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

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FOREWORD

The National Institute for Petroleum and Energy Research (NIPER) is pleased to submit the "FY91 Annual Research Plan," NIPER-465, in accordance with the provisions of Cooperative Agreement DE-FC22-83FE60149 between the IIT Research Institute and the Department of Energy (DOE). Previous research plans have been prepared as follows:

- "1983-84 Annual Research Plan," NIPER-6 (NTIS No. DE84010565), May 1984.
- "FY85 Annual Research Plan," NIPER-11 (NTIS No. DE85027426), March 1985.
- "FY86 Annual Research Plan," NIPER-85 (NTIS No. DE85000143), October 1985.
- "FY87 Annual Research Plan," NIPER-164 (NTIS No. DE86000303), October 1986.
- "FY88 Annual Research Plan," NIPER-260 (NTIS No. DE8700126), October 1987.
- "FY89 Annual Research Plan," NIPER-357 (NTIS No. DE89000701), December 1988.
- "FY90 Annual Research Plan," NIPER-420 (NTIS No. DE9000210), January 1990.

Annual Reports have also been published as:

- "1984 Annual Report: National Institute for Petroleum and Energy Research," NIPER-20 (NTIS No. DE85000122), April 1985.
- "1985 Annual Report: National Institute for Petroleum and Energy Research," NIPER-120 (NTIS No. DE86000265), March 1986.
- "1986 Annual Report: National Institute for Petroleum and Energy Research," NIPER-220 (NTIS No. DE87001228), March 1987.
- "1987 Annual Report: National Institute for Petroleum and Energy Research," NIPER-320 (NTIS No. DE88001234), October 1988.
- "1988 Annual Report: National Institute for Petroleum and Energy Research," NIPER-400 (NTIS No. DE89000759), September 1989.

These plans and reports describe the initiation and development of the research effort at NIPER, and much of that explanation has been left out of this report.

This eighth plan describes the work to be performed in FY91. Projects in both Energy Production Research and Fuels Research are presented in the program.

We wish to express our appreciation to the Director, Project Managers, and other personnel of the DOE/Bartlesville Project Office for their cooperation in the preparation of this plan.

EXECUTIVE SUMMARY

In line with the Federal Oil Research Program to maximize the economic producibility of the domestic oil resource, the National Institute for Petroleum and Energy Research (NIPER) presents this FY91 Annual Research Plan, which is designed to help the Department of Energy (DOE) meet the following objectives:

- For the near-term, to preserve access to petroleum reservoirs with high potential which are rapidly approaching their economic limits.
- For the near-term, develop analytical and physical property data in heavier feedstocks.
- For the near-term, to develop, test, and help transfer the results of the research to petroleum producers/refiners.
- For the mid- and long-term, to develop and improve the understanding of advanced and novel petroleum recovery processes and process applications for heavier feedstocks.

This Annual Research Plan describes the work to be performed in FY91 for the Department of Energy under provisions of the Base Program in Cooperative Agreement DE-FC22-83FE60149 between the DOE and IIT Research Institute which operates NIPER.

Organization and Facilities

NIPER is organized into two research departments -- Energy Production Research (EPR) and Fuels Research (FR). Projects in EPR deal with various aspects of enhanced oil recovery and include reservoir characterization, chemical flooding, gas injection, steam injection, microbial enhanced oil recovery, and the environmental concerns related to these processes. Projects in FR consider the impact of heavy oil and alternative fuels on the processing and end-use of fuels. This breadth of interest assures that NIPER's work will be significant in advancing petroleum technology and that NIPER, with its staff of about 175 employees, will be a viable place to conduct research for other government agencies and industrial clients.

Research Program

Program planning is the result of a cooperative effort by NIPER employees and BPO project managers. In FY91, the DOE will fund this work through its Enhanced Oil Recovery (EOR) and Advanced Extraction and Process Technology (AEPT) Research Programs. The Base Program accommodates 14 research projects. Of this total, EPR has 12 projects and FR has two. The projects are listed in the following table. The Base Program reflects a strong emphasis on enhanced oil recovery (geoscience and recovery processes) while maintaining an interest in basic

research on the chemistry of crude oils. It is designed primarily for near- and mid-term contributions to the maintenance of the Nation's energy supply.

Energy Production Research

Research in the Base Program addresses the remaining oil resource with research on reservoir engineering, geology, geophysics, geochemistry, oil recovery processes, and environmental science directed toward the goal of increasing economic producibility of petroleum resources.

This research program is mission-oriented, with well-defined goals and objectives specified to meet them. Each project within the program addresses the mission. The research clearly addresses the near- and mid-term needs of the petroleum industry, complementing the program's historical emphasis on long-term research. The program reflects the Nation's concern for the environment. The results of the research will be compiled, analyzed, and submitted to the DOE in a timely manner and suitable for dissemination to the private sector.

The EPR program seeks to improve the integration and coordination of geoscience and extraction research, to improve near-term measures to enhance domestic producibility, and to broaden the context of oil recovery research by addressing mobile as well as immobile oil.

Fuels Research

Research in the Base Program recognizes the need to develop both a basic chemical understanding and basic thermochemical and thermophysical properties data to effectively utilize future resources for transportation fuels. Current refineries are more than 90% efficient when processing light, sweet crudes. This is not the case when processing heavier crudes with higher metals and heteroatom content.

This research effort has defined intermediate goals of developing information on compound types in the heavy feedstocks that are most likely to cause problems in the refining sequence or in the finished fuel performance.

The Fuels Research program seeks to broaden the pool of crudes for the refineries while helping to increase the efficiency of introducing heavy crudes to the process stream.

Base Program for FY91

Project	DOE FE Program*	Manpower, Man-Years	Funding, \$K
<u>ENERGY PRODUCTION RESEARCH</u>			
BE1. Reservoir Assessment and Characterization	EOR-LO	5.8	800
BE2. TORIS Research Support	EOR-LO	3.1	340
BE3. Development of Improved Microbial Flooding Methods	EOR-LO	2.9	300
BE4A. Development of Improved Surfactant Flooding Methods	EOR-LO	4.8	600
BE4B. Development of Improved Alkaline Flooding Methods	EOR-HO	1.0	150
BE4C. Development of Improved Mobility Control Methods	EOR-LO	1.25	200
BE5A. Gas Flooding	EOR-LO	1.2	200
BE5B. Mobility-Control and Sweep Improvement in Gas Flooding	EOR-LO	3.2	440
BE9. Three-Phase Relative Permeability	EOR-LO	3.1	300
BE11A. Thermal Processes for Light Oil Recovery	EOR-LO	1.95	300
BE11B. Thermal Processes for Heavy Oil Recovery	EOR-HO	1.4	250
BE12. Imaging Techniques Applied to the Study of Fluids in Porous Media	AEPT	3.7	545
Total EPR Base Projects		33.4	4,425
<u>FUELS RESEARCH</u>			
BFR2. Development of Analytical Methodology for Analysis of Heavy Crudes	AEPT	2.4	300
BFR3. Thermochemistry and Thermophysical Properties of Organic Nitrogen- and Diheteroatom-Containing Compounds	AEPT	2.1	350
Total FR Base Projects		4.5	650
TOTAL BASE PROJECTS		37.9	5,075

* Abbreviations: EOR = Enhanced Oil Recovery; LO = Light Oil; HO = Heavy Oil;
AEPT = Advanced Extraction and Process Technology

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INTRODUCTION

This is the eighth Annual Research Plan for the National Institute for Petroleum and Energy Research (NIPER). NIPER is operated under a cooperative agreement between the U.S. Department of Energy (DOE) and the IIT Research Institute (IITRI). The cooperative agreement, which became effective October 1, 1983, provides for operation of NIPER as a not-for-profit organization doing research both for the Government and for private companies.

NIPER was established by the DOE to undertake long-range, high-risk research that companies are reluctant to do and to perform contract research for government and industrial clients. This arrangement has enabled NIPER to grow as an independent entity.

The near-term objective of the DOE program is to maintain access to resources presently being produced in domestic oil and gas fields and to decrease the rate of decline of domestic production through the application of current technology. NIPER projects in integrated reservoir characterization, chemical flooding, gas injection, steam injection, and microbial EOR address near-term concerns of domestic oil production. Further, problems associated with the utilization of heavier fossil feedstocks are being addressed as new fuel blends increasingly enter the marketplace. In the near-term, NIPER is uniquely positioned to test new oil and gas technology through industry participation in the Work for Others Program and in government-industry R&D programs.

The near to mid-term objectives of the DOE program are to maximize the recovery efficiency of discovered oil and gas through improved understanding of the resource, to develop advanced extraction and instrumentation techniques, and to work closely with oil producers through DOE-sponsored technology transfer programs. The objective also emphasizes an expanded understanding of the environment, assuring that it keeps pace with new and improved extraction technologies. NIPER projects dealing with the quantification of reservoir heterogeneities, pore structure analysis, and fluid flow in porous media are designed to improve extraction technologies. Current advances in instrumentation and simulation procedures can be expanded to enhance the discovery and ultimate utilization of both conventional and unconventional resource targets. The NIPER program will assist DOE in its evaluation of the environmental impact on new petroleum exploration and production technologies.

Scope and Organization

Research at NIPER is broad in scope and provides for major studies in petroleum and fuels research. The DOE-sponsored projects described in this research plan form the nucleus which enables NIPER to present a broad capability of research for other agencies and private companies. NIPER is engaged in active marketing to offer these opportunities to a wide clientele and, in so doing, has achieved significant success.

The organization at NIPER is shown in figure 1. The research effort is divided between two departments: Energy Production Research (EPR) and Fuels Research (FR). The EPR Department has primary responsibility for enhanced oil recovery projects and is divided into three sections: Geotechnology, Chemical and Microbial Displacement, and Thermal and Gas Displacement. The FR Department is divided into Processing and Thermodynamics, Fuel Chemistry, and Fuels/Engines Sections.

The Bartlesville Project Office (BPO) is collocated with NIPER and serves as the DOE administrator of the cooperative agreement. The BPO is delegated the lead assignment for implementing Fossil Energy programs in Enhanced Oil Recovery (EOR) and Advanced Extraction and Process Technology (AEPT). These programs are carried out by BPO personnel through management of a number of Fossil Energy projects executed by (1) NIPER, which utilizes the Federal equipment and facilities at Bartlesville, (2) industrial and university research organizations, and (3) National Laboratories.

Facilities and Personnel

NIPER's facilities are located in Bartlesville, Oklahoma, and consist of 19 buildings with a total floor space of 156,000 square feet on 17 acres. Many of the buildings were specifically designed for petroleum research activities.

NIPER has a staff of approximately 175 people with over 90 technically trained scientists and engineers having background experience and competence in most areas of petroleum research and technology transfer. Major areas of strength are enhanced oil recovery, geoscience, hydrocarbon processing, fuel characterization, mass spectrometry, thermodynamics, and fuels/engines research.

Equipment available at NIPER includes both state-of-the-art commercial equipment and in-house-developed items that may be prototypes of research equipment for commercial development. New capital equipment is added to keep abreast of improved methods and to try new approaches. The capital equipment proposed for FY91 is listed in appendix A.

Another important part of NIPER is its specialized library with excellent coverage on petroleum and related topics. On-line computer data files, such as the DOE Energy Data Base (RECON) and commercial services, are used. Interlibrary loan facilities extend the capability even further.

**NATIONAL INSTITUTE
FOR
PETROLEUM AND ENERGY RESEARCH**

ORGANIZATION

FIGURE 1. - NIPER Organization.

Program Structure

Under the cooperative agreement, NIPER's research program consists of three elements. The Base Program is specifically designed to assist the DOE in meeting its objectives through EOR processes and geoscience research and fundamental studies for the conversion of available hydrocarbons to quality transportation fuels. The second segment is the Supplemental Government Program, and it includes research for non-DOE government agencies as well as DOE work not included in the Base Program. The third segment is the Work for Others Program which encourages research work from the private sector and others. Only the Base Program is included in this plan.

The numbering system for the project descriptions consists of: a letter (B) indicating the Base Program, a letter designation for the Research Group (E for Energy Production Research and FR for Fuels Research), and a numeral indicating the project number. Thus, BE3 would indicate project 3 of Energy Production Research. The numbers are not consecutive because some projects have been completed and their numbers are not reassigned to new projects.

The projects in the Base Program are described under the following headings:

- (1) Background--history of problem, need for research, connection with DOE goals, previous work.
- (2) Objective--a brief statement of project goals.
- (3) Scope of Work--approach, tools, and techniques to be used. Includes a listing of specific tasks to be performed.
- (4) Deliverables--reports to be submitted to DOE.
- (5) Planned Staffing--listing of positions by categories and man-years. Project Leaders are named.
- (6) Equipment Requirements--major items of equipment needed for the project indicating whether they are available or will have to be purchased.

The funding for the Base Program is \$5.075 million, distributed as shown in table 1. The Base Program provides for technical staffing requirements of 37.8 man-years, as shown in table 2.

TABLE 1. - FY90 funding for Base Program

Project Funding	Base Program DOE, \$K
Energy Production Research	4,425
Fuels Research	<u>650</u>
Total	5,075

TABLE 2. - Technical staffing requirements

Base Program	Manpower, man-years
Energy Production Research	33.4
Fuels Research	<u>4.5</u>
Total	37.9

Program Content

The Annual Research Plan for NIPER describes projects in the Base Program which are fully funded by DOE. It is designed to support near-, mid-, and long-term DOE programs in enhanced oil recovery and advanced extraction and process technology, with emphasis on near-term (5-year) objectives.

For the Base Program, initial guidance in terms of funding profile by work area was given by DOE. Work statements were prepared by NIPER and reviewed by BPO Program Managers and Technical Project Officers and DOE Headquarters Program Managers. Final approval is provided by the Program Guidance Committee. The FY 91 Base Program has been refocused to comply with the objectives of the Federal Oil Research Program Implementation Plan. The new emphases in the Base Program projects are on field work, field support, technology transfer, and synergies among different projects and disciplines. Some projects were continued after being scrutinized for agreement with objectives of the Program Implementation Plan.

Energy Production Research

Base Program research conducted by the Energy Production Research Department (EPR) is designed to improve, in the near-term, the predictability and performance of EOR processes. The program has combined efforts directed at DOE analysis and planning activities, support research, and field work. Previous emphasis on support research should be continued in order for DOE to meet the goals of the Federal Oil Research Program Implementation Plan (PIP). The proposed program parallels the new implementation plan with (1) phased field analysis that identifies near-term opportunities for operators and needs for risk reduction by the federal government for mid-term and long-term opportunities, (2) 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, (3) application of technical advances to specific field applications, and (4) continued research directed toward improving the understanding of the mechanisms of EOR processes.

In this plan, projects are grouped into two major areas of work. The first focuses on improved oil recovery through a better understanding of the basic mechanisms of EOR processes. Physical and mathematical models are developed and used to simulate processes and verify hypotheses. These models also are useful as tools for planning future research. The second major area of work is concerned with quantitative predictions of fluid-flow behavior in reservoirs. Such fluid-flow behavior is affected by the geometry of pores and the reservoir as a whole, wettability, mineralogy, fluid distribution, permeability, heterogeneities on both micro- and macroscopic scales, and the history of the reservoir.

The Base Program proposed for EPR will continue working toward near- and mid-term goals of improving predictability and performance of EOR processes through integrated studies of fluid-flow behavior and process mechanisms. Experimental results will be incorporated into process and reservoir numerical simulators. EPR has a total of 12 projects in the Base Program, 11 of which are funded under DOE's Enhanced Oil Recovery Program and one under the Advanced Extraction and Process Technology Program. The research of BE1 is based on a specific reservoir, while all the others are based on generic reservoir properties and are aimed at producing results usable by domestic producers in the near term.

Fuels Research

The Fuels Research Department has two Base Program projects in DOE's Advanced Extraction and Process Technology Program. The research effort in project BFR2 will be to develop and refine analytical methods for determining the compounds or types of compounds suspected of contributing to problems associated with refining and product acceptability.

Project BFR3 will be a continuation of the program for determining thermodynamic properties of polycyclic, nitrogen-containing aromatic compounds and other polycyclic aromatics containing two heteroatoms. These areas are selected because refinery feedstocks increasingly include more heavy oil and are expected to include tar sand bitumen, shale oil, and coal liquids in the future. These materials contain increasing levels of heteroatom-containing constituents.

Fuels Research is working toward the goal of improving the understanding of upgrading heavy oils and alternative feedstocks to reach a theoretical and fundamental background at least equivalent to that presently used in the refining of conventional crude oils.

Reporting

Reports to the Department of Energy include monthly, quarterly, annual, topical, and status reports. Topical and status reports are identified in the Deliverables section of the project plans. Topical reports may be used as the basis for technical society presentations and/or journal publications once they have been submitted to the DOE.

Monthly Progress Report

The Monthly Report provides financial data and progress toward key milestones. It is designed to be as brief and concise as practical.

Monthly reports for all projects will be delivered to the BPO by the 20th of the month following the reporting period. The Monthly Report contains a research summary for each project addressing progress towards key milestones and a key milestone status report showing that work is ahead of schedule, on schedule, or behind schedule. Proposed remedial action and impact on completion of the project will be addressed for work that is behind schedule.

The Monthly Report will give the financial and manpower status for each project and for the total Base Program. An updated listing of the status of all key milestones and deliverables will also be included.

