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(DE87001049)

Gas Miscible Displacement Enhanced Oil Recovery

Technology Status Report

October 1986

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
MORGANTOWN ENERGY TECHNOLOGY CENTER
MORGANTOWN, WEST VIRGINIA

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MORGANTOWN ENERGY TECHNOLOGY CENTER
TECHNOLOGY STATUS REPORT

Gas Miscible Displacement Enhanced Oil Recovery

Extraction Projects Management Division

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880

October 1986

MASTER

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EXECUTIVE SUMMARY

Gas miscible displacement enhanced oil recovery research is conducted by the U.S. Department of Energy's (DOE's) Morgantown Energy Technology Center (METC) to advance the application of miscible carbon dioxide flooding. This research is an integral part of a multidisciplinary effort to improve the technology for producing additional oil from U.S. resources. This report summarizes the problems of the technology and the 1986 results of the ongoing research that was conducted to solve those problems.

Poor reservoir volumetric sweep efficiency is the major problem associated with gas flooding and all miscible displacements. This problem results from the channeling and viscous fingering that occur due to the large differences between viscosity or density of the displacing and displaced fluids (i.e., carbon dioxide and oil, respectively). Simple modeling and core flooding studies indicate that, because of differences in fluid viscosities, breakthrough can occur after only 30 percent of the total pore volume (PV) of the rock has been injected with gas, while field tests have shown breakthrough occurring much earlier. The differences in fluid densities lead to gravity segregation. The lower density carbon dioxide tends to override the residual fluids in the reservoir. This process would be considerably more efficient if a larger area of the reservoir could be contacted by the gas.

Current research has focused on the mobility control, computer simulation, and reservoir heterogeneity studies. Three mobility control methods have been investigated: (1) the use of polymers for direct thickening of high-density carbon dioxide, (2) mobile "foam-like dispersions" of carbon dioxide and an aqueous surfactant, and (3) in situ deposition of chemical precipitates.

There has been only limited success in the search for carbon dioxide soluble polymers. Polymers that disolve into high-density carbon dioxide have been found but the increase in viscosity has been far less than that required for mobility control. Further work is needed to determine if adequate polymers can be synthesized for successful direct thickening of carbon dioxide.

Mobile foam-like dispersions of carbon dioxide are being investigated. This concept involves altering the flowing viscosity of the gas so that viscous fingers are suppressed and displacement is sustained in a piston-like manner. Unswept regions are thereby contacted as well as the watered-out regions of the reservoir.

Preliminary studies on in situ deposition of chemical precipitates for mobility control are ongoing. Chemicals that react with carbon dioxide under proper conditions will chemically precipitate in the formation and block and divert the injected fluids into previously unswept, high oil saturated regions of the formation.

Computer simulation research is mainly being conducted in-house at METC which is developing and refining two models: (1) a black oil simulator modified for miscible gas enhanced oil recovery (EOR); and (2) a compositional simulator. The computer simulation research is continuing to provide adequate tools for predictive and evaluative support of novel technical concepts, laboratory experiments, and field projects. This research will aid the understanding of how fluid phase behavior and miscible displacement mechanisms enhance oil recovery and how reservoir heterogeneities influence oil recovery.

The role that reservoir heterogeneity plays on the performance of the miscible gas EOR process is being investigated. This effort is aimed at quantifying the effects of reservoir heterogeneity on carbon dioxide floods in reservoirs with large well spacing and relatively low permability. The investigation also includes the overall problem of detection, characterization, and representation of the effects.

Pilot field tests demonstrate the feasibility of emerging gas flood technology. Field testing of concepts demonstrated in the laboratory and by computer simulation provides the only method of concept verification. Actual pilot test results are evaluated and used to predict the feasibility of a full-scale, field-wide gas flooding project.

1.0 INTRODUCTION

Petroleum provided 44.65 percent of the total energy consumed in the United States during the first half of 1986 according to the *Energy Monitor* (October 1986). According to the *Weekly Petroleum Status Report* (August 29, 1986), the amount of liquid fuels (including both crude oil and refined products) imported by the United States averaged 4.95 million barrels per day in the first 8 months of 1986, or 30.9 percent of the total United States' demand. This represents an increase in imports of 27.8 percent over the same period in 1985, and an increase in the percentage of the total United States' demand (26 percent over the same period in 1985).

The United States will continue to require vast amounts of liquid fuels throughout the foreseeable future, even with intensive conservation efforts and the conversion of some power plants to alternate fuels. New sources of liquid fuels from such resources as oil shales, tar sands, coal, and biomass are currently being studied and developed, but since economics and time lag may prevent these activities from contributing significantly to domestic supplies for many years, more effective ways of recovering crude oil from domestic sources must be developed to limit imports and reduce the United States' dependence on foreign oil. Conventional primary recovery and secondary (water-flooding) recovery techniques produce only about one-third of the original oil in place. Therefore, it is essential that enhanced oil recovery (EOR) techniques be made economical so that more oil can be recovered. Oil recovered by EOR technology has been defined as the incremental ultimate oil that can be economically recovered from a petroleum reservoir in excess of the oil that can be economically recovered by conventional primary and secondary recovery methods.

Of the more than 300 billion barrels of crude oil remaining in existing developed fields after conventional production, it has been estimated that between 18 and 52 billion additional barrels can be recovered by all EOR techniques. Present proven conventional reserves amount to 28 billion barrels. A recovery of any significant part of the EOR oil target could greatly reduce the United States' dependence on imported oil.

Of the three categories of EOR processes (thermal, chemical, and miscible), the one generally recognized as most promising is miscible flooding. Miscible floods using carbon dioxide (CO_2), nitrogen, or hydrocarbons as miscible solvents have their greatest potential in the enhanced recovery of low-viscosity light crude oil (> 20° API gravity). CO_2 miscible flooding on a large scale is relatively new and is expected to become the most important of the miscible methods. Many large-scale commercial CO_2 miscible projects will be started in west Texas as CO_2 becomes available from large natural sources in Colorado and New Mexico.

There is increasingly widespread use of CO_2 miscible flooding because of its moderate cost and its favorable miscibility characteristics with crude oil. Miscible displacement of oil by CO_2 can produce virtually all of the oil from contacted parts of the reservoir. For these reasons, miscible methods are considered more promising than thermal and chemical EOR methods, although CO_2 flooding has three major technical problems: (1) availability and cost of CO_2, (2) poor mobility control of injected fluids, and (3) lack of reservoir knowledge and understanding.

In the 1984 National Petroleum Council study of EOR potential in the United States, tertiary oil recovery from gas miscible displacement was estimated, based on currently implemented technology and future advanced technology. Mosbacher (1984) cited that the implemented technology outcome from the $30-per-barrel base case study shows the total miscible EOR resource potential from known United States reservoirs to be 5.5 billion barrels of oil. During the 30-year period of their projection, 3.8 billion barrels of the total miscible EOR resource will be produced. The projected peak rate of production is about 500,000 barrels per day, which is expected to be reached shortly after the year 2000. Production is expected to decline to about 360,000 barrels per day by 2013, the last year in the projection period.

The advanced technology outcome from the $30-per-barrel base case study shows the total miscible EOR resource potential from known United States reservoirs to be 6.1 billion barrels of oil. During the 30-year projection period, 4.6 billion barrels of the total miscible EOR resource will be produced. The projected peak rate of production is about 625,000 barrels per day and is expected to be reached shortly after the year 2006. Production is expected to decline to about 540,000 barrels per day by the year 2013. This would be an increase of about 10 percent over the implemented technology outcome in total miscible EOR resource potential from known United States reservoirs. In addition, over

50 percent of the original oil in place is estimated to remain in the reservoirs after completion of the technologically advanced EOR activities, strongly indicating the need for significant research and development (R&D) to improve gas miscible EOR efficiency.

2.0 PROGRAM OBJECTIVES

The United States DOE EOR program's lead office is the Bartlesville Project Office in Bartlesville, Oklahoma. The EOR program is divided into a light oil (>20° API gravity) enhanced recovery program and a heavy oil (<20° API gravity) enhanced recovery program. The gas miscible EOR processes, including the miscible CO_2 flooding process operated in Morgantown, West Virginia at METC, are best suited for light oil reservoirs and are, therefore, a part of the light oil enhanced recovery program.

The EOR program, as it applies to light oil, has four goals:

1. Improve the predictability of the gas miscible EOR process.
2. Improve the performance of the gas miscible EOR process.
3. Assess the feasibility of very long-range, highly advanced, emerging technologies for the gas miscible EOR process.
4. Extend the range of application of the gas miscible EOR process to reservoirs for which no EOR technology currently exists.

Meeting these goals requires a strategy that combines basic R&D efforts with field validation. The research program in CO_2 EOR has been designed and executed to improve the level of knowledge in each of these areas.

3.0 STATE OF TECHNOLOGY

After the secondary recovery of oil by water-flooding, a certain amount of residual oil remains in the pore spaces of the reservoir rock for either or both of two reasons: (1) the oil was bypassed and not contacted by the injected water; or (2) capillary forces, caused by interfacial effects between two immiscible fluids, retained the oil in the capillary-sized pore spaces.

Carbon dioxide can overcome both of these problems. Although injected CO_2 has a strong tendency to flow through those pores that have been contacted and largely saturated with the displacing water, control of the direction of injection and the flow of injected fluids may be able to direct the CO_2 into previously unswept portions of the reservoir. In addition, many crude oils are miscible with CO_2 under certain temperature and pressure conditions. As miscibility eliminates the interface between fluids, capillary retaining forces are reduced to essentially zero.

There is a difference between CO_2 dissolving in crude oil and CO_2 being miscible with crude oil. As pressure is applied to a CO_2 crude oil system, the CO_2 readily dissolves until the crude oil is saturated with CO_2 at the existing pressure and temperature. At that time, both free CO_2 and CO_2 saturated crude oil are present with an interface between the two materials. Dissolving the CO_2 in this manner results in an expansion of the liquid phase and a reduction of the liquid viscosity. Solution of the CO_2 in this manner takes place regardless of the composition or API gravity of the crude oil. It is obvious that the swelling of the oil increases the oil saturation and, therefore, enhances the relative permeability of the reservoir rock. Both reducing the viscosity and increasing the relative permeability to oil facilitates the flow of the swollen oil to the production well.

The reduction of oil viscosity and the increase in relative permeability to oil also take place in CO_2 miscible displacement. In addition, miscibility entails, by definition, the elimination of the interface between the CO_2 and the oil. Thus, when miscibility occurs, capillary forces become zero and essentially 100 percent of the oil can be displaced from the part of the reservoir contacted by CO_2. Miscibility between CO_2 and crude oil, however, requires more restrictive temperature and pressure conditions than simply the dissolving of CO_2 in the oil. At any given temperature, there is a minimum miscibility pressure (MPP), usually 1,000 pounds per square inch (psi) pressure or greater, below which the interface will remain. In addition, in most cases CO_2 and crude oil will not become miscible on first contact because of differences in their properties and composition, regardless of pressure. These materials have what is called multiple contact miscibility. In other words, the CO_2 must repeatedly contact the oil. Because of the concentration gradient from the oil to the CO_2, many hydrocarbon molecules, especially those of C_5 to C_{30}, must leave the oil and enter the CO_2. After a sufficient

number of contacts, enough of these hydrocarbons will have joined the CO_2 vapor phase so that the vapor phase becomes miscible with the crude oil.

Slim tube tests are performed to determine the minimum miscibility pressure (MMP). Tubing ($\leq$ 0.25 inch internal diameter, and up to 80 feet long) is packed with glass beads or unconsolidated sand, saturated with reservoir oil, and then flooded with CO_2 at reservoir temperature and at various pressures.

Core samples of reservoir rock saturated with reservoir oil and formation water are flooded with CO_2 at reservoir temperature and pressure equal to or greater than the MMP to determine, in a more realistic situation, the residual oil saturation and permeability effects that may be expected in a field application. Wettability of the core samples should be determined and preserved as an aid in predicting the amount of oil that may be trapped by water blocking. Additional reservoir data, such as the permeability profile, the vertical permeability to horizontal permeability ratio, and transmissibility between reservoir strata, are needed for reservoir simulation studies.

A widely varying permeability profile in a reservoir formation with a natural or poorly oriented fracture system would be a poor candidate for CO_2 flooding or most other EOR techniques. Because of the low density of CO_2 gas compared to that of oil, the CO_2 tends to migrate vertically to the top of the formation and form a gravity tongue (i.e., advance more rapidly at the top of the reservoir than in lower portions of the rock). The low viscosity of CO_2 permits the formation of viscous fingers or small channels in which the CO_2 rapidly moves from the injection well to the production well, bypassing a large part of the oil.

The low viscosity of CO_2 and the normally high relative permeability to CO_2 of the rock at low CO_2 saturations result in a very high mobility for the CO_2. Because of the channeling, the fingering, and the absence of oil banking that a high mobility permits, a generally low volumetric sweep efficiency and rapidly increasing CO_2-oil ratio results.

Mobility control is, therefore, an important problem in CO_2 miscible flooding. Several methods have been used to alleviate the situation but none of them have been successful to a satisfactory degree. The point of entry of the CO_2 into the formation can be controlled by seating one or more packers at an appropriate position or by selectively perforating the casing. However, once the CO_2 leaves the immediate vicinity of the wellbore, this method does not control the movement of the CO_2. Production wells can be shut in or flow can be restricted. Without the pressure sink that the wells normally provide, the CO_2 will be less likely to channel until the wells are put into production once more. Foams or emulsions formed with surfactants and water may be successful in partially reducing flow rates in swept channels. The method most widely used in practice to control CO_2 mobility is the water-alternating-with-gas (WAG) procedure where CO_2 gas and water are injected alternately. Although this method may temporarily reduce the channeling tendency of the CO_2, the relative permeability remains high in the already formed channels. Also, any increase in conformance may be lost because of the lower displacement efficiency that occurs as a result of water preceding the CO_2 through the pore spaces. This problem is worse in the case of previously watered-out reservoirs.

At this time, foams or emulsions formed with surfactants and water appear to have the greatest promise in lowering CO_2 mobility. A great deal of study needs to be done, however, in this area of mobility control.

Several operational problems exist in CO_2 flooding that can be solved or alleviated by relatively routine techniques. CO_2, when dissolved in water, forms corrosive carbonic acid. Prior to transporting the gas in pipelines and distribution systems and injecting it down wellbores, the CO_2 should be dehydrated to prevent excessive corrosion. When the WAG injection program is to be used, separate water and gas lines should be used both on the surface and downhole.

In using the WAG process, the saturation of water and gas are constantly being changed around the wellbore. As a result, the relative permeability is reduced for a large part of the injection cycle and, therefore, injectivity is reduced. Counteracting this effect, however, is the decreasing oil saturation in the formation surrounding the wellbore, which facilitates the flow of both CO_2 and water. In carbonate or carbonate-containing rocks, the carbonic acid formed by the CO_2 and water tends to react with and dissolve part of the rocks, thus enlarging the pores and increasing the permeability.

