PETROLEUM, ENHANCED OIL RECOVERY

1. Introduction

Excluding oil sands mining, enhanced oil recovery (EOR) accounted for $\sim$199,000 m^3/day (1.25 million b/day) of the world's total 2000 oil production, $\sim 3 \times 10^5 m^3$/day (1.9×10^6 bbl/day) or 1.6% (1). In 2004, U.S. EOR production [105,740 m^3/day (663,451 bbl/day)] represented 12.2% of total production of crude oil plus gas condensate (2). Most of the oil basins in the United States are mature. These fields will require extensive enhanced oil programs to maintain current production rates or, in some cases, merely to minimize rapidly increasing depletion rates. For example, production in Prudhoe Bay, the largest U.S. field, is declining $\sim$10% annually despite large investments in enhanced oil recovery technology (3).

Primary and secondary oil recovery together recover only 25–50% of the oil originally in place in a reservoir. After conventional oil recovery operations, the U.S. will have 60 billion m^3 (377×10^9) barrels of oil remaining after economic production ceases. The U.S. Department of Energy has estimated as much as 43.3 billion barrels of oil could be produced using EOR technologies (4). The most likely location of large new U.S. oil fields is Alaska and deep water offshore. The costs of discovering and developing these reserves make unrecovered oil in known fields an economically attractive target in part because much of the infrastructure is also already in place.

Another factor promoting use of EOR technology in existing oilfields is that countries with the greatest potential of containing undiscovered conventional oil fields either limit Western investment in oil production (5).

The relatively low oil prices of 1981–2003 have resulted in significant changes in the EOR technology being developed and field tested. Injection of steam (qv) or oil-miscible gases remains of great interest. Micellar polymer flooding can efficiently recover oil and was the focus of a large research and development effort from 1970 to 1986, but this process remains relatively expensive and consequently is seldom applied in field operations.

Using relatively low concentration surfactants (qv) as CO_2 (6) and steam mobility control agents (foam) can improve recovery process cost effectiveness. Combinations of older EOR processes, eg, surfactant-enhanced alkaline flooding and alkaline–surfactant–polymer flooding show promise of improved cost effectiveness.

Enhanced oil recovery, the injection of fluids other than water to increase oil recovery is but one means of recovering more oil from existing fields. Other methods include better siting of injection and production wells due to improved reservoir mapping technologies, infill drilling, horizontal wells, hydraulic fracturing, and acidizing.

With the increase of oil prices since 2003, major oil companies and national oil companies have initiated quite large enhanced oil recovery projects usually using carbon dioxide or steam as the injectants and are planning more such projects. Using industrially generated CO_2 for EOR while simultaneously sequestering the injected CO_2 in the rock formation has the potential to produce more oil while reducing emissions of this greenhouse gas (7).

2. The Nature of Oil Reservoirs

Oil reservoirs are layers of porous sandstone or carbonate rock, usually sedimentary. Impermeable rock layers, usually shales, and rock faults trap the oil in the reservoir. The oil exists in microscopic pores in rock. Various gases and water also occupy rock pores and are often in contact with the oil. These pores are interconnected with a complicated network of microscopic flow channels. The weight of overlaying rock layers places these fluids under pressure. When a well penetrates the rock formation, this pressure drives the fluids into the wellbore. The flow channel size, wettability of flow channel rock surfaces, oil viscosity, and other properties of the crude oil determine the rate of this primary oil production.

As reservoir pressure is reduced by oil production, additional recovery mechanisms may operate. One such mechanism is natural water drive. Water from an adjacent more highly pressured formation is forced into the oil-bearing formation by the pressure differential between the two formations. Another mechanism is gas drive. Expansion of a gas cap above the oil as oil pressure declines can drive additional oil to the wellbore. Produced gas may be reinjected to maintain gas cap pressure as is done on the Alaskan North Slope. Additional oil may also be produced by compaction of the reservoir rock as oil production reduces reservoir pressure.

As the natural pressures in the reservoir decrease, oil production declines. A pump is then used to maintain oil production at economic levels by drawing oil to the surface and lowering the height of the fluid column in the wellbore. 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 the reservoir. 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. Pumping the well can maintain production at economic levels for years.

2.1. Waterflooding.

Injection wells are used when the natural pressures driving fluids to production wells are depleted and pumping alone is no longer economical. Fluid injection repressurizes the reservoir, restoring a driving force and promoting oil production. For economic reasons, water is the usual injection fluid. Water injection or waterflooding is usually termed secondary oil recovery. It accounts for ~40% of total U.S. oil production. Additional oil recovery by waterflooding is typically 15–25% of the oil originally in the reservoir.

Determining and using the optimum pattern and arrangement of production and injection wells for a particular reservoir can have a significant effect on oil recovery and production rates (8). Infill drilling and horizontal production wells can drain oil reservoirs more efficiently (9). Horizontal injection wells have also improved oil recovery by increasing volumetric sweep efficiency and increasing fluid injection rates (10). One 600–1200-m long horizontal well can replace several vertical wells decreasing both overall drilling and operational costs (11).

3. Oil Recovery Mechanisms

There are two principal mechanisms of enhanced oil recovery: increasing volumetric sweep efficiency of the injected fluid and increasing oil displacement efficiency by the injected fluid. In both, chemicals are used to modify the properties of an injected fluid whether water, steam, a miscible gas, eg, CO_2 or natural gas, or an immiscible gas, usually nitrogen. Poor reservoir volumetric sweep efficiency is the greatest obstacle to increasing oil recovery (12).

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface (rock) in the presence of other immiscible fluids (8). As many as 50% of all sandstone reservoirs and 80% of all carbonate reservoirs are oil-wet (13). Strongly water-wet reservoirs are quite rare (14). Rock wettability can affect its relative permeability to water and oil and thus influence fluid injection rates, flow patterns of fluids within the reservoir, and oil displacement efficiency (8,14,15). Alteration of rock wettability by adsorption of polar materials, eg, surfactants and corrosion inhibitors, or by the deposition of polar crude oil components (16), can strongly alter the behavior of the rock (15).

When water is injected into a water-wet reservoir, oil is displaced ahead of the injected fluid. Injection water preferentially invades the small- and medium-sized flow channels or pores. As the water front passes, unrecovered oil is left in the form of spherical, unconnected droplets in the center of pores or globules of oil extending through interconnected rock pores. In both cases, the oil is completely surrounded by water and is immobile. There is little oil production after injection water breakthrough at the production well (8).

In an oil-wet rock, water resides in the larger pores, oil exists in the smaller pores or as a film on flow channel surfaces. Injected water preferentially flows through the larger pores and only slowly invades the smaller flow channels resulting in a higher produced water/oil ratio and a lower oil production rate than in the water-wet case.

3.1. Injection Well Considerations. Fluid injection rate can have a significant effect on oil recovery economics. Flow is radial from the wellbore into the reservoir. Thus the region near the injection wellbore acts as a choke for the entire reservoir.

Addition of surfactant to the injection water (17,18) can displace the oil remaining near the well. The lower oil saturation results in an increase in the water relative permeability (8). Therefore, a greater water injection rate may be maintained at a given injection pressure. Whereas ultimate oil recovery may not be increased, the higher water injection rate can increase oil production rates improving oil recovery economics. The concentration of surfactant in the injection water is relatively high (1–3%). However, the total amount of surfactant used is not great because it is necessary only to displace the oil from a 2–3-m radius around the injection well (see SURFACTANT).

