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Gas Miscible Displacement Enhanced Oil Recovery

Technology Status Report

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EXECUTIVE SUMMARY

Low reservoir volumetric sweep efficiency is the major problem associated with gas flooding and all miscible displacements. This problem results from the channeling and viscous fingering that occur due to the large differences between viscosity or density of the displacing and displaced fluids (i.e., carbon dioxide and oil, respectively). Simple modeling and core flooding studies indicate that, because of differences in fluid viscosities, breakthrough can occur at 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 mobility control, computer simulation, and reservoir heterogeneity studies.

Three mobility control methods have been investigated: the use of polymers for direct thickening of high-density carbon dioxide, mobile "foam-like dispersions" of carbon dioxide and aqueous surfactant, and in situ deposition of chemical precipitates.

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 are being investigated. This concept involves altering the flowing viscosity of the gas so that viscous fingers are suppressed and displacement is sustained in a piston-like manner. Previously unswept regions should be contacted as well as the watered-out regions of the reservoir.

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

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

The role that reservoir heterogeneity plays on the miscible gas enhanced oil recovery process performance is being investigated. This effort is aimed at quantifying the effects of reservoir heterogeneity on carbon dioxide floods in reservoirs with large well spacing and relative low permeability. The overall problem of detection, characterization, and representation of the effects are being investigated.

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

1.0 INTRODUCTION

Petroleum provided 44 percent of the total energy consumed in the United States during three-fourths of 1987, according to the Energy Monitor (1987). Even with intensive conservation efforts and the conversion of some power plants to alternate fuels, the United States will continue to require vast amounts of liquid fuels for the foreseeable future.

According to the Weekly Petroleum Status Report (1987), the amount of liquid fuels (including both crude oil and refined products) imported by the United States averaged 6.0 million barrels per day in the first 9 months of 1987, or 36.4 percent of the total United States' demand. This represents an increase in imports of 6.0 percent over the same period in 1986 and an increase in percentage of the total United States' demand, from 31 percent over the same period in 1986.

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 and secondary (water-flooding) recovery techniques produce only about one-third of the original oil in place. Therefore, it is essential that only enhanced oil recovery (EOR) techniques be made economical so that more oil can be recovered. Oil recovered by EOR technology has been defined as the incremental ultimate oil that can be economically recovered from a petroleum reservoir, in excess of that which can be economically recovered by conventional primary and secondary methods.

Of the more than 300 billion barrels of crude oil remaining in existing developed fields after conventional production, it has been estimated that approximately 45 billion additional barrels can be recovered by all EOR techniques. Present proven conventional reserves amount to 26 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.

There are three EOR processes: thermal, chemical, and miscible. Miscible flooding is generally recognized as most promising process. Miscible floods that use carbon dioxide (CO_2), nitrogen, hydrocarbons as miscible solvents hold great potential in the enhanced recovery of low-viscosity light crude oil (> 20° API gravity). CO_2 miscible flooding on a large scale is relatively new, and is expected to be the most important of the miscible methods in the future. Many large-scale commercial CO_2 miscible projects have been started in west Texas as CO_2 became available from large natural sources in Colorado and New Mexico. In addition, CO_2 miscible projects have been initiated in reservoirs located in Mississippi, Oklahoma, New Mexico, and Colorado.

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 technical problems: (1) availability and cost of CO_2, (2) poor mobility control of injected fluids, and (3) lack of reservoir knowledge and understanding.

In the 1984 National Petroleum Council study of EOR potential in the United States, tertiary oil recovery from gas miscible displacement was estimated based on currently implemented technology and future advanced technology. Mosbacher (1984) cited that the implemented technology outcome from the $30-per-barrel base case study shows 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.

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 is needed to further advance gas miscible EOR.

2.0 PROGRAM OBJECTIVES

The United States Department of Energy (DOE) EOR program's lead office is the Bartlesville Project Office in Bartlesville, Oklahoma. The EOR program is divided into a light oil (> 20° API gravity) enhanced recovery program, a heavy oil (10° to 20° API gravity) enhanced recovery program, and the tar sand program. The gas miscible EOR processes are best suited for light oil reservoirs and are, therefore, a part of the light oil enhanced recovery program. These processes include the miscible CO_2 flooding process operated in Morgantown, West Virginia, at the Morgantown Energy Technology Center (METC).

The CO_2 EOR program, as it applies to light oil, has four goals:

1. Improve the predictability of the CO_2 gas miscible EOR process.

2. Improve the performance of the CO_2 gas miscible EOR process.

3. Assess the feasibility of long-range, high advanced, emerging technologies for the CO_2 gas miscible EOR process.

4. Extend the range of application of the CO_2 gas miscible EOR process to reservoirs for which no EOR technology currently exists.

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

3.0 STATE OF TECHNOLOGY

After the secondary recovery of oil by water flooding, a certain amount of residual oil remains in the pore space 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 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 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. Both reduction of viscosity and the increase in relative permeability to oil will facilitate flow of the swollen oil to the production well.

The reduction of viscosity and the increase in relative permeability also take place in CO_2 miscible displacement. In addition, miscibility entails, by definition, the elimination of the interface between the CO_2 and the oil. Thus, when miscibility occurs, capillary forces will become zero and essentially 100 percent of the oil can be displaced from the part of the reservoir contacted by CO_2. Miscibility between CO_2 and crude oil, however, requires more restrictive conditions of temperature and pressure than simply the dissolving of CO_2 in the oil. At any given temperature, there is a minimum miscibility pressure (MPP), usually 1,000 pounds per square inch (psi) pressure or greater, below which the interface will remain. In addition, 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 CO_2 vapor phase so that the vapor phase becomes miscible with the crude oil.

In order to determine the chances of conducting a successful CO_2 miscible displacement, information must be obtained from several sources. Slim tube tests are used to determine the MMP. In these tests, $\leq$ 0.25 inch internal diameter tubing, possibly 80 feet long are packed with glass beads or unconsolidated sand, saturated with reservoir oil, and flooded with CO_2 at reservoir temperature and various pressures. 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 reservoir formation with a natural or poorly oriented fracture system and a widely varying permeability profile 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 (gravity or buoyancy override) to the top of the formation and form a gravity tongue, i.e., advance more rapidly at the top of the reservoir than in lower portions of the rock. The low viscosity of CO_2 permits the formation of viscous fingers or small channels in which the CO_2 rapidly moves from the injection well to the production well, bypassing a large part of the oil.

The low CO_2 viscosity and the normally high relative permeability to CO_2 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 well bore, this method cannot control its movement. Production wells can be shut in or flow can be restricted. Without the pressure sink which the wells normally provide, the CO_2 will be less likely to channel until the wells are put into production once more. Foams or emulsions formed with surfactants and water may be successful in partially reducing flow rates in swept channels. The method most widely used in practice to control CO_2 mobility is the water-alternating-with-gas (WAG) procedure where CO_2 gas and water are injected alternately. Although this method may temporarily reduce the channeling tendency of the CO_2, 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 time, foams or emulsions formed with surfactants and water appear to have the greatest promise in lowering CO_2 mobility. A great deal of study remains to be done, however, in this area of mobility control.

Several operational problems exist in CO_2 flooding that can be solved or alleviated by relatively routine techniques. CO_2, when dissolved in water, forms corrosive carbonic acid. Prior to transporting the gas in pipelines and distribution systems and injecting it down well bores, 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 well bore. 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 well bore, 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} hydrocarbon components from crude oil in the formation may result in the precipitation of paraffin crystals or asphaltenes. These solid materials may partially or totally plug the formation unless a solvent wash is used to redissolve them.

When CO_2 is produced, it is mixed with hydrocarbon gases. The CO_2 reduces the heating value of the natural gas, and methane mixed with CO_2 increases the MMP substantially. Therefore, the CO_2 must be separated from the hydrocarbons so that the hydrocarbons can go through normal 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, New Mexico, Wyoming, and Mississippi. Pipelines are either in use or under construction to transport this gas to oil field areas 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 normally is 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 composed of the costs of source development, compression, dehydration, transportation, distribution, injection, production, separation and recovery, and recompression. If the cost of CO_2 can be held near $1.50 per thousand cubic feet (Mcf) (1987 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.

4.0 CURRENT RESEARCH IN CARBON DIOXIDE FLOODING ENHANCED OIL RECOVERY

DOE/METC's CO_2 EOR program includes R&D projects with the petroleum industry and universities. The work breakdown structure, shown in Figure 1, shows the specific research topic of each industry and university participant. This comprehensive approach covers the broad technology needs of the CO_2 EOR program. Each fiscal year (FY) 87 project is summarized below.

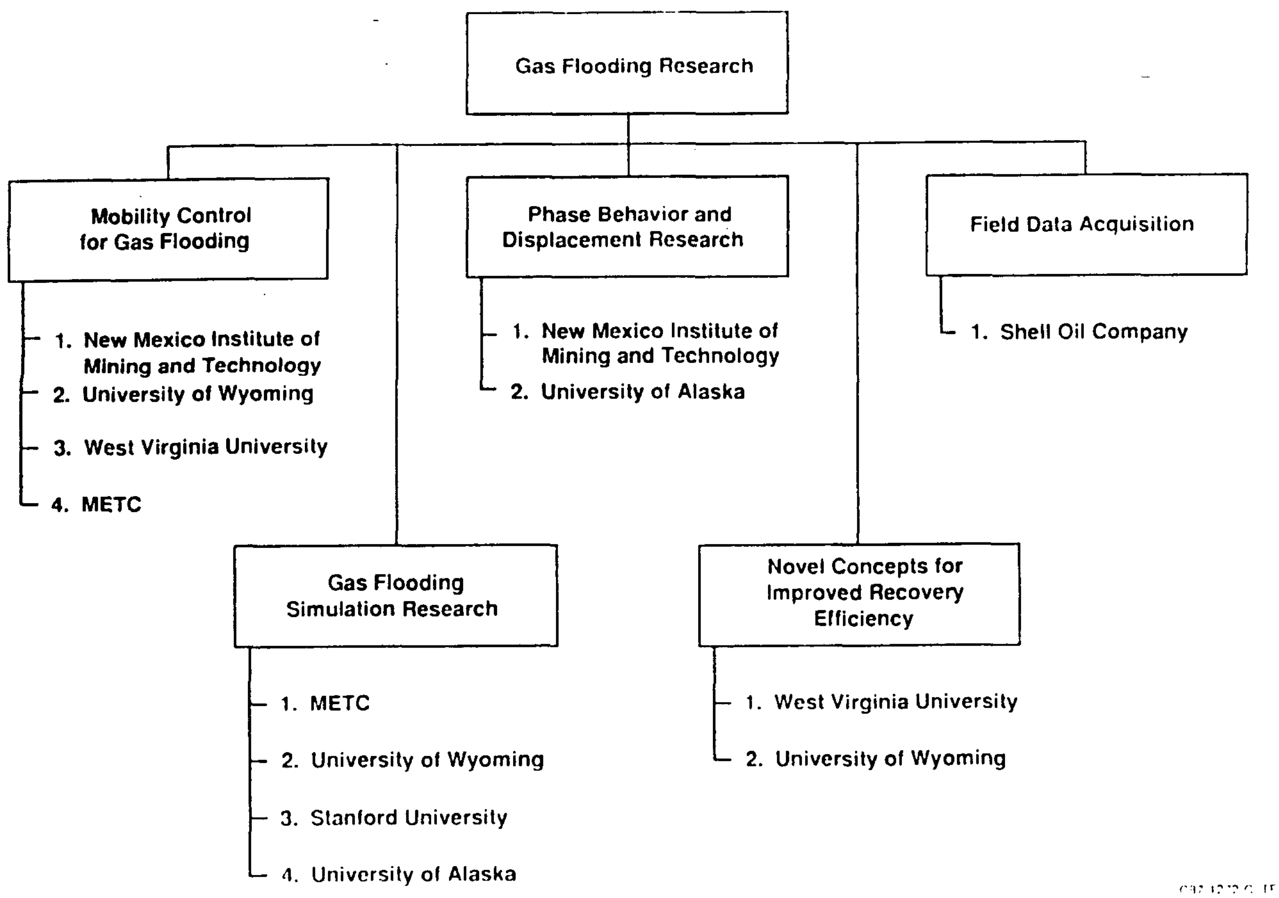

Figure 1. Work Breakdown Structure for CO_2 Gas Flooding Research

4.1 Mobility Control

Three mobility control methods have been investigated: the use of polymers for direct thickening of high-density CO_2, mobile "foam-like dispersions" of CO_2 and aqueous surfactant, and in situ deposition of chemical precipitates.

Success in the search for CO_2-soluble polymers has been limited. Polymers that dissolve into high-density CO_2 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 CO_2.

Mobile foam-like dispersions of CO_2 are also being investigated. This concept involves altering the flowing viscosity of the gas so that viscous fingers are suppressed and displacement is sustained in a piston-like manner. Previously unswept regions should be contacted as well as the watered-out regions of the reservoir.

Several contractors are undertaking research on mobility control. Their progress is summarized below.

4.1.1 Improvement of CO_2 Flood Performance, New Mexico Institute of Mining and Technology

This project has the following objectives:[1]

1. Measure the mobility of CO_2-foam using several surfactants on various oil field rock types over broad ranges of flow rates, surfactant concentrations, and flowing volume ratios. Related measurements 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 the various operation engineering problems that will accompany the field use of mobility control additives in CO_2 floods.

Measurements of CO_2 Foam Mobility

The effect of rock sample permeability on the mobility of CO_2 foam has been investigated. Two different kinds of sandstone were studied -- Rock Creek sandstone with a permeability of 14.8 mD, and Berea sandstone with an average permeability of 305 mD. The magnitude of the relative mobility (the ratio of mobility to rock permeability) for the Rock Creek sandstone is approximately 36 times higher than that for the Berea sandstone, although the

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[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.

inverse ratio of permeabilities is only about 21. Two different kinds of surfactants were tested with each rock sample. Concentrations of 0.1 percent Chembetaine BC-50 (a Zwitterionic surfactant) and (in an earlier experiment) 0.05 percent Alipal CD-128 (an Anionic) were used in tests with Rock Creek sandstone. With Berea sandstone, 0.03 percent Varion CAS (Z) and 0.05 percent Enordet X2001 (A) were used. The effect of sample permeability overshadows that of the type of surfactant, at least in these sandstone samples. In previous tests, the influence of surfactant concentration on foam mobility had been studied, and a first estimate given of the range of mobility that could be attained by varying this parameter.

In the plots of relative mobility versus flow velocity, particularly at high rates of flow, there is sometimes, but not always, an upward trend -- an increase of relative mobility at higher velocity. Classical shear thinning or pseudo-plastic behavior consists of a nearly constant flow-to-pressure ratio for small pressures, increasing by as much as two orders of magnitude with increasing pressure. The resistance of such fluids to the applied pressure decreases with stress, as if these materials are "yielding." The dependence of CO_2-foam mobility on velocity is not this extreme, but some "shear thinning" is evident.

Assessment of Mobility Control Additives in CO_2 Floods

Corefloods remain the most efficient laboratory procedure for assessing mobility control additives, although their results cannot be taken as direct indications of reservoir flooding efficiency. The dimensions of the core must be great enough that viscous fingers can develop from frontal instability, with no interference from transverse dispersion with the largest wavelength disturbances. A set of displacements has been carried out in an approximately 1.9-inch diameter, 28-inch long sample of a quarried dolomite rock. This set included a waterflood to residual saturation, and a tertiary displacement with unthickened propane at 1,200 psi. The core is currently being prepared for a similar series that will culminate in a flood with propane thickened with diamylbutyltin fluoride, one of the more effective of the direct thickeners. The same core will then be used in runs using CO_2 foam as the mobility control agent. The results of these floods are influenced both by the nonuniformity of the rock sample and by the presence in the first flood of fairly strong viscous fingering.

Reservoir Engineering Aspects of CO_2-Foam and Direct Thickeners

In accordance with the initially announced goals of the project, NMIMT has considered the reservoir engineering aspects of these mobility control additives (CO_2 foam and direct thickeners). A major difference between CO_2 foam and direct thickeners is the mechanisms by which the pressure gradient is generated in the region behind the front that is saturated by the displacing fluid. This difference is important for deciding the quantities of additive needed to achieve a desired mobility reduction, and the manner in which it is applied. Less flexibility in achieving a desired mobility can be expected with CO_2 foam than that which will probably be possible with a direct thickener (when one is produced for use in CO_2).

Direct Thickeners

Three general strategies, or methods of synthesis, are being studied in the effort to develop direct-thickening materials that will produce viscous, polymeric solutions in dense gases like CO_2: Methods I, II, and III. Method I concerns the synthesis of multicomponent, high-polymer systems using various higher olefins as monomers. Method II will evolve as a result of the progress made in Method I and is concerned with the synthesis of new ionomers. Method III involves the use of novel organic compounds, e.g., tri-alkyltin fluorides, to make dense CO_2 viscous. Method I polymers have been explored almost as far as the limits originally envisaged. However, work in this area will continue in order to answer some remaining questions concerning the relationship between polymer structure and solubility in dense CO_2. In the general area of Method II, there are many more unknowns yet to be discovered. The pace of the studies on ionomers has been limited to some extent because of the unavailability of appropriate GC columns to monitor the polymerizations during the last several months. Nevertheless, the potential usefulness of this type of direct thickener cannot be ignored, and it is expected that Method II research will receive more attention in the future. Lastly, a great deal of research has been devoted to the study of Method III compounds. This emphasis will continue, as small variations in the structure of RSnF produce strikingly different solubility behavior. It may consequently be possible to improve substantially the solubility of radical tin fluorides (RSnF) in CO_2 by introducing appropriate R groups. As RSnF becomes more soluble in CO_2, CO_2 would become more viscous, as it is a nonpolar solvent.

4.1.2 New Concepts for Improving CO_2 Flooding, University of Wyoming

This project has the following objectives:

1. Investigate the recovery of oil from a large, laboratory-scaled physical model using a CO_2 line-drive injection scheme versus the conventional point-source injection scheme.

2. Investigate the viability of polymerizing CO_2-soluble monomers in order to increase CO_2 viscosity, which would increase control of CO_2 mobility.