Field experience reveals that CO_2 breaks through into the producing wells in a very short time period (i.e., a few weeks to a few months). After breakthrough, the combination of water produced and

CO_2 will corrode the downhole and surface equipment unless corrosion inhibitors, pipe coatings, special steels, or other materials are used.

Extraction of the C_5-C_{30} hydrocarbon components from crude oil in the formation may result in the precipitation of paraffin crystals or asphaltenes. These solid materials may partially or totally plug the formation unless a solvent wash is used to redissolve them.

When CO_2 is produced, it is mixed with hydrocarbon gases. The CO_2 reduces the heating value of the natural gas, and methane mixed with CO_2 increases the MMP substantially. Therefore, the CO_2 must be separated from the hydrocarbons so that the hydrocarbons can go through normal commercial sales outlets and the CO_2 can be reinjected into the formation.

The large quantity of CO_2 needed for oil recovery is available at several locations. The locations, however, are generally far from where the CO_2 is used and it must be transported a great distance. Several large reservoirs containing high concentrations of natural CO_2 are located in Colorado and New Mexico. Pipelines are either in use or under construction to transport this gas to basins where it can be injected into reservoirs. Three major pipelines systems are now moving CO_2 to the west Texas Permian Basin. These are the 30-inch Cortez line operated by Shell Pipeline Corporation, the 24-inch Sheep Mountain line operated by Arco, and the 20-inch Bravo Dome line operated by Amoco Corporation. Additional CO_2 pipelines are in the planning or construction stage throughout the Rocky Mountain region.

Man-made sources (e.g., electrical generation plants, synthetic fuel plants, and refineries) produce large quantities of CO_2. However, it is normally diluted by other gaseous waste products, or exists at essentially atmospheric pressure, or both. These sources, too, are usually located at a considerable distance from the point of application.

The total cost of CO_2 is composed of the costs of source development, compression, dehydration, transportation, distribution, injection, production, separation and recovery, and recompression. If the cost of CO_2 can be held near $1.50 per thousand cubic feet (Mcf) (1986 dollars) and CO_2 requirements can be kept below 8 to 10 Mcf per barrel of oil recovered, economic success can frequently be achieved.

Current reviews of gas miscible displacement EOR techniques are generally encouraging. While both miscible and immiscible CO_2 flooding can frequently achieve economic as well as technical success, some problems remain. Mobility control is probably the most serious technical problem at the present time. Lack of understanding of the interaction between the gas miscible process and the reservoir is also a serious problem. Phase behavior and miscibility are not completely understood, and field data are insufficient to develop models that can adequately predict project performance. Work in these areas should provide at least partial solutions to these problems.

4.0 CURRENT RESEARCH IN CARBON DIOXIDE ENHANCED OIL RECOVERY

The United States CO_2 EOR program at DOE/METC includes research and development (R&D) projects with the petroleum industry and universities. This comprehensive approach covers the broad technology needs of the CO_2 EOR program.

4.1 MOBILITY CONTROL

4.1.1 Improvement of CO_2 Flood Performance[1]

Research activities of this project are focused on the investigation of the use of direct thickeners and surfactants for mobility control.

Work in the area of direct thickeners is being carried out under three categories, which have been identified as Methods I, II, and III. Method I concerns the synthesis of multicomponent high polymer systems using various higher α-olefins as monomers. Method II will evolve as a result of the progress made in Method I and is concerned with the synthesis of new ionomers. Method III involves the use of novel organic compounds, e.g., trialkyltin fluorides, to make dense CO_2 viscous.

Several Method I copolymers of 1-hexene/1-decene, 1-pentene/1-decene, and 1-pentene/1-hexene have been synthesized. The reaction conditions used and the results obtained are summarized in Table 1. Method I can synthesize polymers that can make dense, non-polar fluids of poor solvent power more viscous. However, the increases

[1]Elements of this project fall into the Phase Behavior and Miscibility area and the Laboratory Displacement Tests area. Information concerning this project can be found in those sections of this report.

TABLE 1. COPOLYMERIZATION OF HIGHER α-OLEFINS,*

(Source: Heller, Kovarik, and Taber. August 1986.)

Polymer No.	Monomers: M_1 (mole) Initial Feed	Monomers: M_2 (mole) Initial Feed	Monomer Feed Ratio M_1/M_2 (mole)	Polymer Yield g (24 hrs) (2nd Fraction)	Intrinsic Viscosity $[\eta]$ dl/g (2nd Fraction)	Polymer Composition m/m_2 at 5% Conversion	Reactivity Ratios (Fineman Ross Method)
	1-Hexene	*1-Decene*					
86	0.0149	0.1337	0.111	4.03 (1.03)	0.88 (0.34)	1.7037	1-Hexene = 0.86
87	0.0891	0.0891	1.0	5.2 (0.52)	2.01 (0.085)	1.4106	1-Decene = 0.02
88	0.2005	0.0223	8.991	8.09 (0.80)	2.34 (0.04)	9.5454	
	1-Pentene	*1-Decene*					
89	0.0150	0.1351	0.111	5.84 (0.46)	1.99 (0.09)	0.5	1-Pentene = 0.33
90	0.0951	0.0950	1.00	3.96 (0.11)	1.88 (0.11)	1.6052	1-Decene = 0.27
91	0.2333	0.0259	9.00	7.01 (0.57)	1.91 (0.04)	25.60	
	1-Pentene	*1-Hexene*					
93	0.2517	0.0279	9.0125	9.07 (0.53)	1.91 (0.02)	8.0588	1-Pentene = 1.23
94	0.1296	0.1296	1.0	6.28 (0.49)	2.29 (0.07)	1.3392	1-Hexene = 0.34
95	0.0242	0.2175	0.1112	5.57 (0.30)	3.02 (0.08)	0.3789	

*Reaction Conditions—Solvent: n-heptane; Catalyst: $TiCl_4$-$AlEt_3$ Al/Ti:0.85, 4% based on monomer weight; Time: 24 hrs; Temperature: ambient. Reactions were followed by analyzing the concentrations of unreacted monomers using gas chromatographic techniques.

in viscosity using the available Method I polymers are much less than those attained in Method III with the trialkyltin fluorides at comparable concentrations.

The synthesis of Method II base terpolymers is under way. Ionomers will be prepared using these terpolymers and the results of Method I.

Work in the Method III category progressed in several areas. The characterization of the trialkyltin fluorides synthesized thus far is under way. They have been effective in enhancing the viscosity of normal propane. A new apparatus has been built to test the viscosity of solutions in dense gases such as CO_2, propane, and n-butane.

Testing of surfactants was continued during FY 86. Surfactants tested were the Shell Enordet X2000 series, Chembetaine BC-50 from Chevron Corporation, NES-1412, and CADG-LS. The Enordet X2000 series are anionic alcohol ethyl glyceryl sulfonates, NES-1412 is an anionic alcohol ethoxy sulfate, CADG-LS is an amphoteric zwitterionic cocobetaine, and BC-50 is an amphoteric zwitterionic alkyl dimethyl ammonial acetate. The surfactants were tested for their foamability with pH, temperature, and aging. Tests at 150° and 175°F have been completed and tests at 200°F have been started.

In the 150°F aging test, a decrease in pH occurred from initial values of approximately 3.0. This effect was less for the two zwitterionic surfactants than the four anionics. Results of the 175°F test show that the pH initially drops and then shows a slight rise, which is evident in the zwitterionic surfactants. Results of the foamability tests are shown in Table 2. The Enordet X2000 series all had a significant decrease in foamability and pH stability. This could be a result of a higher potential for hydrolysis of anionics in an acidic environment than for the zwitterionic surfactants.

4.1.2 Enhanced Oil Recovery by CO_2 Foam Flooding

During this research project, three types of tests (static foam tests, mini-flow tests, and linear, two-phase flow tests) were performed on surfactants to test their usefulness as CO_2 EOR mobility control additives. According to Patton (1986), the static foam tests, performed on 113 commercial surfactant samples, identified some optimum chemical structures for mobility control additives. The mini-flow test, a unique, dynamic screening process, was developed to quickly identify new, more promising additives. The potential of additives identified in these tests were confirmed in linear, two-phase flow tests in tight, unconsolidated sand packs.

Linear flow experiments on gas mobility control, conducted in the sand-pack models, show only a general correlation with the static foam test. The static test, which uses a blender to generate foam from an aqueous surfactant solution, is useful mainly for studying the effects of pH, temperature, salinity, and crude oil on the relative foamability of any given surfactant. In general, all surfactants that

TABLE 2. SURFACTANT FOAMABILITY

(Source: Heller, Kovarik, and Taber, August 1986)

	Before Aging	150°F		175°F	
	time = 0	24-hour	28-day	24-hour	28-day
Chembetaine BC-50	3/6*	3/7	2/10	8/10	1/3
Enordet X2001	7/10	8/10	0/1 (700)**	7/10	0/1 (600)
Enordet X2002	1/3	0/.5	0/.5 (900)	2/7	0/0
Enordet X2003	3/7	3/8	0/.5 (600)	3/10	0/0
Foamer NES-1412	3/10	4/10	0/3	2/8	0/0
Varion CADG-LS	7/10	2/10	7/10	8/10	5/10

*Foamability is given as two numbers: X/Y. X and Y are the "foam heights" after 100 and 500 inversions, respectively.

**Numbers in parentheses are from low foaming surfactants that required additional inversions to get a measurable "foam height."

produce reasonable quantities of foam in the blender test also impart some degree of mobility control to gas during two-phase flow. Some of the best mobility control additives, however, are only modest foam volume producers. In addition, the best additives spontaneously produce a viscous foam under the flow conditions present in a petroleum reservoir.

Results of the dynamic screening tests correlate very well with both the linear mobility as well as oil displacement experiments. There is considerable evidence that mobility control shows the most promise with four basic chemical structures: Structure 1 — ethoxylated adducts of C_8 - C_{14} linear alcohols, Structure 2 — sulfate esters of ethoxylated C_9 - C_{16} linear alcohols, Structure 3 — low molecular weight co-polymers of ethylene oxide and propylene oxide, and Structure 4 — synthetic organic sulfonates.

The first three types are compatible with normal oil field brines, are unaffected by the presence of crude oil, and are stable under conditions common in a petroleum reservoir. At least one sulfonate also meets the above criteria. Additive stability is of real concern. Limited experimentation suggests that only the sulfate esters might degrade at an unacceptable rate, which would limit their application to lower temperature reservoirs. However, no degradation has been noted for Structures 1 and 3 in aging tests lasting 2 weeks at 125°F. Some synergism exists between additives. Amine oxides and amides improve foam stability for many anionic surfactants but at the expense of some mobility control.

Data collected at different shear rates showed the foam to be mildly pseudoplastic in nature and several orders of magnitude more viscous (i.e., 10-100 centipoise [cP]), than its gas or liquid fraction. Of special significance is the fact that foam viscosity has been shown to be an inverse function of foam density over a wide range of compositions. This fact is very advantageous in oil displacement processes. In areas where has fingering is pronounced, high gas saturation increases foam viscosity thus mitigating further gas channeling.

This high viscosity exhibited by foam at the low shear rates characteristic of oil reservoirs suggests that the displacement of oil by foam, envisioned by early investigators, may not be the dominant mechanism enhancing oil recovery. Alternately, the spontaneous generation of a viscous foam phase may serve to artificially reduce the flowing-gas saturation and thus may provide a dramatic lowering of the gas mobility, due largely to a relative permeability effect. This mechanism could be especially important in the WAG process using carbon dioxide or enriched gas mixtures for the displacement of oil in both miscible and immiscible processes.

The efficacy of CO_2 mobility control in enhancing oil recovery was demonstrated experimentally. Flow tests were conducted with a viscous oil under immiscible displacement conditions. Mobility control increased recovery by 40 percent over a CO_2 enhanced water-flood and 93 percent over a conventional water-flood plus primary production. No adverse effects, such as emulsion formation, due to mobility control additives were noted. Mass transfer of CO_2 from the foam to the oil did not appear to be impeded. In fact, the mobility control experiment was performed without the severe gas and liquid slugging that characterized conventional CO_2 laboratory floods.

Additional experiments involved the miscible displacement of oil by CO_2. Referring first to Figure 1, the data represent a conventional CO_2 tertiary flood of a water-flooded light oil reservoir. It can be seen that the water-flood, represented by the data prior to CO_2 injection, recovered 0.5 pore volume (PV) of octene, the oil used in the floods to ensure CO_2/oil miscibility. This amount represented 76 percent of the oil initially in place and produced a residual oil saturation at the end of the water-flood of 0.16 PV. Both the recovery and residual saturation are consistent with values expected in a water-flood of a light oil. Injection of 1 PV of CO_2 (temperature = 100°F, pressure = 1,370 psi) followed by additional water produced only 0.07 PV of additional oil.

The most dramatic improvement in CO_2-mobility-controlled tertiary oil recovery was obtained using Exxon's LD 776-52. This is a synthetic sulfonate structure whose performance in brine is only average. Screening tests conducted in tap water containing very little calcium ion indicated that its potential for mobility reduction of gas flow in oil reservoirs flooded with fresh water was significantly higher than any additive previously investigated. To corroborate the superiority suggested by the dynamic screening tests, an experiment using LD 776-52 dissolved in tap water was conducted using the same model and technique previously used for miscible displacement studies in the presence of brine.