Quarterly Technical Report

Quarterly Technical Reports are summary presentations of technical progress. They focus on advances made in the technical program and are limited in the amount of material presented. Whenever a phase of a project indicates the need for a comprehensive description, a topical or status report will be written.

Quarterly Technical Reports are to be delivered to the BPO by the last day of the month following the reporting period. The Quarterly report contains a summary of the technical progress on each project during the reporting period and includes pertinent data, research results, and conclusions.

Annual Report

The annual report is a summary of technical progress made on each approved research project. It focuses on the advances made in the technical program and is limited in the amount of material presented.

The annual report will be delivered to the BPO 90 days after the end of the fiscal year. The report contains a brief summary (project by project) of the year's research work and accomplishments.

Topical Report

Completion of a significant phase of the research usually results in a topical report. It encompasses a body of work that completes an assignment (task or tasks) and is a stand-alone document. Often, it may result in a report to a technical society or lead to publication of a journal article.

Topical reports describing work on individual projects are designated throughout the plan as deliverables under the cooperative agreement. Dates shown for these deliverables in the plan are the dates a final draft of the report will be submitted to the BPO for review.

Status Report

Status reports are interim progress reports prepared for DOE Project Managers. They have much the same basis as that of topical reports but represent completion of only a portion of a total research effort. In certain instances, a status report may be only a one or two-page letter summary. If a status report is listed as a deliverable, the designated date refers to the date that the final draft is to be delivered to the BPO.

BASE PROGRAM

The Base Program--fully funded by DOE for \$5.075 million--is a research program designed to support DOE in its effort to maximize the economic producibility of domestic oil and gas resources through field work, field support, technology transfer, geoscience, and EOR research and to determine the processing criteria required in converting available hydrocarbons to quality transportation fuels. The Base Program accommodates 14 research projects. Of this total, EPR has 12 projects and FR has two.

As shown in table 3, EPR's 12 projects are funded from DOE's Enhanced Oil Recovery and Advanced Extraction and Process Technology research programs in the amount of \$4,425K. The two FR projects are funded by Advanced Extraction and Process Technology in the amount of \$650K, bringing the total program to \$5,075K. Each of the 14 projects addresses a problem area in the projected future development of energy resources in the United States. U. S. proved reserves have declined steadily since the 1970s, and imports already constitute more than 50 % of domestic consumption. To halt this increase in dependence on imported oil, the precipitous abandonment of marginal wells has to be arrested, and promising and advanced technologies have to be developed and transferred to operators. NIPER's research program is structured to achieve these goals.

Enhanced oil recovery projects are conducted by NIPER in its Energy Production Research Department, and projects relating to analysis and properties of alternative fuel sources are conducted in the Fuels Research Department. Together, the two groups of projects represent an effort to develop preparedness for the energy problems which appear inevitable.

TABLE 3. - Base Program for FY91

Project	DOE FE Program*	Manpower, man-years	Funding, \$K
<u>ENERGY PRODUCTION RESEARCH</u>			
BE1. Reservoir Assessment and Characterization	EOR-LO	5.8	800
BE2. TORIS Research Support	EOR-LO	3.1	340
BE3. Development of Improved Microbial Flooding Methods	EOR-LO	2.9	300
BE4A. Development of Improved Surfactant Flooding Methods	EOR-LO	4.8	600
BE4B. Development of Improved Alkaline Flooding Methods	EOR-HO	1.0	150
BE4C. Development of Improved Mobility Control Methods	EOR-LO	1.25	200
BE5A. Gas Flooding	EOR-LO	1.2	200
BE5B. Mobility-Control and Sweep Improvement in Gas Flooding	EOR-LO	3.2	440
BE9. Three-Phase Relative Permeability	EOR-LO	3.1	300
BE11A. Thermal Processes for Light Oil Recovery	EOR-LO	1.95	300
BE11B. Thermal Processes for Heavy Oil Recovery	EOR-HO	1.4	250
BE12. Imaging Techniques Applied to the Study of Fluids in Porous Media	AEPT	3.7	545
Total EPR Base Projects		33.4	4,425
<u>FUELS RESEARCH</u>			
BFR2. Development of Analytical Methodology for Analysis of Heavy Crudes	AEPT	2.4	300
BFR3. Thermochemistry and Thermophysical Properties of Organic Nitrogen- and Diheteroatom-Containing Compounds	AEPT	2.1	350
Total FR Base Projects		4.5	650
TOTAL BASE PROJECTS		37.9	5,075

* Abbreviations: EOR = Enhanced Oil Recovery; LO = Light Oil; HO = Heavy Oil;
 AEPT = Advanced Extraction and Process Technology

Energy Production Research

Research in the Base Program is designed to support the Federal Oil Research Program as outlined in DOE's Program Plan for Enhanced Oil Recovery. Federal enhanced oil recovery research is a national effort to maximize the economic producibility of the domestic oil resource. Specifically, the program is designed for the near-term to preserve access to reservoirs with high potential which are rapidly approaching their economic limits; for the mid-term, to develop and transfer advanced oil recovery technologies to operators; and for the long-term, to improve the understanding of oil recovery mechanisms to define new recovery techniques.

The Federal Oil Research Program defines six closely integrated lines of research reflecting the respective EOR processes and the "crosscutting" issues that affect all EOR processes. These are chemical flooding, thermal recovery, gas flooding, microbial EOR, basic geoscience/resource research, and analysis and evaluation.

The Energy Production Research Program has two main parts, as shown in figure 2. The first emphasizes geoscience research, and the second focuses on EOR processes. Results from both parts are combined to develop reservoir and process simulators which are used to predict oil recovery and design EOR projects.

The geoscience research program has combined efforts directed at DOE analysis and planning activities, support research, and field work. The past emphasis on support research should be continued in order for the DOE to meet the goals of the Federal Oil Research Program Implementation Plan (PIP). The proposed NIPER program parallels the new implementation plan with (1) phased field analysis that identifies near-term opportunities for operators and needs for risk reduction by the federal government for mid-term and long-term opportunities, (2) technology transfer directed toward operators to generate interest in the opportunities identified in the field analysis and research support work by NIPER and other organizations, and (3) application of research support technical advances to specific field applications.

Four projects relate to geoscience: BE1 - Assessment and Characterization of Reservoirs, BE2 - TORIS Research Support, BE9 - Three-Phase Relative Permeability, and BE12 - Imaging Techniques Applied to The Study of Fluids in Porous Media. BE1 fits the PIP in the area of supporting research and development directed toward advanced interpretation techniques such as geostatistics, geological scaling and modeling, and integrated interpretation protocols. BE1 also takes advantage of work in other areas such as well testing and reservoir performance simulation. TORIS support in BE2 brings together information from a wide range of activities including the results

ENERGY PRODUCTION RESEARCH INTEGRATED BASE PROGRAM

FIGURE 2. - Energy Production Research Integrated Base Program.

of EOR field projects, reservoir descriptions, the size of the Nation's petroleum reserves, and reservoir performance simulation. The work in BE9 relates to supporting research and development in the areas of reservoir chemistry and physics and rock-fluid systems. Since most oil recovery processes involve two- or three-phase flow phenomena, this work relates directly or indirectly to all advanced tertiary recovery research. Finally, work in BE12 is directed toward the development of advanced techniques in the areas of reservoir chemistry and physics and rock-fluid systems at the pore and core levels. Since EOR methods are directed toward mobilizing a larger fraction of the oil in place, the results of BE12 will be valuable to other research directed toward each of the specific EOR processes, especially in understanding pore level recovery mechanisms and scaling up from pore level to core level or larger. All of these projects have produced near-term results and have allowed NIPER to assist major and independent oil companies solve real production problems. This interface between DOE-supported research at NIPER and oil companies will continue in FY91. The rock-fluid imaging concept used in BE1, BE9 and BE12 research, and the scaling up of reservoir properties from pore to core to field level is shown in figure 3.

Chemical flooding processes are specifically addressed in three Base Program Projects. The effort under project BE4A has been focussed on the structure-property relationships of third-generation, mixed surfactant systems. These mixed systems offer greater flexibility than single-surfactant systems. In FY91, the study of these systems will be continued. In addition, the application of these and other surfactant systems in near-wellbore cleanup (to increase injectivity or paraffin removal) will be initiated. These results can be applied to the field in the near-term. In project BE4B, an alkaline-surfactant-polymer(ASP) process patented by NIPER will be designed for a field in which a pilot test of the recovery method is being considered. The work in project BE4C is to determine the capability of low-molecular-weight polymer gels for improving mobility control. Studies will be conducted to determine the degree of gel penetration into highly permeable zones as well as the degree of hydrolysis required in making cost-effective polymer gels. The previously developed profile modification simulator will also be used to study the effect of in-depth treatments and gel treatment strategies on the rate of oil recovery.

Gas flooding research comprises two projects in the Base Program. A task in BE5A will experiment with an effective alternative to foam for CO₂ flooding. Success in this program would fulfill the near-term objective of the PIP to apply currently defined, advanced EOR technologies in oil fields. Studies on effects of porous media and mass transfer on CO₂ phase behavior and the development of an accurate phase behavior prediction package are also planned for this project. This year's proposal in BE5B includes the expansion of capabilities at NIPER to evaluate foams

FIGURE 3. - NIPER's rock-fluid imaging concept showing the comparison of imaging technique with the scale being investigated.

under radial flow conditions. In addition to mobility-control studies with foam, an attempt will be made to identify cost-effective entrainers, (hydrocarbon or short chain alcohols that can improve extractability of hydrocarbon in CO₂, improve miscibility, and increase CO₂ viscosity) for use in CO₂ field projects. An effective entrainer would, in the near-term, increase sweep efficiency and displacement efficiency and, therefore, the recovery efficiency of CO₂ flooding. Testing the effectiveness of entrainers in cyclic CO₂ processes is also planned to fulfill the near-term objective of the PIP.

Research on thermal processes will concentrate on steamflooding, both for light oil recovery (BE11A) and heavy oil recovery (BE11B). A task in BE11A will evaluate the effect of (steam or hot water) temperature on produced oil composition and remaining oil saturation, using Teapot Dome sand and crude oil. Since a steamflood project in this reservoir is currently under way, the results would immediately help those operating the field project to assess their potential recoveries. A task under BE11B is to compile a supplement to the steamflood operator guide published in FY 90. This will impact on near-term objectives to transfer thermal technologies from California operators to areas not currently using steamflood operations. These areas include the mid-continent region where heavy oil has been identified as a target for exploitation, but currently

little of it is being produced. Another task is to develop an implicit version of NIPER's numerical laboratory thermal simulator.

Microbial enhanced oil recovery (MEOR) methods are being developed in project BE3. The primary objectives of this project are to elucidate the recovery mechanisms for MEOR and to provide a scientific basis for the technology. A two-pronged approach - (1) experimental and (2) simulation - is applied in this project. The experimental program will form the basis for simulator development, and simulation results will provide guidance for further experiments in an attempt to identify mechanisms responsible for recovering oil. Results of this project will be used in designing and operating pilot projects sponsored by DOE .

Complete descriptions of research to be performed under the 12 EPR Base Program projects follow.

BE1. - RESERVOIR ASSESSMENT AND CHARACTERIZATION

BACKGROUND

The broad objectives of the Department of Energy's program for geoscience research are to develop methods for locating residual oil saturation distribution in oil reservoirs and evaluate suitable methods for recovering the oil. NIPER's specific objective formulated in the FY86 Annual Research Plan is to develop a better understanding of heterogeneities that influence the movement and trapping of fluids in barrier island/shoreline barrier reservoirs. Shoreline barriers are ranked in the top 10 of priority reservoir geologic classes in the DOE Oil Research Program Implementation Plan.

Heterogeneities that strongly influence the trapping of oil and control its movement in barrier island reservoirs were identified within a selected reservoir (Bell Creek (MT) field). Effects of the heterogeneities were quantified to improve predictions of fluid production from the barrier island/shoreline barrier. Data were collected from outcrops and analyzed for development of a quantified geological model that would incorporate the effects of all the critical geological heterogeneities. Geological and engineering data from the tertiary incentive project (TIP) portion and surrounding areas of Unit A of Bell Creek field were used to refine the integrated geological-engineering model of the reservoir. A second barrier island/shoreline barrier reservoir (Patrick Draw (WY) field) was then selected, and analysis was begun to refine the shoreline barrier reservoir description methodology and to quantify the effects of critical heterogeneities on fluid production and trapping.

Industry has shown considerable interest in NIPER's reservoir characterization capabilities, many of which have been developed under the BE1 program. A multiclient project which investigated methods to quantify spatial variations in reservoir parameters has been conducted. Consultations to operators of barrier island reservoirs, as well as other reservoir types, using NIPER methodology developed under BE1 for reservoir characterization have been provided. Most of the field projects conducted with industry cosponsorship, such as the MEOR and subsurface production projects, involve considerable reservoir characterization in the early stages. At the two reservoir characterization technical conferences, cosponsored by NIPER and DOE, most of the presentations were made by industry representatives. Companies which have interests in reservoirs investigated by NIPER have been cooperative in providing core, log, and production data. In Patrick Draw field, which NIPER studied during FY90, the operator is planning to implement EOR and could be amenable to a cooperative project to select and design an appropriate EOR method. Industry participation in NIPER's reservoir characterization research and development is expected to continue.

Numerous publications and presentations have resulted from the work performed as part of project BE1 over the past several years. In addition, technology developed under DOE sponsorship has been used for individual industrial clients and in multiclient projects.

OBJECTIVE

The objective of this project is to develop a methodology for the effective characterization of shoreline barrier reservoirs. Shoreline barriers are ranked in the top 10 of priority reservoir geologic classes in the DOE Oil Research Program Implementation Plan. Such a methodology is necessary to predict residual oil saturation distribution and reservoir performance during various recovery processes.

SCOPE OF WORK

This project will develop an improved methodology for effective characterization of shoreline barrier reservoirs to predict residual oil saturation (ROS) at interwell scales in shoreline barrier reservoirs and improve predictions of flow patterns of injected and produced fluids, given the location of injection and production history. Reservoirs for characterization will include a variety of shoreline barriers (spits, shoals, barrier islands, barrier peninsulas, and barrier bars). These formations will be classified according to their relative growth (aggradational, progradational, transgressive). The degree of tide or wave domination and the influence of tidal range (microtidal, mesotidal) will also be used to classify internal reservoir geometry (heterogeneities) and their relative influence on recovery. This project is multiyear, and it is probable that the tasks listed will not be completed during FY91. Technology transfer of the results of this project will be accomplished through the preparation of journal articles subject to peer review and presentations for symposia in addition to the topical report described in the Deliverables section of this plan.

Task 1. Construct quantitative geological shoreline barrier model for Patrick Draw field. (Start date: October 1990. Completion date: September 1991.) (Near- to mid-term)

Patrick Draw field, a mesotidal, giant barrier island reservoir in the Rocky Mountains, will be used for generalization of the shoreline barrier model. Depositional, structural, diagenetic, and geochemical partial models will be constructed and integrated to form a comprehensive, quantitative geological model. Available information from outcrop studies will also be integrated into the comprehensive geological model for interwell scale information.

Because implementation of the task is interdisciplinary, it will provide both near- and intermediate-term results relative to: (1) integrative methodology for enhanced resource utilization from shoreline barrier reservoirs; (2) optimization of data gathering and most effective

data utilization; (3) prediction of location and distribution of residual oil saturation within specific shoreline barrier reservoirs; and (4) technology transfer of the most effective techniques for characterizing shoreline barrier reservoirs.

Task 2. Construct engineering model of Patrick Draw field. (Start date: October 1990. Completion date: September 1991.) (Near- to mid-term)

Accurate reservoir description is a main prerequisite for successful planning and implementation of EOR and infill well drilling programs. This task develops an effective and efficient reservoir description method by using only readily available wireline logs and well production, injection, and pressure data. Conventional techniques such as volumetric calculations, material balance, decline curve, production-injection, and well test analyses will be used to diagnose reservoir heterogeneities. The engineering model will be integrated with the comprehensive geological model to provide an integrated engineering-geological model of Patrick Draw field. The engineering model will provide an independent source of information for reservoir description.

Task 3. Geostatistical analysis of Patrick Draw field. (Start date: October 1990. Completion date: September 1991.) (Near-term)

Geostatistical techniques such as kriging and fractal analysis will be used to estimate interwell reservoir properties in Patrick Draw field. The application of geostatistics to the barrier island reservoir (specifically Patrick Draw field) may reveal additional information to aid in understanding this type of formation. The comprehensive production information will also provide a good opportunity to investigate strengths and weaknesses of different geostatistical techniques. Study of fractal distributions of important formation parameters such as porosity, permeability, saturation, and pay thickness can be used to revise or supplement the geological model of barrier islands.

Task 4. Development of improved methodology for characterizing shoreline barrier reservoirs. (Start date: October 1990. Completion date: September 1991.) (Mid-term)

The methodology developed during the first phase of reservoir characterization of shoreline barrier reservoirs (Bell Creek study) will be expanded with emphasis on mesotidal barrier island deposystems. This methodology will provide guidelines about data-gathering, sequence, quality, and quantity of data required for characterizing shoreline barrier reservoirs. The methodology also addresses possible recovery methods that may be applied for efficient exploitation of mesotidal barrier type of reservoirs. As part of this task, the similarities and

differences among the various shoreline barrier systems will be examined in light of expected production behavior for the respective systems.

