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Use of Carbon Dioxide in Enhanced Oil Recovery

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The use of carbon dioxide for supercritical extraction separation processes (*1, 2*) and supercritical fluid chromatography (*3*) has received much attention in recent years. A less familiar application of supercritical extraction is the use of high-pressure CO_2 to recover crude oil left behind by conventional methods for recovering oil from porous reservoir rocks. The target for more sophisticated enhanced oil recovery techniques is large. Of the more than 400 billion barrels of oil discovered in the United States, around 300 billion barrels will not be recovered by standard methods. Not all of the oil reservoirs included in that total are suitable for CO_2 flooding or other enhanced oil recovery methods, but there is considerable current effort in the oil industry to implement large-scale CO_2 injection projects. At least as measured by volumes of fluids used, CO_2 flooding will be the largest application of supercritical extraction over the next decade.

Summary. Large volumes of oil will remain in U.S. oil reservoirs when standard recovery methods have been completed. Supercritical carbon dioxide can be used to recover part of that remaining oil. If carbon dioxide is dense enough, it extracts hydrocarbons from the oil to make a mixture miscible with crude oil. Such a mixture can recover 95 percent of the oil in controlled laboratory flow settings. Heterogeneity of reservoir rocks and the low viscosity of carbon dioxide reduce the fraction of oil recovered in projects to lower but still significant levels. With the construction of three pipelines to carry naturally occurring carbon dioxide from Colorado and New Mexico to Permian basin oil fields, large-scale implementation of enhanced oil recovery by carbon dioxide flooding is now beginning.

Any successful oil recovery technique must overcome the forces that act to trap oil in the pores of reservoir rocks. At discovery, oil in a reservoir will usually flow to the surface unaided, driven by the natural pressure in the formation and by the expansion of gas dissolved in the oil. In a typical light-oil reservoir, primary production, as this simplest of oil recovery techniques is known, recovers only 10 to 20 percent of the oil originally in place. In reservoirs containing heavy, viscous oils, primary recovery may be significantly less. Since the 1940's, secondary recovery methods—injection of gas or water to maintain reservoir pressure and displace oil into producing wells—have been used to recover an additional 20 to 50 percent of the oil in place in light-oil reservoirs. More recently, steam has been injected into heavy-oil reservoirs to heat the oil and reduce its viscosity. In this article, we focus on the use of CO_2 for recovery of light oils, though CO_2 has also been used to reduce the viscosity of heavy oils (*4*).

Until the 1970's, the most important factor in the choice of a secondary recovery fluid was cost. Water and natural gas were used because they were inexpensive and readily available. However, gas is a poor displacing fluid because of its low viscosity; it costs more to compress and inject than water and its fuel value has increased markedly in recent years. Therefore, most secondary oil recovery is carried out by waterflooding, which now accounts for approximately half of the oil production in the United States. Unfortunately, water is not miscible with crude oil, and hence numerous interfaces are present in the reservoir rock as the displacement proceeds. The resulting capillary forces, which arise from oil-water interfacial tensions, trap oil in the very small converging and diverging channels that make up the pore space in reservoir rocks. Enhanced oil recovery processes for light oils are designed to reduce the effects of the capillary forces, which limit the performance of current secondary oil recovery techniques. One way to reduce the magnitude of capillary forces is to reduce the oil-water interfacial tension by adding surfactants—molecules with water-soluble heads and oil-soluble tails—to the injected water. Very low interfacial tensions can be achieved with the right choice of surfactants for a particular crude oil and particular reservoir conditions, and a variety of process designs have been tested in both laboratory and field displacements (*5*).

If interfaces between the injected fluid and the oil could be eliminated entirely, the effects of capillary forces would not arise. Thus, injection of a fluid miscible with oil could eventually recover essentially all of the oil. Unfortunately, solvents that are miscible with crude oil are likely to be hydrocarbons or hydrocarbon mixtures obtained from crude oil in the first place and therefore significantly more valuable than the crude oil displaced. Miscible floods with liquid hydrocarbon solvents are likely to be conducted only in special situations, for instance, where light hydrocarbon liquids such as propane or butane cannot be conveniently transported to market.

While injection of liquid solvents is not economically attractive, in situ genera-

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tion of a fluid miscible with crude oil can be. In this article we review the use of supercritical CO_2 for such an application. The principal mechanisms that lead to oil recovery are discussed, as are factors that act to limit process performance in actual oil field use. Finally, we summarize the status of efforts to implement full-scale CO_2 floods in U.S. oil reservoirs.

