

1987



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47, 48, 49 & 50

DOE/BC—88/4/SP
Date Published—March 1988

For the Period
January-December 1987

Bartlesville Project Office
U.S. Department of Energy
Bartlesville, Oklahoma 74005



PREFACE

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LIST OF BPO PUBLICATIONS

For the period

January-December 1987

Compiled by

Herbert A. Tiedemann

Bartlesville Project Office
P.O. Box 1398
Bartlesville, Oklahoma 74005

Date Published—March 1988

UNITED STATES DEPARTMENT OF ENERGY

LIST OF PUBLICATIONS

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Bartlesville Project Office

Robert L. Folstein, Director

DOE/BC-87/4/SP

January-March 1987

DATE PUBLISHED—APRIL 1987

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GENERAL RESEARCH

Quarterly Reports

DOE/BC-86/1 Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery. Progress Review No. 45. Quarter ending December 31, 1985. December 1986. 119 pp. NTIS Order No. DE86000294. Status reports are given for various enhanced oil and gas recovery projects sponsored by the Department of Energy. The field tests and supporting research on enhanced oil recovery include chemical flooding, gas displacement, thermal/heavy oil, resource assessment, extraction technology, and microbial technology.

DOE/BC/99880-15 Strategic Petroleum Reserve Supporting Research. FY86 Annual Report. National Institute for Petroleum and Energy Research. January 1987. 35 pp. NTIS Order No. DE87001215. The DOE Strategic Petroleum Reserve Office (SPRO) has extensive facilities and expertise for underground storage of crude oil but limited analytical laboratory capabilities. The National Institute for Petroleum and Energy Research (NIPER), formerly the Bartlesville Energy Technology Center (BETC), has extensive experience in petroleum testing and has served as the analytical support laboratory for SPRO since 1978. NIPER provides analytical support to SPRO through contract arrangement with the DOE Bartlesville Project Office (BPO). Work performed during the contract period of this report included establishing new and modifying old methodology for expanded and improved crude oil characterization. The expanded comprehensive characterization scheme that was initiated last year was used to analyze 25 samples of crude oil for the SPRO. Inspection type analyses were performed on 28 SPR crude oil samples. The number of tests performed for each sample has significantly increased over those done in previous years, and the characterization scheme continues to expand. Accurate characterization data are essential to define and monitor the quality of crude oil in the Strategic Petroleum

Reserve, the Nation's emergency crude oil reserve. Exploratory research into the chemistry of sludge formation was initiated this past year to provide information for directing future research in this area. Apparently, sludge forms during any long term storage of crude oil and it is present in the SPR caverns. A series of sludge samples was obtained from SPR storage caverns for research and analyses. Some of the samples were separated into acid, base and neutral fractions using liquid chromatographic techniques. These fractions were further analyzed using a variety of instrumental and chemical methods to yield the elemental and structural information in this report.

Enhanced Oil Recovery—Chemical Flooding

DOE/BC/10844-5 Associative Polymers for Mobility Control in Enhanced Oil Recovery—First Annual Report. University of Southern Mississippi. February 1987. 268 pp. NTIS Order No. DE87001218. Research during the first year of this contract focused on synthesis, characterization, and rheology of copolymers of acrylamide (AM) with analogs of 3-acrylamido-3-methylbutanoate (AMB). In the initial phase, however, emphasis was given to the placement of hydrophobic substituents along the polymer backbone which would allow intermolecular associations to occur at low polymer concentration. Comparisons of N-substituted AMB and unsubstituted copolymers prepared under a previous grant are being made currently. The viscosity behavior and the electrolyte tolerance of these copolymers are of special interest to the researchers. Rheological, potentiometry, and ion binding studies of the substituted models indicate less tolerance to calcium ions than the NaAMB/AM system and support the proposed intramolecular chelation suggested previously in DOE report number, DOE/BC/10321-20. Solution behavior has been studied as a function of microstructure and molecular weight for N-substituted AMB/AM copolymers utilizing potentiometry, turbidimetry in conjunction with C-13 NMR and low angle laser light scattering. N-propyl-substituted NaAMB/AM copolymers have shown surfactant-like characteristics including the ability to emulsify hydrocarbons and greatly enhance solution viscosity in aqueous solution. Further studies on these and other N-substituted acrylamido systems are planned for FY-87. A new variable angle laser light scattering apparatus has been designed and is being assembled. The new scattering device should provide a much higher signal to noise ratio, and thus, provide more accurate EOR polymer characterization.

DOE/BC-86/10/SP Supporting Technology for Enhanced Oil Recovery, Polymer Predictive Model. Venezuela-MEM/USA-DOE Fossil Energy Report III-4. December 1986. 394 pp. NTIS Order No. DE87001207. The Polymer Flood Predictive Model (PFFPM) was developed for and in conjunction with the members of the Chemical Task Group of the National Petroleum Council (NPC) for use in the 1982-1984 NPC study on enhanced oil recovery (EOR) potential. The model was designed to conform to the methodology and structure of the suite of models being used in the study. This insured that all models would calculate and report the predicted oil recovery and economics in an identical manner. As in the other models, the polymer flood model contains an extensive set of default equations to calculate noncritical reservoir properties, flood properties, and economic criteria. The Department of Energy, Bartlesville Project Office, supported the NPC and has maintained the models since the NPC study was completed. The DOE, in a cooperative research program with the Ministry of Energy and Mines of Venezuela (MEMV), has made this predictive model available to Venezuela for documentation. Annex III of the cooperative research program required Venezuela to select and fund a contractor to document the five models used in the 1984 study. SSI was selected as the contractor to document the models. The documen-

tation for PFFM is being published as a joint DOE/MEMV document. The code listing has been added to the end of this report to provide the user maximum use of the documentation package.

DOE/BC-86/11/SP Supporting Technology for Enhanced Oil Recovery, Chemical Flood Predictive Model. Venezuela-MEM/USA-DOE Fossil Energy Report III-5. December 1986. 360 pp. NTIS Order No. DE87001208. The Chemical Flood Predictive Model (CFPM) was developed for the Department of Energy (DOE) by Intercomp Resource Development and Engineering, Inc., which is now part of Scientific Software-Intercomp (SSI), Denver, Colorado. The model was developed to estimate economically recoverable oil from reservoirs amenable to the chemical flood process while requiring publicly available data. Publicly available data is generally limited to average rock and fluid properties and is usually too limited to perform most simulation studies. For this reason, a set of extensive defaults are built into the model - both in the predictive algorithms and the economic routines. For versatility, each model allows the user to supply model-required parameters specific to the reservoir being evaluated. CFPM was used in the 1982-1984 National Petroleum Council (NPC) study on EOR potential. The NPC reviewed and modified the predictive, economic, and data default routines to calibrate the models with field histories and current economic standards. The DOE, in a cooperative research program with the Ministry of Energy and Mines of Venezuela (MEMV), made this predictive model available to Venezuela for documentation. Annex III of the cooperative research program required Venezuela to select and fund a contractor to document the five models used in the 1984 study. SSI was selected as the contractor to document the models. The documentation for CFPM is being published as a joint DOE/MEMV document. The code listing has been added to the end of this report to provide the user maximum use of the documentation package.

NIPER-146 Mobility Control in Oil Recovery by Chemical Flooding State-of-the-Art Review. Topical Report. National Institute for Petroleum and Energy Research. January 1987. 100 pp. NTIS Order No. DE87001210. Mobility control in oil recovery by chemical flooding (polymer, micellar polymer, and alkaline polymer) can be achieved through the use of low-concentration, water-soluble polymers in water or in chemical slugs. Since the late 1950's, water-soluble polymers have been studied extensively in laboratories by many researchers and widely used in many chemical flooding projects to improve sweep efficiency and increase ultimate oil recovery. Effective use of polymers as mobility control agents requires the understanding of the stability of polymers and their rheological behavior in reservoirs. An overview of the scientific literature on the application of water-soluble polymers in enhanced oil recovery is presented. The processes, factors, and mechanisms that influence the stability of polymers and those that cause a reduction in water mobility are discussed. Existing knowledge of polymer flow behavior in porous media, and of surfactant-polymer interactions is reviewed. Also discussed are the case histories of 23 chemical flooding field projects.

NIPER-206 A Simple Mathematical Model for Estimating Mineral-Alkali Reactions in Alkaline Flooding. Topical Report. National Institute for Petroleum and Energy Research. January 1987. 43 pp. NTIS Order No. DE87001211. The problem of characterizing alkali-water-rock reactions in alkaline flooding is complicated because there are many mineral phases and aqueous species to include in a compositional model. The model presented in this report includes the following types of minerals: silicates, carbonates, sulfates, and oxides. Individual mineral reactions are arranged in order of increasing pH. Sulfate and carbonate minerals are converted to oxides and silicates at intermediate pH. The model predicts that calcium, magnesium, and carbonate ions are most important at neutral to intermediate pH and that silicate and aluminate ions become important at high pH. Results from bottle tests quantify the ability of minerals to consume alkaline agents. Studies on individual minerals, including kaolinite and dolomite, are reported. The effects of individual minerals in a mixture were found to be additive. The results

described in this report show that an accurate determination of rock mineralogy is required for a reasonable prediction of alkali consumption in an oilfield.

NIPER-216 Emulsion Steam Blocking Processes-Final Report. National Institute for Petroleum and Energy Research. February 1987. 55 pp. NTIS Order No. DE87001220. Emulsion blocking experiments were conducted in cores, sandpacks, a slimtube, and two types of micromodels. The reservoir materials tested were predominantly from the Kern River, California field. The best and most cost-effective emulsification agent for the Kern River crude oil was sodium hydroxide although one cat-ionic surfactant was also extremely effective. In situ emulsification proved to be effective, but the exact mechanisms responsible for incremental oil production are difficult to quantify because of the increased mobilization of oil which results from lowered interfacial tension. Surfactants were screened for adsorption on the Kern River sand and caustic was tested for reactivity (losses) with the sand. Sodium hydroxide loss was less than expected presumably because of the low clay content of the Kern River sand. Surfactant adsorption was similar to that measured on crushed Berea sandstone. Conclusions drawn from this work are as follows: (1) emulsions can be formed that are stable at high temperatures, survive dilution with low-salinity water, and have the correct droplet size distributions for causing blocking in a porous medium; (2) emulsion blocking is effective for reducing steam mobility in high permeability zones, and emulsion blocking should be field tested; (3) the preferred conditions for a field test of the process are reservoirs with low salinity brine, low clay content, and acidic crude oil; (4) Kern River field, California is a good candidate for a field trial of this blocking process; and (5) caustic, a low cost chemical, was found to be effective with many heavy oils; consequently, the emulsion blocking process may be cost effective.

NIPER-217 Enthalpies of Dilution of Aqueous Dodecyl- and Tetra-Decyltrimethylammonium Bromides From 323 To 448 K and of Aqueous Sodium Chloride From 349 To 498 K. Topical Report. National Institute for Petroleum and Energy Research. February 1987. 71 pp. NTIS Order No. DE87001221. Enthalpies of dilution of aqueous dodecyltrimethylammonium bromide from 323 to 498 K, of aqueous tetradecyltrimethylammonium bromide from 323 to 448 K, and of aqueous sodium chloride from 349 to 448 K have been measured using a flow calorimeter. The surfactant data are fitted using a nonlinear least squares minimization of a cubic spline surface. From these fits, changes in activity and osmotic coefficients with respect to temperature and also the relative apparent molar enthalpies and heat capacities may be calculated. Critical micelle concentration regions are obtained and compared to values obtained from conductance measurements. Pitzer's ion-interaction equation is fitted to the sodium chloride data, and the calculated relative apparent molar enthalpies are compared to literature values. This comparison demonstrates a high degree of reliability of data produced by the Albert-Wood calorimeter used in these studies.

