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

and

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

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005
FOREWORD

Fiscal year 1991 completes the eighth 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 FY91 Annual Report, NIPER-664, covers activities dating from October 1, 1990, through September 30, 1991, as authorized under the approved FY91 Annual Research Plan, NIPER-465.

FY91 marked NIPER's first 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 FY91 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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1. INTRODUCTION

Fiscal year 1991 completed the eighth 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). Research programs at NIPER cover a wide spectrum of specific technical tasks, all of which relate to three broad technology areas: (1) 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. Under the agreement, NIPER's mission has three major thrusts: the first and primary is to perform work for DOE's Office of Fossil Energy (FE) through an approved Base Research Program; second, to conduct research work through a Supplemental Government Program (SGP) for non-DOE government agencies and any additional work for DOE not included in the Base Program; third, to help industrial clients solve their technical problems through a Work for Others (WFO) Program. The Bartlesville Project Office (BPO), which is collocated with NIPER, serves as the DOE administrator of the cooperative agreement.

FY91 marked NIPER's first full year of research under DOE's National Energy Strategy-Advanced Oil Recovery Program (NES-AORP) and Advanced Oil Recovery Program Implementation Plan (AORPIP). The Plan, issued in April 1990, outlines an integrated, highly targeted research, development, and demonstration program focusing on near-, mid-, and long-term objectives to bring new and advanced recovery technologies to the field within the earliest possible time frame. 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 AORPIP details a reservoir classification system identifying reservoir classes having the greatest recovery potential and with the greatest danger of early abandonment. 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 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 an approved Base Program, NIPER provides supporting research in nearly all of the above categories, and the work 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 EPR projects are funded under FE's EOR Light and Heavy Oil Programs. The remaining project (BEI2), 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 strategic goal of environmentally acceptable liquid fuel options. The DOE programs are managed by the 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 FY91 research accomplishments, publications, and presentations for each of the 14 Base Program projects are presented in this report (information on ordering DOE reports prepared by NIPER is provided in Appendix A). First, however, a brief synopsis of NIPER's involvement in certain facets of DOE's AORPIP will be presented.

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1NIPER 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.

2Individual 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
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<th>DOE FE Program</th>
<th>Funding, $K</th>
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1Abbreviations: EOR = Enhanced Oil Recovery; LO = Light Oil; HO = Heavy Oil; AE&PT = Advanced Extraction and Processing Technology
Meeting the Objectives of the AORPIP

In August of 1990, Robert H. Gentile, Assistant Secretary for Fossil Energy, appointed a Task Force to put into place the new AORPIP. One of the first activities of the Task Force, comprised of technical and management expertise, was to gather a consensus opinion from industry, academia, and government on issues relevant to oil recovery from fluvial-dominated deltaic reservoirs which were given Class 1 priority for study under the plan. To address these issues, DOE authorized the formulation of a symposium, entitled "Opportunities to Improve Oil Productivity in Unstructured Deltaic Reservoirs," which was held in Dallas, Texas, in January of 1991. Under the direction of Edith C. Allison, DOE's Manager for Class 1 Reservoirs, NIPER assisted in formulating the program and provided an analysis of the results (DOE/NTIS Rpt. No. DE91002237). The analysis identified several major areas to be assessed in furthering the objectives of the AORPIP: (1) technical constraints affecting resource producibility and the research needed to overcome them; (2) required technological advancements in the areas of reservoir characterization, numerical simulation, EOR recovery processes, directional drilling technology, and data acquisition and analysis; (3) technology transfer; and (4) communication between different segments of industry and the DOE. NIPER's research is supporting the DOE implementation of these Task Force objectives in the following ways:

Identification of Technical Constraints

In October of 1991, NIPER prepared for DOE a 521-page report, complete with references, summarizing individual EOR process constraints, limitations, and additional research needed to maximize the economic producibility of the domestic oil resource (NIPER Rpt. No. 527). Information was gathered from professional society and trade journals, DOE reports, dissertations, and patent literature to determine the state of the art in EOR and drilling technologies. The impacts of EOR on the environment and constraints on the application of EOR due to environmental regulations were also reviewed. An analysis of well-documented EOR field projects indicated that in addition to the technical constraints, management factors could also contribute to lower-than-predicted oil recovery in some instances. One chapter was devoted entirely to the constraints associated with technology transfer, and recommendations for improved information exchange were provided.

Also during FY91, NIPER prepared for the DOE an updated version of a environmental regulations handbook for EOR (NIPER Rpt. No. 546). The environmental regulations handbook was first published in 1981 and updated in 1983. Because of the perceived constraints in meeting environmental requirements, these documents were designed to assist owners and operators of EOR operations by providing introductory knowledge of state and federal laws, rules, and regulations which may have jurisdiction over their permitting and compliance activities. The new handbook was complemented by a NIPER journal article (J. Pet. Tech. v. 43, No. 6, June 1991) that was designed to familiarize practicing engineers and other interested parties with environmental rules and regulations, i.e., air and water quality and hazardous waste disposal, which are of concern when planning thermal EOR processes.
NIPER's thermodynamics laboratory continues research on processing problems brought on by the increased use of heavy crude feedstocks in refinery streams to make up for the shortfall in light petroleum feeds. Because the heavier feeds contain considerable quantities of hetero- and diheteroatomic compounds, polynuclear aromatics, and organometallic compounds—some of which produce reactive components during processing—the production of fuels containing even small quantities of reactive components can cause fuel utilization problems of instability, incompatibility, and gum formation. Thermodynamic properties are being determined, on a priority basis, for those compounds identified as the most troublesome in the refining process and during storage.

Reservoir Assessment and Characterization

One major point widely agreed upon by the Task Force was the importance of reservoir characterization and its relation to data interpretation and effective reservoir management. NIPER is supporting this area through Base Program research and has been involved in developing techniques to predict reservoir variations and in assessing and characterizing reservoirs since 1983. In FY86, a microtidal barrier island system at Bell Creek (MT) field was selected for study. From this work, a combined quantified geological/engineering model was developed and used to identify the types and scales of heterogeneities in the shoreline barrier system at Bell Creek. Based on this model, the influence of various heterogeneities on fluid flow and hydrocarbon trapping was investigated.

To broaden the geological and engineering understanding of comparative aspects of shoreline barrier reservoirs, and to improve the methodologies, a mesotidal shoreline barrier at Patrick Draw (WY) field was selected for study during FY90. By incorporating the Patrick Draw field model into the generalized barrier island model, the product became more broadly applicable. The FY90 work focused on determining the fundamental relationships between geological, petrophysical, and reservoir production/injection characteristics. Another objective was to determine more efficient and economical reservoir characterization and simulation methodologies for shoreline barrier/barrier island reservoirs.

During FY91, characterization of the mesotidal system at Patrick Draw field continued, primarily through work in three areas. First was the continued improvement and quantification of the geological shoreline barrier model for Patrick Draw field. The second area included construction of the engineering model for Patrick Draw through quantification of reservoir characteristics and integration with the geological model. The third area included a geostatistical analysis to aid in estimating interwell reservoir properties in Patrick Draw. This activity provided an opportunity to investigate the strengths and weaknesses of different geostatistical techniques.

Although barrier island reservoirs were chosen as candidates for study several years before the decision was made to classify fluvial-dominated reservoirs as Class I, they are in the top 10 of priority of classes outlined in the AORPIP. It is anticipated that the methodologies developed from the previous mid-term studies will be applicable to the Class I reservoirs.
Numerical Simulation—Data Acquisition and Analysis

DOE’s Tertiary Oil Recovery Information System (TORIS) was instrumental in categorizing fluvial-dominatend deltaic reservoirs as the first (Class 1) in a series of reservoir classes to be investigated. This information system was adopted and validated by the National Petroleum Council in 1984 and has since been maintained and updated by the BPO. TORIS consists of comprehensive reservoir data bases to include field test information resulting from DOE cost-shared and tertiary incentive projects (TIP), reservoir/geological engineering data on domestic oil fields, detailed engineering and economic evaluation predictive models; and reservoir data bases. The analysis of fluvial-dominated deltaic reservoirs was based on 410 such reservoirs within the TORIS system. Although originally targeted to the EOR potential of immobile oil, TORIS was expanded in 1990 to investigate the recovery potential of unrecovered mobile oil as well.

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 the 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 for NIPER. With the expanded emphasis on reservoir-specific research, the requirement for accurate retrieval of reservoir data, based on individual reservoir characteristics, is increasing; and, at the same time, the data are becoming more complex as the number of users increases. Summarized data that are appropriate for modeling are sometimes in conflict with data appropriate for reservoir characterization; thus, the development and implementation of a multi-use reservoir data base management system will be an important future task.

The DOE EOR predictive models are a part of TORIS and are used in most major studies. The credibility of these studies is based on the statistical accuracy with which the model can duplicate the results of numerous EOR projects. Since histories of some projects are difficult to obtain, no statistical application of the modeling results has been made. However, such an analysis is now possible for the incentive projects using data acquired by NIPER over the past 10 years.

In addition to the support for TORIS, NIPER researchers have developed a number of improved simulators based on the BOAST black oil simulator which is available in the public domain. Several major oil companies are now using NIPER’s BEST simulator (modification of BOAST) and BEST VHS (vertical/horizontal/slanted well) simulator. The newest simulator, PC-BEST is based upon the above simulators but contains a number of enhancements. The PC version is operable on a personal computer and enables sophisticated simulation of petroleum reservoir problems at a fraction of the cost of commercial simulators. It is ideal for the consultant, independent producer, or field engineer. NIPER’s BEST-GEL simulator, also recently developed, is a unique tool that enables sophisticated simulation of gel/polymer floods in heterogeneous petroleum reservoirs. It is also capable of modeling tracer tests and can be used to simulate typical field problems and laboratory corefloods for isothermal Darcy flow in three dimensions under three phases: gas, oil, and water. This simulator is particularly well suited to
the consultant, independent producer, or field engineer having problems of early water breakthrough from reservoirs with channeling.

**EOR Recovery Processes**

DOE's AORPIP classifies recovery processes under two categories, i.e., unrecovered mobile oil (UMO) extraction processes and enhanced oil recovery (EOR). Mobile oil is the unswept reservoir oil that remains after water or gas flooding because of barriers to fluid flow, and extraction processes used in its recovery include infill drilling, polymer flooding, permeability profile modification treatments, and selected combinations of these processes. Immobile oil is that trapped in reservoir rock by a variety of chemical and physical forces and cannot be moved by waterflooding. The recovery of immobile oil relies on EOR processes such as the injection of miscible gases, chemicals, or heat.

NIPER's improved oil recovery research covers both EOR and UMO processes, and the work focuses primarily on advanced technologies which DOE defines as methods presently undergoing laboratory and/or field testing but yet not widely available for commercial applications. NIPER's Base Program research is designed to overcome technical and economic constraints and to improve the predictability and performance of EOR processes. The program has combined efforts directed at DOE analysis and planning activities, support research, and field work. It provides (1) phased field analyses that identify near-term opportunities for operators and the needs for risk reduction for mid- and long-term opportunities, (2) application of technical advances to specific reservoirs, (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 analysis and supporting research work by NIPER and other organizations.

**Technology Transfer**

The Task Force elaborated on the importance of technology transfer between research organizations, industry, and the states in meeting mid- to long-term objectives of the AORPIP. NIPER is fully aware of this need and makes contributions of technical information by way of the client programs; through technical publications and presentations; sponsoring and cosponsoring symposia, meetings, and conferences; supplying data base support and development to both DOE and industry; redesigning and improving reservoir simulators; participating in related professional society and association activities; cooperating with other oil-producing countries through DOE-sponsored programs; and working closely with independent oil producers through the SGP and WFO Programs.

During FY91, assistance was provided the DOE in formulating the Third International Reservoir Characterization Technical Conference scheduled for November 3-5, 1991, in Tulsa, Okla. The proposed agenda for this meeting included an opening address by Dr. Donald A. Juckett, director of the DOE Office of Geoscience Research and luncheon addresses by Denise Bode, president of the Independent Petroleum Association of America (IPAA) and Farouk Al-Kasim, consultant, Stavanger, Norway. Tutorials were scheduled for presentation by Noel Tyler and Robert Finley of the Bureau of Economic Geology, University of Texas at Austin; Mohan Kelkar,
University of Tulsa; Jack Caldwell, Schlumberger; and Lawrence Teufel, Sandia National Laboratories. Over 240, scientists, engineers, and oil producers were expected to attend this conference.

During May and June of 1991, NIPER’s FR Department performed an evaluation on 22 light-duty pickup trucks involved in the Society of Automotive Engineers’ Natural Gas Vehicle Challenge. Determinations were made on combustion emissions, fuel consumption, vehicle starting at -5°F, and vehicle safety. The Challenge offered college students the opportunity to show their engineering skills in converting standard gasoline engines to dedicated natural gas operations. Other functions of the Challenge were performed by Argonne National Laboratory and the Oklahoma Energy Center at the University of Oklahoma.

NIPER’s capabilities in monitoring gas-powered vehicles and dual-fuel, gas-gasoline powered vehicles are also being extended to the field. Studies are underway on a portion of the 186 dual-fuel vehicles at Tinker Air Force Base and a representative number of the 52 gas-powered vehicles of the Tulsa (OK) School System. In addition to vehicular testing, NIPER is providing technical assistance to Oklahoma’s Tri-County Technical School (Washington County) which is developing a course for CNG (compressed natural gas) certification.

NIPER’s Petroleum Product Surveys provide fuel property values that are significant both in the manufacture of fuels and in the design of nearly all types of end-use equipment, from small heaters and boilers to jet engines. Biennial reports on motor gasoline (winter and summer) and annual reports on aviation turbine fuels, heating oil, and diesel fuel oils are distributed to some 700 clients which include fuel manufacturers, fuel marketers, designers of heating systems, the military, and consultants. This statistical information is useful in forecasting fuel quality, compiling local and national averages of fuel properties, and supplying the data base needs of various regulatory agencies. These surveys have been conducted at the Bartlesville Center since 1918 and were funded by the DOE and its predecessors for several years; however, the data base is now self-sustaining through a multiclient program established in 1986. The American Petroleum Institute has contributed to this program through the years and continues to provide program guidance.

In FY91, the research program accounted for more than 62 publications by NIPER authors, of which 50 were submitted to DOE as program deliverables. The remaining 12 reports were published either in technical journals or symposia proceedings and resulted from information and data acquired from a combination of Base, SGP, and WFO research. On a quarterly basis, newly developed data generated through the Base Program are provided to the DOE for inclusion in its publication, “Quarterly Progress Review of Research on Enhanced Oil Recovery.” This report is disseminated by the DOE to more than 2,400 recipients, including major oil companies, independent operators, service companies, consultants, and universities. Approximately 250 copies of the report are distributed internationally.

