

REPRINT FROM

LINDE REPORTS

ON SCIENCE AND TECHNOLOGY

No. 40 1985

Gas separation using pressure swing adsorption plants

Dr.-Ing. habil. H.-P. Riquarts, Dr. P. Leitgeb, Höllriegelskreuth



LINDE AKTIENGESELLSCHAFT

Gas separation using pressure swing adsorption plants

Dr.-Ing. habil. H.-P. Riquarts, Dr. P. Leitgeb, Höllriegelskreuth

1. Introduction

The term adsorption is defined as the binding of molecules from a gaseous or liquid phase to the surface of solids. This binding is caused by forces interacting between the molecules and the surface of the solid concerned; the forces are governed on the one hand by the type of molecule and on the other by certain properties of the adsorbent solid itself. Industrial adsorbents commercially available are granulates, beads or extrudates with large surfaces, the external geometrical surface constituting in fact the smallest portion of the overall surface area. The

surface of the solid is formed by the interior porosity of the adsorbents; the well-known adsorbents, such as zeolitic molecular sieves, activated carbons silica gels or activated aluminas (aluminium oxides) have interior surfaces of several hundred square metres per gram.

The adsorptive capacity of the above-mentioned solids can be illustrated with the aid of adsorption isotherms. These indicate, for example, the amount of a given type of gas that can be bound by one gram of a given adsorbent at a given temperature as a function of the partial pressure of this gas. A large number of

isotherms of this kind have been determined by experiment for the many different types of gases and solids. Generally speaking, it is a fact that the extent to which an adsorbent can be loaded increases with the partial pressure of the gas component in the gas phase and with decreasing temperature.

The different bonding forces exerted by the adsorbent upon various types of gas can be utilized to separate gas mixtures into their components or to extract individual components. In addition, the pore system of these adsorbents can contribute

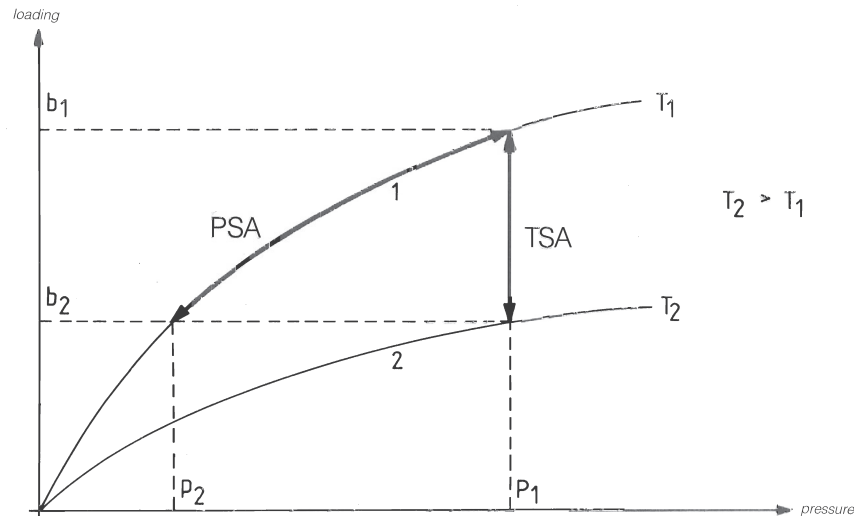


Fig. 1 — Adsorbent regeneration by changing the pressure (PSA) or by changing the temperature (TSA)
1=equilibrium isotherm at temperature T_1
2=equilibrium isotherm at temperature T_2

to gas separation, due to the fact that the pores are more permeable for small molecules than for large ones. Moreover, the difference in the rate of adsorption of the various types of gas can be utilized for a separation process, as will be explained in detail with the example of nitrogen recovery from air by means of carbon molecular sieves. In industrial adsorption processes the utilization of the different bonding forces for gas separation is by far the most important one.

2. Principle of pressure-swing adsorption

Process engineering utilizes the fact that the loading of the adsorbent is a function of pressure and temperature in adsorption processes. Thus the actual adsorption process is designed in such a way that a gas mixture is fed to the adsorber at ambient temperature and increased pressure, a process in which the easily-adsorbed gas components concentrate on the adsorbent surface while the components

that are either adsorbed only slightly or not at all pass right through the bulk; this results in the desired separation of the gas mixture. An adsorbent can be loaded until a state of equilibrium has been reached, then the adsorption capacity is exhausted. To continue the gas-separation process, the loaded adsorbent must be regenerated, which can be done either by increasing the temperature or by reducing the pressure (Fig. 1). These two operations reduce the loading b_1 of the adsorbent at adsorption pressure P_1 and adsorption temperature T_1 to the loading b_2 , either at constant temperature T_1 and reduced pressure P_2 or at constant pressure P_1 and increased temperature T_2 . In the regenerated state the adsorbent has the residual loading b_2 and $(b_1 - b_2)$ is thus the operational capacity for adsorbing the gas concerned. Thermal regeneration, in which the temperature is increased (temperature-swing adsorption or TSA), frequently accompanied by a simultaneous reduction in pressure, is usually carried out when the partial

pressures of the separation components in the feedgas are very low; in other words, when it is a matter of removing impurities, such as water vapor and carbon dioxide, from the feed air of low-temperature air separation plants. The method of regeneration solely by reducing the pressure (pressure-swing adsorption or PSA) can be used when this results in greater differences in partial pressures and thus in adequate differences in loading, as is the case in many gas-separation processes. Both the TSA and the PSA processes are cyclic, alternating between adsorption and regeneration; the cycle periods of the TSA process are a matter of hours, whereas they are in the range of minutes in respect of the PSA processes.