3. Complement the physical model experiments with representative mathematical modeling.

Figure 2 shows schematics of the line-drive injection physical model and the point-source injection physical model. Figure 3 shows the recovery at two pore volumes injected for both the line-drive injection scheme and the point-source injection scheme. These tests were run with n-heptane at 100°F. The figure shows that recovery is consistently about 8 percent of a pore volume higher with the line-drive injection scheme than with the point-source injection scheme. Because the other variables in this model were held constant, the increase can be directly attributed to the injection scheme. This additional recovery represents a 22 percent relative increase in recovery when the MMP is exceeded at 1,200 psi. The percent of additional recovery tends to decrease with increasing recovery.

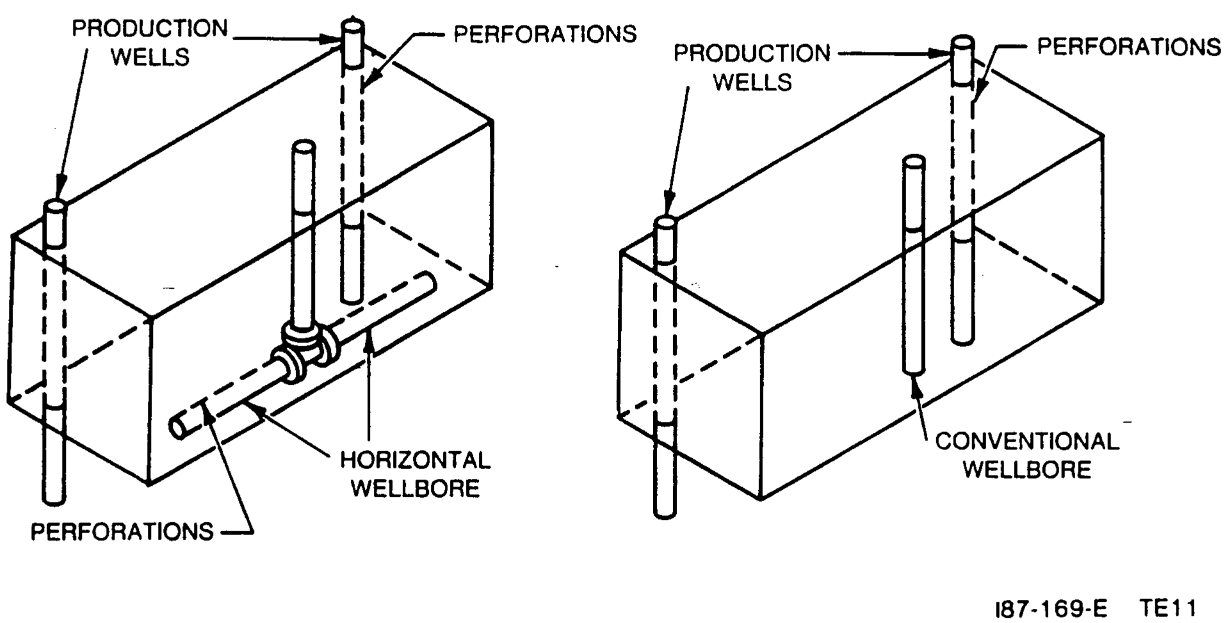

Figure 2. Schematics of the Physical Model

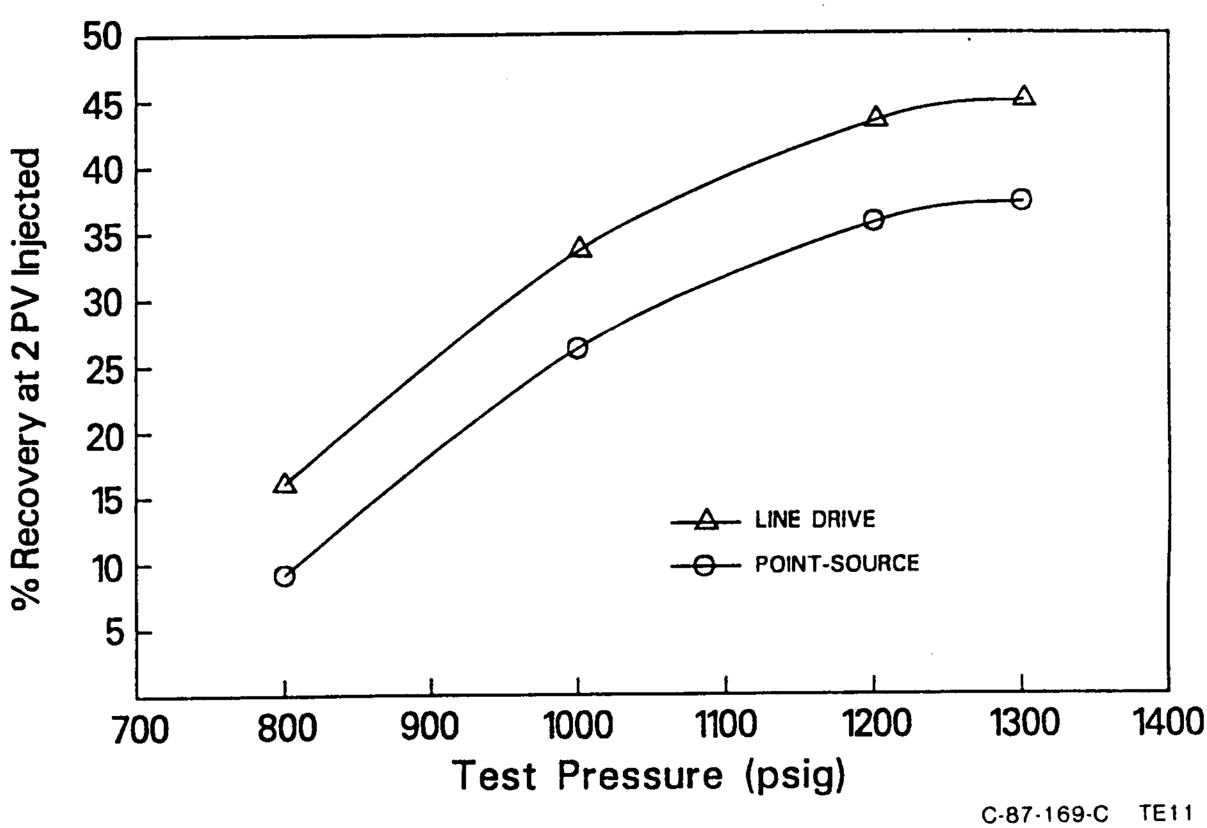

Figure 3. Percent Recovery Versus Pressure at 2 PV Injected for the Line-Drive and Point-Source Injection Schemes

Economic Analysis of Horizontal Injection Techniques

A major effort was to attempt to quantify the profitability of the horizontal injection technique. To do this, an economic analysis was performed. Reservoir characteristics were selected from a field where a CO_2 flood is planned for the near future. A drilling service company provided an estimate of the cost of drilling two horizontal lateral wells into the pay zone from an already existing vertical well. The parameters used in the analysis are given in Table 1.

Table 1. Base Case Data for Economic Analysis

Spacing for Inverted 5-Spot Pattern	40 acres
Net Pay Section	150 ft
Porosity	10.3 percent
Expected Incremental Tertiary Recovery	11.6 percent
Recoverable Oil	3.26 MMbbl
Cost for Two 700-Ft Lateral Wells	$300,000
Oil Price	$24/bbl
Relative Increase in Tertiary Recovery	24 percent

The base case parameters for oil price and relative increase in oil recovery using EOR techniques need some further explanation. The oil price of $24/bbl was chosen before the recent downturn in oil prices. However, subsequent sensitivity studies should allow one to predict the feasibility of the horizontal well scheme in today's oil market. It should also be noted that the $300,000 estimate for the lateral wells was determined before the downturn. Recent discussions with the same service company indicate that the lateral wells could probably be drilled for half to two-thirds of the above cost. Thus, the uncertainties in these two prices would somewhat offset one another.

The 24-percent relative increase in oil production was chosen based on the experimental results that are shown in Table 2. It appears that the increase in oil production that results from the use of the horizontal injector (line source) is fairly independent of how much CO_2 is injected. It should be noted that the results of the laboratory experiments are not, by themselves, directly applicable to what one might expect to see in an actual field test. However, the assumption will be that if the expected incremental oil recovery using EOR techniques is 11.6 percent of the original oil in place (using point-source injection), the resulting production using the horizontal wellbore injection technique will be 1.24, 11.6, or 14.4 percent of the original oil in place.

The three main economic parameters (oil price, cost of the lateral wells, and increase in production) were varied ± 40 percent from their base cases in order to evaluate the sensitivity of the project to them. The results of

Table 2. Recovery at 1,300 psi as a Function of Amount of CO_2 Injected

CO_2 Injection (Percent Pore Volume)	Point Source (Percent)	Line Source (Percent)	Ratio of Line-Source to Point-Source
0.25	9.12	11.56	1.27
0.50	18.00	23.17	1.29
0.75	24.36	31.07	1.28
1.00	29.48	35.82	1.22
1.25	32.40	39.05	1.21
1.50	34.00	41.19	1.21
1.75	35.28	43.08	1.22
2.00	36.71	44.72	1.22
			Overall -- 1.24

this sensitivity study are shown in the spider plot in Figure 4. The oil price was assumed to be essentially 100 percent profit for the additional oil (the difference between the amount of oil recovered from a horizontal well and that recovered from a vertical well) since no additional CO_2 would be injected with the horizontal injector, and all of the required surface facilities for the project would already be in place. The only additional cost for the additional oil production would be the lifting costs associated with the increased rates. The internal rate of return (IRR) was calculated by assuming that the investment was the cost of the lateral wells and that the income generated from the increased production was to be paid out over 10 years in annual annuities. This assumption is an obvious oversimplification since very little revenue is generated in the first few years of an EOR project. Nevertheless, it suffices to give an adequate indication as to the feasibility of drilling the horizontal lateral wells.

As mentioned, Figure 4 shows the sensitivity of the project to the three parameters (oil price, cost of the lateral wells, and increase in production). It should be noted that the variable recovery curve and the variable oil price curve are identical in their effects. The base case IRR is about 72 percent before taxes. The effect of the oil price (or relative recovery increase) on the IRR is for all intents and purposes a linear relationship. The -40 percent range on the oil price represents a selling price of $14.40/bbl. At this price, with the lateral wells costing $300,000 and a 24 percent relative increase in production, the IRR is still around 40 percent. Further calculations have shown that even under the severe conditions of high well cost ($420,000) and low oil price ($14.40/bbl), the IRR is still a respectable 29 percent. The above calculations lead one to conclude, based on this approximate analysis, that the cost of drilling the horizontal lateral wells can be justified for a CO_2 flood.

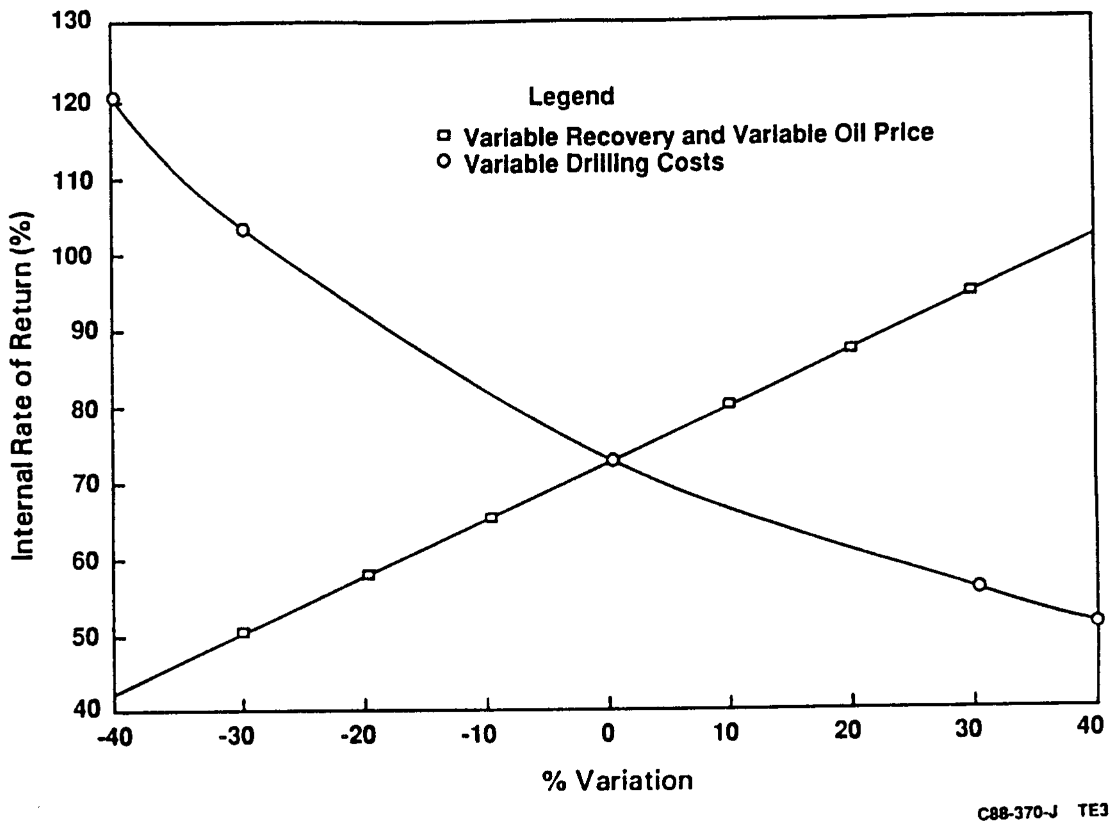

Figure 4. Sensitivity Analysis

Increasing CO_2 Viscosity by Polymerizing CO_2-Soluble Monomers

Polymerization of monomers in the presence of solvents was carried out with various initiators shown in Table 3. Table 3 shows the solvents, initiators, and monomers that were used in the experiments. In the experiments showing a trace of polymer, the trace was never analyzed. The trace usually appeared as a thick, polymer-like residue. In Run 8A, a significant amount of residue was found and analysis showed that the residue contained polyethylene. However, the solubility of the polyethylene, along with the other trace materials, was too low to raise the viscosity of CO_2. A total of 14 runs was conducted, but, while polymerization was achieved, no enhancement of CO_2 viscosity was noted.

4.1.3 Mobility Control, Morgantown Energy Technology Center

METC's in-house research on mobility control concentrates on the use of viscous CO_2 to improve the mobility ratio. The research includes both experimental and theoretical studies. The technique involves the use of surfactants to generate a CO_2 dispersion that would retard the growth of viscous fingers and also act as an in situ diverting agent. The merits of CO_2 dispersion are being determined by performing linear and radial core flow studies on

Table 3. Polymerization Experiments

Run No.	Solvent Used	Monomer Used	Monomer Concentration Volume %	Initiator Used	Initiator Concentration wt % of Monomer	Length of Experiment Hours	Pressure psi	Temperature °F	Polymerization Achieved?	Solvent Viscosity Enhanced?
1	CO_2	1-Octene	8	$2(C_6H_5COO)$	1.3	24	1,900	160	No	No
2	C_6H_{12}	1-Octene	6	$2(C_6H_5COO)$	2.3	24	0	160	Yes	No
3	CO_2	Ethylene	10	$2(C_6H_5COO)$	3.2	48	1,700	157	Yes	No
4	C_6H_{12}	Ethylene*		$2(C_6H_5COO)$	3g*	48	800	160	Yes	No
5	CO_2	Ethylene	20	$2(C_6H_5COO)$	3.0	48	1,800	160	Yes	No
6	CO_2	Ethylene	20	Trigonox-21	6.0	48	1,850	160	Yes	No
7	CO_2	Ethylene	50	Trigonox-21	3.0	35	1,850	170	Yes	No
8	CO_2	1-Decene	10	Trigonox-21	2.0	48	1,625	160	No	No
9	CO_2	Ethylene	20	Trigonox-21	2.0	48	1,750	160	Yes	No
10	CO_2	Ethylene	40	Trigonox-21	3.0	48	1,900	160	Yes	No
11	CO_2	1-Decene	20	Trigonox-21	1.5	48	1,700	160	No	No
12	CO_2	1-Octene	5	Trigonox-21	1.4	48	1,600	169	Yes	No
13	CO_2	Ethylene/ Octene	20	Trigonox-21	1.4	48	1,400	162	No	No
14	CO_2	Ethylene/ Octene	50	Trigonox-21	2.0	48	1,800	169	Yes	No

* Ethylene supply was open to reactor during the experiment. The exact monomer or initiator concentration was not measured.

large-scale laboratory systems. This effort is being supplemented by theoretical and experimental studies of CO_2 dispersions and studies of the effects of altered wettability of rock surfaces. The laboratory data are also being used to test the METC compositional model (CRSIM), and the model is being used to plan experiments.

Knowledge of surfactant/CO_2/oil/water/salt phase diagrams, including the effects of molecular structure, temperature, and pressure, should greatly aid the development of materials and processes for surfactant-based CO_2 mobility control. Often surfactants are sought that form stable fluid-fluid dispersions (emulsions, foams); and stable dispersions greatly increase the time and difficulty of measuring phase diagrams, especially at high pressures. These limitations apply most severely to the detection of boundaries between two- and three-phase regions, for which all previously used methods require separation of the dispersions into bulk phases.

Isoperibolic titration calorimetry provides a convenient method for detecting the phase boundaries in many EOR systems. Previous work has shown how the crossing of a phase boundary can be detected in the thermogram (plot of "temperature," i.e., thermistor voltage, versus "composition," i.e., titration time).

