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MORGANTOWN ENERGY TECHNOLOGY CENTER
TOPICAL REPORT

GAS MISCIBLE DISPLACEMENT ENHANCED OIL RECOVERY

BY

CO_2 PROJECTS BRANCH
EXTRACTION PROJECTS MANAGEMENT DIVISION

This overview report, covering the period 1 October 1982 to 30 September 1983, prepared by the Morgantown Energy Technology Center staff, describes the current status of gas miscible displacement and includes an appendix that provides summary descriptions of individual contracts.

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1.0 SUMMARY

The general goal of the Gas Miscible Displacement Project is to support high-risk, long-term CO_2/EOR research that does not duplicate or displace private and other public R&D efforts. More specifically, the project goals are (1) to understand the CO_2 process displacement mechanisms, (2) to provide predictive capability to forecast recovery from the process, and (3) to improve the process recovery efficiency. In order to accomplish these goals, the following research priorities have been identified: (1) better mobility control of injected fluids; (2) improved techniques for reservoir evaluation through investigating geologic and reservoir heterogeneity, residual oil saturation, and fracturing; (3) improved understanding of oil swelling, viscosity reduction, and extraction/vaporization phenomena; (4) improved predictive modeling; and (5) field-performance appraisal for tertiary oil recovery. The objectives of the research for FY 83 and FY 84 are:

- To provide a better understanding of the mechanism of the carbon dioxide miscible displacement process.
- To increase the displacement and sweep efficiencies of the injected fluids.
- To provide predictive modeling capability for the gas miscible displacement process.
- To study the effects of reservoir heterogeneity.

1.1 PROCESS CHARACTERIZATION AND EVALUATION

Substantial progress has been made in all areas of gas miscible displacement. Although the basic displacement mechanisms are not completely understood, research has provided additional knowledge about how the CO_2 process works. Substantial progress has been made in the area of phase behavior of mixtures of Appalachian crude oil and carbon dioxide. Data were collected in single-contact phase equilibrium experiments using a high-pressure condensate, a Pressure-Volume-Temperature (PVT) cell fitted with a viewing window. Stocktank oils from West Virginia and Ohio were examined in the presence of equimolar amounts of carbon dioxide. The volumetric behavior of the sample mixtures was monitored as a function of increasing pressure at a controlled fixed temperature. Pressures up to 3,600 pounds per square inch and temperatures above and below the carbon dioxide critical temperature were used. Saturated pressures and amount of oil swelling were determined from the PVT measurements.

Significant results show that the phase equilibria determined for carbon dioxide/Appalachian crude oil mixtures behave like those for western crude oil systems. Contaminant gases such as methane and nitrogen can have a pronounced effect on the phase behavior, while oil-swelling indices had little effect. Changes in bubble-point pressure induced by small amounts of additive gas correlate inversely with the gas critical temperature. No solid phase precipitate is formed for the carbon dioxide/crude oil mixtures. These results are important in determining the efficiency of carbon dioxide flooding for oil recovery.

Promising mobility-control techniques aimed at improved CO_2 process recovery have been laboratory tested and identified.

Accomplishments of this research include the following:

- A state-of-the-art literature survey of CO_2 mobility control was completed and published.
- A technique, consisting of the displacement of foam-like dispersions of CO_2, surfactant, and water, was shown to reduce the mobility of CO_2.
- Atmospheric pressure screening tests and surfactant absorption tests were designed and tested with commercially available surfactants. Promising surfactants were identified. The screening tests measured the ability to form a foam-like dispersion and allowed for monitoring the diffusion of the surfactant in the breaking and reforming of foam.
- Several commercially available polymers were tested for their ability to become soluble and increase the CO_2 effective viscosity, but no polymers were soluble enough to increase CO_2 viscosity.
- A highly-instrumented core flood apparatus has been developed to aid in studying CO_2 mobility control.

1.2 GEOSCIENCE RESEARCH

Studies were conducted in the laboratory to evaluate the possibility of formation plugging due to CO_2 flooding. Conditions expected to cause formation damage were simulated in order to evaluate the various possible mechanisms of formation damage.

The results indicate that little or no reservoir damage to carbonate reservoirs will occur by CO_2 miscible flooding. We studied four possible mechanisms of reservoir damage: (1) dissolution of reservoir rock and pore blockage by subsequent precipitation of the carbonates and sulfates; (2) formation of insoluble asphaltene-like solids when CO_2 dissolves in crude oil; (3) formation of immobile phases at the CO_2-oil interface; and (4) carbonic acid attack of carbonates and feldspar, releasing fines that may block pores. Results show that precipitation of either carbonates or organics causes minimal damage that might result in lower gas and water mobilities. Simple kinetic models were used which showed that calcium carbonate precipitates as a nondamaging scale rather than as pore-blocking particulates, and these models were substantiated by experimental results. Precipitation of ferric hydroxide was shown to be the most damaging, but was found to be easily controlled by maintaining back pressure on the producing well (to avoid precipitation). The results indicate that little or no damage to the reservoir will occur by using the CO_2 process to recover additional oil.

1.3 FIELD DATA ACQUISITION AND DISCREPANCY ANALYSES

A carbon dioxide (CO_2) mini-test was conducted with Gulf Oil in the Mission Canyon Formation (lower Mississippian) at Little Knife Field, North Dakota.

The highly instrumented mini-test was conducted by drilling, logging, coring, and completing four closely spaced wells within a 5-acre pattern. Field well testing, coring, and logging, combined with CO_2 injection experiments, provided reservoir characteristics necessary for predicting CO_2 flood performance.

Many diagnostic techniques were successfully used to characterize the reservoir and the field as well as to monitor the test performance. A logging monitor that utilized pulsed neutrons to measure capture cross sections and the ratio of near-to-far detector count-rates monitored fluid saturations to the required precision. Also bottom-hole pressure, fluid samples, tracers, carbon isotope analyses, pulse tests, pressure cores, laboratory tests, computer simulation runs, and a detailed geological study all contributed to the test design and interpretation.

Both the logs and pressure-core results showed zones at a very low oil saturation (less than 5 percent) in regions swept by both CO_2 and water, confirming the development of multiple contact miscibility and high displacement efficiencies observed in the laboratory.

A numerical simulation model provided a satisfactory history match of the pressures, saturations, and fluid compositions observed throughout the test, effectively combining the fluid-property data, reservoir description, and process mechanisms.

No unexpected anisotropies were encountered. Areal sweep was 100 percent of the mini-test pattern. Vertical sweep of CO_2 was incomplete because of stratification and the possible occurrence of viscous fingers. The vertical sweep efficiency was approximately 52 percent. Pattern sweep efficiency for carbon dioxide approached 52 percent.

The displacement efficiency of the CO_2 miscible process, as indicated by the simulation study for the 5-acre mini-test area, was 50 percent of the oil-in-place at the start of the project, compared with an efficiency of 37 percent for a waterflood. Only 3,100 standard cubic feet of CO_2 were required per incremental barrel of displaced oil.

The Little Knife CO_2 mini-test confirmed, by field testing, the results of the laboratory CO_2 miscible displacement tests. It also showed that the CO_2 miscible displacement process has technical potential for commercialization in a dolomitized carbonate reservoir that has not been extensively waterflooded and that has an indicated high-remaining oil saturation.

A study on the potential of enhanced oil recovery from major carbonate oil reservoirs in several western states was completed. Research results predict the amount of oil that could be technically produced using the carbon dioxide miscible displacement process. Reservoir engineering calculations were made for a total of 279 carbonate reservoirs in the Permian, Williston, and several smaller Rocky Mountain basins. Results of the study are summarized as follows:

Basin	No. of Reservoirs	Initial Oil in Place, Gas Free Billion Barrels	Incremental Oil From CO_2, Billion Barrels	CO_2 Required, Billion Cubic Feet	Average CO_2/ Oil Ratio, Thousand Cubic Feet per Barrel
Permian	188	56.50	10.56	114,314	10.8
Williston	68	3.33	0.70	8,830	11.4
Rocky Mountain	23	2.28	0.50	4,656	9.4
Totals	279	62.14	11.82	127,800	10.5

The results show that the Permian Basin reservoirs have, by far, the largest potential for enhanced oil recovery of any of the other areas. The Permian Basin area also contains large sources of naturally occurring carbon dioxide. This area will be the first industry target for using the CO_2 miscible displacement process to recover residual oil from watered-out reservoirs.