In addition to the publications, staff scientists and engineers presented over 20 technical papers at national and international symposia. Participation in such meetings is an essential part of continued progress in developing state-of-the-art technologies and promotes technology transfer. On an international scale, NIPER’s research is supporting DOE’s cooperative research agreement with the Venezuelan Ministry of Energy and Mines through biennial meetings of Annex IV participants. Presentations at these meetings are carefully evaluated as to content and are used to
provide direction for future research in light- and heavy-oil steamflooding. Other organizations participating in Annex IV include INTEVEP, Stanford University, and Lawrence Livermore Laboratories.

**Improving Communication Between Industry and the DOE**

In addition to the interactive communication that results from normal research operations and participation in meetings, conferences, and symposia, etc., NIPER is conducting research on numerous projects jointly funded by DOE and industry. Most of these projects are currently performed under the SGP program and have proved to be beneficial to all participants in that they allow for the rapid dissemination of information, minimize duplication of effort, promote cooperation, and provide a feedback loop for the identification of problem areas and sectors requiring additional research.

One of the most effective ways to develop industry participation in DOE-related research is through the formation of consortia. This type of activity has been successfully established at NIPER for advancing the state of the art in reservoir-condition, multiphase relative permeability measurements applicable to the study of fluid flow behavior in porous media. In addition to facilitating effective technology transfer, the consortium provides industry and DOE the means to leverage research budgets and ensures that the cooperative research is supporting relevant issues on a priority basis.

Technologies developed in NIPER's laboratories are going to the field. During 1990, an expanded microbial-enhanced oil recovery (MEOR) improved waterflood pilot was initiated in Chelsea-Alluwe (OK) field. The project follows a smaller MEOR improved waterflood pilot in Delaware-Childers (OK) field in which oil recovery was improved by a very acceptable 13% over that from waterflooding alone. For both tests, funding was established as a joint-venture between the DOE and independent oil producers under a SGP project. The expanded pilot project is scheduled for completion during the second quarter of FY93. Both of these field tests are in Class I deltaic reservoirs.

In another SGP field project, jointly funded by DOE and an independent operator, NIPER is to test its alkaline-surfactant-polymer (ASP) flooding technology in a Class I reservoir in Hepler (KS) field. The ASP process results from mid-term fundamental research studies on coalescence phenomena and dynamic interfacial tension behavior which indicated that the addition of a small amount of surfactant to moderately alkaline formulations significantly improved recovery efficiency while minimizing the deleterious effects of alkali-mineral reactions—reactions that occur when fluids are in contact with reservoir rock. If this test is successful, the ability to recover more oil with only a small amount of expensive surfactant should benefit the primary goal of the AORPIP which is to maximize the economic producibility of the domestic oil resource.
II. ENERGY PRODUCTION RESEARCH

In FY91, the Energy Production Research Department (EPR) was responsible for 12 Base Program projects, 19 SGP projects, and 24 projects for clients in the WFO Program. The Base Program research, totally funded by the DOE, 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 or 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 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**

The production of unrecovered mobile and immobile oil requires advances in the ability to predict reservoir heterogeneities and flow paths. Mobile oil is the unswept reservoir oil that remains after water or gas flooding because of barriers to fluid flow. A large portion of the unswept oil is a target for advanced recovery methods, but improved geoscientific knowledge and advanced techniques are needed before petroleum engineers can accurately predict its location. Conversely, immobile oil is oil trapped in reservoir rock by a variety of forces and cannot be moved without chemical or physical stimulation.

Through the years, several different EOR techniques have been attempted in more than 800 oil fields. Many have failed to perform as predicted because reservoir variations and flow paths were not well understood. This lack of understanding of reservoir structure and its effects on fluid flow is the single most important technical problem facing oil producers. In most instances, the rock matrix is not homogeneous; rather, it contains heterogeneities that control fluid flow and determine the degree to which the remaining oil and gas can be recovered. NIPER's four projects in geotechnology are addressing problems associated with reservoir characterization and interrelated studies identifying rock and pore structures and fluid flow parameters of reservoirs through computed tomography (CT) imaging, nuclear magnetic resonance imaging (NMRI), and petrographic image analysis. Studies are also designed to advance the technology in measuring two- and three-phase relative permeabilities at reservoir conditions. Accurate reservoir simulations of potential oil recovery cannot be made without reliable relative permeability data. Geotechnology also provides support to DOE’s Tertiary Oil Recovery Information System (TORIS), where research
is continuing the areas of EOR project and reservoir data base management, EOR project technology trends analysis, and computer simulation.

The FY91 research for EPR's four projects in Geotechnology is presented in the following section. Individual project summaries describe (1) the relationship of the work to the DOE program, (2) important research accomplished during the fiscal year, and (3) process utilization and 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.
Objective

The broad objective of the National Energy Strategy is to reduce U.S. vulnerability to crude oil supply disruptions by expanding domestic oil production capacity and strategic stocks. This goal is addressed by three time-specific objectives that (1) preserve access to reservoirs with high potential that are rapidly approaching their economic limits, in the near-term; (2) develop, test, and transfer the best, currently defined, advanced technologies to operators, in the mid-term; and (3) develop sufficient fundamental understanding to define new recovery techniques for the remaining oil, in the long-term.

NIPER's reservoir assessment and characterization research program incorporates elements of each of these objectives. The shoreline barrier reservoirs under study represent a class of reservoirs, located in mature fields, with large amounts of remaining oil in place but which also contain a high number of shut-in and abandoned wells. To help alleviate the problem of well-abandonment, the characterization procedures and geological and engineering models being developed in the course of this research are designed to provide near-term solutions that will directly benefit independent oil producers and integrated oil companies operating in similar types of reservoirs. For example, as a result of this work, the information needed to reposition water injection and production wells is available to operators to optimize production and potentially prevent further well abandonments. Evaluation of a proposed CO\textsubscript{2} pilot project for an independent operator is also being conducted.

Near- to mid-term applications of methodologies developed in this research can be used in the construction of accurate reservoir models to quantify the effects of reservoir heterogeneities. Long-term results of the research will determine the transferability of reservoir and production characteristics to reservoirs of similar depositional histories. Identification of heterogeneities in these reservoirs will allow application of newly developed reservoir management strategies and advanced recovery methods to maximize recovery efficiency. Because of the similarity between shoreline barrier and some delta-front depositional settings, the scope of future work may be expanded to include a comparison of reservoir heterogeneities from selected delta-related barriers with shoreline barriers.

Research Summary

This research project employs an interdisciplinary approach focusing on the high-priority reservoir class of shoreline barrier deposits: (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 methods to effectively
characterize this class of reservoirs to predict residual oil saturation (ROS) on interwell scales and improve the prediction of the flow patterns of injected and produced fluids.

As in previous years, an interdisciplinary team approach was used to characterize Patrick Draw (WY) field and to compare the geological and engineering models developed with models from Bell Creek (MT) field. Accurate descriptions of the spatial distribution of critical reservoir parameters (e.g., permeability, porosity, pore geometry, mineralogy, and oil saturation) are essential for designing and implementing processes to improve sweep efficiency and thereby increase oil recovery. The scope of the work for FY91 consisted of four main areas: (1) development of quantitative geological and engineering models for Patrick Draw field, (2) comparison of the similarities and differences between the mesotidal shoreline barrier reservoir in Patrick Draw field and the microtidal shoreline barrier reservoir in Bell Creek field, (3) the application of geostatistical techniques such as kriging and fractal analysis to estimate interwell reservoir properties in Patrick Draw field, and (4) the continued development of methodologies for improved characterization of shoreline barrier reservoirs.

In the first area, reservoir and outcrop information was used to construct the quantitative geological shoreline barrier model for Patrick Draw field. Investigations indicate that mesotidal processes (2 to 4 m range) dominated the depositional setting at Patrick Draw field. Mesotidal shoreline barrier deposits contain laterally discontinuous sand bodies and are architecturally more complex than micro-tidal barriers. The work in FY91 provided additional detailed information about the reservoir model for Patrick Draw field.

Two broad permeability and porosity classes can be distinguished according to groups of facies. The higher permeability class consists of tidal inlet, tidal channel, and tidal delta facies and is consistent with the higher depositional energies of the facies. Low-permeability intervals within the high-permeability class appear to be the result of carbonate cementation, detrital clay, and clay cement. A lower permeability class consists of tidal creek, tidal flat, swamp, and lagoonal facies. The relative timing of various carbonate cement phases (such as calcite, dolomite/ankerite, and siderite) plays a significant role in determining rock quality. Early carbonate cements strengthened the reservoir rock, preventing or delaying compaction; however, large amounts of cement drastically reduced the storage capacity of the reservoir sandstones and created permeability barriers affecting fluid flow.

Major depositional features of the Almond formation within Arch Unit, Patrick Draw field that are important to fluid flow consist of: (1) sand-thin areas containing low-permeability sediments made up of oyster coquina, carbonaceous shale, and shaley sand; (2) sand-thick areas containing superior reservoir rock quality; (3) facies with limited lateral extent (10's to 1,000's of ft); (4) coal beds prone to parting and fracturing during fluid injection; and (5) calcite cementsed oyster-shell zones.

Lithologic controls on reservoir quality consist of the relatively high proportion of sedimentary rock fragments within the sandstones (average of 16% of total framework grains) which are highly susceptible to compaction and thus reduce permeability. Structural controls on reservoir behavior include faults and fractures. Interpretation of high resolution seismic sections and log-based structural cross-sections through Arch Unit indicate the presence of faults with vertical displacements of 20 to 50 ft. The orientations and distributions of these faults are
currently being determined. Carbonate-filled fractures in cores have been documented; however, the effect of fractures on production behavior in Patrick Draw field is not well understood at this time.

Lateral compartmentalization within the reservoir is indicated by large contrasts in formation water salinity, with anomalously lower salinities downdip in deeper parts of the reservoir; and an anomalously large decrease of formation pressure during primary production in the eastern (downdip) portion of the reservoir. The mechanisms controlling these anomalies are currently being investigated.

Primary and secondary production/injection data were used to construct the engineering model for Patrick Draw field. Analysis of primary production data indicated that initial production (IP) was controlled predominantly by thickness of the sandstone. However, structural features, such as faults or fractures, undoubtedly played a role in the distribution of cumulative primary production. Channeling and poor waterflood sweep efficiency in Arch Unit were indicated by low waterflood recovery and rapid breakthrough times. Fractures were the suspected conduits to fluid flow because matrix permeability contrasts were not high enough to cause such severe channeling.

The second FY91 objective was to compare the microtidal shoreline system of the Muddy formation with the mesotidal shoreline barrier system of the Almond formation. The results of this comparison indicated Almond formation shoreline barrier deposits have a facies architecture that is characterized by short barrier island segments separated by abundant tidal inlets. Tidal inlet fill, tidal delta, and tidal channel/tidal creek deposits are all well represented at Patrick Draw and in the analogous outcrops. Lateral migration of the tidal inlets is the dominant process leading to formation of a broad belt behind the barrier dominated by tidal delta and tidal channel deposits. The dimensions of facies within the mesotidal system at Patrick Draw field are generally smaller than those for the microtidal shoreline barrier systems at Bell Creek field.

Important similarities found between the shoreline barrier reservoirs in Patrick Draw and Bell Creek fields were: (1) both reservoir systems are compartmentalized on a field scale—Bell Creek field has six major producing units and Patrick Draw field has three; (2) pay thicknesses are comparable—23 ft in Bell Creek and 20 ft in Patrick Draw; (3) initial production in both reservoirs appeared to be strongly influenced by the architecture of the depositional systems, while secondary and tertiary production appeared to be more strongly controlled by structural and diagenetic features; and (4) faults played an important role in both reservoirs and contributed to poor sweep efficiency during waterflooding. Significant differences found between Patrick Draw field and Bell Creek field were: (1) diagenetic processes and timing were different, and in Bell Creek field, early stage leaching created oversized pores and enhanced reservoir quality (average permeability is 2,250 mD, average porosity is 28.5%), while in Patrick Draw field, early stage leaching was relatively insignificant, but later stage cementation by carbonates and clays significantly degraded reservoir quality (average permeability is 36 mD, average porosity is 19.6%); (2) the scale of major depositional heterogeneities differs due to the different depositional processes—in the micro-tidal Bell Creek field, major heterogeneities are on the scale of thousands of feet along the depositional strike, whereas in the mesotidal Patrick Draw field, the scale is commonly tens to hundreds of feet; and (3) the production mechanism in Bell Creek field was solution gas drive, whereas in Patrick Draw field oil production resulted from a strong gas-cap drive.
The mean grain sizes for Muddy and Almond formation depositional facies are similar. Sorting of Muddy and Almond formation sandstones also overlaps; however, Almond facies have a much larger range of sorting than do facies from the Muddy formation. These differences reflect different suites of facies that were created by different intensities of wave and tidal depositional processes. The trend of increased grain size with decreased sorting for both Almond and Muddy formations probably represents a fundamental relationship caused by availability of a wider range of grain sizes for the coarser samples.

The lithological and mineralogical compositions of Bell Creek and Patrick Draw reservoir sandstones are a function of both initial lithologies and diagenetic history. Relatively larger amounts of clay-rich sedimentary rock fragments in the Almond formation make the UA-5 reservoir at Patrick Draw field more susceptible to compaction and reduced pore throat sizes, while the distribution and crystallographic habits of kaolinite and illite in the Muddy formation make the reservoir rocks at Bell Creek field sensitive to the migration of fines during completion and production.

The third area of investigation for FY91 consisted of geostatistical analysis of permeability data of the subsurface (Patrick Draw field) and outcrop shoreline barrier Upper Almond formation. More than 600 permeability data, spaced 1 to 3 in. apart, were measured from an outcrop core. Based on variogram analysis of these data, a vertical correlation length for permeability values was found to be between 18 and 27 ft, which is approximately the thickness of one barrier island depositional cycle. Variograms and cross-variograms developed for permeability will be used for mapping interwell porosity and permeability using kriging and co-kriging techniques.

The fourth area addressed was an investigation of economical methods for shoreline barrier/barrier island reservoir description and simulation (methodology development). Two activities were undertaken: (1) development and testing of a mini-permeameter for application of geostatistical techniques to reservoir and outcrop rock samples and (2) wireline log analysis of the effect of subsurface stresses on fluid production at Patrick Draw. The wireline log investigation of subsurface stresses found that: (1) a good estimation of overburden stresses can be obtained from integration of density log data and (2) at Patrick Draw field, variation of shale resistivity with depth is a function of the amount of water in the pores and is also dependent on the salinity of the formation water.

**Process Utilization and Technology Transfer**

With expertise developed over the past several years, the BE1 project staff has been called upon to conduct additional research for the DOE under the SGP Program. Topics addressed during FY91 were in important areas, outside the scope of the Base Program, that provided research data consistent with objectives of the AORPIP.