Phase Behavior

The performance of a CO_2 flood depends strongly on the physical chemistry of mixtures of CO_2 with the crude oil. Despite the fact that CO_2 injection processes are often referred to as miscible floods, pure CO_2 is not miscible with crude oils at typical reservoir temperatures and pressures. It can, however, extract hydrocarbons from the oil if the pressure is high enough. The essentials of the extraction process are illustrated in Fig. 1, where mixtures of CO_2 and crude oil are represented qualitatively at fixed temperature and pressure as mixtures of three components: CO_2; a light hydrocarbon pseudocomponent, which includes hydrocarbons having 2 to 12 carbon atoms (C_2–C_{12}); and a heavy hydrocarbon pseudocomponent, which includes hydrocarbons having 13 or more carbon atoms (C_{13}^+). Clearly, any crude oil has far more than two components, so this simple description of the effects of phase behavior, given first by Hutchinson and Braun (*6*) for natural gas as an injection fluid, has obvious limitations. Nevertheless, it describes qualitatively the key features of the extraction process.

On the pseudoternary diagram shown in Fig. 1, mixtures of CO_2 with crude oil having composition A (containing about 40 percent C_2–C_{12}) lie on the dilution line connecting the CO_2 apex with the oil composition. If a small amount of CO_2 is added to the oil, the mixture composition still lies in the single-phase region. The CO_2 simply dissolves in the oil. As more CO_2 is added, the mole fraction of CO_2 rises until the oil is saturated with CO_2 and has composition L_1. In a CO_2 flood, mixing occurs as CO_2 is injected into the reservoir rock and encounters the oil present. When the mixture composition reaches the boundary of the two-phase region at L_1, the mixture splits into two phases. Any mixture lying inside the binodal curve—the locus of upper- and lower-phase compositions—forms two phases in equilibrium. Each lower-phase composition is in equilibrium with a particular upper-phase composition. Phase compositions in equilibrium are shown in Fig. 1 connected by tie lines. The upper phase in equilibrium with lower phase L_1 is U_1, a phase richer in CO_2 and light hydrocarbons than the original oil. Such a phase has a lower viscosity than the oil-rich phase, and it moves more quickly away from the injection well and contacts fresh oil. The compositions of those mixtures lie along a second dilution line connecting U_1 with oil A. As mixture U_1 is added to oil A, the CO_2 mole fraction again rises until the saturated mixture of L_2 is reached. This time, however, the upper phase U_2 that appears contains even more C_2–C_{12} hydrocarbons because of the preferential extraction of C_2–C_{12} into U_1. When U_2 mixes with fresh reservoir oil, the dilution line lies outside the two-phase region, and hence U_2 is miscible with the original oil A. Thus, preferential extraction of light and intermediate hydrocarbons from the oil generates a mixture that avoids the two-phase region. That mixture can then displace the crude oil without interference from capillary forces. Such behavior is often referred to as multiple contact miscibility.

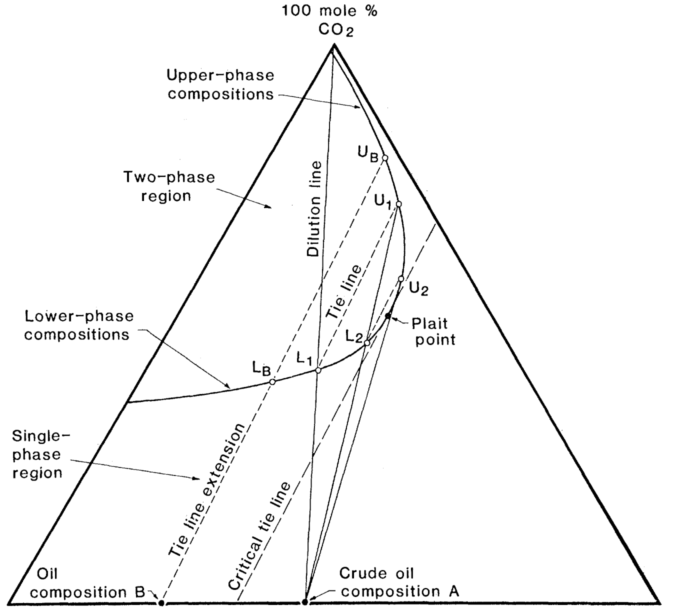

Fig. 1. Extraction of hydrocarbons from crude oil at fixed temperature and pressure to generate mixtures miscible with the oil.

At a given temperature and pressure, whether extraction generates miscible mixtures depends on the composition of the oil. For example, oil of composition B would not produce miscible upper phases. Extraction would proceed as described until the upper phase reached U_B. Mixtures of U_B with original oil would generate additional mixtures lying on the same tie line, and hence no further enrichment of the upper phases would occur. Thus, development of a miscible upper phase occurs only if the oil composition lies outside the region of tie line extensions. The boundary of that region is the critical tie line, the tie line tangent to the binodal curve at the plait point, a critical point at which upper and lower phases are identical.

The compositional effects described above are equivalent to a chromatographic separation of the components of the oil due to differences in the partitioning of components between the phases present. In fact, application of mathematical descriptions of chromatography (*7*) to one-dimensional flow of oil and CO_2 confirms the qualitative argument, provided the fluids are locally well mixed and effects of dispersion or other nonlocal mixing are negligible. As long as the oil composition does not lie within the region of tie line extensions, at a given temperature and pressure, extraction will generate fluids miscible with the oil.

