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October 1, 1991-September 30, 1992

October 1993

Performed Under Cooperative Agreement No. FC22-83FE60149

IIT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma

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1992 Annual Report

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Work Performed Under Cooperative Agreement No. DE-FC22-83FE60149

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U.S. Department of Energy
Assistant Secretary for Fossil Energy

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FOREWORD

Fiscal year 1992 completed the ninth year of research established under Cooperative Agreement DE-FC22-60149 between the U. S. Department of Energy (DOE) and IIT Research Institute (IITRI) for operation of the National Institute for Petroleum and Energy Research (NIPER). This FY92 Annual Report, NIPER-691, covers activities dating from October 1, 1991 through September 30, 1992, as authorized under the approved FY92 Annual Research Plan, NIPER-534.

FY92 marked NIPER's second full year of research under the DOE's National Energy Strategy-Advanced Oil Recovery Program (NES-AORP) and Advanced Oil Recovery Program Implementation Plan (AORPIP). The Plan, issued April 1990, outlines an integrated, highly targeted research, development, and demonstration program focusing on near-, mid-, and long-term objectives to maximize the economic producibility of the domestic oil and gas resource and to assure that new and advanced recovery technologies are implemented in the field within the earliest possible time frame.

NIPER also performs research for the DOE's Advanced Extraction and Processing Technology (AE&PT) Program which is developing crosscutting tools, techniques, and scientific/technical understanding—in both extraction and conversion/upgrading technologies—which can be applied to a broad range of petroleum resources. The Program conducts exploratory research to identify and test novel concepts, and fundamental applied research to develop and apply improved technical and scientific understanding to the solution of generic problems.

This Annual Report provides research accomplishments, publications, and presentations resulting from the FY92 research conducted under 14 Base Program projects, 11 of which were funded under DOE's Light Oil and Heavy Oil Programs, and three funded under the AE&PT Program.

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I. INTRODUCTION

Fiscal year 1992 completed the ninth year of research under a cooperative agreement established in 1983 between the Department of Energy (DOE) and IIT Research Institute (IITRI) for operation of the National Institute for Petroleum and Energy Research (NIPER). As authorized by this agreement, NIPER's mission has three major thrusts. The first and primary is to perform work for DOE's Office of Fossil Energy (FE) under an approved Base Research Program; second, to perform research work by way of a Supplemental Government Program (SGP) for non-DOE government agencies and any additional work for DOE not included in the Base Program; and third, to help industrial clients solve their technical problems through a Work-for-Others (WFO) Program. Research programs at NIPER cover a wide spectrum of tasks, all of which relate to three broad technology areas: (1) chemical, microbial, and thermal enhanced oil recovery (EOR) and all of the associated technical activities such as reservoir characterization and imaging techniques; (2) alternative fuels evaluation and testing, including the supporting technologies of thermodynamics research and fuels characterization; and (3) environmental technology related to production, transportation, and utilization of oil and gas. NIPER receives Base Program funding in these categories through DOE's Fossil Energy Light Oil and Heavy Oil subprograms and through DOE's Advanced Extraction and Processing Technology (AE&PT) Program.

FY92 saw a continuation of the program reorientation that began in FY91 following DOE's issuance of its Advanced Oil Recovery Implementation Plan (AORPIP) which was a part of the National Energy Strategy—Advanced Oil Recovery Program. This Plan was developed following the realization that domestic oil wells were being abandoned rapidly following primary and secondary recovery, and that almost prohibitively high costs would be required in reopening existing wells once they were permanently plugged. The urgency tied to this problem resulted in part from a DOE study, entitled "Abandonment Rates of Known Domestic Oil Reservoirs" (DE89000744, Nov. 1989). This study indicated that as much as 40% of the Nation's oil resource had already been abandoned—up from 30% in 1980—and if prices remained at levels below $20/bbl, the figure could rise to 70% shortly after the year 2000.

In essence, the AORPIP recommends a program of field-based research on prioritized classes of reservoirs to rapidly demonstrate cost-effective advances in recovery technologies. Building upon the predecessor long-term, high-risk program, the Plan establishes a program of highly targeted research, development, and demonstration in collaboration with the states, industry, and academic community. The goal of the new plan is to maximize the economic producibility of the domestic oil and gas resource. The near-term objective (fully effective within 5 years) is to preserve economic access to productive portions of the remaining oil resource by instituting a well-designed technology transfer program—involving the Federal government, the states, service companies, and various research organizations—to ensure that currently proven technologies are made available to oil and gas producers who might benefit from their use. The DOE estimates that meeting the near-term objective could result in production of an additional 15 billion barrels of oil that might otherwise be lost. With successful technology transfer over the near term, DOE projects an additional 61 billion barrels of oil may become recoverable in the mid term (fully effective within 10 years) by implementing currently identified, but yet-to-be-proven technologies. Here, the DOE takes a

problem-solving approach that will maximize specific reservoir producibility by describing reservoir heterogeneities, architecture and flow paths; reservoir simulation and process design; and testing and evaluation of production technologies. The long-term effort, expected to reap benefits the first part of the 21st century, is to develop sufficient fundamental understanding of geoscience and new and novel recovery techniques so that additional oil can be recovered from the 265 billion barrels that remain after near- and mid-term objectives are met.

The first step in preserving reservoir access is in identifying those reservoirs that have significant production potential and are in the most danger of premature abandonment. The AORPIP identifies and prioritizes fluvial-dominated deltaic reservoirs as the most important class (Class 1) for immediate study. This reservoir class is common over a wide geographic area, existing in more than 11 states. As a consequence, NIPER's mid- to long-term research has shifted in scope to focus on the deltaic reservoirs, with some effort going to carbonate reservoirs which are second highest in priority ranking. These changes in scope will become evident under the individual project write-ups presented in this report.

Research aside, one of the most important activities in the FY92 program was DOE's Tiger Team assessment of environmental, safety, and health (ES&H) operations at NIPER. This assessment was in response to Secretary of Energy James Watkin's 10-point initiative to strengthen ES&H programs at DOE facilities. Over a 4-week period in the spring of FY92, the assessment was carried out by a group of about 30 professionals from DOE, its contractors, and consultants, most of whom had participated in previous Tiger Team assessments. As a part of the Tiger Team activities, IITRI/NIPER was required to conduct a ES&H self-assessment, after which any findings were to be compared to those observed by the DOE Tiger Team. NIPER received high points for its self-assessment by identifying 75% of the findings noted by the DOE team.

Further, DOE's team determined that no operations at Bartlesville needed to be reduced in scope or stopped as a result of the assessment. The operations are generally conducted in a safe and environmentally sound manner, with facilities generally in good condition. However, the NIPER ES&H programs were characterized as informal and often lacking in written procedures and documentation, thus being vulnerable to potential future problems. In response, IITRI/NIPER prepared an action plan to address these and other findings and to resolve their underlying root causes. The action plan includes schedules, milestones, and estimated costs associated with specific corrective actions. Unlike other DOE facilities which have undergone Tiger Team Assessments, the Cooperative Agreement between DOE and IITRI for operation of NIPER does not require compliance with all DOE Orders and directives applicable to Management and Operating contractors. However, the BPO, NIPER, and Tiger Team carried out their assessments as if all relevant DOE ES&H Orders and notices were applicable. ES&H has the complete and full support of IITRI management, and the ES&H Manager reports directly to the Director of IITRI/NIPER.

II. NIPER'S RESEARCH PROGRAM

Although the specific focus has changed and is presently concentrating on Class 1 reservoirs, the AORPIP authorizes continued research in five principal categories: (1) reservoir description methods, tools, instrumentation, and modeling; (2) extraction techniques to include reservoir simulation and advanced secondary and tertiary

recovery; (3) environmental technology covering air, water, solid wastes, and wetlands management; (4) petroleum chemistry/processing covering constraints on production and refining problems; and (5) technology transfer.

Under the Base Program, NIPER provides supporting research in nearly all of the above categories. The research is performed and managed under the organization structure shown in figure 1. The Energy Production Research (EPR) Department is responsible for a total of 12 projects in the areas of Geotechnology, Chemical and Microbial EOR, and Thermal and Gas EOR. These projects address categories 1 and 2 of the supporting research outlined above. The Fuels Research (FR) Department is responsible for two Base Program projects in category 4.[1] Presently, no environmental work (category 3) is being performed under the Base Program, but several projects are ongoing under the SGP and WFO Programs. A considerable portion of the present environmental work is the result of expertise gained under former Base Program projects. Category 5, technology transfer, is NIPER's principal product and will be emphasized throughout this report since it plays a crucial role in the successful implementation of the AORPIP.

As shown in table 1, 11 of the projects in Energy Production Research are funded under FE's EOR Light and Heavy Oil Programs. The remaining project (BE12) and the two projects in Fuels Research are funded under FE's Advanced Extraction and Processing Technology (AE&PT) Program.[2] The role of the AE&PT Program is to develop crosscutting tools, techniques, and scientific/technical understanding—in both extraction and conversion/upgrading technologies—which can be applied to a broad range of petroleum resources. The Program conducts exploratory research to identify and test novel concepts and fundamental applied research to develop and apply improved technical and scientific understanding to the solution of generic problems. Accordingly, the Program directly supports the Office of Fossil Energy's strategic goal which is concerned with environmentally acceptable liquid fuel options.

During FY92, 14 projects funded under the SGP Program were conducted to provide near-term research and support to the DOE in areas outside the Base Program. In most instances, these projects coincided with the type of research being performed under the Base Program but were somewhat different in scope. Both the Base Program and SGP Program projects are managed by the Bartlesville Project Office (BPO) which has been delegated the lead assignment in implementing FE's EOR and AE&PT Programs through a number of projects executed by (1) NIPER, which utilizes the federal equipment and facilities at Bartlesville; (2) industrial and university research organizations; and (3) National Laboratories. The BPO is collocated with NIPER at the Bartlesville facility.

The FY92 research accomplishments, publications, and presentations for each of the 14 Base Program projects are presented in this report. Where appropriate, the work being performed under the SGP Program is also addressed. Appendix A indicates the proper procedure for ordering publications prepared for the DOE by NIPER.

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[1] *NIPER is not performing fuels/engines research for DOE under the Base Program although such a category is shown in figure 1 for the Fuels Research Department. The fuels/engines work is, however, important to NIPER's total program as it provides information on the changes and overall acceptability of today's transportation fuels.*

[2] *Individual research projects are numbered in a simple code: A letter "B" representing the Base Program; a letter "E" or "FR" representing the EPR and FR Department, respectively; and a project number. Thus, BE1 indicates Base Program project No. 1 of Energy Projection Research.*

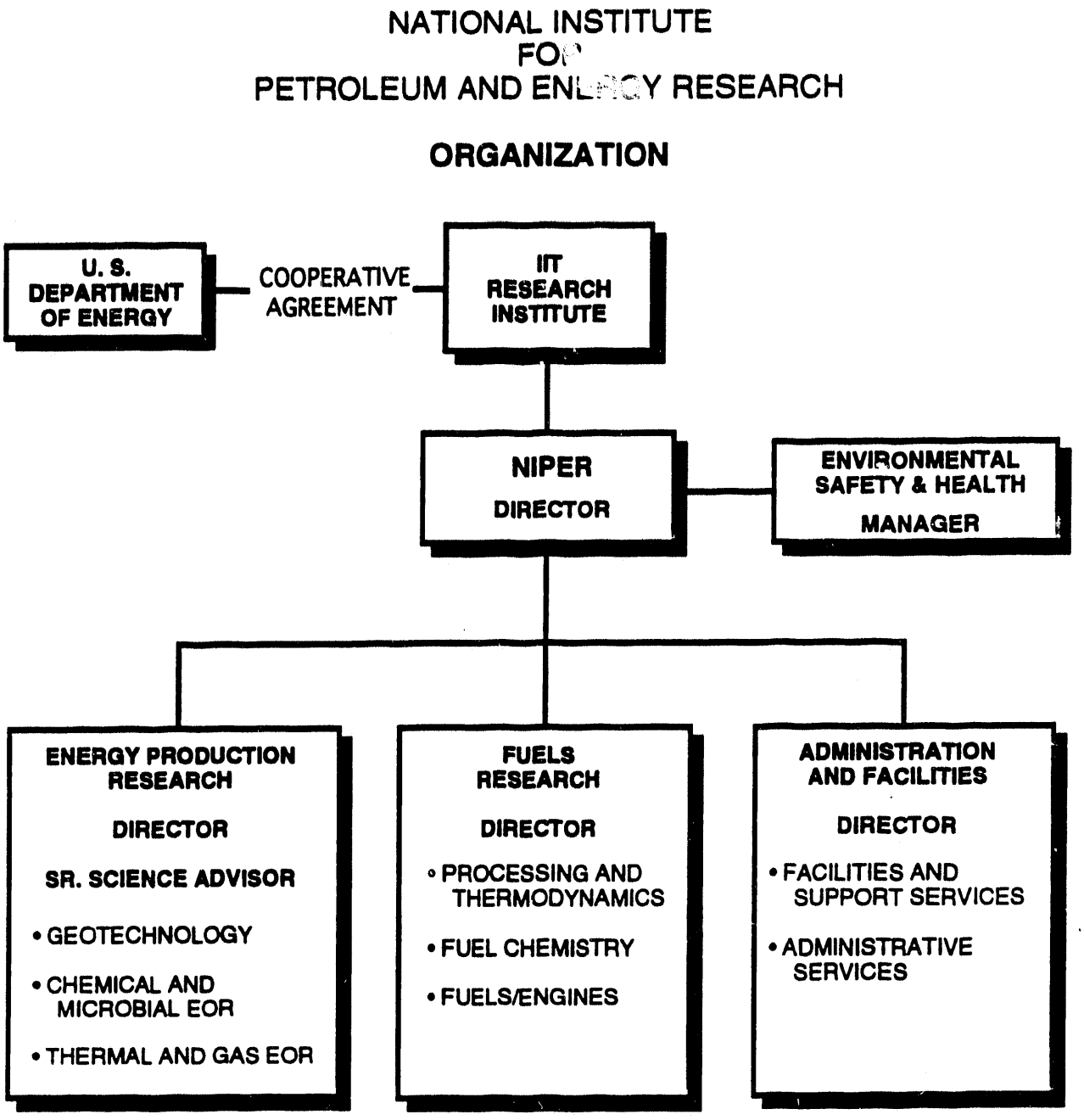

FIGURE 1. - NIPER Organization

TABLE 1. - NIPER FY92 Base Research Program

Project		DOE FE Program[1]	Funding, $K
ENERGY PRODUCTION RESEARCH			
Geotechnology			
BE1	Reservoir Assessment and Characterization	EOR-LO	785
BE2	TORIS Research Support	EOR-LO	340
BE9	Three-Phase Relative Permeability	EOR-LO	290
BE12	Imaging Techniques Applied to the Study of Fluids in Porous Media	AE&PT	545
Chemical and Microbial EOR			
BE4A	Surfactant Flooding Methods	EOR-LO	585
BE4B	Development of Improved Alkaline Flooding Methods	EOR-HO	195
BE4C	Mobility Control and Sweep Improvement in Chemical Flooding	EOR-LO	200
BE3	Development of Improved Microbial Flooding Methods	EOR-LO	295
Thermal and Gas EOR			
BE5A	Gas Flooding Performance Prediction Improvement	EOR-LO	250
BE5B	Mobility Control, Profile Modification, and Sweep Improvement in Gas Flooding	EOR-LO	370
BE11A	Thermal Processes for Light Oil Recovery	EOR-LO	295
BE11B	Thermal Processes for Heavy Oil Recovery	EOR-HO	200
	Total EPR Base Projects		4,350
FUELS RESEARCH			
Processing and Thermodynamics			
BFR3	Thermochemistry and Thermophysical Properties of Organic Nitrogen- and Diheteroatom-Containing Compounds	AE&PT	350
Fuel Chemistry			
BFR2	Development of Analytical Methodology for Analysis of Heavy Crudes	AE&PT	300
	Total FR Base Projects		650
	TOTAL BASE PROJECTS		**5,000**

[1] Abbreviations: EOR = Enhanced Oil Recovery; LO = Light Oil; HO = Heavy Oil; AE&PT = Advanced Extraction and Processing Technology

III. ENERGY PRODUCTION RESEARCH

In FY92, the Energy Production Research Department (EPR) was responsible for 12 DOE-funded Base Program projects and 14 SGP projects receiving full or partial DOE funding. The Base Program research has combined efforts directed toward DOE analysis and planning activities, support research, and field work. The proposed program parallels the new advanced oil research program with (1) phased field analyses that identify near-term opportunities for operators and needs for risk reduction for mid- and long-term opportunities, (2) application of technical advances to specific field applications, (3) continued research directed toward improving the understanding of the mechanisms of EOR processes, and (4) technology transfer directed toward operators to generate interest in the opportunities identified in the field analyses and supporting research work by NIPER and other organizations.

In this report, EPR projects are grouped into three major areas of work. *Geotechnology* provides support for DOE's TORIS data bases and conducts research in the areas of reservoir characterization and the quantitative prediction of fluid-flow behavior in reservoirs. The other two areas, *Chemical and Microbial EOR* and *Thermal and Gas EOR* are concerned with improved oil recovery through a better understanding of the basic mechanisms of EOR processes and the application of EOR technologies in support of field projects. Physical and mathematical models are developed and used to simulate processes and verify hypotheses derived from laboratory and field data. These models are also used to identify areas requiring additional research.

Geotechnology

Research in project BE1, Reservoir Assessment and Characterization, employs an interdisciplinary approach to reservoir characterization and modeling that is targeting the high-priority reservoir class of shoreline barrier deposits: (1) to determine the problems specific to this class of reservoir by identifying the reservoir heterogeneities that influence the movement and trapping of fluids and (2) to develop methods to effectively determine the architecture of this class of reservoirs to predict residual oil saturation on interwell scales and improve the prediction of the flow patterns of injected and produced fluids. In FY92, research was performed to complete the identification and quantification of major reservoir heterogeneities and properties of Patrick Draw (WY) field—analysis of the depositional setting for that field that was started during FY91; to develop an integrated engineering model for Patrick Draw field, based on available petrophysical, well injection, production, and pressure data; and to determine the optimum data set and type of data base required for effective reservoir characterization and data management. BE1 project staff are also involved in the SGP Program. FY92 research in project SGP42 finalized a study authorized by the DOE to develop suitable techniques for mapping the types and volumes of clays from signature analysis of log responses in clayey formations. Under project SGP47, IITRI/NIPER and the DOE/BPO cosponsored the Third International Reservoir Characterization Technical Conference, November 3-5, 1991, at the Westin Hotel, Tulsa, OK. The theme for the conference was "Reservoir Characterization Requirement for Different States of Development." The opening address was given by Donald Juckett, Director of the DOE Office of Geoscience Research. Luncheon addresses were presented by Mrs. Denise Bode, President of the Independent Petroleum Association of America (IPAA) and Farouk Al-Kasim, consultant, Stavanger, Norway. The first conference on

reservoir characterization was held in Dallas in the summer of 1985, with registration of about 175, and the second conference was held in June 1989, also in Dallas, with registration of 234. Total registration for the third conference was 247, and the following countries were represented: England, Norway, Canada, France, Japan, Scotland, China, Hungary, Germany, Sweden, Venezuela, Australia, and the United States.

Project BE2, TORIS Research Support provides specific information to DOE's Tertiary Oil Recovery Information System (TORIS) in the areas of EOR project and reservoir data base management, EOR project technology and trends analysis, and evaluation of computer models and numerical information on hundreds of domestic oil fields. TORIS is being expanded to include most of the known oil resources in major producing states and presently includes geologic and engineering data on 3,700 reservoirs representing 72% of total U.S. oil in place. It has been instrumental in planning the reservoir classification system outlined in the AORPIP and will be used to monitor all new information resulting from future research. Under project SGP60, project staff is performing an analysis of the U.S. domestic resource base and estimating future recoverable oil. This work is scheduled for completion in FY93. Under project SGP56, the DOE has authorized NIPER to upgrade and maintain a high-integrity, on-line, crude oil analysis data base that can be used by the general public.

The objectives of project BE9, Three-Phase Relative Permeability, are to improve the reliability of laboratory measurements of two-and three-phase relative permeabilities for steady- and unsteady-state conditions in core samples; to investigate the influence of rock, fluid, and rock-fluid properties on two- and three-phase relative permeabilities; and to expand the capabilities of measuring relative permeabilities under broader temperature and pressure conditions. FY92 project research focused on two primary areas: examination of the mutual relationships among petrophysical properties and relative permeabilities and improving the state of the art in three-phase measurement at higher temperature and pressure conditions. Tests were conducted on a low-permeability reservoir rock sample rather than the clean, quarried sandstone rock samples commonly used. Testing with actual reservoir rock presented challenges that required many new innovations in testing procedures and designs. Under project BE9, a consortium has been formed with two major petroleum companies. The purpose is to advance the state of the art in reservoir-condition, multiphase relative permeability measurements applicable to the study of fluid flow behavior in porous media. The consortium provides for an interchange of ideas and accrual of advice on areas in which technology developed at NIPER can be of use to the petroleum industry.

The primary goal of project BE12, Imaging Techniques Applied to the Study of Fluids in Porous Media, is to advance the understanding of fundamental processes involved in oil recovery by developing, refining, and applying cross-cutting imaging techniques to include computed tomography (CT) imaging, nuclear magnetic resonance imaging (NMRI), and petrographic imaging. These techniques are being used to assist several Base Program projects in characterizing pore structures and surfaces and determining pore-to-core-scale heterogeneities, rock-fluid interactions, and distribution of fluids in reservoir rock during corefloods. Techniques being developed in this project are being applied for a better understanding of the rock fabric of various facies, determining how various polymer/surfactant combinations affect oil recovery, characterizing and selecting the most representative core plugs for special core analyses, understanding the effect of fractures on EOR processes designed for industrial clients,

characterizing formation heterogeneities and their relation to log responses, and determining the relationship between saturation distributions and the electrical resistivity of core samples.

In the pages that follow, the FY92 research for EPR's four projects in Geotechnology and associated SGP projects is presented. Individual Base Program project summaries describe (1) the relationship of the work to the DOE program, (2) significant research accomplished during the fiscal year, and (3) technology transfer. The projects are addressed in the following order: BE1, Reservoir Assessment and Characterization; BE2, TORIS Research Support; BE9, Three-Phase Relative Permeability; and BE12, Imaging Techniques Applied to the Study of Fluids in Porous Media.

RESERVOIR ASSESSMENT AND CHARACTERIZATION

Principal Investigator:	Susan Jackson
BPO Project Manager:	Edith Allison
Project No.:	BE1
Funding for FY92:	$785,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The FY92 objectives of this project were: (1) to develop geological and engineering methods using existing log, core, and engineering data to predict residual oil distribution and flow characteristics in a shoreline barrier reservoir; (2) to determine the optimum data set and type of data base necessary for effective reservoir characterization and management; and (3) to compare types of shoreline barrier models and determine similarities in the scale and type of heterogeneities and their effect on fluid movement and production/injection performance.

Research Summary

NIPER's reservoir assessment and characterization research program incorporates elements of the near-, mid-, and long-term objectives of the National Energy Strategy—Advanced Oil Recovery Program. The shoreline barrier reservoirs studied as a part of Project BE1 represent a class of reservoirs with large amounts of remaining oil in place (ROIP), located in mature fields with a high number of shut-in and abandoned wells. The analysis and models developed in the course of the research will directly benefit the field operators and companies operating in barrier island reservoirs in the near term.

Near- to mid-term applications of the results of this research comprise a methodology to quantify the effects of heterogeneities and to construct accurate reservoir models. Long-term results of the research will be the determination of the transferability of reservoir and production characteristics among reservoirs of similar depositional histories. Identification of similar heterogeneities will allow application of similar reservoir management strategies and advanced recovery methods to maximize recovery efficiency.

The research program at NIPER employs an interdisciplinary approach focusing on the high-priority reservoir class of shoreline barrier deposits. The studies are designed: (1) to determine the problems specific to this class of reservoirs by identifying the reservoir heterogeneities that influence the movement and trapping of fluids and (2) to develop effective methods for characterizing this class of reservoirs and to be able to predict residual oil saturation (ROS) on interwell scales and the flow patterns of injected and produced fluids.

Accurate descriptions of the spatial distribution of critical reservoir parameters (e.g., permeability, porosity, pore geometry, mineralogy, and oil saturation) are essential in designing and implementing recovery processes that can improve sweep efficiency and thereby increase oil recovery. Most of FY92 was devoted to integrating the previously developed geological and engineering model for the mesotidal shoreline barrier reservoir at Patrick Draw (WY) field with reservoir production performance and previously tested reservoir characterization methods. Newly

developed wireline log analysis, hydrogeochemical analytical techniques, and injection data analysis using Hall plots were validated by integrating analytical results with reservoir information from other sources. These reservoir characterization methods are expected to benefit operators in the selection of cost-effective recovery techniques when applied to domestic fields. The reservoir data generated during model development have been documented and put in electronic format, and an annotated bibliography of shoreline barrier deposit references has been prepared to ensure the technology is effectively transferred to operators and other interested parties.

The scope of the work for FY92 may be subdivided into four main areas: (1) the application of hydrogeochemical techniques to reservoir characterization; (2) the effect of salinity variations in the determination of oil saturations by wireline logs; (3) structural and sedimentological features that control fluid distribution and movement; and (4) analysis of lateral variations of reservoir properties and production/injection performance.

Hydrogeochemical Techniques

The first area of research encompasses the principles and practical applications of hydrogeochemical analytical techniques. Distribution of salinity and the chemical composition of formation waters that coexist with oils within reservoirs can provide important information on reservoir compartmentalization. Interpretation of log signatures and calculation of accurate saturation values from wireline logs are particularly dependent on the variation and spatial distribution of formation water salinity, composition, and consequent resistivity. A hydrogeochemical anomaly has been identified and mapped in the Almond formation of the Washakie Basin where Patrick Draw field is located. High-salinity formation waters (>70 g/L TDS) occur in the updip portions of Arch and Monell production units, whereas brackish waters (≤20 g/L TDS) are found downdip, closer to the oil-water contact.

Distinctly different fluid regimes were identified in portions of Patrick Draw field by quantitative determination of hydrogeochemical facies of reservoir waters. High-salinity gradient zones indicated positions of barriers to lateral flow. Major reservoir compartments and local subcompartments were inferred within the Almond formation on the basis of salinity gradients and differences in chemical composition of the formation waters.

High salinity, and sometimes unique composition of formation waters in the updip portion of Patrick Draw reservoir, cannot be explained by autochthonous (in situ) processes of water-rock interaction. Contrasts in salinity and chemical composition between compartments indicate that allochthonous (of different source and probably origin) fluids migrated into individual compartments of the Almond formation.

Faults are the most probable pathways for interformational migration of fluids from which the fracture fill and matrix cement precipitated. Therefore, the most diagenetically affected parts of the reservoir should occur near structural discontinuities indicated by well log and seismic analyses.

The strong hydrogeochemical indication of fluid compartments within the Almond formation and the probability of vertical migration of fluids through faults provide information for enhanced oil recovery tactics, design of optimum flood patterns, and selection of the best prospective sites for infill drilling into untapped compartments. In Arch Unit of Patrick Draw field, most wells of superior productivity (producing more oil than the general trends) are concentrated in the high-salinity megacompartment. Wells of less than average productivity are

predominantly located within the zone of highest hydrochemical gradient, indicating the position of a barrier to lateral flow. The salinity contrast zones, heterogeneity of water composition, pressure depletion zones, thickness of the major producing sandstone, and productivity of wells are most likely interrelated in Arch Unit. At this point, little is known about such relationships and their geologic reason in Monell Unit due to the paucity of core material.

In Bell Creek field, Montana, lateral compartmentalization of productive units within the Muddy formation is evident based on earlier geological and engineering analysis. A potential for vertical communication of fluids through conductive faults between the Muddy formation and an unidentified aquifer is indicated by strong hydrogeochemical anomalies. They include low salinities and nearly complete homogenization of water composition across Bell Creek field despite the presence of barriers to lateral flow. In contrast to Patrick Draw field, the homogeneity of water composition in all four horizontally separated productive units of the Muddy formation in Bell Creek field indicate a single, dynamic, allochthonous source of water.

Salinity Variations

The second area of research is to determine the effect of salinity variations on oil saturation calculations from wireline logs at Patrick Draw field. Calculation of water saturation profiles, based on water resistivity values ranging from 0.1 to 0.5 ohm-meter, resulted in a range of average water saturations from 34 to 76%—the difference between a good oil reservoir and a residual oil reservoir. A constant value of water resistivity, based on an assumption of a homogeneous distribution of salinity, is often used in interpreting oil reserves from resistivity logs. Work in this project shows that comparison of oil saturation distribution, based on a single R_w value for the entire field and that based on R_w values from accurate salinity data, resulted in a 5 to 12% difference in saturation values in Patrick Draw field. Comparison of various log analysis methods to determine the effect of salinity and clay content indicated that in moderately low-clay-content sandstones (<8% V_{cl}) with relatively small amounts of clays that have high cation exchange capacities (<1%), Simandoux's method gives reliable estimates of S_w.

The recalculation of oil resources, based on the mapped distribution of water salinities and related resistivities, reveals up to 12% more original oil in place in the area of highly saline formation waters in the updip portions of Patrick Draw field, and up to 5% less oil in the portions with much lower salinity. This investigation illustrates the importance of heterogeneous formation water salinity distributions in the estimation of oil resources.

A small change in R_w can cause a relatively large change in S_w values. In the absence of actual R_w measurements, computation of R_w from a SP log may yield acceptable values provided all precautions are taken to remedy the possible sources of errors in this method of calculation. The calculated S_w values by the Dual Water model, which indirectly computes cation exchange capacity (CEC) from the V_{cl} data, were similar to those obtained from Simandoux's method. This confirms that the high CEC clays such as montmorillonite probably had a negligible effect on the S_w calculations in Patrick Draw field.

Structural and Sedimentological Features

In the third research area, the structural and sedimentological controls on fluid distribution and movement

were investigated. Structural cross sections, based on wireline log correlations and seismic data, were used to identify numerous, previously unreported structural faults within the production limits of Patrick Draw field. The fault directions were consistent with lineaments identified in the region and were determined to have a subtle effect on sand depositional patterns, which had previously been correlated with production. Additional controls on fluid distribution and movement at Patrick Draw were related to the areal distribution of an impermeable (coquina) deposit as well as petrophysical properties, some of which were controlled by diagenetic processes such as compaction, cementation, and the creation of secondary porosity and microporosity. In contrast to the results of NIPER's research, Patrick Draw field historically has been considered structurally homogeneous, dipping monoclinally to the east. Previously unrecognized faults within UA-5 and UA-6 sands of the Almond formation have now been identified by NIPER's reservoir characterization team through the correlation of logs and construction of structural cross sections within Arch and Monell Units at Patrick Draw field. Because of the limitations of the correlation, it is probable that other faults with less than 10 ft of throw are also present within the field.