NIPER-221 Design, Construction, and Operation of an Apparatus to Measure Viscosity and Screen Factor of Polymer Solutions at High Temperatures. Topical Report. National Institute for Petroleum and Energy Research. February 1987. 24 pp. NTIS Order No. DE87001222. Water-soluble polymers for applications in harsh reservoirs (high-temperature, salinity, and hardness) for mobility control or profile modification are being developed and manufactured by many chemical companies. For screening the newly developed polymers, apparatuses that can be used to determine the rheological properties of polymers under simulated harsh reservoir conditions are needed. In FY 1986, a high-temperature apparatus was constructed for this purpose. It consists of a capillary viscometer for measuring the screen factor. This report describes the design, construction, and operating procedures for this apparatus. The apparatus can be operated at temperatures up to 392°F. Viscosities can be determined at shear rates from those encountered in the formation (0.1 to 10 sec^{-1}) to those encountered in the near-wellbore region (greater than 500 sec^{-1}).

Rheological Behavior of Pusher 500 Under A Variety of Chemical and Thermal Conditions. Topical Report. National Institute for Petroleum and Energy Research. February 1987. 50 pp. NTIS Order No. DE87001224.

This project was designed to provide information to understand and model the rheological behavior of polymers under a variety of simulated reservoir conditions and to gain the knowledge of the fidelity with which external measurements characterize mobility behavior under changing conditions. The understanding and modeling of the rheological behavior will lead to more effective use of polymers as mobility control agents in enhanced oil recovery processes. This report describes the progress made on the study of the rheological behavior of a partially hydrolyzed polyacrylamide, Dow Pusher 500, under a variety of thermal and chemical conditions. The rheological properties being considered include shear viscosity, screen factor, and flow resistance in cores. Screen factors (constant head) were measured with a modified screen factor viscometer to account for the rate effect. Viscosity and screen factor data were correlated with flow rate, polymer concentration, and salt concentration. The empirical correlations developed were then used to study the effects of alkali and temperature on these parameters. Results suggest that constant-head screen factor gives rheological information which supplements that from standard screen factor. As the screen factor models the flow resistance in porous media, it counteracts the shear-thinning behavior of the polymer. The hydrolysis of Pusher 500 was accelerated by alkali under elevated temperature conditions. Flow resistance studies in a Berea core show that apparent viscosities in the low flow rate regime are lower than bulk solution viscosities and that viscoelasticity effects occur at a friction factor-Reynolds number product less than one. The critical Deborah number corresponding to the onset of viscoelasticity effects is about 0.01. Comparison of the rheological behavior in the Berea sandstone core with that measured outside the core shows that the effects of polymer and salt concentrations on the reduced apparent viscosity measured inside the core are similar to those on the reduced viscosity measured with a shear viscometer at low flow rates. The effects of these variables on the viscoelastic increment to the apparent viscosity are similar to that on the screen factor at high flow rates. These correlations can be used to predict the flow resistance of hydrolyzed polyacrylamides in Berea sandstone cores.

Enhanced Oil Recovery—Carbon Dioxide

Phase Behavior and Minimum Miscibility Pressures for Nitrogen Miscible Displacement. Topical Report. National Institute for Petroleum and Energy Research. March 1987. 56 pp. NTIS Order No. DE87001229.

The phase behavior and minimum miscibility pressure (MMP) for nitrogen with light oils were studied. The phase behavior studies were performed on N_2 +hydrocarbon mixtures as well as N_2 +recombined oil systems at high pressures (above 4,000 psia). The synthetic oil system of N_2 + C_1 + C_4 + C_{10} was studied to approximate the phase behavior of crude oils with nitrogen to investigate the effect of the presence of methane on phase behavior and N_2 MMP values. The phase behavior data are used in a computer simulator to match the slim tube displacement behavior and to provide an estimate of the MMP. The N_2 +recombined oil studies provide the complex behavior of the multicomponent systems. Adjustment of parameters to predict the phase envelope has been made in order to use these parameters in equations of state (EOS) for predictions at various reservoir conditions. This provides a cross check of the conditions of miscibility achieved during the slim tube experiments. Experimental runs were performed in a slim tube apparatus to determine the MMP of stock-tank oils with nitrogen, recombined oils, and synthetic oils at pressures up to 10,000 psia and temperatures from 200 to 300°F. These experiments were performed using stock-tank oils with API gravities of 50.8° and 61.5°, recombined at different gas-oil ratios (GOR). The experimental results indicate the important contribution of the light and intermediate components of crude oil in decreasing the MMP and show the variation in oil recovery as a function of temperature. Similar N_2 MMP tests were performed on two synthetic mixtures containing C_1 , C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} and C_{12} . These studies will provide useful information for the implementation of the N_2 miscible displacement process.

The Miscible Flood Predictive Model (MFFM) was developed for the Department of Energy (DOE) by Intercomp Resource Development and Engineering, Inc., which is now part of Scientific Software-Intercomp (SSI), Denver, Colorado. The model was developed to estimate economically recoverable oil from reservoirs amenable to the CO₂ miscible flood process while requiring publicly available data. Publicly available data is generally limited to average rock and fluid properties and is usually too limited to perform most simulation studies. For this reason, a set of extensive defaults are built into the model – both in the predictive algorithms and the economic routines. For versatility, each model allows the user to supply model-required parameters specific to the reservoir being evaluated. MFFM was used in the 1982-1984 National Petroleum Council (NPC) study on EOR potential. The NPC reviewed and modified the predictive, economic, and data default routines to calibrate the models with field histories and current economic standards. The DOE, in a cooperative research program with the Ministry of Energy and Mines of Venezuela (MEMV), made this predictive model available to Venezuela for documentation. Annex III of the cooperative research program required Venezuela to select and fund a contractor to document the five models used in the 1984 study. SSI was selected as the contractor to document the models. The documentation for MFFM is being published as a joint DOE/MEMV document. The code listing has been added to the end of this report to provide the user maximum use of the documentation package.

This report describes a combination of theory and experiment in each of three key areas: phase behavior, reservoir heterogeneity and viscous instability. The material included here represents progress to date in a continuing research effort aimed at improving understanding of underlying physical mechanisms that influence miscible flood performance. That understanding is an essential part of the progress toward the overall goal of improved performance predictions for field-scale displacements. The combined effects of heterogeneity, viscous instability and phase behavior that limit the accuracy of reservoir simulation predictions of CO₂ flood performance at field scale, are uncertain, however. At laboratory scale, considerable progress has been made in investigations of the combined effects of phase behavior and viscous instability or heterogeneity. Several investigators have shown that the performance of slim tube displacements, in which the effects of nonuniform flow are small, can be predicted quantitatively if the phase behavior of the CO₂-oil mixture is modeled adequately by an equation of state or some other simpler representation. The problem of performance prediction for larger-scale displacements would be straightforward if no new scales of nonuniformity appeared as the displacement length increased. Unfortunately, that is clearly not the case. Instead, new scales of heterogeneity in porosity and permeability appear, and the length scales associated with viscous fingers in large scale displacements must differ from those observed in cores, for example. Thus, if reservoir simulation predictions of CO₂ flood performance are to be improved, better descriptions of the relationships between the various length scales of flow nonuniformities and their interactions with phase behavior are needed.

Enhanced Oil Recovery—Thermal Recovery

The Steam Flood Predictive Model (SFFM) was developed for the Department of Energy (DOE) by Intercomp Resource Development and Engineering, Inc., which is now part of Scientific Software-Intercomp (SSI), Denver, Colorado. The model was developed to estimate economically recoverable oil from reservoirs amenable to the steam flood process while

requiring publicly available data. Publicly available data is generally limited to average rock and fluid properties and is usually too limited to perform most simulation studies. For this reason, a set of extensive defaults are built into the model—both in the predictive algorithms and the economic routines. For versatility, each model allows the user to supply model required parameters specific to the reservoir being evaluated. SFPM was used in the 1982-1984 National Petroleum Council (NPC) study on EOR potential. The NPC reviewed and modified the predictive, economic, and data default routines to calibrate the models with field histories and current economic standards. The DOE, in a cooperative research program with the Ministry of Energy and Mines of Venezuela (MEMV), made this predictive model available to Venezuela for documentation. Annex III of the cooperative research program required Venezuela to select and fund a contractor to document the five models used in the 1984 study. SSI was selected as the contractor to document the models. The documentation for SFPM is being published as a joint DOE/MEMV document. The code listing has been added to the end of this report to provide the user maximum use of the documentation package.

DOE/BC—86/7/SP Supporting Technology for Enhanced Oil Recovery, In-Situ Combustion Predictive Model. Venezuela-MEM/USA-DOE Fossil Energy Report III-3. December 1986. 263 pp. NTIS Order No. DE86000284. The In-situ Combustion Predictive Model (ICPM) was developed for and in conjunction with the members for the Thermal Task Group of the National Petroleum Council (NPC) for use in the 1982-1984 NPC study on enhanced oil recovery (EOR) potential. The model was designed to conform to the methodology and structure of the suite of models being used in the study. This insured that all models would calculate and report the predicted oil recovery and economics in an identical manner. As in the other models, the in-situ combustion model contains an extensive set of default equations to calculate non-critical reservoir properties, flood properties, and economic criteria. The Department of Energy, Bartlesville Project Office, supported the NPC and has maintained the models since the NPC study was completed. The DOE, in a cooperative research program with the Ministry of Energy and Mines of Venezuela (MEMV), has made this predictive model available to Venezuela for documentation. Annex III of the cooperative research program required Venezuela to select and fund a contractor to document the five models used in the 1984 study. SSI was selected as the contractor to document the models. The documentation for ICPM is being published as a joint DOE/MEMV document. The code listing has been added to the end of this report to provide the user maximum use of the documentation package.

Resource Assessment

DOE/BC/10851-5 Dispersivity as an Oil Reservoir Rock Characteristic. Annual Report for Period October 1, 1985-September 30, 1986. University of Oklahoma. March 1987. 57 pp. NTIS Order No. DE87001225. The main objective of this research is to establish dispersivity as an oil reservoir rock characteristic and to use this reservoir rock property to aid in enhancing crude oil recovery. A second objective is to compare the dispersion coefficient and the dispersivity of various reservoir rocks with other rock characteristics such as: porosity, permeability, capillary pressure, and relative permeability. The dispersivity of a rock was identified as one of its physical properties by measuring the mixing of two miscible fluids, one displacing the other in a porous medium. A core was 100% saturated with a liquid oil product (resident fluid) which was displaced by injecting a miscible liquid (displacing fluid). Samples of fluid produced from the outlet end of the core were analyzed for determining the percentage of the resident and the displacing fluid in the producing end. The extent of the spread of the concentration front (mixing) was measured from these samples by use of a refractometer after calibration with the specific fluids. The miscible liquids consisted of crude oil, naphtha, and various mixtures of oil products. Mixtures of miscible liquids were used in order to obtain equal viscosity fluids. Several physical and flow characteristics were measured on the same core in order to investigate the correlation with dispersivity. A standard technique for measuring the dispersion coefficient, K , and the dispersivity

of an oil reservoir rock has been proposed. While conducting this research, a new low-cost, and rapid method of coating cores for laboratory flow studies has been developed. Dispersion coefficients and dispersivities for several Berea sandstone cores were determined and attempts were made to correlate with other standard oil reservoir rock characteristics. A direct relationship between dispersivity and total permeability was observed from the laboratory data. A correlation was also developed to correct for the difference in the viscosities of the two miscible fluids. A new method of calculating the relative permeability ratio of a miscible system was also proposed. Other correlations for dispersivity being attempted were Koval's heterogeneity factor (H-factor) and Peclet number.