The design of an adsorptive separation process with continuous product supply calls for a minimum of two adsorbers, operating in parallel, one of them being in its adsorption phase and the other, during the same period, in the regeneration

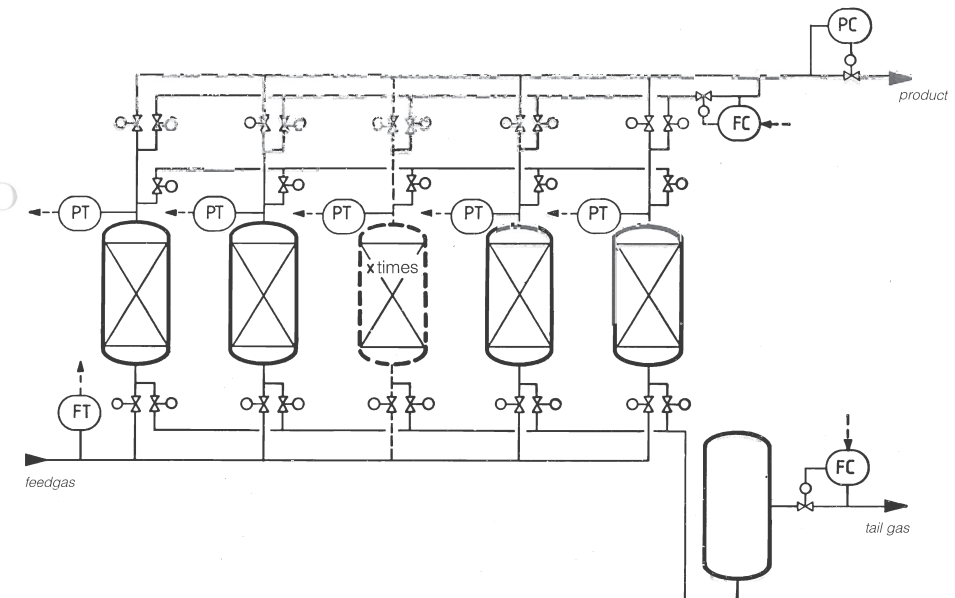


Fig. 2 — Schematic diagram of operating principle of a PSA plant



phase. In actual practice multi-bed systems have become the most commonly-used pressure-swing adsorption plants, numbering up to twelve beds, as shown in the schematic diagram, Fig. 2. The advantage of multi-bed systems is that the expansion gas released during pressure reduction in one adsorber can be used to pressurize and purge other adsorbers. The way in which the various adsorbers act together can best be seen from a pressure/time diagram, as shown in Fig. 3, an example of a pressure-swing adsorption plant with four adsorbers.

Adsorber A 1 is in the adsorption phase at maximum process pressure. During the same period, adsorber A 3 is being pressurized, adsorber A 2 purged and ad-

sorber A 4 de-pressurized. When the adsorption phase of A 1 is terminated, the first procedure is to reduce the pressure by equalizing it with that of A 2 (step E 1). This contributes to reducing expansion losses. The gas leaving A 1 during subsequent depressurization (step E 2), is used to purge adsorber A 4, thus regenerating it. Thereafter, A 1 is depressurized countercurrently (step E 3). The process pressure in adsorber A 1 is at a minimum and now it is purged with expansion gas from adsorber A 3. (step P). Before it is possible to re-load adsorber A 1 with feedgas, the pressure prevailing in A 1 must be raised to maximum process pressure with the aid of expansion gas from A 2 (pressure-equalization step B 1) and product gas from A 4 (step B).