2.0 INTRODUCTION

2.1 PROGRAM PERSPECTIVE

Liquid petroleum provides nearly half of the total energy consumed in the United States. More than 75 percent of this oil is used for transportation and residential heating with few, if any, options for conversion. Even with extensive conservation efforts and conversion of some power plants to alternate fuels, the United States will still require vast amounts of liquid fuels for the foreseeable future.

Even though conservation has reduced demand during the past several years, the cost of imported oil in 1982 was still $60 billion; in 1980 it reached $79 billion.

Although new sources of liquid fuels such as oil shales, tar sands, coal, and biomass are being studied and developed, economics, uncertainties, and time lag may prevent these activities from contributing significantly to increasing domestic supplies for many years. We must develop more effective ways of recovering crude oil from domestic sources in order to limit imports and reduce our dependence on foreign oil in the future. Conventional primary and secondary (waterflooding) recovery techniques produce only about one-third of the original oil in place (OOIP). It is, therefore, essential that enhanced oil recovery (EOR) techniques be made economical so that increased amounts of oil can be recovered.

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 barrels can be recovered by all EOR techniques. Present, proved conventional reserves amount to 28 billion barrels. A recovery of any significant part of the EOR oil target could greatly reduce our dependence on imported oil.

Miscible displacement by carbon dioxide (CO_2) injection is a viable EOR technique for light oils ($>25°$ API). Some of the major problems associated with CO_2 flooding are (1) the availability and cost of CO_2, (2) the mobility control of injected fluids, and (3) the knowledge and understanding of reservoirs. These and other technical, economic, and regulatory constraints have hindered the development of current and advanced CO_2 flooding technologies.

Beginning in 1981, the Federal Government removed some of the regulatory constraints and reoriented its EOR R&D program toward the development of advanced EOR processes, including CO_2 miscible flooding. The current EOR R&D program has evolved over several years.

This evolution has been deliberate — it reflects the Government's intent to refocus its activities as needed.

2.2 PROGRAM OBJECTIVES

The United States Department of Energy's (DOE) EOR program is divided into a light-oil enhanced recovery program and a heavy-oil enhanced recovery program. Among other EOR processes, CO_2 miscible displacement is best suited for light oil reservoirs and is, therefore, a part of the light-oil enhanced recovery program.

The goals of the EOR program, as it applies to light oil, are (1) to develop an improved understanding and predictability of effective, advanced EOR processes; (2) to improve the level of performance and to extend the range of application of advanced EOR processes; and (3) to assess the feasibility of very long-range, highly advanced emerging technologies, and to evaluate the unique problems of reservoirs for which no EOR technology currently exists.

Meeting these goals requires a strategy that combines fundamental basic research and development efforts with field validation.

Although CO_2 flooding performance is sufficiently predictable and its recovery efficiency high enough to justify field-scale projects and very large investments in CO_2 supply in some high-oil-saturation west Texas carbonate and sandstone reservoirs, problems have been encountered. These tests show that CO_2-oil basic 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. 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. A better understanding of the effects of macro- and micro-heterogeneities of the reservoir on CO_2 flooding is required.

We have designed and executed the research program in carbon dioxide enhanced oil recovery in order to increase the level of knowledge in each of these areas.

2.3 STATE OF THE ART

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 ability to overcome both of these factors. Although there is a strong tendency for injected CO_2 to flow though those pores that have been contacted and largely saturated with the displacing water, control of the injection and flow of injected fluids may enable us 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, there will be both free CO_2 and CO_2-saturated crude oil 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 will, 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 consist of swollen oil, which consists of a large volume of CO_2 and a relatively small quantity of hydrocarbon material. The reduction of viscosity and the increase in relative permeability to oil will both 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 miscible CO_2 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 (usually 1,000 psi or greater), MMP, 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 and, because of the concentration gradient from the oil to the CO_2, many hyrocarbon molecules, especially those of C_5-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 contacted part of the reservoir.

The miscible displacement process just described is similar in some respects to the vaporizing gas drive EOR process in which lean, dry gas (essentially methane) is injected into the reservoir. At quite high pressures the C_2-C_6 hydrocarbon components are vaporized and mixed with the lean gas. Eventually, the composition of the gas phase enables it to become miscible with the crude oil. There are some disadvantages to this method that do not apply to CO_2: (1) methane is currently much more expensive than an equivalent amount of CO_2; (2) the high pressure required limits application to relatively deep reservoirs; and (3) the reservoir pressure must not have declined sufficiently from its initial value to permit vaporization and production of a large fraction of the C_2-C_6 components prior to injection of the lean gas.

In order to determine the chances of conducting a successful miscible CO_2 displacement, information must be obtained from several sources. Slim tube tests — in which $\leq$0.25 inch I.D. 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 $\geq$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 in order to determine, in a more realistic situation, the residual oil saturation (S_{or}) and the 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 transmiscibility 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 indicate that this well is 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, there is a tendency for the CO_2 to migrate vertically to the top of the formation and form a "gravity tongue," i.e., to 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 viscosity factor and the normally high relative permeability to gases at low gas saturations result in a very high mobility for the CO_2. This mobility, in turn, because of the channeling and fingering that it produces and the absence of oil banking that it permits, results in a generally low volumetric sweep efficiency, rapidly increasing the producing CO_2-oil ratios, and necessitating the recovery and reinjection of large volumes of CO_2.

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 which they normally provide, there will be less tendency for the CO_2 to channel until they are put on 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 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.

CO_2 has been injected into a growing number of reservoirs. One of the earliest, and certainly the largest, has been the SACROC unit of the Kelly-Snyder field in west Texas. In this giant oil field, which originally held approximately 2×10^9 STB of oil, more than 30,000 acres are being flooded with CO_2. About 90×10^6 STB of oil have been produced as a result of this effort with a gross CO_2 utilization of about 6-7 Mcf/STB of oil recovered. The success of this project has inspired many others, including an immiscible flood in the Lick Creek field that has been economically successful.

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, distribution systems, and injection down wellbores, the CO_2 should be dehydrated to prevent excessive corrosion. When the water-alternating-with-gas (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 is 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 injectivity is, therefore, 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, there is also a tendency for the carbonic acid formed by the CO_2 and water to react with and dissolve part of the rocks, enlarging the pores and increasing the permeability to the injected fluids.

From field experience, it has been found that CO_2 breaks through into the producing wells in a very short time (a few weeks to a few months). After breakthrough, the combination of produced water and CO_2 will corrode the down-hole and surface equipment unless preventive materials, such as corrosion inhibitors, pipe coatings, or special steels, 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 will 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 the methane mixed with the CO_2 increases the MMP substantially. It is necessary, therefore, that the CO_2 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.

Although there are several sources of CO_2 in the quantities needed, they are nearly always located at substantial distances from the oil field where the CO_2 is to be used. Several large reservoirs containing high concentrations of natural CO_2 are located in Texas, Colorado, and New Mexico. Pipelines are either in use or under construction to transport this gas to the basins where it can be injected into the reservoir. Electrical generation plants, synthetic fuel plants, refineries, etc., produce large quantities of CO_2, but it is normally diluted by other gaseous waste products or it is at essentially atmospheric pressure, or both. These sources also are usually located at a considerable distance from the point of application. These and other man-made sources may not be economically feasible at the present time.

The total cost of CO_2 is a sum 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/Mcf (1983 dollars) and CO_2 requirements less than 8-10/Mcf per barrel of oil recovered, economic success can frequently be achieved.

Current reviews of EOR techniques in general are not particularly encouraging. Both miscible and immiscible CO_2 flooding can frequently achieve economic as well as technical success. Problems, however, remain. Mobility control is probably the most serious technical problem at the present time. Phase behavior and misciblity are not completely understood, and there is insufficient field data available to develop models that can adequately predict project performance. Work done in these areas should provide at least partial solutions to these problems.