Enhanced Oil Recovery—Microbial Technology

DOE/BC/10852-2 MEOR Technical Status and Assessment of Needs—1986. Hardin-Simmons University. March 1987. 49 pp. NTIS Order No. DE87001227. This report summarizes the need for, the potential of, and the research still required for microbial enhanced oil recovery (MEOR). Enhanced oil recovery processes are those which recover oil unrecoverable by primary or secondary methods. To date, only chemical flooding, miscible flooding, and thermal recovery have been considered as economical recovery techniques. Last year, the DOE sponsored an international MEOR workshop which concluded that MEOR has merit as a cost-effective method for recovering residual oil. However, there has been no reliable and documented assessment of the technical and economic aspects of MEOR as compared to other EOR techniques. A review of the literature and the conclusions of the MEOR workshop have been summarized to determine the state-of-the-art of MEOR technology, its advantages and limitations, and its future.

DOE/BC/10852-1 Proceedings of the First International MEOR Workshop, April 1-3, 1986. Hardin-Simmons University. January 1987. 376 pp. NTIS Order No. DE87001216. The goal of this workshop was to bring together experienced investigators from around the world to review MEOR state-of-the-art as related to effectiveness as an advanced novel extraction process. Furthermore, it was determined that goal would be most successfully attained in a workshop environment where an evaluation and determination from the available information could be made about the potential for MEOR as a viable technology for increasing oil production where primary recovery is no longer effective. The DOE sponsored the workshop and the Hardin-Simmons Fairleigh Dickinson Research Center hosted the workshop in Abilene, Texas. The format used to achieve the goals of this workshop included: (1) overview presentations and discussions on field evaluation, microbiology and special applications of MEOR; and (2) workshop groups specifically selected to discuss and summarize MEOR topics. In a final session, reports were summarized, conclusions were drawn, and recommendations were made. (1) A "hands-on" laboratory workshop for those participants desiring a demonstration of the microbiological techniques; and (2) a field trip where an actual oil well MEOR injection was demonstrated were optional activities for interested participants.

Environmental

NIPER-179 Significance of the Survival and Performance of Bacillus Species in Porous Media for Enhanced Oil Recovery. Topical Report. National Institute for Petroleum and Energy Research. March 1987. 24 pp. NTIS Order No. DE87001226. Microbial enhanced oil recovery (MEOR) has advanced to the stage in which several field tests have been performed and others are still in progress. The potential for microbial injection into petroleum reservoirs to cause environmental problems has not been determined. Ongoing research at NIPER has placed emphasis upon determining whether MEOR processes can be used safely and successfully in oilfields. Two microorganisms used frequently for MEOR field projects are *Clostridium* and *Bacillus* spp. This report presents data on several species of *Bacillus* and their characteristics in porous media, their compatibility with other microbial species, and their oil recovery

efficiencies. Significant findings include the following: (1) contaminating microorganisms from nutrients or the reservoir can interfere with *Bacillus* species; (2) many Gram-negative bacteria overgrow *Bacillus* spp. after one week residence time in porous media; and (3) *Bacillus* species can, because of their spore formation, survive in porous media for almost seven months without additional nutrients. It was concluded that the compatibility of MEOR microorganisms to be injected and field microbial flora and fluids must be determined before field testing. *Bacillus* appears to behave more consistently in porous media and with other microorganisms than the *Clostridium* species investigated last year.

PROCESSING AND THERMODYNAMICS

Processing

NIPER-186 Trends in Refinery Feedstock Properties and Refining Problems. Topical Report.

National Institute for Petroleum and Energy Research. January 1987. 37 pp. NTIS Order No. DE87001214. Trends in quality of crude feedstocks to U.S. refineries and the problems in processing and utilization caused by the changing feed quality were reviewed. The quality of feedstocks declined in the period 1978-1985. This is shown, for example, by declining API gravity from 34.3 to 32.4 and an increase in sulfur content from 0.78 to 0.91%. The percentage of heavy crude (API gravity less than 20) being processed domestically increased from 1.8 weight percent in 1978 to 5.3 weight percent in 1985. The lower quality was due primarily to a decline in quality of imported rather than domestic crudes. The shift in crude quality was not caused by a shortage of conventional crude, but resulted from economic factors which encouraged the utilization of cheaper heavier crudes. While domestic throughput decreased significantly during this period, the fraction of the residual material being upgraded increased. The increased conversion was driven by heavier feedstocks, a sustained demand for distillate products, a decreased demand for residual fuels, and an increased conversion capacity by industry. The majority of the upgrading relied largely on carbon rejection techniques. A variety of problems are associated with the utilization of lower-quality feedstocks and increased resid processing. These include both problems in the refinery and problems with product quality. The understanding of fundamental petroleum chemistry of heavy crudes and resids is inadequate to predict their processing behavior. Processing flexibility for resids from heavy crudes is limited due largely to their metals content and propensity for coke formation. Other problems discussed include those with desalting, naphthenic acids, hydrotreating, cat cracking, and thermal operations. The change in feedstock quality and increased resid upgrading did not negatively affect overall gasoline quality, but have negatively affected quality of heavier fuels. Heavier feedstocks and increased resid processing result in more aromatic diesel cuts with poorer diesel ignition quality. Stability of diesel cuts is negatively affected. Quality of residual fuels is also negatively affected, with increased problems with stability and compatibility.

NIPER-222 Stability, Compatibility, and Related Problems of Additives in Naval Distillate

Fuels Derived from Lower Quality Feedstocks. Topical Report. National Institute for Petroleum and Energy Research and Naval Research Laboratory. February 1987. 63 pp. NTIS Order No. DE87001223. This report describes the first two years of a study cosponsored by the DOE and the U.S. Navy to determine which antioxidant additives are most effective in delaying fuel degradation in a variety of middle distillate straight run/light cycle oil blends. In this study, straight-run middle distillate and catalytically cracked product were mixed at ratios of 85:15, 70:30, and 60:40, respectively. All of these blended fuels were immediately treated with commercially available additives. Usual dosages were 12 and 24 ppm (volume) percent. Stability testing and fuel characterizations performed at four different laboratories were used to evaluate the additives. Each laboratory used a different type

of stability test. The characterization studies were performed to ensure that the base fuel blends tested were within the range allowed by MIL-F-16884H and to determine whether any of the additives would make the fuels unacceptable for Navy use. Because of the high degree of stability of several of the control (additive-free) fuels, it was difficult to differentiate additive effectiveness in these fuels. Some studies were performed to see if controlled aging techniques prior to actual stability testing could increase the amount of sediment in the fuel. Results indicated that this would increase sediment in some cases and would have no effect in others. Sample collection techniques at the refineries were also investigated. Both lined and unlined cans were used in these studies. Samples were blanketed with argon, sparged with air, or left with an air blanket. Water was added to some samples to determine the effect that the moisture would have on stability. In studies on the West Coast fuel, the unlined cans increased sediment formation considerably. However, the type of cans had virtually no effect on the stability of fuel from the Gulf Coast. In cases where control fuels exhibited instability, it was possible to demonstrate the relative effectiveness of the 12 stabilizer additives. Five of the additives (2, 3, 10, 11, and 12) have been shown to be superior to the remaining seven. However, all 12 will continue to be tested during the remainder of this study.

Thermodynamics

NIPER-83 Thermodynamic Properties of Organic Nitrogen Compounds that Occur in

Shale Oil and Heavy Petroleum. Topical Report. National Institute for Petroleum and Energy Research. January 1987. 38 pp. NTIS Order No. DE87001213. Condensed-phase heat capacities and enthalpies were determined at temperatures from near 10 to 400 K for N-methylpyrrole, 2,5-dimethylpyrrole, piperidine, 2-methylpiperidine, 4-methylpyridine, and N-methylcarbazole and were used to provide the Gibbs energy, enthalpy, entropy, and heat capacity along the vapor saturation line at temperatures from 0 to 400 K. The corresponding ideal gas thermodynamic properties were derived with available vapor pressure and enthalpy of vaporization data. The Gibbs energy, enthalpy, and entropy of formation were derived for the ideal gas at selected temperatures with available enthalpy of combustion data.

NIPER-223 Thermodynamic Model for Surfactant Adsorption. Topical Report. National

Institute for Petroleum and Energy Research. January 1987. 26 pp. NTIS Order No. DE87001212. A simple, semi-empirical thermodynamic model was constructed for the adsorption of solutions of surfactants onto solid surfaces. Essentially, a modified finite-layer BET theory, the model is complete in that it predicts all surface thermodynamic properties. The properties of bulk solutions are considered in an exact way, and the availability of bulk thermodynamic properties is assumed. The theory has been applied satisfactorily to both the adsorption isotherm and the heat of adsorption curve for the adsorption of decyltrimethylammonium bromide (DTAB) on silica gel. In this system, the observed adsorption which occurs above the critical micelle concentration (CMC) depends on the detailed behavior of the bulk thermodynamic properties; since the measured surface properties are sensitive to bulk properties, the latter must be accounted for accurately. DTAB is the only reported surfactant system for which both the isotherm and the heat have been measured and for which the bulk solution properties are known. A critical test of the theory awaits more data of this type; however, the theory has been tested against isotherms measured by Scamehorn, et al., and has been found to fit within experimental error below the CMC. There are many areas in which the adsorption of surfactants is of practical importance, such as minerals processing, lubrication, and enhanced oil recovery. The theory should prove useful to all of these areas. In the scope of enhanced oil recovery, this theory is intended to be developed into an adsorption module for a reservoir simulator for surfactant-mineral systems whose behavior is too complex to be modeled by Henry's law or even a Langmuir isotherm.



PUBLICATIONS LIST

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Bartlesville Project Office
Robert L. Folstein, Director

DOE/BC-87/6/SP

April-June 1987

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Bartlesville, Oklahoma 74005
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GENERAL RESEARCH

NIPER-224 Trends of Petroleum Fuels. Topical Report. National Institute for Petroleum and Energy Research. May 1987. 36 pp. NTIS Order No. DE87001237. Trends in properties of motor gasolines for the years 1942-1986; diesel fuels for the years 1950 through 1986; aviation fuels for the years 1947 through 1986; and heating oils for the years 1955 through 1986, have been evaluated based upon data contained in surveys prepared and published by the National Institute for Petroleum and Energy Research (NIPER) and its predecessor organizations. The surveys for motor gasolines were conducted under a cooperative agreement with the Coordinating Research Council (CRC) and the Bureau of Mines from 1935 through 1948 and in cooperation with the American Petroleum Institute (API) since 1948 for all surveys. The motor gasoline surveys have been published twice annually since 1935 describing the properties of motor gasolines produced and marketed throughout the country. Other surveys prepared in cooperation with the API and the Bureau of Mines, the Energy Research and Development Administration, the Department of Energy, and currently NIPER, were aviation gasolines beginning in 1947, diesel fuels in 1950, aviation turbine fuels in 1951, and heating oils, formerly burner fuel oils, in 1955. Various companies throughout the country obtain samples of motor gasolines from retail outlets and refinery samples for the other surveys, and analyze the samples using American Society for Testing and Materials (ASTM) procedures. The analytical data are sent to the Bartlesville Center for survey preparation and distribution. A summary report has been assembled from data in 87 semiannual surveys for motor gasolines that shows trends throughout the entire era from winter 1942-1943 to the present. Trends of diesel fuels are shown for type C-B/grade 1-D and type T-T/grade 2-D fuels. Trends for properties of heating oils have been plotted for grades 1, 2, and 6, and for properties of grades JP-4, JP-5, and Jet A aviation turbine fuels.