Fault zones identified by analysis of structural cross sections are aligned parallel to several surface-mapped faults located immediately west of Patrick Draw field. The fault zones identified by mapping fault locations identified on structural cross sections are dominantly oriented east-northeast and are offset approximately 30° to the two most dominant surface lineament directions. The dominant fault zones identified by combined seismic and log data are offset 20° and 46° from the major and second major lineament directions. A genetic relationship may exist between the regional surface and subsurface structural features. Carbonate-filled fractures within UA-5 sands have been recognized in cored intervals so there is reason to believe that other fractures may also be present within the field.

The documentation of fractures and faults within UA-5 sands of the Almond formation at Patrick Draw field, some of which are filled or partly filled with carbonate cement, suggest that tectonic forces may have played an important role in determining fluid migration and distribution within the reservoir. Currently, the effect of faults and fractures on production in Patrick Draw field is not well understood, and additional work is required to determine if specific fault or fracture sets are open or closed, thereby creating baffles, channels for fluid flow, or reservoir compartments. Production is generally best in the thickest reservoir sands, and no obvious correlation exists between the distribution of faults and production maps for Arch and Monell Units; however, the coincidence of faults bounding the highly productive sand thick that straddles the Arch-Monell Unit boundary provides an indication that some synsedimentary structural control of sand accumulation probably exists.

The distribution of faults, identified by analysis of log cross sections, correlates with the distribution of some portions of the isosalinity map, particularly those areas marked by a strong gradient. The eastward projection of a tongue of high-formation water salinity, located within a shallow graben (determined by log correlations) in the southern half of Arch Unit, provides the strongest evidence for a relationship between at least some faults and formation water salinity distribution.

The fault map constructed with seismic and wireline log data indicates a fairly large number of faults, some with very few vertical throws, crisscrossing Patrick Draw field. The effect of these faults on primary oil production appears to be relatively minor; however, in certain parts of Arch Unit brittle, carbonate-cemented rocks are encountered, and the detrimental effect on sweep efficiency due to these faults appears to be significant. Fractures may be generated within the more brittle intervals by some of the faults, and they resulted in relatively fast breakthrough times in certain areas, particularly in the Arch Unit part of the field.

The area of high salinity gradient, located in the eastern part of Arch Unit, generally coincides with the location of high resistivities, reflecting coquina development. Evidence for chemical compaction within the coquina, including microstylolitic grain contacts, solution seams, and embayed oyster shells, points to a local abundant source for the carbonate cement. The correspondence between the occurrence of carbonate-cemented sands and the high gradient areas of the salinity map of Patrick Draw field indicates that carbonate cement may have precipitated along a geochemical, rather than a lithological boundary.

Log-derived V_{cl} data indicate greater variability in clay content within the UA-5 sand than do XRD samples. Because of the variation in clay content encountered, XRD samples should be used to calibrate V_{cl} values. For one well, Arch 120, true clay content is 3% lower than the V_{cl} value.

The relatively large spatial variability of petrophysical properties within the reservoir, and possibly within mesotidal shoreline barrier reservoirs in general, results in better correlation of petrophysical properties within a single well than between wells. Empirically derived median pore throat diameters from four wells correlate with permeability; however, the correlation coefficient is higher on a single-well basis. This is significant for field development because it means that relationships between petrophysical properties in a given well (e.g., permeability vs. porosity) may not be the same or may not be accurately predicted, even in nearby wells.

For the samples tested, the amount of microporosity generally increased with total porosity and clay content. The more porous reservoir sands often contain larger proportions of microporosity within leached or altered feldspars or lithic fragments. Also, the more porous intervals tend to have proportionately more loosely associated books of kaolinite within interparticle pores. Petrographic analysis indicates that sands with originally unstable grains have been leached and altered so that they have a tendency toward increased total porosity, microporosity, and clay content.

The microporous nature of the more porous UA-5 sands may be important to production. Although the micro-network of clay particles may have a negligible effect on porosity, the pore geometry could lead to abundant dead-end pore configurations resulting in poor sweep efficiency. Thus, pore system texture may be the reason for relatively low permeability within the reservoir and may explain the tendency of these sands to have production problems that are often incorrectly ascribed to mobile fines.

Distribution of the coquina that acts as a barrier to fluid flow between western and eastern portions of Arch Unit was determined by mapping its occurrence. The correspondence between coquina and log signatures is excellent. The greatest thickness of coquina is indicated along the sand thin that occurs between the western and eastern bars; however, the distribution of the coquina indicates more than one band of isolated thicks. Two sub-

parallel accumulations formed and were probably genetically distinct. The fluid barrier between eastern and western bars may be created by a combination of thin, calcite-cemented sand in the northern part and impermeable coquina in the southern part of Arch Unit. The carbonate-cemented areas may have formed relatively early and remained topographically high during UA-5A deposition, diverting UA-5A sands from the area except in the topographic low between the eastern and western UA-5B bars.

Vertical distribution of facies within cored wells indicates that the coquina deposits are on the back or lagoonal side of the barrier. They are most often associated with tidal channel or tidal delta sandstones. Stratigraphic cross sections show that the deposit consists of several successively offlapping thin wedges with their geometry formed by overall seaward migration of the barrier system, with relatively little lateral (along strike) migration of the inlet/tidal delta complex.

Lateral Variations of Reservoir Properties

The fourth broad area of research consisted of an evaluation of the lateral variations in production performance. Determining the effectiveness of primary and waterflood recovery operations at Patrick Draw field requires a precise estimation of water saturations of the producing sandstones during different stages of production from the field. The efficiency of waterflood recovery was found to increase with the mean permeability of reservoir rock among 12 five-spot patterns in Monell Unit. This relationship is believed to exist due to the relatively high ratio of oil relative permeability to water relative permeability (k_{ro}/k_{rw}) for the rocks of higher permeability values in this strongly water-wet system. No correlation was found between oil recovery efficiencies and Dykstra-Parsons coefficients in either Arch Unit or Monell Unit, and this suggests that the Dykstra-Parsons coefficient is not a good indicator of production performance at Patrick Draw field. Comparison of the permeability distributions indicates that Monell wells have a lower mean permeability but a more homogeneous permeability distribution, as evidenced by the lower value of Dykstra-Parsons coefficient. Because of a greater pay thickness, Monell wells have a larger mean-well reserve than Arch wells. In addition to reservoir pressure and petrophysical properties, the importance of the lateral distribution of oil saturation in the reservoir at different phases of recovery is demonstrated.

Reservoir-volume-balance calculations in three regions of Arch Unit show no evidence of loss of injection water to sands other than UA-5 and UA-6 sands. This indicates that no major conduits connect the UA-5 and UA-6 sands to other sands. Because of the gas cap in the western edge, the western region of Arch Unit shows a smaller ratio of injection to production volume than the eastern region.

The best production of Patrick Draw field lies primarily in the area of good oil reserve, with a thick pay and a high oil saturation value. The expansion of a neighboring gas cap, and water injection, contributed to successful production from the southwestern area of Arch Unit and the northwestern area of Monell Unit. Waterflood recovery is generally poor in Arch Unit, ranging from 7 to 288 MBBL/well, because of the fast water breakthrough and short periods of oil bank. Mean waterflood recovery from 39 Arch wells is 62.7 MBBL. This corresponds to about 6% OOIP and about one-third to one-half of primary recovery of Arch wells. In Monell Unit, oil production decreases smoothly from the northwest area of good reserves toward the southeast, which has poor reserves. The smooth

decrease in oil production is due to a gradual variation of pay thickness and oil saturation. Monell Unit has relatively good recovery efficiencies (primary plus waterflooding), ranging from 20 to more than 50%. The Arch Unit has a relatively poor recovery efficiency (<30%) except for the northern area and the area immediately west of the low-permeability, thin-pay area. Mass balance calculations show that the water injection volume is proportional to waterflood production of nearby producers in Monell Unit. The injected water ranged from 15 to 60% PV for most Monell wells and 10 to 40% PV for most Arch wells. Evidence of a high degree of reservoir heterogeneity in Arch Unit is: (1) sand discontinuity or compartments reflected by gross changes in pay thickness and fluid saturations; (2) poor sweep efficiency and low waterflood recovery compared to that in Monell Unit; and (3) the large contrast in water breakthrough times which ranged from less than 1 month to more than 100 months.

Waterflood production in Monell Unit ranged from 50 to 1,366 MBBL oil per well, with a mean of 321.7 MBBL and a median of 244.4 MBBL/well. This is comparable to the primary recovery (mean 290.7 MBBL per well) and equivalent to a recovery of approximately 23% OOIP. The decrease of producing gas-oil ratio and formation of oil banks indicated by the increase of oil rates in both Arch and Monell Units suggest a normal response to the waterflood. Decline of reservoir pressure and little water production before the initiation of waterflood suggest an inactive aquifer or poor lateral communication with the Almond formation aquifer downdip at the oil-water contact. The majority of wells in the western region of Patrick Draw field have been producing at low water cuts due to communication with the gas cap. A continued injection of water in areas of low water cut can help recover additional oil.

The northwestern and the central parts of Monell Unit have potential for EOR because they are relatively homogeneous and have a significant ROS in the reservoir. Carbon dioxide flooding shows promise as a recovery process for Monell Unit because: (1) reservoir pressure in the Unit is higher than the minimum miscibility pressure for a miscible flood; and (2) a nearby source of CO_2 is available. Horizontal well drilling has potential for recovering additional oil in Arch Unit by overcoming compartmentalization and formation channeling—if the ROS in eastern Arch Unit can be verified from volumetric and production calculations.

No significant wellbore damage was identified in Hall plot analysis of most of the injection wells in Arch Unit, evidence of which is a constant slope of the Hall plot after the gas space in the reservoir was filled with water. The Hall plot slope for the Arch Unit is related to the flow barrier or deterioration of pay sands. Some sharp increases in the Hall plot slopes during the late injection stage were caused by the shut in of surrounding production wells. Numerical simulations demonstrate that the slope of Hall plot increases with the number of nearby barriers and with the decrease of the distance between barriers and the injection well. Analytical calculations of injection pressures show a significant increase when one barrier is less than 200 ft away—or two intersecting barriers are less than 400 ft away. The effect of the orientation of barriers on injection pressure is not as significant as the distance of barriers from the injector.

A data base resulting from work performed from 1989 through 1992 by the reservoir characterization team at NIPER was developed as part of Project BE1 and consists of electronic data files containing geologic, petrophysical, and petrographic data resulting from reservoir studies of Bell Creek and Patrick Draw fields. The files include

production/injection data, core petrophysical properties, petrographic, reservoir fluid, and wireline log data. The data set is designed for oil companies, operators, and other organizations needing realistic rock property values and information on the spatial distribution of reservoir parameters. Potential uses for the data base include testing of various mapping algorithms and geostatistical techniques, data input for reservoir models, log-core correlations, and sensitivity studies using numerical simulators. The data are primarily from Almond formation, Patrick Draw field. Fracture azimuth data from outcrop exposures of Almond formation, located southeast of Rock Springs, WY, are also included in the data set. The data are on six 3.5-in., 1.44-megabyte, Macintosh-formatted floppy disks in Excel™ spreadsheet files. The data include general well information, production data, core data, fluid data, log data, and outcrop data.

In addition to the detailed information about the Almond and Bell Creek formations, the TORIS data bases were used to investigate 319 shoreline barrier reservoirs to develop a summary of shoreline barrier reservoir characteristics. The dominant age of the barriers is Tertiary and the dominant subenvironment represented is strandplain/barrier core. Histograms of permeability, porosity, oil gravity, and formation water salinity indicate a high degree of variability.

Other tasks for FY92 were (1) to outline the types of data, data sources, and measurement tools required for effective reservoir characterization, (2) to identify the data required for specific enhanced oil recovery (EOR) processes, and (3) to discuss the optimum data density for reservoir characterization and reservoir modeling.

The two basic sources of data for reservoir characterization are the specific reservoir and analogous reservoirs, outcrops, and modern environments. Reservoir data can be divided into three broad categories: (1) rock properties (the container), (2) fluid properties (the contents), and (3) rock-fluid interaction. Both static and dynamic measurements are required.

Reservoir characterization requires data on a range of scales from basin and field scale to pore-size scale. Field-scale information establishes the spatial framework and the general architecture of the reservoir for describing and predicting smaller-scale reservoir geometries and heterogeneities along with their associated petrophysical and fluid-flow properties. Mesoscopic scale information addresses variations of properties within the facies or reservoir units, while microscopic or pore-scale information includes pore size, pore throat, surface roughness, grain size, and sorting.

Outcrop exposures of reservoir rocks provide laterally continuous sampling of rock characteristics and lateral information on scales not available from reservoir data. Studies of outcrops and analogous modern environments can be valuable low-cost sources of high-quality geological and petrophysical data. Outcrop studies can provide a wealth of quantitative information on the dimensions and geometries of sandbodies, fluid flow barriers forming compartments, permeability baffles, and the spatial distribution of matrix permeability and porosity. The constraint in applying outcrop data to reservoirs is the inability to determine the degree of transferability of characteristics between different deposits, even within the same depositional system.

Although much of the effort in reservoir characterization is focused on pore- to bedding-scale features, the larger-scale reservoir architecture controls the communication between wells and exerts a very strong influence on

sweep and recovery efficiency. Regional-scale studies are essential for understanding the origin of the reservoir architecture and predicting the occurrence and location of heterogeneities.

The scale of heterogeneities dominating production are different for particular stages of field development. As the stages of field development progress from primary to secondary to tertiary recovery, the scale of important heterogeneities generally decreases and is dependent on the recovery process applied.

The value of data can be assessed as the equivalent loss resulting from poor or incomplete data; however, determining the optimum data density for reservoir characterization is difficult, because the value of the data often is not known until it is acquired and analyzed. Extensive simulation studies are needed to evaluate the magnitude and direction of errors that can be expected in oil recovery prediction with varying amounts of data. A quantitative approach using the variogram is proposed, where the correlation length is used as a guide to the minimum sampling distance for data collection.

Techniques were developed to map the types, volumes, and distribution of clay in petroleum reservoirs and to determine the effects of clays on oil production in project SGP42. Log signatures were correlated with information on the distribution of the types and volumes of clays in sandstone pore spaces determined from detailed CT-scans, XRD, SEM, and thin-section analyses of core samples from three sandstone reservoirs. The log signatures were then analyzed to learn if suitable mathematical/statistical parameter(s) could be calculated from the logs to determine their effects on permeability and oil production.

When a reservoir sandstone has dominantly one type of clay, an easy way to distinguish such a clay is from crossplots of the volume of clay against the bulk density and the neutron porosity of the sandstone. The pattern of distribution of the points in a crossplot is sometimes a good indicator of the type of clay in a sandstone. Because of differences in cementation and consequent changes in pore throat size distribution, two sandstones having the same quantity of identical clay types may have very different production characteristics. These sandstones can be easily identified from a clay-volume density plot. The variation in the vertical distribution of clays within a sandstone seem to have a more drastic effect on permeability of reservoir sandstones than the total volume of clays. Estimates of total clay content from gamma ray logs are always on the high side because of the presence of non-clay radioactive minerals. The effect of non-clay minerals must be eliminated before good estimates of total clay content in sandstone reservoirs can be made.

From correlations of CT-scans and density, gamma ray, sonic, and neutron log data, it was observed that certain thin, shaley beds (thickness <1 ft) could not always be resolved from the density or the sonic logs when the shale beds had the same density as the matrix rocks; however, these beds could usually be identified from gamma ray and neutron logs.

A quantitative measure of the overall variation in clay content of sandstone reservoirs could be obtained from the frequency domain analysis of a reservoir property, like permeability, or wireline logs such as gamma ray, sonic, density, and neutron which are strongly affected by clay content in reservoir rocks. The reservoir property distributions available as functions of depth are first broken down into a continuous distribution of waves of different frequencies each having a distinct amplitude and phase.

The distribution of power (square of amplitude) with frequency, known as a power spectrum, indicates that the variability in clay content may be estimated from the attenuation of power with frequency. An effective method for obtaining power distribution is from time-series analysis of wireline log data in clayey formations. For homogeneous clean sandstones, the distribution of power in the log data as a function of frequency sharply decreases at higher frequencies. In heterogeneous clayey sandstones, the power content at the high-frequency end remains high, and the power does not drop off sharply with frequency. Depending upon the presence of beds with certain stratification, the power distribution has distinct peaks at certain frequencies. The characteristic distribution of power with frequency provides a good measure of clay types and lithological heterogeneity in a sandstone reservoir.

The variability measures obtained from power spectral analysis of permeability and wireline log data in clayey formations were correlated with oil production from two oil fields. Compared with the conventional measures of permeability variations like the Dykstra-Parsons coefficients, the new measure appears to correlate better with oil production.

Technology Transfer

One of the most important activities related to technology transfer during FY92 was the Third International Reservoir Characterization Technical Conference sponsored by DOE and conducted by NIPER. The steering committee for the conference consisted of a broad representation of the government and oil industry: DOE, state geological surveys, major oil companies, service companies, independent oil companies, and academic institutions. The conference was held in Tulsa, OK and had a registration of 247 from the United States and 12 foreign countries. The proceedings of the presentations and the poster session were distributed (see publications list on page 19).

The opening address of the 2-day conference was given by Dr. Donald Juckett, Director of DOE's Office of Geoscience Research. Other keynote addresses were given by Denise Bode, President of the Independent Petroleum Association of America, and Farouk Al-Kasim, a consultant from Stavanger, Norway. Prior to the conference, four tutorial short courses were given in the areas of recovery strategies for mature oil and gas reservoirs, geostatistics, geomechanics, and seismic waves. The conference itself consisted of four technical sessions with 28 papers and a poster session with 24 papers. The topics for the technical sessions were: (1) heterogeneities and anisotropies, (2) field studies and data needs, (3) modeling and interwell description, and (4) optimization of reservoir management.

NIPER researchers presented a paper at the conference describing the results of a multi-client sponsored study to determine the effect of the spatial arrangement and density of core-plug scale permeability data in deriving grid-block scale values for numerical simulation. Various averaging techniques were applied to closely spaced outcrop permeability data to generate input permeability models for simulation. The effect of permeability models with varying amounts of detail, as well as viscosity ratio and grid-block size on waterflood oil recovery, was determined by numerical simulation using BEST, NIPER's improved version of BOAST, which has been shown to be adequate in performing waterflood simulations in heterogeneous reservoirs. The results of the study provide a guideline for the degree of detail required for numerical simulator input permeability models for the specific type of rocks and

conditions investigated. In the absence of the required detail, an indication of the magnitude and direction of errors that can be expected in oil recovery prediction is possible.

Results of some of the research conducted in Project BE1 were presented to petroleum engineers and geologists at Union Pacific Resources Company (UPRC) in Fort Worth, TX. UPRC is currently the operator of Patrick Draw field and has been cooperating with NIPER in the investigation of the field. A paper on major controls on production in Patrick Draw field and methods that enable analysis of injection and production behavior was presented at the joint Tulsa Geological Society and Society of Petroleum Engineers Midcontinent Section annual dinner meeting.

The reservoir characterization team cooperated with researchers on other Base Program projects to identify and characterize fluvial-dominated deltaic (Class 1) rock appropriate for computed tomographic (CT) investigation as part of project BE12. Also, the team helped select Almond formation rock for relative permeability investigations as part of project BE9. Reservoir characterization techniques developed in BE1 were applied to the characterization of Hepler (KS) field which is the site of a surfactant-enhanced alkaline flooding field pilot being conducted under project SGP41. Building upon the work in FY91 to assist the DOE in initiating targeted research on Class 1 reservoirs, a monograph was prepared that described the geological and production characteristics of deltaic reservoirs including an annotated bibliography.

Work was conducted to assist in the operation of two of DOE's Naval Petroleum Reserve oil fields: NPR No. 1 at Elk Hills, CA (SGP57), and NPR No. 3 at Teapot Dome, WY (SGP52). A well was drilled in a new zone at Elk Hills, and NIPER investigators are examining the core using CT imaging and comparing the CT images with logs and other reservoir information. This work is continuing into FY93 with the goal of recommending appropriate recovery strategies. In Teapot Dome, NIPER staff analyzed Shannon reservoir information to assist the operators in optimizing steamflood production.

A project (SGP69) was initiated to compile and analyze outcrop data from the Muddy and Almond formations, so that the data and analyses generated in this project can be used by other workers. In conjunction with a sample-collecting field trip to the Almond formation outcrop, NIPER staff conducted a tour of the outcrop for representatives of two major oil companies.

Publications

Third International Reservoir Characterization Technical Conference, Tulsa, OK, Nov. 3-5, 1991. Reservoir Characterization III Proceedings, C.C. Linville, Ed., PennWell, Tulsa, OK, 1008 pages.

Integrated Geological-Engineering Model of Patrick Draw Field and Examples of Similarities and Differences Among Various Shoreline Barrier Systems, by R.A. Schatzinger, M.J. Szpakiewicz, S.R. Jackson, M.M. Chang, B. Sharma, and M.K. Tham. Dept. of Energy Report No. NIPER-575, Apr. 1992. NTIS Order No. DE92001037.

Petrographic Correlations and Mathematical Analysis of Log Signatures for Clay Identification, by B. Sharma. Dept. of Energy Report No. NIPER-589, Apr. 1992. NTIS Order No. DE92001038.

General Geological and Production Characteristics of Deltaic Reservoirs with Annotated Bibliography, by S.R. Jackson, R.A. Schatzinger, V. Rawn-Schatzinger, M.K. Tham, and M.M. Chang. Dept. of Energy Report, June 1992. NTIS Order No. EPR/OP-92/14.

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Presentations

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Geological Controls on the Production of a Mesotidal Barrier Island Sandstone Deposit, by B. Sharma, S.R. Jackson, and M.M. Chang. Poster Session pres. at the Society of Exploration Geophysicists Development and Production Forum, Big Sky, MT, June 1992.

Results of Reservoir Characterization, Simulation, and Production Analysis of the Steamflood Area of Teapot Dome, NPR #3, by S.R. Jackson, M.M. Chang, D.K. Olsen, and M.P. Madden. Pres. to NPR No. 3 engineers and geologists during field trip to Shannon outcrop, Casper, WY, Aug. 1992.

A New Technique To Estimate Vertical Variability of Rock Properties for Reservoir Rock Evaluation, by B. Sharma. To be pres. at the 67th SPE Annual Technical Conference and Exhibition, Washington, DC, Oct. 1992. SPE paper 24724.

TORIS RESEARCH SUPPORT

Principal Investigator:	James Pautz
BPO Project Manager:	Chandra Nautiyal
Project No.:	BE2
Funding for FY92	$340,000
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The objective of this project is to provide research support for the Tertiary Oil Recovery Information System (TORIS) in the areas of EOR project and reservoir database management, EOR project technology and trends analysis, and evaluation of computer models and numerical simulators.

Research Summary

To be fully effective, TORIS must have accurate information that can be retrieved quickly on EOR projects and petroleum reservoirs. Reliable computer models and numerical simulators are also required for use by the DOE in planning and project assessment. NIPER maintains EOR project and reservoir data bases with currently available information and efficient retrieval. NIPER analyzes trends in the application of EOR and computer models and simulators as they relate to TORIS and its support of the Advanced Oil Recovery Program. Analyses of EOR trends have resulted in annual reports on the application of EOR technology. Analyses of simulators have resulted in subsequent improvements in simulators before they are accepted by the DOE for distribution.

A comprehensive enhanced oil recovery (EOR) project data base is maintained and updated at the Bartlesville Project Office of the Department of Energy. This data base provides an information resource that is used to analyze the advancement and application of EOR technology. The data base has extensive information on 1,388 EOR projects in 569 different oil fields from 1949 until the present. A report published this year contains over 90% of that information in tables and graphs. The projects are presented by EOR process, and an index by location is provided.

NIPER's analysis of the EOR project data base indicates significant technical advances have been made in the various EOR methods. For example, the history of EOR project starts, with and without the projects of the 1978 Tertiary Incentive Program, was compared to annual average crude oil prices. It was found that without the incentive program, EOR project starts lagged the major oil price increase of 1980 by 2 years and lagged the price drop in the mid-1980s by about 1 year. When projects participating in the incentive program were included with other projects, the trends in project starts matched the oil price changes in the early to mid 1980s.

Primary sources of information for the project data base have been reports of EOR projects certified in the Incentives Program, the DOE Cost-Shared Tertiary Program, and data supplied by contractors who search the literature for project information. The information in the data base represents all pertinent data on EOR projects.

Over 330 data elements are populated with information from the field and reservoir, project location and ownership, EOR process used, fluid production and injection criteria, and miscellaneous factors.

When discussing the extent of the data base, two distinct groups of projects are obvious—those that were part of the Tertiary Incentive Program and those that were not. The 433 incentive projects represent only 31% of the projects in the data base but provide more than 80% of the data. The number of incentive projects has decreased slightly from the 430 projects reported in 1984 because operators have combined and split some projects. In the non-incentive-program-project category, 955 projects in about 500 oil fields have been identified by Gulf Universities Research Consortium and NIPER. Twenty-seven DOE cost-shared projects also have been conducted.

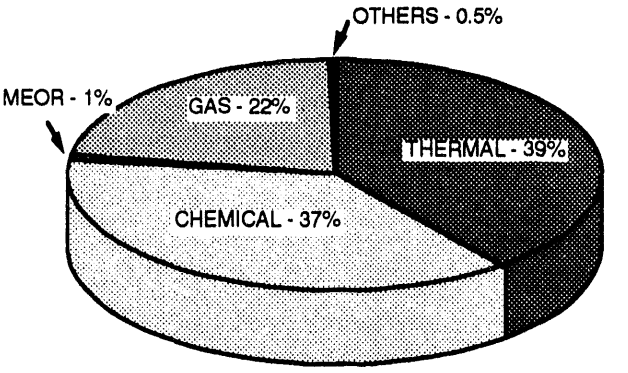

FIGURE 2. - Number of EOR projects by method technology.

The data base maintained by BPO is a historical file; it includes completed and terminated projects as well as current EOR projects. The data base contains information on most projects that have been started. The few that have been missed are those that were small and not widely known or more recent projects for which data reporting is incomplete. Trends are based solely on the information in this data base and may not agree with other published data. This does not imply that the data base is of lesser value; no other known source of data is as complete as the EOR project data contained in this data base.

In 1984, EOR methods were classified by three major processes: thermal (41%), chemical (34%), and gas displacement (24%). The distribution of the number of projects by recovery process contained in the current data base is shown in figure 2. A slight shift in the numbers has occurred that appears significant. Although the process classification system has added microbial-enhanced oil recovery (MEOR) as a major method, this new classification accounts for only 1% of the project total. From levels reported in 1984, project starts for thermal and gas recovery methods have decreased by 5 and 10%, respectively, whereas chemical methods have increased by 10%.

The incremental oil production attributable to the three recovery methods has not followed the same trends as the frequency of projects, as shown in figure 3. Total EOR production in 1990 was up almost 50% from 1984 production levels. Oil production from gas displacement methods more than doubled during the same time period, whereas production attributable to thermal methods increased by 30%. Production attributable to chemical methods decreased by 13%.

The current data base contains 422 steam injection projects, including 23 cyclic injection projects, 383 conventional steam drive projects, and 39 unconventional steam drives. Since 1984, the number of steam projects documented in the data base has increased 180%. The number of hot water projects has increased from 4 to 12 for a

200% increase. The number of in situ combustion projects in the data base has increased 20%, from 75 to 91. Chemical projects in the current data base are the most numerous at 496, an increase of 126% from 1984.

Chemical projects include 359 polymer, 82 surfactant, and 55 alkaline injection projects. Gas injection projects as a group have increased the least in the data base since 1984 when compared to chemical and thermal projects—a 90% increase from 153 to 290 projects. A significant portion of the gas displacement projects added to the data base since 1984 had started before 1984.

Although EOR projects are recorded in 25 states, the projects are concentrated in only a few states. Roughly 35% of the projects are located in California and another 22% in Texas, representing well over half of the projects in the data base. A quarter of the projects are in three other states: Wyoming, Oklahoma, and Louisiana. By adding Illinois, Kansas, and New Mexico, 90% of the projects started are contained in only eight states. The number of new project starts for each year is presented in figure 4 along with the annual average wellhead price of crude oil. Although the number of project starts appears volatile, when compared to average oil prices, the match between 1974 and 1986 is very close. Both curves reflect a slight increase in the 1960s and early 1970s, a moderate rise in the late 70s, and the tremendous increase in 1980 followed by the sharp decline in 1982 and again in 1984-85. There appears to be a very slight delayed reaction by project starts to some of the major changes in oil price. Other economic factors influencing the project starts include the windfall profits tax and the DOE Tertiary Oil Recovery Incentive Program, both of which were initiated in 1980 and served to encourage production of tertiary oil. Technological improvements are also reflected in the curve of process starts. The relatively large number of projects initiated in 1964-65 may reflect industry acceptance of steam injection technology.

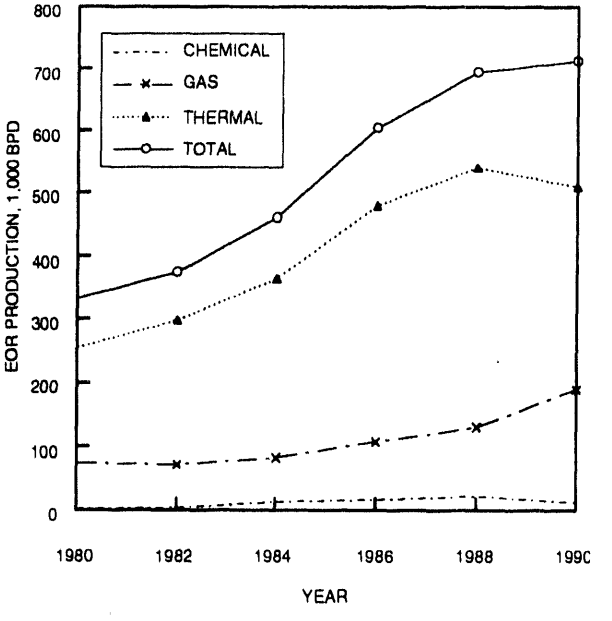

FIGURE 3. - EOR production by process method.

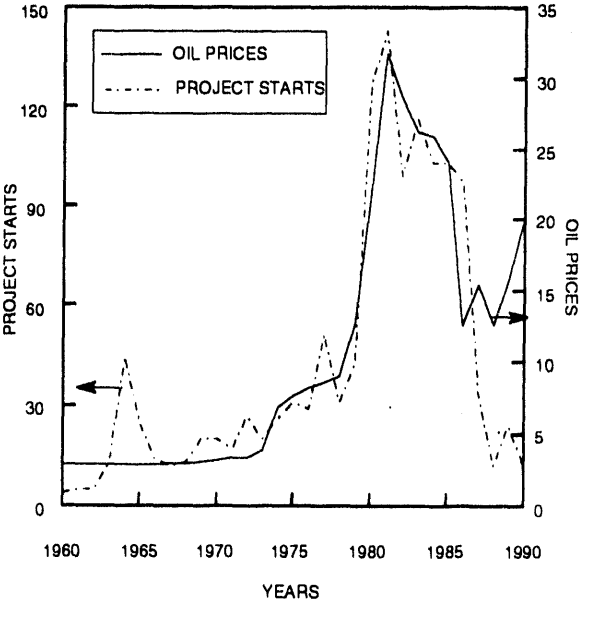

FIGURE 4. - EOR project starts and crude oil prices from 1960 to the present.

