85
2-13-90 JS (2)

NIPER-420
(DE90000210)

FY90 ANNUAL RESEARCH PLAN

National Institute for Petroleum and Energy Research

January 1990

**DO NOT MICROFILM
COVER**

Performed Under Cooperative Agreement No. FC22-83FE60149

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

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office Of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

Price: Printed   A06
Microfiche A01

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

NIPER--420

DE90 000210

NIPER-420

Distribution Category UC-122 and 125

FY90 ANNUAL RESEARCH PLAN

National Institute for Petroleum and Energy Research

January 1990

Work Performed Under Cooperative Agreement No. FC22-83FE60149

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

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

**Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
Box 2128
Bartlesville, OK 74005**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DO NOT MICROFILM
THIS PAGE

(This page intentionally left blank.)

FOREWORD

The National Institute for Petroleum and Energy Research (NIPER) is pleased to submit the "FY90 Annual Research Plan," NIPER-420, 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.

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-DE87001228), March 1987.
- "1987 Annual Report: National Institute for Petroleum and Energy Research" NIPER-320. (NTIS-DE88001234), October 1988.
- "1988 Annual Report: National Institute for Petroleum and Energy Research" NIPER-400.

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 seventh plan describes the work to be performed in FY90. 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.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

7

EXECUTIVE SUMMARY

The National Institute for Petroleum and Energy Research (NIPER) will enter its seventh year of operation October 1, 1989, and this Annual Research Plan describes the work to be performed in FY90. NIPER is operated for the Department of Energy (DOE) by the IIT Research Institute (IITRI) through a cooperative agreement.

The agreement authorizes NIPER to perform research under three different programs. First is a multi million dollar Base Program funded by the DOE to provide research for meeting its Strategic Goal of significantly increasing the economic producibility of domestic oil and gas through geoscience research and related activities. The goal is to be achieved through near-term (5-years or less), mid-term (10-years or less), and long-term (beyond 10 years) research efforts. A second program, the Supplemental Government Program, includes work placed at NIPER through the cooperative agreement by other government agencies and by DOE for work not included in the Base Program. The third program is designated as Work for Others. It encourages NIPER to solicit work from the private sector, thereby contributing to DOE's ultimate goal of expanding the nation's inventory of economically producible resources through the cooperation and participation of industry. This Annual Research Plan covers only the Base Program. Projects in the other two programs are generally of short duration being approved and initiated at different time intervals during the fiscal year.

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 processing and 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 200 employees, will be a viable place to conduct research for other government agencies and industrial clients.

NIPER is located on a 17-acre tract of land in Bartlesville, Oklahoma. The facility consists of 19 buildings containing over 156,000 square feet of floor space. The Bartlesville Project Office (BPO) is collocated with NIPER to administer the DOE research program.

Research Program

Program planning is the result of cooperative effort by NIPER employees and BPO project officers.

In FY90, 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 for both near- and long-term contributions to the maintenance of the Nation's energy supply.

BASE PROGRAM-FY90

Project	DOE FE Program*	Manpower, Man-Years	Funding, \$K
<u>ENERGY PRODUCTION RESEARCH</u>			
BE1. Reservoir Assessment and Characterization	EOR-LO	5.0	800
BE2. TORIS Research Support	EOR-LO	1.7	150
	EOR-HO		60
BE3. Development of Improved Microbial Flooding Methods	EOR-LO	3.3	300
BE4A. Development of Improved Surfactant Flooding Methods	EOR-LO	4.2	605
BE4B. Development of Improved Alkaline Flooding Methods	EOR-HO	1.0	140
BE4C. Development of Improved Mobility Control Methods	EOR-LO	1.2	200
BE5A. Gas Miscible Displacement	EOR-LO	2.7	380
BE5B. Development of Methods to Improve Mobility Control and Sweep Efficiency in Gas Flooding	EOR-LO	2.0	260
BE9. Three-Phase Relative Permeability	EOR-LO	2.4	305
BE11A. Thermal Processes for Light Oil Recovery	EOR-LO	2.6	300
BE11B. Thermal Processes for Heavy Oil Recovery	EOR-HO	1.6	200
BE12. Imaging Techniques Applied to the Study of Fluids in Porous Media	AEPT	<u>2.8</u>	<u>395</u>
Total EPR Base Projects		30.5	4,095
<u>FUELS RESEARCH</u>			
BFR2. Development of Analytical Methodology for Analysis of Heavy Crudes	AEPT	2.5	300
BFR3. Thermochemistry and Thermophysical Properties of Organic Nitrogen- and Ditheteroatom-Containing Compounds	AEPT	<u>2.2</u>	<u>355</u>
Total FR Base Projects		4.7	655
TOTAL BASE PROJECTS		35.2	4,750

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

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	iii
EXECUTIVE SUMMARY.....	v
INTRODUCTION.....	1
Scope and Organization.....	2
Facilities and Personnel.....	4
Program Structure.....	4
Program Content.....	6
Energy Production Research.....	6
Fuels Research.....	7
Reporting	7
Monthly Progress Report.....	7
Quarterly Technical Report.....	8
Annual Report.....	8
Topical Report.....	8
Status Report.....	9
BASE PROGRAM.....	11
Energy Production Research.....	11
BE1. Reservoir Assessment and Characterization.....	17
BE2. Toris Research Support.....	25
BE3. Development of Improved Microbial Flooding Methods.....	29
BE4A. Development of Improved Surfactant Flooding Methods.....	37
BE4B. Development of Improved Alkaline Flooding Methods.....	47
BE4C. Development of Improved Mobility Control Methods.....	54
BE5A. Gas Miscible Displacement.....	61
BE5B. Development of Methods to Improve Mobility Control and Sweep Efficiency in Gas Flooding.....	67
BE9. Three-Phase Relative Permeability.....	72
BE11A. Thermal Processes for Light Oil Recovery.....	80
BE11B. Thermal Processes for Heavy Oil Recovery.....	87
BE12. Imaging Techniques Applied to the Study of Fluids in Porous Media.....	91
Fuels Research.....	97
BFR2. Development of Analytical Methodology for Analysis of Heavy Crudes.....	98
BFR3. Thermochemistry and Thermophysical Properties of Organic Nitrogen-and Diheteroatom-Containing Compounds.....	102
APPENDIX 1. Capital Equipment Requirements.....	109

INTRODUCTION

This is the seventh 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.

More recently, the emphasis of the DOE program has changed from strictly long-term, high-risk research to the more immediate near- and mid-term concerns of domestic oil and gas producibility. Although the long-term objective remains, its primary purpose is to improve the fundamental understanding of domestic oil and gas resources and the chemical, physical, and biological phenomena that govern the occurrence and recovery of these resources in addition to their associated environmental issues. As in previous years, the great majority of work for NIPER's FY90 research projects is geared to improving the fundamental understanding of fossil energy technologies. The results of the research effort are expected to be more directly focused under DOE's geoscience program.

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 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.

The mid-term objective of the DOE program is to maximize the recovery efficiency of discovered oil and gas through improved understanding of the

resource and to develop advanced extraction and instrumentation techniques. 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 near- and mid-term 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.

NATIONAL INSTITUTE
FOR
PETROLEUM AND ENERGY RESEARCH

ORGANIZATION

FIGURE 1. - NIPER Organization.

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 200 people with over 100 technically trained scientists and engineers having background experience and competence in most areas of petroleum research. 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 FY90 is listed in Appendix 1.

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. Inter-library loan facilities extend the capability even further.

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, 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. 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 \$4.75 million distributed as shown in table 1. The Base Program provides for technical staffing requirements of 35.2 man-years as shown in table 2.

TABLE 1. - FY90 funding for Base Program

Project Funding	Base Program DOE, \$K
Energy Production Research	4,095
Fuels Research	655
Total	4,750

TABLE 2. - Technical staffing requirements

Base Program	Manpower, Man-years
Energy Production Research	30.5
Fuels Research	4.7
Total	35.2

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.

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 the BPO program managers and technical project officers and DOE headquarters program managers. Final approval was to be provided by the Program Guidance Committee. With but few exceptions, the FY90 Base Program has been designed as a continuation of the FY89 research program.

Energy Production Research

The Energy Production Research Department's base research program is designed to improve predictability and performance of EOR processes. In this plan, the projects are grouped by major areas of work for two main thrusts.

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 the processes and to verify hypotheses. These models are also useful as tools for planning future research. The other major area of work is concerned with the quantitative prediction of fluid flow behavior in a reservoir. Such fluid-flow behavior is affected by the geometry (reservoir and pore), wettability, mineralogy, fluid distribution, permeability, heterogeneities (microscale and macroscale), and history of the reservoir.

The Base Program proposed for EPR will continue working toward the goal of improving predictability and performance of EOR processes through integrated studies of fluid flow behavior and process mechanisms. The experimental results will be incorporated into process and reservoir 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 1 under the Advanced Extraction and Process Technology Program.

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 short 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 individual 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 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 the 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 the DOE project managers. They have much the same basis as the topical report but represent completion of only a portion of the 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.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

BASE PROGRAM

The Base Program--fully funded by DOE for \$4.75 million--is a basic research program designed to improve the fundamental understanding of domestic oil and gas resources through EOR processes and geoscience 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 2.

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 \$4,095,000. The two FR projects are funded by advanced extraction and process technology in the amount of \$655,000, bringing the total program to \$4,750,000. Each of the 14 projects addresses a problem area in the projected future development of energy resources in the United States. Although there is presently adequate oil available to the U.S. and the world, it is recognized that international emergencies could change this situation rapidly, and that long-term depletion of the finite resource base will ultimately result in the necessity to turn to alternate forms of fossil fuel resources.

The 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.

Energy Production Research

Research in the Base Program is designed to furnish information for the Federal EOR program as outlined in DOE's Program Plan for Enhanced Oil Recovery. Federal Enhanced Oil Recovery Research is a national effort to increase the understanding of the 300-billion barrel residual and unswept mobile resources and to develop the technologies to produce them. Specifically, the program seeks to improve the ability to describe reservoir rocks and fluids quantitatively, to define specific EOR designs to produce the target oil effectively, and to predict accurately EOR production performance as a function of reservoir/fluid properties and specific EOR process designs.

Table 3. Base Program for FY90

Project	DOE FE Program*	Manpower, Man-Years	Funding, \$K
<u>ENERGY PRODUCTION RESEARCH</u>			
BE1. Reservoir Assessment and Characterization	EOR-LO	5.0	800
BE2. TORIS Research Support	EOR-LO EOR-HO	1.7	150 60
BE3. Development of Improved Microbial Flooding Methods	EOR-LO	3.3	300
BE4A. Development of Improved Surfactant Flooding Methods	EOR-LO	4.2	605
BE4B. Development of Improved Alkaline Flooding Methods	EOR-HO	1.0	140
BE4C. Development of Improved Mobility Control Methods	EOR-LO	1.2	200
BE5A. Gas Miscible Displacement	EOR-LO	2.7	380
BE5B. Development of Methods to Improve Mobility Control and Sweep Efficiency in Gas Flooding	EOR-LO	2.0	260
BE9. Three-Phase Relative Permeability	EOR-LO	2.4	305
BE11A. Thermal Processes for Light Oil Recovery	EOR-LO	2.6	300
BE11B. Thermal Processes for Heavy Oil Recovery	EOR-HO	1.6	200
BE12. Imaging Techniques Applied to the Study of Fluids in Porous Media	AEPT	<u>2.8</u>	<u>395</u>
Total EPR Base Projects		30.5	4,095
<u>FUELS RESEARCH</u>			
BFR2. Development of Analytical Methodology for Analysis of Heavy Crudes	AEPT	2.5	300
BFR3. Thermochemistry and Thermophysical Properties of Organic Nitrogen- and Diheteroatom-Containing Compounds	AEPT	<u>2.2</u>	<u>355</u>
Total FR Base Projects		4.7	655
TOTAL BASE PROJECTS		35.2	4,750

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

The Federal program defines six closely integrated lines of research reflecting the respective EOR processes and the "cross-cutting" 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 recovery processes. Results from both parts are combined to develop reservoir and process simulators.

There are three projects relating to geoscience research: assessment and characterization of reservoirs (BE1), the application of imaging techniques to enhance the study of fluids in porous media (BE12), and three-phase relative permeability (BE9). Results from research being performed under these projects will be used to develop basic concepts for EOR technology.

Chemical flooding processes are specifically addressed in three Base Program projects. The effort under project BE4A will focus on the structure-property relationships of third generation, mixed-surfactant systems. These mixed systems offer greater flexibility than single-surfactant systems, but existing data on their salinity tolerance, chromatographic properties, and adsorption behavior are insufficient. All of these parameters will be studied in FY90. Research under project BE4B is to determine the applicability of alkaline surfactant flooding in reservoirs having crude oils with very low acid numbers. Recent successful experiments with the relatively acidic Wilmington, CA crude will be extended to determine the recovery enhancement potential of alkaline/surfactant flooding systems for reservoir crudes having low acid numbers. 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.

Gas flooding research comprises two projects in the Base Program. The work outlined in this plan for project BE5A considers the development of two models that will aid in the implementation of miscible gas flooding methods. The first is a mathematical model capable of describing the adsorption and

ENERGY PRODUCTION RESEARCH INTEGRATED BASE PROGRAM

FIGURE 2. - Energy Production Research Integrated Base Program.

transport of foaming agents in reservoir rock. Foam generation and propagation in porous media have the potential for improving mobility control in miscible flooding. The second model will be designed to predict the degree of precipitation that may result from the heavy organic substances in crude oil during gas flooding operations. The study for project BE5B will focus on further development of methods to improve sweep efficiency and the potential of available predictive models for determining the properties and behavior of CO₂-entrainer systems. Studies will also be made to determine the behavior of foam in the near-wellbore region of a reservoir. This is necessary because the injection of foam nearly always causes a pressure drop within a short distance of an injection well.

Research on thermal processes will concentrate on steamflooding, both for light oil recovery (BE11A) and heavy oil recovery (BE11B). A portion of the work planned for project BE11A is to evaluate the potential of oil recovery by steamflooding previously waterflooded reservoirs which are oil-wet. The performance data resulting from this work will be compared to that obtained in FY88 for water-wet reservoirs. Further, an empirical model is to be developed for use in numerical simulations of steamfloods that will use capillary pressure data from centrifuge experiments rather than the more time consuming and costly two-phase relative permeability measurements. An additional task is designed to evaluate a series of novel diverting agents for increasing oil recovery during light oil steamflooding. One- and two-dimensional sandpacks will be used to evaluate foam and emulsion for steam diversion. Finally, a scaling study will be conducted prior to the development of a new two-dimensional steamflood apparatus. The work under BE11B is to investigate the effectiveness of high-temperature surfactants for steam diversion and improved mobility control. Also, the numerical simulator developed in FY89 will be further evaluated to history match laboratory experiments for parameter sensitivity studies. A final task is to prepare a guidebook for steamflood field operations.

Microbial enhanced oil recovery (MEOR) methods development is conducted in project BE3. The research effort planned for this project will determine the range of conditions under which microbial EOR methods are most applicable. This will be accomplished by conducting a series of statistically designed experiments for determining the interrelationships and relative importance of

variables such as salinity, temperature, pH, rock lithology, and the specific crude under study. Laboratory procedures will be examined to determine how changes in test conditions might affect microbial growth, metabolite production, phase behavior, and oil recovery efficiency. Once the critical parameters of MEOR have been determined, a reservoir model will be selected as a starting point for developing an improved MEOR simulator.

Program analysis and technology transfer includes DOE's Tertiary Oil Recovery Information System (TORIS). Developed by DOE, TORIS consists of EOR project data bases, oil reservoir data bases, and EOR simplified predictive numerical models. NIPER's primary function, under project BE2, is to provide research support to the DOE Program Manager. Task assignments are identified by priority need and may be redirected at any time by the Program Manager. Tasks planned thus far for FY90 include continued support (updating and refining) of the EOR project data base and reservoir data base. A report on the analysis of EOR project trends will be provided at the end of the fiscal year.

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

FY90 ANNUAL RESEARCH PLAN

BE1. RESERVOIR ASSESSMENT AND CHARACTERIZATION

BACKGROUND

The broad objectives of the Department of Energy program for geoscience research are to develop methods for determining mobile and immobile oil saturation distribution in reservoirs and evaluating suitable methods for recovering oil. With these broad objectives in mind, a generic approach for reservoir characterization was formulated in the NIPER FY86 Annual Research Plan. The specific objective was to develop a better understanding of heterogeneity factors that influence the movement and trapping of fluids in reservoirs. Accurate descriptions of the spatial distribution of critical reservoir parameters (e.g., permeability, porosity, pore geometry, mineralogy, and oil saturation) were considered essential for adequate sweep efficiency by implementation of fluid diversion techniques and for reliable predictions of oil recovery. This information, in the near- to mid-term, will assist producers in placing infill wells, or planning polymer gel fluid diversion methods, or other reservoir management strategies.

The research strategy presented in the NIPER FY86 Plan was first to select a deposystem representative of several enhanced oil recovery (EOR) target reservoirs. The barrier island system was selected, and heterogeneities that strongly influence the trapping of oil and control its movement in barrier island reservoirs were identified. The effects of the heterogeneities were quantified for predictions of fluid production from barrier island reservoirs. This method incorporates, to the extent possible, generic factors which determine the influence of heterogeneities on reservoir performance. If the method can account for produced oil and remaining oil, it can be applied to other reservoirs belonging to the same deposystem.

