

# Symposium

## Enhanced Oil Recovery—Facts and Challenges

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### Carbon Dioxide Flooding for Enhanced Oil Recovery: Promise and Problems

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#### ABSTRACT

Of the enhanced oil recovery methods currently being considered for application to many of the nation's older oil fields, carbon dioxide flooding may offer the largest potential for additional oil recovery. The physical mechanisms by which CO<sub>2</sub> contacts and mobilizes crude oil are reviewed. Influence on the displacement process of factors such as the phase behavior of CO<sub>2</sub>-crude oil mixtures, swelling of oil by dissolved CO<sub>2</sub>, and reduction of oil viscosity are considered. Adverse effects of the viscous instability which occurs when very low viscosity CO<sub>2</sub> displaces the more viscous oil and water are discussed. Advantages and disadvantages of three potential methods for controlling the mobility of CO<sub>2</sub> are reviewed: thickening CO<sub>2</sub> with polymeric additives, reduction of CO<sub>2</sub> mobility by high water saturations, and use of surfactants to generate foam-like emulsions of water and CO<sub>2</sub>. Field experience to date and the recent surge in field activity are discussed. Finally, a brief assessment of the future of CO<sub>2</sub> flooding research and practice is offered.

#### INTRODUCTION

Enhanced oil recovery processes attempt to recover oil left behind by conventional primary and secondary recovery methods. When an oil field is first discovered, oil will usually flow into a producing well under the natural pressure of the fluids present in the porous reservoir rocks. As fluid is removed from the reservoir, however, the pressure declines. Oil flows more slowly into the wells and may not flow to the surface without pumping. Even if pumps are installed to bring the oil to the surface, primary production usually recovers only about 15-20% of the oil originally in place in the reservoir. To supply additional energy to drive oil out of the porous rock and into the producing well,

fluid must be injected into the reservoir. Secondary recovery methods use injection of gas or water to restore the driving force for flow through the reservoir rock. Much of the oil now being produced in the United States comes from fields which are being waterflooded. Because water is a very inexpensive fluid and because waterflooding usually produces as much or more oil than is obtained during primary production, waterflooding has become the standard technique for recovering oil left after primary production methods. However, water is not an ideal fluid for forcing oil from the very small pores of a reservoir rock. Because water and oil are immiscible, capillary forces, which arise from the interfacial tension between oil and water, act to trap a significant portion of the oil as isolated droplets. As water displaces oil from the reservoir rock, the oil saturation, or fraction of the volume of the pore space occupied by oil, decreases until it reaches a limiting value, the "residual oil saturation." At this point, all of the remaining oil is trapped and no longer flowing. Of the more than 400 billion barrels of oil discovered in the U.S., nearly 300 billion barrels will remain after primary and secondary recovery methods have been applied. Thus, the target for enhanced oil recovery processes is a large one, indeed.

Tertiary recovery methods are designed to overcome, in one way or another, the capillary forces which trap the oil during waterflooding. In some methods, surfactants are injected which reduce the interfacial tension between oil and water and thus allow the trapped oil droplets to be mobilized. In other methods, fluids which are miscible with oil are injected. Because there are no interfaces between the oil and the injected fluid, capillary forces are not present,

and in principle, all the oil which can be contacted can be recovered. Unfortunately, fluids such as liquid propane, which are truly miscible with oil, are now much too expensive for most field applications. The volume of fluid required is large, so that the fluid chosen must be inexpensive and available in large quantities.

One fluid which meets those requirements is carbon dioxide. Large natural supplies of nearly pure CO<sub>2</sub> have been found in New Mexico and Colorado, and several large pipelines to carry that CO<sub>2</sub> to Permian Basin oil fields are planned. CO<sub>2</sub> may also be available from power plant stack gases, ammonia plants and coal gasification plants (1).

CO<sub>2</sub> is not strictly miscible with crude oil, however. If mixed with oil, it forms two phases at typical reservoir conditions. Under the right conditions, however, it can displace oil nearly as efficiently as a truly miscible solvent. The key to understanding how CO<sub>2</sub> can displace oil efficiently lies in the phase behavior and fluid properties of CO<sub>2</sub>-oil mixtures. This paper reviews the physical mechanisms by which CO<sub>2</sub> contacts and mobilizes crude oil, describes the problems which will be encountered in field applications of CO<sub>2</sub> flooding, and documents the recent surge in field activity.

**Displacement Mechanisms**

When CO<sub>2</sub> is injected into a waterflooded oil reservoir, it displaces some of the water and mixes with the oil left behind by the waterflood. Figure 1 describes the behavior of binary mixtures of CO<sub>2</sub> and crude oil (containing dissolved natural gas) from the Wasson field, a large field in West Texas for which a CO<sub>2</sub> flood is planned. The behavior of a particular mixture depends on the CO<sub>2</sub> concentration and the pressure. For instance, the original oil (0% CO<sub>2</sub>) is a liquid at pressures above 900 psia but splits into liquid and vapor below that pressure. A mixture con-

taining 40 mol % CO<sub>2</sub> forms a single liquid phase above 1,350 psia and a liquid and a vapor at lower pressures. At high CO<sub>2</sub> concentrations, the phase behavior is more complex. At low pressures, liquid and vapor phases form. As the pressure is increased, the vapor phase, which contains CO<sub>2</sub> and the light hydrocarbon gases, condenses into a second liquid phase. There is a narrow pressure range over which two liquids and a vapor coexist. Above those pressures, two liquids form, a CO<sub>2</sub>-rich liquid and an oil-rich liquid. The phase behavior shown in Figure 1 is typical of that observed for crude oils from reservoirs at temperatures below about 120 F (50 C) (1-4). At higher temperatures, the two-phase region has the same general shape, but there is no three-phase region. Instead, the CO<sub>2</sub>-rich phase is a low-density vapor at low pressures and a dense, supercritical phase at high pressures.