Decreased injection rates resulting from formation damage, ie, reduction of the rock fluid carrying capacity, near injection wells can reduce oil production rates at offset (adjacent) production wells. Formation damage may result from invasion of rock capillaries by solid particles in wellbore fluids during well drilling and completion. Plugging of rock capillaries adjacent to fractures by fine solid particles in fracturing fluids may also occur. Acidizing the rock immediately adjacent to the wellbore can dissolve clays (qv), silica particles to improve the rock permeability. However, treatments must be carefully designed to prevent formation of precipitates that can plug rock flow channels.

Precipitate formation can occur upon contact of injection water ions and counterions in formation fluids. Solids initially present in the injection fluid, bacterial corrosion products, and corrosion products from metal surfaces in the injection system can all reduce near-wellbore permeability. Injectivity may also be reduced by bacterial slime that can grow on polymer deposits left in the wellbore and adjacent rock. Strong oxidizing agents such as hydrogen peroxide, sodium perborate, and occasionally sodium hypochlorite can be used to remove these bacterial deposits (19–21).

Formation damage can also be caused by chemical and physical interactions of fluid and rock. Low salinity injection fluids are often preferred to obtain maximum viscosity from a given amount of water-soluble polymer. However, low salinity fluids can cause swelling of water-expandable clays. This swelling reduces the fluid-carrying capacity of rock flow channels. Because clays act as the cementing medium in many sandstone formations, this swelling weakens cementation and can result in the release of mineral fine particles which can migrate to constrictions and plug the flow channels.

Long-lasting stabilization of water-swelling clays may be achieved by using materials, eg, hydroxyaluminum (22) and certain quaternary ammonium salt polymers (23). Quaternary ammonium salt polymers have been used in drilling fluids, completion fluids, acidizing treatments, and hydraulic fracturing as well as in injection water and injected steam for enhanced oil recovery (23). Adsorption is long lasting and limited chemical treatment volumes are needed. Treatment concentration is usually 0.1–1.0% by weight. For injection water and injected steam, it is usually necessary to treat a 2–3-m radius from the injection wellbore. The addition of potassium hydroxide to injection waters has also been used to stabilize clays and maintain injection rates (24).

3.2. Injection Fluids.

Whereas water is the most commonly used injection fluid, other fluids can provide higher oil recovery efficiency. Injecting gases miscible with reservoir crude oil can result in low interfacial tension promoting high oil displacement efficiency (25). The process of miscible gas flooding using carbon dioxide (qv) is depicted in Fig. 1. The primary source of CO_2 is high pressure natural reservoirs of highly pure CO_2. Any CO_2 produced with the crude oil is recovered, purified, and reused. However, CO_2 produced in industrial operations, eg, separation from produced natural gas and coal gasification is increasingly being used while use of flue gases from power plants, refinery units, and other industrial operations is under consideration (26). For example, Norway's Sleipner Field project stores 1 million tonnes/year of CO_2 associated with natural gas production in a saline geologic aquifer. Norway's carbon emission tax of 315 krone/tonne CO_2 equivalent ($45/metric ton) encourages this storage (26). Other suitable gases include natural gas and flue gas.

Overall, CO_2 flooding can increase oil recovery by 7–15% of the oil originally in place and can be sustained for 10–30 years (25). Improvement of CO_2 flood performance has resulted from advances in computer simulation of CO_2 flood performance and greater experience in handling carbon dioxide–water mixtures.

Other recently reduced technology that can increase oil recovery includes horizontal injection and production wells, four-dimensional (4D) seismic analyses to track injected CO_2 flow, automated field monitoring systems, and injecting larger volumes of CO_2 than were used in earlier EOR projects (27).

Many CO_2 miscible EOR projects are located in the west Texas Permian Basin where as much as two-thirds of the oil remains after waterflooding. An incremental (10%) recovery is typical for Permian Basin CO_2 floods, which could correspond to as much as $0.5 \times 10^9 m^3$ ($3{-}4 \times 10^9$ bbl) (28). Pipelines (qv) connect these large EOR projects to natural CO_2 sources in Colorado and New Mexico. Industrial point sources of CO_2 have also been used for projects in other areas.

Combining an *in situ* thermal enhanced oil recovery process (see below) with CO_2 injection and subterranean storage has been reported in the patent literature (29).

The pressure–composition requirement for miscibility limits the oil reservoirs in which CO_2 enhanced oil recovery has been applied. The low injected fluid viscosity often results in poor volumetic sweep efficiency (see below). Despite these concerns, a Department of Energy study indicates that carbon dioxide injection has the potential of recovering 43 billion barrels of oil currently "stranded" in six mature U.S. oil-producing regions (30).

Supercritical CO_2 (25,31) and various hydrocarbon injectants (25,32) undergo physical interactions with crude oil that result in stripping out of the low molecular weight components, which increases oil production (see SUPERCRITICAL FLUIDS). The rapid or gradual development of miscibility with the remaining crude oil constituents results in oil mobilization. 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. However, interaction of the injectant with the crude oil can alter rock wettability and thus reduce injection rates and decrease oil recovery.

Another method of using CO_2 is called cyclic CO_2 stimulation or huff'n'puff (33). A limited amount of CO_2 is injected into a reservoir over hours or days. The well is then shut in for a soak period of days to weeks to allow the CO_2 to interact with the crude oil, swelling the oil and reducing its viscosity. The well is then opened, the CO_2 provides a solution gas drive, and oil mobilized by the CO_2 soak is produced.

3.3. Reducing Greenhouse Gas Emissions. Carbon dioxide EOR could also play a role in reducing greenhouse gas emissions. Carbon dioxide capture and storage (CCS) underground could constitute as much as one-half of the global emissions reduction by 2050, according to the International Energy Agency (34). Carbon dioxide sequestration can provide two added economic incentives for CO_2 EOR in addition to the value of the additional oil recovered. First, by reducing CO_2 emissions, field operators can avoid being subject to paying CO_2 emissions penalties. Second, they can receive credits for reducing their CO_2 emissions; credits that can be sold to other firms that have high levels of CO_2 emissions. While these systems are being deployed in Norway and other European countries, they are not yet in place in the U.S. Eight commercial CO_2 sequestration projects are underway in the Norwegian sector of the North Sea, Algeria, Alaska and Saskatchewan, Canada. Governments in Canada, Norway and other oil-producing areas are providing financial incentives for the underground sequestration of CO_2.

CCS involves three distinct processes: capturing CO_2 from the gas streams emitted during electric power production, industrial processes, or fuel processing; transporting the captured CO_2; and storing it underground in rock formations where it cannot leak to the surface. Using this CO_2 to increase oil production would offset the costs of CCS and perhaps even render it profitable (after factoring in governmental financial incentives).

3.4. Injection of Other Gases. Nonmiscible gases, eg, nitrogen, have been used as EOR injection fluids. Increasingly, the nitrogen used is separated at the oil field from produced natural gas rather than being produced in industrial gases plants. Oil recovery mechanisms include volatilization of low molecular weight components of the crude oil and displacement of oil from the top of the reservoir (27). The latter mechanism occurs as a result of gravity override of the low density injectant.

Gas injection into a gas cap overlaying an oil reservoir is considered an EOR method. The resulting repressurization of the reservoir promotes additional oil production. Reinjection of natural gas is responsible for a significant fraction of Alaskan North Slope oil production. With the construction of a pipeline to transport North Slope natural gas to world markets, CO_2 may be used instead.