In many cases, the derivative of the thermogram is helpful for detecting a crossing of a phase boundary. Figure 5 is a plot of the derivative versus the titration time. The maximum in the derivative marks the beginning of the titration which ends at about 1,200 seconds. The crossing of the limiting

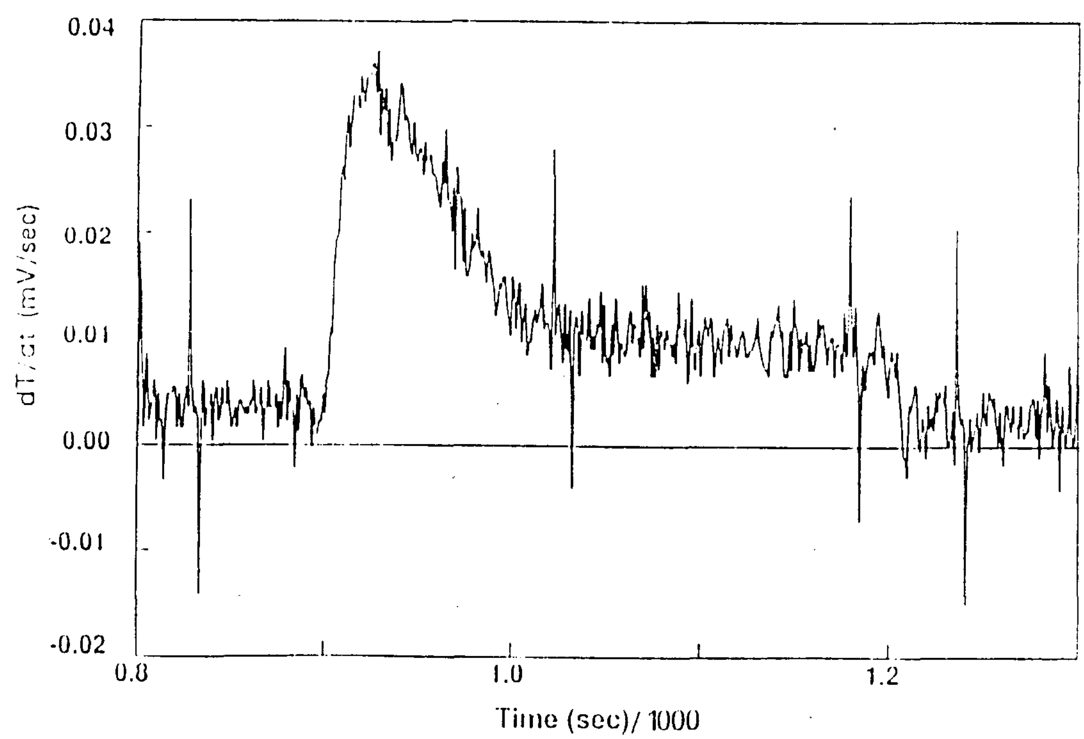

Figure 5. Derivation Versus the Titration Time for Detecting a Crossing of a Phase Boundary

tieline between two and three phases is seen as a large change of slope at about 1,000 seconds.

By suitable calibrations and calculations, the thermistor voltages can be converted to corrected experimental heats. Figure 6 shows the heat evolved during the titration of Figure 5. The heat curve becomes linear when the number of phases changes from two to three. (In Figure 6, unlike Figure 5, the start of the titration is defined as zero time.)

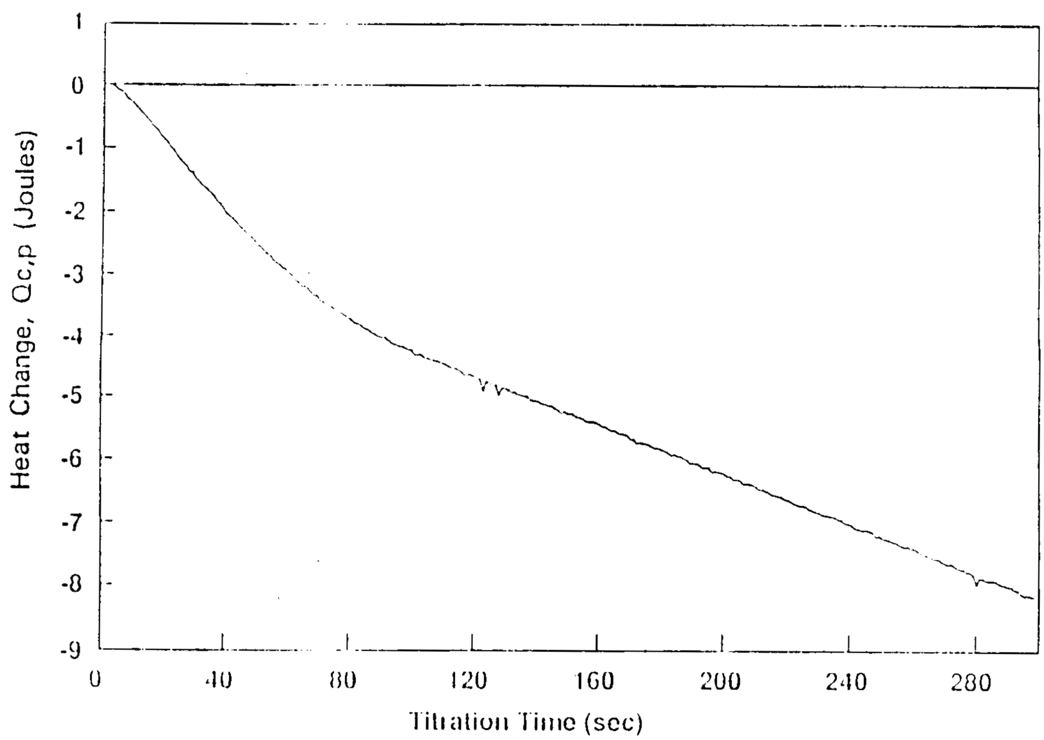

Figure 6. Heat Evolved During Titration

The following systems and temperatures have now been studied: CE/n-decane/water - 24.0° and 24.9°C; CE/n-hexadecane/water - 24.0°, 30.0°, and 35.0°C [CE = 2-butoxyethanol; CE = CH(OCH)OH].

Figure 7 shows the complete phase diagram of the CE/n-decane/water system at 24.9°C, as determined by isoperibol titration calorimetry. The central tie triangle defines the system compositions which form three phases; the corners of the tietriangle are the compositions of these three phases. (Note that the phase compositions were determined without any sampling or conventional analyses of the phases.) Two phases form in the areas on each side of the tietriangle, while a single liquid forms in the remaining portion of the phase diagram.

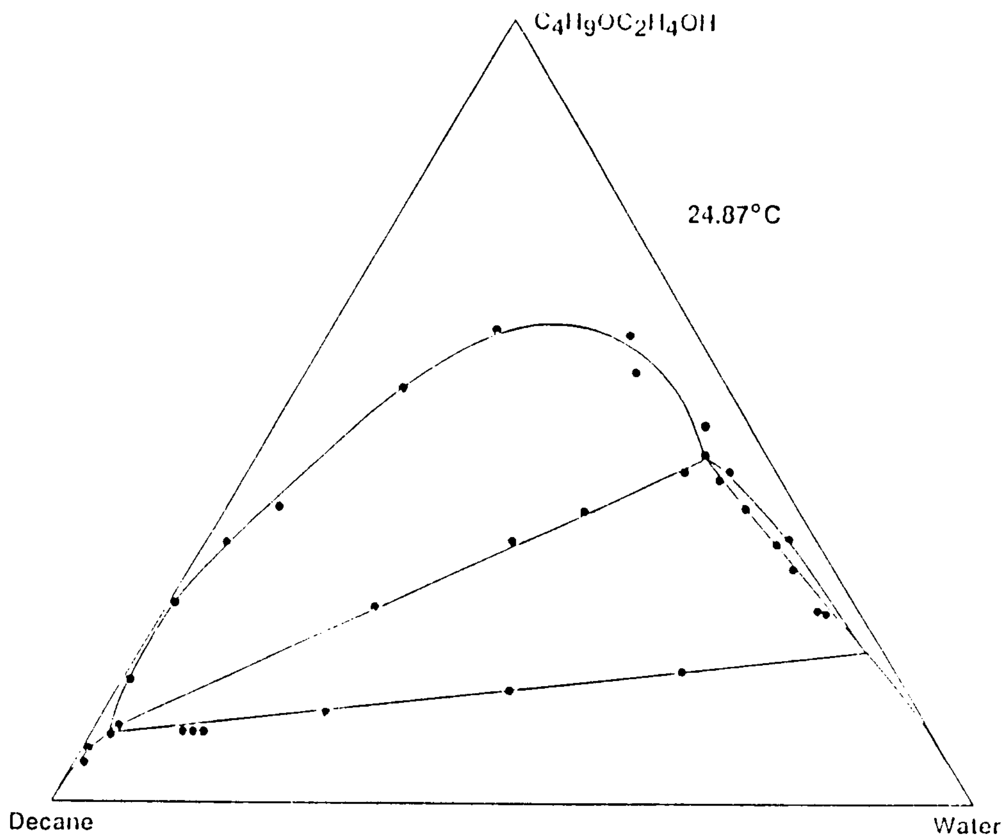

Figure 7. Phase Diagram for the CE/n-Decane/Water System

At 24°C (about 1°C above the lower critical endpoint temperature of the system of Figure 7), it was also possible to detect the "critical micelle concentration" (CMC) for formation of aqueous "micelles" saturated with decane. This fact is of particular interest because it appears to be the first time that the distance between the phase-boundary CMC and the aqueous corner of the tietriangle has been resolved. For amphiphiles of higher molecular weight, the middle phase and micelles appear to form at the same surfactant concentration.

Thermodynamic measurements on surfactant systems are usually made on single-phase solutions that are more or less distant from the compositions of two or more conjugate phases. However, as oil recovery almost always involves multiphase flow, it is the thermodynamic properties of conjugate phases that are needed for the design of EOR materials and processes.

Using isoperibol titration calorimetry, the EOR Group of DOE has made initial measurements of the "heats of formation" of the triconjugate (lower, middle, and upper) phases in a model amphiphile/oil/water system. The system and temperature chosen were n-butanol/n-hexadecane/water at 30.0°C, which are representative of the cosurfactants, equivalent alkane carbon numbers, and reservoir temperatures that are often encountered in the enhanced recovery of light oil.

Table 4 shows reported compositions for the triconjugate phases, along with our current "best values" for their heats of formation. The heat of formation is defined to be the heat produced per unit amount of the triconjugate phase from its formation by mixing of its constituent components. Heats of formation, along with entropies, are the fundamental chemical thermodynamic parameters that control the compositions and, thus, the physical properties of the conjugate phases. The heats in Table 4 are (to our knowledge) the first reported values of the heats of formation of triconjugate phases in an EOR system.

Table 4. Triconjugate Phase Compositions and Their Heats of Formation in n-Butanol, Hexadecane, and Water at 30°C

Phase	n-Butanol	Composition* Hexadecane	Water	Heat (J/100 ml)
Upper	15.4	83.8	0.80	+425
Middle	70.7	16.6	12.7	+798
Lower	6.69	< .003	93.3	-518

* Volume percent as mixed (Seeto, et al. 1983).

The instrument and techniques used to measure the heats of formation are similar to those that have been used to measure phase compositions by isoperibol calorimetry.

4.1.4 Radial Core Experiments, Morgantown Energy Technology Center

The objective of this research is to perform CO_2 miscible displacements of multi-alkane oils in a radial-flow system with compositional analyses of the effluents.

The radial-flow system shown in Figure 7 had a 1-foot-diameter core of 2-inch thickness and was equipped with accessories similar to those of a linear system. A miscible CO_2 injection test was conducted using the same 10-component hydrocarbon mixture as that used in the linear core. The injection rate of 150 milliliters per hour was used for all stages of flooding. (This was equivalent to a Darcy velocity of 23.2 feet per day at the injection face and 0.24 feet per day at the production face, with a mean value of 0.49 feet per day.)

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

Because of the problems of the equipment design, no further experiments will be performed until the apparatus has been redesigned.

4.1.5 In Situ Deposition of Chemical Precipitates, West Virginia University

Another method of mobility control is in situ deposition of chemical precipitates. Preliminary studies on this method of mobility control are ongoing. Chemicals that react with CO_2 under certain conditions will chemically precipitate in a formation, and block and divert the injected fluids into previously unswept regions of the formation that are highly saturated with oil.

This project has the following objectives:

1. Determine conditions and materials for optimum in situ chemical precipitation over 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 (1) the amount of precipitate formed under any condition of temperature, pressure, and concentration; (2) the degree to which chemical precipitates alter permeability and permeability profile in a reservoir; and (3) the improvement in volumetric sweep efficiency in the reservoir and the increase in oil recovery that result from using in situ chemical precipitation.

4. Define reservoirs to which in situ chemical precipitation is applicable.

Clean-Core Flow Tests

After preliminary testing was completed, a series of 19 clean-core flow tests was run with $BaCl_2$ and $CaCl_2$ at four pressures and four temperatures. A second series of tests was run with multiple slugs of the salt solution, CO_2, and NaOH. A third series of tests was run using single-slug treatments with two cores in series and with two cores in parallel. The soluble salts precipitated to carbonates to block permeability. Results are presented in Tables 5 and 6.

Table 5. Clean-Core Flow Test Schedule

Test No.	Chemical	Pressure	Temperature (°F)
Series One -- Single Core, Single Slug			
1	$CaCl_2$	1,500 psi	75
2	$CaCl_2$	1,500 psi	100
3	$CaCl_2$	1,500 psi	150
4	$CaCl_2$	1,500 psi	200
5	$CaCl_2$	2,000 psi	100
6	$CaCl_2$	2,000 psi	150
7	$CaCl_2$	2,000 psi	200
8	$BaCl_2$	1,000 psi	75
9	$BaCl_2$	1,000 psi	100
10	$BaCl_2$	1,500 psi	75
11	$BaCl_2$	1,500 psi	100
12	$BaCl_2$	1,500 psi	150
13	$BaCl_2$	1,500 psi	200
14	$BaCl_2$	2,000 psi	100
15	$BaCl_2$	2,000 psi	150
16	$BaCl_2$	2,000 psi	200
17	$BaCl_2$	2,500 psi	100
18	$BaCl_2$	2,500 psi	150
19	$BaCl_2$	2,500 psi	200
Series Two -- Multiple Slug			
1	$CaCl_2$	1,500 psi	100
2*	$CaCl_2$	2,000 psi	150
3	$BaCl_2$	1,500 psi	100
4*	$BaCl_2$	2,000 psi	150
Series Three -- Multiple Core			
1 Parallel	$CaCl_2$	1,500 psi	100
2 Parallel	$BaCl_2$	2,000 psi	150
3 Parallel	$CaCl_2$	1,500 psi	100
4 Parallel	$BaCl_2$	2,000 psi	150
5 Series	$CaCl_2$	1,500 psi	100
6 Series	$CaCl_2$	2,000 psi	150
7 Series	$BaCl_2$	1,500 psi	100
8 Series	$BaCl_2$	2,000 psi	150

* The 2,000 psi, 150°F tests for both chemicals were run using two different procedures (see text).

Table 6. Results From Clean-Core Flow Tests

Test No.	Pressure (psig)	Temperature (°F)	Porosity	Beginning Permeability	Ending Permeability	Percent Reduction
		Series One -- Single Core, Single Slug, 2.5 Percent $CaCl_2$				
1	1,000	75	17.72	150	111	26
2	1,000	100	16.41	180	83	54
3	1,500	75	16.33	156	61	61
4	1,500	100	17.62	135	71	47
5	1,500	150	16.86	120	56	53
6	1,500	200	16.41	101	77	24
7	2,000	100	17.72	149	76	49
8	2,000	150	16.41	131	70	47
9	2,000	200	18.24	137	57	58
10	2,500	100	17.62	112	48	57
11	2,500	150	18.24	163	67	59
12	2,500	200	16.86	105	44	58
13	1,500	75	17.72	91	51	40
14	1,500	100	17.99	138	67	51
15	1,500	150	17.62	164	69	60
16	1,500	200	16.33	138	68	51
17	2,000	100	17.72	141	57	60
18	2,000	150	17.72	119	77	37
19	2,000	200	16.33	149	83	44
			Series Two -- Single Core, Multiple Slug			
1	$CaCl_2$	1,500	100	164	98	40
2	$CaCl_2$	2,000	150	178	73	59
*3 1st	$CaCl_2$	2,000	150	119	77	35
2nd				77	70	9
3rd				70	52	26
Total				119	52	56
4	$BaCl_2$	1,500	100	97	27	72
5	$BaCl_2$	2,000	150	80	12	85
*6 1st	$BaCl_2$	2,000	150	195	58	70
2nd				58	38	34
3rd				38	25	34
Total				195	25	87

* The best test for each chemical species was repeated measuring the permeability between each slug in order to evaluate when the precipitation formed and when the greatest reduction in permeability occurred.

Table 6. Results From Clean-Core Flow Tests
(Continued)

Test No.	Core Location	Chemical	Pressure (psig)	Temp. (°F)	Beginning Perm.	Ending Perm.	Percent Reduction
			Series Three -- Multiple Cores, Single Slug				
1 Series	Upstream	$CaCl_2$	1,500	100	160	118	24
	Downstream				149	76	49
2 Series	Upstream	$CaCl_2$	2,000	150	149	77	48
	Downstream				149	49	67
3 Series	Upstream	$BaCl_2$	1,500	100	125	83	34
	Downstream				124	60	52
4 Series	Upstream	$BaCl_2$	2,000	150	133	85	36
	Downstream				141	68	52
5 Parallel	High Perm	$CaCl_2$	1,500	100	140	53	62
	Low Perm				74	25	66
6 Parallel	High Perm	$CaCl_2$	2,000	150	145	35	76
	Low Perm				121	33	73
7 Parallel	High Perm	$BaCl_2$	1,500	100	143	39	73
	Low Perm				104	38	63
8 Parallel	High Perm	$BaCl_2$	2,000	150	201	37	81
	Low Perm				111	13	88

Several significant conclusions can be drawn from the clean-core flow tests. For the single core and single slug tests, chemical precipitation reduced permeabilities by 25 percent to 60 percent. The tests showed that the $CaCO_3$ reduced permeability more than the $BaCO_3$ did. This was the opposite of what was expected based on the results of the pressure-volume-temperature (PVT) experiments in the first year of the study. However, further examination revealed that these results were caused by the particle size of the carbonates. The $BaCO_3$ particles are very fine and are much smaller than the $CaCO_3$ particles. In the more permeable cores, a portion of the $BaCO_3$ that forms in the core is carried out of the core with the displacement fluid and can be seen at the outlet of the test apparatus. In the case of the $CaCO_3$, the effluent at the outlet is clear, indicating that the precipitate stays in place and does not migrate through the core.

In the test series that used multiple slugs and a single core, permeability reduction ranged from 40 percent to 87 percent. The largest percentage of reduction occurred with the first slug with lesser amounts of reduction in the second and third slugs. In these tests, the $BaCO_3$ reduced the permeability more than the $CaCO_3$ did. These results are caused again by the smaller $BaCO_3$ particles. The $BaCO_3$ particles of each additional slug "build up" behind the precipitation from the previous slugs, thus further reducing the permeability.

The third series of tests was conducted with single slugs and multiple cores. The tests were run both in series (one core after the other) and in parallel (the cores side by side). Where the tests were run in series, the permeability was reduced in both cores, indicating that precipitation was distributed throughout the entire system and was not limited to the upstream section. Permeability reduction in these tests ranged from 24 percent to 67 percent. The tests that were run in parallel were conducted by simultaneously flowing the chemicals through two cores of varying permeabilities. The general trend of the test results indicates that the permeabilities of both cores were reduced to a more nearly equal value, thus creating a more even flow distribution between the two cores. Permeability reduction in these tests ranged from 62 percent to 88 percent.