Detailed analyses of heterogeneities as proposed in the FY86 Plan required the analysis of closely spaced core samples that represented locations both vertically and laterally in the pay zone. Since the only readily available source for such closely spaced cores was analogous outcrops, the emphasis of the NIPER reservoir characterization program was placed on collecting ample outcrop samples and combining the resulting geological data with the reservoir data to model reservoir heterogeneities.

After a deposystem with high potential for enhanced oil recovery (EOR) was selected, the critical heterogeneities in that deposystem were selected for research. Development of equipment and methodology for outcrop studies was completed, and theoretical studies relating to the development of generic techniques for handling reservoir data were carried out. A list of selected heterogeneities was prepared, and a few critical heterogeneities from that list were selected for further research. The Bell Creek field in Montana and a nearby outcrop site were selected for collecting data for studies of the fluid flow characteristics of the barrier island and genetically associated deposystem. Methods for scaling up and interpolating critical reservoir parameters were developed. Some 1,000 samples from analogous outcrops were collected, and reservoir data from the waterflooded part of the reservoir were compiled to construct a geological model of the reservoir's waterflooded area.

In FY87, the data collected from the outcrops and reservoir were analyzed for development of a quantitative geological model that would incorporate the effects of all critical geological heterogeneities. Waterflood simulations were performed to investigate the influence of critical heterogeneities on waterflood performance. Reservoir data from the waterflooded portion of the reservoir were augmented with the outcrop data for further refinement of the geological model of the waterflooded area. The combined quantified, calibrated, and scaled geological data were used to construct a geological/engineering model of the reservoir in a form suitable for computer simulation. The model was used to evaluate the influence of heterogeneities on reservoir performance. Additional data were collected for further improvement of the model. Through integrated geological/engineering analysis of reservoir data, development plans for a reservoir can be improved by (1) selecting the most favorable location and orientation for well patterns especially for infill drilling, (2) designing injection well completions to avoid high-permeability zones or channels that can cause early water breakthrough and result in poor sweep efficiency and increased operating costs, (3) implementing permeability modification treatments to mitigate channeling and improve sweep efficiency, and (4) designing most appropriate EOR method for mobilizing trapped oil.

In FY88, geological data from the tertiary incentive project (TIP) portion and the surrounding area of Unit 'A' of Bell Creek field were used to refine the geological model of the reservoir in the TIP area. Then the refined geological model of the TIP area was augmented with refined outcrop data to construct a refined geological/engineering model of the barrier island deposystem. This model was used to evaluate quantitatively the influence of critical heterogeneities on the reservoir performance of the TIP area. The optimized methodology was outlined and coded. This methodology is the first published comprehensive, scientific, and multidisciplinary approach for characterizing hydrocarbon reservoirs. It provides an effective means for transfer of technology among disciplines. Although many sophisticated techniques are available to develop information about reservoir fluid flow patterns and residual oil distribution, in this methodology, the integration of conventional data for providing useful information has been emphasized.

In FY89, additional barrier island reservoirs, as described in the literature, were evaluated for the development of a more generalized geological/engineering model. Also, to improve the predictability of barrier island production performance, correlations of petrophysical, petrographical, geological, and production data were prepared. With the information of a generalized barrier island system, EOR simulation was performed to study the effects of several important reservoir factors on the performance of micellar-polymer flooding. The results of a synergetic approach to analyzing a barrier island system were used to further refine the methodology for reservoir characterization. In the mid-term, predictability of production performance will be developed based on generalized characteristics of various depositional environments. This will help producers select the most effective methods for improving recovery efficiency of their reservoirs.

During the past five years, NIPER scientists have helped organize two international conferences addressing state-of-the-art technologies in reservoir characterization and have provided channels for communication among leading scientists in this field. Several joint projects have been organized with industrial clients and international companies to find new ways for characterizing hydrocarbon reservoirs. These conferences, mutual cooperation, and the publication of several articles in the trade journals have provided technology transfer to independent producers, major oil companies, and other

oil producing countries. This direct dissemination of information to the operators, can have an immediate impact on improving oil production efficiency.

OBJECTIVES

To develop an improved methodology for effective characterization of barrier island reservoirs to predict the following:

1. The residual oil saturation (ROS) at interwell scales in reservoirs.
2. The flow patterns of injected and produced fluids, given the location of injection and production.

In particular, the objectives for FY90 are:

1. To select a second barrier island system for testing the developed reservoir characterization methodology.
2. To apply the detailed results of systematic reservoir characterization to production prediction in a barrier island system.
3. To develop and improve reservoir description techniques to provide reliable input data for performing reservoir simulation.

SCOPE OF WORK

The proposed work of FY90 will consist of three main areas. First, a second barrier island reservoir system will be selected for testing and refining the reservoir characterization methodology developed over the past 4 years. Ideally, this system should have a complete suite of geological and engineering data, which includes seismic, drilling, log, core, fluid, and production data. Second, the fundamental relationships between geological, petrophysical, and reservoir production characteristics will be studied. Third, more efficient and effective methods for reservoir description and EOR simulation for a barrier island system will be investigated. The recently developed fractal distributions will be utilized to quantify reservoir heterogeneities. Previously acquired data for Bell Creek field and several related outcrops will be used in the second and third areas of work.

Task 1. Select a second barrier island reservoir system for testing NIPER reservoir characterization methodology. (Start date: October 1989. Completion date: May 1990.)

To validate NIPER reservoir characterization methodology for barrier island systems, a second similar system must be selected for testing.

Ideally, this system should be in the Rocky Mountain region and should have a complete suite of geological and engineering data for analysis. In addition, it is preferable to select a system that has gone through primary, secondary, and tertiary stages of production, which will provide complete information on how reservoir heterogeneities affect the production performance of the system. Once a system has been selected, testing of NIPER methodology will commence, and the methodology will be refined if necessary. The verification and refinement of the methodology will be contingent on the final selection of a second barrier island system.

Task 2. Analysis of fundamental relationships between geological, petrophysical, and reservoir production characteristics to improve quantification of the barrier island model. (Start date: October 1989. Completion date: September 1990.)

Geological and engineering studies will continue to investigate and identify fundamental relationships between barrier island reservoir rocks and characteristics of rocks from analogous outcrops. Production/injection performance of the reservoir will be examined to identify interrelationships between geological and engineering parameters. Correlations between geological parameters, engineering data, and production performance will be developed to complete this task. The need for additional petrophysical and petrographical measurements will be identified, and some measurements will be performed.

Location of faults within Unit 'A' of Bell Creek field will be determined. Geological and engineering studies will then assess the effects of faults on drainage areas of wells, continuity between wells, and petrophysical/petrographic properties of these drainage areas. Production analyses and petrophysical properties will be incorporated with the geological studies to better define the overall effects of faults on the size and shape of drainage areas within the barrier island reservoir.

Task 3. Improve quantitative barrier island model from detailed correlation of log signatures with geological heterogeneities and other features. (Start date: October 1989. Completion date: September 1990.)

Log-core correlations developed thus far with Bell Creek field data show that most of the important geological heterogeneities and other

structural/stratigraphic features have typical log signatures on some of the logs. In many cases, the log signatures are very subtle and may not be readily identified with the geological feature of interest. Through further statistical and mathematical processing of log data and from correlation of the signatures with petrographical and other geological data, it may be possible to map depositional facies with greater detail or to delineate trends in the distribution of mineralogical and diagenetic heterogeneities.

Another important aspect of log-core correlation and signature analysis will be the application of certain mathematical tools (e.g., the 'filter theory') to separate the effects of different types of heterogeneities, such as depositional, diagenetic, and structural. An effective separation of various types of heterogeneities will allow an investigation of certain fundamental aspects of these heterogeneities such as their mode of origin, distribution, effect on fluid flow properties, and severity of occurrence in different types of depositional environments.

An important aspect of the integrated log-core studies will be to develop techniques to quantify effects of different types of heterogeneities. This will allow studies of effects of various heterogeneities on fluid production through reservoir simulation.

Task 4. Investigate the use of fractal distributions for improvement of a quantitative barrier island model. (Start date: October 1989. Completion date: September 1990.)

In 1986, the concept of fractals for generating interwell properties was first applied by some researchers in the oil industry to improve interwell input data used in reservoir simulation. The main advantage of using fractals is that they capture the characteristic rock variability at various scales. By using fractals and a geostatistical approach for reservoir description, the conventional process of history matching before performing reservoir simulation prediction could be greatly reduced or even eliminated. The use of fractal geostatistics for reservoir description combined with conditional simulation is especially preferable when a reservoir system has very limited well and production data for history matching. Conditional simulation is a geostatistical method to generate property distributions with prescribed spatial correlations and match measured data at sampling locations of the distributions. In FY90, the application of fractal geostatistics for the

improvement of a quantitative barrier island model will be investigated. Reservoir parameters such as porosity and permeability will be generated on the interwell region using kriging with fractal-based variograms. In particular, core-log correlations developed in task 3 will be used in calculating fractal dimensions of a barrier island system. The generated data are to be compared with those previously obtained from reservoir mapping and the generalized barrier island geological model as well as results obtained from task 2. If the fractal data appear to be valid, reservoir simulation will be performed in FY90 to confirm the accuracy of using fractals.

DELIVERABLES

- May 90   Status report on selection of second barrier island system for verification of NIPER reservoir characterization methodology.
- Sep 90   Topical report on analysis of fundamental relationships between geological, petrophysical, reservoir production characteristics and the use of fractal distribution to improve quantification of a barrier island reservoir.

PLANNED STAFFING

	<u>Man-years</u>
Senior Research Engineer, Physicist	1.2
Senior Geologist, Research Geologist	1.4
Associate Research Geologist, Petrographer	0.5
Research Engineer	1.1
Technician	<u>0.8</u>
Total	5.0

Project Leader

Matt M. Honarpour Program Manager, Geotechnology

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Binocular microscope	1	
Modern binocular microscope with photographic capability	1	
Automation of mercury porosimeter	1	
Microcomputer		2

BE2. TORIS RESEARCH SUPPORT

BACKGROUND

This project is designed to assist and enhance the efforts of the DOE to apply the Tertiary Oil Recovery Information System (TORIS) for the analysis of EOR research. TORIS is made up of EOR project data bases, oil reservoir data bases, and EOR simplified predictive numerical models. In addition to the data bases and predictive models, the application of TORIS is improved by utilization of commercially and publicly available numerical simulators, investigation of the success or failure of EOR field projects, and the incorporation of newly developed technology into the evaluation of the potential of EOR to increase domestic production. This project has an obvious near-term applicability since a data base that contains information about ongoing EOR projects is continually being updated and maintained. It also has a longer-term view since it tracks the utilization of various EOR methods over the years and evaluates the trends.

During the first and second quarters of FY89, the following tasks were completed:

- (1) 1986 incentive and cost-shared data were loaded to the USAEOR, EOR project data base at the EIA System 2000 (S2k) in Washington and the PROJ EOR project data base in Bartlesville;
- (2) two updates of new EOR projects were loaded into the S2k and the PROJ data bases;
- (3) numerous corrections and additions were made to the data on DOE cost-shared and incentive EOR projects in the S2k data base and the PROJ data base;
- (4) two security tapes were prepared for the USAEOR S2k data base;
- (5) a report was written describing an evaluation of the MASTER numerical simulator; and
- (6) a topical report was written on the application of EOR technology.

Efforts will be continued in FY90 to improve TORIS consistent with the changing priorities of the TORIS program. The current data bases will be maintained and improved through additions of new EOR project data as they become available. Data on new EOR projects and existing EOR projects will be

collected from publicly available publications. The data in the project data base will be analyzed to determine trends in applications of EOR technology, and a report on the results will be prepared. New dictionary elements will be added to the EOR project and reservoir data bases when the appropriate modifications are determined. This support is for both light oil and heavy oil projects and models. This project will be responsive to the tasks and priorities assigned by the DOE Program Manager for TORIS.

OBJECTIVE

To provide research support to the DOE Program Manager for TORIS in the areas of EOR project and reservoir data base management, EOR project and technology and trends analysis, and oil production modeling.

SCOPE OF WORK

During FY90, NIPER will provide research support on tasks identified and assigned priority by the TORIS Program Manager at the financial and manpower levels available for this project. This support is for both light oil and heavy oil projects. Some of the tasks already assigned are listed below. Additional tasks may be identified, or priorities of tasks underway may be altered during the course of the year. In such cases, the Program Manager will have the opportunity to redirect the efforts being placed on project tasks. To facilitate the TORIS Program Manager's direction, review meetings will be held between the TORIS Program Manager and project staff to present current project status and to establish short- and long-term project plans. All changes or additions to project assignments, project scope, and expected deliverables will be identified in writing to the DOE. Because of the broad nature of some of the following described tasks and the required input from other organizations, some tasks may be incomplete by the end of the year and others substituted.

Task 1. EOR project data base research support. (Start date: October 1989. Completion date: September 1990.)

Areas of work in FY90 are as follows:

- A. Transfer the 1987 production data for DOE cost-shared and incentive projects from a DOE-supplied computer tape into the EIA S2k and the BPO PROJ systems. Deliver to BPO a security copy of the EIA S2k data base and a brief status report.

- B. Review the literature for new data on EOR projects and new EOR projects. Install the collected data on both the EIA S2k and BPO PROJ systems.
- C. Analyze trends in new EOR projects and assess the current state-of-the-art. Prepare a topical report presenting this analysis.
- D. Maintain the EIA and PROJ data bases and routines to be current with new versions of S2k and RELIANCE, communications, and operating systems.
- E. Modify and update the project data as necessary with the code information from DOE form 748 and other inputs from BPO.

Task 2. Reservoir data base research support. (Start date: October 1989. Completion date: September 1990.)

Areas of work in FY90 are as follows:

- A. Maintain the EIA RSVR data base and routines to be current with new versions of S2k, communications, and operating systems.
- B. Modify reservoir data bases to include new geologic elements proposed by the Texas study on infill drilling and the new infill drilling predictive model.
- C. Add and modify reservoir data as required.

DELIVERABLES

- Sep 90 Status report on the 1987 data additions to the project data bases and a security tape of the S2k project data base.
- Sep 90 Topical report analyzing EOR project trends.

PLANNED STAFFING

	<u>Man-Years</u>
Research Data Analyst	0.3
Associate Data Analyst	0.9
Associate Engineer	0.1
Support Personnel	<u>0.4</u>
Total	1.7

Project Leader

James F. Pautz, Research Data Analyst

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
DOE/BPO (TORIS) computer, Concurrent 3230	1	
Personal Computer (IBM-AT/compatible)	1	1

BE3. DEVELOPMENT OF IMPROVED MICROBIAL FLOODING METHODS

BACKGROUND

Microbial methods for increasing oil recovery are potentially cost-effective even at relatively low crude oil prices. If crude oil prices remain at current levels, as much as three quarters of the known remaining resource may be lost in the next 15 years because of unfavorable economics. Today in the U.S. 73 percent 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. Domestic oil production and reserves have declined steadily as our domestic oil fields have been depleted. New discoveries have failed to provide new reserves in an amount adequate to arrest the decline. The relatively low crude oil prices and increased environmental regulations have also been an economic deterrent to expensive exploration and drilling activities that are required to find and develop new oilfields. The development and application of methods to increase oil production from aging stripper wells is necessary to decrease the rate of abandonment and maintain access to a significant fraction of our nation's resources for the future.

Microbial methods are particularly well suited to application in today's economic conditions. The technology is flexible, relatively inexpensive, and is amenable to application by independent producers who operate many of the stripper wells in the U.S. 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, are 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 production 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. Well stimulation methods offer the least expensive way to apply the technology but do not have as great a potential for ultimate recovery as does microbial-enhanced waterflooding.

Successful application of microbial 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. Microbial technology is potentially very flexible and useful, but it must be applied properly through careful engineering design if the economic return and oil recovery is to be maximized. 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. Development of an engineering methodology to design and optimize microbial formulations for specific field applications is needed to exploit the potential of this technology.

NIPER has implemented an integrated program to develop microbial technology for the U.S. Department of Energy. This integrated program includes long-term research, mid-term research and development, and near-term field applications. The long-term research program has led to improved understanding of the mechanisms of oil mobilization by microbial formulations and transport of microbes and metabolites in porous media. Glass micromodels were used to visualize the oil displacement process in a simulated porous media. Laboratory studies also helped to determine how microbes, nutrient, and metabolites transport in a porous media. Results have shown that a key component of the oil mobilization mechanism is the ability of the microorganisms to produce localized high concentrations of products at the oil-water interface. The concepts and data from the basic research formed the basis of applied research needed to develop an engineering methodology for designing and optimizing microbial formulations for specific applications. Laboratory tests were conducted both in flasks and reservoir cores to test the compatibility of injected microbes with indigenous microbes that were isolated from oil reservoir produced fluids, various nutrients, crude oil, and reservoir rocks. Oil displacement tests were conducted in reservoir rock to optimize the parameters that affect oil recovery efficiency. The effects of additives and injection strategy were evaluated. Potential environmental effects were addressed by an extensive program that included toxicity testing and development of a procedure for obtaining samples of microbes from oil reservoirs.

Results from the applied research program led to development of microbial formulations that were effective in mobilizing crude oil. A microbial-enhanced waterflooding field pilot project was initiated in the 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 midcontinent sandstone reservoir. The results of the field pilot test are addressed under Supplemental Government Program project SGP-13. Both the 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 the nation's reserves of crude oil.

