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Chapter 1

Chemicals Used in Oil-Field Operations

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Chemicals of various types are used in every stage of drilling, completing, and producing oil and gas wells. This review describes these chemicals, why they are used, and recent developments. These chemicals include common inorganic salts, transition metal compounds, common organic chemicals and solvents, water-soluble and oil-soluble polymers, and surfactants. As existing fields become depleted, use of chemistry to maintain production via well stimulation, more efficient secondary recovery operations, and enhanced oil recovery become ever more important.

The modern chemical industry is highly dependent on crude oil and natural gas feedstocks. Conversely, chemicals, the science of chemistry and chemical engineering join petroleum engineering to play an important roll in the production of oil and gas. The discovery rate of of major new oil fields is declining, particularly in the United States. As the petroleum industry becomes more dependent on increasing production from existing fields, the use of chemicals to more efficiently drill and operate oil and gas wells and enhance productivity from these fields will grow. Environmental considerations will probably be an increasingly important in the choice of chemicals used in well treatment fluids particularly in offshore locations. While geochemistry plays a role in the discovery of oil and gas and production chemicals are used to break produced oil-water emulsions and as friction reducers in pipelines, this review will be restricted to the chemistry and chemicals involved in drilling, completing, stimulating, and operating production and injection wells and in enhanced oil recovery.

Drilling Fluids

Drilling fluids (1-3) are often called drilling muds because of their appearance. This is due to the dispersed clays added to most

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drilling fluids. The drilling fluid is circulated down the drill pipe, around the drill bit, and up the wellbore while drilling is in progress. The purpose of the drilling fluid is to cool and lubricate the drill bit, suspend formation cuttings and lift them to the surface, and control formation pressure reducing pressure surges up the wellbore (thereby reducing the possibility of blowouts). By cooling the drill bit and removing the cuttings from the bottom of the well bore, the rate of drilling can be increased. The drilling fluid is designed to be thixotropic i.e., have high viscosity under low shear conditions when moving up the wellbore carrying suspended solids and have low viscosity under the high shear conditions near the drill bit where rapid fluid movement is necessary to cool the drill bit.

Drilling fluids usually contain water as the primary component. However, oil-based muds may be used for high temperature operations and for drilling highly water-sensitive formations. Oil-based muds are of two types, oil-external emulsions containing as much as 50% water in the internal phase or an oil-based fluid containing little if any water.

A great many additives can be used to impart desired properties to the drilling fluid. In general, the deeper and hotter the well, the more chemical additives are needed to obtain the desired fluid properties. These additives can be classified into different types by function. These include:

Weighting materials which are used to adjust fluid density and thus hydrostatic pressure exerted on the formation by the wellbore fluid. The objective is to prevent sudden pressure surges or blowouts during drilling while simulataneously avoiding excessive fluid leak-off into formations being penetrated by the well bore. Barium sulfate (barite) is the most commonly used weighting agent. Other insoluble minerals used include hematite, siderite, and lead sulfide. Salts may be dissolved in the base water to increase fluid viscosity. The use of high density calcium chloride, sodium and calcium bromides, and zinc bromide solutions and blends thereof has become common in the U.S. Gulf Coast region (4-6). These fluids are somewhat corrosive (7) and the use of corrosion inhibitors such as thiocyanate ion has been recommended. However, these fluids have excellent formation damage characteristics; fluid leakoff from the wellbore into the formation has little adverse effect on rock permeability (8,9).

Fluid loss additives such as solid particles and water-thickening polymers may be added to the drilling mud to reduce fluid loss from the well bore to the formation. Insoluble and partially soluble fluid loss additives include bentonite and other clays, starch from various sources, crushed walnut hulls, lignite treated with caustic or amines, resins of various types, gilsonite, benzoic acid flakes, and carefully sized particles of calcium borate, sodium borate, and mica. Soluble fluid loss additives include carboxymethyl cellulose (CMC), low molecular weight hydroxyethyl cellulose (HEC), carboxymethylhydroxyethyl cellulose (CMHEC), and sodium acrylate. A large number of water-soluble vinyl copolymers and terpolymers have been described as fluid loss additives for drilling and completion fluids in the patent literature. However, relatively few appear to be used in field operations.

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Controlling fluid loss loss is particularly important in the case of the expensive high density brine completion fluids. While copolymers and terpolymers of vinyl monomers such as sodium poly(2-acrylamido-2-methylpropanesulfonate-co-N,N-dimethylacrylamide-co-acrylic acid) has been used (10), hydroxyethyl cellulose is the most commonly used fluid loss additive (11). It is difficult to get most polymers to hydrate in these brines (which may contain less than 50% wt. water). The treatment of HEC particle surfaces with aldehydes such as glyoxal can delay hydration until the HEC particles are well dispersed (12). Slurries in low viscosity oils (13) and alcohols have been used to disperse HEC particles prior to their addition to high density brines. This and the use of hot brines has been found to aid HEC dissolution. Wetting agents such as sulfosuccinate diesters have been found to result in increased permeability in cores invaded by high density brines (14).

Foaming agents provide another way to reduce fluid loss is in the drilling fluids. Mist or foam drilling is used in relatively shallow formations; commonly used foaming agents include C_{14-16} alpha-olefin sulfonates and alcohol ethoxysulfates. While these drilling fluids have not been used extensively in recent years, the development of improved foaming agents and systems containing water thickening polymer to stabilize the foam has been reported (15). Defoamers are used to reduce undesirable foaming which often occurs when saline drilling fluids exit the well bore. Tributylphosphate, low molecular weight aliphatic alcohols, polyglycols, fatty alcohol glycol ethers, acetylenic glycols, aluminum stearate, potassium chloride, silicone-based defoamers, and sodium alkylaromatic sulfonates have been used.

Lost circulation chemical treatments are necessary when the drill bit penetrates a "thief" zone and very large amounts of drilling fluid are lost to the formation. In this situation, the addition of water thickeners or solid particles may not be sufficient. The face of the formation can be plugged using a rapidly setting cement slurry or a process involving the in-situ gelation/precipitation of sodium silicate, treatment with Portland cement, and in less serious cases by plugging the formation face with shredded cellophane, crushed walnut and almond hulls, cedar and cane fibers, and carefully sized sodium chloride and calcium carbonate particles.

Viscosifiers are used as rheology modifiers to aid in suspending rock cuttings as they are carried to the surface. Many of the fluid loss additives described above are used in this application. Clays such as bentonite (montmorillonite) are the most commonly used rheology modifiers. The main organic polymers that are used, polysaccharides and acrylamide and acrylate polymers, often have limited temperature stability or exhibit excessive temperature thinning in deep hot wells. At concentrations below 2.8 g/L, xanthan gum is a more effective solids suspending agent than HEC, CMC, and partially hydrolyzed polyacrylamide (16).

While starches are commonly used, they are relatively poor viscosifiers. Acids and bacterial enzymes readily attack the acetal linkages resulting in facile depolymerization. Both formaldehyde and isothiazolones have been used as starch biocides (17). Development of improved high temperature water viscosifiers for drilling and other oil field applications is underway. For the

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present, oil-based drilling fluids offer the best alternative for elevated temperature applications despite their relatively high cost.

Stabilizing agents are used to maintain drilling fluid rheological properties at highly elevated downhole temperatures. Chromium and chromium-free lignosulfonates, polyglycol ethers, sodium poly-(styrene sulfonate-co-maleic anhydride), and a melanin polymer have been used in this application. Additives such as sodium diethyldithiocarbamate have been used to stabilize aqueous polysaccharides such as xanthan gum (18).

Flocculants cause colloidal clay particles to coagulate thus promoting separation from the drilling fluid which has been circulated down the wellbore and returned to the surface. The treated fluid may then be pumped back down the well bore. Sodium chloride, hydrated lime, gypsum, sodium tetraphosphate, polyacrylamide, poly(acrylamide-co-acrylic acid), cationic polyacrylamides, and poly(ethylene oxide) have been used commercially.

Thinners and dispersants are used to prevent excessive flocculation of clay particles and maintain pumpability of the fluid. Tannins, various lignosulfonate salts, sodium tetraphosphate and other phosphates, and synthetic polymers such as sodium poly(styrene sulfonate-co-maleic anhydride) have been used.

Friction reducers such as partially hydrolyzed polyacrylamide may also be used in drilling fluids (19). They allow fluid to be circulated through the well bore more easily thereby reducing horsepower requirements for the circulating pumps and thus decreasing well treatment costs.

Lubricants offer a means of reducing torque and increasing the effective horsepower to the drillbit by reducing friction. Various vegetable oils, graphite powder, soaps, asphalt blends, air-blown asphalt colloids, diesel oil, and fatty acid esters have been used.

Pipe-freeing agents are used to reduce friction and increase lubricity in areas of expected drill pipe sticking such as angles in deviated wellbores. Soaps, surfactants, oils, soda lime, glass beads, and cationic polyacrylamide have been used.

Corrosion inhibitors are used to reduce the corrosion of surface equipment, surface casing, and the drill string by drilling and well treatment fluids. Many different corrosion inhibitors have been used. These include amine salts such as ammonium sulfite -bisulfite blends, zinc carbonate, zinc chromate, hydrated lime, fatty amine salts of alkylphosphates, cationic polar amines, ethoxylated amines, and tertiary cyclic amines. Commercial products are usually proprietary blends of chemicals.

Bactericides are used to control bacterial growth which can cause corrosion, plugging of the fomation face, and alteration of drilling fluid rheological properties. Paraformaldehyde, glutaraldehyde, sodium hydroxide, lime derivatives, dithiocarbamates, isothiazolones, and diethylamine have all been used.

pH control aids in reducing corrosion and scaling and in controlling interaction of the drilling fluid with formation minerals. Sodium hydroxide, calcium carbonate, sodium bicarbonate, sodium carbonate, potassium hydroxide, magnesium oxide, calcium oxide, fumaric acid, and formic acid have all been used commercially in this application.

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Formation damage control chemicals are added to reduce the permeability damage that occurs when drilling fluid enters the formation. This also aids in preventing erosion of the formation into the wellbore. Maintaining the cylindrical geometry and uniform diameter of the welbore aids in subsequent cementing operations. Potassium chloride, ammonium chloride, sodium chloride, gypsum, sodium silicate, partially hydrolyzed polyacrylamide and poly(acrylamide-co-acrylic acid), certain polymers having quaternary ammonium groups in the repeat unit (see Chapter 10), and lignosulfonate derivatives have all been used to reduce formation damage.

Scale inhibitors are used to prevent the formation of insoluble calcium salts when the drilling fluid contacts formation minerals and saline formation waters. Commonly used scale inhibitors include sodium hydroxide, sodium carbonate, sodium bicarbonate, polyacrylates, polyphosphates, and phosphonates.

Emulsifiers have been used to prepare oil-external emulsion drilling fluids. Surfactants used as emulsifiers include fatty acid salts. fatty acid amides, petroleum sulfonates, and lignosulfonates.

Because of the relatively low cost of many of the chemicals used in drilling fluids, development of more cost effective additives is a major challenge. However, improved high temperature polymers, surfactants, and corrosion inhibitors are under development in many laboratories.

Cementing Fluids (20,21)

After completion of the drilling operation, steel casing is lowered down the well bore and into the drilling fluid. A spacer fluid is then pumped down the well bore to remove the drilling fluid and prevent contact of the drilling mud with the cement slurry. Efficient displacement of the drilling mud also promotes bonding of the cement slurry to rock surfaces.

Intermixing of the spacer and the drilling fluid should not produce solids or a high viscosity phase. Most spacers are aqueous and contain polymers to increase fluid viscosity. Spacer density is usually intermediate between that of the drilling fluid and the cement slurry (22). Salts may be added to control fluid density and pH. Surfactants are used to aid removal of drilling mud from formation surfaces. Water-wetting surfactants also aid in making the casing and exposed rock surfaces water-wet to promote good cement bonding (23). This is particularly important when using oil-based drilling fluids.

Turbulent flow at reasonable pump rates aids in removal of drilling mud from surfaces (24). Downhole devices called scratchers can be installed on the casing to scrape drilling mud residues from formation surfaces. Other devices called centralizers may be attached to the casing to center it in the wellbore.

With increased development work from offshore platforms, more non-vertical (deviated) wells are being drilled. Settling of mud solids to the low side of the well bore can result in a continuous channel of undisplaced drilling mud solids in the casing annulus

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that reduce the effectiveness of cement bonding (25,26). Conversely, cement solids can settle from the slurry before it sets resulting in a channel of water in the high side of the casing annulus. Proper design of both the drilling fluid (particularly through use of surfactants as dispersants) and the cement slurry (including good control over cement set time) are necessary to prevent this.

The cement slurry is pumped down the casing and up the annular space between the casing and the formation. The spacer and drilling fluid are thus displaced by the cement slurry. A compatible fluid (one that does not substantially alter the set time of the cement slurry) is pumped into the wellbore to displace nearly all the cement slurry into the annular space between the casing and the formation. The well is then shut in to allow the cement to set. This bonds the casing to the formation and isolates oil- and gas-bearing formations from aquifers and brine-containing formations. Fluid communication between formations can adversely affect production operations or lead to contamination of potable water aquifers.

Incomplete displacement of fluid from the annular space can result in gaps in the cement sheath through which fluids from different formations can intermingle. In this situation, a "squeeze cementing" treatment is required to plug these gaps. Portland cement or rapidly setting sodium silicate slurries can be used in this operation.

When cementing high pressure gas formations, the gas can penetrate the cement slurry before it sets greatly weakening the set cement (27). Various solutions to this problem have been proposed including the use of cement slurry formulations which expand as they harden thereby resisting gas invasion (28). Foamed cement slurries have been used to provide a low density cement slurry to reduce permeability damage to highly sensitive formations through reduced fluid loss (29). Glass microspheres have also been used to substantially reduce cement slurry density (30, 31). Other additives which reduce cement slurry density to a lesser extent include bentonite, fly ash, silicates, perlite, gilsonite, diatomaceous earth, and oil emulsions (see citations in reference 29).

Corrosion-resistant cements have been developed for use in wells used to inject supercritical carbon dioxide for enhanced oil recovery (32). These are based on Portland cement and high levels (as much as 40% wt.) of additives such as fly ash. Epoxy resins have been successfully used as cements in corrosive environments (33).

Lignosulfonates and lignosulfonate derivatives are used extensively as cement set time retarders (20, 21). Many of the same additives used in drilling muds are used in cement slurries and spacer fluids for similar purposes.

Completion Fluids and Operations (1,20,34)

After cementing the well, communication must be established with the productive formation. This is done in an operation called perforating. The wellbore is filled with a non-damaging fluid of

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the proper density to control pressure surges while not exhibiting excessive fluid loss to the formation. A perforating tool or "gun" is lowered into the well bore and placed opposite the productive formation. The gun fires projectiles or powerful jets of gas generated in small explosions to penetrate the casing and cement sheath. Perforations are generated in a controlled pattern and spacing chosen after considering the formation properties and productive capacity. A small amount of acid may be used to wash the perforations to remove pulverized debris which reduces the fluid carrying capacity of the perforations and adjacent formation. Production tubing is then lowered into the hole and the productive portion(s) of the well isolated using sealing tools called packers (21). This is done to produce from more than one formation simultaneously and to minimize the volume of oil and gas in the wellbore during production.

Fluid loss from the wellbore to the formation may be reduced using the less permeability damaging drilling fluid loss additives described above. In saturated brines, carefully sized sodium chloride particles have been used to temporarily plug the formation face (35). The particles may be dissolved by pumping a less saline fluid down the wellbore.

Sand production from poorly consolidation formations is a significant problem in important oil producing areas such as the U.S. Gulf Coast; Kern County, California; Venezuela; Alberta; Nigeria; and Indonesia. The most commonly used technique for sand control is called gravel packing. A slurry of as much as 1.8 kg of carefully-sized sand particles per liter of aqueous fluid is pumped downhole. The sand particle size is chosen based on size analyses of the formation sand (19,36). The sand-carrying capacity of the water is enhanced by increasing its viscosity using 20-80 lb polysaccharide per 1000 gallon. The most commonly used polysaccharide is hydroxyethyl cellulose because its low content of insoluble solids minimizes permeability damage to the formation (37).

Carboxymethyl cellulose and derivitized guars are occasionally used in this application (1). Methods of stabilizing polysaccharides originally developed for hydraulic fracturing applications (see below) hold promise for increasing the range of temperatures at which polysaccharide polymers can be used in gravel packing applications.

Certain mixtures of polymers have been shown to form complexes which exhibit substantially higher than expected solution viscosity under low shear conditions. Xanthan gum blends with guar gum (38, 39), sodium poly(styrene sulfonate) (40), polyacrylamide (41), sulfonated guar gum (38), sodium poly(vinylsulfonate) (40), hydrolyzed sodium poly(styrene sulfonate-co-maleic anhydride) (38), and poly(ethylene oxide) (41) and blends of xanthan gum and locust bean gum have exhibited substantially higher than expected solution viscosity (42, 43).

An enzyme, acid, or oxidative "breaker" is added to effect a controlled depolymerization and thus a programmed loss of fluid viscosity. This depolymerization is timed to occur when the sand-laden fluid is opposite the productive formation. The sand then drops out of suspension and is packed against the formation. The sand creates a high permeability fluid pathway from the formation

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into the wellbore while substantially preventing the migration of formation particles. Downhole tools such as wire-wrapped screens or liners are used in conjunction with gravel packing. These devices serve to hold the sand in place.

Since formation damage is a critical factor in successful gravel pack treatments, continuing efforts are being made to improve the formation damage characteristics of polysaccharide fluids both before and after depolymerization (37). Recently, grades of hydroxyethyl cellolose having improved formation damage characteristics were introduced into the market place.

Injecting epoxy, furan, or furan-formaldehyde resins into poorly consolidated formations to consolidate them was a common sand control practice for thin highly productive formations (44-46). Organic solvents (46) and silane coupling agents (47) are used to promote adhesion of the resin to the rock surface. Excess resin is flushed deeper into the formation to minimize resin hardening in the flow channels since this would reduce formation permeability.

While effective, the relatively high cost of this sand control method as compared to gravel packing has restricted its use. The use of aqueous slurries of epoxy resins can reduce solvent costs (44). Surfactants, particularly fluorochemicals, may hold promise for increasing epoxy resin fluidity (49). The *in situ* crosslinking of polybutadiene has been proposed as a method of reducing resin costs (50). The gravel packing technique could be used to place resin-coated sand against a poorly consolidated formation (51-53). The resin is then cured resulting in a hard, but permeable mass holding formation sand grains in place. Silica dissolution in high temperature steam injection wells can destroy the integrity of a gravel pack and lead to sand production when the well is placed back on production (54). Use of a resin-coated sand could aid in maintaining gravel pack stability and effectiveness.