4.2 Computer Simulation

Computer simulation research, which is being conducted to improve the predictability of CO_2 floods, is mainly being performed in-house at METC. METC is developing and refining two models: (1) a black oil simulator modified for miscible gas EOR and (2) a compositional simulator. The computer simulation research will be continued to provide adequate tools for predictive and evaluative support of novel technical concepts, laboratory experiments, and field projects. The research will aid the understanding of how fluid phase behavior and miscible displacement mechanisms enhance oil recovery and how reservoir heterogeneities influence oil recovery.

4.2.1 Development of a Compositional Simulator, Morgantown Energy Technology Center

The overall objective of this work is to develop expertise in compositional modeling and to provide simulation support for experimental studies conducted in the laboratory at METC. These studies will aid researchers in understanding the mechanisms of miscible displacement and mobility associated with EOR processes that use CO_2. This work is expected to improve predictive capability for project field operations, increase understanding of methods for improving reservoir sweep efficiency, and improve laboratory research through effective simulation support. The specific objectives of FY 87 were to develop, test, document, and perform a model validation analysis on the three-dimensional, fully compositional reservoir simulator (CRSIM-3D) and to continue development of a PVT package for this model.

A compositional reservoir simulator is required to accurately model a reservoir process in which significant mass transfer occurs between the oil and gas phases. Examples of such reservoir processes are volatile oil reservoirs, depletion of gas condensate reservoirs, depletion of gas cycling operations, and EOR processes including miscible and immiscible flooding using fluids such as CO_2, nitrogen, and lean natural gas.

METC's CRSIM-3D is being developed as an improvement on the CRSIM-1D. A Conformal Solution Model modified equation of state and a modified oil-gas viscosity correlation have been added as options to the compositional model. These additions should help in studying the accuracy of the different fluid physical property correlations to achieving dynamic miscibility in a miscible displacement process. The viscosity correlation is probably the most accurate oil-gas viscosity correlation available, and an initial comparison with the oil viscosity of an actual reservoir (0.11 cp calculated viscosity compared to 0.1107 cp experimental viscosity) seems to confirm this claim (see Figures 8 and 9). The equation of state is a noncubic equation, and it may not be used in a large simulation, but it is considered to be more accurate than the cubic equation of state. It should prove useful in preliminary simulations.

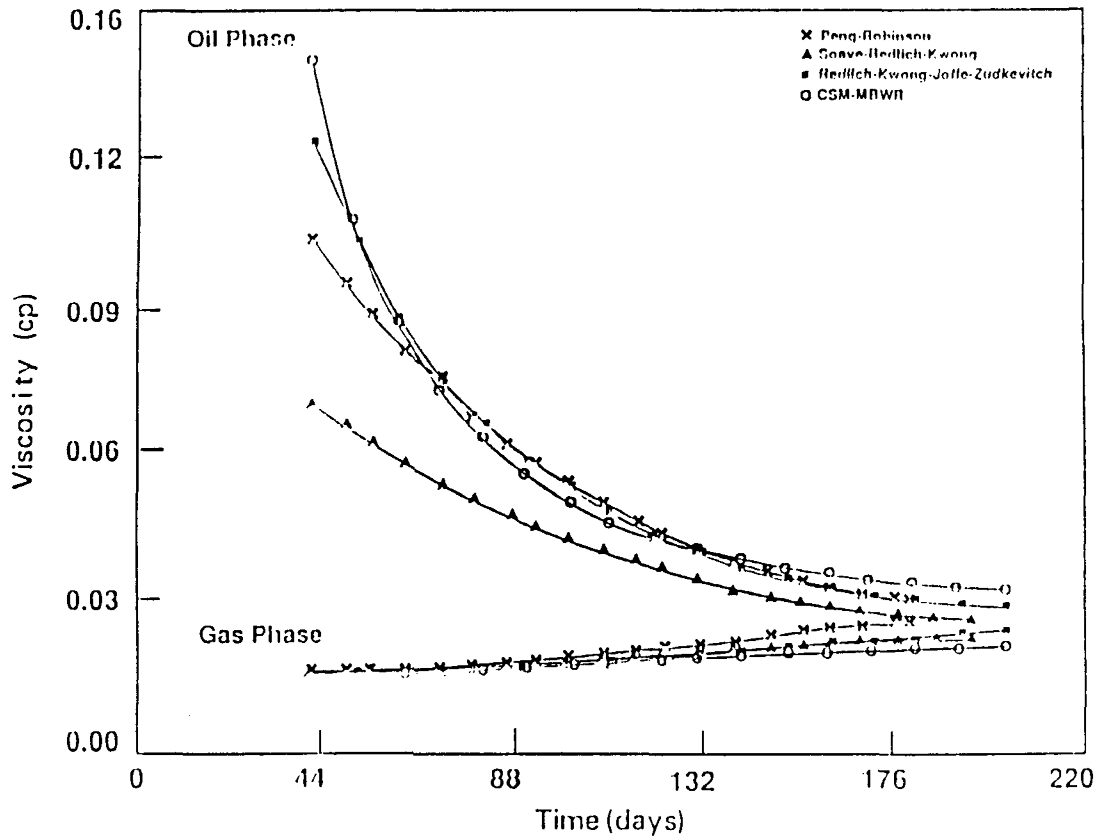

Figure 8. Variation of Oil and Gas Viscosities as a Function of Time Using Different Equations of State

A Substitution Scheme has been added to the compositional simulator as an option for solving the outer loop of the pressure equation. This new solution method should increase the stability and convergence rate of the approximate Newton's method, which is currently being used in the simulator for unstable problems. This scheme uses the band algorithm for the periodic update of the Jacobian matrix. The next phase of implementation will involve using the Preconditioned Conjugate Gradient algorithm for the periodic update of the Jacobian matrix.

Computational efficiency in a compositional simulator is necessary for simulating large, "field-size" problems. For a typical simulation, the flash calculation, with its equation-of-state evaluations, accounts for 50 to

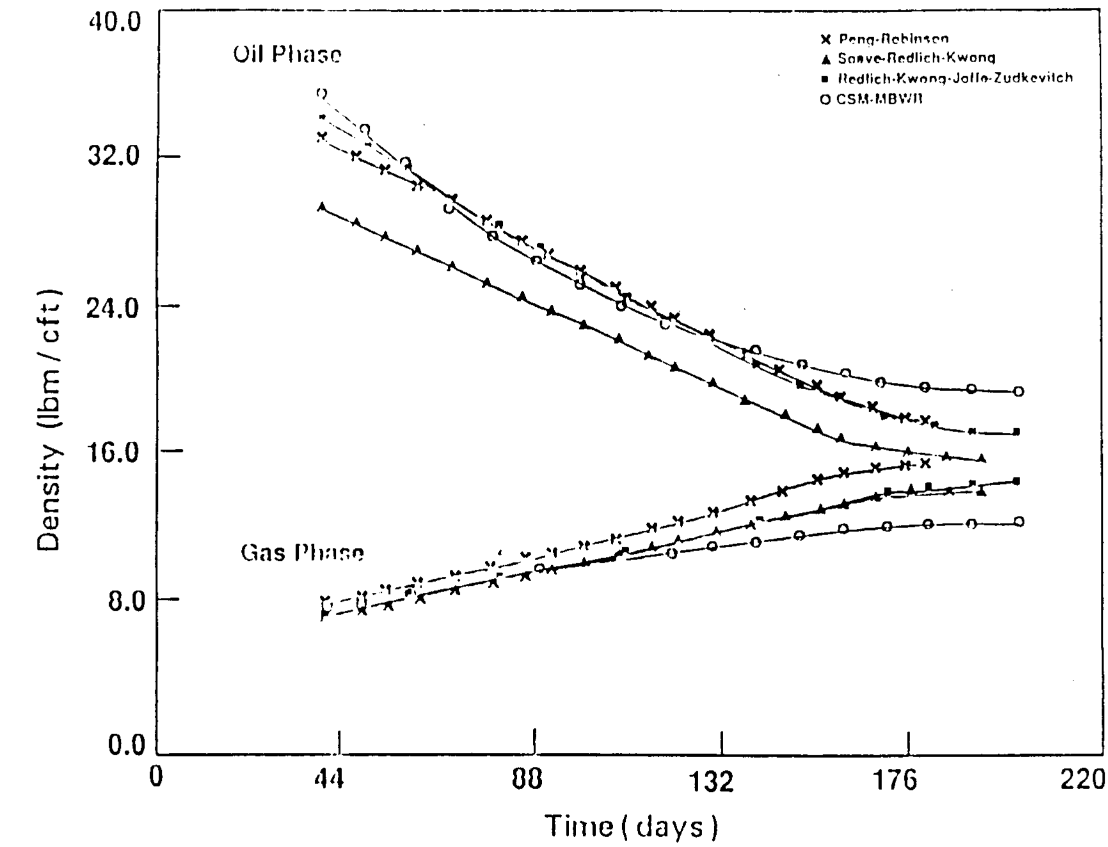

Figure 9. Variation of Oil and Gas Densities as a Function of Time Using Different Equations of State

75 percent of the overall computational time. To improve the speed of this calculation, a feature has been added to the simulator that provides a more accurate initial starting guess for the preliminary values. This feature goes into effect during the second pressure iteration of a time step, where the feature entails the use of the converged permeability values from the previous iteration. Testing of this method for a two-dimensional problem showed the overall computational time of the simulator decreased from 105 to 60 CPU minutes. Further testing is planned for three-dimensional problems.

A multiwell and multilayer option has been developed and incorporated into CRSIM-3D. These options are required when simulating "field-size" two- and three-dimensional problems where multiple wells commonly exist and where the reservoir is complex and must be characterized using multiple layers. Because of the multilayer option, several new arrays had to be added to the simulator, and several subroutines where the time stepping occurs (main, injection, and production routines) had to be revised extensively. Initial testing involved converting a two-dimensional problem into three dimensions by introducing layers along the z-direction. The terms for the well model are currently computed by an explicit procedure. This procedure will be modified to make the calculation more implicit and, hence, more stable.

In a compositional simulator, quantities such as relative permeability and capillary pressure are functions of the phase saturations. A subroutine has been constructed for evaluating the saturation-dependent relative permeability and capillary pressure for CRSIM-3D.

A secondary option exists for data the user supplies. The user can enter the data as an arbitrarily spaced data set or as coefficients for relative permeability and capillary pressure functions. The routine has been successfully tested outside the simulator environment. The next stage of development will involve incorporating the routine into the three-dimensional simulator.

CRSIM-1D assumed that the water phase in the reservoir has no effect on the phase behavior of the remaining fluids. This is a poor assumption for CO_2 flooding of a reservoir because CO_2 is soluble in water under reservoir conditions and, hence, this effect must be considered. A model has been developed and incorporated into the CRSIM-3D that accounts for the solubility of CO_2 in the aqueous phase of the reservoir fluids. In addition, this model accounts for the concentrations of solids and salt in the aqueous phase (brine), as well as the injected fluid phase and the effect of these solids on CO_2 solubility. The tracking and mixing of solids in a reservoir simulator is a novel concept that has not yet appeared in the literature.

A preliminary version of a restart feature has been implemented in CRSIM-3D. The restart feature, which already exists in the one-dimensional simulator, enhances simulator productivity by allowing the user to continue a simulation from an intermediate point during a simulation run without having to repeat the total simulation. This will save a large amount of computer time when "field-size" reservoir problems are being simulated, where CPU time can become excessive. For example, suppose a reservoir simulation has been running for several CPU hours and a convergence problem suddenly develops as a result of a large time step size. The restart feature can be used to continue the simulation from that point in the simulation time with a smaller time step, thus eliminating the need to rerun the simulation from time zero.

As part of a continuing effort to ensure proper validation and verification of CRSIM-3D, several comparisons of simulation results with literature results are being attempted. Scenario I of the Fifth SPE Comparative Solution Problem was simulated using preliminary version No. 1 of CRSIM-3D. The simulation problem was a WAG process with primary depletion occurring for 2 years, followed by injection of water and gas on a yearly cycle. The maximum simulation time was 20 years and the simulation was to be stopped if the gas-oil ratio (GOR) exceeded 10 Mcf per STB or the water-oil ratio (WOR) exceeded 5 stock tank barrels (STB) per STB. The following companies simulated this problem using their compositional simulators: ARCO; British Petroleum; Chevron; Computer Modeling Group; Reservoir Simulation Research; and Todd, Dietrich, and Chase. The results obtained from METC's compositional simulator fall within the band of results obtained from these companies, as illustrated in Figures 10 and 11.

Scenario II of the Fifth SPE Comparative Solution Problem was successfully simulated using the latest version of CRSIM-3D. The simulation problem was a WAG process with the injection of water and gas repeated on a 3-month cycle for a maximum period of 20 years. In addition, the average reservoir pressure was maintained at or above the MMP of the original reservoir oil. Results of cumulative oil production versus time, cumulative oil production versus cumulative water injected, gas-oil ratios, water-oil ratios, and

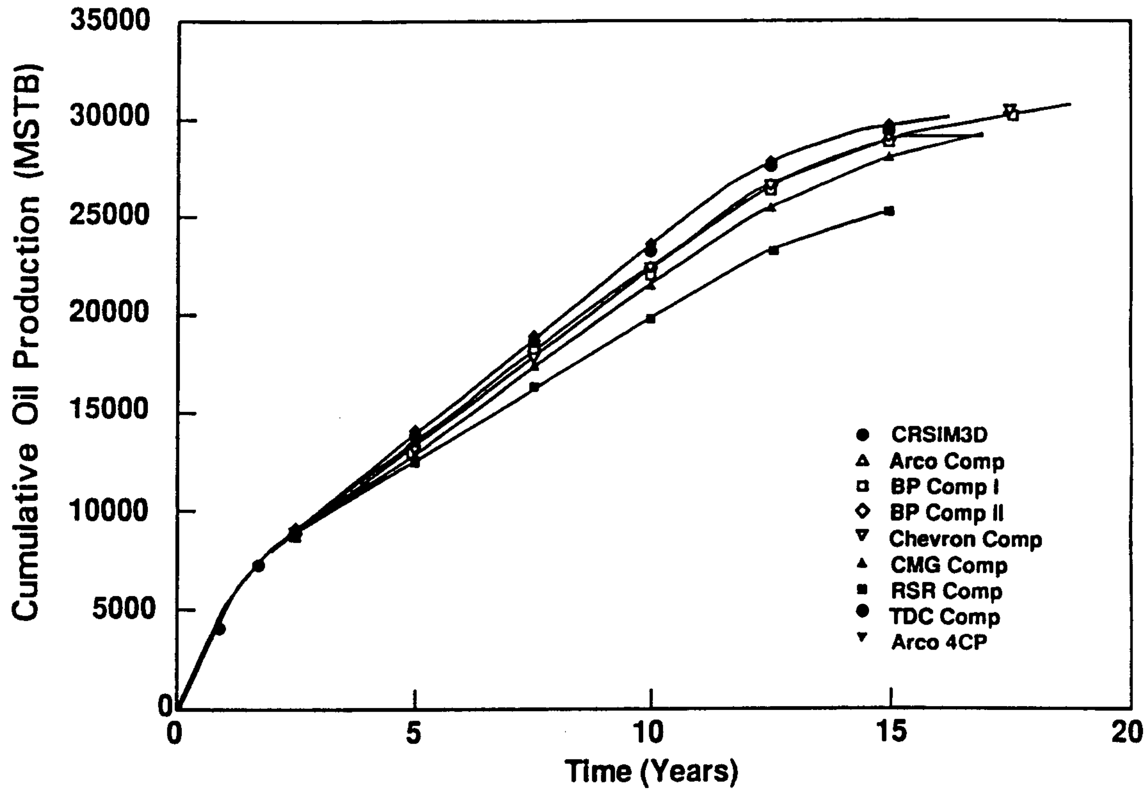

Figure 10. Comparison of Cumulative Oil Production, Scenario One, Compositional Models

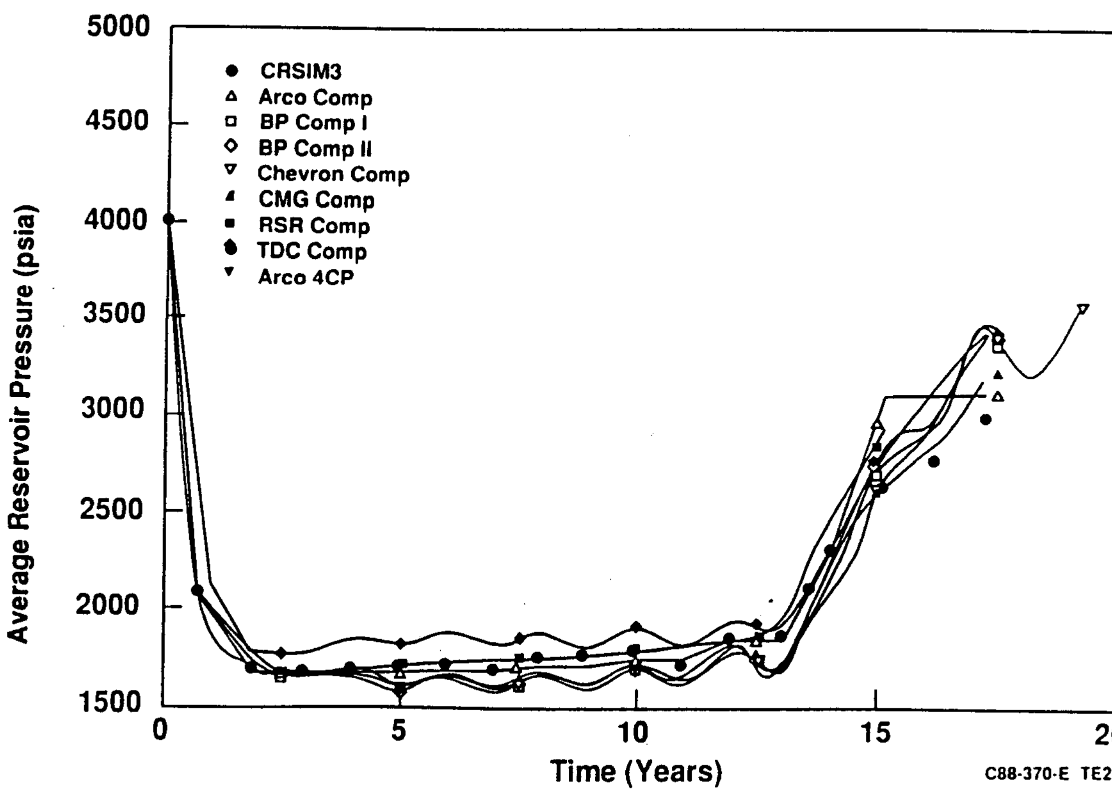

Figure 11. Comparison of Average Reservoir Pressures, Scenario One, Compositional Models

average reservoir pressure versus time predicted by the three-dimensional simulator are in good agreement with results predicted from seven industrial simulators used to simulate the same problem. Figures 12 and 13 represent two typical comparisons.