High temperature steam (qv) is also used for recovery of viscous crude oils (28). Heat from the steam thins the oil, reducing viscosity and increasing mobility. The mobilized oil is produced at offset production wells. In heavy oil fields, water flooding is often omitted and steam injection begun immediately after primary production. Steam injection temperature is typically 175–230°C in California oil fields. Injection temperature can reach 300°C in Canadian and Venezuelan EOR projects.

The injection of large volumes of steam, steam flooding, also called steam-assisted gravity drainage (SAGD), is used to mobilize oil, which is produced at offset production wells. By reducing oil viscosity, the oil flows more readily through the reservoir to production well bores. Smaller volumes of steam are injected in the cyclic steam stimulation or huff'n'puff process (Fig. 2). Many wells are placed on several cycles of steam stimulation and then used as injection or production wells in steam flood projects. Large-scale steam projects can be quite expensive. For example, a steamflood project in Oman's Mukhaizna heavy oil field is projected to cost $>$ \$2 billion and involve drilling 1800–2200 new wells (35). Production is expected to increase from the current 10,000 to 150,000 bbl/day.

An organic chemical may be added to the steam to provide additional oil viscosity reduction in addition to the heat-thinning effect provided by injected steam. For example, after the oil recovery rate in a steam flood reaches 25–75% of the predicted maximum recovery rate, a hydrocarbon solvent may be injected to recover additional heavy oil from an oil reservoir (36). Alternatively, steam or hot water and solvent may be injected simultaneously in a ratio of $> 5{:}1$ (37). The C_{1-5} alcohols have been used as additives to high temperature steam and injected into heavy oil reservoirs in such a manner that the injectant does not form an emulsion with the crude oil (38).

3.5. Heavy Oil Upgrading.

Upgrading of heavy oil prior to conventional refining is increasingly being used to improve SAGD economics. For example, Iraq's Qaiyarah Field produces heavy oil that cannot be refined in conventional refineries and is used mainly for asphalt (39). However, upgrading processes have been developed by several oil companies that convert heavy crude oils to light oils that can be processed in conventional refineries. Such an upgrading plant will be build to process the Qaiyarah heavy oil and several plants are already operating in Canada and Venezuela to process the bitumen and very heavy oil recovered in SAGD and oil mining projects. Syngas has been used to initiate predominantly gas-phase heavy oil upgrading reactions (40). There is also increased interest in the catalytic reaction of very heavy crude oil and resid, the bottoms product remaining after vacuum distillation in a conventional refinery, with steam to produce methane (41).

Bitumen mining in Canada using open-pit mines has reached commercial status. Upgrading of this often solid-appearing material is required before it can be processed in conventional refineries.

3.6. 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. High permeability rock 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 rock volumetric sweep efficiency. Low viscosity injection fluids exhibit poor volumetric sweep efficiency, which leads to low oil production. Thus, proper diagnosis of the cause of poor volumetric sweep efficiency is critical in designing a successful well treatment. For example, sealing fractures requires different well treatment designs than reducing the permeability of thief zones.

Both sodium silicate gelation (42) and *in situ* cross-linking of organic polymers (43,44) can reduce the permeability of fractures and high permeability streaks. Polymers are usually injected at concentrations of 1000–5000 ppm. *In situ* cross-linking treatments are restricted to fractures and the near-wellbore region owing to the kinetics of the cross-linking process. The polymer may be injected into the well with a cross-linker or the cross-linker may be injected after the polymer. The well is shut in for from 1–7 days and then normal injection operations are resumed.

The most commonly used polymers are partially hydrolyzed polyacrylamides (45). The optimum degree of hydrolysis depends on the application, injection water composition, and reservoir conditions (46,47). More salt-tolerant acrylamide copolymers may permit using this technology in higher salinity injection water (48). Field applications of cross-linked xanthan gum have also been reported (49).

Chromium(III), Cr(III), compounds have largely replaced Al(III) compounds as cross-linkers (48–52). The Cr(III) acetate [1066-30-4] cross-links acrylamide polymers rapidly. The Cr(III) complexes composed of strong ligands, eg, glycolate or malonate give extended polyacrylamide gelation times compared to salts such as Cr(III) acetate (53). Delaying cross-linking permits the use of this technology at higher (up to 150°C) reservoir temperatures. Sodium bisulfite and thiourea have been used to reduce injected Cr(VI) to the reactive Cr(III) species that promotes cross-linking (54). Gradual dissolution of colloidal $Cr(OH)_3$ can also delay cross-linking (55) as can Cr(III) propionate (56). Encapsulation of the cross-linking agent permits deeper penetration of gel-forming compositions into oil-bearing formations (57). Injection of unhydrolyzed polyacrylamide followed by *in situ* hydrolysis also delays cross-linking (58).

Cross-linked xanthan gums have also been used to reduce the permeability of thief zones. Trivalent chromium is the preferred cross-linker (59). Cross-linker effectiveness is less at high salinity. However, Cr(III) has been used in the field at salinities as great as 166,000 ppm total dissolved solids (60).

Proper placement of the treatment fluid in the reservoir is critical to treatment success. Careful sizing of the treatment and choice of injection rates are required because overtreatment can cause plugging of the oil-containing rock and excessive reduction of the injection rate. Even after a well-designed treatment, the fluid injection rate is often significantly less than before well treatment. Many successful applications of this technology in waterfloods and in surfactant polymer floods have been reported. Wells in CO_2 EOR projects have also been treated using this technology.

Polymerization may also occur *in situ*. Reactive monomers, eg, acrylamide in concentrations of 2–5 wt% and various additives including a free-radical polymerization initiator may be used (61,62). A difunctional monomer, eg, *N,N′*-methylenebis(acrylamide), can be added to the injected formulation to form a cross-linked polymer *in situ*. Low viscosity aqueous monomer solutions can be injected at higher rates and preferentially enter high permeability zones to a greater extent than do non-Newtonian polymer solutions (63). If no difunctional monomer is used, the viscous polymer mass may be slowly dissolved by injection water increasing water viscosity and providing a second means of increasing oil recovery.

Lignosulfonates may be cross-linked *in situ* using Cr(III) (64) or an acidic gas, eg, CO_2 (65). Cross-linked lignosulfonate can be an effective plugging agent at high temperatures, such as in steam injection wells. Lignosulfonate concentration is usually 2–3 wt%. Blends of lignosulfonate and sodium silicate have also been used (66). Other systems cross-linked *in situ* for water or stream injection wells are phenol–formaldehyde (67), urea–formaldehyde (68), furfuryl alcohol (69), formaldehyde resin plus sulfonated tannin extract (70), and formaldehyde resin and alkali kraft lignin (71).

Using foamed gels can reduce the overall amount of chemicals required to form a given volume of gel within a subterranean formation. For example, a foamed gel formed from a cross-linkable carboxylate-containing polymer, a reactive transition metal cross-linking agent, polyvinyl alcohol, an aqueous solvent and an added gas has been described (72).

Surfactant precipitation may be used for in-depth permeability reduction of thief zones (73). Thief zones have a low oil saturation owing to the preferential flow of injected fluids through high permeability rock. This process is based on the sequential injection of a slowly propagating ionic surfactant followed by an aqueous spacer containing no surfactant. Then a more rapidly propagating ionic surfactant of the opposite charge type is injected. The oppositely charged surfactants gradually mix in the high permeability portions of the reservoir (thief zones) causing precipitation, which plugs flow channels reducing permeability in the most flooded portions of the reservoir thereby diverting injectant to rock zones containing higher oil saturations. The economically limiting factors in the use of this process are cost and low propagation rate of the cationic surfactant.