The number of EOR project starts continued to drop after 1986 in spite of stabilizing oil prices. There are a number of possible reasons for the drop. In figure 3, EOR production is shown to continue to rise from 1980 through 1990. Two general factors may be at play. First, the continual increase in EOR production may indicate that resources and technology are being applied by expanding existing projects rather than starting new projects. Second, existing projects may have a positive cash flow, but new projects would not be profitable at current or expected oil prices. Whatever the reason, companies are not investing in new EOR projects at the rate they were through 1986.

An analysis of the reservoir and fluid characteristics of in situ combustion (or fireflood) projects shows that this technology has made no significant advances since the 70s. The reported total acreage in which production was started peaked during the 70s at roughly 15,000 acres, while about 10% of that has been reported for the past 5 years. The frequency count also indicates a decrease in interest for this process. The change in depth over time does not show any deeper reservoirs nor any increase in average depth. Reporting of information such as the deepest reservoir, the most projects with depth data, and the deepest average depth occurred during the 70s. Trends in the oil properties of in situ combustion projects are similar to the trends in depth data, i.e., the lowest gravity and highest viscosities were attempted during the 70s, and this implies that the technology target has not expanded since the 70s and may even have contracted. One interesting trend is the decrease in the maximum API gravity with time. The correlation between gravity and viscosity is shown to be misleading when data for the late 80s are compared until the reservoir temperature is considered. The two projects with gravity and viscosity data show the importance of viscosity at reservoir temperature. Although the gravities are very different (10° vs. 18°), the viscosities at reservoir temperature are about the same at 1,006 and 1,200 centipoise (cP), respectively. The porosity of reservoirs where in situ combustion projects were started ranged from 19 to 42%, but the averages are in a narrow range of 29 to 33%. Both the highest and lowest porosities occurred in the 60s. Temperature (105° F average) and salinity data (43,900 ppm TDS average) are not very meaningful since they have no effect on the process. The broad range of permeability between the minimum and maximum indicate a broad range of reservoirs that have been fireflooded. The average permeability is 1.3 darcies which might indicate that high permeability and unconsolidated sands are favored for this process.

Steam projects are located in California (88% of projects) and 11 other states. Texas, Wyoming, and Oklahoma have a significant but much lower representation of steam projects (4% for Texas and 2% each for Wyoming and Oklahoma). Steam injection projects have relatively small areas (200-acre average) and even these have declined through time. In the late 80s, the average size of 111 acres was 77% smaller than the average project size reported for projects starting in the 60s. The 45,000 acres of steam projects started in the 60s are more than twice that of any other period. Note that the source of project information should be considered when interpreting areal statistics. Acreage or area statistics reported at the beginning of a project can have multiple meanings: the reported area could be the ultimate area planned for a project that has a few initial patterns in the start-up year, or it could be the area of the initial patterns with major expansion planned for later. These two reporting scenarios might have the same area under development at the same time, but the statistics in the data base would be significantly

different. The average depth of steam projects has increased very slightly since the 60s. This process has the lowest average depth of all the major EOR processes but has had the most successful production history. The maximum depths attempted in steam projects during the 60s have not been exceeded in spite of improvements in tubular insulation. Evidently, going to deeper depths is not profitable enough to justify the higher initial investment.

Steam projects are generally targeted toward reservoirs with the heavier, lower-gravity oils that are also the more viscous. The statistics confirm the general trend but also show that light oils have been steamed in each of the time periods. The average API gravity for each time period has varied less than 4% from the average of 13.6°. The trend toward lower oil viscosities appears to be significant. The maximum oil viscosity recovery attempted during each period has either dropped or been the same as that of the prior period. The average viscosity in the late 80s was 80% less than that in the 60s and even the early 80s. This may indicate that marketing the heaviest and most viscous of the oils is more difficult. The push for higher quality transportation fuels and less pollution at the refineries and well sites may be reflected in these statistics. As previously suggested, the required viscosity for the data base is at reservoir temperature. Unfortunately, viscosities reported in the literature can reflect conditions different from that of the reservoir, i.e., oil delivered at the refinery, dead oil, or at surface conditions. Although there are no trends in the porosity of reservoirs targeted by steam projects, the average porosity of 31.8% is relatively high compared to that of other processes. An average porosity of 29.2% for the other thermal processes is the next highest porosity of the major processes. Average salinity of the reservoir water is 20,735 ppm TDS and has decreased 70% from the levels in the 60s—the reason for this decrease is undefined at this time. The average permeability of steam projects is 2.05 darcies and decreased 20% from the 60s to the early 80s, but jumped back to the 60s permeability levels during the late 80s. There is a definite trend in maximum permeability in that it has increased by 32% from the 60s to the late 80s. This indicates that technology improvements have been made in handling sand that flows into the wellbore from unconsolidated sand reservoirs.

Unlike steam, no single state dominates surfactant or alkaline flooding. The state with the most surfactant projects is Illinois, closely followed by Texas. Many of the states using this process are not significant oil states, e.g., Kentucky, Nebraska, Indiana, and Pennsylvania. With 80% of the total acres being started during the early 80s for alkaline and surfactant flooding, these are the least mature of the processes. Projects roughly tripled in size from the 60s to the 70s and then quadrupled from the higher level into the early 80s. The average depth increased 326% from the 60s to the late 80s. The average depth for all project is 3,120 ft or roughly twice the average depth for steam projects and 50% deeper than in situ combustion projects. The average reservoir temperature has increased with time as expected from the increase in project depth. Since the average reservoir temperature for all alkaline and surfactant projects is 110° F, the increase in average temperature to 118° F and 115° F, respectively, in the early and late 80s would appear to be definite progress. Operators have attempted to expand salinity tolerance, but no progress is obvious. The maximum salinity of projects attempted in the 60s is roughly one-fifth of the maximum in the early 80s. With the data for the 60s being very limited, this trend may be overstated. Since the average salinity of all reservoir waters is 57,875 ppm, the high average of 60,503 ppm in the early 80s does not appear to represent much progress. The lack of projects, and the low salinity of the few started in the late 80s, may indicate that the

economics and related technical problems with reservoir water salinity and absorption have not been solved. Very little change in API gravity and viscosity of the oil recovered by alkaline and surfactant projects has occurred with time. The average API gravity is 32.5°, and the average viscosity is 14.2 cP for the oil of all alkaline and surfactant projects. The porosity of reservoir rock has been slightly decreasing with time. The average of all projects is 21.3%. This is higher than that of gas and polymer projects, but lower than the average porosity for thermal projects. The average permeability for all alkaline and surfactant projects in the data base is 334 millidarcies (mD), and this number is matched by the average permeability in the late 80s. Other than a small drop in the average in the 70s, permeability has changed very little. Although there is not a trend in the minimum permeability, there is a trend away from attempting unconsolidated high-permeability reservoirs, indicating that other processes, such as waterflooding and polymer-augmented waterflooding, are more effective. The statistics on the alkaline and surfactant projects indicate that the technology has advanced some but that the current economics are marginal at best for the state of the technology. By the late 80s, surfactant and alkaline flooding projects were hardly being considered; however, of those initiated prior to 1980, 83% of the starts and 70% of the reported acreage represented projects that were still using the same recovery process. Results of combined alkaline-surfactant-polymer process projects have been encouraging, and additional pilot projects are planned. Although some projects have been completed, they have not been reported and thus are not in the data base. This process variation has the potential to advance the technology at favorable economics.

Nineteen different states have had polymer projects within their borders. Texas and Wyoming have had the most with each showing 96 project starts; Oklahoma ranks next with 76 project starts. These three states have 73% of the polymer projects. Six other states each have between 8 and 19 projects. Polymer project starts have continued through all 10-year time periods, and the size of the projects has continued to increase. Total acreage per period has trended higher, from 11,000 in the 60s to 26,100 in the 70s to 175,600 in the early 80s to 148,000 in the late 80s. This 14-fold increase in total acreage from the 60s to the final time period is the largest of the EOR methods discussed so far. The average project size has increased 230%, and the largest (maximum) project started has increased 240% during the same time. The depths of reservoirs for polymer projects have increased dramatically—140% from the 60s to the late 80s. The maximum depth attempted during this time period nearly doubled, and the shallowest depth was reduced by half.

Early synthetic polymers were subject to thermal degradation and thus a limiting factor in early polymer projects. Generally, the early polymers started to degrade at 160° F and could not be used above 180° F. One of the areas of technical improvement has been in the development of high-temperature polymers that are stable to 300° F. With the high-temperature tolerance comes a much higher polymer price—as high as $5/lb compared to $1/lb or less for other polymers. The marked increase in average temperature in the late 80s, above the average of 117° F (47° C) for polymer projects before 1985, shows application of these new polymers. Generally, the temperature of a reservoir is related to the depth of a reservoir. The average temperature for the 60s does not seem consistent with the depth trends previously discussed. The quality of a reservoir water has an effect on the development of viscosity by a polymer. Although divalent ions such as Ca^{++} are more detrimental than others, the value of total dissolved

solids, or salinity, is one relative measure of water quality as it pertains to this phenomenon. The higher the salinity of reservoir water, the less effective a polymer might be as a mobility control agent or in profile modification. One direction of polymer technology has been in the development of more salt-tolerant polymers; however, insufficient information is in the data base to establish a trend. A slight increase in API gravity and a slight decrease in viscosity of the oil recovered by polymer projects have occurred with time. The average API gravity is 32.4° and average viscosity is 12 cP for the oil of all polymer projects. Although the average API gravity is not significantly different than the average for each of the periods analyzed, the decrease in viscosity is. The decrease in viscosity between the 70s and the late 80s is consistent with the higher reservoir temperatures noted previously. The higher average viscosity in the 60s may be due to the measurement of some viscosities at room temperature instead of reservoir temperature. Porosity of the reservoir rock has been slightly decreasing with time. The average of all projects is 17.9%. This is higher than that of gas but lower than the average for the other types of projects discussed. The average permeability for all polymer projects in the data base is 345 mD or about the same as that for the chemical processes previously discussed. The average permeability has trended lower with a 68% reduction from that of the 60s. The minimum permeabilities have also trended lower toward relative tight reservoirs. The maximum permeability indicates that polymer projects continue to be applied to unconsolidated sands. The statistics on polymer projects indicate that the technology has advanced with high-temperature-tolerant polymers. The characteristics of reservoirs amenable to the process have been expanding. The average depth is deeper, the average temperature is higher, and the rock porosity and permeability are tighter than that in the 60s and 70s. Even during difficult economic times, polymer project starts have continued.

Eighteen different states have gas displacement projects represented in the data base. Texas has the most, with 130 project starts, followed by Louisiana with 68, and Wyoming with 21. Together, these states have 73% of the gas displacement projects. Seven other states each have more than 7 projects. Gas displacement projects were not a popular EOR method during the 60s but have developed into a major source of oil production. At least 533,000 acres have been planned for this process, about 50% more than the total area indicated in the polymer project statistics. Although there were few projects in the 60s, these were six times the size of polymer projects which have the next largest project area. These statistics might imply that most of the early gas projects were not piloted in the 60s but were projects of convenience—the gas was available without ready markets. Although the average project area increased from the early to late 80s, this upward trend is only 13% of the average size of gas projects in the late 80s and is the same as the average size of all projects at 2,690 acres. There has been a six-fold increase in total acreage from the 60s to the final time period, indicating the increase in popularity of the process. The average depth of reservoirs for gas displacement projects has increased by 77% from the 60s to the late 80s and consistently shows increases each period. The maximum depth attempted during a time period has increased roughly 57%, and the shallowest depth has decreased 42%. There is a general trend of increasing salinity of the formation waters in gas displacement project reservoirs. This is consistent with the trend to deeper reservoirs. Although there is a slight decrease in the oil gravity values, this trend is not confirmed in the viscosity data. The average oil gravity is 35.3° API, and the average viscosity is 18.2 cP for all gas projects. Both surfactant/alkaline

and polymer project classifications have lower average gravities, and they both have lower oil viscosities. A difference of less than 10 cP is not very significant. There is a general trend toward lower rock porosity over time as evidenced by the final period being about 10% less than the average of all gas projects. There has been a general trend toward higher permeabilities, but the average permeability in the late 80s was only 3% higher than the average permeability for all gas displacement projects. The statistics show that gas displacement is applied over a wide range of permeabilities. When specific processes are analyzed within this method, reservoir characteristics show a different trend. When projects that can be classified as miscible and immiscible are analyzed separately, the data show that the permeabilities for each process have decreased with time; however, the number of immiscible projects increased faster during the 1980s than other gas displacement projects which explains why the average permeability for all gas projects increased in the 1980s. Gas displacement technology advanced from the 60s to the late 80s. The processes have been widely applied under a broad variety of reservoir conditions. The production is increasing despite low oil prices, and projects are still being started.

Screening criteria for the various EOR processes have been proposed that are all reasonably consistent (Dept. of Energy Report No. NIPER-579). These reflect the technological limitations of the various processes. Most thermal projects meet the screening criteria with the following minor exceptions: 18 steam projects are deeper than 3,000 ft, 19 in situ combustion projects are in reservoirs with net pays less than 20-ft thick, and 29 thermal projects have oil gravities not meeting the criteria. Gas injection projects have few screening criteria, and few projects fall outside the recommended limitations: eight miscible projects have API gravities lower than 25°. Surfactant/alkaline projects have the most critical limitations and, as previously indicated, have made significant technical advances to expand beyond those limitations. Unfortunately, the technical progress has not overcome the economic realities of lower oil prices and adequate supply alternatives. So, although the technical screening criteria for these technologies should be expanded, the economic limitations are likely to limit their application.

A task to compare actual results of the tertiary incentive projects with the output of the TORIS predictive models was begun, but the effort is in an early stage and the results are not conclusive. Data for the incentive projects are being taken directly from the EOR Project Data Base, converted to the TORIS reservoir format, and then analyzed using a TORIS model similar to those used in the 1984 National Petroleum Council EOR study. The only assumption being modified from the 1984 study is the average wellhead oil price. The TORIS models are expected to predict the total production of all projects, but the results of individual projects are expected to differ due to the inherent development timing assumption that does not apply to actual projects.

To obtain information on the incentive projects for 1990 for inclusion in the EOR Project Data Base, FE-748 forms (Annual Report for Enhanced Oil Recovery Incentive Program) were sent to operators of EOR projects requesting information for calendar year 1990 and previous years. Telephone follow-ups were conducted for operators who did not respond. A total of 61 FE-748 forms were received for 1990. Based on the forms, 52 incentive projects are active, four have been terminated, three have been deferred, one has been completed, and one has been sold. In addition, information on 22 projects was received for 1987, 1988, and 1989. In addition to the data additions, the data bases were examined for errors in format, typographical errors, reporting errors, and missing

data. A total of 6,408 changes were made to the EIA EOR Project Data Base based on our review. A security back-up tape was made of the data base and forwarded to the Bartlesville Project Office.

Technology Transfer

NIPER supports TORIS by providing data from the TIP projects, by performing analyses on the system's numerical simulators, and by establishing trends in the application of the various EOR processes. These analyses provide DOE with improved versions of the simulators before they are distributed, and the TIP and trends data provide DOE information on significant changes in EOR technology utilization. The retrieval of reservoir-specific data for defined targets will continue to be an important task under this project.

In addition to the support for TORIS, staff researchers have developed a number of improved simulators based on the BOAST black oil simulator which is available in the public domain. In project SGP40, inflow performance relationships (IPRs) for slanted and horizontal wells producing from heterogeneous solution-gas drive reservoirs were developed. As part of this project, a simulator adapted from DOE's BOAST black-oil reservoir simulator (modified at NIPER to simulate non-vertical wells) was used. Six variables in well configuration and reservoir properties were investigated to develop the IPRs: ratio of vertical to horizontal permeability, wellbore eccentricity, stratification, perforated length, formation thickness, and permeability heterogeneity.

Horizontal wells show a better productivity improvement with additional pressure drawdown than vertical wells at the early stage of depletion. Horizontal well IPR curves increase their curvature with depletion of up to 8%, then slightly decrease in curvature at later stages of oil recovery. This behavior, different from that for vertical wells, is due to a high gas production rate from horizontal wells, at low bottomhole pressures, before oil recovery reaches 8%. The decrease in curvature when recovery is greater than 8% is due to a slightly higher formation pressure around the wellbore at lower flowing bottomhole pressures at later stages of depletion.

In addition, a PC-version of the horizontal well simulator, BOAST-VHS for the PC, along with a user's manual, was delivered to the DOE (SGP40). This new version of BOAST allows a user to modify the problem size without having to rewrite computer code.

The knowledge gained from developing the horizontal well simulator was used to analyze a number of simpler analytical formulas that are used to quickly estimate relative productivity of a horizontal well as compared to that of a vertical well. The existing estimating techniques do not take the effects of gravity into account which in some situations can be considerable. An *Oil and Gas Journal* (v. 90, No. 33, Aug. 17, 1992) article detailed this effect as well as comparing BOAST-VHS to the formulas and the Society of Petroleum Engineer's comparative solution for horizontal well reservoir simulators (projects BE2 and SGP40).

A project (SGP56) to upgrade the DOE's Crude Oil Analysis data base and to analyze crude oils for inclusion in the data base was begun. This data base is widely used by industry but has not been upgraded in content or management software since the early 1980s.

The TORIS data bases and models were also used by NIPER staff to assist the assessment of the heavy oil resources in the U.S. as part of Project SGP37.

NIPER staff participated in a panel to assess the oil resource base of the U.S. as part of Project SGP60. The project was a joint effort by NIPER and the Bureau of Economic Geology (BEG) of the University of Texas at Austin. Panelists for the assessment included representatives of ICF Resources, Gunn Oil Company, Office of Fossil Energy of DOE, Minerals Management Service of the Department of the Interior, Oklahoma Geological Survey, U.S. Geological Survey, Phillips Petroleum Company, NRG Associates, Office of Technology Assessment, BP Exploration, Thomasson Partner Associates, Dallas Field Office of the DOE, Dal Woods Corporation, Gas Research Institute, BEG, and NIPER. The panel estimated that the remaining recoverable volume of crude oil in the U.S. ranges from 99 to 204 billion barrels, depending on variables of price and technology.

Texas Independent Petroleum Royalty Owners (TIPRO), DOE, and Gas Research Institute (GRI) cosponsored a 2-day seminar in Austin, Texas, specifically for technology transfer to Texas independent oil producers. One of the better attended open sessions was a demonstration by NIPER of the DOE BOAST-VHS for the PC reservoir simulator. The addition of a quick-input routine developed for this show (SGP64) assists independents in using this sophisticated software.

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THREE-PHASE RELATIVE PERMEABILITY

Principal Investigator:	Dan Maloney
BPO Project Manager:	Rhonda Patterson Lindsey
Project No.:	BE9
Funding for FY92	$290,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 – September 30, 1992

Objective

The objectives of this project are to: (1) improve the reliability of laboratory measurements of two- and three-phase relative permeabilities at steady- and unsteady-state conditions in core samples; (2) investigate the influence of rock, fluid, and rock-fluid properties on two- and three-phase relative permeabilities; and (3) expand the state-of-the-art of measuring relative permeabilities to higher temperature and pressure to reflect known reservoir conditions more realistically.

Research Summary

The direction and results of this project are in concert with the goals of the Advanced Oil Recovery Program of maintaining domestic oil production and targeting research toward high priority reservoirs. NIPER's relative permeability laboratory is one of the most utilized facilities on behalf of industrial clients and provides a frequent avenue for direct transfer of technology developed under the Base Program to the oil industry. This technology is used for immediate application to optimize oil production. Multiphase relative permeability information is an indispensable component of accurate reservoir simulation, a technique used in the oil industry to plan reservoir management and advanced recovery strategies to produce oil effectively and economically.

Multiphase flow is a common phenomenon in production from petroleum reservoirs. The initial or primary production from a reservoir may include gas, oil, brine, or combinations of the three. Later during the productive life of a reservoir, two-phase flow occurs as fluid such as brine is injected into a reservoir to boost production. Finally, if enhanced oil recovery techniques are used to maximize hydrocarbon recovery, multiphase flow processes are virtually guaranteed to occur. With multiphase flow, the fluids compete for the same flow paths through the reservoir rock. The additional resistance to flow is described by normalizing permeabilities for each of the flowing phases at each fluid saturation condition with respect to a base permeability. This measurement and normalization process yields relative permeability data.

The concept of relative permeability for two-phase flow is not new. Work on developing two-phase flow relationships probably began in 1859, and through the years techniques for using the results have been refined for estimating petroleum reservoir productivity and performance. Efforts to extend the techniques for three-phase flow began in 1941, but difficulties limited progress in this area. Three-phase flow experiments for determining relative permeability relationships are very difficult to perform. Measuring fluid saturations in a rock during three-phase steady-state flow experiments was virtually impossible until the recent advent of techniques to monitor in situ fluid

saturations directly during flow experiments. Correlations have been developed to predict three-phase flow effects from two-phase flow measurements, but such correlations are not always correct or accurate. The primary reasons for the limited knowledge with respect to three-phase flow systems are the scarcity of accurate three-phase relative permeability laboratory data and laboratory measurement systems.

Project efforts were concentrated in two primary areas: examination of the mutual relationships among petrophysical properties and relative permeabilities; and improving the state-of-the art in three-phase measurements at higher pressure and temperature conditions. During this project year, tests were conducted on a low-permeability reservoir rock sample. In comparison with previous work to characterize and measure properties of clean, quarried sandstone rock samples, testing reservoir rock presented some interesting challenges and required many innovations in test procedures and designs.

The rock selected for investigation was from the Almond formation in Patrick Draw field, Wyoming. The Almond is a shoreline barrier reservoir, one of the high-priority reservoir classes identified in the Advanced Oil Recovery Program. Use of Almond formation rock is especially advantageous since it has been the subject of intense investigation by NIPER's reservoir characterization group for more than 3 years. Thus, the rock is well characterized in terms of physical and environmental parameters.

Specifically, core from Well 120, Arch Unit, Patrick Draw field, was selected for investigation. Computed tomography (CT) scanning of whole core sections from depths of 4,953, 4,959, and 4,961 ft revealed that the cores were fairly homogeneous; however, three-dimensional reconstructions of the CT images indicated the presence of bedding features. Visual observation of the core indicated silty bedding features that coincided with the CT images.

Plugs and other samples were cut from the core sections. Several blocks with rectangular cross sections were cut for three-phase flow experiments. Plugs with 1-in. diameters were drilled for mercury injection porosimetry and centrifuge tests. Plugs with 1.5-in. diameters were drilled for two-phase unsteady-state relative permeability tests, resistivity tests, and centrifuge capillary pressure experiments. Other pieces were obtained for thin section evaluation and for X-ray diffraction analyses.

Visual and thin-section examination showed that the core material can be classified as feldspathic litharenite. Microporosity was abundant and comprised 38 to 67% of total porosity. Grain sizes were log-normally distributed. The results of routine air permeability and porosity measurements, along with the mean and median grain sizes from thin sections are shown in table 2. The median pore diameter calculated from mercury injection tests on core 4953 was 1.48 μm. Considerable microporosity was evident as well from mercury injection.

Air-brine capillary pressure results were calculated from the mercury intrusion data. The calculated results were compared with the results from an air-brine porous plate experiment and with centrifuge capillary pressure vs. end-face saturation results. While the data trends were similar, the porous plate data appeared to start with an 85% water saturation for $P_c = 0$, whereas that of mercury was approximately 95%. To better compare the shapes of the curves, all porous plate saturations were adjusted by adding 0.10 saturation fraction units to the measured saturations. Results are shown in figure 5. The air-brine capillary pressures calculated from the mercury intrusion

TABLE 2. - Routine k and ø results for samples 4953, 4959, and 4961

Sample	k, mD	ø, %	Mean grain size from point counts, µm	Calculated median throat size, µm
4953	40.5	19.6	161	3.4
4959	30.9	18.2	144	2.2
4961	41.5	20.1	102	3.3

data are in very good agreement with the corrected porous plate results and the centrifuge capillary pressure vs. end-face saturation data.

Unsteady-state relative permeability tests were conducted on 1.5-in.-diameter by 2.5-in.-long plugs of rock from the three depth intervals. Test fluids were a 1-cP viscosity brine, containing 2 wt % potassium chloride, and a mineral oil of 21 cP viscosity. The test temperature was 74° F. The plugs were subjected to 1,000 psig confining pressure. The permeability of each dry plug was measured with nitrogen gas. Brine permeabilities were measured after saturating the plugs with brine. The plugs were oil flooded to residual water saturation conditions in preparation for waterflood tests. Constant rate waterflood tests were conducted with injection rates of 40 or 65 mL/hr. Two of the plugs were also tested using constant pressure techniques.

Table 3 provides a summary of end-point results from the tests. For each plug, brine absolute permeabilities were lower than absolute permeabilities to gas. The brine permeabilities under conditions of complete brine saturation were also lower than oil permeabilities measured at residual water saturation conditions. Whereas the end-point permeability and saturation data were useful and accurate, the unsteady-state results were not as good as

TABLE 3. - End-point results from unsteady-state tests

Plug	4953	4959A	4959B	4961
k_{air}, mD[1]	40.5	30.9	34.2	41.5
Pore volume, cm^3	12.35	11.39	11.82	12.20
L, cm	6.04	5.90	5.87	5.76
D, cm	3.79	3.78	3.79	3.79
Ø, fraction	0.196	0.182	0.186	0.201
k_w, mD	8.5	3.5	4.3	8.3
k_o at S_{wr}, mD	9.0	5.5	6.3	12.2
S_{wr}, fraction	0.379	0.317	0.332	0.398
k_w at S_{or}, mD	0.35	0.16	0.18	0.42
S_{or} fraction	0.309	0.398	0.361	0.291

[1] Measured with 100 psig confining pressure.

expected. Apparently, gas trapped within the syringe pump that was used for several test measurements caused the brine injection rate to vary during "constant rate" tests. This effect was eliminated, and tests on plug 4959B were repeated. A second test with the plug and an additional test using plug 4961 provided similar results.

All steady-state measurements were conducted with 100 psig backpressure on the flow system. X-ray and microwave scans were used to measure the saturation distributions within the samples during steady-state tests. Permeability and saturation measurements were recorded for first-imbibition and second-drainage saturation cycles. Gas/water imbibition cycle results are shown in figure 6. Imbibition and second-drainage oil/water relative permeability tests and gas/oil tests with a residual water saturation present were conducted next. Oil/water results are shown in figure 7. The oil relative permeability results of figure 7 are in good agreementwith those from the unsteady-state oil/brine test, whereas the brine results do not match. The gas/oil test was conducted with a residual water saturation present within the rock. Gas relative permeability results from the gas/oil test are shown in figure 8. The gas relative permeability results from both gas/water and oil/water tests were very similar. The range of oil saturations which resulted during the gas/oil relative permeability test was narrow and close to the residual oil saturation condition.

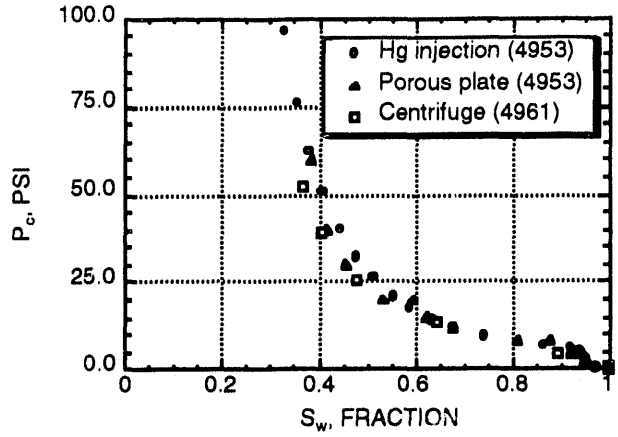

FIGURE 5. - Comparison of air-brine capillary pressures measured by mercury injection, porous plate, and centrifuge techniques for Almond formation rock.

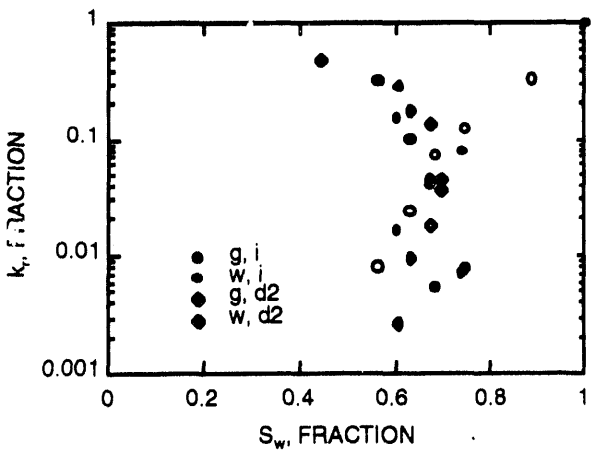

FIGURE 6. - Steady-state gas/water relative permeability results for plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w= 1.000.

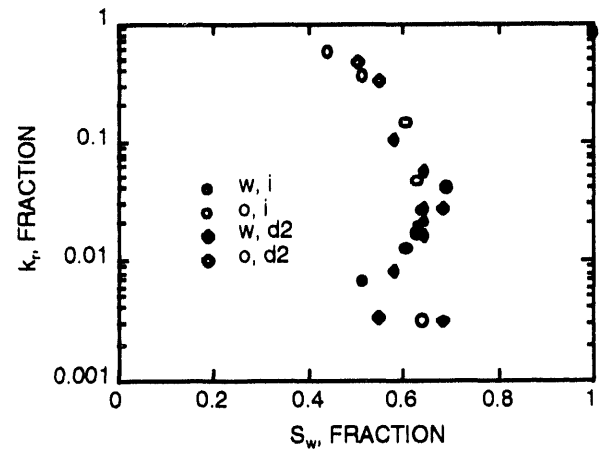

FIGURE 7. - Steady-state oil/water relative permeability results for plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w = 1.000.

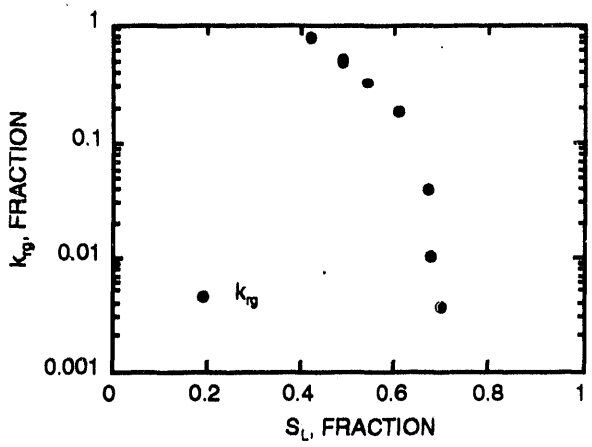

FIGURE 8. - Gas results from a steady-state gas/oil/ residual water test with plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w = 1.000.