It is apparent from Figure 1 that CO<sub>2</sub> is quite soluble in crude oil at typical reservoir pressures, but it is not miscible in all proportions at any reasonable pressure. For instance, at 2,500 psia, the CO<sub>2</sub> mole fraction must be nearly 0.7 before a second, CO<sub>2</sub>-rich phase appears. Thus, when CO<sub>2</sub> is injected into rock and contacts trapped oil, at first it simply dissolves in the oil droplets. The dissolved CO<sub>2</sub> does occupy some volume, however. Figure 2 illustrates how dissolved CO<sub>2</sub> swells several Permian Basin crude oils. The swelling factor reported in Figure 2 is defined as the volume of the saturated CO<sub>2</sub>-oil mixture divided by the volume of the oil alone. Figures 1 and 2 indicate that, as the amount of CO<sub>2</sub> present increases, higher pressure is needed to force all of the CO<sub>2</sub> into solution, and the oil expands as additional CO<sub>2</sub> dissolves in it. Thus, as CO<sub>2</sub> is injected into a waterflooded reservoir, trapped oil droplets will swell, some droplets will coalesce, and hence, some oil will begin to flow. The total amount of oil which can be mobilized by swelling, however, is limited. Only the oil which has a saturation greater than the residual oil saturation can flow and be recovered by an immiscible displacement. Thus, if swelling alone accounted for the recovery of oil by CO<sub>2</sub> flooding, the incremental recovery of oil would be relatively low.

Fortunately, there is an additional mechanism which, under the right circumstances, can lead to a more efficient displacement. This mechanism is similar to the "Vaporizing Gas Drive" in which high-pressure methane is used to displace oil (5). As more CO<sub>2</sub> is injected, the oil eventually becomes saturated and a CO<sub>2</sub>-rich phase appears. This phase is not pure CO<sub>2</sub>, however, but is a mixture of CO<sub>2</sub> and hydrocarbons extracted from the oil. Figure 3 illustrates the compositional behavior of mixtures of CO<sub>2</sub> with recom-

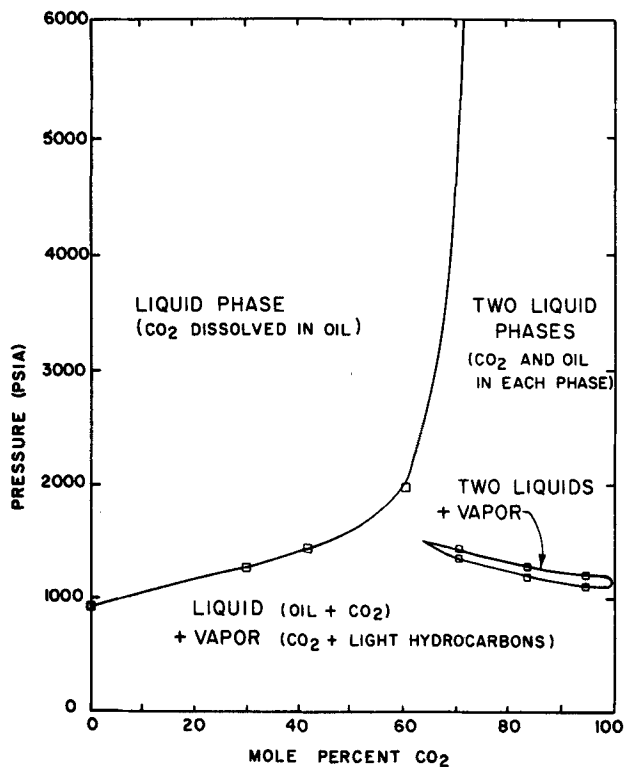


FIG. 1. Phase behavior at 90 F (32 C) of binary mixtures of CO<sub>2</sub> with a recombinant Wasson oil containing 312 SCF/BBL.

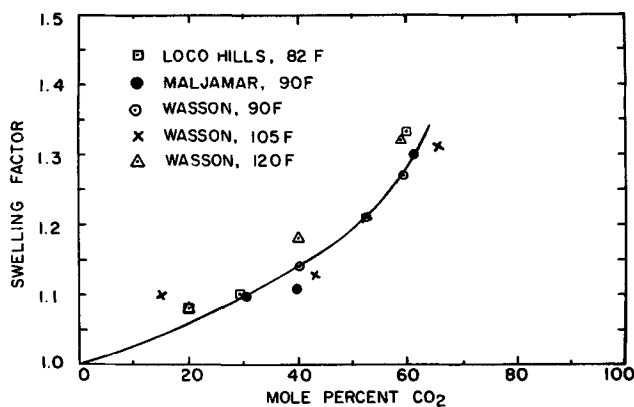


FIG. 2. Swelling of oil by CO<sub>2</sub> (volume of oil saturated with CO<sub>2</sub> divided by the volume of the oil).