Task 5. Development of a data base for shoreline barrier formations. (Start date: October 1990. Completion date: September 1991.) (Near-term)

The objective of this task is to organize all geological and engineering information available about the shoreline barrier systems investigated as a part of this project. This data base will provide the capability to perform quantitative and integrative analysis as well as assist in the construction of crossplots and maps. This data base will provide guidelines for the identification of expected heterogeneities in shoreline barrier systems to major and independent oil companies in addition to the DOE. The preliminary data base will be developed using data from Patrick Draw field.

DELIVERABLES

Sep 91 Topical Report — to include (1) a discussion of the most effective techniques for characterizing shoreline barrier reservoirs, including similarities and differences among the various shoreline barrier systems; (2) a description of the integrated engineering-geological model of Patrick Draw field; and (3) a description of the shoreline barrier data base.

PLANNED STAFFING

	<u>Man-Years</u>
Senior and Research Engineers	1.3
Senior and Research Geoscientists	2.8
Technicians	1.7
Total	5.8

Project Leader

Matt Honarpour, Senior Engineer

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Core saw		1
Core Polisher		1
Apparatus for UV and Visible Photography of Cores		1
Cathodoluminescence Apparatus		1

BE2. - TORIS RESEARCH SUPPORT

BACKGROUND

This project provides research support for the Tertiary Oil Recovery Information System (TORIS) in the areas of EOR project and reservoir data base management; EOR project technology and trends analysis; and evaluation of computer models and numerical simulators. It is necessary for TORIS to have accurate information on EOR projects and reservoirs that can be retrieved quickly. It is also necessary to have reliable computer models and numerical simulators. NIPER maintains EOR project and reservoir data bases with currently available information and efficient retrieval. NIPER analyzes data trends in EOR and computer models and numerical simulators as they relate to needs of TORIS. This work has resulted in annual reports on the trends in applying EOR technology. Analyses of simulators have resulted in subsequent improvements in the simulators before they were accepted by DOE for distribution.

Information that is incorporated into the TORIS project database is provided by oil companies. These companies participate in DOE ECR Incentives projects and provide information on production and other activities. Upon approval by the DOE Program Manager, the system is used to provide statistical analysis of information on reservoirs and EOR projects to industrial clients, which include independent oil companies and service companies. Information is also provided to other DOE-sponsored research projects.

OBJECTIVES

To provide research support for the Tertiary Oil Recovery Information System (TORIS) in the areas of EOR project and reservoir data base management, EOR project technology and trends analysis, and evaluation of computer models and numerical simulators.

SCOPE OF WORK

Task 1. EOR project data base research support. (Start date: October 1990. Completion date: September 1991.) (Near-term)

Areas of work in FY91 are as follows:

- A. Maintain the EIA and RELIANCE versions of the EOR project data bases and associated routines to be current with active versions of S2k, RELIANCE, communications, and operating systems. Maintain and update data as necessary for input from BPO.
- B. Transfer 1989 (if available) production data for DOE cost-shared and incentive projects into the EOR project data bases. Solicit completed FE-748 forms for the active EOR incentive projects for 1990. Deliver to BPO a security copy of the EIA S2k version of the data base and a status report on data additions and solicitation results.

- C. Review literature for new data on existing and new EOR projects. Install collected data on EOR project data bases. Analyze trends in the application of EOR technology and prepare a topical report presenting this analysis.
- D. Assist BPO in publishing an updated description of the EOR project data bases.

Task 2. Reservoir data base research support. (Start date: October 1990.

Completion date: September 1991.) (Near-term)

Areas of work in FY91 are as follows:

- A. Maintain the EIA RSVR data base and routines to be current with new versions of S2k, communication, and operating systems.
- B. Continue the development of a reservoir data base management system started in FY90 as part of Project SGP28, "Development of Reservoir Data Base - Phase 1." Work will progress to the point of an operating DBMS. Refinements and a user's manual will be written in FY92.
- C. Add and modify reservoir data as required.

Tasks 3. Computer modelling research support. (Start date: October 1990.

Completion date: September 1991.) (Near-term)

Areas of work in FY91 are as follows:

- A. Evaluate simulators and computer models as required for the TORIS program. Assist BPO in answering inquiries concerning publicly available simulators.

DELIVERABLES

- Sep 91 Topical Report on EOR Trends
- Sep 91 Status Report on Additions to the Data Bases

PLANNED STAFFING

	<u>Man-Years</u>
Data Analysts	1.6
Engineers	0.2
Geoscientists	0.8
Technicians	<u>0.5</u>
Total	3.1

Project Leader

James F. Pautz, Research Data Analyst

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Personal Computer		1

BE3. DEVELOPMENT OF IMPROVED MICROBIAL FLOODING METHODS

BACKGROUND

Due to increased use of processes based on biotechnology, renewed interest has been given to the use of microorganisms for enhanced oil recovery (EOR). Several major oil companies are currently conducting field pilots, or laboratory research leading to field pilots. A Fossil Energy staff study, "The EOR Initiative", has stressed the need for shorter term oil recovery activities for independent petroleum producers, declining oil fields and stripper wells. These activities are particularly important because "independent operators produce about 40% of the total oil recovered, but cannot conduct needed EOR research." Microbial methods for improving oil recovery are potentially cost-effective, and particularly well suited to be applied in today's economic climate. The technology is flexible, currently available, relatively inexpensive, and can be applied by independent producers to extend well life in the near-term. Microbial formulations can be applied in a variety of methods including well stimulation treatments, permeability modification treatments, and microbial-enhanced waterflooding. Well stimulation treatments are relatively inexpensive, easy to implement, and can provide rapid recovery of the minimal investment costs. Microbial-enhanced waterflooding is a method that has significant potential for increasing producing from aging oil fields that are currently under waterflood. The incremental cost for injecting microbes and nutrient is relatively small in an existing waterflooding operation, which may make this method applicable at low oil prices when more expensive methods are not economically feasible.

Application of this novel EOR technology to increase oil production requires careful laboratory design of the microbial formulation to optimize its performance for the particular application, reservoir characterization to define the important geological parameters, and reservoir engineering design to ensure that the method is applied in an efficient and cost-effective manner. As an example, a microbial formulation that is effective in modifying permeability and increasing sweep efficiency is not necessarily effective in emulsifying paraffin deposits or increasing microscopic oil displacement efficiency.

To date this project has achieved both long-term and near-term goals, including the improved understanding of the mechanisms of oil mobilization by microbial formulations and transport of microbes and their metabolites in porous media. The concepts and data from this research project formed the basis of applied research needed to develop engineering methodologies for field applications.

A key result from NIPER's BE3 applied research program is the development of a microbial culture bank consisting of different types of microorganisms that can improve oil mobilization under a wide variety of conditions. NIPER is currently applying MEOR processes to a reservoir

that is a member of one of the higher priority reservoir classes (Fluvial-dominated deltaic) based upon geologic history outlined in the Oil Research Program Implementation Plan. A microbial-enhanced waterflooding field pilot project was initiated in Delaware-Childers field near Nowata, Oklahoma, to address the near-term needs of independent producers to apply this technology. The project was initiated in a mature waterflood with producing oil wells that are in the stripper category. The reservoir is typical of a mid-continent sandstone reservoir. The results of the field pilot test are addressed under project SGP-13. Both this base program project (BE3) and the near-term field pilot test (SGP-13) have been in progress concurrently for the past several years. They are both part of NIPER's integrated program to develop and apply MEOR technology to increase our nation's reserves of crude oil.

Because of the potential opportunities for independent oil producers to use a cost-effective enhanced oil recovery (EOR) technology, NIPER has prepared and given short courses for independent petroleum producers on microbial EOR. Approximately 150 independent oil producers, major oil company representatives, and interested participants from other nations have attended these short courses. A major goal of these short courses is to demonstrate the potential for microbial technology to assist 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. Stripper wells are responsible for 15% of domestic oil production, but produce an average of less than 3 barrels per day. The short courses emphasize the potential for MEOR, yet stress the need for applying the technology properly through careful engineering design for maximum economic return and oil recovery.

One of the major constraints to MEOR technology has been the lack of simulation data to adequately describe and predict the MEOR processes both in the laboratory and in the field. During the 1980's, researchers at the University of Oklahoma, and Southern California University studied transport of several different types of bacteria to produce one-dimensional models. It became apparent that microbial transport in porous media was an extremely complex phenomenon that required further laboratory and field data to adequately model. While several attempts have been made to modify existing reservoir simulators to describe microbial processes, no model has yet fully incorporated all of the complex phenomena that are believed to be important. Thus, an accurate reservoir simulator for MEOR methods can best be developed through an integrated program of acquisition of laboratory and field data with the feedback loop being the reservoir simulation model. The uniqueness of this project is the integration of laboratory and field data in a numerical simulator to adequately describe the recovery mechanisms and microbial transport processes. Technology transfer will be accomplished through dissemination of field and laboratory information to independent operators through personal

contacts, tour of MEOR field site and publication of refereed technical journal articles and presentations at symposia

The unusual complexity of oil recovery by microbial formulations will obviously require close coordination between laboratory mechanistic studies and oil displacement experiments under carefully controlled conditions to develop and validate a computer model.

NIPER has amassed a wealth of laboratory and field data on the mechanisms of oil mobilization of microbial formulations and the effects of various design parameters on oil recovery efficiency. Research using laboratory experiments in FY90 began to define key mechanisms of oil mobilization. Work for FY91 will continue to develop the critical parameters, correlations and mathematical models to describe the physical phenomena that are important in MEOR methods, and development of a mathematical computer simulator to model and predict performance of microbial formulations in oil recovery applications.

OBJECTIVE

The objective is to develop microbial technology for enhanced oil recovery field applications using an integrated laboratory and field effort to define the critical parameters required for modeling MEOR processes.

SCOPE OF WORK

Laboratory data from NIPER will be used to develop correlations and mathematical models for specific phenomena and linear coreflooding data will be used to test the simulator in an iterative process. The simulator development and laboratory testing aspects of this project will be carefully coordinated so that the results from testing the simulator with oil displacement experiments will be used to design laboratory experiments to clarify and quantify certain physical effects from which correlations will be refined and modified that will be incorporated into the simulator. The numerical simulator will be the primary deliverable from this research, and studies for its development and use will probably result in several journal articles that will be subject to peer review. The overall goal of the project is to develop a method for predicting and evaluating microbial EOR processes in porous media.

Task 1. Review all laboratory data and modify (if necessary) the plan developed in FY90 for laboratory evaluations of MEOR processes. (Start date: October 1990. Completion date: November 1990.)

Laboratory simulation of MEOR processes will continuously be modified in accordance with specifications in the plan. The data obtained from displacement studies will be incorporated into the model, and then used to define further displacement experiments. Based upon last year's results, further definitions of the parameters that are required to predict the behavior of

microorganisms will be made. Preliminary data from last year's experiments indicated that microbial oil mobilization in porous media probably occurs by a combination of chemicals produced by the microorganisms in situ at the oil/water interface. These chemicals can alter wettability of water-wet rock, and reduce interfacial tension at the oil/water interface. More experiments are required to validate this hypothesis.

Task 2. Develop mathematical descriptions for oil mobilization by microorganisms. (Start date: October 1990. Completion date: December 1990.)

Data obtained from experiments dealing with the interfacial phenomena associated with microbial oil mobilization will be used to develop mathematical descriptions that describe the process. Because of the complexity of these phenomena, there are no existing mathematical equations that adequately describe microbial oil mobilization in porous media. Probably the most critical question to be answered in the development of these equations is, does one incorporate all of the microbial products responsible for oil mobilization, or which ones are important?

Task 3. Correlate laboratory displacement tests with mathematical descriptions. (Start date: January 1991. Completion date: August 1991.)

Based on the mathematical descriptions, laboratory displacement tests in porous media will be conducted to fit the mathematical model. By continually adapting the model to fit laboratory data, we can make an accurate assessment of microbial oil recovery technology, predict the behavior of the process, and have the ability to make modifications of the process.

Task 4. Using laboratory displacement tests, compare mechanisms of oil mobilization by selected microbial species currently used in permeability modification field tests with those microbial species used in microscopic oil displacement. (Start date: October 1990. Completion date: August 1991.)

The experiments designed for microbial oil displacement studies will be used to evaluate those microorganisms that are being developed for permeability modification. The mechanisms of oil mobilization by these microorganisms are entirely distinct from the microorganisms that mobilize oil by surfactant, gas, acid and alcohol production. The same types of experiments describing the interfacial phenomena between microorganisms and oil will be designed for microorganisms that produce polymer and biomass.

Task 5. Develop mathematical descriptions for oil mobilization by microorganisms used in permeability modification tests. (Start date: June 1991. Completion date: September 1991.)

Based upon the above experiments, a set of mathematical equations will be developed for predicting how the oil mobilization process is affected by polymer-producing microorganisms.

Task 6. Fine-tune computer model for laboratory corefloods. (Start date: May 1991. Completion date: September 1991.)

The mathematical equations will be used to fit laboratory coreflood data in order to predict oil recovery with the microbial process.

DELIVERABLES

- May 91 Status report on development of mathematical descriptions to represent microbial oil mobilization phenomena
- Aug 91 Topical report on development of computer model for microbial oil displacement.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Biologist	0.7
Sr. Reservoir Engineer	0.2
Associate Biologist	0.7
Sr. Bioexperimentalist	0.6
Sr. Technician	<u>0.7</u>
Total	2.9

Project Leader

Dr. Rebecca Smith-Bryant, Sr. Biologist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Laboratory coreflood apparatus	3	
Gas chromatograph	1	
Video-enhanced microscope	1	
Phase contrast microscope	1	
Coreflooding apparatus with intermittent pressure transducers	1	
Anaerobic glove box	1	
Capital Equipment Required:		
Personal computer		1

BE4A. - DEVELOPMENT OF IMPROVED SURFACTANT FLOODING METHODS

BACKGROUND

Chemical flooding has the potential of mobilizing more residual crude oil than any other method of enhanced oil recovery. In addition, for many shallow U.S. domestic reservoirs in which steam and gas flooding are not applicable, chemical flooding may be the only viable EOR method. Chemical flooding is technically very flexible because of the ability to vary an injected chemical formulation to provide oil recovery capability for a number of different reservoir conditions. However, from the point of view of economics, surfactant/polymer flooding is an EOR process that will need mid- to long-term research and development to overcome problems associated with successful application of the technology. Problem areas that need to be addressed include chromatographic separation of components from the chemical formulation, surfactant adsorption, precipitation, phase trapping, incompatibility with reservoir brines, and economics.

The application of improved chemical flooding methods will be directed towards a priority class of reservoirs. Emphasis will be made on well established chemical flooding EOR screening criteria to match the guidelines stipulated in the Federal Oil Research Program Implementation Plan. Information obtained from the National Reservoir Data Base and the DOE Bartlesville Project Office Crude Oil Analysis Data Bank has been used to identify the range of conditions of temperature, salinities, and API gravities of reservoirs that can be considered as potential candidates for surfactant-based EOR methods. About 60% of the reservoir conditions fall within a fairly broad range of temperature (<180°F) and salinity (<10.3% TDS). The remaining 40% of these reservoirs have harsher conditions.

The goal of the NIPER research is based on the need to improve the application of surfactant flooding methods of producing oil over a fairly broad range of conditions that otherwise would not be recoverable by other technically proven or more economical methods. The results from this on-going research is conveyed to the petroleum industry through NIPER and DOE reports, SPE papers, and technical articles in the open literature.

The first area of research will provide basic knowledge to develop the methodology of using mixed surfactant systems for cost-effective chemical flooding. Mixed surfactant systems offer a mechanism to provide a surfactant system with adequate interfacial tension (IFT) reduction and relatively high oil recovery potential coupled with improved temperature, salinity, and hardness tolerance. Variation in the relative composition of the mixed surfactant system can be used to fine-tune and broaden the conditions of optimum behavior to those existing in a specific reservoir. The existence of a positive synergistic effect can be exploited in such a way that the overall surfactant system will retain relatively low IFT values over a fairly broad range of reservoir

conditions. This project provides mid- to long-term research efforts which can support near-term application of surfactant flooding methods in appropriately chosen reservoirs.

Studies of mixed surfactant systems were initiated in FY90. These studies included alkylaryl sulfonates with carboxyethoxylated surfactants or alpha olefin sulfonates and observed low IFT values for salinities up to 10%. For FY91, NIPER proposes to build on this base of information. Studies will include phase behavior, solution calorimetry, surfactant loss, and oil recovery efficiency of selected surfactant systems. Methods to correlate structure-property relationships will continue to be evaluated to facilitate the rapid selection of surfactant systems for specific reservoir conditions. In addition, development of the technology for successful application of surfactant flooding will include evaluation of methods to reduce surfactant loss and to improve surfactant propagation through the reservoir, with the objective of reducing the cost of surfactant flooding.

The successful application of surfactant systems over broad conditions of salinity and temperature requires an understanding of how these surfactants behave under such conditions. NIPER's calorimetric capability will be used to correlate the solution behavior of surfactant systems with their performance. Such correlations were begun in FY89 and continued in FY90. Recovery of petroleum from a reservoir using chemical flooding involves reducing drive fluid-oil IFT. The most effective reduction in IFT usually occurs at or above the critical micelle concentration (CMC) of the aqueous surfactant solution. The CMC of surfactant systems increases with temperature and decreases with electrolyte concentration. If the CMC of the drive fluid is unknown at reservoir temperature and salinity, then the most economic concentration of surfactant is unknown. High-temperature calorimetry will be applied to some of the more promising surfactant systems selected above to provide auxiliary information on their CMC's and solution properties.