NIPER-220 1986 Annual Report. National Institute for Petroleum and Energy Research. March 1987. 426 pp. NTIS Order No. DE87001228. In its third year of operation under a cooperative agreement with the Department of Energy (DOE), National Institute for Petroleum and Energy Research (NIPER) continues to demonstrate its usefulness to both government and industry. Under the provisions of the cooperative agreement between DOE and IIT Research Institute, NIPER's parent organization, DOE funding decreases each year so industry and other government participants may play an increasing role in the operation of NIPER. The organization is divided into two research departments: Energy Production Research and Fuels Research. Objectives of the Energy Production Research Division are aimed largely at enhanced oil recovery (EOR) technology; the focus of the Fuels Research Division is on the effect of the changing of feedstocks from predominantly light petroleum crudes to include heavy oils, tar sand liquids, shale oil, and coal liquids for both processing and utilization. The DOE supports two NIPER programs: a fully-funded Base program that is designed for basic, long-term, high-risk research, and an Optional program that is cooperatively funded by DOE and other organizations (both government and industry) and designed for studies of current technological problems. In addition, NIPER has a "Work for Others" program for proprietary work that is funded outside the cooperative agreement and therefore not described in this report. A detailed discussion of NIPER's 35 projects and their accomplishments is included in the Project Reports section of this report.

DOE/BC-87/5/SP BPO Crude Oil Analysis Data Bank User's Guide BPO Staff. June 1987. 36 pp. This manual describes in detail the computer access method for obtaining data from the BPO crude oil analysis data bank. The guide discusses the system of computer programs used to search, retrieve, sort, and generate reports from the data in the bank. It also includes information on options available to the user, a sample report from the data bank, telephone assistance numbers for computer access users, and U.S. foreign location name codes to use in conjunction with the system.

Enhanced Oil Recovery—Quarterly Reports

DOE/BC-86/2 Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery. Progress Review No. 46. Quarter ending March 31, 1986. April 1987. 113 pp. NTIS Order No. DE86000295. Status reports are given for various enhanced oil and gas recovery projects sponsored by the Department of Energy. The field tests and supporting research on enhanced oil recovery include chemical flooding, gas displacement, thermal/heavy oil, resource assessment, extraction technology, and microbial technology.

Enhanced Oil Recovery—Chemical Flooding

DOE/BC/10845-5 Enhanced Oil Recovery by Surfactant-Enhanced Volumetric Sweep Efficiency. First Annual Report for the Period September 30, 1985-September 30, 1986. University of Oklahoma. May 1987. 79 pp. NTIS Order No. DE87001241. This annual report summarizes research performed during the past year on surfactant-enhanced volumetric sweep efficiency, a novel EOR method which utilizes precipitation/coacervation of surfactants to plug the most permeable regions of the reservoir, to improve the efficiency of a waterflooding operation. The technique described does not rely on reduction of interfacial tension between aqueous and oleic phases to enhance oil recovery. Though surfactants are involved in

the technique, it is not a substitute or improvement on classical surfactant flooding. It does, however, have the potential to compete with polymer flooding as an alternative sweep efficiency improvement method. Studies with sandpacks of different permeabilities in parallel configuration using mixtures of anionic and cationic surfactants have demonstrated the capability of this method to reduce flow rates through a more permeable sandpack more than that through a less permeable sandpack.

DOE/BC/10848-5 Adsorption from Flooding Solutions in Porous Media—A Study of Interactions of Surfactants and Polymers with Reservoir Minerals—First Annual Report for October 1985-October 1986. Columbia University. April 1987. 145 pp. NTIS Order No. DE87001233. Surfactants in reservoir systems undergo a multitude of interactions that are strongly dependent on properties of the minerals as well as dissolved inorganics like calcium. As part of a major effort to examine the role of structural modification of surfactants in limiting their loss, adsorption behavior of ethoxylated sulfonates and alcohols were studied; particular attention was given to the effects of change of ethoxylation. The fundamental goal of these research efforts is to develop a molecular understanding of the interactions of surfactants, oils, alcohols, inorganics, and polymers at the solid-liquid interface. In this respect, the conventional methodology (adsorption, zeta potential, particle wettability) for study of such systems has been limited to providing a relatively macroscopic picture of adsorption. There is a dire need for in situ spectroscopic techniques that are capable of directly probing the structure of the adsorbed layer. Techniques are being developed for this purpose. For example, results from a fluorescence spectroscopic analysis of a model system viz., dodecylsulfate-alumina are promising. The overall spectroscopic investigation reveals a molecular model that is in close agreement with the concept of hemimicellization.

DOE/BC/10830-5 An Evaluation of the Alkaline Waterflooding Demonstration Project, Ranger Zone, Wilmington Field, California. Topical Report. Keplinger Technology Consultants, Inc. May 1987. 120 pp. NTIS Order No. DE87001240. An alkaline flood enhanced oil recovery project was conducted in the Ranger Zone of the Wilmington Field in California, the largest field in the state. Alkaline flooding was considered for Wilmington since the crude oil is rich in organic acids and reacts with alkaline fluids to produce surfactants. Oil recovery can potentially be improved by increased displacement efficiency and by improved sweep. Oil recovery from the project has been poor. However, water production was reduced in some wells. The key factors for the lower than expected oil recovery are attributed to high consumption of the alkaline fluids and to wellbore plugging problems. High consumption was due in part to the mixing of alkaline fluids with waters of high hardness and to reactions of the alkaline fluids with the reservoir rock. The plugging problems were due to the formation of calcium carbonate scale, magnesium silicate scale, and to silicate-containing precipitates. Workovers to remove the damage were only partially successful. Interpretation of the pilot could have been improved by additional analyses of the produced waters. Such tests would have helped to define the mechanisms for the excessive consumption of the alkaline fluids. It is recommended that future research be directed toward improving the tolerance of the alkaline fluids to hardness of formation waters. Such research may include work on the incorporation of cosurfactants and additional synthetic surfactants.

NIPER-248 Drop-Drop Coalescence: The Effect of Temperature and Equilibration Time on Wilmington Crude Oil in A Weakly Alkaline Brine—Topical Report. National Institute for Petroleum and Energy Research. June 1987. 20 pp. NTIS Order No. DE87001242. Coalescence data were obtained for Wilmington crude oil droplets in sodium bicarbonate brine using a vertically inclined spinning drop tensiometer. The effect of temperature and aging on drop-drop coalescence was evaluated. In most cases, film drainage is considered to be the rate-limiting process prior to coalescence. Results indicate that coalescence time is dependent on temperature, being long at low temperature and short at high temperatures.

Aging of the oil drops in alkaline brine appeared to decrease coalescence time although the effect was more noticeable at high temperature. Natural surfactants produced from the reaction of bicarbonate brine with strong acids in Wilmington crude oil appeared to inhibit drop-drop coalescence, probably due to a surfactant concentration gradient which was providing resistance to flow at the interface. The period of time that interfacial tension remained at a dynamic minimum was directly related to coalescence time. A spinning drop tensiometer was found to be useful in obtaining drop-drop coalescence data. The apparatus is simple to operate and could be used in laboratory optimization of the mechanisms of oil mobilization and oil bank formation.

Enhanced Oil Recovery—Carbon Dioxide

DOE/MC/21136-10 Improvement of CO₂ Flood Performance. Annual Report for the Period October 1985-October 1986. New Mexico Institute of Mining and Technology. May 1987. 108 pp. NTIS Order No. DE87001236. During the second year of this project, progress is reported in three specific research areas. These areas of research include: (1) the phase behavior and fluid properties of CO₂-hydrocarbon mixtures; (2) the interaction of mixing and phase behavior in CO₂ flood performance; and (3) the added problems faced by CO₂ displacement because of the unfavorable mobility ratio. In Area I, the development of the oscillating quartz crystal viscometers has been completed. The viscometers have been validated using pure component and multiple component CO₂ hydrocarbon systems. This was the last major improvement to the Continuous Phase Equilibrium (CMC) apparatus over the past 18 months. In Area II, a new, low-temperature CO₂ coreflood unit was designed, constructed, and debugged. The first suite of experiments was run to verify the reproducibility and accuracy of the data. The one-dimensional simulation of the CO₂ coreflood data is now underway. Integrating the information gathered from the single-phase and two-phase dispersion experiments (the reservoir core mixing parameters) with the CO₂ coreflood oil and gas production data is the focus of this work. The goal of this research is to develop methods for representing mechanisms which operate at the microscopic scale for use in the prediction of performance at the field scale. In Area III, the work to develop field-usable mobility control additives has also shown great progress. Most surfactants have been tested for suitability in stabilizing CO₂-foam in reservoirs, and further developments have been made in the procedure and apparatus required for measurement of high-pressure mobility in reservoir core samples.

Enhanced Oil Recovery—Microbial Enhanced Oil Recovery

DOE/BC/10507-41 Application of Microbial Processes to Viscosity Reduction of Heavy Crude Oil—Final Report. University of Georgia. May 1987. 23 pp. NTIS Order No. DE87001238. This report summarizes results obtained from research conducted during 1981-1986. The objectives of the research program were to determine whether microorganisms and/or microbial processes are applicable to the modification of heavy oil. The rationale underlying the screening for microorganisms and/or microbial activities effective in heavy oil viscosity reduction was based on two possible mechanisms: (1) reduction of the average molecular weight of oil; and, (2) the production of specific biological products that would alter the physical properties of heavy oil. The reduction of the average molecular weight of heavy oils would necessitate the microbial depolymerization and/or degradation of the high molecular weight constituents such as asphaltenes and resin acids to smaller molecular weight components, thus effectively reducing the average molecular weight of the oil. Alternatively, the production of surface-active products by microorganisms growing at the expense of oil or nonhydrocarbon substrates would serve to generate macro- and/or micro-emulsions of oil-in-water having lower viscosities than the parent crude oil.

PROCESSING AND THERMODYNAMICS

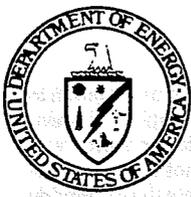
Processing

DOE/BC/10525-16 Mechanisms of Syncrude/Synfuel Degradation. Fourth and Final Report for October 1, 1984-December 31, 1986. Department of the Navy, Naval Research Laboratory. April 1987. 146 pp. NTIS Order No. DE87001232. A major part of the effort during the final phase of this project dealt with the interactions between codopants added to a stable shale derived diesel fuel. Five classes of nitrogen compounds have been examined in detail. A substituted pyridine and a substituted quinoline behave similarly, exhibiting only minor interactions with t-butylhydroperoxide (TBHP), organic bases and weak organic acids, but forming large amounts of insolubles with a sulfonic acid. Dimethylpyrrole (DMP) interacted strongly with TBHP, weak and strong organic acids to produce increased amounts of sediments but interacted only weakly with organic bases. 3-Methylindole exhibited interaction behavior similar to DMP but the positive interaction was significantly enhanced by venting of sample flasks. Dodecahydrocarbazole showed a distinctive pattern of behavior, a strong positive increase in insolubles with TBHP or tributylamine but a substantial decrease with acids, both carboxylic and sulfonic. Widely used fuel stabilizers were ineffective in reducing sediment formation by 2,5-DMP. An intermediate stream from a shale refining process was moderately stable although it was high in nitrogen content, (2290 ppm w/v). Consecutive treatments with dilute HCl and silica gel significantly improved the stability of this liquid. The extracts contained substantial amounts of pyridines and tetrahydroquinolines with smaller amounts of hydrocarbons and other nitrogen compounds. The most polar of the extracts, that stripped from the silica gel by methanol, was a potent sediment producer, on par with DMP on an equivalent nitrogen basis. Light scattering easily detected formation of larger molecules for stressed shale derived diesel fuel containing DMP. However, formation of copious amounts of insolubles prevented the use of this technique as a useful quantitative tool for evaluating fuel instability.