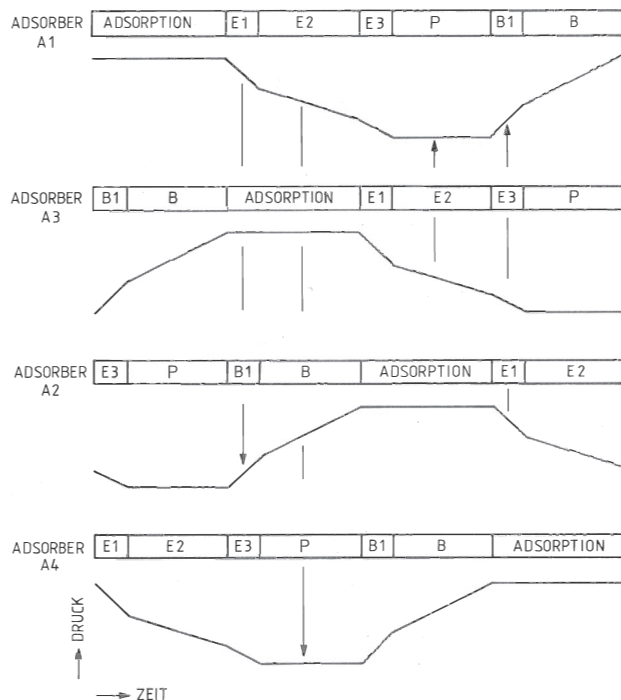


Fig. 3 — Pressure-time diagram of a pressure-swing adsorption plant with 4 adsorbers

Adsorption processes with thermal regeneration usually have only two adsorbers in alternating operation. In this paper it is not intended to go into detail about the temperature-swing adsorption process but to discuss various types of pressure-swing adsorption plants built by Linde.

3. Pressure-swing adsorption plants built

3.1 H₂ plants

The largest and most numerous pressure-swing adsorption plants are those for the recovery of hydrogen from various gas mixtures, such as reformer, refinery and coke oven gases. The process-engineering features of these hydrogen PSA plants vary with the feedgas used [1].

A. H₂ from reformer gas

Fig. 4 is a basic flowsheet of a hydrogen plant in which H₂ is recovered by steam-reforming of natural gas and gas purification by pressure-swing adsorption. The natural-gas feedstock is desulphurized because of the high sulphur sensitivity of the catalysts used in the reformer and the conversion reactor; it is then mixed with steam and pre-heated to reformer inlet temperature using waste heat of the reformer. The catalytic conversion of the natural gas with the steam into a mixture rich in H₂/CO takes place in the reformer pipes. As a result of the CO shift reaction in the conversion reactor the carbon monoxide is transformed into hydrogen and after cool-down of the gas mixture to ambient temperature and separation of the condensate, a feedgas is produced for the pressure-swing adsorption plant, consisting of about 75% by volume of hydrogen. The mixture, which is saturated with water vapour, also contains some CH₄ and CO that have not been converted, and in addition N₂ and CO₂. With the exception of the hydrogen itself, all the components of the hydrogen-rich gas mixture are adsorbed at adsorption pressures usually up to 30 bars in the pressure-swing adsorption plant, which may include up to twelve beds, depending on the capacity of the plant. In this process H₂ yields of more than 90% can be obtained and, if necessary, H₂ purity grades up to 99.999%. The tail gas of the PSA

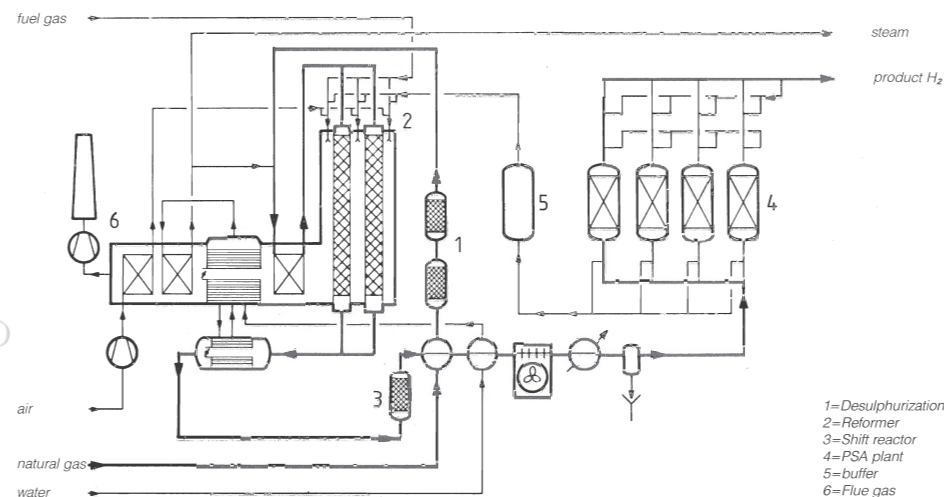


Fig. 4 — Hydrogen production by steam reforming and gas purification by pressure-swing adsorption

plant, containing the sum of feedgas impurities, is fed to a buffer (mixing drum) and together with additional fuel gas it is used as heating gas for the reformer burners.

The fact that high hydrogen-purities can be obtained with pressure-swing adsorption plants and the simplicity of operation, combined with low investment costs, have resulted in other gas-purification processes largely receding from this field of activity. Fig. 5 shows a Linde-built PSA plant for the recovery of hydrogen from reformer gas; it is designed for a feed of 15,000 Nm³/h and came on stream in 1979. In the meantime, H₂ plants with considerably higher capacities have been built: the largest PSA plant built for this purpose and designed for a feed of 116,000 Nm³/h, will go on stream in 1985.

