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MICROBIAL ENHANCED OIL RECOVERY AND WETTABILITY RESEARCH PROGRAM

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ABSTRACT

This report covers research results for FY 1990 for the microbial enhanced oil recovery (MEOR) and wettability research program conducted by EG&G Idaho, Inc. at the Idaho National Engineering Laboratory (INEL) for the U.S. Department of Energy (DOE). The research program is funded by the Office of Fossil Energy and managed by the Idaho Opeations Office and the Bartlesville Project Office. The objective of the multi-year MEOR project is to develop microbial enhanced oil recovery (MEOR) systems for application to reservoirs containing medium to heavy crude oils and the design and implementation of an industry cost-shared field demonstration project of the MEOR technology. An understanding of the controlling mechanisms will first be developed through the use of laboratory scale testing to determine the ability of microbially mediated processes to recover oil under reservoir conditions and to develop the design criteria for scale-up to the field. Concurrently with this work, the isolation and characterization of microbial species collected from various locations including target oil field environments is underway to develop more effective oil recovery systems for specific applications. The wettability research is a multi-year collaborative effort with the New Mexico Petroleum Recovery Research Center (NMPRRC) at the New Mexico Institue of Mining and Technology, Socorro, NM to evaluate reservoir wettabiltiy and its effects on oil recovery. Results from the wettability research will be applied to determine if alteration of wettability is a significant contributing mechanism for MEOR systems.

Eight facultatively anaerobic surfactant producing isolates able to function in the reservoir conditions of the Minnelusa A Sands of the Powder River Basin in Wyoming have been isolated from naturally occurring oil-laden environments. The isolates have been characterized according to morphology, thermostability, halotolerance, growth substrates, affinity to crude oil/brine interfaces, degradative effects on crude oils, and biochemical profiles.

The MEOR research at the INEL in FY 1990 has focused on the elucidation of microbial mechanisms by which crude oil may be recovered from a reservoir and the chemical and physical properties of the reservoir that may impact the effectiveness of MEOR. During FY 1990, Bacillus licheniformis JF-2 (ATCC 39307) has been used as a benchmark organism to quantify MEOR of medium weight crude oils (17.5 to 38.1°API). Bacillus licheniformis was chosen because of its past and current use in the field of MEOR. The capacity for oil recovery of Bacillus licheniformis JF-2 utilizing a sucrose-based nutrient has been elucidated using Berea sandstone cores (permeability 85 to 400 md). Depending on method of injection (washed or unwashed cells) and type of oil, recoveries up to 28% of the original oil-in-place have been achieved. Spacial distribution of cells after microbial flooding has been analyzed with scanning electron microscopy. These data indicate complete distribution of cells with a predominance of organisms located distal to the point of injection. Oil recovery appears to be surfactant mediated. The effect of microbial surfactants on the interfacial tensions (IFT) of aqueous/crude oil systems has been measured utilizing an interfacial tensiometer based on real time digital imaging of a hanging drop (designed and constructed at the INEL). Cell free supernatants prepared from Bacillus licheniformis JF-2 resulted in decrease in IFT for all the crude oils tested.

The results of the wettabiltiy research are summarized and the contributions to the permanant literature are listed.

SUMMARY

This report covers research results for FY 1990 for the microbial enhanced oil recovery (MEOR) and wettability research program conducted by EG&G Idaho, Inc. at the Idaho National Engineering Laboratory (INEL) for the U.S. Department of Energy (DOE). The research program is funded by the Office of Fossil Energy and managed by the Idaho Opeations Office and the Bartlesville Project Office.

The global objective of this multi-year project is to develop microbial enhanced oil recovery (MEOR) systems for application to reservoirs containing medium to heavy crude oils and the design and implementation of an industry cost-shared field demonstration project of the MEOR technology. An understanding of the controlling mechanisms will first be developed through the use of laboratory scale testing to determine the ability of microbially mediated processes to recover oil under reservoir conditions and to develop the design criteria for scale-up to the field. Concurrently with this work, the isolation and characterization of microbial species collected from various locations including target oil field environments is underway to develop more effective oil recovery systems for specific applications.

An understanding of the mechanisms by which microbial systems displace oil under reservoir conditions is being developed through such avenues as core flooding, interfacial tension (IFT) measurements, and other laboratory techniques. The determination of the mechanisms of oil recovery by microbial systems, the range of applicability, and the economic viability of MEOR processes compared to other enhanced oil recovery (EOR) processes will be a significant contribution to EOR and specifically to MEOR technology. The mechanisms of MEOR are not fully understood or specifically known for a wide variety of reservoir conditions, crude oils, and microbial and nutrient systems. Bacteria that have characteristics such as the capability to emulsify crude oils and lower IFT are ideal candidates for improved oil recovery. Organisms that have the ability to produce acids or gases or both and organisms that are capable of asphaltic degradation are also significant

to the technology and are presently being collected and isolated for application in EOR research activities.

Two fields in the Powder River Basin, Wyoming have been selected as targets for focus of the MEOR research. These reservoirs produce from the Minnelusa formation and provide an opportunity to study and evaluate reservoirs in two stages of depletion; primary and secondary. The crude oil produced from these reservoirs is about 20°API gravity at 60°F. Assembly of existing field and reservoir data is underway for these candidates. Water analyses to determine the characteristics of the produced brine and injection water has been completed.

Companies that operate oil reservoirs of the target type will benefit through the geological, engineering, and microbial characterization of potential field test sites. Geoscience research will be expanded as required by characteristics of the target reservoir for a successful EOR field design and demonstration project. The industry will also benefit through technology transfer of data resulting from research and field demonstrations of the EOR technology.

Eight facultatively anaerobic surfactant producing isolates able to function in the reservoir conditions of the Minnelusa A Sands of the Powder River Basin in Wyoming have been isolated from naturally occurring oil-laden environments. The isolates have been characterized according to morphology, thermostability, halotolerance, growth substrates, affinity to crude oil/brine interfaces, degradative effects on crude oils, and biochemical profiles.

A series of core flood experiments were performed to investigate parameters such as crude oil type, crude oil viscosity, aging and incubation time, IFT, and brine composition. The first set of cores were inoculated, incubated, and again waterflooded with varying degrees of success for the Bacillus licheniformis JF-2 (ATCC 39307) microbial system with the different oils. Six oils were used in the experimental core flood work ranging in API gravity from 17.5 to 50.5°API at 60°F. The experimental program consisted of various core floods being performed with each oil. Non-fired Berea sandstone cores

encapsulated in epoxy were used in all core floods. A 2.4% NaCl brine solution was used to saturate the cores and for waterflooding the cores. All core floods were performed at room temperature, including the evacuation and saturation phase of the experimental work.

Viscosities of all oils have been measured and a characterization determined for each oil. The produced oil (postflood) samples were fractionated and analyzed with gas chromatography to determine any changes in the oil because of the conditions experienced in the core during the MEOR core flood. The oils remained basically unchanged after being subjected to the conditions of the MEOR core floods. Residual oil saturations are determined for both the waterflood and the microbial flood.

Base line (control) experiments have been performed for each oil. The control cores were injected with nutrient only (no microbes were injected), incubated at the same temperature and for the same period of time as the MEOR cores.

Numerous MEOR core floods were performed with varying degrees of success. The lower gravity oils tended to produce additional oil beyond waterflood more readily than the higher gravity oils. Microbial oil was produced from all MEOR cores with the exception of the core containing a refined oil (Soltrol 220). The Soltrol test was an early test and the microbes may have been poisoned by toluene used to clean the system. Subsequent testing has shown that Bacillus licheniformis will grow in the presence of and emulsify Soltrol 220. The oil recovery test will be repeated in the future.

Spacial distribution of cells in a Berea sandstone core (110 md) following a microbial flood was analyzed with scanning electron microscopy. The data indicate complete distribution of cells with a predominance of organisms located near the outlet end of the core.

Dilution studies of supernatant solutions indicate the concentration of Bacillus licheniformis surfactant is about 2.5 times greater than the critical micelle concentration (CMC) of the surfactant. Interfacial tensions were measured for various dilutions of supernatant and plotted verses supernatant

concentration. A break in the IFT-concentration curve occurs at a supernatant:water dilution of 2:5. Maximum oil recoveries with a given surfactant will be obtained if the surfactant concentration is at or above the CMC.

Thin layer chromatography (TLC) studies have been initiated to identify the compound(s) that give rise to the surfactant activity found. A search of the literature on microbial oil recovery indicates that the surfactant produced by Bacillus licheniformis is a glycolipid. TLC of an ethyl acetate extract of the supernatant (silica gel, 9:1 ethanol:water) shows one major and five minor spots.

The importance of microbial attachment at the oil-water interface as compared to the isolated metabolites to increase oil mobility by way of change in interfacial properties is currently being determined. These experiments employ the BATH (Bacterial Adherence to Hydrocarbons) test to ascertain the hydrophobicity of cell surfaces and the direct measurement of interfacial tensions.

Results of the research with Bacillus licheniformis indicate that the oil recovery is surfactant mediated.

Research activities in the collaborative effort for wettability research at the New Mexico Petroleum Recovery Research Center (NMPRRC) are continuing. Work is progressing in several areas related to oil recovery studies and the effects of wettability on core flooding results. Interim results for the studies to determine the repeatability of the adhesion mapping technique have been completed. Initial results of research to evaluate the effects of drilling mud filtrates on the wettability of cores have been collected.

The effects of wettability changes on residual oil to waterflooding were significant in that they indicate that a highly water-wet state is not necessarily the best condition for achieving the lowest residual oil saturation. The effect of changing crude oil composition, either by dilution

with solvents, fractionation, or evaporation of the lighter components has also been investigated.

A simple adhesion test, adapted from the contact angle measurements of a captive bubble, has been developed to characterize crude oils based on their surface interactions with smooth solids and varying brine composition. Adhesion tests have been performed for more than 20 different crude oils. Adhesion tests were performed using a West Texas crude, Moutray, diluted with a solvent to simulate the action of bacteria that may work to break down large molecules of crude to smaller ones. Results indicate the pH adhesion/non-adhesion cutoff was lowered from that of Moutray alone.

The ability to establish a range of intermediate wettabilities in Berea cores with crude oils has been developed. Extensive tests have been conducted on Berea sandstone cores to determine the effect of wettability on oil recovery. Wettability is measured by Amott tests, supplemented in some cases by measurements of imbibition rates. Weakly water-wet or mixed-wet cores have been observed to give much higher oil recoveries than reference cores of strongly water-wet conditions, even at breakthrough. Post-breakthrough recoveries also showed a wide variety of recovery rates.

Emulsions of several crude oils have been tested to determine mobilities of emulsion droplets. The isoelectric points (IEP) are estimated from the plotted zeta potential data by measurement fr[illegible] graphs of pH value at which the line between the positive and negative zeta potentials closest to zero passes through zero. Reproducibility of the mobility measurements for a given emulsion batch for both a fresh emulsion and a 2 week old emulsion is very good. For most of the oils studied, some aging was observed.

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1. INTRODUCTION

1.1 Program Purpose

The global objective of this multi-year project is to develcp microbial enhanced oil recovery (MEOR) systems for application to reservoirs containing medium to heavy crude oils, and the design and implementation of an industry cost-shared field demonstration project of the MEOR technology. An understanding of the controlling mechanisms must first be developed through the use of laboratory scale testing to determine the ability of microbial processes to recover oil under reservoir conditions. A multi-disciplinary geological, biological, chemical, and engineering characterization of the target reservoir will be conducted to ensure a successful design and application of the process. The technical and economic potential of enhanced oil recovery in the target reservoir type will be determined to provide an evaluation of the ultimate technology potential. The feasibility of combining microbial systems with other EOR methods such as gas and chemical flooding will be addressed. The effects of following other EOR processes such as polymer flooding with an MEOR application also needs to be determined. The applicability and oil recovery potential of MEOR processes in actual reservoir environments will be evaluated by single well injectivity testing and back-flow production before initiation of an MEOR flood.

This report is organized into seven sections; Introduction, Oil Selection and Analysis, Microbial Analysis and Phenomena, Measurement of Interfacial Tensions, Laboratory Core Floods with Microbial Systems, Target Reservoir Selection, and Reservoir Wettability and its Effect on Oil Recovery. It is a progress report of on-going research and is not intended as a final report. Whenever possible, definitive conclusions have been drawn based on the experimental data. However, due to the dynamic nature of this research, final conclusions are not possible at this time.

1.2 BACKGROUND

Reviews of MEOR from an historical perspective have appeared in the literature and will not be discussed here.[1] MEOR is a process that allows for the introduction of miscible and chemical fluids in the form of metabolic end-products by way of either injection of microorganisms into the reservoir or stimulation of naturally occurring populations. These microorganisms represent a replenishable in situ source of acid, gas, biopolymer, solvent, or surfactant or combinations of these microbially mediated products that can be supported and manipulated by the addition of simple and inexpensive nutrients. The potential application of MEOR technologies may be realized in microbial product ability to overcome common recovery problems. MEOR (while representing a valuable tool for increased oil recovery and available world energy) is the least understood EOR method, and thus offers a broad forum of investigation.

It is extremely important that the mechanisms of oil recovery for the many possible variations of MEOR processes be understood and the recovery potentials quantified. Only after an adequate understanding is developed can MEOR processes be engineered to address specific recovery problems for a broad range of reservoir types and crude oil characteristics. More field tests that are designed, implemented, and conducted in a manner that allows a clear determination of the mechanisms and effectiveness of the process are needed. Most of the field tests to date have failed to establish baseline data or have not been conducted under reservoir or operational situations that allow unequivocal determination of the effectiveness of the MEOR process. Poor or incomplete characterization of the reservoir before implementation has been a frequent cause of failure of the test. Thus, a multi-disciplinary approach involving geology, petroleum engineering, microbiology, and chemistry is essential for an effective, environmentally-safe, research, and demonstration project.

Field research has and is being conducted to prove the effectiveness of microbes to enhance the recovery of oil.[2,3] Microbes responsible for oil

recovery are reasonably well characterized but their activities, kinetics of bio-product production, and nutrient requirements in reservoirs are not well understood. The mechanisms of increased production are unknown and could be caused by several metabolic functions attributed to the introduced or indigenous bacteria. Results from field tests are encouraging, but it is important to understand and control microbial phenomena so that it can be optimized for specific reservoir problems. Microbial processes may fail because of a lack of understanding of environmental conditions under which the process is occurring or because of a lack of understanding of the microbes being used. This is especially true for microbial processes conducted in heterogeneous, remote environments such as oil reservoirs, which are implicitly difficult to understand and control.

1.3 INEL Research

The use of microbes for EOR is a difficult process to understand and predict. Therefore, basic experiments are being conducted in simulated reservoir environments with known collections of microbes that show promise for enhancing oil recovery. These microbes have been obtained from enrichment of environmental samples, culture collections, and other investigators. Specific activities of the microbes (the ability to alter wettability, change interfacial properties, and produce acids, gases, solvents, surfactants, and polymers) are monitored based on conditions in the test medium and produced fluids.

Development of an understanding of the mechanisms by which specific microbial systems displace oil under reservoir conditions through such avenues as core flooding, measurement of IFT and viscosities, and other laboratory techniques will be a significant contribution to EOR technology and specifically MEOR technology. The mechanisms of MEOR are not specifically known or well understood for a wide variety of reservoir conditions, crude oils, and microbial/nutrient systems.

The first objective of the current research is to determine the important biologically induced factors that increase oil recovery by analysis and experimentation with the microbes, oil, and production waters. Research will proceed from determination of displacement mechanisms to development of process design variables for target field conditions. The determination of oil field project design variables will allow comparisons of MEOR process economics with those of chemical EOR systems. The objective is to place MEOR in the mainstream of EOR technology by removing the uncertainty that currently discourages acceptance of MEOR as a viable EOR process by the mainstream of the petroleum industry. It is imperative to bring MEOR to the same scientific and engineering level as other EOR processes that have benefitted from detailed research, which has been openly reported and discussed in the petroleum literature. An integrated research program is necessary for the development of MEOR as a viable EOR process for use by the oil industry.

Field process designs for testing of microbial systems in target reservoirs are being developed and evaluated. Crude oil samples and reservoir cores need to be obtained from target reservoirs for testing of microbial processes under the most realistic conditions possible in the laboratory.

Research at the INEL is focusing on the underlying fundamental mechanisms of MEOR and is not limited to understanding the microbial mechanisms that facilitate the displacement of oil. Instead, a more comprehensive understanding of the microbial mechanisms and the chemical and physical attributes of the rock/fluid interactions controlling microbial processes and mechanisms in reservoirs are being studied. The intention of this research is to gain a better understanding of how and why MEOR works. Efforts have been made to perform realistic and definitive laboratory testing, to collect and preserve oil samples that will best represent reservoir composition, and to carefully conduct all experimental protocols to answer the appropriate questions. The amount of oil that may be recovered under optimum laboratory conditions is of less value at this stage of development of MEOR processes than the development of a fundamental understanding of MEOR gained through realistic laboratory simulation. A better fundamental understanding is

necessary before MEOR processes can be tailored for specific recovery problems in specific reservoirs.

The wettability research program is a collaborative effort between EG&G Idaho, Inc. and the New Mexico Petroleum Recovery Research Center at the New Mexico Institute of Mining and Technology. The research program is directed by Dr. N. R. Morrow and co-funded by industry and the State of New Mexico. The results of the research program have been presented at several industry symposia and through contributions to the permanent literature and are not repeated in this report.

1.4 Publications and Presentations

The following publications and presentations have resulted from the MEOR and Wettability research program.

1. G. A. Bala and M. L. Duvall, "Microbial Enhanced Oil Recovery: Current Status and Future Direction," A Group of Independent Oil Operators and Industry Consultants, Denver, Colorado, July 24, 1990.

2. K. B. Barrett and F. S. Colwell, "Microbial Attachment at the Oil-water Interface Versus Soluble Microbial Products to Increase Emulsification," American Society of Microbiology (ASM) Annual Meeting, Anaheim, California, May 13-18, 1990.

3. J. S. Buckley, "Control of Core Wettability with Crude Oil," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

4. J. S. Buckley, "Multiphase Displacements in Micromodels," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekker, 1990, pp. 157-189.

5. J. S. Buckley, "Prediction of Crude Oil/Rock Wettability," Society of Core Analysts Fourth Annual Technical Conference, Dallas, Texas, August 14-16, 1990.

6. J. S. Buckley, "Wettability Effects of Crude Oils," American Geophysical Union Spring Meeting, Baltimore, Maryland, May 29-June 1, 1990.

7. J. S. Buckley, "Wetting Behavior of Crude Oil/Brine/Solid Surfaces from Adhesion Tests and Electrophoretic Mobilities," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

8. J. S. Buckley and N. R. Morrow, "Characterization of Crude Oil Wetting Behavior by Adhesion Tests," Society of Petroleum Engineers/Department of Energy Seventh Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 21-25, 1990, SPE/DOE 20263, to be published, Society of Petroleum Engineers Formation Evaluation.

9. J. S. Buckley and N. R. Morrow, "Crude Oil Wetting," poster, International Symposium on Contact Angles and Wetting Phenomena, Society of Chemical Industry, Toronto, Canada, June 21-23, 1990.

10. M. E. Cather, "Diagenesis, Pore Structure, and Surface Properties of Reservoir Rocks," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

11. M. E. Cather, N. R. Morrow, and I. Klich, "Characterization of Porosity and Pore Quality in Sedimentary Rocks," Second IUPAC Symposium on Characterization of Porous Solids, Alicante, May, 1990.

12. V. A. Deason, R. L. Miller, A. D. Watkins, M. B. Ward, and K. B. Barrett, "Measurements of Interfacial Tension by Automated Video Techniques," Society of Photo-optical Instrumentation Engineers Conference, San Diego, California, July 8-13, 1990.

13. J. Duo, "Effect of Drilling Mud Filtrates on Mixed Wettability Rock," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

14. M. L. Duvall, G. A. Bala, K. B. Barrett and M. D. Herd, "MEOR: Current Research at the INEL," Society of Petroleum Engineers Forum Series, Crested Butte, Colorado, August 5-10, 1990.

15. M. L. Duvall and C. P. Thomas, "Microbial Enhanced Oil Recovery: EOR Process of the Future?," Society of Petroleum Engineers Forum Series, Crested Butte, Colorado, August 5-10, 1990.

16. P. Jadhunandan, "Effect of Brine Composition, Crude Oil, and Aging Conditions on Wettability and Oil Recovery," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

17. P. Jadhunandan and N. R. Morrow, "Crude Oil Recovery in Laboratory Water Floods," Fifth IFP Research Conference on Exploration and Production, Fundamentals of Fluid Transport in Porous Media, Arles, May 14-18, 1990.

18. D. Jia, J. S. Buckley, and N. R. Morrow, "Control of Core Wettability with Crude Oil," Society of Petroleum Engineers International Symposium on Oilfield Chemistry, Anaheim, California, February 20-22, 1991, SPE 21041.

19. S. Ma and N. R. Morrow, "Effect of Firing on Fluid Flow Properties in Berea Sandstone," Society of Petroleum Engineers International Symposium on Oilfield Chemistry, Anaheim, California, February 20-22, 1991, SPE 21045.

20. G. Mason and N. R. Morrow, "Capillary Behavior of a Wetting Liquid in Irregular Triangular Tubes," to be published, Journal of Colloid and Interface Science.

21. N. R. Morrow, "Capillary Properties of Single Pores," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

22. N. R. Morrow, "Introduction to Interfacial Phenomena in Oil Recovery," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekker, 1990, pp. 1-21.

23. N. R. Morrow, "Measurement of Wettability and Its Effect on Oil Recovery," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

24. N. R. Morrow, "Surfaces and Interfaces," keynote address, Fifth IFP Research Conference on Exploration and Production, Fundamentals of Fluid Transport in Porous Media, Arles, May 14-18, 1990.

25. N. R. Morrow, "Wettability and Its Effect on Oil Recovery," Society of Petroleum Engineers Distinguished Author Series, Journal of Petroleum Technology, 42, 12, 1990, pp. 1476-1484.

26. N. R. Morrow and J. C. Melrose, "Application of Capillary Pressure Data to the Determination of Connate Water Saturation," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekkar, 1990, pp. 257-287.

27. N. R. Morrow and J. C. Melrose, "Application of Capillary Pressure Data to the Determination of Connate Water Saturation," keynote address, European Core Analysis Symposium, London, May, 1990.

28. A. Ouenes, "Numerical Simulation of Core Floods," First International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery, Socorro, New Mexico, September 18-21, 1990.

29. C. P. Thomas, "MEOR: An Overview," Society of Petroleum Engineers Forum Series, Crested Butte, Colorado, August 5-10, 1990.

30. C. P. Thomas, G. A. Bala, K. B. Barrett and M. L. Duvall, "MEOR Research on Heavy Oils," Microbial Enhanced Oil Recovery International Conference, Norman, Oklahoma, May 27-June 1, 1990.

31. C. P. Thomas, W. A. Apel, G. A. Bala, K. B. Barrett, F. S. Colwell, P. R. Dugan, M. L. Duvall, M. E. McIlwain and R. L. Miller, "MEOR Research Program: Idaho National Engineering Laboratory," First Technical Meeting of the United States Department of Energy/Venezuela Ministry of Energy and Mines Energy Research and Development Agreement, Annex XIII, Cooperation in the Area of Microbial Enhanced Oil Recovery, Norman, Oklahoma, May 27, 1990.

32. A. D. Wells, "Microbial Enhanced Oil Recovery: A Novel Approach," Associated Western Universities Summer Research Fellows Conference, Idaho Falls, Idaho, August 1, 1990.

1.5 REFERENCES

1. D. M. Updegraff, "Early Research on Microbial Enhanced Oil Recovery," Developments in Industrial Microbiology,31, 1990, pp. 135-148.

2. R. S. Bryant, T. E. Burchfield, D. M. Dennis, and D. O. Hitzman, "Microbial-Enhanced Waterflooding: Mink Unit Project," Society of Petroleum Engineers/Department of Energy Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, 1988, SPE/DOE 17341.

3. R. M. Knapp, M. J. McInerney, D. E. Menzie, and R. A. Raiders, "MEOR Field Pilot Study," Contracts for Field Projects and Supporting Research on Enhanced Oil Recovery, Progress Review No. 53, 1987, DOE/BC-88/1 (DE88001233).

2. OIL SELECTION AND ANALYSIS

Data obtained from the analysis of crude oil provides valuable information on the physical and chemical characteristics of the oil. These characteristics may influence microbial recovery and the mechanisms by which microbial recoveries are facilitated. Monitoring these characteristics is an integral part of the INEL MEOR research program. Although microbial enhanced oil recovery under economically favorable conditions may be advantageous, the advantage could be quickly lost if the value of the oil or the reservoir are not maintained. This could occur through microbial degradation of the oil, microbial souring of the oil, or microbially mediated plugging of the reservoir.

Oils were selected for use in the MEOR program primarily on gravimetric characteristics. Medium to heavy oils (17.5 to 38.1°API) were selected. A refined mineral oil, Soltrol[a] 220 (50.5°API) was also chosen for control purposes. Suitable oils were found that originated in a variety of geographical locations. Oils selected are presented in Table 2-1.

2.1 METHODOLOGIES

The methodologies used to analyze and characterize the oils include fractionation of the oils, gas chromatography (GC), gas chromatography/mass spectroscopy (GC/MS), elemental analysis, and viscosity determination (temperature variant). Gravimetric analysis of phase separated effluents was the method used to determine the volume of oil produced from core floods.

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a. Soltrol - Registered Trademark, Phillips 66 Company, Bartlesville, OK 74004.

Table 2-1. Oils selected for MEOR research

Oil	Source Sand	County	State	Gravity API°	Viscosity at 23°C (Pa·s)[a]
Soltrol 220	Commercial[b]	--	--	50.5	0.003
Burbank	Burbank	Osage	OK	38.1	0.006
Schuricht	Minnelusa	Crook	WY	25.4	0.054
Moorcroft	Minnelusa	Crook	WY	22.3	0.142
Alworth	Cole	Jim Hogg	TX	19.1	0.134
Lick Creek	Meakin	Union	AR	17.5	0.288

a. Pa·s = centipoise x (1.0×10^{-3})

b. Phillips 66 Company, Specialty Chemicals, Bartlesville, OK

2.1.1 Fractionation (Liquid Chromatography) of Crude Oils

Paraffinic, aromatic, and asphaltic components of the selected crude oils were fractionated utilizing modified procedures of R.M. Atlas,[1] and D.W. Later.[2] 500 mg of crude was weighed directly into a 50 mL glass tube and washed with 40 mL of n-pentane. This was allowed to stand at room temperature for 30 min following complete mixing. The sample was centrifuged at 1800 rpm (International TableTop centrifuge) to facilitate precipitation of the pentane insoluble asphaltics. The supernatant was removed from the tube and the precipitate was taken up in 1 mL toluene and the tube was washed 5 x 1 mL with the same. The toluene eluents were combined into a pre-tared 10 mL crimp top vial (teflon lined septa) and the solvent was removed under nitrogen at room temperature and the vial was weighed and capped. The supernatant fraction was placed in a glass Kontes reflux tube and evaporated to critical volume (ascertained by a constant weight) at room temperature and taken up in 3 mL of

chloroform. The 3 mL of chloroform/oil was mixed with 3 g of Brockman neutral alumina and the chloroform was allowed to evaporate. The oil loaded alumina was then placed in an 11 mm ID column stopped with a modular flow valve topped with a piece of glass wool filter paper held in place with 10 μm-mesh teflon cloth. The column contained 6 g of dry packed neutral alumina. The paraffinic, aromatic, and non-pentane precipitable (ppt) asphaltic resins were eluted sequentially with 20 mL hexane, 50 mL benzene, and 70 mL chloroform/methanol at 2:1 ratio. Individual component fractions were collected into 250 mL Erlenmeyer flasks and solvents were allowed to evaporate at room temperature. All components were taken up in 4 x 1 mL of elution solvent and placed in individual pre-tared vials, taken to critical volume, weighed, and sealed under nitrogen for further analysis.

2.1.2 Gas Chromatography of Crude Oils

Samples (deasphalnated "total oil" or liquid chromatography eluents) were brought to 60 mg/mL in hexane and injected in either 1, 2, or 5 μL aliquots for peak visualization of hydrocarbons C_6 to C_{34}.

A 30 m x 0.244 mm J&W scientific DB-5 column with a film thickness of 0.25 μm was used on a Hewlett Packard 5890A GC equipped with a 7673A autosampler and a 3396A integrator. Conditions were as follows: Column head pressure was 16 psi yielding a gas velocity of 1.1 mL/min. Make-up gas was added at detection such that total flow was 30 mL/min. A purge of 1.5 mL/min was maintained at the inlet except during injection at which time there was no purge. Split vent flow was at 20 mL/min. An initial oven temperature of 80°C was held for 4 min after injection and then increased to 300°C at a rate of 8°C/min and held at 300°C for 16 min. Detection was with flame ionization at 325°C. A reasonable baseline was obtained at an attenuation of 3.

A known hydrocarbon mixture used for methods development (constituents from PolyScience Corporation) was mixed to contain n-Dodecane, n-Tridecane, n-Tetradecane, n-Hexadecane, n-Octadecane, n-Nonadecane, n-Heneicosane, and n-Docosane.

2.1.3 Gas Chromatography/Mass Spectroscopy of Schuricht Crude

Pyrolysis GC/MS analysis of Schuricht crude was performed at the University of Utah Center for Micro-Analysis and Reaction Chemistry. Samples were prepared by liquid chromatography fractionation of the oil into aliphatic, aromatic, pentane precipitable asphaltics, and non-pentane precipitable asphaltics.