3.0 SUMMARY OF PROJECTS IN CARBON DIOXIDE ENHANCED OIL RECOVERY

The Department of Energy carbon dioxide enhanced oil recovery program has included research and development projects with industry, research institutes, and universities. This comprehensive approach covers the broad technology needs of the carbon dioxide program. Additional R&D projects can be initiated and those that are completed or unsuccessful can be eliminated in order to address the needed targets.

Each project is summarized in Sections 3.1 through 3.5 below according to the technology needs. Appendix A provides more specific information on each project, such as contractor, principal investigator, major problem area addressed, and other pertinent material. Appendix B provides a bibliography of published papers and oral reports presented at scientific or engineering meetings. Refer to these for further project details. All of these reports are based on work done in the specified project.

3.1 PHASE BEHAVIOR AND MISCIBILITY

3.1.1 Determination of Miscibility Pressure by Direct Observation Method, University of Alabama

The objectives of this project are to (1) develop a fast and accurate method for determining minimum miscibility pressure (MMP), (2) gain new knowledge of CO_2 miscibility through chemical analysis and microphotography, and (3) determine the feasibility of in situ foam generation by using visual observation and microscopic photography through a transparent tube.

This project has resulted in the following developments and observations:

- A high-pressure, transparent cell has been developed to measure MMP.
- The in situ foam/diverting technique for mobility control can significantly increase recovery in laboratory sand packs.
- CO_2 begins to extract hydrocarbons from crude oil at some minimum pressure.
- CO_2 foams delay CO_2 breakthrough in flow experiments and improve recovery efficiency.
- CO_2 foams can be generated in situ in laboratory sand packs.
- The extraction-vaporizationof hydrocarbons by CO_2 can be observed.

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

The objectives of this project are to (1) conduct phase behavior studies of carbon dioxide with synthtic 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; and (5) improve miscible pressure correlations and develop a reservoir screening procedure for identifying target reservoirs.

This project has resulted in the following developments and observations:

- The presence of aromatic and naphthenic components improves miscibility.
- Slim-tube displacement recoveries are not sensitive to the presence of water.
- Numerical models can be used to verify slim-tube experimental data.

3.1.3 Investigations of Enhanced Oil Recovery Through Use of Carbon Dioxide, Louisiana State University

The objectives of this project are to (1) determine the mechanisms by which CO_2 displaces oil; (2) determine the effect of various CO_2/crude oil components on minimum miscibility pressure, displacement efficiency, and displacement mechanisms; (3) analyze the effect of water saturation on displacement efficiency and mechanisms; and (4) identify the factors involved when CO_2 displaces a discontinuous residual oil phase.

This project has resulted in the following developments and observations:

- Displacement tests, consisting of two runs in 6-foot Berea cores and 15 runs in 20-foot sand packs, were run with the following observations:
    - A second immiscible phase was produced when CO_2 displaced Brookhaven crude oil miscibly at 109°F.
    - CO_2 was able to bank discontinuous waterflood residual crude oil.
    - An increase in displacement temperature caused a significant increase in minimum miscibility pressure.
    - Analysis of compositional data through the transitional region can only be made under gravity stable conditions.

3.1.4 EOR by CO_2 Flooding — Enhanced Recovery of Oil from Subsurface Reservoirs with CO_2, Texas A&M University

The objectives of this project are to (1) determine oil recoveries for various degrees of miscibility in consolidated and unconsolidated laboratory models using the CO_2 displacement process; (2) perform displacement tests under various conditions of core length, oil gravity, dip angle, and reservoir heterogeneity; and (3) evaluate oil recovery sensitivity to various parameters.

This project has resulted in the following developments and observations:

- Seventeen displacement runs were conducted on 15-foot Berea cores. A 30 percent hydrocarbon pore volume CO_2 slug appears to be the optimum size for maximum recovery efficiency.
- These results agree with earlier studies in which 5-foot Berea cores were used.
- Premature CO_2 breakthrough in displacement tests has resulted in inefficient recovery.

3.2 MOBILITY CONTROL

3.2.1 Mobility Control Techniques, New Mexico Institute of Mining and Technology

The objectives of this project are to:

- Develop an instrumented core flooding system which can evaluate the effectiveness of additives for mobility control.
- Study the mechanisms by which foam-like dispersions of dense CO_2 in water are operative in decreasing overall mobility of CO_2.
- Screen and identify CO_2-based "foams" of controllably low mobility.
- Identify CO_2-soluble polymers having mobilities similar to oil or water.

This project has resulted in the following developments and observations:

- A state-of-the-art review of mobility control for CO_2 EOR has been completed.
- Promising surfactants for mobility control were screened and identified.
- An instrumented core flood system was developed to study mobility control.
- Mobility control experiments indicated that foam mobility decreases with increasing surfactant concentration.
- Mobility control requirements were identified.
- No CO_2-soluble polymers are commercially available that can provide adequate mobility control.
- Foam-like dispersions of dense CO_2 in a surfactant aqueous solution can reduce viscous fingering and reduce premature breakthrough of CO_2.

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

The objectives of this project are to:

- Provide laboratory support in the design of the mobility control experiments in the DOE/Pennzoil mini-flood project by:
    - Determining properties of Rock Creek field reservoir materials and compatibilities.
    - Screening a wide field of surfactants/polymers to find (if possible) a suitable mobility control additive.
- Provide assistance in slug design for field experiment implementation.
- Analyze and assess field experimental results.

This project has resulted in the following developments and observations:

- Screening tests were devised and used to identify a suitable foaming agent for the Rock Creek CO_2 mini-flood.
- An injection plan suitable for the Rock Creek mini-flood project was designed.
- A method of monitoring field experiments and relative success of the flood was designed.

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

The overall objective of this project is to finalize the development of lowcost, effective chemical additives capable of lowering the mobility of gases, especially CO_2, for use in EOR. Specific objectives are to (1) evaluate dynamic foam stability or CO_2 mobility reduction, (2) determine foam rheology, (3) conduct CO_2 displacement tests using various mobility control fluids, and (4) conduct computer simulation of linear displacement tests.

This project has resulted in the following developments and observations:

- Some promising chemical structures for mobility control additives have been identified.
- Linear flow tests have been conducted in sand packs that demonstrate mobility control effectiveness for the more promising additives.
- Design and construction of a dynamic foam-stability test apparatus have been completed.
- New additives for mobility control have been identified.
- Dynamic screening tests of brine and the most promising additives have been completed in order to calibrate further experiments.

3.3 LABORATORY DISPLACEMENT TESTS

3.3.1 Displacement of Oil by CO_2, New Mexico Institute of Mining and Technology

The objectives of this project are to (1) determine how CO_2 contacts and displaces oil trapped during a waterflood, (2) determine how density and viscosity of fluids in the transition zone between CO_2 and oil affect the development of an oil bank, (3) determine how mobility control additives affect favorable phase behavior of CO_2-crude oil mixtures, and (4) determine how field operations should be conducted to minimize the effects of gravity segregation and viscous fingering.

This project has resulted in the following developments and observations:

- A new device, a continuous oil-water separator of low dead volume, was developed for use in the two-phase displacement tests.
- A synthetic porous network was developed for visual observations of CO_2 displacement.
- The continuous multiple contact experiment used to study crude oil extraction has been automated for data collection and analysis.
- Displacement of oil by CO_2 in a slim tube is efficient because of extraction of hydrocarbons by a CO_2-rich phase.
- Isolation (or trapping) of oil by water causes lower recovery of oil by CO_2 injection.
- Phase composition and density data ob-

tained from multiple contact experiments can be used to predict slim-tube performance.