Prior work at NIPER has identified the mechanisms of oil mobilization by certain microbial formulations. Mechanisms found to be important include wettability alteration, emulsification, solubilization, and alteration in interfacial forces. Recent experiments at NIPER have demonstrated that oil mobilization by microbial formulations is more than merely the result of the effects of metabolic products from the in situ fermentation of nutrients. Further investigation into the interfacial properties of microorganisms and the localized transient concentrations of metabolic products at the oil-water interface is needed to further determine the mechanisms of oil mobilization. The relationships between transport of microbes, nutrients, metabolic products, and mobilized crude oil need to be clarified and interpreted with mathematical models for fluid flow in porous media. The effects of reservoir conditions such as salinity, temperature, pH, and compositions of reservoir brine and rock need to be studied to develop methods for designing microbial formulations that are optimal for recovering crude oil under specific reservoir conditions. The effects of injection strategies on oil recovery efficiency also need to be determined.

Physical phenomena that affect the microbial oil recovery process include: (1) dynamic growth of microorganisms; (2) mass transfer and transport of microorganisms, nutrients, metabolic chemical products, oil, and brine; (3) changes in microscopic properties such as interfacial tension, wettability, and adsorption that govern oil mobilization and affect fractional

flow and relative permeabilities; (4) changes in rheology of the flowing phases; and (5) certain other physical phenomena that are peculiar to microorganisms. The phenomena that affect oil mobilization by microorganisms must be understood, and mathematical models and correlations developed to relate the phenomena to oil recovery efficiency.

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. The complexity of oil recovery using microbial enhancement 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. The accuracy of a simulator that is designed for MEOR processes will be strongly dependent upon the accuracy of equations used to describe the important phenomena. It is also important to recognize the unique constraints and variations in conditions that occur in actual field applications but are not always accounted for in controlled laboratory experiments. Thus, an accurate reservoir simulator for MEOR methods can best be developed through an integrated program for acquiring laboratory and field data, with feedback data coming from the reservoir simulation model.

In FY90 this project will address three key issues that affect the development and application of MEOR technology: (1) the role of interfacial properties in oil mobilization by microbial formulations, (2) the effects of variations in process variables on performance, and (3) the development of a simulator to match and predict oil recovery efficiency of MEOR processes. These three issues address the long-term, mid-term, and near-term goals of the DOE. Laboratory experiments will be conducted to further define key mechanisms of oil mobilization, correlations and mathematical models will be developed 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 will be initiated.

OBJECTIVES

To develop an engineering methodology for designing and applying microbial methods to improve oil recovery.

SCOPE OF WORK

Prior research at NIPER has demonstrated that the presence of bacterial cells is important in the oil mobilization process. A microbial formulation was found to be much more effective in mobilizing oil than the supernatant solution from which the cells had been removed. Aggregation of the bacteria at the oil-water interface may produce localized high concentrations of metabolic chemical products that result in oil mobilization. Additional research is needed to determine the role of microorganisms on the interfacial properties of crude oil-brine systems. Prior work has also indicated that certain microbial formulations exhibit optimal behavior at specific salinities that are somewhat similar to those of surfactant systems. Interfacial tensions of selected microbial formulations with crude oils will be measured to determine the effects of salinity and composition of microbial formulations. Dynamic oil mobilization experiments will be conducted in micromodels to further examine the mechanisms of interfacial activity of microbial formulations. Prior work at NIPER demonstrated that oil mobilization by microbial systems in micromodels was correlated with oil recovery efficiency in coreflooding tests. Innovative techniques for specifically studying the interfacial activity of microorganisms will also be investigated.

A series of screening tests will be conducted to determine the range of conditions under which microbial EOR methods are likely to be applicable. A series of statistically designed experiments will be conducted to determine the effects of salinity, crude oil, temperature, pH, and rock lithology on the effectiveness of selected microbial formulations. The ranges of conditions will be selected based on a prior NIPER survey of the conditions and properties of a large number of oil reservoirs in the United States. The effects of changes in test conditions on microbial growth, metabolite production, phase behavior, and oil recovery efficiency will be evaluated. Organisms that are particularly tolerant to harsh conditions will be collected and tested to identify their properties and to determine how changes in

temperature and salinity affect their growth and composition of metabolic products. The results will be used to further refine screening criteria for applications of MEOR and to identify conditions for which new organisms should be developed.

All prior work, both in the laboratory and the field, will be reviewed to identify and rank the various phenomena that are believed to significantly affect oil mobilization by microbial formulations. Previous efforts to develop mathematical models and reservoir simulators for various EOR processes, including MEOR methods, will be considered, and a plan will be formulated to develop an improved and comprehensive reservoir simulator for microbial EOR applications. 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 can be used to design laboratory experiments to clarify and quantify certain physical effects from which correlations will be refined and modified and incorporated into the simulator. The goal is to develop a flexible and accurate reservoir simulator that can be extended to match and predict performance in actual field applications.

Task 1. Review laboratory and field data on MEOR and design a development plan for an improved simulator. (Start date: October 1989. Completion date: January 1990.)

Previous work on MEOR will be reviewed to identify the key variables and phenomena that are likely to affect oil recovery by microbial formulations. Once the variables have been identified, mathematical models or correlations will be established for the operable phenomena. Based on an analysis of prior data and NIPER's expertise in reservoir simulation and microbial EOR, a development plan will be formulated for an improved reservoir simulator.

Task 2. Determine effects of microbial formulations on interfacial properties. (Start date: October 1989. Completion date: March 1990.)

The interfacial tensions of a selected microbial formulation will be tested with at least two crude oil samples that have been found to give

distinctly different oil recovery efficiencies. Preferably, crude oils exhibiting high- and low-recovery efficiencies will be selected for comparison. The salinities of the microbial formulation will be varied to determine if the interfacial tension goes through a minimum. Transient IFT will be measured. Comparisons will be made with saline brines containing only the nutrient, and with microbial metabolite solutions from which the active cells have been removed by filtration, to isolate the specific effects of the microorganisms.

Task 3. Determine the importance of process variables in the application of microbial methods. (Start date: October 1989. Completion date: March 1990.)

A series of statistically designed screening experiments will be conducted to determine the relative importance of a number of variables. A series of flask tests and oil-displacement experiments will be conducted over a limited range of conditions of salinity, crude oil, temperature, pH, and rock lithology to determine how these variables affect the performance of microbial formulations. Organisms that have been developed specifically for their tolerance to adverse conditions will be included in the tests, and the effects of temperature and salinity on their growth and composition of metabolic products will be determined.

Task 4. Investigate the mechanisms of interfacial activity of selected microbial formulations. (Start date: January 1990. Completion date: August 1990.)

Based on the results from task 1 and prior work, one or more specific systems will be selected for study of the microscopic mechanisms of oil mobilization by microbial formulations. Dynamic oil mobilization experiments will be conducted in micromodels to observe the physical phenomena and identify the mechanisms of oil mobilization. Some innovative techniques may be employed to further clarify the role of microorganisms in oil mobilization. The selection of systems to be studied and the design of the experiments will be closely coordinated with results being obtained in task 2.

Task 5. Initiate development of an improved MEOR simulator. (Start date: January 1990. Completion date: August 1990.)

Based on the results from task 1, select a reservoir model as a starting point for development of an improved MEOR reservoir simulator and implement the initial steps in the development plan. Initial efforts will primarily focus on incorporating the most important phenomena for which mathematical models or correlations are available or can be developed in a reasonably brief time.

DELIVERABLES

- May 90 Topical report on revised screening criteria for applications of MEOR.
- Sep 90 Topical report on effects of microorganisms on interfacial properties and mechanisms of oil mobilization.
- Sep 90 Status report on development of MEOR simulator.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Biologist	0.7
Senior Chemist	0.1
Research Engineer	0.1
Associate Biologist	0.8
Senior Bioexperimentalist	0.8
Senior Technician	<u>0.8</u>
Total	3.3

Project Leader

Rebecca S. Bryant, Senior Biologist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Coreflood apparatus	4	
Micromodel/video microscope	1	
Anaerobic glove box	1	
Microscope	1	
Gas chromatograph		1

BE4A. DEVELOPMENT OF IMPROVED SURFACTANT FLOODING METHODS

BACKGROUND

For many U.S. domestic reservoirs surfactant flooding will be the only viable EOR method. Steamflooding is generally applicable for recovery of heavy, viscous crude oils in relatively shallow reservoirs with fairly high permeability. Heat losses limit the depth at which this method can be applied. Miscible flooding with carbon dioxide, hydrocarbons, and nitrogen are most applicable in light oil reservoirs that are deep enough to achieve a miscible condition. In practice, steamflooding is being applied in California heavy oil reservoirs and carbon dioxide miscible flooding is being applied in reservoirs in West Texas. Thus, chemical flooding methods represent one of the few remaining technologies applicable to the recovery of crude oils with low to medium viscosities, particularly in relatively shallow sandstone reservoirs. Depth is not a major constraint for surfactant flooding except when the reservoir temperature is so great that the injected surfactants, cosurfactants, and polymers are no longer stable.

Surfactant flooding is potentially a very flexible method because of the ability to optimize formulations for a wide range of reservoir conditions and crude oil types. By varying the type and concentration of surfactant and cosurfactant, formulations with optimal displacement efficiencies can be designed to recover crude oil from a reservoir with a specific salinity, brine composition, temperature, and rock mineralogy. In 1984, the NPC reported that chemical flooding could ultimately recover 1.0 billion barrels of oil at a crude oil price of \$20/bbl with a minimum rate of return of 10% with implemented technology. At a crude oil price of \$30/bbl the ultimate recovery increased to 2.5 billion barrels. Of the various EOR technologies, including thermal, miscible, and chemical methods, surfactant flooding was judged the one most likely to benefit from advances in technology. The projected ultimate incremental recovery for surfactant flooding increased from 2.1 billion barrels for the implemented technology case to 9.9 billion barrels if advanced technologies can be developed.

Recent estimates by the U.S. Department of Energy indicate that there are 198 billion barrels of crude oil remaining in known domestic reservoirs with API gravities ranging from 20° to 45° that is immobile. A portion of this vast resource of oil is the target for surfactant flooding. Properly designed

surfactant formulations have been shown in laboratory and field tests to be capable of achieving very high oil displacement efficiencies in reservoir rock. A number of field pilot tests have produced significant amounts of incremental oil and have been technically but not economically successful. The high initial capital investment for purchase of chemicals, the long delay until payout, technical difficulties in maintaining the effectiveness of the chemical slug, problems in obtaining accurate predictions of process performance in field applications, problems with inadequate reservoir characterization, and relatively low and volatile oil prices have prevented the wide-spread commercial application of this technology.

The potential of surfactant flooding can be achieved by developing systems that are (1) relatively inexpensive, (2) tolerant to changes in reservoir conditions (i.e., changes in salinity, divalent ion concentrations, and rock type), (3) relatively unaffected by losses caused by adsorption, phase trapping, and partitioning, and (4) stable and robust at reservoir conditions for relatively long periods of time (i.e., years). While prior research efforts have been successful in developing methods for designing and optimizing surfactant formulations with high displacement efficiency, the cost has been too great and their performance too unsure in field applications.

The goal of the NIPER program in surfactant flooding is to develop systems that are cost-effective for recovering light crude oils. The focus has been on (1) identifying surfactant formulations or methods that are more cost effective than current technologies, and (2) mitigating problems that have been shown to have adverse effects on the performance and economics of surfactant flooding processes. Major reasons for degradation of effectiveness of surfactant formulations during propagation through rock formations are loss through adsorption onto rock surfaces, partitioning into the water and oil phases, and precipitation. NIPER's long-term basic research has led to development of advanced methods for studying the retention behavior of surfactants on reservoir rocks and fundamental understanding of the mechanisms of retention. Mid-term research and development efforts have been focused on screening various novel surfactants to identify those that are more tolerant to changes in salinity and divalent ion concentration, and are applicable over wider ranges of temperature. Techniques have been developed to evaluate the chromatographic separation of multicomponent formulations. The use of

relatively inexpensive sacrificial agents to reduce losses of the more expensive surfactants is also being investigated. Reducing the concentration of surfactant that must be injected to maintain effective displacement for a distance into the reservoir that is sufficient to form and propagate an oil bank will make a direct improvement in the economics of applying this process.

In early research on surfactant flooding, a search was made for cost-effective surfactants that were capable of reducing interfacial tension (IFT) and were stable at typical reservoir brine concentrations and temperatures. Petroleum sulfonates were usually the class of surfactant that was investigated, primarily because they were relatively inexpensive. Furthermore, as is common to most sulfonate surfactants, they were relatively stable to thermal degradation in aqueous systems and would not precipitate out of solution in reservoir brines as readily as some other types of surfactants. Although sufficiently low IFT values were generated with these systems, optimal conditions needed to produce these low IFT values occurred at salinities that were lower than that of most petroleum reservoirs. By adding alcohols, the optimal salinity of the system could be adjusted to that of the reservoir brine. Certain injection strategies were also found to broaden the salinity range where petroleum sulfonates were applicable. Field results proved disappointing, and difficulties such as reservoir heterogeneity, phase separation, ion-exchange processes, and chromatographic separation processes were identified as reasons for poor performance.

These difficulties motivated researchers to investigate second-generation surfactants with much higher optimal salinities (more salt tolerant) and without the requirement of additional alcohol cosurfactants. Most of these surfactants have been ethoxylated sulfonates, although a variety of other surfactants have also been studied. Ethylene oxide groups have been added to alkyl- and alkylaryl sulfonate chains to shift the hydrophilic-lipophilic balance (HLB) to values more compatible with high salt concentrations. Although investigations of these types of surfactants continue today, some difficulties have been encountered, including a strong tendency to form liquid crystals and gels. Furthermore, improved robustness of these surfactants to variations in temperature and salinity has been obtained only at the expense of overall effectiveness.

Consequently, an investigation into a third generation of surfactant systems is being initiated. These surfactant systems include binary surfactant mixtures that have properties similar enough to minimize chromatographic separation problems, but different enough to improve the overall effectiveness of the surfactant system. The overall HLB would be similar to that of ethoxysulfonates, and other related surfactants previously studied, to take advantage of the higher optimal salinities that were achieved. In addition, the structural features of the two surfactants may be different enough to complement each other and reduce some of the other unfavorable properties observed for second-generation surfactant systems. Although not particularly new, this approach has received very little attention in the literature. Furthermore, relationships developed based on HLB, solubilities, salinities, temperature, etc., for first- and second-generation surfactant systems, are insufficient to predict which particular surfactant combinations would be best.

Some structure-property relationships have been investigated for surfactant systems. One of these includes a linear relationship between HLB and $\log(\text{CMC})$. This relationship, which is based on room-temperature CMC measurements, was developed from data for a homologous series of surfactants with varying chain length. However, this relationship has not been extended to higher temperatures or to surfactants with widely differing molecular structures. A study is planned for FY90 to determine CMC values of selected binary surfactant systems at elevated temperatures. The data will be correlated with emulsifying characteristics of the binary surfactant systems to develop a coherent and simple method for describing complex surfactant systems through extended knowledge of their structure-property relationships.

The surfactants and surfactant blends being developed in this project cost more per pound than petroleum sulfonates; thus, to be used successfully, acceptable adsorption limits for these materials must be even lower than that of petroleum sulfonates. Studies of mixed surfactants conducted in FY89 found that interaction of surfactants may appreciably alter the adsorption behavior of individual surfactants to solid surfaces. Furthermore, organic materials such as alcohols, sulfonates, and carboxylates are known to adsorb and desorb at different rates leading to chromatographic separation of components in addition to permanent adsorption. Therefore, a comprehensive study is planned

for FY90 to identify which combination of surfactants act beneficially to reduce the effects of adsorption and chromatographic separation. Adsorption studies initiated in FY89 will continue for other mixtures of surfactants. Also, methods for quickly evaluating chromatographic separation processes will be developed for future studies in this area. Some of the technologies developed in other areas of chromatography should be transferable to this problem.

Addition of alkaline additives to surfactant formulations has been found to be beneficial by reducing losses of surfactant and polymer, reducing concentrations of divalent cations that cause losses of surfactant by partitioning and precipitation, and by affecting interfacial properties. Recent research has indicated that alkaline/surfactant formulations may be effective in the recovery of light crude oils. Further research on the interactions between the complex components of crude oils and both alkaline and surfactant chemicals is still needed to determine how best to optimize chemical flooding formulations and to determine how broadly this method may be applicable. Alkaline/surfactant formulations may be more tolerant to changes in reservoir conditions and may also be applicable to crude oils with a wide range of gravities, including light crude oils.

OBJECTIVES

To develop more effective surfactant flooding systems that have a broader tolerance to variations in salinity. Underlying this objective is the understanding that IFT values need only be sufficiently low to enhance the production of oil over the broadest possible range of salinities.

Specific objectives for FY90 are to (1) determine if different systems with similar HLB and solubility parameter values vary significantly with respect to optimal salinity and salinity tolerance; (2) use the information gained from this study to develop improved structure-property relationships; (3) develop an experimental technique to evaluate chromatographic separation problems; and (4) determine the adsorption behavior of binary surfactant systems.

SCOPE OF WORK

The emphasis of the work for FY90 will be oriented toward surfactant systems designed from existing technologies based on structure-property correlations and the improvement of those structure-property relationships based on new experimental results. This approach will enable the investigation to be conducted more efficiently and productively using available resources. In addition, the use of experimental design techniques will be implemented, where appropriate, to maximize the efficiency of the tests conducted.