Scenario III of the SPE Comparative Solution Problem was also successfully simulated using the latest version of CRSIM-3D. This problem used primary depletion for the first year of production followed by water injection for the second year of production. The third year of production started the WAG process on a 3-month cycle. WAG was continued for a maximum period of 20 years subject to GOR and WOR constraints. During early times of the simulation, the average reservoir pressure fell to a level below the saturation pressure, and then, as a result of rapid injection, rose to a level above the MMP, thus simulating a multi-contact miscible displacement process. Cumulative oil production versus time, cumulative oil production versus cumulative water injected, gas-oil ratios, water-oil ratios, and average reservoir pressure versus time predicted by the three-dimensional simulator are in good agreement with the results predicted from the seven industrial simulators used to simulate the same problem. Figures 14 and 15 represent two typical comparisons.

A preliminary version of the PVT package has been completed. The PVT package is an important addition to METC's simulation capabilities. When modeling field applications of EOR processes, it is crucial that the crude oil in the reservoir be sufficiently characterized. A PVT package, which is usually used for oil characterization, better characterizes the reservoir hydrocarbon mixture, i.e., oil and/or gas, to provide more accurate equation-of-state calculations in a compositional simulator. The PVT package uses a regression-based gamma or beta distribution program to characterize the oil or gas mixture into 2 to 10 fractions or pseudo-components depending on the user specification.

After these pseudo-components have been defined, a nonlinear regression package is used to fine tune the binary interaction parameters of the equation of state using sets of laboratory data obtained for the hydrocarbon of interest. The interaction parameters are then input into the compositional simulator.

4.2.2 Validation and Operation of a Modified Black Oil Simulator, Morgantown Energy Technology Center

The objectives of this study were to validate the black oil miscible/immiscible simulator, MASTER (Miscible Applied Simulation Techniques for Energy Recovery), and to conduct sensitivity studies on the effects of the input parameters of MASTER on oil recovery.

Before validation began, the Preconditioned Conjugate Gradient method was implemented into MASTER. Almost no modification of the existing code was needed to perform the initial implementation other than a call from the main program and the addition of the new routines. Further modifications may be needed at a later time before the implementation is user ready and testing of the solution method is completed. A two-dimensional version of the Preconditioned Conjugate Gradient method has also been implemented into MASTER. This

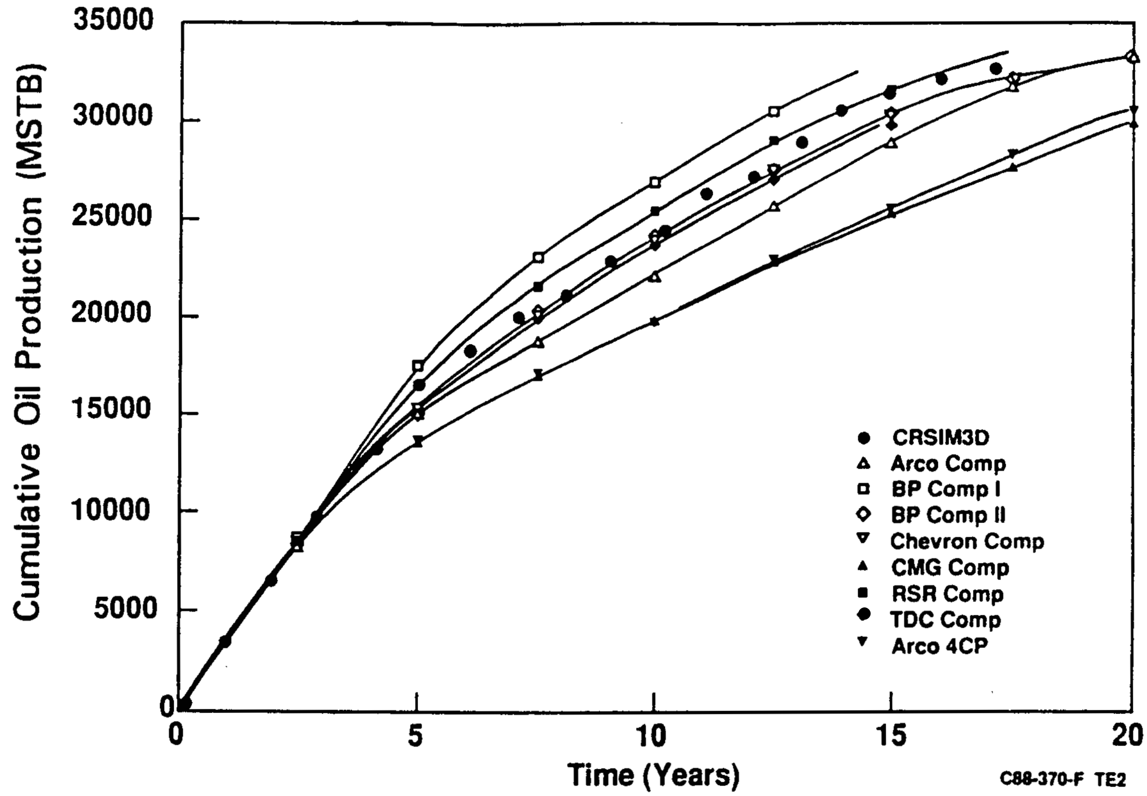

Figure 12. Comparison of Cumulative Oil Production, Scenario Two, Compositional Models

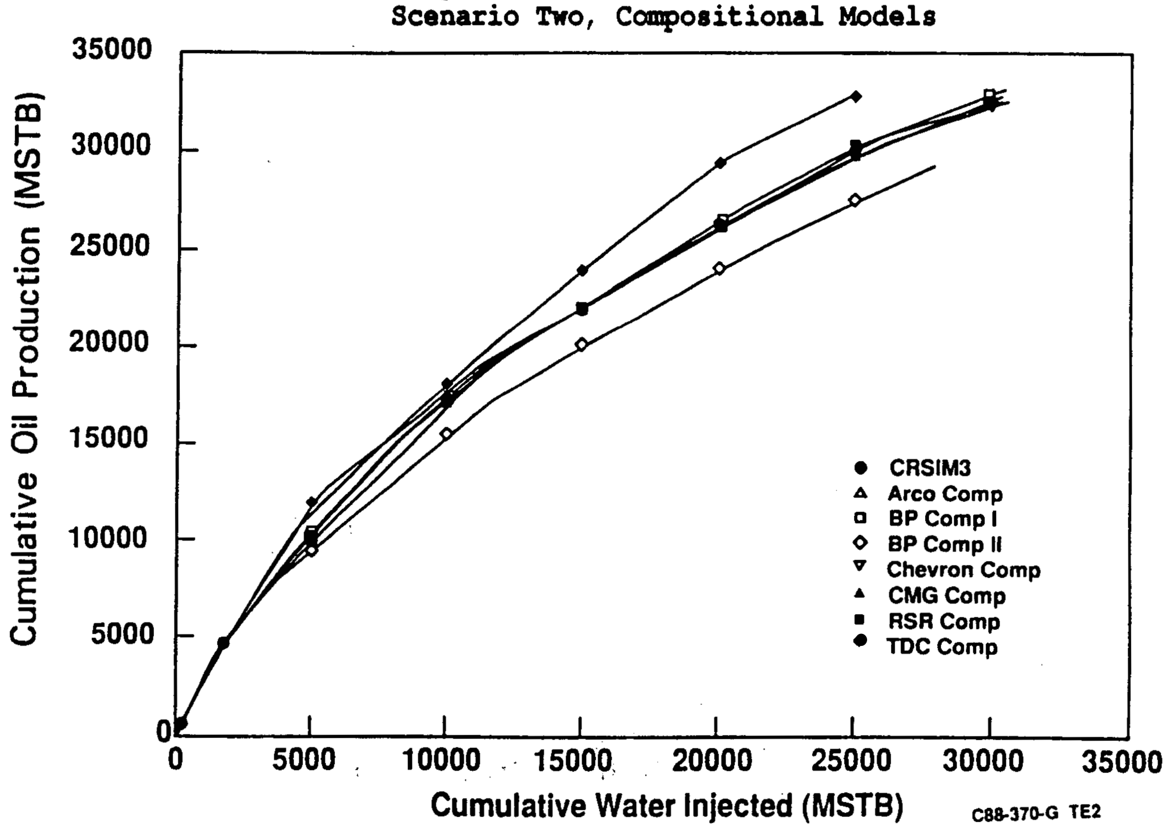

Figure 13. Comparison of Cumulative Oil Production Versus Cumulative Water Injection, Scenario Two, Compositional Models

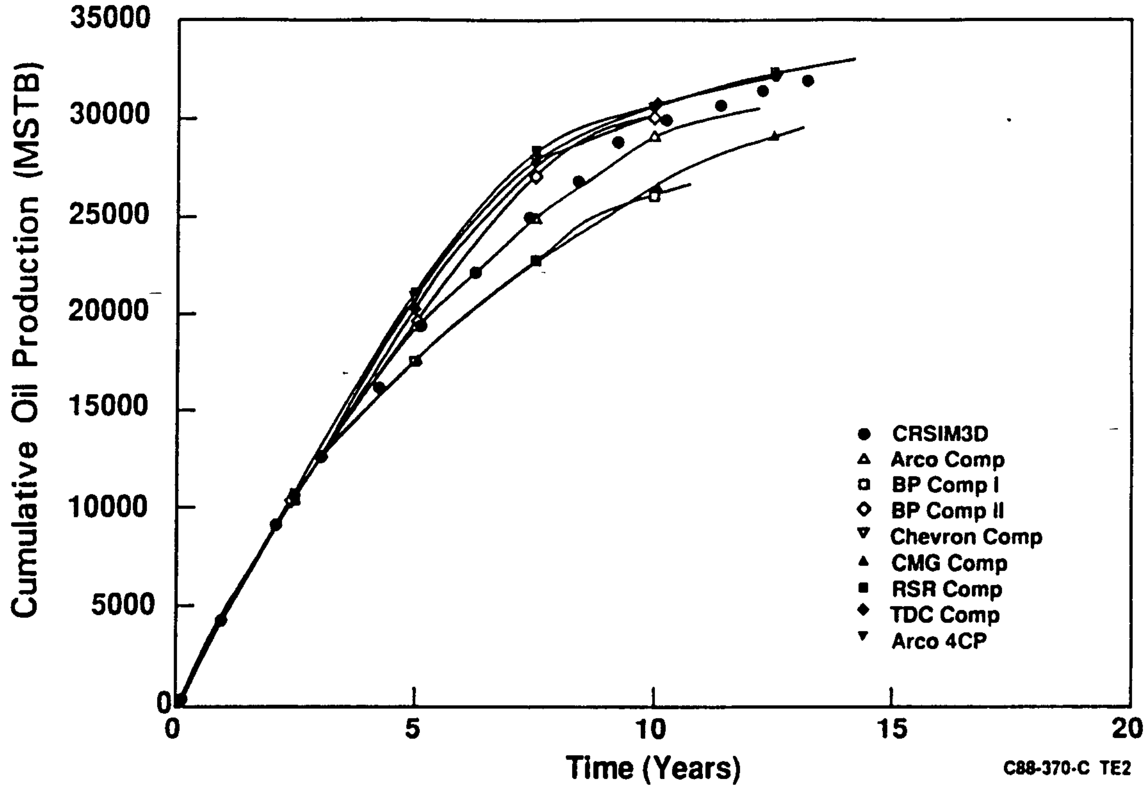

Figure 14. Comparison of Cumulative Oil Production, Scenario Three, Compositional Models

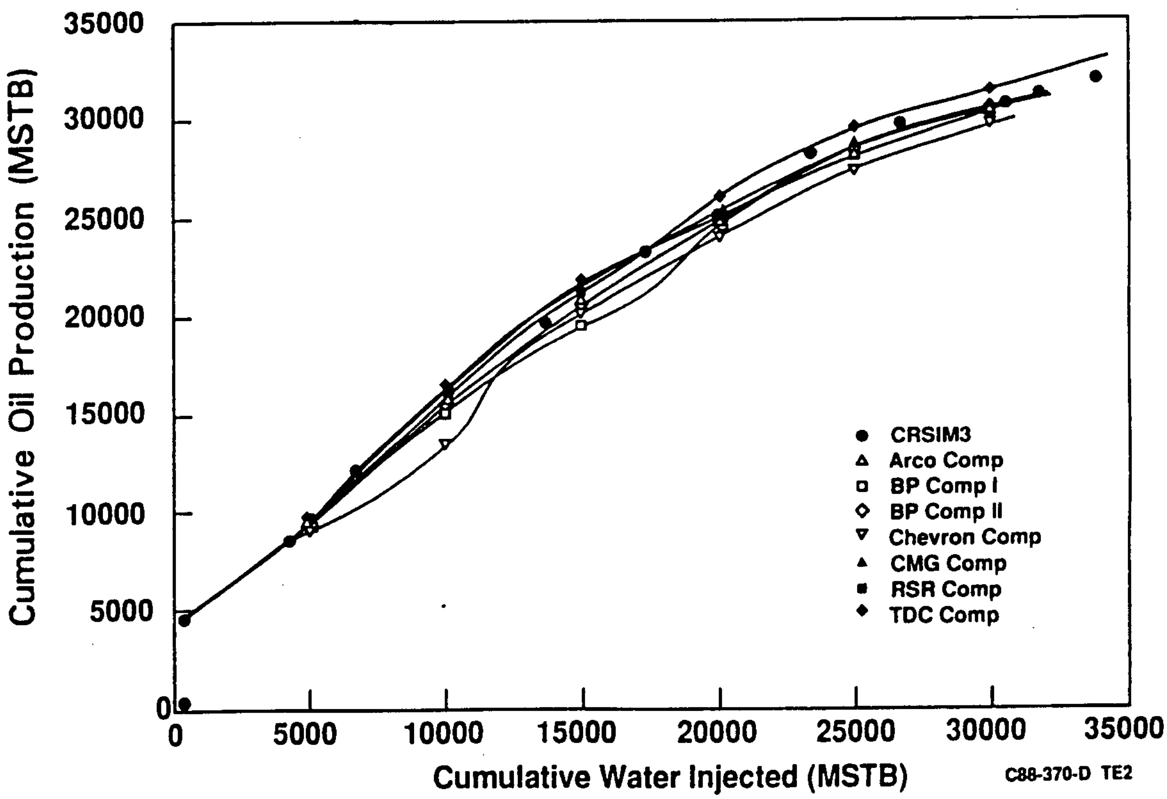

Figure 15. Comparison of Cumulative Oil Production Versus Cumulative Water Injection, Scenario Three, Compositional Models

option is more efficient than using the three-dimensional version for two-dimensional problems. Initial testing of the new solution technique has yielded almost identical results to results using the direct solution technique. Extensive testing of the new solution option will indicate whether the code has to be converted to double precision arithmetic to maintain diagonal dominance and symmetry for the coefficiency matrix. Other testing will determine CPU requirements and will investigate when to use the Preconditioned Conjugate Gradient algorithm over other solution methods.

Results predicted by MASTER for immiscible problems were compared to results presented in technical papers (e.g., the comparative problem for three-dimensional black oil simulators, in which seven major oil and modeling companies participated), and to results predicted by Scientific Software -- Intercomp, Inc.'s (SSI) SIMBEST reservoir simulator. Comparison of results show that MASTER accurately predicts reservoir performance for immiscible problems. Problems specifically designed to test the repressurization algorithm show that some minor problems exist with the current algorithm.

Base case runs for the sensitivity study showed large material balance errors (mbe) when the solid precipitation option was involved. Evaluation of the source code revealed that whenever the solid precipitation option was used with the automatic time-step control option, various parameters were not being reset to their previous values for repeated time-steps. By resetting these parameters for repeated time-steps and making a few other code changes, the large mbe's were removed.

An evaluation of MASTER has been completed. As a result of this evaluation, the following enhancements to the MASTER computer code were made: (1) revise the bubble-point tracking scheme using a variable substitution scheme, in which the primary variables will be switched depending on whether the fluid on the grid block is above or below the bubble-point pressure, (2) revise the solution method for the calculation of grid-block pressure to an iterative Newton Raphson scheme, and (3) revise the calculation for the solubility of the injected fluid.

As part of the bubble-point tracking algorithm, the variable switching technique for undersaturated oil has been implemented in the code. The code has been tested on a 6-foot by 5-foot by 5-foot gas injected problem. The method converges and reduces the mbe's significantly when compared with the old repressurization algorithm.

Results from MASTER were compared with results presented in paper titled "Fifth Comparative Solution Project: Evaluation of Miscible Flood Simulators" (Killough and Kossack 1987). The paper compares the results of four-component miscible simulators and fully compositional reservoir simulators for miscible and immiscible problems. Seven major oil companies and consulting firms involved in reservoir simulation participated in the project. The results that MASTER predicted for the miscible run (Case 2) compared well (typically within 7 percent of the other predictions) for cumulative oil production, gas/oil ratio, oil saturations, and average reservoir pressure. Cumulative mbe's were less than 0.1 percent for all four components after 20 years of production and injection. Figures 16 and 17 compare results predicted by MASTER and ARCO's four-component miscible simulator for cumulative oil production and gas/oil ratio, respectively.

