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Contracts for field projects
and supporting research on . . .

Enhanced Oil Recovery and Improved Drilling Technology

34

DOE/BETC-83/2
PROGRESS REVIEW
Quarter Ending March 31, 1983

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PROGRESS REVIEW NO. 34

CONTRACTS FOR FIELD PROJECTS AND SUPPORTING RESEARCH ON ENHANCED OIL RECOVERY AND IMPROVED DRILLING TECHNOLOGY

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Date Published — July 1983

UNITED STATES DEPARTMENT OF ENERGY

LOCATION OF DOE CONTRACTS FOR RESEARCH ON ENHANCED OIL RECOVERY

Program	Funding (Millions)			Performer	Location
	Total	Contractor	Government		
Chemical Flooding	13.1	7.7	5.4	Cities Service Company	El Dorado, KS
	11.6	7.0	4.6	City of Long Beach (caustic)	Wilmington Field, CA
	35.0	20.1	0.5	Conoco, Inc.	Big Muddy Field, WY
	3.8	2.2	1.6	Energy Resources Co., Inc.	Storms Pool Unit, IL
	43.0	29.6	14.0	Marathon Oil Co.	Robinson Field, IL
CF TOTALS	107.7	72.6	35.1		
Carbon Dioxide Flooding	5.6	2.8	2.8	Gulf Oil Exploration & Production Co.	Little Knife Field, ND
	0.0	3.8	2.8	Pennzoil Co.	Rock Creek Field, WV
	6.5	4.0	2.5	Shell Oil Co.	Iberia Parish, LA
CO₂ TOTALS	18.7	10.6	8.1		
Thermal Recovery	8.2	5.1	3.1	Cities Service Co.	Bellevue Field, LA
	23.2	0.0	23.2	Sandia Laboratories	Albuquerque, NM
	8.2	0.5	1.7	Santa Fe Energy Corp.	Midway Sunset Field, CA
	2.2	0.0	2.2	Stanford Univ. Pet. Research Inc.	Bakersfield, CA
TR TOTALS	41.8	11.6	30.2		
GRAND TOTALS	168.2	94.8	73.4		

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In the June 1983 issue of World Oil, J. Stephen Moore of Gulf Oil Exploration and Production Co., New Orleans, reports on a CO₂ EOR pilot that is recovering additional oil from a watered-out reservoir in a Mississippi Delta area Miocene field. The CO₂-WAG (water-alternating-gas) miscible pilot flood is in Quarantine Bay field, Louisiana, about 50 miles southeast of New Orleans.

Cumulative production through September was 26,600 bbl of oil and 512,000 bbl of water. Cumulative injection was 19,000 tons of liquid CO₂ and 200,000 bbl of water. The CO₂-WAG process appears to be working, as evidenced by a cumulative ratio of 4.03 Mcf of CO₂ per barrel of produced oil from an essentially watered-out reservoir. The comprehensive article describes the project, method of CO₂ acquisition, field facilities required, and production response. Operational problems encountered are also discussed.

Union Oil Co. of California has announced a polymer flood for recovery of tertiary oil from a unit in Healdton field, Oklahoma. The remaining reserves under waterflood are estimated at 2.4 million bbl. Projected remaining reserves with polymer injection are 3,366,000 bbl. A synthetic polyacrylamide polymer along with a chromium ion solution alternated with a bisulfite solution will be injected.

Texaco plans a polymer-augmented waterflood in Carthage Northeast Morrow A Unit, Texas County, Okla., and Morton County, Kans. Initially, a 99,000-lb slug of complexed polysaccharide will be injected. Subsequent polymer injection will be determined by project performance. Texaco owns about 66.5 percent of the working interest. The rest is held by Anadarko Production Co. (Oil & Gas Journal, June 13, 1983.)

Crude oil inputs to refineries averaged 12.0 million bbl/day for the 4 weeks ending June 10, 1983, when stocks of crude oil stood at 355.3 million bbl. For that period, net imports of crude oil (including imports for the SPR) and petroleum products together averaged 4.0 million bbl/day, about 3 percent below the average a year ago. The estimated weighted average international price of crude oil as of June 15, 1983, was \$28.59/bbl. (Weekly Petroleum Status Report/Energy Information Administration report No. DOE/EIA-0208, 83/24.)

In the June issue of Drilling, Robert O. Frederick continues his series on enhanced oil recovery with "EOR--The Peregrinations of Chemical Tracers." Using his expert writing style, Bob translates the

complex jargon of radioactive tracers and chemical tracers into an easy-to-read, interesting article and includes a brief bibliography. We're hoping that Drilling will offer this series as a reprint when it is completed; it would be an excellent addition to the EOR literature.

The 405-mile Sheep Mountain Pipeline will furnish carbon dioxide for the Seminole, Texas, San Andres Unit EOR project operated by Amerada Hess for itself and 87 other companies and individuals. According to Mike Slaton in the June issue of Drilling, a maximum rate of about 320 million cfd of CO₂ will be injected, with a total of 1.2 trillion cf of CO₂. The project is expected to recover 175 million additional bbl of oil. The throughput capacity of the pipeline is 500 million cfd.

Drill Bit Editor Renee Wash, reporting on the San Andres EOR project in her June issue, describes the opening ceremonies held April 15. In the opening address, Philip Kramer, president of Amerada Hess, said, "The capital required to develop and equip the Seminole Unit for tertiary recovery is in excess of a half-billion dollars. The pipeline cost more than \$240 million, and the ultimate development of the CO₂ fields at Bravo Dome and Sheep Mountain will require in excess of \$1 billion."

An additional 35.2 million bbl of oil is expected to be recovered from the injection of CO₂ in a portion of the Means San Andres Unit. Exxon is planning to start injection in January 1984. It is predicted that 252 billion cf of CO₂ will be required for the project, with 144 billion cf purchased from the Sheep Mountain field and the balance recycled.

Darnell Peacock of The Land Rig Newsletter (P.O. Box 73647, Houston, TX 77273), in his June issue, says latest monthly comparisons show the international rig count holding steady. The Hughes Tool tabulation (excluding the U.S. and Canada) shows 1,273 units active in May, down from 1,279 the previous month and from 1,486 a year earlier.

Gulf Oil is planning a miscible CO₂ EOR project for West Texas. The \$7.6 million project covers injection of CO₂ alternating with water in Waddell East Ranch Unit, University Waddell (Devonian) field, Crane County.

Cumulative production of crude oil from the North Sea was 3.6 billion bbl as of Jan. 1, 1982, and there is an estimated 25.5 billion bbl of recoverable crude oil remaining. That cumulative production brought the total estimated ultimate oil recovery to 29.1 billion bbl and the recovery efficiency to 30.5 percent of the original oil-in-place. From both known and undiscovered oil deposits, production could be maintained to the year 2013 at a constant rate of 2.5 million bbl/day; at 3.25 million bbl/day, to the year 2004; and at 4 million bbl/day, to the year 1998. (The Petroleum Resources of the North Sea, Energy Information Administration, (202) 252-8800.)

Tar sands recovery projects underway in Maverick and Zavala Counties, Texas, are targeted beyond the short-term oversupply of crude oil to the day when the country needs every available ounce of fossil fuel, reports Vernetta Mickey in May 1983 Drill Bit. Conoco, Exxon, Enpex, and Chaparrosa Oil are named as being involved in shooting for an estimated 2 billion to 3 billion bbl of -2° API tar that underlies 90 sq. miles of arid South Texas 30 miles northeast of Eagle Pass.

By reinjecting produced gas into the formation, Petromax Energy Corp., Denver, says it can maintain the integrity of the Codell, reap maximum condensate recovery, and store the gas until marketing conditions improve. The Codell Formation is sensitive. Petromax is conducting a pilot test of the production method on two of its Weld County, Colo., prospects. (Western Oil Reporter, May 1983.)

Various sources can supply CO₂ for EOR projects. One source is boiler flue gas, which is generated by burning natural gas, oil, petroleum coke, or coal. Roland E. Meissner III, Ralph M. Parsons Co., reports on "Removing Carbon Dioxide From Boiler Flue Gas" in the June 1983 issue of Oil & Gas Digest. He says several alternative processing schemes for removing CO₂ from boiler flue gas use an aqueous amine solution; however, before the CO₂ can be removed, particulates and sulfur and nitrogen oxides must be removed. Particulates cause amine solution foaming, and sulfur and nitrogen oxides form non-regenerable, highly corrosive salts by reaction with amine.

In the July issue of Drilling magazine, Greg Holloway, reporting on domestic rig activity, says, "Although the domestic count is beginning to build up steam, there's still a lot of iron in the domestic patch that's being mothballed or cannibalized. Our estimates indicate that as many as 1,000 rigs will have been taken out of 3,000 ft and deeper domestic service by the end of July. We know of one company that predicts a loss of 2,000 rigs."

The Supply and Demand Committee of the IPAA reached the following conclusions concerning the domestic economy and the petroleum industry for 1983 during its mid-year meeting in late May: Economic activity will register a 2.6-percent real increase in 1983, following the 1.7-percent decline in 1982. Energy consumption will show a 0.4-percent rise in 1983, reversing a 3-year decline. Oil demand will decrease slightly to 15.2 million bbl/day in 1983, which is 88,000 bbl/day less than in 1982. Oil imports will remain at about 4.9 million bbl/day in 1983. Crude oil production will decline slightly in 1983, after marginal gains in 1982. Natural gas consumption is expected to fall in 1983, following an earlier decline in 1982.

For the second month in a row, the Nation's seismic crew count moved upward in May, according to the Society of Exploration Geophysicists, based in Tulsa. The increase in the number of seismic land

crews and marine vessels searching for oil and gas in the U.S. and U.S. waters is regarded as a bright sign in the exploration picture.

The SPE paper entitled "Prospects of Commercialization, Surfactant/Polymer Flooding, North Burbank Unit, Osage County, Okla.," by the late Dr. J. C. Trantham, was published by the SPE in the May 1983 issue of Journal of Petroleum Technology. This project provides a thoroughly documented case history of a surfactant-polymer flood from the planning stage to final evaluation.

The May 1983 issue of J. Pet. Tech. also contains an article by S. Robert Aydelotte of Intercomp and Gary A. Pope of the University of Texas entitled "A Simplified Predictive Model for Steamdrive Performance." Through a DOE contract administered by BETC, a model has been constructed to facilitate screening and evaluation of reservoirs for application of steamdrive as an EOR process. The model extends existing analytical heat-balance models to include fractional-flow characteristics, vertical and areal sweep effects, steam injectivity, and heat losses in well bores and surface pipes in a single, easy-to-use computer program.

In the past 33 years, the average U.S. well depth has barely increased, standing in the 1980's at the 4,531 ft for a meager gain of 539 ft over the 3,992 ft recorded in the '50s, says Alvara Franco in the July 1983 issue of Drilling Contractor. He reports that if an average can be taken from the 33 yearly figures, the mean depth of the typical U.S. well stands at 4,452 ft for the 3-decade span.

Results of the Forest Hill field (Texas) oxygen-enriched in situ combustion test show that essentially pure oxygen can be handled and injected safely in a typical oil-producing field and that oxygen-enriched air can be used to advantage in oil recovery by means of in situ combustion. Test results are reported in the June 1983 issue of J. Pet. Tech.

If you're interested in improving oil recovery by injection of nitrogen, read Bruce Bleakley's article "Nitrogen From Air Aids Condensate Recovery" in the July 1983 issue of Petroleum Engineer. He says, "Of all the fluids being injected to improve recovery from hydrocarbon reservoirs, including those being considered for injection, nitrogen is grabbing the lion's share of attention." For example, just north of Evanston, Wyo., Chevron U.S.A. Inc. is injecting nitrogen to enhance oil recovery in the Painter field from an on-site air separation plant operated by Niject, which has increased capacity to more than 45 MMcfd. The purpose of nitrogen injection is to maintain reservoir pressure to promote miscible displacement of oil in the reservoir.

Bill Linville

Editor

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GENERAL RESEARCH

Quarterly Reports

DOE/BETC/QPR-82/3. Liquid Fossil Fuel Technology. Quarter ending September 30, 1982. Edited by Bill Linville. January 1983. 76 pp. Progress reports on research projects conducted by Bartlesville Energy Technology Center personnel and contractors are given, with emphasis on liquid fossil fuel projects. Reports are included from BETC's Divisions of Extraction Research, Processing and Thermodynamics Research, Utilization Research, and Project Integration and Technology Transfer. Free subscription available upon request.

Special Publications

DOE/BETC/SP-83/7. List of BETC Publications. BETC staff. March 1983. 28 pp. This report is a compilation of the 1982 BETC publications lists and includes abstracts of all reports published by BETC from January through December 1982.

EXTRACTION

Enhanced Oil Recovery—General

DOE/BETC-82/4. Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery and Improved Drilling Technology. Progress Review No. 32, Quarter ending September 30, 1982. Edited by Bill Linville. January 1983. 116 pp. Status reports are given of various enhanced oil and gas recovery

projects sponsored by the Department of Energy. The field tests and supporting research on enhanced oil recovery include chemical flooding, carbon dioxide injection, thermal/heavy oil recovery, microbial recovery, and residual oil determination. Other research includes resource assessment, extraction research, improved drilling methods, environmental technology, and oil recovery by gravity mining. Free subscription available upon request.

DOE/ET/14010-1. Enhanced Oil Recovery in the Gulf of Mexico. Lewin and Associates. January 1983. 422 pp. This project was designed to identify reservoirs in the Gulf that are geologically, technologically, and economically amenable to enhanced oil recovery (EOR). Reservoirs containing 56 percent of the Gulf's oil-in-place were studied individually. A subset of reservoirs, accounting for about 20 percent of the overall resource, was assessed in detail using engineering and economic models. The results indicate that the EOR potential could be up to 4.4 billion barrels in known reservoirs. Technological performance could have a great effect on the EOR potential, especially the ability to recover oil from zones of the reservoirs previously unswept by conventional operations. The rapid decline of many fields in the Gulf will lead to the abandonment and removal of platforms, which would economically prevent recovery of substantial portions of the EOR potential. Therefore, collaboration by industry and government research and development agencies is needed to realize the offshore Gulf potential.

DOE/BC/10115-2. Oilfield Water Analyses Data Bank. University of Oklahoma. February 1983. 26 pp. This report describes the work performed in collecting, evaluating, and computerizing oilfield water analyses for the Oilfield Water Analyses Data Bank. The computer file containing these analyses is known as the BRIN file. The file currently contains 77,650 analyses obtained by contacts with industry sources, state and federal agencies, and publication searches. Each listing gives the API well number, well classification, depth from which the sample was taken, lithology of the well, name of producing formation, porosity and permeability of pay zone, bottom hole pressure, and any additional information available.

DOE/PC/30259-1. An Evaluation of Heavy Oil Mining, Final Report, Volumes 1 and 2. Energy Development Consultants/Stone & Webster Engineering Corp. March 1983. Vol. 1: 266 pp. Vol. 2: 316 pp. Oil mining is one technology that shows promise for recovery of heavy oil from U.S. resources unrecoverable by conventional production methods. Three mining techniques—surface extractive mining, underground extractive mining, and mining for access—were studied for their technical, environmental, and economic feasibility for heavy oil recovery. The study was divided into three areas: (1) evaluation of heavy oil resources amenable to mining based on DOE screening criteria, (2) evaluation of various mining technologies to select those most promising for heavy oil recovery, and (3) study of specific sites for development of preliminary mining concepts and economics.

DOE/SF/11564-1. Analysis of Unit Mobility Ratio Well-to-Well Tracer Flow to Determine Reservoir Heterogeneity. Stanford University Petroleum Research Institute. February 1983. 198 pp. Exact analytic equations were derived to define breakthrough curves for different developed flooding well patterns for unit mobility ratio. Breakthrough areal sweep efficiencies at various mobility ratios were shown to be nearly independent of mobility ratios, while the post breakthrough data were different for each mobility ratio. The study also investigated flow of a tracer slug in various patterns. The results show that the effluent tracer concentration depends upon the pattern geometry and size and the dispersion constant of the formation.

A computer program was developed based on a non-linear optimization technique that decomposes a detected tracer breakthrough profile from a multilayered system into responses from individual layers. A five-spot field example that was successfully decomposed into several layers is shown to illustrate the use of this research.

Enhanced Oil Recovery—Chemical

DOE/BC/10082-12. Adsorption from Flooding Solutions in Porous Media—A Study of Interactions of Surfactants and Polymers with Reservoir Minerals, Third Annual Report. Columbia University. January 1983. 228 pp. Loss of surfactants by adsorption and related processes is a complex phenomenon dependent upon many system parameters. In order to develop a full understanding of the phenomena involved, tests were conducted with well characterized systems of increasing complexity. Initial tests involved adsorption of isomerically pure sulfonates on alumina. Subsequently, clay, oil, and alcohol were gradually incorporated into the study. Studies also have been initiated with problem minerals such as gypsum and limestone under high temperature and salinity conditions.

DOE/ET/10145-74. Data Requirements for EOR Surfactant-Polymer Process Simulation and Analysis of El Dorado Pilot Project Simulation, Butler County, Kansas, Volume I: Technical Report, Volume II: Appendices. Gulf Universities Research Consortium. January 1983. Vol. I: 66 pp. Vol. II: 246 pp. The results of computer simulation of the El Dorado pilot project indicated that conventional data from the project and other data in the public domain were not adequate for geologic, reservoir, and process characterizations in a complex numerical simulation. Based upon this study, a comprehensive body of data requirements for EOR simulation is defined in detail. Geologic characterization includes descriptors for rock, interwell, and intrasystem correlations; reservoir characterization includes descriptors for fluid/rock, production, and flow rate properties; process characterization includes descriptors for chemical properties, interactions, and functions. The appendices include a flow chart for surfactant-polymer process simulation and reports describing the CFTE simulator program used in this study.

DOE/BC/10033-6. Evaluation of the North Stanley Polymer Demonstration Project. Keplinger and Associates. February 1983. 38 pp. The objective of the cost-shared project was to evaluate the technical efficiency and economic feasibility of polymer-enhanced waterflooding in a sandstone reservoir that has been waterflooded successfully and is approaching the economic limits of waterflooding. The ultimate incremental oil recovery from the polymer flood was estimated to be about 570,000 bbl (or about 1.4 percent of the original oil-in-place), significantly less than original recovery predictions. The lower-than-anticipated recovery is attributed principally to the extremely heterogeneous nature of the reservoir.

Enhanced Oil Recovery—Thermal

DOE/ET/12056-28. Comprehensive Analysis of the Carbon/Oxygen Log. Stanford University Petroleum Research Institute. January 1983. 76 pp. This report reviews the current interpretation methods and presents a cross-plotting technique to compute hydrocarbon saturation for induced gamma ray spectroscopy logs. The technique assumes that each reservoir component has a specific ratio of elemental ratios, and the total log response is a linear function of each ratio in the matrix, the hydrocarbon, the formation water, and the shale. The technique has three unknowns: porosity and volumetric fraction of shale (obtained from a standard set of open hole logs) and oil saturation, which is computed from a linear equation that approximates the bulk carbon-to-oxygen response. The equation contains four terms representing both matrix and fluid responses in the reservoir. An example of the empirical cross-plotting approach is given of an observation well of a steam-foam pilot in Kern County, Calif.

DOE/SF/10762-3. Field Demonstration of the Conventional Steam Drive Process with Ancillary Materials. Chemical Oil Recovery Co. March 1983. 212 pp. The most important factors observed regarding the steam foam treated wells in this study were the use of injection profiles, chemical tracers, and production data to show that the creation of an *in situ* foaming agent in a steam drive alters the flow path of the injected steam. Steam diversion created improved sweep efficiency in each of the four treated patterns; however, only two showed improved oil production rates. This indicates that steam must be diverted into areas of the reservoir higher in oil saturation to augment production.

Enhanced Oil Recovery—Microbial

CONF-8205140. Proceedings of 1982 International Conference on Microbial Enhancement of Oil Recovery. Edited by E. C. Donaldson and J. B. Clark. February 1983. 224 pp. An International Conference on Microbial Enhancement of Oil Recovery (MEOR) was held May 16-21, 1982, at Afton, Okla., and was sponsored by the U.S. Department of Energy, the University of Oklahoma Energy Resources Center, and the Engineering Foundation. More than 140 microbiologists and engineers from around the world attended to discuss the development of methods for the application of microbial systems to the petroleum industry. This proceedings contains papers presented at the conference in the following areas: microbes and their metabolites, transport of bacteria in porous geological materials, application to heavy oils, and MEOR field applications.

Western Gas Sands

DOE/NV/10249-4. Western Gas Sands Project Status Report, April-June 1982. CER Corp. January 1983. 102 pp. This report summarizes the quarterly progress of government-sponsored projects to increase gas production from low permeability gas sands of the Western United States. CER Corp. is investigating downhole shut-off to develop a shut-off tool. The University of Oklahoma completed the two-dimensional lenticular well simulator model consisting of the necessary mathematical equations to simulate reservoir fracture and well performance under a variety of specified conditions. Lawrence Livermore National Laboratories completed a two-dimensional crack model, and work has begun on developing a pseudo three-dimensional crack model. Preparations have begun at Los Alamos National Laboratory to test the 6-inch permanent magnet pre-prototype tool; at Sandia National Laboratories, an analytical version of the Surface Electric Potential mathematical model was completed. For the Multi-Well Experiment program, researchers completed cased hole logging, directional surveys, and two geophysical surveys. The data provided by DOE Well Test Facility's drill stem test of MWX-1 indicated wellbore storage was predominant during the buildup period of the test and essentially masks the pressure transient normally used in the analysis. Free subscription available upon request.

DOE/BC/10498-5. Sonic and Electrical Properties of Partially Saturated Tight Gas Sands, Final Report. Stanford University. March 1983. 60 pp. This study was aimed at relating the seismic and the electrical properties of tight gas rocks to their pore space geometry, permeability, and level of water saturation. Results of laboratory experiments of wave propagation in Cotton Valley and Spirit River sandstones as a function of partial water saturation and wave frequency showed that wave velocities and the velocity ratio are sensitive to the presence of gas. Furthermore, wave attenuation is sensitive to the amount of gas in the pore space. Ultrasonic measurements in tight gas sands tend to yield higher velocity values due to the inability of the pore fluid pressure to homogenize during the passage of waves. Laboratory measurements were made of the complex electrical response of selected tight rocks and compared with normal permeability Berea sandstone. The results show that the dielectric property of tight gas sands is very sensitive to partial water saturation and may give insight into the nature of the pore space and provide a practical measure of *in situ* water saturation.

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DIRECTORY

Name	Phone number	Name of contractor
U.S. Department of Energy Office of Oil, Gas and Shale Mail Stop, D-116 GTN, Washington, D.C. 20545		
J.J. Stosur	301/353-2877 — FTS 233-2877	Gulf Universities Research Consortium
Bartlesville Energy Technology Center P.O. Box 1398 Bartlesville, Okla. 74003		
T.E. Burchfield	918/336-2400 — FTS 735-4320	Louisiana State University University of Oklahoma
F.W. Burtch	918/336-2400 — FTS 735-4208	Cities Service Co. Conoco, Inc. Energy Resources Co., Inc. Oak Ridge National Laboratory Petroleum Training & Technology Services University of Tulsa
H.B. Carroll	918/336-2400 — FTS 735-4297	Fuel and Mineral Resources, Inc. University of Kansas Center for Research, Inc. University of Texas
M.E. Crocker	918/336-2400 — FTS 735-4298	GeoChem Research Inc. New Mexico Institute of Mining & Technology
E.C. Donaldson	918/336-2400 — FTS 735-4292	Argonne National Laboratory City of Long Beach GeoChem Research, Inc. Lawrence Livermore Laboratories Oklahoma State University University of Georgia University of Oklahoma University of Southern California
B.L. Gall	918/336-2400 — FTS 735-4386	University of Florida University of Tulsa
B.E. Gammon	918/336-2400 — FTS 735-4210	University of Kansas Center for Research Inc.
M.B. Kayser	918/336-2400 — FTS 735-4357	Lehigh University University of Oklahoma
R.F. Kendall	918/336-2400 — FTS 735-4343	Brookhaven National Laboratory Gulf Universities Research Mitre Corporation Spears & Associates, Inc.
Sandia National Laboratories Division 4755 P.O. Box 5800 Albuquerque, New Mex. 87185		
B.W. Marshall	505/844-2964 — FTS 844-2964	Sandia National Laboratories (Deep Steam)

Name	Phone number	Name of contractor
P.B. Lorenz	918/336-2400 — FTS 735-4272	Columbia University Illinois Institute of Technology State University of New York University of Mississippi
J.W. McGhee	918/336-2400 — FTS 735-4375	Texas Tech University
L.A. Noll	918/336-2400 — FTS 735-4392	New Mexico Institute of Mining & Technology
C.J. Raible	918/336-2400 — FTS 735-4287	New Mexico Institute of Mining & Technology Terra Tek, Inc.
K.L. Spence	918/336-2400 — FTS 735-4319	Colorado State University Gulf Oil Exploration and Production Co. Marathon Oil Co. New Mexico State University
M.K. Tham	918/336-2400 — FTS 735-4387	University of Texas at Austin University of Minnesota
T.C. Wesson	918/336-2400 — FTS 735-4278	Gary Energy Corp. Gulf Universities Research Consortium
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San Francisco Operations Office

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1333 Broadway

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Laramie, Wyo. 82071

L. Dockter	307/721-4011 — FTS 328-4351	Utah Tar Sands
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CHEMICAL FLOODING

FIELD PROJECTS

IMPROVED OIL RECOVERY BY CONTROLLED WATERFLOODING, CAUSTIC

Contract No. DE-AC03-76ET12047

**City of Long Beach
Long Beach, Calif.**

Contract Date: Sept. 30, 1976

Anticipated Completion: December 1982

Total Project Cost:

DOE	\$ 4,633,829
Contractor	6,950,743
Total	<u>\$11,584,572</u>

**Principal Investigator:
Parker Kemp**

**Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office**

Reporting Period: Jan. 1 - Apr. 30, 1983

Objective

The project is an improved waterflood demonstration of alkaline waterflooding in a typical, well flood pattern of the Ranger Zone of the Long Beach Unit portion of the Wilmington Field. A mixture of 4 percent sodium hydroxide and sodium silicate in fresh water containing 0.75 to 1 percent salt is being injected to improve oil recovery.

The demonstration pattern in which DOE participates involves the input of approximately 30,000 to 34,000 bpd water in 8 injection wells which surround 11 active producers in an area of 93 acres. Reservoir engineering studies have shown that the total area being affected by the injection in these 8 wells is much larger, being approximately 200 acres including areas situated both north and south. If the alkaline injection is successful, improved flood efficiency should occur as demonstrated by reduced water-oil ratios and increased oil recovery.

Summary of Technical Progress

Chemical injection continued in the quarter. A simple long-term solution to the floc formed on mixing the dilute alkaline solution with the concentrated salt brine was not found. Alternating 1-week slug injection of soft water with alkali and then soft water with salt continued throughout the quarter. A 4-hour soft water spacer with no chemicals was placed between the slugs.

The injection data for the period are:

1982-1983	No. days in period:		B/D injection rate (total of 8 wells)	Composite composition	
	of soft water- salt injection	of soft water- alkali injection		Weight- percent salt	Weight- percent sodium orthosilicate
Dec. ¹	15	16	35,538	0.6076	0.3691
Jan. ¹	14	17	33,376	0.5877	0.4196
Feb. ¹	14	14	35,107	0.6709	0.3934
Mar. ²	15	16	35,542	0.7284	0.4077

¹ Final figures.

² Preliminary data.

The lower, but satisfactory injection rate for January is a result of downtime in three wells for servicing of B-826-IA. The lower brine contents in the quarter are a result of the brine system's automation being temporarily out of service and plugging of strainers from insoluble salt residues early in the quarter. The injection pump's motor developed defective bearings and was replaced in February.

The brine tanks were cleaned of insoluble materials in January. While the strainers (screens) on the brine system required relatively frequent cleaning, plugging by the insolubles did not seem as severe as at the end of the prior quarter. Because of restricted throughput capacity, water softener No. 2 was cleaned out in February; little or no oil plugging and minor solids contamination of the resin were noted; the restriction appeared to be due to a defective valve which was replaced and capacity of the softener restored. Additional or replacement metering is being installed to permit the softener's operation to be optimized.