The types of surfactants selected for evaluation will include binary surfactant systems with somewhat dissimilar surfactants. This area is largely unexplored, particularly the development of structure-property relationships for mixed surfactant systems. Furthermore, these types of surfactant formulations offer flexibility not available in single-surfactant systems. Anticipated difficulties such as chromatographic separation and adsorption will be addressed to determine the combinations of surfactants that are beneficial in minimizing surfactant slug disintegration in a reservoir.

A series of light crude oils will be screened by phase-behavior and interfacial-tension measurements with various surfactant/alkaline formulations to identify those that exhibit behavior favorable for oil mobilization. Compositions of the crude oils will be examined, and an effort made to determine if interfacial activity is related to certain constituents in the crude oils. Blank tests with the surfactant and alkaline chemicals will be conducted separately to identify cases where a synergistic effect occurs. Salinity requirement diagrams will be constructed to determine how the alkaline component of the formulation alters the conditions where optimal behavior is obtained. The effectiveness of selected systems in oil recovery will also be determined.

Task 1. Select three binary systems which have similar HLB values.

(Start date: October 1989. Completion date: November 1989.)

Current development of surfactants for EOR have included effective systems that do not require the addition of alcohols or the application of salinity gradients for use in moderate to high salinity environments. Although partially successful, other problems have been encountered that have limited

the usefulness of these systems for efficient oil recovery. A study of systems with two somewhat dissimilar surfactants whose synergistic effects exceed the combined individual effects is proposed. Structure-property relationships will be used to minimize the number of combinations of surfactants to be studied.

State-of-the-art techniques in predicting structure-property relationships will be collected and summarized, and improvements will be made when warranted. Using these relationships, binary surfactant systems will be selected which differ in individual compositions (molecular weight, polarity, branching, etc.) but are nearly equivalent with respect to HLB.

Task 2. Develop salinity requirement diagrams using synthetic reservoir waters for binary surfactant systems. (Start date: December 1989. Completion date: August 1990.)

Salinity requirement diagrams will be developed to describe solubilization boundaries as a function of surfactant concentration for optimal formulations. In addition, factors such as temperature, oil type, and individual effects of specific ions, such as calcium and magnesium, will be considered. This information will be needed to begin developing structure-property relationships for these types of systems. At present, concrete relationships for surfactant properties with chemical structure indices are confused and largely undefined for binary surfactant systems.

Task 3. Develop experimental methods to evaluate chromatographic separation of surfactants in reservoir cores. (Start date: October 1989. Completion date: August 1990.)

Traditional systems containing cosurfactants, such as sec-butanol, have suffered from chromatographic separation in field pilot tests. Once separated, the systems have become ineffective. This task is included to develop methods for accurately and rapidly evaluating the impact of chromatographic separation on binary surfactant systems, similar to those being studied in tasks 1 and 2.

Several coreflood experiments with different reservoir cores, amounts of clays, and types of clays will be performed to determine the chromatographic separation properties of some binary surfactant systems (not necessarily those selected in task 1). Standard chromatographic methods that can approximate

these results over a much shorter time period will then be developed. Factors such as flow rate, temperature, surfactant composition, and salinity will be considered.

Task 4. Determine the adsorption properties of the binary surfactant systems selected in task 1. (Start date: December 1989. Completion date: August 1990.)

Since these surfactants are likely to be more expensive than some petroleum sulfonates previously studied, losses due to adsorption would be even more critical to any economically successful application. Consequently, a realistic determination of the parameters that influence adsorption behavior for these systems is needed. A representative sandstone (not Berea) will be selected from a well-characterized reservoir system, and adsorption studies will be conducted to determine the effect of one surfactant on the adsorption of the other. Adsorption values will be determined by extracting the adsorbed materials from the solid matrix. Some other properties of interest include effects of total surfactant concentration, temperature, and salinity. Results from this task will augment the effort conducted under task 3.

Task 5. Measure the CMC values of the binary surfactant systems selected in task 1. (Start date: December 1989. Completion date: August 1990.)

Prior work has shown that HLB and $\log(\text{CMC})$ can be linearly related for such surfactants as sodium fatty acid soaps, alkyl sulfates, and alkyl sulfonates. Based on this relationship, very small differences in CMC ought to exist for the systems selected in task 1. However, temperature and chemical structure are known to affect micellar structure, and because these parameters will be widely varied in the experiments of task 2, CMC values may change radically from system to system even though the HLB values are nearly identical. If such differences are found, a better relationship between CMC and HLB may be developed to account for some of the properties of surfactants not incorporated in the original HLB concept.

Consequently, CMC values will be measured for the surfactant systems selected in task 1 at elevated temperatures to determine what effects such mixtures might have on micellar structure and stability. The unique capabilities at NIPER to measure CMC at elevated temperatures provide an opportunity for investigating some unusual properties of these systems applicable to reservoir conditions.

Task 6. Determine the effectiveness of surfactant/alkaline formulations for recovery of light crude oils. (Start date: December 1989. Completion date: August 1990.)

Light crude oils and brines will be obtained from several midcontinent oil reservoirs. Various surfactant and surfactant/alkaline formulations will be tested with the crude oil samples near the salinity of the reservoir brines to identify samples that show interfacial activity. Transient interfacial tension measurements will be made to compare the changes in IFT with time, for both the surfactant formulation and the surfactant/alkaline formulation, to determine conditions where the additive improves interfacial activity. The results will also be compared with similar tests for a formulation containing only the alkaline component to isolate the synergistic effect of the additive/surfactant combination. Oil-displacement tests will be conducted in sandstone cores to compare the effectiveness of selected alkali/surfactant formulations in recovering crude oil and to determine the degree of surfactant loss.

DELIVERABLES

Sep 90 Topical report on the design of improved surfactant systems.
Sep 90 Topical report on the effects of additives on performance of surfactant systems.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemists	2.5
Research Engineer	0.8
Senior Experimentalist	0.4
Technician	<u>0.5</u>
Total	4.2

Project Leaders

Leo A. Noll, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Coreflood 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

Alkaline flooding is a promising method for recovering a significant amount of oil from aging oil fields in the United States. Surfactant-enhanced alkaline flooding technology, which has been developed recently, is a potentially cost-effective method for recovering oil from the vast numbers of oil reservoirs that have been waterflooded for many years and will soon be abandoned if oil prices remain near current levels.

Surfactant-enhanced alkaline flooding formulations are potentially more cost-effective at current oil prices than some other chemical flooding methods such as surfactant flooding because the cost of the alkaline chemicals is considerably less than that of synthetic surfactants. The initial investment costs for purchasing chemicals for the injected formulation has been a significant economic disincentive that has hindered the commercial application of some chemical flooding technologies.

Alkaline agents such as sodium hydroxide and sodium orthosilicate, which increase pH values to greater than 12, are able to extract surface-active components from certain crude oils and produce ultralow interfacial tensions that result in efficient oil mobilization. However, such formulations are also frequently reactive with reservoir rocks, particularly those containing clay minerals. A recent NIPER study of 24 alkaline flooding field projects indicated that one third of the projects experienced problems caused by scale formation. Reaction of high pH alkaline formulations with reservoir rocks causes loss of effectiveness of the injected alkaline slug and dissolution of ions that can cause deposition of mineral scales in producing wells.

In recent years research at NIPER and elsewhere has shown that alkaline chemicals such as sodium carbonate and sodium bicarbonate, which have moderately basic pH values (i.e., less than 11), can be effective in mobilizing residual oil when relatively low concentrations of surfactant are added to the formulation. These formulations are less reactive with reservoir rocks and offer the advantages of remaining effective for a longer period of time and having less potential for causing scaling problems. NIPER has patented a surfactant-enhanced alkaline flooding method using alkaline formulations that are less reactive with reservoir rocks but effective in oil mobilization.

Prior field tests using conventional alkaline flooding methods have been disappointing. A number of tests were conducted in California to recover heavy oils that usually have high acid content and are particularly amenable to conventional alkaline flooding methods. A recent study (Lorenz and Peru) indicates that surfactant-enhanced alkaline flooding methods may be applicable to light oil as well as heavy oil reservoirs. This substantially increases the target resource for application of this technology. Initial results from recent field tests using surfactant-enhanced formulations appear to be promising. In recent years, most activity in alkaline flooding has been in Wyoming, Louisiana, and Texas. These three states account for more than 90 billion barrels of immobile oil (DOE, 1989), which is 37% of the immobile oil that remains in U.S. domestic reservoirs. The huge resource of immobile oil that remains in the reservoirs in these three states is primarily in reservoirs that have been waterflooded, many of which are approaching their economic limit. Development and application of surfactant-enhanced alkaline flooding technology can help to extend the productive life of these reservoirs and increase domestic reserves of crude oil.

NIPER's research program in alkaline flooding has been focused on development of a cost-effective technology that can be applied in mature waterflooded reservoirs. Fundamental research on reaction kinetics of alkaline formulations with reservoir minerals indicated that it is difficult or impossible to prevent the deleterious reactions that occur with highly alkaline chemical formulations in most reservoir formations. This led to investigation of milder alkaline agents that are less reactive with reservoir rocks. Initial studies on formulations using sodium carbonate and sodium bicarbonate indicated that the displacement efficiency was much less effective with certain crude oils than that obtainable with highly alkaline chemicals such as sodium hydroxide and sodium orthosilicate. Fundamental research on coalescence phenomena and dynamic interfacial tension behavior indicated that addition of small amounts of surfactants to moderately alkaline formulations significantly improved the properties of the system. The efficacy of these surfactant-enhanced alkaline flooding formulations was subsequently verified in oil displacement tests in cores.

NIPER's long-term basic research effort led to the development of a new patented surfactant-enhanced alkaline flooding method and of criteria for

screening candidate reservoirs for application of this technology. The research program then focused on mid-term application of the technology in specific target reservoirs. Several target reservoirs were selected for study based on reservoir and fluid property data, the size of the target resource, and potential for application of alkaline flooding. A DOE cost-shared alkaline flooding field pilot test was conducted previously in the Ranger zone of the Wilmington field in California that experienced severe problems which were, at least in part, attributed to alkaline consumption and scale formation. The Wilmington field was selected as the principal target reservoir because it is the largest oil field in California, the crude oil is highly acidic and particularly amenable to alkaline flooding, and it was viewed as being representative of a significant number of heavy oil reservoirs in California. Mid-term development efforts were then focused on design of a surfactant-enhanced alkaline flooding formulation for the Ranger zone of the Wilmington field. A formulation was developed that provided effective oil recovery, low reactivity with the reservoir sand, low losses of alkalinity and surfactant, and favorable economics based upon laboratory studies.

NIPER's work on alkaline flooding in the base program has been augmented with research under the cooperative program that was jointly sponsored by DOE and industrial clients, and also under proprietary contracts with industrial clients. Long-term fundamental research on reaction kinetics and interfacial phenomena provided understanding of how surfactant-enhanced alkaline formulations reduce interfacial tension and lead to oil mobilization. This led to the development of a technology that minimizes the deleterious alkali-mineral reactions while maintaining effective oil mobilization. Mid-term applied research focused on the Wilmington field demonstrated that a surfactant-enhanced alkaline formulation could be designed that was effective in laboratory studies in recovering this oil under simulated reservoir conditions. NIPER has developed a plan to conduct a field pilot test in the Wilmington field under joint DOE-industry sponsorship to demonstrate the applicability of this technology and to obtain data to evaluate the economics in field applications. This will be a near-term application of the advanced alkaline flooding technology that has been developed by DOE.

OBJECTIVES

To develop cost-effective and efficient chemical flooding formulations using surfactant-enhanced, low-pH alkaline systems. Specific objectives for FY90 are to (1) investigate the applicability of alkaline-surfactant flooding for use in reservoirs with crude oils having very low acid numbers, and (2) compare the effect of divalent ions on surfactant loss and the transient IFT behavior of carbonate/surfactant systems with the effects previously observed for carbonate/phosphate/surfactant mixtures.

SCOPE OF WORK

Prior work has shown that the acidic content of a crude oil, which is usually expressed as acid number, is not necessarily a reliable indicator of how amenable an oil is to alkaline flooding. If surfactant-enhanced alkaline flooding methods can be applied to recover crude oils with low acid content, then the target resource for this technology would be greater than was previously thought. In FY90 our research efforts are focused on screening crude oils with a range of acid numbers from several candidate reservoirs to further define the limits over which surfactant-enhanced alkaline formulations can be effective. Phase behavior tests will be used to rapidly screen candidate crude oils and interfacial tension measurements will be made to verify the efficacy of the systems and to identify optimal conditions. Oil displacement tests will be conducted with systems that show the greatest promise to evaluate oil recovery efficiency.

Prior work at NIPER has indicated that surfactant-enhanced alkaline flooding formulations using sodium carbonate can be effective in oil recovery in certain types of carbonate reservoirs. The effects of divalent cations, which are typically present in formation waters in carbonate reservoirs, on interfacial tensions are important in designing systems for application in these reservoirs. In this year's program we will investigate the effects of calcium and magnesium cations on interfacial behavior and the advantages of adding sequestering agents such as phosphates to the alkaline formulations.

The work performed with one low TAN crude oil in FY89 should be extended to one or more additional low TAN crudes in FY90. If encouraging results are achieved with several crude oils, from several reservoirs, then a firm conclusion can be reached about the applicability of surfactant-enhanced

alkaline flooding to reservoirs that contain low acid crude oils. If surfactant-enhanced alkaline flooding is applicable to those reservoirs, it will greatly broaden the applicability of the method.

The experiments with low TAN crude oils will include coreflood experiments at optimal conditions. These results can then be compared to the coreflood tests for crudes with high acid numbers that were performed in FY88 and FY89.

The effect of divalent ions on transient IFT behavior will be extended in FY90. The current work is being performed with phosphate/carbonate systems and needs to be compared with systems containing only carbonate.

The research on surfactant loss should be continued with a series of rapid bottle tests. These measurements will allow direct quantitative comparison of surfactant losses with carbonate and phosphate/carbonate systems.

Task 1. Analyze and select experimental crude oils having low acid numbers. (Start date: October 1989. Completion date: December 1989.)

Information regarding crude oil and reservoir properties will be reviewed to identify reservoirs containing crude oils with low acid numbers that are good candidates for surfactant-enhanced alkaline flooding. Samples of crude oil and brine will be obtained from various oilfield operators and analyzed to determine API gravity and total acid number. Reservoir brine samples will also be analyzed to determine if the salinity is appropriate for designing a surfactant-enhanced alkaline flooding system. Based on these analyses, two or three crude oils will be selected for further study.

Task 2. Determine transient IFT behavior of selected crude oils with various surfactant/alkali systems. (Start date: November 1989. Completion date: June 1990.)

The transient IFT behavior of selected crude oil-alkali systems will be measured at several salt concentrations. Tests will be conducted to determine if surfactant-enhanced alkaline formulations that produce ultralow interfacial tensions with selected crude oils can be designed. The results will indicate if the decrease in initial IFT from adding alkali is related to a shift in optimal salinity. The results from tasks 1 and 2 will be used to determine if surfactant-enhanced alkaline flooding is generally applicable to low TAN crude oils and to identify optimal conditions.

Task 3. Conduct oil-displacement tests to determine oil recovery efficiency of selected crude oils by optimized surfactant/alkali formulations. (Start date: January 1990. Completion date: August 1990.)

Based on the results from task 2, oil-displacement tests will be designed and conducted in Berea sandstone cores or sandpacks to determine the recovery efficiency of optimized surfactant-alkali formulations. The results will be compared with previous results obtained on more acidic oils.

Task 4. Measure the effects of low concentrations of divalent ions on the transient IFT behavior of carbonate-containing systems. (Start date: January 1990. Completion date: August 1990.)

The effects of low concentrations of calcium and magnesium, and perhaps iron, on transient IFT behavior of surfactant-enhanced alkaline systems will be determined. Studies will be conducted using a selected crude oil. Results will be compared with data from similar studies using an alkane, with the same EACN of the selected crude oil, to identify synergistic effects that occur between surface-active compounds that are extracted from the crude oil and the added synthetic surfactant. The results will be compared with results obtained in FY89 for phosphate/carbonate systems.

Task 5. Compare surfactant loss for carbonate and carbonate/phosphate mixtures. (Start date: January 1990. Completion date: August 1990.)

The loss of surfactant for a surfactant-carbonate formulation with added phosphate will be compared with that for a similar system that does not contain added phosphate. The tests will be performed with an anionic surfactant, and analyses will be accomplished using an HPLC method. Tests will be conducted on various rock and mineral samples which may include Berea sandstone and reservoir core samples from both sandstone and carbonate formations.

DELIVERABLES

Sep 90   Topical report on design of surfactant-enhanced alkaline flooding systems.