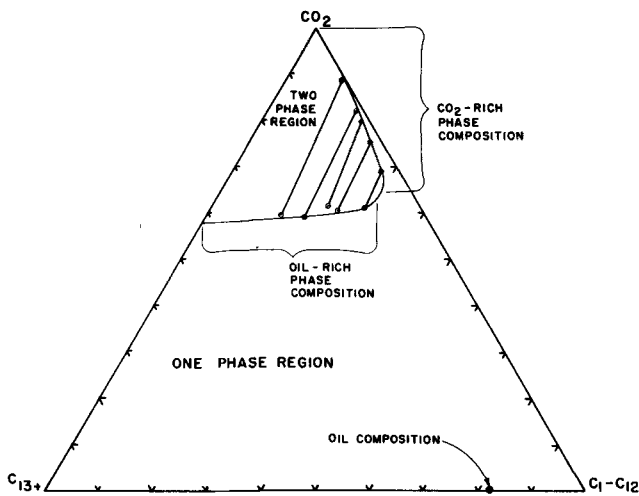


FIG. 3. Pseudoternary phase diagram at 2,500 psia and 90 F (32 C) for mixtures of CO<sub>2</sub> with a recombined Maljamar oil containing 650 SCF/BBL solution gas.

bined crude oil from the Maljamar field (4), in which a pilot CO<sub>2</sub> flooding is being performed. In Figure 3, the compositions of CO<sub>2</sub>-oil mixtures are represented in terms of three pseudocomponents: CO<sub>2</sub>, light hydrocarbons (C<sub>1</sub>-C<sub>12</sub>), and heavy hydrocarbons (C<sub>13</sub> and heavier), though the mixtures actually contain many more components. In the system shown in Figure 3, mixtures of CO<sub>2</sub> and oil containing more than about 60 mol % CO<sub>2</sub> fall into the two-phase region, in which a CO<sub>2</sub>-rich phase is in equilibrium with an oil-rich phase. Tie lines, which connect compositions of phases in the equilibrium, are shown in the two-phase region. Any mixture which has an overall composition lying on a tie line will split into phases whose compositions lie at the ends of the tie lines. As Figure 3 shows, the CO<sub>2</sub>-rich phases can contain substantial mole fractions of hydrocarbons if the overall mixture contains enough of the light hydrocarbons which are preferentially extracted by the CO<sub>2</sub>.

The effect of this extraction behavior on the displacement process is illustrated in Figure 4. Mixtures of reservoir oil A with CO<sub>2</sub> lie on the straight line connecting the CO<sub>2</sub> apex with the oil composition. As CO<sub>2</sub> is added to reservoir oil A, as it would be during CO<sub>2</sub> injection into a reservoir, the overall composition moves along that straight line (with CO<sub>2</sub> dissolving in and swelling the oil) until the two-phase envelope is reached at the composition L<sub>1</sub> (5). At this point, a CO<sub>2</sub>-rich phase of composition U<sub>1</sub> appears. As discussed later, this phase is much less viscous than the oil, so it moves more rapidly under the imposed pressure gradient; thus, the fluids of composition U<sub>1</sub> mix with fresh reservoir oil. Mixtures of upper phase U<sub>1</sub> with reservoir oil A lie on a second straight line connecting their compositions. As the oil is diluted with phase U<sub>1</sub>, the overall composition changes along that line until the composition L<sub>2</sub> is reached. This time, the CO<sub>2</sub>-rich phase has composition U<sub>2</sub>. The contacting process is then repeated, with the upper phases becoming increasingly enriched with light hydrocarbons (L). With repeated contacts, the upper phase eventually contains enough extracted hydrocarbons that it is miscible with reservoir oil A. That is, the straight line connecting the upper phase composition with the oil composition no longer passes through the two-phase region. In this case, CO<sub>2</sub> is said to have "developed" miscibility with the oil through a "multiple contact" process.

If the oil had had a different composition, say that of

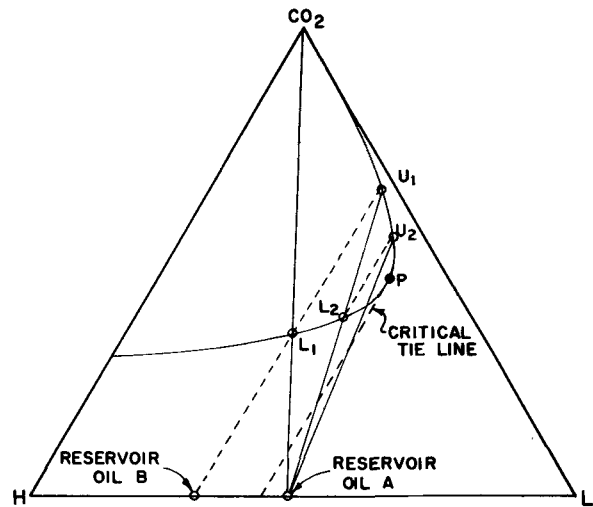


FIG. 4. Development of miscibility in CO<sub>2</sub>-crude oil systems.

reservoir oil B in Figure 4, the development of miscibility would not have occurred. The contacting process would have proceeded as just described until the upper phase composition had reached U<sub>1</sub>. Then, further contacts of the U<sub>1</sub> phase with oil B would produce no composition change, since those mixtures would always fall on the same tie line. Thus, oil compositions which lie in the region of tie line extensions do not contain enough light hydrocarbons (L) to develop miscibility. The dividing line between oil compositions which develop miscibility and those which do not is the "critical tie line" shown in Figure 4, the tie line which is tangent to the phase envelope at the plait point (P) where upper and lower phase compositions are identical.