3.4 RESERVOIR MODELING IN CO_2 FLOODING

3.4.1 Research/Reservoir Characterization and Recovery Process Studies, Lewin and Associates

The objectives of this project are to (1) document and critically review the simplified CO_2 flooding model used by Lewin for reservoir analysis, (2) demonstrate how the Lewin recovery and technology submodels predict oil recovery as a function of alternate reservoir and process parameters, (3) examine the costing and financial components of the Lewin CO_2 economics submodel, and (4) review the experimental work performed for Lewin by the University of Southern California School of Petroleum Engineering on their scaled model runs of the CO_2 process, particularly its applicability for strengthening the CO_2 recovery/technology submodel.

This project has resulted in the following developments:

- A model predicting CO_2 performance has been entered, debugged, and made operational on the DOE-METC computer.
- The capability of performing economic analyses of predicted oil recovery and resistivity analyses of model parameters has been developed.
- The CO_2 model has been "fine-tuned" by using the published CO_2 field performance data from several field CO_2 floods.
- A user's guide to the CO_2 model has been written and submitted.

3.5 FIELD TESTS

Since 1976, DOE has developed cost-sharing CO_2 injection projects with industry to examine the technical feasibility of CO_2 injection by conducting highly instrumented field experiments, pilot and mini-test pattern injection, and injectivity research related to improved methods for increasing CO_2 recovery efficiency. A summary of current and completed DOE cost-sharing CO_2 injection tests is given in Section 3.5.4.

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

The objectives of this project are (1) to demonstrate the efficiency and economics of recovering oil from a shallow, low-temperature reservoir using carbon dioxide and water to displace oil in tertiary recovery, and (2) to investigate, following a CO_2 pilot test, the feasibility of using mobility control techniques to improve the recovery efficiency of the CO_2 process.

This project has resulted in the following observations and developments:

- CO_2 displacement efficiency is excellent in the contacted portions of the reservoir.
- For the following reasons, tertiary recovery by CO_2 flooding is not economical in the Rock Creek oil field:
  - CO_2 requirements, 10 to 14 Mcf per barrel of oil recovered, are much too high for economical recovery.
  - Volumetric sweep efficiency is only about 25 percent. Mobility control is required in order for CO_2 to contact additional oil.

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

The objectives of this project are (1) to demonstrate that CO_2 miscible displacement can be accomplished in deep, hot reservoirs which are unsuitable for surfactant flooding, (2) to provide incentive for developing other CO_2 projects along the Gulf Coast and developing adequate CO_2 supplies, and (3) to transfer the developed technology to private industry for further commercial application.

This project has resulted in the following observations and results:

- Similar waterflood residual oil saturations were obtained from both core analysis and the log-inject-log technique.
- Displacement observations indicate that a gravity-stable CO_2 displacement occurred in the "S" sand, reservoir B.
- State-of-the-art, three-phase relative

permeability models could not predict oil recovery in the "S" sand.

- A post-test evaluation well was drilled by Shell to evaluate project results.
- Total cumulative recovery as of September 30, 1983, totalled 125,000 barrels of oil. Of this production, 60,000 barrels were due to CO_2 injection.

3.5.3 Enhanced Oil Recovery by CO_2 Miscible Displacement in Little Knife Field, Billings County, North Dakota; Gulf Oil Company

The objective of this project was to confirm laboratory CO_2 displacement tests in the field and show viability of CO_2 miscible displacement in high oil saturation carbonate reservoirs that have not been extensively waterflooded.

This project has resulted in the following observations and developments:

- One injection and three observation wells were drilled, logged, and completed.
- Highly-instrumented well diagnostic tests were conducted on the mini-test wells.
- Reservoir simulators have been used to characterize the reservoir, match production history, and compute water injection rates.
- A 25 percent hydrocarbon pore volume slug (2,000 tons) of CO_2 was injected into the pattern.
- Post-test pressure core analysis indicates that CO_2 reduced the residual oil saturation to less than 10 percent in the swept portion of the reservoir.
- Reservoir flood performance predictions by Gulf's reservoir simulator indicate that CO_2 requirements per barrel of oil for secondary and tertiary recovery are 5 and 7 Mcf per bbl, respectively.

3.5.4 Summary of Current and Completed DOE Cost-Sharing CO_2 Injection Tests

	Rock Creek Field Pilot Area	Rock Creek Field Mini-Test Area	Granny's Creek Field Pilot Area	Granny's Creek Field Mini-Test Area	Hilly Upland Field	Little Knife Field	Weeks Island Field
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	23 (Oil Column)
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 Waterflood)
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)	1.05	1.05	1.05	1.05	1.05	1.77	1.652
Formation Volume Factor	1.54 (CO_2@ 1,300 psi)	1.54 (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)

3.5.4 Summary of Current and Completed DOE Cost-Sharing CO_2 Injection Tests (Continued)

	Rock Creek Field Pilot Area	Rock Creek Field Mini-Test Area	Granny's Creek Field Pilot Area	Granny's Creek Field Mini-Test Area	Hilly Upland Field	Little Knife Field	Weeks Island Field
Area, Acres	19.65	1.55	6.7	0.85	10	5.0	39
Pattern	2 Normal 5-Spot	1 Normal 4-Spot	1 Normal 5-Spot	1 Inverted 4-Spot	Single Injection Well	1 Inverted 4-Spot	Single Injection Well
Bottom Hole Pressure, psi	1,834	1,834	1,800	1,800	1,250	3,500	4,950
Minimum Miscibility Pressure, psi	1,000	1,000	1,000-1,050	1,000-1,050	1,050	3,400	N/A
Primary Production, Barrels/Acre	2,900	2,900	2,900	2,900	2,850	N/A	N/A
Secondary Production (Waterflood), Barrels/Acre	529	821	4,100	4,100	N/A	N/A	N/A
EOR Production (CO_2), Barrels/Acre	880	2,415	1,296	2,362	410	N/A	1,665
CO_2 Injected, Tons	35,849	8,189	9,880	2,118	1,546	2,095	50,000
Effective CO_2 Injected, Tons	13,569	1,851	1,186	2,118	1,546	2,095	50,000
CO_2/Oil Ratio, scf/bbl (Minimum)	13,500	8,500	19,626	18,192	6,333	3,100 (By simulator)	13,220 (10/83)

APPENDIX A — CONTRACT RESEARCH ON CARBON DIOXIDE ENHANCED OIL RECOVERY

A.1 PHASE BEHAVIOR AND MISCIBILITY

A.1.1

Title:

Determination of Miscibility Pressure by Direct Observation Method

Contractor:

University of Alabama, Tuscaloosa, Alabama

Principal Investigator:

George Wang, Professor of Mineral Engineering

Objectives:

- Develop a fast and accurate method for determining minimum miscibility pressure (MMP).
- Gain new knowledge of CO_2 miscibility through chemical analysis and microphotography.
- Determine the feasibility of in situ foam generation throughvisual observation and microscopic photography using a transparent tube.

Abstract:

A method is described for direct determination of MMP between CO_2 and crude oil by utilizing a high-pressure visual cell. CO_2 was allowed to mix, circulate, and recycle through the crude oil in the visual cell. The development of different phases, the swelling of crude oil, and the disappearance of the phase boundary between displacing CO_2 and displaced crude oil, marking the MMP, were clearly observed and photographed. MMP tests were conducted on crude oils ranging from 15° API to 48° API at temperatures between 70°F and 140°F. Liquid and vapor samples were extracted from the transparent cell at the miscibility condition in order to understand CO_2-crude oil miscibility through chemical analysis by a gas chromatograph.

A CO_2-rich, less dense liquid phase, believed to be formed by the extraction of the C_5-C_{20} components of the crude oil, was found to be miscible at the forward contacts of the miscible transition zone due to enrichment through multiple contacts. Chemical analysis with the gas chromatograph showed that the amount of the CO_2-rich, less dense liquid, and thus the quality of the miscible transition zone, are determined by oil composition. It is, in particular, a function of the quantity of C_5-C_{20} components in the crude oil. A small amount of CO_2-rich, less dense liquid was generated for a crude oil with a low C_5-C_{20} content; the displacement was primarily of the immiscible type and recovery largely due to viscosity reduction and swelling. Liquid CO_2 also extracted C_5-C_{20} components and eventually became miscible with crude oil.