NIPER-210 Catalytic Cracking of a Wilmington Vacuum Gas Oil and Selected Hydro-

treated Products. Topical Report. National Institute for Petroleum and Energy Research. May 1987. 44 pp. NTIS Order No. DE87001234. The catalytic cracking of a Wilmington vacuum gas oil and the products from mild hydrotreating and severe hydrotreating of this gas oil was evaluated over a low metal equilibrium catalyst in a microconfined bed unit (MCBU). Two levels of catalytic cracking severity were evaluated for these three samples. The performance and product analysis showed that hydrotreating improves the quality of catalytic cracker feedstock and the resultant products. The results also indicate that level of hydrotreating exists above which the quality of the liquid products and the yields of coke and heavy cycle oil are not affected significantly by the severity of the catalytic cracking process. As expected, the sulfur and nitrogen content of the liquid products (gasolines, light cycle oil, and heavy cycle oil) were found to decrease as the severity of the feed hydrotreating increased. The distribution of sulfur and nitrogen in the liquid products was found to be independent of cracking conditions or product yields for a given level of hydrogenation. Analysis of the gas products shows that the degree of hydrogen transfer increases with the severity of hydrogenation. As cracking severity increases, the apparent degree of hydrogen transfer decreases, and the concentration of olefinic compounds increases relative to the saturated compounds. In the future, these results will be compared to similar results from a Mayan vacuum gas oil.

NIPER-239 Thermochemical and Thermophysical Properties of Organic Compounds Derived from Fossil Substances—Thermodynamic Studies Related to the Hydrogenation of Anthracene. Topical Report. National Institute for Petroleum and Energy Research. May 1987. 74 pp. NTIS Order No. DE87001235. Experimental details of vapor pressure, enthalpy of combustion, and condensed-phase heat capacity studies are reported for 9,10-dihydroanthracene, phenyl-o-tolymethane, and 1,2,3,4-tetrahydroanthracene. The results are combined to produce values of the Gibbs energy of formation in the ideal-gas state at selected temperatures for each molecule. The derived Gibbs energies are used in equilibria calculations that provide insights into the roles of temperature and hydrogen pressure in the control of product slate in the hydrogenation of anthracene.



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Bartlesville Project Office
Robert L. Folstein, Director

DOE/BC-87/7/SP

July-September 1987

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ENHANCED OIL RECOVERY

Quarterly Reports

DOE/BC-86/3 **Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery. Progress Review No. 47. Quarter ending June 30, 1986. August 1987. 98 pp. NTIS Order No. DE87001206.** Status reports are given for various enhanced oil and gas recovery projects sponsored by the Department of Energy. The field tests and supporting research on enhanced oil recovery include chemical flooding, gas displacement, thermal/heavy oil, resource assessment, extraction technology, and microbial technology.

Chemical Flooding

NIPER-127 **Sodium Bicarbonate in Chemical Flooding: Part I. Topical Report. National Institute for Petroleum and Energy Research. July 1987. 37 pp. NTIS Order No. DE87001246.** Coreflood experiments were performed with viscosified sodium bicarbonate and viscosified sodium carbonate solutions to compare oil recovery and alkali consumption in alkaline flooding using sodium bicarbonate with other alkaline agents. Oil recovery was monitored, and the effluent brine from these corefloods was analyzed for silicon, aluminum, pH, and total inorganic carbon. The results indicate that viscosified sodium bicarbonate recovered more of the asphaltic Cerro-Negro crude than of the less asphaltic Wilmington crude oil. The recovery efficiency using the viscosified sodium carbonate was similar for the two crudes. For both crudes, the percent oil recovery using viscosified sodium carbonate was slightly higher than that using the viscosified sodium bicarbonate. Mineral dissolution and decrease in pH were found to be greater in corefloods using viscosified sodium carbonate. Total inorganic carbon recovery can be obtained in corefloods with either agent, provided that a sufficient water drive follows the chemical

slug. Long-term experiments were performed by recirculating alkaline solutions through oil-free, unfired Berea sandstone to monitor the rock/alkali interactions. The experimental results indicate an eight-fold decrease in quartz dissolution by sodium bicarbonate compared with sodium carbonate. Moderate magnesium solubility was observed at the pH of the bicarbonate solution. Low solubility of magnesium and aluminum at the pH of the carbonate indicates the possible formation of precipitates. In these experiments, 13% of the carbonate was converted to bicarbonate. Total alkalinity was not significantly decreased with either agent.

NIPER-147 **Sodium Bicarbonate in Chemical Flooding: Part II. Topical Report. National Institute for Petroleum and Energy Research. July 1987. 37 pp. NTIS Order No. DE87001251.** In this report, the results are presented from three areas: (1) the use of low pH alkaline chemicals for wettability alteration; (2) the development of a correlation between interfacial shear viscosity and water breakout for oil-brine microemulsions; and (3) the evaluation of bicarbonate as a chemical for use in oil recovery. The main objective of this work is to develop an understanding of the mechanisms involved in bicarbonate flooding and to make specific recommendations for its potential use in enhanced oil recovery. Emulsification and coalescence test results were compared with interfacial shear viscosities to evaluate the use of bicarbonate as an emulsion destabilizer. In two of the three systems studied, an inverse relationship was found between the maximum rate of water breakout and interfacial shear viscosity. Temperature and aging of the interface was a major factor affecting these results. Sodium bicarbonate and sodium carbonate were used to determine their effect on rock wettability. Sodium bicarbonate was found to change the wettability of Berea sandstone toward the water-wet state more effectively than sodium carbonate for the low-acid oil, Noone crude. Highly acidic crude oils appeared to react with bicarbonate creating highly absorbed surfactants. This caused Berea sandstone to become more oil-wet. The major mechanisms of oil recovery using sodium bicarbonate include wettability alteration, emulsification followed by coalescence, and lowered interfacial shear viscosity. These mechanisms alone did not cause significant recovery of the low-acid oil, Noone crude. Previous oil displacement tests indicate that bicarbonate is more effective when using acidic crude oils. The range of oils that can be recovered using bicarbonate can be extended by adding small amounts of surfactants to the bicarbonate slug.

NIPER-228 **Carboxymethylated Ethoxylated Surfactants. Annual Report. National Institute for Petroleum and Energy Research. August 1987. 58 pp. NTIS Order No. DE87001258.** A method of selecting surfactants for chemical enhanced oil recovery using carboxymethylated ethoxylated surfactants (CES) is described. Structure/performance correlations for hydrophobe, ethylene oxide content, and nonionic-anionic ratio have been developed for a series of CES with alkane carbon number, pH, salinity, phase inversion temperature, and solubilization parameter to provide a guide in selecting candidate surfactants for enhanced oil recovery. Carboxymethylated ethoxylated surfactants are a class of surfactants that generate low interfacial tension against crude oils at high temperatures, high salinities and high divalent ion concentrations. Selection of the surfactant for a specific reservoir can be made based upon determination of the phase inversion temperature (PIT) of the surfactant at reservoir salinity with live crude. An additional scan for phase behavior (salinity scan) can then establish salinity tolerance and solubilization parameters for the selected surfactant system. Correlations of PIT with surfactant structure, salinity, and hydrocarbon have been determined for a number of U.S. reservoirs using CES as the only surfactant.

DOE/BC/10841-5 Modeling and Optimizing Surfactant Structure to Improve Oil Recovery by Chemical Flooding at the University of Texas. First Annual Report for the Period October 1985-September 1986. The University of Texas at Austin. July 1987. 83 pp. NTIS Order No. DE87001250.

Adsorption of surfactant from aqueous solutions is a complex function of a relatively large set of variables including the solution pH, electrolyte composition, temperature and surfactant concentration as well as the surface characteristics of the mineral and the surfactant molecular structure. Because of this complexity, one cannot hope to optimize a micellar system for enhanced oil recovery without the aid of an accurate model tying together all of the significant variables. The development of an adsorption theory is the focus of this research at the present. A model surface, titanium dioxide, has been selected for the initial studies. A particular sample of TiO_2 has been studied extensively (surface titration, ESCA, electrophoretic mobility, electronmicroscopy) and will be used as a model system for comparison with predictions. The parameters describing naturally occurring minerals (clays, silica, etc.) will be incorporated into the theory once the titanium dioxide system is successfully modeled. Work this year has revealed that surfactant adsorption takes place on neutral as well as protonated sites. In contrast, cations such as chlorides, for example, appear to adsorb primarily on the positive, protonated sites. At low surfactant concentrations, surfactant adsorption on oppositely charged surfaces is reduced by increased electrolyte concentration. Surface heterogeneities are modeled by varying the charge density rather than varying the density of the total number of sites. This appears to be physically reasonable, but the approach has not yet been confirmed. All experiments (for example, electrical conductivities) show a gradual change in the microstructure attending the transition from oil to water-continuous systems. While there have been a number of thermodynamic treatments of microemulsions none have addressed this crucial question. In this study, a microemulsion has been represented as a single phase composed of regions which are a dispersion of oil drops in water coexisting in the same solution with other regions having precisely the same overall composition but are a dispersion of water drops in oil. This model then takes into account for the first time the entropy stemming from the chaotic fluctuations of the interfacial region separating oil from water. One satisfying result of this new theory is that it establishes a link between measurable quantities and the interfacial bending energy, a quantity which is believed to be intimately connected to the surfactant structure. Thus, the theory provides a pathway through which the important properties of micellar solutions can be predicted based on the structure of the surfactant thereby permitting the selection of optimized surfactant structures. This is one of the primary goals of this research.

DOE/BC/10846-5 Modelling and Scale-up of Chemical Flooding. First Annual Report for the Period October 1985-September 1986. The University of Texas at Austin. July 1987. 301 pp. NTIS Order No. DE87001245.

The development and application of the chemical flooding simulator (UTCHEM) has been the focus of this research during the past year. Many improvements have been made in UTCHEM and it has been used to evaluate field tracer data, oil recovery from a field surfactant flood, and laboratory coreflood data. A large number of simulations have also been made to study process scale up, process design, and process performance. Many additional simulations were done to study the accuracy and speed of the code, for example, comparison of various solvers. Supporting experimental studies during the past year included relative permeability and trapping for various compositions, microemulsion viscosities, and polymer gel properties. These and other recent data have enabled us to continue to improve the physical property models. Specific improvements and additions made to UTCHEM during the past year include: (1) a slightly compressible option has been added; (2) a variable grid-size option has been added; (3) well representation changes such as skin and partial completion as well as the "concentration well model" have been added; (4) three tracer components have been added; (5) various improvements in the physical property models such as the three-phase trapping model have been made; (6) polymer gel kinetics have been added as an option for use in three-dimensional profile control studies with or without surfactant; (7) alkaline reactions including precipitation-

dissolution reactions with the formation have been added as an option to use in 3-D alkaline surfactant-polymer studies; (8) computational speed has been increased 10 fold by a combination of faster solver and vectorization for the Cray. Perhaps the most significant application of UTCHEM during the past year has been its use to simulate the Big Muddy surfactant pilot. This was the first attempt to simulate an actual field test although field scale studies had been done before this. Both the tracer data Conoco used in the Big Muddy preflush and the oil recovery used during the surfactant-polymer flood have been successfully simulated. Detailed comparisons have been made with these field data without adjustment of input parameters or history matching but rather by using both Conoco's data and our own when needed to fill in the gaps for the surfactant and polymer properties. The reservoir description was based on core data reported by Conoco. The input for the tracer and surfactant flood simulations was exactly the same except for injection rates in the five spot which they reported and which varied during the pilot. The agreement with the tracer data is probably within the accuracy of the field data. The agreement with the oil recovery data is good but not as good as it could be. The simulated value for the final oil recovery is within 1% of the actual field value indicating that there were evidently no major phenomena not accounted for nor any serious errors in the controlling physical property data measured in the laboratory for the surfactant system Conoco used. Another significant implication of this study is that it is possible in at least some cases to get quantitative agreement between interwell tracer data (in this case tritium in one well and thiocyanate in another well).

DOE/BC/10847-5 Enhanced Oil Recovery Through In-Situ Generated Surfactants Augmented by Chemical Injection. First Annual Report for the Period October 1985-September 1986. Illinois Institute of Technology. July 1987. 119 pp. NTIS Order No. DE87001244.