The replacement brine system control panel is on order with delivery expected shortly. Throughout the quarter, the brine system was operated manually because the old panel failed. The new manifold for controlling salt input into the injection stream was placed in service. The replacement rotary alkaline chemical pumps and their new low RPM motors were placed in service in February. Their operation has been troublefree in contrast to prior problems with the variable stroke length pumps that were replaced.

FIG. 1 — Ranger economic block 9

A Corrat probe was installed and continuous corrosion rate and O₂ content readings of the injection water were taken. It was found the O₂ content seemed to be related to air introduced into the brine system when the bulk salt was offloaded into the tanks; addition of the oxygen scavenger to the brine tanks/system is being considered. Because of the high rates of corrosion noted during input of the soft water with no chemical spacer slugs, corrosion inhibitor is now added during this 4-hour period. The brine as well as the orthosilicate corrosion rates was substantially less in the quarter.

Additional drilling occurred in the undeveloped portion (downstructure) of the northern area. Injector B-765-I completed in the prior quarter was acid-stimulated. B-759 was completed as a producer in the F, H and upper X sands. Another downstructure (aquifer) injection well, B-769-I, was completed in the F, H, and X sands, produced briefly, and at the end of the quarter was awaiting conversion to injection. Another downstructure injector, B-767-I is scheduled to be drilled early in the next quarter.

Easterly observation producer B-118 was found to have a bad liner which was repaired by installation of an inner liner. The liner of southern area well B-830 was found to be bad; the well was shut-in pending repair. In pattern area injector B-110-1A an attempt was made to change the flow controller regulating injection into the Fo sand; because of loose plastic from the internal coating on the tubing the work could not be completed; work in the well was discontinued until it requires pulling for other reasons. In pattern area injector B-826-1A, fill over the lower subzones was cleaned out and the well returned to injection. In easterly observation injector B-829-1, an attempt was made to install dual tubing strings; the liner's segregation was found to be incompetent and the work cancelled as a result.

Well bore/pump scaling continued to create production operating problems. A sample of scale from B-838 that was taken in the last quarter, but results of its testing received in this quarter indicated a combination carbonate and silicate scale. Samples from B-712 which suffered frequent failures in the quarter indicated a magnesium silicate scale. Prior scale samples in the pilot were acid soluble with no indication of the silicate scale.

B-838, the first well in the pilot that received a scale inhibitor squeeze, ran from January 1 - February 20 when it failed again. The scale squeeze and continuous annular treatment used NL's SURFLO H-35 inhibitor, which is primarily effective for carbonate scale. At the end of the quarter the well was awaiting pulling to evaluate the cause of the most recent pump failure once it again becomes accessible to a well pulling unit.

B-712 became troublesome due to scaling in the quarter and a number of failures of its pump. In early February it

received a small HCl acid job and a SURFLO H-35 scale inhibitor squeezed (designed for carbonate scale). Despite continuous annular treatment with SURFLO H-35 the well produced less than 12 days before the pump failed again. With the receipt of laboratory analyses indicating a magnesium silicate scale, the well subsequently received a larger HCl/mud acid treatment, and a scale inhibitor squeeze that employed NL's SURFLO H-35 and SURFLO RD-1853 scale inhibitors. When placed on production, the SURFLO RD-1853 was used for the continuous annular scale inhibitor treatment. The RD-1853 was formulated to combat scaling problems recently encountered in a Santa Maria basin orthosilicate flood. The well was returned to production on March 15 after the most recent work; as of the date of preparation of this report, the well was still producing.

B-830, a southern area well, was pulled and found to be scaled as well as having a problem with its inner liner. Further pulling work was discontinued until a program for replacement of the inner liner is approved. B-101-A's pump failed in the quarter and the well suspected to be scaled. Diagnostic pulling is planned as soon as it again becomes accessible to well pulling equipment.

There were 12 acid jobs for scale removal including the jobs mentioned above performed in conjunction with scale squeezes in B-712. All but the second job in B-712 were small volume HCl treatments. There were 10 pilot area pump changes in the quarter plus one in a westerly observation well, one in an easterly observation producer and two in an undeveloped portion northern area well. Three and possibly four of these changes were related to scaling problems. Three of these were in B-712 alone.

Six static pressure surveys were made; three were in pilot area wells, two in downstructure undeveloped portion of northern area wells and 1 in an easterly observation well. PHD (downhole electric sensor) operating pressure measurements were taken in one northern area well. No water entry surveys were run; three spinner surveys were completed in two pattern area injectors.

Well testing continued to be a problem with well cuts on many wells, especially those with higher cuts, remaining anomalous since late November or December, 1982. Calibration work on the tester for the pilot was completed, a new interface probe (controller) installed, and new computer hardware/software to monitor the tester's operation were placed in service. Preliminary data indicate a possible problem with the tester's cut monitor. Because the oil rate was in doubt as a result of the well tester difficulties, no attempt has been made to compare current oil rates with those in early 1982.

Gross rates were not adversely effected by the tester problem. Three wells, B-105 in the northern area offset to

alkaline injection, B-117 in the pattern area's north row offset to alkaline injection and B-121 in the northern area offset to alkaline injection were added to the prior group of 12 wells making a total of 15 wells showing reduced water production rates. The attached table gives data on these; cut and WOR data is in doubt, however, because of the tester problem.

Produced water samples were taken monthly and tested. Noteworthy results and well water rate performance data are as follows:

B-101-A, Southern Area, Row B. PH climbed to over 9.7, silica increased to 560 mg/l (the highest value observed

to dated in the pilot), while salinity dropped to 8800 mg/l and hardness to 200 mg/l. Had scaling problem despite continuous annular inhibitor treatment. Had substantial loss of water production.

Because of the well testing problem described above, the last 3 months' oil rate and WOR data may be substantially in error; as a result no conclusions should be made on recent oil rate and cut trends.

In the pattern area injection rate was up reflecting the change-out of the injection pump and motor and a lack of system/well downtime. The gross rate continued its decline that began in 1981. January's and February's oil rates were

TABLE 1 — DOE alkaline pilot producers showing reduced water production

Well No.	Location	Prior rates				Date	Current rates ⁵				Change in produced water chemistry	Date Simulator predicted first alkali*
		B/D gross	BO/D	WOR	FOP		B/D gross	BO/D	WOR	FOP		
**B-101-A	Southern area, row B ...	1,370	70	18.57	284'	12/80	— ¹³	— ¹³	—	—	Yes	2nd half '81
**B-105-A	Northern area, row A ...	1,690	75	21.53	363'	8/81	1,620 ¹	11 ¹	146.27	N/A	Yes	2nd half '81
B-111	Northern area, row A ...	1,850	95	18.47	318'	1/81	1,320	7?	187.57	189'	Yes?	1st half '83
B-112	Pattern area, north row .	850	45	17.89	107'	9/81	490	22?	21.27	10'	No	1st half '81
B-117	Pattern area, north row .	1,550	130	10.92	28'	1/81	1,060	65?	15.31	12'	No	1st half '82
B-121	Northern area, row A ...	1,250	80	14.63	255'	1/81	900	35?	24.71	80'	No	1st half '84
B-410	Pattern area, north row .	1,600	65	23.62	18'	11/80	800	15?	52.33	0'	Yes	1st half '82
B-705	Southern area, row D ...	1,550	115	12.48	245'	1/81	1,350	55?	23.55	813'	No	1st half '83
B-706	Southern area, row D	930	105	7.86	88'	4/81	820 ¹	70?	10.71	178'	No	2nd half '86
B-711	Southern area, row B ...	1,800	40	44.00	435'	3/81	530	3?	175.67	13'	No?	1st half '81
B-712	Pattern area, south row .	790	45	16.56	501'	2/81	520 ¹	10?	51.00	N/A	Yes	2nd half '83
**B-830	Southern area, row D ...	900	2(?)	450.00	6'	1/81	— ¹³	— ¹³	—	—	Yes	2nd half '81
B-834-A	Pattern area, south row .	2,500	90	26.78	877'	3/81	490	20?	23.50	120'	No?	2nd half '81
**B-838	Pattern area, south row .	1,570	55	27.55	202'	2/81	— ¹³	— ¹³	—	—	Yes	3rd qtr. '80
B-839	Pattern area, north row .	1,550	55	27.18	404'	4/81	1,180	25?	46.20	246''	No?	1st half '82
TOTALS (excluding B-101, B-105 B-830, and B-838)		16,220	865	17.75			9,460	327 ⁴	27.93			

*Alkaline flood simulation #2; other wells producing first alkali.

1st half 1984 B-114

**Excluded from totals because of non representative recent test data or lack of tests following recent work.

¹Stabilizing after pump and/or rotation changes; stimulation

²Possible pumping problem

³Change in water chemistry

⁴All March '83 well cuts, oil rates and WOR's are in doubt a/c well tester problem

⁵Possible tester problem

⁶No test in month

⁷Acidized in mid August '82

⁸Acidized in early August '82

⁹Acidized twice in Sept. '82

¹⁰Suspect pump is reversed

¹¹Two pump failures in Nov. '82. Down all of Dec. On prod. 1-1-83

¹²No tests after pump change and acidizing in month

¹³Idle waiting repair or pump change

N/A: Not available

down anomalously and WORs up as a result of the testing problem.

In the undeveloped portion of the Northern Area, gross rate continued to decline from its early 1982 high. Oil rate for

all 3 months in the quarter was down and WOR up reflecting the testing problems.

In the Southern Area, gross rate continued to decline from its mid 1982 high. Net rate was down and WOR up in January and February as a result of the testing problem.

**IMPROVED OIL RECOVERY BY
MICELLAR-POLYMER FLOODING
EL DORADO, KANSAS FIELD**

Contract No. ET-AC03-78ET13070

**Cities Service Co.
Tulsa, Okla.**

Contract Date: June 26, 1974

Anticipated Completion: Nov. 30, 1982

Total Project Cost:

DOE	\$ 5,392,490
Contractor	7,670,077
Total	\$13,062,567

**Principal Investigator:
Larry E. VanHorn**

**Technical Project Officer:
Fred W. Burtch
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this field test is to demonstrate the efficiency and economics of recovering tertiary oil from a successfully depleted waterflood using a micellar fluid followed by a mobility-controlled buffer zone (polymer solution) displaced through the reservoir by a driving fluid (water).

Summary of Technical Progress

The final report for the project should be published during the latter part of the next quarter.

**BIG MUDDY FIELD — WYOMING
MULTI-PATTERN LOW-TENSION FLOOD**

Contract No. DE-AC03-78SF01424

**Conoco, Inc.
Casper, Wyo.**

Contract Date: Jan. 1, 1978

Anticipated Completion: June 15, 1987

Total Project Cost:

DOE	\$ 9,500,000
Contractor	<u>26,060,000</u>
Total	\$35,560,000

**Principal Investigator:
Tom Painter**

**Technical Project Officer:
Fred W. Burtch
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The object of this field project is to demonstrate the commercial feasibility of the low-tension process in a typical Rocky Mountain reservoir with low matrix permeability, low salinity, and which fractures at bottom-hole injection pressures near and often less than hydrostatic.

Summary of Technical Progress

Polymer injection continued through the first quarter of 1983, bringing the total polymer-pusher slug size to 361,000 barrels.* The average injection rate for the quarter was 1,648 bpd, and the rate for March averaged 1,706 bpd (Fig. 1). This higher rate, compared to the 1982 fourth quarter average of 1,515 bpd, was due to increased injection into R.B. Whiteside No. 101 (Fig. 2).

Injection into R.B. Whiteside No. 101 was increased by placing a Triplex pump at the well in mid-February. The rate jumped from 28 bpd in January to 173 bpd in March; however, the bottom-hole injection pressure also increased from 1,323 psi to 1,620 psi. Pressure-parting (step-rate) tests were unsuccessful in defining the fracturing pressure. Further analysis will include tracer surveys, fall-off tests and observation-well pressure measurements in order to monitor the effects of the increased injection.

Oil production continued to increase during the quarter with sales averaging 175 bopd, 167 bopd and 172 bopd for January, February and March, respectively (Fig. 3). January was high due to 400 barrels of bad oil produced in December; actual production for January was 162 bopd. Cumulative project production is 93,685 barrels of oil as of March 31, 1983.

Minor sulfonate production (200-500 ppm) was observed in Well Nos. 83, 87, 88 and 95; however, no serious treating problems have occurred yet. The sulfonated oil auxiliary treating facility is very close to completion and will be ready for startup by late May.

The C/O log was again run in mid-February in R.B. Whiteside No. 74 (Fig. 2). The average saturation from this run was 47 percent. Previous runs showed oil saturations of 33 percent in June 1980, 36 percent in February 1982, and 44 percent in August 1982.

*Please note: An incorrect total polymer volume of 231,000 barrels was reported in the last quarterly report. The correct volume through December 31, 1982, was 213,000 barrels.

FIG. 1 — Big Muddy DOE project injection rate vs. time

J.C. KINNEY

R.B. WHITESIDE

DEMONSTRATION AREA – SUBSURFACE WELL LOCATION

LEGEND

- △ INJECTION WELL
- PRODUCTION WELL
- LOGGING MONITOR WELL

0 250' 500'
SCALE

FIG. 2 — Demonstration area — subsurface well location

FIG. 3 — Big Muddy DOE project oil and water rate vs. time

**COMMERCIAL SCALE
DEMONSTRATION
ENHANCED OIL RECOVERY BY
MICELLAR-POLYMER FLOODING**

Contract No. DE-AC19-78ET13077-77

**Marathon Oil Co.
Findlay, Ohio**

Contract Date: Sept. 30, 1976

Anticipated Completion: Dec. 31, 1986

Total Project Cost:

DOE	\$14,000,000
Contractor	<u>29,560,000</u>
Total	\$43,560,000

**Principal Investigator:
J.C. Howell**

**Technical Project Officer:
Ken Spence
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this demonstration is to conduct a commercial-scale test of the micellar-polymer flooding process for improved oil recovery. The size of the test, 407 acres, is adequate to evaluate effectively the economic and technical viability of the process as an economic means of oil recovery.

Summary of Technical Progress

The target pore volume of 12.0 percent for 411 ppm polymer injection was reached Jan. 20, 1983. A total of 1,274,500 bbl of 411 ppm polymer solution was injected. The 411 ppm polymer phase was reduced to 200 ppm. During the month of January, 36,546 bbl of 200 ppm polymer solution was injected. This equates to 0.3 percent of a pore volume. The target pore volume of the 200 ppm phase is 11.0 percent.

From Jan. 1, 1983 through March 31, 1983, the oil cut on the 2.5-acre pattern dropped from 5.9 to 5.4 percent. In the same period of time on the 5.0-acre pattern, the oil cut increased from 11.1 to 11.6 percent.

The table summarizes the progress of the demonstration.

TABLE 1 — Fluid summary data sheet for Marathon Oil Company Maraflood process, M-1 project, Crawford County, Illinois

1983	2.5 Acre			5.0 Acre			Total Project		
	Jan	Feb	Mar	Jan	Feb	Mar	Jan	Feb	Mar
Oil production									
BPD	228	255	253	241	212	195	469	467	448
BPM	7,082	7,126	7,838	7,473	5,924	6,041	14,555	13,051	13,879
Cumulative,									
bbls	626,342	633,469	641,307	283,278	289,202	295,243	909,620	922,671	936,550
Pct-PV	5.89	5.96	6.03	4.72	4.82	4.92	5.47	5.55	5.63
Oil cut -pct									
This month	5.9	5.5	5.4	11.1	11.4	11.6	7.8	7.2	7.0
Last month	6.0	5.4	5.5	11.1	10.6	11.4	7.8	7.2	7.2
Cumulative	8.0	7.9	7.9	6.7	6.8	6.8	7.5	7.5	7.5
Fluid production									
BPD	3,886	4,639	4,710	2,164	1,854	1,675	6,050	6,493	6,385
BPM	120,426	129,903	146,010	67,099	51,904	51,936	187,807	181,807	197,946
Cumulative,									
bbls	7,847,948	7,988,926	8,134,935	4,227,515	4,282,902	4,334,837	12,075,463	12,271,822	12,469,772
Pct-PV	73.85	75.17	76.55	70.50	71.42	72.99	72.64	73.82	75.01
Fluid injection									
BPD	5,387	5,399	5,233	1,453	1,456	1,425	6,840	6,855	6,658
BPM	166,984	151,168	162,300	44,958	40,743	44,199	211,942	191,911	206,499
Cumulative,									
bbls	8,955,942	9,106,284	9,268,583	2,866,676	2,907,366	2,951,566	11,822,678	12,013,650	12,220,149
Pct-PV	84.26	85.69	87.21	47.80	48.80	49.22	71.11	72.27	73.51
Injection/production ratio									
This month ..	1.36	1.14	1.09	0.85	1.01	1.09	1.18	1.10	1.09
Last month ..	1.35	1.24	1.14	0.92	0.83	1.01	1.19	1.10	1.10
Cumulative ..	1.08	1.08	1.08	0.96	0.96	0.96	1.04	1.04	1.04

TABLE 2 — Fluid summary data sheet, Marathon Oil Company Maraflood process, M-1 project, Crawford County, Illinois

1983	2.5 Acre			5.0 Acre			Total project
	Jan	Feb	Mar	Jan	Feb	Mar	
Reservoir pore volume	10,627,513	same	10,627,513	same	same	5,996,535	16,624,048
Plant pressure, psig	636	642	631	644	634	639	—
Polymer viscosity, cp @ 77°F	5.1	4.1	4.1	19.6	18.7	19.3	—
Polymer screen factor @ 77°F	14.2	10.5	8.8	19.4	18.7	16.6	—
Injection rate (BPD/PNF)	2.07	2.08	2.01	1.94	1.95	1.91	—
Wells							
Producers	same	same	91	same	same	41	132
Injectors							
Micellar fluid	same	same	85	same	same	29	114
Water	same	same	6	same	same	6	12
Water disposal	same	same	1	same	same	1	12
Abandoned	6	same	6	same	same	0	6
Polymer, ppm							
Fluid injection schedule	Slug	1156	800	625	411	200	
2.5 acre							
Starting date	2/10/77	11/21/78	5/20/79	7/28/80	5/26/82	1/20/83	
Pct-PV actual	10.0	11.0	19.0	32.0	12.0	3.3	
Pct-PV ultimate	10.0	11.0	19.0	32.0	12.0	11.0	
Cumulative, bbls	1,063,446	1,169,677	2,019,170	3,401,604	3,401,604	350,014	
5.0 acre							
Starting date	2/10/77	11/21/78	1/14/80	3/05/82			
Pct-PV actual	10.0	11.0	19.0	9.2			
Pct-PV ultimate	10.0	11.0	19.0	32.0			
Cumulative, bbls	599,679	658,999	1,139,370	553,570			

**ENHANCED OIL RECOVERY BY
IMPROVED WATERFLOODING
STORMS POOL, ILLINOIS**

Contract No. DE-AC19-78ET12065

**Energy Resources Co., Inc. (ERCO)
Cambridge, Mass.**

Contract Date: Sept. 26, 1977

Anticipated Completion: Dec. 31, 1983

Total Project Cost:

DOE	\$1,585,477
ERCO	<u>2,164,667</u>
Total	\$3,750,144

**Principal Investigator:
John Piret**

**Technical Project Officer:
Fred W. Burtch
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this contract is to demonstrate the technical capability and economic feasibility of conducting improved waterflooding techniques to recover additional oil from a reservoir which contains a water-filled depleted gas cap and underlying inactive aquifer. A further project objective is to improve the vertical sweep efficiency.

Summary of Technical Progress

There has been no reported field activity during the quarter. An evaluation of the project from a technical and economic standpoint continues to be made by ERCO personnel. It now appears that ERCO is considering the termination of the project. If so, a final report will be prepared by the contractor.

CHEMICAL FLOODING

SUPPORTING RESEARCH

MOBILITY CONTROL AND SCALEUP FOR CHEMICAL FLOODING

Contract No. DE-AC19-80BC10095

**University of Texas
Austin, Tex.**

**Contract Date: Aug. 1, 1979
Anticipated Completion: Sept. 30, 1983
Government Award: \$166,250
(Fourth year)**

**Principal Investigator:
Gary A. Pope**

**Technical Project Officer:
Min K. Tham
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this project are to determine quantitatively the effects of dispersion, relative permeabilities, apparent viscosity and inaccessible pore volume on mobility control under one-, two-, and three-phase flow of micellar-polymer fluids, and to develop a three-dimensional chemical flooding simulator.

Summary of Technical Progress

The capillary desaturation and two-phase relative permeability curves were measured for a three-phase micellar fluid in a 2-ft Berea sandstone core. Continuous and slug displacements of radioactive tracers were also run during steady-state.

The fluids used in all the experiments were the three equilibrated phases of a micellar system containing 1.5 vol-pct active Witco TRS10-410, 1.5 vol-pct isobutanol, 50 vol-pct n-decane, and brine consisting of water, sodium chloride, and calcium chloride.

The micellar formulation at 1.1 percent NaCl was used for experimental flooding. The physical properties and the

information on the core sample are tabulated in Tables 1 and 2. The composition of the microemulsion was 39.25 vol-pct brine, 55.5 vol-pct n-decane, 1.79 vol-pct IBA and 3.5 vol-pct TRS10-410.

TABLE 1 — Physical properties of fluids

	Lower phase	Middle phase	Upper phase
Volume fraction	0.279	0.451	0.268
Density, g/cc	1.0008	0.8508	0.7275
Viscosity, cp	0.84	4.0	0.780
Calcium content, ppm ..	0.86	21.9	0.0
Brine content, vol-pct..	97.87	39.25	0.0
N-decane content,			
vol-pct	0.0	55.46	99.65
Alcohol (IBA) content			
vol-pct	2.1	1.79	0.30
TRS10-410 content,			
vol-pct	0.03	3.5	0.05
Interfacial tension.			
dyne/cm	7.6×10^{-4}		4×10^{-4}

TABLE 2 — Characteristics of Berea core

Length	24 in. (60.96 cm)
Cross-section area	3.95 in ² (25.5 cm ²)
Bulk volume	1554.5 cc
Pore volume	303.0 cc
Porosity	0.212
100 pct brine permeability	0.739 darcy
Residual brine (S_{wr})	0.35
Residual oil (S_{or})	0.30
Dispersivity at $S_w = 1$	0.224 cm

Four different types of capillary desaturation data were obtained in a Berea core. In obtaining each of these, the core was saturated with one phase, then flooded with one of the other two phases at different flow rates. The same fluid containing the radioactive tracer was run at steady-state to enable evaluation of saturations by both material balance calculations and tracer breakthrough curves. There are a number of different definitions of the capillary number proposed by various authors.^{1,2} Here, all data are plotted in terms of

$$N_c = \frac{K\Delta\Phi}{L\sigma}$$

where K is the absolute permeability to brine
 $\Delta\Phi$ is the potential drop,
 L is the porous sample length,
 and σ is the interfacial tension.

Fig. 1 shows the residual microemulsion saturation to brine and residual brine saturation to microemulsion as a function of capillary number. The phase saturations plotted

are from dispersion data. The most significant finding of these capillary-desaturation curves is that residual microemulsion to brine does not go to zero until a capillary number on the order of 0.4 is reached, which is even higher than that of residual brine. These results suggest that the microemulsion phase is more wetting compared to the brine phase.

Capillary desaturation data for oil and microemulsion are also shown in Fig. 1. The residual oil to microemulsion is already zero at the lowest capillary number measured of 3.8×10^{-3} while residual microemulsion to oil is about 10 percent at about the same capillary number.

FIG. 1 — Residual saturation as a function of capillary number in Berea

The same fluids and core were used to determine the relative permeability curves for oil and middle-phase microemulsion in the direction of increasing microemulsion saturations and at a constant capillary number 10^{-2} . At each of the oil cuts, continuous injection of tracers in both phases was done at steady-state in order to determine the phase saturations and dispersion coefficients.

Relative permeability curves for oil and microemulsion based on both material balance calculations and dispersion data are shown in Fig. 2.

The relative permeabilities are plotted as a function of both oil and microemulsion saturations. The end points of this curve, based on material balance calculations, are at $S_{1r} = 0.117$, $S_{2r} = 0.096$, and $S_{3r} = 0.0436$. The relative permeabilities are less curved at this high capillary number of 10^{-2} than at low capillary number, but are still different from straight lines.

Last, microemulsion and brine two-phase behavior at a capillary number of 6.6×10^{-3} and in the direction of increasing brine saturation was investigated. In this experiment, some of the dispersion curves were determined using slugs of tracer rather than continuous tracers. Although the study of miscible slug displacements goes back to 1965 by Raimondi and Torcaso³, this is the first time that slug-type runs have been done for two-phase, low-tension flow.

EXPERIMENT # SMO

Ncap = 0.010

FIG. 2 — Relative permeability curves for microemulsion and oil flow in Berea

At each water cut, a 15.6 percent pore volume slug of microemulsion and brine containing radioactive tracers, followed by fluids without tracer, was injected into the core.

The microemulsion/brine relative permeabilities are plotted as a function of both brine and microemulsion saturations in Fig. 3. A constant residual oil saturation of $S_{2r} = 0.096$ was present during the experiment. The saturations

EXPERIMENT # SMW

Ncap = 0.0066

FIG. 3 — Relative permeability curves for microemulsion and brine flow in Berea

are evaluated using material balance calculations since a complete analysis of the tracer data is not yet available.

References

- ¹ Abrams, A., "The Influence of Fluid Viscosity, Interfacial Tension, and Flow Velocity on Residual Oil Saturation Left by Waterflood," SPEJ, pp. 437-447 (1973).
- ² Gupta, S.P. and Trushenski, S.P., "Micellar Flooding — Compositional Effects on Oil Displacement," SPE 7063 (1978).
- ³ Raimondi, P. and Torcaso, M.A., "Mass Transfer Between Phases in a Porous Media: A Study of Equilibrium," SPEJ, pp. 51-59 (1965).

THE MECHANISM OF OIL-BANK FORMATION AND COALESCENCE IN POROUS MEDIA

Contract No. DE-AC19-80BC10069

Illinois Institute of Technology
Chicago, Ill.

Contract Date: October 1981
Anticipated Completion: September 1983
Government Award: \$102,000
(Current year)

Principal Investigator:
Darsh T. Wasan

Technical Project Officer:
Philip B. Lorenz
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this project is to make a basic study of coalescence of oil droplets in water, and to correlate this process with oil recovery. The program is designed:

1. To observe the coalescence of individual droplets with interfaces and with each other, the coalescence of emulsions, and the formation of the oil bank in chemical flooding.
2. To measure the interfacial tensions, the interfacial shear viscosity, the interfacial dilational viscosity, and the interfacial charge.
3. To find correlations among these observations under a variety of physicochemical conditions, such as pure and mixed surfactants, caustic, different concentrations, changes in salinity, presence of divalent ions, variations in oil composition and cosurfactants and temperature.
4. To compare oil bank formation and oil recovery in sandstone cores and visual models, and to establish as to what extent tertiary oil recovery in laboratory cores is influenced by emulsion formation and coalescence behavior of drops.

Summary of Technical Progress

In an alkaline flooding process, the extent to which interfacial tension is lowered depends on the specific properties of the crude oil and the flood water. The relationship for interfacial tension was established in terms of a simple chemical model by Ramakrishnan and Wasan.¹ It is possible to use this information on interfacial activity in an equi-

librium flow model for predicting enhanced oil recovery through the use of fractional flow theory. However, such an approach requires information on relative permeability for the specific situation under consideration. During this quarter the popular cut and rejoin porous media model of Wyllie and Gardiner² was extended to apply to both drainage and imbibition. The model was originally applied only to drainage. Relative permeability curves have been derived. Moreover, an analysis based on percolation theory for nonwetting phase trapping makes it possible to generalize the model for varying capillary numbers.

The inputs for the model calculations are (1) the experimental data on capillary pressure, from which the statistical parameters for pore throat distribution are derived, and (2) the residual nonwetting phase saturation.

The analysis constructs the whole of saturation history (for both drainage and imbibition).