As shown in Figure 2, the water-flood produced about the same amount of primary plus secondary

FIGURE 1. CONVENTIONAL CO_2 FLOOD: PLOT OF CUMULATIVE OIL PRODUCED VERSUS CUMULATIVE VOLUME INJECTED (Source: Patton 1986)

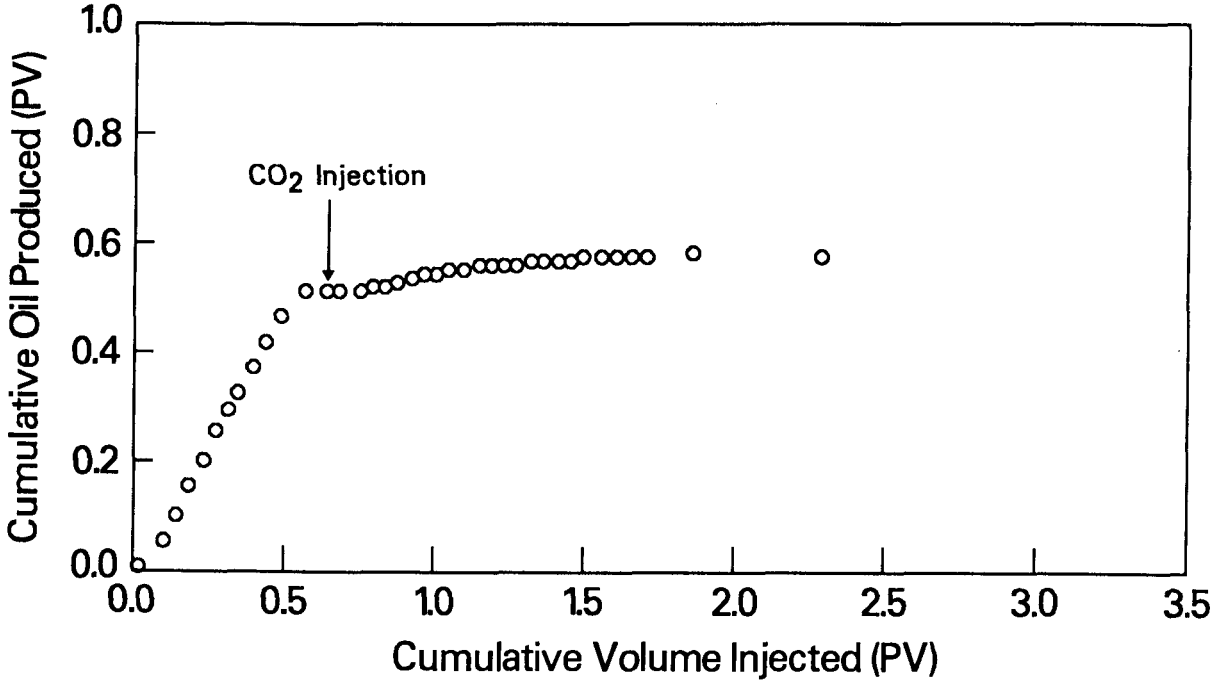

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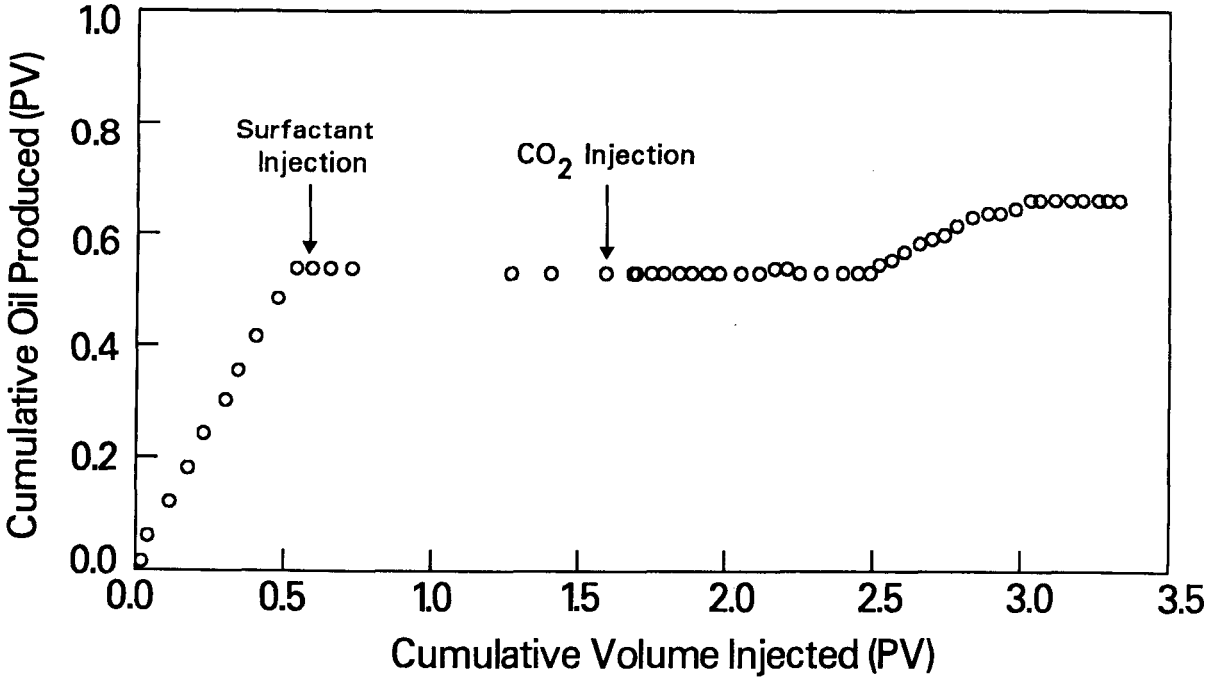
FIGURE 2. EXXON LD776-52 MOBILITY-CONTROLLED CO_2 FLOOD: PLOT OF CUMULATIVE OIL PRODUCED VERSUS CUMULATIVE VOLUME INJECTED (Source: Patton 1986)



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oil as observed in the other experiment, or 0.54 PV. The water phase was then carefully replaced with surfactant solution at a pressure drop of 2 psi/ft. Carbon dioxide injection was initiated and tertiary oil production did not occur until after 0.8 PV of supercritical CO_2 had been injected (temperature = 100°F, pressure = 1,400 psi). Enhanced oil production continued at a low water-oil ratio until 14 percent-PV of additional oil had been produced and residual oil saturation had been reduced to zero. This amount of tertiary oil represents almost a three-fold increase over the average obtained in a conventional CO_2 flood. It is the strongest experimental corroboration of the feasibility of CO_2 mobility control. It also indicates that it may be possible to tailor molecular structures to obtain even more potent additives for use in brine. These results corroborate the immiscible results and, thus, provide additional evidence to support the commercial feasibility of CO_2 mobility control. Equally significant is the fact that the improvement in miscible displacement efficiency correlates with the two-phase flow mobility control data obtained in the dynamic screening experiments.

Computer simulation of mobility-controlled CO_2 floods provided mixed results. For an immiscible CO_2 flood, reducing CO_2 mobility by a factor of 10 increased overall recovery by 20 percent. More importantly, incremental oil production was more than doubled during the early phase when only CO_2 was injected. The earlier oil kick resulting from mobility control could be more significant commercially than the final incremental improvement.

The attempts to simulate the mobility-controlled miscible CO_2 process were not completely successful. Although the base case flood was adequately predicted without problems, it was not possible within the time frame of this project to model lower mobility miscible CO_2 without generating spurious effects on the reservoir oil phase.

4.1.3 Mobility Control for CO_2 Injection

The focus of this project was to provide support for design and evaluation of the Rock Creek Field CO_2 mobility control experiment.

According to Heller (1986) and Heller, Boone, and Watts (1985), the mobility control test at the Rock Creek field did not produce any appreciable volume of oil. Production from the uppermost zone of the Big Injun would have been remarkable because of the very low (about 4.5 percent) residual saturation oil that had been left by the previous conventional CO_2 flood. There had been some expectation, however, that an oil bank might be generated in the central horizon where higher oil saturation existed. If such an oil bank was formed, it was not propagated 75 feet from the injector to the observation well.

Unfortunately, it was not possible to determine the ratio of flow in the two horizons of the Big Injun sand. Analysis of core from the two zones (performed after they were extracted to measure the oil remaining after the first CO_2 flood) had shown no striking permeability difference between the two layers, but the relatively large difference in residual oil had led to some expectation that flow could be somewhat greater in the uppermost zone.

There are several possible explanations for this. It is possible that the difference between flow rates was so great that some sort of small diameter oil bank exists in the central and lower zones of the sand surrounding the injection well, but not reaching as far as the observation well.

A second possibility is that the mobility control efforts were not effective, and for some reason the co-injected surfactant was not able to prevent the CO_2 from forming instability fingers in the formation. This does not seem entirely reasonable, based on the fact that CO_2 had not broken through as a separtate phase into the observation well until after December 21 (and probably not until the pressure was lowered on December 28). It is true that an increasing amount of CO_2 was entering the observation well up to that time, but the quantities were not sufficient to interfere with the flow of liquid samples. This was not the case during the second period of sample taking, when liquid was "slugging" out of the well for shorter times, and between longer periods of gas production. This is evidence that the CO_2 introduced as CO_2-foam did not form fingers. The behavior of fluids in the observation well during the second period of the test is what could be expected after CO_2 actually reached the well.

A third possibility is that the major part of the fluid injected into the injection well did not flow outward uniformly, but took some other route determined by an unexpected permeability heterogeneity. This possibility is supported by the lack of the ammonium thiocyanate tracer in the observation well. Unless the thiocyanate was adsorbed on the rock (although this salt has no record of adsorption in other formations) the tracer tests show either that

none of the injected tracer reached the observation well or that the tracer band passed by unobserved in one or more of the intervals between samplings.

Co-existing with these possible reasons as to why no oil bank was observed at the observation well is the fact that injectivity of CO_2-foam was only about 40 percent of the established value of water injectivity into the injection well. Such an observation (especially if, as here, it is sustained long enough for the injected fluid to be displaced outward more than 10 or 20 feet from the well) can be taken as reliable evidence of reduced mobility. This apparent viscosity of CO_2-foam in Rock Creek sandstone is approximately the same as was observed in the laboratory, as was expected. The reduced mobility apparently was not coupled with an increased mobilization of oil, however.

The injection well was reentered for a radioactive tracer injection, with the observations that no leaks behind casing were detected, that fluid did enter the Big Injun sand, and that the calculated saturations indicated no more oil had been displaced from the lower zones of the formation.

Although no oil was produced, the test provided the following results: (1) it is possible to inject dense CO_2 and a surfactant solution simultaneously, without insurmountable problems of either corrosion or control of the ratio; and (2) the injection of CO_2-foam was effective to some extent in retarding the flow of free CO_2 to a producing observation well located 75 feet from the injection well.

The Rock Creek mobility control test yielded some results that can be of use to the industry. It is possible to inject dense CO_2 and surfactant solution simultaneously into a regular injection well. The reduced injectivity can be interpreted as being caused by the reduced mobility of CO_2-foam, an injection fluid with an apparent viscosity (in this geometry) about 2 1/2 times that of water.

The second test result of some interest is that the simultaneous injection of surfactant with the CO_2 was apparently successful in retarding the formation of viscous fingers and early breakthrough of CO_2 into a producing observation well only 75 feet away. A total of 8,000 reservoir bbl of dense CO_2 were injected (simultaneously with about 2,500 bbl of surfactant solution), with no massive CO_2 breakthrough experienced at the observation well.

4.1.4 New Concepts for Improved Oil Recovery in CO_2 Flooding

The focus of this project is to investigate the recovery of oil from a large, laboratory-scaled, physical model using a CO_2 line drive injection scheme versus the conventional point source injection scheme and to investigate the viability of polymerizing CO_2-soluble monomers in order to increase CO_2 viscosity for better CO_2 mobility control.

A schematic of the line drive injection physical model and the point source injection physical model is shown in Figure 3. The recovery at two PV's injected for both the line drive injection

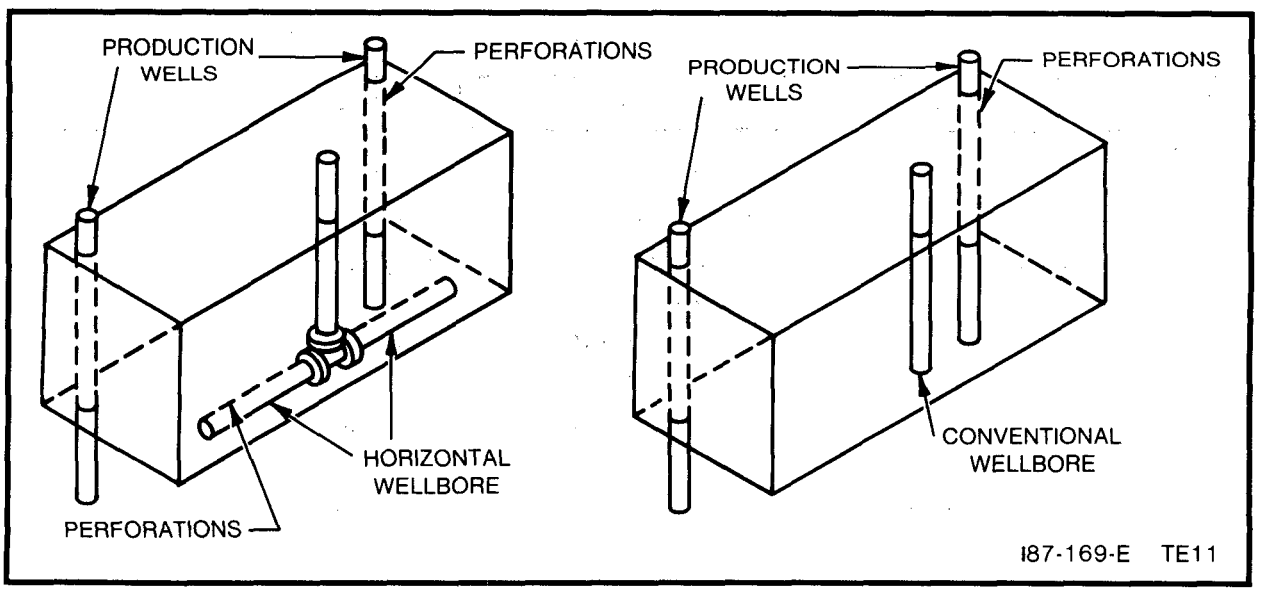
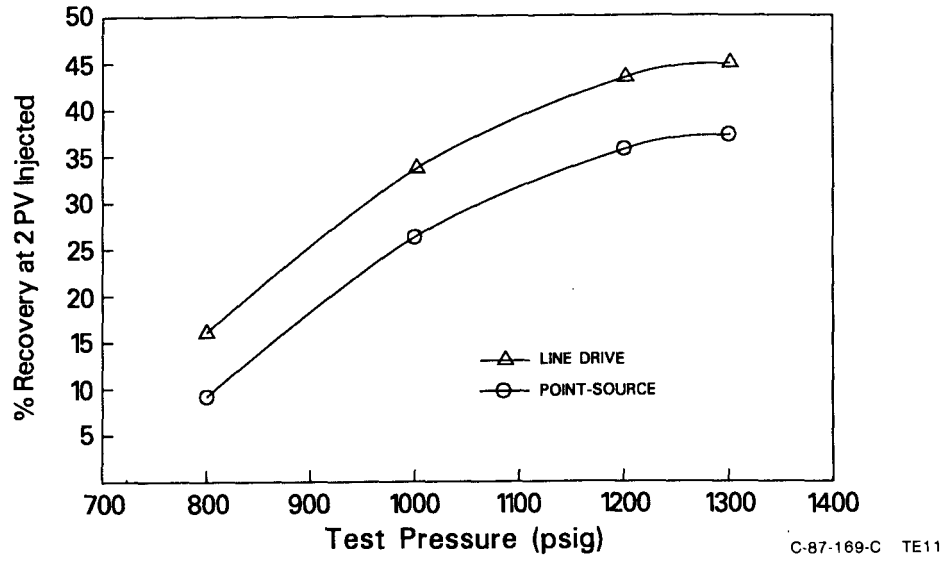


FIGURE 3. SCHEMATIC OF THE PHYSICAL MODEL (Source: Jones 1986)

FIGURE 4. PERCENT RECOVERY VERSUS PRESSURE AT 2 PV INJECTED FOR THE LINE DRIVE AND POINT SOURCE INJECTION SCHEMES (Source: Jones 1986)



scheme and the point source injection scheme is shown in Figure 4. These tests were run with n-heptane at 100°F. The figure shows a consistent increase in recovery of about 8 percent of a PV with the line drive injection scheme in comparison to the point source injection scheme. Due to the fact that the other variables in this model were held constant, the increase can be directly attributed to the injection scheme. This additional recovery represents a 22 percent relative increase in recovery when the MMP is exceeded at 1,200 psi. At 800 psi, the recovery nearly doubles. The percent of additional recovery tends to decrease with increasing recovery.