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>
Spinning drop interfacial tensiometer	1	
Coreflooding apparatus	2	
Liquid chromatograph	1	

BE4C. DEVELOPMENT OF IMPROVED MOBILITY CONTROL METHODS

BACKGROUND

Oil recovery efficiency is directly related to both displacement and volumetric sweep efficiencies. An efficient oil recovery process must be effective in recovering oil from the pores of the rock at a microscopic level and also must contact as large a portion of the reservoir as possible. Differences in viscosity, density, and mobility of the injected fluids such as water and the oil being displaced from the reservoir result in poor sweep efficiency. Permeability heterogeneity in layered reservoirs also causes channeling that leaves lower permeability layers unswept by the injected fluid. Recent estimates by the U.S. Department of Energy indicate that almost 100 billion barrels of mobile oil is uncontacted or bypassed by conventional waterflooding or steam drive methods. Polymer flooding is one method that is used to make the mobility ratio between the displacing and the displaced fluids more favorable thereby improving mobility control. Gelled polymers are used in permeability modification methods to divert the flow of injected water into regions of the reservoir that have not been swept completely. Application of any type of chemical flooding method requires mobility control to ensure that the chemical slug contacts as much of the reservoir as possible.

Polymer flooding is among one of the most inexpensive EOR methods, primarily because suitable water-soluble polymers are available at a relatively low cost and typically low concentrations of polymer are required in designing a polymer slug that has a favorable mobility ratio with light crude oils. Permeability modification treatments using gelled polymers have been successfully applied in both water injection wells, to cause fluid diversion and increase sweep efficiency, and in producing wells, to prevent channeling of injected water to reduce water-oil ratios. Polymer flooding can recover oil economically but the ultimate incremental recovery is usually rather low. Polymers are typically added to the chase water or directly to the chemical slug in both alkaline and surfactant flooding to improve mobility control. Gelled polymer treatments provide a near-term benefit because they can be economically applied even at low oil prices. They are being used to correct problems of early breakthrough of injected water in waterflooding and typically can improve the economics of a producing property by decreasing the volume of water produced, which reduces water handling and treating costs, and

by increasing oil production. Both polymer flooding and gelled polymer treatments have been successfully applied by both independent oil producers and major oil companies.

NIPER's research program in mobility control methods addresses the development of improved mobility control agents, which are needed for application of any type of chemical flooding, and permeability modification treatments. At NIPER, a cost-shared project by the U.S. Department of Energy and an industrial participant led to the development of a crosslinking system for a powdered biopolymer product. Through technology transfer to an independent producer, a field test was conducted that showed successful near-term results. Previous research efforts have focused on understanding the complex rheology of viscoelastic polymers under various but typically encountered conditions of salinity, temperature, and shear rate to determine how best to select polymers for specific applications. Mid-term research has provided the basic understanding of the relationship between rheology of polymer solutions and injectivity and transport in porous media. Work in recent years has focused on development of an improved mobility control method that utilizes crosslinked low molecular weight polymers. The research led to the development of a novel viscometry apparatus which has been used to provide near-term results on the rheological properties of polymers that are being developed for application in deep reservoirs that have high temperatures such as those in the North Sea.

One of the major issues that is hindering the application of gelled polymers for permeability modification treatments is the lack of an accurate reservoir simulator that can be used to optimize injection strategies and predict economic performance. NIPER's mid-term research efforts have resulted in the development of such a simulation program. Results from the long-term basic research program have provided mathematical correlations for determining the rheological and physical properties needed in developing a three-dimensional simulator. The simulator has been used to compare the oil recovery efficiency and economics of various injection strategies and the effects of crossflow on the effectiveness of permeability modification treatments. This model, as an example of near-term technology transfer, will be an important engineering design tool for the petroleum industry to use in maximizing profits from gelled polymer treatments.

In FY90, NIPER's mobility control program is focused on two critical elements of oil production technology: (1) further development of an improved mobility control method using crosslinked low molecular weight polymers, and (2) further development and application of the permeability modification simulator. The further mid-term development of the mobility control method should confirm the utility of this technology. The permeability modification simulator will be used in the near future to make a near-term impact through providing data that can be used to optimize gelled polymer treatments. For specific reservoirs being produced by independents and major oil companies.

Mobility-Control Agents

Dilute, high-molecular-weight polyacrylamide solutions have been used in many chemical flooding projects to improve sweep efficiency. One drawback in using polyacrylamides is their susceptibility to mechanical degradation, which is irreversible and can greatly reduce their effectiveness as mobility-control agents. 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.

Research at NIPER on the development of crosslinked low-molecular-weight polymer gels for mobility control began in FY88. Screening 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.) Thus far, the crosslinking conditions determined have not considered the effect of the degree of hydrolysis. The degree of hydrolysis has been shown to affect the gelation rate of a conventional polyacrylamide with a metal crosslinking agent. In mobility control, a fast gelation rate and a fast rehealing rate of a gel system are desirable. Screening tests and rehealing tests on polymer samples

with different degrees of hydrolysis will lead to the optimal degree of hydrolysis for making cost-effective polymer gels for mobility control.

Shear experiments have shown that crosslinking bonds can be broken under a high shear condition and will reheel under a low shear condition. The ability of broken bonds to reform under low shear conditions will permit a gelled polymer to regain viscosity and to reduce water mobility as it flows through reservoirs. Since gelation and gel properties are dependent upon shear history, it is desirable to develop a mixing procedure that will optimize the gel strength and provide samples with consistent rheological properties.

Permeability Modification

Polymer gel treatment has been used in many oil fields to improve oil production. Successful implementation of gel treatments requires knowledge of the transport, gelation kinetics, and interaction of the gel system in porous media and knowledge of reservoir characteristics. In planning treatments for permeability modification, producers usually have the problems of determining the best time to begin a treatment and how far the gel should penetrate in high-permeability layers. Problems like these can easily be answered by using a simulator. In FY88, a three-dimensional, three-phase simulator was developed by incorporating an in situ gelation model into a black oil simulator. This simulator was then used to determine the best initiation time for a gel treatment in reservoirs of different degrees of crossflow. Results showed that the best initiation time for a gel treatment in an injection well was the time shortly before water breakthrough, regardless of the degree of crossflow. Little is known about the effect of layer permeability contrast on the best initiation time and the effect of the degree of gel penetration in high-permeability layers on oil recovery. This information would be very helpful for assessing potential fields for polymer gel treatments.

OBJECTIVES

To determine the applicability of low-molecular-weight polymer gels for mobility-control applications and to determine the effects of permeability and depth of penetration of gel on oil recovery efficiency.

SCOPE OF WORK

In FY90, screening tests will be continued to determine the effect of the degree of hydrolysis on the crosslinking conditions. Depending upon commercial availability, polymers having different degrees of hydrolysis may have to be prepared by hydrolyzing a low-molecular-weight polyacrylamide. The degrees of hydrolysis of hydrolyzed polyacrylamides will be determined using a conductimetric method. Screening tests to be conducted in FY90, and later, rhealability tests, would lead to the identification of the optimal degree of hydrolysis for making cost-effective polymer gels for mobility control.

A series of gelation tests of some selected polymer/crosslinker systems, developed in FY88 and FY89, will be conducted in a flow system. The effect of apparent shear rate in porous media on gelation kinetics and gel strength will be examined. Viscosity and pressure gradient measurements will be used to monitor gelation and gel strength as a function of time. Screen factors will also be measured after gelation reactions have been completed. The results will be used to develop a mixing procedure that will optimize the gel strength and gelation time of polymer/crosslinker systems.

NIPER's three-dimensional, three-phase simulator for permeability modification, developed in FY88, will be used to investigate the effects of layer permeability contrast and the degree of crossflow on the incremental oil recovery for a polymer gel treatment. The effect of the degree of gel penetration in the high-permeability layer on oil recovery will also be investigated.

Task 1. Conduct screening tests to determine the effects of hydrolysis on gel formation. (Start date: October 1989. Completion date: August 1990.)

Low-molecular-weight polyacrylamide polymers having the same molecular weight but different degrees of hydrolysis will be prepared in the laboratory if they are not available from polymer manufacturers. A conductimetric method will be used to determine the degree of hydrolysis. Polymer concentration, concentration of crosslinking agent, and extent of hydrolysis will be varied to determine conditions under which gels can be formed which are suitable for mobility-control applications. Cr(III) and aluminum citrate will be used as crosslinking agents. The effects of the degree of hydrolysis on gelation kinetics, gel strength, and viscosity will be determined.

Task 2. Develop a laboratory mixing procedure that produces polymer gels with consistent rheological properties. (Start date: January 1990. Completion date: August 1990.)

Several gel systems, developed in FY88 and FY89, will be selected for gelation reaction kinetics studies, using short silica sandpacks or glass bead packs as porous media, to determine conditions under which gels can be formed with consistent rheological properties. Each gel system will be continuously circulated through the porous media. Viscosities and pressure gradients will be measured at various times to determine the kinetics of gelation. Screen factor of the gel will also be measured after the gelation reaction is complete. The effect of apparent shear rate on the gelation time, viscosity, and screen factor will be assessed.

Task 3. Conduct sensitivity runs using NIPER's simulator for permeability modification. (Start date: January 1990. Completion date: July 1990.)

Sensitivity runs using NIPER's three-dimensional, three-phase simulator for permeability modification will be conducted, using a two-layer reservoir model, to investigate the effect of layer permeability contrast on incremental oil recovery for a gel treatment and the effect of the degree of gel penetration in the high-permeability layer on oil recovery.

DELIVERABLES

- Sep 90 Topical report on the effect of shear and degree of hydrolysis on gelation reaction kinetics and gel strength.
- Sep 90 Status report on the effect of layer-permeability contrast on the best initiation time and the effect of the degree of gel penetration on oil recovery.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemist	0.1
Research Engineer	0.9
Technician	<u>0.2</u>
Total	1.2

Project Leader

Troy R. French, Senior Chemist

EQUIPMENT REQUIREMENTS

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

BE5A. GAS MISCIBLE DISPLACEMENT

BACKGROUND

Gas miscible displacement methods are effective for tertiary oil recovery. Carbon dioxide gas and flue gas are the most popular injection gases. Several large-scale gas floods are in progress in the southwestern United States. Nitrogen gas injection also has a great potential for EOR applications in condensate reservoirs and offshore reservoirs. Recent trends in EOR activities indicate that gas miscible flooding will become the most widely practiced EOR method within the next decade.

The most common problems in gas miscible flooding are: (1) poor sweep efficiency resulting from the low viscosity and density of the injected gas, (2) the deposition of heavy organic materials which can reduce productivity of producing wells, and (3) acceleration of corrosion of injection, production, and surface tubing caused by injection of carbon dioxide. This research program is designed to address the first two problems.

Laboratory tests have shown that gas miscible displacement methods are very effective for oil recovery. Oil-recovery efficiencies of nearly 100% can be achieved under ideal conditions. A major constraint to successful field application for all gas flooding methods is the poor sweep efficiency that results from gravity segregation, viscous fingering, and channeling due to formation heterogeneity. The development of improved methods for gas mobility control can significantly increase the recovery efficiency of this method. When applied on a field scale, even a modest improvement in sweep efficiency can result in a significant increase in oil recovery.

The use of surfactant solutions to generate foams is a promising method for gas mobility control and sweep efficiency improvement. Laboratory experiments have indicated that foam can be generated in rocks and can reduce the mobility of injected gas; however, field applications of foam technology have not been very successful. The reason is that foam generation and propagation in porous media are very complicated processes controlled by many factors. Improved understanding of foam generation and propagation in porous media under reservoir conditions is needed to provide a basis for developing engineering methods to design foam applications that are successful in the field.

Previous research at NIPER has indicated that surfactant adsorption and the rate and sequence of injection of gas and surfactant solution are the major factors which determine the success of foam performance in reservoir formations. The essential conditions for the successful application of foam mobility-control methods are: (1) the surfactant concentration in the solution must be great enough for a stable foam to form and (2) the injected surfactant solution must preferentially propagate into channels where gas would normally flow and redirect the gas into unswept areas of the reservoir. The surfactant concentration required to generate a stable foam under dynamic conditions in reservoir rock depends on the foaming ability of the surfactant. The degree of improvement in sweep efficiency also depends on the injection rate and sequence of gas and surfactant solution and size of the injected surfactant slugs. For successful field applications, these two conditions should be optimized to maximize sweep efficiency and oil recovery.

Improved understanding of the mechanisms of foam generation and propagation in porous media and additional laboratory data are needed to develop an engineering methodology for optimizing foam methods for improving mobility control in miscible flooding. In FY90, this research project will focus on the fundamental study of dynamic sorption (adsorption and desorption) and chromatographic separation of surfactants in various rock types. These goals are mid- to long-range goals. The applications of foam technology require that dynamic sorption and chromatographic separation problems be solved, but research in these areas with related EOR methods have shown these problems to be complicated and not easily addressed with quick-fix type measures. A flow experimental technique has been designed, and a mathematical model has to be developed to determine the kinetic and transport parameters. The completion of this task will provide not only information and data on surfactant adsorption on various reservoir rocks but also result in a method to predict changes in surfactant concentration under reservoir conditions.

The study of the problem of organic deposition induced by gas miscible flooding was initiated in FY89. Deposition of asphaltic or paraffinic materials often occurs at or near wellbores and plugs producing wells, which results in increased costs for workovers and decreased productivity of wells. In addition, deposition of organic materials in a reservoir rock matrix may alter wettability and relative permeability and affect the flow of

reservoir fluids. Further data are needed to determine the composition of deposited materials, the mechanisms of deposition, and to understand how to remediate or avoid the problem. In FY90, the objective of the research on organic deposition will be to study the relationship between organic deposition and oil composition and to determine how this affects the composition of oil during miscible displacement. The goal of this research is to understand how miscible gas flooding induces deposition of heavy organic substances and to develop a predictive method that can be used to estimate the degree of deposition and to tell at which condition and where the deposition may occur. Because the problem of organic deposition exists now in the field, some near-term benefits are expected from a clearer understanding of the cause. However, once the causes of organic deposition are delineated, longer range project tasks may be needed before this current field-related problem can be solved.

OBJECTIVES

To develop improved methods for designing gas miscible methods for enhanced oil recovery by (1) developing a mathematical model that can describe the adsorption and transport of foaming agents in reservoir rock and (2) developing a model to describe the deposition of organic materials under miscible conditions.

SCOPE OF WORK

In FY89, NIPER's research on gas miscible displacement methods was focused on studying the two major problems of gas mobility control and organic deposition. This research on improved methods for mobility control has focused on the application of foam technology. Foam flow characteristics, apparent viscosities of foam, effective gas relative permeability, and the effectiveness of foam for gas sweep improvement were determined. This research on organic deposition has focused on characterization of the asphaltic material that precipitates from crude oil when contacted with various solvents. The FY90 research plan is based on previous results and proposes a continuation of the research in these important areas. The work on foams for mobility control would be applicable to both nitrogen and carbon dioxide miscible flooding.

Studies on the role of surfactant adsorption in the design of foam formulations will focus on surfactant adsorption measurements under dynamic conditions. This study of surfactant adsorption is a mid-term goal aimed at improving the effectiveness of surfactant formulations. Experimental data will be obtained, and a mathematical model will be developed, and both will be integrated to determine adsorption-desorption rate constants, equilibrium surface concentrations of surfactants, and transport coefficients. Two different types of surfactants and a typical Berea sandstone and a typical limestone will be selected for this study. The effects of flow rate, temperature, and pressure on surfactant adsorption will also be investigated. In addition, the chromatographic separation of components of a surfactant mixture due to adsorption will be investigated.

Research on organic deposition will focus on investigation of the phase behavior of gas-crude oil systems to determine the relationship between crude oil composition and organic material precipitation. A technique to predict the precipitation of heavy organic substances from crude oil during gas flooding will be developed. Accurate experimental data will be obtained and used to provide a basis for development of a model for the deposition process. Information will also be obtained regarding the mechanisms of organic deposition. Although organic deposition from crude oils are current, long-range goals such as the ones described here are necessary to solve these problems.

Task 1. Determine surfactant sorption and chromatographic separation in sand-packed tubes by flow experiments. (Start date: October 1989. Completion date: July 1990.)

A flow adsorption experimental apparatus will be constructed to measure the surfactant concentration profile at the effluent of a sand-packed tube. Various formation sands will be used for this experiment. Experiments will also be conducted at various conditions to investigate the effects of temperature, pressure, and flow rate on surfactant adsorption. Commercially available foaming agents will be selected for use in the experiments. The surfactant concentration profile in the effluent from the sand-packed tube will be monitored. The data obtained will be fitted with a mathematical model, which will be developed in task 2.

Task 2. Determine the degree of organic deposition and changes in oil composition under miscible conditions. (Start date: October 1989. Completion date: July 1990.)

A specialized apparatus has been constructed to simulate a multiple-contact miscibility process. The apparatus will be used to determine the changes in composition of crude oil at each stage of contact with CO₂ and the resulting degree of solid precipitation. This experiment will provide data that are required for task 4 in developing a model for the phase behavior of CO₂ crude oil systems that exhibit organic deposition.

Task 3. Mathematical modeling of surfactant transport. (Start date: October 1989. Completion date: August 1990.)

The development of a mathematical model to describe the transport of surfactant under flowing conditions, which was initiated in FY89, will be continued. An automatic matching technique will be developed to fit the experimental results obtained from task 1. The kinetic constants and transport parameters such as adsorption-desorption rate constants, equilibrium surfactant concentration on solid surface, and dispersion coefficient will be determined from fitting data for each surfactant-rock system.

Task 4. Develop a preliminary model to describe organic precipitation under miscible conditions. (Start date: January 1990. Completion date: August 1990.)

Based on the results from task 3 for the deposit materials, a characterization technique for the deposited materials will be developed by treating them as pseudo-components or colloidal particles. A phase equilibrium predictive package for predicting gas-liquid-solid coexistence curves will be developed and tested with the experimental data from task 3.

