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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

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EXECUTIVE SUMMARY

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 breakthrough can occur at just 30 percent pore volume injection of 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. The 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 problems of carbon dioxide in enhanced oil recovery (EOR) applications.

Two mobility control methods have been investigated recently under United States Department of Energy (DOE) contract. These are the use of polymers for direct thickening of high-density carbon dioxide and mobile "foam-like dispersions" of carbon dioxide and aqueous surfactant.

Success in the search for carbon dioxide soluble polymers has been limited. Polymers that dissolve 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 have been 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. Previously unswept regions should be contacted as well as the watered-out regions of the reservoir.

Both direct and indirect research concerning mobility control are discussed in Section 3.0 of this report.

1.0 INTRODUCTION

1.1 PROGRAM PERSPECTIVE

Liquid fuels provided 41.5 percentof the total energy consumed in the United States during the first half of 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.

The amount of liquid fuels (including both crude oil and refined products) imported by the United States averaged 4.72 million barrels per day, or 30.3 percent of the total United States' demand for the first half of 1985. It is predicted that, for the entire year, imports will represent 32.5 percent of the total demand. This figure reveals a slight decline over 1984 imports, which provided 33 percent of the total demand. In 1985, the price of imported oil will be 45 to 50 billion dollars. A cost of this magnitude is of serious concern to the United States in a time of record balance-of-trade deficits.

Although new sources of liquid fuels from such resources as oil shales, tar sands, coal, and biomass are being studied and developed, 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 in order 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 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 dependence of the United States on imported oil.

One category of the three EOR processes (thermal, chemical, and miscible) 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). CO_2 miscible flooding on a large scale is relatively new and is expected to be the most important of the miscible methods in the future. 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.

The reasons for the increasingly widespread use of CO_2 miscible flooding are 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. Still, CO_2 flooding has three major 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 cited that the implemented technology outcome from the $30-per-barrel base case study shows 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 peak rate of production is projected to be 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 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 peak rate of production is projected to be 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 (Mosbacher 1984).

The advanced technology outcome from the $30-per-barrel base case study indicates 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. These are strong indications that research and development (R&D) is needed to further advance gas miscible EOR.

1.2 PROGRAM OBJECTIVES

DOE's EOR program is divided into a light oil (>20° API) enhanced recovery program and a heavy oil (<20° API) enhanced recovery program. The gas miscible EOR processes, including CO_2 flooding, 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 level of 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.

CO_2 flooding performance is sufficiently predictable. In some high oil saturation, west Texas carbonate and sandstone reservoirs, CO_2 EOR recovery efficiency is high enough to justify field-scale projects and very large investments in CO_2 supply. However, problems have been encountered. Tests reveal that basic CO_2-oil displacement mechanisms are not understood well enough to permit adequate performance prediction. The interrelationships between miscibility, stripping, oil swelling, and viscosity effects are not clearly defined and probably reflect variations in reservoir rock and fluid properties that are poorly characterized at present. Fundamental phase behavior in the reservoir is not clearly understood. Furthermore, volumetric sweep efficiency in CO_2 flooding is reduced by fingering through the oil and by the tendency of the CO_2 to override the oil. In addition, understanding of the effects of macro- and microheterogeneities of the reservoir on CO_2 flooding is required.

The research program in CO_2 EOR has been designed and executed to improve the level of knowledge in each of these areas.

1.3 STATE OF TECHNOLOGY

After the secondary recovery of oil by waterflooding, a certain amount of residual oil remains in the pore spaces of the reservoir rock for one 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 has the potential to overcome both of these factors. 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 injection and 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 conditions of temperature and pressure. 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 will readily dissolve 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 will be present with an interface between the two materials. Dissolving the CO_2 in this manner will result in an expansion of the liquid phase and a reduction of the liquid viscosity. Solution of the CO_2 in this manner will take place regardless of the composition or API gravity of the crude oil. It is obvious that the swelling of the oil will increase the oil saturation and, therefore, enhance the relative permeability of the reservoir rock to oil. In addition, the residual oil saturation that remains after recovery operations are complete will be swollen with a relatively large volume of CO_2 (when compared to the small quantity of oil). Both reduction of viscosity and the increase in relative permeability to oil will facilitate flow of the swollen oil to the production well. Thus, immiscible displacement, a result of dissolving CO_2 in crude oil, may frequently be an effective enhanced oil recovery technique.

The processes described above also take place in CO_2 miscible displacement. Miscibility between CO_2 and crude oil, however, requires more restrictive conditions of temperature and pressure than simply the dissolving of CO_2 in the oil. Miscibility entails, by definition, the elimination of the interface between the CO_2 and the oil. At any given temperature there is a minimum miscibility pressure (MPP), usually 1,000 psi or greater, below which the interface will remain. In addition, CO_2 and crude oil, because of differences in their properties and composition, will not become miscible on first contact, regardless of pressure, in most cases. 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 vapor (CO_2) phase so that the vapor phase becomes miscible with the crude oil. At that time the interface between the phases will disappear, capillary forces will become zero, and essentially 100 percent of the oil can be displaced from the CO_2 contacted part of the reservoir.

In order to determine the chances of conducting a successful CO_2 miscible displacement, information must be obtained from several sources. Slim tube tests, in which ≤ 0.25 inch internal diameter tubing, possibly 80 feet long, packed with glass beads or unconsolidated sand, and saturated with reservoir oil is flooded with CO_2 at reservoir temperature and various pressures, are used to determine the MMP. In these tests multiple contact miscibility can be attained at pressures equal to or greater than MMP.

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 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 preserved and determined 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 permeability profile having widely varying permeabilities in a reservoir formation with natural or poorly oriented fracture systems 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 gas 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 gas viscosity and the normally high relative permeability to gases at low saturations result in a very high mobility for the CO_2. Because of the channeling and fingering and the absence of oil banking that a high mobility permits, a generally low volumetric sweep efficiency and rapidly increasing producing CO_2-oil ratios result.

Mobility control is, therefore, an important problem in CO_2 miscible flooding. Several methods have been used in attempts 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(s) or by perforating the casing selectively. However, once the CO_2 leaves the immediate vicinity of the wellbore, this method cannot control its movement. 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 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, relative permeability to water and CO_2 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 point, the foam or emulsion injection technique appears to have the most promise. A great deal of study remains to be done, however, in the 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 to the injected phase 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 to the injected fluids.

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 produced water 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} 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 sales channels 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 pipeline 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, exists at essentially atmospheric pressure, or both. These sources also are usually located at a considerable distance from the point of application.

The total cost of CO_2 is comprised 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) (1983 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 is insufficient to develop models that can adequately predict project performance. Work in these areas should provide at least partial solutions to these problems.

2.0 CURRENT RESEARCH IN CARBON DIOXIDE ENHANCED OIL RECOVERY

The Department of Energy CO_2 EOR program at the Morgantown Energy Technology Center (METC) includes research and development projects with the petroleum industry and universities. This comprehensive approach covers the broad technology needs of the CO_2 EOR program.

Each fiscal year (FY) 85 project is summarized below. Section 8.0 provides a list of FY 85 Government-published reports. Section 6.0 and 7.0 provide the reference materials for this report. A list of acronyms and symbols appears in Section 5.0.

2.1 MOBILITY CONTROL

2.1.1 Improvement of CO_2 Flood Performance, New Mexico Institute of Mining and Technology[1]

Principal Investigators: J.P. Heller and J.J. Taber

Objectives: This project has the following objectives:

1. Perform CO_2-foam mobility measurements for several surfactants and oil field rock types over broad ranges of flow rates, surfactant concentrations and flowing volume ratios. Related measurements will include adsorption and thermal stability tests to evaluate prospective surfactants for such CO_2 foams.
2. Synthesize and test promising types of dense CO_2-soluble polymers in search of suitable direct thickeners.
3. Perform a sequence of unprotected and mobility controlled CO_2 floods to test by direct comparison the utility of available mobility control methods.
4. Search for other credible but less time-consuming methods to assess the usefulness of particular mobility control methods.
5. Investigate reservoir engineering aspects of the application of mobility control methods, including studies of optimum level of thickening, slug design criteria, and economic process constraints.
6. Assist in the definition and solution of various operation engineering problems that will accompany the field use of mobility control additives in CO_2 floods.