Another method of sand control is use of a silicon halide which reacts with water at the surface of sand grains forms SiO_2 which can bond the grains together (55). Reducing the cost of sand consolidation could be very useful since the applicability of gravel packing methods is limited by the bottom hole circulating temperature and the limited temperature stability of polysaccharide polymers.

Hydraulic Fracturing (20,56)

Since hydraulic fracturing is reviewed in a subsequent chapter, this important production stimulation technique will be only briefly discussed. Hydraulic fracturing is a process whereby the permeability of a formation is increased by generating high permeability cracks in the rock. Particulate suspensions (usually sand slurries) are injected at sufficiently high rates (which require high injection pressures) to generate fractures in the rock which are held open by the suspended proppant in the fracturing fluid. The majority of hydraulic fracturing treatments are performed using water-based fluids; foams (with nitrogen or carbon dioxide as the gas phase) have been used extensively in recent years to reduce formation damage. Oil-external emulsions have also been used for

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the same purpose. Ingredients used in hydraulic fracturing are chosen from the following:

A viscosifier, usually a polysaccharide, is used to suspend the proppant during pumping and placement in the rock fracture. Generally 2-7g of guar per liter of fracturing fluid is used. Hydrolytic depolymerization beings at 79.6°C (34). The degradation rate in alkaline media, acid, and in the presence of cellulase and hemicellulase enzymes has been determined (1). Most fracturing treatments employ a crosslinked polymer.

A disadvantage of guar is the relatively high level of insoluble materials normally left in the product after processing, 10-14% wt. (57). Alkaline refining can reduce the insoluble materials level substantially, to ca. 3.9% wt. (58). Guar derivatives such as HPG and carboxymethylhydroxypropyl guar (CMHPG) contain fewer insolubles, <2% wt. (59,60). HPG also exhibits better high temperature stability and resistance to hydrolytic decomposition as compared to guar (1). Locust bean gum, karaya gum, and gum traganth have been used to a limited extent as viscosifiers and fluid loss additives (61-63).

Hydroxyethyl cellulose has been used in fracturing fluids not requiring the increased viscosity and longer break times provided by crosslinking. Until recently, it has been difficult to crosslink HEC (64). This has limited its use in hydraulic fracturing applications despite its excellent formation damage characteristics. Hydroxyethyl celluloses containing vicinal hydroxy groups are more easily crosslinked (65) and exhibit better shear stability (66). Zr(IV) has been used to crosslink HEC (64). Crosslinked CMHEC tends to show more shear degradation on passing through pumps and small orifices in downhole tools than crosslinked HPG fluids (67).

Other viscosifiers described in the literature include acrylate copolymers such as poly(acrylamide-co-dodecylmethacrylate) (68) and poly(vinyl alcohol) (69). The driving force behind using synthetic polymers is presumably better high temperature stability.

The use of ionomers such as lightly sulfonated polystyrene as an oil-based fracturing fluid viscosifier has been studied (70). The most commonly used oil-based viscosifiers are phosphate esters of various types (56,71,72).

Fluid loss additives are used are used to reduce the rate of fluid loss from the fracture to the formation and to naturally occurring macro- and micro-fractures within the formation. Silica flour (73,74), oil-soluble resins (75), diesel oil emulsions (5% by volume) (74) have also been used.

Proppants are solid particles used to hold open the fracture after conclusion of the well treatment. Criteria to choose the economically most effective proppant for a given set of formation conditions have been discussed (76). While sand is the most commonly used proppant because of its low cost, resin-coated sand, sintered bauxite, and Al_2O_3 particles have also been used because of their greater compressive strength and resistance to dissolution at high temperature and pH (55). While epoxy resins are most commonly used, the use of other resins such as phenol-formaldehyde has been described.

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Sand has been treated with oil-soluble organosilicon compounds to form a hydrophobic proppant (77). A double layer resin coating has also been developed. The inner layer coating the sand particle is a cured gamma-aminopropyltriethoxysilane - hexamethylenetetramine. The outer layer is an uncured mixture of the same two chemicals which cures within the fracture to form a consolidated permeable mass holding the fracture open (78).

Crosslinking agents are used to increase solution viscosity and thus solids suspending properties of fluids at T>150°F. The most commonly used crosslinking agents are organotitanates, borates, and zirconium compounds. Organozirconates are the preferred crosslinkers for hydroxyethyl cellulose (79-81). Antimonates and aluminum compounds have also been used as polysaccharide crosslinkers. Encapsulation of crosslinkers and the use of ligands to complex with the transition metal atom have been used to delay crosslinking (82). Delayed crosslinking which occurs within the formation under lower shear conditions can provide higher and more predictable crosslinked fluid viscosity (83). Polyamines such as tetramethylenediamine can be used to accelerate crosslinking reactions (84).

A breaker: an enzyme (at T<140°F), strong oxidizing agent, or an acid, is used to depolymerize polysaccharides and break crosslinks such that viscosity declines at a controlled rate so that the proppant may be deposited in the fracture. Too rapid proppant dropout would cause a premature "sand-out" which prevents future extension of the fracture. Peroxydisulfates are the most frequently used breakers. Less reactive organic peroxides may be preferred for high temperature formations (85).

Chemical stabilizers have been used to reduce the rate of oxygen-promoted degradation of polysaccharides at T>225°F. Methanol and sodium thiosulfate are the most commonly used (86). Sodium dithiocarbamate, alkanolamines, and thiol derivatives of imidazolines, thiazolines, and other heterocyclic compounds have also been tested for this application. Calcined dolomite (87) and Cu(I) and Cu(II) salts (88) have been reported to increase the thermal stability of HEC.

Biocides are used to prevent aerobic bacterial degradation of fracturing fluids in surface mixing and storage tanks. Anaerobic bacterial growth in the wellbore and within the formation has to be controlled to prevent introduction and/or growth of these bacteria within the formation during the fracturing treatment and subsequent generation and production of hydrogen sulfide. Glutaraldehyde, chlorophenates, quaternary amines, and isothiazoline derivatives have been used (89,90). The biocide is best added to the base fluid before addition of the polysaccharide viscosifier.

pH buffers are added to the base fluid to keep the pH basic. This promotes rapid polymer particle dispersion and controls polysaccharide hydration rate to avoid formation of large, partially hydrated particles.

Other techniques to promote complete polymer hydration include vigorous mixing and slow addition of the polysaccharide. Specially designed mixing devices have been used to promote rapid particle dispersion (91). Adding already prepared dispersions of guar, HPG, and HEC in nonaqueous media is another means of promoting rapid

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polymer particle dispersion and complete hydration (81,92). Wetting polymer surfaces with ethylene glycol (92) or isopropanol (93) has also been used as a means of promoting rapid polymer dispersion prior to the onset of hydration.

Various particle surface treatments have been used to delay polymer hydration until polymer particles have been thoroughly dispersed. These include guar treatment with borax (2,94) and HEC treatment with glyoxal (95).

Buffers also are used to maintain the proper pH for the cross-linking reaction to occur at an optimum rate. Sodium bicarbonate and sodium carbonate are used to attain basic pH while weak acids: acetic, fumaric, formic, and adipic, are generally used to obtain acidic pH values.

Formation damage control additives are added to reduce permeability damage caused by clay swelling and consequent fine particle migration (which can also occur in the absence of clay swelling). Potassium chloride, ammonium chloride, sodium chloride, and, for longer term treatment effectiveness, organic polymers containing quaternary ammonium groups in the repeat unit have been used for this application. While avoiding permeability damage to the formation adjacent to the propped fracture is critical in determining initial hydrocarbon production rate, fluid conductivity in the propped fracture is the primary determinant of long-term productivity (96).

Surfactants are used to stabilize water-in-oil emulsions and to promote rapid return of injected fluids and a faster return of the well to hydrocarbon production. Although they are expensive, water-soluble fluorochemicals have been shown to be effective in this application (97,98).

Foams have become widely used to limit the fluid lost to the formation and thus reduce formation damage. Foam cell size plays a major role in determining fluid rheology (99). Guar, HPG, and xanthan gum stabilize the foam bubbles by increasing the viscosity of the surrounding aqueous fluid. Both nitrogen and carbon dioxide have been used as the internal phase of the foam (100-102) and foams based on each exhibit similar rheological behavior in laminar flow (102) and similar fluid loss behavior (103,104). The carbon dioxide is pumped as a supercritical fluid which changes to a gas downhole (105).

Acidizing Chemicals (20,106)

Acid treatments fall into three general types:

Acid washing is used to dissolve acid-soluble scales from the well bore and to open gravel packs and perforations plugged by such scales.

Matrix acidizing is the injection of acids into the formation at a pressure below the formation parting pressure (the pressure at which natural fractures are forced open by injected fluids). Properly designed, the injected acid enters the flow channels of the formation and flows radially outward from the wellbore dissolving mineral fine particles in the flow channels. Minerals forming the flow channel walls also react with the acids. These processes increase formation permeability near the wellbore. The end result

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is to increase well productivity without increasing the produced water:oil or gas:oil ratios.

So-called "wormholes" can be formed when the injected acid primarily enters the largest diameter flow channels in carbonate rock further widening them (107). Acid only invades the small flow channels a short distance greatly reducing treatment effectiveness. High fluid loss rates, low injection rates, and reduced rates of acid-rock reactions decrease the wormhole length.

In the third type of acidizing, fracture acidizing, acid is injected above the parting or fracture pressure of the formation. The acid reacts with the minerals on the exposed fracture face in a process called etching. With sufficient etching, the fracture does not reseal when normal well production or injection operations are resumed.

Acids can sometimes break emulsions within the formation either by reducing the pH or by dissolving fine particles which can stabilize emulsions. Breaking the emulsion reduces fluid viscosity thus increases the fluid carrying capacity of the flow channel. Acids may be used as breakers to reduce the viscosity of acid-sensitive fracturing gels.

Acids are sometimes used ahead of fracturing fluids to dissolve mineral fine particles and allow more rapid injection of the fracturing fluid. When used as the initial stage of a squeeze cementing treatment, the acid-promoted mineral and drilling mud particle dissolution can result in increased entry of the cement slurry into the desired portions of the formation.

Acids are selected based on the nature of the well treatment and the mineralogy of the formation. The critical chemical factors in properly selecting an acid are: stoichiometry (how much formation material is dissolved by a given amount of acid), the equilibrium constant (complete reaction of the acid is desired), and reaction rate between the acid and the formation material (106).

Mineral acids include hydrochloric acid and blends of hydrochloric and hydrofluoric acid (usually 12% HCl/3% HF). Hydrochloric acid is used to acidize carbonate formations. Its advantages are relatively low cost, high carbonate mineral dissolving power, and the formation of soluble reaction products (which minimizes formation damage). The primary disadvantage of hydrochloric acid is its corrosive nature.

Hydrofluoric acid may be prepared by dilution of a concentrated aqueous solution or by reaction of enough ammonium bifluoride with aqueous 15% HCl to prepare a 12% HCl/3% HF solution. Hydrochloric - hydrofluoric acid blends have the major advantage of dissolving silicaceous mineral including clays and silica fine particles. HCl/HF blends are quite corrosive.

Earlier corrosion inhibitors limited the maximum strength of the acid to 15% by weight. Improved corrosion inhibitors (see below) have made the use of higher acid concentrations, such as 28% HCl more common. More dilute solutions may initially be injected in sandstone acidizing to reduce the formation of insoluble sodium and potassium fluorosilicates by displacing saline formation water before injection of hydrochloric acid.

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Organic acids used in carbonate rock acidizing include formic, acetic, sulfamic, and chloroacetic acids. These have the advantage of being less corrosive than the mineral acids. This permits use in applications requiring a long contact time with pipe (as perforating fluids) or with aluminum- or chrome- plated pump parts. It is also easier to retard (inhibit) reaction of organic acids with carbonates at elevated temperatures. This permits deeper penetration of the acid treatment fluid into the formation. Organic acids are used to a much smaller extent than mineral acids due to their higher cost and incomplete reaction with many carbonate minerals. Sulfamic and chloroacetic acids are seldom used except in situations such as remote well locations where their solid form (100% activity) makes transportation costs a critical consideration. The 180°F decomposition temperature limits the use of sulfamic acid to temperatures below ca. 160°F.

Mixed acid systems are blends of mineral acids and organic acids. Combinations that have been used in carbonate acidizing include acetic acid/HCl and formic acid/HCl. While these are less corrosive than hydrochloric acid alone, the organic acid may not react completely with the rock. Blends of formic acid and hydrofluoric acid have been used in high temperature sandstone acidizing and are less corrosive than HCl/HF blends.

High fluid injection rates are often required. For this reason, friction reducers are often used in acid fracturing. These include polyacrylamide and acrylamide copolymers, guar gum, hydroxyethyl cellulose, and karaya gum (108)

In many cases, it is desirable to retard the rate of acid - rock reactions to permit deeper penetration of the treatment fluid into the formation. Four techniques hve been used to accomplish this: using retarded acids which generate HF in situ, chemically retarding the acid by placing an organic film on rock surfaces, using polymers to increase acid viscosity (use of so-called "gelled" acids), and foaming or emulsifying the acid to increase the apparent viscosity.

Retarded acids are primarily applicable to sandstone acidizing. Fluoroboric acid slowly hydrolyzes to form the more reactive hydrofluoric acid (109,110). The time required for this hydrolysis process may enable deeper penetration of the HF into the formation although one report contradicts these findings (111). Na_2TiF_6 and similar salts also slowly generate HF in acid media (112). Phosphorous acid addition to hydrochloric acid has been used to reduce the HCl reaction rate with limestone (113).

Organic polymers have been used to increase the viscosity of acids. The primary application is in fracture acidizing. Binary and ternary acrylamide copolymers are the most commonly used chemicals for this application. Many of these polymers degrade rapidly in strong acids at temperatures $\geq$130°F; development of more stable polymers suitable for high temperatures is desirable. Recently developed polymers for this application include acrylamide copolymers with:

- methacryloyltrimethylammonium chloride (114)
- 2-acrylamido-2-methylpropanesulfonic acid (115)
- methacryloyloxyethyltrimethylammonium methosulfate (116).
- N-vinyl lactam (117)

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Other polymers used in this application include:

poly(vinylpyrrolidinone) (118,119)
sodium poly(vinylsulfonate-co-vinylamide) (120)
sodium poly(acrylamide-co-N-vinyl lactam-co-vinyl sulfonate) (119)

and mixtures of sodium poly(2-acrylamido-2-methylpropanesulfonate-co-N-vinylacetamide) and poly(acrylic acid-co-vinylformamide-co-vinylpyrrolidinone) (120).

Despite its limited stability in acid (1), guar gum has been used to thicken 3-15% hydrochloric acid (121). An allyl ether - guar gum adduct has been proposed for use as an acid viscosifier (122). Zr(IV) crosslinked CMHEC has been used to thicken hydrochloric acid (81).

Low viscosity oil-external retarded hydrochloric acid micro-emulsions exhibiting quite low acid diffusion rates (ca. 1% of that of aqueous HCl) have been developed (123,124). Foaming (125) or emulsifying acid (106) also has the effect of limiting the contact of the acid with formation surfaces and increasing acid viscosity thereby reducing the rate of acid-rock chemical reactions. The foaming agents are generally nonionic surfactants and the gas phase is usually nitrogen. The acid is usually the internal phase of emulsified acids and the fluid contains 10-30% of a low viscosity hydrocarbon as the external phase. Polyacrylamide has been used to thicken the aqueous phase of hydrochloric acid emulsions (126) while nonionic surfactants have been used as the emulsifiers (127). Overall, emulsified acids appear to be the most suitable for high temperature formations.

By adding an oil-wetting surfactant to an acid, one can promote the temporary formation of a film on formation surfaces thus reducing the rate of rock dissolution. Acids containing these surfactants are known as chemically retarded acids.

Surfactants are also used to break low mobility oil emulsions. Organic amines and quaternary ammonium salts (128), alkylphenol ethoxylates (128), poly(ethylene oxide-co-propylene oxide-co-propylene glycol) (129) and alkyl- or alkylaryl polyoxyalkylene phosphate esters (130) are among the surfactants that have been used.

Mutual solvents have been used to reduce surfactant adsorption on formation minerals, particularly oil-wetting surfactants (131). Ethylene glycol monobutyl ether is the most commonly used mutual solvent.

Formation permeability damage caused by precipitation of dissolved minerals such as colloidal silica, aluminum hydroxide, and aluminum fluoride can reduce the benefits of acidizing (132-134). Careful treatment design, particularly in the concentration and amount of HF used is needed to minimize this problem. Hydrofluoric acid initially reacts with clays and feldspars to form silicon and aluminum fluorides. These species can react with additional clays and feldspars depositing hydrated silica in rock flow channels (106). This usually occurs before the spent acid can be recovered from the formation. However, some workers have concluded that permeability damage due to silica precipitation is much less than previously thought (135).

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Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include 5-sulfosalicylic acid and citric acid (136); dihydroxymaleic acid (137); ethylenediaminetetraacetic acid (138); lactic acid (138); blends of hydroxylamine hydrochloride, citric acid, and glucono-delta-lactone (139); nitriloacetic acid; blends of citric acid and acetic acid; lactic acid; and gluconic acid (140).

Diverting agents assist in distributing acid more uniformly through the perforated formation interval (141). These are usually oil-soluble hydrocarbon resin particles. They may be dissolved by post-acid injection of xylene or similar solvents. Oil-soluble waxes, naphthalene, and solid organic acids such as benzoic acid have also been used (142). Best results are obtained using a broad range of particle sizes.

Blends of sodium hypochlorite with 15% HCl and with 12% HCl/3% HF have been used to stimulate aqueous fluid injection wells(143). Waterflood injection wells have also been stimulated by injecting linear alcohol propoxyethoxysulfate salts in the absence of any acid (144). The oil near the well bore is mobilized thus increasing the relative permeability of the rock to water (145). Temperature effects on interfacial tension and on surfactant solubility can be a critical factor in surfactant selection for this application (146).

Corrosion inhibition is primarily associated with acidizing. Buffered hydrofluoric acid compositions have been shown to be less corrosive (147). Corrosion inhibitors are designed to reduce the rate of reaction of fluid with metal surfaces, generally by forming films on the surfaces. Acetylenic alcohols and amines are frequently components of corrosion inhibitor blends. Other compounds that have been used include nitrogen heterocyclics, substituted thioureas, thiophenols, and alpha-aminoalkyl thioethers (148).

Arsenic compounds can be very effective corrosion inhibitors but their toxicity, ineffectiveness in hydrochloric acids above 17% active and in the presence of H_2S, and their ability to poison refinery catalysts has limited their use (148). Epoxy resins have been coated onto metal surfaces and cured with a polyamine to reduce corrosion (149).