DELIVERABLES

- Sep 90 Topical report describing results of surfactant adsorption study.
- Sep 90 Topical report describing results of organic deposition study.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Engineer	0.6
Senior Physicist	0.4
Research Engineer	0.4
Assistant Engineer	1.0
Senior Experimentalist	<u>0.3</u>
Total	2.7

Project Leader

Frank Chung, Senior Engineer

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Variable volume PVT cell	1	
Constant rate injection pumps	1	
Gas chromatograph		1
High pressure UV-VIS spectrometer (HPLC)		1

BE5B. DEVELOPMENT OF METHODS TO IMPROVE MOBILITY CONTROL AND SWEEP EFFICIENCY IN GAS FLOODING

BACKGROUND

Gas flooding methods can be effective in recovering both light and heavy crude oils even under miscible and immiscible conditions. The efficiency depends on the extent of contact between the oil and the injected gas. Poor sweep efficiency resulting from gravity override and viscous fingering is one of the major problems that hinders the efficiency of the process. The gas-mobility problem is even more severe in immiscible flooding conditions than in miscible cases. NIPER's research efforts have been directed towards development of methods for improving mobility control (entrainers), sweep efficiency (foams), and displacement efficiency of gas flooding processes. These are long-range goals with some anticipated near- or mid-term benefits.

Previous research at NIPER has identified several areas where further development is needed. One area of interest is the use of entrainers or cosolvents as additives to improve mobility control in CO₂ flooding. Improvement in oil recovery using this method can result from a combination of several factors: (1) an entrainer enhances the solubility of the oil components in the dense phase CO₂; (2) the addition of an entrainer contributes to an increase in the viscosity of the CO₂-rich phase; (3) the enhanced solubility of high-molecular-weight components of the crude oil further increases the viscosity of the displacing phase; and (4) increases in the density of the displacing gas reduces gravity override and increases sweep efficiency.

The entrainer method has been tested in FY88 and FY89 research programs with promising results. In FY90, the goal of this research will be to verify the feasibility of this method for field applications. The project is designed to investigate potential constraints to the application of entrainer technology and to develop a rapid screening technique to identify and compare different candidate entrainers. The development of screening and predictive methods will be useful in identifying entrainers that are most effective and in optimizing conditions for gas flooding applications. Provided the promising results obtained in FY88 and FY89 can be successfully demonstrated as an alternative to surfactant foams, gas flooding pilot projects now being conducted could benefit in the near-term. Even if unforeseen difficulties

prevent immediate applications, impact of this new technology to field wide applications should considerably enhance oil production by gas flooding.

The development of effective methods for using foam for gas mobility control also requires considerable attention because of its great potential in contributing to improved oil recovery. Many factors affect foam performance. Reproducibility of results has always been a major concern in foam research, and historical information has shown that flooding performance in pilot field applications has not always reflected the same degree of effectiveness as had been indicated in laboratory-scale experiments. The complexity of foam behavior has been the major stumbling block in understanding ways to apply this method effectively. Previous efforts undertaken in this project have been directed toward identifying and determining the mechanisms of foam propagation and improvement in sweep efficiency in porous media. Flow experiments in sand-packed tubes and cores have provided insights on how foam propagates in porous media. Research on foam properties in capillary tubes under controlled conditions have also been initiated. Knowledge of foam rheology in conjunction with studies of foam properties are essential foundations to understanding its potential for mobility-control applications. These efforts, as well as information in the literature, will provide the basis for developing effective means for utilizing foam in gas flooding.

OBJECTIVE

To develop methods for improving sweep efficiency and mobility control for gas flooding.

SCOPE OF WORK

Research efforts for FY90 will continue to focus on further developing the entrainer method. This project is oriented towards long-term goals that pursue the development of a new approach for improving sweep efficiency and mobility control. A rapid experimental screening method will be developed to evaluate candidate entrainers. These screening experiments will be conducted to identify potential cosolvents that can be used effectively to enhance the properties of the CO₂-rich phase. Experiments will also be conducted to

determine the degree to which losses caused by adsorption, condensation and phase partitioning of the entrainer may reduce its effectiveness.

The availability of predictive methods for properties of CO₂-entrainer systems is necessary in understanding and effectively applying the entrainer method. One task in this research program is the evaluation of available predictive models to predict the behavior of candidate cosolvents in CO₂. These models will be useful in optimizing the conditions of temperature and pressure as well as composition where screened entrainers can be applied.

Understanding the complex behavior of foam in porous media is necessary to achieve the potential of this method for improving the mobility control of immiscible gas displacement methods. Foam performance can be affected by many factors. In order to determine conditions that may affect foam behavior, a parametric study of the conditions and variables that can alter foam flow characteristics will be conducted in FY90. The experiments will be conducted in short, packed tubes at low pressure conditions.

Injection of foam nearly always decreases the injectivity of a well. Because of the nature of radial flow, a significant portion of interwell pressure drop occurs within a short distance from an injection well. A study of near-wellbore behavior of foam will be conducted to determine means of improving foam injectivity and propagation. An improvement in injectivity can be achieved by altering flow in a near-wellbore region without materially affecting propagation of foam throughout most of a reservoir.

Task 1. Develop an experimental screening method for evaluation of entrainers for CO₂ gas flooding. (Start date: October 1989. Completion date: July 1990.)

An experimental screening technique will be developed and utilized to evaluate and compare a broad class of compounds that have potential as entrainers. The study will consist of measurement of cosolvent affinity to CO₂ and heavy hydrocarbons. Supercritical fluid extraction (SFE) experiments will be conducted to evaluate the effectiveness of selected cosolvents in enhancing hydrocarbon solubility in CO₂.

Task 2. Determine characteristics of foam under flowing conditions in porous media. (Start date: October 1989. Completion date: August 1990.)

Steady-state flow experiments will be conducted by injection of gas and surfactant solution in short, sand-packed tubes to determine changes in flow characteristics as a function of surfactant concentration, foam quality, and flow rate. Foam flow characteristics will be determined in different packing materials and at various experimental conditions. The effects of foam on gas injectivity will be studied by means of experiments under radial flow conditions. Injection sequences of the different fluids will be varied, as well as flow velocity, foaming agent concentration, and slug sizes, to determine their effects on gas injectivity.

Task 3. Evaluate predictive methods for properties of CO₂ entrainer systems. (Start date: October 1989. Completion date: September 1990.)

The goal of this task is to initiate the evaluation of available models to predict the behavior of candidate cosolvents in CO₂ and their effect on the enhancement in supercritical extraction. These predictive models will be used to predict the solubility of entrainers in CO₂ as well as properties including viscosity and density of the CO₂-entrainer system. Experimental and literature data on systems containing CO₂ will be used in the evaluation.

Task 4. Evaluate entrainer loss due to adsorption, condensation, and phase partitioning in porous media. (Start date: April 1989. Completion date: August 1990.)

Laboratory experiments will be conducted to identify potential constraints related to the application of entrainer technology to gas flooding. Flow experiments in cores will be conducted to evaluate the loss of entrainers. Phase equilibria measurements will also be performed to study the extent of partitioning of entrainer in aqueous phase.

DELIVERABLE

- Sep 90   Topical report describing the application of foams for improving sweep efficiency and entrainers for improving mobility control in gas flooding.

PLANNED STAFFING

	<u>Man-Years</u>
Research Chemist	0.3
Associate Engineer	1.0
Senior Experimentalist	<u>0.7</u>
Total	2.0

Project Leader

Arden R. Strycker, Research Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Viscosity measurement apparatus	1	
Coreflooding apparatus	1	
PVT apparatus	1	
Gas chromatograph		1

BE9. THREE-PHASE RELATIVE PERMEABILITY

BACKGROUND

Relative permeability data accurately depicting multiphase flow effects are frequently required for reservoir engineering calculations. Considerations often include the displacement of oil by simultaneous gas and water flow and an estimation of the volume of oil recovered as well as that left in place after primary and secondary production. Enhanced recovery processes also involve three-phase flow in which one of the flowing phases is injected to modify reservoir behavior or to improve petroleum production.

Current reservoir engineering practices include the use of numerical simulators to predict reservoir performance. The appropriateness of the output from a numerical simulator in modeling reservoir performance is directly related to the quality of the data or correlations, representing fluid flow characteristics, entered into the simulator. In the absence of correlations from three-phase relative permeability test data, three-phase flow characteristics are generally determined from more readily available two-phase gas-oil and water-oil data. However, two-phase flow characteristics may not adequately represent three-phase characteristics. For these reasons, it is important to understand three-phase flow processes and to develop correlations and predictive methods for modeling relative permeabilities under multiphase flow conditions. A knowledge of three-phase relative permeability and flow behavior is especially useful to smaller companies, without extensive laboratory facilities, for use in publicly available reservoir simulators and hence can be beneficial to independent operators in the near-term.

Various factors influence multiphase relative permeability characteristics. Several studies have shown the relationship between capillary number and two-phase relative permeability. Fluid velocity, interfacial tension, and viscosity effects on two-phase relative permeability have been studied to some extent, and guidelines for producing quality data for two-phase flow tests have been recommended. However, guidelines or studies showing the effect of rock, fluid, and rock-fluid properties and hysteresis on relative permeabilities are scarce.

The limited results reported for three-phase flow characteristics have shown that the fluid saturation envelope for three-phase flow is narrow and is

affected by rock properties, wettability, and hysteresis among other factors. Since rock and wettability properties are responsible for cycle dependent hysteresis in relative permeability characteristics, an understanding of the relationships among the three is important. Cycle dependent hysteresis has significant implications on reservoir performance prediction. In the process of waterflooding a water-wet reservoir, the rock in front of the oil bank experiences a drainage process (water saturation decreasing) as the oil bank moves towards the production well. The rock behind the oil bank experiences an imbibition process (water saturation increasing). After the oil bank reaches the production well, the reservoir rock undergoes additional drainage and imbibition cycles as oil production continues. Each cycle may yield different relative permeability characteristics which are manifested as hysteresis. Any changes in flooding patterns or profile modification, infill drilling, or application of EOR processes subject the rock to additional hysteresis cycles. The coring, cleaning, and handling of rock samples obtained from the reservoir are often accompanied by one or more hysteresis cycles. Knowledge of the extent of variation in relative permeabilities due to hysteresis provides guidelines for adjusting or using representative relative permeability data in reservoir simulators. Before an understanding of multiphase flow phenomena can be attained, high-quality three-phase flow data recorded under characteristic reservoir conditions must be obtained.

Laboratory measurement of multiphase relative permeability is a very difficult task. Primary test constraints include long test times while waiting for steady-state conditions to be manifested, the measurement of fluid saturation distributions, and the development of test procedures which provide accurate and repeatable results. For a flow system in which N flowing phases are present, at least $N-1$ of the saturation phases must be measured independently to characterize the saturation distributions. In situ methods for monitoring fluid saturations are most appropriate for characterizing fluid distributions.

NIPER has conducted research on three-phase relative permeability determination for the U.S. Department of Energy for the past 6 years. During that time, NIPER has developed the apparatus and capability to measure two- and three-phase relative permeability using x-ray and microwave technology.

Much of the measurement apparatus has been automated. The range of experimental conditions, including core type and size, pressure and temperature, is continually being increased. The effects of interfacial tension, wetting and nonwetting phases, viscosities, pore structures, etc. on three-phase flow behavior are studied. The early goals for these projects included implementing and evaluating saturation determination techniques, designing and assembling equipment for measuring fluid saturations in rock samples during flow experiments, automating relative permeability test measurements and data logging, and conducting three-phase relative permeability tests on Berea sandstone cores. At NIPER, both X-ray and microwave absorption methods are used to characterize oil and brine saturation distributions within rock samples during multiphase flow experiments. While working to meet project objectives, NIPER personnel constantly strive to improve the relative permeability measurement system, measurement accuracy, and experimental techniques. Some of the important achievements from this ongoing project include:

- evaluation of conventional saturation measurement techniques,
- implementation of more accurate in situ measurement techniques based on X-ray and microwave absorption,
- automation of the saturation measurement equipment,
- improvement of data analysis techniques,
- two- and three-phase relative permeability measurements on Berea sandstone cores demonstrating viscous effects,
- evaluation and continual improvement of test procedures,
- design and evaluation of a coreholder which is semitransparent to both X-ray and microwave signals, and
- improvement of microwave scanning technology by implementing a state-of-the-art detection system for measuring saturation in cores with thickness greater than 0.75 in.

While this long-term research into the understanding of three-phase flow behavior has been progressing, several potential industrial clients have expressed an interest in NIPER's expertise for near-term application. We have trained personnel from industry in the techniques involved in measuring three-phase relative permeability. We have conducted difficult investigations (at

extreme temperature and pressure) for industrial clients on the relative permeability characteristics of specific fluids and porous media of interest at the temperature and pressure of the reservoir. Finally, we have worked with equipment suppliers to develop three-phase relative permeability measurements apparatus for sale and installation at industrial facilities. Supply of this equipment includes technology transfer, equipment installation, and training.

Although NIPER is working to transfer the technology developed through this project for its near-term applicability to oil and gas production problems, the longer-term research continues. During FY90, the work is to be concentrated in two areas: examination of mutual relationships among petrophysical properties, rock-fluid characteristics, and relative permeabilities; and improvement of three-phase relative permeability measurements.

OBJECTIVES

To improve laboratory measurements of three-phase relative permeability for steady- and unsteady-state conditions in core samples so that reliable measurements are achieved. To investigate the influence of rock, fluid, and rock-fluid properties on two- and three-phase relative permeability.

SCOPE OF WORK

During FY89, two similar sandstone samples were extensively characterized, and their relative permeabilities were measured to identify influences of rock characteristics on flow behavior. The objective of the work was to characterize two samples to the extent that differences in relative permeability results could be associated with differences in petrophysical or rock-fluid characteristics.

The major objectives of this project for FY90 are concentrated in two primary areas: continuing the examination of mutual relationships among petrophysical properties, rock-fluid characteristics, and relative permeabilities; and improvement in three-phase relative permeability measurements.

Another objective in FY90 is to further investigate the influence of pore geometry, roughness, and hysteresis on two- and three-phase relative

permeabilities. Some of the factors that control pore geometries are texture, clay type, amount, and distribution. The FY90 objectives evolved as the natural continuation of research work conducted in FY89 that showed two sandstone samples having similar wettability characteristics, slight variations in pore throat and pore size variation, but substantial differences in relative permeability performances. Static parameters such as grain size, shape, sorting, packing, clay type, and distribution will be measured by application of image analysis on microscopic samples of the rock and pore casts with SEM. Additionally, rock-fluid properties such as capillary pressure, electrical resistivities, pH, and wettability will be measured.

Two-phase gas-brine, oil-brine, and gas-oil relative permeability tests will be performed on Berea and Bentheimer core samples that were used in the FY89 project year and the new sandstone sample that will be selected. The intent is to study effect of pore geometry on relative permeability hysteresis. Three-phase relative permeability using brine-oil-gas will also be measured in the direction of brine saturation increasing, oil saturation decreasing, and gas saturation increasing. A limited number of unsteady-state two-phase relative permeability tests will be conducted to compare steady- and unsteady-state results with the help of the CT scanner.

Two- and three-phase relative permeability experiments will be performed on the samples in a systematic, highly controlled manner to produce high-quality data reflecting both drainage and imbibition cycles. The major thrust of the work will be to produce high-quality relative permeability data for an additional well-characterized sandstone sample as well as two previously tested samples with different pore geometries -- a prerequisite for establishing test guidelines and multiphase relative permeability correlations. The work conducted on this project will build upon the foundation established during FY89, ultimately leading to the development or verification of correlations among three-phase relative permeability and other influential parameters.

Task 1. Select sandstone sample for test program and characterize their physical properties. (Start date: October 1989. Completion date: March 1990.)

One sandstone sample will be selected for the FY90 experimental program. The sample will be of intermediate permeability compared to the high-

permeability samples that were characterized during FY89. Sources for the rock to be considered include outcrops, petroleum reservoir rock, quarried rock, and synthetic (man-made) cores.

The selected sample will be characterized for petrophysical and petrographical properties, including porosity, permeability, grain density, XRD, SEM, EDS, and CEC measurements. Quantitative microscopic evaluation through petrographic image analysis will be conducted on thin sections of the rock sample to characterize pore geometry, roughness, pore size distribution, and other statistical parameters. Mercury capillary pressure measurements will be conducted on the samples at intrusion pressures from 0 to 2,000 psia. In addition, imbibition and drainage capillary pressure and wettability index will be measured on the sample with the oil and brine that will be used for flow experiments.

Task 2. Modify instrumentation and evaluate temperature effects on microwave and X-ray absorption characteristics. (Start date: October 1989. Completion date: March 1990.)

An experiment will be conducted to evaluate changes in X-ray and microwave attenuation characteristics of a fully brine saturated Berea sandstone rock sample as a function of temperature. Thereafter, the sample will be desaturated to residual liquid saturation by flooding with gas. The rock sample will then be dried at temperatures from 100° to 1,000° F, in 100° F increments, while measuring the X-ray and microwave attenuation after each temperature exposure. This work is intended to help define the shape/linearity for X-ray and microwave calibrations to liquid saturations in the low-liquid-saturation region. In addition, the results will be evaluated to examine whether the scanning procedure has the potential for detecting mineral and physical alterations within a rock sample during a flow test that could affect the X-ray or microwave signals.