Polymerization of monomers in the presence of solvents was carried out with various initiators as shown in Table 3. Table 3 shows the solvents, initiators, and monomers that were used in the experiments. In the experiments showing a trace of polymer, the trace, which usually appeared as a thick, polymer-like residue, was never analyzed. In Run 8A, a significant amount of residue was found and analysis showed that the residue contained polyethylene. However, the solubility of the polyethylene, along with the other trace materials, was too low to raise the viscosity of carbon dioxide.

TABLE 3. POLYMERIZATION OF MONOMERS

RUN	SOLVENT	INITIATOR	MONOMER	POLYMERIZATION
1	Carbon Dioxide	Benzoyl Peroxide	Octene	None
2	Cyclohexane	Benzoyl Peroxide	Octene	Trace
3	Carbon Dioxide	Benzoyl Peroxide in Toluene	Ethylene	Trace
4	Cyclohexane	Benzoyl Peroxide in Toluene	Ethylene	Trace
5	Carbon Dioxide	Benzoyl Peroxide in Toluene	Ethylene	Trace
7	Carbon Dioxide	Trigonox 21	Ethylene	Trace
8A	Carbon Dioxide	Trigonox 21	Ethylene	Polyethylene
8B	Carbon Dioxide	Trigonox 21	1-Decene	None

4.1.5 Linear Core Experiments

Laboratory research focused on CO_2-miscible displacements of multi-alkane oils with compositional analyses of the effluents.

A successful shakedown CO_2 flood was completed in high-pressure apparatus (Figure 5) with a 4-in diameter by 5-ft long core of Berea sandstone. The equipment included a logging system and laboratory computer for data acquisition and reduction. The experiment was performed with a four-component (C_9-C_{12}) hydrocarbon system at 72°F and 1,000 psi. This miscible flood was expected to show a very high recovery efficiency.

Test results indicated that the injection of 1.07 hydrocarbon pore volume (HCPV) of CO_2 reduced the water flooded residual oil saturation of 32.3 percent to a final value of 21.7 percent. This corresponded to a tertiary recovery of 21 percent original oil in place. Gas chromatographic analysis of the effluent samples collected at various stages of the flood did not show any compositional change for this particular synthetic oil.

A second CO_2 miscible flood was conducted using a 10-component C_5-C_{16}) hydrocarbon system in a new large core holder obtained from a different vendor. The data from the second test showed that the injection of 1.07 HCPV of CO_2 reduced the residual oil saturation from 37.9 percent to 24.0 percent, corresponding to a recovery of 23 percent original oil in place. Unlike the first test, the gas chromatograph data showed a gradual decline with time of the concentration of lighter hydrocarbon in the liquid produced and the presence of a significant amount of pentane and hexane in the gas produced. These trends are in conformity with the thermodynamic K-values for hydrocarbon/CO_2 mixtures.

These experiments will be repeated for the 10-component hydrocarbon mixture and with improved apparatus. The results will be interpreted with the aid of the METC compositional simulator.

4.1.6 Radial Core Experiments, Morgantown Energy Technology Center

For comparison with the linear flow model, CO_2-miscible displacements of multi-alkane oils were conducted in a radial-flow system with compositional analyses of the effluents.

The radial-flow system shown in Figure 6 has a 1-ft diameter core of 2-in thickness and was equipped with accessories similar to the linear system. A miscible CO_2 injection test was conducted using the same 10-component hydrocarbon mixture as used in the linear core. The injection rate of 150 mL/hr was used for all stages of flooding. (This was equivalent to a Darcy velocity of 23.2 ft/d at the injection face and 0.24 ft/d at the production face, with a mean value of 0.49 ft/d.)

Injection of 1.2 HCPV of CO_2 into the system resulted in a very small recovery of oil (only 7.2 percent original oil in place) with a reduction of residual oil saturation from 31.6 percent to 28.0 percent. The low recovery was ascribed to channeling between the injection port and the production outlet, caused by the configuration of the core holder. The non-occurrence of radial flow in the core was subsequently confirmed by a tracer test.

A summary report on the radial-core flood experiments will be issued, but because of the problems with the equipment design, no further experiments will be performed until the apparatus has been redesigned.

4.1.7 In Situ Deposition of Chemical Precipitates

The focus of this research is to determine conditions and materials for optimum in situ chemical precipitation for mobility control of CO_2 and to determine potential reservoirs that are applicable to in situ chemical precipitation.

Three different solution concentrations (0.1, 1.0, and 2.5 percent by weight) of barium chloride ($BaCl_2$), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$) have been tested for precipitation of carbonates at ambient conditions in the presence of CO_2. The 0.1 percent concentration consists of three-tenths of a gram of salt in 300 cubic centimeters (cm^3) of deionized water. This concentration produces a minimal amount of precipitation. As a result of the low amount of precipitation, tests were directed to the 1 percent concentration.

The 1 percent concentration test consists of 3 grams of salt in 300 cm^3 of water. This set of tests produced significant amounts of carbonate relative to the $CaCl_2$ and $BaCl_2$ tests. All precipitates were tested on the infrared spectra and were proven to be carbonates.

Finally, the 2.5 percent concentration tests were run. By doubling the concentration, a two-fold

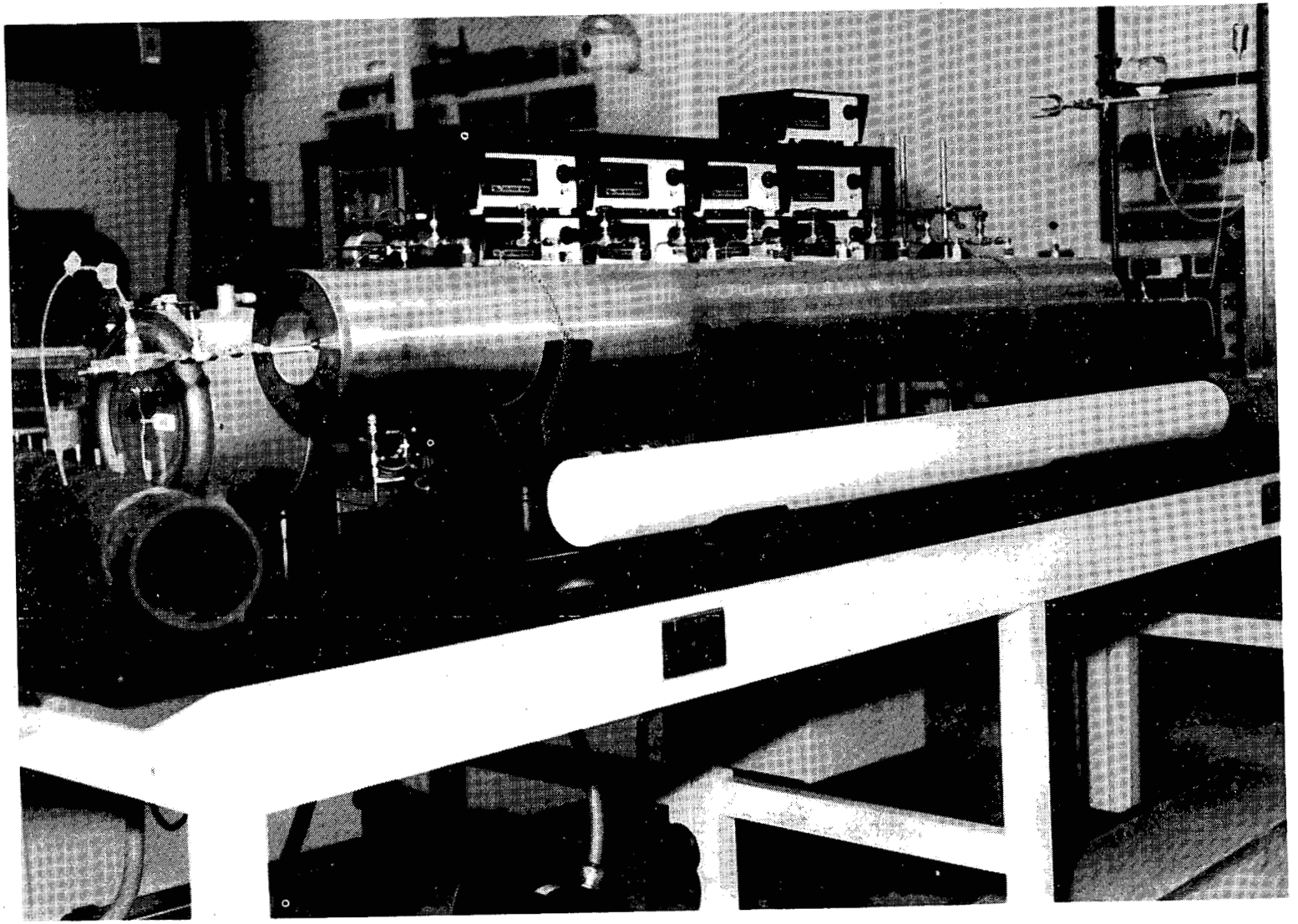


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FIGURE 5. LINEAR CORE APPARATUS

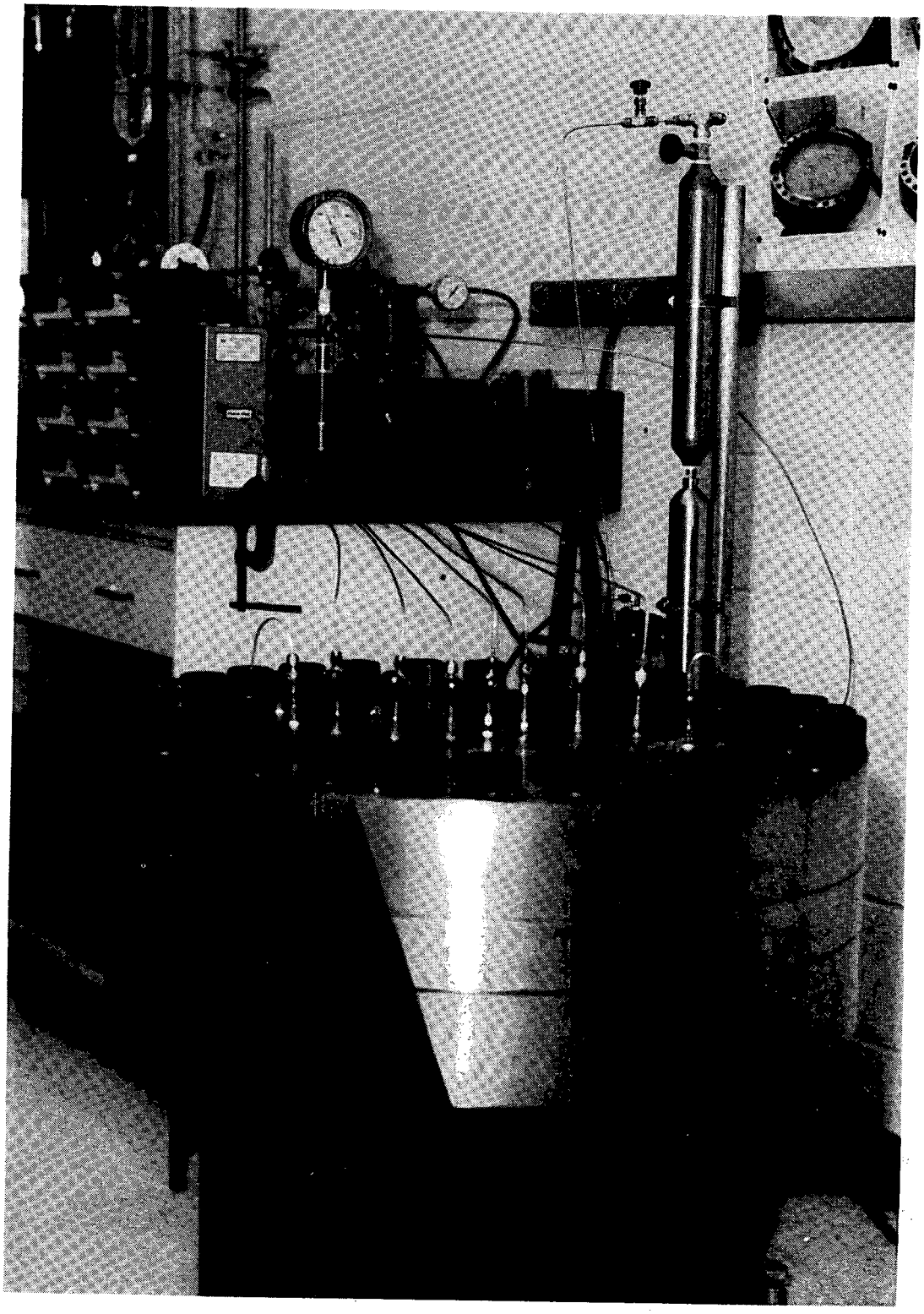

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FIGURE 6. RADIAL CORE APPARATUS

increase in the precipitate was anticipated. However, this was not the case. The 2.5 percent tests produced an amount of precipitate equal to the 1 percent tests. These tests were repeated, and the results were duplicated. Therefore, when tests are resumed in the pressure-volume-temperature (PVT) cell, 1 percent concentrations will be the primary solutions tested.

Tests were conducted at pH values of 3, 4, 5, 6, 7, 8, 9, and 10. These tests indicated that no precipitation could be formed at low pH. Thus, further tests were limited to pH values of 6 through 10. Initially, these pH values were set before CO_2 flow using buffers, and after CO_2 flow using sodium hydroxide (NaOH). After running several samples, the tests indicated that the initial pH of the solution does not affect the amount of precipitation. A common behavior observed in all of the tests is that the pH drops to approximately 4, regardless of the initial pH. Because of this observation, later tests were performed without the addition of buffer to the initial salt solution. NaOH was selected for use because it is relatively inexpensive and has the pH value needed to cause carbonate precipitation.

During all tests, the pH change was recorded as a function of time. The salt solutions were all subjected to 15 minutes of CO_2 flow. After the first 3 to 6 minutes, the pH of the solution would stabilize and remain the same throughout the remaining CO_2 flow time. The tests indicated that the aqueous solution becomes CO_2 saturated within this initial time period. Therefore, all the carbonate capable of precipitation is produced during this time. To prove this hypothesis, a salt solution was subjected to 2 hours of CO_2 flow. The precipitate from this test was then compared to a precipitate from a 5-minute CO_2 flow test. The amount of precipitate from both tests was the same.