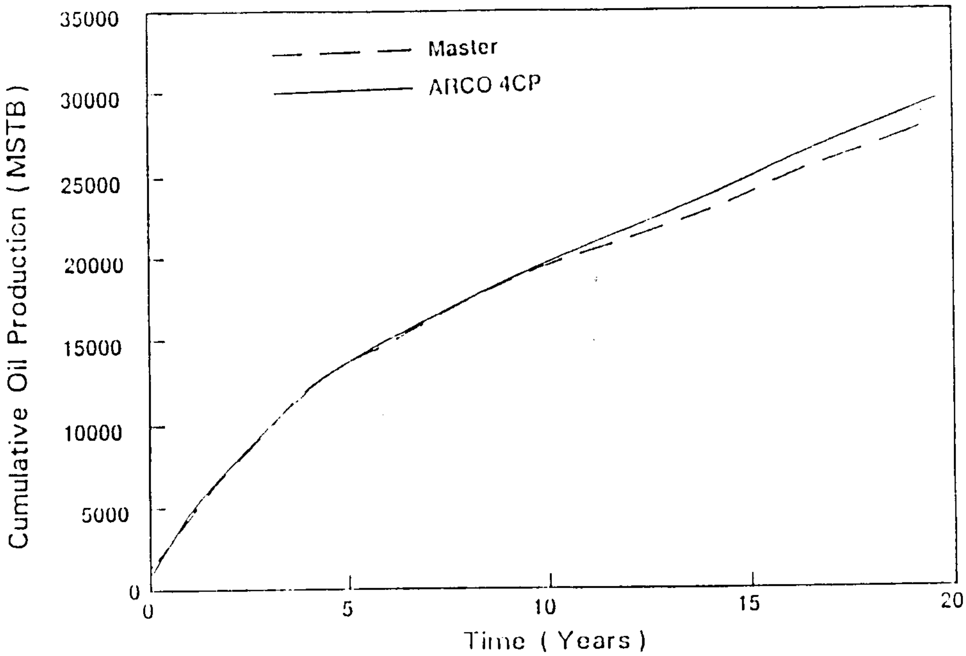

Figure 16. Comparison of MASTER With Arco Four-Component Model -- Cumulative Oil Production

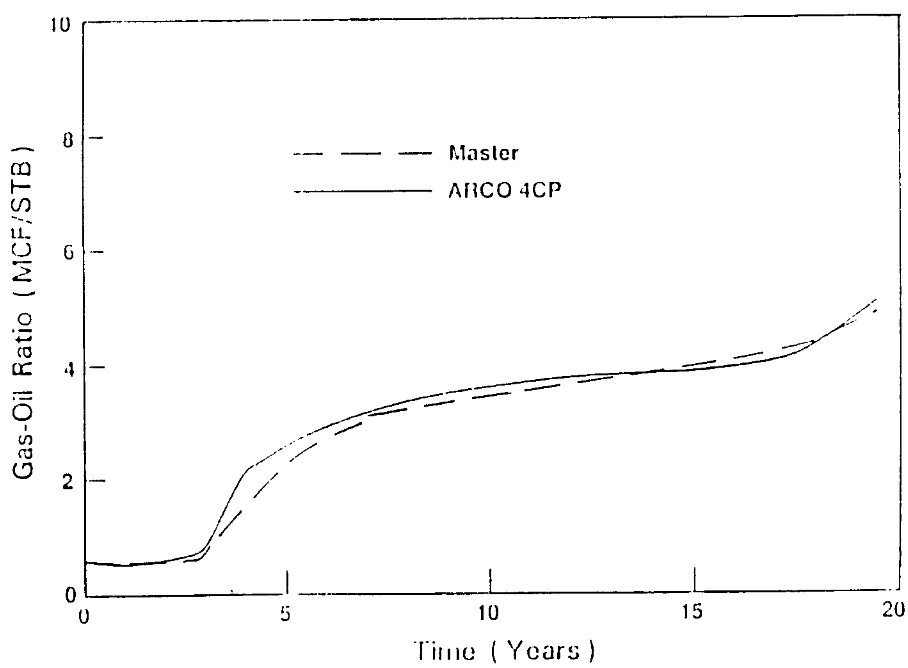

Figure 17. Comparison of MASTER With Arco Four-Component Model -- Producing Gas-Oil Ratios

A comparative study of MASTER and METC's one-dimensional compositional simulator, CRSIM-1D, was completed. The results that MASTER predicted were very close to those that CRSIM-1D predicted, typically within 6 percent. The simulated case was a one-dimensional, miscible hydrocarbon, EOR project in which the injected fluid and reservoir oil were miscible upon first contact, which is the basic assumption behind MASTER. A PVT package, developed in-house, was used to ensure consistent PVT data between the two codes. Figure 18 shows the results predicted by MASTER and CRSIM-1D for cumulative oil production. Figure 19 shows the calculated oil viscosity in the first grid block for the two codes. The good agreement between calculated viscosities is enlightening because MASTER calculates miscible fluid properties based on the saturations of the fluids making up the miscible fluid, whereas CRSIM-1D calculates the miscible fluid properties based on the properties of each component in the fluid. This validation was an essential step in determining if MASTER could accurately predict reservoir performance for miscible floods. Since the fully compositional simulator is a much more rigorous code in predicting reservoir performance for processes where phase transfer is dominant, the verification of results increases the confidence in both models and indicates that under certain scenarios, predictions by MASTER that require less CPU time can adequately match the more rigorous CRSIM-1D.

Computer runs with SSI's reservoir simulator, NHANCE, are being conducted to further validate MASTER's predictability for miscible processes. Runs have been made for different mixture rule parameters and different residual oil saturations, and for a CO_2 repressurization problem. In addition, a and a one-dimensional run was made to test the code for multiple contact miscibility (MCM) processes. Because of differences in the methods used to calculate layer injection rates and production rates in the two codes, exact comparison of the results cannot yet be made. Once the difference is determined, a comparison of results will be conducted.

Phase 2 modifications to correct mbe's that occur during gas injection are continuing. The current work is on the computation of the Jacobian matrix and on the variable update equations. In the original version of MASTER, the coefficients in the pressure equation failed to distinguish the form of these coefficients for the undersaturated case and always used the form appropriate for the saturated case. The correct expressions for these coefficients have been derived and are being implemented in MASTER. The variable update equations have also been modified in order to be consistent with the new methodology. Phase 2 work on the repressurization algorithm is nearly completed. Computer testing of the code has begun.

4.2.3 Pattern Alignment, Blocking, and Horizontal Borehole Studies, Morgantown Energy Technology Center

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

MASTER, the numerical simulator discussed in Section 4.2.2, will be used in this study. No conclusions have been reached because work began in FY 88.

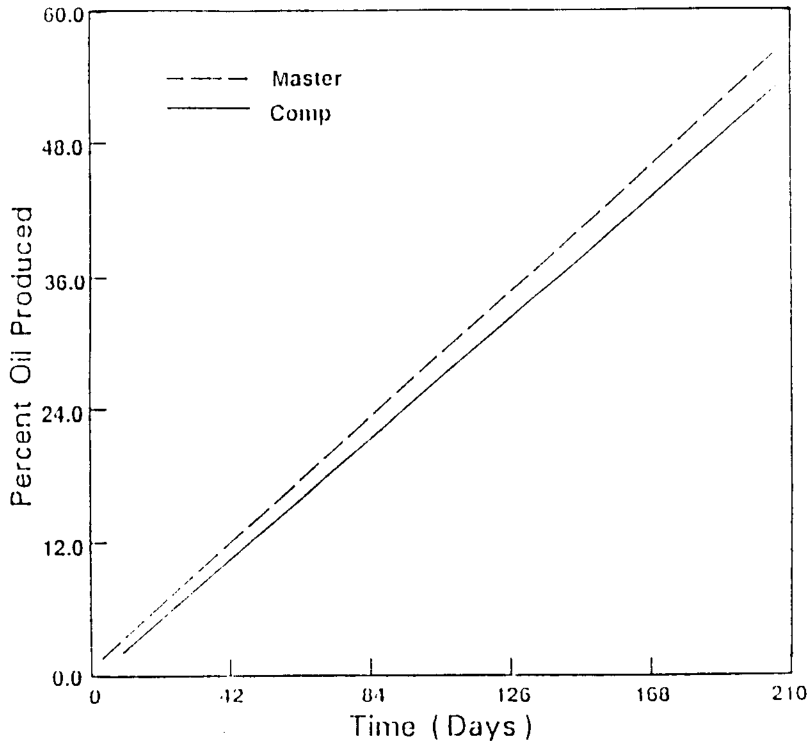

Figure 18. Comparison of MASTER With a Fully Compositional Simulator -- Percent Oil Produced

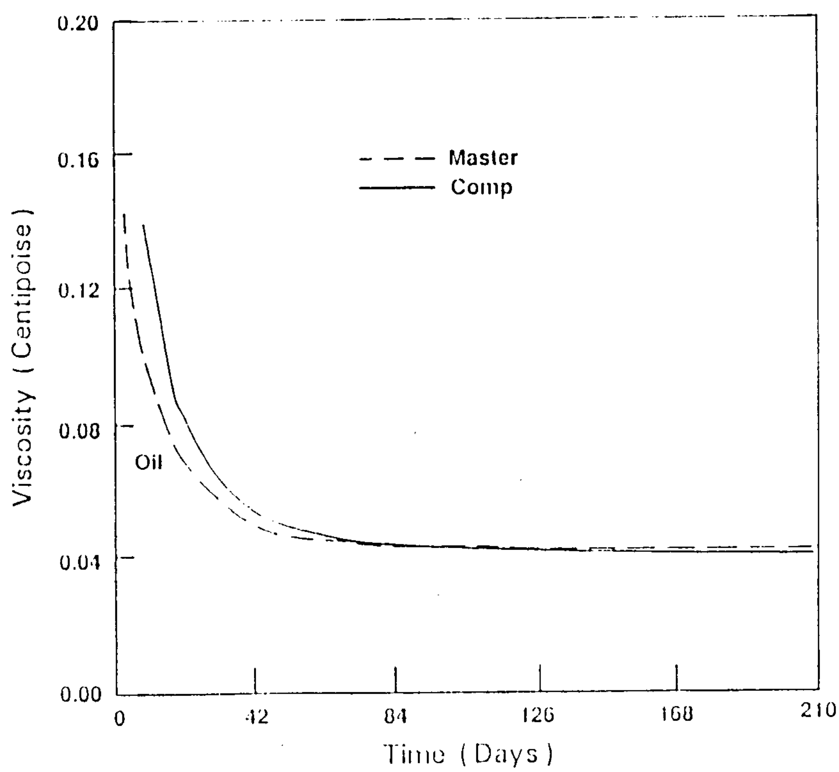

Figure 19. Comparison of MASTER With a Fully Compositional Simulator -- Oil Viscosity

Field Model Operations

METC and an oil field operator entered into an agreement to conduct a joint study on the effect of CO_2 flooding in a large-scale EOR project. The study will use a METC-developed computer simulator (MASTER) to evaluate the operator's field data. This joint effort promotes transfer of METC research results to the private sector by providing operators with the capability for more accurate predictions and assessment of CO_2 EOR projects. In the study, field performance from primary production and secondary waterflood will be simulated to better understand reservoir characteristics. Field performance for the CO_2 flood will also be simulated using currently implemented technology to compare predicted with actual production.

Simulations of the use of advanced technologies such as horizontal wellbores and surfactant mobility control, which are currently being studied at METC, will also be done to evaluate the potential of these technologies for additional oil production.

The oil field operator has received the most recent version of MASTER, and METC has obtained hard copies of completion reports, well logs, core analyses, PVT data, and contour maps, along with floppy disks containing production history, bottom-hole pressure history, and core data. Initial analysis of the data and the start of the study will begin shortly.

Data gathered from the oil field operating company for the cooperative field simulation study was thoroughly reviewed. Only annual production data (estimated for most wells, actual for the leases) exist for the first 6 years of primary production. Biannual pressure data is available for almost all wells. A geologic team was established to develop a detailed three-dimensional description of the reservoir. Gamma ray logs and core analysis are available for nearly all the wells in the field to complete this task. This three-dimensional description will be used to assign reservoir properties for the constructed grid system necessary for the computer simulation study. A literature review on the field and geologic formation is also being conducted.

4.3 Reservoir Heterogeneity

The role that reservoir heterogeneity plays in the performance of the miscible gas EOR process is being investigated. Reservoir heterogeneity, which affects recovery efficiency, is mainly determined by fluid flow, which, in turn, is determined by permeability. This effort is aimed at quantifying the effects of reservoir heterogeneity on CO_2 floods in reservoirs with large well spacing and relatively low permeability. The problems of detection, characterization, and representation of the effects are being investigated.

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

The main objective of this research is to develop new concepts for characterizing and describing the interwell area of a petroleum reservoir suitable for the CO_2 EOR process. To accomplish this objective, the research effort is organized into four tasks:

1. Describe several model reservoirs that have reasonably typical types of heterogeneities. The descriptions will be based on knowledge of depositional environments and digenetic 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.

The following specific work was done in FY 87:

The relationship between reservoir heterogeneity and flow is being examined. It is the flow aspects of heterogeneity that determine which scales of heterogeneity have the greatest influence on the performance of any EOR process. Calculations of the performance of ideal miscible displacements in single layer systems with various distributions of permeability indicate clearly that the way in which high and low permeability zones are connected is as important as the range of permeability variation. For example, permeabilities with the same statistical descriptors (mean permeability, variance, and correlation length) in which the length scale of the heterogeneity is a significant fraction of the displacement length can show very different flow behavior depending on the orientation of zones of high and low permeability with respect to the local average flow direction. If high permeability zones lie transverse to the average flow, they have little effect on solvent breakthrough times. If they are aligned, however, early breakthrough is guaranteed. Thus, any successful description of reservoir heterogeneity for a flow process must include some representation of the orientations of the heterogeneities with respect to average flow directions.

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

The assembly of the apparatus for measurement of equilibrium phase compositions, densities, and viscosities has been completed, and testing and calibration have begun. Figure 20 shows the current configuration of the apparatus. Calibration experiments include measurements of overall cell compressibility, calibration of cell volume versus interface height as a function of temperature and pressure, and determination of calibration constants for the Mettler/Paar densitometers and for the capillary tubes used for viscosity

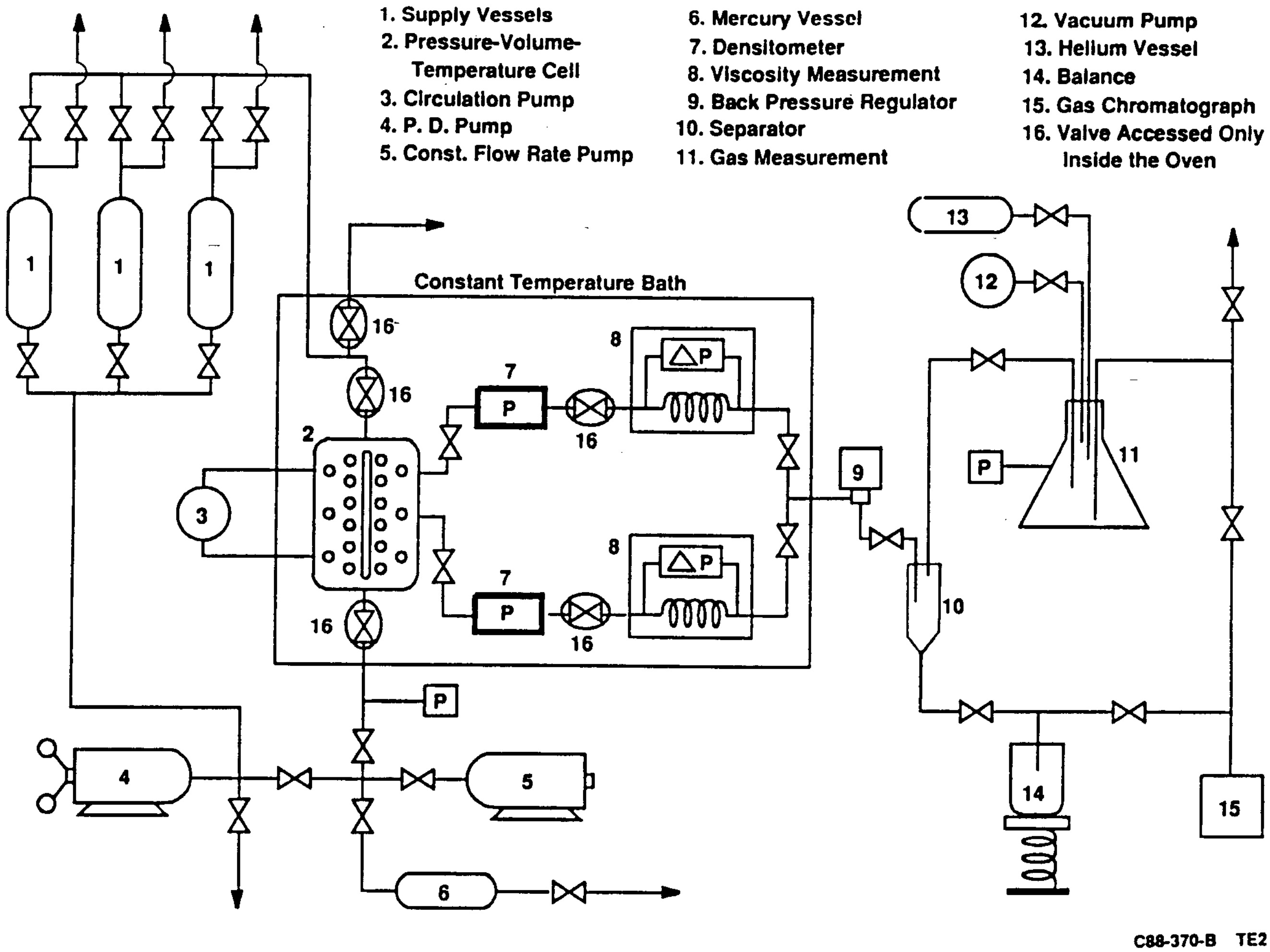

Figure 20. Apparatus for Phase Composition and Fluid Property Measurements

measurements. Initial flow experiments with pentane indicated that the TEMCO back pressure regulator controlled pressure accurately with minimal pressure fluctuation, and that the computer-controlled pump (Petrophysical Services) gave stable displacement rates. Initial calibration experiments with the Setra 204 transducers used to measure pressure drop across the capillary viscometer tubes indicated that for low viscosity fluids at low flow rates, additional accuracy will be required if reasonably precise viscosity measurements are to be obtained for vapor phases.

A computer program that simulates the operation of the apparatus shown in Figure 20 has also been completed. The program uses a microcomputer with a graphics board to simulate the full sequence of valve and pump operations required to load fluids into the PVT cell, compress or expand a mixture at constant temperature, and remove samples from the cell. The program uses the Peng-Robinson equation-of-state to calculate phase compositions and densities. The program will be used to teach students how phase behavior experiments are performed and to prepare for actual experiments. For example, the new program can easily estimate effects on overall composition of samples and varying amounts of components added. Documentation of the code is nearing completion.