Rock surface chemistry can affect volumetric treatment effectiveness and economics. Metal ion cross-linkers and cationic polymers can adsorb on mineral surfaces, particularly clays, by ion-exchange (qv) processes. The subsequently lower concentration of materials in solution decreases treatment effectiveness by reducing the rate of polymer cross-linking and decreasing gel strength.

Both *in situ* cross-linking of partially hydrolyzed polyacrylamides (74) and injection of quaternary ammonium salt polymers having long hydrophilic side chains (75) have been used to reduce the permeability of water-producing zones adjacent to production wells. This permeability reduction decreases the produced water/oil ratio as does injection of polyacrylamide in high hardness brine to reduce rock permeability (76). The polymers exist in saline solution as tightly coiled chains and are readily adsorbed owing to relatively low solubility in hard water. Subsequent injection of soft, low salinity water uncoils the adsorbed polymer chains increasing water viscosity and reducing rock permeability. This technology could also be used to reduce the permeability of thief zones adjacent to injection wells. However, mechanical isolation of these zones may be necessary for cost-effective treatments.

3.7. Polymer Flooding. 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, the mobility of the injected water in the highly flooded (low oil saturation) rock, m_w, divided by the mobility of the oil in oil-bearing portions of the reservoir, m_o (77,78). The mobility ratio is related to the rock permeability to oil, k_{ro}, and injected water, k_{rw}, and to the viscosity of these fluids by the following equation:

$$M = m_{\text{w}}/m_{\text{o}} = (k_{\text{rw}}/\eta_{\text{w}})/(k_{\text{ro}}/\eta_{\text{o}})$$

The terms h_{w} and h_{o} represent the viscosity of the aqueous and oil phases, respectively.

The polymer flooding process is depicted in Fig. 3. The displacing or driving fluid may be steam, supercritical carbon dioxide, hydrocarbon miscible gases, nitrogen, or solutions of surfactants or polymers instead of water. The volumetric sweep efficiency increases with lower mobility ratio values (79). A mobility ratio of 1.0 or lower is considered optimum. The mobility of water is often high relative to that of oil. Steam and oil-miscible gases, eg, supercritical carbon dioxide exhibit even higher mobility ratios. Consequently, these more expensive injectants can have low volumetric sweep efficiencies.

Mobility control agents reduce the mobility ratio. Virtually all polymer flood field projects have used hydrolyzed polyacrylamides having molecular weights of $1-5 \times 10^6$ or xanthan gum, a biopolymer (80). Variations in polymer molecular weight and structure have been made to improve performance properties. Relatively low (100 ppm for fresh water, 1000 ppm or more for saline systems) polymer concentrations can significantly increase injected water viscosity. Adsorption of these polymers on rock can result in a long-term decrease in rock permeability to aqueous fluids (residual resistance). Some polymer field projects have exhibited injected water permeability reductions, attributed to residual resistance effects, that have lasted for more than three years after polymer injection (81).

Each EOR polymer type has important advantages and significant disadvantages (Table 1). When dissolved in more saline waters, xanthan gum produces a higher apparent viscosity than the same concentration of partially hydrolyzed polyacrylamide (82). Xanthan gum is more soluble in saline waters than are polyacrylamides, particularly in injection waters containing divalent metal ions. Xanthan gum also generally adsorbs less on rock surfaces and is substantially more resistant to shear degradation than polyacrylamides (83). However, xanthan gum is also more expensive and the extensional viscosity of the semirigid xanthan molecule is less than that of the flexible polyacrylamide (84). Both polymers cross-link easily in the presence of transition metals.

In addition to the normal problems of completely dissolving particles of water-thickening polymers, xanthan gum contains insoluble residues that decrease polymer injectivity. Various methods of reducing insolubles content and improving xanthan solution injectivity are available (86–92). None appears economically viable. Oxygen scavengers (93) and bactericides (85,94) are commonly used to stabilize injected polyacrylamide and xanthan gum solutions (95–108).

At low polymer concentrations, xanthan containing the intact pyruvate ring exhibits higher brine solution viscosity and better filterability than its ring-opened analogue (109). A xanthan gum containing pyruvate rings in most of the polymer repeat units has been produced by a proprietary strain of *Xanthamonas campestris* (102). Genetic engineering techniques were used to obtain mutant *X. campestris* bacterial strains that provided genetic control of the extent of acetylation and pyruvation of xanthan polymers that provided improved performance in polymer flooding (110). Xanthamonas bacteria have also been used to produce a polymer, having a glucose and mannose unit in a 2:1 ratio, which is claimed to be a better water viscosifier than xanthan gum (111). Another promising microbial polysaccharide is scleroglucan (112), which has been evaluated for North Sea applications. The high temperature behavior of different microbial polysaccharides (qv) has been studied (113). In highly saline media, another biopolymer, succinoglycan, more readily flows through microporous media than does xanthan gum (113). This glycan forms higher viscosity solutions than does xanthan gum at equal concentrations.

Most polyacrylamides used as mobility control agents are partially hydrolyzed or are acrylamide−acrylic acid (or sodium acrylate) copolymers produced by emulsion copolymerization (114). Emulsion polymers are used to avoid high shear degradation and undissolved solid particle problems. Another method of avoiding these problems 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 (115). Polyarylamide is usually hydrolyzed in base to produce a random distribution of acrylate groups (116). Acid hydrolysis results in a more block-like distribution of acrylate units (117). Electrostatic repulsion of the anionic carboxylate groups elongates the polymer chain of partially hydrolyzed polyacrylamides, increasing the hydrodynamic volume and solution viscosity. Cobalt-60, ^{60}Co, irradiation has been used to initiate polymerization and prepare particularly high molecular weight polyacrylamides (118).

Maximum freshwater viscosity of polyacrylamide occurs at ~35% hydrolysis; maximum viscosity in a Ca^{2+}-containing brine occurs at 10–15% hydrolysis (119). 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 (120). Chelating and sequestering agents have been proposed to reduce the adverse effect of divalent (119) and multivalent metal ions on polyacrylamide solution viscosity (120,121). Proper well completion, particularly perforation design, reduces polyacrylamide shear degradation during injection (122).

Excessive hydrolysis of polyacrylamide *in situ* can promote undesirable polymer precipitation in the reservoir. Acrylamide block and random copolymers designed to reduce undesired amide group hydrolysis, increase thermal stability, and improve solubility in saline media have been studied for EOR applications (123–132).

Acrylamide graft copolymers such as those with starch (qv) (133), dextran (134), and lignin (qv) (135), have been studied to try to reduce copolymer costs. A general disadvantage of acrylamide copolymers is greater cost compared to partially hydrolyzed polyacrylamides.

Among the other types of polymers showing promise for polymer flooding are hydrophilic *N*-vinyl lactams (136).

Propagation of enhanced oil recovery chemicals through rock is critical to the success of an EOR project. Mechanical entrapment of polymers as well as adsorption can reduce the effective polymer concentration (137,138). Calcium ions in formation and injection waters increase anionic polymer adsorption (139). Sacrificial adsorption agents such as lignosulfonates (141–143) can be used to reduce the adsorption of more expensive polymers and surfactants. Other chemicals tested include poly(vinyl alcohol) (144), sulfonated poly(vinyl alcohol) (145), sulfonated poly(vinylpyrrolidinone) (146), low molecular weight polyacrylates (147), and sodium carbonate (148).