2.1.4 Elemental Analysis of Crude Oils

Elemental analysis was performed with a Carlo Erba CHNOS EA1108 elemental analyzer equipped with an AS200 autosampler. Separation was with a PoraPak QS (80 to 100) mesh 2 m x 4 mm column operated at 65°C with a flow rate of 100 mL/min. Combustion of the sample was at 1000°C in a combustion chamber packed with 50 g reduced copper proximal and 40 g tungstic anhydride distal, separated, and capped on both ends with 10 mm of quartz wool. Detection was with a thermal conductivity detector operated at a filament temperature of 190°C.

Analysis was performed on samples of deasphalnated crude (pentane ppt asphaltics removed). Each sample (4 to 5 mg) was placed into a pre-tared tin cup filled with Brockman neutral alumina, weighed, and placed in the autosampler. An isotiourea standard was used for instrument calibration.

2.1.5 Viscosity Determination of Crude Oils

Viscosity measurements were performed on the selected crudes at temperatures from 22°C to reservoir temperature (dependant on the origin of the oil). All viscosity measurements were made using a Wells-Brookfield Cone and Plate Digital Viscometer, model LTVDV II with a CP-40 spindle.

The viscometer was zeroed according to the manufacturers protocol.[3] This procedure was performed each time the spindle was removed from the viscometer and replaced or when the temperature at which viscosity measurements were to be taken was changed. Calibration was checked using Brookfield Viscosity Standards under controlled temperature conditions.

A sample volume of 0.5 mL was used to accommodate the CP-40 spindle. This was sufficient to wet the entire face of the spindle and about 1.0 mm up the outside edge of the spindle. The sample was placed in the cup taking care that it was bubble-free and spread evenly over the surface of the cup.

2.1.6 Crude Oil Quantification Following Coreflood Experimentation

Crude oil volume in fluid effluents from water and microbial floods was analyzed gravimetrically following separation of the aqueous and organic phases. Tubes to be used in coreflood experimentation were pre-weighed using a Fisher XD400 analytical balance interfaced directly (RS232) to an IBM AT computer formatted for data acquisition and reduction (Lotus 123). Following aliquoted effluent collection (2 to 3 mL), tubes containing no visual oil were reweighed and emptied. The volume of brine was calculated by density corrected gravimetric analysis. Tubes containing oil and brine were also weighed and then subjected to phase separation. Separation was facilitated by the addition of hexane (3 x 2 mL). The aqueous brine phase was collected into pre-tared tubes and volume was calculated as above. Oil volume was calculated by difference. The hexane/oil phase from all tubes of one experiment are collected in bulk, the solvent is removed and the oil is stored for later analysis. Data were reduced using Lotus 123.

2.2 Results

Results for analysis of oils with respect for fractionation, gas chromatography, coupled gas chromatography/mass spectroscopy, elemental analysis, viscosity, and quantification of oils following coreflood experimentation are presented.

2.2.1 Fractionation (Liquid Chromatography) of Crude Oils

Five crude oils and one refined mineral oil (see Subsection 2.1), were analyzed for aliphatic, aromatic pentane (C_5) soluble asphaltics, and C_5 insoluble asphaltics with fractionation techniques. Data are presented

collectively in Table 2-2. It should be noted that it is unlikely that Soltrol 220 contains C_5 insoluble asphaltics and this is assumed to be experimental error for samples containing little or no C_5 insoluble asphaltics. This consideration effects Soltrol 220, Burbank crude, and Alworth crude.

Table 2-2. Liquid Chromatography Fractionation of Selected Crudes

	% Component (weight fraction/weight sample)			
Oil	Aliphatic	Aromatic	C_5 Soluble[a]	C_5 Insoluble[b]
Soltrol 220	98.22	1.26	0.00	0.60
Burbank	84.59	11.64	2.91	0.60
Schuricht	62.68	22.53	6.38	6.40
Moorcroft	55.44	27.23	7.69	7.60
Alworth	82.84	13.15	3.67	0.60
Lick Creek	50.19	26.85	5.25	16.60

a. Non-pentane precipitable resins.

b. Pentane precipitable asphaltics.

Recoveries of oil from this process vary from 60.54% (Soltrol) and 93.72% (Lick Creek). There is a positive correlation between oil gravity and recovery. This is caused by loss of the light-end hydrocarbons in the fractionation procedure.

2.2.2 Chromatography of Crude Oils

GC analysis was performed with known hydrocarbon standards, and the six oils shown in Table 2.1. Samples analyzed for each sample were "total oil" (deasphalnated sample), aliphatic, and aromatic constituents. Chromatographs are presented in Figures 2-1 to 2-7.

As noted in the fractionation of oils and as evidenced by the aliphatic chromatographs (Figures 2-3a, 2-4a, 2-5a, 2-6a, and 2-7a) components from C_6 to C_{15} are lost in the sample fractionation process. Loss is assumed to occur during solvent removal processes. It is clear in the GC analysis of the "total oil" (deasphalnated) samples that the light ends are present (Figures 2-3c, 2-4c, 2-5c, 2-6c, and 2-7c). Soltrol (60.54% recovery), for example, shows little difference between the fractionated chromatogram (Figure 2-2a) and the "total oil" chromatogram (Figure 2-2b). This indicates an equivalent loss (expected because Soltrol is 98% aliphatic) of all components (manifested by the similarity of the chromatograms). Schuricht (76.16% recovery, 62% aliphatic) however, shows a clear difference between the aliphatic (Figure 2-4a) and "total oil" (Figure 2-4c) chromatograms, in the light end region. Lick Creek, like Schuricht, shows differences in the chromatogram (Figure 2-7a and 2-7c) but unlike Schuricht had a 93% recovery. This is attributed to the relative heavy composition of the Lick Creek crude.

2.2.3 Gas Chromatography/Mass Spectroscopy of Schuricht Crude

A total ion chromatograph of Schuricht crude is presented as Figure 2-8. GC/MS analysis indicates an oil of phytoplankton origin as evidenced by a predominance of C_{17}.[4] Even though the Moorcroft West lease is in close proximity to the Schuricht lease and both are produced from Minnelusa A Sands, similar conclusions should not be drawn about the origin of the Moorcroft West oil based on Schuricht results.

2.2.4 Elemental Analysis of Crude Oils

Elemental analysis was performed on deasphalnated samples. Data are presented collectively in Table 2-3. It is unknown if sulfur reported is in the form of sulfur heterocycles or present as elemental sulfur. The sample exhibiting the highest sulfur content (Moorcroft West) is, interestingly, the only sour oil of those selected. Schuricht, an oil from the same sands and in close geographical proximity to Moorcroft West, is not sour and has a lower sulfur content.

Table 2-3. Elemental Analysis of Selected Crude Oils (Data presented as wt%)

	Element			
Oil	Carbon	Hydrogen	Nitrogen	Sulfur
Soltrol 220	83.68	15.01	0.10	0.00
Burbank	79.36	12.24	0.13	0.00
Schuricht	82.37	11.60	0.35	3.24
Moorcroft	81.99	11.28	0.38	4.21
Alworth	88.36	12.23	0.12	0.00
Lick Creek	85.47	11.46	0.29	3.31

2.2.5 Viscosity Determination of Crude Oils

Data from viscosity determination of Soltrol 220 and the five crudes are presented graphically in Figures 2-9 through 2-14. Viscosity determination of Media E (microbiological growth media) is presented in Figure 2-16.

Viscosities measured at 23°C correlated well with API gravities. In general, as API gravity decreased, viscosity increased. However, Moorcroft West and Alworth were inverted when viscosity is compared to API gravity. Moorcroft West (22.3°API) has a viscosity of 142 cp and Alworth (19.1°API) has a viscosity of 134 cp. The apparent inversion of data is easily understood when the compositions of the oils are taken into account. Alworth is a "heavier" oil than Moorcroft West but is comprised of only 3.67% asphaltic residues while Moorcroft West is comprised of 15.29% asphaltic residues. The majority of the class constituents of Alworth are aliphatic (82.8% versus 55.4% for Moorcroft West). Because viscosity is strongly influenced by the heavier constituents, this inversion is not unusual.

2.2.6 Crude Oil Quantification Following Coreflood Experimentation

Values obtained with this methodology compare very favorably to the direct core weight technique (previously used but not included in this report - values correlate within 1% or less) but have the added advantage of obtaining not only beginning and end point data but dynamic interim data as well.

Comparison of true oil volumes and calculated oil volumes from methodology development experiments indicate close agreement between the measured and expected values. A linear curve between 13 and 250 μL crude oil is achieved (see Figure 2-16). Brine volumes of 2 to 3 mL are typically collected during coreflood experimentation and volume measurement is also very good (see Figure 2-17).

2.3 Discussion

Collective oil analysis data provide useful information on the preflood (water or microbial) conditions and composition of the oils. It is clear that the oils contain quantifiable differences. Data will be used for comparison purposes to monitor changes occurring during coreflood experimentation and to ascertain microbial alterations to the oils. Data will also be used to

monitor changes in oil composition (if any) over time as samples are collected from the field.

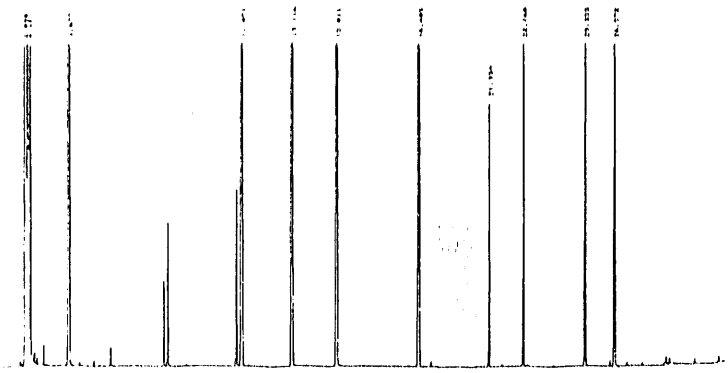

Figure 2-1a. GC spectra of standard hydrocarbon mixture. Injection volume = 1 μL. Respective peaks from right: C_{22}, C_{21}, C_{19}, C_{18}, C_{16}, C_{14}, C_{13}, C_{12}, ethylbenzene (carrier solvent), and hexane (carrier solvent).

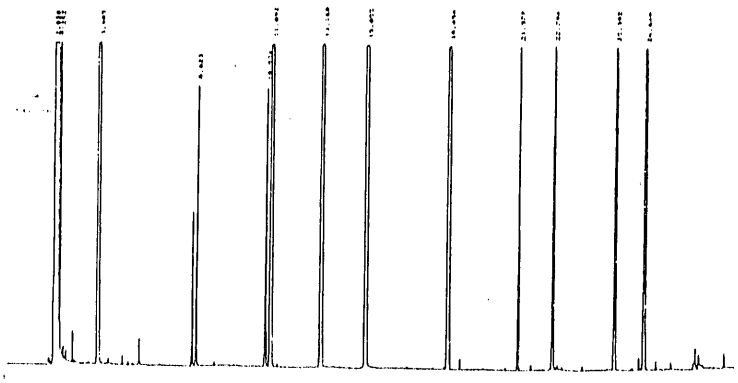

Figure 2-1b. GC spectra of standard hydrocarbon mixture. Injection volume = 2 μL. Respective peaks from right: C_{22}, C_{21}, C_{19}, C_{18}, C_{16}, C_{14}, C_{13}, C_{12}, ethylbenzene (carrier solvent), and hexane (carrier solvent).

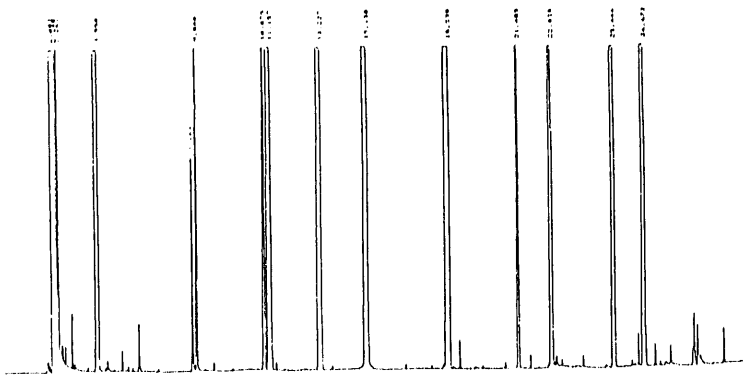

Figure 2-1c. GC spectra of standard hydrocarbon mixture. Injection volume = 5 μL. Respective peaks from right: C_{22}, C_{21}, C_{19}, C_{18}, C_{16}, C_{14}, C_{13}, C_{12}, ethylbenzene (carrier solvent), and hexane (carrier solvent).

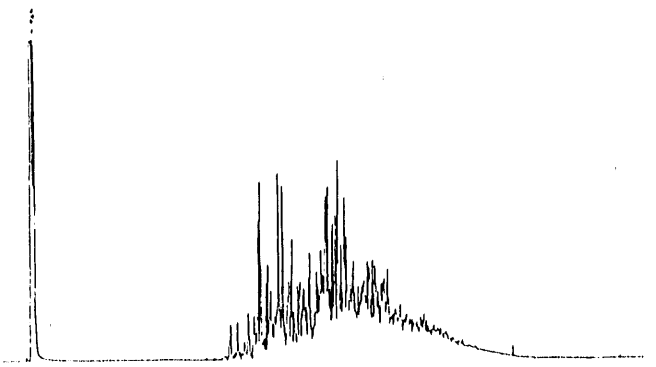

Figure 2-2a. GC spectra of Soltrol 220 aliphatic eluent. Injection volume = 1 μL.

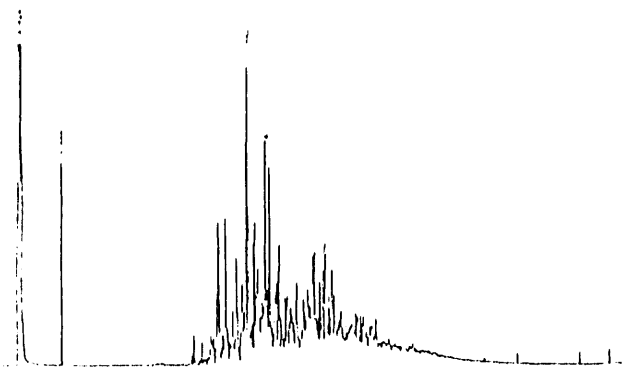

Figure 2-2b. GC spectra of Soltrol 220 total oil (deasphalnated sample). Injection volume = 1 μL.

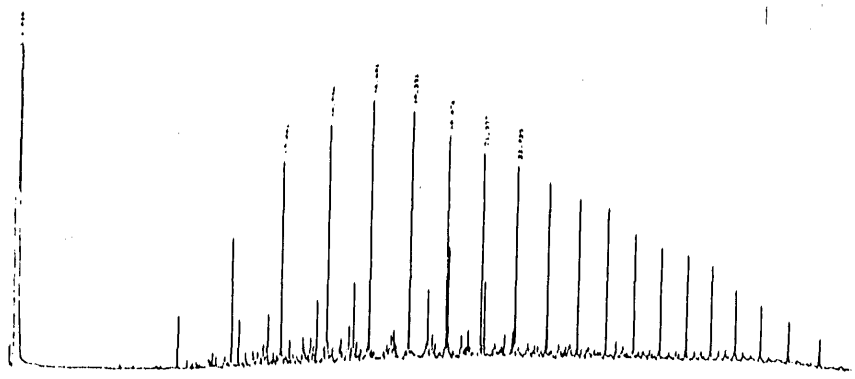

Figure 2-3a. GC spectra of Burbank crude aliphatic eluent. Injection volume = 1 μL.

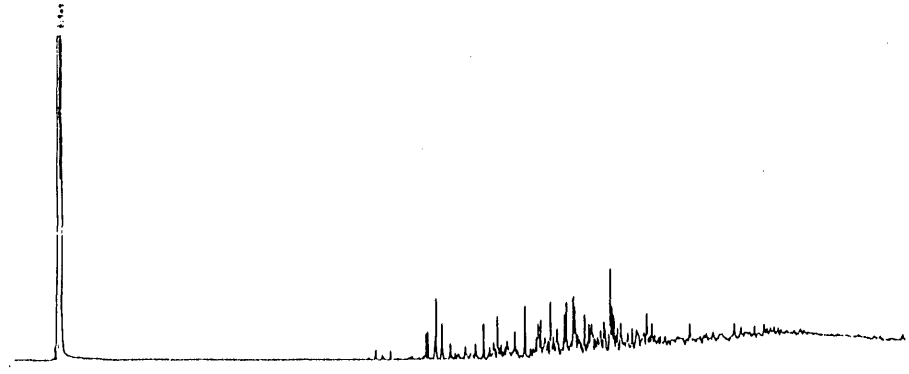

Figure 2-3b. GC spectra of Burbank crude aromatic eluent. Injection volume = 1 μL.

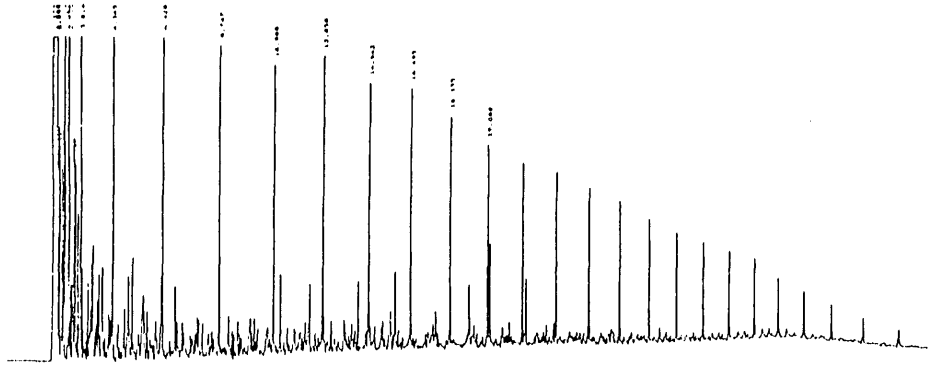

Figure 2-3c. GC spectra of Burbank crude total oil (deasphalnated sample). Injection volume = 1 μL.

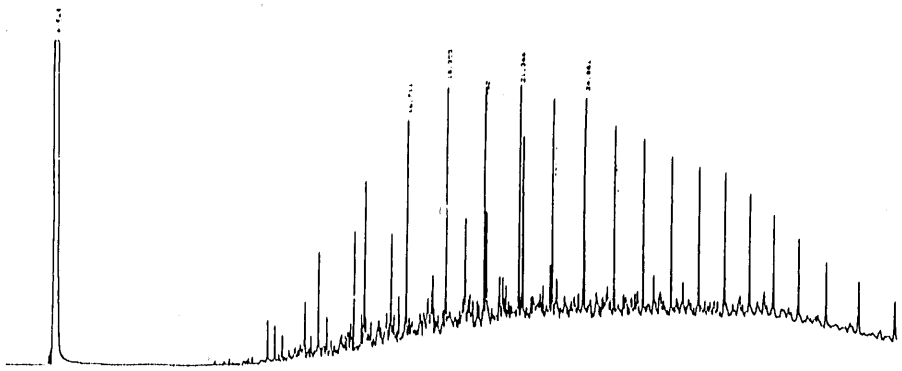

Figure 2-4a. GC spectra of Schuricht crude aliphatic eluent. Injection volume = 2 μL.

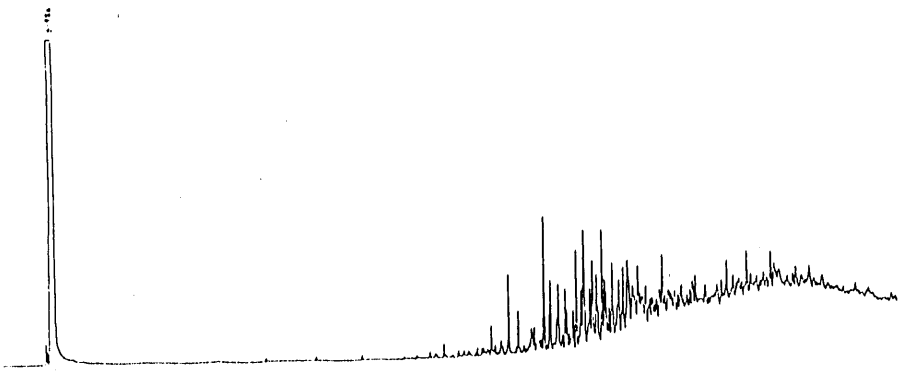

Figure 2-4b. GC spectra of Schuricht crude aromatic eluent. Injection volume = 5 μL.

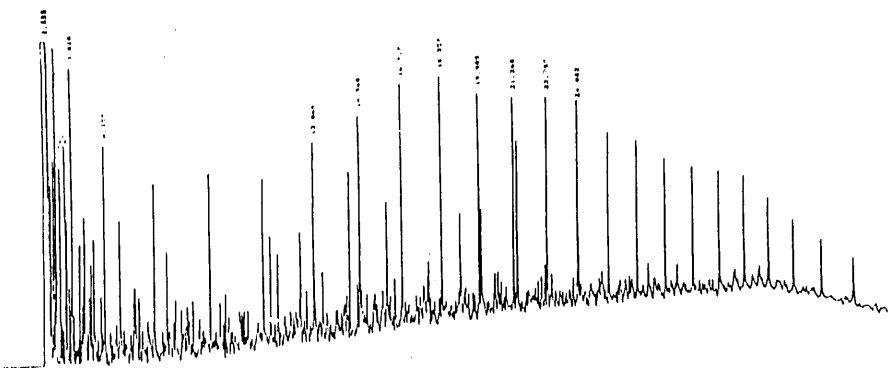

Figure 2-4c. GC spectra of Schuricht total oil (deasphalnated sample). Injection volume = 2 μL.

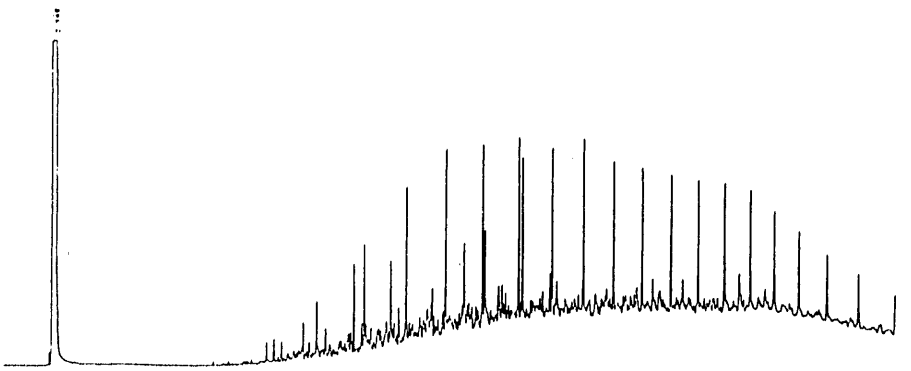

Figure 2-5a. GC spectra of Moorcroft West crude aliphatic eluent. Injection volume = 2 μL.

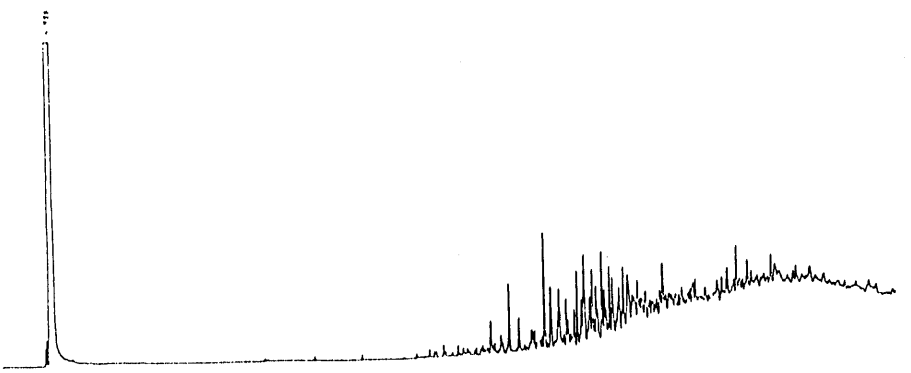

Figure 2-5b. GC spectra of Moorcroft West crude aromatic eluent. Injection volume = 5 μL.

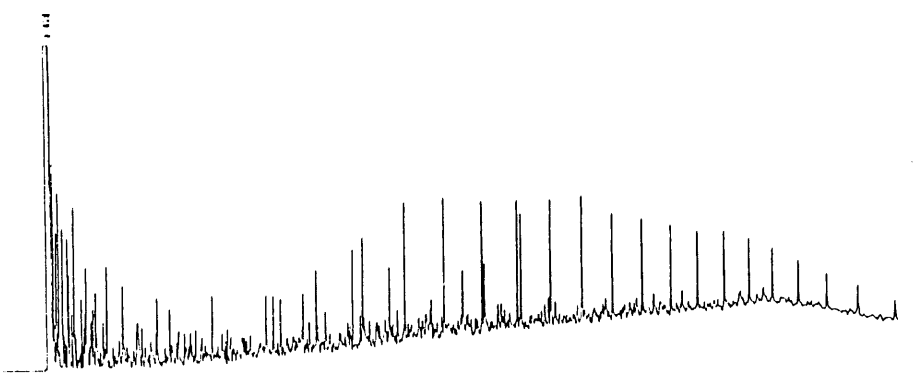

Figure 2-5c. GC spectra of Moorcroft West crude total oil (deasphalnated sample). Injection volume = 2 μL.

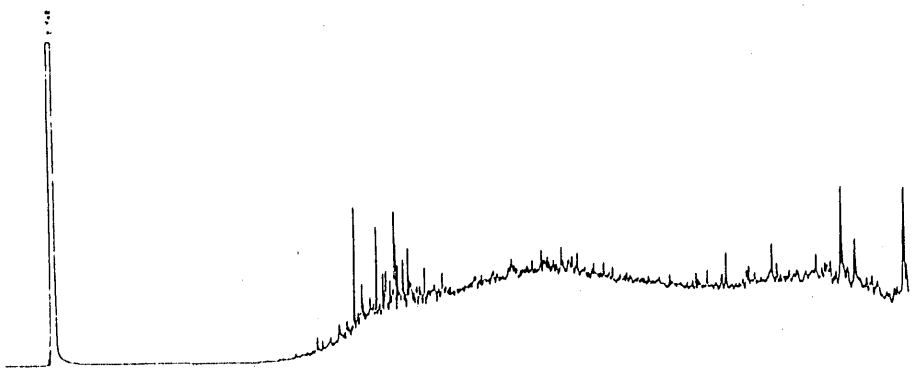

Figure 2-6a. GC spectra of Alworth crude aliphatic eluent. Injection volume = 2 μL.

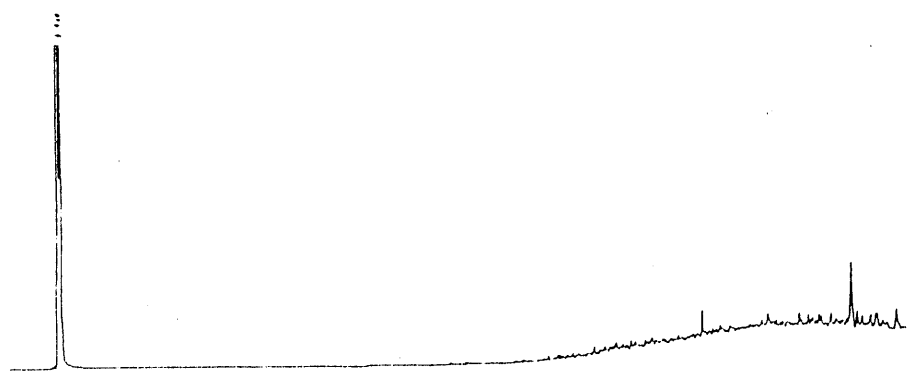

Figure 2-6b. GC spectra of Alworth crude aromatic eluent. Injection volume = 1 μL.

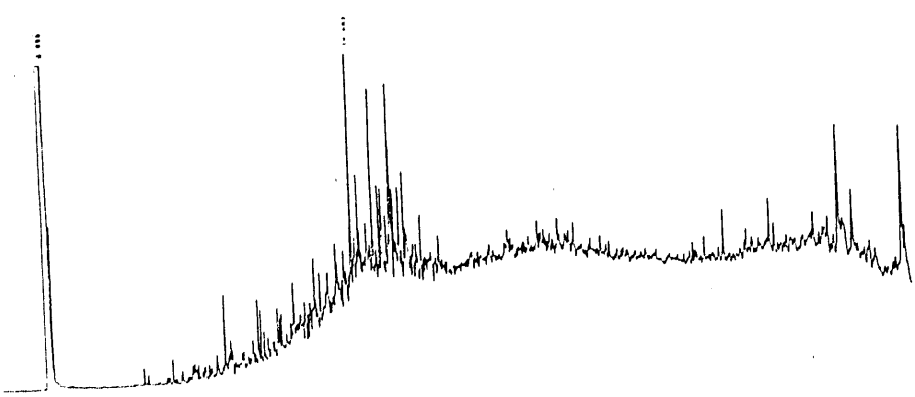

Figure 2-6c. GC spectra of Alworth crude total oil (deasphalnated sample). Injection volume = 2 μL.

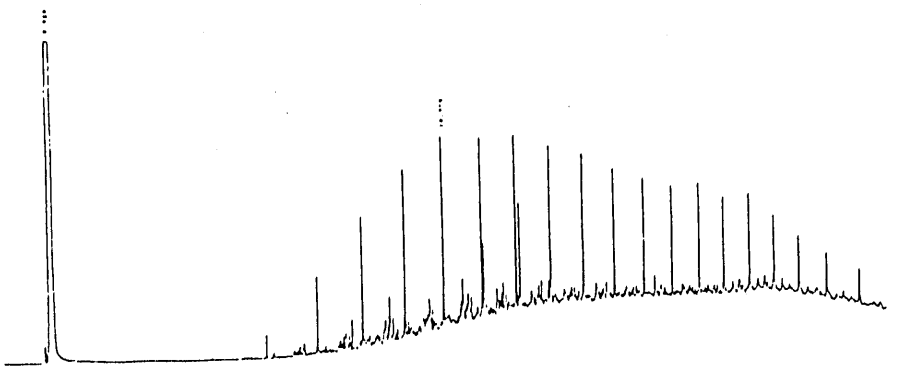

Figure 2-7a. GC spectra of Lick Creek crude aliphatic eluent. Injection volume = 2 μL.