One SGP project had the objective of expanding inflow performance relationships (IPRs) to horizontal and slanted oil wells producing from solution-gas drive. The work followed that of Vogel (J. Pet. Tech., Jan. 1968) who developed successful procedures for determining oil well productivity of vertical wells producing under solution-gas drive. In developing IPRs for horizontal and slanted wells, NIPER scientists employed a specially designed vertical/horizontal/slanted well reservoir simulator that allowed the determination of IPRs under a variety of reservoir and well parameters. In addition to the simulation studies, the project scope of work calls for the preparation of a
"User's Manual" for determining IPRs on a personal computer. Both the manual and results of the simulation studies are scheduled for publication early in FY92.

A second SGP project provided the DOE with geological and production characteristics of Class 1, clastic deltaic system reservoirs receiving top priority for study as outlined in the AORPIP. Documentation of this work included a summation of presentations given at a symposium on Class 1 fluvial-dominated deltaic reservoirs and the key points of audience discussion, followed by a literature-based summary of general reservoir characteristics and properties of deltaic deposits. Specific topics included a general review of the sedimentological aspects of deltaic systems; a discussion of reservoir heterogeneities related to deltaic depositional processes and the effect of fluid movement within the reservoir; a review of geological factors affecting recovery in 26 EOR pilot projects; and a description of the average reservoir properties and production characteristics derived from data acquired on 229 fluvial-dominated, unstructured deltaic reservoirs in the Tertiary Oil Recovery Information System (TORIS) data base. The document contained over 300 annotated references on deltaic deposits and reservoirs, which should greatly aid future research on deltaic reservoirs.

The objective of a third SGP project was to determine the degree of hydraulic communication and fluid flow between productive reservoir horizons using naturally occurring stable and radioactive isotopes. The emphasis of the first phase of the project was to conduct a literature review (1) to seek evidence of dynamic conditions and crossflow associated with multireservoir systems, (2) to identify which stable and environmentally acceptable radioactive isotopes were best suited for studying crossflow phenomena, (3) to review successful field applications where crossformational flow was identified by geochemical isotopic techniques, and (4) to identify major field-specific aspects of conjunctural cross-formational fluid migration and mixing in candidate oil and gas fields preselected for demonstrating the method. Results of the study showed that (1) leakage of hydrocarbons between horizons through geologic discontinuities may negatively affect all production stages and (2) the isotopic analysis technique is effective in identifying interformational cross flow in those instances where the use of conventional methods would be difficult and expensive.

A fourth SGP project was established to develop techniques for determining clay content and lithology of sandstone reservoirs from wireline log data. Correlations of log signatures with CT-scan density and measurements from X-ray defraction, scanning-electron-microscopic, and pretographic-imaging analyses were conducted to determine the clay characteristics and the ultimate effect of different clays on the log signatures. Investigations were conducted to determine the role of mathematical and/or statistical calculations of logs in identifying the types and volumes of clay materials present in sandstone reservoirs. Logs were analyzed from Bell Creek and Patrick Draw fields, and the results indicated that the distribution of power in the log data, as a function of frequency (power spectrum), gave high values at low frequencies; and that the characteristic distribution of power with frequency provided a good measure of the overall clay content and lithologic heterogeneities in sandstone reservoirs.

Late in FY91, a new SGP project was initiated to provide technical support to DOE's Naval Petroleum Reserve No. 3 operations at Teapot Dome (WY) field. The objective of this project is to apply NIPER's integrated multidisciplinary approach to reservoir characterization and EOR process design and simulation to enhance oil
recovery in NPR No. 3 reservoirs. Emphasis is to be placed on three primary tasks: (1) use of surfactant additives to improve sweep efficiency in ongoing steamflooding projects in Shannon reservoir, (2) evaluation of the density and distribution of fractures in Shannon sandstone, and (3) orientation of technology transfer mechanisms to ensure effective problem solving, laboratory testing, and data analysis.

**Seminars and Training**

A 3-day field seminar was conducted for three geologists from a major oil company who were interested in Shannon outcrop formations north of Casper, Wyo. NIPER's characterization of these outcrops began in 1985 as part of the research for the DOE-sponsored BE1 project on Reservoir Assessment and Characterization and continued as a 2-year, multi-client, industry-sponsored project "Quantified Spatial Variations of Reservoir Parameters" from 1988-90. The above-mentioned oil company participated in the industry-sponsored multiclient project in 1990, where permeability and porosity from closely spaced core plugs were used to determine the effect of the spatial arrangement and density of core-plug scale permeability data on waterflood efficiency. Sedimentological, diagenetic, and structural features of the Shannon were reviewed, as well as the attendant petrophysical properties.

A 7-day field seminar and 3-month, on-site training course were conducted for two scientists from the Scientific Research Institute of Petroleum Exploration and Development, Beijing, China. This field seminar was conducted on Almond outcrops in the Rock Springs, Wyo., area and addressed methods of data collection to include rock descriptions and the measurement of geologic sections. Three days were spent at the U.S. Geological Survey core repository, which houses over 1 million ft of core material. During this time, training was provided on methods of core description, documentation, and sampling for instrumental and petrophysical analyses. Activities during the 3-month, on-site training included instruction on the use and design of the minipermeameter, ways in which geostatistical methods are used for mapping reservoir parameters, and how the trainees perceived NIPER's research in relation to the geologic work being performed in China.

**Publications**


Presentations


Determination of Favorable Areas for EOR From Differential Oil-in-Place Calculations in Bell Creek Field, Montana, by A.M. Cheng and B. Sharma. Pres. at the SPE Joint Rocky Mountain Regional Meeting and Low Permeability Reservoir Symposium, Denver, CO, Apr. 15-17, 1991.

TORIS RESEARCH SUPPORT

Principal Investigator: James F. Pautz
BPO Project Monitor: Chandra Nautiyal
Project No.: BE2
Funding for FY91: $340,000 (EOR-Light Oil)

Objective

The objective of this project is to provide research support to DOE's Tertiary Oil Recovery Information System (TORIS) in the areas of EOR project and reservoir data base management, EOR project technology trends analysis, and computer simulation.

Research Summary

Information acquired in this project concerning ongoing EOR projects and EOR technology is used to continually update the TORIS-EOR Project Data Base. Providing the DOE with current information on EOR projects helps to improve the understanding of specific EOR technologies and how and where these technologies are being applied.

Since 1982, the DOE has collected data from operators participating in the tertiary enhanced oil recovery incentives program. During FY91, data on these incentive projects for calendar year 1989 were entered into the two versions of the EOR project data base on computers located at the Bartlesville Project Office and at the Energy Information Administration in Washington, D.C. Monthly production data were entered on 59 projects for 1989 of which 56 continue to be active. Additional projects reported data for 1988 and 1987, bringing the total number reporting to 89 and 77 projects, respectively. Eighty incentive projects were reported as active at the end of 1987 and 70 projects at the end of 1988. Data were collected on 29 projects for 1990 and promised for another 28 projects. Before being entered into the data bases, these data undergo several phases of verification: visual checking of the accuracy of data entry, comparison of several data fields of new data with data already in the data bases, checking of numeric and character format, and verification of annual production figures. A report on this work is scheduled for publication during the second quarter of FY92. To date, the data have been reviewed for accuracy, and information on project characteristics has been expanded by including data on geologic age and field discovery date. Graphs have been prepared for the production and injection data for approximately 160 incentive projects for which at least 2 years of data have been collected.

Trends in the application of EOR technology in the United States are analyzed annually to determine significant technological changes. These analyses are based on current literature, the news media, and the project data bases that contain information on over 1,300 projects. Changes in the frequency, EOR process type, and reservoir characteristics of project starts show how the application of EOR is progressing. Data on 32 new EOR project starts were added to the data base during FY91. Between 1981 and 1988, the number of project starts declined
corresponding to a decline in oil prices. The figure for 1989, 22 new starts, indicated a modest recovery in EOR activity as a result of increasing oil prices since 1987 but again dropped to a low of 12 new projects in both 1988 and 1990. Changes in project starts usually lag behind changes in oil prices. Polymer flooding projects have decreased both in actual numbers and relative to other EOR methods since 1986. Implementation of the longer-term, higher-cost methods such as CO₂ flooding in West Texas and steamflooding in California is continuing. The correlation of project starts with oil price is shown in figure 2.

![Figure 2: EOR projects starts compared to oil price (refiner's cost).](image)

Although the number of EOR project starts has declined drastically since 1986, production due to EOR has not declined correspondingly. In fact, production at the end of 1989 was 18% higher than that in 1986 when oil prices dropped by 50%. Production from both chemical and thermal methods has decreased, while production from gas projects has increased. EOR is being implemented selectively when it fits in with existing long-term plans and where the necessary extensive infrastructure exists. The trends indicate continued application of EOR in spite of price decreases. A comparison of the production from various EOR methods is presented in figure 3.
The interest in novel EOR technologies (microbial EOR, mine-assisted EOR, radio frequency oil production, alkaline/surfactant/polymer processes, etc.) is continuing at a low, but increasing level. Plans for microbial EOR projects continue, and applications that incorporate horizontal drilling are being considered. Field applications of these novel methods are cautious and on a small scale.

![EOR Production in the United States, including Alaska.](image)

**FIGURE 3.** EOR Production in the United States, including Alaska.

Inquiries concerning the operation of the DOE’s publicly available simulators such as BOAST, BOAST-II, and MASTER are addressed by project staff as requested by the DOE. These simulators are the part of TORIS used by industry to model reservoirs and thereby determine the best solution to production problems before applying a specific process in the field.

**Process Utilization and Technology Transfer**

Other Base Program projects use the information gained in project BE2. Information on the various types of EOR projects and known reservoir characteristics is used to guide the direction of research. For the application of a new process, general screening criteria are compared to characteristics contained in the data base to determine the most compatible type of reservoir. Knowledge of the application of EOR for general process types, as well as for specific projects, helps identify the best direction for future research.
One SGP project in particular, which is designed to determine the geological and production characteristics of Class 1 reservoirs (top priority Class outlined for study in the AORPIP), relies heavily on the updated information provided to the TORIS data bases. The application and success (or lack of success) of a particular reservoir class need to be considered in developing the future course of EOR research.

Improving the availability of reservoir data to both the DOE and industry is an important technology transfer issue. This information is currently in a flat file, and limited retrieval capabilities exist. The data contain a mix of public information and proprietary information obtained from companies during the 1984 EOR study by the National Petroleum Council and now used in DOE EOR production studies. The goal is to put the data into an expanded data base management system (DBMS) that will allow broader retrieval and storage capabilities while maintaining secure data. A preliminary design for a reservoir data base that uses the relational model common in many commercial DBMS systems was prepared for DOE under a SGP project. The design has provisions for expanded availability of the reservoir information collected by the TORIS program during the past 9 years by protecting proprietary information and enhancing search capabilities. Also under the SGP Program, production data for projects from the DOE 1978 tertiary incentive program for the years 1987, 1988, and 1989 were collected and added to the EOR project databases to give complete histories on a wide spectrum of EOR projects—both successful and unsuccessful. Information is frequently requested from this data base by DOE, industry, and NIPER personnel.

The availability of DOE computer simulation models was enhanced with the addition of a personal computer (PC) version of BOAST that models horizontal, slanted, and vertical wells. The BOAST line of computer simulators is widely used by independent oil producers, educational faculties, and petroleum consultants to model reservoirs for improved oil production.

The TORIS EOR predictive models are being updated under the SGP program to assist in development of the DOE heavy oil recovery plan. The histories of thermal EOR projects in the data base are used to identify required modifications in the screening criteria and to improve predictability of oil production and economics in the two thermal processes—steam and in situ combustion.

Publications


Objective

The objectives of this project are to improve the reliability of laboratory measurements of three-phase relative permeability for steady- and unsteady-state conditions in core samples, and to investigate the influence of rock, fluid, and rock-fluid properties on two- and three-phase relative permeabilities.

Research Summary

During FY91, a laboratory investigation was conducted to determine relative permeabilities and other characteristics of a 260-mD fired Berea sandstone core sample. The mineralogical and physical characteristics of the sample were determined by X-ray diffraction measurements, thin section analyses, mercury injection tests, and centrifuge capillary pressure and wettability tests. These tests were performed to provide results for comparing rocks having different relative permeability characteristics. Two-phase unsteady-state and steady-state oil/water relative permeabilities were measured under several stress conditions. Resistivity characteristics of the rock were also evaluated during several of the oil/water tests. Oil/gas and gas/water relative permeabilities were measured during steady-state tests. Three-phase steady-state oil/gas/water tests were performed for six DDI (decreasing brine and oil saturations, increasing gas saturation) saturation trajectories in which the sample was not cleaned between saturation trajectories.

Comparisons of two- and three-phase relative permeabilities were made for samples tested at conditions with and without confining pressure. These comparisons were possible because the samples were tested under identical conditions. Although relative permeability results for samples confined at 500 and 3,200 psig were similar, relative permeability curves for unconfined samples were not identical to those of confined samples of the same rock. Applying specific test results (permeabilities, residual saturations, etc.) from unconfined core plugs to the study of specific reservoir processes, where high confining stresses are present, should be done with caution. Changes in pore dimensions and closure of microfractures with stress, as demonstrated by the characteristic decrease in pore volume with stress that most rocks exhibit, are probably responsible for many of the differences in the unconfined and confined test results. The application of some confining pressure is recommended, however, when test results must be related to reservoir-specific processes.

Results of relative permeabilities and resistivities measured during a waterflood test on the 260-mD rock did not agree with measurements from steady-state tests. Water retention at the outlet face of the rock, as shown by CT scans conducted during the flood, probably contributed heavily toward the erroneous nature of the unsteady-state
relative permeability results. These findings showed that particular care should be taken when evaluating laboratory
resistivity and relative permeability results from tests in which saturation conditions were nonuniform. Thin
sections of the sample were also cut from the unconfined rock, allowing comparisons of pore size distributions from
thin sections with permeability results.

The rock was not cleaned after each DDI saturation cycle during the three-phase tests. Instead, the rock was
flooded with brine to drive the oil and gas saturations to residual conditions before starting a new saturation
trajectory. Two- and three-phase relative permeabilities for each fluid phase were primarily affected by the saturation
of that phase when the wetting phase (brine) was also present and for conditions of appreciable flow of all of the
phases. Water relative permeability vs. water saturation results were similar for both two-phase and three-phase flow
systems. This result, which indicates that the wetting phase relative permeability is a unique function of the wetting
phase saturation, agrees with the results from other investigations. Within the range of saturation conditions
imposed during the laboratory tests, gas relative permeability vs. gas saturation results were similar from two-phase
gas-brine and three-phase gas-oil-brine tests. During these tests, gas relative permeabilities were primarily dependent
upon gas saturations. Lower oil saturations were achieved during three-phase tests compared to two-phase results.
Oil saturations as low as 20% were achieved with oil flowing in the three-phase system, whereas the residual oil
saturations during two-phase oil/brine tests were approximately 37%. Since mobilization of the oil phase was
possible at lower saturations in the three-phase system, as compared to the two-phase system, two-phase oil relative
permeability data were inadequate for describing oil relative permeabilities at oil saturations close to or less than the
two-phase residual oil saturation condition. With oil saturations greater than the two-phase residual oil condition,
two- and three-phase oil relative permeability results were similar, and the three-phase oil results tended to fall within
the two-phase oil hysteresis envelopes.