Summary: The displacement behavior of CO_2 foams (dispersions of dense CO_2 in water) and the synthesis of polymeric materials soluble directly in CO_2 are being explored as a means of thickening CO_2 to improve reservoir sweep efficiency. Improved experimental techniques for rapid evaluation of mobility control additives are being developed. Mobility data needed to design field applications are being measured, and criteria for slug design and successful field operation are being considered.

Conclusions: Direct Thickness for CO_2 — Polymers (poly-α-olefins) were synthesized to study the effect of catalyst combination, reaction temperature, and time during polymerization. Based on these synthesis reactions, further polymerization work was performed at ambient temperature using the following materials: (1) $TiCl_4$ and $AlEt_3$ (catalysts); (2) heptane (solvent); and (3) 1-hexane, 1-pentane, 1-decane, 1,4-hexadiene, and 5-ethylidene-2-norbornene (monomers).

For 1-hexane, reduced viscosity (a measure of the specific capacity of the polymers' increase in relative viscosity) generally remained in the range of 2.0 to 3.5 throughout the course of polymerization. The polymer yield was shown to increase with time.

The molecular weight distributions of several synthesized poly-1-hexenes were studied by gel permeation chromatography. All poly-1-hexenes generally showed broad molecular weight distributions. Polymers synthesized with 4 to 5 percent catalyst showed many high molecular weight fractions, while polymers synthesized with 1 percent catalyst showed many low molecular weight fractions.

The solubility of poly-1-hexenes in dense CO_2 ranged between 0 and 10 grams per liter but was shown to increase with decreasing intrinsic viscosity. The intrinsic viscosity ranged between 0 and 4 deciliters per gram for the above-mentioned solubility range.

The effect of increasing alkyl chain length on the solubility of trialkyltin fluorides in lower hydrocarbon solvents and in CO_2 is being studied. Accordingly, triamyltin fluoride and diamylbutyltin fluoride were tested. The enhancement in solubility of these two tin compounds with increased alkyl

[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.

chain length was clearly proven. The solvents hexane and pentane became significantly more viscous after a critical concentration of a tin compound was added.

At a concentration of approximately 0.25 percent in n-butane, triamyltin fluoride increased the solvent viscosity three-fold, while tributyltin fluoride resulted in a five-fold increase. The former, however, was much more soluble in n-butane than the latter and consequently raised the viscosity of n-butane nine-fold at a concentration of 0.43 percent.

Surfactants — Thermal degradation of surfactants can be evidenced by changes in various surfactant solution properties such as pH, foamability, concentration of surface actives, and solution clarity.

A 28-day 200°F aging test was conducted and showed that pH levels changed for some surfactants. Those surfactants that were affected most severely include such molecular types as cocoamid betaines, ethoxy diphenyl desulfonates, a cocosuperamide, alcohol ethoxy sulfates, alcohol ethoxylates, cocobetaines, and cocosulfobetaines. Almost all surfactants exhibited some thermal degradation at 200°F. However, results indicate that most surfactants tested were not adversely affected at 150°F with respect to pH.

Many surfactants that foamed prior to the 28-day thermal exposure test suffered a reduction in foamability after the test. Several surfactants were able to withstand at least 24 hours of exposure, but at further thermal aging, lost their ability to foam.

A reduction in solubility, or solution cloudiness, occurred in several samples during the thermal exposure.

2.1.2 Enhanced Oil Recovery by CO_2 Foam Flooding, New Mexico State University

Principal Investigator: J. Patton

Objectives: This project has the following objectives:

1. Evaluate dynamic foam stability in CO_2 mobility reduction tests during three-phase flow including crude oil and brine.
2. Determine foam rheology as a function of foam quality, temperature, and system composition.
3. Conduct CO_2 displacement tests using various mobility control fluids at reservoir temperature in cores taken from candidate reservoirs for CO_2 flooding.
4. Conduct computer simulation of linear displacement tests to assist in mathematical modeling of mobility controlled CO_2 flooding.

Summary: Objectives 3 and 4 were the focus of FY 85 research. The final CO_2 displacement tests to quantify the mobility control effect of various additives were conducted. A linear high-pressure, sandpacked model containing both oil and water was used for testing.

Mathematical techniques to interpret data were only available for examining two-phase flow. Accordingly, the experiments were designed so that the oil phase would be immobile, and mobility control would be measured under conditions expected behind the flood front in commercial carbon dioxide flooding operations.

Numerous tests were conducted using straight brine and brine containing two of the most potent mobility control additives found by New Mexico State University, Pluradyne SF-27 and Stepanflo 50. In other tests, these two additives produced similar results in lowering the mobility of nitrogen-water flow at pressures between 15 to 50 pounds force per square inch absolute (psia) and also in mobility controlled carbon dioxide displacement of light and heavy crude oils under reservoir conditions. The only significant difference observed between the additives is that Pluradyne SF-27 apparently mobilizes the residual oil (possibly by solubilization) during the carbon dioxide flood.

Fluid samples obtained in the experiments using Pluradyne SF-27 all had an opaque brownish color, indicating dissolution of small quantities of crude oil. In contrast, fluid samples taken with straight brine or with Stepanflo 50 as the mobility control additive were clear, oil-free samples.

In addition to these tests, the computer simulation model was refined to describe the mobility lowering of a gas by surfactants. Mobility lowering was modeled as a pseudoincrease in viscosity rather than a shift in the relative permeability curve for the flow of a viscous foam phase.

Conclusions: Displacement tests in linear sandpacked models using Pluradyne SF-27 and Stepanflo 50, the two best mobility control surfactants found by New Mexico State University, produced comparable results. Mobility lowering of a gas by surfactants was simulated as an increase in viscosity rather than a shift in the relative permeability curve.

2.1.3 Mobility Control for CO_2 Injection, New Mexico Institute of Mining and Technology

Principal Investigator: J.P. Heller

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

Summary: Major aspects of a mobility controlled CO_2 injection program in the Rock Creek Oil Field of Roane County, West Virginia, are reported. A foam-like dispersion of CO_2 in surfactant water is being tested as a high viscosity form of CO_2 to minimize viscous fingering, increase volumetric sweep efficiency, delay CO_2 breakthrough, and maximize CO_2 utilization. Mobility control by this method has the potential to significantly improve oil recovery in both secondary and tertiary CO_2 floods compared to that attained with pure CO_2 or the WAG procedure. By maximizing CO_2 utilization, the economics of the recovery method should be improved.

Although the area of the test and the anticipated oil recovery are small, the implications are great. The test may lead to widespread consideration of mobility control in CO_2 floods as a means of increasing oil recovery and CO_2 EOR profitability.

Conclusions: The design of the field project has been completed; the actual field project is still in progress. The design research has impacted the field project with the following conclusions:

1. The surfactant Alipal CD-128 was found to remain active in laboratory-simulated reservoir conditions over an extended period of time (30 days).
2. The design submitted for the Rock Creek mobility control test included the continuous injection of CO_2 foam followed by an ordinary waterflood. The design called for the foam slug to be preceded by a pad of Alipal CD-128 surfactant solution to supply the surfactant required for adsorption onto the rock.

   The foam slug design consisted of simultaneous injection of CO_2 and 0.05 percent aqueous surfactant solution, giving a foam of 80 percent flowing quality.

2.1.4 New Concepts for Improved Oil Recovery in CO_2 Flooding, University of Wyoming

Principal Investigators: D.L. Whitman, R.E. Terry, and R.E. Ewing

Objectives: This project has the following objectives:

1. Provide new knowledge in methods of stabilizing the advancing flood front of CO_2 during petroleum reservoir flooding with CO_2.
2. Develop new concepts for improving the recovery efficiency of CO_2 so that previously unswept oil-bearing regions of a reservoir can be swept.
3. Improve the current level of technology for recovery efficiency of CO_2 in enhanced oil recovery so that better economics can be expected in future commercial CO_2 floods.