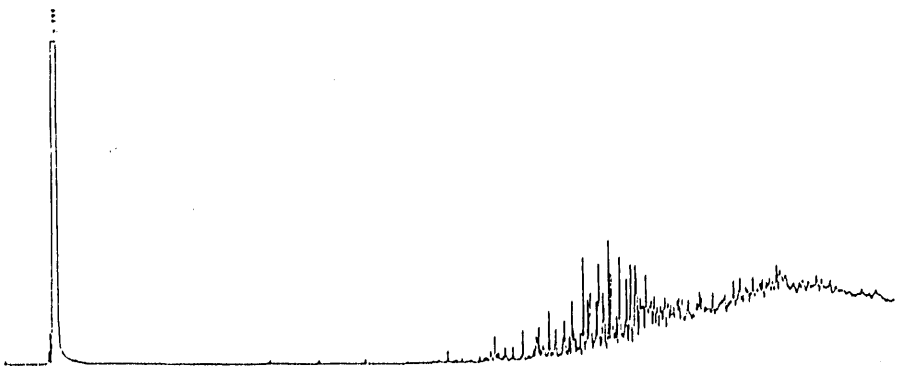

Figure 2-7b. GC spectra of Lick Creek crude aromatic eluent. Injection volume = 5 μL.

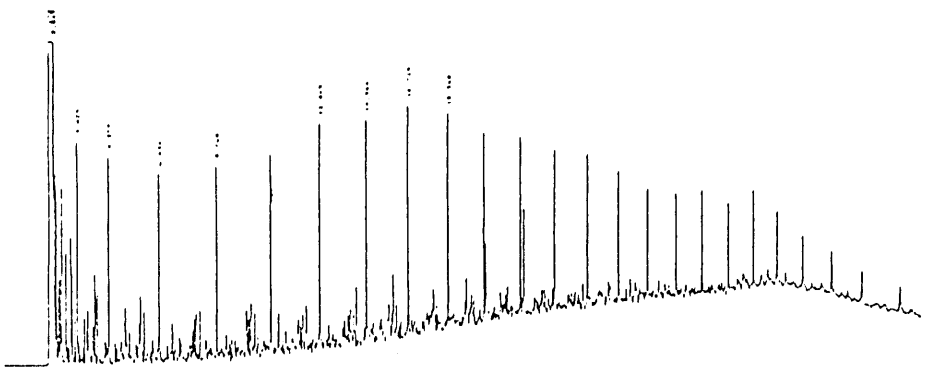

Figure 2-7c. GC spectra of Lick Creek crude total oil (deasphalnated sample). Injection volume = 2 μL.

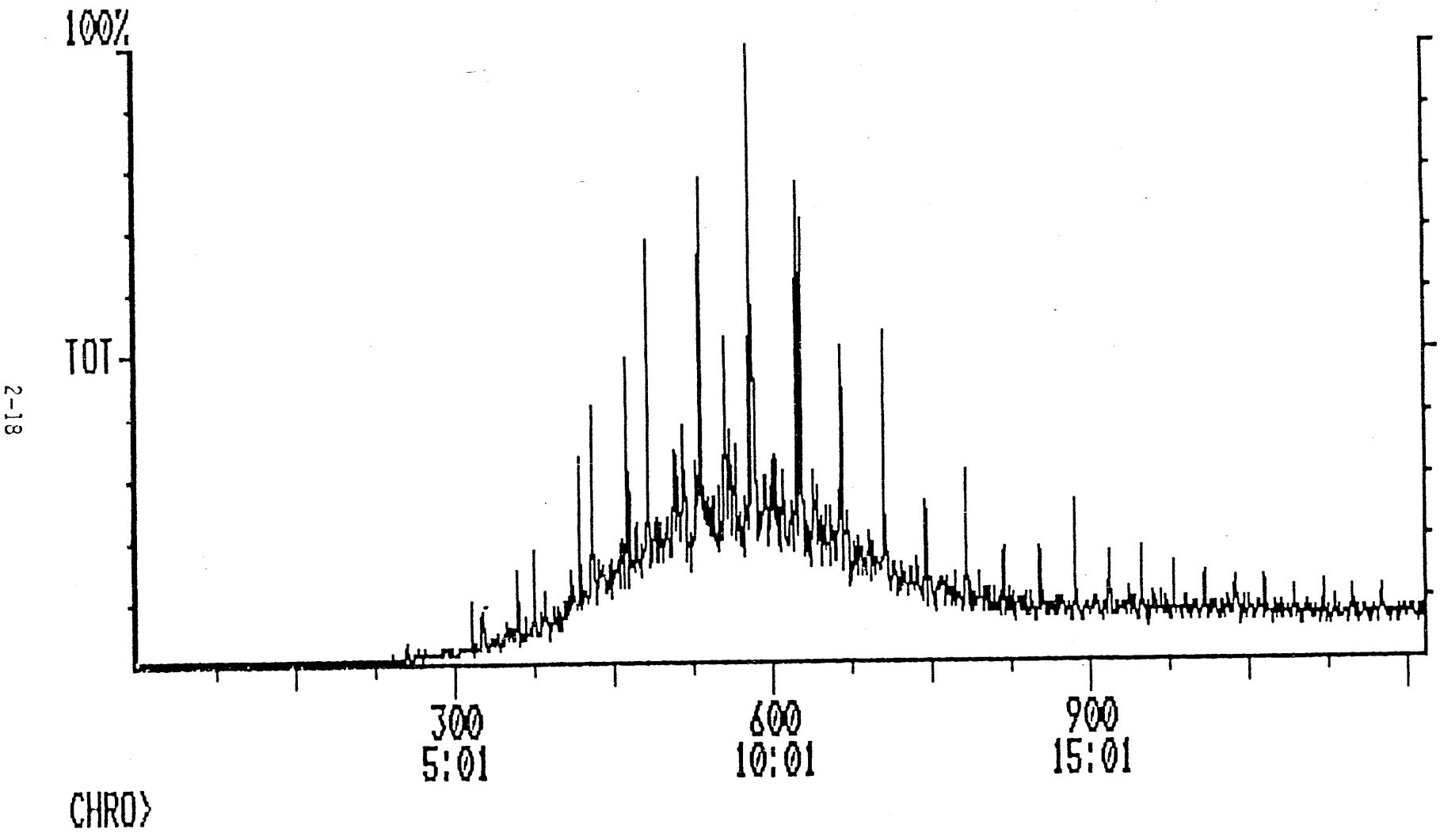

Figure 2-8. GC/MS spectra (total ion current) of Schuricht crude total oil (deasphalnated sample).

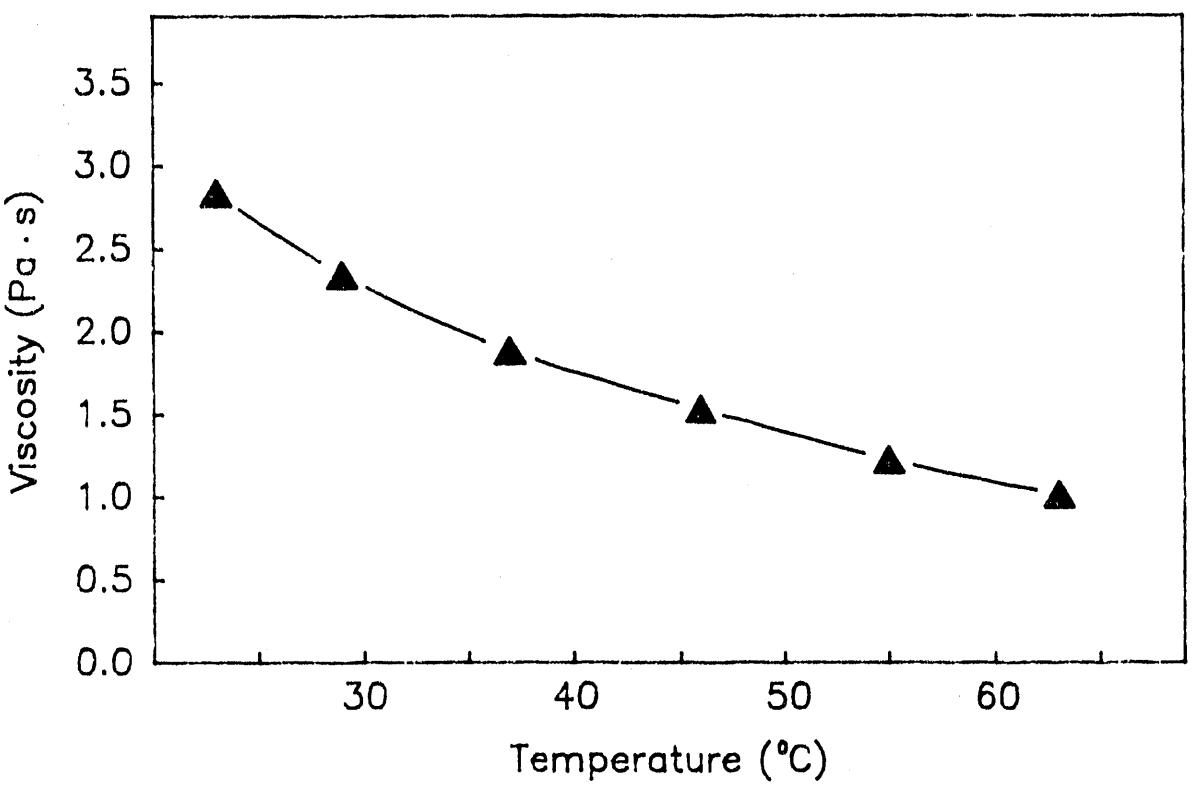

Figure 2-9. Temperature dependence of viscosity of Soltrol 220, 50.5°API @ 60°F.

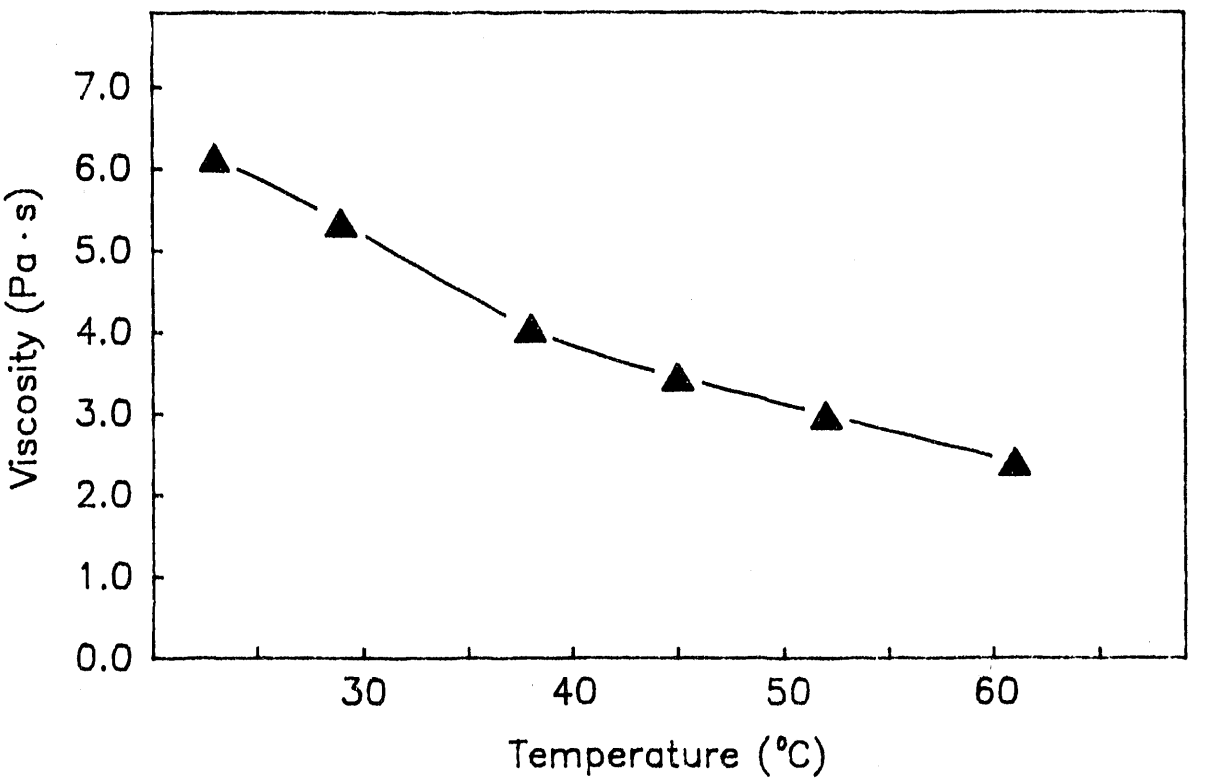

Figure 2-10. Temperature dependence of viscosity for Burbank Crude. Burbank Field, Osage County, OK, 38.1°API @ 60°F.

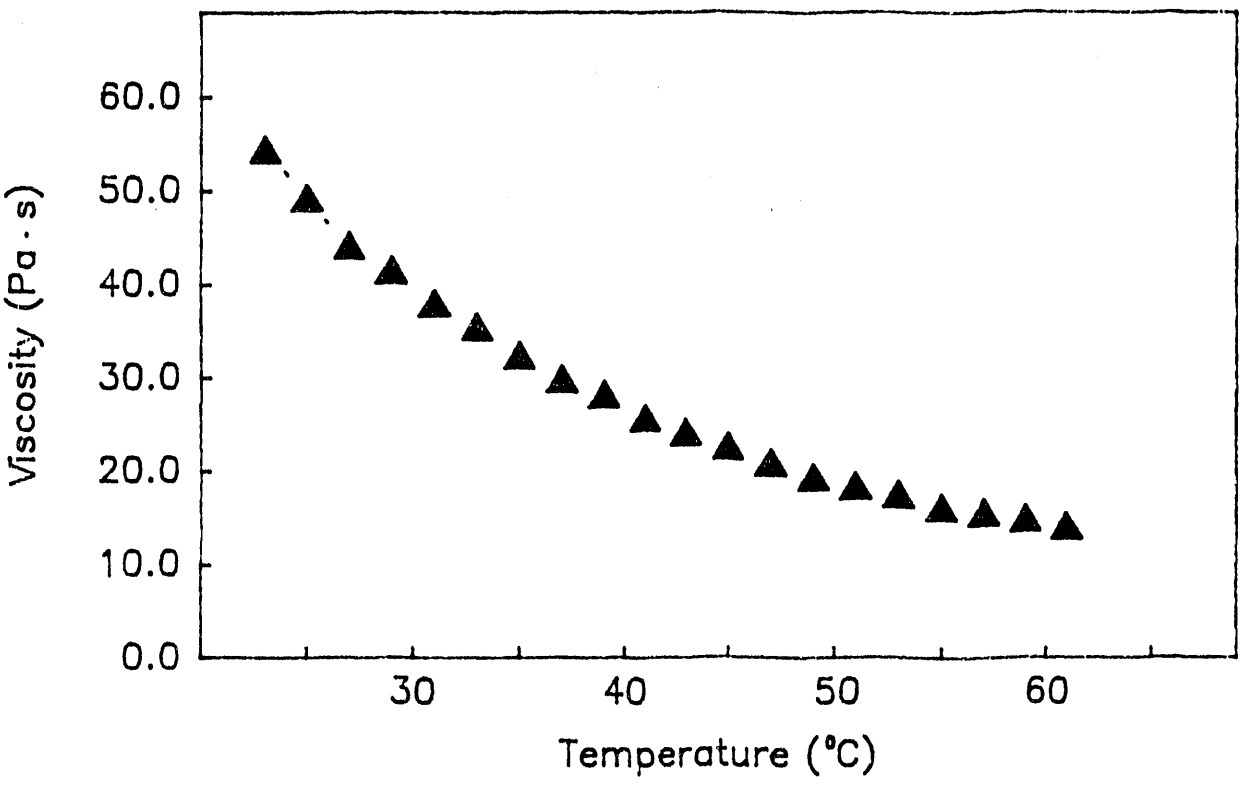

Figure 2-11. Temperature dependence of viscosity of Schuricht Crude. Schuricht Lease, Crook County, WY, 25.4° @ 60°F.

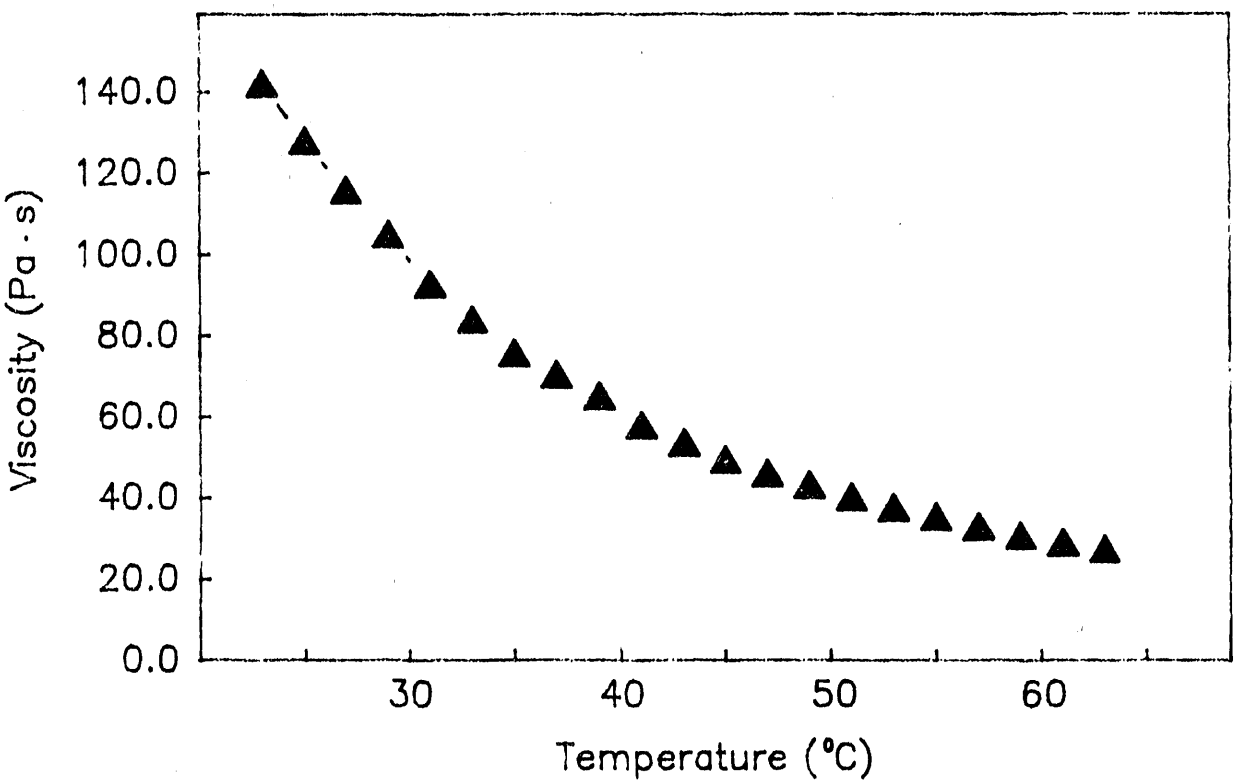

Figure 2-12. Temperature dependence of viscosity of Moorcroft West Crude. Texas Trails #1 Lease, Crook County, WY, 22.3°API @ 60°F.

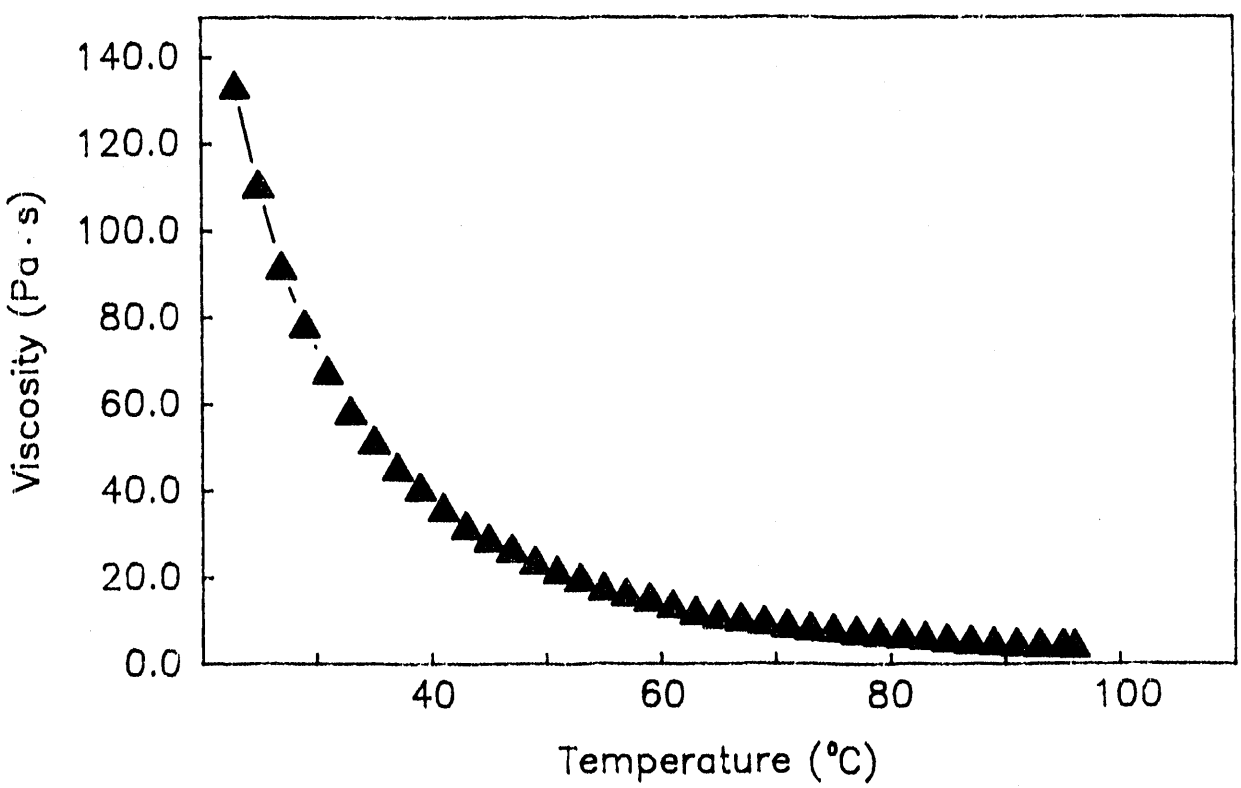

Figure 2-13. Temperature dependence of viscosity of Alworth Crude. Alworth Field, Jim Hogg County, TX, 19.1°API @ 60°F.

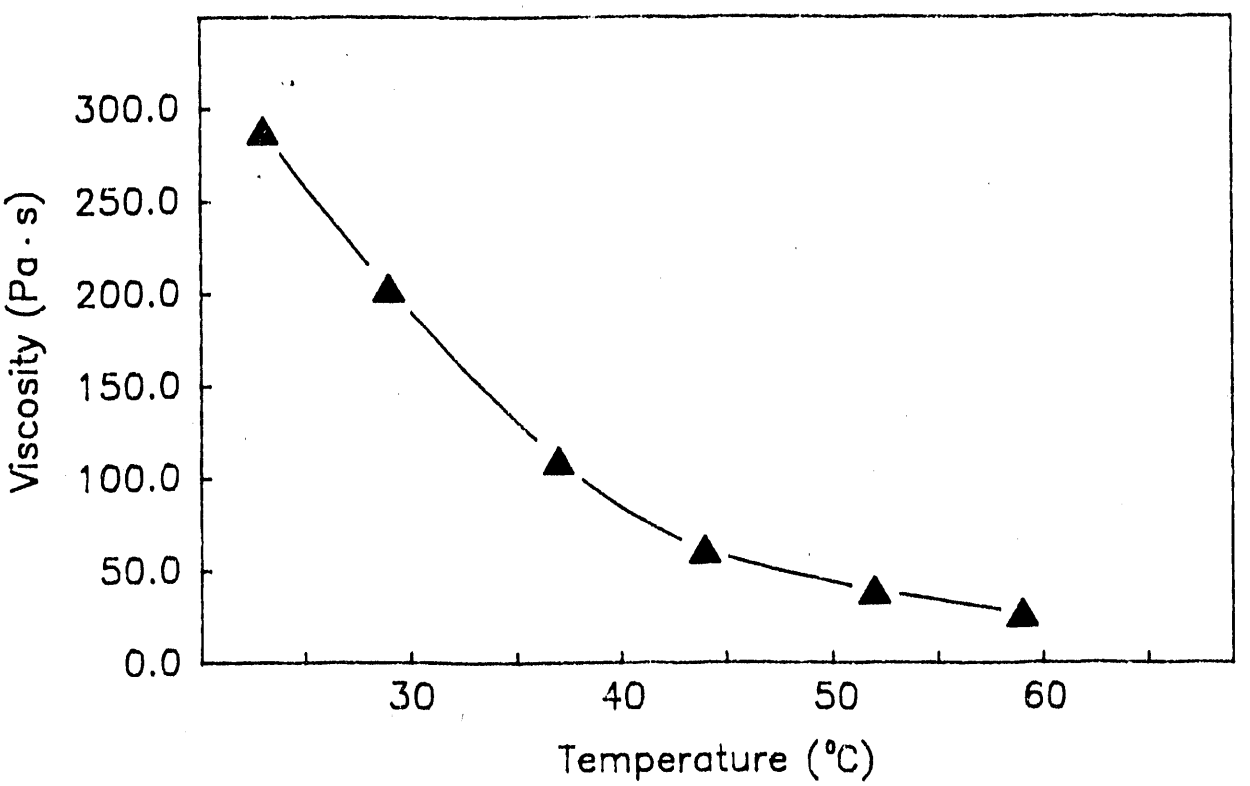

Figure 2-14. Temperature dependence of viscosity of Lick Creed Crude. Lick Creek Meakin Sand Unit, Union County, AR, 17.5°API @ 60°F.

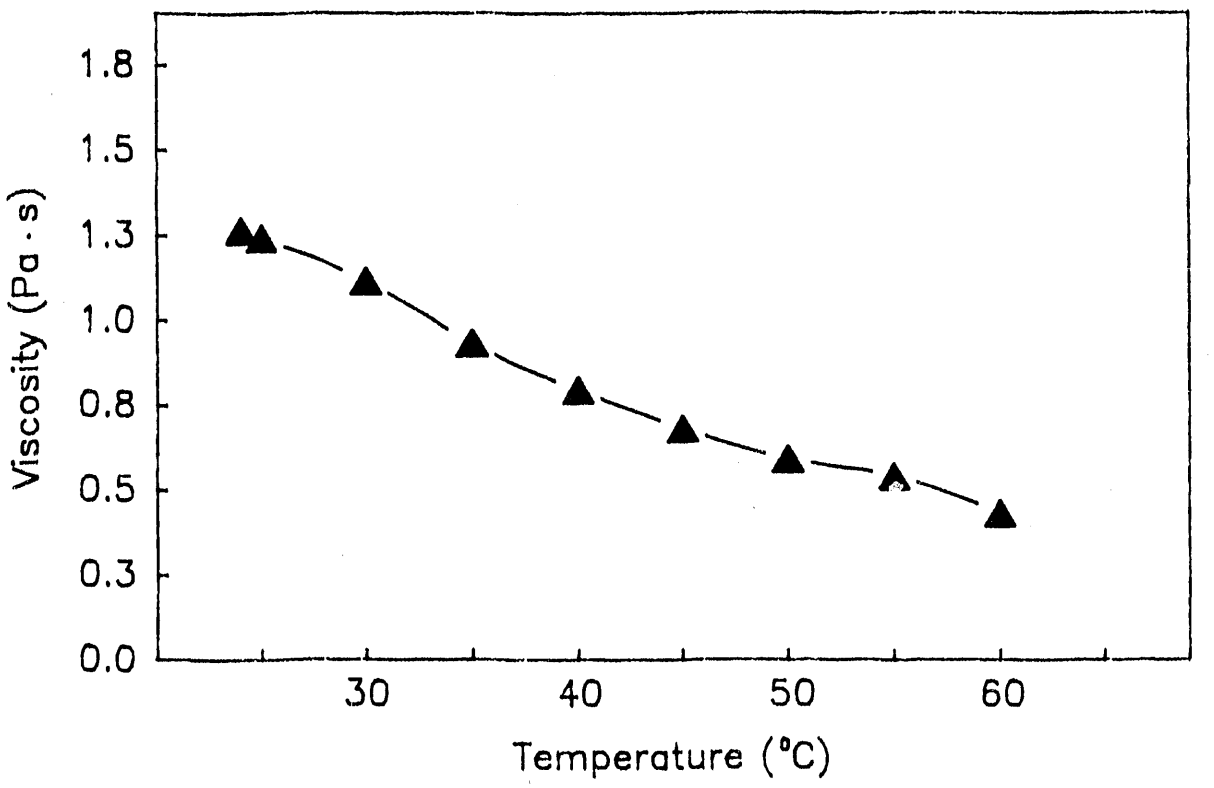

Figure 2-15. Temperature dependence of viscosity of Media E (bacteriological media).