The second area addressed by this research program is to improve the economics of surfactant enhanced oil recovery processes. One promising technology for light oil recovery application includes the addition of alkaline additives to reduce surfactant loss, enhance interfacial tension reduction, and allow the use of lower concentration of expensive surfactant chemicals. Research on the use of alkaline agents as additives to surfactant formulations has evolved over the past few years as a possible low-cost surfactant-based EOR method. This work was first conducted using acidic oils. It was believed that the primary effect of the alkali was neutralization of carboxylic acids present in acidic crude oils. However, it has been shown recently that a synergism exists between surfactants and alkaline additives, even when the oils have very low acid numbers. This leads to the possibility of a more near-term application of this technology to a larger number of reservoirs, including many midcontinent reservoirs that contain slightly acidic, light crude oils. In the presence of alkaline additives, very dilute (0.1 - 0.2%) concentrations of synthetic surfactants are sufficient to mobilize significant amounts of residual oil. Since synthetic

surfactants are expensive components, this can lead to more favorable economics in surfactant flooding field projects.

For FY90, research was conducted with two midcontinent crude oils: one from Teapot Dome (WY) field and the other from Delaware-Childers (OK) field. For FY91, these experiments will be extended to include several reservoirs that meet the selection criteria set forth in the Federal Oil Research Program Implementation Plan. The research will be conducted using oil, brine, and cores from the selected fields. If the results of laboratory tests are favorable, and the economics of oil recovery appears to be favorable, recommendations will be made for a near-term application of this technology in a midcontinent reservoir under the Supplemental Government Program (SGP).

The third area of research for this program provides near-term adaptation of chemical flooding technology to the solution of near-wellbore injectivity problems. The application of chemical flooding technology is not limited to conventional micellar-polymer flooding. The current available chemical flooding technology can be further extended for application in well stimulation and cleanup to extend the life of low-cost secondary recovery mechanisms. Problems relating to loss of fluid injectivity and paraffin deposition and plugging represent major concerns for small independent and major oil producers who may be helped by methods using currently established chemical flooding technology. Chemical flooding based methods represent a viable alternative to conventional thermal-based treatments.

Loss of drive-fluid injectivity can result from a variety of factors, particularly those related to completion and treatment methods. In some cases, formation damage is a direct result of the presence of residual oil in formation pore spaces in the near-wellbore region. The application of surfactant-based methods will help remove or sweep the residual oil saturation from this region and thereby improve overall injectivity. The increase in injectivity does not directly correspond to an increase in amount of oil recovered but rather relates to an accelerated rate of recovery of oil, thereby improving the economics of conventional waterflood processes.

The precipitation and deposition of paraffin particles has been a recurring problem related to crude oil production. The relatively high cost of conventional treatment methods can lead to abandonment of marginal stripper wells. The deposition of these solid or waxy materials frequently occurs in well bores and on tubing strings. The mechanism of deposition is brought about when the oil is cooled below the cloud point of the crude oil components. The common methods for dealing with this buildup are mechanical, thermal, and chemical. The chemical based treatments used are predominantly either dispersant mixtures or a variety of solvents having high aromatic content. Some of these conventional methods, such as hot oil treatments, have been demonstrated to cause further paraffin precipitation and formation damage. Surfactant-based methods can provide a better alternative for the control of paraffin deposition and removal of

these deposits. Methods involving surfactants used in combination with conventional methods such as "hot surfactant" or "hot oil" treatment can be developed to improve the efficiency of the overall treatment process.

A task has been outlined for FY91 to evaluate the extension of current chemical flooding technology to alleviate low near-well bore injectivity and deposition problems and to conduct chemical flood research to reduce the cost of well stimulation. Successful implementation of this technology extension will translate into possible near-term field application of the developed chemical-based methods. Technology transfer of the results of this project will be accomplished through the preparation of peer-reviewed journal articles and presentations for symposia in addition to the topical and status reports described in the Deliverables section of this plan.

OBJECTIVES

To improve chemical flooding technology through the development of mixed-surfactant systems which are more tolerant to changes in chemical composition in the reservoir. The focus will be to mitigate problems which have been shown to have adverse effects on the performance and economics of surfactant flooding processes. To improve the economics of surfactant enhanced oil recovery through the development of effective oil recovery systems that contain very low concentrations of synthetic surfactants and alkaline additives. To investigate the application or extension of current chemical flooding technology to near-term problem solving for near wellbore paraffin removal and waterflood injectivity improvement.

SCOPE OF WORK

Task 1. Evaluation of mixed surfactant systems for chemical flooding application. (Start date: October 1990. Completion date. September 1991.) (Mid-term)

Evaluate mixed surfactant systems that may have potential application for well-to-well chemical flooding, single-well chemical flooding, and near-wellbore remediation treatments (wettability change and injectivity improvement). These studies include phase behavior, IFT, adsorption measurements, and determination of CMC's and solution behavior. Properties will be correlated with structure differences if possible. Oil recovery efficiencies will be determined from laboratory coreflood experiments, and deficiencies of surfactant recovery from produced fluids will be evaluated. A laboratory evaluation of single-well chemical flooding methods will also be conducted in anticipation of selection of field application. A candidate surfactant system will be selected for a target reservoir.

Task 2. Laboratory evaluation of surfactant flooding with alkaline additives for selected reservoir rocks and fluids. (Start date: October 1990. Completion date : September 1991.) (Near-term)

Select four light oil reservoirs from the mid-continent region that meet the selection criteria set forth in the Federal Oil Research Program Implementation Plan. Obtain oil, brine, and core samples from at least two of these reservoirs for laboratory evaluation of surfactant flooding with alkaline additives in the selected fields. Interfacial tension tests and alkali consumption measurements will be used to design a surfactant system with alkaline additives that can be applied in the selected reservoirs.

Task 3. Investigation of application of surfactant-enhanced oil recovery techniques for near-wellbore permeability improvement. (Start date: October 1990. Completion date: August 1991.) (Near-term)

Evaluate available information on the causes of loss of permeability in the near-wellbore region. Determine which types of permeability impairment are amenable to remediation by chemical methods, in particular, surfactant systems that will mobilize oil or components of the oil that block flow channels or change wettability to improve relative permeability to the component of interest. Wettability and oil/water relative permeability measurements will be conducted before and after treatment with selected surfactant systems to determine effectiveness of the treatments for improving injectivity or oil-production in the near-wellbore region during secondary waterflood operations. Selection of targeted reservoir core and operating conditions will be based on anticipated selection of field application and technology transfer to independent operators in the near-term time frame. Evaluate and compare efficiency and economics of the surfactant remediation technique with that of other remediation techniques such as hot oil treatments and solvent extraction. The ultimate goal will be to prepare guidelines to aid oil producers in selection of appropriate treatments to extend the life and efficiency of the more economical secondary oil recovery operations.

DELIVERABLES

Sep 91	Topical report on applications of improved surfactant flooding methods
Sep 91	Topical report on applications of surfactant flooding with alkaline additives
Aug 91	Status report on application of surfactant flooding technology for near-wellbore permeability improvement

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemists	1.80
Senior Engineer	0.80
Senior Experimentalist	0.60
Technicians	<u>1.60</u>
Total	4.80

Project Leader

Leo A. Noll, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Coreflow apparatus	1	
High-temperature mixing calorimeter	1	
Sorption calorimeter	1	
Spinning drop interfacial tensiometer	2	
Titration calorimeter	1	
Conductance apparatus	1	
Ion conductivity detector	1	
CT scanner	1	

BE4B. - DEVELOPMENT OF IMPROVED ALKALINE FLOODING METHODS

BACKGROUND

The emerging technology in alkaline flooding of heavy oil is the use of a combination of surfactant and alkali. This has the potential for alleviating some of the problems associated with the use of either surfactant alone or alkali alone. In favorable cases, chemical requirements are reduced, displacement efficiency is improved, and scale formation is suppressed. Several mechanisms are involved that are partly understood and consist of both equilibrium and dynamic effects. The former includes interfacial activity, adsorption, and ionic equilibria (precipitation and complex formation) and are addressed by the design of the injected formulation. The latter includes chromatographic effects, flow diversion by precipitates, and emulsification, and are addressed by injection strategy.

Several injection strategies have been used or suggested. Some examples are (1) the combination of alkali, surfactant, and polymer into a single slug followed by more polymer, (2) the combination of alkali and surfactant into a single slug, followed by polymer, (3) pre-injection of alkali to condition the reservoir, (4) surfactant followed by alkaline polymer, (5) injection of oil soluble acids followed by alkali, and (6) various injection strategies that utilize surfactant concentration gradients.

Proper design of injection strategy can be viewed as a near-term project as well as long-term research. In the near term, this research will support the design of the proposed surfactant-enhanced alkaline flooding field pilot test which will be conducted under the SGP. After the identification and selection of a project site and establishment of a joint venture between the participants, oil and cores from the site can be used for the optimization studies. In the long term, the results of injection strategy research will provide a base of information for future field tests.

OBJECTIVES

To develop improved alkali-surfactant flooding systems and to provide support for an SGP field project.

SCOPE OF WORK

Injection strategy is an aspect of optimization that needs to be addressed by coreflood and slim tube sandpack tests. The tests that are performed will be selected from the following tasks. To isolate effects, some tests are best performed in the presence of divalent ions and some in the absence of divalent ions. Crude oil from the site of the SGP field pilot will be used for some of the tests after that site is selected. If the crude oil from the SGP site is different from the oils previously tested, then interfacial tension and phase behavior tests will be required for the new oil.

Task 1. Injection strategies in the absence of divalent ions. (Start date: November 1990. Completion date: August 1990.) (Near-term)

Investigation of the best injection strategy is an aspect of optimization that needs to be addressed by corefloods. The effect of injection strategies on the interactions between the chemicals used for flooding and the oil are best studied in the absence of divalent ions. Several injection strategies will be studied and may include any of the following: (1) alkali and surfactant followed by polymer, (2) surfactant followed by alkaline polymer, (3) oil soluble acids followed by alkaline polymer, and (4) surfactant concentration gradient injection.

Task 2. Injection strategies designed to mitigate the adverse effects of divalent ions. (Start date: February 1991. Completion date: August 1991.) (Near-term)

The use of injection strategies designed to protect the injected chemicals from the adverse effects of divalent cations will be the focus of this task. The several injection strategies will include: (1) surfactant followed by alkaline polymer and (2) preinjection of alkali.

DELIVERABLE

Sep 91 Topical report comparing the various injection strategies, economics and suggestions on the best strategies for field use.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemist	0.6
Senior Experimentalist	<u>0.4</u>
Total	1.0

Project Leader

Troy R. French, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Coreflooding equipment	1	
Spinning drop interfacial tensionmeter	1	1

BE4C. - DEVELOPMENT OF IMPROVED MOBILITY-CONTROL METHODS

BACKGROUND

This project aims at developing two products that are essential to improved waterflooding and chemical flooding. Improved waterflooding through improving sweep efficiency, reservoir conformance, and profile modification is an economic process, currently being applied by operators, and is one of the processes proposed in the Oil Research Program Implementation Plan as having the potential, in the near-term, to arrest the rate of well abandonment. The first product is a mobile, and flexible low-molecular-weight polyacrylamide gel which can alleviate the problems of poor injectivity and mechanical degradation one encounters in the traditional high-molecular-weight polyacrylamide. The second product is a simulator for the design and prediction of the recovery efficiency of profile modification process using high-molecular-weight gels which has been studied by Wilhite and Green at the University of Kansas for more than a decade. NIPER's research program complements the efforts at the University of Kansas.

Mobility-Control Agents

Dilute solutions of high-molecular-weight polyacrylamides and biopolymers have been used by many independent oil producers and major oil companies in oil fields as mobility control agents to improve sweep efficiency and to increase oil recovery. The drawback in using polyacrylamides are their susceptibility to mechanical degradation, which is irreversible and can reduce their effectiveness as mobility-control agents and cause losses in injectivity. One strategy for mitigating the effects of mechanical degradation is the use of low-molecular-weight polymers. However, use of low-molecular-weight polymers requires considerably greater polymer concentrations to achieve an increase in viscosity equivalent to that with a high molecular-weight polymer. One alternative is to use crosslinked low-molecular-weight polymer formulations which should not be as susceptible to mechanical degradation and could provide good injectivity under high shear conditions.

NIPER is the only laboratory undertaking this kind of study. Research at NIPER on the development of unique crosslinked relative low-molecular-weight polymer gels for mobility control (rather than for profile modification) began in FY88. Screen tests have shown that crosslinked low-molecular-weight polyacrylamide gels for mobility control can be formulated with Cr(III) (pH = 4.8) and Cr(VI)/thiourea (pH = 6.8) using low-molecular-weight polyacrylamides. Gels that can be formed at neutral pH have also been formulated with a low-molecular-weight polyacrylamide and an aluminum citrate crosslinker. (These formulations are less likely to present environmental problems than chromium salts). Screening tests conducted in FY88 on two partially hydrolyzed low-molecular-weight polyacrylamides also revealed that gelation conditions were affected by the degree of hydrolysis. The degree of hydrolysis has also been shown to affect the gelation rate of

a conventional polyacrylamide with a metal crosslinking agent. In FY90, screening tests were conducted to determine the effect of the degree of hydrolysis on gelation kinetics and gel strength. These studies will allow the selection of the optimal degree of hydrolysis for making cost-effective low-molecular-weight polymer gels for mobility control.

Shear experiments in a pack of five randomly packed 100-mesh screens have shown that crosslinking bonds can be broken under a high shear condition and will reheal (reform) under a subsequent low shear condition. The ability of broken bonds to reform under low shear conditions will permit the healed gelled polymer to regain viscosity and to reduce water mobility as it flows through reservoirs. These results demonstrate that crosslinked low-molecular-weight gels not only can overcome the shear degradation problem but also can improve injectivity over that of conventional high-molecular-weight polyacrylamides. In FY91, shear experiments will be extended to porous media that have lower permeabilities. Results will be compared with those of a conventional polyacrylamide. If it can be shown that crosslinked low-molecular-weight polymer gels are more effective in controlling mobility than conventional polyacrylamides, some gel systems will be formulated and optimized for selected reservoirs in a high-priority class. If field tests are successful technically and economically, this near-term technology will be transferred to independent oil producers to improve oil recovery.

Permeability Modification

Many high-viscosity polymer gel systems have been developed for profile modification. Some of them have been successfully applied to many oil fields by independent oil producers and major oil companies to improve volumetric sweep efficiency and increase oil production.

In planning the treatments for permeability modification, the producers usually have the problems of determining the best initiation time for a gel treatment and how far the gel should penetrate in high-permeability layers. Problems like these can easily be answered by using a simulator. Such a simulator must be able to describe the transport of the chemical species and gelation reaction kinetics of the gel system in stratified reservoirs. It must also be able to account for phenomena such as inaccessible pore volume to macromolecules, adsorption of chemical species on rock surfaces, and retention of polymer gels on the rock matrix. Studies of these phenomena have been conducted in many university and industry laboratories. In FY88, a unique simulator that includes the above features was developed at NIPER for the first time for reservoirs that contain gas as a component. This simulator is very useful for simulating and optimizing any combination of primary production, waterflooding, polymer flooding, and permeability modification. This simulator has been used to determine the best initiation time for a gel treatment in a waterflood in reservoirs of different degrees of crossflow. Results showed that the best initiation time for a gel treatment in the injection well was the time immediately after water

breakthrough occurred, regardless of the degree of crossflow. In FY90, simulation runs were conducted to investigate the effect of layer permeability contrast on the best initiation time and the effect of the depth of gel penetration on oil recovery. Specific reservoir evaluation using this simulator should be very helpful for independent oil producers in assessing potential fields for polymer gel treatments. In FY91, the work will be extended to investigate the effect of a gel treatment on oil recovery in a conventional polymer flood.

Through various means of technology transfer including reports prepared as deliverables to the DOE, technical papers for presentations at society meetings, and refereed journal articles, the results of this project will be disseminated to the petroleum industry and others interested in this subject.

OBJECTIVES

To determine the applicability of low-molecular-weight polymer gels for mobility-control applications and to investigate the effect of a gel treatment on oil recovery in a polymer flood.

SCOPE OF WORK

Comparison of the effect of shear degradation on the flow resistance of solutions of a few crosslinked low-molecular-weight gel systems and on that of a solution of a conventional polyacrylamide polymer will be made in low-permeability porous media to prove that crosslinked low-molecular-weight polymer gels are better mobility-control agents than conventional polyacrylamide polymers. Flow resistance of selected gel systems will be measured at both high (typical of near-wellbore conditions) and low (typical of conditions far away from wellbores) flow rates. Results will be compared with that of a solution of conventional polyacrylamide (Pusher 500 in similar porous media under similar shear conditions).

NIPER's three-dimensional, three-phase simulator for permeability modification, developed in FY88, will be used to investigate the effect of a gel treatment on oil recovery in a conventional polymer flood. The merit of a gel treatment in a polymer flood will be assessed.

Task 1. Compare the effect of shear degradation on the flow resistance of selected crosslinked low-molecular-weight gel systems and on that of a solution of Pusher 500 in porous media. (Start date: October 1990. Completion date: August 1991) (Mid-term)

Flow resistance of selected crosslinked low-molecular-weight gel systems and that of a solution of Pusher 500 in porous media will be measured at both high and low flow rates typically encountered in reservoirs. The sequence of injection rates in each test will be (1) a low flow rate, (2) a high flow rate, and (3) a low flow rate. The effect of shear degradation on the flow resistance of all solutions before and after shear degradation occurs in porous media will be assessed. The

effects of shear degradation on the flow resistance of crosslinked low-molecular-weight gelled polymers and on that of a solution of Pusher 500 will be compared.