It was concluded that a pH of 8 is optimum. As pH is increased above 8, the amount of NaOH used increased but the amount of precipitation remained the same. In the next quarter, the PVT cell will be used to test the effects of pressure and temperature on precipitation and pH.

The tests indicated that $MgCl_2$ solutions can form the same amount of precipitate as $CaCl_2$ solutions. However, this can only be achieved at a pH of 10 or higher. Furthermore, 75 cm^3 of NaOH is required in order to reach a pH of 10. This is 25 cm^3 more than in the $CaCl_2$ tests. Thus, $MgCl_2$ is not a feasible chemical for our research task.

$BaCl_2$ causes the largest amount, by weight, of precipitate. However, the barium ion is much heavier than the calcium ion. The $BaCl_2$ solutions used the same amount of NaOH as did the $CaCl_2$. The main drawback of $BaCl_2$ is the type of precipitate that forms. Barium carbonate ($BaCO_3$) is an extremely fine precipitate. The finest, smallest-pore, filter paper was used during filtration, and the $BaCO_3$ still passed through it. Since it is so fine, it may not block off as much pore volume as the calcium carbonate ($CaCO_3$). The $CaCO_3$ is not as fine, and does not pass through the filter paper.

Initial PVT cell tests consisted of a 1 percent $CaCl_2$ solution, raised to a pH of 8 after contact by CO_2 using 50 cm^3 of NaOH, since these had proven to be the optimum test conditions. Precipitation will occur within minimal CO_2 contact, as long as the pH can be raised to a value of 8. Precipitation of carbonates will not occur at pH values less than 6. The optimum pH value is 8. The amount of carbonate precipitation is independent of the initial solution pH. NaOH is a relatively inexpensive base and is efficient in raising the pH of the solution to conditions favorable for carbonate precipitation.

$CaCl_2$ was found to be the most promising prospect during preliminary precipitation tests on the ability of $CaCl_2$, $BaCl_2$, and $MgCl_2$ to improve carbon dioxide sweep efficiency through selective plugging.

4.2 COMPUTER SIMULATION

4.2.1 Development of a Compositional Simulator

The overall objective of this work is to develop expertise in compositional modeling and to provide simulation support for experimental studies conducted in the laboratory at METC. These studies will aid researchers in understanding the miscible displacement mechanisms and mobility mechanisms associated with enhanced oil recovery processes using carbon dioxide. This work is expected to result in improved predictive capability for project field operations, increased understanding of methods for improving reservoir sweep efficiency, and improved laboratory research through effective simulation support. The specific objectives of FY 86 were to document the development, testing, and validation of the one-dimensional (1-D), fully compositional reservoir simulator.

A compositional reservoir simulator is required to accurately model a reservoir process where signifi-

cant mass transfer between the oil and gas phases occurs. Examples of such reservoir processes are: volatile oil reservoir depletion, gas condensate reservoir depletion, gas cycling operations, and enhanced oil recovery processes (including miscible and immiscible flooding using fluids such as carbon dioxide, nitrogen and lean natural gas).

A 1-D, compositional reservoir simulator has been developed. The model can simulate multicomponent (up to 30 components) and multiphase (up to three phases) fluid flow in a porous medium. The model formulation is an implicit pressure, explicit saturation and composition (IMPESC) solution method. The relative amounts of each component in the oil and gas phases are calculated by assuming phase equilibrium and calculating the individual phase compositions using a flash algorithm coupled with an equation of state.

The 1-D compositional simulator is comprised of a set of semi self-consistent correlations used to calculate fluid thermodynamic, transport, and surface properties. Oil and gas phase thermodynamic properties are calculated using an equation of state, while water density and water viscosity are calculated using a correlation. Oil and gas viscosities and the oil-gas interfacial tension are calculated using correlations which are functions of density. Oil and gas densities are calculated using an equation of state. Therefore, a link has been established between all the oil and gas phase thermodynamic, transport, and surface properties through the thermodynamic property: density. By its nature, an equation of state converges at the critical point where the oil and gas phase properties are equal to one another. This self-consistency in fluid property calculations is important in miscible flooding especially when miscibility is achieved through a multiple contact mechanism with miscibility occurring as the fluid system passes through the critical point. A good example of this phenomena can be seen in Figure 7 where the ternary diagram shows the path of the reservoir oil traveling through the critical point where miscibility is then achieved.

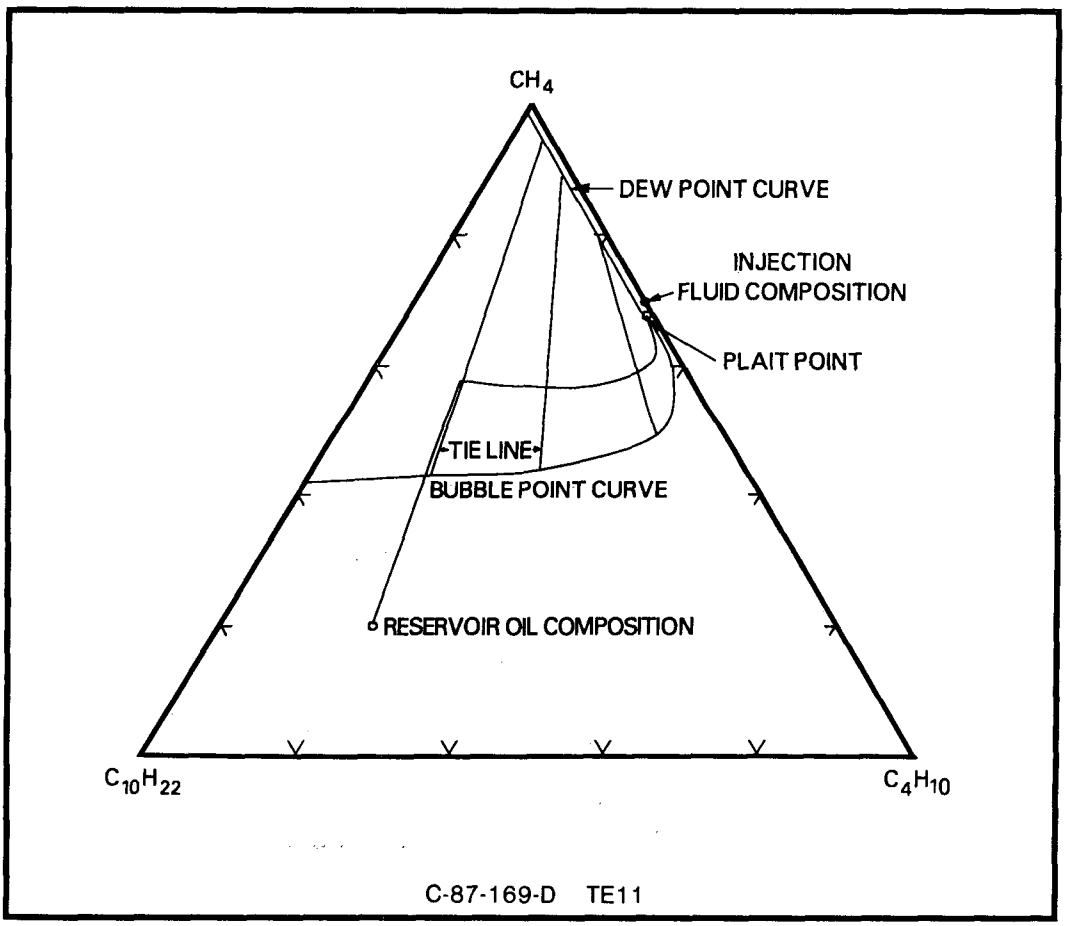

FIGURE 7. COMPOSITION ROUTE OF RESERVOIR OIL FOR A MULTIPLE-CONTACT MISCIBLE DISPLACEMENT PROCESS

Model validation is crucial in establishing the acceptability of compositional simulation results. The model validation was divided into three phases. Phase one, which involved checking all user options to eliminate logic errors, has been successfully completed.

The objective for phase two was to compare results obtained from the simulator with results obtained from literature and the METC laboratory core flooding experiments. Comparison studies have been conducted between the simulator and three literature problems: (1) a 3-component oil displaced by a lean natural gas mixture (miscible case); (2) a 3-component oil displaced by a rich natural gas mixture (immiscible case); and (3) a 15-component oil displaced by carbon dioxide (laboratory case). Figures 8 and 9 show a comparison of composition profiles for methane and decane for the 3-component miscible case and the 3-component immiscible case, respectively. The results generated by METC's 1-D compositional simulator are in

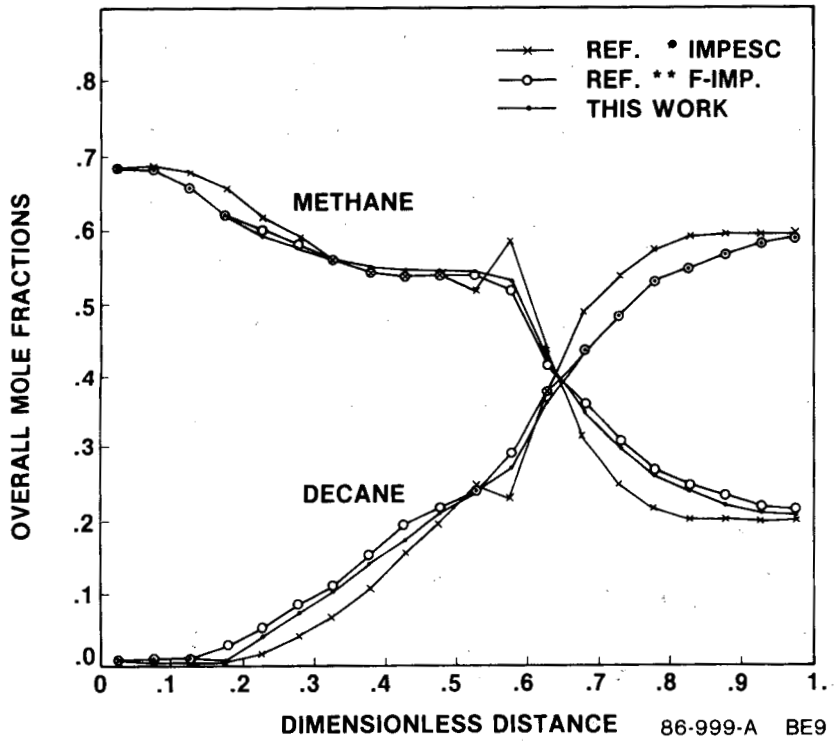

FIGURE 8. COMPOSITION PROFILE FOR METHANE AND DECANE FOR 3-COMPONENT MISCIBLE CASE
(Sources: Ngheim 1981; Coats 1980)

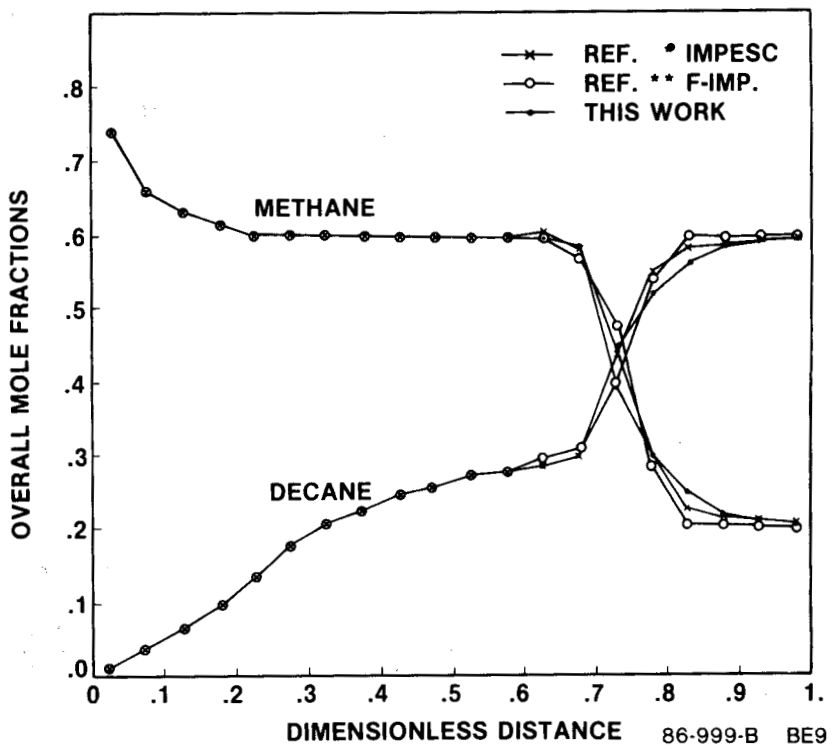

FIGURE 9. COMPOSITION PROFILE FOR METHANE AND DECANE FOR 3-COMPONENT IMMISCIBLE CASE
(Sources: Ngheim 1981; Coats 1980)

close agreement with the results from the two industrial compositional simulators. Figure 10 shows a comparison between the prediction of METC's simulator and the experimental data from a 1-D core flooding experiment. For this comparison, two important input data were unavailable and, thus, had to be estimated. Taking this into account, the results are again in close agreement. The significance of phase two will not be completely realized until comparisons with METC core flooding experiments are completed.

Phase three, an in-depth sensitivity study, has been completed. Examples of the sensitivities examined are: fluid injection rate on oil recovery; productivity index on oil recovery; and bottom hole flowing pressure on oil recovery. Results will be reported in FY 87.

The accurate prediction of phase behavior in a compositional simulator is important in obtaining reliable simulation results. Development has begun on a PVT package. A PVT package is used to better characterize a hydrocarbon mixture, such as crude oil, to improve PVT predictions from an equation of state and to increase the accuracy of simulator results.

4.2.2 Validation of a Modified Black Oil Simulator

The focus of this study is to validate the black oil miscible/immiscible simulator, MASTER (Miscible Applied Simulation Techniques for Energy Recovery), and to conduct sensitivity studies for oil recovery as a function of the input parameters of MASTER.