High density brine completion fluids also often require the use of corrosion inhibitors (8,9). Blends of thioglycolates and thiourea; alkyl, alkenyl, or alkynyl phosphonium salts; thiocyanate salts; mercaptoacetic acid and its salts; and the reaction products of pyridine or pyrazine derivatives with dicarboxylic acid monoanhydrides have been used as high density brine corrosion inhibitors.

Hydrogen sulfide promoted corrosion can be a serious problem (150); the best solution is prevention. Corrosion problems can be minimized by choice of the proper grades of steel or corrosion resistant alloys, usually containing chromium or nickel (150, 151) and avoiding generation of H_2S by sulfate reducing bacteria in situations where H_2S is not initially present. Cathodic protection of casing is often effective for wells less than 10,000 feet deep (150).

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Scale inhibitors may also be used in acidizing. These include alcohol ethoxysulfonic acids (152). Scale inhibitors are also used in water and enhanced oil recovery injection wells and include low molecular weight poly(vinylsulfonate), poly(methylmethacrylate-co-ethylenediamine) (153), bis(phosphonomethylene)aminomethylene carboxylic acid, and poly(acrylic acid-co-3-acrylamido-3-methylbutanoic acid). Ethylenediaminetetraacetic acid and similar complex-ing agents have been used to remove scale from formation surfaces near wellbores.

Formation Damage Control Chemicals

The fluid flow capacity of rock, particularly the rock adjacent to an oil or gas well is critical in determining well productivity. The region near the wellbore acts as a choke for the entire formation; because the flow is radial more and more fluid is flowing through a given volume of rock as the fluid approaches the well bore. The reduction of the rock fluid carrying capacity is referred to as formation damage.

Formation damage may be due to invasion of rock capillaries by solid particles in wellbore fluids (drilling and completion fluids) and plugging of rock capillaries adjacent to fractures by fine solid particles in fracturing fluids. These fines may be generated when sand-laden fracturing fluid passes through small orifices such as choke valves at high flow rates and pressures (67) or by proppant crushing within the fracture. They may also be due to the use of solid fluid loss additives. This type of formation damage may be reduced by filtration of fluids before their entry into the well bore and by proper choice and sizing of solid particles used in drilling, gravel packing, and fracturing fluids. Acidizing the rock immediately adjacent to the wellbore can dissolve clays, silica particles, and precipitates plugging rock flow channels. However, precipitation of hydrated silica, fluoroaluminates, and iron compounds (above pH 2.2) in acidizing can cause formation damage reducing well treatment effectiveness (see above).

Reduced injectivity due to formation damage can be a significant problem in injection wells. Precipitate formation due to ions present in the injection water contacting counterions in formation fluids, solids initially present in the injection fluid (scaling), bacterial corrosion products, and corrosion products from metal surfaces in the injection system can all reduce permeability near the wellbore (153). The consequent reduced injection rate can result in a lower rate of oil production at offset wells. Dealing with corrosion and bacterial problems, compatibility of ions in the injection water and formation fluids, and filtration can all alleviate formation damage.

Formation damage can also be caused by chemical and physical interactions of fluid and rock. Low salinity fluids can cause swelling of water-expandable clays. The resulting larger clay dimensions can reduce the fluid carrying capacity of rock flow channels. The expanded clay particles are more susceptible to the shear forces of flowing fluids. In addition, clays act as the cementing medium in many sandstone formations. Swelling weakens this cementation and can cause the release of mineral fine

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particles. Fines migration in Berea sandstone occurs when the salinity of the flowing phase drops below a critical salt concentration (CSC) (155,156). The CSC varies for different monovalent cations in solution and decreases with increasing ion exchange affinity of the clay for the cation. The CSC of multivalent cations is very low (157). Flowing fluids can carry these fine particles to constrictions in the flow channels where they form a plug.

Inorganic salts: KCl, NH_4Cl, $CaCl_2$, or high concentrations of NaCl have been used in wellbore fluids, fracturing fluids, and injection fluids to temporarily reduce formation damage by converting the more water-expandable smectite and mixed layer clays to less swelling forms through ion exchange processes. However, the potassium, ammonium, or calcium ions on the clays are themselves subject to ion exchange processes and the clays may later be converted back to the more water-expandable sodium form. Once clay swelling has occurred, injection of salts will not reverse formation damage. An acidizing treatment to partially dissolve the clays is required for this.

The addition of potassium hydroxide to injection waters has been used to stabilize clays and maintain injectivity (158). Some degree of permanence appears to result from this treatment since injectivity appeared to be substantially maintained during subse-quent injection of low salinity water.

More permanent stabilization of water-swelling clays may be achieved by bonding the clay surface cation exchange sites together so that simultaneous ion exchange at a large number of sites is required for desorption of the clay stabilizer. This may be accomplished by injection of hydroxyaluminum, zirconyl chloride, or certain quaternary ammonium salt polymers. A 6-12 hour well shut-in period is required to allow polymerization of hydroxyaluminum on formation surfaces to occur (159). Because hydroxyaluminum is removed from mineral surfaces by fluids at pH<3, it cannot be used in conjunction with acidizing treatments. However, treated clays are stable to high temperatures and hydroxyaluminum can be used in 500°F steam injection wells.

Zirconyl chloride can be used to stabilize swelling clays in both acidic environments and in the presence of 600°F steam (160). No well shut-in time is required for polymerization to occur so zirconyl chloride may be used in conjunction with hydraulic fracturing treatments (161).

Quaternary ammonium salt polymers are more versatile and have been used in drilling fluids, completion fluids, acidizing treatments, and hydraulic fracturing. No well shut-in period is required. Care in choosing the particular polymer to be employed in a frac-turing treatment is needed because some polymers can interfere with the function of the crosslinker. Some of these polymers are also stable to high temperature steam and have been successfully used to treat high temperature steam injection wells. Recent developments in organic polymer formation damage control polymers are discussed in chapter 10 of this book.

Fine particle migration can occur in the absence of water-swelling clays. Migrating fines can include the migrating clays kaolinite, illite, chlorite, and some mixed layer clays and fine silica particles (162,163). Fine particle migration is promoted when the

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flowing phase is the rock wetting phase (162), is affected by flowing fluid salinity (155-157) and pH (164), and is accelerated by rapid flow rates (165). A critical flow velocity exists below which fines migration is greatly reduced (166).

Conventional inorganic and cationic organic polymer clay stabilizers have been shown to be effective in substantially preventing permeability damage due to clay swelling and consequent fines migration (see Table 1, Chapter 10). However, most of these polymers are much less effective at preventing fines migration in the substantial absence of swelling clays. Recently developed quaternary ammonium salt polymers have been shown to be effective in reducing migration of a variety of mineral fine particles in the absence of swelling clays (see Chapter 10).

Adsorption of corrosion inhibitors or cationic surfactants can reduce sandstone formation permeability. Alcohols can be used to remove corrosion inhibitors from rock surfaces. Oil-soluble corrosion inhibitors may be dissolved by organic solvents such as xylene or toluene containing a mutual solvent, most often ethylene glycol monobutyl ether, EGMBE (167). Aqueous fluids containing 5-10% EGMBE can be used to dissolve cationic surfactants.

Paraffin deposits adjacent to production wells can greatly reduce productivity by plugging fluid flow channels. Deposition of these waxy crude oil deposits can also occur in perforations and production tubing. Scraping has been used to remove deposits from production tubing. Hot oil washes have been used to dissolve paraffins above the perforations. Washing with organic solvents such as xylene or toluene has been used to remove paraffins from perforations and the formation (167). Addition of amines to these solvents can aid in solubilizing asphaltene deposits (167).

Emulsion blocks within the formation can form as a result of various well treatments and are more easily prevented (by using surfactants in conjunction with well treatments, see above) than removed. Aromatic solvents can be used to reduce the viscosity and mobilize oil-external emulsions (167). Low molecular weight urea-formaldehyde resins have been claimed to function in a similar manner in steam and water injection wells (168,169). Water-external emulsion blocks can be mobilized by injection of water to reduce emulsion viscosity.

Gypsum scaling (calcium sulfate precipitation) can occur as aqueous formation fluids cool and experience pressure drops near and in the production wellbore. In wells producing from more than one oil-bearing formation, mixing of different formation waters can also give rise to this scaling problem. The most common solution is washing the wellbore with basic solutions of potassium acetate, potassium glycolate, potassium citrate or potassium hydroxide. Scale deposits are converted to dispersed particles which can be circulated out of the wellbore. A chelating agent such as ethylenediamine tetraacetic acid can aid in dissolving calcium sulfate deposits. Hydrochloric acid following the basic treatment can also be used to dissolve calcium sulfate (167).

Injectivity can be reduced by bacterial slime which can grow on polysaccharides and other polymer deposits left in the wellbore and adjacent rock. Strong oxidizing agents such as hydrogen

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peroxide, sodium perborate, and occasionally sodium hypochlorite can be used to remove these bacterial deposits (143,170,171).

Rock Wettability

Wettability is defined as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids" (145). Rock wettability can strongly affect its relative permeability to water and oil (145,172). Wettability can affect the initial distribution of fluids in a formation and their subsequent flow behavior. When rock is water-wet, water occupies most of the small flow channels and is in contact with most of the rock surfaces. The converse is true in oil-wet rock. When the rock surface does not have a strong preference for either water or oil, it is termed to be of intermediate or neutral wettability. Inadvertent alteration of rock wettability can strong alter its behavior in laboratory core floods (172).
In water-wet reservoirs being waterflooded, oil is displaced ahead of the water. The injection water tends to invade the small and medium-sized flow channels (or pores). As the water front passes, the remaining oil is left in the form of spherical, unconnected droplets in the center of pores or globules of oil extended through interconnected rock pores but completely surrounded by water. This oil is immobile and there is little oil production after injection water breakthrough at the production well (145).

In a strongly oil-wet rock, water will tend to invade the larger pores as oil is found in the smaller pores or as a film on rock surfaces. Because the water preferentially flows through the larger pores, flow channels to the producing well develop and water only slowly invades the smaller flow channels. This results in a higher produced water:oil ratio and a lower oil production rate than in the water-wet case.

Care must be taken in all well treatment and injection operations not to alter rock wettability in an undesired manner. Use of carefully selected surfactants in well treatment fluids is a way to accomplish this. Rock wettability can be altered by adsorption of polar materials such as surfactants and corrosion inhibitors, or by the deposition of polar crude oil components (173). Pressure appears to have little influence on rock wettability (174). The two techniques used to study wettability, contact and and relative permeability measurements, show qualitative agreement (175-177). Deposition of polar asphaltenes can be particularly significant in carbon dioxide enhanced oil recovery.

Primary and Secondary Oil Recovery

Primary oil recovery is the production of oil driven to wellbores by the energy of fluids under pressure in the reservoir. As reservoir pressure is reduced by oil production, additional recovery mechanisms may operate. One is natural water drive as water from an adjacent more highly pressured formation is forced into the oil-bearing formation by the pressure differential between the formations. Gas drive, expansion of a gas cap above the oil as

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oil pressure declines can also drive additional oil to the wellbore. Additional oil may be produced by compaction of the reservoir rock as this pressure is reduced by oil production. Generally the additional oil produced by reservoir compaction is small. As the natural pressures in the reservoir decrease, oil production declines. The oil well may then be placed "on pump" to maintain production at economic levels; the pump is used to draw oil to the surface and keep the production well relatively free of fluid. (The pressure of a column of fluid can decrease the rate of fluid entry into the wellbore.)

Primary production typically recovers 10-25% of the oil originally in place in the reservoir. The efficiency of primary production is related to oil properties, reservoir properties, geometric placement of oil wells, and the drilling and completion technology used to drill the wells and prepare them for production. Waterflooding or secondary oil recovery is a means of adding energy to the reservoir. Water injection through some wells results in a pressure differential across a reservoir resulting in the movement of oil and injected water to offset production wells. The geographic arrangement of production and injection wells is critical to maximizing oil recovery and can be related to the geology of the reservoir (145). Salinity of the available injection water can have an important effect on the efficiency of oil recovery. Scaling, the formation of insoluble precipitates when the saline injection water contacts a formation brine, is a particularly common problem and many scale inhibitors have been developed to reduce precipitation near the injection wells where permeability reduction can greatly reduce injection rate (see above).

Injection rate can have a major effect on the economics of secondary oil recovery. Acidizing or carefully designed hydraulic fracturing treatments can be used in increase injection rates. More recently well treatments that do not interrupt normal water injection operations have increased in frequency. Addition of surfactant to the injection water (144,146) can displace the oil remaining near the production well. The lower oil saturation results in an increase in the water relative permeability (145). Consequently a greater water injection rate may be maintained at a given injection pressure or a lower injection pressure. Thus smaller and cheaper injection pumps may be used to maintain a given injection rate. While the concentration of surfactant in the injection water is relatively high, the total amount of surfactant used is not great since it is necessary only to displace the oil from a 6-10 foot radius around the injection well.

Extensive waterflooding began in the 1940's. Currently waterflooding accounts for about 40% of domestic oil production. Waterflooding typically recovers 15-25% of the oil originally in place.

Organic and inorganic polymers have been used to improve the results obtained in waterflooding. Crosslinked polymers (see below) have been used to reduce the permeability of fractures and high permeability streaks so that injected water flows through a larger fraction of the reservoir volume. The polymer is injected with a crosslinker or the crosslinker may be injected after the

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polymer. In either case, crosslinking occurs in situ. Sodium silicate gelation has also been used in this application (178,179). The use of organic polymers in injection wells is discussed below. Both in situ crosslinking of partially hydrolyzed polyacrylamides (180) and quaternary ammonium salt polymers with long sidechains (181) have been used to reduce the permeability of water producing zones adjacent to production wells and decrease the produced water:oil ratio.

Enhanced Oil Recovery

Primary and secondary oil recovery together recovery only 25-50% of the oil originally in place in a reservoir. Cumulative U.S. production of 133 billion barrels of oil and remaining reserves of 27.5 billion barrels account for only 33% of the 488 billion barrels of oil discovery to date (182). In a more recent reference (183), recoverable reserves as of Jan. 1, 1989 were estimated to be 26.5 billion barrels. The increasing cost of discovering major new oil reserves in the U.S. (which most likely exist in frontier regions of Alaska and deep water offshore) make unrecovered oil in known fields an attractive target. Its location is known and much of the infrastructure: wells, storage tanks, pipelines, roads, etc. are already in place.

Major disincentives to enhanced oil recovery are the lack of tax incentives and a substantial decline in the price of oil since the end of 1981. All the investment in new wells and surface facilities and injectants must take place before any incremental oil is produced.

This decline in the price of oil has resulted in major changes in the types of enhanced oil recovery (EOR) being studied in the laboratory and field tested. Steam injection and injection of miscible gases, primarily CO_2, remain of great interest due to the relatively low cost of the injectants (although they are quite expensive as compared to water). More expensive injectants such as used in micellar polymer flooding can often efficiently recover oil. However, the large concentration of surfactant (often as much as 2-5% wt plus the additional cost of the polymer used to provide mobility control (see below), usually used in concentrations of 100-1000ppm, have made these fluids prohibitively expensive.

Recent research and field tests have focused on the use of relatively low concentrations or volumes of chemicals as additives to other oil recovery processes. Of particular interest is the use of surfactants as CO_2 (184) and steam mobility control agents (foam). Also combinations of older EOR processes such as surfactant enhanced alkaline flooding and alkaline-surfactant-polymer flooding have been the subjects of recent interest. Older technologies: polymer flooding (185,186) and micellar flooding (187-189) have been the subject of recent reviews. In 1988 84 commercial products: polymers, surfactants, and other additives, were listed as being marketed by 19 companies for various enhanced oil recovery applications (190).

Other important issues influencing the economics of oil recovery include methods of determining fluid movement and behavior within the reservoir (191); the effect of oil composition on oil

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recovery, particularly in miscible flooding (192); and corrosion control (193). Seismic, geotomographic, controlled-source audio magnetotelluric, and pressure analyses as well as tracer chemical injection and analyses are all used to understand fluid movement within the reservoir and monitor EOR processes (191).

Oil Recovery Mechanisms

The amount of oil recovery promoted by an injected fluid is related to its ability to displace the oil it contacts in the reservoir, termed the oil displacement efficiency (ODE), and to the relative amount of the reservoir invaded by the injected fluid, termed the volumetric sweep efficiency (VSE). Total oil recovery may be expressed as:

$$\text{Oil Recovery} = \text{VSE} \times \text{ODE}$$

For example, consider a reservoir which has produced 40% of the oil originally in place. If an injection fluid contacts 70% of the reservoir and has an oil displacement efficiency of 70% of the remaining oil (42% of the oil originally in place) then the maximum enhanced oil recovery is 49% of the oil remaining in place or 29% of the oil originally present in the reservoir. (Trapping and other oil loss mechanisms are neglected in this simplified treatment.) Total oil recovery has increased to 69%.

This example illustrates the importance of using chemicals to improve both the volumetric sweep efficiency and the oil displacement efficiency. Although the greatest attention has been given to increasing the oil displacement efficiency, primarily though the use of surfactants, a government study indicated that volumetric sweep efficiency is the greatest obstacle to increasing oil recovery (194).

Improving Volumetric Sweep Efficiency

Volumetric sweep efficiency is determined by the permeability and wettability distribution in the reservoir and by the properties of injected fluids. Waterflooding characteristically exhibits poor volumetric sweep efficiency. The more expensive the injection fluid, the more important it is to have a high volumetric sweep efficiency so that the injected fluid contacts and thus mobilizes a larger volume of oil. High permeability streaks or layers (thief zones) and natural or induced rock fractures can channel the injected fluid through a small portion of the reservoir resulting in a low volumetric sweep efficiency.

Crosslinked polymers have been widely used to substantially seal these thief zones and fractures thus directing subsequently injected fluids to different parts of the reservoir increasing VSE in waterflooding and chemical flooding. The most commonly used polymers are partially hydrolyzed polyacrylamides (195) although field applications of crosslinked xanthan gum have also been reported (196). These are generally injected at concentrations of 1000-5000 ppm and crosslinked *in situ*. Treatments are restricted to the near-wellbore region due to the kinetics of the crosslinking

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process. The most commonly used crosslinkers are Al(III) (196-198) and Cr(III) compounds(199). The injected fluid preferentially enters the thief zone. The well is shut in to allow crosslinking to occur. After 1-7 days depending on the treatment, normal injection operations are resumed.