Task 2. Conduct sensitivity runs using NIPER's simulator for effect of permeability modification on oil recovery in a conventional polymer flood. (Start date: January 1991. Completion date: June 1991.) (Mid-term)

To investigate the effect of a gel treatment on oil recovery in a polymer flood, sensitivity runs using NIPER's three-dimensional, three-phase simulator for permeability modification will be conducted using three-layer reservoir models (representative of Unit A, Bell Creek field studied in BE1) of different degrees of crossflow.

DELIVERABLES

- Sep 91 Topical report on the flow behavior of polymer gels for mobility control in porous media
- Aug 91 Status report on the effect of gel treatment on oil recovery in a polymer flood

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemist	0.05
Senior Engineers	1.00
Technician	<u>0.20</u>
Total	1.25

Project Leader

Troy R. French, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Contraves viscometer	1	
Coreflood apparatus	1	
Rotating reciprocating pump	1	

BE5A. - GAS FLOODING

BACKGROUND

Gas flooding is an effective method for enhanced oil recovery (EOR). Many large-scale CO₂ and hydrocarbon floods are in progress in the United States. Nitrogen gas flooding processes also have great potential for enhancing recovery in condensate reservoirs and offshore reservoirs. According to the trend of recent EOR activities, gas flooding will become the most applied EOR method in the next decade. Widespread application of gas flooding is hindered by the poor mobility control and the uncertainty in predicting recovery efficiency in field projects. Although most research efforts are now concentrated on these problems, this project will focus on the effect of capillarity and porous medium on CO₂-crude phase behavior, and on the development of techniques to improve the accuracy for predicting solid precipitation in CO₂ flooding. Solid precipitation is a major near-term problem in CO₂ field projects that causes formation damage and reduction in productivity. The ability to predict the conditions for solid precipitation to occur will allow engineers to design suitable methods to alleviate this precipitation problem.

In previous research at NIPER, systematic studies on nitrogen miscible displacement included phase behavior measurements and slim-tube and coreflooding tests. The displacement mechanisms have been investigated, and a minimum miscibility pressure (MMP) correlation has been developed. In the CO₂ displacement studies, NIPER researchers have developed an accurate property prediction package for CO₂ density and viscosity and physical property correlations for CO₂-heavy oil mixtures. These results have been used by industry for gas EOR process design. The immediate application by industry of past results from laboratory research at NIPER demonstrates that short-term benefits often result from projects with long-term goals. In the past 2 years, research on gas mobility control and organic deposition occurring during gas miscible floods has been emphasized.

Phase behavior of injected gas with actual reservoir formation fluids may be different from that determined in a laboratory equilibrium cell. In an equilibrium cell, all fluids are well mixed and rapidly achieve equilibrium; however, recent studies with molecular simulations have shown that fluid phase behavior inside micropores is quite different. The solid surface may induce liquid condensation, and phase equilibrium may not be achieved because of the restriction of a porous medium. Also, injected gas contacts only a small part of oil within a simulated time step. Therefore, the usual assumption of instantaneous equilibrium in reservoir simulations is unrealistic and may generate erroneous results. This phenomenon will be studied in FY91.

A study of the problem of organic precipitation induced by gas flooding was initiated in FY 89. Deposition of asphaltic or paraffinic materials often occurs at or near wellbores and plugs or restricts flow producing wells. This deposition results in increased production costs and reduced productivity. In addition, deposition of these materials may alter rock wettability and relative permeability, thereby affecting fluid flow and recovery efficiency. In FY 91, the effect of asphaltene deposition on rock properties during gas flooding will be studied.

Parallel to the experimental studies, a more accurate prediction method for phase behavior will also be developed. The accuracy of phase behavior predictions using equations of state are still insufficient for systems such as CO_2 - H_2O -crude oils, and CO_2 -crude oils. Inaccuracy is even more serious in the supercritical region of CO_2 , which is extremely important to the CO_2 miscible process. An improved equation of state is needed to accurately describe supercritical extraction and solid precipitation phenomena. An existing cubic equation of state (e.g RK-EOS) will be modified to improve its accuracy for predicting phase behavior, and to enhance its capability to be able to predict solid precipitation phenomenon.

The results of this project will be made available to the petroleum industry and the research community. In addition to reports to the DOE, refereed journal articles and presentations to professional societies will be prepared.

OBJECTIVES

The objectives of this project are to develop methods to mitigate the deleterious effects of solid precipitation in gas flooding, and to determine the effect of porous media on gas-oil phase behavior.

SCOPE OF WORK

The equations of state currently used in the petroleum industry will be modified to develop a technique for predicting solid (wax, asphaltene, etc.) precipitation and for predicting supercritical extraction with CO_2 -perfluorinated hydrocarbon fluids. Techniques to improve the accuracy in phase property predictions for CO_2 -crude oil systems will also be developed. PVT and coreflooding experiments will be conducted to determine the effect of porous media on gas-oil phase behavior, and recovery efficiency. Through coreflooding experiments, formation damage from asphaltene precipitation during gas flooding will also be studied.

Task 1 - Laboratory experiments to investigate the effect of porous media on CO_2 -oil phase behavior. (Start date: October 1, 1990. Completion date: August 31, 1991) (Near-term)

Perform phase equilibrium experiments using CO_2 -oil systems in an equilibrium PVT cell and compare the results with those in which the oil is stored inside a porous medium. Determine

gas phase compositions as a function of time for both cases, and results from these two different experiments will show the effect of porous media on CO₂-oil phase behavior. Conduct coreflooding experiments to study the effect of gas flow rate on phase equilibrium and displacement efficiency. Measure effluent compositions from these core flooding experiments to obtain information on the dynamic gas-oil phase behavior. This research will provide information for correlating the effect of porous media on phase behavior during simulation and will help to clarify the effects of this factor on solids precipitation being studied in task 3. Because this is a scoping task, the level of effort for this task will depend upon the initial results.

Task 2 - Laboratory experiments to investigate the conditions for asphaltene precipitation and its effect on formation damage. (Start date: November 1, 1990, completion date: September 30, 1991) (Near-term)

Conduct CO₂ coreflooding experiments to induce asphaltene precipitation. Measure the asphaltene contents of the crude oil before and after contacting CO₂ to determine the quantity of precipitated asphaltene. Measure the permeability, and other physical properties of the cores before and after the coreflooding experiment to determine the degree of formation damage.

Task 3 - Prediction technique development for the description of solid precipitation. (Start date: October 1, 1990, completion date: September 30, 1991) (Mid-term)

Modify a cubic-type equation of state (e.g. RK-EOS) to predict solid (wax, asphaltene, etc.) precipitation. The preliminary organic precipitation model developed during FY90 will be further refined and improved using experimental data from task 1 and task 2 of BE 5B.

DELIVERABLE

Sep 91 Topical report to describe all experimental results, the newly developed predictive technique, and computer codes.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Engineer	0.5
Research Engineer	0.2
Assistant Engineer	<u>0.5</u>
Total	1.2

Project Leader

Frank Chung, Senior Engineer

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Gas chromatograph	1	
Phase equilibrium measurement apparatus	1	
Coreflooding apparatus	1	
Data-acquisition system		1

BE5B. - MOBILITY CONTROL AND SWEEP IMPROVEMENT IN GAS FLOODING

BACKGROUND

Gas flooding is an effective oil recovery process. Commercial scale carbon dioxide floods and hydrocarbon floods are in progress in the United States. Nitrogen gas flooding processes also have great potential for EOR applications in condensate reservoirs and offshore reservoirs. According to the trend of recent EOR activities, gas flooding, and in particular carbon dioxide flooding, could become the most popular EOR method in the next decade. The success of gas flooding in the United States is mainly attributed to the excellent displacement efficiencies usually obtained with miscible carbon dioxide flooding. However, low fluid densities and viscosities of the injected gases, as compared to common reservoir fluids, usually results in low sweep efficiencies. Consequently, extensive studies have been initiated to develop improved method of mobility control for miscible carbon dioxide displacement processes.

In previous research at NIPER, the use of foam for mobility control has been extensively studied and reported. Two papers describing research on foam conducted over the past 2 years were accepted for the 1990 SPE/DOE Symposium on EOR. Variations of injection strategies have been shown to substantially alter the distance and effectiveness of foam flowing through slim tubes and linear corefloods. As a result of this work, additional questions, such as the following, were raised. Can these results be extrapolated geometrically to typical radial dimensions encountered near well-bores? Can foams be successfully generated and propagated by adjusting critical surfactant solution volumes, concentrations, and injection sequences for idealized radial flow, or must these parameters be further adjusted to account for discontinuous and heterogeneous fluid flow patterns?

The work proposed for this project in FY91 will include the expansion of capabilities at NIPER to evaluate foams under radial flow conditions. Preliminary research conducted during FY90 evaluated radial flow of foams using small cores. An initial assessment was needed to determine if differential pressure profiles and flow patterns could be altered and optimized by selecting appropriate injection strategies. Although the FY90 objectives were met, the small design of the radial core system (6 in. diameter) could be used to study only areas near the wellbore (< 5 ft) and did not allow sufficient time for foam flow to attain steady state conditions. Consequently, an expanded radial flow physical model will be constructed and tested in FY91.

In addition to mobility-control studies with foam, evaluation of entrainers will continue into FY91. Entrainers are supercritical fluid additives capable of enhancing the phase behaviors or solvency properties of fluids. In other applications, entrainers have been able to increase the selectivity in supercritical extraction processes. For gas miscible flooding, these materials have the potential to improve displacement efficiency by increasing the solubility of marginally soluble

components in crude oils; these materials also have the potential to improve mobility control from the viscosity contributions of the entrainer and additional hydrocarbon components solubilized by the entrainer. Studies conducted in FY89 and FY90 have shown that certain materials demonstrate some of the beneficial properties necessary for enhanced mobility control. Current practices in the field have shown that for any method that can enhance gas mobility, immediate economic benefits are obtained by reducing the costs of re-injecting produced gas, and long-term economic benefits are obtained by increasing the total amount of oil produced for the gas injected. Research studies proposed for FY91 are to investigate some of the questions that remain to be answered before the technology can be applied in the field. The most immediate application under investigation (and the one getting the most attention) is with cyclic CO₂ processes. Although mobility control may be less critical in cyclic processes, displacement efficiency is more critical. The additional crude oil components extracted by CO₂ with added entrainer may reduce the soak time and improve the recovery efficiency of the cyclic CO₂ processes. Such benefits would make the process more economically attractive to independent producers, particularly since cyclic CO₂ processes would not incur high front-end costs. Furthermore, cyclic CO₂ processes can be adjusted to fit the size of the operation, making this method very attractive to small operators. In contrast, traditional gas injection projects are often quite expensive and restricted to the larger operators having sufficient capital to cover the front-end costs. If the entrainer process shows promise in the studies conducted in FY92, a recommendation will be made to field test this technology with an operator, as a means of technology transfer.

In addition to evaluating entrainers for cyclic CO₂ processes, additional evaluations will be made to further improve the entrainer technology. In FY90, some feasibility studies suggested that in addition to alcohols and branched alkanes (i.e., 2-ethyl hexanol and isooctane evaluated in FY89 and FY90), other classes of compounds may be even more suited as an entrainer for typical crude oils encountered in the field. Tasks proposed in FY91 will evaluate some selected compounds from these other compound classes. Included among these compound classes are perfluorinated alkanes. Although very little information is available on these compounds, what has been published indicates that certain compounds impart unusual properties to supercritical CO₂ which results in substantially increased viscosities. Because of the inability of most compounds already tested to match these properties, it was proposed to include them in the entrainer evaluation. Environmental hazards by these compounds are expected to be minimal. Toxicity studies have indicated no adverse affects to animals, and these compounds would not be expected to endanger the upper atmosphere due to their absence of chlorine and their low volatilities.

The last phase of entrainer evaluation includes a study of the performance sensitivity to various injection conditions. The effect of concentration, WAG cycles, and multiple entrainer injection cycles will be considered. The evaluation of these factors will provide a basis for making economic projections of this technique in a field environment.

Another unique approach to improving sweep efficiencies of injected gases that is proposed for FY91 is based on the premise that the solubilities of certain polymers are reduced by orders of magnitude in the presence of CO₂. When properly placed, this precipitated polymer would effectively block the flow of injected gas from the high permeable zone and improve the sweep efficiency of the overall process. Because polymer injection is a well established procedure in the field, little difficulty is anticipated in applying this technology once a suitable polymer is found. So, although designated as a mid-term task, this technology could become a near-term solution to a difficult problem if a suitable polymer is quickly identified. This procedure would then be implemented in a field test as a means of transferring the technology to oil field operators.

OBJECTIVE

The objectives of this project are:

(1) for entrainers: address the critical issues that remain before their application in field trials can be justified. These issues include identifying the best class of compounds from which to choose the most cost effective entrainers, and identifying the best injection strategy for entrainers in gas flooding. For the latter, cyclic CO₂ processes will also be tested for potential near-term applications;

(2) for other additives: evaluate unique approaches to improving sweep efficiency in gas flooding EOR processes. This year, precipitation of polymers and perfluorinated alkanes will be evaluated for potential mid-term applications; and

(3) for foam: initiate studies to evaluate foam flow behavior in radial corefloods. Although many have studied foam for mobility control, very few have actually studied the flow of foam under radial flow conditions--conditions more typical of the oil field environment.

SCOPE OF WORK

DOE's new Oil Research Program Implementation Plan recognizes that the application of CO₂ will be fundamentally crucial in the near-term and mid-term time periods for recovering much of the mobile oil in the high priority geological classes (i.e., Open Shelf Platform, W. Texas). Problem: unfortunately, the effectiveness of currently applied technologies (EOR gas flooding) are often limited by low sweep efficiencies of the injected gases. The majority of tasks proposed for this project evaluate unique or untested approaches to improving mobility control and sweep

efficiency. Use of entrainers for enhancing mobility control started at NIPER, and NIPER is currently the primary contributor to the evaluation of this technique. Use of perfluorinated alkanes has received very little attention in the literature. Also, the injection of polymers which are insoluble in the presence of CO₂ to improve sweep efficiency remains untested by anyone, as far as we know. Each of these approaches will be tested in FY91.

Although most of the listed tasks are mid-term oriented, task 1 was inserted to help address DOE's near-term goals, and task 1 will be given the greatest emphasis for this project. As stated in DOE's Oil Research Program Implementation Plan, the near-term overall objective is to preserve access to defined, high-potential classes that are rapidly approaching their economic limits with currently available technologies. Problem: many of these reservoirs that could benefit from CO₂ injection do not have access to cheap pipeline gas. Cyclic CO₂ processes have demonstrated to be effective for these situations, but are virtually unknown by many of the independents operating marginal wells in targeted areas that are being shut in, abandoned, or plugged. NIPER has previously demonstrated that entrainers can improve mobility control in continuous CO₂ injection processes. If similar improvements are demonstrated for cyclic CO₂ injection processes as proposed for FY91, recommendations will be made to test the process in the field. The opportunities for applying entrainers with cyclic as opposed to continuous injection of gas is greater because the economic restriction of being conveniently close to an existing CO₂ pipeline is removed; also because the total investment is less, the process could be implemented by independent operators. The overall impact on domestic oil production rates should be favorable, and the rate of well abandonment for marginal wells should decrease.

Finally, a long-term oriented task on foam characterization was inserted, because it was felt the current practices of extrapolating linear flow experiments to typical radial flow regimes encountered in the field are unrealistic for foam. Very few research laboratory studies on foam flow mechanisms are based on actual radial flow experiments, and very little work is currently being done in this area. NIPER and other laboratories have previously conducted many experiments on foam, and our past experience will be invaluable in guiding the planned experiments.

Product: In addition to the topical reports generated directly from this project, those technologies developed under this project that are found to be successful will be made available to the petroleum industry through journal articles and presentations at technical meetings.

Task 1 - Determine and compare the beneficial effects of entrainers in cyclic CO₂ processes to those measured under flowing conditions. (Start Date: October 1, 1990. Completion Date: September 30, 1991.) (Near-term)

Several operating companies are currently trying the application of cyclic CO₂ in their reservoirs. Certain entrainers have been found (project BE5B, FY89) to increase the range of

hydrocarbon components extractable with CO₂ and improve the mobility control of injected fluid in flow-through systems. Laboratory studies will be conducted under this task to determine if a similar benefit is observed in a cyclic mode. All of the conditions will be the same as those for previous experiments, except the core will be shut in for a certain time period to allow the system to "soak." Provided substantial benefits are evident, the process will be recommended for field trial.

Task 2 - Evaluate alternative compounds as entrainers for gas flooding.

(Start Date: October 1, 1990. Completion Date: September 30, 1991.) (Mid-term)

It was determined in FY90 that other entrainer compounds have even greater potential for enhancing mobility control of injected gases in recovering oil than those previously tested. These compounds will be evaluated under this task for their ability to increase viscosity, improve mobility control, and enhance oil production. Vapor-Liquid Equilibrium (VLE) may also be determined for such unusually behaving mixtures as CO₂-perfluorinated alkanes at a typical reservoir temperature. In addition to conducting the screening tests previously described (fluid density, viscosity, etc.), alternative methods of screening candidate entrainers will be explored.

Task 3 - Test alternative injection strategies to optimize application procedures for entrainers in gas flooding.