In the imbibition cycle the trapped nonwetting phase is considered to be a function of the historical maximum nonwetting phase saturation and the history of capillary number. The dependence of trapping on the capillary number history arises due to the compelling evidence that mobilization of isolated nonwetting phase is more difficult than prevention of entrapment of connected nonwetting phase.

Typical results for low capillary number, showing the hysteresis, are presented in Fig. 1. The imbibition curves are based on Land's relationship for nonwetting phase residual saturation.³ The dotted curves are for imbibition following incomplete drainage.

FIG. 1 — Drainage and imbibition relative permeability; maximum residual nonwetting phase saturation = 0.4; maximum residual wetting phase saturation = 0.2; S_{iw} = initial wetting phase saturation

Figures 2 and 3 compare the results of the model with the data of Amaefule and Handy for Berea sandstone.⁴ By and large, the model compares favorably with their observations; however, the curve for the nonwetting phase shows a systematic deviation in the imbibition case.

References

- ¹ Ramakrishnan, T.S., Wasan, D.T., "A Model for Interfacial Activity of Acidic Crude Oil-Caustic Systems for Alkaline Flooding," Soc. Pet. Eng. J. to be published (1983).

FIG. 2 — Drainage relative permeability for Berea sandstone; ● — experimental nonwetting phase relative permeability (k_{rnw}); ○ — experimental wetting phase relative permeability (k_{rw}); — — model results.

FIG. 3 — Imbibition relative permeability for Berea sandstone; ● — experimental nonwetting phase relative permeability (k_{rnw}); ○ — experimental wetting phase relative permeability (k_{rw}); — — model results.

²Wyllie, M.R.J., Gardner, G.H.F., "The Generalized Kozeny-Carman Equation," World Oil, (1958) 146, 210-228.

³Land, C.S., "Calculation of Imbibition Relative Permeabilities for Two and Three Phase Flow from Rock Properties," Soc. Pet. Eng. J., (1968) 102, 149-156.

⁴Amaefule, J.O., Handy, L.L., "The Effect of Interfacial Tensions on Relative Oil-Water Permeabilities of Consolidated Porous Media," Soc. Pet. Eng. J., (1982) 3, 371-381.

Publications

Manev, E.D., Sazdanova, S.V., Rao, A.A., and Wasan, D.T., "Foam Stability-The Effect of a Liquid Crystalline Phase on the Drainage and Transition Behavior of Foam Films," Journal of Dispersion Science & Technology, 3, No. 4, 1982, pp. 435-463.

Zapryanov, Z., Malhotra, A.K., Aderangi, N., and Wasan, D.T., "Emulsion Stability: An Analysis of the Effects of Bulk and Interfacial Properties on Film Mobility and Drainage Rate," International Journal of Multiphase Flow, 9, No. 2, 1983, pp. 105-219.

Ting, L., and Wasan, D.T., Miyano, K. and Xu, S-Q, "Longitudinal Surface Waves for the Study of Dynamic Properties of Surfactant Systems," paper presented at the Division of Colloid & Surface Chemistry, 185th ACS National Meeting, Seattle, Washington, March 20-25, 1983.

Malhotra, A.K., Manev, E.D., Christov, C., and Wasan, D.T., "The Effect of Film Size on Film Drainage in Emulsion and Foam Systems," paper presented at the Symposium on Thin Fluid Film Phenomena, AIChE National Meeting, Houston, Texas, March 27-31, 1983.

ENHANCED-OIL-RECOVERY RESEARCH

Contract No. W-7405-eng-26

Oak Ridge National Laboratory
Oak Ridge, Tenn.

Amphiphilic Compounds in Enhanced Oil Recovery
(Formerly Ion Exchange Characteristics of Enhanced-Oil-Recovery Systems)

Contract Date: Apr. 1, 1977

Anticipated Completion: Indefinite

Government Award: Suspended for FY 1983

Principal Investigator:

James S. Johnson, Jr.

Technical Project Officer:

Fred W. Burtch

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Research sponsored by Oil, Gas, and Shale Technology, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

Objectives

To clarify the complex interactions which occur between the components of micellar floods and between fluids and oil-bearing formations, by studies of well defined, chemically related systems, with emphasis on small-angle neutron scattering and phase behavior.

Summary of Technical Progress

Small-angle neutron scattering from micellar systems.

Contrast measurements

In the preceding report, we presented scattering patterns of tetramethyl ammonium dodecyl sulfates as a function of solvent H_2O/D_2O ratios. By varying the ratio, one attempts to match the scattering length density of the solute (or of regions of the aggregates formed by the solute) with that of the solvent and thereby to obtain information on the structure of the micelles. For the quarter before last, we presented preliminary fits of the interaction peaks observed with sodium p(1-pentylheptyl)benzene sulfonate with use of the Mean Spherical Approximation (MSA). Structural functions computed from MSA accounts for the interparticle ordering in solution arising from hard-sphere and coulombic repulsion between micelles. When no added inorganic salt was present, agreement between experiment and computations was good.

It is always difficult to be sure that a specified model is the only one plausible for a given system, but the ambiguity can be decreased by showing that the same parameters are derived over a range of contrast between solute and solvent scattering power. Fig. 1 presents the MSA fits obtained for 0.055 M sodium p(1-pentylheptyl)benzene sulfonate in 57 to 100 percent D₂O.

The model comprises an essentially hydrocarbon core of 11.9 Å radius surrounded by a shell of the rest of the methylene groups, the benzene sulfonate, complexed counterions, and solvent. The parameters derived from the fit are summarized in Table 1. Number of monomers/micelle and micellar charge do not vary

TABLE 1 — Parameters derived from fit to SANS data

Fraction D ₂ O	Aggregation Number	Charge Z	δ^*	Diameter σ , Å
1.00	54	19	3.2	42.0
0.90	53	20	3.1	41.6
0.80	52	19	3.1	41.6
0.70	52	19	3.1	41.6
0.57	51	18	3.0	41.0
0.57 (repeat) ..	51	17	3.0	41.0
Average ...	54	18	3.1	41.5

*Number of methylenes in core.

MSA FITS TO CONTRAST PATTERNS OF 0.055 M SODIUM p (1-PENTYLHEPTYL) BENZENE SULFONATE SOLUTIONS.

--- PARTICLE SCATTERING FORMATION, $P(k)$
 ... STRUCTURAL FUNCTIONS, $S(k)$
 — COMPUTED INTENSITIES

D ₂ O VOL. %		
A. 100	C. 80	E. 57%
B. 90	D. 70	F. 57% (REPEAT)

FIG. 1 — MSA fits to contrast patterns of 0.055 M sodium P (1-pentylheptyl) benzene sulfonate solutions.

substantially over the range covered. The thickness of the outer shell implied suggests a rough micellar surface.

Publications

Submitted during quarter

L.J. Magid, R. Triolo, R.M. Jones, and J.S. Johnson, Jr., "Small-Angle Neutron Scattering from an Oil-in-Water Microemulsion as a Function of Temperature," *Chemical Physics Letters*, in press.

P.C. Ho, M.A. Kahlou, T.M. Bender, and J.S. Johnson, Jr., "Osmotic Coefficients of Low-Equivalent-Weight Organic Salts," submitted to *J. Physical Chemistry*.

MATHEMATICAL METHODOLOGY FOR EVALUATING SIMULATIONS OF FLOW IN POROUS MEDIA

Contract No. DE-AC19-80BC10257

Texas Tech University
Lubbock, Tex.

Contract Date: Feb. 1, 1980

Anticipated Completion: Aug. 31, 1983

Government Award:

DOE	\$141,367
Contractor	20,000
Total	\$161,367

Principal Investigator:

Wayne T. Ford

Technical Project Officer:

John W. McGhee

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

To use the fundamental mathematical structure of problems of porous media flow to develop and apply a mathematical methodology for validation of simulators of such flow, and to demonstrate the practicality of the methodology in selection of a simulator; with the expectation that the resulting techniques will be valuable in the study of such flows in projects in enhanced oil recovery.

Summary of Technical Progress

Fluid flow of immiscible phases in a linear, homogenous medium can be formulated in the equation,

$$(1) \quad \frac{\partial [\bar{R}(\bar{U})]}{\partial t} = \frac{\partial}{\partial x} \left[M(\bar{U}) \frac{\partial \bar{U}}{\partial x} \right],$$

which we refer to as a Porous Media System (PMS). It can be analysed in terms of the equation,

$$(2) \quad \frac{d}{d\xi} \left[M(\bar{U}) \frac{d\bar{U}}{d\xi} \right] + F(\xi) \left[M(\bar{U}) \frac{d\bar{U}}{d\xi} \right] +$$

$$G(\xi) \frac{d[\bar{R}(\bar{U})]}{d\xi} = 0,$$

which we refer to as a Similarity Porous Media System (SPMS).

If the PMS is considered in a radial reservoir with angular symmetry, it takes on the form,

$$(3) \quad \frac{\partial [\bar{R}(\bar{U})]}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[r M(\bar{U}) \frac{\partial \bar{U}}{\partial r} \right].$$

The similarity concept can be applied to this radial problem in terms of a function, $\xi = f[r^2/(t-b)]$, such that a coordinate transformation from (r,t) to (ξ,η) can be presumed to be such that $\partial \bar{U} / \partial \eta$ is always zero. The Radial Porous Media System (RPMS) is then transformed to exactly the same form as the SPMS which results from application of the similarity concept to the PMS. However, specification of the $F(\xi)$ and the $G(\xi)$ in the SPMS differ in the two cases.

Transformation of the (linear) PMS to the SPMS involved either $\xi = f[(x-a)/(t-b)]$ or $\xi = f[ax+bt]$ while transformation of the RPMS to the SPMS involves $\mu = f[r^2/(t-b)]$. In any event, the SPMS can best be used, at least in introducing the similarity concept to those who find it unfamiliar, by reducing the discussion to a single phase problem in the form,

$$(4) \quad \frac{d}{d\xi} \left[M(u) \frac{du}{d\xi} \right] + F(\xi) \left[M(u) \frac{du}{d\xi} \right] +$$

$$G(\xi) \frac{d[R(u)]}{d\xi} = 0.$$

This equation can be written in the form

$$(5) \quad \frac{d}{d\xi} \left[H(\xi) M(u) \frac{du}{d\xi} \right] + H(\xi) G(\xi) \frac{d[R(u)]}{d\xi} = 0,$$

where

$$(6) \quad H(\xi) = \exp \left[\int F(\xi) d\xi \right].$$

A change of independent variable, from μ to ζ as defined by the ordinary differential equation,

$$(7) \quad \frac{d\zeta}{d\xi} = \frac{1}{H(\xi)},$$

transforms (5) to the form,

$$(8) \quad \frac{d}{d\zeta} \left[M(u) \frac{du}{d\zeta} \right] + H(\zeta) G(\zeta) \frac{d[R(u)]}{d\zeta} = 0,$$

where

$$(9) \quad H(\zeta) = H(\xi) \text{ and } G(\zeta) = H(\xi).$$

Similarly, a change of dependent variable, for u to v as defined by the ordinary differential equation,

$$(10) \quad \frac{dv}{du} = M(u),$$

transforms (8) to the form,

$$(11) \quad \frac{d}{d\zeta} \left[\frac{dv}{d\zeta} \right] + H(\zeta)G(\zeta) \frac{d[R(v)]}{d\zeta} = 0,$$

where

$$(12) \quad R(v) = R(u)$$

Although (4) through (9) extend easily to the multi-phase case, (10) and (11) extend with more technical details. Thus, the ideas leading to (11) are more easily seen for the single phase case. Specifically, (10) is illustrated by

$$(13) \quad u = P, M(u) = \frac{\rho(P)}{\mu(P)}, \text{ and } v(u) = \int \frac{\rho(P)}{\mu(P)} dP.$$

Reference

W.T. Ford and R.M. Anderson, "Use of Similarity Methods in Evaluation of Reservoir Simulators," Bartlesville Energy Technology Center (BETC/DOE), Summary of Research, Jan., 1981, pp. B1-B14.

R.M. Anderson, W.T. Ford, A. Rutan and M.J. Strauss, "Formulation of Similarity Porous Media Systems," *Transport Theory and Statistical Physics*, vol. 11, no. 2, 1982, pp. 123-140.

FLOW IN POROUS MEDIA, PHASE BEHAVIOR AND ULTRALOW INTERFACIAL TENSIONS: MECHANISMS OF ENHANCED PETROLEUM RECOVERY

Contract No. DE-AC19-79BC10116

**University of Minnesota
Minneapolis, Minn.**

Contract Date: Oct. 1, 1981

Anticipated Completion: Sept. 30, 1983

**Government Award: \$290,750
(Second Year)**

Principal Investigators:

H.T. Davis

L.E. Scriven

Technical Project Officer:

M.K. Tham

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The Minnesota research program is aimed at understanding why conventional oil recovery averages only about one-third of original oil-in-place, and of how additional oil recovery can be enhanced economically. Towards achieving this goal, the topics of the program are: (1) the character of pore space and pore walls in oil-bearing sedimentary rocks; (2) the distribution of fluids in and displacement of one by another from permeable rocks; (3) the strength and transport properties of permeable rocks, especially as influenced by fluid contents; (4) the origins and

roles of phase behavior and interfacial tensions in chemical flooding processes (surfactant, micellar, carbon dioxide, nitrogen, caustic, etc.); (5) the physical chemistry and rheology of microstructured fluids occurring in such processes; (6) the molecular design of surfactant/amphiphile systems possessing ultralow tensions tolerant to hostile and variable environments; (7) the principles of chemical and thermal flooding design.

Summary of Technical Progress

Results relating primarily to fluid microstructures and phase behavior

The phase behavior of sodium 4-(1'-heptylnonyl)-benzenesulfonate, SHBS, in water or brine from 20 to 90°C is dominated by a broad biphasic region consisting of a lamellar liquid crystalline phase in equilibrium with a dilute isotropic SHBS solution. In the isotropic phase the SHBS is not micellar, though conductimetry and nmr spectroscopy indicate weak, concentration dependent aggregation. At 25°C the lamellar phase is approximately 100° above the gel-liquid crystal phase transition temperature and the sulfonate head group undergoes rapid though anisotropic motion. The lamellar phase is very fluid and easily deformable, whether dispersed in the saturated aqueous phase or as the bulk lamellar phase. Mechanical agitation and other sample preparation techniques give closed shell liposome dispersions; the mean size and size distribution depend markedly on the sample history. Sonication of a dilute dispersion leads to long lived, nonequilibrium vesicles. Addition of a suitable cosurfactant, sodium dodecylsulfate, leads to a mixed micellar solution while the addition of a cosolvent, e.g., n-pentanol leads to a non-micellar solution.

Many preparations of SHPS-H₂O(NaCl)-(cosolvent, cosurfactant) show ultralow tension against hydrocarbon. In formulations in which the tension measurements depend on time and preparation technique, an opaque, viscous, thin, surfactant-rich third phase forms at the oil-water interface. The microstructures present in this low volume fraction

surfactant-rich middle phase are unknown. The tension behavior, however, correlates with the nature of the microstructure present in the precontacted aqueous surfactant dispersion. Formulations containing alcohols which produce low, equilibrium tensions that do not depend on the method of preparation yield a low-viscosity, translucent middle phase, a microemulsion. The microemulsion middle phase is shown in this case to be continuous in both water and oil; it is not a swollen micellar microstructure. *W.G. Miller, F.D. Blum, H.T. Davis, E.I. Franses, E.W. Kaler, P.K. Kilpatrick, K.E. Nietering, J.E. Puig and L.E. Scriven, "Fluid microstructures of Texas No. 1 mixtures," in Proceedings of International Symposium on Solution Behavior of Surfactants, ed. K.E. Mittal, Lund University, Lund, Sweden (to appear 1983).*

A square-lattice model of amphiphile-oil-water systems is developed in which oil and water molecules occupy single sites and amphiphiles occupy chains of sites. Energies and free energies estimated by Monte Carlo sampling of configuration space show that when the head, or water-loving portion, of the amphiphile has no tendency to hydrate or surround itself with water, as opposed to surrounding itself with other heads, the capability of even long amphiphiles to solubilize repellant oil and water into a single phase is weak. Although the Monte Carlo free energies deviate markedly from those given by quasi-chemical theory, the deviation of the phase behavior is modest. Computer drawings of typical equilibrium configurations show highly irregular interfaces, apparently owing to capillary waves. *R.G. Larson, L.E. Scriven and H.T. Davis, "Monte Carlo simulation of model amphiphile-oil-water systems," J. Chemical Physics (submitted for publication).*

Measurements of total absorbance at wavelengths 350 to 780 nm of aqueous dispersions of polymer latex microspheres of diameters 0.091 μm , 0.254 μm , 0.325 μm , and 1.10 μm were used to interpret systematic observations of them. Lightscattering dissymmetries and scattering ratios of dispersions of the 0.091 μm microspheres were measured at varying concentration and path length at 546 nm and 436 nm. Spectroturbidimetry and observations were also made in binary mixtures of the above particle sizes and in dispersions of microspheres with added dye, the sodium salt of methyl red.

For absorbance due to scattering, A_{scat} , exceeding 0.05 but not 2, the absorbance and its wavelength dependence yield reliable estimates of particle size, even though the dissymmetry and the scattering ratio do not. Observations of nonabsorbing systems under ordinary illumination are most reliably interpreted when $0.1 < A_{\text{scat}} < 1$. That the Tyndall effect, or a variant of it when absorption is important, is visible implies that particles smaller than 0.1 μm are present. In Part II the results are used to devise rules for interpreting the appearance of dispersed surfactant systems, with due regard for path length, particle size, particle concentration, and multiple scattering. *E.I. Franses, L.E. Scriven, W.G. Miller and H.T. Davis, "Interpreting the appearance of*

dispersed latex systems. Part I. Model dispersions of polymer latex microspheres," Journal of American Oil Chemists' Society (accepted for publication).

We first analyze how color and transparency are perceived. Drawing on principles of light scattering investigated in Part I, we suggest simple rules and procedures in a diagnostic form for visually observing fluid surfactant systems to estimate sizes of dispersed particles. Rules and procedures are organized into a guide, the use of which we illustrate by observing certain important surfactant systems. We conclude that it is possible to estimate particle sizes in the Rayleigh, Rayleigh-Debye-Gans, and Mie scattering regimes from such observations alone. *E.I. Franses, L.E. Scriven, W.G. Miller and H.T. Davis, "Interpreting the appearance of dispersed latex systems. Part II. Model dispersions of polymer latex microspheres," Journal of American Oil Chemists' Society (accepted for publication).*

Results relating primarily to interfacial tension and wetting phenomena

The way fluid wets a solid in the presence of another fluid, i.e., the wettability behavior, is now understood to be of primary importance to oil recovery processes. As a part of systematic experimental and theoretical studies of the wetting process, we are investigating the molecular theory of contact angles and the perfect wetting transition.

Here, we resolve a controversial difference between two recently proposed theories of the equilibrium contact angle, the angle at which a fluid interface meets a solid surface, by investigating integral and gradient theories of fluid at a solid. Van der Waals integral theory, of which Sullivan's model is a special case, in fact admits either a first or second-order transition from a nonzero contact angle to perfect wetting as a critical point is approached. So also does gradient theory, of which the constant coefficient version we examined previously is a special case. *G.F. Teletzke, L.E. Scriven and H.T. Davis, "Wetting transitions II: First-order or second-order?," J. Chemical Physics (accepted for publication).*

The physics of fluid-fluid interfaces is investigated with the gradient theory of inhomogeneous fluid. The theory is used to predict component density and principal pressure (negative of stress) profiles in *flat* and *curved* interfaces formed in carbon dioxide and decane mixtures. In some cases the component density (and total density) profiles are not monotonic, with CO_2 being prominently surface active. In composition regions near where a perfect-wetting third phase splits out, the composition and pressure profiles are especially structured, a thin-film appearing which is akin to the perfect-wetting phase and which almost separates two distinct interfaces. This precursor to the third phase gives rise to Antonov's rule for the interfacial tension between the two phases that are nearly in equilibrium with the third, perfect-wetting phase. Below a perfect-wetting transition temperature, T_{cw} , such thin-films do not arise near compositions of the three phase region.

Curvature of sufficiently small drops or bubbles significantly affects adsorption at interfaces. The theory predicts that the Young-Laplace equation as traditionally applied overestimates the pressure drop across the interface in some cases (as found earlier in the case of one-component drops), but underestimates the pressure drop across interfaces related to perfect-wetting structures. The minimum work of forming critical nuclei is predicted. *A.H. Falls, L.E. Scriven and H.T. Davis, "Adsorption, structure, and stress in binary interfaces," J. Chemical Physics (accepted for publication).*

Macromolecules which find themselves in interfacial zones experience spatially inhomogeneous interactions. Spatial distributions of chain segments are therefore different in interfacial regions than in bulk fluid phases. This difference may manifest itself as a segment density profile in the direction normal to the interface and/or as altered distributions of chain conformations (even at constant total segment density) in the interfacial zone. These inhomogeneities exist at equilibrium in interfacial regions and profoundly alter the dynamics of nonequilibrium processes occurring near interfaces. In this paper we report on our studies of these problems by two different theoretical methods and by model experiments, confining ourselves here to studies of dilute and semidilute polymer solutions. *M. Tirrell, J.H. Aubert, D. Adolf and H.T. Davis, "Dynamic properties of macromolecules near interfaces," IUPAC, Proceedings 28th Macromolecular Symposium, Amherst, 12-16 July 1982.*

Results relating primarily to porous media, fluid distribution and fluid flow therein

We report results of Monte Carlo investigations of dispersion in one- and two-phase flow through disordered porous media represented by square and simple cubic networks of pores of random radii. Dispersion results from the different flow paths and consequent different transit times available to tracer particles crossing from one plane to another in a porous medium. Dispersion is found to be diffusive for the process simulated, i.e. a concentration front of solute particles can be described macroscopically by a convective-diffusion equation. Dispersivity in the direction of mean flow (i.e., longitudinal dispersivity) is found to be an order of magnitude larger than dispersivity transverse to the

direction of mean flow. In two-phase flow, longitudinal dispersivity in a given phase increases greatly as the saturation of that phase approaches its percolation threshold; transverse dispersivity also increases, but more slowly. As the percolation threshold is neared, the backbone of the sublattice occupied by the phase becomes increasingly tortuous, with numerous subloops which provide alternate particle paths that are evidently highly effective in dispersing a concentration front of tracer particles. *M. Sahimi, H.T. Davis and L.E. Scriven, "Dispersion in disordered porous media," Chemical Engineering Communications (accepted for publication).*

The Bethe lattice, which has proven useful for modeling hydraulic conduction and relative permeabilities of disordered porous media, is investigated theoretically as a lattice model for conductive or diffusive random walk behavior. The random walk problem for an inhomogeneous Bethe lattice is solved exactly. It is shown that the percolation threshold (related to residual saturations in the percolation theory of two phase flow in porous media, *Larson et al., Chem. Eng. Sci. 36, 57 (1981); 36, 75 (1981)* and *Heiba et al., SPE No. 11015, 57th Annual SPE meeting, New Orleans, 26-29 September 1982*) of a Bethe lattice is equal to the probability that a random walker will return to a previously visited site. *B.D. Hughes and M. Sahimi, "Random walks on a Bethe lattice," J. Statistical Physics 29, 781 (1982).*

The percolation threshold, directly related to residual oil saturations by percolation theory, has long been thought to be related to the topology of the disordered medium in which two or more materials are distributed. This has been shown experimentally by establishing a connection between residual oil saturation and the genus of the porous medium (*P. Pathak, H.T. Davis and L.E. Scriven, "Dependence of residual nonwetting liquid on pore topology," SPE No. 11016, New Orleans, 1982*).

In the work reported here a conjectured connection between the percolation threshold and the lattice Green function (a topological function) is firmly established on the basis of experimental, theoretical, and Monte Carlo simulation results. *M. Sahimi, B.D. Hughes, L.E. Scriven and H.T. Davis, "On Pólya random walks, lattice Green functions, and the bond percolation threshold," Journal Physics A (accepted for publication).*

ADSORPTION FROM FLOODING SOLUTIONS IN POROUS MEDIA

Contract No. DE-AC19-79BC10082

Columbia University
New York, NY

Contract Date: June 1979
Anticipated Completion: Sept. 1983
Government Award: \$90,000
(Current year)

Principal Investigator:
P. Somasundaran

Technical Project Officer:
Philip B. Lorenz
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

Objectives of this work are to do research on the chemical effects that lead to loss of surfactant in micellar-polymer flooding.

The work consists of research efforts on adsorption and precipitation of surfactants under a wide variety of physical and chemical conditions. Adsorption will be at both solid and liquid interfaces and will be subject to thermodynamic and kinetic analysis, in particular including reversibility. Correlation will be made with the state of surfactants in solution (association complexes, micellization) and the electrochemical nature of the solid.

Summary of Technical Progress

Introduction

Earlier work with limestone has shown the depletion of sulfonate upon contact with it to be much more severe than in systems containing quartz, kaolinite, or alumina, tested under similar conditions. Two major phenomena to be considered in these systems due to the presence of dissolved inorganics are the sulfonate precipitation and activation of inert minerals such as quartz for adsorption. During this quarter, the adsorption behavior of kaolinite and alumina systems containing gypsum was examined as a function of relevant variables. Since precipitation of sulfonate by the dissolved gypsum species appears to be the major phenomenon controlling the system behavior, a detailed thermodynamic analysis of the solubility and stability of gypsum and precipitation of sulfonate is also included.

The isotherm for the abstraction of *n*-decylbenzene sulfonate by gypsum is characterized by a slow-rising region,

followed by an almost vertical rise at about $4 - 6 \times 10^{-5}$ kmol/m³ sulfonate. This behavior is indicative of surfactant depletion by precipitation.

Gypsum type minerals which have relatively high solubility are often present only in trace amounts in the reservoir rock. Therefore, sulfonate depletion in the presence of 1 percent by weight of gypsum along with alumina and kaolinite was also determined. Results given in Figs. 1 and 2 show that addition of gypsum to alumina resulted in an increase in sulfonate uptake at all sulfonate levels; and gypsum caused a marked increase in sulfonate abstraction above 9×10^{-5} kmol/m³ of the surfactant in kaolinite-gypsum system.

FIG. 1 — Effect of 0.99 percent of gypsum on the adsorption on *n*-DBS on alumina.

The above effects of gypsum in mixed mineral systems could be either due to the presence of it as solid particles which can act as substrate for sulfonate abstraction, or the dissolved species can either interact with the sulfonate in bulk solution or can directly enhance or hinder the adsorption process on the major component. Separate tests showed that all the gypsum at 1 percent level of addition would dissolve under the adsorption conditions.

A detailed thermodynamic analysis of the solubility behavior of gypsum is conducted here and the precipitation behavior of sulfonate in Ca solutions is examined.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can also exist as anhydrite (CaSO_4) or hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) depending upon the temperature and other solution conditions.

FIG. 2 — Effect of 0.99 percent of gypsum on the adsorption on *n*-DBS on Na-Kaolinite.

The free energy changes involved in the reactions can be readily calculated

using data available at room temperature. Calculations were made for other temperatures from estimated values of heat capacities.

The free energy change involved in reaction (1), given in Fig. 3, shows that ΔG° becomes negative at about 46°C, indicating that anhydrite is the stable phase above this temperature. Similar calculations made for the hemihydrate suggest that the formation of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ will not take place under the experimental conditions ($\Delta G^\circ_{298} = 1.135$ kcal/mole, $\Delta G^\circ_{348} = 1.057$ kcal/mole).

Even though anhydrite is the stable phase at 75°C, information on the kinetics of this reaction, particularly in aqueous solutions, is not available. Thus, while calcium sulfate, under reservoir conditions may be present as anhydrite, the exact nature of the solid in laboratory adsorption tests is in question. Therefore, the activity of bivalent calcium in equilibrium with the solid phase is estimated for both gypsum and anhydrite. The chemical equilibria involved in the dissolution process are:

FIG. 3 — The free energy change of the system gypsum — anhydrite with temperature.