Summary: This project is basically two-directional with one area being the study of CO_2 injection into the reservoir in a line drive configuration. The second area is the study of CO_2 viscosity increase through the polymerization of hydrocarbon monomers after the monomers have been dissolved into the dense CO_2 phase.

The first study effort includes the construction of a two-dimensional physical model consisting of a sand pack saturated with oil and capable of handling CO_2 miscibility pressures. Line drive displacement processes are being tested in this model. Concurrent with the development and operation of the experimental apparatus, a mathematical model is being developed to represent line drive injection of CO_2 into a reservoir.

The second effort is an investigation of the possibility of generating soluble, viscosity-increasing polymers in liquid CO_2 by first dissolving the corresponding monomer (olefin) or monomer system and chemical initiator in liquid CO_2 and reacting the monomers (in a controlled, repeatable manner) into polymers. After a polymer/CO_2 solution has been made, a high-pressure displacement pump will be used to (1) measure the mobility alteration of the CO_2 in a glass core flood by pumping the solution through it and measuring the resultant pressure drop, (2) displace some of the solution into a high pressure sample bomb for analysis, and (3) displace the solution into a high-pressure Ruska rolling ball viscometer for viscosity measurement.

Several monomers as well as initiation and cross-linking agents will be selected for use in the experiments. After an optimum polymer/CO_2 system has been selected, the final part of the study will be conducted as classical core floods on cores containing residual oil saturations. Some preliminary economic questions such as cost per barrel, incremental oil recovery due to increased sweep efficiency, and cost per unit viscosity change will be addressed.

Conclusions: Six experiments were conducted with the two-dimensional physical model using a point source injection well and a point sink production well. Results show that at two pore volumes (pv) of CO_2 injection, the recovery appears to level off at about 37 percent of the original oil in place. This indicates that the injected CO_2 is bypassing some of the oil. Other evidence of the bypassing phenomenon is the fact that CO_2 is being produced almost immediately after injection begins and that, at about 0.5 percent pv CO_2 injection, CO_2 breakthrough occurs.

2.1.5 Linear Core Experiments, Morgantown Energy Technology Center

Principal Investigators: A.M. Zammerilli and K. Das

Objectives: The objective of this research is to increase the recovery efficiency of CO_2 miscible flooding by the use of mobility control foams. Laboratory flow test systems will be used to test the injectivity and flow properties of CO_2 combined with mobility control foams.

Summary: A large-scale linear core flow system (core size of 5 feet length by 4 inches diameter) was installed and successfully pressure tested. This system will be used to simulate the flow conditions that exist further out in a reservoir flow pattern. Unprotected (CO_2 alone) and protected (CO_2 + foam) floods will be performed using a synthetic crude to assure miscibility at test conditions of 1,200 pounds force per square inch (psi) and 75°F and of 1,500 psi and 100°F. The test plan includes the use of a 70 percent quality foam. The foam will be obtained by combining 0.05 percent concentration of surfactant (foaming agent) with CO_2. Foams will be generated in situ and externally.

Measurements will be taken to acquire the following data:

1. Pressure versus time (pressure will be electronically monitored).
2. Volume, rate, and quality of effluent versus time.

The measured data will be used to calculate the following variables:

1. Mobilities.
2. Permeabilities.
3. Saturations.
4. Volumes.
5. Rates.
6. Injected/produced fluid qualities (compositional analysis).
7. Gas-oil ratios, water-oil ratios, and gas-water ratios.
8. Recovery efficiencies.
9. Incremental recoveries.
10. Breakthrough times.

The data that is collected and the subsequent calculations that are made will be used for numerical model input, verification, and modification.

The successful completion of this research will determine the feasibility of using viscosity modifiers (mobility control agents) to improve CO_2 flood performance. The data collected can be used to develop field tests for CO_2 EOR operations.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.1.6 Radial Core Experiments, Morgantown Energy Technology Center

Principal Investigators: A.M. Zammerilli and K. Das

Objectives: The objective of this research is to improve the recovery efficiency of carbon dioxide miscible flooding. A large-scale laboratory flow test system will be used to test the injectivity and flow properties of CO_2 combined with mobility control foams.

Summary: A large-scale, radial core flow system (maximum core size of 2 feet diameter by 2 inches height), was installed and successfully pressure tested. This system will be used to simulate the flow conditions that exist during the injection of CO_2 foam during actual field tests (i.e., conditions at the wellbore). Foaming agents, concentrations of surfactant, amounts of CO_2, temperatures, and injection rates will be varied and tested using this system. Successful injection conditions will then be determined and applied to actual field tests.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.1.7 In Situ Deposition of Chemical Precipitates, West Virginia University

Principal Investigators: S. Ameri and K. Aminian

Objectives: This project has the following objectives:

1. Determine conditions and materials for optimum in situ chemical precipitation of a realistic range of reservoir temperatures and pressures.
2. Conduct flow tests and in situ precipitation tests in mounted cores.
3. Develop computer models to predict: the amount of precipitate formed under any condition of temperature, pressure, and concentration; the degree of alteration of permeability and permability profile in the reservoir; and the improvement of volumetric sweep efficiency in the reservoir and increase in oil recovery by using in situ chemical precipitation.

4. Determine potential reservoirs that are applicable to in situ chemical precipitation.

Summary: One way to overcome the high mobility of CO_2 is to fully or partially close the large pores within the reservoir rock by placing solid material in them. Since solids suspended in an injected fluid do not penetrate the rock more than a few feet from the wellbore, it would be beneficial to form the solid in the individual pore spaces throughout the formation by chemical precipitation.

Several relatively inexpensive chemicals that are soluble in water will react with CO_2 to form a solid carbonate. One example is CaO. When an aqueous solution of CaO is contacted by CO_2, solid $CaCO_3$ is formed. Other chemicals such as $CaCl_2$, $MgCl_2$, or $BaCl_2$ will react with CO_2 to form a solid.

One procedure used in CO_2 flooding, WAG, is conducted by injecting a slug of water and following it with a slug of CO_2. If the water phase is a solution of a chemical such as those suggested above, chemical precipitation will take place in each pore where the CO_2 slug contacts the chemical. The largest pores will hold the largest volume of solution and, therefore, the greatest amount of chemical. The CO_2 gas will flow most readily into the largest pores. As a result, most of the precipitate will form in the largest, most permeable pores, thereby partially plugging those pores and reducing their permeability. Each WAG cycle will repeat the process with additional precipitate forming and permeability adjustment. If, at any time, it appears that additional precipitate formation would not be desirable, the chemical additive in the injected water can be discontinued. Continued injection of pure water or oil field brine will terminate the precipitating reaction.

Once the precipitate is formed in the larger pores and the permeability has been reduced there, subsequent fluid flow will be forced to take place through alternate pore paths. Additional WAG cycles will cause precipitation in progressively smaller pore spaces, diverting the injected fluids into still smaller pores and increasing the volumetric sweep efficiency of the displacement mechanism.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.1.8 Development of a Method for Evaluating Carbon Dioxide Miscible Flooding Prospects, University of Kansas

Principal Investigators: D.W. Green and G.W. Swift

Objectives: This project had the following objectives:

1. Conduct phase behavior studies of carbon dioxide using synthetic and actual reservoir oils.
2. Use the equation-of-state to predict phase behavior of CO_2, crude oil, and water mixtures.
3. Conduct linear displacements/extractions of both synthetic and actual reservoir oils.
4. Develop a linear compositional simulator.
5. Improve miscible pressure correlations and develop a reservoir screening procedure for identifying target reservoirs.

Conclusions: Work in FY 85 consisted of writing the final report. In the final report, Green and Swift cited the following conclusions:

Bubble-point phase behavior data were taken for binary and ternary systems containing carbon dioxide. These data were judged to be reliable based on agreement with similar data reported in the literature. The phase behavior was adequately simulated with the Suave-Redlick-Kwong (SRK) equation-of-state when suitable interaction coefficients were used. Addition of water to the CO_2-hydrocarbon system reduced the bubble point due to absorption of CO_2 into the water phase. However, when absorption of CO_2 was accounted for, phase behavior on a water-free basis was essentially unchanged from the case when no water was in the system.