3.8. Surfactants for Mobility Control.

Water, which can have a mobility up to 10 times that of oil, has been used to decrease the mobility of gases and supercritical CO_2 (mobility on the order of 50 times that of oil) used in miscible flooding. Gas/oil mobility ratios, M, can be calculated by the following (26):

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

where k refers to permeability, μ to viscosity, and the subscripts 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 (149) compared to injection of CO_2 alone. The design parameters most affecting WAG CO_2 flood oil recovery are CO_2 and water slug sizes, produced gas:oil ratio as a function of time, and total volume of injected CO_2 (150) (see Fig. 1). Injecting water saturated with pressurized CO_2 and relieving the pressure after injection results in gas bubble formation in the smallest rock pores forcing oil into more permeable portions of the formation thereby increasing oil recovery. This strategy can increase the oil recovery beyond that typically reached in WAG processes (151).

The WAG process has been used extensively in the field, particularly in supercritical CO_2 injection, with considerable success (25,150,152). However, a method to further increase the viscosity of injected gas or supercritical fluid is desirable. One means of increasing the viscosity of CO_2 is through the use of supercritical CO_2-soluble polymers and other additives (147). The use of surfactants to form low mobility foams or supercritical CO_2 dispersions within the formation has received more attention (153–155). Foam has also been used to reduce mobility of hydrocarbon gases and nitrogen. X-ray computerized tomographic analysis of core floods indicate that addition of 500 ppm of an alcohol ethoxyglycerylsulfonate increased volumetric sweep efficiency substantially over that obtained in a WAG process (150).

One reason for widespread interest in the use of surfactants as gas mobility control agents is the effectiveness at concentrations of ≤ 0.1 wt% (149,156). Some surfactants are effective below their critical micelle concentration (157). This low chemical requirement can significantly improve process economics.

Among the classes of surfactants studied for this application are alcohol ethoxylates and their sulfate and sulfonate (150,158–161) and carboxylate (162) derivatives, alkylphenol ethoxylates (163), alpha-olefin sulfonates (162), and alkylated diphenylether disulfonates (164). Increased linear carbon chain length, decreased branching, and increased ethoxy group chain length increase foam stability (158). Addition of a water-thickening polymer to the aqueous phase may stabilize the foam (165). Using a blend of an alkaline agent, a surfactant and a polymer as the supercritical CO_2 foaming agent has been proposed (166).

In addition to the mobility control characteristics of surfactants, critical issues in gas mobility control processes are surfactant salinity tolerance, hydrolytic stability under reservoir conditions, surfactant propagation through the reservoir, and foam stability in the presence of crude oil saturations. Lignosulfonate has been reported to increase foam stability and function as a sacrificial adsorption agent (167). Addition of sodium carbonate or sodium bicarbonate to the surfactant solution reduces surfactant adsorption by increasing the aqueous-phase pH (168).

Alcohol ethoxysulfates have been used in field tests as nitrogen (169) and carbon dioxide (170) foaming agents. Field use of alcohol ethoxysulfates is restricted to low temperature formations owing to its limited hydrolytic stability at low pH and elevated temperature (171). It has been reported that some foams can reduce residual oil saturation, not by oil displacement, but by emulsification and imbibition of the oil into the foam (172).

Gravity override of low density steam leads to poor volumetric sweep efficiency and low oil recovery in steam floods. Nonchemical methods of improving steam volumetric sweep efficiency include completing the injection well so steam is only injected in the lower part of the oil-bearing zone (173), alternating the injection of water and steam (174), and horizontal steam injection wells (175,176). Surfactants frequently are used as steam mobility control agents to reduce gravity override (177). Field-proven surfactants include C_{16-18} alpha-olefin sulfonates (AOS), alkyltoluene sulfonates, and neutralized dimerized alpha-olefin sulfonic acid.

Addition of long-chain (C_{8-20}) alcohols to AOS or alkylaromatic sulfonates increases foam strength and permits the use of lower surfactant concentrations (178). Increasing the carbon number in alpha-olefin sulfonates to >25 increases foam strength (179,180). In alkylaromatic sulfonates, longer linear alkyl groups (181,182) or dialkyl substitution (183) has the same effect. Other alkylaromatic sulfonates containing benzene, toluene, or xylene rings (182,184), two fused aromatic groups (185), and the diarylether group (186) have been evaluated favorably as steam-foaming agents. The neutralized dimer of an alpha-olefin sulfonate has also been used (187).

To maintain foam strength as the steam cools and eventually condenses, a noncondensible gas, usually nitrogen or methane, is often added to the injectant composition (188).

Critical parameters affecting surfactant performance are surfactant propagation rate and surfactant stability at steam temperatures that can reach $>316^\circ C$. Surfactant propagation rate can be reduced by adsorption, precipitation, and partitioning into the oil phase. Anionic surfactant adsorption increases with increasing salinity and decreases with increasing temperature (189).

Additives can improve surfactant propagation. Both anionic surfactant partitioning and precipitation increase with increasing calcium ion concentration (190) so minimizing divalent metal ion concentration in the surfactant solution is desirable. Injection of a surfactant preslug containing NaCl converts clays from the calcium to the sodium form and reduces later ion-exchange processes that add Ca^{2+} ions to the surfactant solution (191,192). The use of a hydrotrope such as sodium xylene sulfonate has been reported to increase oil recovery in laboratory steam-foam flood tests (193). Hydrotropes are additives that increase surfactant solubility. They also may function as sacrificial adsorption agents or act as foam stabilization agents.

Steam-foaming agents that efficiently mobilize heavy crude oil by heat transfer can reduce the residual oil saturation. This can increase foam stability and improve the diversion of subsequently injected steam into oil saturated zones thereby increasing oil recovery (194).

Thermal stability of the foaming agent in the presence of high temperature steam is essential. Alkylaromatic sulfonates possess superior chemical stability at elevated temperatures (195,196). However, alpha-olefin sulfonates have sufficient chemical stability to permit their use at steam temperatures characteristic of most U.S. steamflood operations.

The addition of high pH agents, eg, sodium hydroxide to the surfactant solution has been reported to increase foam strength, stability and surfactant propagation (197–199). 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 organic acids naturally found in the crude oil. The resulting soap generation provides surfactant to more efficiently displace oil (197). The consequent lower oil saturation can result in a more stable foam.

Water-soluble polymers (qv) can increase the viscosity of the foam external phase. This improves foam stability and reduces mobility. Gelation of the foam external phase can reduce chemical requirements to plug thief zones and fractures (200).

3.9. Improving Oil Displacement Efficiency. The use of relatively large (~2–5 wt%) concentrations of surfactants to increase oil displacement efficiency has been studied extensively (35,201,202). This method, called the micellar flooding or surfactant–polymer flooding, usually involves the injection of a brine preflush to adjust reservoir salinity. The preflush is followed by injection of a micellar slug comprised of the surfactant, a cosurfactant (usually a C_{4-6} alcohol), and a hydrocarbon. A polymer solution is then injected to reduce viscous fingering of the drive fluid into and through the micellar slug. Viscous fingering causes dilution of the surfactant, reduced contact of the micellar slug with the crude oil, and trapping of some of the micellar slug in the reservoir. These effects reduce oil recovery. A freshwater buffer to protect the polymer follows, prior to injection of the driving fluid, ie, saline water (an oilfield brine), to move the chemicals and the resulting oil bank to the well.