The extractive power of CO_2 changes with changes in temperature and pressure. Since in most oil fields the temperature can be taken as fixed, the discussion here will focus on effects of pressure changes at constant temperature. The solvent strength of CO_2 for hydrocarbon molecules depends strongly on CO_2 density (*8*). For binary CO_2-hydrocarbon mixtures, the weight of hydrocarbon extracted into a unit volume of CO_2-rich phase increases by orders of magnitude as the density of CO_2 changes from low values (below about 0.2 g/cm^3) to high values (above 0.5 g/cm^3) (*3, 8, 9*). At a given pressure, small hydrocarbon molecules are extracted in greater quantities than large ones (*9*), and as pressure is increased, extraction of lighter molecules increases faster than that of heavy ones. Thus, the size of the two-phase region on a pseudoternary diagram (Fig. 1) decreases with an increase in pressure, and tie lines change slope. As the two-phase region shrinks, the region of tie line extensions also shrinks, the critical tie line moves to the left, and hence a greater range of oil compositions meets the criterion for development of miscibility. The pressure at which the critical tie line passes the oil composition is usually called the minimum miscibility pressure (MMP). It should be emphasized that CO_2 is not miscible with the oil at the MMP, but extraction can generate CO_2-hydrocarbon mixtures that are.

While this simple qualitative description illustrates how extraction can generate miscible fluids in a two-phase system, the phase behavior of CO_2–crude oil mixtures can be significantly more complex than that shown in Fig. 1. Figure 2 shows phase behavior typical of binary mixtures of CO_2 with crude oil. The data are for a crude oil from the Wasson field in west Texas, a field in which several operators are beginning large-scale CO_2 flood projects (*10*). Data like those reported in Fig. 2 are obtained in standard pressure-volume-temperature (*PVT*) measurements (*11*). In such an experiment, known volumes of oil and CO_2 are metered into a windowed cell. The volume, and hence the pressure, of the resulting mixture is varied by injecting or removing mercury. At each pressure the number of phases and their volumes are determined visually.

The volumetric behavior of various mixtures of CO_2 and the oil at 32°, 40°, and 50°C is shown in Fig. 2. At CO_2 mole fractions below about 70 mole percent, standard liquid-vapor phase behavior was observed. For instance, at low pressures a mixture containing 40 mole percent CO_2 formed a CO_2-rich vapor phase in equilibrium with an oil-rich phase containing some dissolved CO_2. As the pressure was increased, the vapor volume decreased as more CO_2 was forced into the oil. At each temperature, the last bubble of vapor disappeared when the liquid-vapor bubble point pressure (LVB) was reached. At higher pressures, only a single phase of oil and dissolved CO_2 was present. At fixed mole fraction of CO_2, the pressure required to force all of the CO_2 into solution increased with increasing temperature. At fixed temperature, the bubble point pressure increased with increasing CO_2 mole fraction.

At high CO_2 concentrations (above about 70 mole percent CO_2), more complex behavior was observed. For instance, at 32° and 40°C compression of a mixture containing 80 mole percent CO_2 first caused the vapor volume to decrease, as at lower CO_2 concentrations, but with additional pressure increases a second liquid phase appeared as the CO_2-rich vapor condensed. With a small additional pressure increase, the CO_2-rich vapor was all liquefied. Two liquid phases—a CO_2-rich liquid containing hydrocarbons extracted from the oil, and an oil-rich liquid containing considerable dissolved CO_2—persisted to the maximum pressure investigated. At 50°C, no three-phase region was observed. Instead, the CO_2-rich phase was a highly compressible, low-density phase at low pressure and a low-compressibility, dense phase at high pressure. At high CO_2 concentrations, separation of a small amount of heavy, asphaltic material was also observed (not shown in Fig. 2). Thus, for low-temperature CO_2–crude oil systems, up to four phases can appear for some CO_2 concentrations and pressures.

The complexity of CO_2–crude oil phase behavior is consistent, however, with that observed for simpler CO_2-hydrocarbon systems. Binary CO_2-alkane mixtures form two liquid phases as well as two liquids and a vapor for heptane and heavier hydrocarbons. If the alkane is tetradecane (C_{14}) or heavier, such behavior occurs at temperatures above the critical temperature of CO_2 (*12, 13*). The maximum temperature at which L_1-L_2 and L_1-L_2-V separations occur increases with increasing size of the hydrocarbon molecule (*13–15*). Because most crude oils contain substantial fractions heavier