Several displacements were conducted in a slim-tube apparatus. For ternary systems (CO_2 plus two hydrocarbon components), measured MMP values were in good agreement with values predicted based on known phase behavior. The presence of immobile water in these displacements had negligible effect on MMP. Miscibility pressures were measured for a number of Kansas crude oils. MMP was a function of API gravity, decreasing as API gravity increased. MMP also increased with temperature and decreased when lower molecular weight hydrocarbons were added to the crude (C_4-C_6).

The SRK equation-of-state was used to generate pseudoternary diagrams for two oils described in the literature and three Kansas crudes. For the literature oils, calculations were based on reported compositions. The Kansas oil compositions were estimated from ASTM D-86 and true boiling-point distillation curves. Literature sources were used in conjunction with the estimated compositions to calculate required physical properties.

The pseduoternary diagrams were applied to estimate MMP values obtained for slim-tube displacements. It was determined that the best results were obtained when a linear range of interaction coefficients were used in the SRK equation-of-state. The smallest coefficient in magnitude was assigned to C_5 and the largest to C_{25}^+. When a suitable set of interaction coefficients was used in the equation-of-state, the MMP was correctly predicted for a given crude. The dependence of MMP on temperature was also described satisfactorily. It was not, however, possible to model adequately all of the oils studied with a single set of interaction coefficients. The value of the lowest coefficient (assigned to C_5) had to be adjusted to produce a satisfactory prediction of MMP.

The method was relatively insensitive to the specifications of the pseudocomponents in the pseudoternary representation. Also, the method was not very sensitive to the interaction coefficient value assigned to the heavy component (C_{25}^+).

Finally, the slim-tube displacement results were simulated mathematically using a modification of a model reported in the literature. The model was based on the use of pseudoternary diagrams to describe phase behavior. The model, in general, did a good job of describing displacement performance in a slim-tube apparatus. However, history matching was required. Use of the model allows prediction of MMP and displacement performance in an ideal porous media system (Green and Swift 1985, 121, 122).

2.2 COMPUTER SIMULATION

2.2.1 Compositional Model Study, EG&G Washington Analytical Services Center, Morgantown Operations

Principal Investigator: K.H. Kumar

Objectives: The overall objective of this work is to develop expertise in compositional modeling and to provide simulation support for experimental studies in the laboratory at METC. These studies will aid researchers in understanding the miscible displacement mechanisms of enhanced oil recovery processes using carbon dioxide and mobility control techniques. The objective for FY 85 was to develop the basic computer code for a one-dimensional fully compositional reservoir simulator.

Summary: The basic computer code for a general purpose one-dimensional multipoint compositional reservoir simulator was developed. An implicit pressure, explicit saturation (IMPES) and composition solution method was used. The relative amounts of each component in the oil and gas phases were calculated by assuming phase equilibrium, and the computations are carried out using a flash algorithim and an equation-of-state. Initial testing of the computer code was carried out using 3- and 5-grid block reservoir problems. Later the model was used to sumulate a one-dimensional multipoint miscibility problem from the literature.

Conclusions: A basic one-dimensional computational model using an equation of state was developed. Although several additional features must be added to the model before it is user-ready, the current version successfully simulates a multipoint miscibility problem.

2.2.2 Development of a Modified Black Oil Reservoir Simulator, Lewin and Associates, Inc., and Mathematical and Computer Services, Inc.

Principal Investigators: V.A. Kuuskraa and W.K. Sawyer

Objectives: The objective of this work is to develop a modified black oil simulator for application to miscible flooding processes, with emphasis on the miscible carbon dioxide flooding process. The modified black oil simulator "MASTER" (Miscible Applied Simulation Tool for Energy Recovery) is being developed by modifying "BOAST" (Black Oil Applied Simulation Tool), an existing black oil model. MASTER will be a three-dimensional, three-phase "black oil" finite difference IMPES simulator that incorporates both direct elimination and iterative solution options. The model will permit simulation of immiscible and miscible displacements.

Summary: Enhanced oil recovery by carbon dioxide flooding operates by a variety of mechanisms. It is desirable to computer simulate the most significant of these recovery mechanisms that naturally dictate the process behavior. This can be achieved through modifications of conventional "black oil" recovery models.

The basic modifications to BOAST included the addition of these options:

1. An option to inject and track, by mass balance, up to four different solvent slugs in any time sequence desired.
2. An option to represent multiple contact miscibility features of the carbon dioxide flooding process.
3. An option to represent precipitation of solids or heavy components from the flowing phase.
4. An option to represent water blocking oil from contact with carbon dioxide.
5. An option to represent mobility control of carbon dioxide via injection of a surfactant slug into the aqueous phase of the carbon dioxide slug.
6. An option to permit reductions of computer storage and computation time through use of pseudorelative permeability and pseudocapillary pressure functions.

   The resulting modified black oil model, MASTER, will serve METC as both a research tool and a vehicle to evaluate Government-funded carbon dioxide field projects.

Conclusions: The first five options were completed in FY 85. The first option to the code allows four solvents to be injected and tracked in the reservoir. Thus, there are seven conservation equations: oil, water, hydrocarbon gas, and four solvents. Any injection schedule of an infinite number of slugs can be used as long as each slug is comprised of any one of the four chosen solvents. The slugs can be injected at varying rates or pressures.

In the second option, hydrocarbon gas and injected solvents are assumed to be fully miscible at all reservoir pressures. Accordingly, the hydrocarbon gas-solvent phase capillary pressure is zero, and mixing rules are used to obtain effective densities, viscosities, and relative permeabilities of the hydrocarbon gas-solvent miscible phase.

Above a specified miscibility pressure (P_{MISC}), hydrocarbon gas, oil, and injected solvents are assumed to be fully miscible. In this case, the hydrocarbon gas-oil-solvent phase capillary pressure is zero and the mixing rules again are used to calculate effective densities, viscosities, and relative permeabilities of the hydrocarbon gas-oil-solvent miscible phase.

Multicontact miscibility pressure (P_{MCM}) is defined to be a specified fraction (f_{PM}) of the miscibility pressure, i.e.,

$$P_{MCM} = f_{PM} \cdot P_{MISC}$$

The multicontact miscibility region is defined to be the following pressure range:

$$P_{MCM} \leq P < P_{MISC}$$

In the multicontact miscibility pressure range, immiscible and miscible properties are weighted by the parameter α, defined by

$$\alpha = \frac{P - P_{MCM}}{P_{MISC} - P_{MCM}}, \quad 0 \leq \alpha < 1$$

to give effective capillary pressures, densities, viscosities, and relative permeabilities.

The third option, which represents precipitation of solids from the flowing oil phase, reduces the pore volume by the volume of oil precipitated. All other saturations (water, gas, and slug saturations) are adjusted accordingly. Permeabilities are reduced and new transmiscibilities are calculated.

If the grid block is at residual water saturation, the water saturation is not altered. This results in small water material balance errors that are acceptable in order to prevent mobile water from being created.

In the fourth option, water blocked oil saturation (S_{twb}) is determined from the following equation:

$$S_{twb} = \frac{S_{orw}}{1 + BETA\ (krn/krw)}$$

where krn and krw are the nonaqueous phase and aqueous phase relative permeabilities, respectively. If BETA equals zero, no oil is contacted by the solvent slug. If BETA is very large, essentially all of the oil is immediately contacted by the solvent slug.

In the fifth option, the mobility control agent is assumed to be a percent concentration of surfactant in injected water. The water that contains the surfactant is completely miscible with reservoir water. Using the pore volume concentration of the water that contains the surfactant, the fractional mobility reduction is calculated.

The sixth option, as well as the final report, will be completed in FY 86.

2.2.3 Pattern Alignment and Blocking Studies, Morgantown Energy Technology Center

Principal Investigator: J.R. Ammer

Objectives: The objective of this study is to examine sweep efficiencies for a variety of process conditions. A numerical simulator will be used to study how injection of blocking fluids might divert flow into unswept zones for different pattern alignments.

Summary: MASTER, the numerical simulator discussed in Section 2.2.2, will be used in this study.