To validate MASTER, the results from a three-dimensional, immiscible gas injection problem were compared to seven major oil industry models. The results from the seven companies were published by Odeh (1981). Two cases were modeled: Case 1 was a constant bubble-point problem and

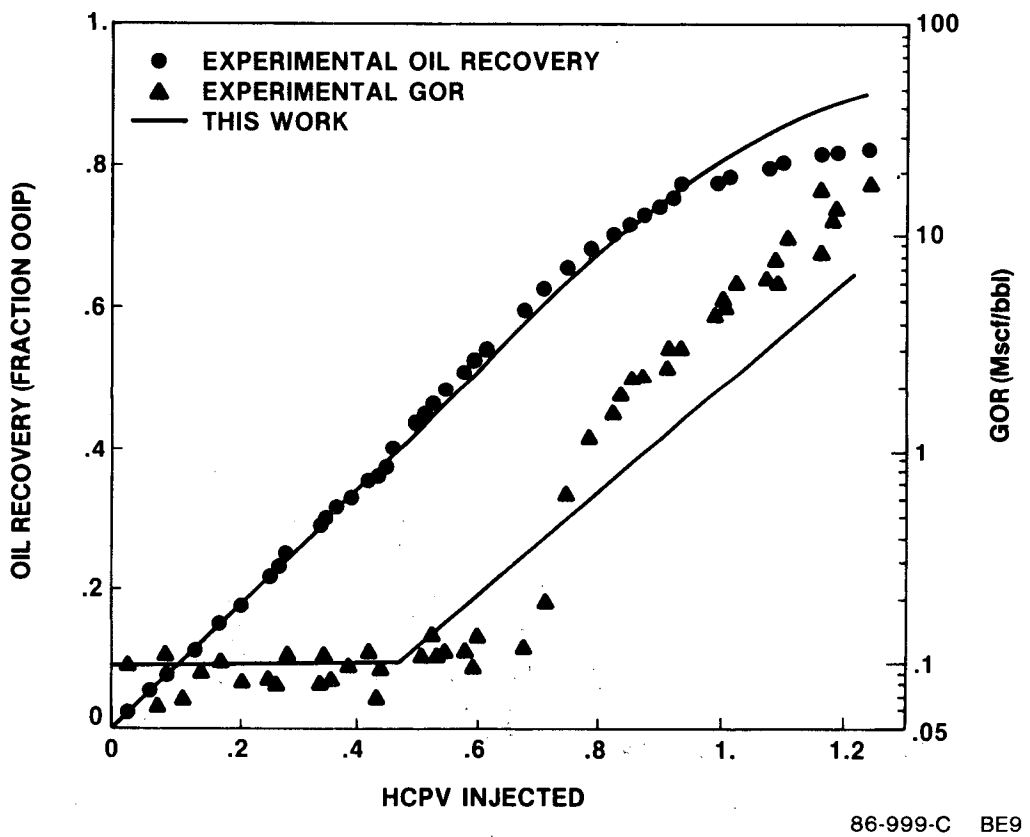

FIGURE 10. COMPARISON OF OIL RECOVERY AND GAS-TO-OIL RATIO FOR 15-COMPONENT LABORATORY CASE
(Source: Kremesec and Sebastian 1985)

Case 2 was a variable bubble-point problem where the bubble-point varied with pressure and gas saturation.

The special options of MASTER have also been tested. The mobility control option was compared to laboratory results published by Bernard, Holm, and Harvey (1980). The water blocking and solid precipitation options were compared to the results of the Todd, Dietrich, and Chase (TDC) Model from the results published by Todd, Cobb, and McCarter (1982). Because all of the necessary input data for MASTER were not available in the literature, only a qualitative comparison of results was made.

Preliminary analysis has shown that MASTER is accurately predicting reservoir performance. Figures 11 and 12 show plots of pressure versus time for both Case 1 and Case 2. As can be seen, the results predicted by MASTER compare favorably to the results of the seven industry models. The

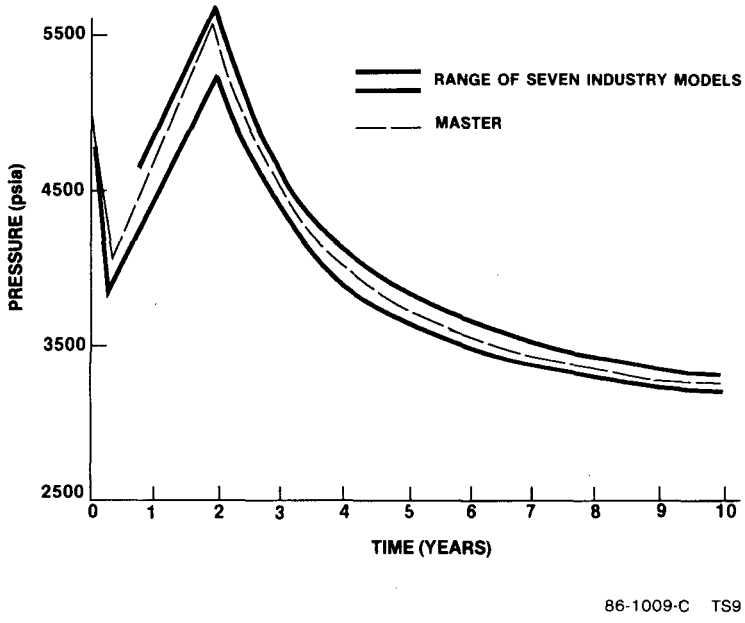

FIGURE 11. COMPARISON OF MASTER TO INDUSTRY MODELS—CASE 1, PRESSURE VERSUS TIME FOR THE PRODUCING WELL NODE
(Source: Odeh 1981)

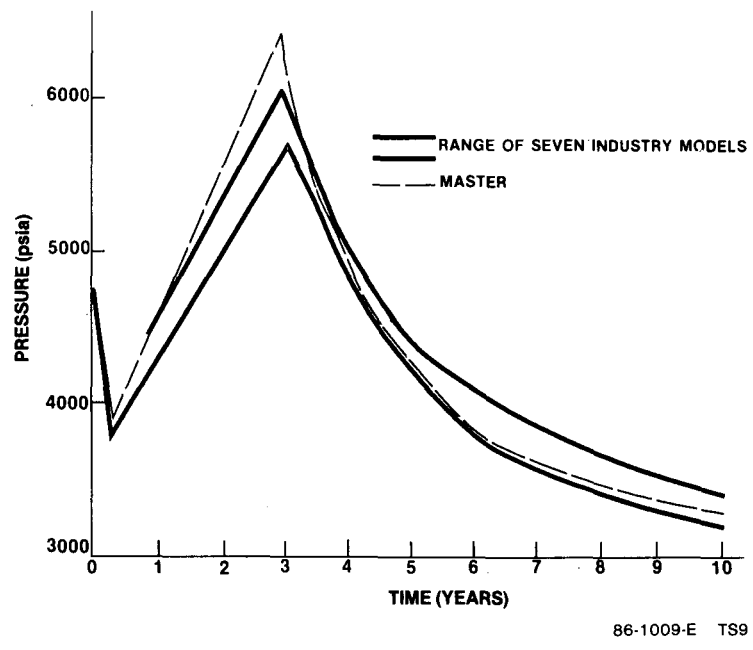

FIGURE 12. COMPARISON OF MASTER TO INDUSTRY MODELS—CASE 2, PRESSURE VERSUS TIME FOR THE PRODUCING WELL NODE
(Source: Odeh 1981)

special options of MASTER provide output that qualitatively compares with laboratory results and a similar simulator. CO_2 mobility data as a function of surfactant concentration will be generated in the laboratory for further validation of the mobility control option and the reservoir behavior resulting from solid precipitation will be investigated. The miscible portion of MASTER will also be validated and sensitivity studies using the various input parameters of MASTER will be conducted to determine their effect on oil recovery. This work will continue into FY 87.

4.2.3 Pattern Alignment and Blocking Studies

The main objective will be to investigate methods designed to increase reservoir sweep efficiency of the CO_2 miscible displacement process using MASTER. Methods to be studied include horizontal wellbores, in situ blocking, and injector/producer pattern optimization.

MASTER, the numerical simulator discussed in Section 3.2.2, will be used in this study.

4.2.4 The Rock Creek Field Simulation Study

The focus of this work was to conduct a reservoir and economic study of the Rock Creek CO_2 flood using the CO_2 miscible flood predictive model.

The miscible CO_2 predictive model (CO2PM) was used to evaluate a CO_2 enhanced oil recovery flood at the Rock Creek Field. The CO2PM represents a fast and effective way to technically screen oil fields for CO_2 miscible flooding prior to a more in-depth analysis. CO2PM predicts oil recovery from a normal, five-spot pattern. The reservoir performance predicted for the single pattern is superposed with a pattern development schedule to predict oil recovery for a given field.

Reservoir and fluid parameters obtained from the pilot tests conducted at Rock Creek, along with operating costs and oil and CO_2 prices, were used for the base-case study. A sensitivity analysis of the Rock Creek design parameters (pattern size, water-alternating-with-gas [WAG] ratio, total hydrocarbon pore volume of WAG injected, and injection rate) was conducted. A sensitivity analysis was also conducted on the economic parameters to determine how the changes in oil price, CO_2 costs, and operating costs affect project economics for a given project performance.

This study has shown that miscible CO_2 enhanced oil recovery is technically feasible in shallow, low-temperature, Appalachian reservoirs. The economic environment, however, is the major factor governing the practicality of conducting a full-field flood. The base-case study showed that an oil price of $39 per barrel is necessary to obtain a discounted cash flow rate-of-return of 15 percent.

A sensitivity analysis of the design parameters showed that a more optimal design of the field, with respect to the base case, could be developed. A more rigorous simulation study with a reservoir simulator is warranted to optimize operating conditions and, thus, improve the project economics. The economic sensitivity analysis showed that a CO_2 pipeline is necessary to conduct a full-field flood and that oil price and CO_2 costs play a major role in project economics. Tables 4 and 5 give the results of the two sensitivity studies.

4.3 RESERVOIR HETEROGENEITY

4.3.1 Reservoir Characterization for Numerical Simulation of the CO_2 Enhanced Oil Recovery Process

The focus of this research is to develop new concepts for characterization and description of the interwell area of a petroleum reservoir suitable to the CO_2 EOR process. The relationship between reservoir heterogeneity and flow are being examined. It is the flow aspects of heterogeneity that determine which scales of heterogeneity have the greatest influence on performance of any EOR process. Calculations of the performance of ideal miscible displacements in single layer systems with various distributions of permeability indicate clearly that the way in which high and low permeability zones are connected is as important as the range of variation. For example, permeability realizations with the same statistical descriptors (i.e., mean permeability, variance, and correlation length) in which the length scale of the heterogeneity is a significant fraction of the displacement length, can show very different flow behavior depending on the orientation of zones of high and low permeability with respect to the local average flow direction. If high permeability zones lie transverse to the average flow, they have little effect on solvent break-through times. If, however, they are aligned, early breakthrough is guaranteed. Thus, any successful description of reservoir heterogeneity for a

TABLE 4. SENSITIVITY ANALYSIS OF ROCK CREEK DESIGN PARAMETERS

Adjusted Input Parameters	Output Parameters					
	Project Life (Years)	Enhanced Oil Recovery (% OOIP)	Gross CO_2 Utilization (Mscf/bbl)	Mean DCF at a 15% Discount Rate ($MM)	DCF ROR (%)	Payback (Years)
Pattern Size (acres)						
5	11	13.0	10.7	-21.8	0.6	No Paybacks
10*	13	12.7	10.4	3.7	15.1	10.7
15	15	11.9	11.6	-0.8	13.0	No Payback
WAG Ratio						
0.1	14	21.8	13.9	38.0	27.1	5.8
0.5	14	19.1	11.7	36.0	30.0	5.5
1.5*	13	12.7	10.4	3.7	15.1	10.7
Total HCPV WAG Injected						
1.0*	13	12.7	10.4	3.7	15.1	10.7
1.5	15	17.2	11.4	8.3	16.9	10.3
2.0	17	20.5	12.7	6.1	15.7	11.6
Injection Rate (bbl/d/pattern)						
170	14	12.7	10.6	-3.4	11.6	No Payback
200*	13	12.7	10.4	3.7	15.1	10.7
230	12	12.9	10.4	8.6	18.0	9.4

*Base case.

TABLE 5. SENSITIVITY ANALYSIS OF ROCK CREEK ECONOMIC PARAMETERS

Adjusted Input Parameters	Output Parameters: Mean DCF at a 15% Discount Rate ($MM)	DCF ROR (%)	Payback (Years)
Oil Price ($/bbl)			
31.00	-24.7	0.2	No Payback
39.00*	3.7	15.1	10.7
47.00	32.5	31.4	5.3
C_2 Cost ($/Mscf)			
0.75	11.3	19.6	7.9
1.00*	3.7	15.1	10.7
1.50	-12.0	7.4	No Payback
2.50**	-35.4	-2.2	No Payback
Water Treatment/ Injection Costs ($/bbl)			
0.15	9.6	18.5	9.3
0.30*	3.7	15.1	10.7
0.45	-2.2	12.0	No Payback
CO_2 Recycle Cost ($/Mscf)			
0.24	5.6	16.4	10.0
0.40*	3.7	15.1	10.7
0.55	1.4	13.9	11.7
Pipeline Capital ($MM)			
13.0	4.8	15.8	10.3
15.3*	3.7	15.1	10.7
17.6	2.6	14.5	11.0

*Base case.
**CO_2 cost and trucking cost; no pipeline capital.

flow process must include some representation of the orientations of the heterogeneities with respect to average flow directions.

The question of how to represent the effects of heterogeneities for simulation with large grid blocks is being examined. In particular, the use of modified block transmissibilities to represent the effects of heterogeneities with length scales smaller than the grid block is being considered. This work shows that grid-scale transmissibilities must be anisotropic to capture the effects of the smaller scale heterogeneity, even when the local permeability field is isotropic. This study is motivated by the recognition that heterogeneity may control the stability and efficiency of recovery processes. In general, neglecting heterogeneity will produce optimistically biased recovery predictions.

A sample transmissibility (T) scaling calculation has been performed. A 20-by-20 grid with a permeability distribution was scaled to a 4-by-4 grid. The scaling algorithm calculates the fluxes between the grid blocks and the average grid block pressures for 40 sets of boundary conditions. The different sets of pressure boundary conditions cause variations in the local pressure field. The normal and shear transmissibilities are then estimated by linear least

squares at those values that give the best match to the calculated fluxes for the various pressure boundary conditions. For constant permeability grid, all the cross terms T_{xy} and T_{yx} are zero. For the variable permeability case, the shear terms were as large or larger than the normal terms. This result demonstrates the importance of using the full permeability tensor when scaling the effects of permeability variations.

The extent to which pressure transient tests can be used to detect reservoir heterogeneity is also being considered. Current work is investigating the effects of line boundary skin in a true composite reservoir on transient pressure testing. The reservoir is composed of two distinct regions separated by a boundary which presents an increased resistance to flow. Such a boundary may be associated with a sequence of shale lenses, a natural fault that is partially conductive, or an artificial boundary created by fluid banks. These skin boundaries are large-scale reservoir heterogeneities and may impose a significant effect on CO_2 flooding operations, especially in large well spacing projects.

The pressure transient test analysis performed to date indicates that: (1) the early time-pressure response is controlled by the properties of the inner region for finite and semi-infinite reservoirs; (2) the deviation from the infinite acting transient linear response depends on the distance to the discontinuity; (3) linear systems with a closed outer boundary approach pseudo steady-state flow, and the value of discontinuity skin is added to the homogeneous solution; and (4) linear systems with a constant pressure outer boundary approach steady-state, and the value of discontinuity skin is added to the homogeneous solution. The inverse problem, determining solution parameters from pressure data, is now being considered.