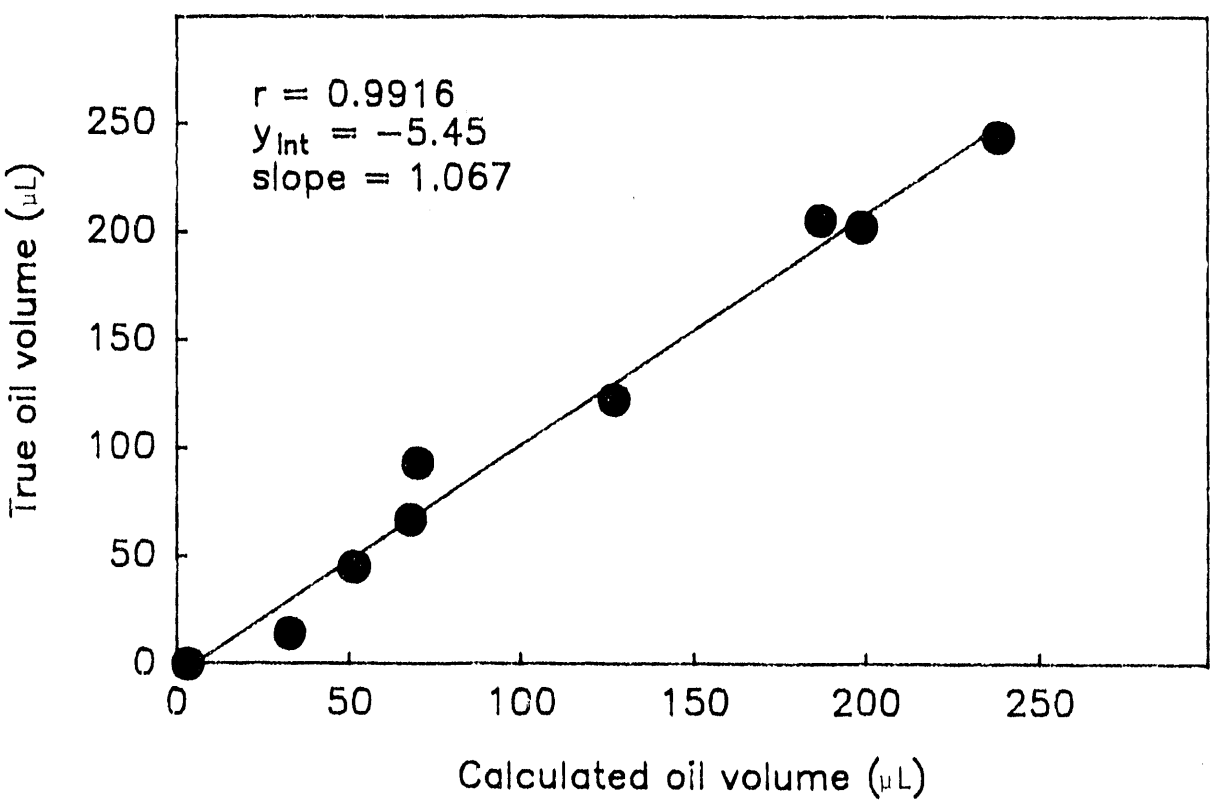

Figure 2-16. Comparison of true and calculated oil volumes resulting from separation and subsequent gravimetric analysis of mixed oil/water systems. Experiment performed according to method outlined in Section 2.3.6.

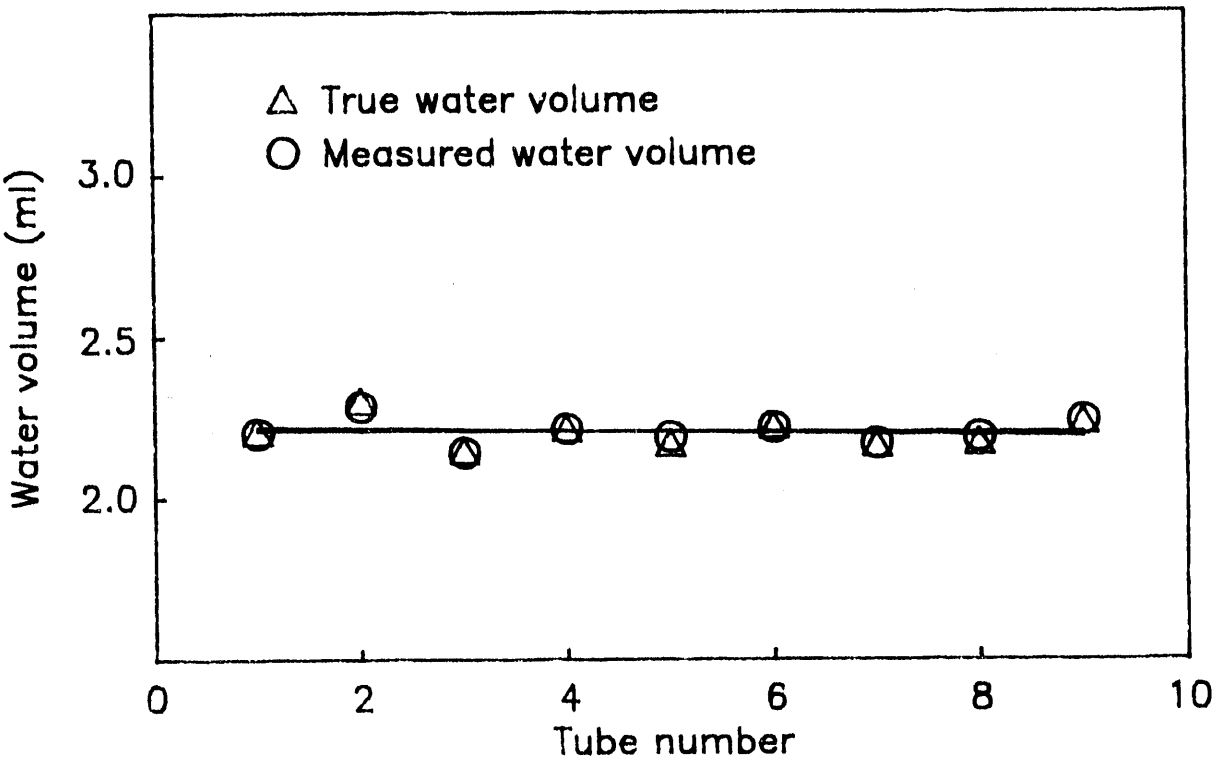

Figure 2-17. Comparison of true and measured water volumes resulting from separation and subsequent gravimetric analysis of mixed oil/water system.

2.5 References

1. R.M. Atlas, "Effects of Temperature and Crude Oil Composition on Petroleum Biodegradation," Applied Microbiology, 30, 3, 1975, pp. 396-403.

2. D.W. Later, M.L. Lee, K.D. Bartle, R.C. Kong, and D.L Vassilaros, "Chemical Class Separation and Characterization of Organic Compounds in Synthetic Fuels," Analytical Chemistry, 53, 11, 1981, pp. 1612-1620.

3. Manual No. M/85-106-F, "The Brookfield Digital Viscometer Model DV-II, Operating Instructions."

4. R.P. Philip, "Biological Markers in Fossil Fuel Production," Mass Spectrometry Reviews, 4, 1985, pp. 1-54.

3. MICROBIAL ANALYSIS AND PHENOMENA

Microbial isolates selected for analysis in the MEOR program were screened for phenotypic and genotypic properties that allow them to function in oil reservoir environments such as those found in the Minnelusa sands of the Powder River Basin, WY. These properties are facultative anaerobicity, thermotolerance to 45°C, halotolerance to 2.5% (in the form of NaCl), and a desirable MEOR phenotype. Desirable phenotypes for MEOR include organisms capable of producing acids, gases, solvents, polymers, surfactants, or any combination of these. Also desirable would be the ability to degrade asphaltic oil components or significantly perturb the oil water interface through direct physical interactions. For application of MEOR technologies, the organisms should have no significant detrimental effect on the economically valuable constituents of crude oil.

To facilitate the selection and comparison of collected isolates and strains, a benchmark organism, Bacillus licheniformis strain JF-2 (ATCC 39307)[1] was chosen. Bacillus licheniformis JF-2 was chosen because it produces a surfactant that has been isolated and characterized by other laboratories[2,3] and because it has been previously used in a field test of MEOR.[4]

Other organisms selected for study were collected from the Powder River Basin in Wyoming, Yellowstone National Park in Wyoming, Tinker Air Force Base in Norman, OK, and the Idaho Falls sewage treatment plant in Idaho Falls, ID. See Table 3-1 for a summary of selected isolates, morphology, geographical origin, and MEOR phenotype.

3.1 Isolation of Field Isolates

Samples were collected aseptically in screw cap containers from the noted locations. All isolates were screened for thermotolerance to 45°C, halotolerance to 2.5% NaCl, and growth on minimal 1502 Medium E for Bacillus[5]

Table 3-1. Origin, morphology and desirable MEOR phenotype of selected field isolates

Isolate	Origin	Gram Rxn./Morph.	MEOR Phenotype
B. licheniformis	a	+ Rod, Linear	Acid, Surfactant, Polymer
SEW BL	b	+ Rod	Acid, Surfactant
COW BL	c	+ Rod, Linear	Acid, Surfactant
SPCDW	d	+ Rod	Acid
SPCDY	e	+ Rod	Acid, Surfactant
COWPY1	c	+ Cocci, Linear	Acid, Surfactant
FSC6DW	e	+ Lrg. Rod, Linear	Acid
YELDY	e	+ Rod	Acid, Surfactant
TNK3PY	f	- Small Rod	Gas, Surfactant
MWWH	g	- Small Rod	Gas, Surfactant

a. American Type Culture Collection (ATCC 39307).

b. Activated sewage from the Idaho Falls sewage treatment plant.

c. Oil soaked cow dung outside the Moorcroft West heater treater.

d. External spill of produced brines and oil at the Moorcroft West heater treater.

e. Natural hydrocarbon seeps in the Rainbow Springs area, Yellowstone National Park.

f. Mixed waste stream (industrial metal plating/stripping, air/land vehicle maintenance, and human sewage) at Tinker Air Force Base, Norman OK.

g. Oil sample from the wellhead at the Moorcroft West Unit.

(all constituents per liter: 1 g $(NH_4)_2SO_4$, 0.51 g $MgSO_4$, 2.5 g NaCl, 5.3 g KH_2PO_4, 10.6 g K_2PO_4, 0.01 g Na_2EDTA, 0.03 g $MnSO_4$, 0.001 g $CaCL_2$, 0.001 g $FeSO_4$, 0.001 g $ZnSO_4$, 0.001 g $CoCL_2$, 0.0001 g $CuSO_4$, 0.0001 g Na_2MoO_4, 0.0001 g $AlK(SO_4)_2$) with 1% sucrose as the sole carbon source. All selections were conducted under aerobic conditions. Halotolerance and minimal media experiments were conducted at 30°C. Sucrose was chosen as the carbon source because it represents the major carbohydrate constituent of beet molasses (molasses has historically been the feedstock of choice for MEOR applications in the field).[6] Sucrose represents 63.5% of total solids in beet molasses and 95.4% of all carbohydrate present.[7]

Samples were streaked onto Trypticase Soy Agar (TSA) containing 2.5% NaCl and incubated under anaerobic conditions at room temperature. Colonies were picked and re-streaked for secondary anaerobic incubation. Isolated colonies were picked and streaked again onto TSA for primary aerobic incubation at 30°C. Facultative anaerobes (organisms growing under anaerobic and aerobic conditions) were picked from the aerobic plates and re-streaked. Well isolated colonies were picked and inoculated into 3 mL of Trypticase Soy Broth (TSB) with 2.5% NaCl and grown at 30°C overnight, gram stained to check homology and gram reaction and held at 4°C as stock cultures.

3.2 Biochemical Characterization of *Bacillus licheniformis* JF-2 and Selected Field Isolates

Characteristics common to all organisms are thermo and halo-tolerance, aerobic growth on Media E (1502) with sucrose as the sole carbon source (1%), no production of H_2S on Triple Sugar Iron Agar (TSI), no affinity for hydrocarbon/water interfaces as assayed by the Bacterial Adherence To Hydrocarbon (BATH) assay,[8] and no degradative capacity for Schuricht crude oil (see Section 2 for characteristics) in the presence of 1% sucrose. Schuricht crude oil was chosen to determine the effects of MEOR isolates and *Bacillus licheniformis* JF-2 on the composition of crude oil because it comes from a relatively pristane field that is under primary production, has not been

perturbed with a waterflood, and has had no chemical intervention. It also represents a median of those oils selected for MEOR research at the INEL.

Isolates with the ability to aerobically emulsify oil were found by inoculating 30 mL Trypticase Soy Broth containing 2.5% NaCl and 1% Schuricht crude oil with 100 μL of the 4°C stocks. Isolates emulsifying oil after 10 d were taken as surfactant producers. Emulsification was judged based on a positive control (Bacillus licheniformis JF-2). Isolates producing acids were found by monitoring pH changes in liquid culture using phenol red as the pH indicator. Gas producers were found using Durham tube culture techniques.

Degradative effects of Bacillus licheniformis JF-2 on Schuricht crude oil composition was determined by comparing volume (as percent) of crude oil constituents (liquid chromatography) of oil extracted from aerobic emulsifications with oil extracted from abiotic culture flasks incubated under identical conditions (see Figure 3-1a to 3-1d). Extraction was facilitated with 2 x 5 mL aliquots of hexane (culture volume = 50 mL, crude = 500 μL). Gas chromatographs of the aliphatic and aromatic fractions of Schuricht crude were also obtained for aerobic and anaerobic emulsification studies extracted as above. Comparisons of gas chromatography (GC) data was made by comparing pristane/C_{17} and phytane/C_{18} ratios of biotic and abiotic culture flasks and GC profiles. Data for pristane/C_{17} and phytane/C_{18} ratios obtained during aerobic emulsification experiments are presented in Table 3-2, data obtained from anaerobic emulsification experiments are presented in Table 3-3. Chromatography profiles from both anaerobic and aerobic experiments concur with the pristane/C_{17} and phytane/C_{18} ratios and indicate no degradation. Anaerobic experiments were monitored for anaerobicity with head space analysis of all samples (GC analysis performed on a Gow Mac series 550P GC fitted with a 6 ft Alltech CTR 1 concentric column). Degradative effects of MEOR isolates on Schuricht crude were determined by comparative gas chromatography. No fractionation data were obtained.

Bacillus licheniformis JF-2 (ATCC 39307) has a highly varigated white surface morphology and was observed to have positive reactions for oxidase and catalase and also observed to possess arginine dihydrolase, gelatinase, alpha

Table 3-2. Pristane/C_{17} and phytane/C_{18} ratios obtained following aerobic emulsification of Schuricht crude oil

Isolate	Pristane/C_{17}	Phytane/C_{18}
Aseptic control	0.66	0.98
B. licheniformis	0.65	0.94
SEW BL	0.66	1.00
COW BL	0.67	0.89
SPCDW	0.67	1.01
SPCDY	0.65	0.93
COWPY1	0.54	0.94
FSC6DW	0.74	0.96
YELDY	0.68	1.00
TNK3PY	0.68	0.96
MWWH	0.69	0.94

amylase, and beta galactosidase. The organism was able to use acetate, pyruvate citrate, and malate as growth substrates. Nitrate was reduced to nitrite but not to nitrogen gas. Acid, but not acid and gas, was formed during growth on glucose. Bacillus licheniformis JF-2 was found to produce a polymer (levan) as well as a surfactant.

SEW BL is a gram positive rod having a creamy white variegated surface morphology on agar plates. SEW BL originated from activated sewage from the Idaho Falls, ID sewage treatment plant. SEW BL was observed to have positive reactions for oxidase and catalase, and also observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-gluconate, acetate, pyruvate,

Table 3.3. Pristane/C_{17} and phytane/C_{18} ratios obtained following anaerobic emulsification of Schuricht crude oil

Isolate	Pristane/C_{17}	Phytane/C_{18}
Aseptic control	0.497	0.853
B. licheniformis	0.558	0.912
SEW BL	0.695	0.988
COW BL	0.787	0.980
SPCDW	0.808	1.021
SPCDY	0.699	0.932
COWPY1	0.676	0.959
FSC6DW	0.686	0.959
YELDY	0.718	0.996
TNK3PY	0.728	0.982
MWWH	0.649	0.957

malate, and citrate as growth substrates. Nitrate was reduced to nitrite but not to nitrogen gas. Acid (but not acid and gas) was formed during growth on glucose. SEW BL was found to produce a surfactant in aerobic and anaerobic shake flasks.

COW BL is a gram positive rod having a mucoid white variegated surface morphology on agar plates. COW BL originated from oil laden cow dung positioned just outside the Moorcroft West heater treater. COW BL was observed to have positive reactions for oxidase and catalase and was also observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-

gluconate, acetate, pyruvate, malate, and citrate as growth substrates. Nitrate was reduced to nitrite but not to nitrogen gas. Acid (but not acid and gas) was formed during growth on glucose. COW BL was found to produce a surfactant in aerobic and anaerobic shake flasks.

SPCDW is a gram positive rod having a dense, pinpoint white surface morphology on agar plates. SPCDW originated from a spill of produced brines and oil just outside the Moorcroft West heater treater. SPCDW was negative for oxidase and catalase but was observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-gluconate, malate, and citrate as growth substrates. Acid (but not acid and gas) was formed during growth on glucose. SPCDW was found to produce a surfactant in anaerobic shake flasks but not in aerobic shake flasks.

SPCDY is a gram positive rod having a dense, pinpoint yellow surface morphology on agar plates. SPCDY originated from a spill of produced brines and oil just outside the Moorcroft West heater treater. SPCDY was negative for oxidase and catalase but was observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-gluconate, pyruvate, malate, and citrate as growth substrates. Acid (but not acid and gas) was formed during growth on glucose. SPCDY was found to produce a surfactant in aerobic and anaerobic shake flasks.

COWPY1 is a gram positive cocci or small rod having a dense, pinpoint yellow surface morphology on agar plates. COWPY1 originated from oil laden cow dung positioned just outside the Moorcroft West heater treater. COWPY1 was negative for oxidase and catalase but was observed to possess beta galactosidase. Acid (but not acid and gas) was formed during growth on glucose. COWPY1 was found to produce a surfactant in aerobic and anaerobic shake flasks.

FSC6DW is a large gram positive rod having a creamy white diffuse surface morphology on agar plates. FSC6DW originated from an active algal matt in the

Rainbow Springs area in Yellowstone National Park, an area known for natural hydrocarbon seeps. FSC6DW was observed to have a positive reaction for oxidase and a negative reaction for catalase and also observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-gluconate, adipate, phenylacetate, acetate, malate, and citrate as growth substrates. Acid (but not acid and gas) was formed during growth on glucose. FSC6DW was found to produce a surfactant in anaerobic but not aerobic shake flasks.

YELDY is a gram positive rod having a dense yellow surface morphology on agar plates. YELDY originated from an oil laden soil sample from the Rainbow Springs area in Yellowstone National Park. YELDY was negative for oxidase and catalase but was observed to possess gelatinase, and beta galactosidase. The organism was able to use arabinose, D-mannose, D-mannitol, acetyl-D-glucosamine, maltose, D-gluconate, adipate, phenylacetate, acetate, and citrate as growth substrates. Acid (but not acid and gas) was formed during growth on glucose. YELDY was found to produce a surfactant in aerobic and anaerobic shake flasks.

TNK3PY is a gram negative rod having a dense yellow surface morphology on agar plates. TNK3PY originated from a mixed waste stream comprised of human sewage effluent, effluent from a metals plating/stripping facility, and effluent from a vehicle maintenance shop all located on Tinker Air Force Base Norman, Oklahoma. TNK3PY was observed to have a positive reaction for oxidase and a negative reaction for catalase. The organism was able to use D-gluconate, caprate, acetate, pyruvate, and citrate as growth substrates. Nitrate was reduced to nitrite. Gas (weak production) was formed during growth on glucose. TNK3PY was found to produce a surfactant in aerobic and anaerobic shake flasks.

MWWH is a small gram negative rod having a glossy yellow surface morphology on agar plates. MWWH originated from a sample of gravel taken from the Moorcroft West wellhead. MWWH was observed to have a positive reaction for oxidase and catalase. The organism was able to use D-gluconate, caprate, acetate, pyruvate, and citrate as growth substrates. Nitrate was reduced to nitrite.

Gas (weak production) was formed during growth on glucose. MWWH was found to produce a surfactant in aerobic and anaerobic shake flasks.

Collective properties of all strains are listed in Table 3-4.

3.3 Properties of Bacillus licheniformis Strain JF-2

Properties of Bacillus licheniformis strain JF-2 with respect to culture characteristics, transport through and spacial distribution in Berea sandstone, surfactant production, and polymer production were elucidated. Culture characteristics, surfactant production, and polymer production were investigated using Media E (1502) with sucrose as the sole carbon source.

Growth protocols for coreflood experimentation in Media E (1502) with sucrose are also delineated.

3.3.1 Culture Properties of Bacillus licheniformis Strain JF-2

Experiments were conducted aerobically in media E (1502) with sucrose as the carbon source. These experiments indicate a temperature optimum at 37°C with a tolerance to at least 50°C (Figure 3-2), a salinity tolerance of 1 to 6 w%/v (as NaCl, Figure 3-3), and a pH tolerance of 6 to at least 8.5 (Figure 3-4).

Temperature data indicate a sharp response at 37°C that peaks by 72 h. After 72 h the cells most likely begin to sporulate and therefore the optical density decreases. At 45°C growth continues at 144 h and has not began to subside. This is indicative of slower metabolism at this temperature. Temperatures of 55°C were found to be lethal for the organism.

Salinity data indicate pronounced sensitivity to salt only during the first few days of growth. By 90 h (3.75 d) a broad tolerance to salt (as NaCl) is observed. Optical densities of 1.0 and greater were obtained after 1 d because of an increased inoculum size in this experiment.

Table 3-4. Biochemical characterization of MEOR field isolates.

Isolate	Biochemical Test																					
	OX	CAT	ACET	PYR	NO_3	H_2S	SUC	ADH	ESC	GEL	PNPG	ARA	MNE	MAN	NAG	MAL	GNT	CAP	ADI	MLT	CIT	PAC
B.L.	+	+	+	+	+	-	+/+	+	+	+	+	-	-	-	-	-	-	-	-	+	+	-
SEW BL	+	+	+	+	+	-	+/NT	-	+	+	+	+	+	+	+	+	+	-	-	+	+	-
COW BL	+	+	+	+	+	-	+/NT	-	+	+	+	+	+	+	+	+	+	-	-	+	+	-
SPCDW	-	-	-	-	-	-	+/NT	-	+	+	+	+	+	+	+	+	+	-	-	+	+	-
SPCDY	-	-	-	+	-	-	+/NT	-	+	+	+	+	+	+	+	+	+	-	-	+	+	-
COWPY1	-	-	-	-	-	-	+/NT	-	+	-	+	-	-	-	-	-	-	-	-	-	-	-
FSC6DW	+	-	+	-	-	-	+/NT	-	+	+	+	+	+	+	+	+	+	-	+	+	+	+
YELDY	-	-	-	-	-	-	+/NT	-	+	+	+	+	+	+	+	-	+	-	-	+	+	-
TNK3PY	+	-	+	+	+	-	+/NT	-	-	-	-	-	-	-	-	-	+	+	-	+	+	-
MWWH	+	+	+	+	+	-	+/NT	-	-	-	-	-	-	-	-	-	+	+	-	+	+	-

Other biochemical tests performed were tryptophanase and urease, tests were negative for all isolates. NT, no test performed.

OX = Oxidase
CAT = Catalase
ACET = Acetate
PYR = Pyruvate
NO_3 = Nitrate
TRP = Tryptophanase
GLU = Sucrose aerobic/anaerobic
ADH = Arginine Dihydrolase
URE = Urease
ESC = Esculin hydrolysis
GEL = Gelatinase
H_2S = Hydrogen Sulfide

PNPG = Beta Galactosidase
ARA = Arabinose
MNE = D-Mannose
MAN = D-Mannitol
NAG = Acetyl-D-Glucosamine
MAL = Maltose
GNT = D-Gluconate
CAP = Caprate
ADI = Adipate
MLT = Malate
CIT = Citrate
PAC = Phenylacetate

Experiments conducted to ascertain response to pH indicate Bacillus licheniformis JF-2 will grow in a pH range from 6 to at least 8.5. Growth may occur at a pH >8.5 but precipitation of media constituents at pH 9.0 precluded data collection beyond this point.

The temperature, salinity, and pH data for Bacillus licheniformis JF-2 when grown in Media E (1502) indicate the organism will most likely be adaptable to the reservoir environment of the Minnelusa Sands in the Powder River Basin, WY. The primary MEOR metabolite of the organism, a surfactant, has been discussed in the literature[2] and reported to function well at the reservoir conditions of the Powder River Basin, WY. Optimal surfactant activity was reported to occur at salinities >4% and temperatures of 50°C. The salinity of the Moorcroft West Unit is about 2.8% and appears to be increasing. Concentrations of Ca^{++} at 7 w%/v are reported to decrease surfactant activity compared to concentrations of 2 and 10%. The Ca^{++} concentrations in the Moorcroft West Unit in the Minnelusa Sands in the Powder River Basin are in the range of 0.10 ± 0.006% (personal communication, Julie Smith TIORCO Inc.).

3.3.2 Growth of Bacillus licheniformis JF-2 for Coreflood Experimentation

Organisms used in core flood experimentation (Bacillus licheniformis JF-2) were routinely grown by inoculating 50 mL Media E (1502, supplemented with 1% sucrose and 2.4% NaCl, see Subsection 3.2) with 100 μL of a fresh overnight culture (trypticase soy broth). Incubation was conducted aerobically at 30°C until the cultures reached an optical density of 1.0 ± 0.15. The cells were harvested by centrifugation (3000 rpm x 10 min at room temperature, Sorvall rotor SS34) and resuspended in fresh Media E (1502) with sucrose (1.0%) and NaCl (2.5%) added. This procedure was followed to allow differentiation between metabolic products produced outside of the core and those metabolites produced in the core. Under this regiment, only the cells themselves were used for inoculum and therefore oil displacement that occurred was caused by either in situ production of metabolic products or the physical presence of bacterial cells. Cells were injected into epoxy coated Berea sandstone cores using a 6 mL accumulator operated at 1.5 mL/h.

Where noted, unwashed cells (cells plus metabolites liberated in culture) were used for comparitave experimentation.

3.3.3 Scanning Electron Microscopy (SEM) of Berea Sandstone Cores

Spacial distribution of Bacillus licheniformis JF-2 in Berea sandstone cores following microbial flood experiments was analyzed with SEM. Controls for SEM experiments were coarse (permeability 300 to 500 md, Figure 3-5) and fine (permeability 100 to 300 md, Figure 3-6) virgin Berea sandstone and oil coated Berea sandstone cores (Figure 3-7) that had been previously waterflooded to residual oil (Schuricht crude). The SEM of microbial coreflood experiments was performed after the core had been waterflooded for production following a microbial flood. The core was broken into three distinct regions, the inlet (Figure 3-8), mid section (Figure 3-9) and the outlet (Figure 3-10).

The SEM was performed with an AMRAY scanning electron microscope. All samples (biotic and abiotic) were treated the same. Small pieces (5 to 10 mm) of material were broken from larger core elements and placed in 4% glutaraldehyde in Sorensens buffer[9] (phosphate buffer, pH 7) and allowed to fix for 4 h. The samples were then washed 5x in the buffer and transferred to a 1% osmium tetroxide (in Sorensens buffer) and allowed to stand for 2 h. Each sample was placed on a standard SEM aluminum stub and glued in place using silver paint. The samples were then coated with a thin layer of gold (75 Å) to ensure conductivity.

Although organisms were found to be distributed completely through the core (Figures 3-8, 3-9, 3-10), a predominance of organisms were found in the region distal to injection (Figure 3-10). Based on the size of the cells, it is hypothesized that spores and germinative cells are present. It is not known if the cells were committed to sporulation before they were injected or if the cells sporulated once inside the core.

3.3.4 Surfactant Production by Bacillus licheniformis JF-2

Bacillus licheniformis JF-2 was proven to produce a surfactant when grown on minimal Media E (1502) in the presence of sucrose. Interfacial tensions were measured on cell free supernatants using various crude oils as the organic phase. The production, characterization, and IFT measurements of Bacillus licheniformis JF-2 surfactant is presented and discussed in Section 4.

3.3.5 Polymer Production by Bacillus licheniformis JF-2

Levan production by Bacillus licheniformis strain NRC 9012 has been previously reported in the literature.[10] Levan, *B*-D-fructofuranose linked primarily 2,6 with branched chains linked 2,1,[11] produced by Bacillus licheniformis strain JF-2 has been demonstrated. Initial experiments were conducted aerobically at 30°C in Media E (1502) supplemented with 0.5% sucrose. Cultures, abiotic controls, and abiotic media + levan were incubated for 7 d.

Levan was isolated with modifications based on the procedure of Leeper.[12] Ice cold methanol was added to the cultures as a three fold excess (v/v) and allowed to stand at 4°C overnight. The insoluble material was harvested by centrifugation at 2,000 rpm (International table top centrifuge) for 10 min at room temperature. The supernatant was discarded and the pellet was overlaid with pyridine and agitated to mix. The insoluble material was harvested as above and brought up in distilled water. Levan concentrations were ascertained by a spectrophotometric assay based on the ability of hydrolyzed levan (fructose) to reduce 3,5-dinitrosalicylic acid to a colored product.[13] 500 µL of the isolated material was added to 1.0 mL of 1.0 M oxalic acid and incubated at 100°C for 30 min to facilitate hydrolysis. Following hydrolysis, 100 µL of the sample was reacted with 1.0 mL of 3,5-dinitrosalicylic acid for 10 min at 100° C. Samples were analyzed spectrophotometrically at 590 nm. Net levan production was calculated based on the difference between hydrolyzed and unhydrolyzed samples. Previous experiments indicate no difference between glucose and fructose with respect to reduction of 3,5-dinitrosalicylic acid to its colored product under nonhydrolyzing or hydrolyzing conditions (data not shown).

Although polymer production was nominal, research will continue to elucidate the importance of production under field conditions in conjunction with surfactant.