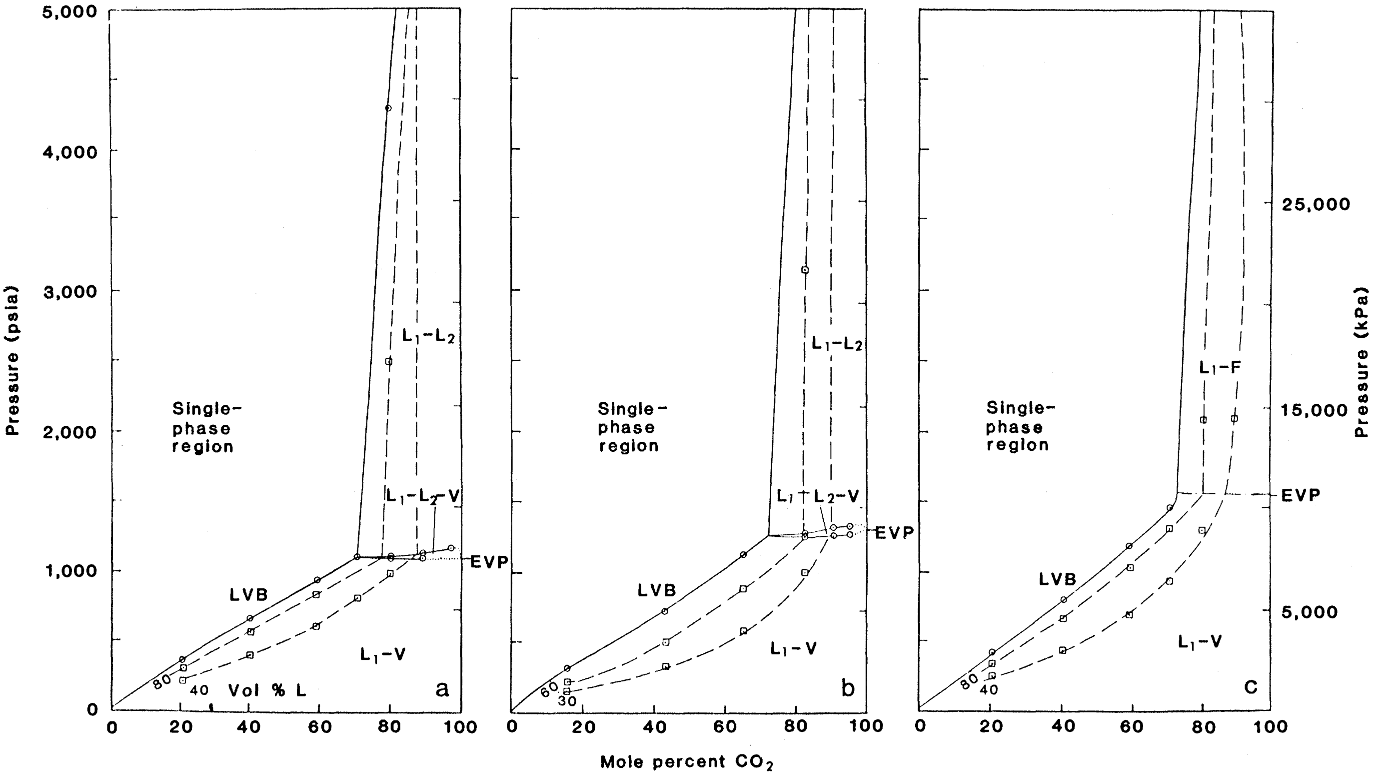

Fig. 2. Phase behavior of binary mixtures of CO_2 with Wasson oil (*10*). Dashed lines indicate volume fraction of the oil-rich liquid phase.

than C_{14}, L_1-L_2 and L_1-L_2-V behavior should be expected at temperatures above the critical temperature of CO_2. A review of phase diagrams reported for CO_2–crude oil mixtures (*15*) suggests that the maximum temperature for L_1-L_2-V behavior is about 50°C.

Phase Behavior and Flow

The simple explanation of compositional effects was given in terms of staged mixing operations. In actual CO_2 floods, however, the mixing takes place during flow of the various phases in the porous rock. The standard experiment for measuring the effects of phase behavior in a flowing system is the slim tube displacement. In a typical experiment, oil is displaced by CO_2 from a long (10 to 20 m), small-diameter (0.5 cm) tube packed with sand or glass beads. In this simple flow system, the porous medium is nearly uniform, and the flow diameter is small enough compared to the length that effects of flow instabilities which arise when a viscous fluid is displaced by a less viscous one are minimal. Hence, the flow is nearly one-dimensional, and effects of phase behavior dominate displacement performance. Displacements are performed at several pressures at fixed temperature, and the amount of oil recovered at each pressure is measured (*12*).

Typical results of slim tube displacements performed for one crude oil at different temperatures by Yellig and Metcalfe (*16*) are shown in Fig. 3. At each temperature, the amount of oil recovered at fixed injection volume (1.2 times the pore volume of the sand pack) initially increased with increases in pressure, but above some pressure no further increase in recovery was observed. That pressure is the same as the MMP described in the discussion of Fig. 1. Different investigators have used slightly different definitions of the MMP, but it is generally taken as the pressure above which additional increases in recovery are insignificant. At the higher temperatures, the pressure required to achieve high displacement efficiency also increased, and recovery increased more slowly with increasing pressure. That behavior is consistent with the idea that the pressure needed to produce a CO_2 density high enough for efficient extraction increases with increasing temperature and that density increases more slowly with increasing pressure at higher temperatures (*17*).