Because the phase behavior of CO<sub>2</sub>-crude oil mixtures depends on the pressure (see Fig. 1), the location of the critical tie line can be changed by changing the system pressure. An increase in pressure causes the two-phase region to shrink, which displaces the critical tie line to the left, as shown in Figure 5. Tie line slopes may also change to reflect more effective extraction of hydrocarbons at higher pressures. Thus, an oil for which the multiple contact process did not develop miscibility at a low pressure could develop miscibility at a higher pressure.

Figure 6 shows the effect of displacement pressure on the recovery of oil from a long (40-ft), slim (0.25 in. id) tube packed with small glass beads (4) (see ref. 6 for a review of laboratory techniques used to evaluate reservoir oils for CO<sub>2</sub> flooding). At 800 psia, the displacement was relatively inefficient. Only about 50% of the oil was recovered. At 1,000 psi, the displacement recovered 90% of the oil and at 1,200 and 1,400 psi, nearly 95% of the oil was displaced. Clearly, CO<sub>2</sub> displacement efficiency in this ideal porous flow system can be very high.

Detailed numerical simulations of the displacement process (7,8) are consistent with the qualitative description already given for ideal displacements such as those performed in laboratory slim tubes. In field-scale CO<sub>2</sub> floods, there are additional complexities, the effects of which are not completely understood. For instance, in tertiary CO<sub>2</sub> floods, the water which surrounds trapped oil droplets may restrict the access of injected CO<sub>2</sub> to the oil droplets. If mixing of CO<sub>2</sub> with trapped oil were less efficient, then the benefits of the multiple contact extraction process described would also be reduced.

An additional and, perhaps, more important complexity

affecting field-scale CO<sub>2</sub> displacements arises from nonuniformities of flow, particularly if the reservoirs are heterogeneous (as most are). This problem is seriously magnified by the low viscosity of CO<sub>2</sub> compared to oil. When CO<sub>2</sub> dissolves in oil, the viscosity of the resulting mixture is lower than that of the original oil. Figure 7 shows a correlation given by Simon and Graue (9) for the effect on viscosity of saturating oil with CO<sub>2</sub> at 120 F (32 C). If the saturation pressure is high enough, substantial viscosity reductions can occur. Unfortunately, however, the viscosity of the CO<sub>2</sub>-oil mixture is still much higher than that of pure CO<sub>2</sub>, and much of the difficulty remains.

**Viscous Instability and Mobility Control**

Discussion so far has focused on the microscopic or local behavior of CO<sub>2</sub>-oil mixtures, but the performance of a CO<sub>2</sub> flood on a reservoir scale is also influenced by the macroscopic behavior of the displacement regions which occur as CO<sub>2</sub> pushes oil. In any flood in which a less viscous fluid displaces a more viscous one, the displacement front is unstable. As a result of the instability, an initially

sharp displacement front becomes convoluted and develops "fingers."

In Figure 8, modified from Habermann (10), the difference between stable and unstable displacements is illustrated for a symmetry element of a two-dimensional reservoir. In Figure 8a, the injected fluid has a viscosity equal to or greater than that of the fluid in place. The displacement front advances uniformly through the porous medium and at time t<sub>3</sub>, when injected fluid breaks through into the producing well, most of the reservoir has been swept. In Figure 8b, the injected fluid has a viscosity which is significantly lower than that of the fluid in place. In this case, the displacement is no longer uniform. At time t<sub>1</sub>, the displacement front is irregular. The nonuniformities (viscous fingers) grow with additional injection, and a much smaller portion of the reservoir has been swept when injected fluid breaks through at time t<sub>2</sub>. Thus, in displacements in which a fluid of low viscosity, such as CO<sub>2</sub>, drives one of higher viscosity, oil, the displacement front is inherently unstable. Such adverse mobility displacements are characterized by early breakthrough and poor areal sweep efficiency.

At reservoir pressures and temperatures, CO<sub>2</sub> has a viscosity of a few hundredths of a centipoise, whereas the viscosities of oils for which CO<sub>2</sub> floods are planned usually lie in the range of 1-10 centipoise. Thus, in CO<sub>2</sub> floods, the mobility ratio (ratio of oil viscosity to CO<sub>2</sub> viscosity) is in the range 10-100, so that viscous instabilities will cause early breakthrough of CO<sub>2</sub>. By establishing high-mobility paths from injection to production wells, viscous fingering also reduces the recovery rate of oil. Thus, the overall efficiency of the displacement process is much lower in a reservoir than in the ideal slim tube displacement. An analogous instability occurs if a denser fluid overlies a less dense one in a porous medium. Indeed, the two situations can be treated simultaneously and even played-off against each other if they are of opposite signs. A downward displacement of a heavy, viscous liquid by a lower density, less viscous fluid can be gravitationally stabilized if the displacement front velocity is less than a critical value. In fact, CO<sub>2</sub> floods at Weeks Island and Bay St. Elaine, both in Louisiana, have been designed to take advantage of the difference in density between injected fluid and oil to stabilize downward displacements.

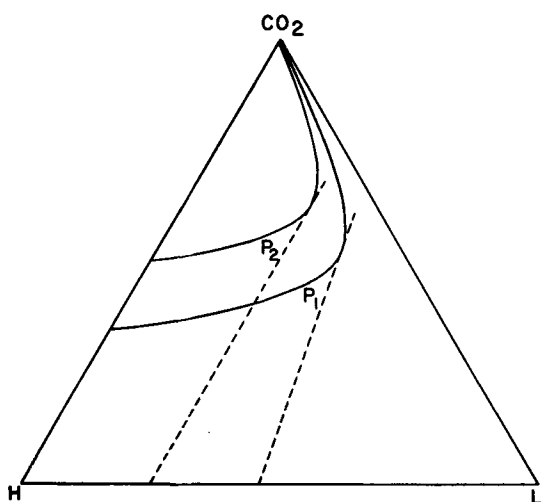


FIG. 5. Effect of pressure ( $P_2 > P_1$ ) on critical tie line position.