3.4 Discussion

Development of an understanding on the mechanisms by which microbial systems displace oil under reservoir conditions through such avenues as core flooding and other laboratory techniques will be a significant contribution to EOR technology and specifically MEOR technology. The mechanisms of MEOR are not fully understood or specifically known for a wide variety of reservoir conditions, crude oils, microbial, and nutrient systems. Bacteria that have characteristics such as the capability to emulsify crude oils and lower IFT are ideal candidates for improved oil recovery. Organisms that have the ability to produce acids or gas or both and organisms that are capable of asphaltic degradation are also significant to the technology and are presently being collected, isolated, and characterized for application in EOR research activities.

The utilization of Bacillus licheniformis JF-2 as a benchmark organism has allowed the selection of promising microbial isolates with selected phenotypic and genotypic properties to facilitate MEOR as well as providing for a systematic comparison of the effects of different oil characteristics.

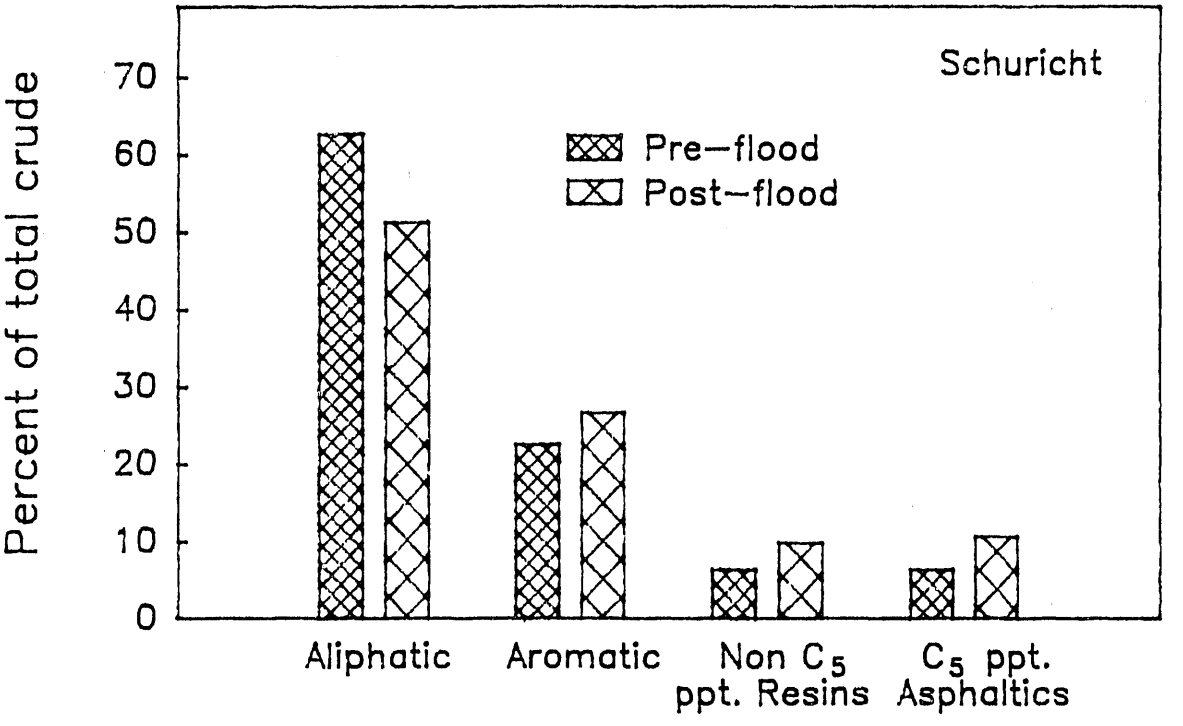

Figure 3-1a. Comparison of pre- and post-flood (microbial) chromatography fractions, Schuricht crude.

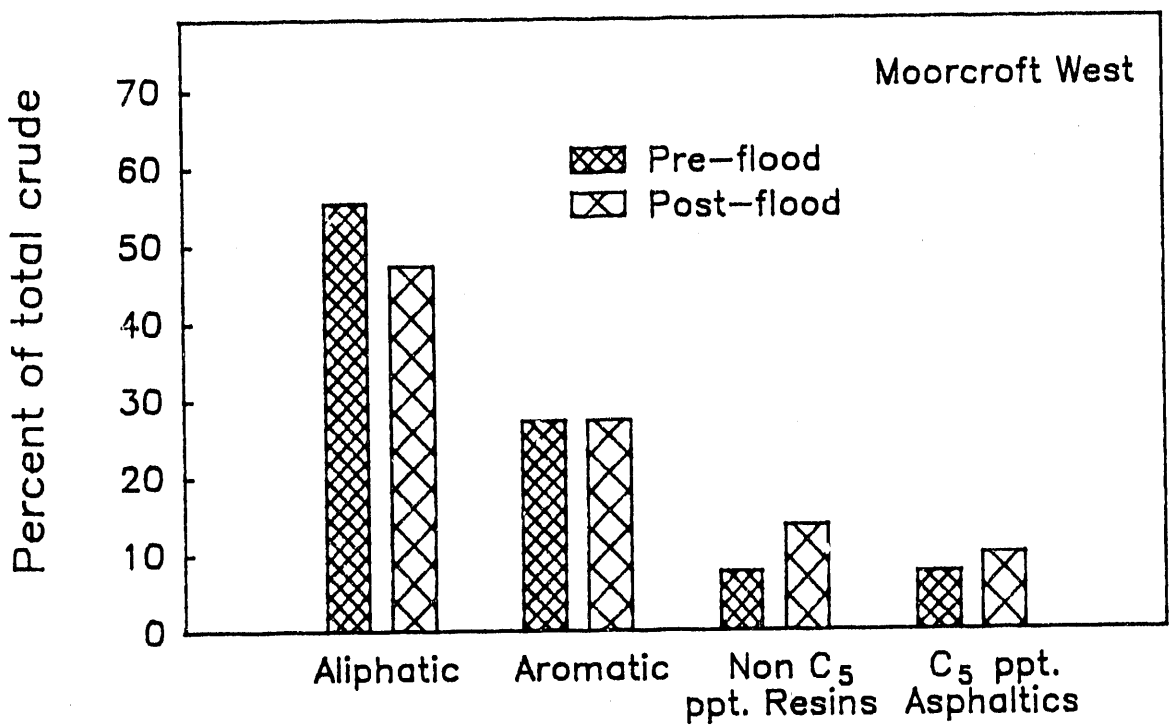

Figure 3-1b. Comparison of pre- and post-flood (microbial) chromatography fractions, Moorcroft West crude.

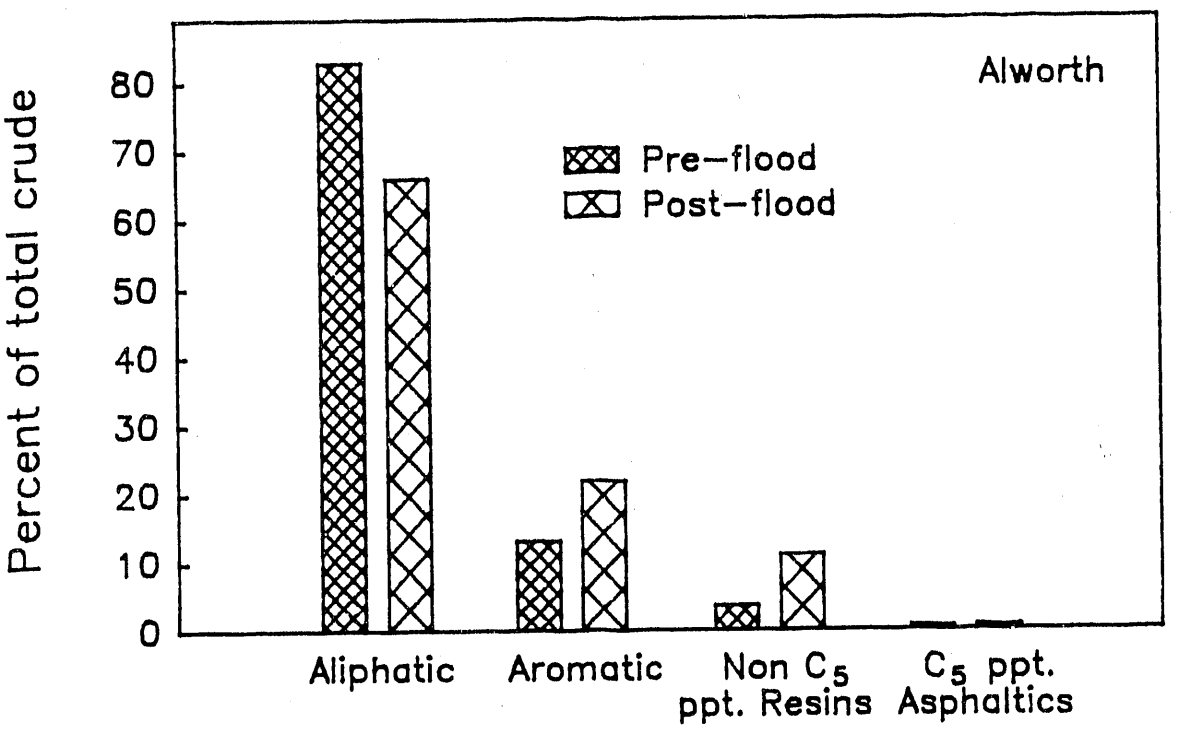

Figure 3-1c. Comparison of pre- and post-flood (microbial) chromatography fractions, Alworth crude.

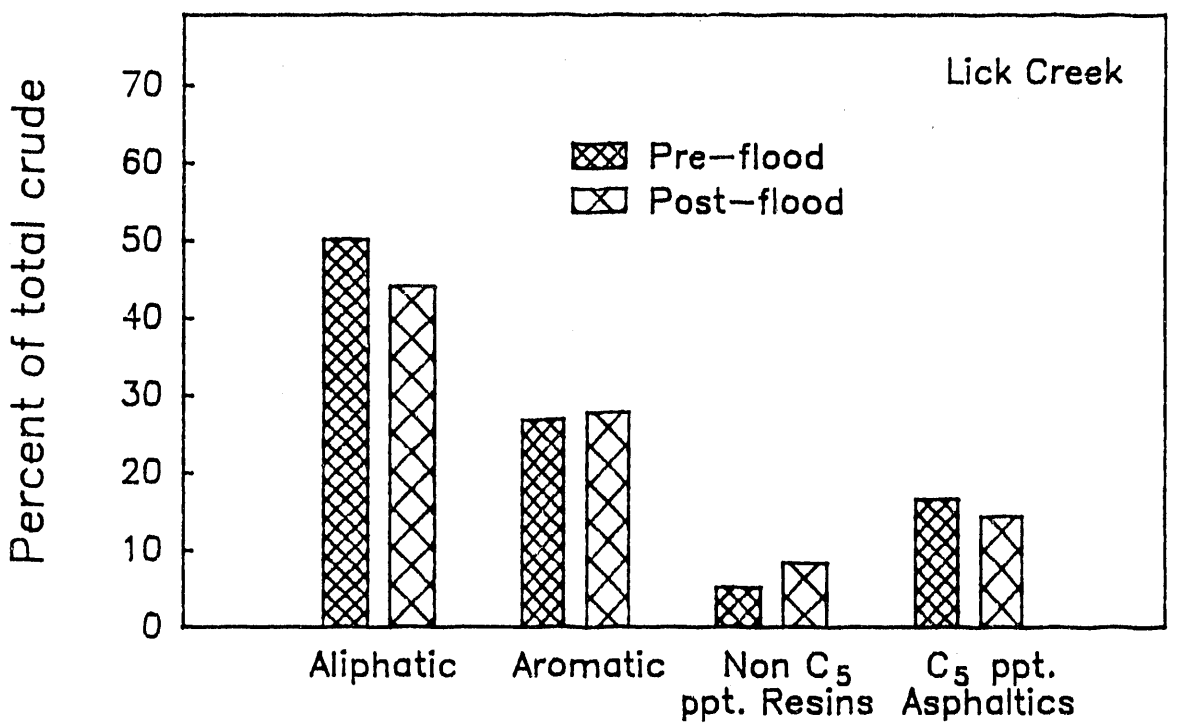

Figure 3-1d. Comparison of pre- and post-flood (microbial) chromatography fractions, Lick Creek crude.

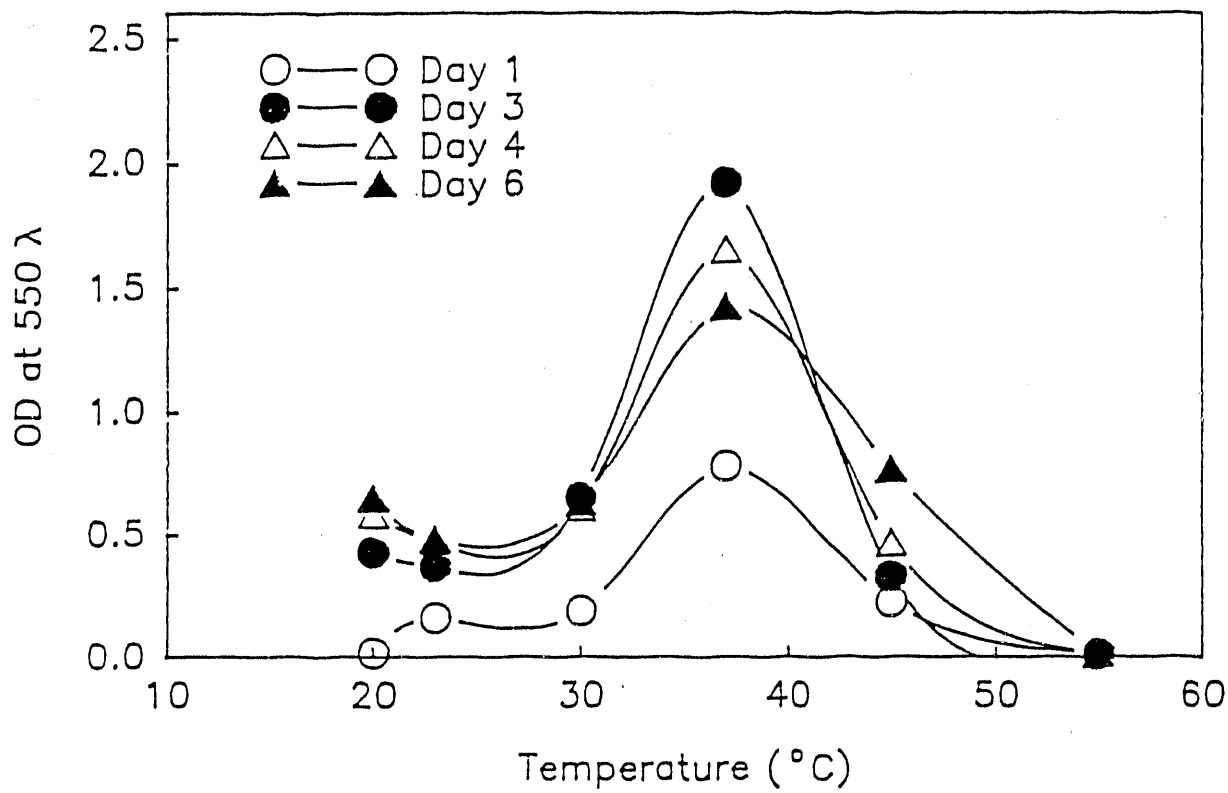

Figure 3-2. Growth response of Bacillus licheniformis JF-2 as a function of temperature.

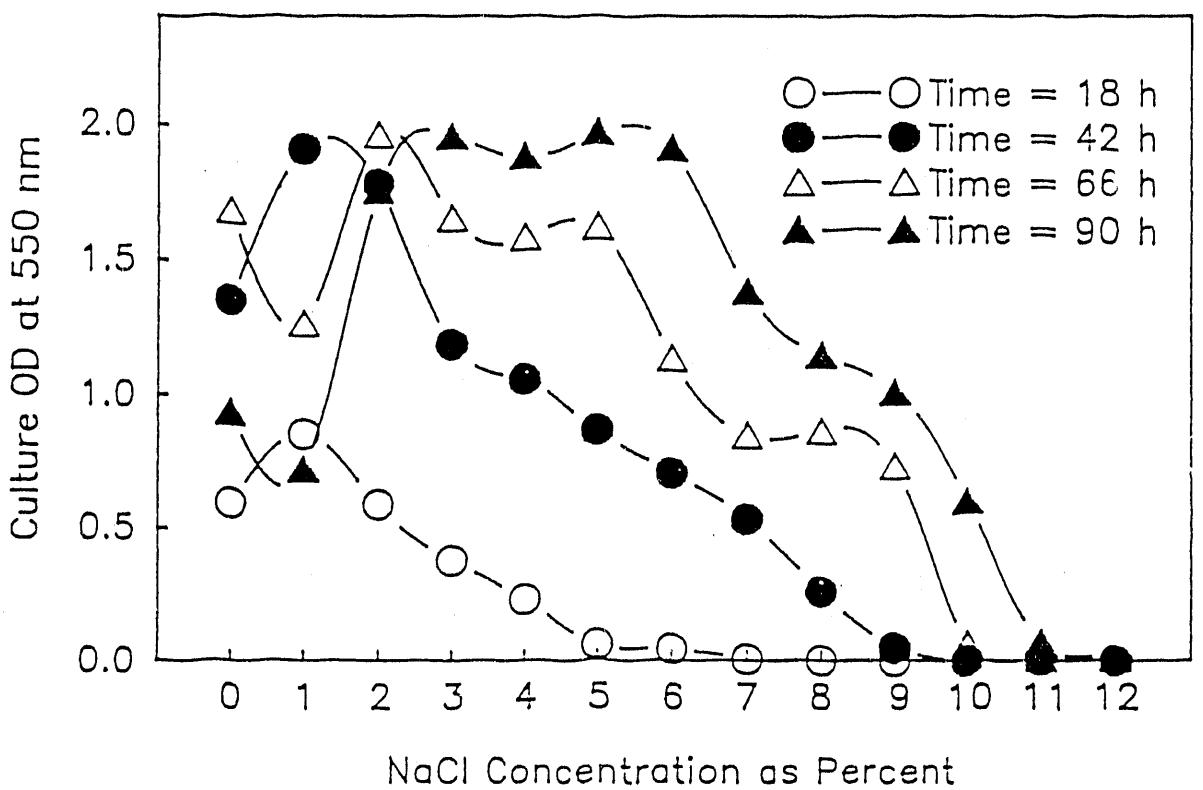

Figure 3-3. Growth response of Bacillus licheniformis JF-2 as a function of salt (NaCl) concentration.

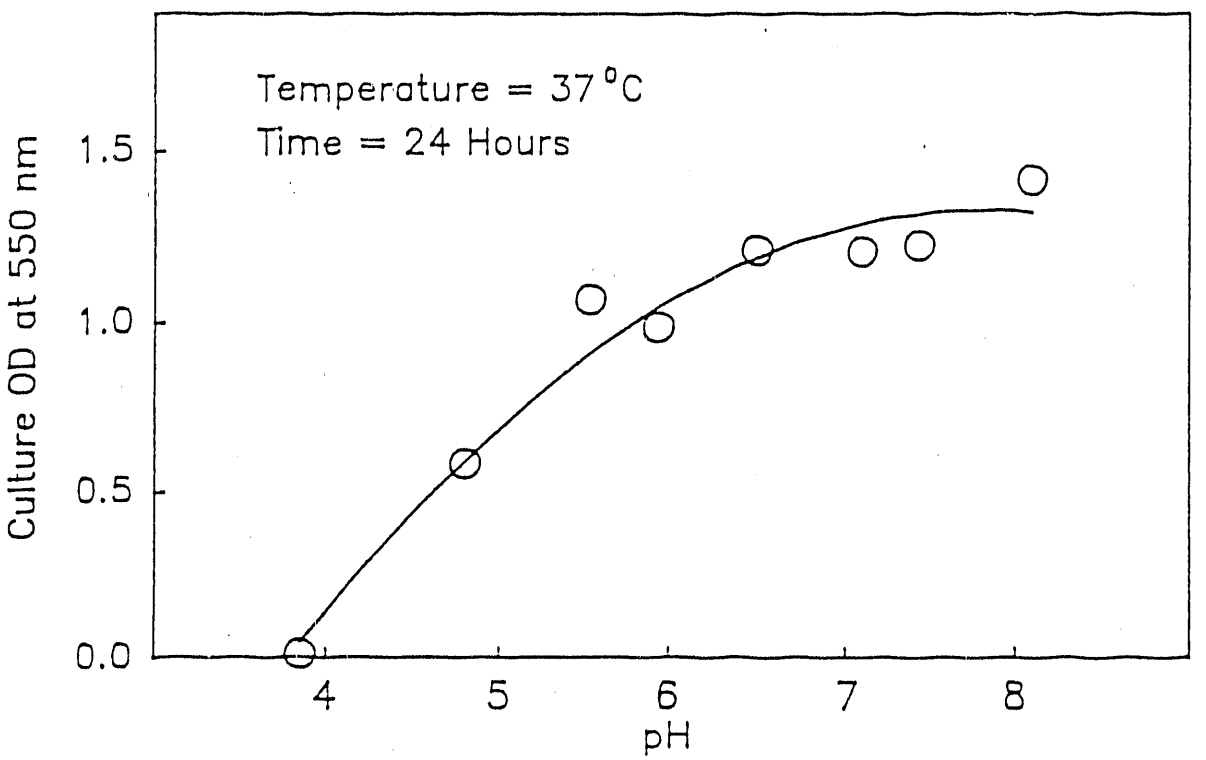

Figure 3-4. Growth response of Bacillus licheniformis JF-2 as a function of pH.

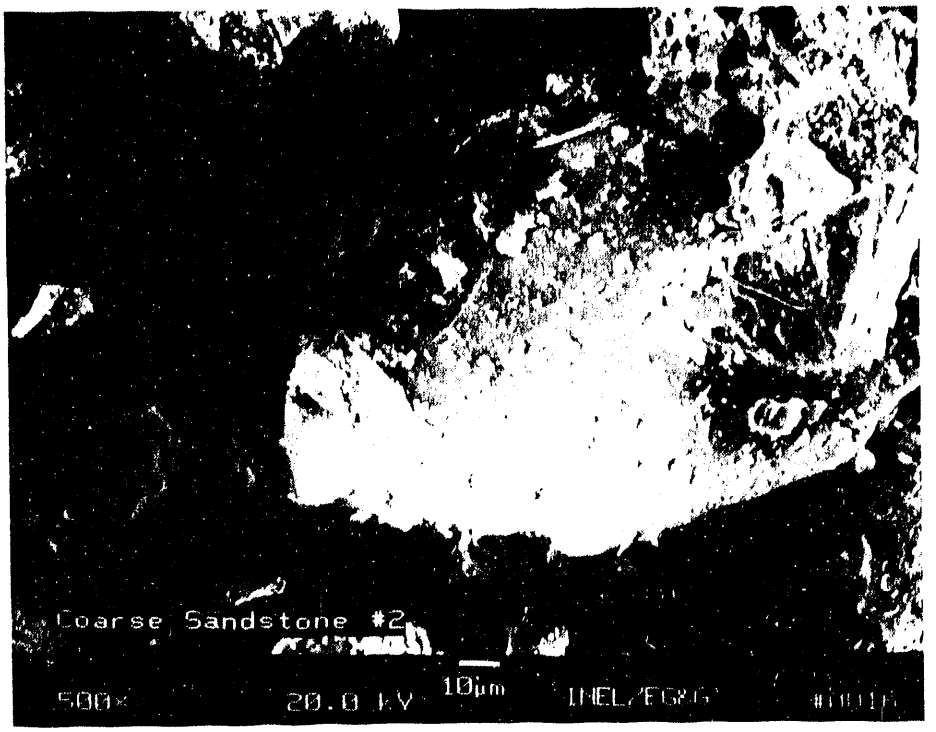

Figure 3-5. Scanning electron micrograph of virgin coarse (300 to 500 md permeability) Berea sandstone.

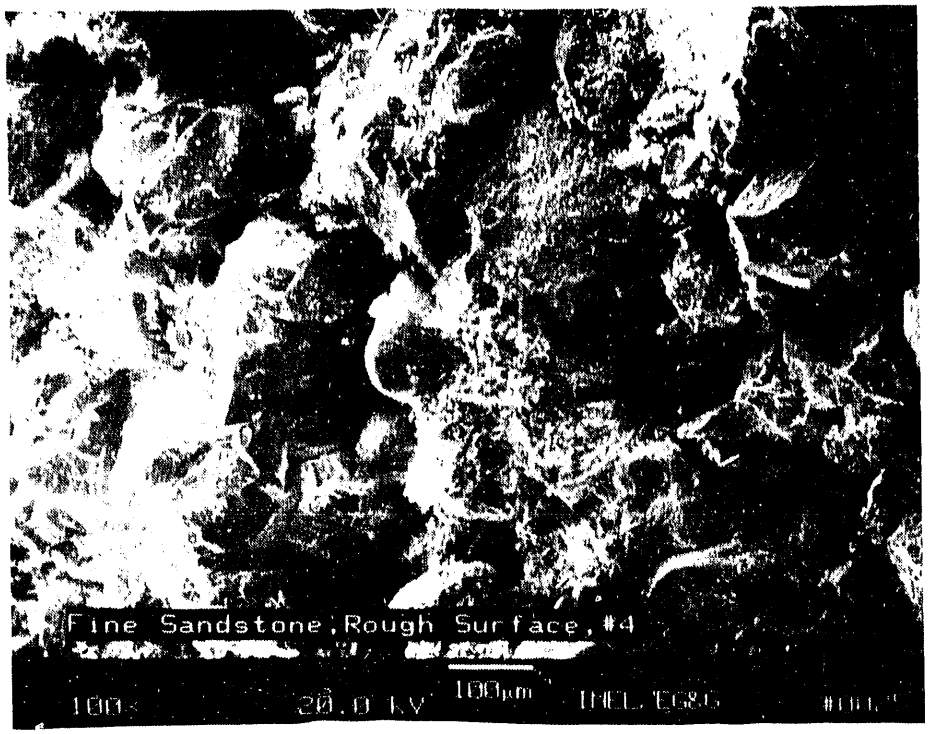

Figure 3-6. Scanning electron micrograph of virgin fine (100 to 300 md permeability) Berea sandstone.

Figure 3-7. Scanning electron micrograph of oil coated (Schuricht) fine (100 to 300 md permeability) Berea sandstone.

Figure 3-8. Scanning electron micrograph (inlet region) of a Berea sandstone core (fine) obtained from a microbial (Bacillus licheniformis JF-2) coreflood experiment. Schuricht crude at water flood residual.

Figure 3-9. Scanning electron micrograph (mid region) of a Berea sandstone core (fine) obtained from a microbial (Bacillus licheniformis JF-2) coreflood experiment. Schuricht crude at water flood residual.

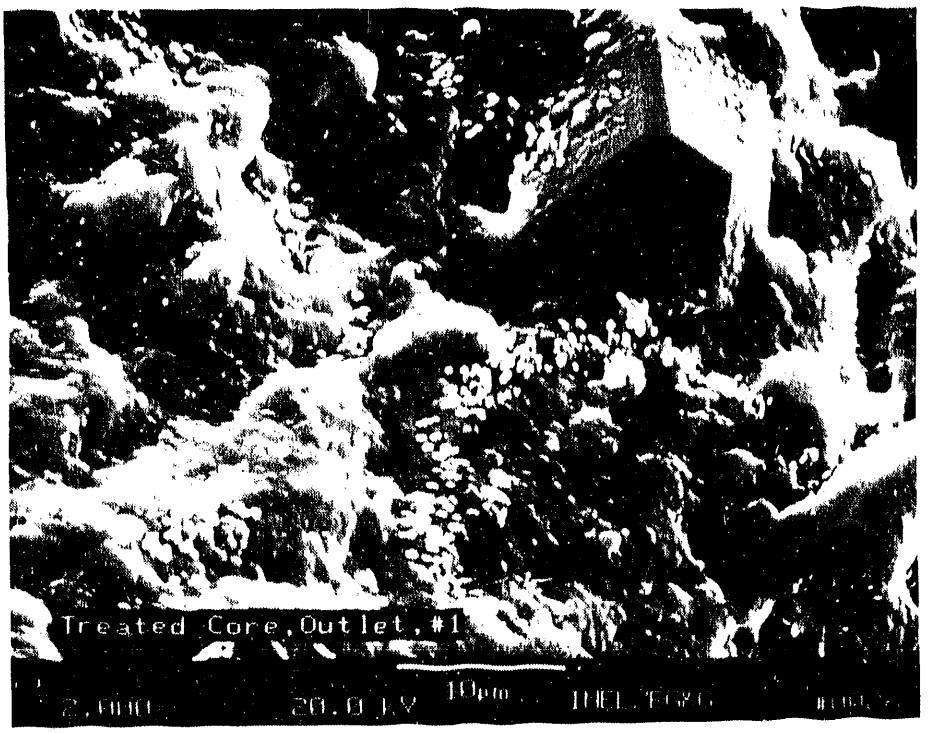

Figure 3-10. Scanning electron micrograph (outlet region) of a Berea sandstone core (fine) obtained from a microbial (Bacillus licheniformis JF-2) coreflood experiment. Schuricht crude at water flood residual.

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4. MEASUREMENT OF INTERFACIAL TENSIONS

About 2/3 of the oil that has been discovered remains trapped in the original reservoir. This oil is trapped by capillary forces in the pore structure of the formation and is resistant to displacement by waterflooding techniques. Capillary forces between the oil and formation water determine the pressures needed to displace the oil from the rock. The pressure required to displace this oil is higher than can be generated in secondary waterflood oil recovery operations. The pressure requirement can be lowered if the interfacial tension between the oil and water (typically 30-40 mN/m) is lowered. Calculations using models of trapped oil have estimated that interfacial tensions lower than 0.1 mN/m are needed for improved oil recovery.[1,2,3,4] Interfacial tension (IFT) is defined as the minimum amount of work required to create the boundary between two immiscible phases, such as oil and water. Ultralow IFTs (about 10^{-3} mN/m) are capable of mobilizing the oil trapped by capillary forces. Lowering the IFT by use of surfactants (which align between the two phases at the boundary) decreases the pressure required to force a non-wetting phase (oil) through a small capillary. Oil trapped in a reservoir can therefore be displaced by flooding the reservoir with a surfactant solution capable of lowering the IFT to the values required by the reservoir conditions.