(Start Date: October 1, 1990. Completion Date: September 30, 1991.) (Mid-term)

Certain compounds, such as isooctane and 2-ethyl hexanol have been shown to enhance the mobility of CO₂ in corefloods. However, effects of entrainer concentration, WAG cycles, and multiple entrainer slugs on performance have not been evaluated. This task is design to evaluate these factors based on coreflood experiments. Answers to these questions are critical to the application of this unique technology in the field.

Task 4 - Laboratory experiments to investigate polymer precipitation by CO₂.

(Start date: October 1, 1990. Completion date: August 31, 1991) (Mid-term)

Polymer solution properties will be studied first at ambient conditions. Experiments will be designed to determine the phase changes of polymer solutions with respect to the solution pH-value. From these preliminary screening tests, a polymer will be selected for high pressure experiments to investigate polymer precipitation by CO₂. In the high pressure experiments, the polymer solution will be mixed with high pressure CO₂ gas inside a PVT cell and the precipitation will be determined by flowing the solution through filters. If the results are positive, coreflooding tests will be conducted to determine the effectiveness of this method for CO₂ mobility control.

Task 5. Assemble and make operational a suitably sized radial core apparatus. (Start Date: October 1, 1990. Completion date: September 30, 1991.) (Long-term)

Small (6-in.-diameter) radial coreflood experiments were conducted in FY90 to study various injection strategies to improve the injectivity gradient for foams in the near-wellbore region. However, because of the varied volume of foam, larger radial cores are needed for extending these studies to an accurate investigation of foam flow properties in a radial environment. Under this task, a larger diameter radial coreflood apparatus will be constructed, and preliminary experiments will be conducted on foam flow to develop suitable methods for tracking the foam front. It is anticipated that in FY91 or FY92, a unique approach to describing radial foam flow, such as through chaos theory, will be developed and the laboratory capability developed under this task will be used to confirm the approach. Currently, most experiments are conducted in slim-tubes and linear cores, and the results are mathematically extrapolated to radial flow. Micromodel studies of gas flow in two or three dimensions have shown that complexities are considerable increased, and simple geometrical extrapolation from linear to radial dimensions is not expected to adequately describe fluid flow patterns with gas and foam.

DELIVERABLES

- Sep 91 Topical report describing the results obtained from the entrainer studies.
- Sep 91 Topical report discussing the feasibility studies with unique mobility control additives and with foam flow in radial cores.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Engineer	0.4
Senior Physicist	0.8
Research Chemist	0.3
Associate Engineer	0.2
Assistant Engineer	0.5
Senior Experimentalist	<u>1.0</u>
Total	3.2

Project Leaders

Frank Chung, Senior Engineer
Clarence Raible, Senior Physicist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Viscosity measurement apparatus	1	
Coreflooding apparatus	1	
PVT apparatus	1	
Data acquisition system		1
High-pressure electromagnetic viscometer		1

BE9. - THREE-PHASE RELATIVE PERMEABILITY RESEARCH

BACKGROUND

Multiphase flow is a common phenomenon in petroleum reservoirs. The initial or primary production from a reservoir may include gas, oil, brine, or combinations of the three. Later during the productive life of a reservoir, two-phase flow occurs when a fluid such as brine is injected into a reservoir to boost production. Finally, if enhanced oil recovery techniques, such as chemical or immiscible gas flooding, are used to maximize hydrocarbon recovery, multiphase flow phenomena probably will occur. With multiphase flow, fluids compete for the same flow paths through reservoir rock. The additional resistance to flow is described by normalizing permeabilities for each of the flowing phases at each fluid saturation condition with respect to a base permeability. This measurement and normalization process yields relative permeability data. The FY91 research program is designed to build upon the previous results for the project with emphasis on studying the relationships among pore and grain size distributions, trapping, tortuosity, and relative permeabilities. Existing two- and three-phase relative permeability apparatuses have been used in assisting several industrial clients.

The concept of relative permeability for two-phase flow is not new. Work on developing two-phase flow relationships probably began in 1859, and through the years techniques for using the results have been refined for estimating petroleum reservoir productivity and performance. Efforts to extend the techniques for three-phase flow began in 1941, but difficulties limited progress in this area. Keeping track of fluid saturations in a rock during three-phase, steady-state flow experiments was virtually impossible until the recent advent of techniques, such as X-ray and microwave attenuation, to monitor in situ fluid saturations directly during flow experiments. Correlations have been developed to predict three-phase flow effects from two-phase flow measurements, but such correlations are not always correct or accurate. The primary reasons for the limited knowledge with respect to three-phase flow systems are the scarcity of accurate three-phase relative permeability laboratory data and laboratory measurement systems.

Three-phase flow characteristics are affected by rock properties, wettability, and hysteresis, among other factors. Because quantification of the relationships between rock properties and multi-phase flow behavior has not been completed, additional study is clearly required. The major problem that the availability of accurate measurement of multiphase relative permeability will solve is unrealistic numerical reservoir simulation. Relative permeability is a major input for reservoir simulation and if accurate data are not available for the behavior of fluids in the reservoir at actual reservoir conditions, a reasonable simulation cannot be made. Simulations are used by operating companies to decide how to develop a field, whether to conduct an improved recovery project, where to drill infill wells, to identify the cause of formation damages, and whether it is cost-effective

to continue production. NIPER uses the relative permeability equipment for industrial clients who must decide how to manage their reservoirs. Tests for industrial clients are conducted as closely as possible to actual reservoir temperatures and pressures. Thus, the equipment developed in this project has an immediate applicability and provides a means of technology transfer to the petroleum industry.

NIPER has conducted DOE-funded relative permeability research for the past 6 years. The objectives of this work have been to improve laboratory measurements of three-phase relative permeability so that reliable measurements are achieved and to investigate the influences of rock, fluid, and rock/fluid properties on two- and three-phase relative permeabilities. This work has yielded improvements in measurement techniques and equipment including the development of an X-ray and microwave scanning instrument for monitoring fluid saturations during relative permeability experiments; the development of a high-pressure coreholder that is semitransparent to microwaves; improvement in microwave technology for scanning rocks with thicknesses greater than 1 inch; and continual improvements in relative permeability measurement systems and techniques. Several models for computing three-phase flow characteristics have been evaluated using three-phase data from laboratory experiments conducted by Corey Naar-Wygal, Naar-Henderson, and Stone. Of the models evaluated, none predicted the experimental data adequately, demonstrating that additional research is necessary. NIPER's two- and three-phase laboratory investigations have yielded important results. Three-phase experiments with Berea sandstone to demonstrate viscous effects on relative permeability showed variations in permeabilities as a result of variations in rock characteristics; brine and gas relative permeabilities were functions of the brine and gas saturations, respectively; oil relative permeabilities were functions of all three-saturations; and oil and water relative permeabilities were essentially independent of oil viscosity for viscosities in the 1 to 50 cP range. Water relative permeabilities decreased with increasing wetting phase viscosity.

During FY89, NIPER investigated the effects of rock characteristics on relative permeabilities by comparing the results from experiments on Berea and Bentheimer sandstones. Relative permeabilities for the two sandstones were noticeably different, and these differences were attributed to variations in pore size distributions. Comparison of oil-brine flow test results showed that residual oil saturations for the Bentheimer sample were lower than those of the Berea sample; the range of mobile saturations for the Bentheimer sample were broader; and data from both samples were subject to hysteresis effects.

Recently, considerable industrial interest has been shown in determining when it is necessary to conduct relative permeability measurements at reservoir conditions and when it is sufficient to conduct the measurements at room temperature. NIPER is recognized by the industry as having considerable expertise in conducting relative permeability measurements at

elevated temperatures and pressures and is pursuing a multiclient project to answer this question. Such a project will provide an excellent technology transfer opportunity. Additional technology transfer will be accomplished by the preparation of journal articles subject to peer review and presentations for symposia.

OBJECTIVES

The objectives of this project are as follows:

1. To improve the reliability of laboratory measurements of two- and three-phase relative permeabilities for steady- and unsteady-state conditions in core samples.
2. To investigate the influence of rock, fluid, and rock-fluid properties on two- and three-phase relative permeabilities.

SCOPE OF WORK

Project efforts will be concentrated in two primary areas: examination of mutual relationships among petrophysical properties and relative permeabilities; and improvement in three-phase relative permeability measurements. A homogeneous sandstone sample with absolute permeability in the 150 to 400 md range will be selected for complete characterization. The sample will be nearly identical to high-permeability samples tested during FY89 and FY90, except with respect to pore and grain size distributions. Two- and three-phase relative permeability experiments will be performed on the sample in a systematic, highly controlled manner to produce high-quality data reflecting both drainage and imbibition cycles. Test results will be compiled and compared with those for the 600- and 2,000-md samples tested in previous years. It is anticipated that this work will build upon the foundation for the project established during FY89, ultimately leading to the development or verification of correlations between three-phase permeability and other rock properties.

Tasks to improve laboratory measurements will focus on comparing steady- and unsteady-state relative permeability measurements; comparing fluid saturation distributions from CT imaging with resistivity measurements to study variation in resistivity with saturation distribution; and improvements in laboratory automation. Finally, automation of the experimental system will continue with hardware and software modifications such that the laboratory computer will determine when coreflood flow conditions have reached steady-state conditions, then automatically scan the rock to determine the saturation distribution, and finally change pump rates to achieve a new steady-state condition. This automatic mode will result in more reproducible determinations of steady-state conditions and more efficient time management.

Task 1. Select and characterize sandstone sample in preparation for two- and three-phase relative permeability experiments. (Start date: October 1990. Completion date: March 1991.) (Near-term)

One sandstone sample with absolute permeability in the 150 to 400 md range will be selected for the FY91 experimental program. The petrophysical and petrographical properties of the sample will be characterized, including porosity, permeability, grain density, XRD and SEM measurements. Quantitative microscopic evaluation through petrographic image analysis will be conducted on thin sections of the rock sample to characterize pore and grain size distributions. Mercury injection and centrifuge capillary pressures will be measured. The wettability index for the sample will be determined from centrifuge capillary pressure results using the same oil and brine that will be used during flow experiments.

Task 2. Conduct and analyze two- and three-phase relative permeability experiments. (Start date: November 1990. Completion date: September 1991.) (Near-term)

Two- and three-phase steady-state relative permeability experiments will be conducted under controlled ambient conditions. Electrical properties of the rock and pH of the effluent will also be measured as appropriate to provide additional insight into the process of achieving steady-state conditions. The overall objective of this task is to obtain high-quality data that can be related to other measurements for development of correlations. Results will be compared with those from FY89 and FY90.

Task 3. Conduct unsteady-state oil/water relative permeability tests on the selected sandstone. (Start date: December 1990. Completion date: September 1991.) (Near-term)

A literature review of factors affecting unsteady-state relative permeability results will be conducted to determine guidelines for producing unsteady-state results which are comparable with steady-state results. Tests will be conducted at ambient conditions, and results will be compared with steady-state results from task 3. Additional tests will be performed as necessary with higher viscosity oils or different injection rates and pressures to determine optimum test conditions for matching unsteady- and steady-state results.

Task 4. Compare saturation dependent electrical properties with saturation distributions from CT Imaging. (Start date: January 1991. Completion date: June 1991.) (Near-term)

The flow of electricity through porous media is thought to be analogous to the flow of a fluid of zero viscosity. If so, the resistivity of a brine-saturated rock depends primarily on lengths of the shortest paths through the pores and on the rock's porosity rather than on permeability and pore

shapes and sizes. Resistivity factors have been used to calculate effective pore lengths in brine-saturated rocks. Resistivities also have been correlated for partially saturated rocks as a function of water saturation, but such correlations are accurate only when the brine is uniformly distributed.

The effect of saturation distribution will be studied for Berea rock samples under various saturation conditions. Nonuniform saturations will be imposed through controlled dynamic flow experiments or by using a high-speed centrifuge. Electrical properties of partially saturated rocks will be measured, then the rocks will be CT scanned. Variations in electrical properties with variations in saturation distribution will be studied. This is important to field applications since resistivity is a common field measurement.

DELIVERABLE

Sep 91 Topical report describing two- and three-phase relative permeability results and their interrelationships.

PLANNED STAFFING

	<u>Man-Years</u>
Senior, Research, and Associate Engineers	1.3
Technicians and Support Staff	<u>1.8</u>
Total	3.1
<u>Project Leader</u>	
Daniel R. Maloney, Research Engineer	

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
X-ray/microwave sources and detectors	1	
Pumps for unsteady-state tests		2
Coreholder for unsteady-state tests		1

BE11A. - THERMAL PROCESSES FOR LIGHT OIL RECOVERY

BACKGROUND

Steamflooding of heavy oil reservoirs (<20° API) is a mature technology and currently contributes nearly 7% of domestic daily oil production; however, heavy oil constitutes only about 10% of the total domestic petroleum reserves. This project was initiated to determine if steamflooding light crude oil reservoirs can be as successful as for heavy oil.

DOE is conducting steamflood field pilots in light oil zones in two reservoirs: one in the Elk Hills field in California, and the other in Teapot Dome (WY) field. Both projects demonstrate steamflooding in different environments. The California steamflood is in a highly permeable sand at a depth of 2,000 ft, and the Teapot Dome pilot is in a fractured consolidated tighter Shannon sand at 500 ft depth.

NIPER research has shown that steamflooding previously waterflooded water-wet reservoirs is infeasible. Physical model 2-D steamflooding studies on previously waterflooded sands that are oil-wet, and of intermediate wettability, indicate that oil-wet reservoirs are prime candidates for steamflooding. Oil-wet reservoirs respond poorly to waterflooding and become stripper wells early in their productive life. Thus, oil-wet reservoir sands have high oil saturations as compared with water-wet reservoirs. Steamflooding in addition to supplying pressure and lowering the viscosity of the oil, changes the wettability to a more water-wet condition as part of the mechanism of light oil steamflooding. Thus, application of steam to oil-wet light oil reservoirs may help to maximize the economic producibility of this nation's oil resource—the major goal in DOE's Oil Research Program Implementation Plan. Steamflooding in even water-wet sands has been shown to reduce the oil saturation beyond what is achievable by waterflooding. Research at NIPER has shown that contrary to earlier simulation results, gravity override and fingering can be major problems.

During the past few years, NIPER has been analyzing oils and their thermal oil recovery potential. These oils were chosen because of their chemical composition. In FY90, NIPER analyzed base case 2-D steamfloods from a current California light oil steamflooding pilot. This study then correlated the composition of the produced oil with time and temperature (hot water vs. steam at various temperatures), analyzed potential override and fingering tendencies, and compared the results from light oil studies on proposed light oil steamflooding sites.

The ability to predict the effect of light oil steamflooding on a field scale requires a simulator that not only has thermal capabilities but also has mass transfer capabilities. Expansion of light oil steamflooding technology to the independent small producer will require a simulator in the public domain that has this capability. The personal computer-based semianalytical predictive models

developed for heavy oil need to be analyzed for their adaptability in predicting behavior of steamflooding light oils.

Transferring the technology resulting from the project will be accomplished by reports on the results of the work prepared for the DOE, participation in symposia and meetings of professional societies, and publication, as warranted, in professional and trade journals. Personal contacts, as requested, will be made with representatives of the petroleum industry in fulfillment of requests for information and data about the work.

OBJECTIVES

Specifically for FY91, the objectives are as follows:

(1) determine the effect of steam temperature on composition of the produced oil and residual oil saturation (hot water vs. steam at various temperatures). Determine potential override and fingering tendencies in a 2-D model using oil and sand from Teapot Dome (WY) field. Compare Teapot Dome results with oils analyzed from proposed light oils steamfloods.;

(2) examine the applicability of the semianalytical thermal predictive models for applicability in evaluating light oil steam flood potential;

(3) construct a new multidimensional steamflood physical model; and

(4) support the DOE in its cooperative effort with Venezuela in thermal technology transfer by participating in the Annex IV meetings that are scheduled twice a year.

SCOPE OF WORK

Task 1. Analyze semi-analytical numerical predictive models. (Start date: October 1990. Completion date: December 1990.) (Near-term)

This task is designed to analyze the current semi-analytical thermal predictive models for their applicability for use in evaluating light oil steamflood potential. Based upon the analysis, a compositional package could be added in FY 92. This simulator could be used to screen mid-continent reservoirs for light oil steamflooding.

Task 2. Compare the oil recovery efficiency of hot water versus steam from the 2-D model using Teapot Dome core and oil. (Start date: December 1990. Completion date: July 1991.) (Near-term)

This task is designed to analyze base case 2-D steamfloods using field sand and oil from Teapot Dome. This study will be conducted to study the produced oil composition with time and temperature (hot water vs. steam at various temperatures), and potential override and fingering tendencies in this field pilot. The data collected in this task will be compared with previous light oils that have been analyzed for their potential recovery by steamflooding. Results from this task can be immediately used by operators of this field pilot.

Task 3. Design of a multidimensional steamflood physical model. (Start date: October 1990. Completion date: September 1991) (Mid- to long-term)

This task is proposed based on the results of task 5 of BE11A in FY90. A scaling study and analysis of the current 2-D model was conducted to determine whether a new design is needed. A multidimensional steamflood physical model will be constructed in FY 91 and FY92 to add to NIPER and DOE's capability to conduct research in steam EOR. This task will be implemented in cooperation with BE11B.