Preliminary calculations showed that the major species in the pH range of 4 to 9 are Ca^{2+} , SO_4^{2-} and $\text{CaSO}_{4(\text{aq})}$. Activities of Ca^{2+} in equilibrium with anhydrite and gypsum are given in Table 1. As expected from the phase stability

TABLE 1 — Activity of Ca^{2+} in equilibrium with anhydrite and gypsum at 75° C

pH	Ca^{2+} activity, kmol/m³	
	Anhydrite	Gypsum
5	3.45×10^{-3}	4.54×10^{-3}
6	3.449×10^{-3}	4.535×10^{-3}
7	3.448×10^{-3}	4.534×10^{-3}
8	3.448×10^{-3}	4.534×10^{-3}
9	3.448×10^{-3}	4.534×10^{-3}

considerations, the activity of Ca^{2+} in equilibrium with gypsum is higher than that with anhydrite.

Lack of thermodynamic data for CaSO_4 (aq) makes it difficult to estimate the total solubility from thermodynamic considerations. The solubility of gypsum under the test conditions was therefore determined experimentally and the results are given in Table 2.

TABLE 2 — Total dissolved calcium under adsorption conditions with temperature 75°C, NaCl 10^{-1} kmol/m³

Condition	Dissolved calcium kmol/m ³
Gypsum (excess)	2×10^{-2}
10 mg in 10 ml of NaCl.....	5.8×10^{-3}
Alumina + 10 mg gypsum in 10 ml NaCl	3.9×10^{-3}
Kaolinite + 20 mg gypsum in 10 ml NaCl.....	7.8×10^{-3}

The solubility product of $\text{Ca}(\text{DBS})_2$ at 75°C was determined by contacting sulfonate solutions of different concentrations with 5×10^{-4} kmol/m³ CaCl_2 in 10^{-1} kmol/m³ NaCl. The onset of precipitation was at $2.8 - 3 \times 10^{-4}$ kmol/m³ sulfonate. The solubility product of $\text{Ca}(\text{DBS})_2$ was calculated using γ , the activity coefficient.

$$\log y_i = -0.568 Z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I$$

(I = ionic strength.) The value of K_{sp} obtained, $7 - 8 \times 10^{-12}$ (kmol/m³)³, led to the results that while anhydrite will cause precipitation around $6 - 6.4 \times 10^{-5}$ kmol/m³ sulfonate, gypsum will cause precipitation around $5.2 - 5.5 \times 10^{-5}$ kmol/m³. (Compare the sharp rise in the abstraction isotherm which is around $4 - 6 \times 10^{-5}$ kmol/m³ sulfonate.) On the other hand, from results in Table 2, precipitation of $\text{Ca}(\text{DBS})_2$ is expected in alumina and kaolinite systems at

1.1×10^{-4} and 7.1×10^{-5} kmol/m³ sulfonate, respectively. On this basis, it is possible to predict values of abstraction in the gypsum + kaolinite system, Γ_{GK} , assuming that,

$$\Gamma_{GK} = \Gamma_K + \Gamma_P$$

where Γ_P is the contribution from precipitation. Table 3 shows that the predicted values of abstraction are in fair agreement with the experimental results. Similar predictions for gypsum + alumina system given in Table 4 also are in agreement with the experimental values obtained for abstraction.

TABLE 3 — Experimental vs. calculated abstraction in gypsum + kaolinite system

Total dissolved calcium = 7.8×10^{-3} kmol/m³
Calculated abstraction = $\Gamma_{GK} = \Gamma_K + \Gamma_P$

Residual sulfonate kmol/m ³	Experimental abstraction mol/g	Calculated abstraction mol/g
1×10^{-4}	6×10^{-6}	3.2×10^{-5}
1.5×10^{-4}	3.5×10^{-5}	6.3×10^{-5}
2×10^{-4}	6×10^{-5}	7.3×10^{-5}
3×10^{-4}	9×10^{-5}	8.3×10^{-5}

TABLE 4 — Experimental vs. calculated abstraction in alumina + gypsum system

Total dissolved calcium = 3.9×10^{-3} kmol/m³
Calculated abstraction = $\Gamma_{AG} = \Gamma_A + \Gamma_P$

Residual sulfonate kmol/m ³	Experimental abstraction mol/g	Calculated abstraction mol/g
2×10^{-4}	3.4×10^{-5}	6.5×10^{-5}
3×10^{-4}	7.5×10^{-5}	9.3×10^{-5}
5×10^{-4}	1.2×10^{-4}	1.2×10^{-4}
6×10^{-4}	1.2×10^{-4}	1.3×10^{-4}

VAPOR PRESSURE STUDIES OF THE SOLUBILIZATION OF HYDROCARBONS BY SURFACTANT MICELLES

Contract No. DE-AT19-81BC10476

**University of Oklahoma
Norman, Okla.**

Contract Date: Aug. 31, 1982

Anticipated Completion: Sept. 30, 1983

Government Award: \$50,510

Principal Investigators:

Sherril D. Christian

Edwin E. Tucker

Technical Project Officer:

Thomas E. Burchfield

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of the project are to determine accurate thermodynamic constants to characterize the solubilization of hydrocarbons by aqueous surfactant solutions. A prototype system, sodium octylsulfate in pure water and in aqueous solutions with added NaCl, is being investigated with vapor pressure, surface tension, and osmometry methods.

Summary of Technical Progress

Data for the system sodium octylsulfate-benzene-NaCl (0.4M)-water have been analyzed with a mass action model described previously^{1,2} to infer equilibrium constants for (a) the 1:1 interaction between the octylsulfate anion and benzene and (b) the incorporation of single benzene molecules into the octylsulfate micelle.

At 25°C, the 1:1 equilibrium constant is 0.88 L/mol for the solutions with added NaCl, compared with 0.62 L/mol reported for the 1:1 complex in pure water. Thus, addition of salt appears to favor the hydrophobic interaction of benzene

with the alkyl group of octylsulfate. The interaction constant for molecules of benzene with micellar octylsulfate (normalized to the same concentration of octylsulfate in the micelle) is 11.4 L/mol in the solutions containing NaCl, compared with 10.8 L/mol for the solutions in pure water. However, this comparison pertains to the ideal dilute solution standard states (unit molarity) for benzene and the surfactant monomer in the two media. When a standard state of pure benzene is used, it is inferred that the solubilization of benzene into the micelles is actually about 15 percent smaller in the 0.4 M NaCl solutions than in the solutions with no salt.

Another comparison that can be made is that of values of b , the interaction coefficient between benzene molecules within the micelle. This constant has a value of 0.055 in the 0.4 M NaCl solutions, compared with a value of 0.049 in the solutions in pure water (for micelles of comparable size). Thus although the present results indicate that the addition of NaCl somewhat reduces the ability of octylsulfate micelles to solubilize benzene at low benzene activities, the effect of salt is less important at higher benzene activities.

We have recently installed and calibrated a Wescan Model 232A molecular weight apparatus. This instrument is being used to determine activities and osmotic coefficients of aqueous solutions of surfactants and surfactants plus solubilizates. It appears that reliable degrees of association can be obtained with the method at solute molarities as low as 0.001 M. Combined with surface tension measurements, the osmometry method should yield thermodynamic information that will be useful in describing the formation of micelles and the solubilization of nonpolar species by surfactant solutions.

A recent article indicates the importance of heat capacity effects in relation to the formation of aggregates of hydrocarbons and hydrocarbon groups in aqueous solutions.³ Large negative heat capacity changes typically occur when solutes associate hydrophobically, and such effects are characteristic of the surfactant-hydrocarbon interactions under study here. It will be important to investigate these effects quantitatively in order to be able to predict the changes in properties of micellar solutions and micelle solubilizates that will occur at temperatures in the range 40° to 70°C.

References

- ¹E. E. Tucker and S.D. Christian, Faraday Symposium No. 17 on The Hydrophobic Interaction, J. Chem. Soc., in press.
- ²S.D. Christian and E.E. Tucker, Annual Report 1982 DOE/BC/10476-4.
- ³S.D. Christian and E.E. Tucker, J. Solution Chem. 11, 749 (1982).

TERTIARY OIL RECOVERY PROCESSES

Contract No. DE-AS19-83BC10345

**University of Texas
Austin, Tex.**

**Contract Date: Oct. 1, 1982
Anticipated Completion: Sept. 30, 1983
Government Award: \$224,000**

Principal Investigators:

**R.S. Schechter
W.H. Wade**

Technical Project Officer:

**Min K. Tham
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this research program are to develop the following: (1) surfactant systems that yield both low interfacial tensions and maximum amount of middle-phase per unit volume of surfactant with minimal adsorption at high salinities and high-divalent ion concentrations; (2) scaling rules for middle-phase formation, hopefully using the same approach developed to predict interfacial tension; (3) the relationship between surfactant structure, cosurfactants, and the rate and extent of adsorption on reservoir rock; (4) an understanding of the state of aggregation of surfactants in mixed micelle systems and the relationship of this state to ultralow interfacial tensions; adsorption, and fractionation due to adsorption; (5) an understanding of the mechanism of spontaneous emulsification, its relationship to residual oil mobilization, and comparison with mobilization by low tensions.

Summary of Technical Progress

The spontaneous imbibition of fluids in porous masses is of obvious importance in many chemical processes and the pore sizes can vary from 10 to 10^6 Å. The hope is that imbibition can be treated as a classical hydrodynamic flow problem, but for the lower limit in pore dimensions given above there are possible problems in using macroscopic properties. The results of the studies presented here show that the macroscopic flow equations are valid with bulk viscosity as the retarding force and the measured surface tension as the driving force.

W.H. Wade and J.A. Wingrave. "Macroscopic Properties of Fluids in Micropores. RILEM/CNR Symposium, Milan, Italy, April 26-28, 1983.

Conventional wisdom says that the continuous phase of a macroemulsion is the one into which the surfactant is preferentially partitioned. The equilibrium partition coefficient is in turn related to many system variable — character of the oil phase, temperature, electrolyte type and concentration and surfactant composition. The surfactant variables are tail length and branching in addition to extent of ethoxylation. When one maps the phase behavior with electrolyte concentration and percent EO content as variables, the regimes where surfactant is partitioned into oil and into water are found to be separated by a three phase regime. It is the common observation that in the initial stages of macroemulsion breakage, i.e., while under drainage control, the two maximally stable emulsion systems exist at the phase boundaries separating the three-phase regime from the two two-phase regimes. As creaming proceeds and emulsion breaking comes under coalescence control, the maximally stable w/o and o/w emulsions move further from the above mentioned phase boundaries. Nevertheless the equilibrium phase map serves as a starting point for identifying the most stable emulsion systems.

A. Graciaa, R.S. Schechter and W.H. Wade. "Macroemulsion Stability, Phase Behavior, and HLB of Ethylene Oxide Type Non-ionic Surfactant." Middle Atlantic ACS Regional Meeting, White Haven, PA, April 6-8, 1983.

Many, if not most, surfactants potentially useful for EOR will form precipitates or liquid crystals in oil/water systems, showing complex phase behavior or injection difficulties. One standard cure is the addition of alcohols. Unfortunately, this leads to reduced solubilization (elevated interfacial tensions) and possible chromatographic separation problems. The function of the alcohols appears to be to bond to the polar head group, propping apart the surfactant molecules and diminishing the attractive lateral interactions between surfactant tails. Linear surfactant species simultaneously have the greatest inherent solubilization capabilities and the greatest need for alcohol to destroy liquid crystals. This greatly complicates the choice of surfactant. Fortunately, recent experimental results show that the alcohol requirements can be greatly reduced by 1) elevating the system temperature and "melting" the more highly organized structures, 2) reducing electrolyte concentration or increasing head group polarity to enhance repulsion between the heads, 3) increasing the lateral dimensions of the surfactant molecules by branching the alkyl tails, adding phenyl rings or ethylene oxide, or decreasing tail length. All such structural modifications must be done judiciously since they disturb the necessary partitioning balance of surfactants between oil and water. Although many of these modifications also reduce the solubilization parameter, the extent of reduction is less than with alcohols. Moreover, mixed surfactant systems can be

identified which require little or no alcohol, have very large salinity tolerances, and produce high solubilization parameters at optimum.

C. Lalanne-Cassou, I. Carmona, P. Cowley, L.N. Fortney, C.J. Pearce, D.S. Schechter, R.S. Schechter, W.H. Wade, U. Weerasooriya, V. Weerasooriya, and S.H. Yiv. "The Interplay of Factors Affecting the Liquid Crystal/Microemulsion Phase Transition and their influence on Solubilization Parameter at Optimum." Gordon Conferences, Tilton, N.H. July 25-29, 1983.

CARBON DIOXIDE INJECTION FIELD PROJECTS

**ENHANCED OIL RECOVERY BY CO₂
MISCIBLE DISPLACEMENT IN THE
LITTLE KNIFE FIELD,
BILLINGS COUNTY, NORTH DAKOTA**

Contract No. DE-AC21-79MC08383

**Gulf Oil Exploration and Production Co.
Oklahoma City, Okla.**

Contract Date: July 17, 1979

Anticipated Completion: Dec. 30, 1982

Total Project Cost

DOE	\$ 2,811,000
Contractor	<u>2,811,000</u>
Total	\$ 5,622,000

**Principal Investigator:
J.E. Upton**

**Technical Project Officer:
Ken Spence
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this task is to confirm by field testing the results of laboratory CO₂ displacement tests and show that the CO₂ miscible displacement process has potential for commercialization in carbonate oil reservoirs that have not been extensively waterflooded and have a high remaining oil saturation.

Summary of Technical Progress

The final report for this project is being prepared for publication.

**WEEKS ISLAND "S" SAND RESERVOIR B
GRAVITY STABLE MISCIBLE CO₂
DISPLACEMENT
IBERIA PARISH, LOUISIANA**

Contract No. DE-AC05-77ET12004

**Shell Oil Co.
Houston, Texas**

Contract Date: June 10, 1977

Anticipated Completion Date: March 1983

Total Project Cost:

DOE	\$ 2,475,000
Contractor	4,039,000
Total	\$ 6,514,000

**Principal Investigator:
George E. Perry**

**Technical Project Officer:
R.J. Watts
Morgantown Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

**OIL RECOVERY BY CARBON DIOXIDE
INJECTION ROCK CREEK FIELD, ROANE
COUNTY, WEST VIRGINIA**

Contract No. DE-AC21-76ET12002

**Pennzoil Co.
Parkersburg, W. Va.**

Contract Date: June 30, 1976

Anticipated Completion: December 1983

Total Project Cost:

DOE	\$2,823,000
Contractor	3,760,000
Total	\$6,583,000

**Principal Investigators:
John Blomberg
Paul King**

**Technical Project Officer:
R.J. Watts
Morgantown Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

1. To demonstrate that CO₂ miscible displacement can be successfully accomplished in deep hot reservoirs which are unsuitable for surfactant flooding. This is a unique and different application of CO₂ injection in tertiary oil production projects.

2. Provide incentive for development of other CO₂ projects along the Gulf Coast and the development of adequate CO₂ supplies.

3. Transfer technology developed to private companies for further commercial application in other similar situations along the Gulf Coast.

Summary of Technical Progress

Drilling of the CO₂ displacement evaluation well, Weeks Island State Unit A well, was completed during this reporting period. The well is now being tested and all well data analyzed. During this period, the oil production well has been shut in. Oil production will resume when the evaluation well testing is completed.

Objective

The objective of this project is to demonstrate the efficiency and economics of recovering oil from a shallow, low-temperature reservoir using carbon dioxide and water to displace the oil for tertiary recovery.

Summary of Technical Progress

The project was shut down during this reporting period. All injection and production wells were shut in. The pilot area has been flooded out. Activities for a mobility control field experiment will be initiated during the next quarter.

CARBON DIOXIDE INJECTION

SUPPORTING RESEARCH

DISPLACEMENT OF OIL BY CARBON DIOXIDE

Contract No. DE-AS19-80BC10331

**New Mexico Institute of Mining and
Technology**

Contract Date: Sept. 1, 1980

Anticipated Completion: Aug. 31, 1983

Total Project Cost:

DOE	\$372,501
Contractor	170,678
Total	\$543,179

Principal Investigators:

Franklin M. Orr, Jr.

Joseph J. Taber

Technical Project Officer:

Leo A. Noll

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

This project will produce quantitative measurements of the extent to which CO₂ contacts and recovers oil in the presence of the high water saturations normally present in tertiary CO₂ floods. There are three areas of study:

1. Phase behavior and fluid property measurements. Static equilibrium experiments measure phase volumes as functions of pressure and compositions. Continuous multiple contact experiments measure compositions and densities for two phases in equilibrium.

2. Core flood experiments. Miscible displacements in the absence of water with fluids of matched density and viscosity characterize the flow properties of the rock (dispersion, heterogeneity). Steady-state miscible displacements with water present, again with fluids of matched density and viscosity, study shielding of trapped oil by water films. Gravity stabilized displacements of oil by CO₂ in the presence of water examine the efficiency with which CO₂ contacts trapped oil. Effects of phase behavior and fluid properties must be accounted for in interpreting such displacements.

3. Mathematical modeling and numerical simulation of the displacement process to investigate interactions of phase behavior, fluid properties, gravity segregation and viscous fingering.

Summary of Technical Progress

Phase behavior and fluid property measurements

Static equilibrium PVT equipment has been modified to reduce the volume of sample lines between cells and to improve the accuracy of viscosity measurements. A check of cell volume and viscometer tube calibrations will begin shortly.

Work on the use of an oscillating quartz crystal to measure fluid viscosities has continued. A crystal holder in which the crystal was suspended on Teflon blades was tested but was found to have too much damping of the crystal. Tests were then performed with the original mounting system (wires at the midpoint) for several hydrocarbons. Viscosities measured with the crystal viscometer agreed closely with published values. Additional tests to establish performance of the instrument over a wide range of viscosities, densities, and operating conditions are underway.

A sequence of continuous multiple contact (CMC) measurements of phase compositions and densities has been completed for three synthetic oil systems. A comparison of component partitioning in mixtures of CO₂ with paraffinic and naphthenic synthetic oils indicates the following:

1. The solubility of CO₂ was highest in the isoalkane mixture, lower in the normal alkane mixture, and lowest in the naphthenic mixture.

2. CO₂ extracted hydrocarbons most effectively from the isoalkane oil, and less effectively from the normal alkane oil, and least effectively from the naphthenic oil.

Displacement experiments

Software for on-line data acquisition in core flood experiments was completed and tested. Experimental procedures for those experiments have been modified to reduce the time required for core cleaning and preparation and to reduce the effects of dead volume on composition measurements for small cores.

The use of 0.5-inch-diameter cores in place of 1.5-inch cores was investigated. The smaller cores can be cleaned and

saturated more rapidly, though their smaller pore volume makes control of dead volume more important. A new conductivity cell with a volume of 15 μ l was constructed to replace a commercial cell with a volume of 0.3 cm³ and new, lower-volume end caps were fabricated.

Since refractive index measurements have been substituted for chromatography, normal hydrocarbon mixtures were chosen for miscible displacements in the oil phase. Normal decane (C₁₀) and C₁₀ containing a small amount of normal undecane (C₁₁) were chosen because they show linear refractive index response. Ethylbenzene and ethylbutyrate, the oils used previously, did not.

Test experiments for miscible displacements using these fluids have been carried out. These displacements successfully demonstrated the use of the differential refractometer to measure compositions of produced hydrocarbons.

Development of computer code for interpretation of single-phase miscible displacements has been completed. A simple numerical scheme was adopted for solution of the Coats-Smith model. The scheme is based on the use of truncation error (numerical dispersion) to represent a portion of the physical dispersion in core floods. That approach reduces computational costs significantly.

This model has been used to fit the results of miscible floods in both sandstone and carbonate cores. The parameters of interest which are obtained from the fit include values of the flowing fraction, Peclet number, and mass transfer group.

Simulation

Numerical simulation efforts have centered on the modification of the one-dimensional simulator to model the effects of a dendritic oil saturation on the compositional behavior of the CO₂ flood process. Dendritic oil ganglia have been observed in flow visualization experiments. The computational effort to model such behavior is an attempt to understand how the exchange of material between flowing and stagnant phases alters mixing between oil and CO₂, hence how it affects the local displacement efficiency of the process.

MOBILITY CONTROL FOR CO₂ INJECTION

Contract No. DE-AC21-81MC16426

**New Mexico Institute of Mining and Technology
Petroleum Recovery Research Center**

Contract Date: May 20, 1981

Anticipated Completion: Sept. 30, 1983

Government Award:

DOE	\$213,902
Contractor	-0-
Total	\$213,902

Principal Investigator:

John P. Heller

Technical Project Officer:

A.B. Yost, II

Morgantown Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

This research project is in support of an enhanced oil recovery experiment to be performed by the Pennzoil Company with the Department of Energy. This operation, to be conducted in the Rock Creek Field in Roane County, West Virginia, is a test of mobility control methods to improve the efficiency of carbon dioxide floods. The goals of the contract with New Mexico Tech's Petroleum Recovery Research Center are:

1. To continue activities under a companion project, DE-AC21-79MC10689, which are aimed at the development of mobility control additives or procedures. These are to be specialized, where possible, to apply to the particular problems of the Rock Creek Field.
2. To conduct additional laboratory tests designed to study the compatibility of Rock Creek oil, brine, and reservoir rock with CO₂ and with other chemicals which might be involved in mobility-controlled CO₂ floods.
3. To provide support in the design of field mobility control tests themselves.
4. To assist in the assessment of field results and in the design of tests to be used for such assessment.

Summary of Technical Progress

A draft topical report on the design of mobility control experiments at Rock Creek Field has been completed and is being reviewed by DOE and Pennzoil personnel.

METHODS FOR MOBILITY CONTROL IN CO₂ EOR PROCESSES

Contract No. DE-AC21-79MC10689

**New Mexico Institute of Mining and Technology
Petroleum Recovery Research Center**

Contract Date: Sept. 30, 1979

Anticipated Completion: May 31, 1983

Government Award:

DOE	\$248,683
Contractor	256,275
Total	\$504,958

Principal Investigators:

John P. Heller

J.J. Taber

Technical Project Officer:

A.B. Yost, II

Morgantown Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The goals of this research project are to develop mobility control methods for CO₂ floods. The project is divided into three tasks, reflecting the need not only to develop particular additives for this use but also to perfect laboratory methods by which their effectiveness may be evaluated. The three objectives are:

1. To develop an instrumented core flooding system in which the effectiveness of various mobility control procedures and additives can be tested.
2. To study the mechanisms by which foam-like dispersions of dense CO₂ in water are operative in decreasing the overall mobility of CO₂ through rock and to develop CO₂-based "foams" of controllably low mobility for use in the oil field.
3. To develop the method of direct thickened solutions of polymer(s) in dense CO₂ which will exhibit a viscosity of a few centipoise and thus be capable of immediate use as a mobility control additive.

Summary of Technical Progress

The draft final report on this contract is in preparation by NMIMT personnel. The final report will be out for printing by early June, 1983.

ENHANCED OIL RECOVERY BY CO₂ FOAM FLOODING

Contract No. DE-AC21-78ET12083

New Mexico State University
Las Cruces, N.M.

Contract Date: Sept. 30, 1981

Anticipated Completion: Sept. 29, 1984

Total Project Cost:

DOE	\$390,921
Contractor	390,772
Total	\$781,693

Principal Investigator:

John T. Patton

Technical Project Officer:

Ken Spence
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this study is to identify commercially available additives effective in reducing the mobility of carbon dioxide, CO₂, thereby improving its efficiency in the recovery of tertiary oil at a price which will be economically attractive.

Summary of Technical Progress

Task 1.1 - Apparatus design and construction

Significant progress was achieved during this quarter. A third, high-pressure model was packed with unconsolidated silica flour which had been carefully sized to produce a permeability of about 500 millidarcys. To accommodate the high efficiency of the mobility control additives now being tested, it was necessary to pack the model with the higher permeability sand in order to achieve timely results. Previous models, having permeabilities below 200 millidarcys require 5 to 6 weeks to accomplish one experiment. This lengthy experiment time was adversely affecting the experimental progress.

Task 2.1 - Foam generation and static stability

Six tailored surfactants were submitted by Exxon Chemical for evaluation as improved mobility control additives. Initial static stability tests indicate that the

surfactants in general, are above average in comparison to those previously reported. It is Exxon's intention to utilize the initial screening data in the design of a second generation of mobility control additives that will have superior mobility control properties tailored into the molecule.

Task 3.1 - Dynamic foam stability

Work during the period was concentrated on a chemical additive with a structure previously identified as being very effective but having a slightly higher molecular weight. The additive, Pluradyne SF-27, is produced by Wyandotte Chemical. It is similar to Neodol 23-6.5 with the exception that the hydrophobe, consisting of a linear alcohol, is C₁₄₋₁₅ rather than C₁₂₋₁₃. In addition, it has an extra 1/2 mole of ethylene oxide added to the hydrophylic portion of the molecule. The mobility ratio curve obtained with this additive is shown in Fig. 1. For comparison similar curves

FIG. 1 — Mobility ratio vs. time for Pluradyne S.F.-27; pH = 2.5.

for the Neodol 23-6.5 as well as Alipal CD-128 are shown as Figs. 2 and 3. It can be noted that the Pluradyne SF-27

FIG. 2 — Mobility ratio vs. time for Neodol 23-6.5, pH = 2.9, 1/28/83.

shows superior mobility control in the dynamic screening test. Additional studies will be undertaken during the next quarter to see if this superiority is still apparent in oil displacement tests utilizing high pressure carbon dioxide.

FIG. 3 — Mobility ratio vs. time for Alipal CD-128, pH = 2.85, 20/11/82.

Task 4.1 - Foam stabilizers

No additives submitted for testing.

Task 5.1 - Immiscible displacement

No displacement tests were completed during the period. The model has been repacked with a more permeable sand. Permeability and porosity measurements are in progress.

Task 6.1 - Miscible displacement

Experiments on this task operated continuously during the period. Due to the very low permeability to gas, rendered by the mobility control additives, this task has taken most of the quarter to complete. In the experiment, Stepanflo 50 was used as a mobility control additive for the miscible displacement of octane by high pressure carbon dioxide. Effluent samples are now being analyzed and it appears that the presence of the mobility control additive had no adverse effect on the almost complete miscible displacement of the octane. This experiment was conducted to demonstrate that the formation of foam, in a matrix, characteristic of an oil reservoir, would not materially interfere with the miscible displacement of oil by carbon dioxide.

Summary status, assessment and forecast

A special item of significant importance is the news that Exxon USA is considering the use of mobility control additives for their giant nitrogen floods in the Jay and Blackjack fields. Detailed data, relative to the most promising mobility control additives, have been forwarded to Exxon to assist them in their project planning.

ENHANCED RECOVERY OF OIL FROM SUBSURFACE RESERVOIRS WITH CARBON DIOXIDE

Contract No. DE-AC21-79MC10509

**Texas A&M Research Foundation
College Station, Tex.**

**Contract Date: Feb. 23, 1979
Anticipated Completion: Sept. 30, 1983
Government Award: \$225,000**

**Principal Investigator:
Dr. Joseph S. Osoba**

**Technical Project Officer:
A.B. Yost, II
Morgantown Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

To determine oil recoveries for various degrees of miscibility in consolidated (sandstone and carbonates) and unconsolidated laboratory models for different sample

lengths, oil gravities, dip angles and reservoir heterogeneities.

Summary of Technical Progress

Data from previous displacement studies were used to plot oil recoveries as functions of CO₂ slug size. These results are shown in Figure 1.

FIG. 1 — Determination of the optimum CO₂ bank size (water propellant). Oil recoveries from the two horizontal 15 ft and the 5 ft long consolidated Berea sandstone cores as functions of CO₂ slug size. T = 110°F, 120°F; 1500 psig ≤ pressure ≤ 1650 psig, 2500 psig ≤ pressure ≤ 2650 psig)

Four displacement runs have been conducted on the 15 ft. long Berea cores. In Run #1, 0.7 HPV CO₂ slug propelled by 0.1N KCl solution was used to displace Foster field crude oil from the core. The displacement was conducted at a pressure of 1597 psig. Similar runs were conducted at 1610 psig, 1590 psig, and 1614 psig when 0.5, 0.3, and 0.1 HPV CO₂ slugs propelled by KCl solution were injected to displace Foster field crude oil from the core. CO₂ and KCl solution were injected at a rate of 6cc/min. The temperature of the system was maintained at 110°F during the test. The result is shown in Table 1. Oil recovery ranged from 91.27 percent OIP for the 0.7 HPV CO₂ slug to 76.69 percent OIP for the 0.1 HPV CO₂ slug.