Measurement of IFTs has been accomplished by a variety of methods, including pendant drop,[5,6,7] sessile drop,[8] and spinning drop[9] methods. The pendant or sessile drop methods of determining IFTs was first suggested by Worthington[10] and Ferguson.[11] These methods place a drop of oil into a surfactant solution, and then measure the shape of the drop. All of these methods require difficult measurements to be performed on the drop that is formed. In the past, a photographic record was made of the drop size, and the measurements of drop shape were determined from this record. Current developments in personal computers coupled with the ability to digitize video images makes it possible to automate the process, and to provide a faster means to determine the IFT.[12,13,14]

4.1 Current INEL Interfacial Tension Measurement Technology

A simple automated system for measuring interfacial tensions using the sessile drop method has been developed at the INEL.[15] The size and shape of a transparent or opaque drop of one fluid (crude oil) immersed in a second transparent fluid (surfactant solution) is displayed on a monitor with a CCD video camera. The video image is digitized and stored by a computer-controlled system. Custom software (developed at the INEL) determines various drop shape measurements and then computes the interfacial tension. The video image can be stored on the computer disk, or could be stored on video tape. In the sessile drop method, an outline of the drop is recorded and used to determine the IFT. The detailed theoretical derivations for the determination of the interfacial tension are given in different literature reports.[16,17,18] The currently used analysis utilizes an empirical procedure[19] that defines a function, S, to determine the drop shape. The maximum diameter, de, of the drop is determined and then used in the determination of the horizontal dimension, ds, of the drop as shown in Figure 4-1. Using algorithms developed by Fordham,[20] the IFT between the drop and the external solution can be estimated. The ratio of these two measurements, ds/de (called the drop shape factor, S) can be used to determine the IFT. The equation used to calculate the interfacial tension is given in Equation 1.

$$\gamma = \Delta\rho \bullet g \bullet \left(\frac{de^2}{H}\right) \qquad (4\text{-}1)$$

where

γ = *interfacial tension*
$\Delta\rho$ = *density difference of the two liquids*
g = *gravitational acceleration*
de = *maximum diameter of drop*
$H = \dfrac{1}{0.312 \bullet S^{-2.64}}$.

The relationship between the drop shape factor S and the IFT has been quantified in a look-up table resident in the computer.

The complete IFT system consists of four major components: illumination, drop forming cell, video camera, and computer. These subsystems are described below.

The droplet cell is illuminated from behind so that the image of an opaque drop is black on a white background. Transparent drops appear as dark outlines surrounding a lighter interior caused by lensing effects. A fiber optics illumination system is used to provide the background light. The fiber optics source is desirable because of the reduced heating effects on the droplet cell and simplified mounting design. A ground glass diffusion lens is used to ensure uniform illumination of the drop.

The droplet forming cell has two windows and holds the surfactant solution to be tested (see Figure 4-2). The cell is backlit by the illumination system. For simplicity and cost, the windows are standard microscope slides. The windows can be easily removed for cleaning or can be replaced when contaminated. About 7 mL of surfactant solution is used in the test procedure. The crude oil is introduced into the cell through an injector situated at the bottom of the cell. External to the cell is a micrometer driven syringe used to inject a drop of oil (or other fluid) into the cell. In the sessile version, the drop floats above and is attached to the injector. The drop can be formed to any desired size (up to the buoyant release point) and the drop size and shape recorded. It is possible to record the sequence of such data with a video recorder while the drop is growing or changing shape because of equilibration or after terminal volume is reached.

The latest versions of the cell permits temperature control by flowing heated or cooled water through channels in the metal frame of the cell. Cells have been redesigned with a smaller path length in addition to the temperature control feature to permit IFT measurements of turbid bacterial cultures containing biosurfactants. These turbid bacterial cultures are translucent instead of transparent.

Various video cameras and lenses were used in developing the system. The current camera utilized is a Cohu model 6515 CCD camera with external controls

of gamma, black level, and AGC. Extension tubes provide various magnification ranges as required by different drop diameters (see Figure 4-3). Sensor pixel count and magnification are chosen so that one obtains at least 200 pixels across the minimum dimension to be measured. The goal is to have measurements of at least 1% precision.

A PC based system was selected to control the video system and to perform the calculations. An IBM-AT personal computer was equipped with a Data Translation DT2853 video frame digitizer board. The computer controls data acquisition, computation, and display functions. An auxiliary video monitor displays the video image output by the DT2853. If desired, a video cassette recorder can be used to record longer image sets for later evaluation.

The software is designed to control the video frame digitizer and to acquire, reduce, and display the data. It uses commercially available Data Translation DT-IRIS device drivers. The software is a combination of Specifically developed routines intermixed with the DT-IRIS driver routines. The user interacts with the program by depressing special function keys indicated by the displayed menus. Among the functions available are calibration, video adjustments, and plots of video intensity. Other options include saving and restoration of video images or of reduced data and printing of IFT data and of two-dimensional blocks of pixel intensities centered on a user selected image point.

Before an actual series of tests, a calibration object consisting of a sphere of known diameter comparable to that expected for the drop is installed in the test cell (see Figure 4-4). An automated calibration procedure computes the number of pixels per millimeter at the object in both the x and y axes. These calibration values are used to convert all pixel measurements into actual dimensions. In both the calibration process and the interfacial tension measurements, the edge of the drop image is fit with a second order polynomial curve so that subpixel locations can be determined. The operator generates a drop of the test liquid in the cell and then adjusts the focus, magnification, and illumination to match predetermined criteria (see Figure 4-5). When the sample has equilibrated, an automated data acquisition and data reduction

process is initiated. The system acquires a video image of the drop, then locates the maximum horizontal diameter, de, and the top of the drop. These values are then used to locate and measure the drop diameter ds. The program requests certain physical properties of the test fluids (density difference), then computes the IFT of the system.

4.2 Interfacial Tension Measurements

Bacillus licheniformis JF-2 is a known surfactant producing organism. The IFTs on culture supernatants of Bacillus licheniformis JF-2 (see Subsection 3.3.2 for growth parameters) were determined using various crude oils as the organic phase. The calibration of the tensiometer was verified using n-butanol/water and n-hexane/water, which have interfacial tensions of 1.8 mN/m at 20°C[21] and 51.1 mN/m at 20°C[22], respectively.

4.2.1 Calibration of Interfacial Tensiometer

Systems of known interfacial tensions were used to verify the accuracy of the system calibration. The system was verified to 1.8 mN/m using a system consisting of nano-pure water and n-butanol at 22.3°C following video calibration with 0.0625 and 0.1564 in. calibration standards. The IFT measurements were made using 0.22 μm capillary tubing (0.0625 in. calibration ball) and 0.0625 in. tubing (0.1564 in. calibration ball). Data for the n-butanol system are given in Table 4-1. The system calibration was verified to an interfacial tension of 51.1 mN/m using nano-pure water and n-hexane at 22.3°C following video calibration with a 0.1564 in. calibration ball with 0.0625 in. tubing. These data are given in Table 4-2.

4.2.2 Determination of CMC for Bacillus licheniformis JF-2 Biosurfactant

Bacillus licheniformis JF-2 was grown as delineated in Subsection 3.4.2 and the resulting cell free supernatant was used in a dilution experiment to determine the critical micelle concentration (CMC) of the biosurfactant. Schuricht crude was used as the organic phase. No effort was made to purify

Table 4-1. IFT measurements for n-butanol/water (1.8 mN/m @ 20°C) systems (measurements made @ 22.3°C)

Trial	IFT[a]	Calibration Std.	Trial	IFT[b]	Calibration Std.
1	1.9107	0.0625	1	1.3690	0.1564
2	1.9466	0.0625	2	1.8869	0.1564
3	1.9104	0.0625	3	1.9696	0.1564
4	1.9203	0.0625	4	1.8619	0.1564
5	1.8918	0.0625	5	1.9079	0.1564
6	1.7387	0.0625	6	1.8084	0.1564
7	1.8362	0.0625	7	1.9335	0.1564

a. Average = 1.8792 mN/m, standard deviation = ± 0.0706 mN/m.

b. Average = 1.8196 mN/m, standard deviation = ± 0.2052 mN/m.

Table 4-2. IFT measurements for n-hexane/water (51.1 mN/m @ 20°C) system (measurements made @ 22.3°C)

Trial	IFT[a]	Calibration Std.	Trial	IFT[a]	Calibration Std.
1	51.47	0.1564	8	48.96	0.1564
2	47.26	0.1564	9	47.91	0.1564
3	48.80	0.1564	10	47.20	0.1564
4	46.60	0.1564	11	47.61	0.1564
5	49.11	0.1564	12	45.69	0.1564
6	49.38	0.1564	13	48.08	0.1564
7	47.58	0.1564			

a. Average = 48.12 mN/m, standard deviation = ± 1.45 mN/m.

the biosurfactant and the resulting data could therefore more appropriately be labeled "CMC of cell free supernatant of Bacillus licheniformis JF-2". The CMC is taken as the inflection point of the curve. Graphical data are presented in Figure 4-6. The concentration of the undiluted biosurfactant produced under these conditions is 2.5 times the CMC.

4.2.3 IFT Measurements of Bacillus licheniformis biosurfactant using various crude oils

Cell free supernatants prepared from cells grown as delineated in Section 3.4.2 were used to establish IFTs relative to sterile Media E (1502). Without exception, the supernatants resulted in a decrease in IFT of about a factor of ten when tested against Moorcroft West, Schuricht, Alworth, and Lick Creek crude oils.

4.3 Discussion

A simple automated system to measure IFTs of two-phase liquid systems has been developed at the INEL. Data have been collected that proves validity of measurements between 1.8 and 51.1 mN/m. Future efforts will center on lowering the limits of measurement through testing of systems with known IFTs. Although standardization experiments indicate a sensitivity to component purity and operator fidelity, it is believed that meaningful data have been (and can continue to be) generated with this instrument. Ultralow IFT measurements, in the 10^{-3} mN/m range, have been reported using pendant drops.[16]

Results from IFT experiments indicate a definitive lowering of IFTs of crude oil/biosurfactant systems in comparison to crude oil/Media E controls. When Bacillus licheniformis JF-2 is grown as specified, the resulting surfactant (undiluted) is 2.5 times the CMC. Although IFTs in the 10^{-3} mN/m range are reported to be necessary for improved oil recovery, we believe the oil recovery mediated by Bacillus licheniformis JF-2 in experimental systems at the INEL to be surfactant mediated (see Section 5). The possibility of synergistic contributions of other cell mediated components, such as polymers,

proteins, and biomass, cannot be overlooked. Future experiments will be designed to control these and other parameters.

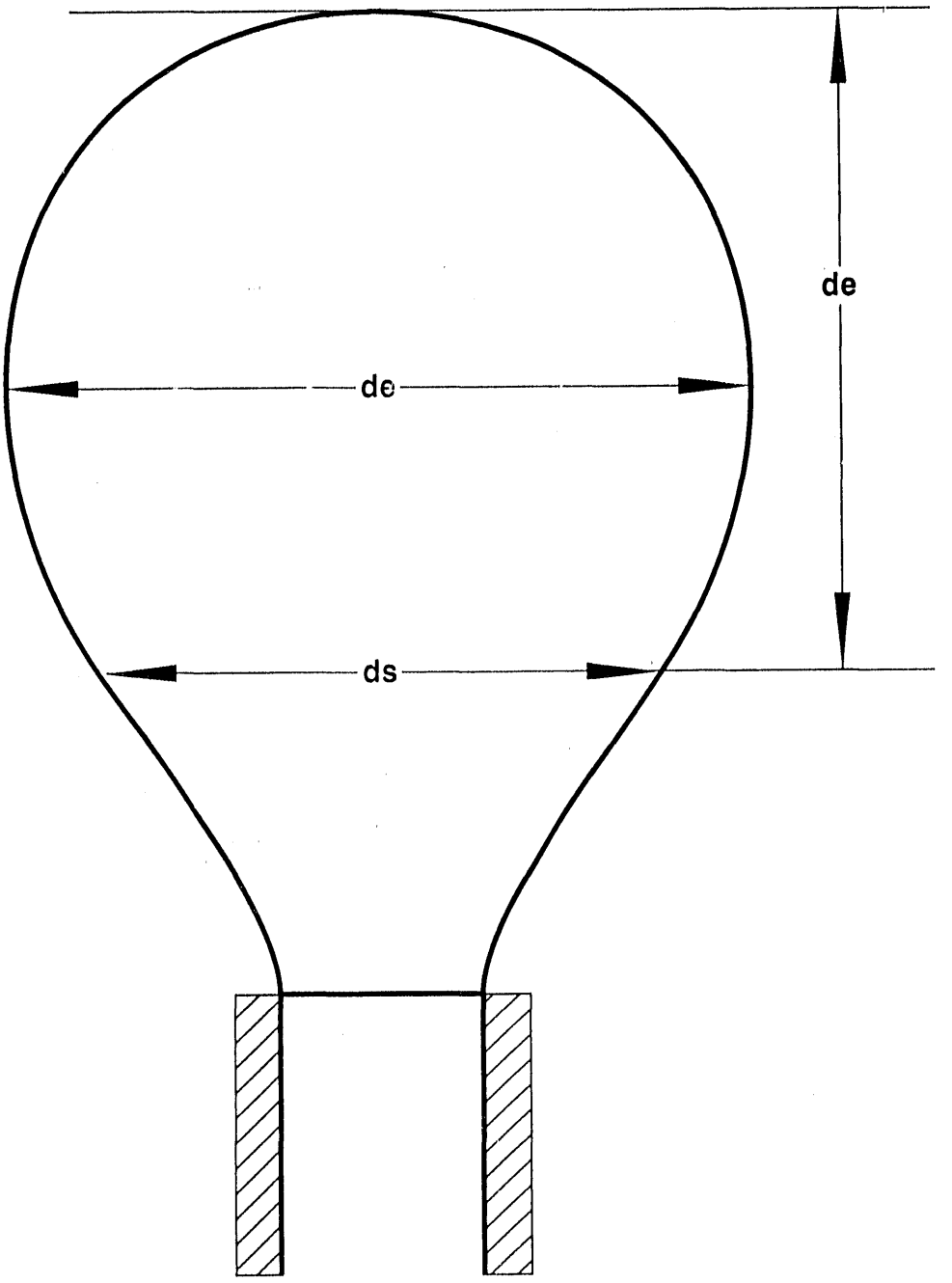

Figure 4-1. Critical dimensions used in calculating interfacial tensions.

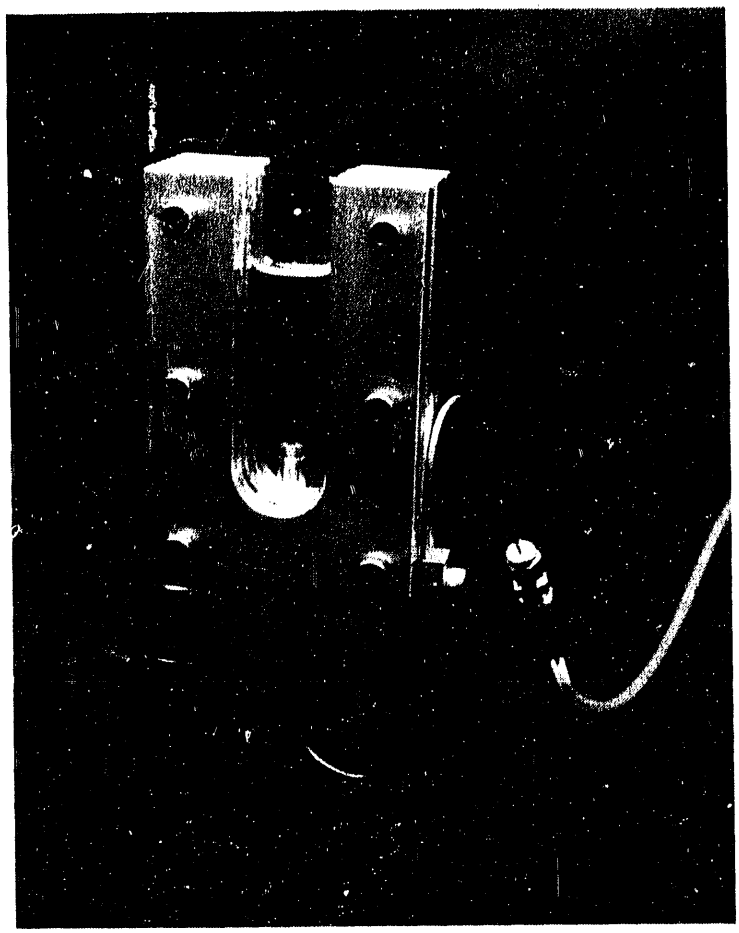

Figure 4-2. Drop forming cell for interfacial tensiometer.

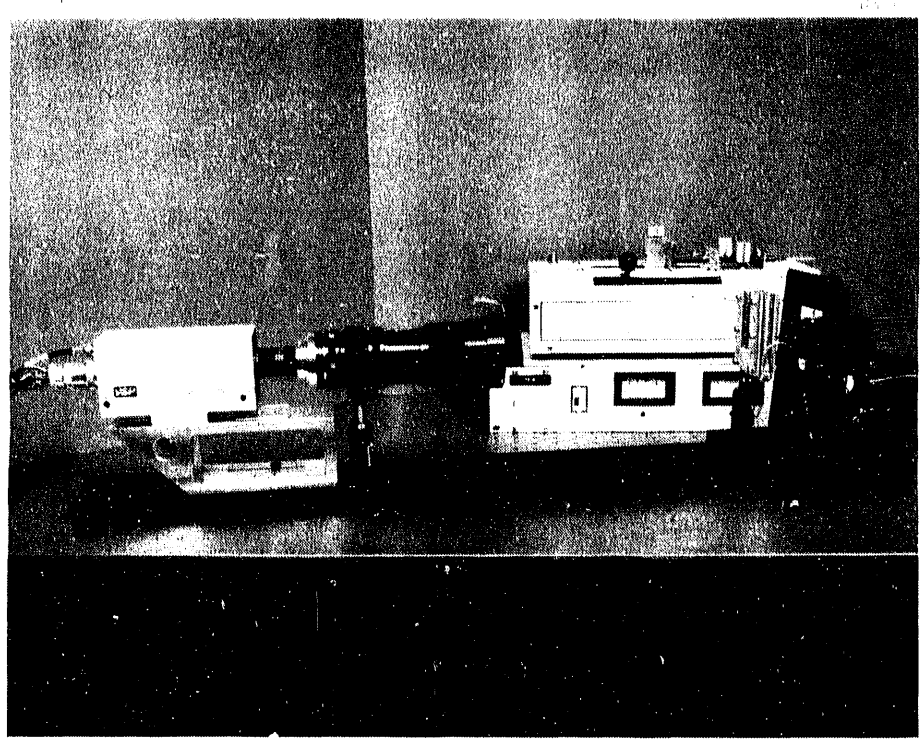

Figure 4-3. Video camera, lenses, magnification system setup for interfacial tensiometer.

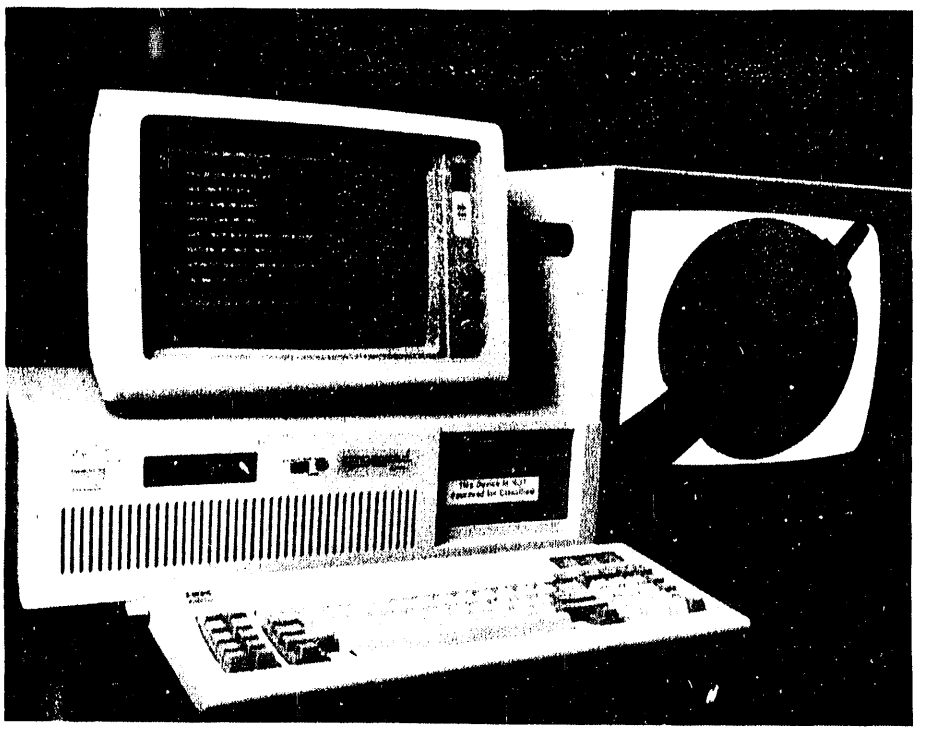

Figure 4-4. Calibration of interfacial tensiometer.

Figure 4-5. Video image of drop for interfacial tension measurement.

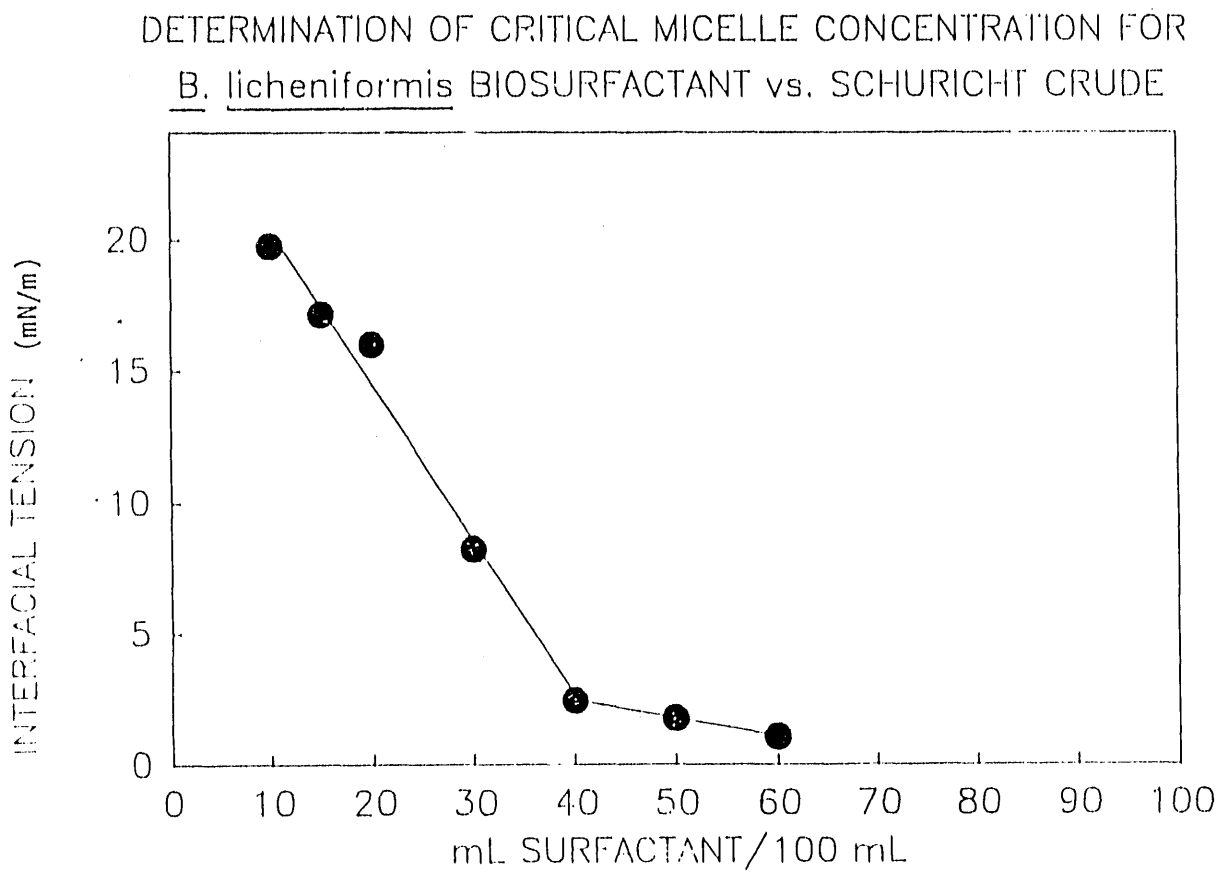

Figure 4-6. Determination of critical micelle concentration for cell free supernatants of Bacillus licheniformis JF-2.

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5. LABORATORY CORE FLOODS WITH MICROBIAL SYSTEMS

The objective of the core flooding program is to investigate the effect on oil recovery with selected microbial systems of parameters such as crude oil type, crude oil viscosity, aging and incubation time, IFT, and brine composition. All MEOR core floods completed to date have been flooded with the Bacillus licheniformis JF-2 microbial system (see Section 3). The core flooding apparatus, experimental procedures, and resulting core flood data are presented and discussed in this chapter.

5.1 Experimental Program

The experimental program consists of core floods being performed with six different oils. The six oils range in API gravity from 17.5 to 50.5°API at 60°F. Five of the oils are crude oils and one is a refined oil (Soltrol 220). The selected oils are listed in Table 2.1 and the analysis procedures and results were presented in Section 2.

All of the experiments use non-fired Berea sandstone cores coated with epoxy and fitted with end plates. The dimensions of the cores are 1 in. in diameter and 6 in. in length. A 2.4 wt% NaCl brine solution is used to saturate the cores and to displace the oil as the cores are flooded. The brine solution is filtered through a 0.45 μm Millipore membrane and de-aerated. All core floods have been performed at room temperature, including the evacuation and saturation phase of the experimental work. All MEOR cores are incubated for 2 weeks at 37°C after the injection of the microbial system. Control experiments have been performed for each of the oils. The control cores were injected with nutrient only (Medium E + 1% sucrose - no microbes) and incubated at the same temperature and length of time as the MEOR cores.

5.2 Core Flood Apparatus

The core flood apparatus used for all core floods is similar to that used by other researchers[1,2,3] and is shown in Figure 5-1. Milton Roy Slo Speed miniPumps are used for fluid delivery and Temco Floating Piston Accumulators are used to keep fluids separated. The accumulators have a floating piston that enables the injection of microbial solutions and other fluids into the cores while preventing corrosive fluids from contacting the pumps. Nupro pressure relief valves are used on the pump discharges as safety relief. Adjustable Nupro back pressure valves are used to provide back pressure on the cores as needed. All components of the system are connected using 1/8 in. OD nylon tubing with Swagelok connectors. Effluent from the cores is collected at various time intervals in an automated tube collection device (fraction collector). Omega Type T Test Gauges are utilized on both the inlet and outlet of the core. The differential pressure across the core is determined using a Validyne DP15TL differential pressure transducer coupled to a Validyne CD223 digital transducer indicator.

5.3 Core Preparation And Handling

Cores were cut from Berea sandstone blocks and air dried at room temperature for a minimum of 72 h. End plates for the cores were made from brass or stainless steel bar-stock and were used for connection of injection and production lines to the cores. They were then placed in a suitable holder (vise or clamp) with the end plates positioned in preparation for epoxy application. The epoxy (Epoxy Patch made by the Dexter Co.) was prepared as outlined by the manufacturer. Working time of the epoxy was about 20 min.

The end plates were mounted to the cores by applying epoxy along the edges of the plate using a wooden tongue depressor. After the epoxy was allowed to harden for a minimum of 2 h at room temperature, it was wiped with alcohol to ensure the removal of all debris and oils caused by handling. A new batch of epoxy was mixed and applied to the core using a wooden tongue depressor to evenly spread the epoxy over the entire core and edge of the end plates. This

was done with an end-to-end motion over the core. The second coat was applied following the same precautions and guidelines used for the first coat and was allowed to age at room temperature for a minimum of 24 h before proceeding with further core preparation procedures.

5.4 Brine Saturation of Cores

With end plates and connections in place, the core was weighed and the weight recorded as the dry weight of the core (Wd). Care was taken to ensure the surface of the core and the associated connections and hardware were free of debris and any external adhering fluids. The core was then placed in the evacuation/saturation apparatus and evacuation was initiated. Brine solution to be used for saturating the core was prepared, filtered through a 0.45 μm Millipore membrane, and de-aerated.

After the core was saturated by passing a minimum of 10 pore volumes (PV) of brine through the core, the core was weighed and the weight recorded as the initial saturation weight. The saturation procedure continued for a minimum of 3 h or 10 PV throughput, whichever occurred last. The total volume of brine that had passed through the core was recorded.

5.5 Determination of Core Parameters

The core was placed in the core flood apparatus once the saturation procedure had been completed. A back pressure valve was installed on the outlet end of the core and set to apply a minimum constant back pressure of 15 psig against the outlet of the core while flooding. The injection pump was set at a constant rate for the permeability determination procedure. Several time intervals were recorded during the procedure with a minimal 10 pore volumes being pumped through the core. Darcy's law was used to determine the absolute permeability to brine of the core. The core was then re-weighed and if the weight had increased from the initial saturation weight, additional brine was pumped through the core. The core was weighed an additional time and this procedure of pumping brine through the core and re-weighing continued until

the core weight was unchanged after consecutive trials. This final weight was recorded as the saturated core weight (Ww).