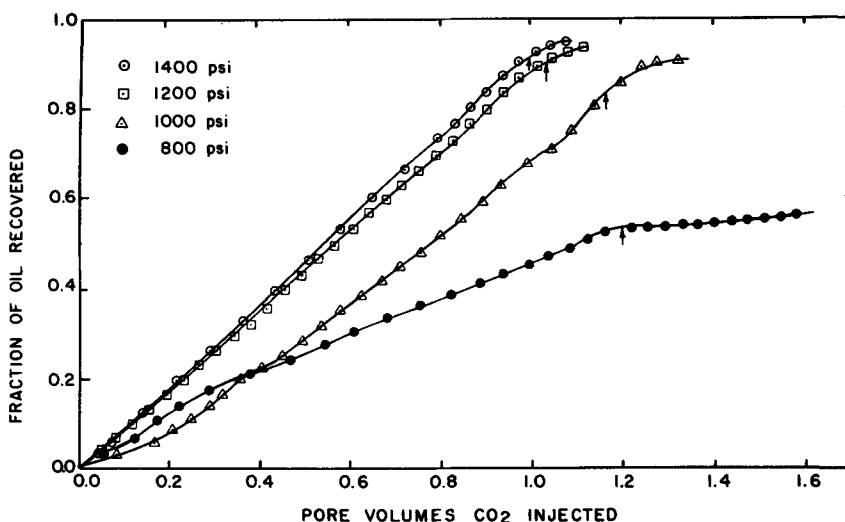


FIG. 6. Effect of pressure on oil recovery by CO<sub>2</sub> flooding in an ideal porous flow system (slim tube) for CO<sub>2</sub> displacing Maljamar oil at 90 F (32 C).

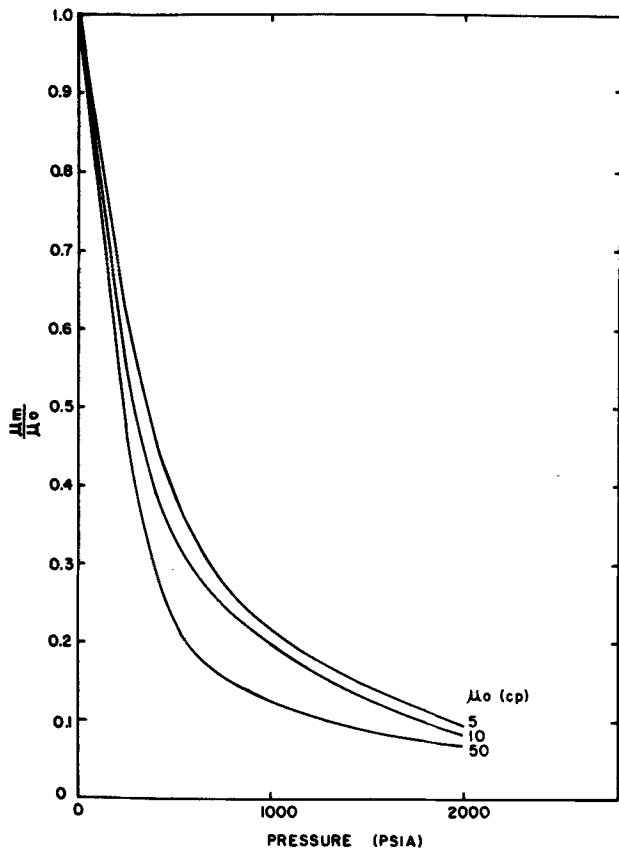


FIG. 7. Effect of dissolved CO<sub>2</sub> on oil viscosity.

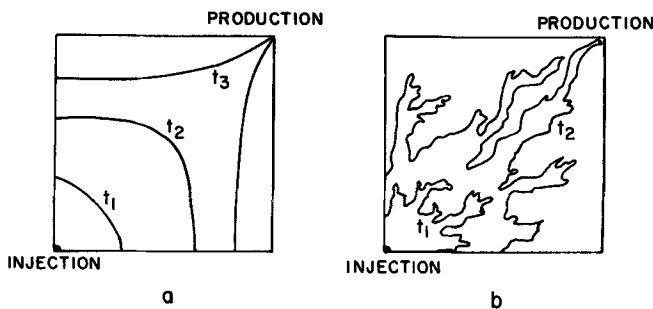


FIG. 8. Comparison of stable and unstable displacements: (a) favorable mobility ratio (stable); (b) unfavorable mobility ratio (unstable).

In many reservoirs, however, the flow from injection to production well is nearly horizontal, density differences cannot be used to stabilize the flow, and frontal instabilities will occur if the mobility ratio is adverse. It is apparent, therefore, that investigation of methods for controlling viscous fingering, often referred to as mobility control methods, is an important area of CO<sub>2</sub> flooding research.

Mobility control methods which have been proposed all aim at eliminating the basic cause of the problem. By somehow decreasing the mobility of the injected CO<sub>2</sub>, and thus increasing the pressure gradient behind the frontal region, the forces which give rise to the growth of fingers can be lessened or eliminated. This approach has its drawbacks—after all, making the displacing fluid less mobile inevitably

decreases the rate at which it can be injected, and thus decreases the rate at which the oil can be produced. Nevertheless, the alternate effects of early breakthrough and poor reservoir sweep are usually less attractive. Potential methods for controlling the mobility of injected CO<sub>2</sub> are described next.