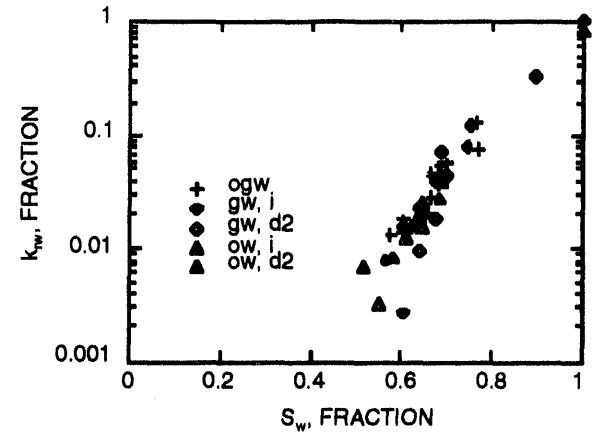

FIGURE 9. - Two- and three-phase brine steady-state relative permeability results for plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w = 1.000.

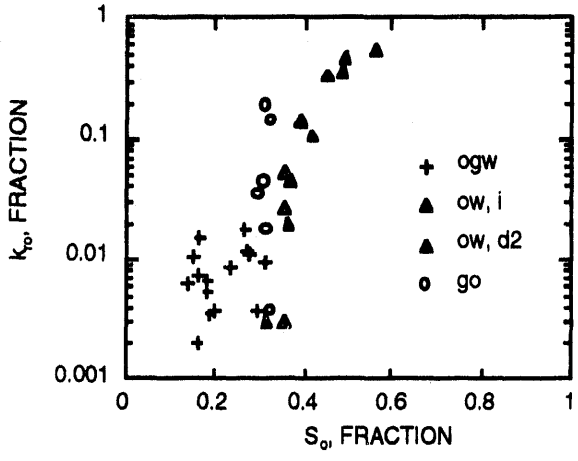

FIGURE 10. - Two- and three-phase oil steady-state relative permeability results for plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w = 1.000.

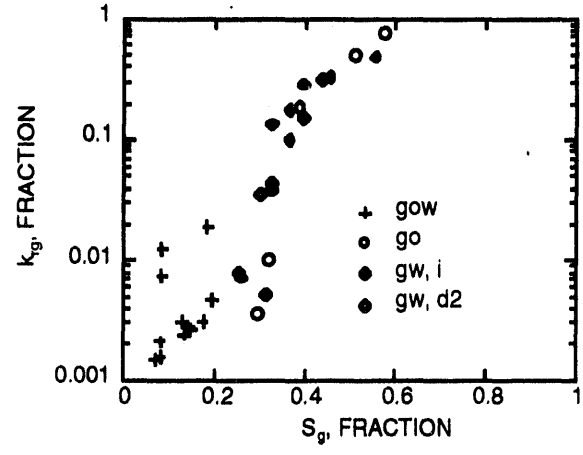

FIGURE 11. - Two- and three-phase gas steady-state relative permeability results for plug 4959. Results are normalized with respect to k_w = 5.78 mD at S_w = 1.000.

Three-phase results are shown in figures 9, 10, and 11 along with two-phase steady-state results for comparison. Three-phase brine relative permeability results are very similar to those from two-phase measurements. Gas and oil three-phase results are clustered near their two-phase residual saturation conditions. The three-phase gas and oil results are similar to those from the two-phase tests at comparable saturation conditions. Gas and oil saturations below their two-phase residual conditions were achieved during the three-phase tests.

Air-brine capillary pressure vs. brine saturation results were in good agreement from centrifuge, mercury injection, and porous plate experiments. Insufficient centrifugal forces were developed, using available centrifuge

equipment, to obtain full oil/brine capillary pressure vs. brine saturation curves. For these low-permeability samples, the use of an ultracentrifuge for oil/brine centrifuge tests is more appropriate.

The prediction that fluid trapping would affect laboratory flow experiments with this rock appears to have been true since residual brine saturations were high during relative permeability experiments. The range of relative permeability vs. saturation data measured during the three-phase flow experiments was narrow. Fines migration and clay effects did not appear to be a problem in laboratory experiments.

The experimental sample for steady-state relative permeability tests was cut from a section of reservoir core. The sample was prepared to test the rock with flow parallel to the bedding planes. This constraint yielded a sample which was much shorter than earlier samples used in this project. However, reasonably good two- and three-phase steady-state relative permeability results were obtained using the sample. The microwaveable coreholder and core preparation techniques worked well and provided for steady-state oil/water, gas/water, and gas/oil/water measurements on the same sample.

Oil relative permeability results were in good agreement from both unsteady- and steady-state oil/water tests, whereas the brine results were not similar. The brine relative permeability vs. saturation plots from the steady-state oil/water test showed a more pronounced change in relative permeability with changes in saturation compared to the unsteady-state result. The steady-state brine data projected to the $k_{rw} = 1$ at $S_w = 1$ end point, whereas the unsteady-state data appeared to have a $k_{rw} = 0.1$ at $S_w = 1$ end point. The unsteady-state water relative permeability data appear to be incorrect. Better agreement might have been achieved had the sample been longer or if other test conditions had been imposed.

Working with Almond formation rock instead of quarried rock such as Berea increased the level of complexity involved in testing the rock, but not excessively. Limiting the maximum pore pressure within the rock to 400 psig reduced the range of relative permeability results that could be obtained in a reasonable length of time using the available laboratory equipment. A higher-permeability sample would have provided better opportunities experimentally, but the core analyst must work with the rock of interest rather than idealized samples.

Comparing the results for this Almond formation sample (taken from 4,959 ft depth) to FY91 project results for 260-mD fired Berea yields the following observations:

1. With each sample, two- and three-phase k_{rw} vs. S_w trends were similar. For equivalent saturations below $S_w = 75\%$, the water relative permeabilities for Almond formation rock were somewhat lower than those of Berea.
2. In comparing oil relative permeability results, those of Almond formation rock were generally greater than those of Berea at equivalent oil saturations for both two- and three-phase flow systems. The Almond formation rock oil relative permeability results showed more scatter than those of the Berea.
3. Two-phase gas results for Almond formation rock were generally less than those of Berea. Three-phase relative permeabilities for Almond formation rock were generally greater than those of Berea at equivalent gas saturations. Three-phase gas relative permeability vs. gas saturation results for both samples were scattered.

Some conclusions from this work are as follows:

1. The samples tested were strongly water-wet. USBM wettability indices from centrifuge tests were close to 1.
2. Air-brine capillary pressure vs. saturation characteristics were measured for one of the Almond formation samples using a variety of techniques. Air-brine capillary pressure data from porous plate, mercury injection, and air/brine centrifuge tests were very similar.
3. Oil/brine centrifuge capillary pressure vs. saturation results were nearly identical regardless of whether decane or Soltrol 100 was used as the oil phase.
4. Thin section evaluations indicated that for the Almond formation samples examined, microporosity comprises 38 to 60% of the rock porosity. Clay filaments crossed many pore throats. The microporosity and clay were predicted to trap fluids during flow tests.
5. Unsteady-state and steady-state oil relative permeability results from oil/brine tests were almost identical. However, brine relative permeability results from the same tests were significantly different. In general, brine relative permeability measurements from the steady-state tests were lower than those of the unsteady-state tests. This is believed to result from the shortness of the unsteady-state test plugs and from laboratory testing techniques.
6. Sample preparation and testing techniques that were developed for the steady-state testing program were successful. Three-phase measurements were conducted with the sample subjected to 1,000 psig confining pressure.
7. Comparing relative permeability results for the Almond formation sample from the 4,959 ft depth to the 260-mD fired Berea results from FY91:
    a. With each sample, two- and three-phase k_{rw} vs. S_w trends were similar. For equivalent saturations below S_w = 75%, the water relative permeabilities for Almond formation rock were somewhat lower than those of Berea.
    b. Comparing oil relative permeability results, those of Almond formation rock were generally greater than those of Berea at equivalent oil saturations for both two- and three-phase flow systems. The Almond formation rock oil relative permeability results showed more scatter than those of Berea.
    c. Two-phase gas results for Almond formation rock were generally less than those of Berea. Three-phase relative permeabilities for Almond formation rock were generally greater than those of Berea at equivalent gas saturations. Three-phase gas relative permeability vs. gas saturation results for both samples were scattered.

Technology Transfer

A consortium has been formed with two major petroleum companies. The purpose of the consortium is to advance the state of the art in reservoir-condition, multiphase relative permeability measurements applicable to the

study of fluid flow behavior in porous media. The consortium provides for an interchange of ideas and accrual of advice on areas in which technology developed at NIPER can be of use to the petroleum industry. Discussions conducted with the consortium members give the project staff a better appreciation of the types of information required by reservoir engineers and special core analysts for simulation and reservoir evaluation.

Laboratory projects undertaken during FY92 for industry clients were diversified and challenging. These projects included:

- Experiments to evaluate scale-up of relative permeability measurements from plug to reservoir scale
- Gas/water steady-state relative permeability measurements under extreme temperature and pressure conditions (offshore, North America)
- Comparisons of capillary pressure and wettability results for reservoir core plugs at temperatures from ambient to 300° F to assess thermal changes in rock/fluid properties (offshore, Europe)
- Tests to evaluate formation damage potential from scale and corrosion inhibitors (offshore, Europe)
- Steady- and unsteady-state relative permeability and centrifuge capillary pressure measurements (offshore, Asia)
- Contact angle, capillary pressure, and wettability measurements (continental, South America)
- Development of training materials and computer software for X-ray fluid saturation measurement in a joint project with an equipment manufacturer for a major South American research laboratory.

Technology transfer was also accomplished through many tour-group presentations, by giving local students opportunities to learn about the laboratory during Engineers Week, through career day presentations by the laboratory staff at area schools, by using AWU scholarship students for summer work, and by general communication with other members of the scientific community.

Project staff members attended the Sisters City Technical Seminar in April which was conducted by Exxon Production Research Company, Esso Norge, and Rogaland Research in Houston, TX. The seminar covered various aspects of reservoir-condition special core analysis tests. After the seminar, the staff members visited a special core analysis laboratory of one of the major oil companies in Houston and discussed measurements and experimental design with the core analysts.

Talks on reservoir-condition core analysis measurements were presented to participants of a major oil company during its special core analysis workshop held in April and to NIPER researchers and the AWU scholars who were at NIPER in May.

Staff members attended the SCA/SPWLA Joint Annual Technical Conference and Exhibition in Oklahoma City in June. NIPER had an exhibition booth at the SCA/SPWLA meeting. Many copies of topical reports on project BE9 research were distributed to SCA/SPWLA members visiting the NIPER booth. Several API subcommittee meetings on routine core analysis were attended during the project year.

Relative permeability measurement technology was transferred directly to the oil industry as part of special core analysis projects through NIPER's Work-for-Others Program. These projects utilize the technology of measuring relative permeability at reservoir conditions developed under DOE sponsorship at NIPER. In addition,

considerable research and development is conducted under industrial funding, and knowledge gained in projects sponsored by industrial clients is valuable in the work performed specifically for DOE.

Publications

Special Core Analysis and Relative Permeability Measurements on Almond Formation Reservoir Rocks, by D. Maloney, K. Doggett, and A. Brinkmeyer. Dept. of Energy Report No. NIPER-648, Oct. 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Presentations

Reservoir Condition Core Analysis Measurements, by D. Maloney. Pres. at special core analysis workshop held at a major oil company, Apr. 1992.

Reservoir Condition Core Analysis Measurements, by D. Maloney, Pres. to AWU scholars at NIPER, May 1992.

IMAGING TECHNIQUES APPLIED TO THE STUDY OF FLUIDS IN POROUS MEDIA

Principal Investigator:	Liviu Tomutsa
BPO Project Manager:	Robert Lemmon
Project No.:	Project BE12
Funding for FY92	$545,000 (AE&PT)
Period of Performance:	October 1, 1991 – September 30, 1992

Objective

The objectives of this project are to: (1) develop a methodology to derive reservoir engineering parameters from petrographic, computed tomography (CT) scanning, and nuclear magnetic resonance imaging (NMRI); (2) characterize the recovery efficiency and measure the saturation distribution in cores for EOR processes applicable to specific reservoirs, including Class 1, by using the state-of-the-art imaging technology developed; (3) investigate the applicability of imaging technologies to the development of scale-up procedures from core plugs to whole cores to interwell scales; and (4) strongly encourage and seek cost-sharing of collaborative research by industrial participants.

Research Summary

This project supports reservoir description and advanced oil recovery processes research and development, especially in the areas of reservoir chemistry, physics, and rock-fluid interactions at the micro- and macroscopic scales. This work is aimed at advancing the understanding of the effect of small-scale rock heterogeneities (pore to whole core scales) on fundamental processes involved in oil recovery by developing, applying and refining cross-cutting imaging techniques and technologies. Imaging techniques are currently used at NIPER to provide near-term field RD&D support in the characterization of pore structures and surfaces, and rock/fluid interactions as applied to the evaluation of enhanced oil recovery processes for Class 1, 2, and other reservoirs. The emphasis of Project BE12, however, is on the longer-term application of these techniques to the study of oil trapping, recovery mechanisms, and scaling-up procedures from core plug to whole core to interwell scales.

Numerical reservoir simulation provides critical information for reservoir management, initiation of secondary recovery projects, and selection of optimum enhanced oil recovery (EOR) processes. Without a realistic geological and engineering reservoir description, simulation results may be substantially in error. Depending on the degree and scale of reservoir heterogeneities, the level of detail obtainable from subsurface sampling is often inadequate to assign simulation parameters accurately to predict fluid flow on the interwell scale. Quantitative descriptions for simulation at scales less than well spacing can be obtained by combining available subsurface reservoir data with a detailed quantitative model of rock composition and fluid flow characteristics constructed through statistical sampling and analysis of analogous outcrops.

Although studies of outcrops, analogous reservoir, and simulation sensitivity can provide improved understanding of reservoir architecture, the inherent incompleteness of reservoir data prevents us from accurately

determining the effect of reservoir heterogeneity on fluid flow. The advent of nondestructive imaging technologies such as CT and NMRI allows direct visualization and measurement of rock properties and of fluid distributions in rock samples. Thus, they provide the necessary tool needed to verify directly, in the laboratory, the various scaling-up techniques which up until now could be verified only indirectly in the field. In the present work, values for rock parameters (porosity, permeability), generated by CT, minipermeameter, and computer-aided petrographic image analysis are used either directly as input data for simulating floods which are monitored by CT, or they are used to generate realizations of rock properties (ø, k) statistically and spatially compatible with the observed values by means of Turning Bands methods, and these realizations are used as simulator input. The effect of permeability models with varying amounts of detail, as well as viscosity ratio and grid block size, on waterflood oil recovery was determined. The numerical simulator used in this study was BOAST-VHS, NIPER's improved version of BOAST (Dept. of Energy Report No. NIPER-542).

To derive engineering parameters, one must determine the small (millimeter)-scale porosity, permeability, and saturation variations in heterogeneous cores in which laboratory floods are performed. The first step is to measure the surface permeabilities of the core using a minipermeameter with a fine tip (3-mm ID O-ring). By calibrating the minipermeameter often with homogeneous core plugs of known permeabilities, the accuracy of the measurements is maintained at ±10%. Minipermeameter measurements are used to determine variations in rock permeability due to small-scale heterogeneities. The limitation of the minipermeameter is that it can perform only surface measurements. To determine permeabilities within a rock sample, thin section image analysis is used.

After minipermeameter measurements are performed, thin slabs from which thin sections will be made are cut at the same locations where the minipermeameter measurements were taken. The permeability and porosity values from image analyses are averaged and compared with their CT value counterparts and the minipermeameter measured values, respectively. Small adjustments in the porosity and permeability values generated by image analysis can be made by adjusting the segmentation threshold and the tortuosity. The permeability-porosity correlation is determined from the image analysis data.

The porosity values determined by CT and the permeability-porosity correlation from the thin section image analysis are used to construct the three-dimensional permeability distribution within the core sample. By comparing the simulations using the porosity and permeability values determined above to the distributions observed by CT, the accuracy of the above approach for a specific sample can be evaluated.

NMR microscopy is used to provide three-dimensional pore network images to understand how pore-scale rock geometry and fluid distributions relate to larger scale permeabilities and fluid saturations. A maximum image resolution of 20 μm has been achieved. The high resolution enables visualization of the effect of rock/fluid interaction on oil, water, and gas distributions within pore spaces of reservoir rocks. Previous resolution limitations have been overcome by interfacing two desk top computers with the NMR spectrometer. One computer controls the current in the recently built high magnetic field gradient coils and the image data acquisition sequence using a recently built probe. The second computer, which has a high-speed RISC processor, performs all the computations necessary to generate the fluid image. For small-scale studies by NMRI, small core plugs (4 to 5 mm diameter, 4 to

5 mm long) are needed. A micro-coring apparatus has been built to cut such core plugs from large plugs in regions identified by CT as being of interest. Two basic methods are available for reconstructing the 3-D image from the raw projection data in projection reconstruction NMRI: (1) a direct approach based on the application of the Radon transform in three dimensions and (2) a two-stage reconstruction involving two successive applications of standard 2-D Radon transforms. The two-stage method is more efficient involving approximately $2N^4$ operations to reconstruct the entire 3-D image, where N is the cubical dimension of the image in pixels. The major shortcoming in this approach is the impossibility of reconstructing only part of the image, i.e., the complete image must be reconstructed. This increases the overall requirements both for time and large file handling and storage capability. With the direct approach, reconstruction of the complete 3-D image involves approximately N^5 operations which would require much more time if the reconstruction of the entire image would be required; however, the direct approach does permit a partial reconstruction of selected regions of the image; for example, a single slice view of arbitrary orientation or a reduced volume image using only a subset of the raw data. Because the acquisition of the data is the limiting factor, imaging the central volume of a sample at high resolution is possible with a reduced number of raw projections using the direct approach. The direct method also does not seem to be as susceptible to image artifacts that appear in reconstructed images. The direct image reconstruction approach allows spatial resolutions down to 25 μm in sandstones with low iron content. Also, the use of animation in successive displays of cross sections through the volume studied appears to have the potential of aiding the extraction of topological characteristics of the pore network from NMRI images. The integration of these techniques enables a more definitive assessment of the roles of heterogeneities in oil entrapment, fluid flow, and fluid saturation distribution.

To carry out the scaling-up work, information on various scales is needed. The use of outcrops provides information at scales from hundreds of meters to centimeters. Outcrops in a Northeastern Oklahoma field (Bartlesville sandstone formation) are used for the acquisition of samples containing heterogeneities at various scales. Fluvial-dominated deltaic (Class 1) outcrops are available in locations close to NIPER. From these locations, rock samples containing generic heterogeneities characteristic to fluvial deltaic deposition environments (small-scale crossbedding and ripple bedding) are collected and cut in rectangular shapes for observation of small-scale heterogeneities and for minipermeameter measurements.

To accelerate the CT scanning of long cores, the topogram capability of the scanner has been combined with the high-accuracy positioning system to generate longitudinal cross sections of the cores in one pass. The topogram, which generates a projection of the core in only one plane, similar to the traditional medical X-ray radiography, can provide rapid identification of sedimentary, diagenetic and structural features in unslabbed, unprocessed cores. A longitudinal cross section of a 10-in.-long section of core can be generated in approximately 20 seconds, a reduction in time and file sizes by a factor of at least 30 compared to the previous approach in which transverse cross sections were combined in a three-dimensional array and a longitudinal cross section was generated from the array. By selecting three different projection planes parallel to the core axis (0°, 45° and 90°), the optimum locations and directions for cutting plug samples and the preferential slabbing plane can be rapidly determined.

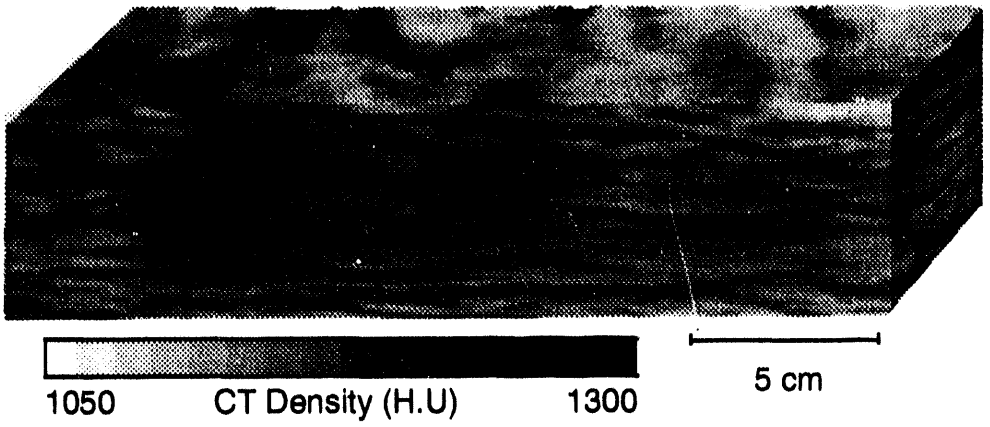

FIGURE 12. - CT reconstruction of Tallant sandstone block showing climbing ripples.

For this study, a sample with climbing ripples was selected (Fig. 12). This sample was cut parallel to the laminations from a block collected from an outcrop exposure of the Tallant formation in northeastern Oklahoma. Its dimensions are 25.5 x 5.6 x 5.1 cm. Its porosity measured volumetrically is 26.0%, and the air permeability measured parallel to the laminations is 210 mD. Images were captured from a thin section, and permeability and porosity were calculated by image analysis.

Mercury intrusion porosimetry indicated a relatively large percentage of the pore throats (60%) have diameters larger than 5 μm, while a significant percentage of the pore throats (15%) have diameters smaller than 0.5 μm. This reflects the fact, that while most of the sample contains clean high-permeability sandstone, a significant fraction has lower porosity and lower permeability values which are localized in the clay-rich, more cemented laminae. NMR microscopy also shows that in the regions with clay-rich laminae the pores are smaller than those in the cleaner zones.

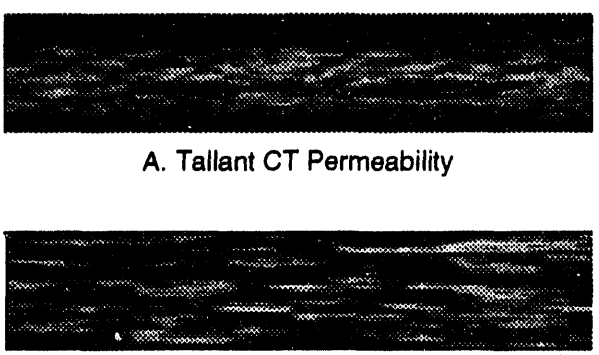

FIGURE 13. - Permeability distribution in a vertical, longitudinal plane: (A) from CT/thin section image analysis and (B) from Turning Bands.

To identify dynamically the permeability contrasts due to rock heterogeneities, tracer tests were performed on the Tallant block. The block was first encapsulated in Castolite™ and saturated with untagged 2% KCl brine, and the porosity of the sample was determined by CT scanning. The corresponding permeability distribution generated using the correlation from thin section image analysis is shown in figure 13A. The average permeability was calculated to be 210 mD using the CT porosity and the permeability/porosity correlation from thin section image analysis. For comparison, the permeability distribution generated using the Turning Bands method

(as applied in the TUBA computer program), in which correlation lengths of 3.2 cm horizontally and 0.3 cm vertically were used, is shown in figure 13B. As the figure shows, the Turning Bands method adequately describes the spatial distribution of the rock heterogeneity.

A slug of 7% NaI tagged brine was injected and followed again by untagged brine. The observed and simulated tracer test fluid distributions are shown in figures 14 – 16. The CT image of the tracer test shows fine fingering due to the permeability contrast at millimeter scale. Also observed is a large central finger due to a central zone of higher permeability. The simulations, using a 63 x 126 grid, corresponding to grid block sizes of the CT voxel size (0.5 mm x 0.5 mm x 4 mm long), while reproducing the general front movement observed by CT scanning, show less fingering. The factors contributing to the discrepancy between CT and simulation results are related to the limitations in both simulations and CT observations. With respect to simulations, the main factors to consider are: (1) the relatively coarse grid compared to the heterogeneity scale; (2) the fact that this simulator does not take into account dispersion effects, and (3) performing a two-dimensional simulation (in the xz plane) of a system, which, although displays layering in the z direction, has a significant lack of translational symmetry in the y direction.

To study the effect of climbing ripples on initial and residual oil saturations and the fluid paths during oil removal, oil floods and waterfloods were performed using 1.0, 2.6 and 23 cP oil. Simulations were performed using the CT measured porosity and permeability values and the Turning Bands method generated values.

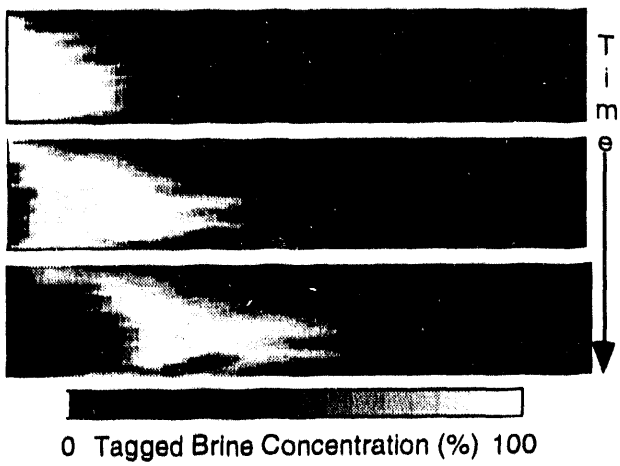

FIGURE 14. - Fluid distributions during tracer test as observed by CT.

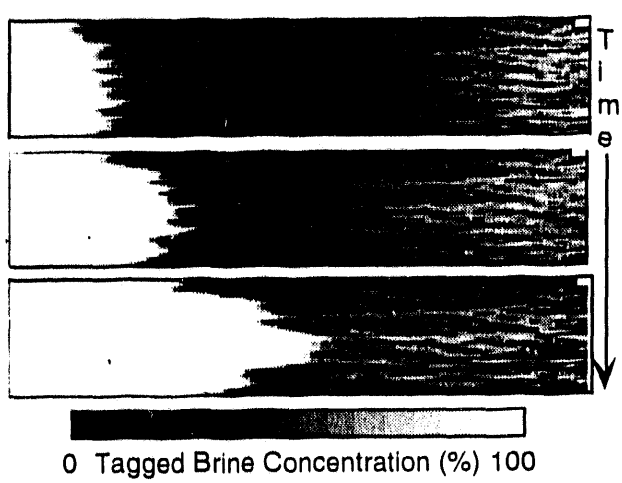

FIGURE 15. - Fluid distribution during a tracer test as simulated by BOAST-VHS.

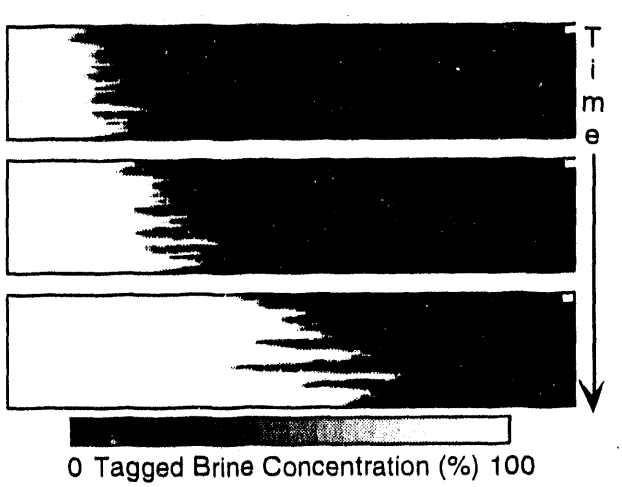

FIGURE 16. - Fluid distribution during tracer test with data generated by the Turning Bands method.

The first oil flood consisted of flooding the core, previously saturated with brine tagged with 7% NaI with 90 pore volumes (PV) of 1-cP mineral oil. The oil front movement during the 1-cP oilflood is shown in figure 17, and the corresponding simulations using the CT image analysis data in figure 18 and Turning Bands generated data in figure 19. The strong oil frontfingering present in figure 17 is controlled by the small scale heterogeneities (climbing ripples). An average saturation of 71.8% was observed by CT and 67% was measured volumetrically. The simulation-generated oil front displayed in figure 18, while reproducing the three main fingers, due to the factors mentioned previously, is not able to reproduce the details of the front shown in figure 17. The front displayed in figure 19 reproduces statistically the oil flood behavior shown in figure 17. The oil saturation at the end of the oil flood (two pore volumes of oil injected) displayed a dependence on the rock heterogeneity with the lower saturations in the lower porosity laminations (figure 20).

Waterfloods were performed at a rate of 1 ft/day using a 7% NaI tagged brine for the cases with 1.0-, 2.6- and 23-cP oil. The floods, as observed by CT, for the three oil viscosities showed relatively sharp fronts in all cases. The 1-cP case is illustrated in figure 21. The residual oil saturation at the end of the waterflood was relatively uniform across the sample with no significant difference between the high- and low-porosity locations.

Minipermeameter measurements of three profiles at the end of the sample perpendicular to the laminations show less permeability contrast than the thin section data, as expected. The minipermeameter tip diameter size (3 mm) is larger than the laminations

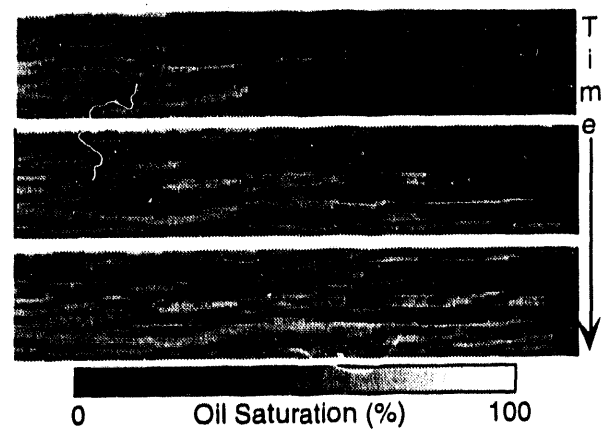

FIGURE 17. - Movement of the oil front during the 1-cP oilflood as observed by CT.