Additional instrumentation will be incorporated to provide for rock electrical resistivity and pH measurements during relative permeability experiments. This will allow simultaneous measurements of rock permeabilities, fluid saturations, pH, and electrical properties under dynamic flow conditions. Because of the analogous nature of both electrical and fluid conductivities, one may be correlated to the other. A high-speed centrifuge at NIPER will be used to measure capillary pressure and wettability

characteristics of 1.5 in. diameter by 1.5 in. long cores. A new microcomputer is to be installed to handle automated laboratory measurement and control functions. The computer currently in use lacks sufficient capabilities to allow levels of automation and control necessary for this project.

Task 3. Conduct and analyze two- and three-phase relative permeability experiments on core characterized in task 1. (Start date: December 1989. Completion date: September 1990.)

Two-phase steady- and unsteady-state and three-phase relative permeability experiments will be conducted under controlled ambient conditions. The Berea and Bentheimer core samples used in FY89 will be further tested to study the effect of saturation history on relative permeability. Additionally, brine pH, and dynamic core electrical resistivity will be monitored continuously to observe transient and steady-state behaviors of electrical (resistivity and pH) and fluid flow properties as the new core sample is tested. This process of monitoring various dynamic parameters will provide 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.

Relative permeability test results will be analyzed and compared. Experimental results from flow tests, electrical resistivity data, and rock characteristics obtained from petrophysical and petrographical analysis will be evaluated to seek improved empirical or statistical techniques for correlating three-phase relative permeability with other more easily measured properties, parameters, and characteristics.

DELIVERABLES

Sep 90   Topical report describing two- and three-phase relative permeability results and their interrelationships.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Research Engineer	0.4
Research Engineer	0.8
Associate Engineer	0.5
Technician	<u>0.7</u>
Total	2.4

Project Leader

Dan R. Maloney, Project Leader

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Microcomputer		1
CT scanner		1
Resistivity meter		1

BE11A. THERMAL PROCESSES FOR LIGHT OIL RECOVERY

BACKGROUND

Steamflooding of heavy oil reservoirs ($<20^\circ$ API) is a mature technology and currently contributes nearly 7% of domestic daily oil production. Steamflooding currently contributes 73% of the total EOR oil produced. However, heavy oil constitutes only about 10% of the total domestic petroleum reserves. To reduce the rate of resource abandonment and exploit the potential of many shallow, pressure-depleted, and even previously waterflooded light oil reservoirs, steamflooding is being considered because steam has demonstrated effectiveness in recovering commercial quantities of oil.

Steamflooding light oil reservoirs that are amenable to waterflooding is being tried. The DOE is conducting field pilots in light oil zones in two reservoirs: Elk Hills, California, and Teapot Dome, Wyoming.

Although the principal mechanism for light oil steamflood (LOS) is distillation, as opposed to viscosity reduction for heavy oil, application of diverting agents to improve steam sweep will become as critical as in heavy oil steamflooding. Research at NIPER has shown that contrary to earlier simulation results, sweep efficiency, gravity override and fingering are still some of the major problems.

In FY88, experiments in the two-dimensional (2-D) steamflooding physical model and use of the DOE screening model predicted that steamflooding water-wet, light oil reservoirs that have been extensively waterflooded would be unfeasible. In the experiments, there was a long delay in oil production as steam heated the water and then followed previously waterflooded channels. The resulting poor oil recovery was the product of both low oil saturation and excessive heat loss to the aqueous phase. Steamflooding light oils, not previously waterflooded, did not experience similar time delays. Both processes, steamflooding light oils and waterflooding followed by steamflooding, reduced the oil saturation to lower than that of waterflooding alone. Not all waterfloodable reservoirs have been reduced to residual oil saturation before their average 30-year life. Oil-wet reservoirs release their oil very slowly, and many oil-wet reservoirs are strippers or are abandoned but still contain significant oil. Changing the wettability of cores from oil-wet to more water-wet is one mechanism of oil production

identified in the FY89 steamflooding research. The effects of steamflooding light oil, oil-wet, reservoirs need to be investigated to determine if this technology could economically recover significant light crude oil before these older fields are abandoned well-by-well as pumping costs increase because of increasing water cuts.

Evaluation and formation of model oil-wet surfaces have been pursued at NIPER over the past 5 years. A more convenient method for preparing oil-wet cores was developed in late FY89 and a determination of the effects the surface has on steamflood performance is being undertaken. In FY85, the use of polar and asphaltic fractions of crude oil for wettability conversion was investigated. This more promising route to oil-wet cores uses silylating agents but until recently they have been used only at low temperatures (<205° F). The thermal stability of these treatments has just been evaluated showing they can be used under steamflood conditions (>350° F). This will permit laboratory simulation of the tighter oil-wet sands that may be expected in LOS candidate reservoirs, as opposed to California heavy oil reservoirs with high permeability.

In FY89, the work on high-temperature capillary pressure measurements showed that increasing temperature greatly affects wettability and moves a system to a more water-wet environment. The correlation of capillary pressure data generated from well characterized cores in centrifuge experiments and two-phase relative permeabilities determined at elevated temperatures is needed for numerical simulators to predict the performance of steamflood projects. Capillary pressure centrifuge measurements require far less time and are easier to generate than two-phase relative permeability curves. If correlations and an empirical model can be generated, the design and evaluation of both heavy and light oil steamflooding projects will be accelerated.

The two-dimensional (2-D) steamflood model which has been used for both light and heavy oil research is outdated, and a new physical model is needed. As part of a 2-year project to construct a new steamflood model, an analysis of scaling and design criteria of the physical model and of proposed experiments will be conducted in FY90. The second year would be devoted to construction and testing the physical model. This project could be accelerated if an appropriate high-pressure chamber and supporting surplus equipment were available.

The previous NIPER research used light crude oils from a number of fields, none of which are now being considered for steamflooding because of both technical and economic constraints within those specific fields. Elk Hills is a prime candidate for future work because the oil reservoir is large and there is potential to expand light oil steamflooding within the field, as well as adjacent fields with similar depositional environments. If possible, light oil steamflooding experiments will be conducted with Elk Hills oil and cores to evaluate steam diverters and oil recovery. This work anticipates future incorporation of NIPER expertise in addressing field related problems in the DOE Elk Hills light oil steamflood pilot project. Use of the developed expertise in addressing near-term related problems is a direct response to the current rate of U.S. petroleum resource abandonment.

OBJECTIVES

To improve the understanding of the basic mechanisms responsible for the improvement of light oil production using steam, and to use this understanding for accelerating development of this production technology.

Specifically for FY90, the objectives are as follows:

- (1) support the DOE in its cooperative effort with Venezuela in thermal technology transfer by participating in the Annex IV meetings;
- (2) determine the potential of oil recovery by steamflooding previously waterflooded light oil reservoirs which are oil-wet rather than water-wet;
- (3) correlate capillary pressure experimental results obtained from high-temperature centrifuge data with two-phase relative permeability experiments performed at high temperatures. Design an empirical model that would be useful in existing numerical simulators which describe this behavior for use in steamflood projects;
- (4) investigate the use of novel steam diverters for steamflooding of light oils; and
- (5) design a scaled, two-dimensional steamflood physical model with capability to model various steamflooding conditions.

SCOPE OF WORK

The use of our expertise in addressing near-term and mid-term related problems is the major emphasis for this project and is a direct response to the current rate of U.S. petroleum resource abandonment. More specifically, each of the objectives listed are being addressed by the corresponding tasks.

In support of the cooperative effort between DOE and Venezuela at the Annex IV meetings, immediate feedback on current activities is provided by other experts doing work in the same field. Thus, all near-term, mid-term and long-range goals are enhanced.

Work related to the second goal utilizes mid-continent light crude oils to investigate the production differences between oil-wet and water-wet reservoirs. A separately proposed survey/feasibility study of mid-continent light oil reservoirs in oil-wet formations would determine the potential benefits from steamfloods. Preliminary studies at NIPER have shown that steamflooding oil-wet reservoirs is an unexploited opportunity that deserves serious attention. Successful results on this task would impact the field in 1 to 3 years after the study is completed.

Objectives 3 and 5 are long-term in nature. However, results from objective 3 is expected to be published in 6 to 18 months, and the results would be incorporated in current simulation work being done at other research centers developing related technologies.

Finally, objective 4 is being addressed in anticipation of future involvement with a field pilot light oil steamflood project. Steamflood experiments are planned using Elk Hills shallow sand crude oil and core to provide guidance for the DOE cosponsored project. This task is near-term and is expected to address field related problems as they arise.

Task 1. Support the DOE in its cooperative effort with Venezuela by presenting the results of this project at the Annex IV meetings. (Start date: November 1989. Completion date: May 1990.)

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.

Task 2. Determine the oil recovery potential of steamflooding previously waterflooded light oil reservoirs which are oil-wet and compare results with those from water-wet reservoirs. (Start date: October 1989. Completion date: July 1990.)

This task is designed to compare the performance of steamflood recovery of light oil from waterflooded water-wet (work completed in FY88) and oil-wet reservoirs in the NIPER 2-D model. Experiments will use Delaware-Childers crude to duplicate previous experiments.

Task 3. Conduct steamflood experiments using light crude oil and diverting-mobility control agents. (Start date: October 1989. Completion date: August 1990.)

This task is designed to evaluate a series of novel diverting agents for increasing the oil recovery from steamflooding light oils. One- and two-dimensional sandpacks will be used to evaluate foam and emulsion for steam diversion using Elk Hills oil and sand.

Task 4. Contrast capillary pressure results obtained from centrifuge experiments with two-phase relative permeability experiments at high temperatures. (Start date: October 1989. Completion date: September 1990.)

This task is designed to provide an empirical model that can be used in numerical simulation of steamfloods that will use capillary pressure data from centrifuge experiments rather than the more time-consuming and costly two-phase relative permeability measurements as input for steamflood design. A correlation will be developed between relative permeability and capillary pressure as a function of temperature by measuring capillary pressures and unsteady-state, two-phase relative permeabilities of a well characterized set of oil- and water-wet cores at different temperatures. The centrifuge drainage data will then be history matched and the generated relative permeability compared with the measured value. The parameters of the model will then be adjusted to obtain a satisfactory match between measured and generated relative permeability. The task will also allow the evaluation of the thermal stability of artificially oil-wet surfaces to determine if the gas-phase silylation procedure of converting water-wet cores to oil-wet cores provides a suitable oil-wet surface that will allow this method to be used to simulate oil-wet reservoirs for steam recovery experiments.

Task 5. Conduct scaling study and dimensional analysis in preparation of constructing a new 2-D steamflood apparatus. (Start date: October 1989. Completion date: September 1990.)

The objective of this research is to design a new 2-D physical steamflooding apparatus that is scaled or partially scaled. The experience gained over the past 3 years using the 2-D, unscaled, thick-wall physical apparatus will be used to design the scaled apparatus. Scaling criteria accommodating various parameters to be investigated and the constraints of the design imposed by a number of different designs will be analyzed. Through analyses, the critical scaling factor will be determined and steamflooding experiments designed for each apparatus using statistical techniques of experimental design to minimize the number of experiments and maximize the quality of results compared with the cost and difficulty involved in construction and operation.

DELIVERABLES

- May 90 Summary report of the activities under this project for inclusion in the annual report of the Annex IV meetings that covers the work since the last report.
- Sep 90 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	0.8
Research and Associate Engineers	1.0
Technicians	<u>0.8</u>
Total	2.6

Project Leader

David K. Olsen, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
One- and two-dimensional steamflood apparatus	1	
High-temperature capillary pressure wettability apparatus	1	
High-temperature two-phase relative permeability apparatus	1	
HPLC pumps	2	
Microcomputer		1

BE11B. THERMAL PROCESSES FOR HEAVY OIL RECOVERY

BACKGROUND

Steamflooding currently produces nearly 7% of the domestic daily oil production and produces more oil (73%) than all the other EOR methods combined. Steamflood technology has concentrated on heavy oil ($<20^\circ$ API) recovery; however, this resource represents about 10% of domestic petroleum reserves, and the U.S. development of the technology has concentrated on the heavy oil reserves in Kern County, California.

The major problems of steamflooding are mobility control and sweep of the steam. In FY85 and FY86, a two-dimensional (2-D) steamflood model was constructed and tested. Since that time, the model has evolved to include multilayers to simulate multiple sand zones, each with different permeabilities. Altering the flow of steam into zones not originally contacted by steam has been the goal of this research. Several high-temperature, stable surfactants have been developed by other groups. The cost-effective application of surfactants as steam foam diverters is a near-term goal for this project. These surfactants offer the potential for increasing the resistance to flow formulations which could provide the steam diversion capability that is needed in current thermal projects. In FY90, laboratory tests in 1-D and 2-D models will be conducted to evaluate these formulations under conditions corresponding with Kern County, California, steamflooding operations.

In FY89, a numerical steamflood simulator was developed to assist in the evaluation and design of steamflooding laboratory experiments with and without the use of steam diverters. Modifications and validation of the simulator will be conducted in coordination with project BE11A to produce a simulator that will assist researchers in evaluating and designing future steamflood experiments.

Although several excellent monographs have been published on steamflooding and on the theory and design of the process, no comprehensive analysis of a field operation of a steamflood has been reported. Much of the petroleum resource abandonment is attributed to stripper well operations conducted by the small independent operator. State-of-the-art technology needs to be directed for the benefit of these independent operators who cannot support an

engineering and research staff. A literature analysis and coordinated effort to solicit contributions from industry to document field operations of cyclic and steamdrive field operations will be undertaken with the intention of publishing a comprehensive analysis. The benefits of such a report would impact the field operators in 1 to 2 years, and therefore, is a near-term goal-oriented task.

OBJECTIVES

To improve the understanding of the basic mechanisms responsible for the improvement of heavy oil production using steam and to use this understanding for further development of this production method..

Specifically for FY90, the objectives are as follows:

- (1) investigate the effectiveness of mobility control and diverting agents in diverting steam from a zone of high permeability to a zone of lower permeability;
- (2) compare the predicted values obtained with the numerical simulator with laboratory-measured values of steamflood performance; and
- (3) compile and write a state-of-the-art summary on the operation of steamfloods.

SCOPE OF WORK

Task 1. Conduct multiple-zone steamflood experiments using crude oil and mobility-control agents. (Start date: October 1989. Completion date: August 1990.)

The objective is to evaluate the use of high-temperature surfactants for diversion of steam using the existing 2-D model. Low-pH alkaline chemicals will be added to reduce surfactant requirements along with high-temperature tolerant surfactants. These formulations are being combined to accelerate the propagation of the foam front. Statistical design and sensitivity analysis of experiments will be used to minimize the number of experiments and obtain the best results.

Task 2. Test numerical simulator developed in FY89 and publish results.

(Start date: October 1989. Completion date: September 1990.)

The objective of this research is to utilize the numerical simulator developed during FY89 to history match laboratory experiments and conduct parameter sensitivity studies to define controlling factors in laboratory steam experiments to improve laboratory evaluations. This simulator will be used to statistically design laboratory experiments.

Task 3. Conduct state-of-the-art review of steamflood field operations.

(Start date: October 1989. Completion date: September 1990.)

The objective of this task is to write a state-of-the-art review of steamflood field operations. This will encompass a literature review and coordination of contributions from field operating personnel to assemble a guide for field operators with minimal thermal oil production experience.

DELIVERABLES

- Sep 90   Status report that describes research conducted on heavy oil in support of thermal processes for heavy oil recovery under this program.

- Sep 90   Status report on the state-of-the-art in steamflood field operations.

- Sep 90   Topical report on numerical simulator.

PLANNED STAFFING

	<u>Man-Years</u>
Senior and Research Chemists	0.3
Research and Associate Engineers	0.8
Technicians	<u>0.5</u>
Total	1.6

Project Leader

David K. Olsen, Senior Chemist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
One- and two-dimensional steamflood apparatus	2	
High-temperature wettability apparatus	1	
Gas chromatograph	1	
HPLC pumps	2	
Microcomputer		1

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

BACKGROUND

Methods designed to maximize oil and gas production from a reservoir can be improved by having a detailed understanding of rock structure within the reservoir. The pore-space geometry of reservoir rocks strongly influences water, oil-gas distribution, oil-gas entrapment, and fluid-flow properties within a reservoir. Knowledge of interrelationships between measurements at pore to whole core scales is required to evaluate the applicability and accuracy of various core measuring techniques. Application of image analysis techniques for characterizing drill cuttings and sidewall core samples, which are commonly available, can be especially useful for determining the petrophysical properties, fluid flow, and trapping parameters of reservoirs. This research has near-term potential of improving oil recovery by contributing to the accuracy of modeling the internal anatomy of reservoirs.

Direct visual examinations of the pore-space geometry, fluid distributions in the pores, and fluid distribution at the core level are necessary steps in understanding mechanisms controlling fluid-flow and trapping within the reservoir rock. Such observations are necessary initial steps prior to building realistic mathematical models which can predict the effect of pore level heterogeneity on core level flow parameters. The improved mathematical models are expected to lead to near-term applications in oil recovery prediction.

Pore level measurements can be performed by the use of computer-assisted image analyses of thin sections and micromodel observations. While thin section measurements yield geometry-related pore data, observations with micromodels generate an understanding of the actual multiphase fluid flow within a certain porous medium.