TABLE 1

Pressure psig	CO ₂ slug size HPV	Oil recovery pct OIP
1597	0.7	91.27
1610	0.5	90.00
1590	0.3	87.12
1614	0.1	76.29

INVESTIGATION OF ENHANCED OIL RECOVERY THROUGH USE OF CARBON DIOXIDE

Contract No. DE-AS19-80BC10344

**Louisiana State University
Baton Rouge, La.**

**Contract Date: Oct. 1, 1980
Anticipated Completion: Sept. 30, 1983
Government Award: \$485,335**

**Principal Investigators:
Teresa G. Monger
John. H. McMullan**

**Technical Project Officer:
Thomas E. Burchfield
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this project include the determination of: (1) the mechanism by which carbon dioxide displaces oil; (2) the effects of various components (e.g., ethane, propane, and butane) in the injection fluid and in the oil on minimum miscibility pressure, displacement efficiency, and

displacement mechanism; (3) the effect of water saturation on the ability of carbon dioxide to displace oil and on the mechanism of the displacement process; (4) the factors involved when carbon dioxide is used to displace oil which exists as a discontinuous residual phase following a waterflood or natural water drive. This research involves the displacement of synthetic and crude oils from unconsolidated sand packs and Berea sandstone cores and the analysis of produced fluids.

Summary of Technical Progress

Introduction

During the past quarter, the project was dedicated to the analyses of data accumulated on earlier experiments. These results are discussed in detail in the project's second annual report No. DOE/BC/10344-8. An abstract was also submitted to the Society of Petroleum Engineers for consideration of presentation at its annual meeting.

Extensive modifications to the contract were prepared to reflect a reduced level of support and redirection of research into areas not documented in the existing contract. A reduced experimental effort resulted from the unusual amount of administrative responsibilities during the past quarter.

Phase behavior studies

Single-contact phase behavior measurements have been initiated for mixtures of CO₂ and Brookhaven reservoir oil which probe low-molecular-weight oil compositional affects. These studies are designed to illuminate the relationship between the displacement mechanism, and minimum miscibility pressure results from sand pack displacements of Brookhaven crude (summarized in the project's second annual report). Pressure-volume isotherms and swelling indices are being determined at 109°F and 140°F for CO₂-crude oil mixtures which span the CO₂ compositional range. Phase compositions and densities are being determined at 109°F, and about 1,800 psi for selected sample mixtures.

Samples of Brookhaven reservoir oil produced during sand pack displacements performed to determine minimum miscibility pressures for dead Brookhaven crude as a function of temperature are being analyzed by gas chromatography and carbon-13 nuclear magnetic resonance spectrometry to delineate oil compositional and chemistry effects.

Displacement studies

Construction of a second rack to hold the new high-pressure core holders continued during the last quarter. A second core holder has been mounted vertically, and design and installation of the heating system has begun. These core holders will be heated externally rather than internally like the existing core holders mounted on the rotating rack.

While this will require a significantly longer time to heat the cores to run temperature, it should facilitate the removal and installation of the cores as well as provide a more uniform temperature distribution. At present we plan to use this consolidated core system to study the effects of water saturation and also to investigate gravity stable flooding with natural crude oil.

Preparation of a core in the existing rotating core rack has begun to allow displacements using synthetic oils. The phase behavior of these oils has been studied extensively, and the displacements are designed to supplement what has been interpreted as the role of oil aromaticity in multiple-contract miscibility.

One additional plugging experiment has been performed using live Brookhaven crude. This experiment was done at the same temperature and pressure as the earlier reported experiment using dead Brookhaven crude. The results of the experiment suggest that plugging was not as severe using the live oil. The live oil displacement encountered operational problems, however, and a repeat live oil displacement at the same conditions is planned.

COMPUTER SIMULATION OF RECOVERY OF HEAVY CRUDE OIL USING CARBON DIOXIDE DRIVE OR HUFF-N-PUFF

Contract No. DE-AC19-81BC10640

**Colorado State University
Fort Collins, Colo.**

**Contract Date: Mar. 1, 1981
Anticipated Completion: Dec. 31, 1982
Government Award: \$31,087**

**Principal Investigator:
David A. Krueger**

**Technical Project Officer:
Ken Spence
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this work is to determine by computer simulation the feasibility of CO₂ drive and CO₂ huff-n-puff

methods in laboratory tests using heavy oil and future field tests in shallow heavy oil reservoirs.

Along with the CO₂ computer simulation, an investigation will be made of the *in situ* combustion experiment at Bartlett, Kansas. The site has been mapped by a CSAMT resistivity method to investigate the stability and extent of the burn front. These maps, along with experimental data obtained from the *in situ* burn will provide information to develop and/or improve a prediction model for the *in situ* combustion process.

Summary of Technical Progress

The final report for this project is being prepared for publication.

DETERMINATION OF MISCIBILITY PRESSURE BY DIRECT OBSERVATION METHOD

Contract No. DE-AC21-81MC16140

University of Alabama

**Contract Date: July 7, 1981
Anticipated Completion: Feb. 28, 1983
Government Award: \$77,235**

**Principal Investigator:
George C. Wang**

**Technical Project Officer:
A.B. Yost, II
Morgantown Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The overall major objectives of this contract are to conduct all necessary laboratory experiments to (1) develop a fast and accurate method for the determination of minimum miscibility pressure (MMP), (2) gain new knowledge in CO₂ miscibility through chemical analysis and microphotography, and (3) determine the feasibility of *in situ* foam generation through visual observation and microscopic photography through a transparent tube.

Summary of Technical Progress

The final report is expected by April 15th.

CARBON DIOXIDE MISCIBLE FLOODING PROSPECTS

Contract No. DE-AC19-79BC10122

**University of Kansas Center for Research Inc.
Lawrence, Kan.**

Contract Date: Oct. 1979

Anticipated Completion: Aug. 15, 1983

Government Award: \$237,923

Principal Investigators:

Don W. Green

George W. Swift

Technical Project Officer:

Bruce E. Gammon

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this work is to develop an effective method for evaluating the potential of CO₂ miscible flooding of various petroleum reservoirs. This will lead to a set of criteria based on information acquired from standard drilling and production records and on reservoir fluid analyses. The phase behavior of carbon dioxide with a synthetic oil and some well-characterized candidate oils in the presence of brine will be obtained, and the results will be correlated with a suitable equation of state. A method will be used to simulate the repeated contact conditions encountered in flow through reservoirs. These results will be used in a computer model for fluid flow in porous reservoirs. The latter results will be checked against laboratory studies to be done with sand-packed cores and Berea sandstone cores. In these studies, the effects of temperature and pressure are to be investigated over a range comparable to those required for field applications.

Summary of Technical Progress

Bulk Phase Behavior Studies

Methods of metering components and measuring the bubble point pressures of mixtures were improved to minimize the problems associated with dead volume in the apparatus. In addition, the dead volume was calibrated to allow determination of saturated and compressed liquid densities of mixtures. Six different mixtures of the CO₂-n-butane-n-decane system were studied using the improved procedures. Binary interaction coefficients regressed from the new data at 160°F and 1400 psia, from the data of

Metcalf and Yarborough, and from both sets together vary no more than 1.6 percent. When plotted, there is no visual difference between the phase envelopes calculated with the different sets of interaction coefficients in the API-SRK equation of state.

From these data, the maximum miscibility composition for the CO₂-n-butane-n-decane system at 160°F and 1400 psia is 0.2765 mole fraction decane. The maximum miscibility composition is the maximum amount of the heavy ends (decane) in a mixture (butane-decane) which can become miscible with CO₂ at a given temperature (160°F and pressure (1400 psia). Sensitivity analysis indicates that the maximum miscibility composition is known for this system within 0.008 mole fraction units.

Table 1 presents the saturated liquid densities for these mixtures and those calculated from the correlation of Hankinson and Thomsom (1979). The mixtures are listed in order of increasing butane composition from the CO₂-decane binary toward the critical region. It is clear from the table that as the critical region is approached, the correlation becomes unable to predict the densities within reasonable error.

TABLE 1 — Saturated liquid densities at 160°F (nominal pressure 1400 psia)

CO ₂	Mole fraction butane	Decane	ρ exp. g/cm ³	ρ calc. g/cm ³	Pct. Δ
0.6704	0.0000	0.3296	0.735	0.748	1.8
0.6742	0.0682	0.2576	0.713	0.720	1.0
0.6814	0.1383	0.1803	0.695	0.676	2.7
0.7118	0.1998	0.0885	0.642	0.577	-10.1
0.7539	0.2059	0.0403	0.543	0.338	-37.7
0.7538	0.2067	0.0396	0.548	0.332	-39.4

Experimental Linear Displacement Studies

The miscibility pressure was measured for different Kansas crude oils. The samples were stock-tank oils and therefore were relatively dead oils. However, the reservoirs represented are producing at very low gas-oil ratios and thus the stock-tank oils are probably representative of the reservoir oils. The crude oils for which miscibility pressures were measured, and results are shown in Table 2.

TABLE 2 — Miscibility pressures

Crude oil	°API	Temp., °F	Viscosity at 25°C, cp	Miscibility pressure, psi
Olson B #6	34.5	105	11.6	1600
Newcomer #4	36.1	105	12.6	1350
Olive	39.5	105	7.7	1250

Additional displacements were made in which relatively light hydrocarbons were added to selected crudes to

determine the effect on miscibility pressure. A mixture of 10 percent n-hexane and 90 percent Abernathy crude oil (by volume) was prepared. The miscibility pressure of Abernathy crude was previously determined to be 1600 psi at 126° F. With the hexane added, the miscibility pressure decreased to 1500 psi. Results are shown in Fig 1. Olson A #3

FIG. 1 — Slim-tube displacements with and without n-hexane added.

crude was saturated with n-butane. This crude oil was previously determined to have a miscibility pressure of 1250 psi at 105° F. The addition of the n-butane decreased the miscibility pressure to 1100 psi. The average GOR was 60 SCF/STB during the displacement. Results are given in Fig. 2.

Numerical Model of Fluid Flow

The mathematical model of Orr (1980) was modified to include the effects of variable density. The modification is about 80 percent complete. Investigations were made on methods of characterizing crude oils for miscibility pressure

FIG. 2 — Slim-tube displacements with and without n-butane added.

predictions. The current version of the Soave-Redlick-Kwong (SRK) computer simulator for computation of ternary or pseudo-ternary diagrams was examined, and the current program is being rewritten in Fortran for application on the University's Honeywell computer. The code for doing flashes and bubble-point and dew-point calculations was completed.

Literature Cited

- Hankinson, R.W., Thomson, G.H., *AIChE J.*, 25, No. 4 (1979) 653-663.
- Metcalfe, R.S. and Yarbrough, L.: "The Effect of Phase Equilibria on the CO₂ Displacement Mechanism", *Soc. Pet. Eng. J.* (Aug. 1979) 243-252; Trans., AIME.
- Orr, F.M. Jr., 1980. "Simulation of the One Dimensional Convection of Four-Phase, Four Component Mixtures," Topical Report, Dept. of Energy.

THERMAL/HEAVY OIL FIELD PROJECTS

**IMPROVED OIL RECOVERY BY
STEAMFLOODING, CAT CANYON FIELD,
CALIFORNIA**

Contract No. DE-AC03-76ET12058

**Getty Oil
Ventura, Calif.**

Contract Date: June 25, 1976

Anticipated Completion: Nov. 30, 1982

Total Project Cost:

DOE	\$2,000,000
Contractor	<u>\$6,700,000</u>
Total	\$8,700,000

**Principal Investigator:
D.R. Greene**

**Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this project is to demonstrate and evaluate by a pilot operation the technical efficiency and economics of producing a highly viscous crude oil from an unconsolidated sand by steamflood in conjunction with short-term steam stimulations of producing wells.

Summary of Technical Progress

The project has been completed, and the final report is being published as report No. DOE/ET/12058-6. Single copies are available from BETC.

FIELD PILOT OF STEAM DRIVE WITH IN SITU FOAMING

Contract No. DE-AC03-80SF11445

Stanford University Petroleum Research
Institute
Stanford, Calif.

Contract Date: Oct. 1, 1980

Anticipated Completion: Mar. 31, 1983

Government Award: \$2,181,301

Principal Investigator:
W.E. Brigham

Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

Stanford University Petroleum Research Institute contracted to perform a field test of steam drive with *in situ* foaming for heavy oil recovery. This field test is designed to obtain field-scale data unattainable in a laboratory study. The many variables in an actual *in situ* test present a challenge that puts to a severe test, the ability of researchers to achieve positive results, and to adjust planned operations for changing conditions.

The general procedure is to select a test site (the McManus leases located in the Kern River field); run tests on surfactants; evaluate the reservoir to select two patterns for the field test; drill observation wells; perform laboratory studies of surfactant reaction; determine injection profiles; run tracer and injectivity tests; determine final design of surfactant as to slug size, injection rates, etc.; monitor responses of the test, both as to injectivity and production of oil and steam; utilize models for studies of production; drill post-pilot core holes to determine saturation distribution; and finally, analyze the data to evaluate technical and economic merits of using surfactants with steam drive process.

Summary of Technical Progress

A joint meeting of personnel from Stanford, DOE, and subcontractors (CORCO and GeothermEx) was held in early January for the purpose of completing plans for the third major slug treatment program. On Jan. 31, the

surfactant treatment of the steam injection well, McManus 208, was initiated.

Numerous steam generator failures occurred during February primarily due to outdated control systems and severe weather conditions. Controls were replaced late in February and longer run periods were observable. The monthly run time increased from a low 81 percent in February to a more consistent 92 percent during March. Surfactant, nitrogen gas and steam were being injected simultaneously. The target injection rates are: 1) 0.25 gpm (360 gpd) surfactant, 2) 10 SCFM (14,000 SCFD) nitrogen gas, and 3) a projected 180 bwpd steam. Through the first 29 days of treatment, actual injection rates were: 1) 0.27 gpm surfactant, 2) 9.5 SCFM nitrogen gas, and 3) 182 bwpd steam. The low rate injection of Suntech IV continued through March. The surfactant injection is planned for completion in mid-April. Wellhead pressure increased from a pre-treatment 80 to 160 psig in late March. A total of five injection profile surveys were run during the quarter and each profile indicated a significant vertical injection migration at the well bore as compared to its prior profile.

Although too soon to reach firm conclusions, the production data presented on the attached graph show a significant increase in oil recovery caused by the surfactant injection. The start of the injection of the second slug on October 7, 1982 was premature (the effect of the first slug had not completely disappeared), but the production after the second slug behaved in a manner very similar to the first slug response. Incremental production is difficult to calculate due to the poor production data prior to injection of surfactant. If one estimates the average daily production of the test pattern prior to injection at 60 bbl/day (most probable case), incremental production caused by the first two slugs is in excess of 10,000 bbl. Further analysis of the data is in progress.

FIG. 1 —

**ENHANCED OIL RECOVERY
BY STEAMFLOODING
MIDWAY-SUNSET FIELD, CALIFORNIA**

Contract No. DE-AC03-79ET12059

**Santa Fe Energy Co.
Los Angeles, Calif.**

Contract Date: June 16, 1976

Anticipated Completion: June 30, 1983

Total Project Cost:

DOE	\$1,700,000
Contractor	6,547,266
Total	\$8,247,266

**Principal Investigator:
Willie O. Alford**

**Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this field project is to demonstrate the operational and economic aspects of steamflooding a typical, low-pressure, flat, heavy-oil reservoir which has had unfavorable response to cyclic steam stimulation.

Summary of Technical Progress

Steam injection continued in all 14 injectors. Oil and water production was slightly higher for the quarter. Minor maintenance work including sand bails, pump performance checks, temperature surveys, and fluid level checks and cycle stimulations were performed on some wells. Recovery from the vapor recovery system averaged over 100 barrels per month.

The summary of production for the quarter and cumulative production figures through February 1983 are as follows:

Production	Quarter	Cumulative
Oil, bbl	34,487	430,328
Water, bbl	250,645	1,728,191
Steam inj., bbl	775,064	5,685,839

THERMAL/HEAVY OIL SUPPORTING RESEARCH

MAXIMIZING STEAM DRIVE IN LIGHT OIL SYSTEMS

Contract No. DE-AC19-80BC10316

**Petroleum Training and Technical Services
Norman, Okla.**

Contract Date: Sept. 30, 1980

Anticipated Completion: Dec. 31, 1982

Government Award: \$279,027

**Principal Investigator:
Henry Crichlow**

**Technical Project Officer:
Fred W. Burtch
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this project is to extend the use of steam drive technology to light oil reservoirs and attain the set goal of increasing the ultimate recovery of oil using this technique. Extend and verify the technical and economic feasibility of the steam drive recovery process in light oil reservoirs by laboratory research and conduct a technical pilot demonstration of the steam drive process in an appropriate light oil reservoir.

Summary of Technical Progress

The final report was received and reviewed by BETC personnel. It should be published during the latter part of the next quarter.

SECONDARY RECOVERY BY THERMAL METHODS

Contract No. DE-AC03-81SF11564

**Stanford University Petroleum Research
Institute (SUPRI)
Stanford University**

Contract Date: Oct. 1, 1981

Anticipated Completion: Sept. 29, 1986

Government Award: \$3,931,202

**Principal Investigator:
W.E. Brigham**

**Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The ultimate goal of the Stanford University Petroleum Research Institute is to conduct research directed toward increasing the efficiency in the recovery of heavy oils. Presently SUPRI is working in five main directions.

1. Flow Properties Research — to assess the influence of different reservoir conditions (temperature, pressure, etc.) on the absolute and relative permeabilities to oil and water, on capillary pressure and electrical resistivity.
2. *In Situ* Combustion Studies — to evaluate the effects of different parameters on the *in situ* combustion process. This project includes the study of the kinetics of the reactions.
3. Additives To Improve Steam Injection — to develop a process using commercially available chemicals to reduce gravity override and channeling of steam.
4. Formation Evaluation — to develop and improve techniques of formation evaluation such as tracer tests, well logging and pressure transient tests.
5. Field Support Services — to provide technical support for design and monitoring of DOE sponsored field projects.

Summary of Technical Progress

Project 1: Flow properties studies

The effect of temperature on the absolute permeability to water is being studied on consolidated cores. The first runs are being made on a clean Fontainebleau sandstone. Berea cores will be studied later to study the effect of the clays.

The equipment used to study temperature and pressure effects on relative permeabilities of oil water systems has been modified to allow the use of consolidated cores. Calibration of the different parts is progressing. The literature search has been updated and completed.

The equipment for the experiments on determination of capillary pressure at high temperature and at different pressures is being calibrated. Pressure tests were performed. The first runs are planned for Spring 1983.

Project 2: In situ combustion

Oil has been obtained from Mobil's Newport Beach field. The literature search was continued on the kinetics of *in situ* combustion. The experimental tube designed to study the intermediate temperature reactions is being tested and calibrated.

Preliminary studies have been undertaken on high-oxygen-concentration runs. Design of an apparatus to perform these tube runs has been started. Safety factors are also being studied.

Project 3: Additives to improve steam injection

The project on two-dimensional glass models is continuing. The literature search was completed. References, abstracts and papers are now organized for easy retrieval. A technical report summarizing the results is in preparation. After a comprehensive evaluation of all the experimental data to date has been made, a simple one-dimensional model will be built in order to determine the residual oil saturations after foam flow under various experimental conditions.

A new experiment was initiated to measure oil-surfactant interfacial systems by the spinning-drop technique at different temperature levels. Suntech IV was used at different concentrations. Kaydol (white mineral oil) was the oil phase. To date, concentrations from 0.0005 percent to 5 percent (by weight) active were studied at temperatures of 25, 45, and 65°C. A graph of the results is attached. Salt effect has also been studied.

Work on the long-term temperature stability of additives is being continued. New runs using alpha olefin sulfonates of different chain length which were obtained from Shell, Ethyl and Stepan and other surfactants will be started at the beginning of April 1983.

Material balance and temperature profiles obtained from the linear steam apparatus were analyzed. In this analysis, empirical correlations are used to determine the density and enthalpy of each phase and component during a run. The experimental procedure will be modified to make the experiment more realistic. Surfactant will be injected into the model after steam injection to simulate foaming in a desaturated zone of the reservoir.

FIG. 1 — Oil-surfactant interfacial systems by spinning-drop technique.

Project 4: Formation evaluation

Well Testing

The mathematical formulation of interference testing with skin and wellbore storage at both wells is in progress. A solution to the dimensionless system of equations in Laplace space has been obtained and inverted numerically using the

Stehfest algorithm. Analysis of the results and validation of the solution technique is in progress.

Simulation

Thermal numerical simulators will be used for further analysis of the pressure-falloff tests in thermal recovery. The simulators to be used in this project are the ISCOM simulator from the Computer Modelling Group in Calgary, Canada and an experimental thermal simulator in APL developed by Dr. Rodman Jenkins.

A new project, "Use of Advance Graphics in Reservoir Simulation," has started. The primary goals for this project are to simplify and to expedite the process of input and output for reservoir simulation. Secondary goals are to achieve interactive control during a simulation run in order to ease the process of history matching.

Tracer Flow

The mathematical formulation of the single-well tracer problem is in progress. A technical report on that project is expected in the near future.

Solution of the well-to-well tracer-response curve interpretation has been presented by M. Abbaszadeh for a mobility ratio equal to one. The non-unit mobility ratio case cannot be solved analytically because streamtube shapes change with time. Numerical methods will be used to solve this problem. A literature search on numerical techniques to solve the convection-diffusion equation has been performed to select the most appropriate numerical scheme.

Well Logging

Analysis of data from the SUPRI steam foam field experiment continues.

Project 5: Field support services

SUPRI has been active in support of the steam foam field experiment located in the Kern River Field. Work this quarter has focused on laboratory experiments with Suntech IV.

**USE OF SULFUR TRIOXIDE AS AN
ENHANCED RECOVERY AGENT**

Contract No. DE-AS19-83BC10762

**University of Oklahoma
Norman, Okla.**

Contract Date: Sept. 30, 1982

Anticipated Completion: Sept. 30, 1983

Government Award: \$15,000

Principal Investigator:

Charles W. Terrell

Technical Project Officer:

Marshall Kayser

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

SO₃ reacts vigorously with reservoir water to release a considerable amount of energy ($\approx 87.5^{\text{KJ}}/\text{gmole}$). Since the heat is produced in the reservoir, the process has a high thermal efficiency. Other aspects of the use of SO₃ are its miscibility in various hydrocarbon fractions and its ability to act as a sulfonation agent in the presence of the sulfuric acid generated by the SO₃-H₂O interaction. This project is to determine the feasibility of using SO₃ as an EOR agent.

Summary of Technical Progress

During the January 1 - March 31, 1983 period the SO₃ experimental setup has been rebuilt in an engine test cell on the north campus of the University of Oklahoma. The SO₃, which had partially frozen during shipment, has been returned to the liquid state.

An unconsolidated core (pure SiO₂) has been loaded into the reaction chamber. During April known quantities of water and oil will be loaded into the sand. Details of the loading procedure are not yet firm.

During the summer, a field model will be defined in order to obtain a first economic evaluation in terms of dollars per BTU of heat delivered to the formation. Since SO₃ becomes a gas at 113°F the implications of forcing the SO₃ into the formation as a gas are now being considered.

RESOURCE ASSESSMENT TECHNOLOGY

MEASUREMENT AND CORRELATION OF CONDITIONS FOR ENTRAPMENT AND MOBILIZATION OF RESIDUAL OIL

Contract No. DE-AC19-80BC10310

**New Mexico Institute of Mining
and Technology
Socorro, N. Mex.**

Contract Date: Dec. 1, 1980

Anticipated Completion: Sept. 30, 1983

Government Award:

DOE (first year) \$133,514

Contractor 133,514

Total \$267,028

Principal Investigator:

Norman R. Morrow

Technical Project Officer:

Michael E. Crocker

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this work are:

1. Variations in Residual Saturations Measured by Laboratory Core Flooding: This task is to establish limits for the reliability of laboratory waterflooding as an evaluation tool. The sensitivity of laboratory-measured residual saturations to the effects of test procedure, properties of displaced and displacing fluids, core material, and rock-fluid interactions will be investigated.

2. Effect of High-Pressure Gradients and Residual Oil Saturations: Current studies of trapping and mobilization will be extended to include wetting effects and residuals trapped in carbonate rocks. This work will address the problem of flushing that occurs when attempting to determine residual oil by coring or by logging measurements that involve regions close to the wellbore.

3. Mechanisms of Mobilization and Entrapment of Oil: This task is to demonstrate mechanisms by which oil can become trapped and how it can be mobilized. The effect of pore structure and pore-fluid interactions on the development and behavior of residual oil blobs will be investigated in pore models of wide-ranging complexity.

4. Residual Oil Structure: Work on residual oil structure and the size distribution of trapped oil blobs in sandstone will be studied. The technique of using a nonwetting phase which, after being trapped as a liquid, can be solidified and recovered, will be used.

Summary of Technical Progress

Task 1: Experiments on the contact angle behavior of crude oil and its use as a wettability control agent have been reported previously. One particular crude, Moutray, which was obtained in bulk quantity, was used to alter the wettability of Berea sandstone, which initially had been fired at 800°C. Although flooding characteristics were changed, it was observed that residual oil saturation was about the same as that observed for waterflooding under water-wet conditions. However, evidence of marked change in detailed distribution was provided by capillary number behavior. For a total of five runs to date, results were closely reproducible with capillary numbers for mobilization being about 5 times higher than corresponding results obtained under strongly water-wet conditions.

Task 2: From the obtained capillary number displacement data on various cores, it appears that unusually high flushing of residual oil might be anticipated in regions close to the wellbore during drilling and coring operations. Relationships between overbalance pressure and flushing are now being computed for capillary number relationships comparable to those measured for the Caddo limestone.

Task 3: The work summarized in the previous quarterly report indicated that instabilities developed in oil-surfactant solution displacements at low interfacial tensions. It also became obvious that gravity separation played a significant role in inducing instability.

These experiments are being carried out in artificial porous media consisting of consolidated glass beads. The displacement cells are three-dimensional, their thickness being about 10 bead diameters. When using two fluids of different density (such as isooctane as the oil phase and surfactant solution as the water phase), the lighter fluid may be mobilized by gravity forces and rise in the porous medium to float on top of the heavier fluid.

With the aim of eliminating such buoyancy effects, special fluid-fluid pairs have been prepared that possess identical density for both phases. In order to compare displacement patterns in water-displacing-oil and oil-displacing-water experiments, the viscosities of the two fluids were also matched.

Task 4: In the process of rechecking interfacial tension measurements with styrene as the oil phase, it was observed that the value of interfacial tension (σ) previously employed in capillary number ($K_w \Delta P / L \sigma$) calculations for various core floods was probably obtained with an aged styrene monomer. This value (22 dynes/cm) was lower by

about 30 percent than the value of 29.7 dynes/cm observed for fresh styrene (containing 1 wt-pct benzoylperoxide)/2 wt-pct CaCl_2 brine system at room conditions ($\sim 24^\circ\text{C}$) — after a 5-hour equilibration period. These recent measurements were consistent with other observed trends of reduced interfacial tensions with aging time. Current work has therefore been interpreted using the higher value of σ (29.7 dynes/cm).

INVESTIGATION OF PULSED NEUTRON TECHNIQUE FOR OIL WELL LOGGING

Contract No. DE-AC19-80BC10308

Argonne National Laboratory
Argonne, Ill.

Contract Date: Aug. 1, 1980
Anticipated Completion: Oct. 31, 1982
Government Award: \$245,000

Principal Investigator:
Ronald J. Pecina
Martin G. Seitz

Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

This objective of this work to investigate nuclear logging methods for determining residual oil saturation and to assess their limitations, evaluate accuracy, and propose improvements. The program includes a literature search, detailed studies, and a laboratory investigation to verify whether or not such techniques are feasible; for promising techniques, the program will recommend field testing or additional developmental needs leading to commercial applications.