Results of theoretical studies in high-pH flooding are presented in this report. The objective of this work was to develop a reasonable chemical model that would account for interactions between the alkali in the flood water and the acids in the crude oil, the enhanced mobility of oil due to the generated surfactants, and finally the interaction of alkali with the rock surface. The chemical model itself aims to predict saturation profiles, composition profiles and histories, and cumulative oil production. The conclusions from these high-pH flooding models are given: (1) a major finding of the theoretical study was that low interfacial tension at intermediate sodium hydroxide concentrations plays a dominant role in recovering oil; (2) the dominance of the optimum region was found to persist only for favorable viscosity ratios; (3) as long as viscosity ratio is favorable, factors such as injection sodium hydroxide concentration, sodium chloride concentration and velocity have little effect in recovering oil; (4) reversible ion exchange leads to a delay in the chemical front whenever the NaCl or the inlet NaOH concentration is decreased; (5) adsorption reduces the influence of the low interfacial tension region in recovering oil; therefore, a faster chemical front using higher NaOH and NaCl values can actually be detrimental to ultimate oil recovery; and (6) there is a small reduction in the advantages of using a favorable mobility ratio as far as ultimate oil recovery is concerned. However, this is offset by the prediction that the commencement of oil production is affected more in the case of unfavorable viscosity ratios.

Thermal Processes

DOE/SF/11564-22 The Comparative Economics of Thermal Recovery Projects. SUPRI TR-56. Stanford University. July 1987. 88 pp. NTIS Order No. DE87001247.

The purpose of this study is twofold. First, an attempt to predict the oil recoveries for two thermal recovery methods was made. The Marx and Langenheim model was used to determine the ultimate oil recovery in a steam-injection project, while the Gates and Ramey oil recovered volume burned model was used to determine the oil recovery in an in-situ combustion project. Second, an economic analysis using the Monte-Carlo simulation technique was done for both methods. A discounted net present value was obtained from the oil recovery schedules to facilitate comparison between the two thermal methods. It was found

that both methods are economically competitive. The comparative economics of steam injection vs. in-situ combustion must be reexamined in the light of recent technical and economic reports. This study attempts to dispel some misconceptions and confusion surrounding the two thermal recovery processes, and presents a general method for comparing the two mechanisms that is easily altered to suit specific field cases.

DOE/SF/11564-24 Two Dimensional Displacement of Oil by Gas and Surfactant Solution Under Foaming Conditions. SUPRI TR-58. Stanford University. July 1987. 171 pp. NTIS Order No. DE87001249. Gas displacement in the presence of surfactant under foaming conditions has been shown to enhance oil recovery, but it is a complex process because surface phenomenon is involved in it. The lack of understanding is a barrier for its commercial-scale testing and application. A major difficulty in analyzing the production performance of such displacement is in deciding whether to treat gas and surfactant solution as a two-phase mixture or as a single-phase homogeneous fluid (foam). Another uncertainty is in determining the rheological behavior of gas and surfactant solution mixture flowing in the porous media. The problem is further complicated if two-dimensional flow is taking place, since the frontal geometry may also influence the performance significantly. This study was performed to investigate these problems. Flow was visually observed through a two-dimensional (x,y) sandpack of 4' length and 1' height, having 14 darcies permeability and 35% porosity. Since analytical treatment of the flow and oil recovery data has not been possible, the objectives were to get a basic understanding of the flow behavior under foaming conditions, devise conceptual models with the help of flow processes seen, and then analyze the data quantitatively using semi-analytical approaches. A model meeting these objectives was developed and successfully matched with experimental data obtained in the two-dimensional sandpack.

DOE/SF/11564-25 SUPRI Heavy Oil Research Program. Tenth Annual Report for the Period October 1, 1985-December 31, 1986. SUPRI TR-59. Stanford University Petroleum Research Institute. August 1987. 137 pp. NTIS Order No. DE87001255. The Stanford University Petroleum Research Institute (SUPRI) was established in 1976 with the primary purpose of pursuing enhanced oil recovery research in heavy oils. SUPRI's five overall research objectives are summarized as follows: (1) Flow Properties Study—the purpose is to assess the effects of temperature and pressure on relative permeability to oil and water, and capillary pressure in petroleum reservoirs; and to correlate the data obtained in the laboratory with those at reservoir conditions. Early results indicate that the absolute permeability to water decreases with a rise in temperature. These results were in agreement with some research work, but differ from other work. Recent efforts show that the absolute permeability to water seems to be dependent on whether the core is fired or not. This was found even with Ottawa sand cores. (2) In-Situ Combustion—the goal of this project is to evaluate the different parameters affecting combustion field projects, including the study of the reaction kinetics of combustion in the presence of reservoir matrix and crude oil. The effect of CO₂ is being studied for systems including steam and heavy oil at high pressure and temperature. The approach is analytical, whereby the equations defining the flow, the equilibrium relationships, and the enthalpies are combined into a set of Buckley-Leverett type equations which can be solved simultaneously. Such solutions form a matrix of possible frontal velocities which must be identified. (3) Steam Injection With Additives—the purpose of this project is to develop a process allowing mobility control in steam drives in order to reduce gravity override and channeling of steam, primarily by use of surfactants/foams, and to understand the nature of the flow for such systems. Recent efforts have centered on several aspects of basic understanding of foam flow. (4) Reservoir Definition—the main purpose of this project is to improve the techniques of well-to-well formation evaluation such as tracer tests and pressure transient tests, and to facilitate the interpretation of such tests. On well testing, a study is being made of the pressure derivative technique for analyzing well tests. Of particular importance are cases of high mobility ratio and high compressibility which are the types of systems found in thermal recovery. Another study has found a way to detect faults in many

cases where they could not be detected. Also a study has begun on analytically solving the flow to perforations. An exact solution has been developed for the single well tracer test technique. This solution requires complex integrations to be evaluated and it is being compared with the approximate solutions developed by Antunez several years ago. (5) Field Support Services—the purpose is to provide technical support in design and monitoring of enhanced oil recovery field experiments. Studies are in progress on the economics of thermal recovery and on optimization of cyclic steam injection.

DOE/BC-87/2/SP Supporting Technology for Enhanced Oil Recovery—EOR Thermal Processes. Republic of Venezuela Ministry of Energy and Mines and U.S. Department of Energy. July 1987. 285 pp. NTIS Order No. DE87001217. This report contains the results of efforts under the several tasks of the Third Amendment and Extension of Annex IV, Enhanced Oil Recovery Thermal Processes of the Venezuela/USA/ Energy Agreement. The report is presented in sections by tasks and each section contains one or more reports prepared by various individuals or groups describing the results of each particular task. A statement of each task is presented at the beginning of each section. The tasks are numbered 25 through 31. The first, second, and third reports of Annex IV, DOE/BETC/SP-83/15, DOE/BC-84/6/SP, and DOE/BC-86/2/SP, contain the results from the first 24 tasks.

Resource Assessment Technology

NIPER-214 Geological Characterization and Statistical Comparison of Outcrop and Subsurface Facies: Shannon Shelf Sand Ridges. Topical Report. National Institute for Petroleum and Energy Research. September 1987. 64 pp. NTIS Order No. DE87001243. This study was designed to provide a preliminary evaluation of the usefulness of outcrop information in characterizing analogous reservoirs and to develop research techniques necessary for model development. The primary objective of the research is to develop a methodology for constructing accurate quantitative models of reservoir heterogeneities. The resulting models are expected to improve predictions of flow patterns, spatial distribution of residual oil after secondary and tertiary recovery operations, and ultimate oil recovery. The Shannon Sandstone, a shelf sand ridge deposit in the Powder River Basin, Wyoming, was studied. The sedimentologic and petrophysical features of an outcrop exposure of the High-Energy Ridge-Margin facies (HERM) within the Shannon were compared with those from a Shannon sandstone reservoir in Teapot Dome field. Comparisons of outcrop and subsurface permeability and porosity histograms, cumulative distribution functions, correlation lengths and natural logarithm of permeability versus porosity plots indicate a strong similarity between Shannon outcrop and Teapot Dome HERM Facies petrophysical properties. Permeability classes found in outcrop samples can be related to crossbedded zones and shaley, rippled, and bioturbated zones. Similar permeability classes related to similar sedimentologic features were found in Teapot Dome field. The similarities of outcrop and Teapot Dome petrophysical properties, which are from the same geologic facies but from different depositional episodes, suggest that rocks deposited under similar depositional processes within a given deposystem have similar reservoir properties. The results of the study indicate that the use of quantitative outcrop information in characterizing reservoirs may provide a significant improvement in reservoir characterization.

DOE/SF/11564-23 Mathematical Analysis of Single-Well Tracer Test. SUPRI TR-57. Stanford University. July 1987. 91 pp. NTIS Order No. DE87001248. Single-well tracer test as a means of evaluating reservoir in-situ fluid saturation has interested many researchers. The hydrodynamics of single-well tracer test is based on the radial flow of a tracer which can partition in the fluid saturations within the reservoir. At the same time, the tracer is mildly reactive with the mobile phase fluid saturation. This mild, irreversible chemical reaction results in the formation of another tracer species called secondary tracer. The secondary tracer is different from

the parent tracer in its partition and chemical reaction characteristics. Typically, the secondary tracer is not reactive with, and has a near-zero partition coefficient with the immobile phase fluid saturation. The hydrodynamics of the above tracer system is described by a Radial-Diffusion-Convection-Reaction (R-D-C-R) type second order differential equation. The use of this equation to analyze single-well tracer test has, in the past, largely been through the application of numerical techniques. Since these techniques may suffer from inaccuracies due to adverse numerical dispersion or the problem of uniqueness arising from fitting many unknown parameters, there is a need to develop an exact analytical solution to the R-D-C-R type differential equation for accurate single-well tracer test analyses. This work reexamines the R-D-C-R system of differential equations as it applies to single-well tracer tests, and obtains an exact analytical solution which heretofore has been considered impossible. Even though the exact solutions are based on a linear equilibrium adsorption isotherm model for tracer partitioning, it is shown that a solution based on the linear nonequilibrium adsorption model could also be obtained without much additional mathematical difficulties. Using the exact analytical solution as the basic tool, the hydrodynamic models describing all phases of the single-well tracer test were solved analytically. Graphs showing the tracer concentration profiles for each of the phases of the single-well tracer test were constructed.

PROCESSING AND UTILIZATION

NIPER-187 **Research Needs for Heavy Crude Processing and Utilization. Topical Report. National Institute for Petroleum and Energy Research. August 1987. 48 pp. NTIS Order No. DE87001257.** In the future, conventional crudes will not be able to meet the national energy need. At that point, there will be a transition from conventional to alternative crudes. Heavy crudes which are readily available will be utilized first. Because of the volatility of the petroleum market and the net importer status, the U.S. will have little control over the timing of the transition. The current weakness of the domestic petroleum industry and the lack of understanding of heavy crude chemistry and characteristics may complicate the coming transition. The most efficient role for government research in the processing and utilization of heavy crudes is to develop a program which supports the transition in technologies by developing basic data and understanding of heavy crudes. This effort consists of programs which identify and explore the chemistry of processing heavy crudes, define their general characteristics, and measure thermodynamic properties and design data. In addition, because the nature of the fuels from heavy crudes will be different, other programs should develop an understanding of stability and compatibility and engine performance differences which may result from their utilization. In this document, a series of programs to define and explore each of the research needs are given and discussed. Estimates of program content, timing, and cost are also included. To insure the validity of these conclusions, the finding of this study was reviewed by experts from the refining industry and faculty members from universities knowledgeable about the refining industry. In general, the findings strongly support the research needs developed in this document.