**WAG (Water Alternated with Gas)**

A method that first appeared in the literature in the late 1950s is based on the simple principle that the mobility of a fluid can be decreased by decreasing the proportion or “saturation” of that fluid (11). This was first suggested for solvent (such as propane) floods, which suffer from the same difficulty as that described for CO<sub>2</sub>. The rock’s relative permeability to the solvent can be decreased greatly by a relatively small increase in water saturation. This is illustrated in Figure 9a. When water is injected along with the solvent or miscible gas, the overall mobility of the injected fluid is decreased because the water fills some of the flow channels that previously were available to solvent. Hence, the growth of displacement inhomogeneities due to instability is decreased. A schematic of the injection process is shown in Figure 9b. This method is currently being used in a number of CO<sub>2</sub> floods, though there are still some questions regarding the method. Injected water and CO<sub>2</sub> may not be distributed uniformly in the reservoir, and increased water saturations may reduce microscopic displacement efficiency. For instance, there is evidence that with a higher mobile water saturation, a larger fraction of the residual oil stays “trapped” or shielded from contact with the CO<sub>2</sub> (12).

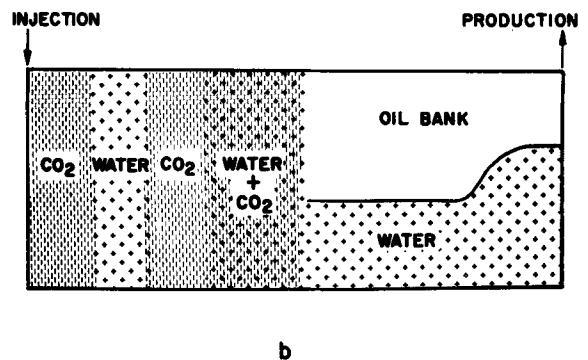
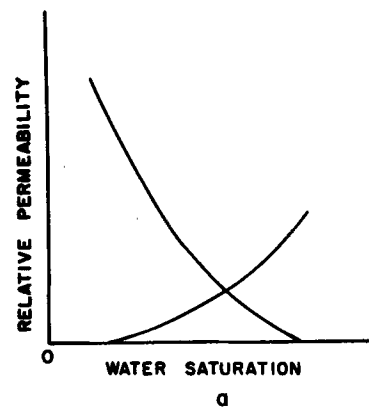


FIG. 9. Mobility control by alternate injection of water and gas: (a) effect of water on the flow of gas; (b) schematic of injection process.

### "Foamulsions"—CO<sub>2</sub> Dispersed in Water

The petroleum literature contains a number of papers which report large pressure drops required to force foam through porous media. Most of these reports describe air foams composed of bubbles or cells of gas in a water-continuous dispersion. With the "quality," or proportion of gas at 70% or greater, the aqueous component exists mostly as a network of thin films surrounding the gas cells. There is general agreement that a principal cause of the low mobility (as evidenced by the higher pressure gradients required) is the thermodynamic work required to distort and move large numbers of water films through the necks of pores in the rock (Fig. 10) (13). Those films are stabilized by the presence of surfactants or "foamants." In the absence of the surfactant, the films disappear and the mode of flow changes back into the usual situation when immiscible fluids are flowing simultaneously in the rock, and where separate, fairly well-defined channels accommodate each flowing fraction.

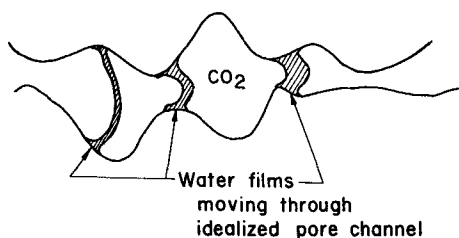


FIG. 10. Schematic of the flow of water films through an idealized porous medium.

The effort to use "foams" composed of CO<sub>2</sub> and water is based partly on the effort to find suitable surfactants. Thus far, the approach has followed the classic ideas of "foam stability" (14), and it appears that a number of surfactants will produce foams which may function well in CO<sub>2</sub>-oil-water systems. For instance, nonionic surfactants with suitably balanced water-hydrocarbon solubilities seem most promising (15). In addition, there is a need to study the differences between dispersions of liquid or supercritical CO<sub>2</sub> in water, and the true foams. One can also ask how much of the reported experimental data resulted from the large compressibility of air foams, and how much resulted from the same phenomena as are seen in the flow of liquid-liquid dispersions.

#### Direct Thickening

Because at reservoir pressure CO<sub>2</sub> is a dense fluid—its density is near that of oil—one can regard it as a potential solvent. In fact, the effectiveness of such dense CO<sub>2</sub> in displacing oil depends on this aspect of the fluid. It turns out that other substances besides hydrocarbons can be dissolved in dense CO<sub>2</sub>, and that is the origin of the mobility control method that we label as "Direct Thickening."

The solutes of most interest, of course, are polymers. Other polymers have been used extensively to thicken water, but these polymers are not soluble in CO<sub>2</sub>. The ideal additive for CO<sub>2</sub> floods would be an inexpensive polymer which, when dissolved at fairly low concentration in liquid CO<sub>2</sub>, would raise the solution viscosity from .075 cp or so to, say, 1.5 cp. Such a moderate increase by a factor of about 20 would be sufficient. A great improvement in "areal sweep pattern" would result, the amount of CO<sub>2</sub> required would decrease, and a very significant gain in over-

all displacement efficiency would be observed.