Task 4. Support the DOE in its cooperative effort with Venezuela by presenting the results of this project at the Annex IV meetings. (Start date: November 1990. Completion date: April 1991.) (Near-term)

This task is designed to support DOE in their technology exchange with the Venezuelan Ministry of Energy and Mines to increase oil production by thermal methods. Activities within this task include attendance at joint meetings, participation in joint discussions, and presentations of results (both oral and written) obtained from light oil research performed in this project.

DELIVERABLES

- May 91 Summary report on the activities under this project for inclusion in the annual report of the Annex IV meetings.
- Sep 91 Status report that describes research conducted on light oil in support of thermal processes for light oil recovery.

PLANNED STAFFING

	<u>Man-Years</u>
Senior and Research Chemists	0.45
Research and Associate Engineers	0.7
Technicians	<u>0.8</u>
Total	1.95

Project Leader

David K. Olsen, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Computer		1
Support equipment for new steamflood model		1
Data backup system		1

BE11B. - THERMAL PROCESSES FOR HEAVY OIL RECOVERY

BACKGROUND

Steamflooding of heavy oil reservoirs ($<20^\circ$ API) is a mature technology and currently contributes nearly 7% of total U.S. daily oil production. Currently, the majority of the Nation's steam injection projects are concentrated in California where most of the oil is produced by major operators. The goal of making this technology available to small independent operators has been slow in developing because the independents do not have access to the technology held by the major operators and must rely on information dispersed throughout the public domain.

To assist in **technology transfer** to independent oil producers, NIPER is developing an operator's guide to thermal EOR based on an assessment conducted during FY90 on California's ongoing thermal operations. This undertaking is much like the early SPE papers and waterflooding papers prepared as part of the technology transfer conducted in the 1950's by the U. S. Bureau of Mines, Bartlesville, Oklahoma, to help independent operators successfully implement waterflooding technology.

Heavy oil reservoirs usually have a high oil saturation, and steam can effectively reduce the viscosity by orders of magnitude. However, the differences in viscosity and density between steam and heavy oil reduces the sweep efficiency of the process. Thus, close spacing and increased sweep efficiency are critical in maximizing oil production.

The NIPER 2-D laboratory physical model is capable of evaluating specific aspects of steam foam and other profile modifying agents needed to help alleviate sweep efficiency problems. Future advances requires a different model to study the process. A study was undertaken as task 5 in BE11A during FY90 to evaluate the model, propose scaled experiments, and suggest alternative physical models that could be used in future research. The proposed model is a compromise between desirable features and cost, while permitting research on other aspects of thermal recovery of heavy oil to continue. Assembly of the model over the next 2 years is achievable under the current funding level. Increased funding would permit the model to be operable in less time. The new model will allow us to resume evaluation of steam diverters and be more representative of actual field conditions, including the chemical and physical processes occurring at the vapor/liquid-solid/liquid interface.

Effective technology transfer of the findings of this research to the petroleum industry will be a major goal of this project. Results will be reported to the DOE as described in the section of this plan on Deliverables. In addition, the project leader and members of the project team will prepare peer-reviewed technical papers about the project for professional society meetings and publication in the scientific literature.

OBJECTIVES

Specifically for FY91, the objectives are as follows:

- (1) as an addition to the thermal (steam) field operators' guide sections prepared in FY90, the costs, sample engineered analysis, schematics, and equipment needed for implementation of a steamflood by an independent operator will be prepared in a format that can be used by independent operators to help assess the economic feasibility of implementing a thermal EOR process;
- (2) advance the current numerical laboratory thermal simulator to assist in the analysis of laboratory experiments using both vertical and horizontal steam injection; and
- (3) construct a new multidimensional steamflood model.

SCOPE OF WORK

Task 1. Compile a supplement to the steamflood operators guide published in FY90. (Start date: October 1990. Completion date: June 1991.) (Near-term)

This task is designed to support DOE in near-term technology transfer to independent operators by publishing a topical report that incorporates the status report on the thermal (steam) field operators guide prepared in FY90. Potential topics in addition to those of FY90 include costs, schematics, and equipment listings for implementation of thermal (steam) EOR. Also, a section of this report will provide an analysis of current screening criteria and describe the development of a system to help the independent operator assess the feasibility of using steam to increase production. In addition, this task will develop a spreadsheet model that may assist the operator in assessing the economic feasibility of implementing steamflooding.

Task 2. Design of a multidimensional steamflood physical model. (Start date: October 1990. Completion date: September 1991.) (Mid- to long-term)

This task is proposed based on the results of task 5 of BE11A in FY90. A scaling study and analysis of the current 2-D model was conducted to determine in FY90 whether a new design is needed. Based upon the funding level, a multidimensional steamflood physical model will be added to the capability of NIPER and DOE to conduct research in thermal EOR.

Task 3. Development of implicit version of numerical laboratory thermal simulator. (Start date: October 1990. Completion date: December 1991.) (Near- to mid-term)

This task is designed to advance the current numerical laboratory thermal simulator to an implicit version running on a personal computer. This will allow simulation of current and future laboratory thermal displacement experiments injecting steam in both vertical and horizontal orientations. No PC level compositional thermal simulator is currently available. A public domain

version will be delivered in the near future based on the effort allocated for this and subsequent tasks.

DELIVERABLES

Jun 91	Topical report on steamflood operators' guide.
Sep 91	Status report that describes research conducted in support of thermal processes for heavy oil recovery (numerical laboratory thermal simulator and design of a multidimensional physical model).

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemists	0.3
Research and Associate Engineers	0.7
Technicians	0.3
Consultant	<u>0.1</u>
Total	1.4

Project Leader

David K. Olsen, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
New 2-D steamflood physical model		1
Thermal heat flux sensors		1

BE12. - IMAGING TECHNIQUES APPLIED TO THE STUDY OF FLUIDS IN POROUS MEDIA

BACKGROUND

This project is in support of reservoir description R&D, especially in the areas of reservoir chemistry, physics, and rock-fluid interactions at the micro- and macroscopic scales.

The techniques developed in this project are being used in characterizing pore to core scale heterogeneities for BE1 and BE9 and, together with techniques developed in BE9 are being applied to solve formation damage and production problems for several oil producers (identities of the producers remain confidential as agreed with these producers). Over the next two years these techniques will be used to provide field RD&D support to assist in the characterization of pore structures and surfaces, rock/fluid interactions, and residual oil distributions for a planned alkaline-surfactant-polymer field project and a potential polymer flooding project in two priority reservoir classes in the midcontinent area. These techniques will also be applied to identify dominant recovery processes associated with each priority reservoir class. Besides the above near- and mid-term goals, the long-term goal is to apply the techniques developed in this project to study oil trapping and recovery mechanisms, so that new and novel enhanced oil recovery processes can be developed.

Considerable progress has been made in rock-fluid imaging technology to quantify the impact of rock heterogeneities on the effectiveness of oil recovery. Accomplishments of this program over the past several years have generated results directly applicable to increased oil production in the near-term. Some of these accomplishments are as follows.

Development of a computerized image analysis system to be used for petrographic measurements. This system allows rapid and automatic measurements of pores, pore throats, and grain sizes in thin sections prepared from reservoir rock and is used to calculate porosity and permeability values. The system can be used with samples from cores, sidewall cores, or drill cuttings. This technique will allow producers to determine the permeability and porosity of reservoir rock without expensive coring and core analysis. NIPER has used this technique to solve formation damage and production problems in oil and gas reservoirs for several oil producers. Industry is currently funding cooperative efforts and additional industry involvement is actively being solicited.

Computerized tomography (CT) technology, already widely used in the medical field, has been gaining acceptance in petroleum research as a powerful tool for nondestructive measurements of variations in rock properties and fluid saturations in reservoir rock. Using CT scanners available at area hospitals, research work has been ongoing at NIPER for more than 4 years to investigate core heterogeneities and fluid flow in cores. By interfacing the CT scanner acquired in 1989 with the computerized image processing and analysis system already

developed, quantitative measurements of oil and brine spatial saturation distributions have been performed during flow experiments through core materials. At present, studies of flow processes are performed at ambient conditions, but operators are often interested in imaging recovery processes occurring at pressures and temperatures similar to those encountered in the reservoirs being studied. NIPER has performed CT-scanning of cores for industrial clients, either as special projects, or as part of other core measurement contracts where CT images are an integral part of the process to select representative core plug samples from whole cores. This technique is useful in determining heterogeneities in cores and their influence on oil recovery processes. Technology transfer has been accomplished by NIPER researchers through peer-reviewed publications and presentations of CT-generated information.

Development of nuclear magnetic resonance imaging (NMRI) is another nondestructive imaging technology transferred from the medical field to the petroleum industry. It is used to image fluids within cores. NIPER has modified an in-house NMR spectrometer. The small bore of the NIPER spectrometer, and other instrument characteristics, should allow image resolutions down to 10 microns. By comparison, NMRI instruments available for medical purposes have resolutions of the order of 500 microns. The high resolution achievable allows visualization of the effect of rock/fluid interaction on oil, water, and gas distributions within pore spaces of small core plugs. Such a capability would help in understanding oil displacement processes taking place at the pore level and is essential in understanding the mechanisms of various oil recovery processes. The NMR instrument has generated images of fluids in cores and beadpacks with resolutions to 125 and 25 microns, respectively. The present limitations to achieving finer resolution are: (1) the computing power of the NMR spectrometer computer, (2) delays caused by demand on multiuser MicroVAX computer, (3) the image processing station, and (4) the speed of the data transmission link between these three computers. A single, high-speed, state-of-the-art graphics work station would reduce the turnaround time tenfold between the NMR high-resolution, 3D image acquisition directly connected to the NMR spectrometer and final image output. NIPER is on the forefront of developments in the area of NMR imaging in, (1) resolution, (2) distinguishing oil and water phases, and (3) image processing.

Pore level fluid displacements using micromodels is a new technique that has been developed at NIPER using thin-slab (3 mm) micromodels built from sandstone samples. Pore-level fluid flow and fluid displacement processes for oil, gas, and water phases have been observed by optical microscopy. This technique, combined with flow experiments performed on cores, is used to improve the understanding of mechanisms by which various oil recovery processes remove oil from reservoir rock. This technique can help in the design of an optimum recovery process for a given reservoir rock by enabling observations, at the pore level, of the effects of various flow regimes, fluid properties, and injected chemicals on oil mobilization.

Integration of the above rock/fluid imaging techniques for understanding effects of small-scale rock heterogeneities on oil trapping in reservoir rocks for processes taking place at conditions relevant to oil recovery is one of the unique features of this project. The integration of these techniques enables a more definitive assessment of the roles of heterogeneities in affecting oil entrapment, fluid flow and fluid saturation distribution. This integration is described in a paper on the effect of small-scale heterogeneities on fluid distribution, to be presented by NIPER researchers at the 1990 SPE Annual Meeting. Several oil and service companies have facilities for one of the rock-fluid imaging techniques, but few have all these techniques for integrated investigations. The combination of these methods enables NIPER to investigate the effects of various scale of heterogeneities (pore to core scale) on oil recovery efficiency.

OBJECTIVES

1. To develop a methodology to derive reservoir engineering parameters from petrographic, computed tomography (CT) scanning, and nuclear magnetic resonance (NMRI) images.
2. To apply state-of-the-art technology as it is developed to provide field support to characterize high-priority reservoirs.
3. To transfer the newly developed technology through an industry consortium, organized to help plan, review, and participate in the research. Opportunities for industry bilateral cooperation in the research will be pursued.

SCOPE OF WORK

In addition to applying these techniques to support BE1 and BE9, they will also be applied to support the reservoir characterization effort of an alkaline-surfactant-polymer field project and a planned polymer flooding project. Both of these projects are to be implemented in priority classes of reservoirs. Active participation in the support of the field work (heterogeneity description) on the selected priority reservoirs described in the PIP, as they are selected, will be pursued. It is necessary to improve the efficiency of image-handling capabilities of both the CT and the NMRI systems to reduce the time between the initiation of data acquisition and resultant fluid saturation maps of cores. This will increase capacities of both CT and NMRI instruments and increase efficiency in processing samples. These capacity increases are necessary to make these technologies more attractive for industry utilization to optimize oil recovery processes in the near-term. Technology transfer will be accomplished by the preparation of DOE reports, journal articles and presentations for symposia.

Applying imaging techniques to the study of fluids in porous media to determine oil trapping and release mechanisms in EOR processes will continue. Study of the effect of microscopic-scale

rock heterogeneities on the trapping of oil in core samples will be expanded to reservoir pressures. The existing experimental setup will be modified to handle high pressure fluids used in immiscible CO₂ and WAG processes. Scaling procedures from microscopic to core plug to whole core will be utilized in experimental design and data analysis. The objectives of these experiments are: (1) improving the reliability of core measurement data used in oil recovery simulations aiding the identification of high priority reservoirs; (2) to quantify and to observe directly and rapidly the various flow regimes and mobilization of trapped oil in EOR processes and improved waterflooding, to aid in the selection of optimal recovery process for a priority reservoir class; and (3) to develop fundamental understanding needed to identify novel techniques for recovering immobile oil. The CT scanner will be used to observe fluid distributions for both miscible and immiscible floods in heterogeneous 2-in.-diameter cores under reservoir pressures. Pore geometries and fluid distribution in locations where oil trapping takes place will be studied by means of computer image analysis of thin sections and high resolution NMRI. Using these techniques, correlations and scaling procedures will be derived for the laboratory corefloods measured. Oil trapping and removal under various flow regimes will be quantified for rock from field projects being implemented in high priority reservoir classes.. (Near to mid-term)

Task 1. Provide support to field projects. (Start date: October 1990. Completion date: September 1991.) (Near-term)

Apply computerized petrographic and CT imaging techniques to characterize cores from the reservoir chosen for the alkaline-surfactant-polymer and polymer flooding (if approved) projects. Support the field work (heterogeneity description) on selected priority reservoirs as described in the PIP.

Task 2. Perform high-pressure corefloods using CT. (Start date: October 1990. Completion date: August 1991.) (Mid-term)

Perform high-pressure coreflood experiments to simulate immiscible CO₂ and water-alternate-gas (WAG) recovery processes. The effect on trapping due to rock heterogeneity; oil, gas, and brine properties; and flow regimes will be studied. The rock will be characterized using CT, SEM, and by computer-assisted petrographic analysis. Acquisition of a high-pressure core holder, displacement pumps, automated flow control and data acquisition, and supporting hardware and software will be required. Increasing the transfer and processing speed of CT images and the size of mass storage for real-time monitoring of the corefloods is necessary. Published scaling laws applied to heterogeneous systems will be used in the design of experiments and analysis of results. Evaluate the possibility of using the dual energy scanning

capability of the Somatom II scanner for multiphase saturation measurements and displaying them in three-dimensional form.

Task 3 Improve the NMRI resolution and data acquisition speed. (Start date: October 1990. Completion date: September 1991.) (Long-term)

Improvements such as adding a workstation for faster image processing and modifying the existing NMR spectrometer hardware and software will be performed to allow application of this technique to study effects of rock/fluid interactions (wettability) on fluid trapping, oil release mechanisms, and residual oil saturations.

DELIVERABLES

- Sep 91 Status Report - summarize the field and laboratory support efforts using techniques developed in this project.
- Sep 91 Topical Report - to include (1) a discussion of equipment modifications, equipment capabilities and operational procedures; (2) experimental design for corefloods conducted in conjunction with CT or NMR imaging; and (3) results of coreflood experiments.

PLANNED STAFFING

	<u>Man-Years</u>
Senior and Research Physicists	1.6
Senior, Research, and Associate Engineers	1.1
Technicians and Support Personnel	<u>1.0</u>
Total	3.7

Project Leader

Liviu Tomutsa, Research Physicist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
CT Scanner	1	
NMR	1	
SEM	1	
Micromodel system	1	
High-pressure coreholder		1
Positive-displacement pumps		2
Work station for NMRI		1
X-Ray tube		1

Fuels Research

The primary emphasis in Fuels Research (FR) is to develop information which will allow the use of heavy or unconventional feedstocks with nearly the same efficiency as is enjoyed with use of light, sweet crudes. These heavier feedstocks are being introduced into processing streams at an increasing rate as supplies of light stocks diminish. These heavier feedstocks are expected to be a substantial part of the refinery feedstocks in the future. Unfortunately, heavier crudes vary considerably in composition. They also usually contain higher concentrations of undesirable chemical constituents which cause problems throughout the refining and end use sequence.

The DOE, through its Advanced Extraction and Process Technology (AEPT) Program, is supporting research to obtain basic data for the technology associated with heavy crudes and other alternative fossil-related feedstocks. NIPER's Fuels Research Department has two projects under AEPT in the Base Program.

The research work in project BFR2 emphasizes the development of methodology to analyze problem components such as metal-containing compounds and compounds which contribute to coke formation. With sufficient data and understanding, processes can be developed which will reduce the risk and increase the efficiency of processing these feedstocks to transportation fuels.

In project BFR3, thermodynamics research continues based on assessment of needs for specific data. Pure compound work will continue on organic nitrogen compounds and compounds which contain two heteroatoms.

A complete description of the two projects in the Fuels Research Base Program follows.

BFR2. - DEVELOPMENT OF ANALYTICAL METHODOLOGY FOR ANALYSIS OF HEAVY CRUDES

BACKGROUND

The trend toward the use of heavier feedstocks by domestic refineries is well documented. Conversion of these higher molecular weight feedstocks to liquid transportation fuels requires continually deeper conversion of the residual materials. The heavier feeds and need for deeper conversion have resulted in increased problems in both refining and in product quality. The proposed analytical technique development addresses both the refining and product quality problems.