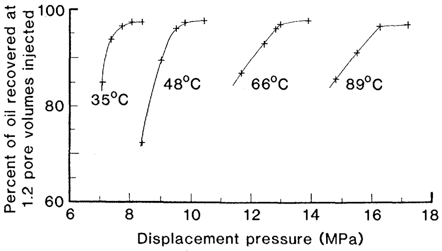

Fig. 3. Oil recovered at different temperatures in slim tube displacement tests with the same oil (*16*).

Several investigators have proposed correlations for the MMP. Yellig and Metcalfe (*16*) suggested an empirical correlation that depends only on temperature. Johnson and Pollin (*18*) offered a more complex empirical correlation, which included effects of temperature, injection gas composition, and a characterization of the aromaticity of the oil. Holm and Josendal (*17*) constructed a correlation based on the idea that for a given oil there is a characteristic density of CO_2 required to give sufficient extraction. They argued that the minimum density for effective extraction is 0.42 g/cm^3 and, in addition, that the density required must depend on the composition of the crude oil. They correlated the density required with the amount of C_5–C_{30} hydrocarbons present in the oil. Oils having high C_5–C_{30} content required relatively low densities, since those hydrocarbons are extracted more effectively than are heavier hydrocarbons, while heavier oils required a higher CO_2 density. Orr and Jensen (*10*) argued, on the basis of an analysis of CO_2–crude oil phase diagrams, that for low-temperature reservoirs (below about 50°C) the vapor pressure, extrapolated if necessary for temperatures above the critical temperature of CO_2, provides a reasonable estimate of the MMP. At temperatures above but close to the critical temperature, the density of CO_2 increases sharply at some pressure. The vapor pressure expression given by Newitt *et al.* (*19*)

$$P = 101.3 \exp\left(\frac{-2015}{T} + 10.91\right) \quad (1)$$

is a good estimate of that pressure. In Eq. 1, P is the pressure in kilopascals and T is the temperature in kelvins. Phase behavior experiments with crude oils have shown that L_1-L_2-V behavior occurs near the extrapolated vapor pressure (EVP), if it occurs at all (*10*). Thus, the EVP is an estimate of the pressure above which the CO_2-rich phase will be a liquid or at least a dense supercritical phase, either of which can extract hydrocarbons well. Such an estimate ignores the effects of oil composition, but at low temperatures such effects are less important than at high temperatures. Because the density increases so rapidly with pressure at the EVP, oil composition variations which require variations in CO_2 density have only a small effect on the pressure required to achieve that density.

The correlations suggested by Yellig and Metcalfe (*16*), Holm and Josendal (*17*), and Orr and Jensen (*10*) are compared with measured MMP's in Fig. 4. Part of the scatter in the experimental points is due to differences in crude oil compositions, but part is probably due to differences in experimental procedure and interpretation and to the use of fairly large pressure increments in slim tube tests. In general, however, the agreement supports the contention that the improvement in slim tube tests with increasing pressure is the result of better extraction of hydrocarbons by higher density CO_2. Figure 4 also gives an indication of the pressures required for efficient displacement at various temperatures. At 30°C, the vapor pressure of CO_2 is about 7 MPa (1000 psia), while at 100°C a typical pressure would be around 25 MPa (3600 psia). Such pressures are usually well within reach in all but the shallowest reservoirs or those in which large gas caps limit the rate at which pressure can be increased by fluid injection. One important advantage of CO_2 over other supercritical fluids is that the pressures required to produce high densities are relatively low, much lower than the pressures required for significant extraction by methane or nitrogen, for instance (*20*).

Attempts to verify the effects of phase behavior on flow through detailed calculations of the performance of slim tube displacements have been made by several investigators (*9, 21, 22*). In such calculations, phase behavior, variations of phase densities and viscosities with phase composition, and effects of the presence of more than one phase on flow velocities (relative permeability effects) are modeled. For instance, Sigmund *et al.* (*21*) used the Peng-Robinson equation of state to calculate equilibrium phase compositions from which fluid properties were calculated. Parameters needed to characterize pseudocomponents used in the calculations were obtained by matching calculated bubble point pressures to results of *PVT* experiments similar to those illustrated in Fig. 2. At the experimental temperature of 97°C only two-phase equilibria were observed. Good agreement was obtained between calculated and experimental results of slim tube displacements. The effects of

L_1-L_2 and L_1-L_2-V phase behavior were studied by Gardner *et al.* (*22*) and Orr *et al.* (*9*). Gardner *et al.* used results of volumetric measurements for CO_2–crude oil mixtures at 41°C to construct pseudoternary phase diagrams like Fig. 1 for both two- and three-phase systems. Those diagrams were then used in the calculations. Orr *et al.* (*9*) used a continuous-flow experiment to obtain detailed phase composition and density measurements for a CO_2–crude oil system at 32°C which showed L-V, L_1-L_2, and L_1-L_2-V at different pressures. Performance of slim tube displacements at the same pressures was then calculated on the basis of pseudoternary representations of the more detailed phase composition data. Calculated and experimental displacement results agreed well, as shown in Fig. 5 (*9*), although a phase density model too simple to reflect the actual behavior of the L_2 phase caused some disagreement late in the run at 6890 kPa. Sensitivity studies with the validated calculation scheme confirmed that phase behavior dominates the performance in the very simple flow geometry of a slim tube. The total amount of oil recovered at a given pressure is determined by the effectiveness of extraction, although the rate of recovery is strongly affected by volume change on mixing of CO_2 and oil (*9*).