Many researchers have studied sweep efficiency for a variety of reservoir settings. Few researchers, however, have examined the sweep efficiency of various reservoir patterns if blocking agents are injected into the high permeability of previously swept zones of the reservoir. Blocking agents injected into these swept zones will serve to alter streamlines and increase sweep efficiency.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.2.4 The Gulf Little Knife Field and the Pennzoil Rock Creek Field Simulation Studies, Morgantown Energy Technology Center

Principal Investigator: J.R. Ammer

Objectives: The main objective of these studies is to match the production history of the Gulf Little Knife Field in North Dakota and the Pennzoil Rock Creek Field in West Virginia. MASTER, a black oil model (discussed in Section 2.2.2), was chosen to simulate the tertiary CO_2 injection phase of each project.

Summary: The efforts to match histories of the primary production phase and the secondary waterflood phase of the Gulf Little Knife Field and the Pennzoil Rock Creek Field were conducted in previous fiscal years using BOAST. These efforts yielded a fair match between actual field data and simulator output data. MASTER will now be used to simulate work on the CO_2 miscible recovery phase in both of these fields.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.3 RESERVOIR HETEROGENEITY

2.3.1 Reservoir Characterization for Numerical Simulation of the CO_2 EOR Process, Stanford University

Principal Investigator: F.M. Orr, Jr.

Objectives: The main objective 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. To accomplish this objective, the research effort will be organized into four tasks:

1. Construct descriptions of several model reservoirs that have reasonably typical types of heterogeneities. The descriptions will be based on knowledge of depositional environments and diagenetic history.
2. Determine which scales of heterogeneity can be detected by the following descriptive methods: core analysis, log analysis, outcrop studies, pressure transient testing, tracer tests, and seismic tomography.
3. Assess the impact of representative scales of heterogeneity on process performance.
4. Develop and test methods for representing heterogeneities.

Summary: In the first task, reservoir models will be constructed for use in the remaining tasks. The models, based on behavior observed in actual reservoir systems, will contain a 160-acre pattern element. Each model will have a unique scale and distribution of heterogeneities. In combination, these models will offer a sufficient range of behavior for investigation. A reasonable sequence of models would include pattern elements with uniform porosity and permeability, layering but no areal variation, areal variation but no layering, and layering and areal variation.

Within each of the heterogeneous cases, more than one distribution of heterogeneity will be investigated. The models will be developed based on reasonable geological descriptions.

In the second task, each technique's ability to detect various scales of reservoir heterogeneities will be assessed. The reservoir models developed in Task 1 will be used in these assessments. Guidelines shall be established for the design of further experimental and numerical studies of CO_2 floods in reservoirs with large spacing to be undertaken in Tasks 3 and 4. The advantages and limitations of techniques available for detecting heterogeneities in the interwell region will be determined.

In the third task, two sets of experiments will be designed to provide the information needed to assess the impact of scale in CO_2 floods. In the first set of experiments, interactions of viscous instability with heterogeneity will be examined in flow visualization experiments conducted in pore networks etched in glass. The micromodels will be constructed with known heterogeneities similar to those of the reservoir descriptions of Task 1, although the micromodel displacements will be limited to two-dimensional variations. The initial set of experiments will be conducted with miscible hydrocarbon liquids that have known or easily measured variations in fluid properties with composition. The composition of fluids as a function of position in the model will be measured. The composition of fluids leaving the model will also be measured.

The second set of experiments involves construction of physical models of some of the heterogeneous flow systems of Task 1. Glass beads of varying sizes, with varying degrees of sintering to control local permeability, will be used to construct scaled models similar to those described in Task 1. As in the first set of experiments, displacements with miscible liquids of varying viscosities will be conducted. A method for taking very small fluid samples from the interior of the packs so that local composition variations can be examined will be developed. Such measurements will be used to assess the interchange of fluids from various parts of the model. The measurements will be very useful in estimating the effect of mixing on local displacement efficiency in a CO_2 flood. The experimental results will also be used for testing reservoir simulations of the effects of heterogeneity with and without viscous instability.

In the fourth task, preferential flow paths will be modeled using the Coats-Smith model or a similar model. Whether such an approach can be used if heterogeneity is not randomly distributed or if viscous instability is a factor are matters for investigation. Finally, the use of the theory of fractals to represent the spacing of viscous fingers will be investigated to obtain information about how greatly finger spacing varies with the scale of the flow system.

Conclusions: No conclusions have been reached since work will begin in FY 86.

2.3.2 Nuclear Magnetic Resonance (NMR) Imaging, Morgantown Energy Technology Center

Principal Investigators: A.M. Zammerilli and K. Das

Objectives: The objective of this research is to develop a nondestructive method of determining oil and water saturations inside sandstone cores during enhanced oil recovery flow tests.

Summary: NMR imaging is currently being extensively used in the medical field. Hydrogen proton resonance is being used because of its high NMR sensitivity and the natural abundance of hydrogen nuclei. In order to distinguish between oil and water using only protons, relaxation time differences or chemical shift differences can be used. This research is in its initial stages with some preliminary results on oil-water saturated sandstone cores. Magnetic materials in the cores (such as iron) distort the NMR signal. Porous material such as porous ceramic cores are being examined to determine if oil-water saturations are distinguishable.

Conclusions: NMR imaging has promise as an important method for nondestructive determination of oil and water saturations in sandstone cores. It may be possible to map fluid saturations along the length of a core while undergoing an EOR flow test.

2.4 PHASE BEHAVIOR AND MISCIBILITY

2.4.1 Investigation of Enhanced Oil Recovery Through Use of Carbon Dioxide, Louisiana State University[2]

Principal Investigator: T. G. Monger

Objectives: This project had the following objectives:

1. Study the miscibility mechanisms associated with CO_2 displacement of crude oil.
2. Study the effects of additives to CO_2, such as hydrocarbon and nitrogen.
3. Study the compositional changes of CO_2 crude oil mixtures.
4. Conduct phase behavior studies.

Conclusions: Work in FY 85 consisted of writing the final report. In the final report, Monger cited the following conclusions:

1. Several features of the phase behavior exhibited by mixtures of CO_2 with complex reservoir fluids can be modeled using synthetic oils created from a small number of hydrocarbon components. This facilitates studies of oil compositional effects in CO_2 flooding because experimental data can be more easily verified by material balance.
2. No solid phase was observed for CO_2 synthetic oil mixtures, and the liquid-liquid phase regions that were observed were notably smaller. Both of these distinctions are likely due to the absence of C_{30} components.
3. The ability of supercritical CO_2 to extract hydrocarbons is influenced by the presence of aromatic components. Phase equilibria results suggest that both heavy paraffinic and heavy aromatic hydrocarbons must be present to demonstrate this compositional effect. This improves our understanding of the CO_2 multiple-contact miscible displacement process because natural reservoir fluids contain heavy hydrocarbons of both chemical types.
4. Paraffins, especially heavy paraffins, are more readily extracted into the CO_2-rich liquid phase in the presence of heavy aromatics. As a consequence of the improved extraction, aromatics impair the CO_2's ability to selectively solubilize lighter hydrocarbon components. Both effects are beneficial in enhanced oil recovery operations using CO_2 because an efficient CO_2 flood depends upon extensive hydrocarbon extraction into a CO_2-rich phase with no selectivity requirements.
5. The phase behavior results provide an explanation for laboratory displacement experiments that showed that, when a highly paraffinic crude oil was enriched with heavy aromatics, the CO_2 miscibility pressure was lowered and oil recovery was improved.
6. No liquid-liquid vapor three-phase region was observed for CO_2-BF (Brookhaven-flashed) oil mixtures at temperatures greater than 111°F. Carbon dioxide-BF oil mixtures in the high CO_2 concentration range were capable of creating a liquid-liquid vapor three-phase region at room temperature.
7. No liquid-fluid (liquid-liquid) critical points were exhibited by CO_2-BF oil mixtures at 111°F or 141.4°F over the pressure range tested.
8. Carbon dioxide is multiple-contact miscible with BF oil at approximately 1,809 psia and 111.9°F by the vaporizing gas drive mechanism.
9. Extensive precipitation of a tar-like solid phase is associated with the development of CO_2-BF oil miscibility.
10. The BF oil precipitate appears to be highly aromatic and constitutes approximately 20 weight percent of the stock tank oil hydrocarbon.
11. The phase equilibria results presented provide multiple contact phase compositions which are necessary to calibrate equations-of-state for reservoir simulation.
12. The results presented provide multiple-contact phase behavior data for a highly asphaltic (aromatic) crude, which is lacking in the literature. The results thus provide a general model for predicting the phase behavior of other highly asphaltic crudes.
13. Very little oil recovery will be realized after the first swept zone contact (second CO_2 contact) in a hydrocarbon vaporization huff-n-puff process

[2] Elements of this project fall into the Laboratory Displacement Tests area. Information concerning the project can be found in that section of this report.

on the BF oil. The cumulative liquid volume recovered by two CO_2 contacts is approximately 35 percent of the original oil in place.