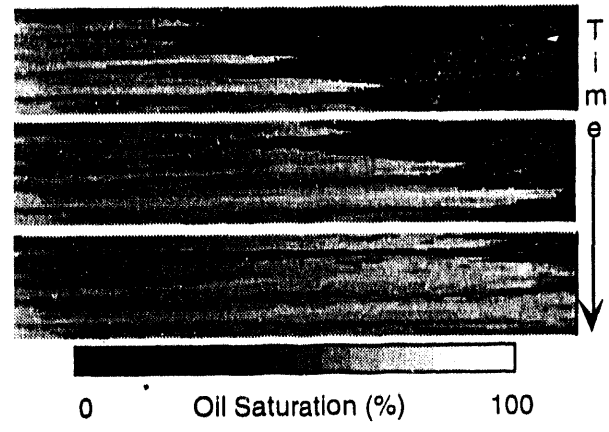

FIGURE 18. - Movement of the oil front during the 1-cP oilflood as simulated from the CT images.

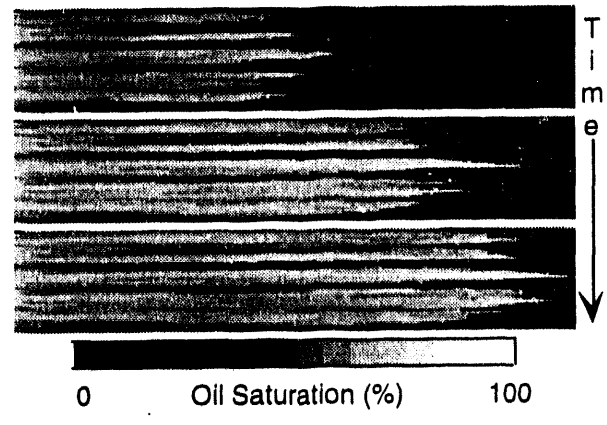

FIGURE 19. - Movement of the oil front during the 1-cP oilflood with data generated from the Turning Bands method.

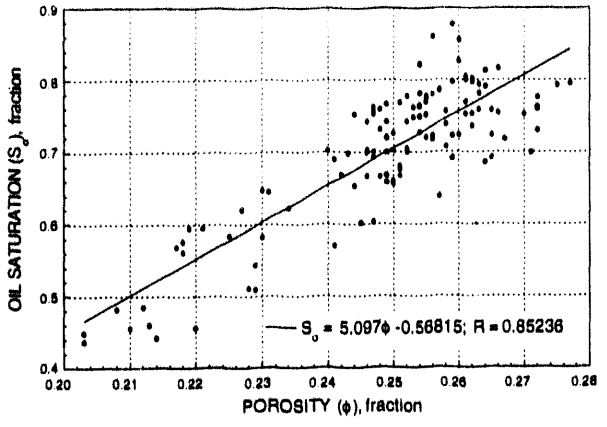

FIGURE 20. - Correlation between porosity and oil saturation at residual brine saturation following oil flood of Tallant sandstone block.

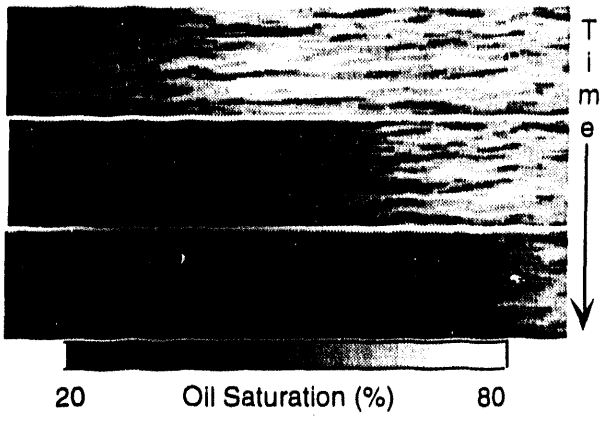

FIGURE 21. - CT scan of waterflood in which the oil has a viscosity of 1 cP.

(1 to 2 mm thick), and an averaging effect is taking place. When permeabilities are measured on the side where the laminations intersect the surface at a small angle such that the entire minipermeameter tip is covered by the laminations, lower values in better agreement with the image analysis values are generated.

By selecting a heterogeneous rock sample with a complex structure on which detailed measurements could be performed and against which the simulation results could be compared, many of the uncertainties are removed in history-matching the floods by simulation when only production curves are used. The waterflood experimental results could be reproduced not only by a detailed simulation, including all the rock data obtained from CT, minipermeameter, and image analysis of thin sections but also by a much coarser simulation using uniform parameters. Two factors contributing to this occurrence are (1) the range of porosity, permeability, and relative permeability contrasts between the two rock types within the sample and (2) the size, geometry, and number of the heterogeneities compared to the size of the sample in which the experiment was performed. The large number of ripples uniformly distributed within the sample during waterflood dispersed the water front and actually prevented channeling, creating the same effect as a homogeneous sample containing much smaller heterogeneities. The implication for laboratory work is that the minimum representative sample size should be determined by the size, number, and contrast in properties of the smaller scale heterogeneities, if the theory used to interpret the data assumes uniform rock properties. Given that in this simulator the actual physical dimensions are not important, these results are generally applicable also at field scale.

Previous work that used only simulations and various permeability distributions derived from outcrop data to study the effect of heterogeneity on oil recovery during waterflood also showed that, at larger scales (meters to tens of meters), homogeneous equivalent models could account for small-scale heterogeneity with respect to the volume studied. Heterogeneities with sizes comparable to the volume studied and which have high contrasts in permeability (ratios up to 1 to 50) have to be taken into account either by deterministic models (considered to be the most accurate) or stochastically (by incorporating the accurate spatial correlation lengths), and the layered or uniform models can give predictions that are considerably different than the deterministic models.

In summary, a synergistic rock characterization methodology, which derives reservoir engineering parameters from CT scanning, computer-assisted petrographic image analysis, minipermeameter measurements, and nuclear magnetic resonance (NMRI) imaging has been developed. This rock characterization methodology, together with fluid distribution measurements by CT, can be effectively used to investigate the effect of small-scale rock heterogeneity on oil distribution and waterflood recovery in a sample containing heterogeneities characteristic to Class I reservoirs. Imaging technologies can be used in the development of scale-up procedures from core plug to whole core, by comparing the saturation distributions resulting from simulations with the saturation distributions resulting from CT scanning. Even highly complex heterogeneous rock samples behave as uniform media if (1) the contrasts between the petrophysical properties of the various rock types are relatively small; (2) the sample size is large compared to the sizes of the heterogeneities; and (3) the number of the heterogeneities is large enough to be amenable to statistical handling.

Technology Transfer

X-ray topograms were used to identify sedimentary, diagenetic, and structural features and to select preferential slabbing planes for cores drilled by researchers at the University of Tulsa behind an outcrop of a Class I reservoir. The topograms and the slabbed cores were used on a field trip to the outcrop conducted during the SPE/DOE EOR Symposium in Tulsa.

Almost all of the special core analysis projects performed for industrial clients as part of NIPER's Work for Others program include CT scanning of the cores prior to and during the testing process. The scanning techniques enable better selection of plug locations and identification of fluid trapping phenomena.

A well was drilled in a new zone at Elk Hills, Naval Petroleum Reserve #3, and NIPER investigators are examining the core using CT and comparing the CT images with logs and other reservoir information as part of Project SGP57. This work is continuing into FY93 with the goal of recommending appropriate recovery strategies.

The techniques developed as part of BE12 were used by researchers on other Base Program projects. In Project BE3, experiments demonstrated that microbes were viable after CT scanning. CT images of a brine-saturated core containing gas-producing bacteria exhibited high gas saturations. Experiments were conducted with cores waterflooded to residual oil saturation and injected with gas-producing bacteria. After incubation, the oil saturation as measured by CT dropped from 33.6 to 29.7% as the pressure rose to 39 psig. Additional flooding tests were conducted with microbial consortia with the saturations monitored by CT.

In Project BE4A, surfactant/polymer corefloods were conducted and monitored by CT: examination of oil saturation changes for (1) surfactant systems known to provide high oil recovery in laboratory tests, (2) systems with an unfavorable mobility ratio, and (3) a system with a surfactant less effective in producing oil. All tests were conducted using Berea sandstone at ambient temperature. The cores contained layers that varied in permeability and porosity. CT images of the effective surfactant systems indicated that fluid fronts could advance in a non-uniform manner so that a higher proportion of chemicals was injected into the higher porosity layers resulting in low, but non-homogeneous, oil saturations. Use of an ineffective mobility control agent failed to move oil that was not

initially displaced by the injected surfactant solution even when an effective surfactant was used. Use of a less effective surfactant with an effective mobility control could produce as much oil as the use of an effective surfactant with inadequate mobility control. The role of mobility control thus becomes a critical parameter for successful application of chemical EOR. Residual oil saturations as measured by CT and volumetrically were in reasonable agreement. The effect of core heterogeneities on chemical movement and oil production during chemical EOR can be examined simultaneously with the evaluation of chemical formulation effectiveness using CT imaging techniques.

In Project BE4C, CT techniques were used in experiments to determine the effect of lamination angles on polymer retention during corefloods. Polymer retention was greater in cores that had laminations parallel to the direction of flow than in cores that had cross-bed laminations, and the retention increased with increasing lamination angle.

In Project SGP41, CT topograms of Hepler (KS) field cores were used to select locations for plugs to be used in coreflooding tests. In Project BE9, whole core sections from well 120 in the Arch Unit of Patrick Draw field were CT-scanned within protective jackets. Images showed that the cores were fairly homogeneous, although three-dimensional reconstructions indicated the presence of bedding features. Silty bedding features that coincided with the CT images were identified by visual examination after the protective jacket was removed.

In Project BE5B, CT techniques were used for visualization of fluid flow and gel placement while investigating profile modification for use in gas flooding. High-permeability layers were identified in the cores, and the lack of crossflow between layers was verified. The results of corefloods indicated that crossflow and damage to oil-productive formations during polymer placement are minimized when the polymer solution has a low viscosity or resistance factor.

Publications

NMR Microscopy for Fluid Imaging at Pore Scale in Reservoir Rock, by D. Doughty and L. Tomutsa. SPWLA/SCA Joint Technical Conference, Oklahoma City, OK, June 1992, SCA paper 9222.

CT Imaging of Surfactant Enhanced Oil Recovery Experiments, by B.L. Gall. Dept. of Energy Report No. NIPER-611, July 1992. NTIS Order No. DE93000102.

The Effect of Lamination Angle on Polymer Retention, by H.W. Gao. Dept. of Energy Report No. NIPER-630, Sept. 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Application of Polymer Gels for Profile Modification and Sweep Improvement of Gas Flooding, by C. Raible and T. Zhu. Dept. of Energy Report No. NIPER-632. In preparation.

Imaging Techniques Applied To The Study Of Fluids In Porous Media – Scaling Up In Class I Reservoir Type Rock, by L. Tomutsa, A. Brinkmeyer, and D. Doughty. Dept. of Energy Report No. NIPER-663. In preparation.

Presentations

NMR Microscopy for Fluid Imaging at Pore Scale in Reservoir Rock, by D. Doughty and L. Tomutsa. Presented at the SPWLA/SCA Joint Technical Conference, Oklahoma City, OK, June 1992. SCA paper 9222.

Integration of Computed Tomography, Nuclear Magnetic Resonance Microscopy, Computer Assisted Petrographic Image Analysis and Flow Simulation for Heterogeneous Core Characterization, by L. Tomutsa, D. Doughty, and A. Brinkmeyer. Pres. as a poster by Liviu Tomutsa at the SPE Forum on Special Core Analysis and its Application to Reservoir Engineering, Snowmass Village, CO, July 12-17, 1992.

Laboratory Studies of Parameters Involved in Modeling Microbial Oil Mobilization, by R.S. Bryant K.M. Bertus, A.K. Stepp, M.M. Chang, and K.L. Chase. Pres. at the Eighth Symposium on Enhanced Oil Recovery, Tulsa, OK, Apr. 22-24, 1992. SPE/DOE paper 24205.

Chemical and Microbial EOR

The capability to adjust an injected chemical formulation over a wide range of reservoir conditions, and crude oil types, remains a strong point for development and application of chemical and microbial flooding processes. NIPER's program in chemical and microbial EOR consists of four projects conducting research in surfactant flooding (BE4A), alkaline flooding (BE4B), improved mobility control (BE4C) and advanced microbial flooding EOR (project BE3). The work in each project is designed to increase recovery efficiency and associated economics, to improve process predictability, and to bring promising technologies on stream as rapidly as possible. The AORPIP addresses oil recovery in the near-term using currently available technology and in the mid- to long-term through application of advanced technologies. NIPER's research covers both of these phases now that a portion of the mid-term research, initiated in 1983, has advanced to the state of field testing.

Research under project BE4A is concentrating on the development of improved surfactant flooding methods primarily directed at waterflooded reservoirs containing crude oils of low to medium viscosity. This chemical flooding process, which usually includes the use of cosurfactants, polymers, and alkaline additives, provides a very flexible means of recovery because specific formulations can be optimized for application over a wide range of reservoir conditions and crude oil types. However, surfactant flooding has a history of questionable economics and limited applicability in high-temperature, high-salinity reservoirs, as well as those with extreme water hardness and high crude oil viscosity. NIPER's research is helping to solve these problems by developing cost-effective surfactant formulations that meet process design requirements of low interfacial tension, low rock adsorption properties, and tolerance to higher brine salinities and reservoir temperatures. Emphasis has been placed on the development of mixed surfactant systems that can be tailored to reservoir salinity conditions. FY92 studies incorporated CT imaging in the determination of fluid distributions during EOR experiments on these mixed surfactant systems. The technique was effective in monitoring oil saturation distributions during various stages of chemical injection. Experiments in FY92 also keyed on examination of surfactant mixtures containing a primary anionic surfactant component (petroleum sulfonate, TRS 10-410) and two types of nonionic surfactants—linear alkyl alcohol ethoxylates (the Genapol™ series) and dialkylphenol surfactants (the Igepal™ series). The hydrophilic-lipophilic balance (HLB) of the mixtures was varied as a measure for predicting favorable solution behavior of the overall chemical system. The TRS system alone had an optimal salinity of less than 2% NaCl. Addition of nonionic surfactants increased salinity tolerance from 4 to 11 wt % NaCl, depending on the HLB of the added surfactant. Shorter hydrocarbon chain length and branching in the secondary ethoxylated components favored improved solubility and salinity tolerance of the overall chemical system.

Recent laboratory studies in project BE4B have resulted in the development of effective alkaline-surfactant-polymer (ASP) flooding formulations and have shown this type of flooding to be cost-effective because the addition of alkali reinforces the surfactant activity and diminishes the depletion of surfactant and polymer, both of which tend to be retained in the reservoir due to adsorption and other factors. Also, chemical requirements are reduced, displacement efficiencies are improved, and scale formation is suppressed. To field test the capabilities of ASP flooding, a DOE/industry jointly funded SGP field project is underway in Hepler (KS) oilfield. The injection of

chemicals is scheduled to begin late in FY93. FY92 studies were designed to determine the impact of the interaction of chemicals used in ASP formulations and to determine what chemical-injection sequence(s) would minimize such interactions. Although it was found that such interactions are very difficult to eliminate, certain injection strategies are favorable over all others.

The success of any chemical EOR process depends not only on the effectiveness of the chemicals used to mobilize the residual crude oil but also on the ability of mobility control agents to maintain effective mobility control throughout the reservoir. Research in project BE4C focuses on the development of advanced mobility-control methods for improving sweep efficiency between injection and producing wells and profile (permeability) modification in the near-wellbore region. NIPER studies have shown that crosslinked low-molecular-weight polyacrylamide gels outperform conventional high-molecular-weight polyacrylamides when subjected to high shear conditions and that under low shear conditions the crosslinking bonds broken at high shear will reheal and thus help alleviate problems of poor injectivity. Another problem is polymer retention in the reservoir, and this is due primarily to polymer adsorption or mechanical entrapment. Adsorption can be reduced by preflushing the reservoir with the proper chemicals, but mechanical entrapment, which is thought to be caused by intercalation of shale layers, particularly in Class 1 reservoirs, is not as easily remedied. Studies conducted in FY92 showed that the direction of laminations in relation to the direction of fluid flow can have a major effect on polymer retention. Studies designed to compare NIPER's permeability modification simulator with field results were initiated but could not be finished in FY92. Additional studies will be proposed for the FY93 research effort.

Individual summaries of the four projects in chemical and microbial EOR are presented next. They are addressed in the following order: BE4A, Surfactant Flooding Methods; BE4B, Development of Improved Alkaline Flooding Methods; BE4C, Mobility-Control and Sweep Improvement in Chemical Flooding; and BE3, Development of Improved Microbial Flooding Methods.

Studies at NIPER indicate that microbial EOR methods are potentially applicable to 31% of the reservoirs in 10 of the largest oil-producing states which, together, contain 230 billion barrels of remaining oil in place. However, even though laboratory studies have been successful, not enough field performance data are available to assess the true potential of this technology. To acquire more field information, NIPER has initiated two microbial-enhanced waterflooding field tests: an original pilot in Delaware-Childers (OK) field and an expanded pilot in Chelsea-Alluwe (OK) field. Both tests received funding under the SGP Program. In the first pilot, incremental oil production was improved by a very acceptable 13% over that by waterflood alone. The expanded pilot will not be completed until the fourth quarter of FY93, but preliminary results are promising. The engineering design that made these tests possible was based on laboratory research performed in Base Program project BE3. Concepts derived from the basic research effort have resulted in the development of an engineering methodology and design of optimal microbial formulations for specific applications including well stimulation treatments, permeability modification treatments, and microbial enhanced waterflooding. These results are being transferred to independent operators through publications, presentations, and a series of short courses that have been presented on an international scale.

SURFACTANT FLOODING METHODS

Principal Investigators:	Bonnie L. Gall Feliciano M. Llave Leo A. Noll
BPO Project Monitor:	Jerry F. Casteel
Project No.:	BE4A
Funding for FY92:	$585,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The FY92 objectives of this project were (1) to determine the applicability of advanced EOR technologies, based on mixed surfactant systems, for improving oil recovery from Class 1 reservoirs; (2) to extend the use of surfactant-based EOR to different salinity and temperature ranges by developing systems chemically compatible with reservoir fluids; and (3) to develop cost-effective chemical systems that efficiently recover oil at reduced concentrations of synthetic surfactants and alkaline additives. The emphasis of these studies will be on problem areas which may adversely affect the performance and economics of chemical flooding processes.

Research Summary

Since 1983, NIPER has conducted laboratory research for the DOE in developing improved chemical flooding methods. The studies have included chemical systems applicable to Class 1 reservoirs and fields operated by the DOE such as Naval Petroleum Reserve NPR No. 3. Emphasis has been placed on the development of mixed surfactant systems that can be tailored to reservoir salinity and on development of cost-effective alkaline/low-concentration-surfactant chemical systems suitable for field application.

Earlier work at NIPER focused on the investigation of problem areas adversely affecting the successful application of chemical EOR techniques. These included surfactant loss studies and investigations of salinity-tolerance improvement using mixtures of ethoxylated and nonethoxylated anionic surfactants. During FY92, research efforts included the evaluation of mixed nonionic and anionic surfactants, within a specific range of conditions identified in prior work, and as established in DOE's Federal Oil Program Implementation Plan. The Phase-Inversion-Temperature (PIT) method was used for rapid evaluation of surfactants to determine approximate optimal salinity and temperature conditions, i.e., conditions where the chemical system was most likely to solubilize and mobilize oil. Comparison with more time-consuming screening methods, such as phase behavior salinity scans, indicated that the PIT method determined optimal salinity within approximately 1-2 wt % NaCl of the phase behavior method.

Tests in FY92 concentrated on the examination of surfactant mixtures containing a primary anionic surfactant component (petroleum sulfonate, TRS 10-410) and two types of nonionic surfactants, linear alkyl alcohol ethoxylates (the Genapol™ series), and dialkyl phenol surfactants (the Igepal™ series). The hydrophilic-lipophilic

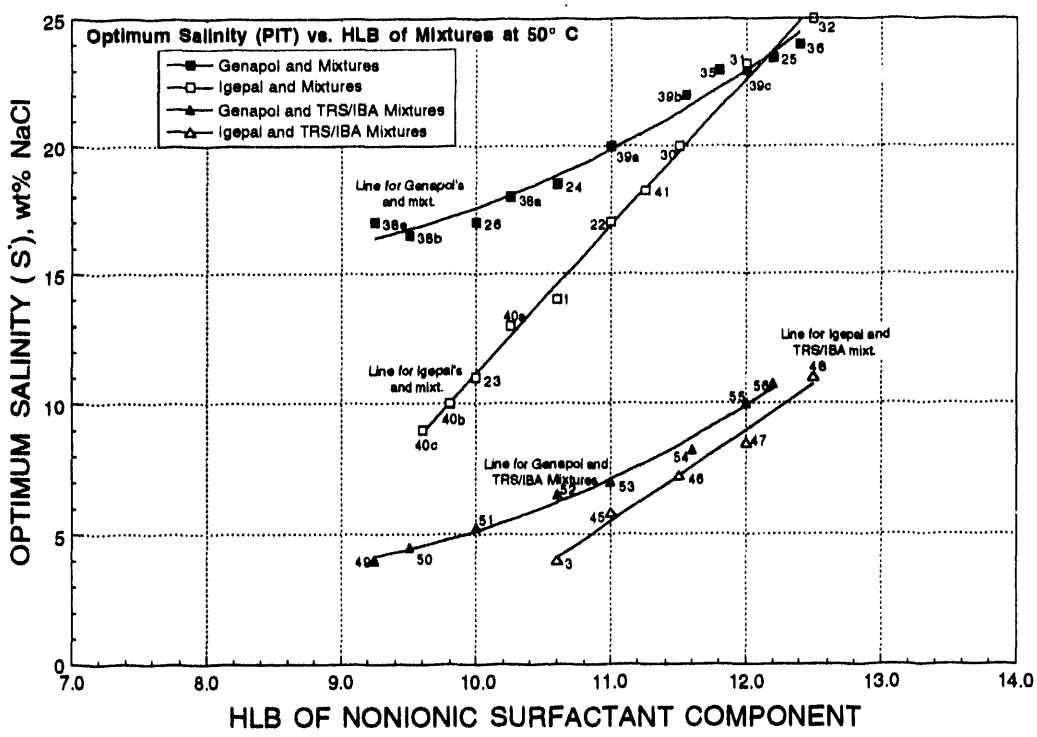

FIGURE 22. - Optimal salinity (PIT-method) vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures with and without TRS 10-410/IBA [1:1] at 50° C with n-decane.

balance (HLB) of the mixtures was varied as a measure of predicting favorable solution behavior of the overall chemical system. Figure 22 shows the variation in optimal salinity as a function of HLB of the nonionic surfactant component for mixtures of nonionic and nonionic-anionic surfactants for one temperature. The TRS system alone has an optimal salinity less than 2% NaCl. Addition of nonionic surfactants increased salinity tolerance to from 4 to 11 wt % NaCl, depending on the HLB of the added surfactant. In many cases, however, an increase in salinity tolerance appeared to be accompanied by a decrease in oil solubilization. Shorter hydrocarbon chain length and branching in the secondary ethoxylated components favored improved solubility and salinity tolerance of the overall chemical system. Surfactant mixtures, therefore, provide a method for tailoring chemicals for use in reservoirs of interest. The HLB value of surfactants provides a basis for building selection criteria to facilitate surfactant testing and/or selection.

Computed tomography (CT) was used to study fluid distributions during coreflooding experiments on mixed-surfactant chemical systems. The technique was effective in monitoring oil saturation distributions during various stages of chemical injection. Nonuniform fluid advance could be observed, even in cores that appeared homogeneous by visual inspection. The role of adequate mobility control was found to be significant. Use of a less favorable surfactant system with adequate mobility control produced as much oil as the use of a good surfactant system with inadequate mobility control. In addition, the effects of core heterogeneities on fluid propagation and oil production were examined simultaneously with the evaluation of chemical formulation effectiveness. Continued use

of CT-imaging techniques to help establish the role of different chemical flooding parameters on oil recovery effectiveness was recommended.

NIPER's efforts in developing cost-effective chemical flooding technologies are focusing on the use of alkaline-enhanced surfactant flooding technology for the recovery of light crude oils. The Naval Petroleum Reserve (NPR) No. 3, Teapot Dome (WY) field is a target for this technology. The primary target for recovery, other than by steam, is the 2nd Wall Creek formation. Particular emphasis is being placed on 2nd Wall Creek because of rapidly declining production that is approaching its economic limit. Alkaline-surfactant systems were evaluated using two oil samples from NPR No. 3. The alkaline additives were incompatible with the Madison water (limestone aquifer) that has been used for 15 years to waterflood the 2nd Wall Creek formation. Divalent ion concentrations in this water must be reduced prior to mixing with added chemicals. Once the water was softened, however, several commercial surfactant mixtures produced very low interfacial tensions (IFT) between oil and water. Therefore, surfactant-enhanced alkaline flooding appears to be have good potential for oil recovery from NPR No. 3 reservoirs. Reservoir permeability and the presence of natural fractures will require a careful geological study and, perhaps, some form of remedial gel treatment to redirect fluid flow away from the fractures.

Experiments were also conducted to determine the effect of partitioning of surfactant between the oil and aqueous phases in alkaline/low-concentration-surfactant systems. Results indicated that the economics of surfactant flooding with low surfactant concentrations are not greatly affected by partitioning. In this study, no demonstrable effect of alkaline additives on the partitioning of synthetic surfactant was observed. Results did show: (1) alkaline additives significantly reduce surfactant adsorption and (2) IFT levels that are very favorable to the mobilization of residual oil can be achieved using dilute surfactant solutions containing alkaline additives.

The volume of research information available on chemical flooding EOR is significant. To identify key areas for future research, NIPER has begun work on an informational data base. The ultimate goal is to develop a system for identifying surfactants that meet specific conditions associated with a given reservoir. The overall system will draw on information from the literature as well as ongoing research. A two-part data base system has been constructed. Part one is primarily a compilation of available literature in the chemical EOR area. The second section of the system will contain information that has been abstracted from the literature. Development of the system will be used to help develop surfactant-performance correlations for application of this technology.

Technology Transfer

Results of research performed in this project are communicated through publications and presentations as noted below. The emphasis on near- and mid-term applications of DOE-sponsored research has encouraged and focused surfactant evaluation on reservoirs of interest to DOE. Therefore, oil recovery experiments have been conducted using oil, salinity, and temperature conditions of Class 1 reservoirs or for Naval Petroleum Reserve No. 3. Joint DOE-industry projects have been initiated using alkaline/-low-concentration-surfactant formulations.

Publications

Low-Concentration Surfactant Flooding: Partitioning of Synthetic Surfactants, by T.R. French and D.A. Evans. Dept. of Energy Report No. NIPER-608, June 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Development of a Chemical Flooding EOR Literature Database System, by F.M. Llave. Dept. of Energy Report No. NIPER-609, August 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

CT Imaging of Surfactant Enhanced Oil Recovery Experiments, by B.L. Gall. Dept. of Energy Report No. NIPER-611, July 1992. NTIS Order No. DE93000102.

Evaluation of Mixed Surfactants for Improved Chemical Flooding, by F.M. Llave, T.R. French, and P.B. Lorenz. Dept. of Energy Report No. NIPER-631, Nov. 1992. NTIS Order No. DE93000117.

Presentations

CT Imaging of Chemical Flooding Experiments, by B.L. Gall. Pres. at the Tulsa Chapter of the Society of Core Analysts Meeting, Tulsa, OK, Mar. 17, 1992.

DEVELOPMENT OF IMPROVED ALKALINE FLOODING METHODS

Principal Investigator:	Troy R. French
BPO Project Monitor:	Thomas B. Reid
Project No:	BE4B
Funding for FY 1992:	$195,000 (EOR-Heavy Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The objective of this project is to develop cost-effective and efficient chemical flooding formulations using surfactant-enhanced, weakly alkaline systems. Specific objectives for FY92 were: (1) to determine the effects of variables on polymer propagation and retention during alkaline flooding (especially the effects resulting from surfactant-polymer interaction), and (2) to perform studies designed to support a field test conducted under the SGP program.

Research Summary

The chemical interactions that can occur during surfactant-enhanced alkaline flooding are complex. Some of the parameters that may contribute are pH level, ionic strength, and properties of the surfactant, cosurfactant (alcohol), and polymer. The presence of crude oil may also affect interaction, as can other chemicals. At least six types of surfactant-polymer complexes have been described, and the interactions that occur between polymers and surfactants are the most significant of the interactions possible during surfactant-enhanced alkaline flooding.

Polymer-surfactant interaction was the focus of FY92 research. Rheological properties of polymer solutions, in the presence of crude oil, were monitored over a 191-day period at different pH levels. A substantial number of experiments were performed on the surfactant-polymer system selected for use in a pilot test to be conducted in Hepler (KS) oilfield under the SGP program.

The experiments were performed with chemicals that included the surfactant and polymer system that will be used for a field test conducted in Hepler field under the SGP program. The reagents and brines used in developing the proper mixture(s) for use in the Hepler pilot are tabulated in table 4. Many of the mixtures were formulated with water from a water supply located in Hepler field. All compositions shown in table 4 are given as weight per volume. A Contraves low-shear viscometer was used for initial measurements of viscosity. However, mechanical problems made it necessary to switch to a Brookfield Model LVT-C/P 1.565° cone and plate viscometer for later measurements. An Orion Model 601 digital pH meter was used for pH measurements. Samples were monitored visually for phase separation, cloudiness, and precipitation. Interfacial tension (IFT) properties of selected systems were measured with a University of Texas spinning drop interfacial tensiometer. Transient (dynamic) IFT behavior was monitored over a time interval of several hours.

TABLE 4. REAGENTS and CHEMICALS

Surfactants:
- Chevron Chaser XP-100, an anionic surfactant, mol wt = 434
- Chevron Chaser CF-100, an experimental anionic surfactant
- Stepan Petrostep B-110, an anionic surfactant, mol wt = 500
- Stepan Petrostep B-105 an anionic surfactant mixture mol wt = 424
- Shell Neodol 25-9, ethoxylated alcohol, mol wt = 610

Polymers:
- Pfizer Flopaam 3230E, a low-molecular weight partially hydrolyzed emulsion polyacrylamide, mol wt = 7-8 X 10^6
- Pfizer Flopaam3230S, a low-molecular weight partially hydrolyzed solid polyacrylamide, mol wt = 7-8 X 10^6
- Pfizer Flocon 4800CX, a biopolymer
- Allied ColloidsAlcoflood 1135, a medium molecular weight partially hydrolyzed solid polyacrylamide

Alkalis:
- Sodium carbonate, analytical reagent
- Sodium bicarbonate, certified ACS
- Sodium hydroxide, certified ACS
- Sodium tripolyphosphate (STPP), tech.