These results were further described in a topical report, entitled "Three-Phase Relative Permeabilities and Other
Characteristics of 260-mD Fired Berea." Techniques for determining two- and three-phase saturation distributions
using X-ray and microwave scanners and a mass-balance method for monitoring oil and brine production during
oil/brine unsteady-state relative permeability tests are described in appendices of the topical report.

**Process Utilization and Technology Transfer**

Several projects were undertaken for various major domestic and international oil companies using the
technology developed as part of this project. These industrial projects were proprietary; however, the breadth of the
work included: formation damage investigations for corrosion and scale inhibitor selection, measurements of residual
oil saturations for an offshore reservoir from centrifuge imbibition experiments, centrifuge capillary pressure and
wettability experiments to characterize rock/fluid systems and to evaluate thermal effects on the shapes of capillary
pressure vs. saturation curves and residual saturations, steady-state gas/brine measurements to provide data for
predicting ultimate recovery from a gas reservoir, steady- and unsteady-state relative permeability measurements on
rock from an offshore reservoir to provide data for determining the feasibility of field development, and steady-state
relative permeability measurements on unconsolidated sand samples to provide data for reservoir engineering
calculations for an offshore field. A scientist with INTEVEP (Venezuela) assisted in this project during FY91 and was assigned to NIPER as part of a training program sponsored by INTEVEP and the DOE.

Publications

IMAGING TECHNIQUES APPLIED TO THE STUDY OF FLUIDS IN POROUS MEDIA

Principal Investigator: Liviu Tomutsa
BPO Project Manager: Robert E. Lemmon
Project No.: BE12
Funding for FY91: $545,000 (AE&PT)
Period of Performance: October 1, 1990 - September 30, 1991

Objective
The objectives of this project in FY91 were (1) to derive reservoir engineering parameters from computed tomography (CT) scanning, petrographic image analysis, and nuclear magnetic resonance imaging (NMRI); (2) to apply newly developed state-of-the-art imaging technologies to the characterization of DOE high-priority reservoirs; and (3) to transfer newly developed imaging technologies through an industry consortium organized to help plan, review, and participate in the research.

Research Summary
The primary goal of this project is to advance the understanding of fundamental processes involved in oil recovery by developing, refining, and applying cross-cutting (CT, NMR, and petrographic) imaging technologies. The techniques developed in this project are being used to characterize pore structures and surfaces, pore-to-core-scale heterogeneities, rock-fluid interactions, and distribution of fluids in reservoir rock during corefloods. The project supports reservoir description and advanced oil recovery research and development, especially in the areas of reservoir chemistry, physics, and rock-fluid interactions at the micro and macroscopic (pore-to-whole-core) scales. Techniques developed in this project have been applied to understanding the rock fabric of various facies, determining the effect of various polymer/surfactant combinations on 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. Other applications include estimates of water and gas content in coal samples from coal bed methane formations.

Computed Tomography Imaging
Computed tomography (CT) imagery is a powerful tool for nondestructive measurement of variations in rock properties and fluid saturations in reservoir rock. NIPER acquired a third-generation medical CT scanner during FY89; and in FY90, developed computer software to provide for quantitative measurement of oil and brine spatial-saturation distributions in cores during flow experiments. In addition, a CT-scanning method was developed for determining porosity distributions within porous media. The method has been expanded to integrate the permeability values generated by the petrographic image analysis (PIA) of thin sections with porosity distributions determined by CT measurement. This provides a reliable method for predicting permeability distribution within a core.
Coreflood simulations were performed to test the validity of the CT/PIA combination method of calculating core permeability distributions. The porosity and permeability data generated above were used as input for the black oil simulator BOAST-VHS. The agreement between the fluid saturations obtained by the CT scanner, shown in figure 4, and by the simulator, shown in figure 5, indicate the excellent potential for this permeability determination method for samples in which a good permeability-porosity correlation can be generated by PIA.

**FIGURE 4.** CT scan of oil flood of Shannon sandstone (direction of flow is from right to left).

**FIGURE 5.** Simulation of oil flood of Shannon sandstone (direction of flow is from right to left).
To measure the recovery efficiency of immiscible CO₂ floods and water-alternating-gas (WAG) recovery processes, accurate determination of spatial three-phase saturation distributions in reservoir rock are needed. To accommodate this need, methods were explored for measuring three-phase (gas, oil, and brine) saturations using the CT scanner. While CT scanning at one X-ray energy is adequate for porosity and two-phase saturation measurements in porous media, it is necessary in three-phase fluid saturation measurements that the media be scanned at two different X-ray energy levels. Dual energy equations were validated by comparing single and dual energy saturations at two-phase conditions. After establishing accurate porosity and two-phase results, a third phase (gas) was introduced into the rock, and three-phase saturations determined by the dual-energy method were compared to volumetric data. Good agreement (within 4%) was obtained between the two methods for three-phase systems and for average gas saturations of less than 35%.

Significant progress has been made in improving the versatility and efficiency of CT imaging technology at NIPER, and this has increased the demand for assistance of other projects performing research in the areas of multiphase fluid distributions in reservoir rock and in the characterization of core samples. To enhance the imaging capabilities and accommodate additional research work, the following technical improvements were made to the CT-imaging laboratory during FY91:

1. Interfacing of the CT scanner's host computer with a Macintosh IIfx-based image processing/analysis workstation for rapid transfer of CT-generated images from the CT scanner to the image processing work station. This modification reduced transfer time of a single CT image from 8 minutes to 10 seconds.

2. Installation of a new, high-accuracy positioning system, with repeatability of 12.5 microns and total travel distance of 5 ft, for precise and simultaneous calculation of porosity and saturation distributions during multiple coreflood experiments.

3. Installation of three-dimensional (3-D) image analysis and processing software on the Macintosh work station to provide for rapid interpretation of the large quantity of spatial data generated during CT-scanning experiments. This processing software allows for rapid computation of porosity and saturation distribution and merging of two-dimensional (2-D) images into 3-D arrays. It also permits viewing of any 3-D arrays in sections along planes parallel to XY, XZ, and YZ planes as well as rotation of the 3-D object around the X, Y, and Z axes. Various color tables, as well as a gray scale, are available for data display. Porosity, permeability, and fluid saturations from CT applications have been readily displayed and analyzed, along with water and oil distributions at pore level from high-resolution NMRI studies.

**Nuclear Magnetic Resonance Imaging**

Nuclear magnetic resonance imaging (NMRI) is another nondestructive imaging technology used to image fluids within core. NIPER is at the forefront of NMR imaging developments in areas of spatial resolution, image processing techniques, and resolution of oil and water phases. A commercial high-resolution Fourier Transform NMR spectrometer has been modified by NIPER staff for use as an imaging instrument. During FY90 the instrument was used to generate 3-D images of fluids in beadpacks with resolution as low as 25 microns. Such
resolution is required for the visualization of oil, water, and gas distributions within the pore spaces of reservoir rocks. This capability aids in understanding pore-level oil displacement processes and is essential for determining the mechanisms of oil recovery processes.

The FY91 research was designed to increase the spatial resolutions in rock samples toward the 20-micron range and was achieved by constructing a new gradient coil assembly that produces imaging gradients approximately seven times stronger than those previously attained. This modification was necessary for identification of pore level behavior of reservoir fluids under different oil recovery mechanisms. A new, more efficient, horizontal-coil NMRI probe was also installed. The radio-frequency (RF) coils can generate the shorter 90° RF pulses required for projection-reconstruction NMRI at higher gradients. The new probe also eliminates interferences from proton-containing materials used in the construction of standard NMR probes. The addition of a high-speed, two-channel A/D board and a 25-MHz 386 computer improved both data acquisition and processing time and permitted digitization of the higher bandwidth signals resulting from the stronger gradients achieved with the new gradient system. The horizontal solenoid NMRI sample probe was fitted with a new sample cell measuring 3 mm in diameter and 6 mm in length. The cell was calibrated using a water-saturated beadpack containing polymer beads in the 250 to 350 micron range. Images of the water protons were obtained at 128 x 128 x 128 and 256 x 256 x 256 pixels with corresponding pixel sizes of 30 and 15 microns, respectively. The pixel size of 15 microns represents the highest spatial resolution achieved to date by this laboratory. Using the new probe and gradient coil, NMRI images were obtained on fluids in a small plug of Bentheimer sandstone, 4 mm in diameter and 7 mm in length. At the highest resolution, the pixel size was 25 microns in the cross-sectional views with 40 microns along the axis. These images represent the highest resolution achievable to date for fluids in a sandstone. Soltrol mineral oil, with viscosity adjusted to 5 cp, was injected into the water-saturated Bentheimer plug. Two images of the plug were made at a pixel resolution of 256 x 256 x 256, one showing total fluid distribution (Fig. 6) and the second showing the residual water phase using an inversion recovery imaging sequence to null the oil phase signal (Fig. 7). Notice the water appears as small isolated droplets with virtually the entire pore space being filled with the oil phase.

Imaging Technology Applied to Other NIPER Projects

The following projects utilized CT imaging or petrographic image analysis (PIA) in deriving needed information not otherwise available.

1. Characterization of grain size distributions in reservoir and outcrop facies by PIA (Joint research with project BE1, Reservoir Assessment and Characterization).

The objective of project BE1 is to develop a methodology for the effective characterization of shoreline barrier reservoirs. For this development, an important part is played by the geological characterization of rock facies from different shoreline barrier reservoirs and corresponding outcrops. The grain size distribution measurement is a necessary component of rock description. By replacing the traditional manual point-count technique with computer-assisted PIA techniques, a larger number of rock thin sections could be analyzed, resulting in the generation of more
representative data. Grain size and sorting were determined for a total of 75 thin sections prepared from cored wells located in Arch Unit of Patrick Draw field, situated in southwestern Wyoming, and from Almond formation outcrops located on the eastern flank of the Rock Springs Uplift, as close as 8 miles west of Patrick Draw field.

Grain sizes among combined Almond outcrop and subsurface samples range from coarse silt to fine sand (30-225 microns) and fall into two groups: (1) a finer-grained and better-sorted group comprising tidal creek and tidal flat facies, with the tidal flat mean grain size being consistently finer than all other facies and (2) a relatively coarser-grained and poorly sorted group, comprising all of the other facies including tidal delta, tidal channel, and tidal inlet facies. Tidal channel grain size distributions are similar for the outcrop and the subsurface samples, while tidal delta, tidal creek, and tidal inlet outcrop samples tend to be coarser grained than their subsurface counterparts. The crossplot of mean grain size vs. standard deviation of grain size (sorting) shows a linear relationship with a high correlation coefficient ($r = 0.95$) for outcrop as well as for subsurface data sets.

Mean grain size for the Almond formation (a mesotidal shoreline barrier system) lies in the 30-225 micron range, which is similar to the mean grain size for the Muddy formation (a microtidal shoreline system, previously studied in project BE1) which lies in the 95-150 micron range. On the other hand, the Muddy formation samples lack grains coarser than 150 microns, the outcrop and subsurface facies have very similar distributions, and the marine facies have a narrower range of sizes. Although the sorting for both formations is similar, the Almond formation facies have consistently poorer sorting than the equivalent Muddy formation facies. Also, both formations show similar good correlations between sorting and mean grain sizes.


The presence of clay minerals has a great impact on petrophysical properties such as rock permeability and porosity. Their presence and type can be determined by thin section, XRD, and SEM analyses on reservoir cores but, due to costs, only a few wells are routinely cored while most of the wells drilled in a field are logged. Research to develop quantitative approaches to the use of logs for determining the presence of clays in a reservoir is being performed using both core and log data and mathematical analysis of this data. Since clays influence both the average density of the core and its mineralogy (two factors which affect X-ray attenuation), it is expected that CT scanning can be a useful tool in characterizing the rock. For example, CT scanning of a number of well-described whole cores from the Almond formation, Patrick Draw (WY) field, provided excellent correlations ($r = 0.98$) between the sonic density and CT density for the relatively homogeneous (uniform clay content) cores and lower correlations for the more heterogeneous cores. Small-scale (<1 in.) heterogeneities in the core (fractured, cemented, or clay-rich zones) were clearly apparent in the CT density profile, but their effect on the density log response was expected to be very small due to the effect of spatial averaging. Although, in general, the correlation between the CT density profile and the gamma ray log was excellent, the CT did not detect the presence of a thin shale layer that caused a gamma ray log response. This was probably due to the small density contrast between the shale and the neighboring sandstone.
3. CT imaging of surfactant/polymer floods (Joint research with project BE4A, Development of Improved Surfactant Flooding Methods).

Chemical flooding has the highest potential of all EOR processes for mobilizing residual crude oil from many U.S. domestic reservoirs because the chemical formulation of injected fluids can be varied to suit specific fluids and minerals for a given reservoir. The goal of NIPER research is to improve surfactant flooding methods of producing oil over a fairly broad set of conditions. The use of noninvasive rock-fluid imaging methods, such as CT, is needed to investigate the actual behavior of injected fluids within the rock during a flood. For a preliminary study in the application of CT to monitor chemical corefloods, two tests were conducted. The same surfactant formulation was used for both tests, but differed in that the surfactant injection was followed by injection of a mobility-control biopolymer with a concentration of 3,500 ppm in one coreflood and 1,200 ppm in the other. CT images showed strong differences in the oil saturation between the two floods. The flood with 3,500-ppm biopolymer concentration had high oil recovery, and formed an oil bank ahead of the surfactant slug. In the other test, no oil bank was observed, and a significant amount of oil was bypassed by the aqueous fluids. To understand the effect of rock on oil recovery, more information regarding the minerals present, the grain size, and pore and pore throat size distributions is needed from thin section, mercury injection, and XRD analyses.

4. Whole core screening by CT for selection of representative core plugs.

An important application of CT scanning is nondestructive evaluation of whole cores for selection of locations where representative core plugs should be taken. X-ray attenuations visible in the CT image are controlled by the porosity and the mineralogy of the rock. In proprietary work, CT scanning was used to screen 30 ft of core for selection of core plug samples for chemical flooding and to understand the low recovery measured in the floods performed on some of the selected core plugs. Highly fractured zones and the extent of the fractures were identified and provided explanations for chemical flooding recovery results.