The performance of most CO_2 floods will be influenced by a combination of the effects of phase behavior, viscous instability, and reservoir heterogeneity. Quantification of the interactions of those contributions to the reservoir flow behavior is an important goal of current research to improve the accuracy of performance predictions. Recent work has focused on two parts of that problem. The first part is the calculation of the performance of flows dominated by viscous instability by simulating the development of viscous fingers. To evaluate the quantitative performance of the model, the displacement experiments performed by Blackwell, Rayne, and Terry (1959) were simulated. Preliminary results indicate that while breakthrough times can be matched by varying grid block size, recovery curves do not match well with continued injection. Additional investigation of the numerical contributions to transverse and longitudinal dispersion is being performed in an attempt to explain the differences between observation and calculation.

In the second part, the influence of phase behavior on displacement performance has been explored further by extending the analysis of Helfferich (1981) and Dumore, Hagoot, and Risseeuw (1981) for one-dimensional flow in ternary systems to four-component systems. The analysis explains why the addition of methane to an oil has minimal impact on the minimum miscibility pressure for the oil. When methane is present in an oil that would develop miscibility in the absence of methane, the methane forms a bank at the leading edge of the displacement. The displacement is immiscible in the sense that is clearly passes through the two-phase region; but the recovery in the displacement is only slightly less than that observed when no methane is present because for much of the displacement length, the injected CO_2 displaces the oil from which the methane has been removed. The calculations also suggest that for some systems Co_2 can displace the oil very efficiently even if it is below its bubble point pressure.

Calculations of the performance of ideal miscible displacements in single-layer systems with various distributions of permeability indicate that the way in which high and low permeability zones are connected is as important as the range of variation. The use of modified block transmissibilities simulation to represent the effects of heterogeneities with length scales smaller than the grid block shows that grid-scale transmissibilities must be anisotropic to capture the effects of the smaller scale heterogeneity, even when the local permeability field is isotropic. Analysis of the extent to which pressure transient tests can be used to detect reservoir heterogeneity shows definite relationships between the reservoir and pressure and flow responses. Preliminary simulation of experiments of flows dominated by viscous instability indicate that while breakthrough times were matched with the simulator by varying grid block size, recovery curves do not match well with continued injection. Investigations of the influence of phase behavior on displacement performance has revealed why the addition of methane to an oil has minimal impact on the minimum miscibility pressure.

4.3.2 X-Ray and Nuclear Magnetic Resonance Imaging

The focus of this research is to examine imaging techniques for possible use in the quantification of surfactant-based mobility control for miscible flood enhanced oil recovery.

Scouting experiments were performed on the use of X-ray computerized tomography (CT) at General Electric in Milwaukee and on the use of nuclear magnetic resonance imaging (NMRI) at the Nuclear Magnetic Resonance Imaging Center in Pittsburgh.

X-ray CT technology appears to be ready for semi-routine use in the quantification of miscible flood mobility control and an X-ray CT unit will be acquired. However, NMRI is much more costly; hence, further experiments will be performed at existing NMRI centers.

4.4 PHASE BEHAVIOR AND MISCIBILITY

4.4.1 Improvement of CO_2 Flood Performance[2]

Emphasis of this study has been on phase behavior studies, where: in the development of the quartz crystal viscometers used on the continuous multiple contact (CMC) experiment has been completed. Average viscosity errors well under 10 percent have been shown for pure compounds (CO_2 and several light hydrocarbons) over temperature and pressure ranges from 100°F to 200°F and 14.7 psi to 4,000 psi, respectively (1986).

Researchers are now simultaneously measuring viscosity, density, and composition of phases for mixtures of CO_2 with several synthetic oils, including CO_2-C_1-C_{16} and CO_2-nC_5-nC_{10}-nC_{16}-nC_{30}. Commonly used viscosity correlations are being evaluated against the data, and new viscosity correlations are under development.

The influence of multiple hydrocarbon phase behavior in process scale-up is under investigation. Recent evidence indicates that the presence of three or four hydrocarbon phases can improve sweep efficiency at reservoir scale. A new slim tube/coreflood apparatus has been designed and is under construction. It will first be used to investigate the effects of solution gas on the development of miscibility.

There is a new emphasis on fluid diversion systems, for example, dense gas foams and polymers. A previous micromodel apparatus is being overhauled and reassembled in a temperature-controlled air bath. The new system will have a pressure and temperature range of 2,000 psi and 150°F, respectively.

Researchers are also developing new phase behavior models and are presently working with cubic equation of state. A literature review on the use of equations of state for reservoir fluids is being completed.

4.5 LABORATORY DISPLACEMENT TESTS

4.5.1 Improvement of CO_2 Flood Performance[3]

Laboratory tests were conducted using a new coreflood unit, as shown in Figure 13, which has been assembled, tested, and is fully operational. In addition, during FY 86, work on CO_2 coreflood experiments progressed with preparation of four Society of Petroleum Engineers (SPE) technical papers.

Bahralolom and Orr (1986) compared the results of secondary and tertiary displacements of Maljamar crude oil by N_2 and CO_2 to examine the effects of solubility and extraction on local displacement efficiency. The flow visualization experiments were performed in pore networks etched in glass plates. In those experiments, the higher solubility of CO_2 in the oil caused only marginal improvement in displacement efficiency over that observed for N_2 which is much less soluble in the oil. At pressures high enough for CO_2 to extract hydrocarbons efficiently, displacements were much more efficient.

They reported the following three conclusions: (1) the performance of secondary displacements of crude oil by CO_2 is much more sensitive to the efficiency of extraction of hydrocarbons by the displacing CO_2-rich phase than it is to the solubility of CO_2 in the crude oil; (2) capillary forces dominate the performance of displacements of crude oil by low-density CO_2 regardless of the level of solubility of CO_2 in the oil; and (3) in displacements at the

[2]Elements of this project fall into the Laboratory Displacement Tests area and the Mobility Control area. Information concerning this project can be found in those sections of this report.

[3]Elements of this project fall into the Phase Behavior and Miscibility area and the Mobility Control area. Information concerning this project can be found in those sections of this report.

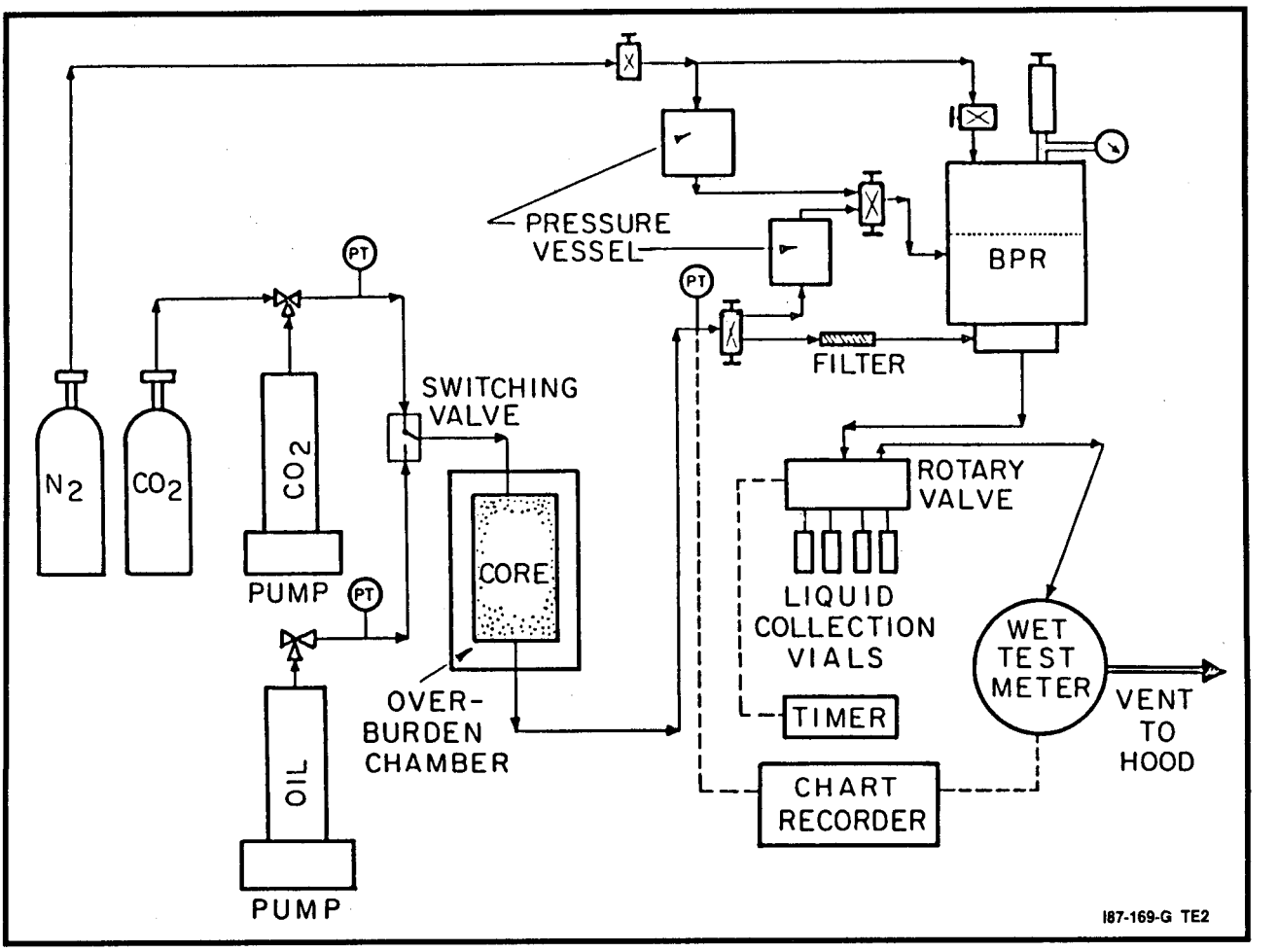

FIGURE 13. CO_2 CORE FLOOD UNIT
(Source: Heller, Kovarik, and Taber 1986)

scale of laboratory pore networks, the presence of significant heterogeneity in the pore space significantly slows the rate at which CO_2 reaches and displaces waterflood residual oil.

Bretz and Orr (1986) presented the results of stable, first-contact miscible displacements for three San Andres carbonate cores from west Texas and eastern New Mexico. All three cores showed evidence of significant heterogeneity at the core scale. Effluent composition measurements were interpreted using two simple models of mixing during flow in a heterogeneous media. They concluded that for reservoirs with scales of heterogeneity larger than those present in core samples, laboratory core displacements do not provide evidence about mixing behavior at field scale.

Observations of pore structure in thin sections were related to the performance of stable, first-contact miscible displacements in reservoir cores and then to simulations of displacement performance of CO_2 corefloods by Bretz, Spector, and Orr (1986). They concluded that simulations of the interactions of phase behavior and flow in non-uniform pore structures indicate that wide pore size distributions and preferential flow paths can significantly increase residual oil saturations in CO_2 floods over those with uniform pore structures. Heterogeneities observable at the scale of a thin section have significant effects in laboratory cores but much smaller effects in displacements at field scale. Large-scale heterogeneities present in field floods probably cause similar increases in residual saturations in some fields.

In examining the changes in fluid distributions and the mixing that occurs in immiscible phases flowing in a porous medium with changes in phase saturations and flow rates, Bretz, Welch, Morrow, and

Orr (1986) primarily concluded that in CO_2 floods in laboratory cores similar to the Berea and Rock Creek cores used, the trapped oil saturations resulting from mobile water saturations would cause a larger reduction in oil recovery than would the effects of mixing between fluids in flowing and stagnant fractions in the oil phase.

4.5.2 Adsorption and Wettability Modification in Enhanced Oil Recovery

The focus of this research was to examine the effects of wettability modification on enhanced oil recovery by CO_2-miscible flooding.

When dilute solutions of chemicals such as asphaltenes and surfactants flow through porous rocks, the rock surface adsorbs the chemicals from solution. In most cases, the adsorption parallels the Langmuir isotherm. Since the isoelectric point for quartz is about pH = 3.0, the adsorption of ionic or polar substances on sandstone will depend on the pH of the solution and the ionic/polar nature of the adsorbate. Our experimental data follow these generalizations.

The chemical retention also manifests itself in altered wettability of the cores, as determined by Amott's method based on imbibition and centrifugal displacement. In our experiments, asphaltene treatments rendered Berea sandstone neutral-wet.

Cationic surfactants made the sandstone oil-wet, whereas anionic and nonionic surfactants made the rock less water-wet. (Untreated Berea sandstone is strongly water-wet.)

The tertiary recovery of oil by CO_2-flooding was found to increase as the Berea cores were rendered neutral or slightly oil-wet. This optimum recovery was also found to be higher than that observed in a strongly oil-wet teflon core of higher permeability.

In all these tests, Penetac white mineral oil was used. This 44° API paraffin oil contains C_{13} to C_{20} hydrocarbon with 94 percent in the C_{15}-C_{18} range and has a viscosity of 3.8 cP at 100°F.

Weakly oil-wet porous media appear to give substantially larger CO_2 oil recoveries than strongly water-wet media. Hence, these experiments will be continued and refined during the next year.

4.6 FIELD TESTS

Since 1976, DOE and industry have shared the cost of CO_2 injection projects to examine the technical feasibility of this process. Projects have included highly instrumented field experiments (pilot test pattern floods, minitest pattern floods, and injectivity tests) related to improving methods for increasing CO_2 recovery efficiency. A summary of current and completed DOE cost-sharing CO_2 tests is shown in Table 6. Figure 14 shows the approximate location of each of these tests on a map of the United States. A discussion of the current tests (those that were active in FY 86) follows.

4.6.1 Oil Recovery by Carbon Dioxide Injection, Rock Creek Field, Roane County, West Virginia

The focus of this field test was to determine the efficiency of injecting CO_2 for oil displacement in a tertiary mode following water-flooding and low-pressure gas recycling in a shallow, low-temperature reservoir and to investigate the feasibility of using mobility control techniques to improve the recovery efficiency of the CO_2 process.

The pilot test consisted of two adjacent 10-acre, normal five-spot patterns surrounded by 13 back-up water injection wells which maintained the MMP of 1,000 psi and prevented much of the CO_2 from escaping from the pilot area. The six pattern injection wells were drilled, cored, and logged to determine reservoir properties. Water injection was initiated in April 1977 to raise the reservoir pressure to the MMP.

In February 1979, CO_2 injection was initiated. By June 1980, 23,842 tons of CO_2 had been injected. Pennzoil then certified the Rock Creek project under the DOE Tertiary Incentive Program, thus allowing the injection of 12,000 additional tons of CO_2 into a 1.55-acre, four-spot minitest pattern, developed within the pilot area. Injection resumed in the fall of 1980 and pattern floodout was completed in January 1982.

Cumulative oil production from the field test was 28,259 barrels through December 1982. The ratio of CO_2 injected per barrel of oil recovered was 13,000 standard cubic feet (scf) per stock tank barrel (STB) in the original two 10-acre, five-spot patterns. This test effort recovered 13,078 STB of oil (3 percent of the original oil in place) but was terminated before all oil capable of being mobilized was recovered and was replaced with a second, smaller test that would yield quicker results.