Process effectiveness depends on maintaining an ultralow [$\sim 10^{-10}$ N/m(10^{-3} dynes/cm)] interfacial tension between the injected surfactant slug and the crude oil (203). The effect of petroleum composition on oil solubilization by surfactants has been the subject of extensive study (204). Other critical surfactant issues are performance in saline injection waters, adsorption on reservoir rock, partitioning into reservoir crude oil, chemical stability in the reservoir, interactions with the mobility control polymer, and production problems caused by resultant emulsions. Reservoir heterogeneity can also greatly reduce process effectiveness. Micellar processes remain relatively high cost relative to other EOR technologies.

Besides crude oil petroleum sulfonates, nonionic surfactants, eg, alcohol ethoxylates, alkylphenol ethoxylates (205) and propoxylates (206), and alcohol propoxylates (206) have been evaluated for this application. More recently, anionic surfactants have been used (207–220). Alpha-olefin sulfonates (AOS) have been found to possess good salt tolerance, chemical stability at elevated temperatures, and good oil solubilization (210,221), whereas less salt tolerant alkylaromatic sulfonates exhibit excellent chemical stability. The nature of the alkyl group, the aryl group, and the aromatic ring isomer distribution can be adjusted to improve surfactant performance under a given set of reservoir conditions (222,223).

Surfactant blends can provide improve cost effectiveness compared to use of a single surfactant. For example, the use of a blend of a synthetic polyisobutylene with a sulfonate surfactant, alcohols or nonionic surfactants has been described (224). Cosurfactant requirements can be minimized using a surfactant having a short-branched hydrophobe or a branched-alkyl substituent on an aromatic group (222,225) and a long ethoxy group chain (225). Blends of surfactants optimized for seawater or reservoir brine salinity include linear alkylxylene sulfonate–alcohol ether sulfate mixtures (226).

High (1–10%) concentrations of lignosulfonate have sufficient interfacial activity to increase oil recovery from unconsolidated sands (227). Lignosulfonates and petroleum sulfonates undergo a synergistic interaction resulting in ultralow interfacial tension and substantially increased oil recovery (228).

The effect of temperature, pressure, and oil composition on oil recovery efficiency have all been the subjects of intensive study (229). Surfactant propagation is a critical factor in determining the EOR process economics (230). Surfactant retention owing to partitioning into residual crude oil can be significant compared to adsorption and reduce surfactant propagation rate appreciably (231).

Various low cost sacrificial agents decrease surfactant adsorption on reservoir rock and increase the surfactant propagation rate. These agents include lignosulfonates and chemically modified lignosulfonates (6,80,143). Alkaline chemicals (198,199), particularly sodium silicate (232), which precipitate in the presence of divalent metal ions, can increase the surfactant propagation rate. Intermixing of polymer mobility control fluid with a previously injected surfactant slug can result in undesirable surfactant–polymer interactions affecting interfacial behavior and reducing oil displacement efficiency (233).

3.10. Alkaline Flooding. Alkaline or caustic flooding involves injection of high pH agents, eg, sodium hydroxide, sodium carbonate, or sodium silicate solutions. At equivalent Na_2O levels, the three alkaline agents gave equivalent recovery of each of nine different crude oils in laboratory core floods (234). However, the use of buffered sodium carbonate rather than strong alkali can result in reduced interaction with mineral surfaces. The lower reagent consumption can reduce the amount of sodium carbonate required.

These chemicals generate surfactants *in situ* by reacting with organic acids present in crude oil (232,235). Several oil recovery mechanisms may be operative. Probably the most significant oil recovery mechanism for this process is lowering of the capillary number (the ratio of viscous to capillary forces) through interfacial tension reduction. Other possible mechanisms are altering rock wettability (usually from oil-wet to water-wet), oil emulsification and entrapment resulting in lower injectant mobility (in turn resulting in a greater injectant volumetric sweep efficiency), oil emulsification and entrainment in the flowing aqueous phase, and possibly the solubilization of rigid films that may form at the oil–water interface.

Caustic flooding chemicals are relatively inexpensive. However, project economics are adversely affected by the large quantities that must be injected. The high pH agents react with reservoir clays (236) and are precipitated by divalent metal ions present in formation waters. Coinjection of a lignosulfonate (237) or a polyacrylate (238) reduces precipitation. This precipitation has been used to advantage to reduce adverse surfactant and polymer interactions with dissolved divalent metal ions. Injecting a caustic preflush causes divalent metal ion precipitation before beginning a micellar polymer flood (239). Ion-exchange processes promoting solubilization of divalent metal ions limit the effectiveness of preflushes injected before the caustic solution (240).

Including a surfactant in the caustic formulation (surfactant-enhanced alkaline flooding) can increase optimal salinity of a saline alkaline formulation. This can reduce interfacial tension and increase oil recovery (239,241,242). Both nonionic and anionic surfactants have been evaluated in this application (243,244). Encouraging field test results have been reported (245). Current (2005) operating costs in a waterflood in Oklahoma's Delaware-Childers Field are $20–22 per barrel of recovered oil (245). An alkaline-surfactant-polymer waterflood is being initiated that will increase the produced oil from 0.3 to 5%

of total produced fluids. At the estimated oil peak production of 4300 barrels/day expected in 2007, the higher oil cut and reduced water pumping costs should reduced operating costs to an estimated $10 per barrel of produced oil.

Surfactants evaluated in surfactant-enhanced alkaline flooding include internal olefin sulfonates (244), linear alkylxylene sulfonates (246), petroleum sulfonates (246), alcohol ethoxysulfates (242,247,248), and alcohol ethoxylates/anionic surfactants (241). Water-thickening polymers, either xanthan or polyacrylamide, can reduce injected fluid mobility in alkaline flooding (249) and surfactant-enhanced alkaline flooding (244,248). Cross-linked polymers have been used to increase volumetric sweep efficiency of surfactant–polymer–alkaline agent formulations (250). The combined use of alkali, surfactant, and water-thickening polymer has been termed the alkali–surfactant–polymer (ASP) process.

4. Other Technologies

Microbial-enhanced oil recovery involves injection of carefully chosen microbes. Subsequent injection of a nutrient is sometimes employed to promote bacterial growth. Molasses is the nutrient of choice owing to its relatively low (~$100/t) cost. In its absence, the main nutrient source for the microbes is often the crude oil in the reservoir. A rapidly growing microbe population can reduce the permeability of thief zones improving volumetric sweep efficiency. Microbes, particularly species of Clostridium and Bacillus, have also been used to produce surfactants, alcohols, solvents, and gases *in situ* (251). These chemicals improve waterflood oil displacement efficiency (see also BIOREMEDIATION).

Microbes adsorb and grow on reservoir rock surfaces fed by injected nutrients (252) and may have application in plugging thief zones near injection well bores. However, there is concern that the microbes can also enter lower permeability zones containing higher oil saturations thereby reducing oil production. Controlling the rate and location of bacterial growth and chemical production can be difficult. Bacterial growth near wellbores has been a common problem causing reduced injection rates and productivity. However, field test results have been promising (253). Variations of this technology continue to be patented (254).

The *in situ* combustion method of enhanced oil recovery through air injection (32,255,256) is a chemically complex process. There are three types of *in situ* combustion: dry, reverse, and wet. In the first, air injection results in ignition of crude oil and continued air injection moves the combustion front toward production wells. Temperatures can reach 300–650°C. Ahead of the combustion front is a 90–180°C steam zone, the temperature of which depends on pressure in the oil reservoir. Zones of hot water, hydrocarbon gases, and finally oil propagate ahead of the steam zone to the production well.