**Process Utilization and Technology Transfer**

The rock-fluid imaging technology developed at NIPER can be beneficial to the oil industry as it contributes to a better understanding of fundamental oil recovery phenomena. When used in conjunction with other technologies available at NIPER, the imaging capability allows a more in-depth analysis of the diverse EOR processes being studied under the Base Program. CT monitoring of front movements in surfactant/polymer floods provides information regarding the interaction of the chemical system with the oil present in the rock, identifies the location of the bypassed oil, and helps in the design of the most effective EOR processes for a given reservoir. CT screening of whole core provides information necessary for the selection of representative core plugs. Permeability distributions within cores, obtained from correlations of petrographic image analysis measurements and combined with porosity distributions from CT scanning, provide data for the accurate simulation of floods within cores and identify the role of rock heterogeneity on oil recovery.

For mid- and long-term research, CT contributes to developing techniques for identifying clays in cores from wireline logs, and computer-assisted PIA provides fast and accurate grain and pore size data needed in understanding
similarities and differences between facies deposited in various depositional environments. Also, high-resolution NMRI microscopy helps in understanding pore structure and fluid distribution in pores and provides the information needed to understand the mechanisms controlling various oil recovery techniques and to design improved recovery technologies. NIPER's imaging capabilities are used in the characterization of cores for industrial clients participating in the WFO Program.

Attempts to form a consortium on imaging technology development, as planned for FY91, was unsuccessful due to the lack of industry participation. Additional technology transfer activities will be conducted in FY92.

Publications


Chemical and Microbial EOR

NIPER's program in chemical and microbial EOR consists of four projects conducting research in advanced microbial, surfactant, and alkaline flooding and improved mobility control. 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 soon as possible. The DOE AORPIP addresses oil recovery in the near term using currently available technology and in the mid and long term through application of advanced technology. NIPER's research covers both of these phases now that a portion of the mid-term research, established in 1983, has advanced to the stage of field testing.

Research to improve microbial enhanced oil recovery (MEOR) has led to an improved understanding of the mechanisms of oil mobilization and transport of microbes and metabolites in porous media. 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. Knowledge gained from the laboratory studies has provided the engineering design for two microbial enhanced oil recovery waterflood projects: an original pilot in Delaware-Childers (OK) field and an expanded pilot in Chelsea-Alluvial (OK) field. Both projects are funded under an SGP project supported by industrial participants and the DOE. 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 second or third quarter of FY93.

Studies for the development of improved surfactant flooding methods are directed primarily at waterflooded reservoirs containing crude oil of low to medium viscosity. This chemical flooding process, which usually has included 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. On the other hand, 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 designed 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.

Laboratory studies over the near term have resulted in the development of effective alkaline-surfactant-polymer (ASP) flooding formulations; they 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. However, to be fully effective, a better understanding of the equilibrium and dynamic mechanisms of ASP flooding is essential. The former mechanism includes interfacial activity, adsorption, and ionic equilibria (precipitation and complex formation). These factors are controlled, to the extent possible, by design of the injected formulation. The latter includes chromatographic effects, flow diversion by precipitates, and emulsifications which are governed by injection strategy. Thus, NIPER's research is designed to
overcome problems associated with these various mechanisms and to develop an optimal injection strategy for use in an upcoming ASP pilot field test to be conducted under a SGP project.

Research to improve mobility-control methods is focusing in two primary areas. One is in the development of a simulator that can be used in the design of profile modification processes and to predict oil recovery efficiency from such processes. The second is development of a flexible low-molecular-weight polyacrylamide gel that will alleviate poor injectivity and mechanical (shear) degradation problems encountered with the traditional high-molecular-weight polyacrylamides. Although low-molecular-weight polyacrylamides provide certain advantages, they have a disadvantage in that considerably higher concentrations of polymer are required in achieving viscosities equivalent to those attainable with high-molecular-weight polyacrylamides. To overcome this disadvantage, NIPER is developing crosslinked low-molecular-weight polymer formulations which are expected to provide good injectivity even under high shear conditions.

Individual summaries of the four projects in chemical and microbial EOR are presented in the following section. They are addressed in the following order: BE3, Development of Improved Microbial Flooding Methods; BE4A, Development of Improved Surfactant Flooding Methods; BE4B, Development of Improved Alkaline Flooding Methods; and BE4C, Development of Improved Mobility-Control Methods.
DEVELOPMENT OF IMPROVED MICROBIAL FLOODING METHODS

Principal Investigator: Rebecca S. Bryant
BPO Project Monitor: Edith C. Allison
Project No.: BE3
Funding for FY91: $300,000 (EOR-Light Oil))
Period of Performance: October 1, 1990 - September 30, 1991

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 DOE since 1983. One of the goals of this research is to maintain a data base of field projects that are using MEOR technology. The data base provides documentation on the characteristics of reservoirs where MEOR is being implemented and is used to revise published screening criteria for MEOR processes. The data base currently contains 69 different microbial field projects, although complete information on many of them is unavailable.

In addition to the data base development, prior work at NIPER has defined the key mechanisms responsible for improved oil mobilization by microbial formulations. The MEOR research team began 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 regarding microbial growth and decay, nutrient consumption, microbial deposition, convective dispersion, and diffusion. Unsteady-state relative permeability data using microbial formulations were used to determine the microbial effects on relative permeability and the 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 can reduce residual oil saturation in porous media.

Process Utilization and 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, a microbial enhanced waterflood was initiated, under a SGP project, in Chelsea-Alluwe field near Alluwe, Oklahoma, based upon data acquired during 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 typical of a Class 1, midcontinent sandstone reservoir. To date, the decline curve of oil production in the expanded project has been arrested by over 6% by microbial treatment. Both this Base Program project and the near-term field pilot tests have been in progress concurrently for the past several years.

Because of the potential opportunities for independent oil producers to use cost-effective enhanced oil recovery (EOR) technologies, NIPER has presented a series of short courses to independent producers on microbial EOR. Some 150 U.S. 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. A major goal of the short course is to demonstrate the potential of microbial technology in improving oil recovery from marginal oil wells. Today 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 course emphasizes the potential for MEOR, yet stresses 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.

Publications


Presentations


DEVELOPMENT OF IMPROVED SURFACTANT FLOODING METHODS

Principal Investigator: Leo A. Noll
BPO Project Manager: Jerry F. Casteel
Project No.: BE4A
Funding for FY91: $600,000 (EOR-Light Oil)
Period of Performance: October 1, 1990 - September 30, 1991

Objective:

The FY91 objective of this project was to develop more effective surfactant flooding systems having broader tolerance to the chemical composition found in petroleum reservoirs. The focus was (1) to mitigate problems known to adversely effect the performance of surfactant flooding processes, (2) to improve the economics of surfactant enhanced oil recovery through the development of effective oil recovery systems containing very low concentrations of synthetic surfactants and alkaline additives, and (3) to investigate the application or extension of current chemical flooding technology to near-term problem solving for near-wellbore permeability improvement.

Research Summary

Chemical flooding processes have considerable flexibility; and, for many U.S. domestic reservoirs, represent the most viable enhanced oil recovery (EOR) method available. The capability to adjust an injected chemical formulation for a wide range of reservoir conditions, and crude oil types, remains a strong point for development and application of this technology. It has been identified by the DOE as an important production technique targeted for Class 1 reservoirs.

In response to guidelines of the National Energy Strategy-Advanced Oil Recovery Program (NES-AORP), the focus of this NIPER research is in the development of chemical flooding systems that are both cost-effective and have improved adaptability to variations in salinity, hardness, temperature, and dilution for recovery of light crude oils from selected Class 1 reservoirs. Research under this program has focused primarily on mixed surfactant systems that have potential advantage over conventional chemical flooding systems. These surfactant systems can be designed to achieve improved tolerance to adverse conditions and the variables encountered following the injection of fluids. These systems can be formulated with surfactant components that have both high oil recovery potential (i.e., high oil solubilization and ultra-low interfacial tension) and improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature. The existence of a synergistic effect with mixed compositions can be evaluated to develop a surfactant system or systems that will retain relatively low interfacial tension (IFT) values over a range of target reservoir conditions, while maintaining overall effectiveness at an acceptable level. Factors influencing the economics of the chemical system(s) have to be considered as well. A balance between cost and oil recovery effectiveness has to be achieved to find the optimal surfactant system for field application.

In FY91, research on mixed surfactant systems was targeted toward a specific range of reservoir conditions. The work conducted in prior fiscal years, along with guidelines from the AORPIP, have helped identify reservoir
conditions necessary for EOR application of mixed surfactant systems. Statistical and experimental design methods were used to identify the variables having significant effects on the performance of these chemical systems, which include temperature, salinity, and hardness. One of the reservoirs selected for this research was that of the North Burbank Unit (NBU), Osage County, Oklahoma, which is classified as a fluvial-dominated deltaic (Class 1) reservoir with salinity and temperature parameters that lie in the mid-range value for reservoirs in the same class. This reservoir has a significant quantity of oil remaining and has been identified as a prime candidate for the application of advanced chemical EOR methods.

Improved salinity and hardness tolerance was achieved for some of these chemical systems. Several combinations of screening methods were used to help identify potential chemical formulations and to determine conditions where a particular chemical system could be applied. The effects of different parameters on the behavior of the overall surfactant system were also studied. The salinity tolerance of these systems was found to be dependent on the molecular weight, surfactant type, and concentration of the surfactant components.

The observed solution behavior was attributed to the structure, molecular weight, and proportion of the different surfactant components. A qualitative dependence of the salinity tolerance on the molecular weight, surfactant type, and concentration of surfactant components in the system was observed. Ethoxylated sulfates were found to be better than the ethoxylated sulfonates for improving the tolerance of the overall chemical system. The molecular weight and the branching structure of both ethoxylated sulfonates and sulfates affected the overall salinity tolerance of the mixture. Shorter chain length and branching favored improved solubility and salinity tolerance. The total surfactant concentration also affected the performance of these mixed systems. As the total concentration increased, the favorable salinity region appeared to have slightly increased. The proportion of the different types of surfactants effectively adjusted the region of favorable salinity for a given surfactant system. The proportion of salinity-tolerant surfactant (e.g., ethoxylated sulfates) was critical as to whether or not the overall system exhibited good phase behavior. The degree of ethoxylation in the primary component (sulfonate-type) was found to be helpful in reducing the salinity-tolerant surfactant requirement and shifted the salinity range of the chemical system. The alcohol content in the chemical solutions also affected behavior of the system, i.e., it enhanced the solubility of the mixture but had a deleterious effect on the IFT and oil solubilization potential.

Oil displacement experiments in Berea sandstone cores showed considerable improvement in the oil recovery potential of these systems as compared to previously studied systems that contained carboxy-methylated ethoxylates (CMEs). Some of the displacement experiments were conducted with the aid of advanced imaging techniques such as NIPER's computed tomography (CT) scanner to determine the progression of the flood. Both the effectiveness of the surfactant formulation and the mobility control system could be monitored using this technique.

For the mixed surfactant systems studied in this project, the oil recovery potential was observed to be dependent on both the efficiency of the surfactant system and on the effectiveness of the polymer mobility-control slug. Core permeability, polymer injectivity, or effective viscosity ratio of the polymer and surfactant/oil solutions were parameters affecting the oil recovery properties of the chemical system. Oil recovery was also observed to be more efficient for mixed surfactant systems with alkaline additives than without these additives. However, this could
have been related to the lower salinity conditions of these tests. Other results showed that for the same surfactant system, little difference was observed between overall recovery efficiency of a lower concentration and larger pore volume injection strategy as compared to a higher concentration and smaller slug. The former method is useful in the investigation and comparison of parameters affecting oil recovery. The latter method, however, would be more favorable for economic considerations.

NIPER's efforts in developing other cost-effective chemical flooding technologies have focused on the use of surfactant-enhanced alkaline flooding technology for the recovery of midcontinent crude oils. The positive influence of alkaline additives on the effectiveness of surfactant formulations is now fairly well known and accepted. Research on the use of alkaline agents as additives to surfactant formulations has evolved over a period of several years. First performed on acidic oils, it was believed that the primary effect of the alkali was neutralization of carboxylic acids present in the acidic crudes. However, recent research has shown that a synergism exists between surfactant and the alkaline additives, even when the oils have very low acid numbers. This opens up the possibility of applying this technology to a larger number of reservoirs, including many midcontinent reservoirs containing slightly acidic light crudes. In the presence of alkaline additives, very dilute (<0.4%) concentrations of synthetic surfactants have the potential to mobilize significant amounts of residual oil. Since synthetic surfactants are expensive components of the chemical formulation, low concentration requirements improve the economics of EOR projects. The results from current research efforts, however, show that each crude oil behaves differently. This finding is the result of comparative testing of crude oils from different reservoirs. The applicability of these chemical systems must then be determined for each target oil, brine, and reservoir type.

Research on the treatment of paraffin deposits in producing wells was also conducted under this project. Such deposits reduce and sometime stop production. The most common way of alleviating this problem is by periodically performing hot oil treatments on the offending well. This process was developed because the application of heat is the most economical method of recovering deposits. Unfortunately, hot oil treatments tend to build up paraffin at the sand face leading to formation damage. Hot xylene treatments avoid the reintroduction of wax to the well and do a good job of cleaning but are more expensive. Surfactants in conjunction with heat or solvents give satisfactory cleanout performance. Dispersant and inhibitors are useful in helping to prevent the deposition of paraffin. These agents can be applied along with descaling materials in squeeze processes. Dispersant and crystal modifiers are very specific, and maximizing the effectiveness of these agents requires screening of a rather large number of potential candidate materials. The effectiveness of paraffin treatment depends on a thorough and complete evaluation of the cause(s) of the problem and needs of the field. When chosen and applied correctly, paraffin treating products can help; however, the use of paraffin control chemicals does not always solve the problem. There is no single method available for the prevention or control of paraffin accumulation.

To achieve a better understanding of the paraffin deposition issue and potential solutions, an extensive literature search on the problem and methods of control was performed, and information was obtained from companies that provide chemicals to aid in well treatment. The resulting documentation included a discussion of the
Some conclusions and recommendations are as follows: (1) There is a need for the development of procedures capable of evaluating and classifying the potential paraffin-forming tendency of a crude. Viscosity-temperature curves of systems of known composition are a step toward achieving this goal, showing the difference in behavior between normal paraffin-containing crudes, asphaltene-containing crudes, and viscous water emulsions. (2) Improvements are required in the collection of representative wax and oil samples. (3) Better deposition tests would be beneficial. The standard deposition tests are quite nonreproducible, especially when considering the cold finger test which only determines deposition of paraffin by the molecular diffusion mechanism and is usually performed without brine in the system. (4) There is a need to be able to test an oil below its cloud point and thus allow determination of the rate of wax deposition in the presence of brine. Once the tests are reproducible and represent conditions as they exist in the field, results of the deposition test can be correlated with the crude oil composition.

It was further suggested that a differential scanning calorimeter (DSC) might be useful in determining the point of first wax crystal formation and then compared with ASTM cloud point and viscosity test results. Visualization techniques, such as the polarizing microscope attached to a video camera and VCR, could be used to view the type of crystals and paraffin masses which accumulate on cooling, with and without additives. These observations need to be correlated with other tests such as composition studies by gas chromatography, DSC, viscosity, and depositional behavior.