Make-up waters:
- Deionized water (DIW)

Hepler supply well water:

Sodium and potassium	830 mg/L
Chlorides	908 mg/L
Calcium and Magnesium	21 mg/L
Bicarbonate	720 mg/L
TDS	2,483 mg/L
pH	7.9

Crude oil:
- Hepler (KS) Tucker sand

The polymer used for the tests was partially hydrolyzed polyacrylamide Alcoflood 1135, a medium-molecular-weight anionic polymer which is furnished in solid form. The surfactant used for the tests was Chevron XP-100, an anionic surfactant. The pH was adjusted with sodium hydroxide, a strong alkali. Weak, buffered alkalis have properties that are advantageous for field use. For these studies, however, the strong alkali was more useful because the pH adjustment can be adjusted by the addition of only a small amount of the strong alkali and resulting small change in ionic strength. Sodium chloride was used in adjusting ionic strength.

The detrimental effect of ionic strength on the rheological properties of polyacrylamide polymers is well known. The effects of salinity and time on apparent viscosity are shown in figure 23, where pH is lower than 7, and figure 24, where pH is higher than 10. The pH level had negligible effect on the rate of viscosity reduction as salinity was increased. Some downward drift in viscosity with time occurred at both pH levels.

For comparison, the rates of change in apparent viscosity for mixtures that contained both polymer and surfactant are shown in figures 25 - 38. Figures 25 and 26 show the results of periodic measurements of polymer - surfactant mixtures at pH 7.04 and 10.70, respectively, in 0.4% NaCl. At pH 7.04, the viscosity decreased sharply for 50 days and continued to decline over the entire time interval. Overall, viscosity decreased from 60 to 19 cP at low shear rate, a decrease of 68%. For pH 10.70, behavior was quite similar. After a slight initial increase in viscosity at early time, viscosity decreased sharply during the first 40 days of measurements. Overall, viscosity decreased from 58 to 27 cP at low shear rate, a decrease of 54%. A slight increase in viscosity at early time was measured for all of the mixtures containing polymer and surfactant.

The rates of change in apparent polymer viscosity for polymer-surfactant-oil mixtures are shown in figures 29 and 30. They constitute the results of periodic measurements of polymer-surfactant-oil mixtures at pH 7.07 and 10.73, respectively, in 0.4% NaCl. At both pH values, initial viscosity was lower, and the rate of viscosity decrease was lower than that for the previously discussed polymer-surfactant mixtures. The aqueous phase of the polymer-surfactant-oil mixtures were more homogeneous in appearance, and there was less scatter in the measurements. At pH 7.07, viscosity decreased from 50 to 19 cP over the time interval, an overall decrease of 62%. At pH 10.73, viscosity decreased from 52 to 40 cP, an overall decrease of only 23%.

In 1.2% NaCl, very similar results were obtained for polymer-surfactant-oil mixtures. At pH 6.87, the overall viscosity decrease at low shear rate was from 20 to 8 cP, or 60%. At pH 10.79, viscosity decrease was from 25 to 15 cP, or 40%.

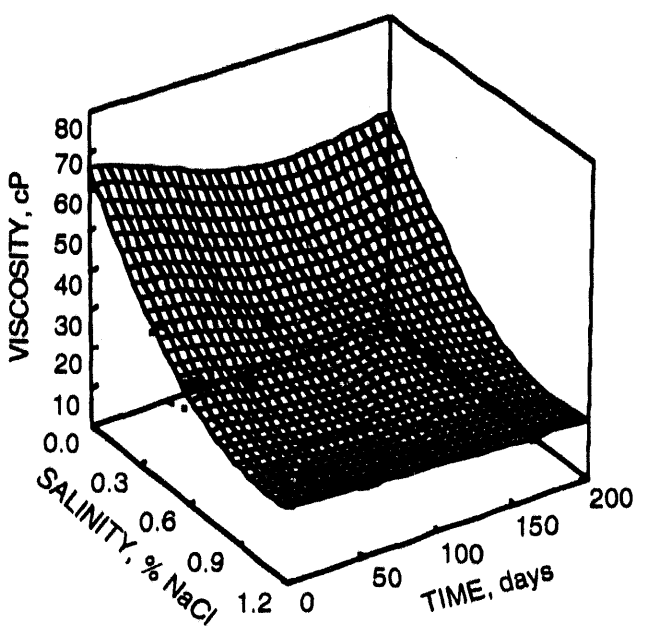

FIGURE 23. - Viscosity of non-alkaline mixtures of 2,000 ppm Alcoflood 1135 polymer and NaCl, 11.5 sec^{-1}, 23° C.

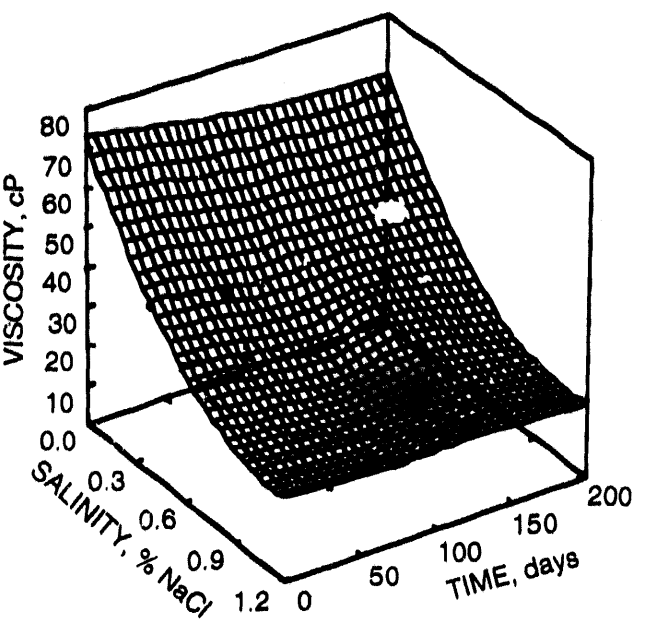

FIGURE 24. - Viscosity of alkaline mixtures of 2,000 ppm Alcoflood 1135 polymer and NaCl, 11.5 sec^{-1}, 23° C.

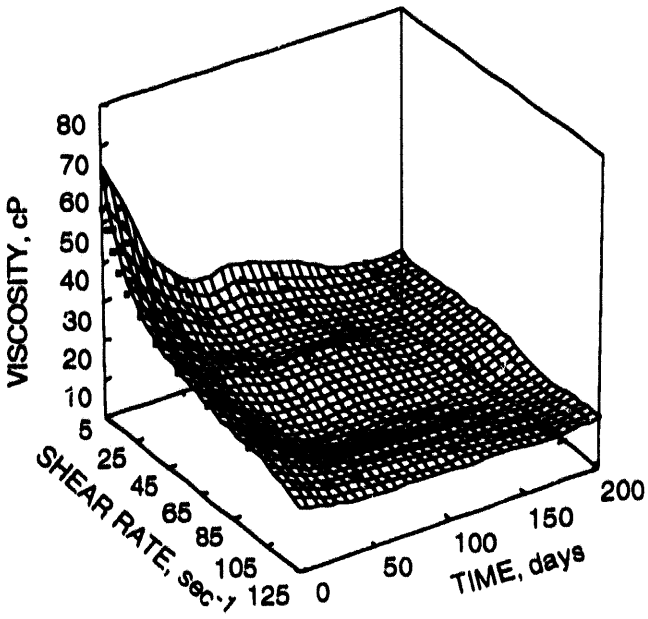

FIGURE 25. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 7.04, 23° C.

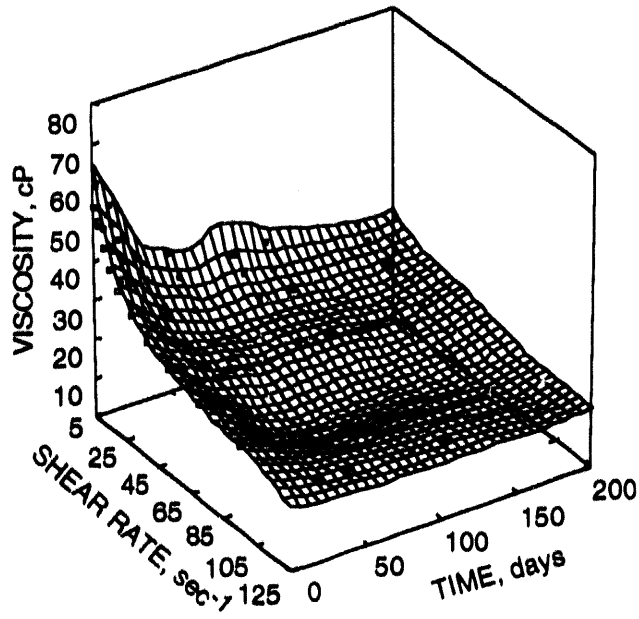

FIGURE 26. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 10.70, 23° C.

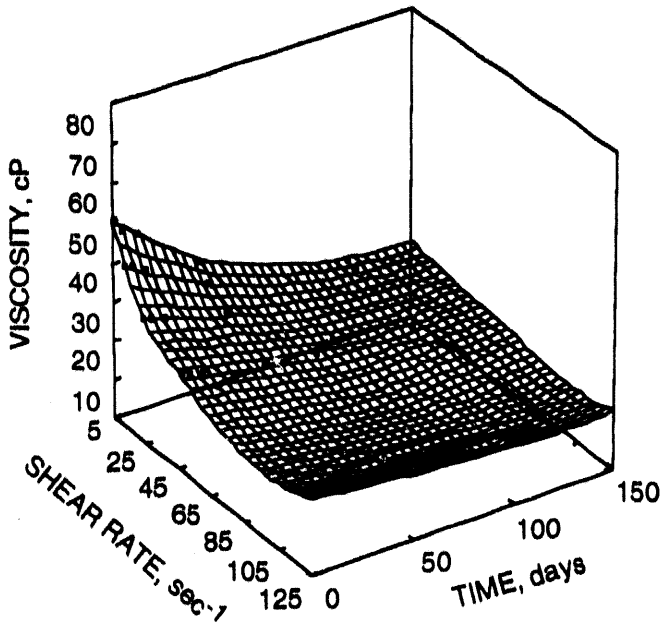

FIGURE 27. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 7.07, 23° C.

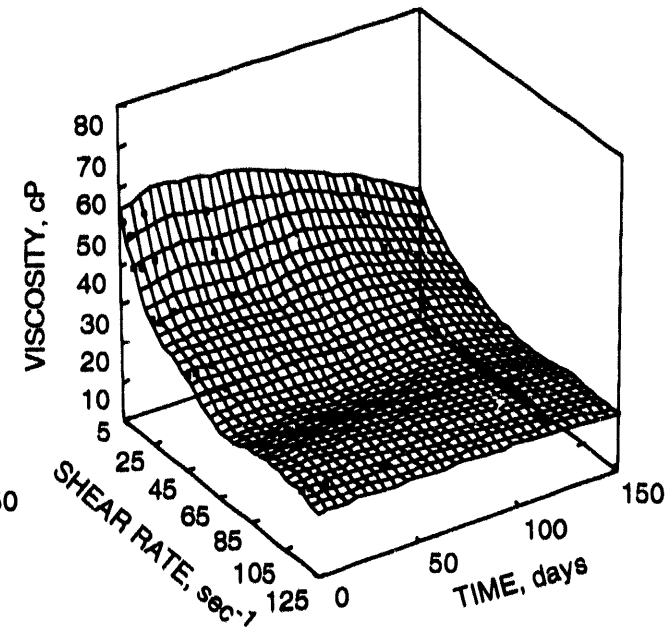

FIGURE 28. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 10.73, 23° C.

The following observations and conclusions were made from results of research performed in FY92.

1. Polymer-surfactant interaction can be expected to have an adverse effect on oil recovery, especially when permeability is low.
2. Polymer-surfactant interaction (phase separation, precipitation, and viscosity loss) occurred between most of the polymers and surfactants that were tested.
3. Polymer-surfactant interaction is difficult to eliminate, and no method was found for completely eliminating interaction.
4. Polymer-surfactant interaction occurred at optimal salinity and below optimal salinity.
5. The magnitude of the interaction was least for non-ionic surfactant and biopolymer.
6. Polymer-surfactant interaction had an adverse effect on polymer rheology.
7. The adverse effect of interaction on polymer rheology was lessened when oil was present.
8. When oil was present, the adverse effect of interaction on polymer rheology was further reduced by increasing pH.

Technology Transfer

NIPER has conducted research on surfactant-enhanced alkaline flooding since 1983. The reservoir screening criteria and other results from this work were utilized for the selection of a field site for testing the process. Design of the chemical formulation was partially accomplished under Project BE4B. The project is designed to demonstrate a successful approach to recover oil from Pennsylvanian Period, Cherokee Group, fluvial-dominated deltaic sandstone reservoirs in oil fields with mature waterfloods. The demonstration project is jointly funded and sponsored by the DOE and Russell Petroleum Company of Chanute, Kansas. Proprietary work on surfactant-enhanced alkaline flooding has also been performed, and this allows NIPER scientists to assist independent oil producers in the evaluation and utilization of surfactant-enhanced alkaline flooding technology.

Publications

The Effect of Polymer-Surfactant Interaction on the Rheological Properties of Surfactant-Enhanced Alkaline Flooding Formulations, by T.R. French and C.B. Josephson. Dept. of Energy Report No. NIPER-635, Oct. 1992. NTIS Order No. DE93000119.

Surfactant-Enhanced Alkaline Flooding Field Project, by T.R. French. Dept. of Energy Report No. NIPER-636, Oct. 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Environmental Investigation of Hepler Field for an Alkali-Surfactant-Polymer Enhanced Oil Recovery Field-Pilot Demonstration Project - Crawford County, Kansas, by W.I. Johnson and T.R. French. Dept. of Energy Report No. NIPER-668. In preparation.

Presentation

Comparison of Analytical Methods for Characterization of a Midcontinent Cherokee Group Fluvial-Dominated Deltaic Sandstone Reservoir, by T.R. French, W.I. Hohnson, R.A. Schatzinger, and L. Tomutsa. Pres. at the Tenth Oil Recovery Conference, Wichita, Kansas, Mar. 10-11, 1993.

MOBILITY CONTROL AND SWEEP IMPROVEMENT IN CHEMICAL FLOODING

Principal Investigators:	Hong W. Gao Troy R. French
BPO Project Manager:	Jerry F. Casteel
Project No.:	BE4C
Funding for FY92:	$200,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objectives:

The objectives of this project are to develop improved methods for maintaining effective mobility control throughout the reservoir in chemical flooding, and to use the permeability modification simulator to design a cost-effective gel treatment using polymer gel systems. Specific objectives in FY92 were to determine the effect of lamination angle on polymer retention and to compare simulation results using NIPER's permeability simulator with field performance on gel treatments.

Research Summary

Successful surfactant/polymer and alkaline/polymer processes rely not only on the effectiveness of chemicals to mobilize residual crude oil but also on the ability of the polymer solution to maintain effective mobility control throughout the reservoir. Maintaining effective mobility control is also important in polymer flooding. If mobility control is ineffective or lost, a less-than-anticipated oil recovery is inevitable. Polymer retention is one of the factors responsible for the lost mobility control. To account for polymer retention, dynamic coreflood experiments with native cores at reservoir conditions should be conducted. Conventionally, the parameters considered for a particular reservoir include polymer concentration, flow rate, and permeability. No research on the effect of mesoscale heterogeneity has been reported. A review of several chemical flood field projects in Class 1 reservoirs revealed that polymer propagation was impeded, resulting in poor mobility control and poor recovery efficiency. Polymer retention in field tests was found to be much higher than that found in corefloods. It was hypothesized that polymer molecules were retained due to entrapment, most probably caused by the intercalation or shale layers known to be present in a fluvial deltaic depositional environment. To reduce layer permeability contrast and to improve sweep efficiency, a permeability modification simulator that has been validated with field performance is useful in designing cost-effective gel treatments.

To determine the effect of lamination angle on polymer retention, a series of corefloods was conducted with three, fired, rectangular Berea sandstone cores in FY92. These cores were cut from the same Berea sandstone block and were cut at 0°, 30° and 90°, respectively, with respect to the direction of laminations. Firing was conducted in an oven at 1000° F for 24 hours. Before biopolymer injection, each core was scanned by computed tomography (CT) to determine the porosity and permeability contrast. Tracer tests were conducted before and after the biopolymer flow to determine how the retained biopolymer affected the fluid advance. A CT scanning method was

used to monitor the advance of the tracer. The polymer solution (1,000 ppm in 0.3% NaCl) used was prepared from Pfizer's FLOCON 4800C. All corefloods and tracer tests were conducted at low flow rates (apparent shear rate was about 10 sec^{-1}) similar to that in reservoirs. Results showed that during polymer flow, core A that had laminations parallel to the flow direction, gave the highest polymer retention, and core B, which had a lamination angle of 30 degrees with respect to the direction of the longest axis, gave the lowest polymer retention. After 8 PV of post brine flood, core A, which gave the highest polymer retention during polymer flow, also gave the highest irreversible retention, and core B, which gave the lowest polymer retention during polymer flow, also gave the lowest irreversible retention. It was concluded that during and after polymer flow, polymer retention is higher in cores that have laminations parallel to the direction of flow than in cores with crossbed laminae. In cores that have crossbed laminae, polymer retention increases with an increase in the lamination angle. One explanation for this was that in core A, some of the polymer that was retained in the low-permeability laminations was by-passed by the injected fluid since the injected fluid did not have to flow across the low-permeability laminations in order to flow through the core. Conversely, in cores B and C, the injection fluid had to flow across the low-permeability laminations. As a consequence, some of the polymer that was retained in the low-permeability laminations was flushed out.

Comparison of tracer tests before and after polymer flow indicated that retained biopolymer has an adverse effect on the stability of the fluid front in cores that have laminations parallel to the flow direction, but is beneficial to the stability of the fluid front in cores that have crossbed laminae.

To simulate and predict oil recovery from field permeability modification treatments using NIPER's permeability modification simulator, field data on permeability modification treatments received from a major chemical company were analyzed, and the site for simulation studies was selected – a 40-acre, five-spot-pattern pilot area. The field is in Claiborne Parish, Louisiana. Hall plots (pressure versus injection rate) showed that an apparent decrease in injectivity was observed in each of the four injection wells after the injection of the polymer gel system, indicating that injection water was diverted to a previously unswept lower-permeability zone. Data from pre- and post-polymer surveys indicated that a significant change in the injection profile occurred in all four injection wells. To simulate this area, additional information, such as the saturation profiles of the four injection wells, PVT data, updated production histories of the five producing wells inside the pilot area and 16 producing wells outside the pilot area, and the rheological properties of gelled polymer, is required. This additional information is being sought from a major chemical company and an independent oil producer who recently acquired this field.

Technology Transfer

Through DOE's technology transfer program, NIPER's permeability modification simulator was released to the public in 1990. Studies on the effects of various process parameters such as the initiation time of a gel treatment, degree of crossflow, and layer permeability contrast on the success or failure of a gel treatment in waterfloods and polymer floods were presented in DOE reports and a journal article and at the SPE/DOE symposium on EOR. These results provided valuable information for oil producers. They can be used to screen reservoirs for cost-effective permeability modification treatments in polymer floods and waterfloods using polymer gels. Because of

public interest in the simulator, a personal computer (PC) version will be developed in FY93 under the Base Program.

Research on the effect of lamination angle on polymer retention was initiated in FY92. Results from this research indicated that lamination angle should be considered in designing a chemical EOR project. These results were reported in a DOE topical report. A Chinese visting scholar under a training program at NIPER assisted in this research.

Publications

Simulation and Prediction of Oil Recovery from Field Permeability Modification Treatments, by H.W. Gao. Dept. of Energy Report No. NIPER-624, 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

The Effect of Lamination Angle on Polymer Retention, by H.W. Gao. Dept. of Energy Report No. NIPER-630, 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Studies of the Effects of Crossflow and Initiation Time of a Polymer Gel Treatment on Oil Recovery in a Waterflood Using a Permeability Modification Simulator, by H.W. Gao, M.M. Chang, T.E. Burchfield, and M.K. Tham. To be published in *SPE Reservoir Engineering.*

Presentation

The Effects of Layer Permeability Contrast and Crossflow on the Effectiveness of Polymer Gel Treatments in Polymer Floods and Waterfloods, by H.W. Gao and T.E. Burchfield. To be presented at the Soc. Pet. Eng. Production Operations Symposium, Oklahoma City, OK, March 21-23, 1993.

DEVELOPMENT OF IMPROVED MICROBIAL FLOODING METHODS

Principal Investigator:	Rebecca S. Bryant
BPO Project Monitor:	Rhonda Patterson Lindsey
Project No.:	BE3
Funding for FY92:	$295,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The continuing objective of this project is to develop microbial technology for improving oil recovery by an integrated research program that includes long-term research, mid-term research and development, and near-term field applications.

Research Summary

NIPER has conducted both laboratory research and field applications in microbial enhanced oil recovery (MEOR) for the U. S. Department of Energy (DOE) since 1983.

Prior work at NIPER has defined the key mechanisms responsible for improved oil mobilization by microbial formulations. The research team began the development of simulation models capable of predicting reservoir and production behavior of MEOR technology. The simulator development and laboratory testing aspects were coordinated, so that a feedback loop existed. Laboratory experiments were conducted to obtain actual data for the simulator in the areas of microbial growth and decay, nutrient consumption, microbial deposition, convective dispersion, and diffusion. Unsteady-state relative permeability data were used to determine the microbial effects on relative permeability and its relationship to oil recovery. After conducting field-scale numerical simulation studies, using data from relative permeability experiments, it was determined that microbial treatment could improve oil recovery over waterflooding alone. Computed tomography (CT) studies demonstrated that gas production by microorganisms in porous media can reduce residual oil saturation in porous media. Wettability experiments were conducted with both water-wet and oil-wet cores. In both cases, it was shown that microbial formulations could alter the wettability to a more water-wet or a more intermediate wettability condition, which was favorable for oil mobilization. This alteration of wettability also reduced the residual oil saturation in the core plugs (figure 29).

Technology Transfer

A key result from the applied research program is the development of an engineering methodology for improving oil production using microorganisms. In 1990, an expanded microbial-enhanced-waterflood field project was initiated in Chelsea-Alluwe field near Alluwe, OK, based upon the data acquired from an earlier pilot project. The expanded project was designed to determine the effects of centralized microbial/nutrient injection in a mature waterflood with producing oil wells in the stripper-well category. The reservoir is a fluvial-dominated deltaic reservoir, typical of Midcontinent sandstone reservoirs, and designated as a Class 1 reservoir by the DOE. As of the end of September, 1992, oil production increased by 13.4% over that of the predicted hyperbolic waterflood decline curve (figure. 30).

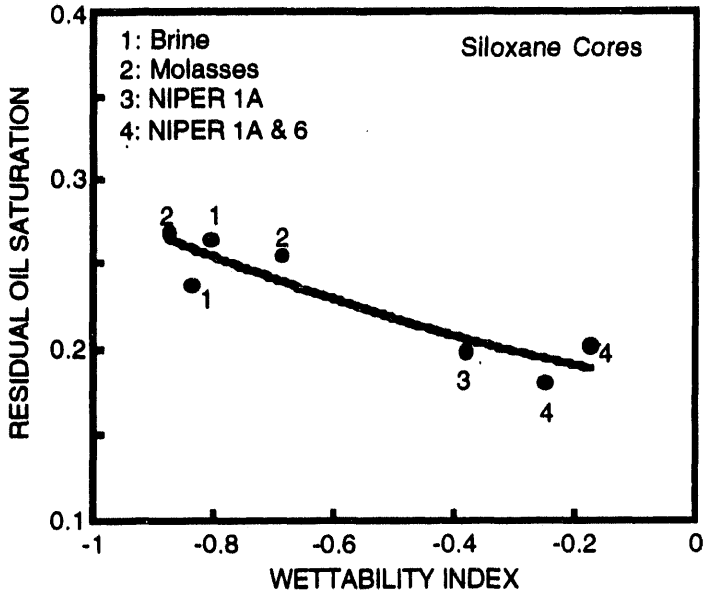

FIGURE 29. - Residual oil saturations in siloxane-treated Berea sandstone cores.

Because of the potential opportunities for independent oil producers to use a cost-effective enhanced oil recovery (EOR) technology, NIPER has presented a series of short courses on MEOR for independent petroleum producers. Approximately 150 independent oil producers, major oil company representatives, and interested participants from other nations have attended these short courses. A MEOR short course was conducted this year in Brazil, and another has been planned for Germany in 1993. A major goal of these short courses is to demonstrate the potential for microbial technology in improving oil recovery from marginal oil wells. In the United States, 73% of all producing oil wells are producing less than 10 barrels per day and are classified as stripper wells. The short courses emphasize the potential for MEOR, yet stress the need for applying the technology properly through careful engineering design for maximum economic return and oil recovery. Some proprietary work on MEOR has been conducted in the WFO Program.

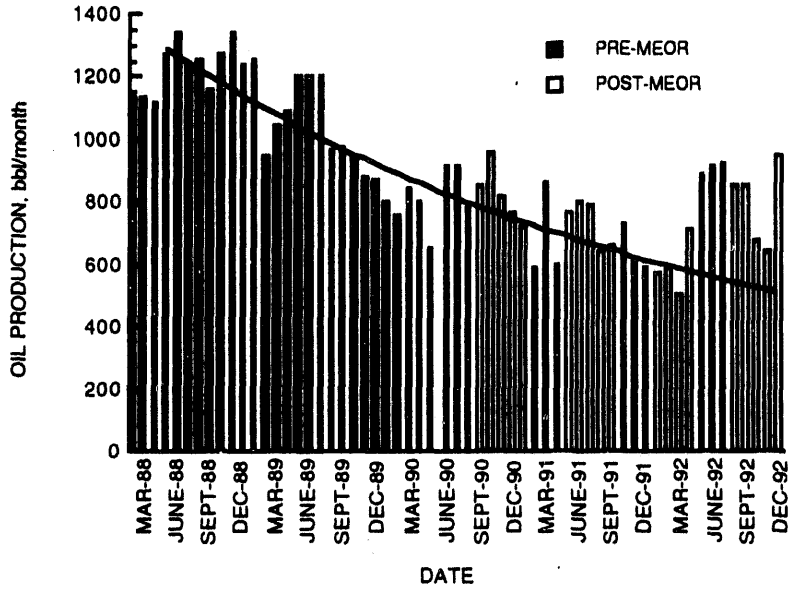

FIGURE 30. - Comparison of oil production with the predicted hyperbolic waterflood decline curve from the Chelsea-Alluwe pilot through September, 1992.

Publications

Parameters Affecting Microbial Oil Mobilization in Porous Media, by A.K. Stepp, R.S. Bryant, K.M. Bertus, and M.M. Chang. Proceedings of the 4th International Microbial Enhanced Oil Recovery Conference, Upton, NY, Sept. 8-11, 1992.

Microbial Alteration of Wettability in Oil-Wet Rock, by A.K. Stepp, R.S. Bryant, and K.M. Bertus. Dept. of Energy Report No. NIPER-618, June 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Modeling and Laboratory Investigations of Microbial Oil Recovery Mechanisms in Porous Media, by M.M. Chang, R S. Bryant, A.K. Stepp, and K.M. Bertus. Dept. of Energy Report No. NIPER-629, Dec. 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Microbial Enhanced Waterflooding Field Pilots, by R.S. Bryant, A.K. Stepp, K.M. Bertus, T.E. Burchfield, and M.D. Dennis. Proceedings of the 4th International Microbial Enhanced Oil Recovery Conference, Upton, NY, Sept. 8-11, 1992.

Laboratory Studies of Parameters Involved in Modeiing Microbial Oil Mobilization, by R.S. Bryant, A.K. Stepp, K.M. Bertus, M.M. Chang, and K.L. Chase. SPE/DOE Enhanced Oil Recovery Symposium, Apr. 22-24, 1992, Tulsa, OK. SPE paper 24205.

Modeling and Laboratory Investigation of Microbial Transport Phenomena in Porous Media, by M.M. Chang, F.T.H. Chung, R.S. Bryant, H.W. Gao, and T.E. Burchfield. SPE paper no. 22845, Annual Society of Petroleum Engineers Technical Conference, Oct. 8, 1991, Dallas, TX.

Presentations

Parameters Affecting Microbial Oil Mobilization in Porous Media, by A.K. Stepp. Pres. at the 4th International Microbial Enhanced Oil Recovery Conference, Upton, NY, Sept. 8-11, 1992.

Microbial Enhanced Waterflooding Field Pilots, by R.S. Bryant. Pres. at the 4th International Microbial Enhanced Oil Recovery Conference, Upton, NY, Sept. 8-11, 1992.

DOE-Funded Microbial EOR Research at NIPER, by R.S. Bryant. Pres. at the DOE Annex XIII Meeting, Upton, NY, Sept. 8, 1992.

Laboratory Studies of Parameters Involved in Modeling Microbial Oil Mobilization, by R.S. Bryant. Pres. at the SPE/DOE Enhanced Oil Recovery Symposium, Apr. 22-24, 1992, Tulsa, OK. SPE paper 24205.

Modeling and Laboratory Investigation of Microbial Transport Phenomena in Porous Media, by M.M. Chang. Pres. at the Annual Society of Petroleum Engineers Technical Conference, Oct. 8, 1991, Dallas, TX.

Thermal and Gas EOR

NIPER's FY92 Base Program research included two projects in the area of gas flooding: one designed to advance the state of the art in miscible gas flooding processes and the other targeted to improved mobility control in gas flooding. Additionally, two projects on thermal recovery were underway with goals of determining the utility of steamflooding for light oil recovery and improving mobility control and sweep efficiency of injectants used in heavy oil recovery.

Gas displacement, miscible or immiscible, accounts for about 30% of commercial EOR production in the United States. Because of its effectiveness, it remains active even when oil prices are low. However, wide application of the technology is hindered by problems of poor sweep efficiency, organic deposition, and uncertainties in the ability to predict recovery efficiency. NIPER is addressing all of these problems in a continuing effort to advance gas flooding technology. Project BE5A is focusing on the development of predictive models to determine when organic deposition might occur in gas flooding due to complex interactions between the crude, reservoir mineral, and CO_2 injectant. These interactions frequently result in the deposition of waxy or asphaltene materials that can cause plugging and other problems in the reservoir, at the wellbore, or in surface equipment. The ability to predict how or when organic deposition might occur can help oil producers design a production strategy to minimize or eliminate these problems. In addition, parameters of DOE's NPR No. 3 reservoirs are being screened to determine if gas EOR methods can be effective in increasing oil recovery.

Although gas flooding is a proven oil recovery method, many technical problems remain to be solved before this process achieves its potential for high recovery efficiency and cost-effectiveness for large-scale application. Many CO_2 field projects, such as Class 2 carbonate reservoirs in West Texas, have experienced early gas breakthrough because of fractures, high-permeability channels, and other reservoir heterogeneities. In project BE5B, NIPER is investigating the application of polymer gels to block these thief zones and prevent early gas breakthrough. The FY92 objectives for this project were to develop gel systems applicable to CO_2 gas flooding conditions and to conduct laboratory experiments to demonstrate the potential for selective placement of gels for profile modification. Using CT-imaging techniques to observe gel placement in porous media, it was determined that a gelant having a low resistance factor would have to be developed if polymer gels are to effectively block high-permeability layers and improve sweep efficiency in CO_2 floods.