Polymers which meet those requirements have not yet been found, but high-pressure experiments have shown that a fairly large assortment of hydrocarbon-soluble polymers are also soluble in CO<sub>2</sub>. Those tested so far raise the viscosity by only 10-20%. It would be convenient to find one or more effective polymers among the product lists of currently active manufacturers, but synthesis of new polymers may be necessary.

Results of solubility measurements for some polymers in CO<sub>2</sub> are shown in Table I. Those listed are atactic, straight-chain polymers of relatively low molecular weight (MW). Higher MW polymers we have tested have been insoluble. Table II reports results of viscosity measurements for some of the systems. Because of the low molecular weights of these polymers, and probably for other reasons, the viscosity increases are much lower than those which can be obtained for aqueous solutions containing similar concentrations of water-soluble polymers.

#### Chemicals for Mobility Control

Two types of chemicals discussed as mobility control agents for CO<sub>2</sub> floods must satisfy several additional requirements. The chemicals must survive in the environment in which they will be used and must not engage in destructive or inconvenient reactions with other materials present. They must not adsorb too readily on rock surfaces, and they must tolerate pressures from 1,000-5,000 psi (depending on the depth of the reservoir) and temperatures from 20-120 C (also depending on the depth). In addition, the reservoir contains crude oil with a variety of organic surfactants which commonly render rock oil-wet and destabilize emulsions. Water is also present which sometimes contains high concentrations of calcium, magnesium, sodium, and carbonate and chloride ions. The effect of these on the solubility, and on the effectiveness of the mobility control methods mentioned, is a subject for future study. Finally, any additive must be available in sufficient quantities at a price low enough to allow economic use.

Although the requirements listed may be difficult to satisfy, the potential value of effective mobility control in CO<sub>2</sub> floods is very large. It can be measured as a reduction in risk, an increase in profitability of EOR projects, and an increase in petroleum supply in the years ahead.

#### Field Activity in CO<sub>2</sub> Flooding

One advantage of CO<sub>2</sub> flooding is the broad range of oil-field types to which it is applicable. The process itself is not sensitive to the presence of divalent cations (calcium and magnesium) which can adversely affect the performance of most surfactant formulations; nor is it affected by the salinity of the reservoir brine. Thus, CO<sub>2</sub> flooding can be applied to both sandstone and carbonate reservoirs. The reservoir must be deep enough that it can withstand, without fracturing, the high pressure required for efficient extraction of hydrocarbons by CO<sub>2</sub>, and it should be permeable enough that CO<sub>2</sub> can be injected at reasonable rates. Because the viscosity of CO<sub>2</sub> is very low and it is therefore easy to inject, all but the lowest-permeability fields meet the injection rate requirement. In fact, CO<sub>2</sub> injection has been used in at least one field (Crossett, Crane County, Texas) because it could be injected where water could not (13). In such low-permeability fields, mobility control may be in conflict with the goal of high injection rate. The most stringent restrictions on CO<sub>2</sub> flooding come, again, from its low viscosity. Because the tendency for viscous fingering increases with the ratio of the viscosity of the oil to that of CO<sub>2</sub>, the process has been

TABLE I  
Solubilities of Polymers in Dense CO<sub>2</sub>

Polymer	Temp. (C)	Pressure (psi)	CO <sub>2</sub> density (g/cc)	Solubility (g/L)	Comments
Polybutene	25	1700	0.82	23.8	Mn 440
Polybutene	25	1700	.82	7.8	Mn 640
Polybutene	25	1700	.82	1.0	Mn 2500
Polybutene	25	1700	.82	0.0	Mn 2700
Polypropylene	25.5	2260	.875	2.17	Atactic
Polypropylene	32.0	1960	.80	1.19	Atactic
Terpeue resin	25.5	1940	.846	4.1	
Polyvinylethyl ether	26	1930	.84	4.0	
Polyundecanamide (Nylon 11)	25	1500-2400	.8-.88	0.0	
Poly-4-vinyl biphenyl	26	2100	.87	0.0	
Polyvinyl stearate	25	2000	.852	1.75	
Polydimethyl siloxane	26	2050	.855	4.91	

TABLE II  
Fall Times and Viscosity of Polymer Solution in Dense CO<sub>2</sub>

Fluid	Pressure (psi)	Temp. (C)	Fall time (sec)	Viscosity (cp)
( Pure CO <sub>2</sub> )	1700	25	1.460	.076
	1900		1.488	.081
	2100		1.514	.087
( Polybutene MW 440 20 g/L in CO <sub>2</sub> )	1700	25	1.540	.080
	1900		1.568	.085
	2100		1.608	.092
( Polybutene MW 640 8.5 g/L in CO <sub>2</sub> )	1700	25	1.565	.081
	1900		1.620	.088
	2100		1.660	.095
( Polybutene MW 2500 1.5 g/L )	1700	25	1.560	.081
	1900		1.575	.086
	2100		1.615	.093
( Polymethyl oxirane 9.57 g/L in CO <sub>2</sub> )	1900	26	1.760	.096

applied mainly in reservoirs in which the oil viscosity is 3 cp or less. Furthermore, the adverse effects of viscous fingering are aggravated by large permeability contrasts because CO<sub>2</sub> tends to break through quickly in high-permeability streaks or fractures establishing preferential flow paths through which most of the CO<sub>2</sub> then flows. Thus, CO<sub>2</sub> flooding will, in general, be more effective in reservoirs which do not have high-permeability streaks or fractures which communicate between wells.