B. H₂ from refinery gases

The increasing demand for high-purity hydrogen for hydrogenation purposes in refineries has resulted in pressure-swing adsorption becoming the method of choice for gas purification, thus recovering high-quality hydrogen from refinery gases. The hydrogen content of refinery gases may be up to 95% by vol. In addi-

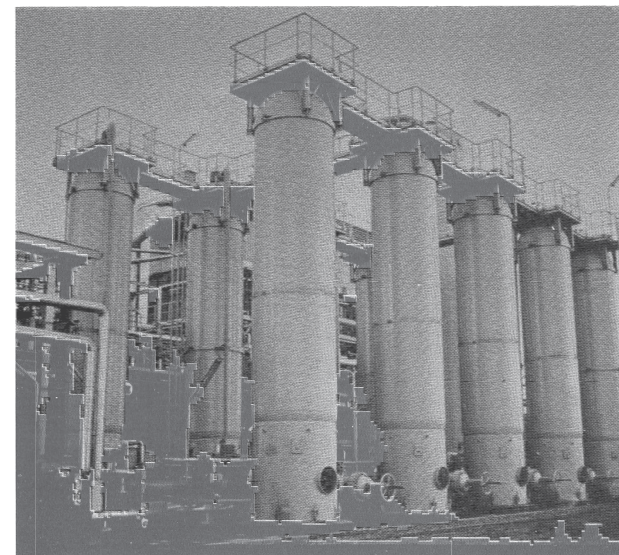


Fig. 5 — PSA plant for the production of H₂ from reformer gas, built for N. V. Bayer S.A.

tion refinery gases contain hydrocarbons ranging from C_4 to C_{10} . The fact that the higher hydrocarbons are very efficiently adsorbed is advantageous for hydrogen purification with the aid of a PSA process, but here the choice of adsorbent must be handled with particular care in order to ensure adequate desorption of the bonded components by pressure reduction and purging. The fact that this technology has been mastered is proved by the single-train pressure-swing adsorption plant operated by UK Wesseling, which is the largest in operation to date and processes 87,000 Nm^3/h of feedgas to produce more than 57,000 Nm^3/h of hydrogen at a purity-grade of 99.5% (Fig. 6). An even larger plant of this type, designed to handle 100,000 Nm^3/h of refinery gas, will go on stream in 1985.

C. H_2 from coke oven gases

Up to the sixties the main hydrogen source was coke oven gas, from which it was recovered with the aid of low-temperature processes. The availability of inexpensive oil and natural gas has made this type of coke oven gas-processing uneconomic; at present-day prices, however, coke oven gas is coming back into favour as a hydrogen source.

Pressure-swing adsorption is a modern process that can be utilized for the recovery of hydrogen from coke oven gas. The demands on PSA technology are very exacting, however, since it is a matter of controlling impurities. Pre-purified coke

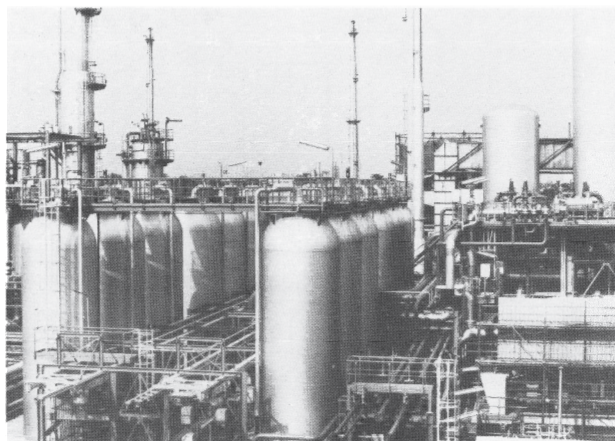


Fig. 6 — PSA plant for the production of H_2 from different gases, including refinery gases, built for Union Rheinische Braunkohlen Kraftstoff AG

oven gases consist mainly of hydrogen and methane, but they also contain more or less appreciable amounts of the higher-boiling hydrocarbons, sulphur compounds, BTX, naphthalene and tar. To obtain high-purity hydrogen despite these impurities, a number of series-connected process stages shown in Fig. 7 are required. First, the heavy components of the coke oven gas are removed by adsorption in a pre-purification stage. The pre-adsorbents are regenerated by purging

with the tail gas from the downstream H_2 PSA unit. CO_2 , hydrocarbons, CO and N_2 are removed from the gas in the pressure-swing adsorption plant for H_2 purification at adsorption pressures of up to 20 bars. To remove oxygen residues (also contained in coke oven gas), from the H_2 product, the hydrogen stream, containing oxygen is conducted through a deoxidant catalyst downstream of the pressure-swing adsorption plant, where O_2 is converted to H_2O .