NIPER-205 **Effects of Lead Level on Emissions and Valve Seat Recession. Final Report. National Institute for Petroleum and Energy Research. August 1987. 42 pp. NTIS Order No. DE87001253.** This report describes testing operations to determine the effect of using unleaded gasoline in engines designed for leaded gasoline. Three tractor engines, one combine engine, one light-duty fire truck engine, and one heavy-duty truck engine were tested using leaded fuel (1.1 gm/gal), unleaded fuel, and low lead fuel (0.10 gm/gal). Results show the higher speed engines experienced valve seat recession using unleaded fuel while lower speed engines did not show valve recession using the unleaded fuel. No valve seat recession occurred using the 1.1 gm/gal leaded fuel. The use of .10 gm/gal lead reduced valve seat recession compared to unleaded fuel, but did not eliminate recession in all cases.

NIPER-245

Stability and Compatibility of Residual Fuel Oils. Topical Report. National Institute for Petroleum and Energy Research. August 1987. 297 pp. NTIS Order No. DE87001254. In recent years, there has been an increased use of low-quality crudes in refinery feedstocks. This results from several factors including the depletion of light, sweet domestic crude oils and the growing dependence upon heavy, sour crudes from both domestic and foreign sources. Refiners have found it necessary to increase the conversion of resid to distillate fuels which has resulted in increased problems in product quality. Problems are particularly severe in residual materials which contain the highest levels of problem compounds such as asphaltenes or heteroatom compounds. Experience has shown that conventional fuel oil analyses are inadequate to allow prevention or prediction of handling problems resulting from fuel instability or incompatibility of fuel mixtures. A number of "problem" or "nonproblem" fuels supplied by utilities were analyzed in an attempt to understand the reasons for the reported problems. These fuels were carefully characterized by the determination of chemical and physical properties. It was apparent, however, that a baseline or reference test was needed to categorize the fuels as "problem" or "nonproblem." Because of the wide variations in hardware used by various utilities, the differences in handling and mixing fuels by utilities, varying storage conditions, and local differences in ambient climatic environments, fuels presenting problems at one utility might be a nonproblem fuel in another. Supplemental samples were obtained through the cooperation of participating utilities, and these and initial samples were subjected to baseline tests for determining stability and compatibility characteristics. These baseline tests were the basis for the evaluation of rapid tests which might be useful for the prediction of potential problems. Some of the simple techniques which were evaluated for usefulness in predicting instability or incompatibility potential included determination of sediment by hot filtration (existent dry sludge), determination of potential dry sludge (Shell accelerated stability test), determination of coke content, a modified spot test and prediction of incompatibility between fuels through the use of the Bureau of Mines Correlation Index and toluene equivalence.

THERMODYNAMICS

NIPER-247 **Thermodynamic Studies Related to the Hydrogenation of Phenanthrene. Topical Report. National Institute for Petroleum and Energy Research. July 1987. 107 pp. NTIS Order No. DE87001252.** If coal liquids are to play an important role in the future energy needs of this country, it is essential that efficient processes for coal liquefaction and coal-liquid upgrading are developed. Heavy crudes, shale oils, bitumens, resids from light sweet crudes, etc., as well as coal liquids contain large quantities of fused-ring aromatics. Efficient conversion of these materials to naphthenes is an important goal in new process development. The hydrocracking of phenanthrene is often used as a model system in kinetics, catalysis, and equilibria studies designed to provide insights into the fundamental processes involved. The application of thermodynamics, more specifically, the calculation and interpretation of equilibrium constants via Gibbs energies, can provide important information concerning the dependence of the product slate upon such key variables as temperature and hydrogen pressure without doing a single reaction. If more than one reaction is allowed thermodynamically, decisions can be made concerning whether to run the reaction under thermodynamic control or to search for a catalyst to promote one allowed reaction over another (i.e., use kinetic control). To search for a catalyst to promote a thermodynamically unfavorable reaction is certain to be a fruitless endeavor. If thermodynamic equilibria calculations are to be reliable, data of high accuracy are required for all molecules to be considered. This report gives details of experimental thermodynamic studies for 1,2,3,4-tetrahydrophenanthrene, 2-ethylbiphenyl, and 2,2-dimethylbiphenyl; three key hydrogenation products of phenanthrene. Additionally, based on new experimental results, revised values of the Gibbs energies of formation for phenanthrene and 9,10-dihydrophenanthrene are derived and tabulated. The utility of the results is demonstrated via chemical equilibria calculations for abbreviated phenanthrene/hydrogen reaction networks. Reaction networks with and without ring opening are considered.



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Bartlesville Project Office

Thomas C. Wesson, Acting Director

DOE/BC-88/3/SP

October-December 1987

DATE PUBLISHED—FEBRUARY 1988

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ENHANCED OIL RECOVERY

Quarterly Reports

DOE/BC-86/4 **Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery. Progress Review No. 48. Quarter ending Sept. 30, 1986. September 1987. 130 pp. NTIS Order No. DE87001231.** Status reports are given for various enhanced oil and gas recovery projects sponsored by the Department of Energy. The field tests and supporting research on enhanced oil recovery include chemical flooding, gas displacement, thermal/heavy oil, resource assessment, extraction technology, and microbial technology.

GENERAL RESEARCH

DOE/BC-88/2/SP **Boast II: A Three-Dimensional, Three-Phase Black Oil Applied Simulation Tool. Topical Report. K&A Technology. December 1987. 420 pp. NTIS Order No. DE88001205.** The Boast II program simulates isothermal, darcy flow in three dimensions. It assumes reservoir fluids can be described by three fluid phases (oil, gas, and water) of constant composition with physical properties that depend on pressure only. These reservoir fluid approximations are acceptable for a large percentage of the world's oil and gas reservoirs. Consequently, Boast II should have a wide range of applicability. For example, Boast II can simulate oil and/or gas recovery by fluid expansion, displacement, gravity drainage, and capillary imbibition mechanisms. Some of the typical field production problems which can be handled by Boast II include: primary depletion studies, pressure maintenance by water and/or gas injection, and evaluation of secondary recovery waterflooding and displacement operations. Technically, Boast II is a finite-difference, implicit pressure-

explicit saturation (IMPES) numerical simulator. It contains both direct and iterative solution techniques for solving systems of algebraic equations. The well model in Boast II allows specification of rate or pressure constraints on well performance, and the user is free to add or recompute wells during the simulation. Multiple rock and PVT regions may be defined, and three aquifer models are available as options. Boast II contains flexible initialization capabilities, a bubble point tracking scheme, an automatic time step control method, and a material balance check on solution stability. Many user-controlled output options are available and include optional final run summary information and line-printer plots of fieldwide performance. Example data sets illustrate the flexibility of the Black Oil Applied Simulation Tool Boast II.

NIPER-260

FY88 Annual Research Plan. National Institute for Petroleum and Energy Research. October 1987. 170 pp. NTIS Order No. DE87001261. The National Institute for Petroleum and Energy Research (NIPER) entered into its fifth year of operation on October 1, 1987. This research plan describes the work to be performed in FY88. NIPER is operated for the Department of Energy (DOE) by the IIT Research Institute (IITRI) under a cooperative agreement for fiscal years 1984-1988. NIPER's research program is a composite of four different programs, but the annual research plan covers only two of those programs, the base and optional programs. The DOE funds a \$5 million Base Program designed for long-range, high-risk petroleum research. An Optional Program is a cost-shared effort between DOE and contributing participants. The Supplemental Program includes work placed at NIPER by other government agencies and DOE work not included in the Base Program. The Work for Others Program allows NIPER to solicit work from the private sector and others. NIPER is organized into two research departments: (1) Energy Production Research (EPR) and Fuels Research (FR). Projects in EPR deal with various aspects of enhanced oil recovery including reservoir characterization, chemical flooding, gas injection, steam injection, and microbial enhanced oil recovery. Projects in FR focus on the impact of heavy oil and alternate fuels on processing and use of fuels. The fifth plan describes the work to be performed in these two research groups under the Base and Optional Programs.

DOE/BC/14000-1

Primary and Secondary Recovery in the Sho-Vel-Tum Oilfield, Oklahoma. Topical Report. Lewin and Associates, Inc. October 1987. NTIS Order No. DE87001262. This study was part of a comprehensive review of the potential for enhanced oil recovery in Oklahoma. Due to the past production and future potential production from the Sho-Vel-Tum oilfield, the largest producing field in the State of Oklahoma and the eleventh largest in the United States, it was chosen for the detailed analyses reported in this document. The original oil in place at Sho-Vel-Tum is estimated in this study to be 3.237 billion barrels of oil. Of this total, 1.235 billion barrels have been produced from the field through 1984 by primary and secondary (waterflood) applications, while reserves are estimated to be an additional 169 million barrels. By subtraction, 1.833 billion barrels still remain as a target for future development, including enhanced oil recovery. Over 99% of the oil produced from Sho-Vel-Tum thus far has come from five formation groups: the Permian aged Pontotoc Group, the Pennsylvania aged Hoxbar, Deese, and Dornick Hills-Springer Groups, and the Mississippian aged Sycamore Limestone. Data from numerous individual wells, along with information from waterflood units and enhanced oil recovery operations, were analyzed to determine the general reservoir characteristics and fluid properties of these groups. Although each group contains a number of individual producing zones which display a wide range of lithological,

reservoir, and fluid characteristics, this study places primary emphasis on the average properties of these important oil producing zones. Oil production by producing zone was determined and includes the contribution by primary, secondary, and tertiary (enhanced) oil recovery. These data permitted detailed calculation of the reservoir performance and oil recovery by producing horizon.

DOE/BC/10830-6 Evaluation of Micellar-Polymer Flood Projects in a Highly Saline Environment in the El Dorado Field. Topical Report. Keplinger Technology Consultants, Inc. December 1987. 136 pp. NTIS Order No. DE88001202. Two different micellar processes were conducted in the El Dorado Field in an effort to develop an EOR method for reducing the high oil saturation after waterflooding. Each process was field tested on adjacent 25-acre blocks of four 5-spot patterns. This report reviews the field performance, geology, formation evaluation, and laboratory support tests for the field tests. Both processes failed to recover additional oil, primarily because of unavoidable exposure to and mixing with divalent ions. An unusual oil saturation distribution also contributed to the failure. Unfortunately, these conditions could have been predicted from study of previous air, water, and steam injection projects in the field.

Chemical Flooding

DOE/BC/10844-10 Polymers for Mobility Control in Enhanced Oil Recovery. Second Annual Report for the Period October 1986-September 1987. University of Southern Mississippi. December 1987. 220 pp. NTIS Order No. DE88001207. Research during FY87 focused on synthesis and characterization of copolymers with intra- or intermolecular associations. Associative copolymers of acrylamide with N-alkylacrylamides, ampholytic copolymers of NaAMPS and AMPDAC, and micelle-forming copolymers with PDAAM have shown unique rheological properties which can be varied by changing microstructure. Dilute-solution studies as well as rheological studies have been conducted on these associative systems in order to probe molecular interactions. Such studies indicate significant potential advantages of these systems in EOR applications. Size exclusion chromatography and dynamic light-scattering analysis techniques are being developed concurrently so that EOR polymer molecular weight distributions can be measured. The two analysis methods are complementary and have been successfully employed to cross-collaborate measurement results.

DOE/BC10842-5 Flow in Porous Media, Phase Behavior and Ultralow Interfacial Tensions: Mechanisms of Enhanced Petroleum Recovery. First Annual Report for the Period October 1, 1985-September 30, 1986. University of Minnesota. October 1987. 240 pp. NTIS Order No. DE87001260. This report summarizes the research highlights of FY85-86. The emphasis of the research program is on understanding basic physical and chemical mechanisms with the goal of transforming this knowledge into concepts and mathematical formulations needed for engineering process design and analysis. The research reported here falls under three broad headings: (1) science of microstructured fluids and application to their phase behavior, interfacial tension, and rheology; (2) science of porous media and flow therein and of chaotic composites; and (3) supercomputer-scale theoretical analyses and mathematical modeling.