One of the principal constraints which affects the field-scale application of CO<sub>2</sub> flooding is the availability of CO<sub>2</sub>. The large quantities of CO<sub>2</sub> needed will come primarily from natural sources, though ammonia plants and coal gasification plants may provide CO<sub>2</sub> if oil fields are located nearby (1). Large natural supplies of CO<sub>2</sub> have been discovered in northeastern New Mexico and in southern Colorado. Figure 11 shows approximate locations of the largest known CO<sub>2</sub>-producing areas as well as areas in which are located oil fields where CO<sub>2</sub> floods are active now or are being planned. Of the areas shown, the Permian Basin, with its very large carbonate reservoirs, and the Gulf Coast area, with its deeper, hotter sandstone reservoirs, appear to offer the greatest potential for oil recovery with CO<sub>2</sub>. For most applications, the costs of delivering CO<sub>2</sub> by any means other than a pipeline are too high except for pilot

tests in which CO<sub>2</sub> is usually delivered by truck. Plans have been announced for two large pipelines, one from the Four Corners area and the other from southern Colorado and northeast New Mexico, to carry CO<sub>2</sub> to the oil fields of the Permian Basin. Cost estimates for those pipelines and associated facilities are in the range of \$2-3 billion. Thus, both the investments and the associated risks required for the development of large CO<sub>2</sub> projects are high, but apparently not too high to prevent implementation.

The projects being planned now, however, have the benefit of extensive field testing of the CO<sub>2</sub> flood process. Field-scale, secondary CO<sub>2</sub> floods have been operating in the Kelly Snyder and Crossett fields since the early 1970s, with good performance (16), and pilot tests in fields of widely varying characteristics have established that CO<sub>2</sub> can displace oil left behind by waterflooding (17,18). Although current oil production from existing CO<sub>2</sub> flood projects is only about 22,000 barrels/day (18), that number should grow substantially as the projects being implemented now begin to produce additional oil. Figure 12 compares the growth in the number of active CO<sub>2</sub> flood projects over the last decade with that of other gas injection projects (18). The number of hydrocarbon miscible projects declined with the increasing price of the hydrocarbon solvents, but the number of CO<sub>2</sub> projects increased. Indeed, the number

of active CO<sub>2</sub> projects nearly doubled from 1980 to 1982, and those numbers do not include the large west Texas projects which are dependent on the CO<sub>2</sub> pipelines. Of 416 projects recently certified in 12 categories of enhanced oil recovery under the U.S. Department of Energy's Tertiary Incentive Program, 91 were CO<sub>2</sub> floods (19). Thus, it appears very likely that the number of active CO<sub>2</sub> projects will continue to grow as will oil production from CO<sub>2</sub> floods. It is equally clear that successful large-scale implementation of CO<sub>2</sub> flooding will continue to provide a variety of challenges to the researchers and engineers who will guide that development.

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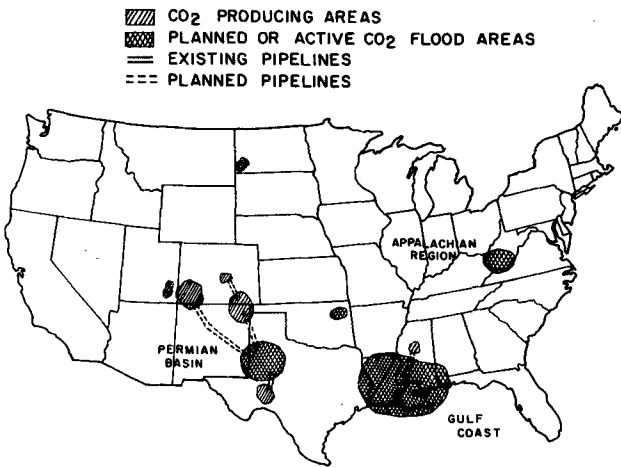


FIG. 11. Locations of natural CO<sub>2</sub> supplies and oil fields for which CO<sub>2</sub> floods are planned.

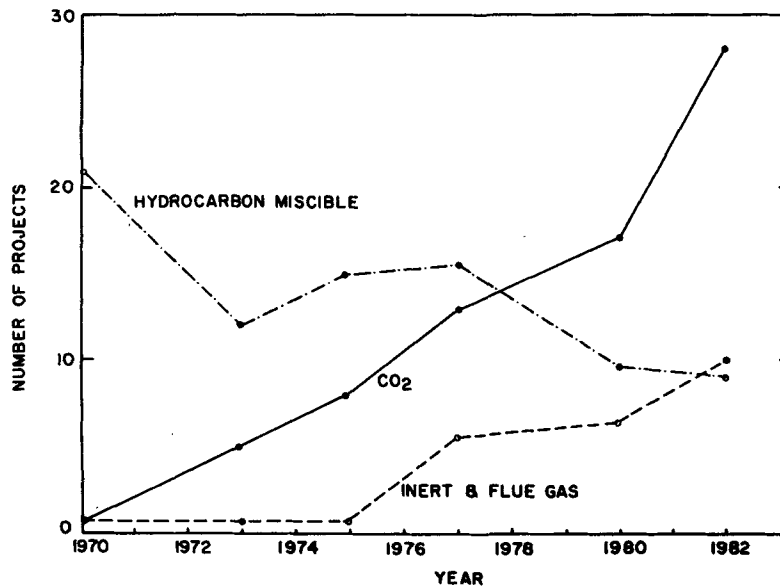


FIG. 12. Active CO<sub>2</sub>, hydrocarbon miscible and inert gas field projects.

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