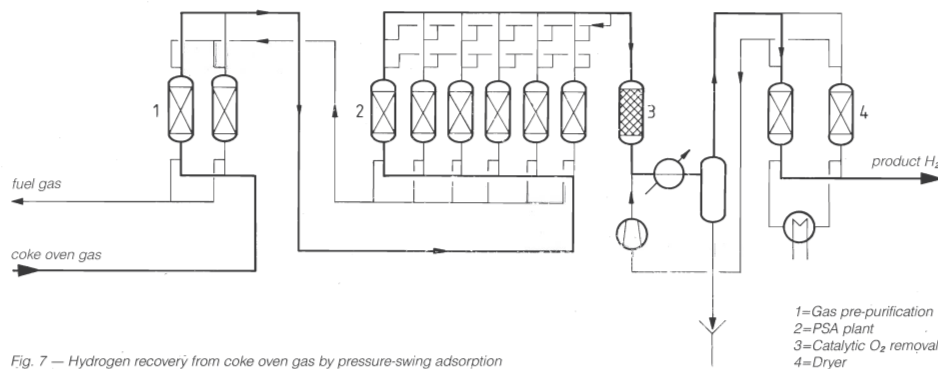


Fig. 7 — Hydrogen recovery from coke oven gas by pressure-swing adsorption

The water is finally removed in a dryer station, consisting of two thermal-regeneration adsorbents.

In the Prosper coke oven plant at Bottrop a hydrogen plant for H_2 -recovery from coke oven gas was erected in 1982 for the Ruhrkohle AG (Fig. 8). The pressure-swing adsorption plant is capable of handling 20,000 Nm^3/h feedgas from which 10,000 Nm^3/h hydrogen of a purity of 99.9% by volume are being recovered; up to now, this is the largest PSA plant ever used for this purpose. The hydrogen product is fed into the hydrogen pipeline system Rhine/Ruhr of Chemische Werke Huls.

A similar PSA plant was erected in Japan, where the H_2 purity grade specified was particularly high, i. e., 99.999%. It has proved possible to meet these specifications with a PSA process producing hydrogen with less than 10 ppm residual impurities; this is a purity-grade that up to that time had been unknown in the recovery of hydrogen from coke oven gas.

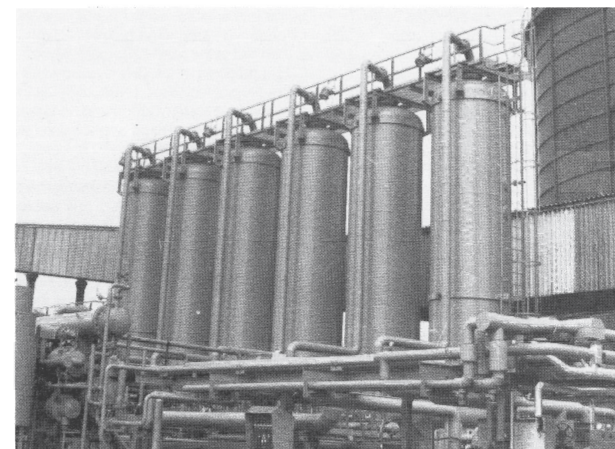


Fig. 8 — PSA plant for the recovery of H_2 from coke oven gas, built for Ruhrkohle AG

The recovery of hydrogen from coke oven gas by means of a PSA process is an extremely cost-effective way of producing H_2 . Leaving out of account the fuel-value loss of the coke oven gas as a result of hydrogen extraction, the plant and operating costs of a pressure-swing adsorption plant are clearly less than 0.10 DM/ Nm^3 H_2 .

In addition to the above-mentioned PSA plants for hydrogen recovery from reformer, refinery and coke oven gases, smaller plants are available for the separation of H_2 from purge gases of NH_3 and methanol plants. Mention should also be made of Sasol plants, where 5 units are used to recover 100,000 Nm^3/h hydrogen from 160,000 Nm^3/h feedgas obtained from a coal-gasification process.

3.2 CO plants

In addition to H_2 , N_2 , CH_4 and CO_2 , waste gases from blast furnaces may contain 70% by vol. or more of carbon monoxide, which is a much requested chemical raw