14. Aromatic hydrocarbons appear to concentrate in the oil-rich phase of CO_2-BF oil mixtures. In the swept zone contacts, these components constitute a large fraction of the unrecoverable oil. In the forward contacts, these components are precipitated out as a solid phase. In both cases, potential problems associated with the refining or disposal of these toxic compounds are alleviated (Monger 1985, 1:22, 126, 128).

2.4.2 Improvement of CO_2 Flood Performance, New Mexico Institute of Mining and Technology[3]

Principal Investigators: J.P. Heller and J.J. Taber

Objectives: This project has the following objectives:

1. Design a high-pressure viscometer based on an oscillating quartz crystal and associated instrumentation.
2. Determine the viscosity, composition, and density of mixtures of CO_2 with well-characterized hydrocarbon systems.
3. Determine the viscosity of mixtures of CO_2 with crude oil.
4. Determine the most accurate correlations for calculation of viscosity of CO_2-crude oil mixtures.
5. Analyze composition paths in displacements of CO_2-C_1-C_4-C_{10} mixtures.
6. Determine a correlation for MMP, based on measurement of component positioning in CO_2-crude oil systems, that accounts for the composition of the oil and the injected fluid.

Summary: An oscillating quartz crystal has been installed in a continuous flow apparatus developed previously to study composition and densities of phases in equilibrium. Simultaneous measurements of phase compositions, densities, and viscosities have allowed testing of the accuracy of viscosity correlations for CO_2-crude oil mixtures and quantitative assessments of the driving force for viscous instability. Additionally, component partitioning data has been used to develop an improved correlation for MMP that accounts for differences in oil and injected fluid compositions.

Conclusions: Two oscillating quartz crystal viscometers have been developed, one of which has been added to the continuous multiple contact (CMC) experiment equipment. The new viscometers have been developed because conventional viscosity measurement techniques, such as the rolling ball viscometer, are overly time consuming, require very large samples, and must be coupled with some type of high-pressure sampling device if phase compositions are also measured. The high-pressure, oscillating quartz crystal viscometer has been coupled with the core equipment, leak tested, and checked electrically. The time required to take a viscosity measurement has been reduced from 2 minutes to 30 seconds. The accuracy is comparable to the original measurements, while the reliability has been increased.

A very simple correlation for MMP that accounts for variations in oil composition has been completed. The correlation is based on a weighted composition parameter of the form

$$F = \sum_{2}^{37} k_i w_i$$

where w_i is the weight fraction of molecules with i carbon atoms in the C_2+ fraction, and k_i is a modified partition coefficient. Estimates of k_i's were obtained from a CMC experiment with CO_2 and Maljamar crude oil at 90°F and 1,200 psia. Data (Holm and Josendal 1982) for nine oils were used to determine a relationship between the weighted composition parameter and the CO_2 density in grams per cubic centimeter at the MMP (ρ_{MMP}). The resulting correlation is

$$\rho MMP = 0.986F + 1.194F < 0.785$$

$$\rho MMP = 0.42 \qquad F > 0.785.$$

Thus, given a carbon number distribution, the weighted composition parameter is calculated and then the CO_2 density at the MMP is obtained. Any suitable CO_2 density data can then be used to estimate the pressure required to produce that density at a given temperature.

Measurements of CO_2 diffusion coefficients at high pressure have been completed. The technique is based on a measurement of the motion of an interface between CO_2 and the fluid of interest. As CO_2 dissolves and diffuses into the oil, it swells the oil

[3] 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.

and causes the interface to move. The rate at which the interface moves depends on the solubilities of CO_2 and the oil in each other, the densities of the phases, and the diffusion coefficients in the two phases. As long as the solubility of oil in the CO_2-rich phase is significantly less than that of CO_2 in the oil-rich phase, the motion of the interface is determined primarily by the diffusion coefficient of CO_2 in the oil phase.

2.5 LABORATORY DISPLACEMENT TESTS

2.5.1 Investigation of Enhanced Oil Recovery Through Use of Carbon Dioxide, Louisiana State University[4]

Principal Investigator: T.G. Monger

Objectives: This project had the following objectives:

1. Study the miscibility mechanisms associated with CO_2 displacement of crude oil.
2. Study the effects of additives to CO_2, such as hydrocarbons and nitrogen.
3. Study the compositional changes of CO_2-crude oil mixtures.
4. Conduct phase behavior studies.

Conclusions: Work in FY 85 consisted of writing the final report. Monger cited the following conclusions:

1. The results of sand pack displacements of Brookhaven reservoir oil support a general picture of the dominant factors which influence the MMP in the CO_2 gas miscible displacement process. Temperature usually has the primary effect, with oil compositional effects of lesser magnitude. The relative importance of the type of oil compositional effect depends upon flood conditions. Three types of oil compositional effects were demonstrated by the displacement experiments completed under this contract, namely, hydrocarbon molecular weight distribution, oil aromaticity, and solution gas.
2. Increasing the temperature increases the required MMP. The MMP temperature dependence was more pronounced in dead oil versus live oil displacements. This MMP difference, attributed to the effects of solution gas, diminished with increasing temperature.
3. The influence of hydrocarbon molecular weight distribution is reflected by compositional analyses of effluent samples from displacements performed at a given temperature. At lower pressures, the major components extracted into the CO_2-rich phase are in the C_9-C_{12} range. As the run pressure is increased to approach the MMP, the ability of CO_2 to extract heavier hydrocarbons improves, thereby achieving greater oil recoveries. An increase in the proportion of intermediate molecular weight hydrocarbons allows sufficient extraction to occur at a lower pressure because CO_2 preferentially solubilizes these hydrocarbons. This explains the well-known observation that for a given temperature, the MMP increases with increasing crude oil molecular weight.
4. As improved hydrocarbon extraction into a CO_2-rich phase proceeds, aromatics concentrate in the stripped oil to promote deposition of a solid phase.
5. The effects of solution gas are mixed. The presence of methane has little effect on the MMP. Sand pack displacements of live Brookhaven oil show that methane is expelled from the crude by CO_2 and moves ahead of the flood front because of its high mobility. Dissolved methane is thus expected to have little impact on the CO_2 gas miscible displacement process for frontal velocities that are not gravity stable. The presence of other light hydrocarbons, however, tends to lower the MMP.
6. Tertiary CO_2 core floods using synthetic oils exhibit improved oil recoveries with increasing aromatic content. Compositional analyses of effluent samples show that the improved oil recoveries correlate with enhanced recovery of the heavier paraffinic components, C_{20} and C_{30}. Visual observations of the phase behavior occurring during these displacements also suggest that the presence of aromatics enhances the CO_2 extraction mechanism, thereby accelerating the development of miscibility in the multiple-contact process.
7. The effect of oil aromaticity shown by the core flood results typifies the well-known relationship between phase behavior and MCM (multiple contact miscibility) displacement efficiency, and establishes that oil chemistry effects can compete with the numerous other variables that control CO_2 flood performance (Monger 1985, 2:33, 35, 76).

[4] Elements of this project fall into the Phase Behavior and Miscibility area. Information concerning this project can be found in that section of this report.