Aluminum (III) citrate and sodium aluminate have been used as crosslinkers. The polymer and crosslinker solutions are injected as alternate slugs. A layer of adsorbed polymer is built up which is then crosslinked to subsequently injected polymer (200). Cationic polyacrylamide may be used in the initial treatment stages to promote rapid polymer adsorption (201). Adjustment of the pH may allow deeper penetration of the fluids in an aluminate crosslinking system prior to gelation (202). A process involving injection of alternate slugs of stoichiometrically equivalent amounts of partially hydrolyzed polyacrylamide and $Al_2(SO_4)_3$ has been evaluated in the laboratory; permeability of sand packs were reduced by more than 96% (203). Mixtures of Al(III) and Zr(IV) have also been evaluated as partially hydrolyzed polyacrylamide crosslinkers (204).

Sodium bisulfite and thiourea have been used to reduce injected Cr(VI) to the reactive Cr(III) species that promotes crosslinking (205,206). Kinetic studies suggest that the crosslink stucture includes two chromium atoms bridged by oxygen (205). Gradual dissolution of colloidal $Cr(OH)_3$ has been used to delay crosslinking to permit deeper polymer penetration in the formation prior to crosslinking (207) as has the use of Cr(III) propionate (208). Injection of unhydrolyzed polyacrylamide followed by *in situ* hydrolysis delays Cr(III) crosslinking (209). The rate of the hydrolysis reaction is dependent on temperature but not on injection and formation water salinity (210). Studies suggest that 5-10% hydrolysis is the optimum to produce a crosslinked polyacrylamide (211).

Occasionally it may be desirable to have a rapid crosslinking take place. Blends of chromium triacetate and hydrochloric acid have been used in this situation (212). Gelation time decreases substantially as applied shear increases (213,214). Thus, static laboratory gelation time experiments should not be used to predict gelation time in actual well treatments.

Organic crosslinkers have also been used. These include glyoxal (215) and formaldehyde. Use of hypohalite salts (216,217) and epichlorohydrin (218,219) have been found to increase gel stability.

Copolymers of sodium acrylate with sodium 2-acrylamido-2-methylpropane sulfonate (220) or N,N-dimethylacrylamide (221) have been found useful for preparing crosslinked systems that must function at high temperatures and relatively high salinity. Chromium crosslinked gels prepared from a 3:1 blend of partially hydrolyzed polyacrylamide and guar gum have been found to have a higher strength and stability than gels prepared from the partially hydrolyzed polyacrylamide alone (222).

Crosslinked xanthan gums have also been used to reduce the permeability of thief zones. Trivalent chromium and aluminum have been used as crosslinkers (223,224). While crosslinker effectiveness is reduced at high salinity, Cr(III) has been used in the field at

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salinities as great as 166,000 ppm total dissolved solids (224). Xanthan gum can be precipitated by quite high concentrations of divalent metal ions to plug thief zones (225). Xanthan gum plus a partially methylated melamine-formaldehyde resin has been used to form a gel (226).

Carboxymethylhydroxyethyl cellulose has been gelled by hydrated lime (227). Succinoglycan has been crosslinked by Cr(III), Al(III), Zr(IV), Ti(IV), and other trivalent metal ions (228,229).

Careful sizing of the treatment and choice of injection rates is required to prevent inadvertent overtreatment i.e., excessive treatment of oil-containing rock. The post-treatment fluid injection rate is usually significantly less than that prior to treatment. While successful applications of this technology in waterfloods and in surfactant polymer floods have been reported, temperature and pH stability limitations of the polymer and the crosslinking chemistry result in few if any applications in steam and CO_2 injection wells.

Reactive monomers such as acrylamide in concentrations of 2-5%w and various additives including a free radical polymerization initiator may be used to form polymers in situ (230-232). An optional reactive difunctional monomer such as N,N'-methylenebis(acrylamide) can be added to the formulation to form a cross-linked polymer in the high permeability zone. The low viscosity aqueous fluid may be injected at relatively high rates and preferentially enters the high permeability zones to a greater extent than do non-Newtonian polymer solutions (233). Polymerization takes place forming a high permeability mass that greatly reduces rock permeability. If no difunctional monomer is used, this mass may be slowly dissolved by injection water. This process increases injection water viscosity (see below).

If the two functional groups of the difunctional monomer differ substantially in reactivity, the difunctional monomer may be injected without any comonomer. An example is 2-hydroxyethylacrylate which can polymerize rapidly through the carbon-carbon double bond and form crosslinks more slowly through hydrogen atom abstraction from the hydroxyl group. Less reactive monomers such as 2-hydroxyethyl acrylate and the use of less reactive polymerization intiators permit the use of this technology in somewhat higher temperature formations.

Lignosulfonates may be crosslinked in situ using Cr(III) (234,235) or an acidic gas such as CO_2 (227) to promote crosslinking. Crosslinked lignosulfonate has been reported to be quite effective at high formation temperatures. Lignosulfonate concentration is usually 2-3% by weight. This gelation technology has been evaluated in field tests in both waterflood and steam injection wells. An advantage of this technology appears to be the ability of this system to crosslink at long distances from the injection well bore. Chemical reactivity at formation temperatures and in situ dilution effects can limit the effective treatment radius of the crosslinked polymer systems described above. Blends of lignosulfonate and sodium silicate have also been evaluated in the field (236).

Phenol-formaldehyde resins (237, 238), urea-formaldehyde resins (239,240), melamine-formaldehyde resins (241), furfuryl

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alcohol resins (242) and resins of formaldehyde plus sulfonated tannin extract (243) or alkali Kraft lignin (244) have been evaluated to seal thief zones near water and steam injection wells. Polymer gels formed in situ from polyvinyl alcohol and aldehydes (245) and by Cr(III) crosslinking of alkylene oxide - styrene block copolymers (246) have also been evaluated.
Surfactant precipitation may be used for in-depth permeability reduction of thief zones (247). This process is based on the sequential injection of a slowly propagating ionic surfactant followed by an aqueous spacer containing no surfactant, and then a more rapidly propagating ionic surfactant of the opposite charge type. In a sandstone reservoir, one would initially inject a cationic surfactant and then an anionic surfactant. The oppositely charged surfactants gradually mix in the high permeability portions of the reservoir resulting in the formation of precipitates. These precipitates plug flow channels and the cumulative effect is to reduce permeability in the most flooded portions of the reservoir diverting injectant to rock zones containing higher oil saturations. The economically limiting factors in the use of this process would probably be the cost and propagation rate of the cationic surfactant.

The use of polyethylene glycol ethers in a process in which a high viscosity emulsion is formed on contact with residual crude oil has also been tested as a means of plugging thief zones using surfactants (248-250). Precipitation of sodium pectate when fresh water solutions contact brine has been proposed as a method of plugging high permeability zones (251).

Polymer Flooding (186,187,252)

Even in the absence of fractures and thief zones, the volumetric sweep efficiency of injected fluids can be quite low. The poor volumetric sweep efficiency exhibited in waterfloods is related to the mobility ratio, M. This is defined as the mobility of the injected water in the highly flooded (watered-out) low oil saturation zone, m_w, divided by the mobility of the oil in oil-bearing portions of the reservoir, m_o, (253,254). The mobility ratio is related to the rock permeability to oil and injected water and to the viscosity of these fluids by the following formula:

$$M = m_w/m_o = (k_{rw}/\mu_w)/(k_{ro}/\mu_o)$$

wherein k_{rw} and k_{ro} represent the relative permeability to water and oil respectively and μ_w and μ_o represent the viscosity of the aqueous and oil phases respectively.

The displacing fluid may be steam, supercritical carbon dioxide, hydrocarbon miscible gases, nitrogen or solutions of surfactants or polymers instead of water. The VSE increases with lower mobility ratio values (253). A mobility ratio of 1.0 is considered optimum. The mobility of water is usually high relative to that of oil. Steam and oil-miscible gases such as supercritical carbon dioxide also exhibit even higher mobility ratios and consequent low volumetric sweep efficiencies.

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The first mobility control agents were partially hydrolyzed polyacrylamides having molecular weights of $1\text{-}5\times10^6$ (254-259) and xanthan gum (biopolymer) (1,34,260). Virtually all field projects have used polymers from one of these two classes although variations in polymer molecular weight and structure have been made to improve performance properties (see below). Relatively low polymer concentrations (down to ca. 100ppm) can significantly increase injected water viscosity. The increase in apparent viscosity in porous media was often sigificantly greater that that exhibited in conventional laboratory viscosity measurements (259). Another benefit of both polyacrylamides and xanthan gum is a long-lasting decrease in rock permeability to aqueous fluids that persists even during long periods of water injection. This residual resistance effect has been observed in laboratory tests and some field trials. After termination of polymer injection, the North Stanley Field and North Burbank Unit 29 polymer field tests exhibited injected water permeability reductions attributed to residual resistance effects that lasted for more than three years and more than seven years respectively (261,262).

Each polymer type has important advantages and significant disadvantages. These are summarized in Table I and discussed below for polymers representative of those presently used.

Table I. Properties of Polyacrylamide and Xanthan Gum EOR Polymers

Property	Polyacrylamide	Xanthan Gum
Brine tolerance	very limited esp. to Ca^{+2}, Mg^{+2}	good tolerance to mono- and divalent cations
Transition metal cations	easily crosslinked	easily crosslinked
Shear stability	undergoes irreversible shear degradation	reversible shear thinning.
Thermal stability	maximum use T 225°-250°F	maximum use T $160\text{-}170^{\circ}$F
Hydrolytic stability	hydrolysis promoted by acid or base. Partially hydrolyzed product more sensitive to Ca^{+2}, Mg^{+2}	hydrolytic depolymerization promoted by acid or base esp. at high T
Oxidative stability	susceptible	particularly susceptible esp. at high T
Microbial degradation	susceptible to attack by yeasts, fungi, bacteria	very susceptible in aerobic conditions

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Compared to partially hydrolyzed polyacrylamide, xanthan gum is more expensive, more susceptible to bacterial degradation, and less stable at elevated temperatures (1). However, xanthan gum is more soluble in saline waters, particularly those containing divalent metal ions; generally adsorbs less on rock surfaces; and is substantially more resistant to shear degradation (1,34). The extensional viscosity of the semi-rigid xanthan molecule is less that that of the flexible polyacrylamide (263).

In addition to the normal problems of completely dissolving particles of water-thickening polymers, xanthan gum contains insoluble residues the cumulative effect of which is to decrease polymer injectivity. Fermentation broths containing 8-15% by weight xanthan can be used to prepare solutions which contain no undissolved polymer particles (264). Flash drying of polymer broths can produce a solid product which dissolves more readily in injection waters (264). Other means of inproving xanthan solution injectivity include brief (30 sec) ultrasonic treatment at 60-80 MHz (265), solid polymer hydration in solutions of metal complexing agents such as sodium citrate (266) or low concentrations of boron species (266), heat treatment (267,268), bentonite treatment followed by filtration through diatomaceous earth (266,269), passing xanthan solutions through a colloid mill (270), treatment with methylenebis(isocyanate) (271), cellulase enzymes (272,273), proteases (272,273), polysaccharide hydrolases (274), or caustic agents plus an enzyme (274). Flow channels adjacent to the well-bore which have been plugged with solid xanthan residues may be reopened by treatment with oxidizing agents such as hydrogen peroxide.

Use of oxygen scavengers (275,276,277) and bactericides (278) is common parctice in field operations. Among the oxidation stabilizers used are thiourea (279), sodium dithionite (280), guanidine acetate (281), and a blend of sodium sulfite, thiourea, and 2-propanol (282). Among the other chemicals studied as xanthan gum and polyacrylamide stabilizers are: sodium bisulfite, sodium 2-mercaptobenzothiazole and benzoimidizol (283), 2-thioimidazolidone (284), 1-tolylbiguanide (285), 2-thiazoline-2-thiolate (286), dithiocarbamates (287), methionine (288), thiosulfuric acid (289), and phosphonic acid esters (290), and mixtures of isobutanol, sodium 2,4,6-trichlorophenate, and sodium diethylenetriaminepentaacetic acid (291).

When dissolved in more saline waters, xanthan gum produces a higher apparent viscosity than the same concentration of polyacrylamide (292). Prehydration of xanthan in fresh water followed by dilution in the saline injection water has been reported to provide higher viscosity than direct polymer dissolution in the same injection water. Optical rotation and intrinsic viscosity dependence on temperature indicate xanthan exists in a more ordered conformation in brine than in fresh water (293).

Although high concentrations of pyruvate ring-opened polymers exhibit increased tolerance to divalent metal ions in high density completion fluids (294), at low polymer concentrations, xanthan containing the intact pyruvate ring exhibits higher brine solution viscosity and better filterability than its ring-opened analog (295). A xanthan gum containing pyruvate rings in most of the

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polymer repeat units has been produced by a proprietary strain of Xanthamonas campestris (296) and evaluated for polymer flooding applications (295).

Other microbial polysaccharides have also been evaluated for use in enhanced oil recovery. These include scleroglucan (299-300) which is thought to exist in solution in a rigid helical conformation, polymers produced by the bacterium Pseudomonas methanica (301), by Leuconostoc mesenteroides (302), by Aerobacterium NC1B11883 (303), the alga Porphyridium aeruginium (304), and nonionic glucose homopolysaccharides produced by fungi (305). Xanthamonas bacteria have also been used to produce a polysaccharide comprising glucose and mannose units in a 2:1 ratio. This polymer has been claimed to be a better water viscosifier than xanthan gum (306). Saccharide polymers may be prepared by the polymerization of 3-O-methacryloyl-D-glucose (307).

Most polyacrylamides used as mobility control agents are actually partially hydrolyzed or are acrylamide - acrylic acid (or sodium acrylate) copolymers produced by emulsion copolymerization (308). Emulsion polymers are used to avoid the high shear degradation and undissolved solid particle problems often associated with solid polyacrylamide dissolution. Another method of avoiding problems associated with hydration of solid polymer particles is acrylamide solution polymerization at the wellhead. The polymerization can be designed to proceed at adequate rates and in saline injection waters to provide polymers of adequate viscosity characteristics (309). Polyacrylamide is usually hydrolyzed in base to produce a random distribution of acrylate groups. This random distribution is similar to that obtained in a copolymer having the same acrylate group content (310). Acid hydrolysis results in a more block-like distribution of acrylate units (311). ^{60}Co irradiation has been used to initiate polymerization and prepare particularly high molecular weight polyacrylamides (312).

Electrostatic repulsion of the anionic carboxylate groups elongates the polymer chain of partially hydrolyzed polyacrylamides increasing the hydrodynamic volume and solution viscosity. The extensional viscosity is responsible for increased resistance to flow at rapid flow rates in high permeability zones (313). The screen factor is primarily a measure of the extensional (elongational) viscosity (314). The solution properties of polyacrylamides have been studied as a function of NaCl concentra-tion and the parameters of the Mark-Houwink-Sakaruda equation calculated (315). Maximum freshwater viscosity occurs at ca. 35% hydrolysis (316) while maximum viscosity in a Ca^{+2}-containing brine occurs at 10-15% hydrolysis. Metal ions interact with carboxylate groups reducing their mutual repulsion and thus decreasing hydrodynamic volume and solution viscosity. Divalent metal ions reduce viscosity more than monovalent ones (317). Above 33-35% hydrolysis, interaction with Ca^{+2} causes polyacrylamide precipitation (318). The major mode of polyacrylamide decomposition at elevated temperature (in the absence of oxygen) is hydrolysis (319,320). Thus, the concentration of divalent metal ions has an effect on viscosity retention at high temperature. Chelating and sequestering agents have been used to reduce the adverse effect of

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divalent (316) and multivalent metal ions on polyacrylamide solution viscosity (321,322).

Proper well completion, particularly perforation design, can reduce polyacrylamide shear degradation during entry into the formation (313).

Acrylamide copolymers designed to reduce undesired amide group hydrolysis, increase thermal stability, and improve solubility in saline media have been synthesized and studied for EOR applications. These polymers still tend to be shear sensitive. Acrylamide comonomers that have been used include 2-acrylamido-2-methylpropane sulfonate, abbreviated AMPS, (1,321-324), 2-sulfoethylmethacrylate (325,326), diacetone acrylamide (324, 326), and vinylpyrrolidinone (327,328). Acrylamide terpolymers include those with sodium acrylate and acrylamido-N-dodecyl-N-butyl sulfonate (329), with AMPS and N,N-dimethylacrylamide (330), with AMPS and N-vinylpyrrolidinone (331), and with sodium acrylate and sodium methacrylate (332). While most copolymers tested have been random copolymers, block copolymers of acrylamide and AMPS also have utility in this application (333).

Acrylamide terpolymers having a heterocyclic ring in the polymer backbone have been shown to exhibit improved viscosity and shear degradation properties (334,335). A disadvantage of acrylamide copolymers is their greater cost as compared to partially hydrolyzed polyacrylamides. Acrylamide graft copolymers have been studied in an effort to reduce copolymer costs. These include acrylamide graft copolymers with starch (336), dextran (337), and lignin (338).

Polymer association complexes (38-43, see above) including those which form micelle structures by association of hydrophobic groups such as nonylphenoxy polyethylene glycol acrylates (339), acrylamide terpolymers containing hydrophobic alkylacrylamides (340-343), and poly(styrene-co-maleic anhydride) vinylbenzylpolyglycol ethers (344) substantially increase water viscosity at quite low polymer concentrations. Similar hydrophobically modified polysaccharides such as hexadecyloxyhydroxyethyl cellulose (345) may be suitable for use in enhanced oil recovery. These polymer association complexes exhibit much higher solution viscosity than equal concentrations of conventional polymers.

The substantial decrease of polyacrylamide solution viscosity in mildly saline waters can be utilized to increase injection rates by adding a quaternary ammonium salt polymer to the polyacrylamide mixing water (346,347). If the cationic charge is in the polymer backbone and substantially shielded from the polyacrylamide by steric hindrance, formation of an insoluble interpolymer complex can be delayed long enough for polymer injection. Upon contacting formation surfaces, the quaternary ammonium salt polymer is adsorbed reducing solution salinity and thus increasing viscosity away from the wellbore where it will not adversely affect injectivity. By using a clay stabilizing quaternary ammonium salt polymer, formation damage associated with low salinity polyacrylamide solvents can be reduced (348).

Propagation of enhanced oil recovery chemicals through rock is critical to the success of an EOR project. Polymer retention in permeable media has been the subject of considerable study (349)

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and mechanical entrapment as well as adsorption has been identified as a cause of polymer loss (350,351). Sacrificial adsorption agents may be used to reduce the adsorption of expensive polymers and surfactants. Lignosulfonates and their derivatives have been extensively evaluated for this application (34,352-356). Other chemicals tested for this application include poly(vinyl alcohol) (357), sulfonated poly(vinyl alcohol) (358), sulfonated poly(vinylpyrrolidinone) (358), low molecular weight polyacrylates (359), and sodium carbonate (360).