Process Utilization and Technology Transfer

The research effort in project BE4A has resulted in the development of improved surfactant formulations which can be tailored for use at a given salinity or temperature. The use of different screening methods and core imaging techniques being developed in project BE12 have been incorporated into the work conducted under this project. The use of CT scanning has become an important tool in achieving a better understanding of the mechanisms of oil displacement. The use of alkali additives with these surfactant formulations has been shown to improve oil recovery and lower chemical losses during injection. Efforts along these lines have been coordinated with research in project BE4B in the development of formulations suitable for use with light midcontinent crude oils. The results of this research were reported in DOE topical reports, client reports, journal articles, and through oral presentations. More than 40 reprints of the paper on adsorption calorimetry have been distributed. In FY91, research work under the WFO program utilized methodologies developed under projects BE4A and BE4B. These included the evaluation of novel methods of surfactant-based mobility control and development of technology for the use of surfactant-alkali-polymer formulations in field tests.

Publications

Flow Adsorption Calorimetry of Surfactants as a Function of Temperature, Salinity, and Wettability, by Leo A. Noll and Bonnie L. Gall. Colloids and Surfaces, v. 54, 1991, pp. 41-60


Presentations

DEVELOPMENT OF IMPROVED ALKALINE FLOODING METHODS

Principal Investigator: Troy French
BPO Project Monitor: Thomas B. Reid
Project No.: BE4B
Funding for FY91: $150,000 (EOR-Heavy Oil)
Period of Performance: October 1, 1990 - September 30, 1991

Objective

The objective of this project is to develop cost-effective and efficient chemical flooding formulations that utilize surfactant-enhanced, weakly alkaline systems. The specific goal for FY91 was to determine optimal injection strategies for use in surfactant-enhanced alkaline flooding EOR. The design of a proposed surfactant-enhanced alkaline flooding field pilot test is also being developed under this project.

Research Summary

The use of a combination of surfactants and weak alkalis for recovery of crude oil is a recent discovery that has been reported in several publications. Prior research conducted at NIPER, under the sponsorship of the DOE and a major chemical corporation, resulted in a novel chemical EOR process that is now patented. The combination of surfactant and weak alkali alleviates some of the problems associated with the use of either surfactant alone or alkali alone. With some crude oils, the addition of small concentrations of synthetic surfactant to weak alkaline solutions significantly improves the interfacial tension (IFT) behavior and increases the mobilization of additional oil. In favorable cases, the combination of weak alkalis and surfactants reduces chemical requirements, suppresses scale formation, and increases displacement efficiency.

Several mechanisms involved in surfactant-enhanced alkaline flooding are only partially understood. These consist of both equilibrium and dynamic effects. The former includes interfacial activity, adsorption, and ionic equilibria (precipitation and complex formation) which are considerations in the design of the injected formulation. The latter includes mobility control, chromatographic effects, flow diversion by precipitates, and emulsifications, which are considerations in the injection strategy. The specific goal for FY91 was to develop an optimal injection strategy for use in surfactant-enhanced alkaline flooding.

In the laboratory, oil recovery was compared for four different injection strategies: (1) surfactant followed by polymer, (2) surfactant followed by alkaline polymer, (3) alkaline surfactant followed by polymer, and (4) alkali, surfactant, and polymer mixed into a single formulation. The effect of alkaline preflush was also studied under two different conditions.

All of the oil recovery experiments were conducted under optimal conditions with a viscous, non-acidic oil from Hepler (KS) oil field. The coreflood experiments were conducted with Berea sandstone cores since field cores were not available in sufficient quantity for coreflood tests. The Tucker sand of Hepler (KS) oil field, a Class 1, fluvial dominated deltaic reservoir, is expected to be the site of a DOE-sponsored field pilot test.
Some observations from the oil recovery tests were as follows:

1. Oil recovery was highest when the injection of alkaline surfactant was followed by polymer.
2. Oil recovery was only slightly decreased when the alkali, surfactant, and polymer were simultaneously injected (mixed in a single slug), and oil production occurred faster.
3. Oil recovery was significantly reduced when surfactant was followed with alkaline polymer.
4. Oil recovery was lowest when surfactant was followed by polymer and there was no alkali in any of the injected solutions.

When different alkaline preflush volumes were injected before injection of the main chemical slug, it was observed that:

1. Oil production increased as the preflush volume was increased from 0 to 0.25 PV.
2. The alkaline preflush increased oil production in all cases, but the effect was most pronounced when the cores were saturated with brine that contained divalent ions.

The conclusion pertinent to application of surfactant-enhanced alkaline flooding in the Tucker sand of Hepler field is that alkali, surfactant, and polymer should be injected in a single slug preceded by injection of at least 0.1 PV of alkaline preflush. This conclusion is based on results obtained with Berea sandstone and will be verified using field core.

**Process Utilization and Technology Transfer**

NIPER has conducted research on surfactant-enhanced alkaline flooding since 1983. The screening criteria and other results from this work are being used for the selection of a field site and for the design of a chemical formulation to be used at that site. The actual field test will be conducted under a SGP project. This pilot test would not be possible without the research that has been accomplished under the Base Program. Proprietary work on surfactant-enhanced alkaline flooding is also being performed, and this allows NIPER scientists to assist independent oil producers in the evaluation and utilization of surfactant-enhanced alkaline flooding technology.

**Publications**


DEVELOPMENT OF IMPROVED MOBILITY-CONTROL METHODS

Principal Investigators: Hong W. Gao
Troy R. French

BPO Project Manager: Jerry F. Casteel

Project No.: BE4C

Funding for FY91: $200,000 (EOR-Light Oil)

Period of Performance: October 1, 1990 - September 30, 1991

Objectives:

The overall objectives of this project are (1) to develop a novel mobility-control system based on crosslinking a low-molecular-weight polymer as an alternative to conventional high-molecular-weight polymer systems and (2) to develop a simulator for permeability modification using gelled polymers. The mid-term objectives are (1) to implement the application of the novel mobility-control formulation for cost-effective mobility control in waterflooding and chemical flooding and (2) to apply the permeability modification simulator to potential fields to arrest the rate of well abandonment.

Specific objectives for FY91 were (1) to examine the flow behavior of gel systems in plastic beadpacks to prove that crosslinked low-molecular-weight polymer gels can provide better injectivity than conventional polyacrylamides and maintain required viscosity as they enter into a formation and (2) to investigate the effect of gel treatment on oil recovery in a polymer flood using the permeability modification simulator.

Research Summary

Conventional high-molecular-weight polyacrylamides have been used in waterflooding and chemical flooding to improve volumetric sweep efficiency and increase oil recovery. Permeability modification treatments using gelled polymers have been successfully applied in both water injection wells and producing wells to prevent channeling of injected water and to reduce water-oil ratios through fluid diversion and increased sweep efficiency. The disadvantages of using the high-molecular-weight polymers as mobility-control agents are (1) their susceptibility to irreversible mechanical (shear) degradation, which can greatly reduce their effectiveness as mobility-control agents and (2) poor injectivity in low-permeability reservoirs. To mitigate these problems, the DOE has authorized continuing research on the development of a mobility-control system based on crosslinking a low-molecular-weight polymer with metallic ions. To improve oil recovery in highly heterogeneous reservoirs, the effect of gel treatment on oil recovery in a polymer flood was investigated.

Mobility-Control Agent

To clarify the flow behavior of flexible, crosslinked low-molecular-weight polymer gels in porous media, two polymer gel systems in 53 meq/L NaCl (pH = 4.8) were tested in several polystyrene beadpacks. Both gel systems contained 15,000 ppm of HPAM1-10 (MW = 400,000 daltons, 10% hydrolyzed). Gel system G1 contained 50 ppm
of Cr(III) and G2 contained 75 ppm of Cr(III). Four high-permeability (ranging from 36 to 45 darcies) and three low-permeability (ranging from 4.3 to 5.8 darcies) polystyrene beadpacks were tested. Plastic beads were used to avoid any possible interaction of polymer gels with the beads.

Flow tests in high-permeability polystyrene beadpacks showed that high shear (higher than 960 sec⁻¹) favored the gelation of G2, which had a fast rate of gelation, but had an adverse effect on the gelation of G1, which had a slow rate of gelation. At low shear conditions (lower than 960 sec⁻¹), gelation reaction occurred in both systems. Both systems were freshly prepared before testing. These results imply that (1) gel systems that have a fast rate of gelation will not produce mechanical degradation problems and will provide good injectivity and (2) gel systems that have a slow rate of gelation will also provide good injectivity due to breakage of the crosslinking bonds at high shear conditions.

Shear degradation tests of gel system G2 that had been agitated in a bottle under a nitrogen atmosphere for more than 1 month and a polymer solution (1,100 ppm Pusher 500) in beadpacks with permeability ranging from 4.3 to 41 darcies showed that both gelled polymer and conventional polymer were degraded after experiencing a high shear condition. Tests in two high-permeability beadpacks showed that under high shear conditions, gel system G2 provided better injectivity than did the polymer solution. At an injection rate of 400 mL/hr, the injectivity of the polymer solution in a 41-darcy beadpack (apparent shear rate = 4,950 sec⁻¹) was 2.9 mL/hr/psi while that of gel system G2 in a 36-darcy beadpack (apparent shear rate = 5,290 sec⁻¹) was 5.2 mL/hr/psi. Under low shear conditions the crosslinking bonds healed, and the original viscosity of the gelled polymer G2 was recovered. Better injectivity over that of the polymer solution and the ability to regain viscosity of the polymer gel demonstrated that a gel system could alleviate the problems of poor injectivity and mechanical degradation encountered in field applications when using high-molecular-weight polyacrylamides as mobility-control agents in chemical flooding.

In two low-permeability (4.3 and 4.4 darcies) beadpacks, strong gel formed inside the beadpacks after injecting G2 through the beadpacks at both high and low shear conditions. A strong gel formed inside the low-permeability beadpacks but not inside a high-permeability beadpacks indicating that permeability had a significant effect on the further gelation of a gel system in a porous medium. Therefore, tests with reservoir cores should be conducted before selecting a gel system for use in a particular reservoir.

Permeability Modification

The technology of applying a polymer gel treatment before or after a polymer flood has the potential of preventing early breakthrough of polymer in highly heterogeneous reservoirs thereby improving sweep efficiency and increasing oil recovery. To investigate the effect of a polymer gel treatment on oil recovery in a polymer flood, simulation runs using NIPER's permeability modification simulator were conducted for polymer flood, gel treatment, and combining polymer flood and gel treatment on a quarter of a five-spot, two-layer reservoir model with \( k_v/k_h \) (ratio of the vertical permeability \( k_v \) to the horizontal permeability \( k_h \)) ranging from 0.1 to 0.001. The permeability in the top layer was 100 mD, and that in the bottom layer was 1,000 mD. The length and width of the reservoir model were each 1,000 ft, and the thickness of each layer was 15 ft. The oil viscosity was 3 cP, and that of
water was 0.8 cP. The porosity was 20%, and the injection rate was 535 bbl/d. During gel treatment, the gel system was injected into the bottom layer only.

It was found that starting a polymer flood early resulted in an early increase in incremental oil recovery regardless of the degree of crossflow. Under simulated conditions, total oil recovery at the end of 15 years of flooding was not affected by the initiation time (between 0 and 5 yr after waterflooding was initiated) of a polymer flood.

In the simulation combining polymer flood and gel treatment, the polymer flood was (1) either initiated at the beginning of a waterflood followed by a water spacer and then a gel treatment or (2) initiated after a gel treatment with or without a water spacer. Results showed that combining near-wellbore gel treatment and polymer flood was effective in increasing incremental oil recovery over that of a polymer flood for a reservoir having a low degree of crossflow ($k_v/k_h = 0.001$) but not in a reservoir with high crossflow ($k_v/k_h = 0.1$).

In the reservoir where $k_v/k_h = 0.001$, a near-wellbore gel treatment followed by a polymer flood was more effective in increasing incremental oil recovery over that of a polymer flood than was a deep gel placement or any combined deep gel placement and polymer flood. In the reservoir of $k_v/k_h = 0.1$, a deep gel placement or combined deep gel placement and polymer flood was not effective in increasing incremental oil recovery over that of a polymer flood. Therefore, the conventional gel treatment is not recommended in a waterflood or a polymer flood in reservoirs with high crossflow.

Under simulated conditions, undesired permeability reduction in the low-permeability layer occurred in reservoirs with low and high crossflow when a large slug size of a gel system was used. The degree of permeability reduction in the low-permeability layer increased with the increase in the slug size of the polymer gel system and the increase in $k_v/k_h$.

**Process Utilization and Technology Transfer**

NIPER's permeability modification simulator was released to the public in 1990. Simulated results on the effects of various process parameters such as initiation time for a gel treatment, degree of crossflow, and depth of gel penetration on the success or failure of a gel treatment and on oil recovery in waterfloods and polymer floods were presented in DOE reports, at the seventh SPE/DOE symposium on EOR, and in a journal article and thus provided valuable information for oil producers. This information can be used to screen reservoirs for cost-effective permeability modification treatments in polymer floods and waterfloods using polymer gels. Recently, the public has expressed interest in a PC version of the simulator; therefore, a proposal for the adaptation of the simulator to a PC version was submitted to DOE.

**Publications**


**Thermal and Gas EOR**

NIPER's Base Program research is being conducted on 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 Base Program projects on thermal recovery are 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 29% 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. In FY91, all of these problems were addressed in a continuing effort to advance gas flooding technology. In one project, the research focused 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 CO₂ 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.

The success of gas flooding in the field can be attributed to the excellent displacement efficiencies obtained with miscible CO₂ flooding; however, oil recovery can be significantly reduced by unfavorable mobilities and gravity segregation caused by the low fluid densities and low viscosities of the injected gases. The resulting poor sweep efficiencies can markedly affect oil recovery and profitability of a given project. To mitigate problems of poor sweep efficiency, NIPER's research is evaluating various processes that have shown promise for improving mobility control. Those studied to date include the water-alternating-gas (WAG) process, the use of surfactant foams to retard gas mobility, and improving the viscosity of the CO₂-rich phase through the addition of cosolvents or entrainers. The research in FY91 was directed toward the selection and testing of cosolvents for improved oil recovery and to determine if polymer precipitation could be considered a viable technique for blocking the flow of gas in the high-permeability zones of a reservoir.

NIPER's past and present research in steamflooding EOR addresses those factors that limit production and impact the economics associated with light oil and heavy oil steamflooding. Problems of poor sweep efficiency, gravity override, and viscous fingering are common to both processes. 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 experiments with one-dimensional sandpacks, 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.