The descriptions of model reservoirs are being used to test whether available techniques for detecting reservoir heterogeneity in the interwell region are sensitive enough to detect heterogeneities that are likely to have a significant effect on process performance at field scale. The resulting simulations are useful for testing methods of dealing with the inverse problem: the unraveling of a reservoir description from the analysis of test data that integrates the effects of reservoir structure. The scaled miscible displacement experiments provide experimental evidence concerning the interaction of viscous instability with heterogeneity and allow an assessment of the effects of phase behavior when heterogeneity and viscous instability are both factors. The experimental results will allow testing of schemes for averaging the combined effects of process mechanisms operating at scales significantly smaller than grid blocks used in simulations of reservoir-scale CO_2 floods. The parallel, experimental, and theoretical approach proposed here is aimed at quantification of the effects of reservoir heterogeneity in CO_2 flooding.

Because CO_2 performance depends strongly on phase behavior, the following are key questions for field-scale floods:

1. What is the optimum displacement pressure when the flow is not one-dimensional (as a result of heterogeneity or viscous instability or both)?

2. Is that pressure substantially different from the MMP measured in nearly one-dimensional (slim tube) displacement experiments?

To answer those questions, detailed information about phase behavior, the length scales of flow nonuniformities, and rates of fluid transfer between zones of fast and slow flow are needed.

Fundamental to all descriptions of miscible flood processes are measurements of the phase behavior and fluid properties of the mixtures that form during the displacements. Volume changes of fluids in the visual cell with changes in pressure have been measured at room temperature and is being measured now for elevated pressures. Measurements of volume above an interface at a given height have also been completed at room temperature. Calibrations of capillary tubes to be used for viscosity measurements has been deferred pending delivery of Sensotec differential transducers (Model HL-Z), which offer precision of $\pm$ 0.125 psia for operating pressures up to 6,000 psia. Calibrations of volume versus interface height at elevated temperature and pressure, the final calibration task, begins in FY 88.

Once data on phase behavior and fluid property are available, they can be used to predict the interactions between phase behavior and flow that are the basis for high displacement efficiency in any successful CO_2 flood. Similar mathematical techniques are being used to study other flow problems in which the effects of phase behavior are important. Reported below are preliminary results of composition path calculations for a CO_2 water-oil ternary system. The calculations are aimed at the description of combined flow of vapor containing CO_2 and water, liquid oil, and liquid water. The calculation scheme includes the effects of temperature variation, though the preliminary results reported are for constant temperature.

Also described below is an application of the method of characterizing two-phase, three-component flow in a two-layer porous medium. That calculation is an attempt to quantify the effects of crossflow on composition paths and, hence, on MMP. When completed, it will provide a semianalytical description of the combined effects of heterogeneity and phase behavior when viscous crossflow is also significant.

In field-scale CO_2 floods, nonuniform flow may be caused by reservoir heterogeneity or by viscous fingering, or, more likely, by both. To examine the interaction of heterogeneity and viscous instability, displacement experiments are being performed in partly scaled models of glass bead packs, as are fine-grid simulations of the growth of viscous fingers. Development of the experimental apparatus continued in FY 87 with the assembly of a flow system that includes a constant rate pump, which injects fluids into the model, and a refractive index detector, which monitors effluent compositions. Calibration of the refractometer (which finds the effluent concentration as a function of refractometer output curve) is now being completed. Sample runs were performed in the uniform pack model, using various mobility ratios. When mobility ratios were adverse, fingers were generated, as expected. Some evidence of faster flow was observed in the layer of glass beads adjacent to the upper glass surface. In subsequent models, the glass beads will be sintered lightly to bond them to each other and to the glass surfaces to reduce such effects.

Analysis of the flow visualization portions of experiments will make use of digital image processing equipment available in the Department of Geophysics at Stanford University. In a typical experiment, the flow observation is recorded on videotape. Using the digital image-processing equipment, any frame of the videotape can be digitized into an array of 512 by 480 intensity values (integers from 0 to 255). The resulting digital image can then be processed further by computer to obtain a quantitative analysis of finger properties. For example, compositions can be averaged across the flow cross section, fronts can be tracked, and shapes and dimensions of fingers can be analyzed. Figure 21 shows contours of image intensity for a displacement with an adverse viscosity ratio of 14. While the digital image contains some artifacts, it clearly shows the locations of fingers. Refinement of the image quality of changes in lighting and digital filtering of noise are being explored.

Development of the computer codes for fine grid simulations of the growth of viscous fingers has continued. However, the model always predicts less oil recovery because it does not include transverse dispersion. Therefore, the model has been modified in the following manner. A streamline and concentration contour are chosen randomly. Their intersection is then the location where the displacement front moves during a time step. Next, that location is perturbed by random amounts corresponding to longitudinal and transverse dispersion. These amounts are also obtained by selecting values from a zero-mean, normal distribution with a variance appropriate to the respective dispersivity. The concentration at that location is then adjusted by increasing or decreasing the injection rate increments. Preliminary runs are now being made for unit mobility ratio to determine if the input transverse and longitudinal dispersion values can be recovered through Peclet number calculations.

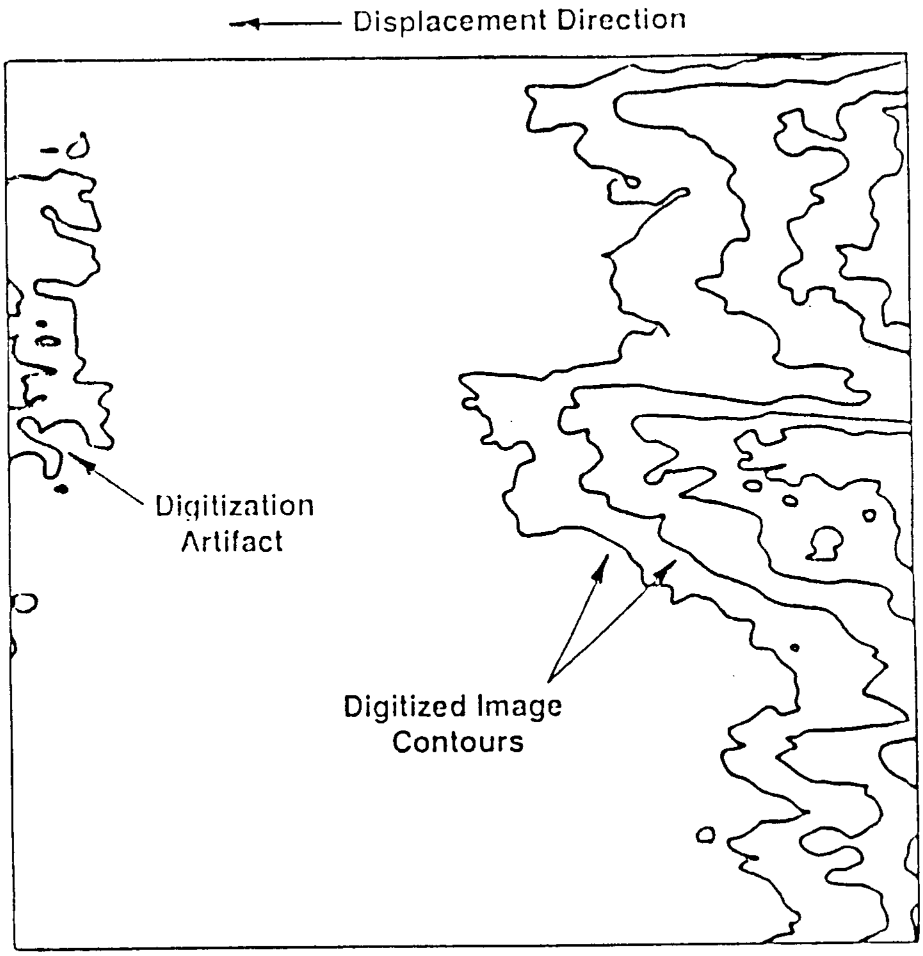

Figure 21. Digital Image of an Unstable Displacement With a Viscosity Ratio of 14

Another model has been developed that uses a finite difference solution of the mbe's to determine the pressure field, given the distribution of permeabilities and the current distribution of fluid viscosities. Tracer particles that carry a finite concentration of injected fluid are then moved with velocities based on the pressure field. Effects of transverse and longitudinal dispersion are included, again, by perturbing the positions of particles by amounts selected from a normal distribution with a mean of zero and a variance that sets the relevant dispersion coefficient. In effect, it is assumed that local velocity variations at scales smaller than a grid block can be represented adequately by dispersion. Once the locations of all tracer particles are determined, local viscosities can be evaluated and the process repeated for the next time step.

This scheme has the advantage that it controls the effects of numerical dispersion, but it requires that many particles be tracked. Preliminary runs for unit mobility cases show that the input values for transverse and longitudinal dispersion are recovered. Currently, the program is being tested for ways to improve computational performance without loss of resolution in the concentration distributions.

4.4 Phase Behavior and Miscibility

4.4.1 Laboratory and Modeling Experiments, New Mexico Institute of Mining and Technology

New Mexico Institute of Mining and Technology is performing laboratory and modeling experiments to better predict phase behavior and miscibility. This project has the following objectives:

1. Design a high-pressure viscometer based on an oscillating quartz crystal and associated instrumentation for the continuous phase equilibrium (CPE) experiment.

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 CO_2 displacements of 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, which accounts for the composition of the oil and the injected fluid.

New-Generation Continuous Phase Equilibrium Experiment

The reliability of the crystal viscometer for use with CO_2/crude oil systems has been fully demonstrated. There were early concerns that asphaltene would deposit onto the quartz would occur, causing anomalous damping of its oscillation and yielding incorrect results. Because of these fears, the design of the CPE apparatus had included means by which the experiment could be stopped and the crystal cleaned by an effective solvent for asphaltene (tetrahydrofuran [THF] is used). Extensive viscosity measurements were obtained during the six scheduled CPE experiments that have been performed with a Permian Basin crude. These measured viscosities have been used in the work detailed below.[2]

Comparison of Viscosity Data to the Lohrenz, Bray, and Clark (LBC) Correlation

The Lohrenz, Bray, and Clark (LBC) viscosity correlation has been used extensively in reservoir simulators because its data requirements are easily

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

met and because of its numerical convenience. The precision of estimates obtained with it has not been generally tested, however, especially for mixtures with CO_2. Calculated results have been compared with the measured viscosities of various CO_2 dilutions of the different oils, and errors as large as 60 percent observed. It should, of course, be noted that although the LBC correlation is often used for CO_2-oil systems, the original data on which the correlation was based did not include such mixtures.

Effect of Solution Gas on the Development of Miscibility

This topic was studied by performing slim tube displacement experiments to measure the MMP of oils containing different amounts of methane. In a series of runs with a synthetic oil that consisted of 1.0 (mol) part n-butane and 1.5 parts decane, it was found that the presence of up to 30 mol percent methane had only a minor effect on the MMP, although analysis of the produced hydrocarbon showed an interesting "methane bank" behavior. This influence is negated by the deleterious effect of methane impurity in the CO_2. The magnitude of this latter effect was reported by Kovarik in 1985. A preliminary run has also been made with Maljamar crude oil containing added methane with similar results, but more data will be collected with this system before conclusions about it can be drawn.

4.5 Laboratory Displacement Tests

4.5.1 Flow Studies, New Mexico Institute of Mining and Technology

This project has the following objectives:[3]

1. Perform single-phase miscible displacements with fluids having matched densities and viscosities 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 the 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 obtain Coats-Smith parameters.

5. Predict performance of gravity-stable tertiary CO_2 floods using a one-dimensional simulator.

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

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 (i.e., physical modeling) to examine qualitative effects of microscopic heterogeneity and flow of foam on mixing of CO_2 and crude oil.

CO_2-Oil Displacements -- Experiments and Simulation

Two preliminary runs were made in a new CO_2-flooding system, in which n-hexane was displaced. These runs demonstrated two causes of low oil recovery: (1) operations below the MMP and (2) operations at rates significantly higher than the critical rate. A second series of floods used simple synthetic oil composed of 33.3 mol percent n-decane and 66.7 mol percent n-hexadecane, in a series of vertical (downward) floods by pure CO_2 at pressures both below and above the MMP, and such that the L_1 L_2 region of the (P,T) diagram was spanned. This latter enabled some assessment to be made of the importance of the decreased mobility resulting from the presence and flow of the additional phases. Results of analysis along these lines are promising, so that continuing research is planned to define the limits in which the effect can be put to practical use in reservoir floods.

Flow Visualization Experiments

During the continuing analysis of these high-pressure micromodel experiments, some new terminology has been defined. <u>Stable foam</u> refers to clusters of CO_2 bubbles (discontinuous phase) when the average bubble diameter is less than the pore width and the bubbles exist in the porous media for a significant length of time. <u>Stable lamellae</u> is the name given to the discontinuous phase when the bubbles are stable, but the average bubble diameter exceeds the pore diameter. These bubbles appear as films, oriented normal to the pore walls, that travel through the porous media without bursting. Unstable lamellae are exactly similar in appearance and performance to stable lamellae, but burst after a short period of time. In the course of experiments designed to measure the effectiveness of foam floods in the micromodel, it was found that continuous foaming can be inefficient in diverting fluids into unswept pores, and that cycles of in-situ foaming, followed by a CO_2 sweep of continuous phase paths, were effective in diverting fluids into unswept pores.

Supplementary Research

Measurements were made of the output fluid concentration from a number of miscible displacements in small-diameter tubes with glass bead packing. These runs were performed with various mobility ratios to obtain data on the factors that influence the growth and apparent length of the transition zone between the fluids. While this research has implications for laboratory core floods, its major application is in the design of slim tube tests and in the interpretation of results from them. The major conclusions concern the fact that in a slim tube, as in a core, the flow is often nonuniform. The flow in a slim tube can be afflicted with serious lateral variations of flow velocity which can arise both from frontal instability and from nonuniform permeability.

4.5.2 Development of Effective Gas Solvents Including CO_2 for the Improved Recovery of West Sak Oil by Steam Flooding, The University of Alaska

This project has the following objectives:

1. Measure phase behavior and physical properties of West Sak solvent mixtures in the laboratory. The purpose of the study is to obtain experimental PVT, phase behavior, and physical property data for West Sak crude in combination with potential displacing fluids including natural gas, natural gas enriched with natural gas liquids (NGLs), CO_2, and steam.

2. Measure the MMP for injection of enriched gas and steam into the West Sak crude. This investigation will provide an appropriate range of minimum enrichment required for possible thermal miscible recovery of West Sak oil.

3. Model multiphase equilibria for systems containing water, enriched gaseous steam with CO_2, and West Sak oil. The goal is to present a user-friendly computer program capable of handling the phase equilibria computation for the thermal miscible drive for West Sak.

4. Perform displacement experiments on steam-solvent process for West Sak oil. The study is to conduct laboratory displacement experiments for evaluation of the feasibility of steam solvent or gas additives for heavy oil recovery from the West Sak reservoir.

The possibility of oil companies sharing the existing Kuparuk River Unit facilities has made the future recovery of these heavy oils in West Sak and Ugnu (Alaska) a near-term target and an economically viable venture. Although there are other horizons in the upper cretaceous and tertiary sections which are known to contain oil (heavy crude), the West Sak sands show the most potential to become commercial in the near future. West Sak alone contains about 15 to 25 billion barrels of intermediate heavy crude in the 260-square mile area outside of the Kuparuk River Unit boundaries and may be one of the largest oil accumulations in North America.

It appears that the most attractive targets for development and exploration are the deeper and warmer portions of the West Sak reservoir. The heavy oil in the West Sak is not recoverable by primary recovery methods; therefore, thermal recovery appears to be the best approach for maximizing the ultimate recovery. However, the key to successful development of West Sak will be to reduce costs for thermal recovery operations. A thermal recovery project in the harsh, cold environments of the Kuparuk River Unit certainly is a unique situation and a challenge.

Based on the characteristics of the West Sak reservoir, thermal recovery (especially steam drive) seems to be the most attractive EOR method. A combination of thermal and miscible drives might be equally attractive and can increase the ultimate recovery of heavy oils. West Sak reservoir data is given by Table 7.

Table 7. West Sak Reservoir Data

Lithology	Very fine- to fine-grained, quartzose, well-sorted sand
Area	260 square miles
Oil-in-Place	15 to 25 billion barrels
Depth	2,000 to 4,500 feet subsea
Oil Gravity	16 to 22 °API
Oil Viscosity	50 to 3,000 centipoise
Gross Pay	200 to 450 feet (average: 300 feet)
Porosity	< 20 percent (typically 18 percent)
Permeability	10 to 140 millidarcies
Dip	130 feet per mile
Temperature	45° to 100°F
Salinity of Formation Water	1,500 to 35,000 parts per million

The co-injection of steam and miscible gas will not be economical for any other reservoir because of the high cost of NGLs required for miscibility at high temperatures. For the Prudhoe Bay miscible project, a gas that is miscible with the injectant is created by the EOR gas processing plant. The separator gas is used as input to create the miscible injectant containing predominantly ethane, propane, and CO_2 as enriching agents; an NGL stream containing the heavier butanes and pentanes plus components is currently blended into the crude oil stream for sale down the pipeline and the residue gas stream is reinjected into the Prudhoe Bay gas cap. Unavailability of a market creates a possibility of utilizing the North Slope gas enriched with NGLs along with steam for the West Sak reservoir. Whether a miscible-enriched gas drive along with steam will be employed will depend on the amount of enrichment needed and the economic situation at that time.

During FY 87, The University of Alaska acquired and installed equipment for the laboratory investigations. The equipment has been calibrated and the first investigations initiated.

4.6 Field Tests

Since 1975, 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 test 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 8. Figure 22 shows the approximate location of each of these tests on a map of the United States. A discussion of the current test (the one that was active in FY 87) follows.

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

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.

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 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 percolate to the top of the watered-out reservoirs. The CO_2 would percolate upward 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 had 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 more than 75 percent of oil left after the water drive.

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, expected in 1988. In October of 1987, two production wells were producing approximately 60 barrels of oil per day. As of July 1987, the test had produced 254,000 barrels of oil or about 62 percent of the oil-in-place at the start of the field test. The ratio of CO_2 injected per barrel of oil recovered is presently 9,000 scf/STB.