Summary of Technical Progress

The final report is being prepared.

**RESIDUAL OIL SATURATION
TECHNOLOGY EVALUATION IN AN
UNCONSOLIDATED SANDSTONE
RESERVOIR
WILMINGTON FIELD, CALIFORNIA**

Contract No. DE-AC03-78ET12044

**City of Long Beach
Long Beach, Calif.**

**Contract Date: Oct. 20, 1978
Anticipated Completion: February 1983
Government Award: \$282,021**

**Principal Investigator:
Harrison L. Staub**

**Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of this project is to conduct a program for obtaining residual-oil-saturation data for the Wilmington micellar-polymer project, utilizing various complementary techniques for determining the residual oil saturations after waterflooding as well as after micellar-polymer flooding in an unconsolidated sandstone reservoir. These techniques will include core analyses, well logging, and single-well tracer tests, as well as analyses of reservoir and individual well performance.

Summary of Technical Progress

ROS determination after waterflooding has been completed, and the detailed Final Report is being prepared.

A summary of the final report was presented at the annual SPE Annual Meeting, San Antonio, Texas, Oct. 5-7, 1981, SPE Paper No. 10298, "Comparison of Methods for Measurement of Oil Saturation."

The final report is being prepared.

**CROSS-BOREHOLE SEISMIC PROBING
FOR PETROLEUM RESERVOIR
ASSESSMENT**

Control No. DE-AT19-79BC10062

**Lawrence Livermore Laboratory
Livermore, Calif.**

**Contract Date: Oct. 1, 1979
Anticipated Completion: Sept. 30, 1983
Total Project Cost: \$400,000**

**Principal Investigator:
E.F. Laine**

**Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The principal objective of this effort is to assess the feasibility and cost of using state-of-the-art instrumentation

and tomography techniques to provide detailed acoustic velocity and attenuation reconstructions of reservoir cross-sections between boreholes. By combining the results generated using these procedures with laboratory and other available geologic data, a more detailed and accurate interpretation is possible than is presently available for the location and quantity of recoverable oil within a production field.

Summary of Technical Progress

A seismic system designed to endure the high temperatures of the Getty boreholes was placed at the test site. The system consists of a downhole packer and a three-axis geophone assembly with a manual clamping assembly. The geophone is lowered to the desired depth and by pulling up on a steel cable, a pantograph type mechanism attached to the geophone assembly wedges the entire assembly to the casing walls. Pulling up on the geophone releases the entire assembly.

We spent one week at the site debugging the system and data-acquisition software before we were able to obtain reasonable seismic signals. The plan now is to return to the site and take enough data in the cooler upper regions to construct a velocity tomograph (about one week's effort to acquire data). After the data are processed or perhaps prior to that time, we will return and acquire another set of data in the steamflood zone; we do not want to risk the equipment in the hot zone immediately.

DEVELOPMENT OF A RAPID AND ACCURATE METHOD FOR DETERMINING PARTITION COEFFICIENTS OF CHEMICAL TRACERS BETWEEN OILS AND BRINES

Contract No. DE-AC19-79BC10100

**Geochem Research, Inc.
Houston, Tex.**

**Contract Date: Jan. 1, 1980
Anticipated Completion: Jan. 1, 1982
Government Award: \$217,890**

**Principal Investigator:
Charles T. Carlisle**

**Technical Project Officer:
Michael Crocker
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

To develop a dynamic system for rapidly and accurately determining partition coefficients of chemical tracers used in the single-well tracer method; investigate their sensitivity to control by oil properties, temperature, and brine salinities; and apply new knowledge obtained from the measurements to the formulation of mathematical relationships by which predictions can be made from reservoir and crude oil parameters.

Summary of Technical Progress

The final report has been received and is being prepared for publication.

OIL SOLUBILIZATION STUDIES

Contract No. DE-FG19-80ET12267

**Lehigh University
Bethlehem, Pa.**

**Contract Date: Aug. 30, 1978
Anticipated Completion: Dec. 30, 1983
Government Award: \$49,986**

**Principal Investigator:
F.M. Fowkes**

**Technical Project Officer:
Marshall Kayser**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

Tertiary recovery of petroleum involves the use of surfactants which promote oil displacement either by

lowering interfacial tension or by solubilizing the petroleum into swollen micelles or microemulsions. There has been much recent study of formulations to reduce interfacial tension but less attention has been given to solubilization.

A better understanding of the principals of solubilization could open up the field to many new types of formulation, some of which could be better and cheaper.

This study concerns the role of the co-surfactant in solubilization. There is reason to believe that its "osmotic" pressure π in the solubilized hydrocarbon core of microemulsion droplets determines how much oil can be solubilized. The co-surfactant is partially dissolved in the solubilized oil and partly adsorbed in the surface of the droplets, where it helps to reduce the interfacial tension γ . As droplets grow during solubilization, γ increases. We suspect that droplets grow to a radius r such that the Laplace pressure $2\gamma/r$ equals the "osmotic" pressure π of the co-surfactant. Experiments are chosen to test this hypothesis.

Summary of Technical Progress

Camera-ready copy of corrected final report is being prepared.

EXTRACTION TECHNOLOGY

PROPPANT TRANSPORT IN MASSIVE HYDRAULIC FRACTURING

Contract No. DE-AC19-80BC10197

**University of Tulsa
Tulsa, Okla.**

Contract Date: Feb. 4, 1983

Anticipated Completion: May 4, 1984

Government Award: \$88,000

Principal Investigators:

P.E. Clark

E.F. Rybicki

Technical Project Officer:

Bonnie L. Gall

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

An experimental and numerical study of dynamic proppant settling rates in fracturing fluids over a wide range of conditions to simulate field application.

Summary of Technical Progress

During this last quarter, the equations describing the proppant concentration were implemented in the computer program. The concentration of the proppant varies from point to point and varies with time at any fixed point. It is observed that the concentration profile adopts an exponential form. The equations leading to the proppant bed build up are also included in the computer program, the resulting bed shape varies in a step-wise fashion. Preliminary results with the model have been obtained. An illustration of the predicted proppant bed is shown in Fig. 1.

Current work is oriented towards finding an optimum pad volume so that the sand does not reach high concentrations at the fracture tip.

Analysis of the experimental proppant settling data has led to some interesting conclusions. The plot in Fig. 2 shows settling data for sand particles in several concentrations of

FIG. 1 — Illustration of settled proppant.

FIG. 2 — Settling data for sand particles.

gelling agent as a function of apparent viscosity. If Stokes' Law was obeyed for all concentrations, points of equal apparent viscosity should have identical settling velocities. The data clearly indicates that this is not the case. More work needs to be done to clarify the source of the discrepancy.

An attempt to correlate the settling data with other measurable parameters has been initiated.

Work in the second quarter will involve collection of data as a function of temperature.

RELATIONSHIP OF PORE STRUCTURE TO FLUID BEHAVIOR IN LOW PERMEABILITY GAS SANDS

Contract No. DE-AS19-80BC10216

New Mexico Institute of Mining and Technology
 Petroleum Recovery Research Center

Contract Date: July 15, 1980

Anticipated Completion: July 15, 1983

Government Award, FY 82: \$85,000

Principal Investigator:

Norman R. Morrow

Technical Project Officer:

Clarence J. Raible

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective of the investigation is to relate the pore structure of low permeability (tight) gas reservoir rocks to their flow characteristics. The two main questions to be researched are:

1. What is the effect of overburden pressure on pore structure? and
2. What is the modifying effect of the presence of water on pore structure as it relates to flow properties? The work will also include research on characterization of samples obtained under the Western Tight Sands Coring Program and core properties of cores from the DOE Multiwell Experiment in the Piceance Basin near Rifle, Colorado.

Summary of Technical Progress

Empirical correlations between core properties and sensitivity to overburden pressure to overburden pressure

The pressure sensitivity measure used most in our recent work is the pressure sensitivity index, which is defined as minus the parameter "a", where "a" is the least-squares slope in

$$\log K = a \log (p/1000) + c \quad (1)$$

for first unloading data. Where K (md) is the permeability at overburden pressure P (psi).

Some empirical relationships have been found to give reasonably good agreement when comparing experimental vs. predicted pressure sensitivity index. Using the pressure sensitivity index, described above, as the independent

variable gave better correlations (statistical significance at a higher confidence level for almost every correlation that was ranked the same) than using the ratio of Klinkenberg permeability at 500 psi to that at 5000 psi. These two different measures of pressure sensitivity are reasonably consistent (see Fig. 1). An example of the types of correlations obtained is plotted in Fig. 2.

FIG. 1 — Comparison of pressure sensitivity measures for multi-core and multiwell samples: pressure sensitivity Index (i.e., minus the slope from linear regression on log permeability vs. log overburden pressure data from first unloading) vs. ratio of Klinkenberg permeability at 500 psi to that at 5000 psi overburden pressure. These two measures of pressure sensitivity are reasonably consistent.

From a number of experimental vs. predicted pressure sensitivity index plots, such as Fig. 2, it appeared that the pressure sensitivity index values of certain samples were consistently being underestimated, while those of some of the other samples were consistently being overestimated. Further investigation confirmed this observation (see Table 1, which also can be used as a key to labels in Fig. 2). This could indicate that there is a significant effect not covered by the independent variables used so far in regression. Further research may help to determine the sources of this effect and to quantify them.

Ultrasonicing effects on permeabilities to liquid and gas

In order to investigate the possible effects of dispersible fine material as a cause of difference in liquid and gas permeabilities, the effect of ultrasonication was tested. Old Man Mountain #2 core sample was selected for this investigation. Permeabilities to gas and liquid were reported

FIG. 2 — An example of experimental pressure sensitivity Index versus an empirical correlation of pressure sensitivity Index.

previously.^{1,2} The procedure involved subjecting the sample to ultrasonic cleaning for 30 minutes. Fig. 3 shows results for this sample. Ultrasonicing is seen to cause a 90 percent reduction in liquid permeability.

It was also desired to determine whether the permeability to gas would return to its previous level. The

FIG. 3 — Brine permeability vs. overburden pressure.

sample was removed from the core holder, subjected to vacuum for 2 hours in a desiccator, and then returned to the core holder. Nitrogen was allowed to flow through the core for 20 minutes. The permeability to gas was measured. Fig. 4 shows the results before and after the ultrasonicating run. After ultrasonicating, the permeability to gas was about 20 percent higher than before. One possible explanation for these phenomena is that ultrasonicating dislodged small particles, many of which blocked channels of the porous medium during liquid flow, thus decreasing permeability to liquid. As the core was dried, the particles probably were drawn to the pore walls by capillary forces and their overall tendency to interfere with gas flow was reduced. Further experiments are in progress.

Investigation of surface areas

Portions of a Multiwell sample were broken up and separated by sieving. Surface areas of two of the resulting fractions were determined by nitrogen adsorption.

FIG. 4 — Gas permeability vs. overburden pressure.

TABLE 1 — Extreme values and means of experimental minus predicted pressure sensitivity index using correlations that are statistically significant at the 99.99 percent confidence level

Sample label	Origin ID	Number of correlations	Experimental minus predicted		
			Minimum	Mean	Maximum
1H	6405	97	-0.198	0.081	0.282
1V	6405	74	-0.314	-0.055	0.156
2H	10570 S BETC	92	-0.425	-0.096	0.158
2V	10570 S BETC	91	-0.553	0.145	0.169
3H	Old Man Mtn. #2	114	-0.125	0.031	0.186
3V	Old Man Mtn. #2	91	-0.139	0.025	0.169
4H	Ralston core	114	-0.380	-0.141	0.110
4V	Ralston core	91	-0.421	-0.206	0.031
5H	BC-1-25	114	-0.151	0.093	0.248
6H	PCUF31-13G	114	-0.218	0.029	0.344
7H	C1G1 21 (depth 4403.3)	109	-0.250	-0.047	0.149
7V	C1G1 21 (depth 4403.3)	86	-0.281	-0.085	0.149
8H	C1G1 21 (depth 8492)	114	-0.396	-0.157	0.130
8V	C1G1 21 (depth 8492)	91	-0.330	-0.123	0.109
9H	C1G1 21 (depth 8503)	114	-0.187	0.010	0.244
10H	U78JP16	100	-0.284	0.052	0.246
11H	U78JP36	35	-0.202	-0.126	0.069
11V	U78JP36	86	-0.415	-0.219	0.019
12H	Wilkin Ridge	114	-0.166	0.078	0.320
12V	Wilkin Ridge	91	-0.075	0.231	0.209
22HT	(MWX-1) 31-32	97	-0.044	0.155	0.409
22VI	(MWX-1) 31-32	97	0.026	0.233	0.511
23HT	(MWX-1) 14-14	97	-0.167	0.140	0.404
23VT	(MWX-1) 14-14	97	-0.050	0.233	0.478
24H	(MWX-2) 48-9	97	-0.056	0.136	0.338
24V	(MWX-2) 48-9	97	-0.105	0.347	0.565
25V	(MWX-2) 56-19	97	-0.094	0.071	0.353
26VT	(MWX-2) 51-19	97	-0.248	-0.030	0.203
27VT	(MWX-2) 52-15	97	-0.294	0.029	0.339
28VB	(MWX-2) 54-11	80	-0.310	-0.150	0.030
29VT	(MWX-2) 55-16	97	-0.379	-0.198	-0.001
30VB	(MWX-2) 57-2	97	-0.402	-0.247	-0.099

H (horizontal) — core cut perpendicular to axis of whole core sample
V (vertical) — core cut parallel to axis of whole core sample
B (bottom) — specimen taken from bottom of whole core sample
T (top) — specimen taken from top of whole core sample

A new method of measuring surface area based on density of $-OH$ groups and hydrogen deuterium exchange is being investigated. The surface of mineral grains consisting primarily of silica is covered by silanol groups, $(-O)_3Si-OH$. Heating to $140-150^\circ C$ at ordinary pressure or $70^\circ C$ under vacuum removes physically adsorbed water but does not dehydrate the silanol groups to siloxene linkages. The surface density of silanol groups has been measured by several methods for varieties of silica ranging from silica gel to quartz. The measurements seem to converge on a value of 4.6 groups per square nanometer for all forms of silica.³ Exposure of the mineral to deuterium oxide in liquid or vapor form causes rapid exchange of hydrogen and deuterium. After being dried again, the surface is covered with $(-O)_3Si-OD$ groups. The total number of groups is determined by reexchange with a measured quantity of ordinary water followed by analysis for the percentage of deuterium. Dividing the number of groups by 4.6×10^{18} groups per square meter gives the surface area in square meters.

The pores are not lined exclusively by silica minerals, and the swelling clay minerals such as montmorillonite play an important role in H-D exchange. Surface areas measured by nitrogen adsorption give only the exterior area of such clay crystals because nitrogen is unable to penetrate the layers. The method of H-D exchange, however, gives the total area, which may be more than ten times greater than the superficial area. The extent to which the H-D area exceeds the BET nitrogen area will reflect the presence of minerals containing interior exchangeable hydrogens. Experimental details and some initial results have been reported elsewhere.¹

Adsorption isotherms

Tight gas sands have generally been observed to be very hygroscopic, a dried core exhibiting rapid weight gain when

exposed to quite low humidity. Adsorption isotherms have been measured by equilibrating cores at various levels of relative humidity. Hysteresis in these isotherms indicates the errors that can arise in achieving reference moisture contents from initially dry or partially saturated cores. Although the surface areas of these sandstones are quite high (approximately two square meters per gram), they are not sufficient to explain the observed amounts of adsorption (up to 25 percent water saturation at 90 percent relative humidity). Similar results have been observed for heptane. This together with observed hysteresis is strongly suggestive of capillary condensation. This topic is obviously of great importance to core analysis techniques for tight gas sands and is being investigated further.

Effect of firing on permeability behavior

One of the Multiwell samples, (MWX-2) 48-9, was selected for detailed study of effects of high temperature firing on permeability vs. overburden behavior. Cores cut from a whole core sample were each heated to a different temperature — 500, 550, 600, 650, 700, 800, 900, or $1000^\circ C$. The general procedure has been reported.^{1,2} Results obtained to date are presented in Table 2. Cores that were fired at $500-600^\circ C$ showed increased permeability before being loaded beyond 500 psi. However, once these cores were loaded to 5000 psi, the permeability was not changed very much from that exhibited by unfired core at the same overburden pressure.

Thus, the permeability of cores fired at $600^\circ C$ or less seemed to be very sensitive to overburden on the first loading, but on the second loading displayed much the same sensitivity as unfired core. Thus, changes caused by firing at temperatures not exceeding $600^\circ C$ did not produce permanent change in the rock's sensitivity to overburden pressure. On the other hand, firing at $650-1000^\circ C$ caused

TABLE 2 — Effects of firing portions of core sample (MWX-2) 48-9 at depth of 5731 feet

Temp. of firing, $^\circ C$	Time of firing, hrs	Pct. porosity	First loading			$K_{\infty, 500}$
			$K_{\infty, 500}$ md	$K_{\infty, 5000}$ md	$\frac{K_{\infty, 500}}{K_{\infty, 5000}}$	$K_{\infty, 5000}$ second loading
—	—	8.52	0.0413	0.0043	9.6	—
—	—	8.31	0.0335	0.0015	22.3	—
500	2.0	10.11	0.072	0.0032	22.5	8.0
500	16.0	9.28	0.053	0.0021	25.2	12.1
550	2.0	9.37	0.10	0.0024	41.7	10.8
600	2.0	9.94	0.13	0.0020	65.0	15.0
650	2.0	10.79	0.12	0.0031	38.7	9.6
700	2.5	10.52	0.25	0.0053	47.2	8.6
800	2.0	10.76	0.34	0.0122	27.9	11.25
*900	6.0	10.84	0.85	0.048	17.7	6.4
1000	2.0	10.99	3.55 x	1.70 x	—	2.09

x — These data for the sample fired at $1000^\circ C$ were obtained on second loading (instead of first loading) and at 150 psi (instead of 350 psi) inlet pressure. K_{500} was obtained by extrapolation to 150 psi on Klinkenberg plot.

*Data for the sample fired at $900^\circ C$ also were obtained with 150 psi inlet pressure.

K_{∞} refers to Klinkenberg permeability

permanent increase in permeability. Firing at 900-1000°C led to a decrease in the ratio of permeability at 500 psi overburden pressure to permeability at 5000 psi. Also, fired core material adsorbed less moisture than corresponding unfired material. Firing at 1000°C did not equalize the permeabilities to gas and liquid, the liquid permeability of the fired material still being much less than gas permeability.

References

- ¹ Morrow, N.R., Brower, K.R., and Kilmer, N.H., "Relationship of Pore Structure to Fluid Behavior in Low Permeability Gas Sands," 1982 Annual Technical Report to the U.S. Department of Energy, Report No. DOE/BC/10216-14 (March 1983).
- ² Morrow, N.R., Brower, K.R., and Kilmer, N.H., "Relationship of Pore Structure to Fluid Behavior in Low Permeability Gas Sands," Quarterly Technical Progress Report for the period Oct. 1-Dec. 31, 1982 to the U.S. Department of Energy, Report No. DOE/BC/10216-10 (Jan. 1983).
- ³ Iler, R.K., *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, Wiley-Interscience, New York (1979).

STOCHASTIC MODEL OF MASSIVE HYDRAULIC FRACTURING

Contract No. DE-AS19-80BC10215

**Oral Roberts University
Tulsa, Okla.**

Contract Date: Aug. 1, 1980

Anticipated Completion: Aug. 31, 1983

Total Project Cost:

DOE	\$75,346
Contractor	28,600
Total	\$103,946

**Principal Investigator:
I.D. Palmer**

**Technical Project Officer:
Keith Westhusing
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this project include: (1) Estimate the effects of statistical variations in rock properties and *in situ* stress upon propagation of fractures generated in the MHF process; (2) extend the two-dimensional Monte Carlo fracture simulator to a three-dimensional model where the fracture tip can propagate out of the plane of the fracture; and (3) determine the effect on three-dimensional fracture geometry of inhomogeneities in basic rock properties obtained from core measurements and logs.

Summary of Technical Progress

1. Blanket fracture simulator with bounding stresses symmetric

a. Useful Approximations to the Fully Iterated Solution

By fully iterated, we mean the solutions for height, $h(x)$, and pressure, $p(x)$, which satisfy the continuity equation. As described previously¹, this requires a double iteration — one to converge the flow rate, $q(x)$, and the other to converge the fracture expansion rate, $a(t)$. Using the following illustrative parameters: $H = 100$ ft, $a = 1,000$ ft, $S_2 - S_1 = 550$ psi, $E = 3 \times 10^6$ psi, $q(0) = 10$ bpm, $\mu = 300$ cp, $C = .0007$ ft/min^{1/2}, it has been found that wellbore height and pressure are well approximated (to within 10 percent) by (i) a model in which $q(x)$ is assumed linear between wellbore and fracture tip at $x = a$, with value zero at the tip (i.e., leakoff neglected), and (ii) a model in which the fracture perimeter is assumed to be an ellipse (in (i) the shape is not assumed, it is derived), and the flow rate is linear as in (i).

This is an important result, because (i) provides us with a good first estimate of wellbore height and pressure (but *not* time), which can be used as a starting point for the refinements of the fully iterated model. In addition, (ii) means that a previously published parameter study² of wellbore height and pressure (but not time), based on an elliptically-shaped fracture, is valid.

b. Revised Results for Previous Paper

A previous paper has been revised for publication in SPEJ. One revision was substantial, and changed the results somewhat. The essence of the revision was an improvement of the fluid flow equation. Previously, the flow equation, taken to be Poiseuille flow (1D, Newtonian) along the direction of the payzone, assumed the channel flow to have an elliptical cross section of height H (payzone height) and width w_0 (which varies with x). This has been changed, and replaced by two limiting cases which are considered to give a more realistic picture of the actual situation:

(i) An elliptical section is again assumed, with width w_0 , but the height of the flow channel is the height of the fracture, h .

(ii) When the fracture height is much larger than the payzone height, the flow is modeled by flow through parallel plates of height H and width w_0 . When h equals H , the flow is the same as in (i) above. For intermediate heights, we interpolate. This situation would correspond to one in which the bulk of the fluid viscous losses occurred in the payzone, and not in the "wings" above and below — this becomes a possibility when the stress contrast between pay and bounding zones becomes high, and consequently the fracture width becomes relatively small in the regions above and below the payzone.

c. Boundary Condition at the Fracture Tip

As explained previously¹, the differential equation for $h(x)$ was obtained by taking as the boundary condition $h \approx H$

at the tip of the long axis. It appeared that the wellbore height and pressure were not sensitive to the value of h chosen at the tip. However, the details of fracture shape do depend on the boundary condition, and so we have examined this in more detail.

Since the region at the tip of the fracture into which the driving fluid has not penetrated is very small⁴, one is justified in neglecting this region and the associated region of high fluid gradients. If one takes as the boundary condition $K_i = K_c$ (the usual fracture expansion criterion) then the question becomes: what values of h and p near the fracture tip satisfy this criterion? Two approaches for calculating K_i were tried (numerical computations by Mastrojannis⁵ and Weaver⁶). Both failed because they could not accommodate the situation in which $h > H$.

A possible solution we are exploring is whether the results of Shah and Kobayashi⁷ can be utilized. The fracture tip would have to be replaced by an elliptical contour which is more realistic than the previously assumed rectangle anyway.

Our fracture perimeters are concave above and below the payzone, but proper accounting of the boundary condition at the fracture tip and of 3D elasticity may alter the shape to convex. The details of the fracture shape near the tip of the long axis may be quite important as far as proppant transport and bedding is concerned, even though not important for the calculation of wellbore height and pressure.

d. Correction to Fluid Flow Equation

The equation used for fluid flow in our recent work⁸ is 1D Newtonian flow along the direction of the payzone. Each vertical section of the fracture is regarded as an ellipse, with height h , and width w . However, the shape is not an ellipse because the higher stress in the bounding layers reduces the width relatively more. We can calculate the exact profile of the vertical width, given the pressure, and now we are programming this width into the fluid flow equation to give a more accurate solution for the height of the fracture.

2. Blanket simulator with bounding stresses asymmetric

Here the payzone is bounded by two zones of higher, but unequal, stresses. The fracture perimeter will be vertically asymmetric about the payzone axis.¹ We have been able to integrate the differential equations for fracture half-heights, $h_1(x)$ and $h_2(x)$, from fracture tip back to

wellbore, but the iterations are tedious. A method has been discovered to automatize the height computations, which should speed up the process tremendously; and this is being debugged at present.

3. Lenticular simulator

Because this is such a difficult problem, the rationale we are following is:

(a) To develop a working blanket sand simulator which can then be applied or adapted to an individual-lens situation.

(b) To develop a model in which a fracture intersects many lenses. To this end we are pursuing:

(i) A general formulation for the width equation $w(p)$ for an arbitrary-shaped fracture opened by an arbitrary pressure distribution $p(x,y)$. A numerical code by Mastrojannis⁵ is available, but the pressure is not completely arbitrary.

(ii) A general formulation for the fluid flow equation, $p(w)$, in 2D. This will have to be a numerical computation as well.

(iii) A general formulation for K_i is the same problem as (i) above. These (i), (ii), and (iii) can be thought of as three separate tools, which need to be combined (actually solved simultaneously). Our plan is to study the behaviour of each separately, then examine the degree to which they are consistent. We intend also to search for approximations which would reduce the complexity of this very difficult problem, viz. the full 3D solution of fracture propagation in inhomogenous media.

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**DETERMINE FEASIBILITY OF
FABRICATING LIGHT WEIGHT
PROPPANTS FOR APPLICATION IN GAS
AND OIL WELL STIMULATION**

Contract No. DC-AC19-79BC10038

**Terra Tek, Inc.
Salt Lake City, Utah**

**Contract Date: July, 1982
Anticipated Completion: July 1, 1983
Government Award: \$100,000**

**Principal Investigators:
A.H. Jones
R.A. Cutler**

**Technical Project Officer:
Clarence J. Raible
Reporting Period: Jan. 1 - Mar. 31, 1983**

Objective

This study is to determine the feasibility of fabricating light weight proppants for application to deep oil and gas well stimulation, and select viable materials and manufacturing techniques.

Summary of Technical Progress

Proppant fabrication

Hollow Proppants

Hollow alumina proppants from the fourth series of spray drying experiments run at Bowen Engineering were evaluated. Three separate batches were made using A-16 superground alumina as the starting material. Polyvinyl alcohol (Gelvatol 20-30), polyethylene glycol (Poly "G" 200), a dispersant (ammonia based Darvan C) and an antifoam were used as shown in Table 1. A porcelain composition, consisting of alumina, kaolin clay and nepheline syenite, was used to see if there were major differences in the spray drying parameters needed to produce different proppant types. A two-fluid nozzle laboratory spray dryer was used and the purpose of these tests was to compare the alumina proppants produced in the small spray dryer to previous runs in the larger single-fluid nozzle dryer. The porcelain ceramic composition was spray dried in conjunction with the A-16 superground alumina to be sure that the multiple voids and network structure previously observed in the alumina system are not material dependent. The advantage of the small dryer is that it allows

more experiments and, hence, more spray drying parameters to be investigated.

TABLE 1 — Composition of ceramic slurries for the fourth set of spray drying runs at Bowen Engineering

Spray drying run #	Weight percent solids	Weight percent based on alumina*			
		Darvan "C"	Gelvatol 20-30	Poly G-200	Anti-foam
1	67	0.75	1.00	0.50	—
2	70	0.75	1.00	0.50	—
3	70	0.75	1.00	0.50	0.03
4	70	0.75	1.00	0.50	0.03

*Porcelain composition A (see Table 1 of 3rd Annual Report for composition) Instead of alumina was used in Run #4.

The spray drying conditions listed in Table 2 are typical of previous alumina slips run in the small dryer. Conditions were kept constant from run to run so that any differences in the properties of the resulting powders could be attributed to the differences in formulations. The slips spray dried readily without any accumulations in the spray dryer, in contrast to samples produced in the single fluid nozzle runs. Wall interactions were a possible reason for multiple voids observed in previous runs.