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During FY91, work began on 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. The manual will explore the concepts behind steam injection processes and provide 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 in the following section. They are addressed in the following order: BE5A, Gas Flooding; BE5B, Mobility-Control and Sweep Improvement in Gas Flooding; BE11A, Thermal Processes for Light Oil Recovery; BE11B, Thermal Processes for Heavy Oil Recovery.
**Objective**

The FY91 objectives of this project were to develop methods to mitigate the deleterious effects of solid precipitation in gas flooding, to determine the effect of porous media on gas-oil phase behavior, and to develop models describing the deposition of organic materials under miscible conditions.

**Research Summary**

Organic solid deposition is often a major problem in petroleum production and processing. The development of a prediction technique is crucial to the solution of this problem. The major task of this research is to develop predictive models to describe the precipitation of asphaltene and wax materials. Two new models were developed in this work: one based on a thermodynamic equilibrium principle and the other on the colloidal stability theory. The thermodynamic model assumes that the asphaltenes and wax are dissolved in oil in a true liquid state and may precipitate due to changes in thermodynamic conditions. It is based on the thermodynamic principle for solid-liquid phase equilibrium with continuous representation for asphaltene molecules. The thermodynamic equilibrium model has been tested to be more accurate than other published models for wax formation predictions. The colloidal stability theory, which was applied only to asphaltenes, assumes that asphaltenes exist in crude oil as solid particles in a colloidal suspension stabilized by the repulsion of the adsorbed resin molecules. These two models are more sophisticated and general than others that have been reported. Two different approaches are needed because experimental results on the characteristics of asphaltene are inconclusive, and it is still not well known whether the asphaltenes in crude oil exist as a true solution or as a colloidal suspension.

Accompanying the modeling work, experimental studies were conducted to study the mechanisms of CO2-induced asphaltene precipitation. Through coreflooding experiments, it was found that asphaltene precipitation occurred after gas breakthrough. As shown in figure 8, asphaltene contents for the produced oil dropped significantly after gas breakthrough because the oil was produced mostly by hydrocarbon extraction. The CO2 flood was conducted under immiscible conditions. The cumulative asphaltene production at oil production of 80% OIP was about 50 wt % of the original asphaltene in the oil. There was about 50 wt % of the asphaltene left inside the core along about 20% of the oil. A significant reduction of permeability in the core was observed. Also, experiments were conducted separately to investigate the effect of hydrocarbon extraction on asphaltene precipitation. At temperature and pressure conditions typical of CO2-coreflooding experiments, the extraction of an amount (about
CO₂ core flooding experiment:
Oil gravity=35° API, 4 wt% asphaltene
T = 120 °F, P = 1,500 psig
Berea sandstone: 2-ft L. x 2-in I.D.
S₀ = 62.98%PV, Sₘ = 37.02%PV
Porosity = 18.62%PV, PV = 207.85 ml.

FIGURE 8: Change of asphaltene content in oil produced during CO₂ flooding.

4% of light hydrocarbons (ranging from C₅ to C₂₁) from the sample oil by CO₂ caused deposition of almost all of the asphaltenes. However, if the oil was saturated only with CO₂ at the same conditions without hydrocarbon extraction, no asphaltene precipitation was found. These experiments showed that swelling is not the mechanism for organic solid precipitation. It was also found that the composition of oil imbibed into the core was not the same as that of the bulk oil. From this study, it was concluded: (1) the major mechanism for CO₂-induced asphaltene precipitation is the change of oil composition caused by CO₂ supercritical extraction; oil swelling by CO₂ dissolution does not cause asphaltene precipitation, and (2) the solubility of asphaltenes in organic solvents depends on the solubility power of the solvents, which is represented by the value of the solubility parameter. This study explains why asphaltene deposition usually occurs at or near the wellbore after CO₂ breakthrough in CO₂-flooded reservoirs.

Process Utilization and 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 project is to develop such a technique. Toward this end, a simplified asphaltene solubility model based on polymer solution theory has been developed and tested. The model is able to predict qualitatively the trends of the effects of
temperature, pressure, and composition. In addition, another thermodynamic model based on solid-liquid solution theory has been developed and successfully applied in the prediction of wax formation. This model is simple and can predict the wax appearance temperature and composition with reasonable accuracy. The techniques developed in this work can help industry tackle the deposition problem. Because the problem of organic deposition exists in the field, some major oil companies have requested technical help.

Publications

MOBILITY CONTROL AND SWEEP IMPROVEMENT IN GAS FLOODING

Principal Investigator: Clarence Raible
BPO Project Manager: Jerry F. Casteel
Project No.: BESB
Funding for FY91: $440,000 (EOR-Light Oil)
Period of Performance: October 1, 1990 - September 30, 1991

Objective

The overall objective of this research is to develop improved gas flooding technology for carbon dioxide (CO2) floods. Unfavorable mobility control of injected CO2 can significantly reduce oil recovery and sweep efficiency. Previous work has shown that the addition of miscible hydrocarbons as cosolvents or entrainers increased solvent power of the gas phase. Research in FY91 continued an evaluation on the application and selection of cosolvents to improve CO2 displacement processes. The research objectives were (1) for entrainers: to address the critical issues that remain before their application in field trials can be justified. These issues included identification of the best class of compounds from which to choose the most cost-effective entrainers, and determination of the best injection strategy for entrainers in gas flooding. For the latter, to test (1) cyclic CO2 processes for potential near-term applications; (2) for other additives: to evaluate unique approaches to improving sweep efficiency in gas flooding EOR processes and to investigate the precipitation of polymers for potential mid-term applications; and (3) for foam: initiate studies to evaluate foam flow behavior in radial corefloods. Although many researchers have studied foam for mobility control, few have actually studied the flow of foam under radial flow conditions—conditions more typical of oil field environments.

Research Summary

Previous project studies have shown that a volatile cosolvent can improve the extraction of crude oil components into the gas phase, resulting in greater gas phase density and viscosity. Work in FY91 was directed to the selection of cosolvents which not only produced the greatest improvement in oil recovery efficiency but also were cost-effective. Physical property measurements of CO2/cosolvent mixtures were used for the evaluation of cosolvents. Gas-phase properties were measured in an equilibrium cell with a capillary viscometer and a high-pressure densitometer. A cosolvent, used as a miscible additive, changed the properties of the supercritical gas phase. The addition of some cosolvents resulted in higher viscosities and densities of the gas mixture and reduced the minimum miscibility pressure of the CO2-rich phase. Also, the reduction of the minimum miscibility pressure enhanced the extraction of crude oil compounds into the gas phase.

Several constraints and requirements were investigated in the selection of a cosolvent for gas flooding. A cosolvent must be volatile and miscible with CO2. In addition, the relative quantity of the cosolvent which partitions into the oil phase was a factor to be considered for the successful application of cosolvents. Corefloods were used to determine the quantity of a cosolvent which partitions into the oil phase. These tests showed the
higher-molecular-weight cosolvents were bypassed by a gas displacement flood. Higher-molecular-weight compounds, although miscible at gas flooding conditions, would not be effective in sustaining improved oil recovery throughout a gas flood. Although the lower-molecular-weight compounds perform much better as cosolvent additives, only a few are actually acceptable.

Coreflood experiments were conducted to measure oil recovery efficiency of cosolvents that were selected from physical property measurements. Test results indicated lower-molecular-weight additives, such as propane, were the most effective cosolvents for increasing oil production in immiscible CO₂ floods. Coreflood tests indicated that propane had a higher oil recovery efficiency than a higher-molecular-weight cosolvent additive such as isooctane. The primary reason was that propane was more effective in achieving miscibility during the coreflood. Physical property measurements indicated that a mixture of propane and CO₂ produced a small increase in gas-phase viscosity which contributed to mobility control and an increase in oil recovery. The effects of light hydrocarbon slugs on oil recovery in immiscible CO₂ corefloods were evaluated. A propane slug (about 10 wt % of the OIP), used in conjunction with an immiscible CO₂ flood, produced about 20% more crude oil (33.6° API gravity, Delaware-Childers field, OK) when compared to a CO₂ flood without the cosolvent.

Another objective for FY91 was the evaluation of cosolvent additives and their application toward increased oil production from cyclic gas floods. Cyclic coreflood tests were made to compare oil production with slugs of CO₂ and blends of CO₂/propane. Comparison of cyclic tests indicated that using a cosolvent did not increase oil production. For increasingly higher cosolvent concentrations of propane, lower amounts of oil were produced for each of the successive cyclic production steps. In laboratory cyclic coreflood experiments, there was no evidence that use of a cosolvent would increase oil production in cyclic gas floods.

Experimental tests were also conducted to investigate the possibility of CO₂-induced polymer precipitation in a high-pressure PVT cell. The objective of polymer precipitation in gas flooding was to block the flow of injected gas from highly permeable zones and improve sweep efficiency. The polymer solutions used for these studies were xanthan gum and polyacrylamide. However, no precipitation was observed in PVT cell experiments when the polymer solutions were saturated with CO₂ under pressures ranging from 1,500 to 2,200 psig and temperatures ranging from 120° to 160° F. Polymer precipitation was observed only when divalent ions were added to the solutions. From these tests, it was concluded that polymer precipitation was generated by the hydrolysis of polymers and salting out by divalent cations.

**Process Utilization and Technology Transfer**

As stated in DOE's AORPIP, advanced gas flooding technology will contribute to increased production of light oil. Development of this recovery technology has been the major focus of this project. Project research of gas flooding has shown that the use of cosolvents can improve oil recovery of immiscible CO₂ gas floods. Potential cosolvent candidates are limited to lower-molecular-weight hydrocarbons, such as LPG. The results of this work have been provided to the industrial community through technical publications such as those listed below for FY91.
The research effort proposed for FY92 is to investigate the application of polymer gels to selectively plug higher-permeability channels of gas floods. For waterflooding, several water-soluble gels have been used to reduce fluid flow in channel zones. However, many of these polymer gels are not sufficiently stable and rigid to restrict flow of CO₂ floods. Therefore, methods will be investigated in FY92 that will initiate placement of stable, rigid gels in channel zones swept by CO₂ and direct the flow of gas to areas normally bypassed during a gas flood.

Publications


THERMAL PROCESSES FOR LIGHT OIL RECOVERY

Principal Investigator: David K. Olsen
BPO Project Monitor: Thomas B. Reid
Project No.: BE11A
Funding for FY91: $300,000 (EOR-Light Oil)
Period of Performance: October 1990 - September 30, 1991

Objective

The objective of the FY91 research program on thermal processes for light oil was to improve the understanding of the basic mechanisms responsible for light oil production using steam and to use this knowledge for further development of production techniques. The FY91 objectives were revised midyear to be more closely aligned with the direction outlined in DOE's AORPIP. These objectives were: (1) determine the applicability of semianalytical thermal predictive models in evaluating light oil steamflood potential; (2) analyze potential override and fingering tendencies using a two-dimensional (2-D) physical model for oil and sand from NPR No. 3, Teapot Dome (WY) field, (3) compare Teapot Dome steam diversion results with those from other heavy and light oil steamfloods; (4) conduct laboratory research (including evaluation of steam diverters) to directly benefit operations of the NPR No. 1, Elk Hills (CA) field light oil steamflooding pilot; and (5) transfer technology developed from this project to others in the field of thermal oil production by participating in Annex IV meetings conducted by the DOE and the Venezuelan Ministry of Energy and Mines (MEM).

Research Summary

Research to determine the applicability of semianalytical predictive models for the evaluation of light oil steamflood potential was conducted in conjunction with work being performed in project BE11B and is reported for that activity.

A series of experiments on steam-foam buildup (rate of pressure increase) and foam degradation (rate of pressure decline when surfactant injection is stopped) was conducted using a commercial high-temperature surfactant in one-dimensional (1-D) quartz sandpacks, or sandpacks containing reservoir sand, that were either oil-free or contained crude oil at low-oil saturation. In the absence of oil, the rate of foam buildup (pressure rise) was rapid when 1% surfactant in deionized water was injected into the sandpack along with steam and nitrogen. However, the presence of oil retarded the foam formation and slowed the initial pressure buildup rate. In these experiments, the oil-saturated sandpack was steamed, and the initial oil-in-place (OIP) was reduced from 75 to 20% before injection of surfactant and nitrogen. The rate of pressure buildup began to accelerate when the oil saturation in the pack was reduced to about 10% of initial OIP. The pressure peaked when the oil saturation in the pack was reduced to less than 5% OIP. Figure 9 shows schematically the difference in identical 1-D steamfloods where the same...
LIGHT OIL OBSERVATIONS

HEAVY OIL OBSERVATIONS

FIGURE 9. - Changes in physical appearance of effluents with decreasing oil saturation and the corresponding pressure response during concurrent injection of steam nitrogen and surfactant solution (1% SD-1020) into a preheated sandpack in the presence of different oils. The heavy oil is 13° API gravity Kern River (CA) crude oil, and the light oil is 32° API gravity Teapot Dome (WY) crude oil.

A surfactant/gas (foam) system was used on two different crude oils of different composition. In the case of heavy oil, foam was generated at a much higher oil saturation than was observed with light oil. This shows the effect of oil composition on foam/emulsion generation.

Foam or emulsion generation (resistance to flow as measured by the pressure drop, psi/ft) is very dependent on the local oil saturation as well as composition of the oil. To predict performance of a steam foam/emulsion diverter, the test must be performed at reservoir steamflood temperature with reservoir sand and oil. Figure 10 shows the pressure response during concurrent injection of steam, nitrogen, and surfactant solution in the presence of different oils. Crude oil composition significantly affected the rate of pressure buildup. These tests indicate that surfactants and gas can form high-temperature-tolerant foams and emulsions that provide high resistance (large pressure drop per foot) to flow in steam-swept areas and thus can be used to mitigate gravity override of steam or diversion of steam from high-permeability or gas-saturated zones. Foams can improve sweep efficiency, and the degree to which this can be achieved depends upon the oil composition and saturation, temperature, surfactant, surfactant concentration, liquid/vapor ratio, permeability of the porous media, adsorption of surfactant, and injection rate. Further work will focus on establishing conditions under which maximum mobility control can be achieved in a target reservoir.

Tests were conducted with the 2-D steamflood model filled with reservoir rock from zones being steamed at NPR No. 1 and NPR No. 3. Steamfloods on sands from NPR No. 1 showed behavior similar to that observed in the field. Scale deposition, high CO₂ production from the reaction of steam and carbonate minerals, fines release
Upon treating the scale with HCl, and a tendency to sweep only the higher permeability areas were observed. In steamfloods with crushed NPR No. 3 Shannon sandstone core, the clays swelled reducing permeability although oil recovery was >80% OIP.

**Process Utilization and Technology Transfer**

NIPER participates with other U.S. laboratories (Stanford University and Lawrence Livermore) in supporting DOE’s cooperative research agreement with the Venezuelan Ministry of Energy and Mines. 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 FY91, results of NIPER’s thermal EOR program were presented at three Annex IV meetings. One meeting was held in Caracas, Venezuela, and the other two at Stanford University. A report on the effect of wettability on light oil steamflooding research was published in the Annex IV Proceedings.