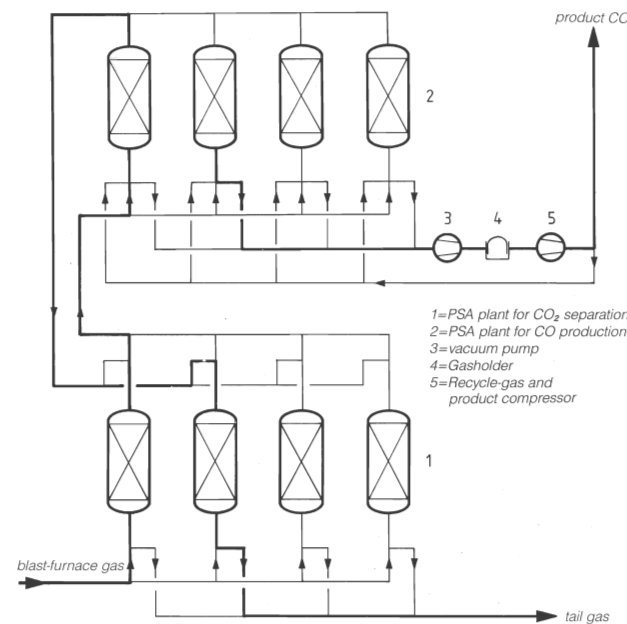


Fig. 9 — PSA plant for the production of CO from blast-furnace gases



material for numerous synthesis processes. Low-temperature processes for the recovery of CO from gas mixtures of this kind are well-known, but it is also possible to use a pressure-swing adsorption plant for separating the gases at ambient temperature. Fig. 9 shows a PSA plant of this kind: in a "first" PSA plant, CO₂ and if necessary higher hydrocarbons, are separated from the blast-furnace gas. The gas that has been pre-purified in this way enters a second PSA plant, in which CO is retained by adsorption, while hydrogen and nitrogen are not adsorbed and are returned to the first PSA plant to act as purging gas. In contrast to hydrogen plants, the CO product is not recovered during the adsorption step but during the desorption stage of the adsorbers, the CO being evacuated. By returning some of the CO fraction that has been drawn off, CO yields of up to 85% and purity grades of up to 99% can be obtained.

3.3 C₂H₄ recovery

To reduce the production costs of ethylene oxide (EO), a plant had to be designed which enabled ethylene to be recovered from the purge gas of the EO production by flushing out the inert gases. A typical EO purge gas contains about 30% C₂H₄ and 50% CH₄, plus oxygen, nitrogen, argon and carbon dioxide. A PSA plant was designed for this job, processing 700 Nm³/h feedgas; it has been in successful operation since 1983 in a chemical factory. Fig. 10 is a schematic diagram of the process. Trace components in the EO

purge gas are retained in thermal-regeneration pre-adsorbers. The pre-purified gas is then fed to the main adsorbers, where C₂H₄ and some of the CH₄ is retained by adsorption at increased pressure, while inert gases, particularly argon and nitrogen, pass through unhindered and are used as regeneration gas for the pre-adsorbers. The ethylene is recovered during the regeneration phase of the main adsorbers at lower pressure. In this way it is possible to recover up to 99% of the C₂H₄; up to 80% of the argon is also eliminated.

In this process special attention must be paid to the oxygen in the purge gas because this oxygen may concentrate in the PSA plant. However, a combination of a suitable order of process stages and the correct choice of adsorbents ensure with complete certainty that no explosive gas mixtures are formed in the adsorbers.

3.4 N₂ plants

Adsorptive nitrogen recovery from air, using the Linde BF process with a carbon molecular sieve (CMS) as an adsorbent is based on a principle that differs from the PSA processes described above. The forces bonding oxygen and nitrogen to CMS are not intrinsically very different; thus O₂/N₂ separation, due to different equilibrium loading capacities of the carbon molecular sieves, is out of the question. On the other hand, the two substances can be efficiently separated on the basis of a kinetic effect. The rate of sorption of oxygen into the CMS is con-

siderably higher than that of nitrogen, thus resulting in the fact that at the discharge end of a CMS bed, N₂ appears first and it is not until after the lapse of some time that O₂ is discharged. In industry, this separation effect can be utilized for adsorptive N₂ recovery. Air is compressed and, after re-cooling and separating from the condensate, is fed through a molecular-sieve adsorber (Fig. 11). N₂, with a purity-grade of up to 99.8%, leaves the adsorber. Before the oxygen breaks through, the adsorption step is terminated and the CMS bed is regenerated by expansion to ambient pressure. The N₂ plant includes two alternating adsorbers and a product buffer for smoothing out the product stream.

A number of plants of this kind have been built, usually for the production of inert gas; the largest plant to date has a yield of 1,500 Nm³/h product N₂. The power required for N₂ production may be no more than 0.4 kWh/Nm³ of N₂, depending on the purity specification and the N₂-supply pressure. Linde have a standard series of N₂ plants available, delivering up to 2000 Nm³/h; if more N₂ were required, nitrogen production by low-temperature air separation would be less expensive.

3.5 O₂ plants

The fact that N₂ adsorption by zeolitic molecular sieve is much higher than is O₂ adsorption is utilized in adsorptive oxygen recovery from air. N₂ is separated from O₂ by passing compressed air through a

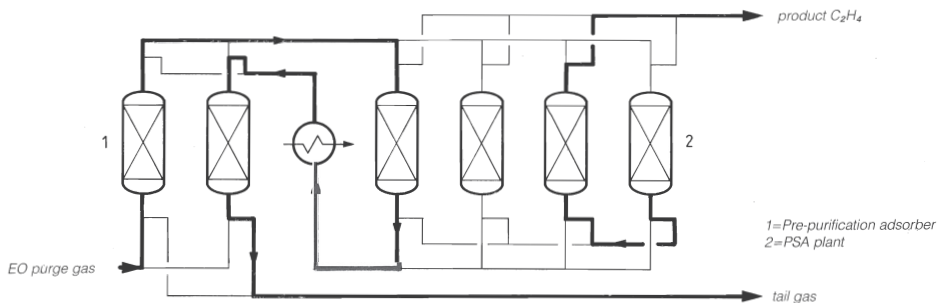


Fig. 10 — PSA plant for ethylene recovery from purge-gases of an ethylene-oxide plant