In additional studies, CO_2-foam properties were investigated at room temperature and atmospheric pressure. Emphasis was given to foam quality, quantity, stability, surfactant concentration, and the CO_2/surfactant ratio. Foam properties were also studied at temperatures up to 140°F and pressures up to 2,500 psi using a vertical glass tube. CO_2-

foam displacement tests of SACROC and Rock Creek crude oils were performed using a 62-inch long Jerguson gauge packed with 0.125 mm glass beads. The CO_2 foam that was generated in the porous medium was susceptible to degeneration when it contacted crude oil. Although the foam may exist only in the the near-wellbore area, it may reduce early channeling tendencies, delay CO_2 breakthrough, and decrease the CO_2/oil ratio. Excessive surfactant concentrations would cause a foam block and decrease oil recovery efficiency.

Conclusions:

The following conclusions were drawn from the results of this study.

- At some minimum pressure, CO_2 will begin to extract hydrocarbons from crude oil. Higher pressures are required to start the process at higher temperatures.
- The emergence of a CO_2-rich liquid appears to be the key to the development of a miscible transition zone. At the forward contacts of this transition zone, the CO_2-rich liquid becomes miscible with fresh crude oil after multiple contacts. At the rear of the transition zone, the CO_2-rich liquid is miscible with the driving CO_2 at pressure above the MMP.
- The CO_2-crude oil MMP can be determined by direct observation through a high-pressure glass cell. It is the minimum pressure at which the CO_2-rich liquid becomes miscible with the CO_2 vapor phase.
- The CO_2-crude oil MMP depends primarily on the temperature and to a lesser degree on oil composition. The amount of C_5-C_{20} components contained in the crude oil determines how much CO_2-rich liquid is generated.
- A stable and high-quality transition zone can be sustained if the crude oil contains adequate amounts of C_5-C_{20}. With low gravity oils where amounts of C_5-C_{20} components are small, miscible displacement is unlikely.
- Liquid CO_2 is also capable of extracting C_5-C_{20} from crude oil. The less-dense liquid formed will mix with liquid CO_2 much more readily than it will with CO_2 vapor.*
- CO_2-foam can be generated within the porous medium at ordinary reservoir temperatures and pressures.
- The CO_2-foam generated in the porous medium cannot be displaced forward. Instead, propagation of the foam front depends on degeneration and regeneration.
- The CO_2 mass input should be considered in designing the slug size. With the same size (fractional hydrocarbon pore volume) slug, liquid CO_2 would have nearly double the mass of the vapor phase slug. Liquid CO_2 develops miscibility more quickly and, because of higher density, is less prone to gravity segregation than vapor phase CO_2.*
- CO_2-foam, generated either internally or externally, is subject to rapid degeneration when it contacts crude oil. The CO_2-foam is more stable in a waterflooded reservoir where the oil saturation is low.
- The CO_2-foam generated near the inlet reduces channeling and gravitational segregation effects. Even though the CO_2-foam degenerates very quickly in the porous medium, it improves CO_2 flooding performance by delaying CO_2 breakthrough and decreasing CO_2 production. After degeneration of the foam, the flood becomes an ordinary CO_2 displacement.
- Excessive surfactant concentrations (1.5 percent) cause foam block and decrease oil recovery efficiency.

*The critical temperature of CO_2 is 88°F. Liquid CO_2 cannot exist at temperatures in excess of 88°F regardless of pressure.

A.1.2

Title:

Development of a Method for Evaluating Carbon Dioxide Flooding Prospects

Contractor:

University of Kansas

Principal Investigators:

Don Green and George Swift

Objectives:

The ultimate goal of this project is to develop an effective method for evaluating various petroleum reservoirs as prospects for carbon dioxide flooding. The method should provide the miscibility (or second liquid phase) pressure plus some measure of expected oil displacement/extraction efficiency as functions of normally available data from such reservoirs (drilling and production records and reservoir fluid analysis).

Abstract:

Phase behavior studies of carbon dioxide with synthetic and actual reservoir oils were conducted. The purpose of the synthetic oil studies is to assess the impact of known Paraffinic-Naphthenic-Aromatic (PNA) components and relative compositions on the phase equilibrium of CO_2-rich systems. Studies can then be made on actual reservoir oils which have been well characterized as to C_7+. Phase behavior on both types of oils will be determined in the presence of water.

The coefficients of an appropriate equation of state are to be "fine tuned" to predict, within engineering precision, the phase behavior of carbon dioxide with hydrocarbons and water as reported in the technical literature.

Linear displacements/extractions of both synthetic and actual reservoir oils have been made with CO_2 in slim tubes.

A linear numerical simulator, using the "fine tuned" equation of state, was developed to improve existing correlations for miscibility pressure and to develop an overall evaluation method for screening reservoirs as potential prospects for carbon dioxide flooding.

Conclusions:

- The presence of aromatic and naphthenic components in the crude oil improves CO_2-oil miscibility.
- Slim-tube displacement recoveries are not sensitive to the presence of water.
- Numerical simulators have been developed and used to verify slim-tube experimental data.

A.1.3

Title:

Investigation of Enhanced Oil Recovery Through Use of Carbon Dioxide

Contractor: Louisiana State University, Baton Rouge, Louisiana

Principal Investigators:

Walter Whitehead and Oscar Kimbler

Objectives:

The objectives of this project were to study the miscibility mechanisms associated with CO_2 displacements, the effects of additives to CO_2 such as hydrocarbons and nitrogen, the compositional changes of CO_2/crude oil mixtures, the effects of water saturation on the displacement process and mass transfer of hydrocarbons from oil to the CO_2-rich phase, and to conduct phase behavior studies.

Abstract:

The phase behavior of 43 mixtures of synthetic oil and carbon dioxide has been studied. Four synthetic oils, composed of selected paraffinic, aromatic, and naphthenic hydrocarbons, were examined in mixtures spanning the CO_2 compositional range. Pressure-volume isotherms and swelling indices have been presented at temperatures below and above the CO_2 critical temperature, and for pressures up to 3,500 psia. Analyses of liquid phase compositions were made for CO_2-synthetic oil mixtures with and without aromatic components. Significant results show that the phase equilibria determined for mixtures of CO_2 with simple synthetic oils generally emulate those reported for complex natural crude oils. Hydrocarbon compositional effects have been discussed in terms of their chemical or physical nature. Chemical effects correlate with the oil's aromatic content or the "molecular type," while physical effects reflect "molecular packing" and can be correlated with oil density. The size of the multiple-liquid phase regions appears to depend upon both the chemical and physical natures of the oil. Oil swelling, or the condensation of CO_2 into an oil-rich phase, is a physical phenomenon. Miscibility, or the extraction of hydrocarbons into a CO_2-rich phase, is a chemical phenomenon. Results for synthetic oils containing unsaturated carbon suggest that aromatics enhance CO_2's ability to extract hydrocarbons by solvating the heavy ends.

Twenty-two displacements of dead Brookhaven oil and one slim-tube displacement of live Brookhaven oil using 100 percent CO_2 as a displacing fluid have been conducted. Minimum miscibility pressures were estimated using ultimate recovery plots supplemented with visual observations of the effluent stream. Temperatures of 109°, 140°, and 175°F were used up to a maximum pressure of 4,000 psia. Analyses of the role of light hydrocarbons on the miscibility mechanism were based upon a comparison of live and dead oil runs. The lower minimum miscibility pressures observed for the live versus dead oil displacements suggest that the C_2 through C_5 hydrocarbons have a major effect on the displacement mechanism. The pressure of methane, however, has a minor effect on miscibility pressure. Methane appears to be expelled from the crude by CO_2 and to move ahead of the front.

Conclusions:

- CO_2 can cause the banking of a discontinuous waterflood residual oil in a watered-out system. Miscibility pressure is directly proportional to system temperature. Analysis of compositional data through the transitional region can apparently be made only under gravity-stable conditions.