Surfactants for Mobility Control

Despite its relatively high mobility, water has been used to decrease the mobility of even higher mobility gases and supercritical CO_2 used in miscible flooding (361). While water mobility can be up to ten times that of oil, the mobility of gases can be 50 times that of oil (362). The following formula is used to calculate gas:oil mobility ratios (363):

$$M = \left[(k_g/\mu_s) + (k_w/\mu_w)\right] \Big/ \left[(k_o/\mu_o) + (k_w/\mu_w)\right]$$

wherein k refers to permeability, μ to viscosity, and g, s, o, and w to gas, miscible solvent, oil, and water respectively. The water may be injected simultaneously with the gas or in alternate slugs with the gas (WAG process). X-ray computerized tomography of core floods has demonstrated the increased volumetric sweep efficiency attained in the WAG process (364).

The WAG process has been used extensively in the field, particularly in connection with supercritical CO_2 injection and some success have been reported.(365-367). However, it would be desirable to develop a method to further reduce the viscosity of injected gas, particularly CO_2, the most commonly used gas (actually injected as a supercritical fluid) in the U.S.. While limited studies on increasing the viscosity of CO_2 though the use of supercritical CO_2-soluble polymers and other additives have been reported (368, see also Chapter 29 and references therein), the major direction of research has been the use of surfactants to form low mobility foams or supercritical CO_2 dispersions within the formation.

The behavior of foam in porous media has been the subject of entensive study and recently a collection of papers on this subject (369), a review of foam rheology (370), and an extensive bibliogra-phy (371) have been published. X-ray computerized tomographic analysis of core floods indicated that addition of 500 ppm of an alcohol ethoxyglycerylsulfonate increased volumetric sweep efficiency substantially over that obtained in a WAG process (364).

The role of various surfactant association structures such as micelles and lyotropic liquid crystals (372), adsorption-desorption kinetics at liquid-gas interfaces (373) and interfacial rheology (373) and capillary pressure (374) on foam lamellae stability has been studied. Microvisual studies in model porous media indicate

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that the predominant mechanisms of in situ foam generation are snap-off at pore constrictions (375,376), lamellae leave-behind (375), and lamellae division (375).

The reason for wide-spread interest in the use of surfactants as gas mobility control agents (369) is their effectiveness at concentrations of 0.1%wt (377) or less (364). This low chemical requirement can significantly improve process economics.

Another advantage is the wide range of surfactant classes and chemical structure variations within each class of surfactant which can be screened to optimize surfactant performance for a given set of reservoir conditions. Any change in surfactant structure should increase the propagation rate and the displacement efficiency. It has been noted that this is possible only by decreasing surface viscosity (378). Among the classes of surfactants studied for this application are alcohol ethoxylates and their sulfate and sulfonate (364,379-384), and carboxylate (385) derivatives, alkylphenol ethoxylates (382), alpha-olefin sulfonates (383), and alkylated diphenylether disulfonates (386). Increased linear hydrophobe carbon chain length, decreased hydrophobe branching, and increased ethoxy group chain length was found to increase foam stability (380). When using mixtures of surfactants or surfactants plus an alcohol, foam stability, injected breakthrough time at the core outlet, and oil recovery were maximized when the two surfactants or the surfactant and the alcohol had the same carbon chain length (387,388). Addition of a water-thickening polymer to the aqueous phase will stabilize the foam (389-391).

In addition to the mobility control characteristics of the surfactants, critical issues in gas mobility control processes are surfactant salinity tolerance, hydrolytic stability under reservoir conditions, and surfactant propagation. Lignosulfonate has been reported to increase foam stability and function as a sacrificial adsorption agent (392). The addition of sodium carbonate or sodium bicarbonate to the surfactant solution reduces surfactant adsorption by increasing the aqueous phase pH (393).

Alcohol ethoxysulfates have been used in field tests as foaming agents for nitrogen (394) and carbon dioxide (395). Application of alcohol ethoxysulfates is restricted due to its limited hydrolytic stability at low pH and elevated temperature (396).

High temperature steam has also been used in enhanced oil recovery, for the recovery of highly viscous crude oils (397). In heavy oil fields, water flooding is often omitted and steam injection begun immediately after primary production. Steam injection temperature, usually 350-450°F in California oil fields, can reach 600°F in Canadian and Venezuelan projects. Heat is transferred from the steam to the rock and crude oil reducing oil viscosity. This increases oil mobility thereby enhancing oil production.

Gravity override is the migration of the steam to the upper portion of the formation and is caused by the low steam density. This results in channeling of the steam through the upper portion of the reservoir and a low volumetric sweep efficiency. Surfactants have been used as steam mobility control agents in both laboratory and field tests to prevent this gravity override thereby increasing volumetric sweep efficiency. Surfactants that have been

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used in field tests include C_{16-18} alpha-olefin sulfonates, alkyltoluene sulfonates, and neutralized dimerized alpha-olefin sulfonic acid.

Careful screening procedures are required to evaluate surfactants as steam foaming agents (398,399). Increasing the hydrophobe carbon number in alpha-olefin sulfonates from 14-16 to 16-18 to >25 has been reported to improve foam strength (400,401). In alkylaromatic sulfonates, longer linear alkyl groups (402) or dialkyl substitution (403) seem to have the same effect. Other alkylaromatic sulfonates containing benzene, toluene, or xylene rings (402, 404); two fused aromatic groups (405); and the diarylether group (406) have been favorably evaluated as steam foaming agents. The neutralized dimer of an alpha-olefin sulfonate has also been used (407).

The high temperature steam will cool and eventually condense as it propagates through the oil reservoir. In order to maintain foam strength as the steam cools, a noncondensible gas, most often nitrogen or methane, is usually added to the injectant composition (408). A method of calculating the optimum amount of noncondensible gas to use has been reported (409).

Critical parameters affecting surfactant performance are surfactant propagation rate and surfactant stability at steam temperatures that can reach more than 600°F. Surfactant propagation rate can be reduced by adsorption, precipitation, and partitioning into the oil phase. Adsorption increases with increasing salinity and decreases with increasing temperature (410). A numerical model of foaming agent transport has been developed which uses the surface excess variable in describing surfactant adsorption (411).

Surfactant propagation can be improved by the use of additives. Both surfactant partitioning and precipitation tend to increase with increasing calcium ion concentration (412) so minimizing divalent metal ion concentration in the surfactant solution is desirable. Injection of a surfactant preslug containing NaCl will convert clays to their sodium form reducing later ion exhange processes that result in the presence of Ca^{+2} ions in the surfactant solution (413,414). The use of a hydrotrope such as sodium xylene sulfonate has been reported to increase oil recovery in laboratory steam foam floods of sandpacks (415). The hydrotropes may function as sacrificial adsorption agents or interact with the foaming agent to stabilize lamellae and increase foam strength. Thermal stability of the foaming agent in the presence of high temperature steam is essential. While alkylaromatic sulfonates possess superior chemical stability at elevated temperatures (416-419), alpha-olefin sulfonates possess sufficient chemical stability to justify their use at steam temperatures characteristic of most U.S. steamflood operations. Decomposition is a desulfonation process which is first order in both surfactant and acid concentrations (417). Since acid is generated in the decomposition, the process is autocatalytic. However, reservoir rock has a substantial buffering effect. The addition of high pH agents such as sodium hydroxide to the surfactant solution has been reported to increase foam strength and stability (420). The sodium hydroxide may function by precipitating with calcium ions to improve surfactant propagation (421). This is also the mechanism

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by which sodium carbonate and trona ($Na_2CO_3/NaHCO_3$) function when used as steam foam additives (422). These additives can also maintain the pH at a high enough value to reduce the rate of surfactant decomposition. In addition, the added base may interact with petroleum soaps naturally found in the crude oil to more efficiently displace oil (420); the consequent lower oil saturation can result in a more stable foam.
High sulfur content heavy crude oil may be recovered more efficiently using transition metal ions such as Ti or V and optionally carbon monoxide as steam additives (423).

Improving Oil Displacement Efficiency

The use of relatively large concentrations of surfactants, usually 2-5%w, to substantially increase oil displacement efficiency has been the subject of very extensive study (188-190,424-426). This complex process usually involves the injection of a brine preflush to adjust reservoir salinity followed by injection of a micellar slug comprising the surfactant, a "cosurfactant" (usually a C_{4-6} alcohol) and a hydrocarbon. A polymer solution is usually injected after the micellar slug to reduce viscous fingering of the drive fluid into and through the micellar slug. This viscous fingering causes dilution of the surfactant, less contact of the micellar slug with the crude oil, and trapping of some of the micellar slug in the reservoir. Process effectiveness depends on maintaining an ultralow interfacial tension (<0.01 dynes/cm) between the injected surfactant slug and the crude oil (427). The surfactant-rich microstructures involved in oil recovery include vesicles as well as micelles (428). Interfacial tension behavior is sensitve to the presence of air and is both temperature and pressure dependent, it can be different for stock tank oil and live (containing dissolved gases under pressure) reservoir crude oil 174). Therefore interfacial tension, phase behavior, and core flood tests should be carefully designed.

By about 1980, the emphasis of research had shifted from inexpensive surfactants such as petroleum sulfonates to more expensive but more effective surfactants tailored to reservoir and crude oil properties. Critical issues are: surfactant performance in saline injection waters, surfactant adsorption on reservoir rock, surfactant partitioning into the crude oil, surfactant chemical stability in the reservoir, surfactant interactions with the mobility control polymer, and production problems caused by produced emulsions. Reservoir heterogeneity can also greatly reduce process effectiveness. The decline in oil prices dating from the end of 1981 halted much of this research due to the relatively high cost of micellar processes (also called surfactant polymer flooding). Since 1982 the number of field projects in progress evaluating this technology has dropped from 20 to 9 (429). Only one field test since 1982 has been successful enough that expansion of the project has been considered (430).

The thrust of surfactant flooding work has been to develop surfactants which provide low interfacial tensions in saline media, require less cosurfactant, are effective at low concentrations, and exhibit less adsorption. The optimal salinity concept and the

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salinity requirement diagram (431,432) are extremely useful when screening surfactants. When comparing the performance of different surfactants, it is important that the comparison be made at the optimal salinity of each surfactant or, if it is not possible to adjust injection water salinity, in the actual injection water to be used in a given field project.

While nonionic surfactants such as alcohol ethoxylates, alkylphenol ethoxylates (433) and propoxylates (434) and alcohol propoxylates (434) have been studied, most recent work has been on anionic surfactants: alcohol propoxysulfates (434), alkylphenol propoxysulfates (434), alcohol alkoxyalkylsulfonates (435), alkylphenol alkoxyalkylsulfonates (435), secondary alkane sulfonates (436), alpha-olefin sulfonates (436), calcium or magnesium salts of alpha-olefin sulfonates (437), internal olefin sulfonates (438), blends of alpha- and internal olefin sulfonates (439), blends of branched olefin sulfonates and polyoxyalkylene alkylphenyl ether sulfates (440) or alkylaryl alkoxysulfate (441), sulfonated Friedel-Crafts alkylation products of benzene, toluene, and xylene with alpha-olefins (442), alkylalkoxyphenol sulfonates (sulfonate group on the benzene ring) (443), styrylaryloxy ether ethylsulfonates (ethylsulfonate group at end of the alkoxy chain) (444), the ethoxyethylsulfonate salt of dicyclopentadiene (445), carboxymethylated linear alcohol ethoxylates (445-448), carboxymethylated alkylphenol ethoxylates (448), carboxypropylated alcohol ethoxylates and alkylphenol ethoxylates (449), and branched (twin-tail) carboxymethylated alcohol ethoxylates (450). Increasing the length of an ethoxy chain reduces the critical micelle concentration (380, 451). Cosurfactant requirements can be minimized using a surfactant having a short branched hydrophobe or branched (vs. linear) alkyl substituent on an aromatic group (452,453) and a long ethoxy group chain (453).

Blends of surfactants optimized for seawater or reservoir brine salinity include linear alkylxylene sulfonate/alcohol ether sulfate mixtures (454,455). Alkyl- and alkylarylalkoxymethylene phosphonates (456), and amphoteric surfactants (457,458) have also been evaluated for use in surfactant flooding.

High concentrations (1-10%) of lignosulfonate have sufficient interfacial activity to increase oil recovery from unconsolidated sands (459) and have been shown to interact synergistically with petroleum sulfonates to produce an ultralow interfacial tension (460) and substantially increase oil recovery (461). Paper industry spent sulfite liquors function in a similar manner if they are not in the Ca^{+2} or Mg^{+2} forms which precipitate the petroleum sulfonates (462). Low molecular weight ethoxylated, sulfated, or sulfonated lignin phenols have been used alone in surfactant floods and found to recover more than 75% of the oil remaining after waterflood (463). The use of alkylated oxidized lignins has also been studied (464).

Of these surfactants, two classes are worthy of further note. The alpha-olefin sulfonates have been found to possess good salt tolerance, chemical stability at elevated temperatures, and appear to exhibit good oil solubilization and low interfacial tension over a wide range of temperatures (438,465). While being less salt tolerant, alkylaromatic sulfonates exhibit excellent chemical

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stability. The nature of the alkyl group, the aryl group, and the ring isomer distribution produced in the Friedel-Crafts alkylation of the aromatic compound (452,466) can all be adjusted to optimize surfactant performance under a given set of reservoir conditions.

The effect of temperature, pressure, and oil composition have all been the subjects of intensive study and only a leading reference (467) will be cited. Surfactant propagation is a critical factor in determining the economics of an oil recovery process and has been the subject of many investigations (468). Recently liquid flow microcalorimetry has been used to study surfactant adsorption and determine the adsorption isotherm and entropy of adsorption (469,470). The use of high pressure liquid chromatography to analyze low surfactant concentration core flood effluents has aided in determining which components of commercially produced surfactants most rapidly propagate through rock (471). Commercial surfactant synthesis synthesis can then be modified to maximize the content of these rapidly propagating components. Mass spectral analysis could also be applied to this problem to identify chromatographic elution peaks and reduce the need to synthesize model compounds. Surfactant retention due to partitioning into residual crude oil can be significant relative to adsorption and reduce surfactant propagation rate appreciably (472).

The use of sacrificial agents to increase the surfactant propagation rate through reservoir rock has been proposed. Lignosulfonates and chemically modified lignosulfonates (34,352-356) and sodium saccharite wastes from wood pulping (473) have been evaluated as sacrificial adsorption agents. Injection of solutions containing K^+, NH_4^+, and zirconium ions prior to surfactant injection has been found to decrease surfactant adsorption (474). This is believed to occur by clay stabilization which reduces later swelling and fines migration (processes which increase the surface area exposed to the surfactant solution). Alkaline chemicals (422,423), particularly sodium silicate (475), which precipitate in the presence of divalent metal ions can increase the surfactant propagation rate.

Intermixing of the polymer mobility control fluid with the surfactant slug can result in surfactant - polymer interactions which have a significant effect on oil recovery (476). Of course, oil - surfactant interactions have a major effect on interfacial behavior and oil displacement efficiency. The effect of petroleum composition on oil solubilization by surfactants has been the subject of extensive study (477).

Caustic flooding involves the injection of high pH agents such as sodium hydroxide, sodium carbonate or sodium silicate to generate surfactants *in situ* by interaction with organic acids present in crude oil (478,479). The crude oil acid number (the number of grams of KOH required to neutralize one gram of crude oil) should be >0.5. A number of different oil recovery mechanisms are thought to be operative: lowering of the capillary number (the ratio of viscous to capillary forces) through interfacial tension reduction, altering rock wettability (usually from oil-wet to water-wet), oil emulsification and entrapment of oil which results in a lower water mobility (in turn resulting in a greater injected water volumetric sweep efficiency), oil emulsification and entrainment in the

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flowing aqueous phase, and possibly the solubilization of rigid films that may form at the oil-water interface.

While the injected chemicals are relatively inexpensive, large quantities must be injected due to reaction of the high pH agents with reservoir clays (480) and by precipitation by divalent metal ions present in formation waters. (This precipitation has been used to reduce adverse surfactant and polymer interactions with divalent metal ions by injecting a caustic preflush prior to a micellar polymer flood (481)). The presence of a lignosulfonate (482) or a polyacrylate (483) in the alkaline injectant has been reported to reduce this precipitation. Ion exchange processes promoting solubilization of divalent metal ions (484) limit the effectiveness of preflushes injected prior to the caustic solution. Which is the best of the three major alkaline agents used in this process: sodium hydroxide, sodium carbonate, and sodium orthosilicate, is the subject of some dispute. At equivalent Na_2O levels, the three alkaline agents gave equivalent recovery of each of nine different crude oils was obtained in laboratory core floods (485). The inclusion of surfactant in the caustic formulation (surfactant enhanced alkaline flooding) can increase optimal salinity of the saline (NaOH is a salt) alkaline formulation thereby reducing interfacial tension and increasing oil recovery (481,486,487). Both nonionic and anionic surfactants have been evaluated in this application (488,489) including internal olefin sulfonates (487, 490), linear alkylxylene sulfonates (490), petroleum sulfonates (491), alcohol ethoxysulfates (487,489,492). Ethoxylated alcohols have been added to some anionic surfactant formulations to improve interfacial properties (486). The use of water thickening polymers, either xanthan or polyacrylamide to reduce injected fluid mobility mobility has been proposed for both alkaline flooding (493) and surfactant enhanced alkaline flooding (492). Crosslinked polymers have been used to increase volumetric sweep efficiency of surfactant - polymer - alkaline agent formulations (493).

While this technology appears quite promising and a field project is in progress (494), field pilot results are unavailable as yet.

Miscible gas flooding is currently the preferred technology to increase oil displacement efficiency. Supercritical CO_2 (361,495, 496) and various hydrocarbon injectants (361,497,498) undergo complicated physical interactions with crude oil that result in stripping out of the low molecular weight components (which increases oil production). In addition, the rapid or gradual development of miscibility with the remaining crude oil constituents results in mobilization of at least some of the oil. Either partial or complete miscibility with the oil may be developed depending on the nature of the injectant, crude oil properties, and reservoir conditions, particularly temperature. In addition, the interaction of the injectant with the crude oil can result in changes in rock wettability which can affect oil recovery and reduce injectivity. As noted previously, both surfactants and polymers may be used to reduce the mobility of these low viscosity injectants.

Steam flooding (397,499,500) can greatly increase the recovery of high viscosity crude oils through heat thinning processes. As noted previously, surfactants can be used to reduce the mobility of

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the high temperature steam. Interfacial tension reduction promoted by steam foaming agents can also increase oil recovery (see Chapter 18). Since heavy crude oils have relatively high acid numbers, it is not surprising that addition of alkaline agents to high temperature steam can increase recovery of these oils (501,502). The in situ combustion method of enhanced oil recovery through air injection (397,503,504) is an exceeding complex process chemically. However, because little work has been done on the effect of chemical additives to oil recovery efficiency, this process will not be discussed herein.