The oil zone is fairly cool, and in a viscous oil reservoir this can result in little oil movement (liquid blocking). Reverse combustion, in which oil ignition occurs near the production well, can avoid this problem. The combustion zone moves countercurrent to the flow of air from the injection well. Oil flows through heated rock and remains mobile. Reverse combustion requires more air and consumes more oil than forward combustion.

In wet combustion, water is injected concurrently and alternately with air, extending the steam zone and aiding heat transfer to the crude oil reducing oil viscosity. This can decrease the injected air/produced oil ratio and improve project economics.

Maintenance and propagation of the combustion front are problems. This has led to a near-wellbore technology in which the same well is used for air injection and oil production. The combustion front needs to be propagated for a relatively short distance (257).

5. Economic Aspects

World EOR production in 2000 averaged 199,000 m^3/day (1.25 million b/day) the world's 2000 oil production (258). In 2004, U.S. EOR production was 105,740 m^3/day (663,451 bbl/day) (259). Due to the rapidly fluctuating price of oil it is difficult to calculate the current value of this level of EOR production.

U.S. 2004 CO_2 EOR production of crude oil was 205,877 b/day (260). The price of crude oil must exceed US$25/bbl before CO_2 injection becomes economical (261). A CO_2 price sensitivity analysis indicates CO_2 must be priced at less that US$0.50 per thousand cubic feet before CO_2 injection becomes more economical than conventional production. Incentives for reduction of CO_2 emissions if industrially generated CO_2 is used would increase the CO_2 price that could be tolerated while achieving economic viability.

Injection of hydrocarbons accounted for 97,300 b/day of U.S. 2004 oil production (260). The amount of crude oil produced by this tehnology has been declining since 1992 due to the increasing price of natural gas. Notrogen injection accounted for 14,700 b/day of the 2004 U.S. oil production (260).

All thermal recovery methods accounted for 345,514 b/day of U.S. 2004 oil production with steam injection accounting for 98.6% of this amount (260). Chemical injection: micellar polymer, polymer, alkaline chemicals, and surfactants, accounted for only 60 b/day of U.S. 2004 oil production (260). The contribution of other EOR technologies to U.S. oil production was negligible.

The value of the oil produced by EOR methods varies with crude oil prices. Given recent oil price volatility, any financial estimates would have limited value.

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JOHN K. BORCHARDT
Shell Development Company

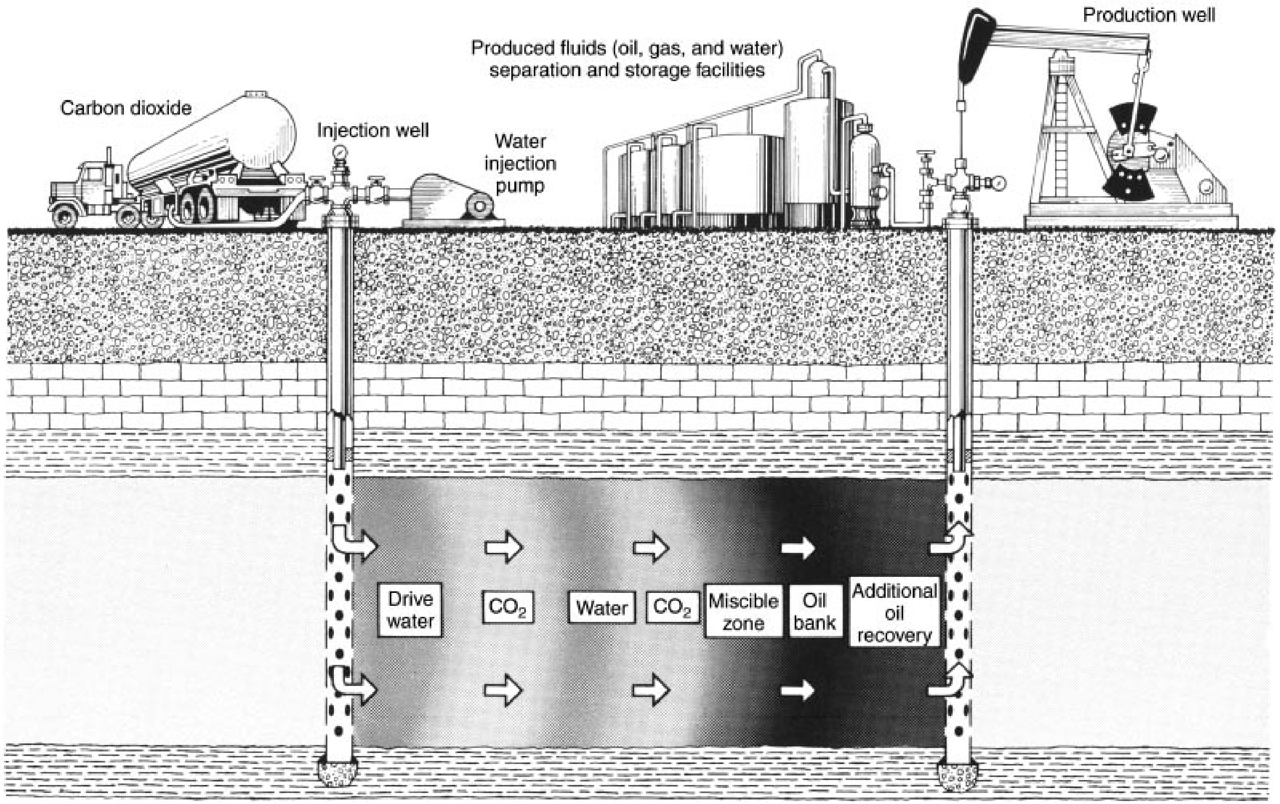

Fig. 1. Carbon dioxide flooding. The WAG process, in which a CO_2 slug is followed by alternate water and CO_2 injections, is usually employed. The viscosity of the oil is reduced providing more efficient miscible displacement. (Courtesy of the U.S. Dept. of Energy).