2.5.2 Enhanced Recovery of Oil from Subsurface Reservoirs With Carbon Dioxide, Texas A&M University

Principal Investigator: J.S. Osoba

Objectives: The principal objective of this project was to determine oil recoveries for various degrees of miscibility in consolidated and unconsolidated laboratory models using the CO_2 displacement process. Other objectives were to study the effects of varying the length of the models, the oil gravity, the angle of dip, and the reservoir heterogeneity on oil recovery.

Conclusions: Work in FY 85 consisted of preparation of the final report. In the final report, Osoba cited the following conclusions:

1. The minimum pressure at which CO_2 appeared to achieve miscibility with a crude oil was the same in a 20-inch long sandpack as in 60- and 240-inch long sandpacks.
2. The fraction of oil displaced from a sandpack in a vertical position increased as the rate of injection decreased.
3. The fraction of oil displaced from a sandpack in a horizontal position increased as the rate of injection increased.
4. Banks of CO_2 displaced a larger fraction of oil from horizontal consolidated cores 15 foot long and 2 x 2 inch cross section when pushed with water than when pushed with nitrogen.
5. The efficiency of the nitrogen solvent slug propellant increased with the flooding pressure while that of the brine propellant was almost unaffected by flooding pressure.
6. A 0.3 HPV (hydrocarbon pore volume) CO_2 bank was found to be the optimum size for displacing crude oil from horizontal 15 foot long consolidated cores with 2 x 2 inch cross section.
7. The total oil recoveries from a core with variable horizontal permeability was only a little lower than those from homogeneous cores at similar flooding conditions.
8. The total oil recoveries showed a slight decrease as the flooding temperature was increased for all slug sizes.
9. Studies of CO_2-dolomite rock interaction showed that CO_2 dissolved part of the rock at high pressures, thus increasing the permeability. The enhancement of the permeability of the rock increased with the flooding pressure.
10. Pressure drawdown along the flow path caused dissolved carbonates to be precipitated and decreased the permeability of the rock. There was a larger reduction in permeability when the pressure reduction was larger (Osoba 1984, 78).

2.5.3 Improvement of CO_2 Flood Performance, New Mexico Institute of Mining and Technology[5]

Principal Investigators: J.P. Heller and J.J. Taber

Objectives: This project has the following objectives:

1. Perform single-phase miscible displacements with fluids having matched density and viscosity at three flow rates in sandstone and carbonate reservoir core samples, and obtain Coats-Smith parameters for the rock by history matching effluent composition data.
2. Predict performance of gravity-stable CO_2 floods (no water present), based on single-phase Coats-Smith parameters and independent measurements of phase behavior and fluid properties, using a one-dimensional process simulator.
3. Perform gravity-stable CO_2 floods and compare performance with prediction.
4. Perform miscible displacements in both oil and water phases after steady-state flow of oil and water is established in the same cores as in Objective 1, and to obtain Coats-Smith parameters.
5. Predict performance of gravity-stable tertiary CO_2 floods using a one-dimensional simulator.
6. Perform gravity-stable tertiary CO_2 floods and compare performance with prediction.
7. Attempt to correlate Coats-Smith parameters with direct observation of rock pore structures.
8. Perform flow visualization experiments to examine qualitative effects of microscopic heterogeneity and flow of foam on mixing of CO_2 and crude oil.

Summary: Miscible displacement experiments with fluids having matched densities and viscosities in reservoir cores were used to measure effects of rock

[5] 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.

pore structure and the distribution of oil and water within the pore space on mixing of oil and CO_2. A one-dimensional simulator was used to predict the performance of gravity-stabilized secondary and tertiary CO_2 floods. Predictions were based on the results of the miscible core floods and independent measurements of phase behavior and fluid properties. CO_2 floods may then be performed in the same cores to test the accuracy of the prediction.

Conclusions: Bretz, Specter, and Orr cited that heterogeneities observed in thin sections account for the behavior of miscible displacements in laboratory cores. A simple technique for detection of preferential flow paths was demonstrated. It is based on the argument that such paths will exist if, on average, large pores are surrounded by other large pores while small ones are close to other small ones. Examination of thin sections for carbonate and sandstone core samples indicated that early breakthrough and significant tailing were observed for those samples with wide pore size distributions and an indication of the existence of preferential flow paths.

Calculations performed with the convection-dispersion equation, the Coats-Smith model, and a porous sphere model indicate that for displacements at a fixed scale, a lumped parameter model, such as the Coats-Smith model, fits displacement behavior reasonably well. A more detailed model, such as the porous sphere model, requires that fewer parameters be determined by fitting experimental data to the model if geometric parameters can be estimated from observations of thin sections or by other means. Parameters that describe the transfer of material between the porous sphere and the matrix still require such estimation. A difficulty with the Coats-Smith model is that it is not clear how appropriate parameter values change with the scale of the flow system. The porous sphere model does, however, allow estimation of the qualitative impact of heterogeneities with large characteristic lengths on displacements at field scale. Estimates of Coats-Smith parameters made using the porous sphere model for larger scale displacements suggest that for some types of heterogeneities, Coats-Smith parameters will have magnitudes similar to those observed in laboratory core displacements. Thus, interactions of phase behavior and heterogeneity, demonstrated previously to have significant impact on residual oil saturations to CO_2 floods in laboratory cores, may also have significant effects at field scale (Bretz, et al. 1985, 26, 27).

2.5.4 Wettability Modification, Morgantown Energy Technology Center

Principal Investigators: A.M. Zammerilli and K. Das

Objectives: This project has the following objectives:

1. Examine foaming agent (surfactant) loss by adsorption to reservoir rock.
2. Determine applications of modifying wettability to CO_2 foam flooding through the identification of target research areas.

Summary: An extensive literature survey of surfactant adsorption loss revealed that the use of sacrificial agents in the micellar flooding process to minimize the adsorption loss may provide a similar solution for surfactant adsorption in CO_2 foam flooding. Research indicates that wettability modification (water-wet to oil-wet) could play an important role in reducing surfactant loss. A complete understanding of how surfactant loss occurs and ways of preventing this loss is needed. To enhance this understanding research is targeted to the following four areas:

1. Displacement Tests — Identified sacrificial agents such as Na_2CO_3, Na_2SO_4, and lignosulfonate will be used on normal and modified wettability sandstone cores saturated with oil and waterflooded to residual oil saturation. The effectiveness of the sacrificial agents on the adsorption loss of a foaming agent can be measured by the amount of foaming agent recovered at the end of the displacement test.
2. Effects of Sacrificial Agents on the Interfacial Tension Between Oil-Surfactant Water System — Interfacial tension between oil and brine with and without sacrificial agents will be examined. The effect of the distribution of surfactant between oil and aqueous phases will be investigated.
3. Effects of Sacrificial Agents on Contact Angle of Rock-Water Oil System — Contact angle measurements can be performed using single crystals of quartz for sandstone and calcite for carbonate rock. It is expected that contact angles will be different for different sacrificial agents. The contact angle can be taken as a measure of rock wettability, and its effect on surfactant loss can readily be related.

4. Heterogeneous Acid-Base Titration — The effect of the sacrificial agent on the adsorption of foams (surfactants) on reservoir rock may also be evaluated by a heterogeneous acid-base titration. The surfactant may be titrated after it is converted to the acid form with hydrochloric acid. The heterogeneous system includes the use of electrolyte, water, and crushed reservoir rock. Major shifts are expected in the resulting titration curves compared to those obtained in the absence of reservoir minerals. The pH shift will be monitored to evaluate the interaction between foaming agents, sacrificial agents, and reservoir rock.

Conclusions: No conclusions have been reached because work will begin in FY 86.

2.6 FIELD TESTS

Since 1976, the Department of Energy and industry have cost-shared CO_2 injection projects to examine the technical feasibility of this process. Projects have included highly instrumented field experiments (pilot tests and minitest pattern floods and injectivity research) related to improving methods for increasing CO_2 recovery efficiency. A summary of current and completed DOE cost-sharing CO_2 injection tests is shown in Table 1. A discussion of the current tests (those that were active in FY 85) follows.