Summary and Conclusions

Current and projected oil prices have resulted in oil recovery processes based on organic chemicals as the primary oil recovery agent being uneconomic. As a result, both R&D and commercial activities have been redirected to the use of relatively low quantities of chemicals to increase the effectiveness of waterflooding, supercritical CO_2 and gas injection EOR, and steam flooding. The recent emphasis has been on the use of chemicals to increase the volumetric sweep efficiency of these EOR processes. While a number of crosslinked polymer systems have been shown to be effective in substantially reducing the permeability of thief zones, methods for achieving greater treatment radii (from the injection well) are desirable. Experience with surfactant foams or dispersions as mobility control agents is more limited so the potential of this technology in economically improving volumetric sweep efficiency is less clear. Additional field tests are needed.

Literature Cited

1. Chatterji, J.; Borchardt, J.K. J. Pet. Technol., 1981, 32 2042-2056.
2. Chilingarian, G.V.; Vorabutr, P. Drilling and Drilling Fluids, Elsevier Scence Publishing Co., Inc. New York, 1981.
3. Clark, R.K.; Nahm, J.J. in Kirk-Othmer Encylcopedia of Chemical Technology, M. Grayson, Ed.; John Wiley & Sons, New York, 1982, 3rd Edit., Vol. 17, pp. 143-167.
4. Saunders, G.C. West German Patent 2 949 741, 1980.
5. Bruton, J.R. World Oil, 1979, 189 (7), 71-4.
6. Poole, G. Oil Gas J., 1981, 79 (28), 159, 161.
7. Ezzat, A.M.; Augsburger, J.J.; Tillis, W.J. J. Pet. Technol., 1988, 40, 491-8.
8. Doty, P.A. SPE Drilling Eng., 1986, 1, 17-30.
9. Morgenthaler, L.M. SPE Production Eng., 1986, 1, 432-436.
10. Borchardt, J.K.; Rao, S.P. U.S. Patent 4 554 081, 1985.
11. House, R.F.; Hoover, L.D. French Patent 2 488 325, 1982.
12. Socha, G.E. U.S. Patent 4 373 959, 1983.
13. Pelezo, J.A.; Corbett, Jr., G.E. French Patent 2 578 549, 1986.
14. Walker, T.E.; Strassner, J.E . West German Patent 3 521 309, 1985.
15. Miura, M.; Harada, E.; Domon, F. Japan Patent 62 153 382, 1987.

PHARAOH, EX. 1014
P. 37

16. Salamone, J.C.; Clough, S.B.; Salamone, A.B.; Reid, K.I.G.; Jamison, D.E. Soc. Pet. Eng. J., 1982, 22, 555 (1982).
17. Haack, T.; Shaw, D.A.; Greenley, D.E. Oil Gas J., 1986, 84 (1), 82.
18. Vio, L.; Meunier, G. French Patent 2 552 441, 1985.
19. Meltzer, Y.L. Water-soluble Polymers: Technology and Applications, Chem. Process Rev., Noyes Data Corp., Park Ridge, N.J., 1972, pp. 17-19.
20. Allan, T.O.; Roberts, A.P. Production Operations, 2nd edit., Oil & Gas Consultants, Inc., Tulsa, 1982, Volumes 1 and 2.
21. Smith, D.K. Cementing, Society of Petroleum Engineers, Dallas, 1974, Monograph No. 4
22. Smith, R.C. Oil Gas J., Nov. 1, 1982, 72-5.
23. Carter, L.G.; Evans, G.W. J. Pet. Technol., 1964, 16, 157-60.
24. Brice, Jr., J.W.; Holmes, B.C. J. Pet. Technol., 1964, 16, 503-8.
25. Keller, S.R.; Crook, R.J.; Haut, R.C.; Kulakofsky, D.S. J. Pet. Technol., 1987, 39, 955-60.
26. Crook, R.J.; Keller, J.; Wilson, M.A. J. Pet. Technol., 1987, 39. 961-6.
27. Cheung, P.R.; Beirute,, R.M. J. Pet. Technol., 1985, 37 (6), 1041-1048.
28. Griffin, T.J.; Spangle, L.B.; Nelson, E.B. Oil Gas J., June 25, 1979, 143-151.
29. Harms, W.M.; Febus, J.S. J. Pet. Technol., 1985, 37 (6), 1049-1057.
30. Smith, R.C.; Powers, C.A.; Dobkins, C.A. J. Pet. Technol., 1980, 32, 1438-44.
31. Harms, W.M.; Lingenfelter, J.T. Oil Gas J., Feb. 2, 1981, 59-66.
32. Bruckdorfer, R.A.; Coleman, S.E. U.S. Patent 4 635 724, 1987.
33. Cole, R.C.; Borchardt, J.K. Drilling, 1985 (4), 44.
34. Borchardt, J.K. Encyclopedia of Science and Engineering, John Wiley & Sons, New York, 1987, Volume 10, 328-369.
35. Mondshine, T.C. U.S. Patent 4 175 042, 1979.
36. Saucier, R.J. J. Pet. Technol., 1974, 26, 205-12.
37. Pober, K.W.; Huff, H.M.; Darlington, R.K. J. Pet. Technol., 1983, 35, 2185.
38. Borchardt, J.K. U.S. Patent 4 524 003, 1985.
39. Norton, C.J.; Falk, D.D. U.S. Patent 3 919 092, 1975.
40. Borchardt, J.K. U.S. Patent 4 508 629, 1985.
41. Knight, R.K. U.S. Patent 4 039 028, 1977.
42. Kovacs, P. Food Technol., 1973, 27, 26.
43. Rocks, J.K., Food Technol., 1971, 25, 22.
44. Hong, K.C.; Milhone, R.S. J. Pet. Technol., 1977, 29, 1657.
45. Muecke, T.W. J. Pet. Technol., 1974, 26, 157.
46. Rensvold, R.F. Soc. Pet. Eng. J., 1983, 23, 238.
47. Penberthy, Jr., W.L.; Shaughnessy, C.M.; Gruesbeck, C.; Salathiel, W.M. J. Pet. Technol., 1978, 30, 845.
48. Young, B.M.; Totty, K.D. U.S. Patent 3 404 735, 1968.
49. Yano, A.; Yasue, T. Japan Kokai Tokkyo Koho 63 23 922, 1988; Chem. Abs., 1988, 109, 232346p.
50. Burger, J.; Gadelle, C.; De Chou, J.S. French Patent 2 575 500, 1986.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

51. Suman, G.O. World Oil, Nov. 1974, 179, 63.
52. Murphey, J.R. U.S. Patent 4 259 205, 1981.
53. Underdown, D.R.; Das, K. J. Pet. Technol.,1985, 37, 2006-12.
54. Watkins, D.R.; Kalfayan, L.J.; Watanabe, D.J.; Holm, J.A. SPE Production Eng., 1986, 1, 471-477.
55. Davies, D.R.; Richardson, E.A.; Van Zanten, M. Eur. Pat. Appl. 30 753, 1981.
56. Economides, M.J.; Nolte, K.G., Eds. Reservoir Stimulation, Schlumberger Educational Services, Houston, 1987.
57. Githens, C.J.; Burnham, J.W. Soc. Pet. Eng. J., 1977, 17, 5.
58. Wu, S.N. Eur. Pat. Appl. 163 271, 1984.
59. Clark, P.E.; Underwood, J.S.; Steiner, T.M. Canadian Patent 1 090 112, 1977.
60. N.R. Morrow and J.P. Heller in Developments in Petroleum Science; Donaldson, E.C.; Chilingarian, G.V.; Yen, T.F. Eds., Elsevier, Amsterdam, 1985, Volume 17A, pp. 47-74.
61. Barker, S.A.; Stacey, M.; Zweifel, G. Chem. Ind. London, 1957, 330.
62. Dill, W.R. U.S. Patent 4 466 893, 1984.
63. Stauffer, K.B. in Handbook of Water-Soluble Gums and Resins; Davidson, R.L., Ed.; McGraw-Hill, New York, 1980, pp. 11/1-11/31.
64. Nierode, D.E.; Kehn, D.M.; Kruk, K.F. U.S. Patent 3 934 651, 1976.
65. Almond, S.W.; Conway, M.W. U.S. Patent 4 553 601, 1985.
66. Brode, G.L.; Stanley, J.P.; Partain, III, E.M. U.S. Patent 4 579 942, 1986.
67. Roll, D.L.; Himes, R.; Ewert, R.; Doerksen, J. SPE Production Eng., 1987, 2, 291-6.
68. Constein, V.G.; King, M.T. U.S. Patent 4 541 935, 1985.
69. Prikryl, J.; Oliva, L.; Kubat, V. Czech. Patent 235 624, 1986.
70. Lundberg, R.D.; Peiffer, D.G.; Sedillo, L.P.; Newlove, J.C. U.S. Patent 4 579 671, 1986.
71. Burnham, J.W.; Tiner, R.L. U.S. Patent 4 200 539 (1980).
72. Griffin, Jr., T.J. U.S. Patent 4 174 283, 1979.
73. Zigrye, J.L.; Whitfill, D.L.; Sievert, J.A. J. Pet. Technol., 1985, 37, 315.
74. Penny, G.S.; Conway, M.W.; Lee, W. J. Pet. Technol., 1985, 37, 1071.
75. Gulbis, J. in reference 56, p. 4-11.
76. Anderson, R.W.; Phillips, A.M. J. Pet. Technol., 1988, 40, 223-8.
77. Needham, R.B.; Thomas, C.P.; Wier, D.R. U.S. Patent 4 231 428, 1980.
78. Graham, J.W.; Sinclair,R.A. U.S. Patent 4 585 064, 1986.
79. Rummo, G.J. Eur. Pat. Appl. 92 756, 1983.
80. Kucera, C.H. British Patent 2 108 112, 1983.
81. Harris, L.E. U.S. Patent 4 324 668, 1982.
82. Reference 75, pp. 4-5, 4-6.
83. Gregory, G.J. Oil Gas J., 1982, 83 (37), 80.
84. Payne, K.L. U.S. Patent 4 579 670, 1986.
85. Misak, M.D. U.S. Patent 3 922 173, 1975.
86. Reference 75, p. 4-9.
87. Malone, T.R.; Foster, J., T.D.; Executrix, S.T. U.S. Patent 4 290 899, 1981.

PHARAOH, EX. 1014
P. 39

88. Rygg, R.H. British Patent 2 090 308, 1982.
89. Reference 75, p. 4-9 and references therein.
90. Millar, S.W. U.S. Patent 4 552 591, 1985.
91. Sortwell, E.T.; Solovinski, M.; Mikkelsen, A.R. U.S. Patent 4 507 450, 1985.
92. Hoover, L.D.; House, R.F. British Patent 2 070 611, 1981.
93. House, R.F.; Hoover, L.D. French Patent 2 488 325, 1982.
94. Bayerlein, F.; Habereder, P.P.; Keramaris, N.; Kottmair, N.; Kuhn, M. French Patent 2 513 265, 1983.
95. Mosier, B.; McCrary, J.L.; Guilbeau, K.G. U.S. Patent 4 530 601, 1982.
96. Reference 75, p. 4-10.
97. Clark, H.B.; Pike, M.T.; Rengel, G.L. J. Pet. Technol., 1982, 34, 1565-9.
98. Penny, G.S.; et. al. U.S. Patent 4 425 242, 1984.
99. Hirt, D.E.; Prud'homme, R.K., Rebenfeld, L. J. Dispersion Sci. Technol., 1987, 8, 55-73.
100. Reference 75, pp. 4-7, 4-8 and references therein.
101. Black, H.N.; Langsford, R.W. J. Pet. Technol., 1982, 34, 135-40.
102. Reidenbach, V.G.; Harris, P.C.; Lee, Y.N.; Lord, D.L. SPE Production Eng., 1986, 1, 31-41.
103. Harris, P.C. SPE Production Eng., 1987, 2, 89-94.
104. Ward, V.L. SPE Production Eng., 1986, 1, 275-8.
105. Garbis, S.J.; Taylor III, J.L. SPE Production Eng., 1986, 1, 351-358.
106. Williams, R.B.; Gidley, J.L.; Schechter, R.S. Acidizing Fundamentals, Society of Petroleum Engineers, Dallas, SPE Monograph No. 6, 1979.
107. Hung, K.M.; Hill, A.D.; Sepehrnoori, K. J. Pet. Technol., 1989, 41, 65-6.
108. Reference 106, p. 97.
109. Thomas, R.L. U.S. Patent 4 151 878, 1979.
110. Thomas, R.L.; Suby, F.A. U.S. Patent 4 160 483, 1979.
111. Kunze, K.R.; Shaughnessy, C.A. Soc. Pet. Eng. J., 1983, 23, 65-72.
112. Blumer, D.J. U.S. Patent 4 703 803, 1987.
113. Dill, W.R. West German Patent 2 925 748, 1980.
114. Nehmer, W.L. British Patent Appl. 2 163 790, 1986.
115. Norman, L.R.; Conway, M.W.; Wilson, J.M. J. Pet. Technol., 1984, 36, 2011.
116. Roper, L.E.; Swanson, B.L. U.S. Patent 4 205 424, 1980.
117. Burns, L.D.; Stahl, G.A. U.S. Patent 4 690 219, 1987.
118. Haltmar, W.C.; Lacey, E.S. U.S. Patent 4 207 946, 1980.
119. Engelhardt, F.; Schmitz, H.; Hax, J.; Gulden, W. European Patent 44 508, 1982.
120. Engelhardt, F.; Piesch, S.; Balzer, J.; Dawson, J.C. PCT Internat. Patent Appl. 82 02 252 (1982).
121. Swanson, B.L. Eur. Patent Appl. 7 012, 1980.
122. Costanza, J.R.; DeMartino, R.N.; Goldstein, A.M. U.S. Patent 4 057 509, 1977.
123. Hoefner, M.L.; Fogler, H.S.; Stenius, P.; Sjoblom, J. J. Pet. Technol., 1987, 39, 203-8.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

124. Hoefner, M.L., Fogler, H.S. Chem. Eng. Prog., 1985, 40.
125. Ford, W.G.F. J. Pet. Technol., 1981, 33, 1203-1210.
126. Khasaev, A.M.; Sadykhov, M.G.; Kurbanova, Kh. G. Azerb. Neft. Khoz., 1978, 32.
127. Jones, W.L. British Patent 2 141 731, 1987.
128. Reference 106, p. 97.
129. Crema, S.C. U.S. Patent 4 676 916, 1987.
130. Walton, W.B. U.S. Patent 4 541 483, 1985.
131. Hall, B.E. J. Pet. Technol., 1975, 27, 1439-42.
132. Walsh, M.P.; Lake, L.W., Schechter, R.S. J. Pet. Technol., 1982, 34, 2097-2112.
133. Dria, M.A.; Schechter, R.S.; Lake, L.W. SPE Production Eng., 1988, 3, 52-62.
134. Labrid, J.C. Soc. Pet. Eng. J., 1975, 15, 117-28.
135. Crowe, C.W. J. Pet. Technol., 1986, 38, 1234-40.
136. Street, Jr., E.H. U.S. Patent 4 167 214, 1979.
137. Dill, W.R.; Walker, M.L.; Ford, W.G.F. U.S. Patent 4 679 631, 1987.
138. Nehmer, W.H.; Coffey, M.D. British Patent Appl. 2 158 487, 1985.
139. Walker, M.L.; Ford, W.G.F.; Dill, W.R.; Gdanski, R.D. U.S. Patent 4 683 954, 1987.
140. Reference 106, pp. 101-102.
141. Brannon, D.H.; Netters, C.K.; Grimmer, P.J. J. Pet. Technol., 1987, 39, 931-42.
142. Reference 106, p. 100.
143. Clementz, D.M.; Patterson, D.E.; Aseltine, R.J.; Young, R.E. J. Pet. Technol., 1982, 34, 2087-96.
144. Taggart, D.L.; Heffern, E.W. U.S. Patent 4 690 217, 1987.
145. Craig, Jr., F.F. The Reservoir Engineering Aspects of Water Flooding, Society of Petroleum Engineers, Dallas, Monograph No.3, 1971, pp. 19-22.
146. Dymond, P.F.; Spurr, P.R. SPE Reservoir Eng., 1988, 3, 165-74.
147. Scheuerman, R.F. SPE Production Eng., 1988, 3, 15-21.
148. Reference 106, pp. 92-95.
149. Wu, Y. British Patent Appl. 2 082 589, 1982.
150. Tuttle, R.N. J. Pet. Technol., 1987, 39, 756-62.
151. Wilhelm, S.M.; Kane, R.D. J. Pet. Technol., 1986, 38, 1051-61.
152. Tate, J.F.; Maddox, Jr., J.; Shupe, R.D. Canadian Patent 1 051 649, 1979.
153. Redmore, D.; Outlaw, B.T. U.S. Patent 4 315 087, 1982.
154. Patton, C.C. J. Pet. Technol., 1988, 40, 1123-6.
155. Khilar, K.C.; Fogler, H.S. Soc. Pet. Eng. J., 1983, 23, 55-64.
156. Khilar, K.C.; Fogler, H.S. J. Colloid Interface Sci., 1984, 101 (1), 214-24.
157. Kia, S.F.; Fogler, H.S.; Reed, M.G.; Vaidya, R.N. SPE Production Eng., 1987, 2, 277-83.
158. Sydansk, R.D. J. Pet. Technol., 1984, 36, 1366-74.
159. Reed, M.G. J. Pet. Technol., 1972, 24, 860-64.
160. Veeley, C.D. J. Pet. Technol., 1969, 21, 1111-18.
161. Peters, F.W.; Stout, C.M. J. Pet. Technol., 1977, 29, 187-94.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