A.1.4

Title:

EOR by CO_2 Flooding — Enhanced Recovery of Oil from Subsurface Reservoirs with CO_2

Contractor:

Texas A&M University, College Station, Texas

Principal Investigator:

Joseph 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. Another objective was to study the effects on oil recovery of varying the length of the models, the oil gravity, the angle of dip, and the reservoir heterogeneity.

Abstract:

Sand-packed columns in 1/2-inch I.D. steel pipe with permeabilities of 500 to 1,000 md and lengths varying from 1 to 60 feet have been used to study the displacement of oil by CO_2 at operating pressures ranging from 200 to 3,000 psi. The columns were saturated with brine and oil to simulate field conditions. The sand was removed from the pipe at the end of each displacement test, and the pipe was then repacked for the following test. The removed sand was analyzed to determine residual oil content and displacement mechanisms. Suites of tests were run in 5-foot sand packs oriented horizontally and at 30°, 60°, and 90° to determine the effect of gravity on displacement efficiency. All other tests were run horizontally only.

Sand pack lengths were 1, 5, 20, and 60 feet. Pressures for each pack were 200; 400; 1,000; 1,500; 2,000; and 3,000 psi. Both light and medium weight west Texas crude oils were used.

Effluents were measured and produced gases were analyzed chromatographically. Residual oil saturation was determined at various points in the sand pack to determine the displacement mechanisms.

Conclusions:

- Results of displacement tests indicate that optimum displacement efficiency can be attained with a 30 percent hydrocarbon pore volume CO_2 slug. This result is substantiated by both 5-foot and 15-foot consolidated (Berea) core displacement tests.
- Premature CO_2 breakthrough was observed in core displacement with resulting reductions in recovery efficiency.

A.2 MOBILITY CONTROL

A.2.1

Title:

Mobility Control Techniques

Contractor:

New Mexico Institute of Mining and Technology, Socorro, New Mexico

Principal Investigators:

John P. Heller, Joseph J. Taber

Objectives:

The objectives of this research included the preparation of a literature review on the background, origin, and proposed remedies for the "mobility ratio problem" as it exists in CO_2 displacement; the screening and selection of "potentially useful additives" to improve the mobility ratio; the conducting of laboratory experiments to determine the cost effectiveness of such additives; and the recommendation of additives and of injection programs for use in field tests.

Abstract:

In certain crude oil reservoir situations, highly compressed CO_2 can be used very effectively to displace the oil from the rock. The advantage of CO_2 over other displacement fluids is that a much higher microscopic displacement efficiency can be attained with CO_2.

Because CO_2 is much less viscous than the reservoir crude oil, the injected fluid does not move through the reservoir uniformly. Viscous fingering, early CO_2 breakthrough, and high CO_2-oil ratios are problems caused by the unfavorable viscosity ratio. Viscous fingering causes a very poor volumetric sweep efficiency and extremely poor CO_2 utilization.

The aim of this project was to prevent or minimize the formation of viscous fingers and improve the volumetric sweep efficiency of the injected CO_2. The viscosity of the CO_2 might be increased by two different methods: (1) using a foam-like dispersion of dense CO_2 in a surfactant solution, and (2) using polymers that are directly soluble in dense CO_2. The foam-like dispersion is to be evaluated in a field test.

Conclusions:

- A Literature Survey relating to viscous fingering, unfavorable mobility ratios, and poor sweep efficiency was compiled.
- It has been shown that low mobility of the CO_2 can be achieved with foam-like dispersions even though the CO_2 has a high density and a relatively low compressibility. The nonaqueous fluid does not need to be a gas to achieve mobility control with this method.
- An atmospheric-pressure screening test for surfactants has been developed that measures properties in the presence of reservoir brine. The test measures the ability to form a foam-like dispersion and the ability of the surfactant to diffuse quickly back to new interfaces in order to re-form films and foam after the initial foam-like dispersion has degenerated. An adsorption test has also been developed.

- No commercially available polymer was found that was capable of increasing CO_2 viscosity by direct addition.
- A highly-instrumented core flood apparatus was developed to aid in studying mobility control.

A.2.2

Title:

Mobility Control for CO_2 Injection

Contractor:

New Mexico Institute of Mining and Technology, Socorro, New Mexico

Principal Investigator:

John P. Heller

Objectives:

The work done on this project was primarily for the purpose of supporting and designing mobility control experiments in the mini-flood area of a CO_2 pilot project conducted by DOE and Pennzoil in the Rock Creek oil field, Roane County, West Virginia.

Abstract:

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 to be 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 unprotected floods or those using the WAG procedure. By maximizing CO_2 utilization, the economics of the recovery method should be improved.

Descriptions of the Rock Creek oil field and the proposed injection program are described, as well as the laboratory tests used in choosing the surfactant (Alipal CD-128). Design calculations are also included. Well site facilities are suggested along with methods of assessing results of the flood.

Although the area of the test and the anticipated oil recovery are small, the implications are large. If the oil bank forms as expected, the test may be expected to lead to widespread consideration of mobility control in CO_2 floods as a means of increasing oil recovery and CO_2 EOR profitability.

Conclusions:

This project is still under way at this time. Therefore, the conclusions are preliminary.

- The surfactant Alipal CD-128 was found to remain active enough in the reservoir over an extended period of time (30 days) to control the CO_2 mobility there and to satisfy all other screening requirements.
-

- The design submitted for the Rock Creek mobility control test includes the continuous injection of a "CO_2-foam" in a slug of a calculated size that is to be displaced by an ordinary water flood. The foam slug is to be preceded by a "pad" of Alipal CD-128 surfactant solution to supply the surfactant required for adsorption onto the rock. The recommended concentration of the surfactant pad is 0.1 percent and the calculated pad volume is 8,130 barrels.
- The slug is to be made by simultaneously injecting four parts by volume of CO_2 to one part of 0.05 percent surfactant solution. The calculated volume of the slug is 32,500 barrels (6,500 barrels of surfactant solution and 26,000 reservoir barrels or 3,660 tons of CO_2).
- Automatic instruments, designed to monitor at frequent intervals the composition of small fluid samples taken from the observation well, are being constructed. Description of the equipment and its operation is not yet available.

A.2.3

Title:

Enhanced Oil Recovery of CO_2 Foam Flooding

Contractor:

New Mexico State University, Las Cruces, New Mexico

Principal Investigator:

John Patton

Objectives:

The objectives of this project were to evaluate dynamic foam stability in CO_2 mobility reduction during three-phase flow, including crude oil and brine; determine foam rheology as a function of foam quality, temperature, and system composition; conduct CO_2 displacement tests using various mobility control fluids at reservoir temperature and pressure in cores taken from candidate reservoirs for CO_2 flooding; and conduct computer simulation of linear displacement tests to assist mathematical modeling of mobility controlled CO_2 flooding.

Abstract:

Experiments on gas mobility control, conducted in linear sand-pack models, have shown only a general correlation with static foam tests. Static tests, which use a blender to generate foam from an aqueous surfactant solution, are mostly useful for studying the effects of pH, temperature, salinity, and crude oil on the relative foamability of any given surfactant. In general, all surfactants which produce reasonable quantities of foam in the blender test also impart some degree of mobility control to gas during two-phase flow. The best mobility control additives, however, produce only modest volumes of foam. All surfactants spontaneously produce a viscous foam under fluid flow similar to reservoir conditions.

Three basic chemical structures appear to show most promise for gas mobility control. They are:

- Ethoxylated adducts of C_8-C_{14} linear alcohols.
- Sulfate esters of ethoxylated C_9-C_{14} linear alcohols.
- Low molecular weight copolymers of ethylene oxide and propylene oxide.

Each of these structures is compatible with normal oil-field brines, unaffected by the presence of crude oil, and stable under conditions common in a petroleum reservoir. Additive stability is of vital concern. Limited experimentation suggests that only the sulfate esters might degrade at an unacceptable rate and, therefore, be limited to lower temperature reservoir application. No degradation was noted for structures 1 and 3 in aging tests lasting two weeks at 125°F.