NIPER's past and present research in steamflooding EOR addresses those factors that limit production and impact the economics associated with both light oil and heavy oil steamflooding. For both processes, problems of poor sweep efficiency, gravity override, and viscous fingering are common. The research has concentrated on the implementation of cost-effective surfactants for the generation of foams to improve in situ diversion of steam. Through laboratory experimentation it has been determined that high-temperature, foam-forming surfactants can control the gravity override of steam by diverting the steam to unswept regions of the reservoir, and the degree to which this can be accomplished depends on steam temperature, reservoir matrix composition, reservoir permeability, oil composition, surfactant, surfactant concentration, nitrogen flow rate, and liquid/vapor fraction. However, the process parameters required in minimizing steam override are reservoir specific and must be tailored accordingly.

During FY92, project BE11A conducted laboratory studies and provided an analysis of the potential use of foam to improve oil production in the Shallow Oil Zone of DOE's Naval Petroleum Reserve (NPR) No. 1, Elk Hills field, CA, and participated with other U.S. laboratories (Stanford University and Lawrence Livermore National Laboratory) in supporting Annex IV—DOE's cooperative research agreement with the Venezuelan Ministry of Energy and Mines—by presenting thermal EOR research results at two meetings. Working through the SGP and BE11A programs, staff personnel supported the DOE in developing a case history of the steam-foam operations at NPR No. 3, Teapot Dome field, WY. As a result, an SPE paper is being prepared for presentation at the International Thermal Operations Symposium in Bakersfield, CA, Feb. 8-10, 1993. Also, through the SGP Program, NIPER will conduct a symposium on Field Application of Foams, in Bakersfield, Feb. 11-12, 1993.

In project BE11B, screening criteria and DOE's steamflood predictive model were used to screen heavy oil reservoirs in the Nacatoch formation of Arkansas and Louisiana for steam drive potential. A commercial steamflood simulator was used to conduct detailed simulations for both cyclic and steamflooding potential. The study showed that EOR steam processes similar to those successfully applied in California heavy oil reservoirs could be implemented in the Cenozoic and Mesozoic Age sandstone reservoirs of Arkansas. Under two SGP projects, NIPER personnel conducted studies (1) to assess the viability of various steam-foam processes in the field and (2) to assess the heavy oil resource of U.S. domestic reservoirs.

During FY91, work in project BE11B began development of a comprehensive steamflood operators handbook designed to assist engineers and small, independent operators who are familiar with routine waterflood operations but have had little exposure to thermal operations. This manual (NIPER-580) was published early in FY92. The manual explores the concepts behind steam injection processes and provides practical information required in designing, implementing, and evaluating steam processes in the field. Environmental and economic considerations associated with steamflood operations are included.

Individual summaries of the four projects in thermal and gas EOR are presented next. They are addressed in the following order: BE5A, Gas Flood Performance Prediction Improvement; BE5B, Mobility Control, Profile Modification, and Sweep Improvement in Gas Flooding; and BE11A, Thermal Processes for Light Oil Recovery; BE11B, and Thermal Processes for Heavy Oil Recovery.

GAS FLOOD PERFORMANCE PREDICTION IMPROVEMENT

Principal Investigator:	Frank T. H. Chung
BPO Project Manager:	Jerry F. Casteel
Project No.:	BE5A
Funding for FY92:	$250,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The FY92 objectives of this project were to develop improved prediction techniques for asphaltene and wax deposition during gas flooding and to conduct a feasibility study for the application of gas displacement in DOE'S NPR oil reservoirs.

Research Summary

Organic deposition is a common problem in oil production and processing. The mixture of organic constituents deposited is complex and may contain problem components such asphaltenes, asphaltic resins, wax, and some heavy hydrocarbons. The major objective of this research is to develop a better predictive model to describe the precipitation of asphaltene and wax materials. Because experimental results on the characteristics of asphaltenes are inconclusive, modeling and prediction of the phase behavior of asphaltenes may also be inconclusive. Currently available models are inconsistent and ambiguous due to their assumptions and may give incorrect predictions even for well-defined simple systems. The predictive model developed herein is based on thermodynamic principles for solid-liquid phase equilibrium with the assumption that asphaltenes are dissolved in oil in a true liquid state and may precipitate as a result of changing thermodynamic conditions. The model takes into account the effects of temperature, composition, and the nonideal solution behavior of wax and asphaltenes in oil. The developed model has been tested with experimental data for wax formation and asphaltene precipitation. The predicted wax appearance temperature is reasonably accurate when tested with available data. The model not only can match the measured asphaltene solubility data but also can be used to predict the solubility of asphaltene in organic solvents or crude oils. A method of using the model to predict the precipitation of asphaltene in crude oil has been developed. The model is thermodynamically consistent and has no ambiguous assumptions. Accompanying the modeling work, an experimental technique has been developed to determine the solubilities of asphaltenes in organic solvents and crude oil.

Another objective of this research is to make a direct contribution to field EOR development. A feasibility study for the application of gas EOR technology to DOE's Naval Petroleum Reserve NPR No. 3 fields has been conducted. The screening study shows that the gas miscible displacement method is not applicable to NPR No. 3 reservoirs because reservoir temperatures and pressures are too low and the reservoir formation is fractured. However, immiscible CO_2 flooding may be applicable to some reservoirs.

Technology Transfer

Organic deposition has been shown to be a major problem associated with oil recovery by gas flooding. Industry is looking for ways of controlling organic deposition and economic methods that can remedy the problem. A predictive technique is crucial to the solution of this problem, and one of the objectives of this research project has been to develop such a technique. This objective has been successfully accomplished. A generalized model, based on thermodynamic equilibrium theory, has been developed and tested. It is capable of predicting the effects of temperature, pressure, and composition on the solubility of asphaltenes in hydrocarbon solutions and crude oil. It can also predict the wax-appearance temperature and composition with reasonable accuracy. The technique can help industry solve the deposition problem. A paper describing this work was presented at the 1992 SPE Annual Technical Conference and Exhibition in Washington, D.C., Oct. 7, 1992. Because the problem of organic deposition exists now in the field, the paper has drawn considerable interest and attention.

The result of the preliminary screening study for the application of gas EOR technology to DOE's NPR-3 reservoirs has been delivered to DOE.

Publications

Modeling of Heavy Organic Deposition, by F.T-H. Chung. Dept. of Energy Report No. NIPER-555, Jan. 1992. NTIS Order No. DE92001016.

Thermodynamic Modeling for Organic Precipitation, by F.T-H. Chung. Dept. of Energy Report No. NIPER-623, Oct. 1992. NTIS Order No. DE93000103.

Thermodynamic Modeling for Organic Solid Precipitation, by F.T-H. Chung. Proceedings of the 1992 SPE Annual Tech. Conf. and Exhib., Washington, DC, Oct. 4-7, 1992. SPE paper 24851.

Presentation

Thermodynamic Modeling for Organic Solid Precipitation by F.T-H. Chung. Pres. at the 1992 SPE Annual Tech. Conf. and Exhib., Washington, D.C., Oct. 4-7, 1992. SPE paper 24851.

MOBILITY CONTROL, PROFILE MODIFICATION, AND SWEEP IMPROVEMENT IN GAS FLOODING

Principal Investigator:	Clarence Raible
BPO Project Manager:	Jerry F. Casteel
Project No.:	BE5B
Funding for FY92:	$375,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The overall objective of this research is to develop improved gas flooding technology for carbon dioxide (CO_2) floods. Unfavorable mobility control of injected CO_2 can significantly reduce oil recovery and sweep efficiency. Research in FY92 focused on the application and selection of polymers and polymer gels to improve CO_2 displacement processes. The research objectives were (1) to develop experimental models to investigate the selective placement of polymer gels for profile modification of gas flooding; (2) to conduct laboratory investigations to select polymer gel systems which are applicable to gas flooding conditions; (3) to investigate selective placement of polymer gel systems using experimental models for profile modification; and (4) to use a three-phase simulator to investigate the effect of polymer gels on gas flow profiles.

Research Summary

Successful gel treatments require placement of a gel in high-permeability zones with minimal damage to the adjacent, less permeable, oil productive reservoir. Crossflow into oil productive zones can seriously impair subsequent gas flooding, and linear corefloods do not permit evaluation of effects of crossflow during placement of diversion agents. Therefore, experimental models were developed to investigate the selective placement of polymer gels. These models, made of layered sandpacks with contrasting permeabilities, were used in studying effects of crossflow and location of diversion fluids such as polymers and gel treatments. Also, X-ray computed tomography (CT) imaging was used to visualize and measure location and flow of injected fluids by using fluids tagged with an X-ray attentuator. CT imaging provided a noninvasive method capable of measuring effects of viscous crossflow. Development of a combination of layered sandpacks and CT imaging techniques allowed viscous fluid crossflow of gelled polymer treatments to be monitored and measured within porous media.

Several candidate gelled polymer treatments were investigated to determine their potential for blocking fractures and high-permeability zones thus allowing oil to be displaced from strata of lower permeability. These investigations indicated crossflow was a fundamental constraint in the application of gelled polymer treatments for fluid diversion. Most conventional gel treatments consist of injecting a viscous polymer solution or gelant with subsequent crosslinking of the polymer to form a gel. Results of the gel placement tests indicated the gel would

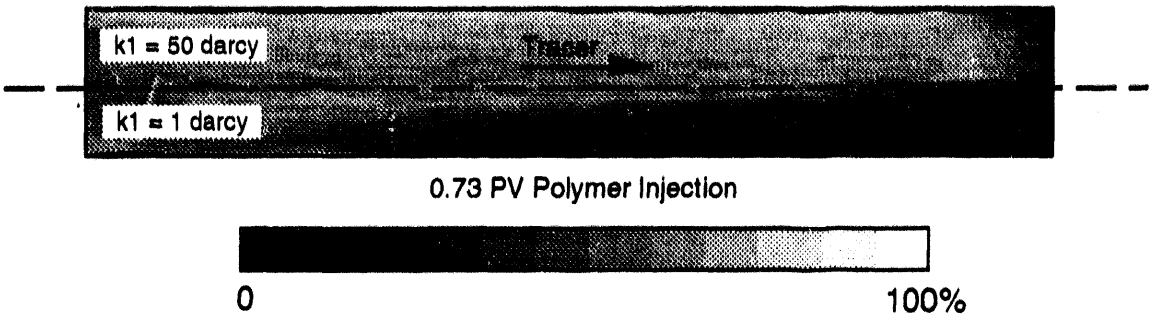

FIGURE 31. - CT cross section of 1,500-ppm biopolymer injection into a layered sandpack with a permeability contrast of 50. The cross section shows the relative position of the polymer solution containing an X-ray tracer after injecting 0.73 PV. For this experiment with a high-permeability contrast, the polymer viscosity was too high for polymer injection without significantly invading the low-permeability layer.

invade zones of lower permeability (due to viscous crossflow) unless there was an extremely high-permeability contrast between layers (e.g., a fracture). An example of viscous crossflow is shown in figure 31.

For this test, a relatively low concentration of biopolymer solution (1,500 ppm) was injected into a sandpack with a high-permeability contrast of 50. Even in this test, with a relatively low-viscosity solution and high-permeability contrast, over 50% of the low-permeability sand layer was invaded and resulted primarily from viscous crossflow.

The effects of viscous crossflow were also demonstrated by numerical simulation using NIPER's profile modification simulator. The simulator was used to investigate gelant placement and viscous crossflow with multiphase systems. Simulation studies indicated polymer invasion is less of a problem in less-permeable zones having more viscous oils and high oil saturations.

In summary, the FY92 research investigated the application of polymer gels as profile modification agents to selectively plug highly permeable channels in gas floods. The development of experimental models and CT-imaging techniques allowed for observation of gel placement in the porous media. However, polymer gels typically require viscous gelant to be injected, and this results in viscous crossflow and damage to less-permeable zones. These investigations indicate that during viscous gelant placement, the polymer solution will penetrate and damage lower permeability zones which will tend to block subsequent gas flooding. The development of a gelant with a low resistance factor during placement is required for polymer gels to effectively block high-permeability layers and to improve the sweep efficiency of CO_2 floods.

Technology Transfer

As noted in the DOE's AORPIP, advanced gas flooding technology will contribute to increased production of light oil. The development of improved recovery technology has been the major focus of this project. Previous project research has shown that the use of cosolvents can improve oil recovery of CO_2 gas floods. These cosolvent candidates are limited to lower-molecular-weight hydrocarbons such as LPG. FY92 research demonstrated the need

for a low-viscosity gelant to be developed. Proposed FY93 work will continue the development of effective polymer gels as mobility agents for gas flooding. Also, the potential for profile modification by the precipitation of salts will be investigated. The results of this work have been provided to the industrial community through technical publications such as those that follow.

Publications

Improvement in Oil Recovery Using Cosolvents with CO_2 Gas Floods, by C. Raible. Dept. of Energy Report No. NIPER-559, Jan. 1992. NTIS Order No. DE92001017.

Application of Polymer Gels for Profile Modification and Sweep Improvement of Gas Flooding, by C. Raible and T. Zhu. Dept. of Energy Report No. NIPER-632,Oct. 1992. NTIS Order No. DE93000106.

THERMAL PROCESSES FOR LIGHT OIL RECOVERY

Principal Investigator:	David K. Olsen
BPO Project Manager:	Thomas B. Reid
Project No.:	BE11A
Funding for FY92:	$295,000 (EOR-Light Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The FY92 objectives were (1) to develop a procedure and apparatus for measuring dynamic saturation changes in steamfloods using X-ray CT scanning and incorporate temperature and pressure measurements to calibrate a numerical simulator for predictive purposes; (2) to conduct laboratory research in support of NPR No. 3, Teapot Dome (WY) field light oil steamfloods; (3) to conduct laboratory research in support of NPR No. 1, Elk Hills (CA) field light oil steamflooding pilot; (4) to transfer technology developed from this project to others in the field of thermal oil production; and (5) to participate in the Annex IV meetings conducted by the DOE and Venezuelan Ministry of Energy and Mines.

Research Summary

As part of the BE11A application of technology to solve near-term problems and provide support to the Naval Petroleum Reserve oil production program, research was directed toward the analysis of field problems and pursuance of known technology for improving the economics of the two DOE-operated light oil steamfloods. During FY92, the light oil steamflood pilot in the Shallow Oil Zone (SOZ) at NPR No. 1, Elk Hills field, was suspended. Early in the year, however, the NIPER thermal research group was actively pursuing research and cooperation with surfactant manufacturers to find a surfactant capable of generating foam under the existing steamflood operating conditions. The field steamflood was experiencing off-pattern oil production, premature steam breakthrough, and excessive scaling in hot wells. The use of foam was being explored to help reduce steam channeling and to improve sweep efficiency. Although foam generation is most effectively evaluated at reservoir conditions, it was successfully generated in clean quartz sand over a wide variety of flow rates, surfactant concentrations, and liquid-to-vapor ratios. NIPER's laboratory studies had previously shown, in two-dimensional steamflood models packed with SOZ sand and oil, that scaling on the production end was a significant problem. This phenomenon was also observed in the field when the steam broke through to the producer. Because of the high temperature and the high calcium-carbonate content and shell fragments in the SOZ reservoir sand, no surfactant was found that could withstand the high divalent ion concentration and produce an adequate resistance to flow as either foam or emulsion. Figure 32 shows the variation in pressure response (delay of pressure buildup indicative of flow resistance) due to oil composition when the steam injection rate, nitrogen flow rate, liquid-to-vapor ratio, and surfactant and surfactant concentration are the same.

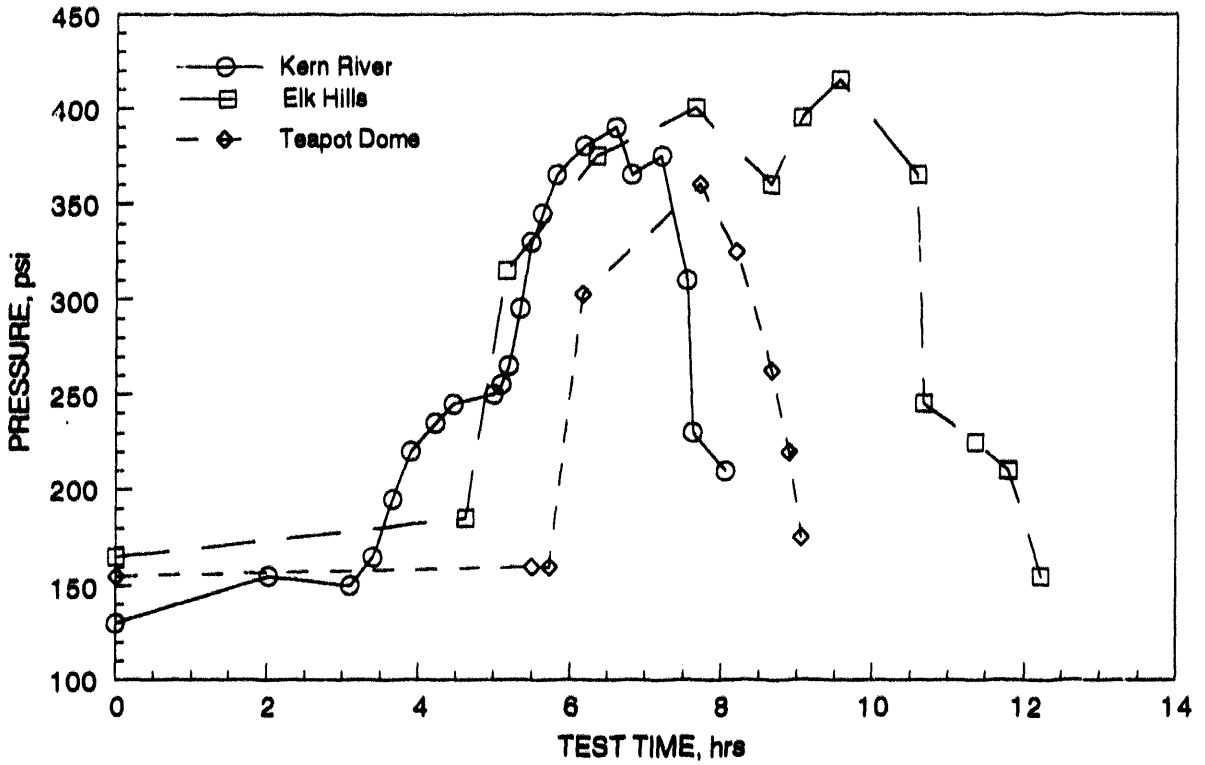

FIGURE 32. - Pressure response during concurrent injection of steam, N_2, and 1% Chaser 1020 into a preheated quartz sandpack in the presence of different oils at residual oil saturation. Backpressure on 1-D sandpack set at 150 psi.

The light oil steamflood in the shallow Shannon sandstone at NPR No. 3, Teapot Dome field (Fig. 33), has progressed to commercial scale with four steam generators flooding 150 acres and a fifth steam generator under construction. The overall objective of the Shannon steamflood is to extend the economic life of NPR No. 3, thus allowing for future development of other producing formations. Research to find suitable commercial materials for use as steam diverters resulted in the identification of two surfactants (Chevron's Chaser 1020 and Shell's AOS 16-18) capable of producing significant flow resistance in one-dimensional sandpacks with Shannon core and oil. Discussions on the progress of the steamflood prompted DOE to fund project SGP52 at NPR No. 3 to assess methods that would improve the sweep efficiency of the steamflood and evaluate the geology in one of the steamflood patterns. Recommendations for remediation treatment of hot wells and a geologic interpretation of pattern 3A were reported to DOE at NPR No. 3. Discussions among DOE, the operating contractor, and NIPER staff resulted in the analysis and documentation of the light oil steamflood case history report with authors from each organization contributing to its preparation. The report is to be presented as SPE paper 25786 at the 1993 International Thermal Operations Symposium, scheduled for Feb. 8-10, in Bakersfield, CA. The paper documents the use of steam to produce light oil (32° API gravity) from a shallow, fractured, very heterogeneous, low-permeability reservoir which defies conventional steamflood screening criteria. Field geology, project history,

FIGURE 33. - Light oil steamflood at NPR No. 3, Teapot Dome field, Wyoming, showing water treatment plant, steam lines, steam injection wells, and producing wells.

pattern design, spacing, completions, operational problems, performance, and economics are detailed. The intent of this paper is to demonstrate how the productive life of many shallow light oil reservoirs may be extended by the application of thermal EOR.

Because of stringent safety requirements, a new location for a high-temperature, high-pressure steamflood laboratory was not approved during FY92. As a result, project staff pursued development of computer data acquisition/control/presentation software that could be readily adapted to laboratory and pilot plant operations. The software was demonstrated at the SPE/DOE Eighth Joint Symposium on Enhanced Oil Recovery in Tulsa and was the subject of a NIPER report. The software and hardware for the steamflood laboratory were tested within the pressure and temperature limitations set by the NIPER Safety Manager.

A symposium, entitled "Field Application of Foam for Oil Production," is being organized under project SGP63. The symposium will be held in Bakersfield, CA, Feb. 11-12, 1993. It will immediately follow the SPE 1993 International Thermal Operations Symposium which will also be held in Bakersfield. The foams symposium is anticipated to draw about 75 international experts who are familiar with field application of foams. The objective of the symposium is to determine the state of the art in field application of foam for oil recovery by providing a forum for information exchange among specialists in the technology. This symposium is expected to enhance the development of the technology through open discussion about the successes and failures associated with the application of foam technologies.

Technology Transfer

NIPER participates with other U.S. laboratories (Stanford University and Lawrence Livermore National Laboratory) in supporting DOE's cooperative research agreement with the Venezuelan Ministry of Energy and Mines (MEM). This cooperative effort has proved to be very beneficial to all participants as it allows for the rapid dissemination of research results, minimizes duplication of effort, combines laboratory and field information, promotes cooperative efforts among researchers at the various laboratories, and provides direction for future research on light- and heavy-oil steamflooding. During FY92, results of NIPER's thermal EOR program were presented at two Annex IV meetings. One meeting was held in Caracas, Venezuela, and the other at Stanford University. A report on the effect of wettability on light oil steamflooding research is to be a part of the Annex IV Proceedings to be published jointly by DOE and MEM.

The results of an analysis of the light oil steamflood being conducted at NPR No. 3 were presented to DOE. Two reports, one on geologic interpretation and one on field practice and processes to increase sweep-efficiency, were prepared and delivered as part of SGP53. The cooperative effort between DOE and its contractors in the analysis of steamflood performance may help increase oil production and recovery from Naval Petroleum Reserve No. 3. Documentation of some of this information was included as part of SPE paper 25786, entitled, "Case History of Steam Injection Operations at Naval Petroleum Reserve No. 3, Teapot Dome Field, Wyoming: A Shallow Heterogeneous Reservoir," which is being prepared for presentation at the International Thermal Operations Symposium to be held in Bakersfield, CA, Feb. 8-10, 1993.

Publications

Preliminary Recommendations for Remediation Treatments to Steamfloods in the Shannon Sandstone Naval Petroleum Reserve No. 3, Teapot Dome Field, Wyoming, by D.K. Olsen. Dept. of Energy Report No. NIPER-591, Mar. 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Analysis of Available Structural and Injection/Production Data in the Steam Generator #3 Area, Shannon Sandstone, Naval Petroleum Reserve No. 3 Teapot Dome Field, Wyoming, by S.R. Jackson, M.M. Chang, and D.K. Olsen. Dept. of Energy Report No. NIPER-602. In preparation.

Results of Task 52 Research on Light Oil Steamflooding, by D.K. Olsen, P.S. Sarathi, S.M. Mahmood, E.B. Ramzel, and S.D. Roark. Dept. of Energy Report No. NIPER-605, July 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Status of Reconstruction of NIPER Steamflood Laboratory, by D.K. Olsen and E.B. Ramzel. Dept. of Energy Report No. NIPER-612, July 1992. Available from DOE Bartlesville Project Office, Bartlesville, OK.

Effect of Wettability on Light Oil Steamflooding, by D.K. Olsen. Dept. of Energy Report No. NIPER-552, Dec. 1991. NTIS Order No. DE92001015.

Evaluation of Surfactants as Steamflood Diverters/Mobility Control Agents in Light Oil Steamfloods: Effect of Oil Composition, Rates and Experimental Conditions, by S.M. Mahmood, D.K. Olsen and E.B. Ramzel. Dept. of Energy Report No. NIPER-554, Dec. 1991. NTIS Order No. DE92001014.

Research Needs to Maximize Economic Producibility of the Domestic Oil Resource, by Min Tham, Thomas Burchfield, Ting-Horng Chung, Phil Lorenz, Rebecca Bryant, Partha Sarathi, Ming-Ming Chang, Susan Jackson, Liviu Tomutsa, and Dwight Dauben. Dept. of Energy Report No. NIPER-527, Oct. 1991. NTIS Order No. DE92001001.

Presentations

Light Oil Steamflooding: A Laboratory Study of Oil Recovery from Oil-Wet and Water-Wet Porous Media from a 2-D Physical Model, by D.K. Olsen, P.S. Sarathi, and S.M. Mahmood. Pres. at the II Latin American Petroleum Engineers Conf., Caracas, Venezuela, Mar. 8-11, 1992.

Light Oil Steamflooding Foams for Steam Diversion DOE/MEM Venezuela, by D.K. Olsen. Pres. at the Annex IV meeting, Caracas, Venezuela, Mar. 12, 1992.

Light Oil Steamflooding at NPR No. 3: Results of Reservoir Characterization, Simulation, and Production Analysis of the Steamflood Area of Teapot Dome, by S.R. Jackson, D.K. Olsen, M.M. Chang, and M.P. Madden. Pres. to DOE at NPR No. 3, Casper, Wyoming, Aug. 27-28, 1992.

THERMAL PROCESSES FOR HEAVY OIL RECOVERY

Principal Investigator:	Partha S. Sarathi
BPO Project Manager:	Thomas B. Reid
Project No.:	BE11B
Funding for FY91:	$200,000 (EOR-Heavy Oil)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The FY92 objectives of this project were (1) to evaluate the Computer Modeling Group (CMG) 'STARS' steamflood simulator, (2) to conduct modeling and reservoir studies to determine the applicability of thermal EOR techniques in the Nacatoch sands of Arkansas and Louisiana, and (3) to collect information/data on the resource and economical recovery of heavy oil from the West Sak reservoirs in Alaska.

Research Summary

A major portion of this project research during FY92 concentrated on defining the thermal heavy oil potential of several fields in southern Arkansas and northern Louisiana, The Nacatoch sands are the principal heavy oil bearing formation in these fields and have been identified (NIPER project SGP37) as one area of the country where there is potential for the development of significant heavy oil production. However, the conventional steam injection process used in heavy oil reservoirs suffers from poor sweep efficiency, and attempts have been made by industry to rectify this situation through the use of foams as a steam mobility-control agent. The technical and economic merits of employing the steam-foam process was evaluated in NIPER project SGP58 since little information on its use in conventional steamdrive reservoirs was available.

Published screening criteria and DOE's steamflood predictive model were utilized to screen the heavy oil reservoirs in the Nacatoch formation of Arkansas and Louisiana and to select reservoirs for further scrutiny. Although several prospects satisfied the steam injection screening criteria, time and manpower constraints precluded an in-depth performance analysis of all the identified reservoirs. Hence, based on the steamflood predictive model performance prediction, the Charivari Creek reservoir was selected for further study.

Charivari Creek is a marginal heavy oil reservoir with thin low-permeability zones and high water saturation. This is typical of many reservoirs in the region. The selection of this marginal heavy oil reservoir permitted the evaluation of the steam injection process in an unconventional heavy oil reservoir and subsequent development of operating strategies. This is in line with the thermal EOR research needs as outlined by Tham et al. in Dept. of Energy Report No. NIPER-527. A commercial steamflood simulator (Computer Modeling Group's 'STARS' simulator) was used to conduct detailed simulation studies.

Both cyclic and steamflood simulations were carried out to test the applicability of a steam injection process in Charivari Creek reservoir. Best-estimate parameters were used for certain unknown reservoir parameters as part of the study associated with steam injection in a marginal reservoir. General levels of performance calculated by the

model were reasonable, and changes noted in temperature, pressure, saturation distribution, and recovery history were believed to be realistic. Only a very preliminary economic analysis of the process was performed to gain some insight into the economics of steam injection in a less than ideal heavy oil reservoir. The economic analysis was based on California development and operation costs.

For cyclic steam simulation, a grid block configuration representing two-dimensional radial flow into a single well was selected. The external drainage radius of the model was set to correspond to the 5-acre spacing. Several runs were made by varying the steam slug size, and the slug size that resulted in the lowest operating costs per barrel of oil produced was selected as the optimum. A base run was performed to analyze the cyclic steam performance in this reservoir. The sensitivities to selected reservoir and process parameters were also investigated.

For steamflood simulation, a 9 x 5 x 5 grid configuration was used to represent the symmetric element (one-eighth) of a 23-ft-thick, 2.5-acre, 5-spot pattern. Several runs were made using different steam injection rates to arrive at an optimum injection rate. The optimum was found to be 250 bbl-steam/d (cold water equivalent) or 4.3 bbl/acre-ft. Both single pattern (a single inverted 5-spot) and multipattern configurations were studied. Sensitivity studies were carried out with respect to well spacing, pattern size, steam quality, and completion intervals. The use of horizontal wells on steamflood performance was also investigated.

The study showed that the reservoir will respond favorably to steamdrive but not to cyclic steaming. The characteristics of low-permeability, thin pay, and low oil saturation are the major reasons for poor cyclic steam performance. Steam stimulation, however, is necessary to improve steam injectivity before the steamdrive. Further, in such marginal reservoirs, conventional steamdrive (i.e., steam injection using vertical wells) would not be economical at an oil price of less than $24.00/bbl, making nonconventional methods necessary under current oil prices. It was found that the use of horizontal well steamdrive technology holds greater potential for economic oil recovery in the reservoir. Although all three horizontal well configurations (horizontal injector/vertical producer, horizontal producer/vertical injector, and horizontal injector/horizontal producer) investigated showed improved recovery performance compared to the conventional (vertical injector/vertical producer) steamflood strategy, the horizontal injector/horizontal producer was clearly the superior. For the cases studied, the conventional steamdrive using vertical wells recovered 53% of the oil in place at an estimated cost of $23.47/bbl, while the horizontal injector/horizontal producer combination recovered 65% of the oil in place at an estimated cost of $15.33/bbl.

Since this study indicated that a steamflood using horizontal wells has good recovery potential in Nacatoch sands, it was recommended that the applicability of horizontal steam injection technology in Nacatoch sands be further investigated.

Steam-Foam-Process Viability Assessment

In addition to the Base Program project, a study is being conducted under project SGP58 to assess the viability of the steam-foam process in the field. The purpose of this study is to analyze the data from selected completed steam-foam pilot projects and to assess under what conditions the process is likely to succeed, both technically and economically. Thus, this study will address the technology transfer objectives of the National

Energy Strategy in that it emphasizes the transfer of a technology that has been partially field tested and demonstrated to recover additional oil economically. A commercial thermal simulator with foam modeling capabilities will be used.