Displacements in Reservoir Rocks

While the interaction of phase behavior and flow is well enough understood that quantitative prediction of performance is possible for slim tube displacements, at least four additional physical effects not present in the simple flows make quantitative predictions for displacements in reservoir rocks much more difficult. In actual reservoir displacements, viscous instabilities, segregation of fluids by gravity, heterogeneity of the reservoir rock, and the presence of water in portions of the pore space can have a considerable impact on displacement performance.

Viscous instabilities occur because the viscosity of CO_2 is very low, typically 0.02 to 0.05 mPa-sec at reservoir conditions. Typical viscosities of oils considered for CO_2 flooding range from about 0.5 to 5 mPa-sec. Thus, in most field applications the oil will be at least an order of magnitude more viscous than the injected CO_2. The displacement of a viscous fluid by a less viscous one is inherently unstable. The low-viscosity fluid fingers through the more viscous fluid, and the reservoir is not swept uniformly. The fact that dissolved CO_2 decreases the viscosity of an oil phase while extracted hydrocarbons increase the viscosity of the CO_2-rich phase reduces but does not eliminate the driving force for the instability (*15*). While the principal effect of viscous instability is to alter macroscopic fluid distributions in the reservoir, it also interacts with phase behavior to influence microscopic displacement efficiency. Gardner and Ypma (*23*) showed, with detailed calculations of the growth of viscous fingers in a CO_2–crude oil displacement, that mixing of uncontacted oil outside the finger with nearly pure CO_2 inside it leads to higher residual oil saturation in the zone swept by the finger. Thus, viscous instability alters both macroscopic and microscopic displacement efficiency.

Gravity segregation occurs when the injected fluid has a density different from that of the fluid present in the reservoir rock. The density of injected CO_2 is often quite close to that of the oil because a high CO_2 density is required for efficient extraction, but it is still substantially less than the density of water. In reservoirs that have high water saturations after waterflooding, good vertical communication, and reasonably thick formations, gravity segregation may also reduce the fraction of the reservoir swept by CO_2. Thus, even if the local displacement efficiency is very high in the swept zone, nonuniform distribution of injected fluid will reduce the average recovery for the whole reservoir.

In some cases it may be possible to take advantage of gravity forces to over-

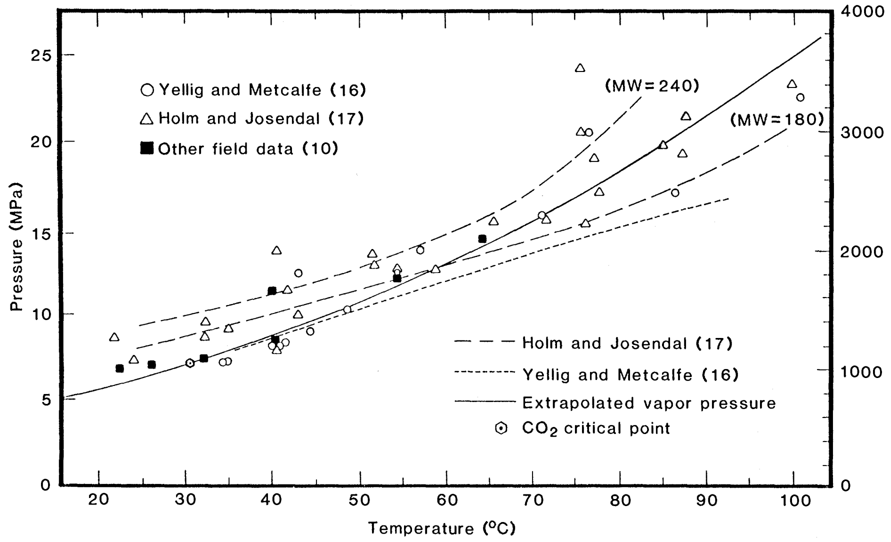

Fig. 4. Comparison of minimum miscibility pressure correlations with measured values.