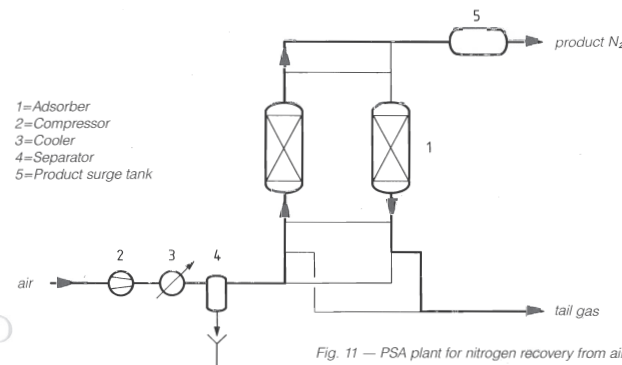


Fig. 11 — PSA plant for nitrogen recovery from air

molecular-sieve bed, the oxygen being drawn off as product at the discharge end of the adsorber. The O₂ purity grade is up to 95%, the remaining gas consisting mainly of argon.

The O₂ PSA plants already built usually contain three adsorbers as shown in Fig. 12. Some small plants, containing only two adsorbers, have also been built.

Fig. 13 shows a special design of O₂ plant. Here, the adsorbers are mounted on a valve block. In this design special importance was attached to compactness and a low trouble factor. Thus the control valves have been integrated into blocks and the adsorbers mounted on top of this assembly. The connections between the adsorbers follow the shortest possible route via the tubing between the block assemblies; the external geometry of the adsorber units allows the plant to be designed very compactly, thus practically eliminating all possibility of damage to sensitive parts. The PSA plant in the illustration has an output of 5 Nm³/h. Fig. 14 shows how this type of plant can be containerized.

PSA oxygen plants are supplied for O₂ outputs up to 1,000 Nm³/h; if more than this is required, a low-temperature air separator would be cheaper to run.

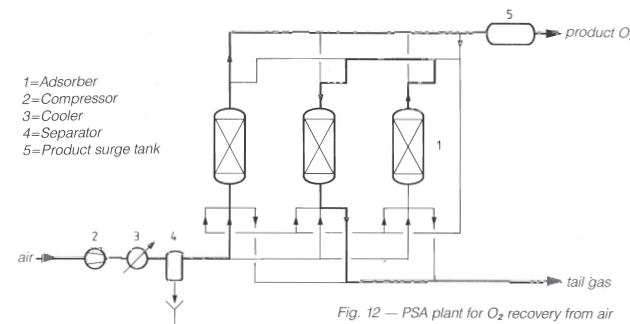


Fig. 12 — PSA plant for O₂ recovery from air

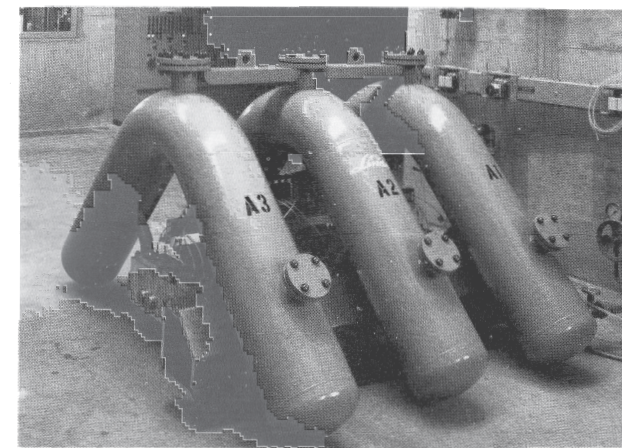


Fig. 13 — Standard plant for the production of small amounts of oxygen by means of pressure-swing adsorption