Table 8. Summary of Current and Completed DOE Cost-Sharing CO_2 Field Tests

	Rock Creek Field Pilot Area, WV	Rock Creek Field Minitest Area, WV	Granny's Creek Field Pilot Area, WV	Granny's Creek Field Minitest Area, WV	Hilly Upland Field, WV	Little Knife Field, ND	Weeks Island Field, LA
Formation	Pocono Big Injun	Pocono Big Injun	Pocono Big Injun	Pocono Big Injun	Greenbrier Big Injun	Mission Canyon	"S" Sand, Reservoir B
Lithology	Sandstone	Sandstone	Sandstone	Sandstone	Carbonate	Dolomitized Carbonate	Sandstone
Reservoir Depth (Ft)	1,975	1,975	2,000-2,100	2,000-2,100	1,800-2,100	9,800	12,750
Reservoir Temperature (°F)	73	73	73	73	77-80	245	225 (Oil Column)
Net Effective Thickness (Ft)	32.4	32.0	28	28	12.5	16	120
Porosity (%)	21.9	21.3	16	16	14.0	19.5	26.0
Permeability (mD)	20.5	27.3	7	7	2-4	16.7	1,800
Oil Saturation (%)	34.4 (After Primary)	34.4 (After Primary)	30 (After Waterflood)	30 (After Waterflood)	70-80 (After Primary)	40.4 (After Waterflood)	22 (After Waterflood)
Water Saturation (%)	50-55 (Initial)	50-55 (Initial)	70 (After Waterflood)	70 (After Waterflood)	20-30 (Initial)	21.8 (Initial)	8 (Initial)
Oil Type	Paraffin Base	Paraffin Base	Paraffin Base	Paraffin Base	Paraffin Base	N/A	N/A
Oil Gravity (°API)	43	43	45	45	42	41	32.3

Table 8. Summary of Current and Completed DOE Cost-Sharing CO_2 Field Tests
(Continued)

	Rock Creek Field Pilot Area, WV	Rock Creek Field Minitest Area, WV	Granny's Creek Field Pilot Area, WV	Granny's Creek Field Minitest Area, WV	Hilly Upland Field, WV	Little Knife Field, ND	Weeks Island Field, LA
Oil Viscosity (cP) (Reservoir Conditions)	1.9	1.9	1.6	1.6	1.73	0.20	0.41
Formation Volume Factor (Original)	1.13	1.13	1.13	1.13	1.13	1.77	1.652
Formation Volume Factor	1.20 (CO_2 @ 1,300 psi)	1.20 (CO_2 @ 1,300 psi)	1.113 (CO_2 @ 492 psi)	1.113 (CO_2 @ 492 psi)	1.145 (CO_2 @ 445 psia)	N/A	1.545 (@ 225° and 5,100 psia)
Area (acres)	19.65	1.55	6.7	0.85	10	5.0	8 (900 acre-feet)
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

Table 8. **Summary of Current and Completed DOE Cost-Sharing CO_2 Field Tests**
(Continued)

	Rock Creek Field Pilot Area, WV	Rock Creek Field Minitest Area, WV	Granny's Creek Field Pilot Area, WV	Granny's Creek Field Minitest Area, WV	Hilly Upland Field, WV	Little Knife Field, ND	Weeks Island Field, LA
Primary Production (bbl/acre)	2,900	2,900	2,900	2,900	2,850	N/A	N/A
Secondary Production (Waterflood) (bbl/acre)	577	577	4,100	4,100	N/A[1]	6,680 (By simulator[2])	N/A
EOR Production (CO_2) (bbl/acre)	666	2,465	1,296	2,362	410	9,020 (By simulator[2])	23,625
CO_2 Injected (tons)	27,454	8,189	9,880	2,118	1,546	2,095	50,000
Effective CO_2 Injected (tons)	6,167	2,012	1,186	2,118	1,546	2,095	50,000
CO_2/Oil Ratio (scf/bbl)	13,000	9,000	19,626	18,192	6,333	3,100 (By simulator[2])	9,000[3] (10/86)

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

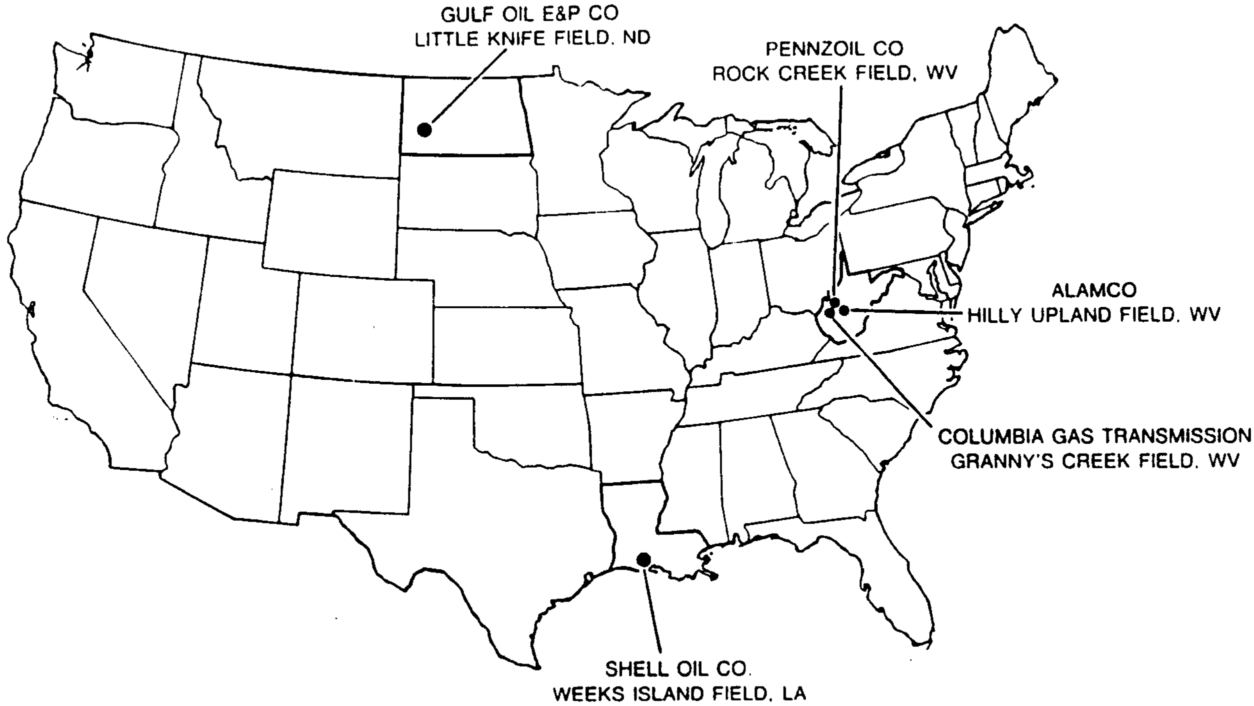

Figure 22. Location of CO_2 Enhanced Oil Recovery Field Tests

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. When economic conditions permit, Shell plans to expand CO_2 process operations to other similar reservoirs.

5.0 RESEARCH ISSUES REMAINING

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

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 able to increase the viscosity of CO_2 enough to affect mobility are still being sought. Mobility control research will be continued at the New Mexico Institute of Mining and Technology, West Virginia University, and METC.

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

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

Finally, in the area of laboratory displacement tests, METC will investigate the role that rock wettability plays in improving CO_2 flood efficiency. Methods to alter rock wettability for improved oil production will also be investigated.

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

6.0 LIST OF ABBREVIATIONS

API	American Petroleum Institute
CE	2-butoxyethanol; CH(OCH)OH
CMC	Continuous Multiple Contact
CO_2PM	CO_2 Predictive Model
cp	Centipoise
CPE	Continuous Phase Equilibrium
CRSIM-1D	One-Dimensional, Compositional Reservoir Simulator
CRSIM-3D	Three-Dimensional, Compositional Reservoir Simulator
CT	Computerized Tomography
DOE	Department of Energy
EOR	Enhanced Oil Recovery
FY	Fiscal Year (Federal: October through September)
GOR	Gas-Oil Ratio
HCPV	Hydrocarbon Pore Volume
IMPESCC	Implicit Pressure, Explicit Saturation Composition
IRR	Internal Rate of Return
LBC	Lohrenz, Bray, and Clark
MASTER	Miscible Applied Simulation Tool for Energy Recovery
MCM	Multiple Contact Miscibility
METC	Morgantown Energy Technology Center
MMP	Minimum Miscibility Pressure
MSTB	Thousand Stock Tank Barrels
NGL	Natural Gas Liquid
NMRI	Nuclear Magnetic Resonance Imaging
pV	Pore Volume
PVT	Pressure-Volume-Temperature
RSnF	Radical Tin Fluorides
SPE	Society of Petroleum Engineers
STB	Stock Tank Barrel
T	Transmissibility
TDC	Todd, Dietrich, and Chase
WAG	Water-Alternating-with-Gas
WOR	Water-Oil Ratio

7.0 REFERENCES

Killough, J.E., and C.A. Kossack. 1987. Fifth comparative solution project: evaluation of miscible flood simulators. Richardson, Texas: Society of Petroleum Engineers. SPE 16000.

Energy Monitor. October 1987. McGraw-Hill.

Jones, S.E. May 1986. The Effects of Horizontal Wellbore Injection Versus Point-Source Injection on the Recovery of Oil by CO_2. M.S. Thesis. Department of Petroleum Engineering, University of Wyoming.

Kovarik, F.S. 1985. For METC Under Contract No. DE-FC21-84MC21136.

Mosbacher, R.A. June 1984. Enhanced oil recovery. National Petroleum Council.

Journal of Colloid Interface Science 96:360.

Weekly Petroleum Status Report. October 21, 1987. Washington, D.C.: Energy Information Administration. DOE/EIA-0208 (87-39).

8.0 BIBLIOGRAPHY

Bahralolom, I.M., and F.M. Orr, Jr. 1986. Solubility and extraction in multiple-control miscible displacements: comparison of N_2 and CO_2 flow visualization experiments. Paper presented at the 56th California Regional Meeting. April 2-4, 1986. SPE 15079.

Bernard, G.G., L.W. Holm, and C.D. Harvey. August 1980. Use of surfactant to reduce CO_2 mobility in oil displacement. Society of Petroleum Engineers Journal 20(4):281-292.

Blackwell, R.J., J.R. Rayne, and W.M. Terry. 1959. Applied Science Publishers, London 206.

Bretz, R.E., and F.M. Orr, Jr. 1986. Interpretation of miscible displacements in laboratory cores. Paper presented at the 5th Symposium on Enhanced Oil Recovery, April 20-23, 1986. SPE/DOE 14898.

Bretz, R.E., R.M. Spector, and F.M. Orr, Jr. 1986. Effect of pore structure on miscible displacements in laboratory cores. Paper presented at the Permean Basin Oil and Gas Recovery Conference, March 13-14, 1986. SPE 15071.

Brummert, A.C., R.J. Watts, D.A. Boone, and J.A. Wasson. 1986. Rock Creek oil field CO_2 pilot tests, Roane County, West Virginia. Paper presented at the 5th Symposium on Enhanced Oil Recovery, April 20-23, 1986. SPE/DOE 14941.

Connor, W.D. October 1983. Tertiary oil recovery by carbon dioxide injection, Granny's Creek Field, West Virginia: final report. 38 pp. DOE/ET/12015-62. NTIS/DE84002601.

Dunmore, J.M., J. Hagoot, and A.S. Risseeuw. 1984. An analytical model for one-dimensional, three component condensing and vaporizing gas drives. Society of Petroleum Engineers Journal 24:169-179.

Helfferich, F.G. 1981. Theory of multicomponent, multiphase displacement in porous media. Society of Petroleum Engineers Journal 21:51-62.

Heller, J.P., D.A. Boone, and R.J. Watts. 1985. Field test of CO_2 mobility control at Rock Creek. Paper presented at the 60th Annual Technical Conference and Exhibition, September 22-25, 1985. SPE 14395.

Heller, J.P., D.A. Boone, and R.J. Watts. 1985. Testing CO_2-foam for mobility control at Rock Creek. Paper presented at the Eastern Regional Conference, November 6-8, 1985. SPE 14519.

Odeh, A.S. January 1981. Comparison of solutions to a three-dimensional black oil reservoir simulation problem. Journal of Petroleum Technology 33(1):13-25.

Patton, J.T. September 1986. <u>Enhanced oil recovery by CO_2 foam flooding: final report, October 1, 1981, to December 31, 1985</u>. 195 pp. DOE/MC/16551-19. NTIS/DE86000300.

Perry, G.E. 1982. Weeks Island "S" sand reservoir gravity-stable miscible CO_2 displacement. Paper presented at the 3rd Symposium on Enhanced Oil Recovery, April 4-7, 1982. SPE/DOE 10695.

Todd, M.R., W.M. Cobb, and C.D. McCarter. October 1982. CO_2 flood performance evaluation for the Cornell Unit, Wasson San Andres Field. <u>Journal of Petroleum Technology</u> 34(10):2271-2282.

Upton, J.E. July 1983. <u>Little Knife field CO_2 mini-test, Billings County, North Dakota: final report, vols. 1 and 2</u>. DOE/MC/08383-45-Vol. 1 and DOE/MC/08383-45-Vol. 2. NTIS/DE83015381 and NTIS/DE83015380.

Watts, R.J., J.B. Gehr, J.A. Wasson, D.M. Evans, and C.D. Locke. August 1982. A single CO_2 injection well minitest in a low-permeability carbonate reservoir. <u>Journal of Petroleum Technology</u> 34(8):1781-1788.

9.0 FISCAL YEAR 1987 GOVERNMENT-SPONSORED PAPERS AND REPORTS CONCERNING MISCIBLE GAS ENHANCED OIL RECOVERY

Ambastha, K.A., and A. Sageev. January 1987. Infinite linear water influx through a partially communicating fault. In Proceedings of the 12th Workshop on Geothermal Reservoir Engineering. Stanford, California.

Ambastha, K.A., P.G. McLeroy, and A. Sageev. 1987. Effects of a partially communicating fault in a composite reservoir on transient pressure testing. Presented at the SPE Annual Technical Conference and Exhibition, SPE of AIME, September 1987, Dallas, Texas, SPE 16764.

Bouett, L.W., A. Sageev, and F.M. Orr, Jr. 1987. Simulation of BPVT experiments. Presented at the 1987 Symposium on Petroleum Industry Applications of Microcomputers, June 23-26, 1987, Houston, Texas. SPE 16502.

Bretz, R.E., S.L. Welch, N.R. Morrow, and F.M. Orr, Jr. 1986. Mixing during two-phase, steady-state laboratory displacements. Presented at the 1986 SPE Annual Meeting, October 5-8, 1986, New Orleans, Louisiana. SPE 15389.

Britto, P., and A. Sageev. April 1987. The effects of shape and orientation of an impermeable region on transient pressure testing. Presented at the California Regional Meeting, SPE of AIME, April 1987, Ventura, California. SPE 16376.

Brummert, A.C., J.R. Ammer, R.J. Watts, P. King, and D.A. Boone. 1986. Economic evaluation of a CO_2 enhanced oil recovery flood at the Rock Creek Field, Roane County, West Virginia. Paper presented at the Eastern Regional Conference, November 12-14, 1986. SPE 15955.

Heller, J.P., F.S. Kovarik, and J.J. Taber. May 1987. Improvement of CO_2 flood performance: annual report for the period October 1985 - October 1986. 101 p. DOE/MC/21136-10. NTIS/DE870001236.

Klara, S.M., and K. Hemanth-Kumar. 1987. Comparisons of computational efficiencies of different equations of state and transport property correlations in a compositional simulator. Presented at the 62nd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, September 27-30, 1987. Dallas, Texas. SPE 16942.

Larsen, L.L., M.K. Silva, M.A. Taylor, and F.M. Orr, Jr. 1986. Temperature dependence of L-L-V phase behavior in CO_2 hydrocarbons systems. Presented at the 1986 SPE Annual Meeting, October 5-8, 1986, New Orleans, Louisiana. SPE 15399.

Monroe, W.W., M.K. Silva, L.L. Larsen, and F.M. Orr, Jr. 1987. Composition paths in four-component systems: the effect of dissolved methane on CO_2 flood performance in one dimension. Presented at the 1987 Fall Meeting of SPE of AIME, September 27-30, 1987, Dallas, Texas. SPE 16712.

Orr, F.M., Jr. 1987. Reservoir characterization for CO_2 flooding. In Proceedings of the 3rd Wyoming Enhanced Oil Recovery Symposium, May 13-14, 1987, Casper, Wyoming.

Orr, F.M., Jr., and A. Sageev. March 1987. Reservoir characterization for the CO_2 enhanced oil recovery process: annual report. 142 pp. DOE/MC/22042-5. NTIS/DE87001230.

Pande, K.K., H.J. Ramey, Jr., W.E. Brigham, and F.M. Orr, Jr. 1987. Frontal advance theory for flow in heterogeneous porous media. Presented at the 1987 California Regional Meeting of SPE of AIME, April 8-10, 1987. Ventura, California. SPE 16344.

Smith, D.H. 1986. New methods for the measurement of phase diagrams for CO_2 mobility control. 1986 Southwest Regional ACS Meeting, November 19-21, 1986, Houston, Texas.

Smith, D.H., K. Das, G. Covatch, and G.C. Allred. 1987. Calorimetric measure of phase diagrams and enthalpies of surfactant systems for enhanced oil recovery. Presented at the symposium on Use of Surfactants for Mobility Control in Enhanced Oil Recovery, June 23-24, 1987, Ann Arbor, Michigan.

Terry, R.E., A. Zaid, C. Angelos, and D.C. Whitman. 1987. Polymerization in supercritical CO_2 to improve CO_2/oil mobility ratios. Presented at the SPE International Symposium on Oil Field Chemistry, February 4-6, 1987, San Antonio, Texas. SPE 16270.

Watts, R.J. March 1984. CO_2 injection must wait for economics. Northeast Oil World 1(3):13-15.

White, C.D., and R.N. Horne. 1987. Computing absolute transmissibility in the presence of fine-scale heterogeneity. Presented at the 9th SPE Simulation Symposium, May 1987, San Antonio, Texas. SPE 16011.

Whitman, D.L., and S.E. Jones. 1987. Laboratory investigation of increasing the sweep efficiency of carbon dioxide flooding by using a horizontal wellbore. Presented at the 2nd Annual International Enhanced Oil Recovery Conference, June 1-3, 1987, Anaheim, California.