The second test was conducted in a 1.55-acre normal four-spot pattern that was contained within the

TABLE 6. SUMMARY OF CURRENT AND COMPLETED DOE COST-SHARING CO_2 FIELD TESTS

	Rock Creek Field Pilot Area, WV	Rock Creek Field Minitest Area, WV	Granny's Creek Field Pilot Area, WV	Granny's Creek Field Minitest Area, WV	Hilly Upland Field, WV	Little Knife Field, ND	Weeks Island Field, LA
Formation	Pocono Big Injun	Pocono Big Injun	Pocono Big Injun	Pocono Big Injun	Greenbrier Big Injun	Mission Canyon	"S" Sand, Reservoir B
Lithology	Sandstone	Sandstone	Sandstone	Sandstone	Carbonate	Dolomitized Carbonate	Sandstone
Reservoir Depth (Ft)	1,975	1,975	2,000-2,100	2,000-2,100	1,800-2,100	9,800	12,750
Reservoir Temperature (°F)	73	73	73	73	77-80	245	225 (Oil Column)
Net Effective Thickness (Ft)	32.4	32.0	28	28	12.5	16	120
Porosity (%)	21.9	21.3	16	16	14.0	19.5	26.0
Permeability (mD)	20.5	27.3	7	7	2-4	16.7	1,800
Oil Saturation (%)	34.4 (After Primary)	34.4 (After Primary)	30 (After Waterflood)	30 (After Waterflood)	70-80 (After Primary)	40.4 (After Waterflood)	22 (After Waterflood)
Water Saturation (%)	50-55 (Initial)	50-55 (Initial)	70 (After Waterflood)	70 (After Waterflood)	20-30 (Initial)	21.8 (Initial)	8 (Initial)
Oil Type	Paraffin Base	Paraffin Base	Paraffin Base	Paraffin Base	Paraffin Base	N/A	N/A
Oil Gravity (°API)	43	43	45	45	42	41	32.3
Oil Viscosity (cP) (Reservoir Conditions)	1.9	1.9	1.6	1.6	1.73	0.20	0.41
Formation Volume Factor (Original)	1.13	1.13	1.13	1.13	1.13	1.77	1.652
Formation Volume Factor	1.20 (CO_2 @ 1,300 psi)	1.20 (CO_2 @ 1,300 psi)	1.113 (CO_2 @ 492 psi)	1.113 (CO_2 @ 492 psi)	1.145 (CO_2 @ 445 psia)	N/A	1.545 @ 225° and 5,100 psia)
Area (acres)	19.65	1.55	6.7	0.85	10	5.0	8 (900 acre-feet)

TABLE 6. SUMMARY OF CURRENT AND COMPLETED DOE COST-SHARING CO_2 FIELD TESTS (Continued)

	Rock Creek Field Pilot Area, WV	Rock Creek Field Minitest Area, WV	Granny's Creek Field Pilot Area, WV	Granny's Creek Field Minitest Area, WV	Hilly Upland Field, WV	Little Knife Field, ND	Weeks Island Field, LA
Pattern	2 Normal 5-Spot	1 Normal 4-Spot	1 Normal 5-Spot	1 Inverted 4-Spot	Single Injection Well	1 Inverted 4-Spot	Single Injection Well
Bottom Hole Pressure (psi)	1,834	1,834	1,800	1,800	1,250	3,500	4,950
Minimum Miscibility Pressure (psi)	1,000	1,000	1,000-1,050	1,000-1,050	1,050	3,400	N/A
Primary Production (bbl/acre)	2,900	2,900	2,900	2,900	2,850	N/A	N/A
Secondary Production (Waterflood) (bbl/acre)	577	577	4,100	4,100	N/A[1]	6,680 (By simulator[2])	N/A
EOR Production (CO_2) (bbl/acre)	666	2,465	1,296	2,362	410	9,020 (By simulator[2])	21,750
CO_2 Injected (tons)	27,454	8,189	9,880	2,118	1,546	2,095	50,000
Effective CO_2 Injected (tons)	6,167	2,012	1,186	2,118	1,546	2,095	50,000
CO_2/Oil Ratio (scf/bbl)	13,000	9,000	19,626	18,192	6,333	3,100 (By simulator[2])	9,000[3] (10/86)

[1]No secondary production.
[2]Nonproducing pilot test.
[3]Including recycled CO_2.

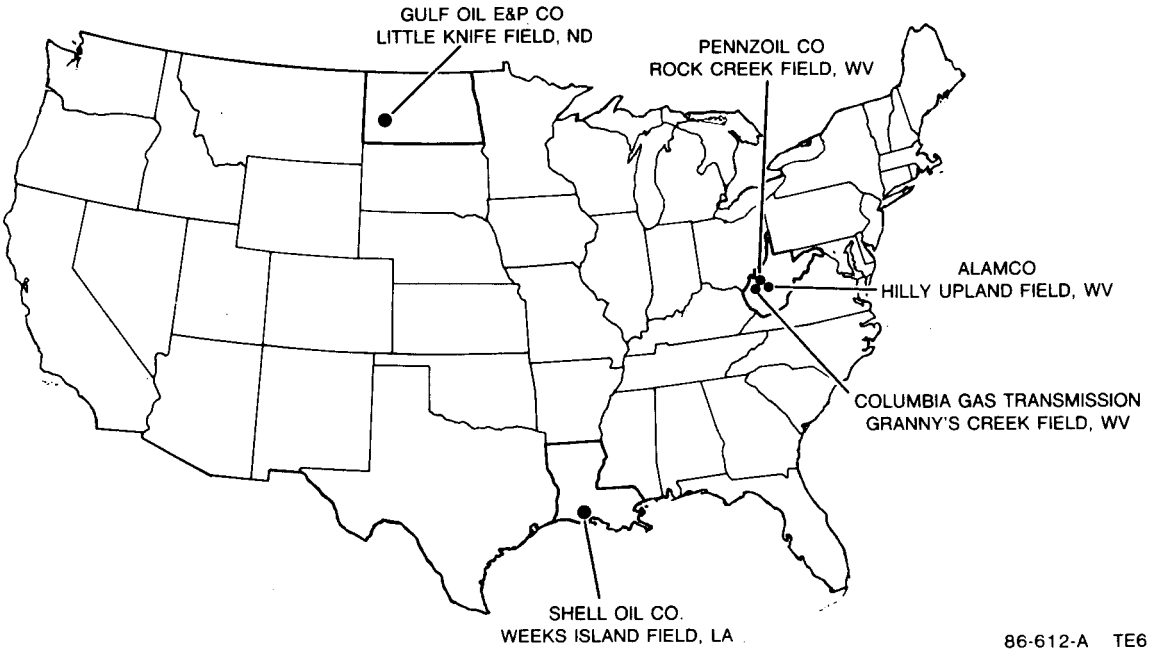

FIGURE 14. LOCATION OF CO_2 ENHANCED OIL RECOVERY FIELD TESTS

original test pattern. In this test, the ratio of CO_2 injected per barrel of oil recovered was approximately 9,000 scf/STB. The oil recovery from this test was 3,821 STB (11 percent of the original oil in place).

Mobility control is a problem in CO_2 enhanced oil recovery. Due to the very low viscosity of the CO_2, it tends to finger through the lower viscosity fluid (water) within the reservoir and bypass the higher viscosity fluid (oil). This viscosity factor results in a very high mobility of the CO_2, which generally leads to a low volumetric sweep efficiency of the reservoir, and leaves much of the oil behind.

In an attempt to address this difficulty, a CO_2-surfactant mobility control test was conducted. This test was conducted within the pilot test area. The test pattern consists of one injection well, one observation well, and one production well. The test area was repressured by water injection to reach the CO_2/oil MMP. A chemical tracer test using thiocyanate was run to determine fluid velocity through the reservoir. This would allow better estimates of later results such as oil bank arrival time. In 1984, following the tracer test, surfactant pad injection was begun to condition the reservoir to prevent any surfactant adsorption on the rock surfaces when the CO_2/surfactant foam injection begins. Neither the tracer, the surfactant, nor the oil bank was detected at the observation well. Completion of this test should verify laboratory experimental results for mobility control of CO_2 flooding to increase oil recovery efficiency.

Brummert, Watts, Boone, and Wasson (1986) concluded that in the original five-spot patterns, CO_2 displacement efficiency was extremely good (residual oil saturation < 5 percent) where CO_2 contacted the oil. However, it was shown that volumetric sweep efficiency was less than 35 percent.

Concerning the mobility control test, Heller, Boone, and Watts (1985) discussed that an unforeseen and unexplained difficulty has been the absence of any sign of an oil bank in the observation well. The following can be listed as the possible causes for the absence of the oil bank:

1. There may not have been enough CO_2 foam injected to push the oil bank to the observation well. This possibility is supported by the fact that no thiocyanate tracer was detected.
2. There may not be enough oil left in the formation being swept to form an oil bank. Although this is probably true in the upper 10 feet of the reservoir, there appears to be a suitable amount

of oil in the lower part of the Big Injun in which the permeability is adequate for flow.

3. The CO_2 foam may have broken down by the following:

   a. Adsorption of surfactant into the formation rock. (This would contradict the adsorption experiments done in the laboratory, but is not impossible; only a small sample of reservoir rock was sampled.)

   b. Thermal/chemical degradation of the surfactant. (Again, various experiments have shown that at the low temperature of 75°F, Alipal can survive for years in water solution. There certainly may be some unexpected, deleterious effects from the rock minerals and CO_2 that become important at longer times.)

   c. Inability to lower the mobility under reservoir conditions. (It is conceivable that the flow of CO_2 foam is so non-uniform in larger sections of porous rock, that the mobility decrease measured on a small scale is not applicable. Scale effects in the displacement of the surfactant solution lamellae might not be as well understood as has been assumed).

4.6.2 Weeks Island "S" Sand, Reservoir B, Gravity-Stable CO_2 Displacement, Iberia Parish, Louisiana

The principal emphasis of this field test was to demonstrate that a gravity-stable, CO_2 miscible displacement could be successfully achieved in a deep, hot, dipping reservoir that was not suitable for surfactant flooding.

Reservoirs similar to the Weeks Island "S" Sand Reservoir B are typically produced by natural water drive mechanisms which leave a significant residual oil volume. The major watered-out reservoirs in the Weeks Island Field alone contain as estimated recovery potential of 26 million barrels of oil which could be recovered by a CO_2 displacement.

Reservoirs of this type are not suitable for surfactant flooding since the temperatures and water salinities are too high for the chemicals currently available. The depth and high oil mobility preclude any significant incremental recovery by thermal processes. The major reservoirs in the Weeks Island Field have such high permeabilities that any CO_2 injected down-dip would tend to float to the top of the watered-out reservoirs. The CO_2 would float because viscous forces are very small compared to gravity forces. Downward CO_2 displacement is designed to use gravity forces to stabilize the displacement and increase the sweep efficiency of the injected CO_2.

During Phase I of the test, the CO_2 injection facilities were installed and a new well, the down-dip producer, was drilled to evaluate the tertiary potential of the reservoir. Measurements in the new well indicated that the sand had watered out until only a 23-foot gassy oil column remained. The watered-out portion of the reservoir contained a 22 percent residual oil saturation which provided a target of 288 barrels of oil per acre-foot.

During Phase II, a 50,000-ton slug of CO_2 containing 5 mole percent natural gas was injected just above the gas-oil contact. The slug was moved down-dip by the production of the down-dip water with a producible oil column moving ahead of the CO_2.

Analysis of the CO_2 displacement indicates that a substantial oil column was developed and that the process displaced in excess of 75 percent of the water drive residual oil saturation.

Contract work with Shell Oil Company was completed in February 1984. The final report is being prepared. Shell Oil Company will continue to operate the project until floodout. In October of 1986, two production wells were producing 65 barrels of oil per day. The test has produced 239,000 barrels of oil or about 10 percent more than was originally predicted and an additional 20,000 to 30,000 barrels are expected over the next 2 years. The ratio of CO_2 injected per barrel of oil recovered is presently 9,000 scf/STB.

Displacement observations indicate that a gravity-stable CO_2 displacement occurred in the "S" sand, Reservoir B. Concurrent research findings by Shell indicate that a gravity-stable immiscible CO_2 displacement can recover substantial oil from watered-out reservoirs.

Water-drive residual oil saturations obtained from core analysis and the log-inject-log technique confirmed these findings. A reservoir evaluation well drilled behind the CO_2 front showed a greatly reduced oil saturation (less than 2 percent), further verifying the process capability.

5.0 RESEARCH ISSUES REMAINING

Research issues in need of further investigation include: (1) mobility control, (2) computer simulation, (3) reservoir hetergeneity, and (4) laboratory displacement tests.

In the area of mobility control, surfactants have proven to be most useful, although much information about surfactants is still needed. Polymers that are both soluble in CO_2 and able to increase viscosity of CO_2 enough to effect mobility are still being sought. Mobility control research will be continued at the New Mexico Institute of Mining and Technology, the University of Wyoming, West Virginia University, and METC.

In the area of computer simulation, gas flooding simulation research will be continued to provide acceptable process predictability for adequate evaluation of novel, technical concepts and completed field projects. This work will be continued at METC.

In the area of reservoir heterogeneity, reservoir evaluation techniques will be investigated to predict any relationships that exist between CO_2 flood outcomes and the heterogeneities that exist in the reservoir. This work is being conducted at Stanford University and METC.

Finally, in the area of laboratory displacement tests, METC will investigate the role that rock wettability plays in improving CO_2 flood efficiency and will explore methods to alter rock wettability to improve outcome.

Overall, the results of the research have shown great promise, but there are many unanswered questions regarding the methods of application and even the practicality of some concepts. Effort is needed to determine if alternate methods for improved gas miscible enhanced oil recovery can be developed or if substantial improvement of present technology is possible.

6.0 LIST OF ACRONYMS AND ABBREVIATIONS

API	American Petroleum Institute
BPR	Back Pressure Regulator
CMC	Continuous Multiple Contact
CO2PM	CO_2 Predictive Model
CT	Computerized Tomography
DCF ROR	Discounted Cash Flow Rate of Return
DOE	Department of Energy
EOR	Enhanced Oil Recovery
F-IMP	Fully Implicit
FY	Fiscal Year (Federal: September 1 through October 31)
GOR	Gas to Oil Ratio
HCPV	Hydrocarbon Pore Volume
IMPESC	Implicit Pressure, Explicit Saturation Composition

M	Thousand
MASTER	Miscible Applied Simulation Tool for Energy Recovery
METC	Morgantown Energy Technology Center
MMP	Minimum Miscibility Pressure
NMRI	Nuclear Magnetic Resonance Imaging
OOIP	Original Oil In Place
PV	Pore Volume
PVT	Pressure-Volume-Temperature
R&D	Research and Development
SPE	Society of Petroleum Engineers
T	Transmissibility
TDC	Todd, Dietrich, and Chase
WAG	Water-Alternating-with-Gas
1-D	One-Dimensional

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