162. Muecke, T.W. J. Pet. Technol., 1979, 31, 144-150.
163. Gruesbeck,C.; Collins, R.E. Soc. Pet. Eng. J., 1982, 22, 847-856.
164. Kia, S.F.; Fogler, H.S.; Reed, M.G. J. Colloid Interface Sci., 1987, 118, 158-68.
165. Reference 20, Volume 2, p. 99.
166. Leone, J.A.; Scott, E.M. SPE Reservoir Eng., 1988, 3, 1279-86.
167. Broaddus, G. J. Pet. Technol., 1988, 40, 685-7.
168. Blair, Jr., C.M. U.S. Patent 4 337 828, 1982.
169. Blair,Jr., C.M.; Stout, C.A. Oil Gas J., May 20, 1985, 83 (55). 133.
170. Cusack, F.; Lappin-Scott, H.M.; Costerton, J.W. Oil Gas J., Nov. 9, 1987, 85, 87.
171. Hensel, Jr., W.N.; Sullivan, R.L.; Stallings, R.H. Pet. Eng. Int., 1981(5), 155.
172. Anderson, W.G., J. Pet. Technol., 1987, 39, 1453-67.
173. Anderson, W.G., J. Pet. Technol., 1986, 38, 1125-44. 173. Reference 144, pp. 19-21.
174. Hjelmeland, O.S.; Larrondo, L.E. SPE Reservoir Engr., 1986, 1, 321-8.
175. Owens, W.W.; Archer, D.L. J. Pet. Technol., 1971, 23, 873-8.
176. Morrow, N.R.; Mungan, , N. Rev. Inst. Franc. Petrole, 1971, 629-50.
177. Treiber, L.E.; Archer, D.L.; Owens, W.W. Soc. Pet. Eng. J., 1972, 12, 531-40.
178. Elphingstone, E.A.; McLaughlin; H.C.; Smith, C.W. Canadian Patent 1 070 936, 1980.
179. Downs, S.L.; Gohel, M.G. J. Pet. Technol., 1974, 26, 557-70.
180. Peddycoart, L.R. Oil Gas J., Feb. 4, 1980, 78, 52.
181. Weaver, J.D.; Harris, L.E.; Harms, W.M. U.S. Patent 4 460 627, 1984.
182. Geosciences Research for Oil and Gas Discovery and Recovery, U.S. Dept. of Energy, Washington, D.C., March, 1987.
183. Oil Gas J., December 26, 1988, 86 (52), 49.
184. Smith, D.H. Surfactant-Based Mobility Control - Progress in Miscible-Flood Enhanced Oil Recovery, ACS Symposium Series No. 373, American Chemical Society, Washington, D.C., 1988.
185. Neale, R.R.; Doe, P.H. J. Pet. Technol., 1987, 39, 1503-7.
186. Kessel, D.G.; Volz, H.; Maitin, B. Proc. World Pet. Congr., 1977, 12th (Vol. 3), 355-64.
187. Ling, T.F.; Lee, H.K.; Shah, D.O. Spec. Publ. - R. Soc. Chem., 1987, 59 (Ind. Appl. Surfactants), 126-78.
188. Miller, C.A.; Qutubuddin, S. Surfactant Sci. Ser., 1987, 21 (Interfacial Phenom. Apolar Media), 117085.
189. Tomich, J.F.; Laplante, D.L.; Snow, T.M. Proc. World Pet. Congr., 1977, 12th (Vol. 3), 337-46.
190. Pet. Eng. Int., May, 1988. 79-81.
191. Leighton, A.J.; Wayland, J.R. J. Pet. Technol., 1987, 39, 129-36.
192. Holm, L.W.; Josendal, V.A. Soc. Pet. Eng. J., 1982, 22, 87-98.
193. Martin, R.L.; Braga, T.G. Mater. Perform., 1987, 26, 16-22.
194. Technical Constraints Limiting Application of Enhanced Oil

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

Recovery Techniques to Petroleum Production in the United States, U.S. Dept. of Energy, DOE/BETC/RI-83/9 (DEB4003910), Jan., 1984.
195. Reference 34, pp. 350-351.
196. Reference 34, p. 344.
197. Norton, C.J.; Fak, D.O. U.S. Patent 4 343 363, 1982.
198. Sandiford, B.B.; Dovan, H.T.; Hutchins, R.D. U.S. Patent 4 413 680, 1983.
199. Prud'homme, R.K.; Uhl, J.T.; Poinsatte, J.P.; Halverson, F. Soc. Pet. Eng. J., 1983, 23, 804.
200. Wilhite, G.P.; Jordan, D.J. Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 1981, 22 (2), 53.
201. Sloat, B. Pet. Eng. Int., 1977, 20.
202. Dovan, H.T.; Hutchins, R.D. SPE Res. Eng., 1987, 2, 177-188.
203. Norton, C.J. Canadian Patent 1 217 629, 1987.
204. Hanlon, D.J.; Almond, S.W. European Patent Appl. 161 858,1985.
205. Prud'homme, R.K.; Uhl, J.T. Proc. Fourth Joint Symposium on Enhanced Oil Recovery, Tulsa, Okla., Apr. 15-18, 1984, Paper No. SPE/DOE 12640 .
206. Jordan, D.J.; Green, D.W.; Terry, R.E.; Willhite, G.P. Soc. Pet. Eng. J., 1982, 22, 463.
207. Routson, W.G. U.S. Patent 3 687 200, 1972.
208. Mumallah, N.A. SPE Reservoir Eng., 1988, 3, 243.
209. Sydansk, R.D. U.S. Patent 4 744 418, 1988.
210. Moradi-Araghi, A.; Doe, P.H. SPE Reservoir Eng., 1987, 2, 189-93.
211. Nanda, S.K.; Kumar, R.; Sindhwani, K.L.; Goyl, K.L. ONGC Bull., 1986, 23, 175-85.
212. Sydansk, R.D. U.S. Patent 4 723 605, 1988.
213. Aslam, S.; Vossoughi, S.; Whillhite, G.P. Chem. Eng. Commun., 1986, 48, 287-301.
214. Hyang, C-G.; Green, D.W.; Willhite, G.P. SPE Reservoir Engr., 1986, 1, 583-592.
215. Vio, L. U.S. Patent 4 155 405, 1979.
216. Sullivan, E.J.; Jones, G.D. U.S. Patent 4 125 478, 1978.
217. Pliny, R.J.; Regulski, T.W. European Patent 5 835, 1979.
218. Sidorov, I.A.; et. al. USSR Patent 1 040 118, 1983.
219. Ech. E.; Lees, R.D. U.S. Patent 4 579 667, 1986.
220. Ryles, R.G.; Robustelli, A.G.; Cicchiello, J.V. European Patent Appl. 200 062, 1986.
221. Ryles, R.G.; et. al. European Patent Appl. 273 210, 1988.
222. Falk, D.O. U.S. Patent 4 688 639, 1987.
223. Hessert, J.E.; Johnston, Jr., CC. U.S. Patent 4 110 230, 1978.
224. Abdo, M.K. U.S. Patent 4 574 887, 1986.
225. Hurd, B.G. U.S. Patent 3 581 824, 1971.
226. Colegrove, G.T. U.S. Patent 4 157 322, 1979.
227. Clear, E.E. U.S. Patent 4 321 968, 1982.
228. Dasinger, B.L.; McArthur, H.A.I. European Patent Appl. 251 638, 1988.
229. Sampath, K. U.S. Patent 4 640 358, 1987.
230. McLaughlin, H.C. U.S. Patent 3 334 689, 1967.
231. Borchardt, J.K. U.S. Patent 4 439 334, 1984.

PHARAOH, EX. 1014
P. 43

232. Argabright, P.A.; Rhudy, J.S. U.S. Patent 4 503 909, 1985.
233. Seright, R.S. Proc. 1989 SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers, Dallas, 1989, pp. 389-402.
234. Felber, B.J.; Dauben, D.L. Soc. Pet. Eng. J., 1977, 17, 391.
235. Felber, B.J.; Christopher, C.A. U.S. Patent 4 428 429, 1984.
236. Lawrence, D.D.; Felber, B.J. U.S. Patent 4 275 789, 1981.
237. Whitworth, A.J.; Tung, S.Y.S.; Hajto, E.A. U.S. 3 686 372, 1972.
238. Allan, B.W. U.S. Patent 4 299 690, 1981.
239. Soreau, M.; Siegel, D. French Patent 2 551 451, 1985.
240. Navritil, M.; Batycky, J.P.; Sovak, M.; Mitchell, M.S. Canada Patent 1 187 404, 1985.
241. Balitskaya, Z.A.; et. al. U.S.S.R. Patent 878 904, 1981.
242. Hess, P.M. J. Pet. Technol., 1980, 32, 1834-42.
243. Navritil, M.; Mitchell, M.S.; Sovak, M. U.S. Patent 4 663 367, 1987.
244. Navritil, M.; Mitchell, M.S.; Sovak, M. Canada Patent 1 217 932, 1987.
245. Marocco, M.L. U.S. Patent 4 664 194, 1987.
246. Chung, H.S.; Sampath, K.; Schwab, F.C. U.S. Patent 4 653 585, 1987.
247. Harwell, J.H.; Scamehorn, J.F. U.S Patent 4 745 976, 1988.
248. Schievelbein, V.H.; Kudchadker, M.V.; Varnon, J.E.; Whittington, L.E. U.S. Patent 4 161 982, 1979.
249. Schievelbein, V.H. U.S. Patent 4 161 983, 1979.
250. Varnon, J.E.; Schievelbein, V.H.; Kudchadker, M.V.; Whittington, L.E. U.S. Patent 4 161 218, 1979.
251. Schievelbein, V.H.; Park, J.H. U.S. Patent 4 160 480, 1979.
252. Stahl, G.A.; Schulz, D.N.; Eds. Water Soluble Polymers for Petroleum Recovery, Plenum, New York, 1988.
253. Crafts, B.C.; Hawkins, M.F. Applied Petroleum Reservoir Engineering, Prentice-Hall, New York, 1959.
254. Reference 145, pp. 45-7.
255. Sandiford, B.B.; Keller, Jr., H.F. U.S. Patent 2 827 964, 1958.
256. Sandiford, B.B.; Keller, Jr., H.F. U.S. Patent 3 116 791, 1964.
257. Sandiford, B.B. U.S. Patent 3 308 885, 1967.
258. Sandiford, B.B. J. Pet. Technol., 1964, 16, 917.
259. Pye, D.J. J. Pet. Technol., 1964, 16, 911.
260. Chang, H.I. J. Pet. Technol., 1978, 30, 1113-1128.
261. Smith, R.V.; Burtch, F.W. Oil Gas J., Nov. 24, 1980, 78, 127.
262. Lorenz, P.B.; Trantham, J.C.; Zornes, P.R.; Dodd, C.G. SPE Reservoir Eng., 1986, 1, 341-53.
263. Jones, D.M.; Walters, K.; Williams, P.R. Rheological Acta, 1986, 26, 20.
264. Cahalan, P.T.; Peterson, J.A.; Arndt, D.A. U.S. Patent 4 053 699, 1977.
265. Carter, W.H.; Christopher, C.A.; Jefferson, T. West German Patent 2 809 136, 1979.
266. Sandford, P.A.; Laskin,A. Eds; Extracellular Microbial Polysaccharides, ACS Symposium Series No. 45; American Chemical Society: Washington, D.C., 1977.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

267. Abdo, M.K., U.S. Patent 3 771 462, 1973.
268. Rhone-Poulenc Specialties Chemique, Japan Kokai Tokkyo Koho 62 39 643, 1987; Chem. Abstr., 1987, 107, 42858u.
269. Casad, B.M.; Conley, D.; Ferrell, H.H.; Stokke, O.M. U.S. Patent 4 212 748, 1980.
270. Bragg, J.R. British Patent Application 2 115 430, 1983.
271. Rinaudo, M.; Milas, M. Int. J. Biol. Macromol., 1980, 2, 45.
272. Holding, T.J.; Pace, J.W. British Patent 2 065 689, 1981.
273. Kohler, N.; Longchamp, D.; Thery, M. J. Pet. Technol., 1897, 39, 835-43.
274. Stokke, O.M. U.S. Patent 4 165 257, 1979.
275. Knight, B.L.; Jones, S.C.; Parsons, R.W. Soc. Pet. Eng. J., 1974, 14, 643.
276. Grollman, U.; Schnable, W., Polymer Degradation and Stability, Applied Science Publishers, London, 1982, pp. 353-362..
277. Wellington, S.L. Soc. Pet. Eng. J., 1983, 23, 901-12.
278. Cadmus, M.C.; et. al. Appl. Environ. Microbiol., Aug. 1982, 5.
279. Lee, S.L. West German Patent 2 715 026, 1977.
280. Philips, C.J. European Patent 106 666, 1984.
281. F. Dawans, Binet, D.; Kohler, N.; Quang, D.V. U.S. Patent 4 454 620, 1984.
282. Wellington, S.L. Canadian Patent 1 070 492, 1980.
283. Kanda, S.; Kawamura, G. U.S. Patent 4 481 316, 1985.
284. Kanda, S.; Kawamura, G. Japan Kokai Tokkyo Koho 61 275 337, 1986.
285. Niita, A.; Arai, T.; Funato, R.; Sato, T. Japan Kokai Tokkyo Koho 62 184 048, 1987.
286. Niita, A.; Arai, T.; Funato, R.; Sato, T. Japan Kokai Tokkyo Koho 62 184 047, 1987.
287. Niita, A.; Arai, T.; Funato, R.; Sato, T. Japan Kokai Tokkyo Koho 62 177 052, 1987.
288. Nakanishi, Y. Japan Kokai Tokkyo Koho 62 277 407, 1987.
289. Judson, C.P. European Patent Application 196 199, 1986.
290. Nitta, A.; Ito, Y.; Nitta, A. Japan Kokai Tokkyo Koho 61 136 545, 1986.
291. Contat, F.; Boutin, J. European Patent Application 241 340, 1987.
292. Chen, C.S.H.; Sheppard, E.W. J. Macromol. Sci. Chem. Part A, 1979, 239.
293. Chen, C.S.H.; Sheppard, E.W. Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem., 1978, 19 (1), 424-9.
294. Wernau, W.C. West German Patent 2 848 984, 1979.
295. Holzwarth, G.M. European Patent 103 483, 1984.
296. Phillips, J.C.; Miller, J.W.; Wernau, W.C.; Tate, B.E.; Auerbach, M.H. Soc. Pet. Eng. J., 1985, 25, 594.
297. Donche, A.F. World Biotech Rep., 1985, 1, 429-36.
298. Meldrum, I.G. Comm. Eur. Communities, {Rep.} EUR, 1985, Vol. 2, 776-83.
299. Doster, M.S.; Nute, A.J.; Christopher, C.A. U.S. Patent 4 457 372, 1984.
300. Rinaudo, M.; Vincendon, M. Carbohydr. Polym., 1982, 2, 135.
301. Hitzman, G.O. U.S. Patent 4 096 073, 1978.
302. Linton, J.D.; Evans, M.W.; Godley, A.R. European Patent 135 953, 1985.

American Chemical Society
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PHARAOH, EX. 1014
P. 45

303. Thompson, B.G.; Jack, T.R. U.S. Patent 4 561 500, 1985.
304. Savins, J.G. U.S. Patent 4 079 544, 1978.
305. Lindoerfu, R.; et. al. West German Patent 3 643 467, 1988.
306. Vanderslice, R.W.; Shanon, P. European Patent Application 211 288, 1987.
307. Graaflund, T. European Patent Application 237 132, 1987.
308. Frank, S.; Coscia, A.T.; Schmitt, J.M. U.S. Patent 4 439 332, 1984.
309. Borchardt, J.K. U.S. Patent 4 439 334, 1984.
310. Klein, J.; Heitzman, R. Makromol. Chem., 1978, 179, 1895.
311. Halverson, F.H.; Lancaster, J.E. Macromolecules, 1985, 18, 1139.
312. Boutin, J.; Contat, F. French Patent 2 495 217, 1982.
313. Southwick, J.G.; Manke, C.W. SPE Reservoir Eng., 1988, 3, 1193-1201.
314. Prud'homme, R.K. SPE Reservoir Eng., 1986, 1, 272-6.
315. Munk, P.; Aminabhavi, T.M.; Williams, P.; Hoffman, D.E.; Chmelir,M. Macromolecules, 1980, 13, 871-5.
316. Muller, G.; Laine, J.P.; Fenyo, J.C. J. Polym. Sci. Polym. Chem. Ed., 1979, 17, 659.
317. Ward, J.S.; Martin, F.D. Soc. Pet. Eng. J., 1981, 21, 623.
318. Chen, G.S.; Neidlinger, H.H.; McCormick, C.L. Prepr. Pap. Nat. Meet. Div. Pet. Chem. Am. Chem. Soc., 1984, 29 (4), 1147.
319. Ryles, R.G. SPE Reservoir Eng., 1988, 3, 23-34.
320. Moradi-Araghi, A.; Doe, P.H. SPE Reservoir Eng., 1987, 2, 189-98.
321. Szabo, M. J. Pet. Technol., 1979, 31, 553.
322. Szabo, M. J. Pet. Technol., 1979, 31, 561.
323. McCormick, C.L.; Johnson, C.B. Biotechnol. Mar. Polysaccharides, Proc. Annu. MIT Sea Grant Coll. Program Lect. Semin., 3rd, 1984 (Pub. 1985), 213-48.
324. McCormick, C.L. J. Macromol. Sci. Chem. Part A. 1985, 22, 955.
325. McCormick, C.L., Hester, R.D.; Neidlinger, H.H.; Wildman, G.C. BETC Prog. Rev., 1979, 20, 61.
326. McCormick, C.L., Blackmon, K.R.; Elliott, D.L. Prepr. Pap. Nat. Meet. Div. Pet. Chem. Am. Chem. Soc., 1984, 29 (4), 1159.
327. Stahl, G.A. U.S. Patent 4 644 020, 1987.
328. Doe, P.H.; Moradi-Araghi, A.; Shaw, J.E.; Stahl, G.A. SPE Res. Eng., 1987, 2, 461.
329. Ching, T.Y. West German Patent 3 627 456, 1987.
330. Ryles, R.G. European Patent Application 233 533, 1987.
331. Engelhardt, P.; Greiner, U.; Schmitz, H.; Gulden, W.; von Halasz, S.P. West German Patent 3 220 503, 1983.
332. Ito, Y.; Niuta, A.; Sudo, Y.; Hayashi, K. Japan Kokai Tokkyo Koho 62 15 279, 1987.
333. Wu, M.M.; Ball, L.E. U.S. Patent 4 540 498, 1985.
334. Martin, F.D.; Hatch, M.J.; Abouelezz, M.; Oxley, J.C. Polym. Mater. Sci. Eng., 1984, 51, 688.
335. Ball, L.E.; Griffin, L.M.; Antloger, K.M.; Nemacek, A.L. U.S. Patent 4 653 584, 1987.
336. Pledger, Jr., H.; Meister, J.J.; Hogen-Esch, T.E.; Butler, G.B. Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 1981, 22 (2), 72.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