TABLE 2 — Spray drying conditions for the fourth set of spray drying runs at Bowen Engineering

Spray Drying run #	Slurry feed rate, ml/min	Air temperature, °C		Atomizing pressure, MPa/psi
		Inlet	Outlet	
1	380	240	148	0.28/40
2	317	240	150	0.28/40
3	265	240	150	0.28/40
4	276	240	148	0.28/40

The size distributions of the spray dried powders are listed in Table 3. The majority of the powder made in the spray dryer was too small to be effectively evaluated. Unsintered particles below 100 mesh were very difficult to cut and observe their internal structure. The resistance to crushing, shown in Table 4, was very poor for the alumina particles despite their relatively high sintered density. All four runs were initially sintered at 1525°C for 1 hour. The porcelain proppants (run #4) were oversintered and individual spheres coalesced. Similar porcelain compositions, mixed and pelletized mechanically, sintered normally at this temperature. The rest of the code 4 porcelain composition was sintered at 1400°C but this temperature was still too high. This means that the more homogeneous composition obtained by mixing the slurry before spray drying results in a substantial reduction in the sintering temperature. More material is needed to establish the correct sintering temperature of the spray dried porcelain composition.

TABLE 3 — Sieve analysis of unsintered powders for the fourth set of spray drying runs at Bowen Engineering

Bowen code	Tap density, g/cc	Particle size distribution (mesh, wt-pct)					
		-40, +60	-60, +80	-80, +100	-100, +120	-120, +140	-140
1	1.40	0.96	2.12	4.83	17.86	44.68	29.55
2	1.32	9.83	5.13	4.58	7.67	39.59	33.20
3	1.29	8.09	5.38	4.58	16.14	28.33	37.48
4	0.87	1.61	4.75	12.78	36.28	15.33	29.27

TABLE 4 — Packed bed strength data at 5,000 psi

Bowen code	Mesh size	Sintered density,* g/cc	Wt-pct crushed	Tap density, g/cc
1	A	2.73	80.2	1.65
	B	3.11	39.8	1.88
2	A	3.09	84.7	1.86
	B	3.20	65.9	1.93
3	A	3.09	83.6	1.86
	B	3.22	47.3	1.95

A: -60, +80 mesh, B: -80, +100 mesh

*All samples were sintered at 1525°C for 1 hour in air.

Optical micrographs show why this series of experiments exhibited low strength. The alumina compositions (Runs 1-3) were much less spherical than the same composition sprayed in the larger dryer. The alumina proppants were mainly non-spherical while the porcelain composition was much more spherical. The angular particles increased the point-to-point contacting between alumina proppants and the strength was inadequate.

A major problem with this series of runs was the high sintered density of the proppants. This resulted because the majority of spray dried materials contained no large voids. There were a few instances in which well formed voids existed, the majority of particles from all four runs contained no major voids. In some cases implosion occurred during the spray drying operation. Although most of the particles didn't contain large voids, multiple voids were still observed as well as non-concentric voids.

The small two-fluid nozzle spray dryer did not produce comparable results with the larger single-fluid nozzle. The sphericity of the porcelain proppants warrants further testing of this material. Discussions with Olev Ratsep of Bowen Engineering will help establish which direction the next set of spray drying experiments will take.

Pan Agglomeration: Arcanum Corporation (Ann Arbor, MI) investigated the possibility of making hollow proppants by pan agglomeration. This method uses a decomposable core which is removed prior to sintering to leave a well formed central void. Arcanum stated that alumina, titania or mullite proppants could be made hollow or with sufficient porosity to reduce the density to the desired levels. It is doubtful, however, that pan agglomeration could meet the economic targets needed to

compete in the proppant business. This is the same conclusion reached by 3M Company. There are no plans to do further work on making hollow proppants using decomposable cores.

Graphite Proppants

Superior Graphite Co. (Chicago, IL) sent two graphitic carbon samples for evaluation as proppants. One grade, Desulco 9001, is a high purity material used as a carbon additive in the steel industry. The other material, HFC-26, is a more spherical graphite made from a petroleum fluid coke. Although graphite is typically not able to withstand tensile loading above 5,000 psi, Superior said that these materials showed a high degree of resiliency and could be compacted without breakage.

The 9001 particles were angular, whereas, the HFC-26 particles were more spherically shaped. The HFC-26 particles became more spherical as the particle diameter decreased. Crush resistance data are presented in Table 5. While the strength of both materials at 10,000 psi is considerably better than sand, it is not nearly as high as intermediate strength proppants. The low tap density, specific gravity (1.8) and chemical inertness of the HFC-26 material are attractive if the strength can be improved. The Desulco 9001 material showed considerable elastic behaviour which would hinder the propping action. The crushing that occurs is probably during initial particle rearrangement since there is little difference in strength between tests at 5,000 and 10,000 psi. Optical micrographs show that the 9001 material is porous while the HFC-26 graphite has large pre-existing cracks before loading. Superior is investigating whether it is possible to obtain more spherical HFC-26 materials.

Fast firing

A research program further investigating the possibility of rapid sintering of proppants has been initiated with Professor D.L. Johnson of Northwestern University. Plasma sintering using a counter flow condition with short dwell times (a few seconds) will be used to see if bauxite, mullite and porcelain compositions can be rapidly densified. Commercial proppant manufacturers are supplying some of the proppants and participating in the evaluation. The advantages of rapid firing are not only the potential to lower processing costs but also the possibility of limiting grain

TABLE 5 — Crush resistance of graphite

Material	Tap density	Size evaluated	Pct. crushed @ 5,000 psi		Pct. crushed @ 10,000 psi	
			-40 mesh	-60 mesh	-40 mesh	-60 mesh
HFC-26	0.87	-25, +40	50.2 ± 1.2	11.3 ± 0.7	—	—
HFC-26	0.91	-40, +60	13.1 ± 0.9	7.8 ± 0.9	24.3 ± 0.8	15.7 ± 0.6
9001	0.58	+40	12.2	5.4	13.7	5.6
9001	0.61	-20, +40	21.8	12.1	23.5 ± 1.6	11.7 ± 1.5

growth and thereby increasing proppant strength. This would permit lower density proppants to have comparable

strength with similar compositions fired in a conventional manner but having higher densities.

RESERVOIR CHARACTERIZATION FOR NUMERICAL SIMULATION

Contract No. DE-AS19-82BC10744

**University of Texas
Austin, Texas**

Contract Date: Sept. 30, 1982

Anticipated Completion: Sept. 30, 1983

Government Award: \$99,968

Principal Investigators:

Larry W. Lake

Alan J. Scott

Technical Project Officer:

Herbert B. Carroll

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives for this project are to:

1. Develop a general reservoir descriptor (GRD) for assigning input properties to numerical reservoir simulations.
2. Structure a reservoir data base to accept the GRD procedures.
3. Test GRD and data base on field projects.

Summary of Technical Progress

During the reporting quarter, more geologic information on the El Dorado field was accumulated and evaluated. The information consists primarily of core descriptions, core plug data, well logs, core photographs, and geologic interpretations of the area centered on the Chesney and Hegberg bases. Standard core data are

available on many wells, both in the Chesney lease and elsewhere. We have reviewed the quality of the information and, though minor discrepancies are present, the data appear to be self-consistent and should prove to be useful. In particular, many of the core descriptions are quite detailed and in a quantized form that appears to lend themselves readily to digitization. If this is possible, it will form an important component of the data base system described below.

Working with the porosities from routine core analysis, we have been attempting to define a single parameter that would indicate if the data in a particular well were internally correlated or random. Initial efforts using one of the serial auto-regression coefficients have been discouraging. Many of the El Dorado wells do appear to have internal correlation — that is, the serial auto-regression coefficients are larger than what could be expected by random variations with depth — but, the coefficients are undesirably sensitive to the definition used in the mean. Moreover, the degree of correlation does not improve as the range of depths included in the measurements is diminished. Such an improvement in correlation would normally be expected as the decreasing range conforms more exactly to homogeneous sections of the reservoir. In many cases, the data do not satisfy all the requirements necessary to use the auto-regression coefficient, and we are attempting to determine if this is the cause for the poor performance. We are investigating ways to interpret or extend (transform) the data so that they will satisfy the requirements. Consideration is also being given to entirely different measures of correlation.

In an effort to systematically separate deterministic from random variations, we have been applying signal processing techniques to the routine core data and logs. This technique looks encouraging as it appears possible to establish frequency limits so that the filtered signal reflects more of the deterministic character of the reservoir data. We have applied the technique only to porosity data on wells that have rather dense (one-half foot), evenly-spaced measurements so the applicability of the technique is undetermined. Currently, we are investigating advanced signal processing techniques based on the idea of or

maximum likelihood which are less susceptible to data bias and the quantity of data.

The reservoir data base now has a prototype version working. We have chosen to concentrate on a well data base, and leave the "reservoir" information as a separate file, or as a file that could be generated by the concatenation of the well data base files. The well data base contains 12 major headings of data which are arranged approximately in the order in which such information is chronologically accumulated under normal conditions. Within each heading, the information is arranged in a sequence of decreasing generality, with appropriate divisions for parallel pieces of information. We are currently working on a technique to efficiently store and display routine core data, digitized log data, and core descriptions (where available) in a parallel fashion.

WELL TEST PERFORMANCE AND ANALYSIS OF GAS WELLS COMPLETED IN NONCONTINUOUS LENTICULAR FORMATIONS

Contract No. DE-AS19-82BC10695

**University of Oklahoma
Norman, Okla.**

**Contract Date: March 1, 1982
Anticipated Completion: Feb. 28, 1983
Government Award: \$40,359**

**Principal Investigator:
Ronald D. Evans**

**Technical Project Officer:
Keith Westhusing
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

Develop refined sand-lens distribution models for channel-fill and point-bar types of sandstone formations characteristic of the Rocky Mountain gas province. In this regard, it is proposed to statistically investigate the noncontinuous nature of the gas bearing formations using random variable theory in order to arrive at the most probable distribution of the sand lenses in a given area. The reservoir simulator developed would be modified such that a given sand lens distribution could be input to the program as a mathematical function.

Modify existing two-dimensional reservoir/well simulator to include the effects of non-Darcy flow in the reservoir and fracture, wellbore and fracture storage, frictional pressure drop in the production string, and pressure-dependent rock properties.

Extend two-dimensional reservoir/well simulator to a fully generalized three-dimensional one which considers three phase flow of gas, water, and condensate fluids through noncontinuous, heterogeneous formations with partial and/or full penetrating infinite and/or finite conductivity vertical fractures.

Summary of Technical Progress

During this period, the following work was accomplished relative to the indicated tasks associated with the contract.

I. Extension and development of a three-dimensional, three-phase simulator for hydraulically fractured lenticular reservoir.

The development of the three-dimensional gas reservoir simulator is complete, and it has been used to make some performance predictions and well performance. These results were based upon artificial data in order to test out the capability of the program. Preliminary results of such simulations have been reported previously. Future plans are to use this simulator to analyze well performance for actual data taken from wells completed in low-permeability gas reservoirs.

II. Investigation into refined sand lense distribution models.

Effort was initiated toward applying a Monte Carlo approach to selecting reservoir cells within the simulator and assigning these cells with a permeability value representative of that of a lenticular sand lense. A Monte Carlo generator has been developed which will be used to select and assign the rock properties for a given portion of the reservoir. This approach may be particularly useful when one attempts to include vertical coupling between sand lenses since a directional permeability tensor can be assigned to a given cell. For example, Fig. 1 illustrates a reservoir area that has been discretized into a 10×7 grid system. A 35 percent concentration of sand lenses is distributed within the area using the Monte Carlo generator. This translates into 25 of the 70 grid points containing sand lense properties. Within each of the 25 grid cells, a sand lense permeability tensor and porosity value could be assigned which are unique to this particular portion of the reservoir. If no vertical coupling is desired, the Z component of the permeability tensor could be set to zero.

Furthermore, such an approach has implications for coupling randomly distributed fractures which could exist with a given sand lense cell. Further work needs to be done

1	0	1	0	0	0	0	0	1	0
0	1	0	1	1	0	0	0	0	0
0	1	1	0	1	0	1	0	0	0
1	1	0	0	1	0	1	0	0	0
0	0	0	1	0	1	1	0	0	0
1	0	0	1	0	0	1	1	0	0
0	1	0	0	1	1	0	0	1	0

SAND LENSE CELLS = 1

SHALE CELLS = 0

FIG. 1 — Random generation of sand lense cells by Monte Carlo method

concerning this approach, and efforts will be expended toward incorporating it into the three-dimensional reservoir simulation model.

As has been pointed out in a previous report point bar type of sand lenses, the shape of a particular lense is not important as long as it is randomly distributed on an areal basis. In general these types of sand lenses are considerably larger than the lenticular type which are characteristic of the Mesa Verde formation¹.

III. Development of a transient wellbore storage model

The mathematical model for the transient wellbore storage model has been completed. We are in the process of developing a computer code, and plans are to try and finalize this by the end of the next reporting period. The present mathematical model consists of a two-phase liquid/gas model based upon the simultaneous solution to the two-phase continuity, momentum, and energy equations including heat lost through the pipe as the fluids flow up the production string. A finite difference approach is being used to numerically solve the coupled system of equations.

IV. Development, analysis and evaluation of a skin damage factor model

A skin damage model has been developed to take into account possible fracture face damage effects. The results were presented in a previous report. Upon further investigation of this problem, we have concluded that to distinguish between lenticularity, fracture face damage effects, proppant embedment, and/or fracture closure is difficult if not impossible to separate as individual effects.

The skin damage factor, s , appears in the reservoir model in the form, $(k F_{nd}/s)$, where k is the reservoir permeability, and F_{nd} is the non-Darcy flow number. If one attempts to do reservoir history matching, it is clear that different combinations of k , F_{nd} , and s can give the same ratio and hence, may lead to non-unique solutions. Although Cinco-Ley and Samaniego⁵ have addressed fracture face damage effects their solutions are based upon the slightly compressible fluid and radial flow assumptions. Such assumptions for gas wells do not seem appropriate.

V. Correlation, parametric and sensitivity analyses of well performance

In order to assess the merits of the existing simulator, results have been compared against work published by other researchers. In particular an earlier version of the simulator was used to predict the well production history of some gas wells completed in low-permeability lenticular reservoirs simulated by massive hydraulic fracturing. Well data from reference 2 was used as input to the simulator and results were generated to predict the production history of a well stimulated by massive hydraulic fracturing technology. The results and a discussion of this study are contained in reference 4. The purpose of the results presented in reference 4 was to point out the difficulty of uniquely separating lenticular effects, skin damage effects, and proppant embedment effects.

As a second check against results presented by other researchers, well data reported in reference 3 was used as input into the simulator for comparison purposes. The input data and simulator results are given in Table 1 and Fig. 2, respectively. As can be seen, a reasonable match is obtained

FIG. 2 — Comparison of simulator results with that contained in Reference 3.

when compared against the results from reference 3. Since the mathematical models used in the two simulators are different, some differences are to be expected. Furthermore, additional data such as fracture permeability and fracture width were not specified in reference 3; hence, they were back calculated from other data, and results are given in this reference. The results shown in Fig. 2 are somewhat sensitive to the time step size. These results were generated by using a time step size of 0.01 day. Since we were interested in early time pressure transient analysis, this approach gave reasonable results. From Fig. 2 it can be seen that excellent agreement is obtained for late times, but there is some disagreement for early time. However, in their paper Agrawal, et al, indicated their simulator results for early

time did not agree as well with actual production data, so it is difficult to say which of the two models is the more accurate. Since they did not indicate magnitudes for the grid spacing and time step size used in their analysis, the results agree reasonable well when compared against the simulator results developed under this DOE contract.

TABLE 1 — Reservoir data from reference 3

Initial Reservoir Pressure, P_i	2394 psi
Reservoir Temperature, T	720° R
Formation Thickness, H	32 ft
Fracture Half-Length, x_f	727 ft
Fracture Width, W	0.1 in
Formation Permeability, k	0.0081 md
Fracture Permeability, k_f	35 darcies
Formation Porosity, Φ	0.107
Initial Gas Viscosity, μ_i	.0176 cp

Over the next reporting period, work will be directed toward simulating well-performance data for other field cases and to conduct some sensitivity analysis in order to

further assess well-performance predictions in low-permeability lenticular reservoirs.

It was originally thought that lenticularity would have a significant effect upon early time pressure transient testing. However, it appears this is not the case. Evidence does exist to substantiate that lenticularity will indeed effect production forecasting.

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ENVIRONMENTAL AND SAFETY

IDENTIFICATION AND ASSESSMENT OF WATER ISSUES RELATED TO ENHANCED OIL RECOVERY

Contract No. DE-AS19-81BC10412

**Gulf Universities Research Consortium
Bellaire, Tex.**

Contract Date: Sept. 1, 1981

Anticipated Completion: Aug. 31, 1982

Government Award: \$125,000

Principal Investigator:

James L. Gumnick

Technical Project Officer:

Ronald F. Kendall

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

It is the purpose of this project to assemble, into a single reference document, the water issues associated with the production of oil by EOR. The information tabulated will provide a ready reference to assist environmentalists, energy planners, and decision makers when assessing the impacts of oil production by EOR methodologies.

The document will contain information only for those states in which EOR is expected to play a major role in future oil production. The contents will include data as to (1) water needs, i.e., water quantity, quality and rate of usage for the individual EOR processes; (2) applicability of various EOR processes to a specific geographic location; (3) water quantity and quality available at a given geographic location; (4) entities that may be in competition for available water supplies; (5) areas where the lack of high quality water may constrain EOR production; and (6) regulatory bodies responsible for control of water supply and use.

Summary of Technical Progress

Technical reviews of the final report from this contract have been completed. The report, entitled "Assessment of Water Issues Associated With Enhanced Oil Recovery: A User's Guide," has been submitted to BETC's Technology Transfer Branch for final publication.

SAFETY ANALYSIS AND REVIEW SYSTEM (SARS) ASSESSMENT

Contract No. DE-AS19-80BC10353

**Mitre Corp.
McLean, Va.**

**Contract Date: Sept. 30, 1980
Anticipated Completion: June 30, 1983
Government Award: \$321,730**

**Principal Investigator:
Tom Wright**

**Technical Project Officer:
Ronald F. Kendall
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

To provide BETC's project managers with guidelines for identifying, quantifying, and prioritizing hazardous materials or conditions in the working environment and to assess risk potentials associated with any identified hazards. The programmatic impact of the Safety Analysis and Review System (SARS) requirement on BETC's developing fossil energy programs will be established along with the need for additional research in areas where hazards and risk potentials are known. Procedures are to be developed to enable project managers to meet and document the SARS requirement from the preplanning stages of project development through the entire life cycle.

Summary of Technical Progress

The anticipated completion date of this project has been extended, on a time only basis, until June 30, 1983. This extension was necessary to provide Mitre Corp. sufficient time to complete its final report, entitled "Health and Safety Handbook for Enhanced Oil Recovery Operations."

SUPPLEMENT TO ENVIRONMENTAL REGULATIONS HANDBOOK FOR ENHANCED OIL RECOVERY

Contract No. DE-RP19-80BC10355

**Spears and Associates, Inc.
Tulsa, Okla.**

**Contract Date: Sept. 26, 1980
Anticipated Completion: June 30, 1983
Government Award: \$16,867**

**Principal Investigator:
John Scott**

**Technical Project Officer:
Ronald F. Kendall
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

To prepare a Supplement to the Department of Energy's Environmental Regulations Handbook for Enhanced Oil Recovery that will provide the public with a technical interpretation and assessment of recent Federal and state regulations and their impact on enhanced oil recovery processes.

Summary of Technical Progress

The decision has been made to incorporate the information obtained under this contract into a new, revised edition of the "Environmental Regulations Handbook for Enhanced Oil Recovery" which was published by the Department of Energy in August 1980. The original intent was simply to publish a supplement to the Handbook but this is no longer being considered because of several changes in Federal Regulations, especially in the area of underground injection control. In order for Spears and Associates to complete this revision, the contract anticipated completion date has been extended until June 30, 1983.

**EVALUATION OF GROUNDWATER
CONTAMINATION FROM ENHANCED
OIL RECOVERY OPERATIONS**

Contract No. DE-AP19-82BC99996

**Brookhaven National Laboratory
Upton, New York**

Contract Date: Sept. 15, 1982

Anticipated Completion: Sept. 15, 1983

Government Award: \$95,000

**Principal Investigator:
Edward Kaplan**

**Technical Project Officer:
Ronald F. Kendall
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

To utilize computerized mathematical models to predict the movement of pollutants in an aquifer. The models will take into account parameters such as advection and dispersion in an aquifer as well as adsorption and pollutant decay. The analysis will consider only those enhanced oil recovery processes which use substances in the production of oil that clearly present a risk to aquifer contamination and will focus on those substances for which sufficient data is available.

Summary of Technical Progress

Several data collection phases of this project have been completed. Many reports identified in computerized bibliographic searches have been received and reviewed. Information has been obtained on three additional groundwater models, bringing the total number of models available for the study to five. Substantial work is to be performed next quarter comparing and evaluating all five models to identify the one which is most applicable to this project.

Personnel in over 25 different federal and state agencies, universities, and industry have been contacted to obtain documented cases of groundwater contamination from oil production. Three cases have been identified which may be sufficient to validate groundwater models; however, only one of these is associated with enhanced oil recovery.

MICROBIAL ENHANCED OIL RECOVERY

ISOLATION AND SCREENING OF ANAEROBIC CLOSTRIDIA FOR CHARACTERISTICS USEFUL IN ENHANCED OIL RECOVERY

Contract No. DE-AS19-80BC10302

**Oklahoma State University
Stillwater, Okla.**

**Contract Date: Sept. 1, 1981
Anticipated Completion: Dec. 31, 1983
Government Award: \$50,000**

**Principal Investigator:
Edward Grula**

**Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

This project has the following objectives: (1) obtain selected microorganisms for use in enhanced oil recovery.

In complex media such as trypticase soy broth supplemented with sucrose (1 percent) gas production by some of our isolates is good and there is a close parallel. These will be screened qualitatively and quantitatively for their ability to produce gases such as carbon dioxide, hydrogen, and methane; acids such as acetic; solvents such as alcohols and acetone, as well as small molecules possessing surfactant properties; (2) isolate and screen mixtures of bacteria capable of producing the greatest amount of the desired metabolic end products which will be tested for their ability to grow with each other under conditions that exist in shallow oil wells; (3) determine which solvent mixtures that are capable of production by bacteria which will optimize solubilization of crude oil; (4) determine if a desired inoculation sequence of bacteria exists; and (5) introduce bacterial mixtures into selected reservoirs.

Summary of Technical Progress

We continue to prepare for field testing of some of our isolates later this spring and summer. Thus far there are at least 3 possible well locations that are probably going to be made available to us. Produced waters from 2 sites have been tested and found to be satisfactory even at a 1-1 dilution using local river and pond water.

between gas production and growth (Fig 1). It is also of definite interest that refeeding of the culture results in a significant stimulation in both growth and gas production (Note: Dr. Yen, University of Southern California made a similar observation). Such refeeding can be done even when the pH of the culture is at its lowest point (pH 4.2-4.3).

FIG. 1 — Growth and gas production by HR-3

Emulsifier production is interesting. Again, a burst of synthesis occurs on re-feeding which is very encouraging. It is also pleasing to observe the synthesis of emulsifier will occur either at the higher or lower pH (data shown in Fig 2). There is a significant drop in emulsifier present in the culture prior to re-feeding. Unless the culture utilizes emulsifier as a carbon-energy source under conditions of nutrient limitation, this drop is difficult to understand. All data are given for 1 ml amounts of unconcentrated spent media. At 4+ reading for emulsifier is equivalent to a surface tension of 40 ± 5 dynes/cm or an interfacial tension of 20 ± 3 dynes/cm. Interfacial tension readings were obtained using mineral oil having a Saybolt viscosity of 125/135. Ability of the growing culture to utilize emulsifier as a carbon-energy source will be directly tested when the emulsifier has been obtained in a sufficiently pure form.

Data given in Table 1 are included to show the effects of 3 growth media and 5 different growth temperatures on gas production by 2 organisms. Exact content of sugar in the 2 molasses media is not known, however, the TSB medium contains no sugar, thus the consistently lower values.

FIG. 2 — Early growth, acid and emulsifier activity by HR-3

TABLE 1 — Growth of two clostridial isolates at five different temperatures in three different media

Isolate	Growth medium*	Temp., °C	Gas prod.,** mm at 72 hr.
69E	TSB	15	0
69E	TSB	20	15
69E	Beet	20	34
69E	Sorghum	20	38
69E	TSB	25	16
69E	Sorghum	25	50
69E	Beet	25	44
69E	TSB	37	20
69E	Sorghum	37	60
69E	Beet	37	60
69E	TSB	45	18
69E	Sorghum	45	60
69E	Beet	45	60
HR-3E	TSB	15	0
HR-3E	TSB	20	0
HR-3E	TSB	25	0
HR-3E	Sorghum	25	10
HR-3E	Beet	25	11
HR-3E	TSB	37	0
HR-3E	Sorghum	37	10
HR-3E	Beet	37	24
HR-3E	TSB	45	20
HR-3E	Beet	45	30

*TSB = trypticase soy broth; beet = 2 percent molasses-salts; sorghum = 2 percent sorghum molasses-salts.

**Average of duplicate tubes using the Vaspar overlay technique.

STUDY OF THE BIODEGRADATION OF COMPOUNDS USED IN ENHANCED OIL RECOVERY

Contract No. DE-AT19-78BC30201

**Oklahoma State University
Stillwater, Okla.**

**Contract Date: July 1, 1979
Completion: Feb. 28, 1982
Government Award: \$162,781**

Principal Investigators:

**Mary M. Grula
Edward A. Grula**

Technical Project Officer:

**Erle C. Donaldson
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The main objective of this project is to determine the biodegradability and toxicity of various materials used in enhanced oil recovery, allowing an environmental assessment of damage resulting from a spill or accidental discharge.

Summary of Technical Progress

Work on this contract has been completed. The final report is being prepared.

THE USE OF MICROORGANISMS IN ENHANCED OIL RECOVERY PROCESSES

Contract No. DE-AC19-80BC10300

**University of Oklahoma
Norman, Okla.**

**Contract Date: Dec. 1, 1982
Anticipated Completion: Nov. 30, 1983
Government Award: \$90,000**

Principal Investigator:

Roy M. Knapp

Technical Project Officer:

**Erle C. Donaldson
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The objectives of this project are as follows: (1) determine if microbial cells can be used to selectively plug high-permeability regions in the oil reservoir and thus improve sweep efficiency; (2) isolate microorganisms

capable of growing in the oil reservoir and then examine their metabolic and biochemical characteristics; (3) examine the potential of using microorganisms for enhanced oil recovery by mechanisms other than selective plugging, such as *in situ* production of biosurfactants and biopolymers; (4) examine ways for oxygenating an oil reservoir to support growth of aerobic microorganisms and thus allow additional metabolic processes to be investigated for possible use in microbial EOR processes; (5) study an oil reservoir as an ecosystem in order to obtain a better understanding of the behavior of microorganisms in the oil-bearing formation; and (6) initiate laboratory core tests and field trial tests on the EOR methods developed.

Summary of Technical Progress

Biosurfactant

During the past quarter, a method has been developed for production and purification of the biosurfactant produced by JF-2. The procedure involves the batch fermentation of a (1 percent w/v) sucrose mineral salts medium by the organism JF-2 at 40C. The fermentation is performed under aerobic conditions and has been scaled up to a working volume of 5 liters thus far; however, no attempt has yet been made to optimize the process.

Foam produced by the surfactant by sparging air into the fermentation broth can be removed during the fermentation process and collected in a sterile vessel via the air exhaust line. This foam, which contains concentrated

biosurfactant, is then centrifuged for 15 minutes at $14,300 \times g$ ($4C$) to remove cells. The spent medium is adjusted to a pH of 1.8 with HCl causing precipitation of surfactant and various other macromolecules. This fraction is then centrifuged at $14,300 \times g$ for 30 min. and the precipitant is collected and the supernatant is discarded. This precipitant can then be freeze-dried until ready for purification.