This study was initiated during the third quarter of FY92, and during this period the limitations of the various foam models available in the simulator were evaluated.

Feasibility of Heavy Oil Recovery

The scope of the heavy oil resource assessment for the Midcontinent states of Kansas, Missouri, and Oklahoma was expanded in FY92 to include an assessment of the heavy oil resource for the entire United States. The oil resource and constraints associated with the geological environment, volume of the resource, oil quality, production, transportation, economics, and refining were evaluated. The reason for investigating domestic heavy oil resources and constraints to production is that this resource may offset some of the projected decline in U.S. oil production, as shown in figure 34. (Data for the figure were developed as part of this project.) Heavy oil production in 1990 was estimated by NIPER and is shown in table 5. A series of publications by geographic area were published. Results have been reported in DOE reports, outside publications, and as a series of presentations to DOE and at technical meetings.

TABLE 5. - Estimated Current (1990) Daily Heavy Oil Production

Area	Daily heavy oil production, bbl
Alabama	990
Arkansas	11,300
California	655,700
Kansas	964
Louisiana	11,085
Mississippi	9,055
Missouri	16
New Mexico	2,000
Oklahoma	3,200
Texas	29,530
Wyoming	>18,250
PADD 2 except states above	<250
PADD 4 except Wyoming	2,000
Alaska	>3,000
All other	<1,000
TOTAL approximately 750,000	

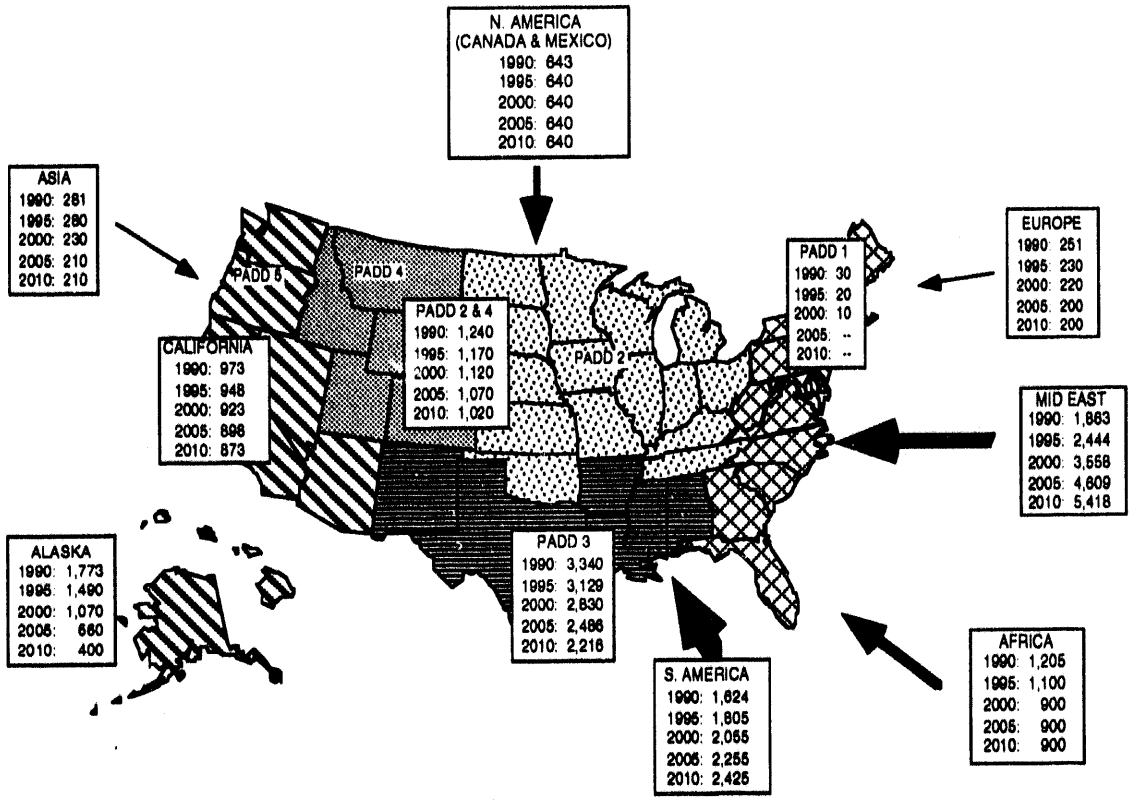

FIGURE 34. - Domestic and imported crude oil (source and volume in thousands of barrels per day) for 1990-2010. Boxes with arrows indicate imports of crude oil and their source and volume. Domestic production is shown in boxes without arrows.

The U.S. heavy oil resource is principally located within two geologic environments, consolidated and unconsolidated sandstones, originally deposited as either fluvial-dominated deltas or as turbidites. Domestic heavy oil is also found in carbonate reservoirs, but oil recovery is difficult and usually uneconomic. The greatest potential for future heavy oil production is in the unconsolidated sands of the U.S. Gulf Coast, and the deeper reservoirs of northern Wyoming. California has the largest heavy oil resource, great potential for additional oil production, and a pipeline and refinery structure are in-place; however, the market is saturated and the cost to transport heavy oil to refiners outside the area is uneconomic. With declining Alaskan North Slope production, some increase in heavy oil production can be anticipated in California. However, heavy oil production in California will not grow significantly as imports of medium and light oil from Pacific rim countries and South and Central America will fill the void. Alaska is projected to have the second largest heavy oil resource, although it is still poorly defined. Limited heavy oil is being produced in Alaska, but large increases in production are not expected because of the high production and transportation costs associated with delivery of this oil to the U.S. West Coast where it would compete with California heavy oil.

The U.S. Midcontinent, Appalachian, and Permian Basins have heavy oil in older formations that are principally consolidated. Over 30 years of field tests in the Midcontinent have shown that economic heavy oil

production is either very low volume (<2 BOPD/well) or from the few unconsolidated, dipping formations where thermal oil recovery (steam) methods are used to produce limited amounts of heavy oil (<10 BOPD/well).

The U.S. Gulf Coast, and its Tertiary-Age unconsolidated sandstones, represent the area of greatest potential for significant future production of additional heavy oil. These reservoirs are more like California heavy oil reservoirs (unconsolidated, thicker, high permeability and porosity) than other lower 48 states heavy oil reservoirs. However, they are generally thinner and have been undeveloped because there was plenty of light oil in the region. The oil is usually of higher quality than asphaltic California heavy oil; and, therefore, should bring a higher market price. The U.S. Gulf Coast refineries have the largest capacity outside of California to process heavy oil. The Gulf Coast lacks heated pipelines for heavy oil transport; however, sufficient light oil is available for dilution of heavy oil to make pipeline transport feasible.

The impact of projected increased domestic heavy oil production from more than 500 heavy oil reservoirs was identified by production levels and general area of production as part of this work. This information was then used to make estimates of the impact of future production on the U.S. refining industry and the cost to achieve acceptable refining capacity. The cost of constructing refining units capable of accommodating an additional 930,000 bbl/d of heavy oil (projected upper limit) was determined to be 7 billion dollars.

Heavy Oil Resources of Alaskan North Slope (West Sak) Reservoirs

As part of a Nationwide assessment of the feasibility of heavy oil recovery, an in-depth analysis of the heavy oil resources in Alaskan North Slope reservoirs was performed, and it was found that significant heavy oil exists in Alaska and is being produced in limited volumes. However, the technical and environmental constraints, and the high cost of transportation to refineries on the U.S. West Coast make the economics unfavorable for increased production. The detailed results of this study are included in Dept. of Energy Report No. NIPER-610.

Technology Transfer

Research performed under project BE11B has shown that steam processes similar to those successfully applied in California heavy oil reservoirs can be successfully implemented in the Cenozoic and Mesozoic Age sandstone reservoirs of Arkansas. These heavy oil resources represent a good future source of domestic liquid fuel and can make a substantial contribution to domestic crude oil production, if exploited. The current research, by identifying the reservoirs amenable to steamflood and the techniques to be followed for economic exploitation, encourages operators to try a proven recovery technique not previously attempted.

Research performed under project SGP37 has identified the U.S. heavy oil resources to include new production opportunities as well as constraints to production, transport, and refining. In addition to making this information available to independent operators, it provides background material for the DOE in making its assessments and targeting research to address the development of the Nation's heavy oil resource.

The recently published document "Practical Aspects of Steam Injection Processes, A Handbook for Independent Operators," published as Dept. of Energy Report No. NIPER-580, was designed to support DOE in the

transfer of steam injection technology to independent operators. This publication was well received by the industry. Several hundred copies of the handbook were distributed to universities in the United States and Canada for use as a thermal EOR textbook.

Publications

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Heavy Oil Production in California: Effects of Compartmentalization and Other Geological Structures, by W.I. Johnson, D.K. Olsen, and A.R. Strycker. Pres. at the ACS National Symp. on Exploration, Characterization, and Utilization of California Heavy Fossil Fuel Resources, San Francisco, CA, Apr. 8, 1992.

IV. FUELS RESEARCH

The Fuels Research (FR) Department continues to develop procedures for the identification of individual compounds and classes of compounds in petroleum and alternative feedstocks, to measure and correlate thermodynamic properties of organic materials, and to determine the performance and emissions of fuels burned in engines. The research supports DOE's AE&PT Program that has responsibility for the cross cutting fundamental and exploratory research related to the evaluation, extraction, processing, and upgrading of oil, gas, oil shale, tar sands, and underground coal gasification resources. NIPER's work encompasses the entire realm of liquid and gaseous fuels—from the time they are extracted, through processing, to commercial utilization. Research within the department is funded about one-third each by DOE, other government agencies, and industry.

FR's Base Program projects focus on the identification of compounds that cause problems in processing of heavy crude distillates, the determination and correlation of thermodynamic properties of organic compounds in heavy and alternative crude oils, and processing options to more efficiently use the heavy feedstocks found in this hemisphere. Although there are only two Base Program projects, they act as the nucleus for the entire realm of work by providing support to the fundamental research in the areas of advanced instrumentation, analytical methods development, and thermodynamic properties measurement. Research in these areas has been ongoing for well over half a century at the Bartlesville Center, first in the analysis and measurement of light petroleum and now the heavier crudes. That research on light, sweet crudes has enabled refineries to maintain efficiencies of over 95%. It is imperative that we develop data for the heavy crudes and heavy ends of lighter crudes to enable efficient processing of those available feedstocks to transportation fuels.

The Fuels Engines Section is comprised of a research team studying the interactions of fuels and the effectiveness of additives on engine performance. As engine parameters change, both fuels and additives must be adapted to maintain efficiency and performance. Reformulated fuels, alcohol fuels, and even natural gas present challenges to engine systems designed for different fuels. Efficiency, performance, and emissions all change with changing engine, fuel, and additive interactions. Although there is no Base Program in this area, the research is synergistic with the other work and provides information on the overall acceptability of present and future transportation fuels. NIPER's laboratory routinely conducts evaluations on parameters such as engine performance, engine wear, and emissions from the burning of diesel fuels, reformulated gasolines, and alternative fuels such as methanol, compressed natural gas, liquefied petroleum gases, and liquid and gaseous fuels from coal.

Processing and Thermodynamics Research

As a result of the shortfall in conventional light petroleum crudes, several refiners throughout the United States are blending small quantities of heavy crudes to refinery process streams. These heavier crudes contain reactive polycyclic aromatic compounds and heteroatom-containing (oxygen, sulfur, and nitrogen) types that cannot be easily converted or removed. Additionally, many refiners are resorting to high-severity conversion processes to utilize more of the residual materials in the production of transportation fuels, especially when the demand for residual fuel oil is low. The use of heavier crudes causes more problems in the refinery and makes it more difficult

to meet current and projected clean air standards. Many small refineries are going out of business because the capital investment needed to meet these standards is beyond their means. Marginal refineries are changing their mix of products by shutting down some of the units resulting in decreased capacity for producing transportation fuels especially from heavier feedstocks. Coking of heavy material is increasing. This is an inefficient process when compared to processing of light crudes and contributes billions of dollars to the deficit as we import more oil. This combination of increasing amounts of heavy components and increased processing severity has created a variety of problems with the resulting fuels including instability, incompatibility when mixed with other fuels, corrosiveness, viscosity increases, and unacceptable engine performance.

The design of processes for conversion of alternative refinery feedstocks into products that can be used as fuels without severe energy penalties and/or harm to the environment requires new thermodynamic data. Although some laboratories have attempted via computer correlations to extend thermodynamic data developed for light petroleum to the heavier crudes, these correlations produce data that can be off by several orders of magnitude when applied to the design of processing streams and result in billions of dollars being needlessly spent on process equipment. NIPER's approach is to build correlations for a given class of compounds based on the extrapolation of data from a selected group of highly purified compounds within that class. These correlations provide the type of precise thermodynamic information needed in calculating optimum conditions required for economic conversions.

The series of heavy components under study were selected from an assessment of thermodynamic needs conducted in 1986 and updated for the DOE in June of 1990 with a five-year planned approach. The priority classes of compounds selected included organic nitrogen compounds, diheteroatomic compounds, organic oxygen compounds, and organometallic compounds. Since 1986, the majority of work has been on the nitrogen and diheteroatomic compounds as they were given first priority. The nitrogen work was completed during FY91; the diheteroatom work is scheduled for completion in FY94.

The summary of FY92 research for Project BFR3 is presented in the following section.

THERMOCHEMISTRY AND THERMOPHYSICAL PROPERTIES OF ORGANIC NITROGEN- AND DIHETEROATOM-CONTAINING COMPOUNDS

Principal Investigator:	William V. Steele
BPO Project Monitor:	William D. Peters
Project No.:	BFR3
Funding for FY 1992:	$350,000 (AE&PT)
Period of Performance:	October 1, 1991 - September 30, 1992

Objective

The continuing objective of this project is to provide, interpret, and correlate with molecular structure and polarity of molecules precise and accurate values of thermochemical and thermophysical properties of organic nitrogen- and diheteroatom-containing compounds that occur in or are readily derivable from heavy petroleum and shale oil. Emphasis is placed on the study of key compounds whose properties are being used in state-of-the-art correlations to predict properties for other compounds that contain the structural features of the key substances. The results will enable the prediction of chemical equilibria for conceptual as well as current processes.

Research Summary

Thermodynamic data are severely lacking for the hetero- and diheteroatomic compounds and polynuclear aromatic compounds found in heavy petroleum feedstocks and ranging through the spectrum of alternate crudes to the products of coal liquefaction. NIPER, through the FE program of cross cutting research, is working to fill these information gaps while assuring the correlations developed from its group-additivity studies are of high quality and suitable for advanced process-design calculations. The group-additivity studies speed acquisition by building correlations for a given class of compounds by extrapolating data from a selected group of highly purified compounds within that class.

The "key compounds" chosen for study in FY92 included: benzo[c]carbazole, benzoxazole, benzothiazole, thianthrene, and phenoxathiin. Measurements (not completed for all compounds) included condensed-phase heat capacities (5-450 K) by adiabatic calorimetry; liquid-phase heat capacities to near T_c by differential-scanning calorimetry; enthalpies of formation by combustion calorimetry; vapor pressures by comparative ebulliometry and inclined-piston manometry (0.02-270 kPa); densities (298-548 K); and critical properties.

A method was developed previously to determine critical properties and heat capacities over a wide temperature range. This technique was used successfully to estimate critical properties accurately (±10 K) for thianthrene and phenoxathiin, both of which decomposed far below (>200 K) their critical temperatures. However, heat-capacity measurements were obtained for each compound until decomposition occurred, extending the range of experimentally determined thermodynamic properties into the region where present commercial heteroatom removal is attempted.

Two high-purity four-ring aromatic, nitrogen-containing molecules were prepared for thermodynamic measurements as a test of correlations developed from information obtained in this project. Measurements were completed on benzo[c]phenanthridine. The complex phase structure observed for this material is expected to be common for large polycyclic compounds, particularly those containing nitrogen as a heteroatom. The complexity of these studies highlights the need for an accurate means to estimate the properties of these materials. A sample of benzo[c]carbazole was purified in FY91, and calorimetric measurements were completed in FY92. That material also showed a complex structure pattern of crystalline phases.

The NIPER thermodynamics research program has advanced continuously on two parallel tracks: (1) The successful completion of state-of-the-art thermodynamic property measurements for key materials and (2) the interpretation of the results of such measurements with emphasis on the design of efficient processes for the removal of heteroatoms in the upgrading of alternate crudes. Property correlations developed within this project provide accurate estimations for gas-phase entropies and enthalpies of formation, which combined yield the Gibbs energies of formation for equilibria calculations to determine optimum reaction pathways. Cross cutting research is to continue as improved thermodynamic data are applied to the efficient processing of all alternate feedstocks.

Technology Transfer

The techniques developed for determining critical properties have been extended to a NIPER project for the quantitative measurement of thermal instability in jet fuels. This capability will allow the design of fuels and fuel-handling systems that will minimize stability problems.

Many oil companies using hydrodenitrogenation (HDN) steps are now looking for a catalyst that will function effectively at relatively low temperatures for the efficient removal of nitrogen from polycyclic aromatic compounds. This results from NIPER's thermodynamic equilibria studies on two- and three-ring aromatic nitrogen compounds (described in Dept. of Energy Reports No. NIPER-544, and NIPER-570 plus earlier reports and journal articles cited therein) that provide convincing evidence that nitrogen can be removed more efficiently from polycyclic aromatic compounds at temperatures below 650° F.

The first thermodynamic equilibria studies based on experimental results for a three-ring nitrogen-containing aromatic compound (carbazole) were completed in FY92, and were published as Dept. of Energy Report No. NIPER-570. The report showed that removal of nitrogen from heterocyclic aromatic nitrogen-containing compounds using conventional hydrodesulfurization catalysts, temperatures, and hydrogen pressures results in processing under thermodynamic control with high hydrogen consumption. These results also indicated that HDN of carbazole will be difficult to accomplish even with high hydrogen consumption.

Most petroleum companies do their correlations in-house and use published literature data to add to their base; other companies buy technology and equipment from engineering firms specializing in design correlations and equipment. Literature references indicate that NIPER's data are widely used throughout the private sector.

NIPER does proprietary work on specialized client projects. The data and correlations allow NIPER scientists to benefit these clients by suggesting reaction conditions to optimize results. One such client was able to

triple the desired product yield by changing temperature and pressure conditions within existing reactors to those more favorable to the reaction equilibria being sought.

The research conducted in this program is complemented by other research performed for AE&PT within project SGP49, entitled "Process-Engineering Property Measurements on Heavy Petroleum Components." Present emphasis is on aromatic and hydroaromatic hydrocarbons that are important not only in the upgrading of heavy petroleum but also in processing the whole range of alternate crudes. Therefore, the research is cross-cutting and increases our knowledge across the whole range of future fuel sources. The results from both programs can be applied to the range of fossil fuels from heavy petroleum, through tar sands and oil shale, to the liquefaction of coal.

A portion of the research under SGP49 is concerned with extension of the capability to measure thermodynamic properties to high temperature (towards temperatures generally met in present processing within the refining industry). The results of that research benefit all the other research programs within the thermodynamics group.

A new high-temperature densitometer was designed, built, and tested successfully within the SGP research program. This new apparatus complements the high-temperature heat-capacity and critical property determinations developed previously by project staff. The methods and apparatus are presently being used within projects for industrial as well as governmental clients.

Publications

Thermodynamics of the Hydrodenitrogenation of Carbazole, by W.V. Steele and R.D. Chirico. Dept. of Energy Report No. NIPER-544, Oct. 1991. NTIS Order No. DE91002255.

Hydrodenitrogenation as Increasingly Important Part of Catalytic Hydroprocessing Interlocking of Thermodynamics and Kinetics, by W.V. Steele and R.D. Chirico. Dept. of Energy Report No. NIPER-570, Feb. 1992. NTIS Order No. DE92001040.

The Thermodynamic Properties of 9-Methylcarbazole and 1,2,3,4-Tetrahydro-9-methylcarbazole, by W.V. Steele, S.E. Knipmeyer, A. Nguyen and R.D. Chirico. *J. Chem. Thermodynamics*, v. 24, pp. 245-271, 1992.

The Thermodynamic Properties of Benzothiazole and Benzoxazole, by W.V. Steele, S.E. Knipmeyer, A. Nguyen, and R.D. Chirico. *J. Chem. Thermodynamics*, v. 24, pp. 499-529, 1992.

Related Publications

Determination of Some Pure Compound Ideal-Gas Enthalpies of Formation: The 1989 Project Results, by W.V. Steele, R.D. Chirico, A. Nguyen, I.A. Hossenlopp, and N.K. Smith. DIPPR Project 871. Published in Experimental Results for Phase Equilibria and Pure Component Properties DIPPR Data Series No. 1, pp. 101-134, 1991, J. R. Cunningham and D. K. Jones, editors.

Fuel Chemistry

Since 1918, the Bartlesville Center has been involved in the development of analytical and instrumental procedures capable of identifying individual compounds and classes of compounds found in petroleum distillates. Work between 1948 and 1972 resulted in the development of analytical procedures for the identification of more than 200 individual sulfur compounds in petroleum. During this period, it was found that separating the distillates into acid, base, and neutral fractions greatly reduced the complexity of the sample and simplified subsequent chromatographic and spectral identification procedures. This separation scheme was later used for the characterization of compound types in heavy ends of light petroleum. In 1983, the DOE recommended this work be extended to the separation and identification of constituents in heavy crudes and provided project funding under an earlier Optional Research Program and later under the Base Program (AE&PT funding). This mid-term study was to be made on Cerro Negro (Venezuelan) heavy crude, known to be one of the most difficult to characterize. Subsequent research on this crude resulted in six major publications and a final report published in Jan. 1990 (Dept. of Energy Report No. NIPER-491).

Following completion of the Cerro Negro work in FY90, the direction of the Base Program research was shifted toward a better understanding of the behavior of the various compound classes during resid upgrading. Coking or carbon deposition is a common occurrence in many refining processes, particularly those employed for upgrading distillation residues. Carbon deposits also typically contain portions of sulfur, nitrogen, and metals that are particularly harmful to catalytic processes because they result in the loss of catalytic activity. Catalyst regeneration processes are ineffective in removal of metals codeposited with carbon, and sulfur and nitrogen oxides that may be present in regeneration gases cause difficulties from an environmental standpoint. During FY90 and 91, the relative tendencies of compound classes to form coke and codeposit heteroatoms were determined. It was found, that for a given resid the carbon residue yield and distributions of sulfur, nitrogen, nickel, vanadium, and iron varied appreciably for the various compound classes. This type of information is useful in optimizing refining processes so that the amount and impact of coke formation can be reduced.

A second area of research in FY91 encompassed the differentiation of primary, secondary, and tertiary aromatic amines by acylation under conditions sufficient for quantitative conversion of all nitrogen-hydrogen moieties to the corresponding trifluoroacetyl amide. This conversion permitted the analysis of reaction products by gas chromatography/mass spectral analysis. The methods developed were applied to a diesel range feed and corresponding hydrotreated products. This type of analysis was quite successful and will be used in future work.

Many of the analytical techniques developed as part of this project were used to support other government agencies and industry in solving problems related to fuel instability and incompatibility, and problems in refining specific feedstocks. This included problems in handling light cycle oils generated by more severe processing and the problems in trying to further process these materials or to incorporate them into fuels of the proper boiling range. Identification of compounds that cause problems is imperative to developing refining methods for their conversion to useful products. This chore becomes more difficult as the molecular weight and the complexity of the mixture increases.

FY92 began a 2-year study to determine the coking behavior of compound classes during catalytic cracking. Materials to be investigated will be selected from Brass River, Maya, Lagomedio, Merey, and Wilmington resids. Studies were also scheduled to improve the analysis of primary, secondary, and tertiary amines in base fractions from petroleum products through chemical derivatization/GS/MS methodology. The results of the FY92 research for project BFR2 are presented in the following.

DEVELOPMENT OF ANALYTICAL METHODOLOGY FOR ANALYSIS OF HEAVY CRUDES

Principal Investigator:	John B. Green
BPO Project Monitor:	William D. Peters
Project No.:	BFR2
Funding for FY 1991:	$300,000 (AE&PT)
Period of Performance:	October 1, 1991 - September 30, 1992

Objectives

General objectives of this project are to identify compounds or classes of compounds with significant positive or negative effects on crude oil and/or product properties and characteristics and to develop methods for their determination in conventional or low grade petroleum and syncrudes.

Specific objectives for FY92 were to determine catalytic cracking behavior of compound classes in petroleum resids, and to complete development of analytical methodology capable of differentiation of primary, secondary, and tertiary aromatic amines in petroleum products and refinery streams.

Research Summary

Initial efforts in catalytic cracking were expended in setting up the apparatus and establishing appropriate experimental conditions. Modifications to the existing bench-scale catalytic cracking unit were necessary because of the desire to obtain quantitative material balances for sulfur and nitrogen in this work, and because of the high viscosity of the feedstocks employed (>650° F resids). The desired severity of cracking was one that would provide acceptable degrees of conversion, yet not obliterate the effects of feedstock composition owing to extremes of temperature, catalyst/oil ratio, etc. The experimental conditions selected were 521° C (970° F) and a catalyst/oil ratio of 8.5. An equilibrium catalyst from a Phillips Petroleum Company refinery was employed. The modified apparatus generally yielded material balances for total mass, Carbon (C), Hydrogen (H), Nitrogen (N) and Sulfur (S) within 95 to 105%.

Concurrent with the above, feedstocks were prepared from >650° F resids from Wilmington (CA), Maya (Mexico) and Brass River (Nigeria) crudes. Liquid chromatography and distillation were used to prepare the following fractions from each resid: >1000° F strong acids, strong bases, weak acids and weak bases; 650°-1000° F total acids and total bases; and >650° F neutrals and sulfide-free neutrals. Each of the acid and base fractions were blended back into aliquots of the >650° F neutrals to obtain blends of about 15% acid/base:85% neutrals.

The resulting blends, whole neutrals, sulfide-free neutrals, and the whole resid from Wilmington crude were cracked at conditions specified above. A minimum of three runs was conducted for each feed. Gas, liquid, and solid (coke) products from each run were analyzed independently; the resulting analytical and run data were entered into a computer program written to calculate material balances and other run parameters. Results from repetitive runs for each feedstock were combined to obtain averages and statistical data for each feedstock. Results from periodic runs

with a conventional gas oil feedstock were used to check for any systematic variations in performance of the catalytic cracking unit or in results from the various analytical procedures.

Analysis of the Wilmington data is still in progress. Preliminary conclusions are listed below. Total coke yield from all feeds is linearly related to microcarbon residue. The y-intercept of this plot indicates catalytic coke (coke formed via catalytic rather than thermal reactions). Gasoline yield is suppressed by basic compounds; the degree of suppression increases with their boiling point (molecular weight). Gasoline composition is highly dependent on the concentration and types of polar compounds present. A significantly higher proportion of the nitrogen initially present in acidic forms (carbazole, etc.) carries over into liquid products than that initially present in basic forms (quinoline, etc.). Sulfide sulfur converts to H_2S to a greater extent than thiophenic S.

Cracking experiments on four additional sets of feedstocks are planned for next year. Also, the concentration dependence of product slate and gasoline composition on selected types of polar compounds will be determined. Also, the existing apparatus will be modified to improve run to run repeatability, via incorporation of an automatic feed-injection device and other refinements.

Development of methodology for GC/MS analysis of aromatic amines was completed and a report prepared. The key feature of the method is its capability to differentiate primary, secondary, and tertiary amines; since, using the conditions described in the report, most primary amines add two and secondary amines add one trifluoroacetyl group. In general, tertiary amines do not react. Since conventional trifluoroacetylation procedures introduce only a single trifluoroacetyl group into both primary and secondary amines, the procedure reported here improves GC/MS identification of the relatively large number of isomers of nitrogen compounds found in petroleum or similarly complex mixtures. For example, using exhaustive trifluoroacetylation, it is possible to differentiate isomeric forms of $C_9H_{11}N$ (e.g., cyclohexenopyridines, aminoindans, 1,2,3,4-tetrahydroquinoline and tetrahydroisoquinolines).

Examples of the application of the method to petroleum and coal liquid products are provided. Because of the limited thermal stability of the derivatives of primary amines, the method is applicable only to distillates boiling below 370° C (700° F).

To expedite utilization of the method by others, GC retention indices and relative GC/MS total ion current response factors for 102 trifluoroacetyl derivatives are included in the body of the report and their 70 ev mass spectra are reported in an appendix.

Technology Transfer

Four papers were presented describing application of analytical techniques partly or wholly developed under this project to fuel stability problems and sludge formation during long-term crude oil storage. That work was funded outside of this project. In addition, a summary of the work done on coking tendencies of compound classes in petroleum resids performed in FY90 and FY91, was also presented.

A liquid chromatographic method developed earlier under this project was adapted by the Strategic Highway Research Program for determination of compound types that significantly impact asphalt performance. The procedure utilizes ion exchange resins to separate acids, bases, neutrals and amphoterics. This, and other methods

developed under the project, were applied in-house in proprietary projects for industrial clients. In-house application of methodology for industry is a very effective means of technology transfer, since the client sees original data from the method and how it applies to a real-world problem.

Publications

GC/MS Determination of Amines Following Exhaustive Trifluoroacetylation, by J.S. Thomson, J B. Green, T.B. McWilliams, and S.K.-T.Yu. Dept. of Energy Report No. NIPER-680. In preparation.

Compound Class Separation of Petroleum Resids: Relating Coke Yields and Heteroatom Content to Chemical Structure, by J.B. Green, G.P. Sturm, Jr., J.Y. Shay, J.A. Green, J.W. Reynolds, L.L. Young, and M.E. White. Preprints, Am. Chem. Soc., Div. Petrol. Chem., v. 37, No. 3, 1992, pp. 956-968.

Presentations

An oral version of the second paper listed above was given at the National American Chemical Society meeting in San Francisco, CA, Apr. 1992.

APPENDIX A - ORDERING INFORMATION FOR REFERENCED PUBLICATIONS

Department of Energy (DOE) publications prepared by NIPER and listed in this Annual Report are individually identified as to availability through either the Office of Scientific and Technical Information (OSTI), the National Technical Information Service (NTIS), or the DOE Bartlesville Project Office (BPO).

Publications identified as obtainable through OSTI and NTIS should be ordered through these organizations. Cost information for the publications (hard copy or microfiche) can be obtained by writing or calling OSTI or NTIS at the following locations:

Office of Scientific and Technical Information
U.S. Department of Energy
P. O. Box 62
Oak Ridge, Tennessee 37831
Telephone No. 615/576-1301

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Telephone No. 703/487-4650

The Bartlesville Project Office maintains a small depository of publications not available through OSTI or NTIS. For information on these publications please contact:

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U. S. Department of Energy
Bartlesville Project Office
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