337. Neidlinger, H.H.; McCormick, C.L. Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 1979, 20 (1), 901.
338. Meister, J.J.; et. al. Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem., 1984, 25 (1), 266.
339. Schulz, D.N.; Kaladas, D.A.; Maurer, J.J.; Bock, J.; Pace, S.J.; Schulz, W.W. Polymer, 1987, 28, 2110-15.
340. Bock, J.; Siano, D.B.; Turner, R. U.S. Patent 4 694 046, 1987.
341. Bock, J.; Valint, P.L. U.S. Patent 4 730 028, 1988.
342. Bock, J.; Valint, P.L.; Pace, S.J. U.S. Patent 4 702 314, 1987.
343. Bock, J.; Pace, S.J.; Schulz, D.N. U.S. Patent 4 709 759, 1987.
344. Evani, S.; Rose, G.D. Polym. Mat. Sci. Eng., 1987, 57, 477-81.
345. Landoll, L.M. Netherlands Patent 80 03 241, 1980.
346. Borchardt, J.K.; Brown, D.L. U.S. Patent 4 409 110, 1983.
347. Borchardt, J.K.; Brown, D.L. Oil Gas J., Sept. 10, 1984, 89, pp. 150,152,154,156.
348. Shuler, P.J.; Kuehne, D.L.; Uhl, J.T.; Walkup, Jr., G.W. SPE Reservoir Engr., 1987, 2, 271-80.
349. Willhite, G.P.; Dominguez, J.G. in Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press, Washington, D.C., 1977, pp. 511-553.
350. Friedmann, F. SPE Reservoir Eng., 1986, 1, 261-271.
351. Cohen, Y.; Christ, F.R. SPE Reservoir Eng., 1986, 1, 113-18.
352. Hong, S.A.; Bae, J.H. SPE Reservoir Eng., 1987, 2, 17-27.
353. Kalfoglou, G. U.S. Patent 4 627 494, 1986.
354. Howard, J.; Stirling, M. U.S. Patent 4 713 185, 1987.
355. Bansal, B.B.; Hornof, V.; Neale, G. Can. J. Chem. Eng., 1979, 57, 203.
356. Novosad, J. Can. J. Pet. Technol., 1984, 23, 24.
357. Chen, C.S.H.; Sheppard, E.W. U.S. Patent 4 284 517, 1981.
358. Clint, J.H.; Hodgson, P.K.G.; Tinley, E.J. British Patent 2 148 356, 1985.
359. Horton, R.L. U.S. Patent 4 574 885, 1986.
360. Arf, T.G.; et. al. SPE Reservoir Eng., 1987, 2, 166-76.
361. Stalkup, Jr., F.I. Miscible Displacement, Monograph Volume 8, Society of Petroleum Engineers, Dallas, 1983, pp. 62-67.
362. Caudle, B.H.; Dye, A.B. Trans. AIME, 1958, 213, 281.
363. Reference 361, p. 32.
364. Wellington, S.L.; Vinegar, H.J. J. Petroleum Technol., 1987, 39, 885-98.
365. Reference 361, pp. 147-158.
366. Stalkup, Jr., F.I. J. Pet. Technol., 1984, 36, 815-826.
367. Desch, J.B.; et. al. J. Pet. Technol., 1984, 36, 1592-1602.
368. Heller, J.P.; Dandge, D.K.; Card, R.J.; Donaruma, L.G. Soc. Pet. Eng. J., 1985, 25, 679-86.
369. Smith, D.H. Surfactant-Based Mobility Control - Progress in Miscible-Flood Enhanced Oil Recovery, ACS Symposium Series No. 373, American Chemical Society, Washington, D.C., 1988.
370. Heller, J.P.; Kuntamukkula, M.S. Ind. Eng. Chem. Res., 1987, 26, 318.

PHARAOH, EX. 1014
P. 47

371. Ali, S.M. Farouq; Selby, R.J. Oil Gas J., 1986, 84 (5), 57, 60-3.
372. Friberg, S.E.; Solans, C. Langmuir, 1986, 2, 121-6.
373. Malhotra, A.K.; Wasan, D.T. Chem. Eng. Commun., 1987 , 55, 95-128.
374. Khatib, Z.I.; Hirasaki, G.J.; Falls, A.H. SPE Reservoir Eng., 1988, 3, 919-26.
375. Ransohoff, T.C.; Radke, C.J. SPE Reservoir Eng., 1988, 3, 573-85.
376. Owete, O.S.; Brigham, W.E. SPE Reservoir Eng., 1987, 2, 315-23.
377. Craig, Jr., F.F.; Lummus, J.L. U.S. Patent 3 185 634, 1965.
378. Hahn, P.S.; Ramamohan, T.R.; Slattery, J.C. AIChE J, 1985, 31, 1029-35.
379. Borchardt,, J.K.; Bright, D.B., Dickson, M.K.; Wellington, S.L. in Reference 338, pp. 163-80.
380. Borchardt, J.K. in Reference 369, pp. 181-204.
381. Holm, L.W. U.S. Patent 4 706 752, 1987.
382. Wellington, S.L. U.S. Patent 4 380 266, 1983.
383. Buckles, J.J. U.S. Patent 4 706 750, 1987.
384. Wellington, S.L.; Resiberg, J.; Lutz, E.F.; Bright, D.B. U.S. Patent 4 502 538, 1985.
385. Borchardt, J.K. U.S. Patent 4 799 547, 1989.
386. Settlemeyer, L.A.; McCoy, M.J. U.S. Patent 4 739 831, 1988.
387. Sharma, M.K.; Shiao, S.Y.; Bansal, V.K.; Shah, D.O. in Macro- and Microemulsions, ACS Symposium Series No. 272, American Chemical Society, Washington, D.C., 1985, pp. 87-103.
388. Sharma, M.K.; Shah, D.O.; Brigham, W.E. SPE Reservoir Eng., 1986, 1, 253-60.
389. Mitchell, T.O. U.S. Patent 4 676 316, 1987.
390. Zhukov, I.N.; Polozova, T.L.; Shatova, O.S. Kolloidn. Zh., 1987, 49, 758-62; Chem. Abstr., 1987, 108, 63029a.
391. Hutchins, R.D.; Dovan, H.T. European Patent Applicaation 212 671, 1987.
392. Djabbarah, N.F. Canadian Patent 1 221 305, 1987.
393. Falls, A.H. U.S. Patent 4 733 727, 1988.
394. Holm, L.W. J. Pet. Technol., 1970, 32, 1499-1506.
395. Holm, L.W.; Garrison, W.H. SPE Reservoir Eng., 1988, 3, 112-118.
396. Talley, L.D. SPE Reservoir Eng., 1988, 3, 235-243.
397. Prats, M. Thermal Recovery, Monograph Volume 7, Society of Petroleum Engineers, Dallas, 1982.
398. Castanier, L.M.; Brigham, W.E. Chem. Eng. Prog., 1985, 81, 37-40.
399. Strycker, A.R.; Madden, M.P.; Sarathi, P. SPE Reservoir Eng., 1987, 2, 543-8.
400. Isaacs, E.E.; McCarthy, F.C.; Maunder, J.D. SPE Reservoir Eng., 1988, 3, 565-72.
401. Muijs, H.M.; Keijzer, P.P.M. U.S. Patent 4 693 311, 1987.
402. Janssen van Rosmalen, R.; Muijs, H.M.; Keijzer, P.P.M. West German Patent 3 510 765, 1985.
403. Muijs, H.M.; Keijzer, P.P.M., West German Patent 3 734 075, 1988.
404. Huang, W.S.; Gassmann, Z.Z.; Hawkins, J.T.; Schievelbein, V.H.; Hall, W.L. West German Patent 3 503 532, 1985.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

405. Angstadt, H.P. U.S. Patent 4 699 214, 1987.
406. Lim, T. PCT International Patent Application 85 05 146, 1985; Chem. Abstr., 1985, 104, 171228a.
407. Duerksen, J.H.; Wall, R.G.; Knight, J.D. U.S. Patent 4 576 232, 1986.
408. Falls, A.H.; Lawson, J.B., Hirasaki, G.J. J. Pet. Technol., 1988, 40, 95-104.
409. Falls, A.H.; Lawson, J.B.; Hirasaki, G.J. U.S. Patent 4 570 711, 1986.
410. Novosad, J.; Maini, B.B.; Huang, A. J. Can. Pet. Technol., 1986, 25, 42-6.
411. Huang, A.Y.; Novosad, J. Proc. Eng. Found. Conf. Fundam. Adsorpt., 2nd, 1986 (Pub. 1987), 265-75.
412. Lau, H.C.; O'Brien, S.M. SPE Reservoir Eng., 1988, 2, 1177-1185.
413. Dilgren, R.E.; Lau, H.C.; Hirasaki, G.J. U.S. Patent 4 597 442, 1986.
414. Lau, H.C. U.S. Patent 4 617 996, 1986.
415. Angstadt, H.P.; Rugen, D.F.; Cayias, J.L. French Patent 2 557 198, 1985.
416. Maini, B.B.; Ma, V. J. Can. Pet. Technol., 1986, 25, 65-9.
417. Angstadt, H.P.; Tsao, H. SPE Reservoir Eng., 1987, 2, 613-8.
418. Isaacs, E.D.; Prowse, D.R. U.S. Patent 4 458 759, 1984.
419. Duerksen, J.H. SPE Reservoir Eng., 1986, 2, 44-52.
420. Shen, C.W. U.S. Patent 4 702 317, 1987.
421. Lau, H.C. U.S. Patent 4 609 044, 1986.
422. Lau, H.C. U.S. Patent 4 727 938, 1988.
423. Hyne, J.B.; Clark, P.D. U.S. Patent 4 506 733, 1985.
424. Shah, D.O.; Schecter, R.S., Eds. Improved Oil Recovery by Surfactant and Polymer Flooding, Academic Press, New York, 1977.
425. Poettmann, F.H. in Improved Oil Recovery, Interstate Oil Compact Commission, Oklahoma City, Okla., 1983, pp. 173-250.
426. van Poolen, H.K. Fundamentals of Enhanced Oil Recovery, pp. 114-151.
427. Morgan, J.C.; Schechter, R.S.; Wade, W.H. in Proc. Sect. 52nd Colloid Surf. Sci. Symp.; Mittal, K.L., Ed.; Plenum Press, New York, 1979, Vol. 2, 749-75.
428. Puig, J.R.; Scriven, L.E.; Davis, H.T.; Miller, W.G. Chem. Eng. Commun., 1988, 65, 169-85.
429. Aalund, L.R. Oil Gas J., 1988, 86, 33-73.
430. B. Cox and J. Schubert, Eds. 1986 EOR Project Source Book, Pasha Publications, Arlington, Va., 1986.
431. Nelson, R.C. Soc. Pet. Eng. J., 1982, 22, 259-70.
432. Puerto, M.C.; Gale, W.W. Soc. Pet. Eng. J., 1977, 17, 193-200.
433. Graciaa, A.; Fortney, L.M.; Schechter, R.S.; Wade, W.H.; Yiv, S. Soc. Pet. Eng. J., 1982, 20, 743-9.
434. Puerto, M.C. West German Patent 3 542 063, 1986.
435. Cardenas, R.L.; Harnsberger, B.G.; Maddox, Jr., J. U.S. Patent 4 270 607, 1981.
436. Barakat, Y.; et. al., Soc. Pet. Eng. J., 1983, 23, 913-18.
437. Morita, H.; Kawada, Y.; Yamada, J.; Ukigai, T. U.S. Patent 4 512 404, 1985.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

438. Morita, H.; Kawada, Y.; Yamada, J.; Ukigai, T. U.S. Patent 4 555 351, 1982.
439. Okada, T.; Morita, H.; Hagiwara, M. Japan Kokai Tokkyo Koho 60 152 794, 1985.
440. Thaver, R. British Patent Application 2 160 242, 1985.
441. Thaver, R. British Patent Application 2 184 763, 1987.
442. Aldrich, H.S.; Ashcraft, T.L.; Puerto, M.C.; Reed, R.L. West German Patent 3 303 894, 1983.
443. Greif, N.; Oppenlaender, K.; Sewe, K.U. West German Patent 3 422 613,1984.
444. Schmidt, R.; Rupp, W.; Schneider, G.; Kohn, E.M. European Patent Application 264 867, 1988.
445. McCoy, D.R.; Gipson, R.M.; Naylor, C.G. U.S. Patent 4 426 302, 1984.
446. Chiu, Y.C.; Hwang, H.J. Colloids Surf., 1987, 28, 53-65.
447. Balzer, D. West German Patent 3 523 355, 1987.
448. Shaw, J.E. J. Am. Oil Chem. Soc., 1984, 61, 1395-9.
449. Liu, K.C. U.S. Patent 4 692 551, 1987.
450. Abe, M.; Schechter, R.S.; Selliah, R.D.; Sheikh, B.; Wade, W.H. J. Dispersion Sci. Technol., 1987, 8, 157-72.
451. Abe, M.; Schechter, D.; Schechter, R.S.; Wade, W.H.; Weerasooriya, U.; Yiv, S. J. Coll. Interface Sci., 1984, 114, 342.
452. Puerto, M.C.; Reed, R.L. Soc. Pet. Eng. J., 1983, 23, 669-82.
453. Lalanne-Cassou, C.; et. al. J. Dispersion Sci. Technol., 1987, 8, 137-56.
454. Fernley, G.W. West German Patent 3 535 371, 1984.
455. Bolsman, T.A.B.M.; Daane, G.J.R. SPE Reservoir Eng., 1986, 1, 53-60.
456. Heiss, L.; Schneider, G.; Trost, A. West German Patent 3 407 565, 1985.
457. Baviere, M.; Durif-Varambon, B.; Salle, R. French Patent 2 547 860, 1984.
458. Kalpacki, B.; Chan, K.S. U.S. Patent 4 554 974, 1985.
459. Bansal, B.B.; Hornof, V.; Neale, G. Can. J. Chem. Eng., 1979, 57, 203.
460. Manasrah, K., Neale, G.H.; Hornof, V. Cellul. Chem. Technol., 1985, 19, 291.
461. Kalfoglou, G. West German Patent 2 918 197, 1980.
462. Babu, D.B.; Neale, G.; Hornof, V. Cellul. Chem. Technol., 1986, 20, 663-72.
463. Nase, D.G.; Whittington, L.E.; Ledoux, W.A.; Debons, F.E. U.S. Patent 4 739 040, 1988.
464. Morrow, L.R.; Dague, M.G.; Whittington, L.E. U.S. Patent 4 739 041, 1986.
465. Baviere, M.; Bazin, B.; Noil, C. SPE Reservoir Eng., 1988, 3, 597-603.
466. Aldrich, H.S.; Puerto, M.C.; Reed, R.L. French Patent 2 589 858, 1987.
467. Hjelmeland, O.S.; Larrondo, L.E. SPE Reservoir Eng., 1986, 1, 321-8.
468. Somasundaran, P.; Shafick, H.H. Soc. Pet. Eng. J., 1985, 25, 343-50 and references therein.

Borchardt and Yen; Oil-Field Chemistry
ACS Symposium Series; American Chemical Society: Washington, DC, 1989.

469. Van Os, N.M.; Haandrikman, G. Langmuir, 1987, 3, 1051-6.
470. Noll, L.A. Colloids Surf., 1987, 26, 43-54.
471. Hofman, Y.L.; Angstadt, H.P. Chromatographia, 1987, 24, 666-70.
472. Lorenz, P.B.; Trantham, J.C.; Zornes, D.R.; Dodd, C.G. SPE Reservoir Engr., 1986, 1, 341-53.
473. Hohnson, J.S.; Jones, R.R.M. Ann. Chim. (Rome), 1987, 77, 229-44.
474. Doleschall, S.; et. al. Hungarian Patent 42 575, 1987.
475. Krumrine, P.H.; Ailin-Pyzik, I.B.; Falcone, Jr., J.S. Prepr. Am. Chem. Soc., Div. Pet. Chem., 1981, 26 (1), 195-8.
476. Methemitis, C.; Morcellet, M.; Sabbadin, J.; Francois, Eur. Polym. J., 1986, 22, 619-27 and references therein..
477. Bourrrel, M.; Verzaro, F.; Chambu, C. SPE Res. Eng., 1987, 2, 41-53.
478. Reference 426, pp. 104-111.
479. Neil, J.D.; Chang, H.L.; and Gefferm, T.M. in Improved Oil Recovery, Interstate Oil Compact Commission, Oklahoma City, 1983, pp. 52-66.
480. Mohnot, S.M.; Bae, J.H.; Foley, W.L. SPE Reservoir Eng., 1987, 2, 653-63.
481. Holm, L.W.; Robertson, S.D. J. Pet. Technol., 1981, 33, 161-72.
482. Chan, K.S.; Majoros, S.J. U.S. Patent 4 466 892, 1984.
483. Mohnot, S.M.; Chakrabarti, P.M. U.S. Patent 4 714 113, 1987.
484. Bunge, A.L.; Radke, C.J. Soc. Pet. Eng. J., 1983, 23, 657-68.
485. Burk, J.K. SPE Reservoir Eng., 1987, 2, 9-16.
486. Shuler, P.J.; Kuehne, D.L.; Lerner, R.M. J. Pet. Technol., 1989, 41, 80-88 and references therein.
487. Nelson, R.C.; Lawson, J.B.; Thigpen, D.R.; Stegemeier, G.L. Proc. 1984 SPE Enhanced Oil Recovery Symposium, Society of Petroleum Engineers, Dallas, 1984, pp. 417-424.
488. Saleem, S.M.; Faber, M.J. Rev. Tec. INTEVEP, 1986, 6, 133-42; Chem. Abstr., 1986, 106, 159007m.
489. Saleem, S.M.; Hernandez, A. J. Surf. Sci. Technol., 1987, 3, 1-10.
490. Pitts, M.J. Prepr. Am. Chem. Soc., Div. Pet. Chem., 1988, 33 (1), 169-72.
491. Peru, D.A. Report, 1986, NIPER 212; Chem. Abstr., 1986, 104, 140693k.
492. Lawson, J.D.; Thigpen, D.R. U.S. Patent 4 502 541, 1985.
493. Neale, G.H.; Khulbe, K.C.; Hornof, V. Can. J. Chem. Eng., 1987, 65, 700-3.
493. Lin, F.F.J.; Besserer, G.J.; Pitts, M.J. J. Can. Pet. Technol., 1987, 26, 54-65.
494. Enhanced Recovery Week, June 16, 1984, pp. 1,4.
495. Mungan, N. in Improved Oil Recovery, Interstate Oil Compact Commission, Oklahoma City, 1983, pp. 113-72.
496. Reference 426, pp. 132-145.
497. Johansen, R.T. in Improved Oil Recovery, Interstate Oil Compact Commission, Oklahoma City, 1983, pp. 91-112.
498. Reference 426, pp. 114-131.
499. Reference 426, pp. 3-40.
500. Ali, S.M. Farouq; Meldau, R.F. in Improved Oil Recovery,

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Interstate Oil Compact Commission, Oklahoma City, 1983, pp. 311-350.
501. Tiab, D.; Okoya, C.U.; Osman, M.M. J. Pet. Technol., 1982, 34, 1817-27.
502. Babu, D.M.; Hornof, V.; Neale, G. Can. J. Chem. Eng., 1984, 62, 156-9.
503. Crawford, P.B.; Cju, C. in Improved Oil Recovery, Interstate Oil Compact Commission, Oklahoma City, 1983, pp. 251-309.
504. Reference 426, pp. 41-55.

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