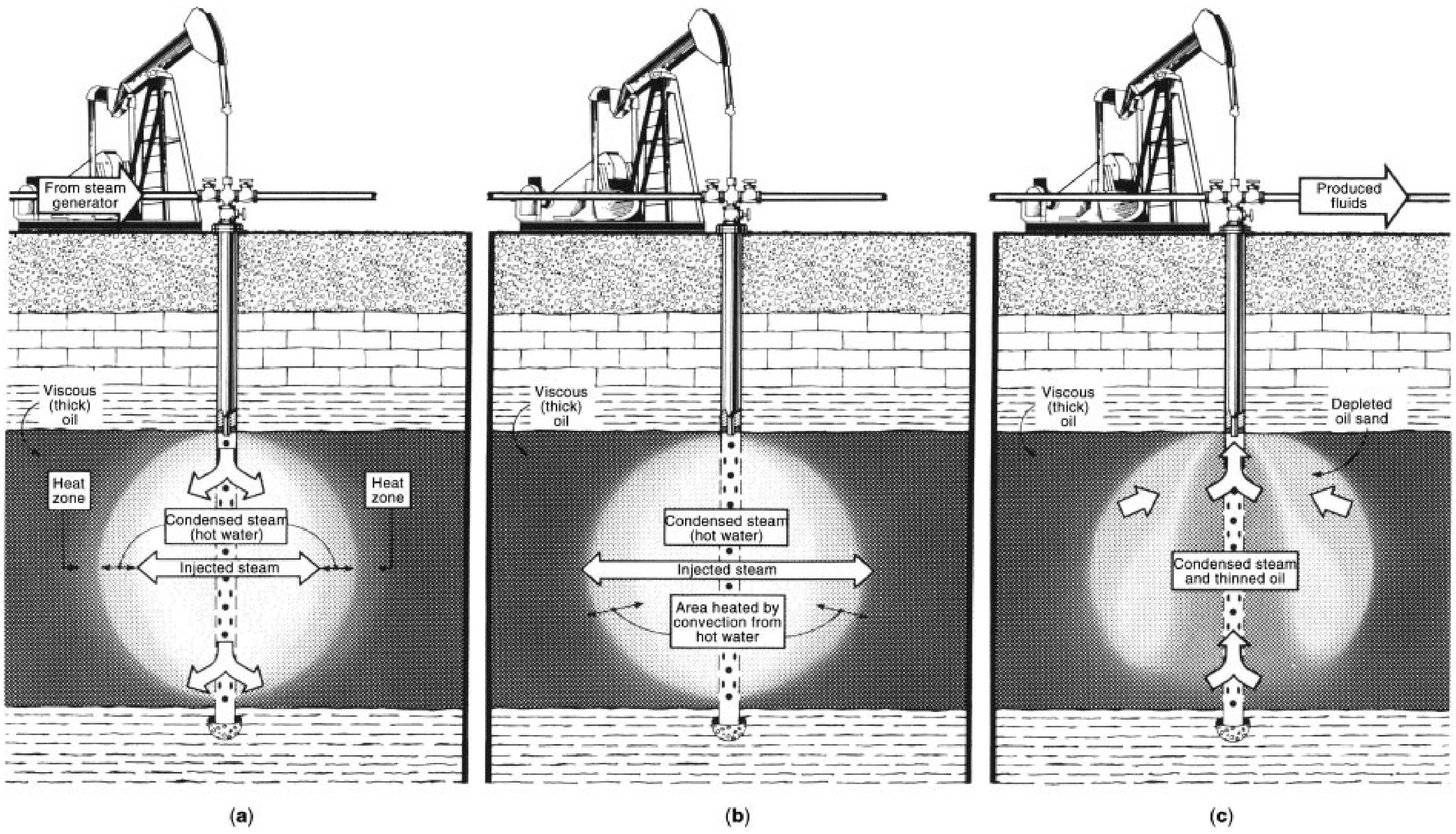

Fig. 2. Cyclic steam stimulation of an oil well: (**a**) steam, injected into a well over a period of days or weeks in a heavy oil reservoir, introduces heat (huff) that, coupled with (**b**), alternate soak periods lasting a few days to allow (**c**) a production phase of weeks or months (puff), thins the oil. This process may be repeated until production falls below a profitable level. (Courtesy of the U.S. Dept. of Energy).

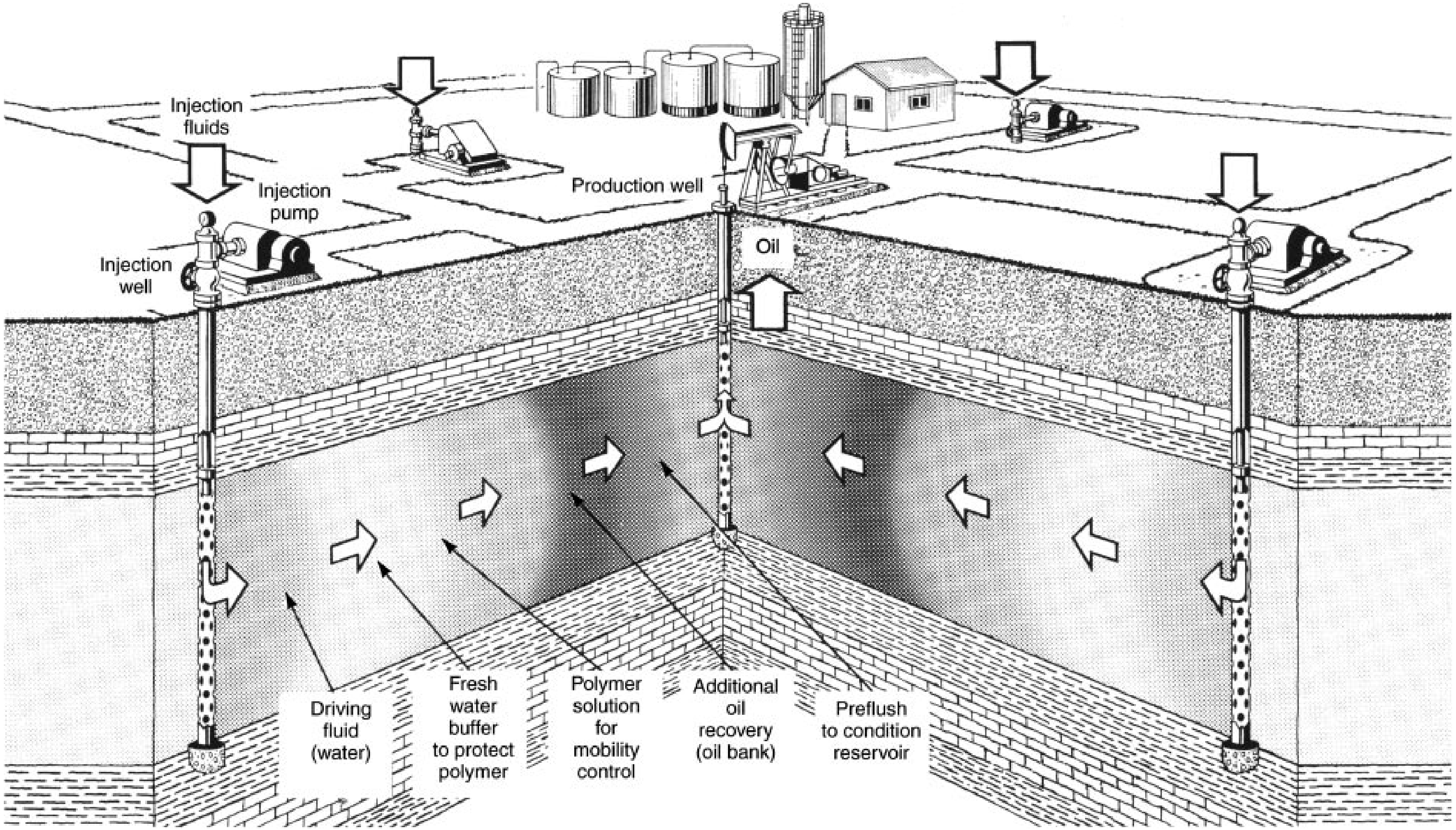

Fig. 3. This polymer flooding method requires a preflush to condition the reservoir, the injection of a polymer solution for mobility control to minimize channeling, and a driving fluid (water) to move the polymer solution and resulting oil bank to production wells. (Courtesy of the U.S. Dept. of Energy).

Table 1. **Properties of EOR Polymers**[a]

Property	Polyacrylamide	Xanthan gum
brine tolerance	very limited, especially to Ca^{2+}, Mg^{2+}	good to both mono- and divalent cations
shear stability	undergoes irreversible shear degradation	reversible shear thinning
maximum use temperature, °C	71–82[b]	71–77
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 especially at high temperatures
oxidative stability	susceptible	particularly susceptible especially at high temperatures
microbial degradation	susceptible	very susceptible

[a] Ref. 75.

[b] In very low salinity reservoirs temperatures can go to 107–121°C.