2.6.1 Oil Recovery by Carbon Dioxide Injection, Rock Creek Field, Roane County, West Virginia, Pennzoil Company

Principal Investigators: P. King and D.A. Boone

Objectives: This field test had the following objectives:

1. Determine the efficiency of injecting CO_2 for oil displacement in a tertiary mode following waterflooding and low-pressure gas recycling in a shallow, low-temperature reservoir.
2. Evaluate the displacement efficiency of the process by obtaining a pressure core in a part of the reservoir that has been contacted by CO_2.
3. Investigate the feasibility of using mobility control techniques to improve the recovery efficiency of the CO_2 process.

Summary: The pilot test consisted of two adjacent 10-acre, normal five-spot patterns surrounded by 13 back-up water injection wells that 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 two original 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 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 in place).

Pressure cores were taken from wells drilled after the test to evaluate displacement and vertical sweep efficiency. Results are currently being evaluated and will be reported at a later date.

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 is being conducted. This test is also being conducted within the pilot test area. The test pattern consists of one injection well, one observation well, and one production well. The test area has been repressured by water injection to reach the CO_2/oil MMP. A chemical

TABLE 1. SUMMARY OF CURRENT AND COMPLETED DOE COST-SHARING CO_2 INJECTION TESTS

	Rock Creek Field Pilot Area, WV	Rock Creek Field Mini-test 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, Feet	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, Feet	32.4	32.0	28	28	12.5	16	120
Porosity, Percent	21.9	21.3	16	16	14.0	19.5	26.0
Permeability, Millidarcys	20.5	27.3	7	7	2-4	125	1,800
Oil Saturation (After Primary), Percent	34.4	34.4	30 (After Waterflood)	30 (After Waterflood)	70-80	78.2	22 (After
Water Saturation (Initial), Percent	50-55	50-55	70 (After Waterflood)	70 (After Waterflood)	20-30	21.8	8
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, Centipoises (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)
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

TABLE 1. SUMMARY OF CURRENT AND COMPLETED DOE COST-SHARING CO_2 INJECTION TESTS (CONTINUED)

	Rock Creek Field Pilot Area, WV	Rock Creek Field Mini-test 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
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, Barrels/Acre	2,900	2,900	2,900	2,900	2,850	N/A	N/A
Secondary Production (Waterflood), Barrels/Acre	577	577	4,100	4,100	N/A[1]	6,680 (By simulator[2])	N/A
EOR Production (CO_2), Barrels/Acre	666	2,465	1,296	2,362	410	9,020 (By simulator[2])	18,125
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/barrel	13,000	9,000	19,626	18,192	6,333	3,100 (By simulator[2])	5,920[3] (09/85)

[1] No secondary production.
[2] Nonproducing pilot test.
[3] Including recycled CO_2, the CO_2-oil ratio $\simeq$ 12,000 scf/bbl.

(thiocyanate) tracer test has been run to determine fluid velocity through the reservoir for 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 for prevention of surfactant absorption on the rock surfaces once the CO_2/surfactant foam injection begins. Neither the tracer, the surfactant, nor the oil bank have been 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.

Conclusions: 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 only about 25 percent.

Concerning the mobility control test, Heller, Boone, and Watts discussed that an unforeseen and unexplained difficulty has been the reduced injectivity due in large part to the surfactant itself. While this has prevented the injection of enough CO_2 foam to test the proposed method adequately, efforts to continue the test until a more definite result can be obtained are presently underway.

In the meantime, the following possibilities can be listed as the causes for the absence of any sign of an 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 has yet been 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, which 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 [24°C], 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 nonuniform 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.) (Heller et al. 1985, 7, 8).

2.6.2 Weeks Island "S" Sand, Reservoir B, Gravity-Stable CO_2 Displacement, Iberia Parish, Louisiana, Shell Oil Company

Principal Investigator: G. Perry

Objectives: The principal objective 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.

Summary: Reservoirs similar to the Weeks Island "S" Sand Reservoir B are typically produced by natural water drive mechanisms that leave a significant residual oil volume. The major watered-out reservoirs in the Weeks Island Field alone contain an estimated recovery potential of 26 million barrels of oil that 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 that provided a target of 288 barrels of oil per acre foot.

During Phase II, a 50,000-ton slug of CO_2 containing 5 mol 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 July of 1985, two production wells were producing 90 barrels of oil per day. Oil production should reach the original project production goal of 210,000 barrels of oil (of which 145,000 barrels were due to CO_2 injection).

Conclusions: Displacement observations indicate that a gravity-stable CO_2 displacement occurred in the "S" sand, Reservoir B. Concurrent Shell research findings 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.

3.0 RELATED INDUSTRIAL ACTIVITIES

Cities Service Oil and Gas Corporation and Mobil R&D Corporation recently conducted work concerning CO_2 mobility control using surfactants. Their findings agreed with the work being funded by the United States Department of Energy's Morgantown Energy Technology Center. Casteel and Djabbarah reached the following conclusions:

1. Foaming agents can improve the sweep efficiency for the carbon dioxide flooding process.
2. The sequence of injection of a foaming agent affects the sweep efficiency of the carbon dioxide flooding process.
3. Foaming agents can improve oil recovery over that obtained from a WAG process or carbon dioxide injected alone.
4. Foaming agents are reservoir-specific and must be evaluated for a given set of reservoir conditions (Casteel and Djabbarah 1985, 4).

Work conducted by Shell Development Company also agrees well with work being funded by METC. Brochardt, Bright, and Wellington found that surfactant foaming properties are related to surfactant chemical structure parameters such as hydrophobe size, ethylene oxide chain length, and hydrophile functional group (Borchardt et al. 1985, 5, 6).

Other work conducted by Wellington and Vinegar of Shell Development Company using computerized tomography on cores suggests that surfactant can provide effective mobility control for tertiary miscible CO_2. The study revealed a combination of mechanisms responsible for the surfactant induced mobility control: large apparent CO_2 viscosity, capillary pressure changes allowing CO_2 to reduce brine saturation below connate water saturation, and an in situ generated brine bank between oil and CO_2. Oil displacement efficiency is not reduced by the surfactant or by the in situ generated brine bank (Wellington and Vinegar 1985, 6).

4.0 RESEARCH ISSUES REMAINING

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

In the area of mobility control, surfactants have proven to be most useful. Still, much information about surfactants is needed. Polymers that are both soluble in CO_2 and are able to increase the viscosity of CO_2 enough to affect mobility are still being sought. No polymers have been found to date that do both. 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 the EG&G Washington Analytical Services Center-Morgantown Operations and 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 will begin 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. Methods to alter rock wettability for an improved outcome will also be investigated.

Overall, the results of mobility control 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.

5.0 LIST OF ACRONYMS AND SYMBOLS

API	American Petroleum Institute
BF	Brookhaven-Flashed
BOAST	Black Oil Applied Simulation Tool
CMC	Continuous Multiple Contact
CO_2	Carbon Dioxide
DOE	U.S. Department of Energy
EOR	Enhanced Oil Recovery
F	Weighted Composition Parameter
f_{PM}	Specified Fraction of the Miscibility Pressure
FY	Fiscal Year (Federal, September 1 through October 31)
IMPES	Implicit Pressure, Explicit Saturation
k_i	Modified Partition Coefficient
MASTER	Miscible Applied Simulation Tool for Energy Recovery
Mcf	Thousand Cubic Feet
METC	Morgantown Energy Technology Center
MMP	Minimum Miscibility Pressure
NMR	Nuclear Magnetic Resonance
P_{MCM}	Multicontact Miscibility Pressure
P_{MISC}	Specified Miscibility Pressure
pH	The Logarithm of the Reciprocal of Hydrogen Ion Concentration in Grams per Liter

psia	Pounds per Square Inch Absolute
psi	Pounds per Square Inch
pv	Pore Volume
R&D	Research and Development
scf	Standard Cubic Feet
S_{orw}	Residual Oil Saturation after Waterflooding
SRK	Soave-Redich-Kwong Equation-of-State
STB	Stock Tank Barrels
S_{twb}	Water Blocked Oil Saturation
WAG	Water-Alternating-with-Gas
w_i	Weight Fraction of Molecules with i Carbon Atoms in the C_2+ Fraction
ρ_{MMP}	CO_2 Density of the MMP
α	Weighted Parameter for Partially Miscible Conditions

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