A presentation on the results of the light oil steamflooding research was made to DOE and Chevron at NPR No. 1. The presentation highlighted common behavior between the performance of steamfloods in the NIPER 2-D steamflood model and a light oil steamflood being conducted in the Shallow Oil Zone at Elk Hills.
Several participants at the UNITAR/UNDP 5th International Conference on Heavy Oil and Tar Sands (see Presentations below) requested NIPER's experimental procedures for preparing artificially oil-wet surfaces for use in laboratory studies.

Publications


Presentations


THERMAL PROCESSES FOR HEAVY OIL RECOVERY

Principal Investigator: Partha S. Sarathi
BPO Project Monitor: Thomas B. Reid
Project No.: BE11B
Funding for FY91: $250,000 (EOR-Heavy Oil)
Period of Performance: October 1990 - September 30, 1991

Objective

The objectives, scope of work, and milestones for this project were modified to reflect the current near-term research priorities of the DOE's AORPIP. The revised project objectives for FY91 were: (1) to expand and improve the thermal (steam injection) field operation handbook, (2) to assess the suitability of the Stanford University semianalytical steam model for field steamflood performance prediction, (3) to upgrade the existing two-dimensional (2-D) steamflood physical model, and (4) to enhance NIPER's thermal simulation capability.

Research Summary

An updated version of a steam injection handbook is being prepared as a ready reference for independent operators considering the use of steam to enhance oil recovery. The handbook is designed to help answer questions regarding steam injection processes and field practices. An earlier version of the handbook, written in FY90, is being considerably expanded to include the rewriting of several chapters incorporating information from California steam injection operators.

The handbook will discuss in detail the operational aspects of the steam injection processes. The concepts behind steamflooding will be explored, along with information required in the evaluation, design, and implementation of steam injection processes. Further, the various surface and subsurface systems and equipment involved in steam injection operations will be discussed, as well as the overall importance of good operational practices and maintenance schedules that reduce overall maintenance and operating costs.

The underlying message of the handbook is to convey that the operation of facilities associated with steam injection operations are not simple, and the economic success of the process depends on the constant review of performance of the equipment and the need to ensure its safe and correct operation. Improperly or poorly maintained facilities can doom otherwise successful steam injection operations.

The semianalytical steamflood predictive model developed at Stanford University was evaluated for its suitability in predicting steamflood field performance. An in-depth evaluation of the performance of this model indicated that it overestimates field production rates. The predicted production rate data had very little resemblance to observed production data, and the predicted production rates were considerably higher than observed values. It was concluded that the model needs modification before it is relied upon for use as a field steamflood performance prediction tool.
The current 2-D physical steamflood model was improved significantly by the addition of new electronic backpressure regulators (EBPR) and a state-of-the-art data acquisition and control system. The addition of the new EBPR eliminated the pressure pulse problems associated with steam-foam experiments and improved steam/foam performance prediction.

As part of NIPER's research in support of BPO in the area of thermal simulation, NIPER senior staff members attended a 4-day training class to learn about the capability and usage of Computer Modeling Group's 'STARS' steamflood simulator. To assist in technology transfer to independent producers, NIPER will use 'STARS' in FY92 to determine the potential for increasing heavy oil production using steam from the Nacatoch sands of Arkansas and Louisiana.

Process Utilization and Technology Transfer

Even though steamflood (heavy oil reservoirs ≤ 20° API) is a mature technology and widely practiced by major operators in California, the process has found very little utilization in heavy oil reservoirs of the other states. It is suspected that one reason for this is that steam injection technology is not readily available to small and medium sized operators, and who own most of the leases. It is anticipated that the steam injection process operator's handbook will help in the rapid dissemination of this proven technology to independent operators. This objective is consistent with the National Energy Strategy which is to increase U.S. oil production using currently-available oil recovery technology.

A condensed version of the chapter on environmental issues affecting steam injection operation from the handbook was presented at the Society of Petroleum Engineer's (SPE) Western Regional Meeting in Long Beach, Calif., Mar. 20-22, 1991. This paper was highly acclaimed for its timeliness and subsequently published in the Journal of Petroleum Technology (JPT) and was selected as the paper of the month by the editors of JPT. This paper was also selected by the SPE Transactions Editorial Committee for inclusion in the 1991 SPE Transactions. The selection of this paper was based on the originality of the work and its lasting significance to petroleum technology.

Publications


Presentations

III. FUELS RESEARCH

The Fuels Research (FR) Department continues its multifaceted program in developing procedures for the separation and identification of individual compounds and classes of compounds in petroleum and alternative feedstocks, in the measurement of thermodynamic properties of organic materials, and in determining the performance and emissions of fuels burned in engines. The research supports DOE's AEPT Program which 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. In FY91, the overall fuels research effort consisted of two Base Program projects, 15 projects under the Supplemental Government Program (SGP), and 55 projects under the Work for Others (WFO) Program.

The two Base Program projects focus on the separation and identification of problematic compounds in heavy crude distillates and determination of thermodynamic properties of organic compounds in heavy and alternative crude oils. 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 work 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.

The Fuels Engines Section is comprised of a research team studying the interactions of the newer fuels and the effectiveness of additives on engine performance. Although there is no Base Program work in this area, the research is synergistic with the other work and provides information on the overall acceptability of today's 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 gasoline, 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 oils is low. 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 to extend thermodynamic data developed for light petroleums to the heavier crudes, these computerized correlations produce data that can be off by several orders of magnitude when applied to the design of processing streams. 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. 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 FY91 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 FY91: $350,000 (AE&PT)
Period of Performance: October 1, 1990 - September 30, 1991

Objective

The 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 which 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 coal liquids. 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 "key compounds" chosen for study included: benzo[c]phenanthridine, 2-aminobiphenyl, and 1,2,3,4-tetrahydrocarbazole. Measurements (not completed for all compounds) included condensed-phase heat capacities (5-450 K) by adiabatic calorimetry; liquid-phase heat capacities to near Tc by differential-scanning calorimetry; enthalpies of formation by combustion calorimetry; vapor pressures by comparative ebulliometry and inclined-piston manometry (0.02-270 kPa); densities (298-423 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 determine critical properties for 2-aminobiphenyl. The other materials studied decomposed far below 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 hydrodenitrogenation (HDN) is attempted.

Two high-purity, four-ring aromatic nitrogen-containing molecules were prepared for thermodynamic measurements as a test of correlations developed based on information obtained in this project. Measurements were begun 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 will follow in FY92. In FY92, additional key compounds representing polynuclear aromatics and diheteroatomic aromatics are proposed for study.

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.

**Process Utilization and 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 HDN steps are now looking for a catalyst which will function effectively at relatively low temperatures for the efficient removal of nitrogen from polycyclic aromatic compounds. The results from NIPER's thermodynamic equilibria studies on two-ring aromatic nitrogen compounds (described in NIPER reports 458, 468, and 469, plus earlier reports and journal articles cited therein) 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 FY91, and were published as NIPER report 544. These preliminary results 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 the Supplemental Government Program (SGP) entitled, "Process-Engineering Property Measurements on Heavy Petroleum Components." Present emphasis within the SGP Program is on aromatic and hydroaromatic hydrocarbons. These compounds are important not only in the upgrading of heavy petroleum, but 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 the SGP Program 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 benefits 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 within this research group. The methods and apparatus are presently being used within projects for industrial as well as governmental clients.

Publications


Related Publications


Fuel Chemistry

Since 1918, the Bartlesville Center has been involved in the development of analytical and instrumental procedures capable of identifying individual 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 January 1990 (NIPER Rpt. No. 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 which are particularly harmful in 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.

The summary of FY91 research for Project BFR2 is presented in the following section.
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 FY91: $300,000 (AE&PT)
Period of Performance: October 1, 1990 - September 30, 1991

Objectives

General objectives 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 FY91 were: (1) to determine relative carbon forming (coking) tendencies of compound classes in petroleum and to relate coke yield and heteroatom content to chemical structure, (2) to develop methods for isolation and identification of metal-containing compounds in petroleum, and (3) to further develop mass spectrometric methods for analysis of nitrogen compounds in petroleum.

Research Summary

Work on coking behavior of compound classes in petroleum resid was completed and the corresponding topical report published. Coke formation is inherent in many refining processes suitable for petroleum resid, heavy oils, and tar sand bitumens. The standard laboratory method for assessing coking tendency is a determination of microcarbon residue (MCR, ASTM D 4530), which provides comparable results to the older Ramsbottom and Conradson carbon residue procedures. Results from laboratory carbon residue determinations correlate well with actual coke yield in refining processes, including delayed coking and catalytic cracking. Synergistic effects in carbonization are rare. Typically, the coke or MCR yield from a combined stream is simply the weighted average of the individual feedstocks. However, this generalization had not previously been tested with regard to the various compound classes within a given sample. In addition, the relative partitioning of sulfur, nitrogen, and metals into carbon residue vs. volatiles as a function of their initial chemical form had not been investigated.

Five petroleum >1000° F resid samples were separated into compound-type fractions using liquid chromatography. The coking tendency of each compound type was assessed using the MCR test. Heteroatom (N, S, Ni, V) partitioning between MCR solids vs. volatiles was determined through analysis of the starting fractions and the corresponding MCR solids.

The weighted sum of MCR solid yields over all of the compound types in a given resid was typically in good agreement with the MCR yield of the whole resid. This finding agrees with prior studies indicating coke yield to be an additive property. Sulfur partitioning was also an additive property, was predictable from MCR yield, and was nearly independent of the initial form (sulfide, thiophenic, sulfoxide) present. Nitrogen and nickel partitioning were
nonadditive and therefore composition dependent. Partitioning of vanadium into solids was essentially quantitative for all resids and their fractions.

MCR solid yield was generally dependent only on H/C ratio. However, there is some evidence indicating secondary dependence on hydrocarbon structure, i.e., that naphthenic rings reduce MCR in proportion to H/C by virtue of their effective hydrogen transfer properties. Deposition of N and Ni into MCR solids over the fractions was often appreciably less than that of the whole resids, thereby indicating that interaction among various compound types was required for maximum incorporation of those elements into coke.

Work on separation of metal-containing compounds in petroleum resids was discontinued at the end of FY91 because the available funding for FY92 was earmarked for catalytic cracking. A topical report was prepared which summarized work over this and the previous two years. Evidence to date has indicated that nonporphyrinic metal complexes are not simply associated or otherwise masked (in terms of visible spectrophotometric response) porphyrinic species. A summary of the work is provided below.

Acid and base fractions from petroleum vacuum resids with no detectable (by visible spectrophotometry) quantities of porphyrinic Ni or V complexes were hydrotreated under various conditions to determine if significant amounts of porphyrinic metals were released, via disassociation or other means, upon hydrotreating. No significant quantities were observed, thereby indicating that nonporphyrinic metals were not simply associated, complexed, or otherwise masked (in terms of visible spectrophotometric response) porphyrinic metal complexes. However, it is possible that hydrotreating was simply not effective in breaking up these associates and/or that some porphyrinic forms of metal were in fact released but were rapidly destroyed by hydrotreating.

In addition, three liquid chromatographic (LC) separation methods were sequentially applied to Cerro Negro (Orinoco belt Venezuelan heavy crude) >700°C resid in an effort to separate and concentrate the metal complexes present. Nonaqueous ion exchange chromatography was used initially to separate the resid into acid, base, and neutral types. A custom synthesized alkylyridyl-bonded silica HPLC column packing was used in the intermediate separation step; plain silica was employed for the final step. Two concentrates containing 19,500 and 13,500 ppm total V, or an estimated 19 and 13 wt % V-containing compounds respectively, were obtained. The degree of enrichment of Ni compounds obtained was significantly lower. By visible spectrophotometry, using vanadyl etioporphyrin as a standard, each of the concentrates contained near a 1:1 ratio of porphyrinic:nonporphyrinic V complexes. Analogous separation behavior for porphyrinic vs. nonporphyrinic metal forms was observed throughout much of the work, thereby suggesting that a comparable diversity of structures existed within each general class of metal compounds. However, strong acid and strong base fractions produced in the nonaqueous ion exchange separation contained largely nonporphyrinic metal complexes, whereas the bulk of the measurable porphyrinic complexes partitioned into the weak base and neutral fractions. Also, nonporphyrinic forms of V tended to elute later in the other LC separations than porphyrinic forms. Thus, the behavior of porphyrinic vs. nonporphyrinic complexes did not directly correspond, but appreciably overlapped. The generally wide dispersion of both Ni and V over the LC separation scheme suggests a structural variety of metal complexes that is comparable to that observed for other heteroatoms (N, S, O) in petroleum.
Significant progress was also achieved toward development of a chemical derivatization procedure which enables differentiation of primary, secondary, and tertiary amines during GC/MS analysis. Exhaustive trifluoroacetylation is carried out which typically substitutes 2, 1, and 0 groups on primary, secondary, and tertiary amines, respectively. Thus, compounds analogous to aniline (primary aromatic amines) can be generally differentiated from homologs of pyridine (tertiary aromatic amines). Also, benzologs of pyrrole (indole, carbazole, etc.) are usually readily distinguished from basic nitrogen compounds of the same molecular weight (e.g., methylcarbazole vs. aminofluorene) after derivatization. A preliminary report on the method was published and subsequently presented at the fall 1991 National ACS meeting.

**Process Utilization and Technology Transfer**

A paper was presented at the 5th UNITAR International Conference on heavy crude and tar sands which discussed prior work done under this project. However, the current low oil prices have effectively stifled interest in heavy oil in general, including analytical methodology for heavy oils. For this reason, the emphasis of this project has shifted toward improving the utilization of conventional crude, specifically conversion of heavy ends to distillates and troubleshooting common refining problems. For example, the recently completed work on coke formation relates to upgrading schemes where coke formation is an integral part of the process (e.g., delayed coking) or an undesirable side reaction (e.g., catalytic cracking or hydrotreating). Also, GC/MS methodology for nitrogen compounds (this year), phenolic compounds (FY89), and carboxylic acids (FY90) is applicable to storage and thermal stability problems with distillate fuels, monitoring process efficiency in removing those species, or other types of troubleshooting activities.

In-house utilization of analytical methodology developed within this project included the following: (1) determination of phenols, carboxylic acids, and polyglycols in brines taken from the U.S. Strategic Petroleum Reserve, (2) determination of alkylindole and phenolic compound distributions in light cycle oils (LCO) and correlating those parameters with storage stability of LCO, (3) analysis of pipeline deposits in a major oilfield to determine compound types contributing to plugging and flow reduction, and (4) separation of asphalts into compound classes in order to determine sulfur speciation within each class. Sponsors for the above work included both governmental agencies and private industry. In-house application of methodology in work for others is a very effective means of technology transfer, since the customer sees original data from a given method, and how it may be applied to a real problem.

**Publications**


Presentations

Oral versions of the last two publications were presented at the 5th UNITAR Conference and Fall 1991 National ACS meeting, respectively.