After the true saturated weight of the core had been determined, the porosity (ϕ) and PV of each core were determined using the dry (Wd) and saturated weights (Ww) of each core and the dimensions of the core (R = radius of core, L = length of core, ϱb = density of brine). This gives

$$PV = \frac{Ww-Wd}{\varrho b} \qquad \text{and} \qquad \phi = \frac{PV}{\pi R^2 L} \quad . \tag{5-1}$$

5.6 Initial Core Saturation Conditions

Oil was then pumped through each core (oil flood) to establish an initial oil saturation condition in the core. A total throughput of 10 pore volumes (minimum) of oil was pumped through each core to ensure proper oil saturation of the core. After the core had been oil saturated, the oil saturated weight (Wo) was recorded. The initial (connate) water saturation (Swi) and initial (original) oil saturation (Soi) of the cores were determined by material balance (ϱw = water density, ϱo = oil density). This gives

$$Swi = \frac{PV-\frac{Ww-Wo}{\varrho w-\varrho o}}{PV} \qquad \text{and} \qquad Soi = 1-Swi \quad . \tag{5-2}$$

5.7 Waterflood Residual Oil Saturation

The core was then placed in the core flooding apparatus in preparation for waterflooding. Pump rates were set to ensure a 1 to 2 ft/d frontal advance rate in the core. The waterflood continued until no oil was visible in several consecutive collection tubes or at least 10 PV had been injected, whichever occurred last. After the waterflood was completed, the core was

weighed and the weight recorded as the waterflood weight (Wwf). The waterflood residual oil saturation was then determined gravimetrically (see subsection 2.1.6). Waterflood residual oil saturation (Sorwf) was checked by material balance (Swwf = waterflood water saturation). This gives

$$Swwf = \frac{PV - \frac{Ww - Wwf}{\varrho w - \varrho o}}{PV} \quad \text{and} \quad Sorwf = 1 - Swwf \quad . \tag{5-3}$$

5.8 Microbial Flood Residual Oil Saturation

The core was then in a waterflood residual oil saturation condition and ready for injection of microbes. The Bacillus licheniformis JF-2 microbial system was injected into the core by use of a small accumulator (see Figure 5-1). The volume of injected microbes and nutrient was 60% PV for each core.

After the Bacillus licheniformis JF-2 microbial system had been injected into the core, it was placed in incubation for 14 d at 37°C. Any pressure increase in the core during the incubation period was monitored to determine the presence of any microbial gas production.

The core was then placed in the core flood apparatus in preparation for the microbial flood. The core was flooded with filtered and de-aerated brine of the same composition as that used in the earlier waterflood. The brine injection rate was identical to that used for the previous waterflood, and core effluent was collected and handled in the same method as for the waterflood. The microbial flood continued until oil production ceased or until 10 PV of throughput were realized, which ever occurred last. When the microbial flood was completed, the core was weighed and the weight recorded as the microbial flood weight (Wmf). The microbial flood residual oil saturation (Sormf) was then determined gravimetrically (see subsection 2.1.6). The

microbial flood residual oil saturation was checked by material balance, which gives (Swmf = microbial flood water saturation)

$$Swmf = \frac{PV - \frac{Ww - Wmf}{\varrho w - \varrho o}}{PV} \quad \text{and} \quad Sormf = 1 - Swmf \quad . \tag{5-4}$$

5.9 Core Flood Results

The cores used (including the control cores) had fairly consistent porosity values from 21.7 to 23.8%. Permeabilities ranged from a low of 85 md to a high of 510 md with an average for all cores of 216 md. Initial oil saturations varied from 53.3 to 79.3% PV. The MEOR cores averaged 68.6% PV initial oil saturation and the control cores averaged 65.6% PV initial oil saturation. Waterflood residual oil saturations varied from 11.9 to 41.3% PV. The MEOR cores averaged 28.8% PV waterflood residual oil saturation and the control cores averaged 28.9% PV waterflood residual oil saturation.

Of the 11 MEOR core floods, 9 produced oil by microbial injection (see Table 5-1). One of the cores containing Burbank oil (Core 14) and the core containing Soltrol 220 (Core 15) did not produce oil. These were both early tests where microbes may have been poisoned with toluene. Bacillus licheniformis JF-2 has been shown to grow in the presence of either of these oils and the repeat core flood test with Burbank crude did produce oil beyond waterflood with the Bacillus licheniformis JF-2 system. Schuricht, Moorcroft West, Alworth, and Lick Creek produced additional oil beyond waterflood in all cores inoculated with the Bacillus licheniformis JF-2 microbial system. Only Moorcroft West and Lick Creek produced oil from their control core (nutrient only injection).

Plots of brine injection versus residual oil saturation for the MEOR core floods are shown in Figures 5-2 through 5-10. Oil production rate for two core floods, Core 13 (Moorcroft West) and Core 23 (Alworth) lagged that of the other MEOR core floods. The residual oil saturations for these two cores dropped rapidly once 2 to 3 PV of brine were injected. The other MEOR core

Table 5-1. MEOR core flood recovery data[a]

CORE[b]	MICROBE[c]	OIL[d]	VIS (Pa·s)	PERM (md)	Soi (%PV)	Sorwf (%PV)	Sormf (%PV)	MEOR[e] REC (%OOIP)	MEOR[f] REC (%OOIP)	(PV)[g]
15	B L[h]	SOL	0.003	86	57.9	25.9	25.9	0	0	(8)
16[i]	-	SOL	0.003	94	58.6	24.3	24.3	0	0	(9+)
14	B L[h]	BUR	0.006	195	63.2	25.8	25.8	0	0	(9)
22	B L[h]	BUR	0.006	214	65.8	32.6	29.6	4.6	4.6	(12)
20[i]	-	BUR	0.006	323	70.7	34.0	34.0	0	0	(9+)
10	B L[h]	SCH	0.054	267	76.7	33.4	29.9	2.7	4.6	(8)
25	B L[h]	SCH	0.054	85	72.3	39.5	37.9	1.4	2.2	(14.5)
19[i]	-	SCH	0.054	432	64.1	27.0	27.0	0	0	(9+)
12	B L[h]	ALW	0.134	119	72.6	18.6	14.1	4.2	6.2	(9.5)
23	B L[h]	ALW	0.134	311	53.3	11.9	7.7	7.1	7.9	(6.5)
18[i]	-	ALW	0.134	134	66.6	25.5	25.5	0	0	(9+)
13	B L[h]	MOO	0.142	123	78.8	25.6	14.7	9.9	13.8	(15.5)
24	B L[h]	MOO	0.142	115	72.3	39.4	38.3	1.3	1.4	(12)
17[i]	-	MOO	0.142	190	58.9	26.1	23.2	--	4.9	(9+)
11	B L[h]	LIC	0.288	109	79.3	39.2	35.8	2.6	4.3	(9.5)
26	B L[j]	LIC	0.288	359	62.8	22.3	4.2	11.5	28.8	(25)
21[i]	-	LIC	0.288	510	74.7	36.5	33.2	--	4.4	(9+)

a. Core parameters; OOIP = original oil in place, VIS = oil viscosity, PERM = absolute brine permeability of core, Soi = initial oil saturation, Sorwf = waterflood residual oil saturation, Sormf = microbial flood residual oil saturation, PV = pore volume of core.

b. For all core floods, temperature = 23°C and brine = 2.4 wt% NaCl.

c. Bacillus licheniformis JF-2 microbial system.

d. Crude oil type; SOL = Soltrol 220, BUR = Burbank, SCH = Schuricht, AlW = Alworth, MOO = Moorcroft West, LIC = Lick Creek.

e. Oil recovery at six pore volumes of brine injected.

f. Oil recovery with brine injection until oil production ceases.

g. PV of brine injected.

h. Washed cells re-suspended in Medium E + 1% sucrose.

i. Control floods - oil recovery when oil production ceases.

j. Unwashed cells in Medium E + 1% sucrose.

floods tended to have a large reduction in the residual oil saturation earlier in their flood life at about 1 PV of brine injection.

Total recovery data for all oils are plotted as percent of the original oil in place (OOIP) for each core (Figure 5-11). Multiple sets of data are shown for each oil; waterflood recovery for the MEOR cores (Cores A and B), microbial flood recovery for Cores A and B, waterflood recovery for the control core (Core C), and recovery of the nutrient only flood for Core C (control core). Only one MEOR core flood was performed with the Soltrol 220. These cores were flooded with brine until oil production ceased. This was at least 10 PV of brine injection in all cases to obtain a waterflood residual oil saturation condition in the cores. After the waterflood residual oil saturation condition had been obtained, cores were either injected with the MEOR system or injected with nutrient only. The MEOR cores (Cores A and B) were injected with the Bacillus licheniformis JF-2 microbial system and placed in incubation at 37°C for 14 d before the reinstatement of waterflooding. The control cores were injected with nutrient only and placed in incubation at the same temperature and for the same period of time as the MEOR cores. Like the MEOR cores, waterflooding was reinstated when the control cores were removed from incubation. Recoveries for both the MEOR and the control cores can be seen in Figure 5-11. The oil recovery efficiencies for each of the microbial flood cores is presented in Figures 5-12 through 5-20. The recovery efficiency for the microbial floods is defined as the fraction of waterflood residual oil that is recovered by the microbial flood. The recovery efficiencies for the microbial floods are plotted for 10 PV of injection, although many of the microbial floods exceeded the 10 PV of throughput for the microbial flood.

Core 26 (Lick Creek oil) produced more microbial oil than the others, 28.8% OOIP or 81.2% of the waterflood residual oil. This was the only core inoculated with unwashed Bacillus licheniformis JF-2 cells. The injectant included the bioproducts produced during the aerobic growth process outside the core in addition to the cells. As a direct comparison, Core 11 (also with Lick Creek oil) using washed and resuspended cells, produced 4.3% OOIP (8.7% of waterflood residual oil). As discussed in Section 4, the supernatant is capable of significantly reducing the interfacial tension between the aqueous

phase and crude oil. All other cores were inoculated with washed Bacillus licheniformis JF-2 cells resuspended in fresh Medium E + 1% sucrose.

5.10 Future Experimental Work

The reason for the observed variation in microbial oil recovery with oil type will be investigated further. Additional core floods and other experimental work such as interfacial tension measurements will be performed to evaluate the variation in oil recovery with oil type. More experimental data points are needed before any definitive correlation of oil recovery with oil type can be made.

An additional series of core flood experiments have been initiated that utilize injection of only bioproducts of Bacillus licheniformis JF-2. These core floods will be used to investigate the recovery of waterflood residual oil with the injection of bioproducts followed by waterflood. Four crude oils ranging in gravity from 19.1 to 38.1°API at 60°F will be utilized in these experiments.

5.11 Conclusions

Based on the core flood experimental work performed, the following conclusions can be made.

1. The waterflooding characteristics of Berea sandstone vary for the different oil tested. This may indicate that different wettability characteristics are being established in the Berea cores because of the differences in oil properties of the various oils.

2. The Bacillus licheniformis JF-2 system used will recover waterflood residual oil for the crude oils tested. It appears to be less effective for the higher gravity crude oils, although oil recovery has been seen with all oils tested with the exception of Soltrol 220, which is thought to be a bad test.

3. Control experiments are critical to separate the effects of the microbial system from other displacement effects.

4. The difference in oil recovery from cores injected with unwashed cells compared to those injected with washed cells of the Bacillus licheniformis JF-2 system is very significant, 28.8% OOIP as compared to 4.3% OOIP (Cores 11 and 26).

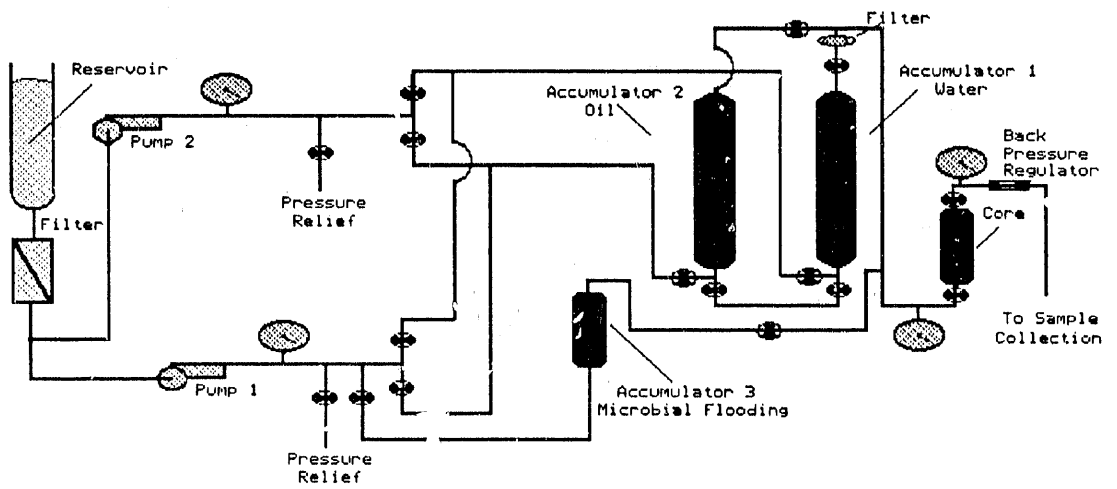

Figure 5-1. Core flood apparatus.

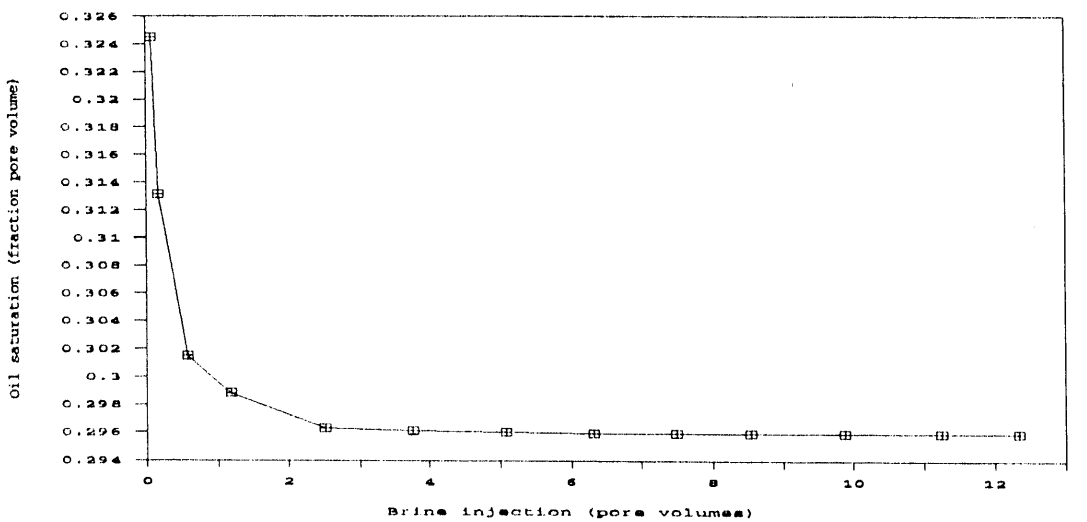

Figure 5-2. Microbial flood oil recovery - Burbank oil - Core 22.

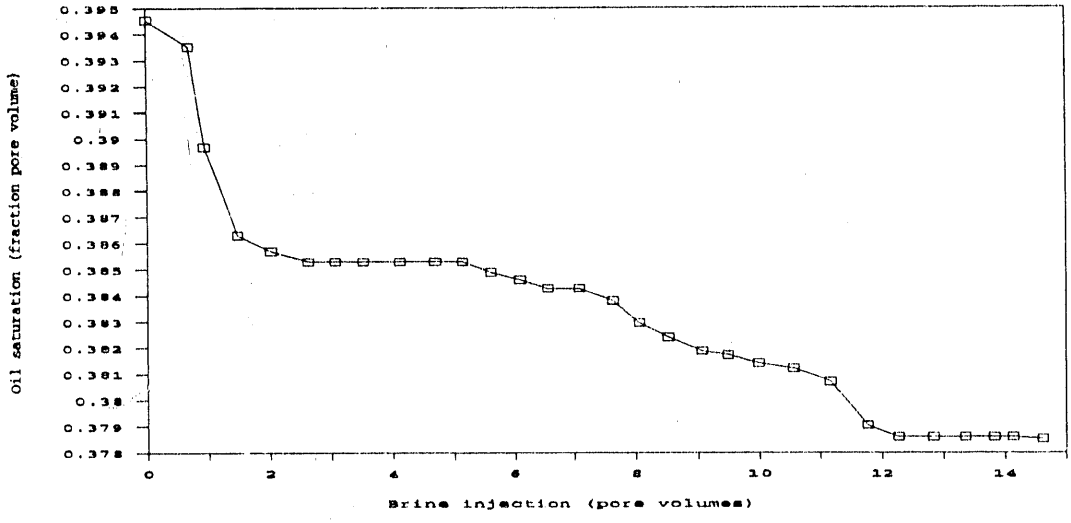

Figure 5-3. Microbial flood oil recovery - Schuricht oil - Core 25.

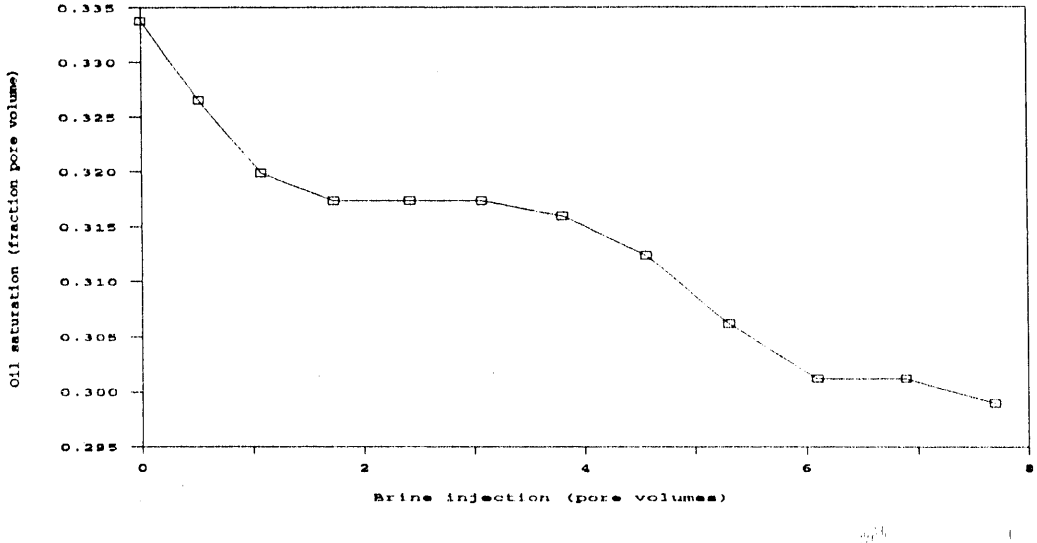

Figure 5-4. Microbial flood oil recovery - Schuricht oil - Core 10.

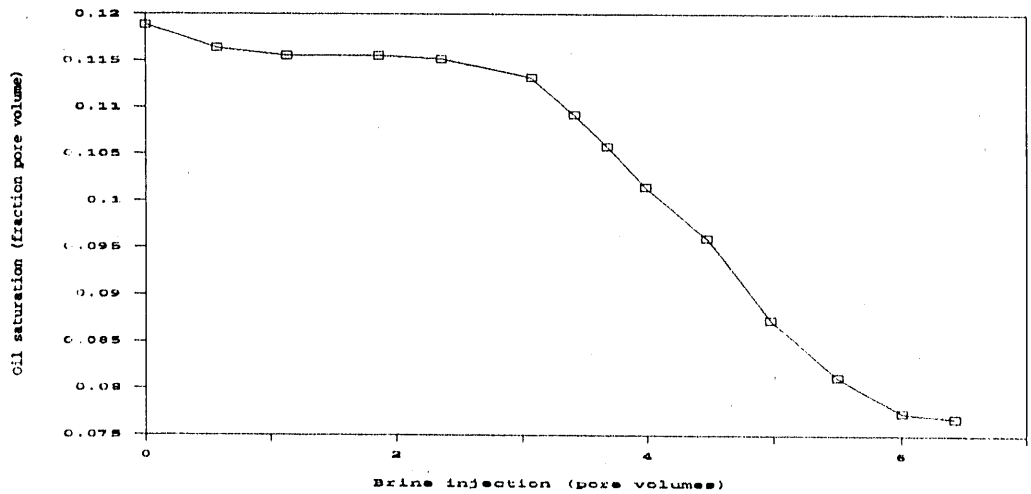

Figure 5-5. Microbial flood oil recovery - Alworth oil - Core 23.

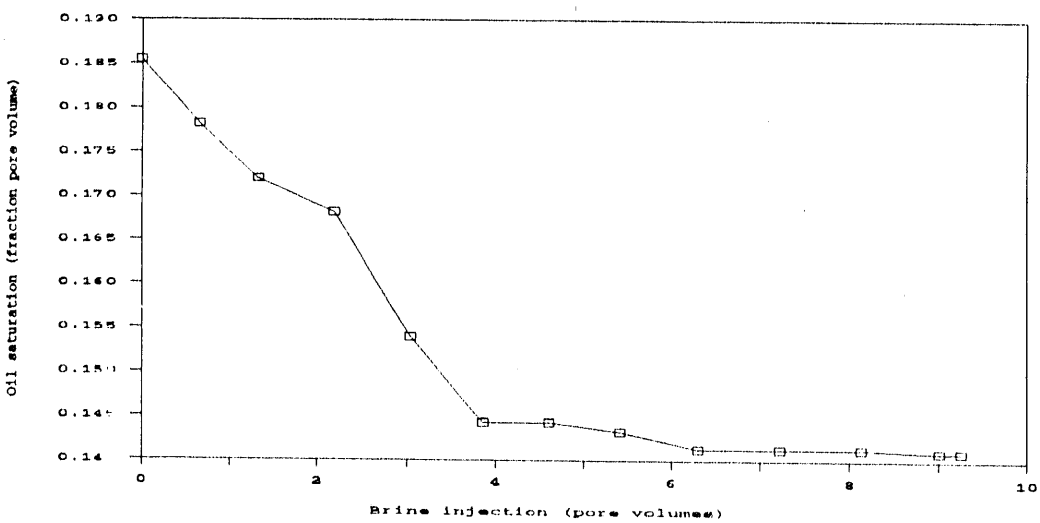

Figure 5-6. Microbial flood oil recovery - Alworth oil - Core 12.

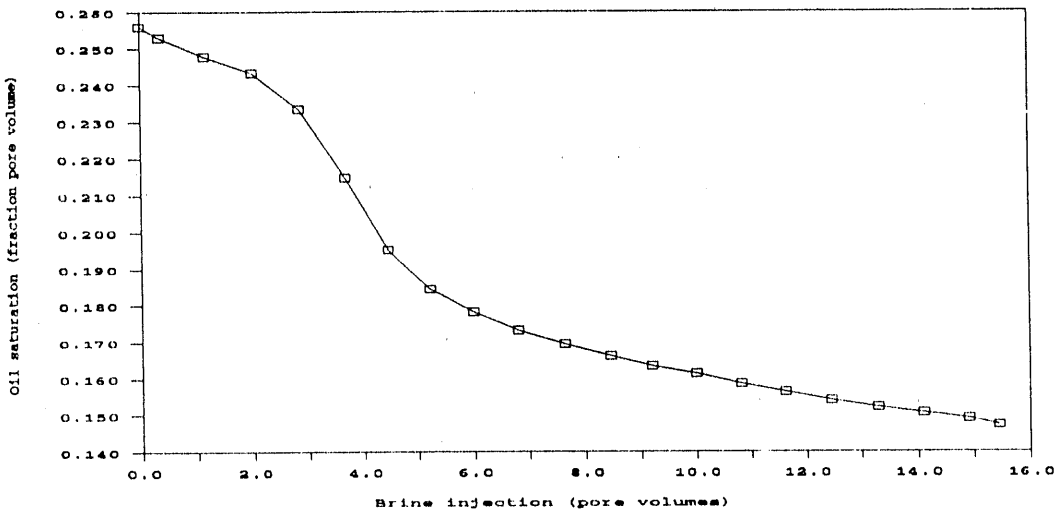

Figure 5-7. Microbial flood oil recovery - Moorcroft West oil - Core 13.

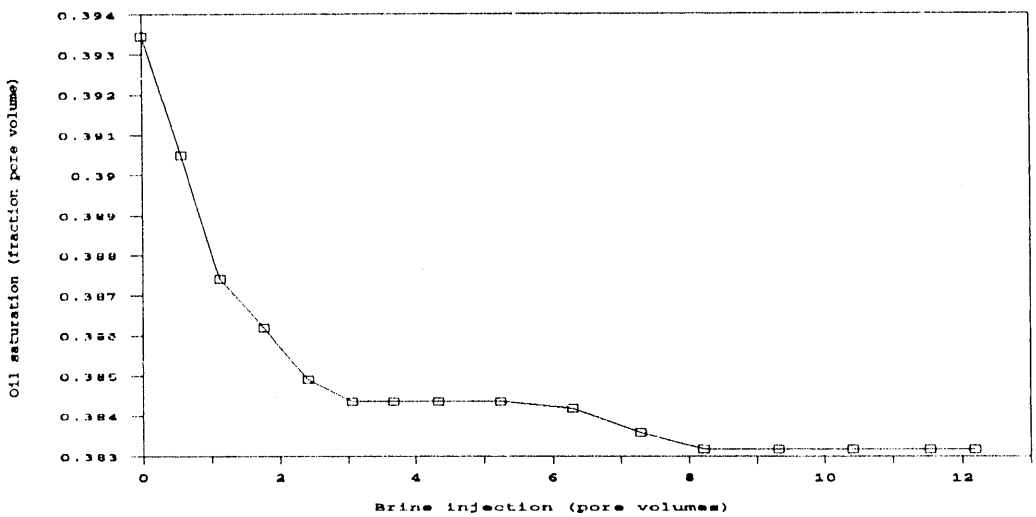

Figure 5-8. Microbial flood oil recovery - Moorcroft West oil - Core 24.

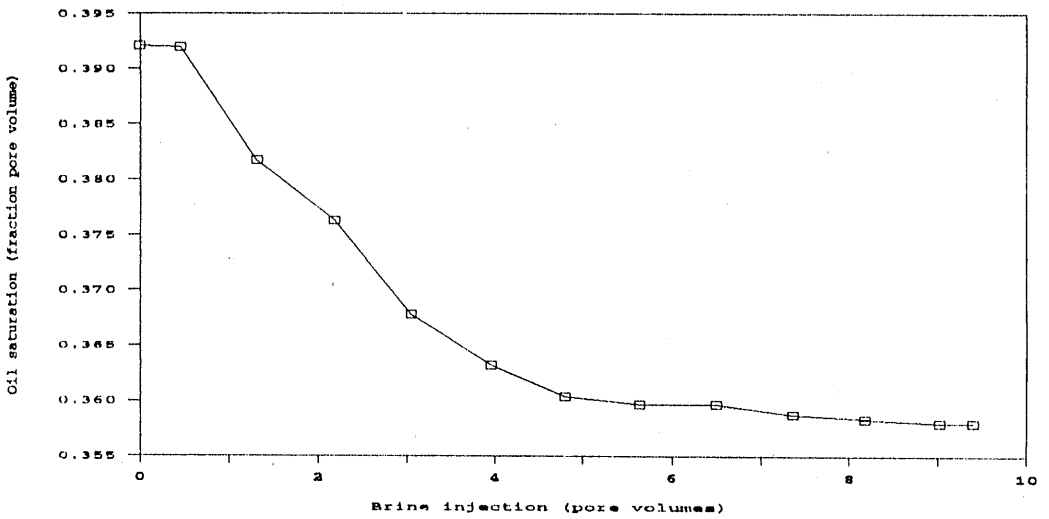

Figure 5-9. Microbial flood oil recovery - Lick Creek oil - Core 11.

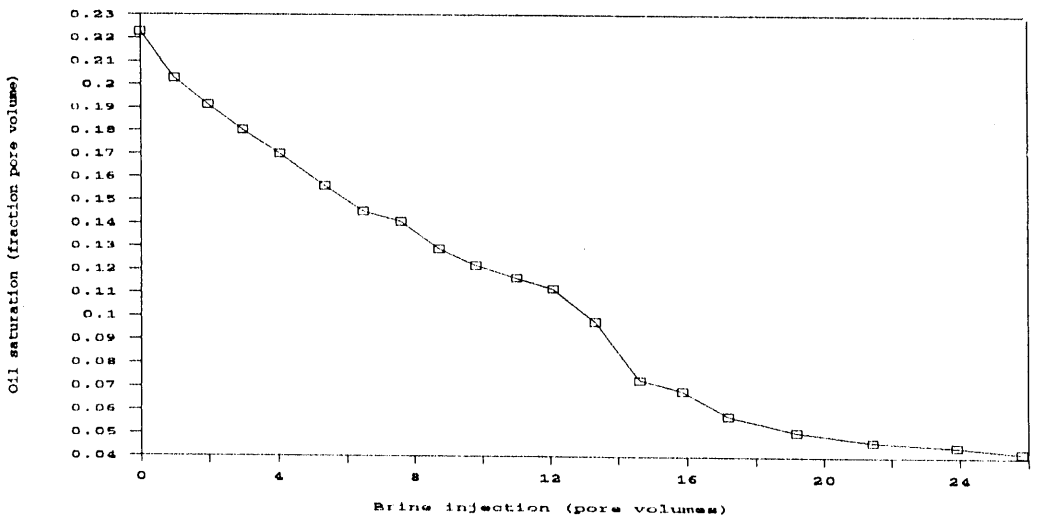

Figure 5-10. Microbial flood oil recovery - Lick Creek oil - Core 26.