Conclusions:

- Apparatus design and construction have been completed, and the apparatus can operate at temperatures up to 170°F. In general, with all other factors being equal, additives that produce generous quantities of foam in static tests also display superior performance in mobility control flow tests in linear sandpacks. The presence of mobility control additives does not interfere or detract from the miscible displacement process.

A.3 LABORATORY DISPLACEMENT TESTS

A.3.1

Title:

Displacement of Oil by Carbon Dioxide

Contractor:

New Mexico Institute of Mining and Technology, Socorro, New Mexico

Principal Investigators:

F. M. Orr, Jr. and J. J. Tabor

Objectives:

The objective of this research was to determine how and to what extent CO_2 contacts, mixes with, and displaces oil trapped during a waterflood; i.e., is the contact and displacement efficiency of the CO_2 impaired by the isolating water?

Core floods are being performed to study the effects of pore structure and the distributions of phases within it on miscible displacement efficiency. Flow visualization experiments examine qualitatively the impact of water on mixing of CO_2 and oil. Phase behavior and fluid property measurements provide the basis for calculations of the impact of phase behavior or displacement efficiency and hence for the interpretation of CO_2 displacements. Simulation work is an attempt to study interactions of mixing effects with phase behavior based on independent measurements.

Other objectives are to determine the effect of density and viscosity of fluids in the transition zone between CO_2 and oil on the development of an oil bank, to determine how mobility control additives affect favorable phase behavior of the CO_2-oil mixture, and to discover how field operations should be conducted in order to minimize the effects of gravity segregation and viscous fingering.

Abstract:

Visual observations were made of high-pressure CO_2 floods. The displacements were performed in two-dimensional pore networks etched in glass plates. Results of secondary and tertiary first-contact miscible displacements and secondary and tertiary multiple-contact miscible displacements were compared.

Three displacements were performed with no water present in each of three pore networks: (1) displacement of a refined oil by the same oil dyed a different color, (2) displacement of a refined oil by CO_2 (first-contact miscible), and (3) displacement of a crude oil at a pressure above the minimum miscibility pressure. In addition, three tertiary displacements were performed in the same pore networks: (4) displacement of refined oil by water followed by displacement by the same refined oil dyed to distinguish it from the original oil, (5) tertiary displacement of the refined oil by CO_2 (first-contact miscible), and (6) tertiary displacement of crude oil by CO_2 at a pressure above the minimum miscibility pressure. In addition, the recovery of oil from dead-end pores, with and without water barriers shielding the oil, was investigated.

Visual observations of pore level displacement events indicate that CO_2 displaced oil much more efficiently in both first-contact and multiple-contact miscible displacements when water was absent. In tertiary displacements of refined oil, CO_2 displaced effectively the oil it contacted, but high water saturations restricted the access of CO_2 to the oil. The low viscosity of CO_2 aggravated the effects of high water saturations because the CO2 did not displace water efficiently. CO_2 did, however, contact trapped oil by diffusing through water to reach, swell, and reconnect isolated droplets. Finally, CO_2 displaced crude oil more efficiently than it did the refined oil in tertiary displacements. Differences in wetting behavior between the refined and crude oils appear to account for the different flow behavior.

Conclusions:

Observations of displacements in two-dimensional pore networks lead to the following conclusions:

- The distance required to develop miscibility in secondary CO_2 floods was significantly less than the length of the pore models.
- A residual oil saturation to CO_2 developed in the region first penetrated by viscous fingers, as predicted by Gardner and Ypma.
- Configurations and movements of interfaces between CO_2-rich and oil-rich phases in CO_2-crude oil displacements suggested that the interfacial tensions were significantly lower than typical oil-water interfacial tensions. In secondary displacements in the models used here, low interfacial tensions appeared to have little effect on recovery efficiency because the second-phase saturation was always very low. In tertiary displacements, much of the displacement of oil occurred with two phases flowing simultaneously. Hence, low interfacial tension probably had a greater effect in the tertiary displacements.
- Displacement of waterflood residual Soltrol by a viscous miscible solvent (Soltrol) was relatively inefficient. Oil production and solvent breakthrough occurred almost simultaneously. While considerable residual oil was reconnected, much of it was recovered slowly by diffusion from dendritic ganglia given their shape by the surroun-

ding water. Significant fractions of the residual oil remained uncontacted by the solvent.

- Tertiary displacements of residual Soltrol were also inefficient because CO_2 did not displace water effectively. Given enough time, however, CO_2 did diffuse through the water to reach and swell trapped oil droplets. Experiments in dead-end pores blocked by water also demonstrated that CO_2 can reach trapped oil where a solvent insoluble in water would not.
- CO_2 contacted residual crude oil much more efficiently than it did residual Soltrol. Observations of oil-water interfaces and independent contact-angle measurements indicated that the crude oil wet the glass more strongly than did the Soltrol. Calculations of the conditions under which oil would occupy grooves at the edges of the pores indicated that continuous paths in the oil phase were more likely in the displacements of crude oil. Hence, differences in wetting behavior probably account for the better performance of the tertiary CO_2-crude oil displacements.
- Soltrol diffused more rapidly from dead-end pores into flowing CO_2 than it did into Soltrol. Phase behavior of CO_2-crude oil mixtures gave rise to capillary forces which acted to remove oil from dead-end pores bounded by capillary grooves.

A.4 RESERVOIR MODELING IN CO_2 FLOODING

A.4.1

Title:

Rsearch/Reservoir Characterizations and Recovery Process Studies

Contractor:

Lewin and Associates, Inc., Washington, DC

Principal Investigator:

Vello Kuuskraa and Edgar Hammershaimb

Objectives:

The work done on this project was performed primarily for the purpose of making the Lewin CO_2 flooding model usable and available for those who might need it. A user's guide was essential. In accomplishing this objective, it was necessary to document and review the model and to demonstrate how integral submodels could predict recovery, costing, and other economic aspects of CO_2 flooding.

Abstract:

The Lewin and Associates' CO_2 flooding model is capable of calculating oil recovery, CO_2 requirements, and economics as a function of process parameters (WAG versus continuous) as well as reservoir and crude oil characteristics. These capabilities permit various flooding processes and R&D improvements to be evaluated on a reservoir-specific basis.

This report is in two parts. The first part describes the model used to estimate EOR by CO_2 flooding and includes the model derivation and verification. The second part illus-

trates how the CO_2 recovery, technology, and economic submodels predict flood performance and economics as a function of alternative processes, reservoirs, and economic parameters.

The model is based on theoretical considerations, scaled physical model results, and a comparison with reported field tests for Crossett, Little Creek, and Slaughter Estate oil fields. Separate models were developed for analysis of pattern flooding in flat reservoirs and of gravity stable, down-dip displacement in inclined reservoirs.

Conclusions:

- The CO_2 flooding model has been made operational on the Morgantown Energy Technology Center computer.
- The model has been refined by using data from field tests.
- A user's guide has been developed for the CO_2 model.

A.5 FIELD TESTS

A.5.1

Title:

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

Contractor:

Pennzoil Company, Parkersburg, West Virginia

Principal Investigators:

John Blomberg and Paul King

Objectives:

The objectives of this field test were (1) to determine the efficiency of injecting CO_2 for oil displacement in a tertiary mode following waterflooding on low-pressure gas recycling in a shallow, low-temperature reservoir and (2) to evaluate the displacement efficiency of the process by obtaining a pressure core in a part of the reservoir that had been contacted by CO_2.

Abstract:

The pilot test consisted of two adjacent, 10-acre, normal five-spot patterns surrounded by 13 water injection wells which maintained the minimum miscibility pressure (MMP) and prevented 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. In June 1980, after the injection of 23,842 tons of CO_2, Pennzoil certified the Rock Creek project under the DOE Tertiary Incentive

Program, which allowed the injection of 12,000 additional tons of CO_2 into the pattern. In addition, a 1.55-acre, four-spot pattern was developed within the pilot area to accommodate a 25 percent pore volume slug of CO_2 (compared with the original 10 percent pore volume slug for the original pilot area). Injection resumed in the fall of 1980 and was completed in January 1982.