The purification begins with a methylene chloride extraction of the precipitant. The methylene chloride extract is then boiled for 5 min. with stirring and then filtered through a $0.45 \mu m$ millipore filter to remove insoluble particulate matter. The filter is then washed with additional boiling methylene chloride. The liquid fraction is dried under reduced pressure at $35C$. The dried fraction is resuspended in water and adjusted to a pH of 7.0 with NaOH. This fraction is then passed through a $0.22 \mu m$ millipore filter after which the pH is adjusted to 2.0 with HCl (recrystallized). This fraction is then centrifuged at $48,400 \times g$ for 40 minutes and the precipitant is then freeze-dried.

The yield obtained in a 5 liter batch fermentation is approximately 0.1 g/5 l or 20.0 mg/l of fermentation broth. Yields in terms of grams of sucrose utilized has not yet been determined. The purity of the surfactant was determined by thin layer chromatography.

The molecular weight determination of the purified fraction was performed utilizing gel permeation techniques. A column packed with Sephadex G25 was run in a buffer containing 0.5 mM phosphate buffer (pH = 7.0). The effluent fractions were pooled and tested for activity (surface tension). It was found that the activity was greatest at very near the fraction where the void volume comes off the column. This would indicate that the molecular weight is estimated between 20,000-25,000 daltons. This figure is in conflict with our earlier estimate of 410 daltons on the crude extract using mass spectroscopy techniques. We are in the process of running molecular weight standards to be able to more precisely evaluate the correct molecular weight. The purified preparation is also being examined by infrared and mass spectroscopy to obtain additional molecular weight as well as structural information.

Growth kinetics of plugging

A. Growth Parameters

Growth parameters of 15 polymer producing organisms is presently being evaluated at growth under O_2 -limiting

conditions and temperatures of $50C$. The growth parameter currently being evaluated for these 15 isolates include the specific growth rates, exopolymer yields, cell mass production, and substrate depletion with time. Specific growth rates for these 15 isolates vary from 0.81 generations/hr to 1.9 generations/hr. When grown on a 1 percent w/v sucrose mineral salts medium containing 0.1 percent w/v $NaNO_3$ and 0.05 percent w/v yeast extract. Determination of other parameters is currently under way. Also presently being examined are the rheological properties of these exopolymers at different shear rates.

B. Modeling

We have been developing a computer program to model the bacterial selective plugging process. The model will be used to understand the process and guide experimental design. As stated by Revus (M.S. Thesis, University of Oklahoma, 1982), "The theory of this process is based upon three major criteria:

1. viable bacteria may be introduced via the aqueous displacing fluid into high permeability regions of the reservoir.
2. a specified amount of preferably cost-effective nutrients may be injected into the reservoir to initiate *in situ* metabolic growth of viable bacteria in targeted regions.
3. *in situ* growth of viable bacteria by nutrient addition to produce sufficient quantities of biomass (cellular and extracellular) for physical selective plugging of high permeability channeling zones."

The reduction of permeability in porous media is caused by the accumulation of microbial cells within the pore spaces by the mechanisms of adsorption and filtration during the transport of cells through the porous media in a form of its suspension in a carrier solution. The carrier solution contains nutrients essential for cell growth along with the carbon source that already exists in the reservoir formation. In general, bacteria growth is nutrient limited and may be controlled by varying nutrient availability. This allows an external control on the process.

A mathematical model for the prediction of the spatial and temporal permeability reduction has been developed based on the fundamental conservation of mass and momentum incorporated with the bacteria growth kinetics and adsorption and filtration models. The model will be limited to a simplified, one-dimensional treatment.

BACTERIA TRANSPORT THROUGH POROUS MEDIA

Contract No. DE-AS19-81BC10508

University of Southern California
Los Angeles, Calif.

Contract Date: Feb. 1, 1982

Anticipated Completion: Feb. 1984

Government Award: \$70,000

Principal Investigator:
Teh Fu Yen

Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

This research effort has the following objectives: (a) examination of the interaction between bacteria and geological porous media containing oil, brine water; (b) study of transport phenomena of bacteria through porous media under applied pressure; and (c) facilitation of bacterial transport through geological porous media under naturally-occurring reservoir conditions.

Summary of Technical Progress

Experiments of microbial EOR.

The experiments of microbial EOR were mainly to utilize the bacterial metabolites generated during the *in situ* growth of the aerobe *Bacillus subtilis*. The oil recovery efficiencies were around 40-50 percent of the residual oil remaining after waterflooding. Oxygen supply could be a limiting factor for the use of this species.

In order to evaluate the efficiency of recovering Long Beach crude from sandpack columns by utilizing anaerobes, we particularly chose *Clostridium sp.* for our study.

To predict the relative efficiencies of recovery by various *Clostridium sp.*, synthetic solutions of organic acid and solvents were injected into sandpack columns containing residual oil. The compositions of the solutions corresponded to the aqueous-phase metabolites produced by fermenting 400 m mole glucose per liter medium using various *Clostridium sp.* (Table I). It was found that recovery efficiencies were 20, 16 and 15 percent by flooding the columns with 20 PV of solutions corresponding to the metabolites produced by *C. acetobutylicum*, *C. butylicum* and *C. sacharotutyricum*, respectively.

The residual oil remaining in the sandpack column after secondary waterflooding was the target for further recovery by *C. acetobutylicum*. In order to investigate exclusively the effects of *C. acetobutylicum*, Long Beach crude was poured into a stainless steel bomb which was sealed and later autoclaved for 40 min to kill the indigenous bacteria to the oil.

About 8 PV *C. acetobutylicum* culture was first injected into Column 1. To investigate if *in situ* bacterial activity can be stimulated and recover oil, the inlet end was then switched to fresh medium. About 20 PV of fresh deoxygenated nutrient broth was injected from the beginning of the experiment. Finally, about 8 PV of brine solution was injected into both column to displace additional amount of oil released from pore spaces.

About 12.9 percent of residual oil was recovered from Column 1 during flooding with *C. acetobutylicum* culture, 34.1 percent was recovered when the inlet end was switched to fresh nutrient broth, an additional 7.1 percent was recovered at the final stage of flooding with brine solution. The overall recovery from Column 1 was around 54 percent. The overall recovery from Column 2 was around 30 percent.

We observed that an appreciable amount of oil was recovered when fresh deoxygenated nutrient broth was injected into Column 1 which has been loaded with old *C. acetobutylicum* cells in the previous stage of flooding with culture. This might indicate that the vigorous *in situ* growth stimulated by fresh medium yielded a high percentage of recovery.*

Surface charge modification of *Bacillus* spores

Attempts were made to alter the surface charge of *Bacillus Subtilis* spores by chemical means since the cells must be viable even after the treatment very mild derivitization conditions were used. All treatments were carried out in aqueous medium unlike some of the earlier attempts will cell walls.

The *Bacillus* spores were spun down from a nutrient broth growth medium and washed 3 times with 0.01 M NaCl solution. The suspension of spores was then treated by 3 chemical methods in an attempt to modify the surface charge. (a) *NBS Treatment* (for-COOH groups) 250 mg of N-Bromosuccinimide (NBS) was added to 50 ml of spore stock solution and the mixture heated to 40°C for 30 minutes. The cells were then centrifuged and washed 3 times with 0.01M NaCl for electrophoretic mobility measurements. (b) *TSCL Treatment* (for-NH₂ groups) 150 mg of p-toluene sulphonyl chloride were added to 50 ml of the stock spore suspension and the mixture refrigerated for 2 to 3 hours. The pH of the solution was ~3. The cells were then centrifuged and washed 3 times with 0.01 M NaCl solution for electrophoretic mobility measurements. (c) *Phosphate Treatment*. 10 ml of 0.01M pyrophosphate solution was added to 50 ml of stock spore suspension and the mixture kept at room temperature for 1/2 hour. The cells were then

TABLE 1 — Examples of acetone-butanol and mixed solvent fermentations*

Products ¹	<i>C. saccharo-</i> <i>butyricum</i> ²	<i>C. aceto-</i> <i>butylicum</i> ²	<i>C. bu-</i> <i>tylicum</i> ³	<i>saccharo-</i> <i>tylicum</i> ⁴	<i>C. thermo-</i> <i>B. aceto-</i> <i>ethylicum</i> ³	<i>B. polymyxa</i> ³
CO ₂	195.5	220.0	207.0	174.0	215.0	195.0
H ₂	233.0	165.9	111.1	229.4	137.0	54.0
Acetate	42.6	24.8	20.3	48.5	16.0	5.0
Butyrate	75.3	7.1	14.5	59.5	—	—
Formate	tr	—	—	—	10.0	—
Lactate	—	—	—	25.7	—	—
Ethanol	—	4.9	—	—	122.0	95.0
Butanol	—	47.4	50.2	—	—	4.5
Acetone	—	22.3	—	—	28.0	6.0
Isopropanol	—	—	18.0	—	—	—
Acetoin	—	5.7	—	—	—	—
2,3-Butanediol ..	—	—	—	—	12.0	39.0
<i>C. rec.</i> , pct	97.0	98.0	93.5	98.0	105.0	100.0
O/R bal	1.02	1.01	1.05	0.99	0.90	1.13

*Amounts are expressed as mmoles per 100 mmoles of glucose use.

²Donker, 1926.

³Osburn, Brown and Werkman, 1937.

⁴Sjolander, 1937.

*A.G. Moat, *Microbial Physiology*, John Wiley & Sons, N.Y., 1979, p. 145.

centrifuged and washed 3 times with 0.01 M NaCl. The pH of the reaction mixture was 9.9.

Results

The results of the Zeta potential measurements are shown in Table II. The pyrophosphate treatment was too strong for the cells as a result of which they are lysed and only protein chains are obtained after centrifuging. No Z. P. measurements could be made.

The results show that the reactions do not cause any significant change in the bacterial surface charge, as had been expected. In the future some new derivitization procedures will be attempted to cause significant changes in the surface charge without causing any change in mobility.

Influence of chemical additives on transport

An experiment of preflushing the sandpack with pyrophosphate solution was conducted. After injecting twelve

TABLE 2

Sample	Temp., °C	Conduvity	ZP. mV	pH
1 Stock sample ...	25.1	996	-44.3	6.3
	24.7	996	-44.1	6.4
2 After NBS treatment	27.0	1044	-45	6.6
	27.4	1089	-53	6.56
3 _a After TSCI treatment	23.6	946	-48.9	6.61
3 _b After TSCI treatment @ pH = 8	25.3	995	-44.0	6.62

*Data for 0.01 M pyrophosphate not available due to lysis of cells.

FIG. 1 — The *Pseudomonas fluorescens* count in the effluent from the sandpack column

pore volume pyrophosphate solution (1.5×10^{-3} M), the *Pseudomonas fluorescens* with concentration about

10^{12} /c.c. was injected into the sandpack. The effluent contraction of *Pseudomonas fluorescens* was increased rapidly to 5×10^{11} /c.c. Comparing with the result of coinjecting with $\text{Na}_4\text{P}_2\text{O}_7$ solution, the effluent concentration of *Pseudomonas fluorescens* is higher when the sandpack was preflushed with pyrophosphate solution. (Fig 1). When the pyrophosphate solution is preflushed with sandpack, the $\text{P}_2\text{O}_7^{4-}$ ions will form complexes with the surface of the sand particles, and this will change the surface charge of sand particles to more negative. Due to the stronger charge repulsion between sand particles and bacteria, the bacteria (*Pseudomonas fluorescens*) can pass through the sandpack easier, which will cause a lower pressure drop in the sandpack.

*Note: Dr. Grula, OSU, observed similar behavior when a bacteria culture was fed with nutrients a second time.

THE APPLICATION OF MICROBIAL PROCESSES FOR THE REDUCTION OF VISCOSITY OF HEAVY CRUDE PETROLEUM

Contract No. DE-AS-AS19-81BC10507

University of Georgia
Athens, Geo.

Contract Date: Feb. 1, 1982
Anticipated Completion: Jan. 1984
Government Award: \$80,000

Principal Investigator:
William R. Finnerty

Technical Project Officer:
Erle C. Donaldson
Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The work will focus on three phases of research development: (1) the selection and examination of microorganisms which exhibit a metabolic capability to reduce the viscosity of heavy crude petroleum. This metabolic activity can serve to reduce the relative viscosity of heavy crudes through direct bacterial oxidation of specific hydrocarbons present in heavy crudes or through the production of metabolic byproducts that effectively alter or

reduce the relative viscosity of in-place oil; (2) those microbial cultures identified as exhibiting the appropriate biological properties — namely, reduction of viscosity — will be studied in greater detail to determine the physical and nutrient requirements for maintenance of culture viability and activity under reservoir conditions; (3) the final phase will involve an examination of the mechanisms involved in the microbial modification of heavy oil with characterization of products formed and their direct relationship to viscosity reduction.

Summary of Technical Progress

Surface properties of glycolipid

The surface properties of the cellular, extracellular, and purified major glycolipid derived from growth of H13A on hexadecane are shown in Table 1. Each glycolipid exhibits the lowest interfacial tensions (10^{-2} - 10^{-3} dynes/cm) against decane. Supplementation with pentanol reduced interfacial tensions to 10^{-5} - 10^{-4} dynes/cm, with a shift in effective alkane carbon number for the surfactant.

TABLE 1 — Surface properties of the glycolipid

Glycolipid ^a	Minimum interfacial tension ^b , dynes/cm	Effective alkane carbon number, N_c	Minimal interfacial tension ^b (plus pentanol), dynes/cm	Effective alkane carbon number N_c
Major glycolipid	4.2×10^{-3}	10	1.2×10^{-4}	12-13
Extra-cellular glycolipid	2.0×10^{-2}	10	6.0×10^{-5}	11
Cellular glycolipid	2.3×10^{-3}	10-11	9.6×10^{-5}	12

^aGlycolipid (1.8 $\mu\text{g}/\text{ml}$ dry weight) was dissolved in basal salts solution (1.7 percent salts).

^bInterfacial tension was measured using a spinning drop tensiometer at 40°C.

Table 2 shows the effect of pH on the extracellular glycolipid. Acidification of the glycolipid results in aggregation and loss of surface activity. The glycolipid exhibits similar interfacial tensions at pH 7.0 and pH 10.0.

TABLE 2 — Effect of pH on surface activity of glycolipid

pH	Interfacial tension, dynes/cm
3.5	—
7.0	0.250
10.0	0.202

Table 3 shows the effect of divalent cations on the extracellular glycolipid. Addition of Ca^{++} , Fe^{++} , or Mg^{++} results in a slight reduction of the interfacial tension.

TABLE 3 — Effect of divalent cations on surface activity of glycolipid

Cation	Interfacial tension, dynes/cm
None.....	0.250
Ca ⁺⁺ (CaCl ₂ 1 mg/ml)	0.141
Fe ⁺⁺ (FeSO ₄ 1 mg/ml)	0.099
Mg ⁺⁺ (MgSO ₄ 10 mg/ml)	0.161
Mg ⁺⁺ (MgSO ₄ 1 mg/ml)	0.099

Phase characteristics of the glycolipid

The extracellular glycolipid was dissolved in basal salts solution (1.7 percent total salts), mixed with an equal volume of undecane, heated to 50°C, and allowed to settle 48 hours at room temperature to permit phase separation. Under these conditions no middle phase was formed, nor were the phase volumes altered significantly. Turbidity of the aqueous phase indicated formation of an oil-in-water emulsion.

When the system was supplemented with 0.5 percent pentanol, a distinctly visible middle phase or microemulsion phase was formed, with a reduction in the volume of the aqueous phase. Turbidity in the oil (undecane) phase

indicated formation of a water-in-oil emulsion. Conductivity measurements confirmed that in the upper phase oil was the continuous phase, having a conductivity of 0 mho/cm. In the lower phase, in both cases, water was the continuous phase, with measured conductivities in the range of 10⁻³ to 10⁻⁴ mho/cm. The middle phase is always associated with ultra-low interfacial tensions.

Physical properties of the glycolipid

When examined microscopically under plane-polarized light, the dried glycolipid was birefringent, having both amorphous and crystalline regions. Upon hydration, the glycolipid undergoes a series of phase transitions, and "maltese cross" figures appear, indicating the formation of liquid crystals. Addition of pentanol appeared to propagate liquid crystal formation.

Chemical characterization of the glycolipid

The glycolipid was shown to contain glycerol and amino sugars in addition to disaccharide and fatty acid. The intact glycolipid was ninhydrin-negative; but water-soluble products of acid hydrolysis were ninhydrin-positive, indicating that the amino group is not free, but is most likely acylated in the intact lipid.

OIL RECOVERY BY GRAVITY MINING

AN EVALUATION OF HEAVY OIL MINING

Contract No. DE-AC22-80PC30259

**Energy Development Consultants
(Stone and Webster Corp.)
Denver, Colo.**

**Contract Date: Sept. 23, 1980
Anticipated Completion: July 23, 1982
Government Award: \$218,096**

**Principle Investigator:
Edwin M. Piper**

**Technical Project Officer:
H.J. Lechtenberg
San Francisco Operations Office**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objective

The objective is to determine the technical and economic feasibility of recovering heavy oil by mining or mining-assisted methods. The project will proceed under three tasks as follows:

Task 1: Evaluate the heavy oil resource amenable to mine production.

Task 2: Evaluate mine technology.

Task 3: Develop preliminary mining concepts for subsets of heavy oil resource.

Summary of Technical Progress

The project has been completed and the final report has been published in two volumes as report No. DOE/PC/30259-1. Free copies of the report are available from BETC.

FEASIBILITY OF LIGHT OIL MINING IN THE UNITED STATES

Contract No. DE-AC19-82BC10704

**Fuel & Mineral Resources, Inc.
Reston, Va..**

**Contract Date: June 15, 1982
Anticipated Completion: Dec. 15, 1982
Government Award: \$60,000**

**Principal Investigator:
Feridun Albayrak**

**Technical Project Officer:
Herbert B. Carroll, Jr.
Bartlesville Energy Technology Center**

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

This study will provide a detailed technical and economic feasibility analysis of three light oil mining methods as applied to three light oil reservoirs. The three preselected methods are:

1. Spoke drilling from bottom of shafts.
2. Spoke drilling from bottom of shafts, of lesser density of drill holes and stimulation of the formation through explosive fracturing of the horizontal holes.
3. Modified fracture caving featuring tunnels only in the upper level, with chambers off the tunnels.

Each of the three mining methods will be applied to each of the three reservoir formations to be exploited by

light oil mining. Thus, nine light oil mining case studies will be performed, including both technical and economic feasibility elements. All key unit operations of each mining method will be identified, and the mining and construction requirements associated with each unit operation will be quantitatively specified. Key unit operations will include, among others, the following: shaft excavation; shaft lining; shaft grouting; tunnel excavation; tunnel lining; oil collection chamber excavation; well bore stimulation (such as explosive fracturing, MHF, etc.); and positive-displacement oil pumping from underground mine workings to the surface.

Summary of Technical Progress

During the final performance period of the project all major efforts have been completed on sections of the Table of Contents of the Draft Final Report. The table of contents was modified to reflect DOE personnel review comments received during a project review meeting.

The final section of work includes the cost calculations for the block caving mining system which requires the most engineering calculations due to the extensive underground development work required. Cost calculations include the estimates for panel drifts, slusher drifts, finger raises, undercut drifts, ventilation crosscuts and ventilation raises. These estimates are very detailed and follow a step-by-step costing of each unit operation. All cost data are based on extensive discussions and communications with equipment manufacturers and underground mining construction contractors. The block caving mining is the costliest of all the methods analyzed in the study in terms of initial development cost. However, this method can be applied to heavy oil fields where gravity drainage with boreholes may not be feasible. The explanatory text to these cost tables will be included in the Draft Final Report.

The Draft Final Report is currently under preparation and is expected to be submitted within a month.

IMPROVED DRILLING TECHNOLOGY

STRESS-INDUCED FATIGUE STUDIES OF DRILL PIPE IMMERSSED IN DRILLING MUD WITH H₂S OR CO₂

Contract No. DE-AC19-80BC10361

**The University of Tulsa
Tulsa, Okla.**

Contract Date: Sept. 30, 1980

Anticipated Completion: Feb. 30, 1983

Total Project Cost:

DOE	\$114,237
T.U.	8,031
Industry	120,240
Total	\$242,508

**Principal Investigator:
John Hendrickson**

**Technical Project Officer:
F.W. Burtch
Bartlesville Energy Technology Center**

Reporting Periods: Jan. 1 - Mar. 31, 1983

Objectives

The main objective of this work is to develop a data base comparing the performance of a variety of drill pipe steels under the action of corrosive mud solutions with dissolved H₂S (and subsequently CO₂). Another objective is to search for identifiable time-dependent changes, such as strain or other techniques, which will signal that pipe failure is imminent. The desired result of the project is to provide drilling engineers with reference data useful in actual field situations, such that bad drill pipe can be identified before it fails. The former objective can definitely be accomplished, but the latter objective is more nebulous in that such correlations may not exist.

Summary of Technical Progress

Two data runs were performed during the January-March, 1983 quarter. Their code designations are E-11 and E-12.

Run E-11 was a comparative data run using two different grades of drill pipe. Segments of normalized and tempered Grade E pipe were placed in slots 2, 4, 6, 8 and 10. Five other segments of a higher-strength quench and tempered steel pipe were placed in slots 1, 3, 5, 7 and 9. The high-strength pipe has a nominal yield strength of 150,000 pounds per square inch, and it was claimed to have better resistance to hydrogen sulfide attack than comparable high-strength steels.

All specimens were subjected to the same level of dynamic plus static stress, the maximum applied stress being approximately 75,000 pounds per square inch. The circulating drilling mud was not heated, but frictional drag effects increased the mud temperature to about 90° F. Hydrogen sulfide content of the mud was increased from 0 to 1314 parts per million during the first 14 hours of the data run. Then it was kept in the neighborhood of 1000 ppm for the remainder of the test.

The overall results are that four of the Grade E specimens cracked and failed, whereas three of the high-strength specimens cracked and failed. The Grade E specimens which failed had fairly straight circumferential cracks extending from $\frac{1}{2}$ to $\frac{3}{4}$ of the distance around the periphery of the specimens (Fig. 1). The high strength specimens had jagged, irregular and branched cracks which sliced the specimens in half (Fig. 2). Our preliminary conclusion from visual inspection is that the high strength specimens tested are considerably more sensitive to hydrogen sulfide attack leading to embrittlement than the Grade E specimens. It remains to be seen whether the high-strength specimens perform better than specimens of comparable high strength steel. The broken specimens will

be subjected to more comprehensive analyses before a final report is compiled.

Data run E-12 was quite similar in most respects to data run E-11, except that five specimens of a different grade of drill pipe were compared with five specimens of normalized and tempered Grade E pipe. The new grade has a nominal yield strength of 95,000 pounds per square inch, and is slightly stronger than Grade E. It has a quench and temper heat treatment. All laboratory conditions were basically the same as for data run E-11. The result of this test was that two of the new specimens cracked and none of the Grade E specimens cracked or failed. One of the failed specimens cracked when stress was first applied, but before it was exposed to hydrogen sulfide.

Our opinion, based on this data run and previous data runs using Grade E pipe, is that the performance of the two pipe grades studied is comparable under the test conditions used. It is quite common for one or more specimens of Grade E to fail during a test run. Moreover, those samples which did crack in this test did not crumble into small pieces as has been seen with high-strength pipe. We found straight, circumferential cracks, similar to cracks of failed Grade E specimens (Fig. 1).

FIG. 1

FIG. 2

GENERAL SUPPORTING RESEARCH

**ENGINEERING AND RESEARCH
SUPPORTING THE DOE ENHANCED OIL
RECOVERY PROGRAM**

Contract No. DE-AS19-81BC10412

**Gulf Universities Research Consortium
Houston, Tex.**

Contract Date: Feb. 12, 1981

Anticipated Completion: Feb. 11, 1983

Government Award: \$350,000

Principal Investigator:

James L. Gumnick

Technical Project Officer:

Thomas C. Wesson

Bartlesville Energy Technology Center

Reporting Period: Jan. 1 - Mar. 31, 1983

Objectives

The current scope of work addresses specific activities represented in the following task statements: University and Industrial Liaison, Identification and Assessment of Water Issues for Enhanced Oil Recovery, Incentives Data Augmentation and Analysis, and Exploration of An Alternative to Simulation Through Critical Parameter Analysis of Reservoir Data Bases.

Summary of Technical Progress

Task I. University and industrial liaison

The GURC EOR Industry Advisory Panel met during February in Houston. Edward J. Lievens, Jr., then Acting Director of BETC, spoke on recent developments relative to EOR research at BETC. S.G. Appan of GURC presented results of work on "SORCES — A Statistically Oriented Reservoir Comparison and Evaluation System, Multi-variate Interrelationships in Heterogeneous Reservoir Systems for EOR Prediction and Assessment," (Task VIII).

GURC prepared an inventory describing its reports and projects completed during the current contract year. The overview list includes eight final reports.

At Brookhaven National Laboratory's Energy and Environment Department, Jim Gumnick discussed continued EOR research, geology, water, data-related matters and reported on the "SORCES" work.

On a visit to the Energy Information Agency in Washington, Gumnick briefed Diane Lique on "SORCES" and other related EOR projects.

At the U.S. Synfuels Corp., Gumnick reviewed DOE/BC/10412-40, "Assessment of Water Issues Associated with Enhanced Oil Recovery: A User's Guide." The discussions included the significance of coordinating the development of energy technologies in areas where synfuels projects might be competing with EOR projects for water resources.

And, during the quarter, Gumnick held a briefing at the Interstate Oil Compact Commission on needs and methods for providing university/industry liaison in support of EOR programs.

A proposal, titled "Enhanced Recovery of Heavy to Intermediate Oils by Alkaline-Steam Flood, Phase III," was reviewed.

Task VII. Identification and assessment of water issues for enhanced oil recovery.

The draft final report for Task VII, titled "Assessment of Water Issues Associated with Enhanced Oil Recovery: A User's Guide," was submitted to Task Manager Ronald F. Kendall in January. The technical and editorial reviews were received and the recommended changes completed in February. The final report (DOE/BC/10412-40) was delivered to BETC March 8.

This report is a single reference user's manual designed to help EOR producers, energy planners and decision makers in assessing the impacts of water issues related to the production of oil by EOR. Water quality and quantity requirements representing the total water needed from all sources are estimated for individual EOR processes on a current and future basis in geographic locations where EOR processes will likely play a major role in future petroleum production. Information for quantity and quality of surface and ground water availability and competing entities by four major categories are presented on a qualitative and quantitative basis by state-county. Information regarding regulatory bodies responsible for control of water supply and use is presented in tabular form by state. The report includes instructions and examples for the use of its charts

and tables to aid the user in data evaluation and decision making.

Task VIII. Investigation of multivariate interrelationships in heterogeneous reservoir systems for EOR prediction and assessment

During January, Task VIII research work was examined in a meeting with Task Manager Herbert B. Carroll, Jr.

In order to subject the new concepts of Task VIII work to frequent peer review, the following presentations were made during the reporting quarter:

- at the Petroleum Data System Advisory Council meeting in Denver,
- at the GURC EOR Industry Advisory Panel meeting in Houston,
- to staff at Brookhaven National Laboratory, Energy and Environment Department,
- at the Energy Information Agency in Washington, Diane Lique.

Also, an abstract was submitted for presentation at the SPE Annual Conference in October 1983, titled "Multivariate Interrelationships in Heterogeneous Reservoir Systems for EOR Prediction and Assessment."

A compendium of the "SORCES" work, as yet untitled, was prepared for publication in the *Journal of Energy and Environment*.

Task IX. Incentives data augmentation

The work in 1982 consisted for the most part of contacting operators and companies and requesting updated and corrected data on the filing of the original Form ERA 424-A, the information requested for entitlement under the Enhanced Oil Recovery Incentives Program. During the first quarter of 1983, the emphasis was on evaluating, tabulating and putting the information in computer-sensible form. This work has been completed, and after some editing will be forwarded to DOE/BETC.

In addition, work is continuing on obtaining the Annual Report data (Form FE-748) from the various companies for the years 1981 and 1982.

On the original 430 projects authorized, we have received responses on 320. There are approximately 110 companies which have not replied to any of our requests for data. An effort will be made in the next quarter to contact and acquire some type of definitive response from the companies and operators.

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