In FY 1990, NIPER began to address the coking and heteroatom deposition tendencies of compound classes in petroleum residues. This work will be continued in FY1991. Coking or carbon deposition is a common occurrence in many refining processes, particularly those employed for upgrading distillation residues. Carbon deposits typically also contain portions of sulfur, nitrogen, and metallic elements originally present in compounds which contributed to coke formation. In connection with catalytic processes, these deposits are particularly harmful because they result in loss of catalytic activity. Catalyst regeneration processes are not effective in removal of metals codeposited with carbon, and sulfur and nitrogen oxides in regeneration gases require removal for environmental reasons. In this project, the relative tendencies of compound classes to (1) form coke and (2) codeposit heteroatoms will be determined and correlations will be derived relating coking tendencies to chemical composition. This information will aid in optimizing refining processes by reducing the amount and impact of coke formation.

The second research area proposed is speciation of metal-containing compounds in petroleum residues. Development of a process for removal of metals from heavy crudes would greatly improve their compatibility with existing refineries as well as the yields of distillate products obtained. Development of demetallization processes would be aided by analyses which define the types and general structures of metal complexes present in a given crude. Analytical research toward development of suitable methods for this will be continued.

The final analytical technique area proposed for further development is a continuation of the means for identification of specific compounds or compound classes responsible for problems in refining and/or product quality. The usual approach for determining these components, typically present at minor or trace levels, involves preconcentration and/or removal of interferences via HPLC or other liquid phase separations, followed by gas chromatography (GC), mass spectrometry (MS), or combined GC/MS determinations. Chemical derivatization techniques are often employed to improve the specificity of the analysis and/or the GC behavior of the components of interest. Prior work under this project led to significantly improved methodology

for oxygen-containing compounds including phenolic species, multiple-hydroxylated aromatic compounds, and carboxylic acids.

OBJECTIVES

Generally, 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 are: (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 procedures for breaking associates formed between metal- and nonmetal-containing compounds which will ultimately lead to methods for isolation and identification of metal-containing compounds in petroleum, and (3) to further develop mass spectrometric methods for analysis of nitrogen and sulfur compounds in petroleum.

SCOPE OF WORK

High performance liquid chromatography (HPLC) will be used to generate fractions of varying chemical composition for carbon residue determinations. Micro carbon residue (MCR) testing will be carried out using the standard ASTM method D 4530. Elemental balances will be determined for N, S, Ni, and V throughout the fractionation and carbonization steps. Fractions obtained from preliminary separations in FY90 will be subfractionated further into more discrete compound groups. Results from their analysis will be used to expand and refine earlier correlations concerning carbon and heteroatom deposition properties of compound classes in petroleum resids.

Dissociation of aggregates comprised of metal and nonmetal-containing compounds in resids will be attempted using a combination of HPLC separations and chemical treatments. Fractions already appreciably enriched in Ni- and V-containing compounds will serve as starting materials. The degree of dissociation achieved by any given process will be determined from elemental analysis of the resulting fractions/products and, if warranted, visible spectrophotometric and MS analysis.

Differentiation of primary, secondary, and tertiary aromatic amines will be attempted by acylation under conditions sufficient for quantitative conversion of all N-H moieties to the corresponding trifluoroacetyl amide. The reaction product will be analyzed by GC/MS. Preliminary work has demonstrated conversion of pure primary aromatic amines (e.g., aniline) to ditrifluoroacetyl derivatives and secondary aromatic amines (e.g., diphenylamine) to monotrifluoroacetyl derivatives. Tertiary amines (e.g., pyridine) do not acylate. The proposed work will evaluate the feasibility of this approach for analysis of base fractions from actual refinery

streams containing aromatic amines (e.g., cat cracked and hydrotreated products). In addition, the degree of derivatization achieved for hindered amines (e.g., 2,6-dialkylanilines) and potential for interference from other compound types will be assessed.

The potential advantages of GC/MS analysis of sulfur compounds as their trifluoroacetyl derivatives will also be explored. In particular, the effectiveness of acylation toward preventing conversion of thiols to disulfides via air oxidation will be investigated.

Task 1 - Coking tendencies of compound classes. (Start date: October 1990. Completion date: September 1991)

Fractions exhibiting unusually high carbon forming or heteroatom deposition tendencies will be further fractionated using existing methodology (see NIPER Report No. 452, December 1989). The resulting subfractions will undergo MCR testing and elemental analysis to determine their relative contributions to that of the whole material. They will also undergo spectroscopic analysis to determine compound types/classes present. The above data will be used to arrive at more detailed correlations of coke formation versus chemical structure than possible from preliminary fractions.

Task 2 - Dissociation and isolation of metal-containing compounds. (Start date: October 1990. Completion date: September 1991)

Existing metal-enriched fractions obtained from HPLC separations on a 2-(4-pyridyl)ethylsilica will be further separated using a different type of HPLC column. In addition, isolation of metal porphyrins from those fractions via precipitation with TiCl_4 or other agents will be attempted. If sufficiently pure metal-containing fractions are obtained, they will be analyzed by spectroscopic methods, including MS with microprobe sample introduction. In addition, their ability to reassociate with nonmetal-containing compounds of varying type will be determined by size exclusion HPLC.

Task 3 - Development of GC/MS methods for nitrogen and sulfur compounds. Start date: October 1990. Completion date: September 1991)

Five to 10 mg quantities of whole base fractions and subfractions enriched in primary aromatic amines will be acylated by heating for one hour at 80° C in the presence of 0.4 mL trifluoroacetic anhydride and 0.5 mL of a 0.8 M 4-dimethylaminopyridine-dichloromethane solution. A wide variety of fractions from light cycle oils, coal liquids, and hydrotreated streams is available. The abundance of primary versus secondary versus tertiary amines from GC/MS analysis of the acylation products will be compared with that predicted from titration and other analyses. Also, prominent structural types for each class of amine present in the various samples will be determined.

Alliquots of pure aromatic and aliphatic thiols will be acylated as above and their GC/MS properties determined. The stability of the derivative will be assessed from reanalysis over a period of several days. Acidic sulfur compounds will be isolated from selected crude oils via caustic extraction, acylated, and analyzed by GC/MS if preliminary results warrant such an effort.

DELIVERABLES

Sep 91	Task 1 - Topical report
Sep 91	Task 2 - Topical report
Sep 91	Task 3 - Topical report

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemist	0.7
Research Chemist	0.4
Assistant Chemist	0.6
Technician	<u>0.7</u>
Total	2.4

Project Leader

John B. Green, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
High performance liquid chromatography (HPLC) systems, also HPLC accessories: columns, specialized detectors, column packing apparatus	6	
Rotary solvent evaporators	4	
Gas chromatographs (GC) with supporting intelligent interfacing	5	
MS-80 GC/MS	1	
MS-50 field ionization, field desorption, electron impact mass spectrometer	1	
HP-5970A mass selective GC detector	1	
Flame/graphite furnace atomic adsorption spectrophotometer	1	
Infrared spectrophotometer	1	
270 MHZ NMR	1	

BFR3. - THERMOCHEMISTRY AND THERMOPHYSICAL PROPERTIES OF ORGANIC NITROGEN- AND DIHETEROATOM-CONTAINING COMPOUNDS

BACKGROUND

The average API gravity of the crude oil run to stills in the United States dropped from approximately 34.2 in 1978 to 32.2 in 1987. The trend continues today. That drop in gravity has been accompanied by an equivalent increase in the amount of petroleum coke exported by the United States. When the cost of the oil imported and the price obtained for the coke are compared, it accounts for approximately one billion dollars of the trade balance deficit per year. The heavier crudes contain more carbon, oxygen, sulfur, and nitrogen (polycyclic aromatics and heteroatom-containing compounds) than the benchmark West Texas Intermediate. These heteroatom-containing compounds are difficult to remove. Processing of crudes containing increasing levels of oxygen, sulfur, and nitrogen using present-day technology has produced fuels with high heteroatom contents and a tendency toward instability. The refractory nature of the heteroatom-containing compounds is the main reason for the increase in coke production. The full utilization of heavy oil to make quality transportation fuels requires an understanding of the chemistry and the thermodynamics of adding hydrogen to the feedstocks. The major goal of this research project is to aid in that understanding.

The design of processes to convert alternative refinery feedstocks (heavy crudes, heavy ends, oil shale, tar sand liquids, and coal liquids) into products that can be used in current technologies without severe energy penalties and/or harm to the environment requires thermodynamic data. Applications of these data include determination of optimum reaction sequences; optimum reaction compositions, temperatures, and pressures for desired conversions; cooling/heating requirements for reaction vessels; capacity of heat exchangers; and size, strength, and complexity of separation vessels.

The data available for light petroleum, which contains a relatively narrow set of classes of compounds, have permitted the design of processes to produce desired products with high efficiency. The precision and accuracy obtained in the measurements on the components of light petroleum performed by this and other research groups was such that they have become part of the "permanent" literature and are used with confidence within industry in process design and development. However, as noted above, the alternative feedstocks contain substances of drastically different and more varied chemical structure, and the procedures developed for light crudes are often not applicable.

The thermodynamic data base for the components of alternate crudes is severely limited. Efficient processing of such crudes requires research programs that study the different compound types present. The programs must include larger, and often more reactive, molecules

than before, studied to higher temperatures, while generally maintaining the accuracy and precision of the results for light petroleum components. This laboratory maintains its position at the cutting edge of technology in thermodynamic property measurements, with significant progress recently made in projects such as the one described here.

Thermodynamics research at NIPER in this area is currently funded by three different DOE Office of Fossil Energy programs: Advanced Extraction & Process Technology (AEPT), Advanced Research section of Coal Liquefaction (AR/CL), and Basic Energy Sciences Office of Energy Research (OER). The crosscutting nature of the research funded by the AEPT, AR&TD, and OER sections of the Office of Fossil Energy is summarized in Exhibit 1. The results obtained in the thermodynamics research programs are applicable across the full range of fossil fuel sources from heavy petroleum through oil shale and tar sands to the utilization of coal.

Topical reports generated in these projects have demonstrated that some of the hydrogenation reactions among heteroatomic species are reversible over a wide range of processing conditions. Consequently, a knowledge of the thermodynamic equilibria among species is essential for the proper interpretation of reaction data, for comparing different catalysts, and for accurate modeling of the overall reactions for such processes as hydrotreating or hydrocracking. Thermodynamics can be used to ascertain the relative stabilities of proposed intermediates, to determine if a given reaction is possible (and, if not, whether shifting the reaction conditions will make it so), and to determine specifically which reactions are reversible.

This section of the NIPER research program, funded by AEPT, is concerned with organic nitrogen- and diheteroatom-containing compounds. The program represents, in part, the results of the comprehensive state-of-the-art assessment undertaken in FY86. Thermodynamic considerations arising from recently developed and current information on heteroatom compounds are being used to interpret the differences observed between heavy crudes and the products arising from their upgrading. The research program goals include answering the following three key questions concerning heteroatom removal reactions:

1. What are the reaction networks? Alternatively, what are the stable intermediates formed?
2. What are the reactivities of the various classes of nitrogen-containing compounds?
3. Are the reaction networks and commonly accepted generalities about reactivities valid for broad groups of catalysts?

Topics of investigation include: the role of equilibria, the interplay of thermodynamics and kinetics, and the effect of choice of catalyst on the aromaticity of the final products.

FOSSIL FUELS

EXHIBIT 1.

In FY91, measurements of selected thermodynamic properties of three 4-ring polycyclic aromatic nitrogen-containing compounds will be performed in conjunction with the estimation of the same properties using the data base derived in this project to date. If, as is expected, good agreement is obtained between the measured and estimated properties, a successful conclusion can be made to the nitrogen-containing compound section of the research. The property data base will then be sufficient to enable property estimations for all significant nitrogen-containing structural types present in the alternate crudes.

In the diheteroatom-containing compound section of the research program, measurements will be made on three compounds. These will be selected on the basis of the assessment exercise completed in FY86 to meet the needs in extending the existing prediction and correlation methodology. A major criterion for selection will be the need for measurements on key compounds to determine the thermodynamic feasibility of pathways for upgrading diheteroatom-containing heterocyclics using the minimum of hydrogen. The overall goal in this portion of the research program is the attainment of a property data base sufficient to enable property estimations for all significant diheteroatom-containing structural types present in the alternate crudes. Present estimation of the time-scale for completion of that task is FY93, assuming present funding and manpower levels.

Compounds chosen for study often are not available from chemical supply houses. Thus, an essential part of this work is the synthesis and purification of selected compounds through a subcontract with an Oklahoma State University group, which has unique capabilities and extensive experience in such preparations. Through close coordination of these efforts, the best compromises are made to select materials that are suitable for obtaining key information and which are possible to prepare in high purity.

OBJECTIVES

To measure, interpret, and correlate with molecular structure and polarity of molecules, precise and accurate values of thermodynamic properties of organic nitrogen and diheteroatom-containing compounds that occur in or are readily derivable from heavy petroleum and oil shale. The results enable the prediction of chemical equilibria for conceptual as well as current processes and the prediction of properties needed downstream from the reactor stages.

SCOPE OF WORK

Task 1. - Thermochemical measurements on organic nitrogen compounds.

(Start date: October 1990. Completion date: September 1991.)

A. Preparation of three compounds of the required purity through the subcontract with Oklahoma State University. These will be selected on the basis of the assessment exercise completed in FY86 to meet the needs in extending the existing prediction and correlation methodology. Major criteria for selection will be the need for measurements on key compounds to determine the thermodynamic feasibility of pathways for upgrading nitrogen heterocyclics using the minimum of hydrogen, and to provide a stringent test of property-estimation techniques for nitrogen-containing compounds.

B. Make measurements of enthalpies of combustion, condensed phase heat-capacities (standard entropies), vapor pressures, and densities on selected key organic nitrogen compounds as equipment becomes available from queued experiments on these substances.

Task 2. - Thermochemical measurements on selected diheteroatom-containing compounds. (Start date: October 1990. Completion date: September 1991.)

A. Preparation of three compounds of the required purity through the subcontract with Oklahoma State University. These will be selected on the basis of the assessment exercise completed in FY86 to meet the needs in extending the existing prediction and correlation methodology. A major criterion for selection will be the need for measurements on key compounds to determine the thermodynamic feasibility of pathways for upgrading diheteroatom-containing heterocyclics using the minimum of hydrogen.

B. Make measurements of enthalpies of combustion, condensed phase heat-capacities (standard entropies), vapor pressures, and densities on selected key diheteroatom-containing compounds as equipment becomes available from queued experiments on these substances.

Task 3. - Thermodynamic analysis of nitrogen removal in heavy petroleum and oil shale upgrading. (Start date: October 1990. Completion date: September 1991.)

This task continues the evaluations (started in FY88) of the thermodynamic equilibria possible during the removal of nitrogen by the hydrotreating/hydrocracking of heavy petroleum and shale oil. In this financial year, thermodynamic analyses will be performed on model systems in an attempt to answer the three key questions posed above. In addition, studies will be made on the thermodynamic conditions necessary for the formation of nitrogen aromatic heterocycles in the alternate crudes. These studies will give insights into whether the processing conditions used currently for heteroatom removal actually produce more refractory heteroatom-containing compounds. Analysis of reaction networks for 3-ring materials will be included.

DELIVERABLES

- Dec 90 Topical report on the thermodynamic properties of tetrahydro-9-methylcarbazole and 9-methylcarbazole.
- Feb 91 Topical report on the thermodynamic properties of 2-amino-biphenyl and the related compounds 2-methylbiphenyl and 2-hydroxybiphenyl.
- Aug 91 Topical report detailing the thermodynamic analyses performed in task 3 with emphasis on 3-ring compounds.
- Sep 91 Status report on the research program summarizing data acquired, its utility, and an updated assessment for future work.

PLANNED STAFFING

	<u>Man-Years</u>
Manager	0.1
Senior Chemists	0.7
Research Chemists	0.3
Research Physicist	0.3
Associate Chemist	0.3
Senior Experimentalist	0.3
Technical Support	<u>0.1</u>
Total	2.1

Project Leader

William V. Steele, Senior Chemist

APPENDIX A. -- CAPITAL EQUIPMENT REQUIREMENTS

Project No.	Equipment	Cost (\$K)
BE1	Core saw	1.0
	Core Polisher	2.0
	Apparatus for UV and Visible Photography of Cores	5.0
	Cathodoluminescence Apparatus	10.0
BE2	Personal Computer	6.0
BE3	Personal Computer	4.0
BE4B	Interfacial tensiometer (spinning drop)	10.6
BE5A	High pressure electromagnetic viscometer	3.0
	Data acquisition system	4.0
BE5B	Data acquisition system	3.0
BE9	Pump for unsteady-state tests (2 each)	19.0
	Coreholder for unsteady-state tests	5.0
BE11A	Personal computer	14.0
	Support equipment for new steamflood model	16.0
	Data backup system	2.0
BE11B	Thermal heat flux sensors	2.0
	New steamflood physical model	18.0
BE12	High pressure core holder	10.0
	Positive displacement pump (2 each)	20.0
	Workstation for NMRI	10.0
	X-Ray Tube	<u>30.0</u>
Total Base Program		194.6
NIPER Support		
	Word processing-reproduction and/or computers	40.0
	Safety	10.0
	Maintenance	<u>10.0</u>
Total NIPER Support		60.0

END

DATE FILMED

02 / 05 / 91