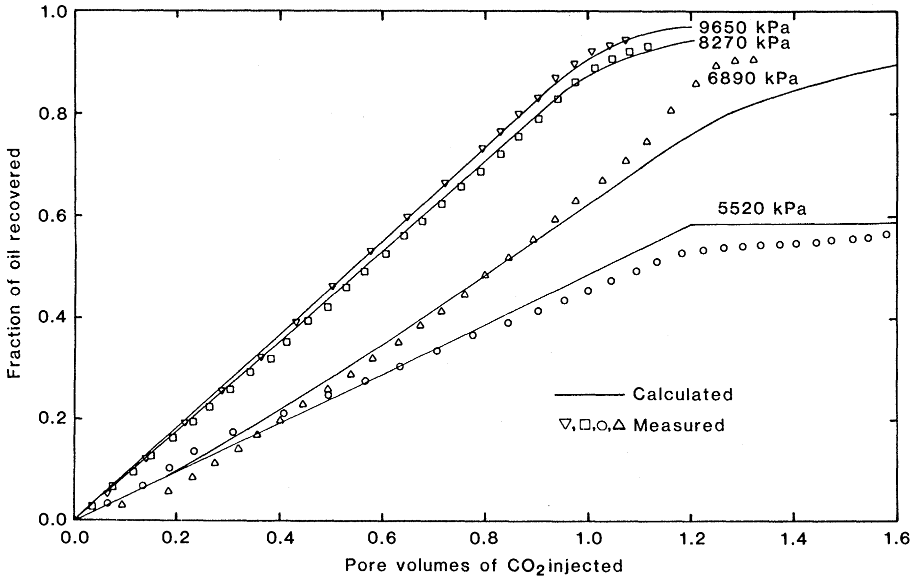

Fig. 5. Comparison of calculated and measured recovery of oil in slim tube displacements at 32°C.

come the adverse effects of viscous instabilities. A low-density, low-viscosity fluid injected near the top of a reservoir can displace oil downward without instability if the rate is low enough. For this reason, the displacement of oil by CO_2 (or another compressed gas such as methane or nitrogen) works best in steeply dipping formations. While gravity-stabilized displacements have been successfully tested (*24*), most reservoirs suitable for CO_2 flooding do not dip steeply enough to allow gravity stabilization.

On a large scale, heterogeneity—the areal and vertical variations in permeability and porosity always present in real reservoir rocks—also reduces the fraction of the reservoir swept by CO_2. In fact, the low viscosity of CO_2 aggravates the effects of heterogeneity as injected CO_2 seeks the easiest flow path from injection well to production well. Once a flow path between injector and producer has been established, large amounts of CO_2 may flow through that high-permeability zone while lower-permeability portions of the reservoir are swept more slowly.

Heterogeneity in reservoir rocks also affects microscopic displacement efficiency. Reservoir rocks show variations in porosity and permeability over length scales that vary from a few pore diameters (100 μm) to the distance between wells (300 m). At reservoir scale, heterogeneity affects gross fluid distributions. At the pore level, local heterogeneity alters mixing as CO_2 flows through paths of locally higher permeability and mixes with oil in less easily swept pores by diffusion (*25*). The presence of water in some fraction of the pore space can also alter the efficiency with which injected fluid contacts and mixes with the oil (*26–28*). If the rock is wet by oil rather than water, then oil occupies the finer pores, and continuous oil flow paths through the rock exist even at high water saturations. In such systems, CO_2 appears to contact oil efficiently even after a waterflood (*28–30*). In water-wet rocks, however, oil is trapped as droplets isolated by water. While CO_2 can diffuse through water to reach and swell trapped droplets, as demonstrated in flow visualization experiments with CO_2, water, and oil at high pressure (*30*), the time and space scales of such mixing are quite different from those in a slim tube. Since mixing of oil and CO_2 is an essential requirement of the mechanism that generates miscible fluids, changes in mixing behavior are likely to alter microscopic displacement efficiency, though the details of such behavior are not yet understood well enough to permit quantitative prediction of the importance of such effects in displacements at field scale.

It is the range of scales on which physical mechanisms operate that makes prediction of performance at reservoir scale so difficult. Reservoir simulators—large computer programs that solve differential equations describing the flow of fluids in a reservoir—are in everyday use in the oil industry. When the fluids are oil, water, and gas and the only compositional effect is the liberation of gas dissolved in the oil as the pressure declines, simulators can do a good job of modeling macroscopic fluid movements, despite the inevitable uncertainty about the description of the reservoir itself. When component transfers between phases and mixing at the pore level strongly affect microscopic displacement efficiency, simulation is much less accurate (*11*). Much remains to be learned about the description of the flow of multicomponent, multiphase fluids in reservoir rock for use in field-scale predictions.

Field Experience

Use of CO_2 has been tested in a wide range of reservoir settings (*20*). Extensive testing in pilot-scale operations began in the 1970's and has continued to the present, with more than 30 field tests performed so far. While not all fields are suitable for CO_2 injection, it is effective in a surprising range of reservoir conditions. The process has been tried in sandstones and carbonate rocks, at temperatures below the critical temperature of CO_2 and as high as 120°C, and in waterflooded reservoirs as well as reservoirs with low water saturations. Some of the field tests have been quite large. A 33,000-acre CO_2 flood, using CO_2 separated from natural gas produced in southwest Texas, began in the Kelly-Snyder field in west Texas in 1972 (*31*). The operators expect to recover 88 million barrels of additional oil with CO_2. Good response was also obtained in the smallest Crossett field nearby (*32*). Pilot tests in the Little Creek field (*33*) and Slaughter Estate Unit (*34*) showed clearly that CO_2 could recover oil from waterflooded reservoirs. Significantly different performance has been observed in field tests performed so far. The amount of oil recovered has ranged from 10 to 40 percent of the remaining oil and the amount of CO_2 required to recover a barrel of oil from 3000 to more than 20,000 cubic feet of CO_2 at standard conditions (*35*). About 2000 cubic feet are required to produce a volume of 1 barrel at reservoir conditions.