Core-scale measurements of spatial distributions of both rock properties and fluid saturations can be performed by computed tomography (CT) and nuclear magnetic resonance imaging (NMRI). These methods have recently emerged as powerful nondestructive investigative techniques. At spatial resolutions of 0.5 mm for CT to 0.05 mm for NMRI, they are ideal tools for studying average properties over a small number of pores.

In FY88 the main effort in this work was directed toward setting up an image analysis laboratory. It has been equipped with a full-color, real-time image analysis system having the capability to measure lengths, areas, angles, and pixel intensities on features defined by operator threshold selection.

The main accomplishments in the micromodel study areas have consisted of developing improved techniques for fabricating thin-slab, pore-cast, etched-glass, cryolite, and sandpack micromodels. Second, appropriate optical observation systems have been set up for each micromodel technique. Third, a NMR spectrometer has been modified, and images of water saturation distribution have been generated for both sandpacks and sandstone cores.

The FY89 work has involved: 1) Upgrading the equipment and software for petrographic image analyses, improving the methodology for generating high-quality images of porous media obtained from thin sections, and developing improved algorithms to generate pore and grain measurements. By statistically processing data obtained from thin sections of plugs or drill cuttings and using formulas based on the Kozeny-Carmen model, accurate values for porosities and permeabilities for relatively clean (<5% clay) sandstone samples have been computed. 2) Micromodel development has yielded more realistic thin-slab, etched-glass, and cryolite models. Using the refined models, two- and three-phase flow studies have been performed under various steady and unsteady state flow conditions. 3) Resolution has been increased by designing and installing an improved magnetic field gradient coil for the NMRI apparatus. 4) A Siemens SOMATOM II, third-generation, medical CT scanner has been purchased and installed. Previous work done on this CT scanner showed it to be extremely useful in core imaging work.

The addition of the HP CT scanner to existing NMR imagery, petrographical image analysis, and micromodel studies provides NIPER a unique and powerfully integrated approach to the study of pore to core scale features. The interrelationships of parameters measured at various scales offers some exciting resolutions of basic questions on reservoir internal anatomy. Accurate, efficient, and cost-effective methods of pore to core scale characterization can be expected using this integrated approach. Predictive equations for fluid flow and oil trapping in hydrocarbon reservoirs should evolve out of this effort. NIPER's image analysis capabilities have been utilized by industrial clients, demonstrating the near-term applicability and interest in this integrated technical approach.

OBJECTIVES

To further development and use of new imaging techniques to measure pore geometry and fluid distribution in reservoir rock at scales varying from pore level and whole core. To study the interrelationships of microscopic-scale rock heterogeneities on oil trapping in core-size rock samples.

SCOPE OF WORK

Application of the above imaging capability will be used to measure pore-related parameters and microscopic fluid distributions. Image analyses of thin sections, micromodels, CT, and NMR scans will be used to study the effect of pore structure on two-phase fluid-flow in reservoir rock. This investigation will provide data regarding the pore geometry of selected rocks and will identify interrelationships between the pore geometry, topology, and fluid distribution within the rock medium at various scales. Through the use of CT scans, NMR images, thin sections, and micromodels that represent successively smaller rock volumes; the interrelationships between petrophysical properties at various scales will be studied. An important contribution of this part of the project will be to correlate micron scale pore data obtained from thin sections and micromodels, with NMR and CT images of fluid distribution obtained at the millimeter to centimeter scale. The resultant data can be used to predict single and multiphase flow in porous media and to design proper scaleup models.

Task 1 addresses the improvement and integration of procedures and software used in image measurements. Tasks 2 through 4 address the study of interrelationships between pore structure and fluid distribution.

Task 1. Adapt the CT scanner for measurements of spatial distributions of two-phase fluid saturations. (Start date: October 1989. Completion date: April 1990.)

Software, measurement techniques, and calibration procedures will be developed to allow the display of quantitative images of two-phase fluid saturations in porous media.

Existing image analysis systems will be interfaced with the CT scanner to allow advanced image processing and measurement.

Task 2. Measurements of single and two-phase spatial fluid distributions in large core plugs. (Start date: October 1989. Completion date: May 1990.)

Large core plugs (1½ to 2 in. diameter, 6 to 12 in. long) containing heterogeneities encountered in typical reservoirs will be analyzed. Cores will be selected from formations (outcrop or subsurface) for which good geological characterization exists, when possible.

Gas permeability and porosity of the coreplugs will be determined. The core will then be imaged using the CT scanner at centimeter intervals under the following reservoir conditions: (1) dry, (2) saturated with tagged brine, (3) saturated with oil (residual brine), and (4) saturated with brine (residual oil). If feasible, flooding will be performed for various mobility ratios. Two-dimensional (2-D) images will be analyzed for variations in rock properties and fluid trapping. If available, a three-dimensional (3-D) reconstruction package will be used for a better understanding of fluid distribution in cores. The CT images from one of the two cores will be used in selecting locations where small core plugs, thin sections, and slabs for micromodels will be taken for subsequent pore-size scale image analysis. Using image analysis techniques from thin sections, the pore size, geometry and topology, pore throat size, and pore coordination numbers will be measured. Pore throat measurements will be verified by using mercury injection. Fluid saturations for groups of pores will be observed by NMRI on the small core plugs.

Task 3. Micromodel study of pore level fluid distributions. (Start date: January 1990. Completion date: June 1990)

Thin-slab micromodels will be manufactured from representative rock samples selected in task 2. Microscopic two-phase fluid-flow, fluids distribution, and trapping will be studied by using optical, CT, and NMR imaging. The results are expected to provide a better understanding of the effect of pore geometry on the in situ movement and trapping of fluids.

Task 4. Study of correlations of pore geometry to fluid distribution in porous media. (Start date: January 1990. Completion date: September 1990)

Rock property and fluid distribution measurements at various scales (from microns in micromodel to centimeter in CT scans) will be correlated. Conclusions will be drawn regarding the effects of small-scale rock heterogeneity on fluid flow and fluid trapping.

The feasibility of correlating 1) pore geometry data, 2) micromodel fluid observation, and 3) saturation data measured by CT and NMRI to current theoretical models and simulation schemes will be evaluated.

DELIVERABLE

Sep 90 Topical report on the applicability of imaging techniques in establishing correlations of pore-level data to core-level fluid distributions.

PLANNED STAFFING

	<u>Man-Years</u>
Research Physicist	0.7
Senior Research Physicist	0.2
Research Engineer	0.5
Associate Engineer	0.6
Associate Geoscientist	0.2
Technician	<u>0.6</u>
Total	2.8

Project Leader

Liviu Tomutsa, Research Physicist

EQUIPMENT REQUIREMENTS

	<u>Available</u>	<u>New</u>
Optical microscope	1	
Image analyses system	1	
SEM	1	
NMR	1	
CT	1	
Low light video camera (b&w)	1	
Low light video camera (color)	1	
Mercury injection apparatus	1	
Upgrading scanning setup		1
CT Scanner		1

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

Fuels Research

At present, the primary emphasis in Fuels Research (FR) is directed toward the analysis, characterization, and upgrading of heavy petroleum feedstocks. These feeds are being introduced into processing streams of an increasing number of petroleum refineries to supplement diminishing supplies of conventional light petroleum stocks and are expected to be a substantial part of the refinery inputs in the future. Unfortunately, heavier crudes vary in composition and generally contain undesirable complex chemical components which cause a multitude of problems during distillation, upgrading, blending, storage, and use.

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 a methodology to analyze heavy fuels. Its objective is to identify compounds which may have significant positive or negative effects on the properties and characteristics of crude oils and their products and to develop methods for their determination in conventional or heavy petroleum and syncrudes. The effort for FY90 focuses on the analysis of coking tendencies of certain compound classes and the extent of association between metal-containing and nonmetal-containing compounds. In addition, data from previous work on the development of mass spectrometric methods for the analysis of acidic compounds will be interpreted and a final report prepared.

In project BFR3, NIPER scientists continue the thermodynamics research effort that is based on an assessment of needs developed in FY86. Thus, work will continue on determining the thermodynamic properties of pure organic nitrogen compounds and compounds containing two heteroatoms (sulfur, nitrogen, oxygen, or a metal). Work will also continue on the evaluation of thermodynamic equilibria possible during the removal of nitrogen by hydrotreating or hydrocracking heavy petroleum and shale oil.

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

Past work in this project emphasized development of methods for the analysis of acidic compounds in heavy petroleum including: NMR analysis of functional groups tagged with ^{13}C - and ^{119}Sn -containing agents, infrared analysis of trifluoroacetyl and trifluoroethyl acid derivatives, GC/MS and MS analysis of the above, and nonaqueous titration with very strong bases. In addition, exploratory work on methods for analysis of metal-containing compounds was conducted and a comprehensive report on analysis of Cerro Negro heavy oil written. Work performed to date on metal-containing compounds indicates that they are extensively associated with nonmetal-containing compounds, thereby making them appear to be higher in molecular weight and more chemically diverse than the true monomeric species.

Although significant progress has been made in analytical method development under this and other DOE projects, as well as in industry-supported research, a major gap persists between analytical capabilities versus the level of understanding needed for their effective application. Thus, the potential benefits of newer analytical techniques are not often realized in practice because: 1) the relevant compositional parameters have not been identified or 2) appropriate relationships between composition and the desired property have not been developed. For example, total nitrogen rather than detailed breakdowns of nitrogen-containing compounds is typically used for predicting process performance because the process chemistry of individual species or even groups of compounds has not been defined. Similarly, physical properties such as thermal stability or corrosion tests are used to define product quality because the species actually responsible for poor fuel performance have not been identified.

It is important to measure every compound in heavy petroleum fractions. Thus, in the course of analytical method development, greater emphasis should be placed on determining the impact of the measured compound or compound class on process chemistry, physical properties and/or other parameters. Then measurements can be tailored for specific compounds to obtain a processing goal. In this context, analytical method development encompasses a broader scope of work which includes elucidation of known chemical/physical phenomena

as well as compound identification with subsequent determination of chemical/physical properties or effects.

OBJECTIVES

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 FY90 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 acidic compounds in petroleum.

SCOPE OF WORK

Distillation and liquid chromatography (LC) will be used to generate fractions of varying boiling range and 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. Results will be interpreted in the context of the probable structure(s) of compounds in each fraction.

The extent of association between metal-containing and nonmetal-containing compounds in the presence and absence of agents designed to break the association will be monitored primarily with the size exclusion LC-inductively coupled plasma technique. In addition, the presence of metal porphyrins will be determined by visible spectroscopy and normal phase LC. Previously separated acid and base fractions from petroleum residues will be used to test the effectiveness of prospective dissociation agents.

Much of the remaining work in development of mass spectrometric methods for acidic compounds consists of data interpretation and report writing. Experimental work will be minimal.

Task 1 - Determine coking tendencies of compound classes. (Start date: October 1989. Completion date: September 1990)

Nominal >1000° F resids from five crude oils will be separated into strong acid, strong base, weak acid, weak base, and neutral fractions using nonaqueous ion exchange LC. Neutrals will be further separated into saturate, neutral-aromatic, sulfide, and polar-neutral fractions. Elemental C, H, N, S, Ni and V will be determined in the whole resid and in the above fractions, as well as in the corresponding carbon residues from each. The percent of a given element present in the chromatographic fractions as well as their corresponding carbon residues will be determined for each resid. These data will be used to relate carbon residue yield to the distribution of compound classes in a given resid, and to identify the compound type(s) primarily responsible for formation of carbon deposits. In addition, the relative deposition of N, S, Ni, and V into carbon residues will be determined as a function of initial chemical form (e.g., sulfide versus thiophenic S).

Task 2 - Develop methods for dissociating and isolating metal-containing compounds (Start date: October 1989. Completion date: September 1990)

A combination of chemical treatments, chromatographic separations, and instrumental analyses will be employed in a series of experiments designed to: 1) assess the extent of association between metal-containing and bulk components and 2) to minimize that association. Development of a normal phase HPLC technique for metal-porphyrin isolation will be continued.

Task 3 - Develop mass spectrometric methods for analysis of acidic compounds (Start date: October 1989. Completion date: September 1990)

A second report on GC/MS analysis of hydroxyl compounds as their trifluoroacetate esters (sequel to NIPER-396) will be written.

DELIVERABLES

Sep 90	Task 1 - Topical report on coking tendencies of various compound types found in resids.
Sep 90	Task 2 - Status report on the development of methods for dissociating and isolating metal-containing compounds.
Sep 90	Task 3 - Topical report on the development of mass spectrometric methods for analysis of acidic compounds.

PLANNED STAFFING

	<u>Man-Years</u>
Senior Chemist	0.7
Research Chemist	0.4
Assistant Chemist	0.7
Technician	<u>0.7</u>
	2.5

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 gravity of crude oil processed in the United States has dropped from an average of 34.2° API in 1978 to 32.2° API in 1987. 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, shale oil, 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. These data are necessary to determine such things as optimum chemical reaction sequences; optimum reaction compositions, temperatures, and pressures to obtain desired conversions; the cooling or heating requirements for reaction vessels; the capacity of heat exchangers; and the size, strength, and complexity of separation vessels.

The data available for light petroleum which contained 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 results and procedures developed for light crudes are often not applicable. The thermodynamic data base for the components of these alternate crudes is severely limited. Efficient processing of such crudes requires research programs to study the different compound types present. These programs will include larger, and often more reactive molecules than before, will have to be studied to higher temperatures than before, and generally will have to maintain the accuracy and precision of the data on 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 and Process Technology (AEPT), Advanced Research (AR) and Basic Energy Sciences Office of Energy Research (OER). The crosscutting nature of the research funded by the AEPT, AR, and OER sections of the Office of Fossil Energy is summarized in Figure 3-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.

The section of the overall research program discussed here is funded by AEPT. It is concerned with organic nitrogen- and diheteroatom-containing compounds. The program represents, in part, the results of the comprehensive

FOSSIL FUELS

FIGURE 3. - Exhibit 1.

state-of-the-art assessment undertaken in FY86. Thermodynamic considerations arising from previously 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 goal is to answer 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?

The investigations cover: the role of equilibria, the interplay of thermodynamics and kinetics, and the effect of choice of catalyst on the aromaticity of the final products.

The substances selected for study quite often are either not available or cannot be purchased from chemical supply houses in the purity required. Thus, an essential part of this work is the synthesis and purification of these compounds through a subcontract with an Oklahoma State University research 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 which 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 shale oil. The results will enable the prediction of chemical equilibria for conceptual as well as current processes and for the prediction of properties needed downstream from the reactor stages.

SCOPE OF WORK

Task 1. - Thermochemical measurements on organic nitrogen compounds.

(Start date: October 1989. Completion date: September 1990.)

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 nitrogen heterocyclics using the minimum quantity of hydrogen.

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 ongoing experiments on these substances.

C. Use the recently reactivated vapor-flow calorimeter to determine vapor-phase heat capacities of isoquinoline over a range of temperatures. Make measurements of the enthalpies of vaporization over a series of pressures and, hence, derive second virial coefficient data for this important class of aromatic nitrogen compounds. The results from this portion of the work plan will produce definitive ideal-gas heat capacities for isoquinoline thus solving the discrepancy between the calorimetric and spectroscopic values reported in NIPER-301. The derived second virial coefficients will add to the meager data available on the properties of aromatic nitrogen compounds in the real gas state and aid in future equation of state development.

Task 2. - Thermochemical measurements on selected diheteroatom-containing compounds. (Start date: October 1989. Completion date: September 1990.)

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 quantity 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 shale oil upgrading. (Start date: October 1989. Completion date: September 1990.)

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.

DELIVERABLES

Nov 89	Topical report on the thermodynamic properties of trans-decahydroquinoline and 2-methylaniline.
Feb 90	Topical report on the the overall hydrodenitrogenation reaction scheme for quinoline.
Jun 90	Topical report on the thermodynamic properties of 2-aminobiphenyl and the related compounds 2-methylbiphenyl and 2-hydroxybiphenyl.
Aug 90	Topical report detailing the thermodynamic analyses performed in task 3.
Sep 90	Status report on the research program summarizing data acquired, its utility, and an updated assessment for future work.

PLANNED STAFFING

Man-Years

Director	0.05
Manager	0.08
Senior Chemists	0.65
Research Chemists	0.32
Research Physicist	0.32
Associate Chemist	0.35
Senior Experimentalist	0.34
Technical Support	<u>0.07</u>
Total	2.18

Project Leader

William V. Steele, Senior Chemist

APPENDIX 1. - CAPITAL EQUIPMENT REQUIREMENTS

Project No.	Equipment	Cost (\$K)
Base Program		
BE1	Microcomputer (2 each)	7.0
BE2	Microcomputer	4.0
BE3	Partial payment for gas chromatograph	5.0
BE4A	Ion conductivity detector	3.0
	Partial payment for CT scanner	2.5
BE4C	Reciprocating pump	1.3
BE5A	Partial payment for gas chromatograph	5.0
	High pressure UV-VIS spectrometer	4.5
BE5B	Partial payment for Gas Chromatograph	5.0
BE9	Microcomputer	5.0
	Partial payment for CT scanner	18.0
	Resistivity meter	4.0
BE11A	Microcomputer	4.0
BE11B	Microcomputer	4.0
BE12	Partial payment for CT scanner	16.5
	Upgrade scanning set-up	<u>10.0</u>
Total Base Program		98.8
NIPER Support		
	Word processing-reproduction and/or computer	40.0
	Safety	10.0
	Maintenance	10.0
	Miscellaneous	<u>10.0</u>
Total NIPER Support		70.0