DOE/BC/10843-5 Investigation of the Application of Gelled Polymer Systems for Permeability Modification in Petroleum Reservoirs. First Annual Report for the Period October 1985-September 1986. The University of Kansas. November 1987. 172 pp. NTIS Order No. DE88001201. The goal of this research program is to improve volumetric sweep of fluid-displacement processes using gelled polymer systems. An inte-

grated program is underway to develop a systematic procedure for the evaluation of gel systems used for in situ permeability modification and methods which can be used for design of gelled polymer applications. The program is organized into three parts: (1) physical and chemical description of gelling systems; (2) experimental investigation of in situ gelation in porous media; and (3) correlation and mathematical modeling of in situ gelation. This report describes progress during the first year of a 3-year program. In the first part, results are reported from polymer characterization studies in progress on the structure of polymers, long-term swelling and syneresis of Cr(III)-xanthan gum gels, and intramolecular cross linking of polyacrylamide in Cr(III)-PAAM gelation processes. The chemical structure of polymer/metal ion complexes was investigated by studying the chemistry of complexes of acrylamide and related compounds with chromium and cobalt. A procedure based on equilibrium dialysis was developed to determine the rate of Cr(III) consumption during crosslinking with PAAM. Experimental methods were developed to study the gelation process in the presence of an imposed shear field. The second part of this project has to do with flow experiments in porous media. Flow studies using xanthan biopolymer were initiated to develop a method of estimating in situ shear rate in unconsolidated sand packs. Preliminary studies of the flow of Cr(III)-xanthan gelling solutions were conducted. In situ gelation studies continued on a thiourea/Cr(IV)/cationic polyacrylamide system. A mechanism of in situ gelation based on retention of polymer/metal ion aggregates appears to explain the observed in situ behavior. In the aluminum citrate process, this effort focused on identification of aluminum species that might be retained or precipitated during the flow of aluminum citrate solutions through porous media. The third part of this program is directed at correlation of data and model development related to in situ gelation process. Research on this part of the program will begin in the second year of the contract.

NIPER-256 Surfactant and Cosurfactant Properties of Mixed and Polysulfonated Surfactant By Phase Volume Measurements. Topical Report. National Institute for Petroleum and Energy Research. October 1987. 112 pp. NTIS Order No. DE87001259. This report covers work performed over a 3-year period with the goal of characterizing the oil-solubilizing properties of alkylaryl compounds with two or more sulfonate groups in the molecule. One material studied was a petroleum fraction, containing a large portion of diphenylalkanes, that had been over-sulfonated. The other was an alkyl-diphenyl ether sulfonate. Several monosulfonates were studied for comparison: a petroleum sulfonate (TRS 10-410), technical grades of sodium pentadecylbenzenesulfonate and sodium dodecylbenzenesulfonate; and two isometrically pure materials, sodium n-octylbenzenesulfonate and a branched-chain sodium tetradecylbenzenesulfonate ("Texas No. 2"). The experimental technique was measurement of phase volumes of surfactant-oil systems in alkane and salinity scans. All oils were pure or mixed alkanes from hexane to dodecane. Each surfactant system was characterized by its values of the parameters in the Salager correlation, along with the solubilization parameter and width of the 3-phase region. The results are reported in terms of how these parameters varied with polysulfonation, equivalent weight, mixing of surfactants, and calcium in the brine. A limited study was made of alcohol and sulfonate partitioning and their effect on interpretation of the data. It was found that many of the properties of polysulfonates are a consequence of their low equivalent weight. However, disulfonates are more water soluble, and act more like alcohols, than do monosulfonates of similar equivalent weight. They have less solubilizing power at the same hydrophilic-lyophilic balance, and they decrease the effect of calcium on the behavior. Principal findings on effects of blending surfactant components were that the optimal salinity and Salager slope are higher for mixtures than the linearly interpolated values and that a component with a low O^* has a disproportionate impact on the solubilization parameter of the mixture. An examination of the way solubilization varied as conditions departed from optimal revealed an asymmetry that was reduced by the first polysulfonate. It is not known whether this was the effect of over-sulfonation or mixing different surfactants.

Microbial Enhanced Oil Recovery

DOE/BC/10300-45 Microbial Strains and Products for Mobility Control and Oil Displacement.

Final Report for the Period July 1, 1980-February 28, 1986. University of Oklahoma. December 1987. 208 pp. NTIS Order No. DE88001203. The Department of Botany and Microbiology and the School of Petroleum Engineering have been involved in a joint research program to investigate the use of nonpathogenic microorganisms to enhance oil recovery. The focus of this research has been the use of microorganisms and their metabolic products to improve volumetric sweep efficiency. One study was undertaken to determine why bacteria could penetrate lengths of consolidated sandstone (Berea) faster when sandstone was sterilized by autoclaving than when dry heat (150° Centigrade) was used. While autoclaving resulted in changed permeability, porosity and pore entrance size distribution, these changes were not sufficient to explain the changes in bacterial penetration rates observed in previous work. Electron dispersion spectroscopy and electron microscopy revealed that autoclaving changed the mineral composition and morphology of the clays. Surface charge changes from chloride adsorption onto the clays caused the increased penetration rates. Therefore, dry heat sterilization is preferable for "native-state" rock modeling. In previous parallel core experiments, it was reported that in situ growth and metabolism of indigenous microorganisms releases residual oil from cores and corrects permeability contrasts. Another parallel core experiment was conducted to formulate a material balance for the process. Bacterial growth occurred throughout the cores, but biomass concentration decreased with increasing length in low permeability cores. Unmetabolized sucrose was detected in the effluent, implying that carbon source did not limit the process when one pore volume of nutrient was injected into the core per treatment. Polymeric carbohydrate was observed in the effluent late in the experiments. Pore size may be the limiting factor for in situ metabolism.

Resource Assessment Technology

DOE/BC/10849-5 A Systematic Procedure for Reservoir

Characterization. Annual Report for the Period October 1, 1985-September 30, 1986. The University of Texas. December 1987. 276 pp. NTIS Order No. DE88001206.

The first part of this report is a discussion of results on conditional simulations of miscible displacements in randomly heterogeneous permeable media. The focus here is on local or macroscopic dispersion, the dispersion experienced at a fixed point in the medium. Macroscopic dispersivity has many of the same dependencies on reservoir properties as does megascopic dispersivity, but it seems to be less time dependent and is always smaller. A major part of the report deals with statistical descriptions. The Lorenz and Dykstra-Parsons coefficient, the bias and precision of standard measures of heterogeneity are investigated. Next is the exploration of the benefits of using a distribution-type characterization parameter in heterogeneity. The distribution type is as sensitive as mobility ratio in determining sweep efficiency. Other statistical topics dealt with the sampling issue in correlating log-derived and core permeabilities and in generating a two-dimensional stochastic field that mimics an actual eolian reservoir. The final part of the report describes mapping efforts on the Page sandstone outcrop in northern Arizona. The mapping is to be used in generating both deterministic descriptions and in calibrating the stochastic descriptions discussed above.

Reprints

DOE/BETC/IC-83/4 Abandoned Oil Fields in Oklahoma. James W. Chism. August 1983. 106 pp.

A considerable amount of petroleum may be economically recoverable at today's oil prices from reservoirs abandoned when prevailing prices were lower. A major barrier to renewed production from these abandoned fields has been the lack of pertinent, readily available, systemized information for oil producers. The DOE developed this listing from the Petroleum Data System at the University of Oklahoma; the list includes the abandoned oil fields in Oklahoma that produced 10,000 or more barrels of oil prior to abandonment.

**BARTLESVILLE PROJECT OFFICE
P.O. BOX 1398
220 NORTH VIRGINIA
BARTLESVILLE, OKLAHOMA 74005**

For your convenience in requesting information, the project managerial staff at the Bartlesville Project Office (BPO) and their areas of professional expertise are listed below.

Project Managers

Telephone Numbers

Thomas C. Wesson, Director	918/337-4401
Edith Allison, Project Manager for Reservoir Data and Analysis	918/337-4390
Fred Burtch, Program Coordinator for Enhanced Oil Recovery	918/337-4413
Jerry Casteel, Project Manager for EOR Gas Flooding	918/337-4412
Alex Crawley, Acting Program Coordinator for Advanced Exploratory Research (AER)	918/337-4406
Ernest B. Nuckols, Project Manager for Geoscience and Microbial Enhanced Oil Recovery	918/337-4410
William D. Peters, Project Manager for Fundamental Petroleum Chemistry/Thermodynamics	918/337-4414
Mike Ray, Deputy Director, Program Coordinator for the Tertiary Oil Recovery Information System (TORIS)	918/337-4403
Thomas Reid, Project Manager for Novel Recovery Technology and Thermal Processes	918/337-4233
Karl Schorno, Project Manager for Geoscience and Extraction	918/337-4405
Herbert A. Tiedemann, Project Manager for Technology Transfer	918/337-4293

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SPE/DOE SIXTH SYMPOSIUM ON ENHANCED OIL RECOVERY

APRIL 17-20, 1988

TULSA CONVENTION CENTER
TULSA, OKLAHOMA

You are invited to the Sixth Symposium on Enhanced Oil Recovery sponsored by the Society of Petroleum Engineers and the U.S. Department of Energy. The Mid-Continent Section of SPE and the DOE Bartlesville Project Office are your hosts. EOR has been forced to "tighten its belt" along with the rest of the industry during the recent difficult times. The practical, viable, and significant technology that has survived will be the emphasis of the 1988 Symposium.

The Monday Morning General Session features four speakers who will address our theme—"EOR: Today's Perspective/Tomorrow's Direction." SPE President R. Lyn Arscott will provide the opening remarks. The Honorable John S. Herrington, Secretary of U.S. Department of Energy, has been invited to speak. Other speakers are Ed Holstein, Manager of Reservoir Engineering for Exxon Company U.S.A.; Timothy Dowd, Executive Director of the Interstate Oil Compact Commission; and Myron Kanik, Deputy Minister of Energy, Province of Alberta, Canada.

The technical program consists of 80 papers on topics ranging from reports of field applications to summaries of university research. Research and development in EOR will be discussed by a panel of experts in that area. At a very practical level, the *Forum for Independents* will be an off the record discussion by independent operators on what does and does not work in their operations.

The Monday luncheon will honor five pioneers in Enhanced Oil Recovery Research and Application. The Honorable Henry Bellmon, Governor of the State of Oklahoma, will give welcoming remarks. The Honorable Donald Hodel, U.S. Secretary of the Interior, has been invited to address luncheon attendees. Dr. T. Don Stacy, President of Amoco Canada Petroleum Company Ltd., will speak at the Tuesday luncheon.

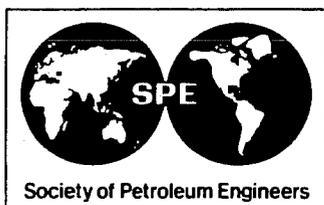
Four short courses and a field trip are scheduled for Saturday and Sunday prior to the meeting. The courses cover EOR Fundamentals, Economic Evaluation of Oil and Gas Investments, EOR by CO₂ Miscible Injection, and Heavy-Oil Recovery.

SEE EOR PREDICTIVE MODELS AT BARTLESVILLE PROJECT OFFICE BOOTH

Be sure to visit our Bartlesville Project Office exhibition booth (Convention Center Booth #724) where we will demonstrate DOE's **EOR Predictive Models**. Bring us your reservoir parameters and see the program find the most efficient EOR process for your

operation. We will also display BPO's **EOR Project Data Base**, covering nearly 1300 historic and current EOR projects. Browse current EOR research publications for information that may help you with your operations or research. See you there!!

DOE-BARTLESVILLE PROJECT OFFICE EXHIBITION BOOTH #724



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