In general, field experience has been good enough that large-scale implementation of CO_2 flooding is now beginning. Two large pipelines have been constructed to transport naturally occurring CO_2 from fields in southwest and southeast Colorado to very large oil fields in the Permian basin at the Texas–New Mexico border. Construction of a third pipeline from northeast New Mexico to the Permian basin is also under way. Investments in pipelines and injection facilities will total in the billions of dollars for operations in the Permian basin alone. There is also considerable activity in Gulf Coast reservoirs in Mississippi and Louisiana.

In the near future, the application of CO_2 for enhanced oil recovery will probably be limited by the availability of CO_2. Natural sources are currently cheapest even with the added cost of pipelines required to deliver CO_2 from long distances (as much as 500 miles). Carbon dioxide is sometimes available as a sidestream from refineries and ammonia plants and may be produced in large quantities if coal gasification projects are implemented. Very large quantities of CO_2 are vented in power plant stack gases, but improvements in separation technology will be required before economic use of CO_2 at such low concentrations will be possible. Despite the remaining uncertainties in the prediction of CO_2 flood performance, CO_2 supplies, and process economics, it is clear that large-scale use of supercritical CO_2 for enhanced oil recovery is assured.

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β-Carotene: An Unusual Type of Lipid Antioxidant

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Summary. The mechanism of lipid peroxidation and the manner in which antioxidants function is reviewed. β-Carotene is a purported anticancer agent, which is believed by some to have antioxidant action of a radical-trapping type. However, definitive experimental support for such action has been lacking. New experiments in vitro show that β-carotene belongs to a previously unknown class of biological antioxidants. Specifically, it exhibits good radical-trapping antioxidant behavior only at partial pressures of oxygen significantly less than 150 torr, the pressure of oxygen in normal air. Such low oxygen partial pressures are found in most tissues under physiological conditions. At higher oxygen pressures, β-carotene loses its antioxidant activity and shows an autocatalytic, prooxidant effect, particularly at relatively high concentrations. Similar oxygen-pressure-dependent behavior may be shown by other compounds containing many conjugated double bonds.

Epidemiological studies indicate that the incidence of cancer may be slightly lower among individuals with an above-average intake of β-carotene and other carotenoids (*1*). Although the association between dietary β-carotene and decreased cancer incidence may not reflect a causal relationship, β-carotene may exert a genuine protective effect against the onset of cancer (*1*). Several mechanisms for its possible protective action have been suggested (*1*). One of the most interesting proposals is that β-carotene deactivates reactive chemical species, such as singlet oxygen and free radicals, that would otherwise initiate harmful reactions such as lipid peroxidation (*2*) and, through this process, eventually induce cancer (*3–15*). There is ample evidence that β-carotene is a very effective quencher of singlet oxygen (*16, 17*), but the scope of its radical-trapping abilities has not yet been defined.

Experimental evidence from our laboratory shows that β-carotene can indeed function as an effective radical-trapping antioxidant. However, because β-carotene represents a previously unknown class of biological antioxidants it is appropriate first to review the mechanism of lipid peroxidation (autoxidation) and the ways in which conventional antioxidants work.

Mechanism of Autoxidation

Lipid peroxidation in vivo provides a steady supply of free radicals since it is a chain reaction in which the chain is carried by free radicals. This process is generally represented as

Initiation: production of $R^\cdot$ from a molecular precursor (1)

Propagation:

$$R^\cdot + O_2 \rightarrow ROO^\cdot \quad (2)$$

$$ROO^\cdot + RH \rightarrow ROOH + R^\cdot \quad (3)$$

Termination:

$$ROO^\cdot + ROO^\cdot \rightarrow \text{nonradical products} \quad (4)$$

In this reaction scheme, RH represents the lipid (generally a polyunsaturated fatty acid moiety) and $R^\cdot$ the carbon-centered radical derived from it. The overall rate of autoxidation can be represented by

$$-d[O_2]/dt = k_3[RH]R_i^{1/2}/(2\ k_4)^{1/2} \quad (5)$$

where R_i is the rate of initiation and the k's are the rate constants for the indicated reactions. It should be noted that the overall rate of autoxidation does not depend on the oxygen pressure. This somewhat unexpected result has been shown to apply to many different classes of oxidizable substrates at ambient temperatures and at oxygen pressures equal to or greater than those of normal air (*18–20*). Reaction 4 is very much slower than most reactions between two free radicals.

Mechanism of Antioxidant Action

The molecular precursor for the initiation process is generally the hydroperoxide product, ROOH. Lipid peroxidation is therefore a branching chain reaction with potentially devastating effects on a living organism. To control and reduce lipid peroxidation, nature makes use of

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