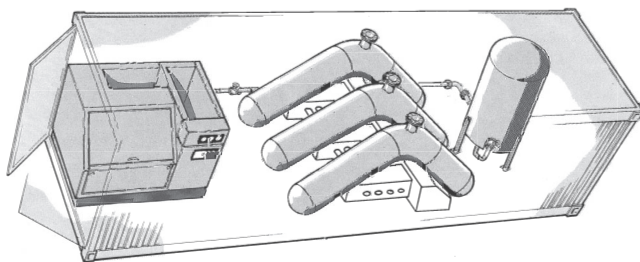


Fig. 14 — Containerized pressure-swing adsorption plant for oxygen recovery

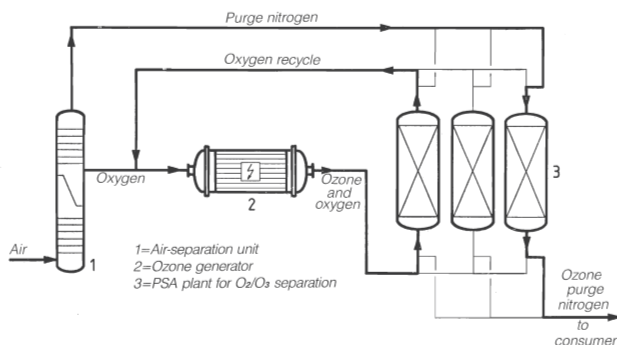
The costs of ozone production are primarily governed by the power requirement of the ozone generator in which ozone is formed from oxygen by a corona discharge. The majority of ozone generators of today still use air as a feedstock; the power required by the generator to produce 3% by weight ozone from the air stream amounts to more than 17 kWh/kg ozone. By way of contrast, O_3 production with oxygen as a feedgas is considerably less expensive, i. e., to produce 3% by weight of O_3 from a stream of oxygen calls for no more than about 7 kWh/kg ozone. Apart from this, it is hardly possible to obtain O_3 concentrations in air above 3% by weight, whereas in ozone generation from oxygen, values of 6% by weight and above can be obtained. This would thus argue in favour of using an ozone-generation process operating with an oxygen feedstock.

The underlying principle of the Linde ozone process is shown in Fig. 15. Oxygen is extracted from air by a low-temperature air-separation process, fed into the ozone generator and converted to ozone in an alternating electric field, the yield being between 5 and 6% by weight. To recover the unused oxygen, ozone is separated off from the O_2/O_3 mixture leaving the generator in a pressure-swing adsorption plant. The ozone is adsorbed while the oxygen passes the adsorber unimpeded. The recovered O_2 is added to the intake oxygen upstream of the ozone generator. When the O_3 -loading capacity of the adsorber has been exhausted, the adsorber must be regenerated, ozone being obtained as product in the regeneration process.

Regeneration and product generation are so designed that the impure nitrogen pro-

duced by the air separation plant is used as purge gas. The ozone is desorbed by the purge gas flowing through the adsorber and is released to the ozone consumer in this form; the O_3 concentration in the purge nitrogen is about 8% by weight. To minimize oxygen losses, adsorbent and power consumption of the separation process, it is possible to constitute the adsorption plant with up to 8 adsorbers. The power required by the plant complex is about 10 kWh/kg ozone.

As an alternative to the above ozone-generation process, another process had already been tested earlier on. In this the air was also separated with a pressure-swing adsorption plant to produce oxygen [2]. Wherever high ozone requirements must be met, the process using a low-temperature air-separation plant is more profitable.

Fig. 15 — Ozone-generation plant with O_2/O_3 separation by pressure-swing adsorption

4. Microprocessor control systems for pressure-swing adsorption

One of the features of a pressure-swing adsorption plant is that the individual adsorbers are operated in a discontinuous process, i. e., pressurizing, adsorption step, depressurizing, purging and repressurizing. It is only when a number of adsorbers, with their individual control and regulation equipment, are so interconnected that the entire adsorption process can be seen as a uniform system, which in turn is a condition for integration of the adsorption process in a complete unit.

Up to a few years ago plants of this kind were controlled and regulated by conventional means until the first PSA plant was erected in 1979, in which a microprocessor, using Linde's own hardware and software concept, controlled the plant. Numerous other plants of this kind followed in rapid succession. The reasons for replacing the usual pneumatic controls by microprocessor controls were as follows:

— Plants that operate on a discontinuity principle, such as PSA plants, call for direct matching of the control of different process variables in order to facilitate continuous operation of the process complex (multi-loop control system). When conventional pneumatic regulators are used it is only possible to achieve the collaboration of a number of control circuits by utilizing a



great deal of equipment and the result would still be imperfect since it is not possible to achieve fully continuous operation. If, however, the regulators are replaced by mathematical control functions, a computer can take over the job of the regulators and their matching. Thus the PSA plants built by Linde no longer contain any "hardware" regulators as their jobs have been taken over by the microprocessor control system.

— Operating personnel have visual access to the process situation and trend indications on a monitor screen at all times.

— If there is a central process control system in a plant complex in which the PSA plant is designed to be integrated, this does not constitute any obstacle to using a microprocessor control system, since this can be incorporated with the aid of the appropriate communication software.

Taken as a whole, a modern control system rounds off the image of pressure-swing adsorption as a progressive gas-separation process. The large number of plants already built have ensured for PSA procedures a firm position in the field of gas-separation technology and its range

of application will go on increasing in the future.

Literature

- [1] P. Häußinger, R. Lohmüller, H.-J. Wernicke: Ullmanns Encyklopädie der technischen Chemie, Vol. 24, Pp. 243-348 „Wasserstoff". Publishers: Verlag Chemie, Weinheim 1983
- [2] E. Laßmann, C. Benkmann: Wirtschaftliche Ozonherzeugung aus Sauerstoff durch die Linde-Druckwechseladsorptionsanlage. Linde-Berichte aus Technik und Wissenschaft, No. 49, July 1981, Pp. 9/13.