Cumulative oil production from the pilot test was 27,694 barrels through December 1982 of which 17,291 barrels could be attributed to CO_2 injection in the 20-acre pilot flood. The CO_2-injected per barrel-of-oil-recovered ratio was 13,500 scf/bbl. A highly successful project might have had a ratio of 5,000 scf/bbl.

Pressure cores were taken from wells drilled after the test to evaluate displacement and vertical sweep efficiency. Results are currently being evaluated.

Conclusions:

The following conclusions were drawn from the results of this study:

- Pressure coring results indicate that tertiary displacement by CO_2 flooding is capable of reducing the oil saturation from 35 percent after waterflooding to 5 percent in the contacted portions of the reservoir.
- Mobility control is required to increase the volumetric sweep efficiency and, in turn, the recovery efficiency.
- The Rock Creek project was a technical success, but because of the excessive CO_2 requirements, it was an economic failure.

A.5.2

Title:

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

Contractor:

Shell Oil Company

Principal Investigator:

George 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. Success in this project should encourage similar projects in other similar Gulf Coast reservoirs.

Abstract:

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

Reservoirs of this type are not suitable for surfactant flooding as the temperatures and water salinities are too high for currently available chemicals. 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 CO_2 injected down-dip would tend to float to the top of the watered-out reservoirs because viscous forces are very small compared to gravity forces. Downward CO_2 displacement is designed to utilize gravitational forces to stabilize the displacement and increase the sweep efficiency of the injected CO_2.

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

During Phase II, a 50,000-ton slug of CO_2 containing 5 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.

During the third quarter of 1983, daily flowing production averaged 352 barrels of oil, 1,273 barrels of water, and 4.47 MMcf of gas. Cumulative oil production was 125,000 barrels by the end of the quarter, and oil production had exceeded the projected remaining water-drive ultimate recovery by 60,000 barrels.

Conclusions:

The following conclusions were drawn from the results of this study:

- Confirmative water-drive residual oil saturations were obtained through core analysis and the log-inject-log technique.
- Observations indicate that a gravity-stable CO_2 displacement has occurred in the "S" Sand, Reservoir B.
- The oil column thickness appeared to have increased from an initial value of 23 feet to 57 feet.
- Concurrent work at Shell's Bellaire Research Center indicated that a gravity-stable immiscible CO_2 displacement can recover substantial oil from watered-out sands having a three-phase oil relative permeability similar to that of the "S" Sand.
- State-of-the-art, three-phase relative premeability models were not applicable to the "S" Sand.

A.5.3

Title:

Enhanced Oil Recovery by CO_2 Miscible Displacement in the Little Knife Field, Billings County, North Dakota

Contractor:

Gulf Oil Company

Principal Investigator:

J. E. Upton

Objective:

The principal objective of this field test was to confirm the results of laboratory CO_2 miscible displacement tests and to show that the CO_2 miscible displacement process has potential for commercialization in southwestern U.S. and Rocky Mountain area carbonate oil reservoirs that had not been extensively waterflooded and that had a high remaining oil saturation.

Abstract:

A CO_2 mini-test was conducted in the Mission Canyon Formation (lower Mississippian) at Little Knife Field, North Dakota. The Mission Canyon is a dolomitized carbonate reservoir which is undergoing primary depletion.

Four wells were drilled in an inverted four-spot configuration covering 5 acres. The central well served as the injection well and was surrounded by three nonproducing observation wells. Oriented cores were cut in each well for detailed reservoir characterization and laboratory testing. In addition, a well test program was conducted which involved two pulse tests and injectivity tests on the individual wells. Results from these tests were used as part of the input data for two reservoir simulation models. Various parameters in the computer models were varied to determine the most efficient injection plan for the specific reservoir characteristics.

A WAG-type injection sequence, selected on the basis of simulation studies, utilized five alternate slugs of formation water and CO_2. Preflush injection began December 11, 1980, followed by the WAG slugs from January 7 to March 25, 1981. Drive-water injection commenced immediately and was completed on September 24, 1981. Injection rates were maintained at 1,150 B/D during water injection and 40 T/D during CO_2 injection. Alcohol tracers were used during the waterflood preflush and with the water during the WAG injection period.

Fluid samples and cased-hole logs from each observation well, obtained on a periodic basis, were used to determine the advance of the injected fluids. In analyzing the data, it was evident that the injected waters and CO_2 did reach each observation well. With the use of CO_2-isotope ratios, the arrival of the injected CO_2 at each observation well was accurately determined.

A pressure core behind the flood front was obtained to confirm residual oil saturations in the project interval. Overall rock recovery was excellent, 90 percent, but sample recovery under reservoir pressure was less than anticipated. Invasion of drilling fluids during coring was measured by introducing a radioactive tracer into the coring fluid.

A compositional simulation model was used to history-match the field performance of the CO_2 mini-test. A detailed reservoir characterization was developed and used in the simulator to match bottom-hole pressures, water and CO_2 breakthrough times, and fluid saturation histories at the observation wells. The effects of gravity segregation, stratification and crossflow, and reservoir heterogeneity were also investigated.

The pattern sweep efficiency for carbon dioxide approached 52 percent in the mini-test area. Displacement efficiency, as indicated by simulation study, was 50 percent of the oil-in-place at the start of the project, compared with an efficiency of 37 percent for waterflood. Thirty-one hundred (3,100 scf) cubic feet of CO_2 were required per incremental barrel of displaced oil. The absence of producing wells and the fact that only one zone within the Mission Canyon Formation was flooded, favorably influenced these figures.

The Little Knife CO_2 mini-test confirmed, by field testing, the results of laboratory CO_2 miscible displacement tests. The minitest indicated that the CO_2 miscible displacement process has technical potential for commercialization in a dolomitized carbonate reservoir that has not been extensively waterflooded and has an indicated high remaining oil saturation.

Conclusions:

The following conclusions were drawn from the results of this study:

- The Little Knife CO_2 mini-test confirmed, by field testing, the results of laboratory CO_2 miscible displacement tests. The mini-test indicated that the CO_2 miscible displacement process has technical potential for commercialization in a dolomitized carbonate reservoir that has not been extensively waterflooded and that has an indicated high remaining oil saturation.
- The mini-test was carried out without major difficulties. CO_2 and water were injected at the planned rates, and pressure was maintained in the 5-acre-project area above the 3,400 psi minimum miscibility pressure.
- Many techniques were successfully used to characterize the reservoir and the fields as well as to monitor the test performance. A logging method that utilized pulsed neutrons to measure capture cross sections and the ratio of near-to-far detector count-rates monitored fluid saturations to the required precision. Also, bottom-hole pressure, fluid samples, tracers, carbon isotope analyses, pulse tests, pressure cores, laboratory tests, simulation runs, and a detailed geological study all contributed to the test design and interpretation.
- Materials used in the mini-test wells performed satisfactorily. However, corrosion may have differed from measured rates had the wells been continuously produced.
- Both the logs and pressure core results showed zones at very low oil saturations (less than 5 percent) in regions swept by both CO_2 and water, confirming the development of multiple contact miscibility and high displacement efficiencies observed in the laboratory.
- A numerical compositional simulation model provided a satisfactory history-match of the pressures, saturations, and fluid compositions observed throughout the test, effectively combining the fluid property data, reservoir description, and process mechanisms.
- No unexpected anisotropies were encountered. Areal sweep was apparently 100 percent of mini-test pattern. Vertical sweep of CO_2 was incomplete because of stratification and the possible occurrence of viscous fingers. The vertical sweep efficiency was approximately 52 percent. Pattern sweep efficiency for carbon dioxide approached 52 percent.
- The displacement efficiency of the CO_2 miscible process, as indicated by the simulation study, for the 5-acre mini-test area was 50 percent of the oil-in-place at the start of the project, compared with an efficiency of 37 percent for a waterflood. Thus, only 3.1 Mscf of CO_2 were required per incremental barrel of displaced oil. The absence of producing wells, and the fact that only one zone within the Mission Canyon Formation was flooded, favorably influenced these figures.

APPENDIX B — BIBLIOGRAPHY OF RECENT DOE PUBLICATIONS

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