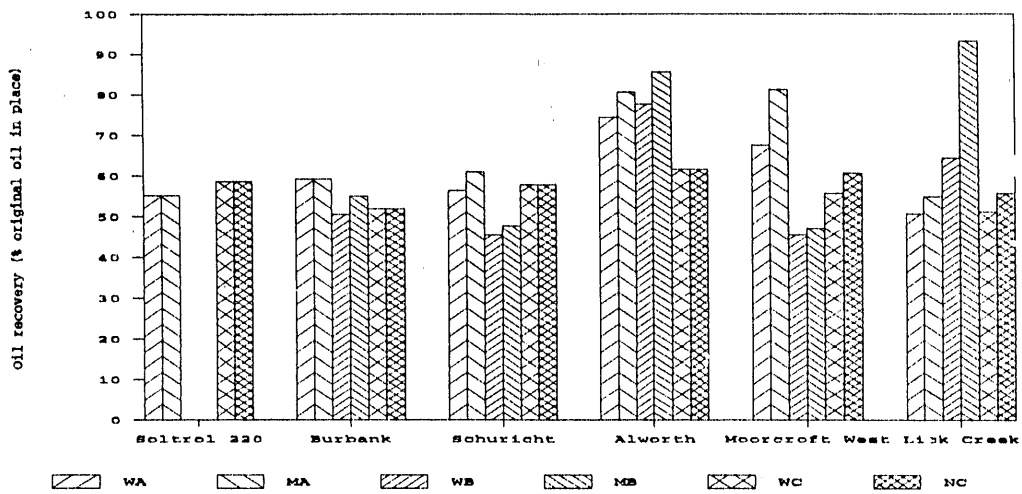

Figure 5-11. Core flood total oil recovery for all oils. (W = waterflood, M = microbial flood , N = nutrient flood, A = first core, B = second core, C = third core - control).

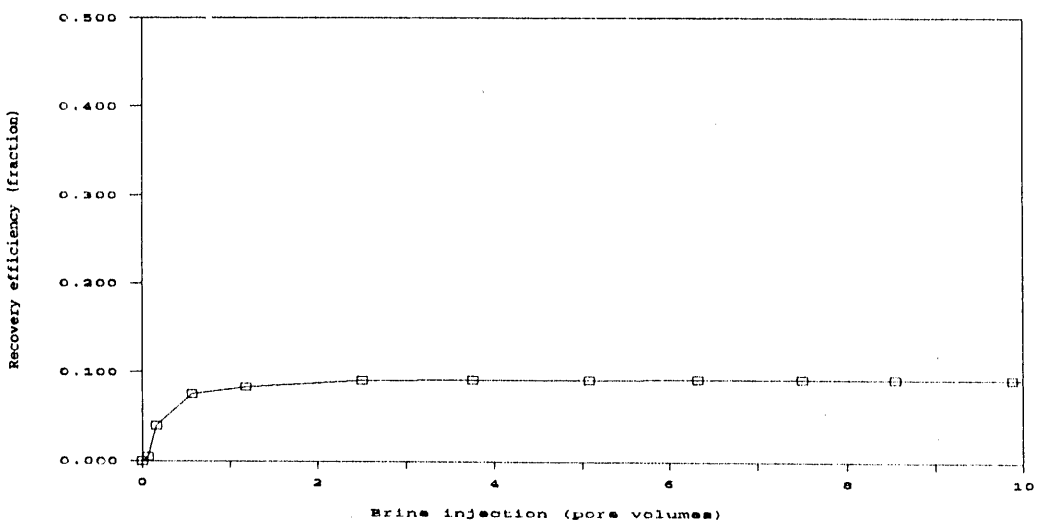

Figure 5-12. Recovery efficiency - Burbank oil - Core 22.

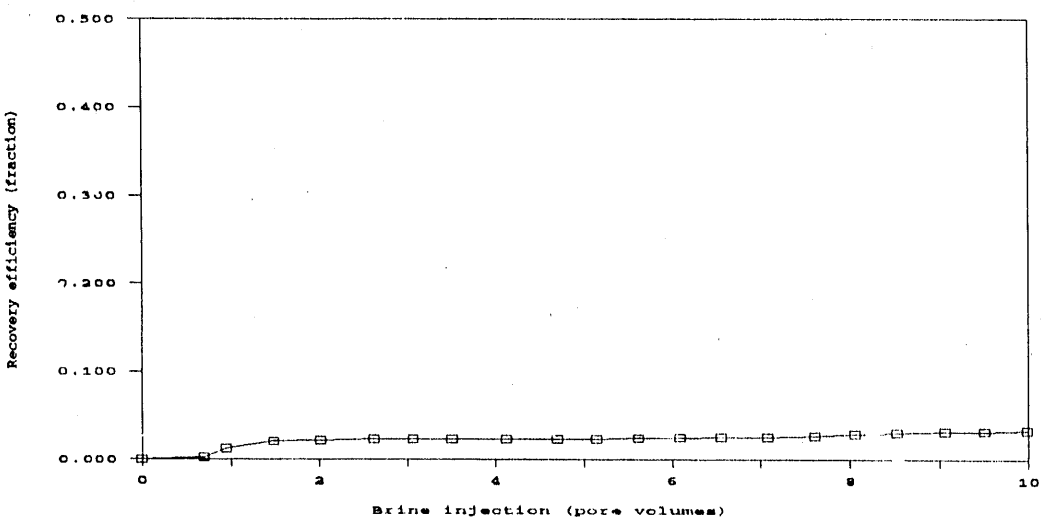

Figure 5-13. Recovery efficiency - Schuricht oil - Core 25.

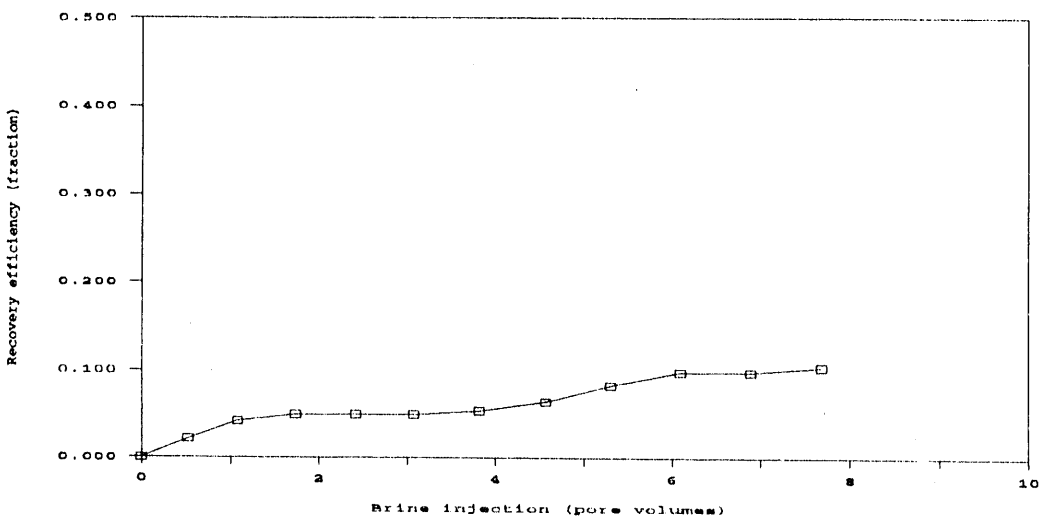

Figure 5-14. Recovery efficiency - Schuricht oil - Core 10.

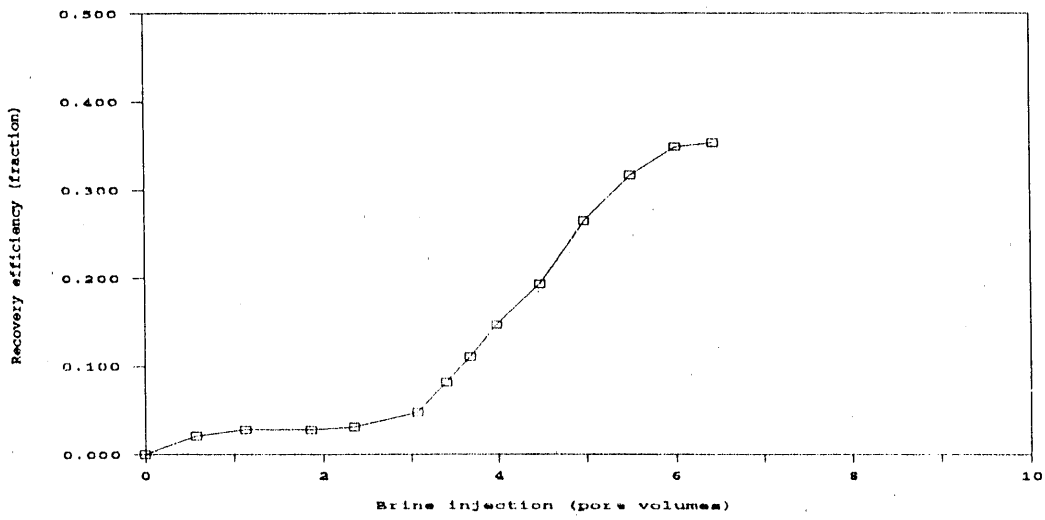

Figure 5-15. Recovery efficiency - Alworth oil - Core 23.

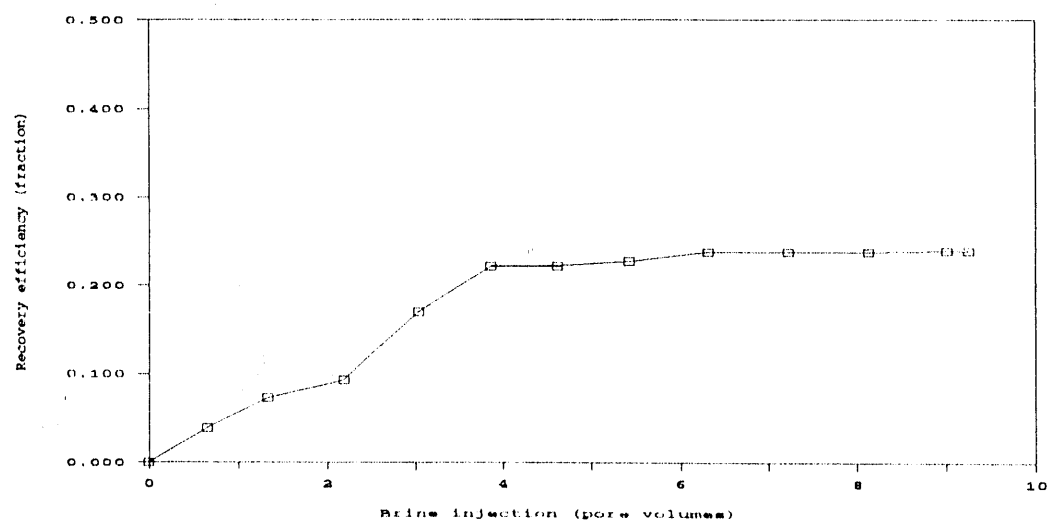

Figure 5-16. Recovery efficiency - Alworth oil - Core 12.

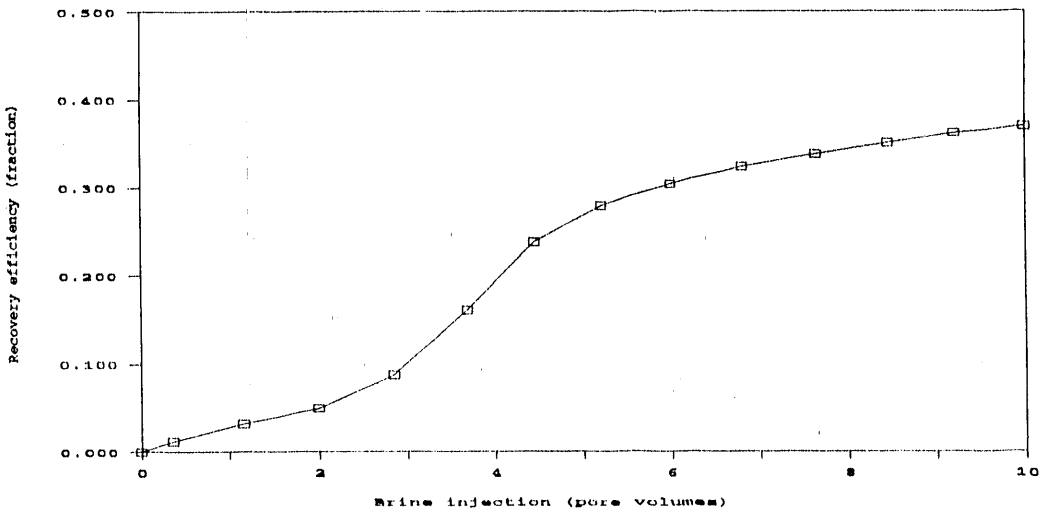

Figure 5-17. Recovery efficiency - Moorcroft West oil - Core 13.

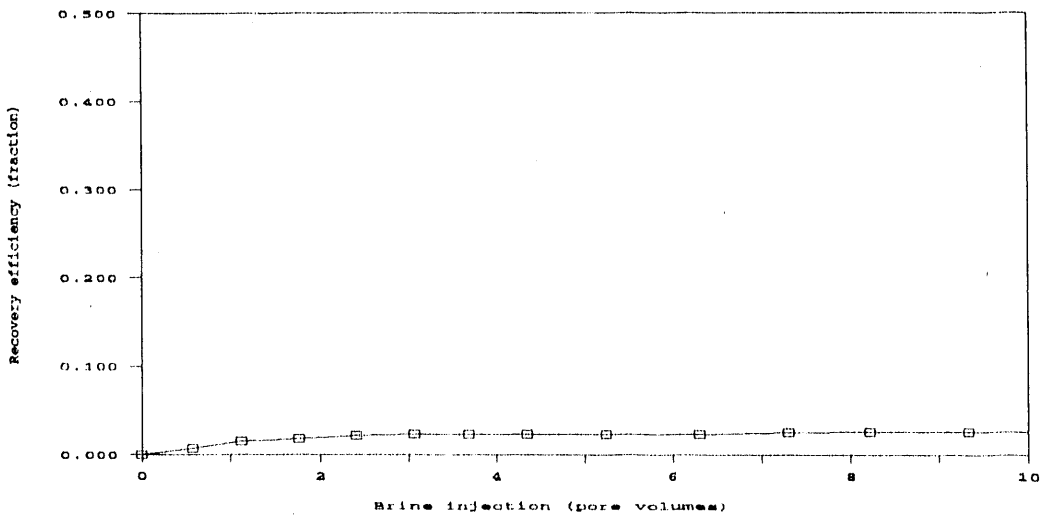

Figure 5-18. Recovery efficiency - Moorcroft West oil - Core 24.

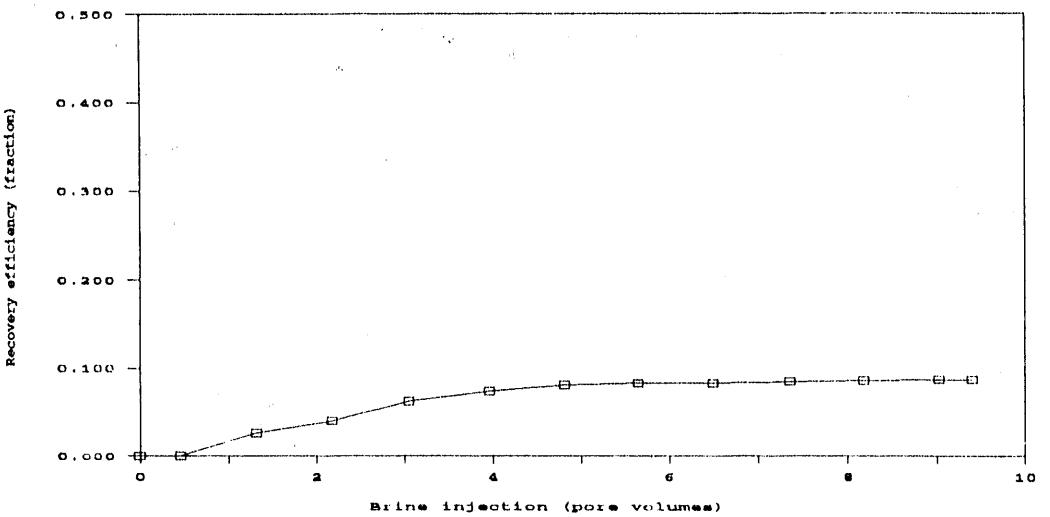

Figure 5-19. Recovery efficiency - Lick Creek oil - Core 11.

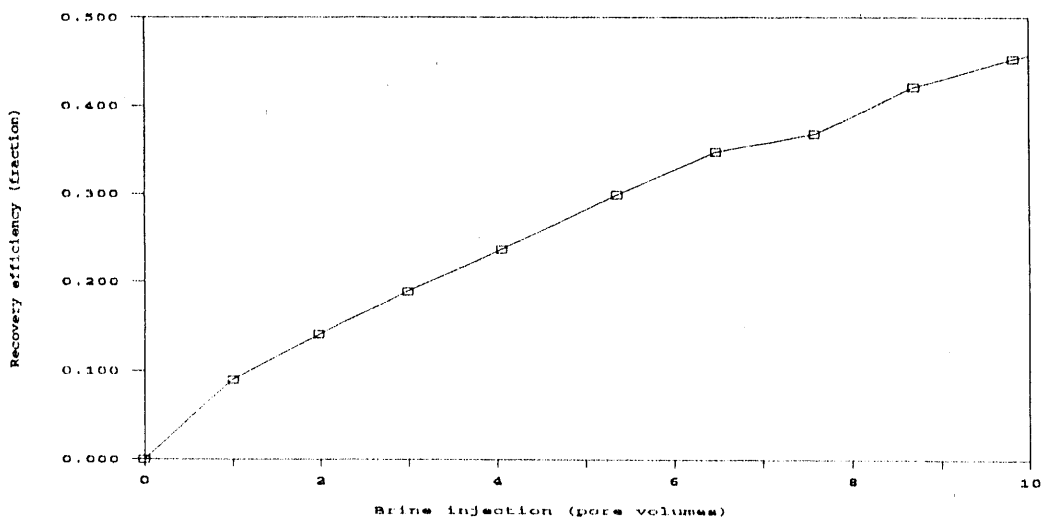

Figure 5-20. Recovery efficiency - Lick Creek oil - Core 26.

5.12 REFERENCES

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2. R. M. Knapp, M. J. McInerney, D. E. Menzie, J. L. Chisholm, Microbial Field Pilot Study - Quarterly Technical Progress Report for the Period March 1, 1989 - June 30, 1989, DOE/BC/14246--T2, July 1989.

3. D. Jia, J. S. Buckley, and N. R. Morrow, "Control of Core Wettability with Crude Oil," Society of Petroleum Engineers International Symposium on Oilfield Chemistry, Anaheim, California, February 20-22, 1991, SPE 21041.

6. TARGET RESERVOIR SELECTION

The guidance received in early 1989 for the EOR and Applied Geoscience Research Program at the INEL was to investigate the application of MEOR to reservoirs containing medium to heavy crude oils in the 12 to 20°API gravity range. Dwight's Energydata database was used to review existing field data in search of fields that contain medium to heavy oils that fit the published criteria[1] for MEOR field applications (see Table 6-1).

Table 6-1. Criteria for reservoir selection for MEOR processes[a]

Total dissolved solids in brine (ppm)	<100,000
Usual reservoir temperatures (°F)	<160
Usual reservoir depths (ft)	<10,000
Residual oil saturation (%)	>25 to 30
Usual brine permeability (md)	>100

a. From Bryant and Burchfield, 1989.[1]

The states of Colorado, Montana, North Dakota, Utah, New Mexico (northern) and Wyoming were searched using an API gravity cut-off of >10° and <22°. These states were chosen because they are all oil producing states within reasonable proximity to the INEL. Having target reservoirs in relative close proximity to the INEL improves ease of accessibility and decreases travel expenses for field fluid sampling and data collection.

The database search of these six states revealed that Wyoming had the largest number of reservoirs with oil in this API gravity range. Numerous reservoirs with appropriate API gravities were found in the Powder River Basin of

Wyoming. Most of the Powder River Basin reservoirs were in the Minnelusa formation with a few in the Tensleep formation.

6.1 Candidate Reservoir Selection For Focus Of MEOR Research

Several operators of Minnelusa and Tensleep Formation fields in the Powder River Basin of Wyoming were contacted. Home Petroleum Corporation and KSL Enterprises, Inc. were both willing to allow sample collection and to cooperate in a study of their reservoirs for potential MEOR application. During this initial stage of MEOR research and process design, operator cooperation is critical to ensure field availability and accessibility for fluid sampling and field and reservoir data collection. Six Minnelusa fields were initially chosen for field fluid sample collection based on operator cooperation and field accessibility. These reservoirs were also screened using reservoir and field data to determine if they contained sufficient residual oil and were viable candidates for application of MEOR technology.

Based on the screening results, three fields in the Powder River Basin, Wyoming were selected as candidates for focus of MEOR research at the INEL. These reservoirs, South Rozet Unit (Section 25-50N-70W, Campbell County, Wyoming), Moorcroft West Unit (Section 12-51N-68W, Crook County, Wyoming), and the Schuricht Lease (Section 24-52N-68W, Crook County, Wyoming) all produce from the Minnelusa formation. When field and reservoir data were obtained and analyzed on these fields, the South Rozet Unit was dropped as a current target reservoir for focus of MEOR research at the INEL. This decision was made because of the 80°C reservoir temperature that may be too high for MEOR applications. During this time period, the South Rozet Unit was also sold and a new operator took over operation of the field. Work continues to determine if Moorcroft West and Schuricht are viable targets for focus of MEOR research and process application.

These two fields provide the opportunity to study and evaluate reservoirs in two stages of depletion. The reported API gravities in Dwight's Energydata database for the crude oils from these fields are below the 22°API gravity

cut-off. Produced fluid samples have been obtained from these fields. The API gravities measured on the crude oil samples are 25.4°API at 60°F for the Schuricht Lease (primary recovery) and 22.3°API at 60°F for the Moorcroft West Unit (waterflood/polymer-augmented waterflood). Produced water quantities at the Schuricht lease are minimal and a sample could not be obtained. The viscosity measurements for the crude oils and brines at temperatures ranging from room temperature to reservoir temperature are shown in Figures 6-1 through 6-3, 2-11, and 2-12. Viscosity data are included for the South Rozet Unit for comparative purposes since it is located in the middle of the Minnelusa trend at a greater depth (about 8000 ft). Analysis of the produced brine and injection water from the Moorcroft West Unit and the South Rozet Unit are shown in Tables 6-2 and 6-3.

Table 6-2. Produced water analysis

Field	Moorcroft West Unit	South Rozet Unit
Operator	KSL Enterprises, Inc.	Home Petroleum Corp.
County, State	Crook County, Wyoming	Campbell County, Wyoming
Location	Section 12-51N-68W	Section 25-50N-70W
Producing Formation	Minnelusa "A"	Minnelusa "B"
Approximate Depth (ft)	5900 subsurface	8000 subsurface
Sample Point	Texas Trail #1 wellhead	Heater Treater wells 3&4
pH	6.7	7.3
TDS (mg/L)	46,000	134,000
Na (ppm)	15,000	51,000
Ca (ppm)	1320	1370
Mg (ppm)	625	448
Ba (ppm)	0	0
Fe (ppm)	0	0
Cl (ppm)	23,800	78,200
SO_4 (ppm)	1800	2650

Table 6-3. Injection water analysis

Field	Moorcroft West Unit	South Rozet Unit
Operator	KSL Enterprises, Inc.	Home Petroleum Corp.
County, State	Crook County, Wyoming	Campbell County, Wyoming
Location	Section 12-51N-68W	Section 25-50N-70W
Producing Formation	Unknown shallow sand	Foxhills
Approximate Depth (ft)	200 subsurface	3500 subsurface
Sample Point	Wellhead	Wellhead
pH	7.3	8.4
TDS (mg/L)	366	800
Na (ppm)	93.0	301
Ca (ppm)	31.3	1.7
Mg (ppm)	14.6	0.04
K (ppm)	5.4	1.6
Fe (ppm)	0	0
Cl (ppm)	1.94	19.4
SO_4 (ppm)	101	107

6.2 Analysis of Schuricht and Moorcroft West Crude Oils

Oils have been analyzed with open column liquid chromatography (LC) for separation and quantification of the paraffinic, aromatic, non-pentane precipitable asphaltics, and pentane precipitable asphaltics. Component fractions from this procedure were analyzed with gas chromatography (GC). A de-asphalnated (pentane precipitable) sample of Schuricht was also analyzed by coupled gas chromatography/mass spectroscopy (GC/MS). Data resulting from the crude oil analyses are presented in Section 2. of this report.

6.3 The Powder River Basin, Wyoming

The Powder River Basin is the second largest structural basin in the Rocky Mountain Structural Province. It includes the Northeastern quarter of Wyoming and a small portion of Southeastern Montana. The Basin is bounded structurally and topographically on the east by the broad asymmetric arch of the Black Hills and on the west by the Big Horn Mountains. The northern

Laramie Range and the structural Hartville uplift lie to the south. The northern limit of the Powder River Basin is less defined, but may logically be placed at the south flank of the broad, north-trending arch separating the Sheep Mountain syncline from the Tongue River syncline (see Figure 6-4).[2] It is a deep, asymmetric, elongated, syncline about 230 mi long and 100 mi wide.

6.4 The Minnelusa Formation

The Minnelusa formation lies in the northeastern portion of the Powder River Basin east of Gillette, WY. The formation outcrops in the Black Hills at Rapid River above Rapid City, SD.[3]

The first well in the Minnelusa having commercial significance was completed in 1957. Exploration for additional Minnelusa discoveries has continued into the 1990s with an extremely high increase in exploration activities with the higher oil prices of the early 1980s. Most of the larger Minnelusa reservoirs were discovered in the earlier phase of Minnelusa exploration, during the 1960s, but numerous smaller discoveries have continued into the 1990s. The original oil in place for the Minnelusa in the Powder river Basin has been estimated at 629 million barrels.[4] With the increased Minnelusa exploration activities starting in the early 1980s and the high degree of acceptance of EOR technology by independent oil producers operating in the Basin, an updated assessment of the remaining primary, secondary, and tertiary reserves is needed.

The Minnelusa formation is comprised predominantly of a white crystalline sandstone containing little clay and is loosely cemented by carbonate and anhydrite. The formation is of Pennsylvanian and Lower Permian age and is entirely marine in origin with the possible exception of the lower basal Bell Sandstone. The upper portion of the Minnelusa formation (Upper Minnelusa) usually contains two producing zones (A and B) and a third major sand (C) which is usually nonproductive and frequently wet.[5,6] A generalized stratigraphic column of the northeastern portion of the Powder River Basin is shown in Figure 6-5 and type logs of the Minnelusa are shown in Figure 6-6.

The C sand is separated from the B sand by alternating intervals of dolomites and anhydrites. The most predominant of the two producing zones is the B sand which generally thins from the southwest to the northeast. The A sand (which is the upper bench) generally thins from the south to the north and from the west to the east.

The Upper Minnelusa consists of shallow marine sandstone, carbonates, and evaporites and the top zone is an erosion surface overlain by impervious red shale of the Opeche formation. A variety of trapping mechanisms exist in the Minnelusa including permeability barriers within the sand lenses, truncation by pre-Opeche erosion, structural closure, and sand wedge-out against older topographic highs. Most of the active fields show both truncation and differential sand deposition on an uneven existing topography.[4,7]

During Minnelusa time, open sea existed to the southeast. The Minnelusa sediments in the Powder River Basin indicate a more restricted marine environment. Sandstones in the Upper Minnelusa can be 100 ft thick and topographic relief of up to 75 ft is common at unconformities. Lithology indicates a sandstone capped by dolomites and anhydrites. These caps are harder than the underlying sandstones and the caps are generally more resistant to erosion than the underlying sandstones. Decrease in interval thickness is usually caused by erosion at the top of the Minnelusa. The Minnelusa dips about 5 ft/mi with regard to the Minnelusa surface and is essentially flat at the unconformity surface.[4]

At the end of Minnelusa time, the entire region was sub-aerially exposed and subjected to erosion. Subsequently, the Opeche sea invaded the area, and deposition continued until Laramide time. Paleotopography developed on the Upper Minnelusa unconformities reflects thick intervals in the overlying Opeche Shale representing valleys in the Upper Minnelusa and thins in the Opeche representing hills in the Upper Minnelusa.

Lithologically, the Upper Minnelusa consists of hard dolomite-anhydrite, alternating with softer sandstones with the practically flat bedding at unconformities indicating essentially a mesa or tableland topography (see

Figure 6-7). The hills are remnants of erosion resistant caprocks, while the valleys are usually eroded into the softer sandstones.[4] In the eastern portion of the area, paleo-highs or hills tend to be relatively small and isolated within broad topographic depressions. A decrease in intensity of relief is seen from east to north and west. The long axes of these hills or mesas tend to be oriented to the northeast or to the northwest. To the west, the paleo-hills merge into larger elevated areas and the valleys become better defined. The northwest-southeast orientation of the long axes of the hills appears to be more prevalent in the western portion than in the east.

A north-south line separates the strongly dissected eastern portion from the lesser dissected western portion. About 85% of the 600 plus million barrels of Minnelusa oil in place (1971 data) has been found in the eastern portion.[4] Erosion apparently proceeded westward and northward until the Opeche sea started to invade the Minnelusa surface. It is not known whether post-Minnelusa topography was produced by water or wind erosion. The Permian period was very arid and wide shallow depressions and isolated hills in the eastern portion make it difficult to place these features within a logical drainage system. This (with the presumably arid climate) may point to the presence of a desert-type of erosion cycle during the late Upper Minnelusa time. Most Minnelusa accumulations occur on the updip or northeast side of the paleo-highs that tend to be orientated in a northwest-southeast or northeast-southwest direction.

6.5 Minnelusa Reservoir Characteristics

In a study of Minnelusa reservoirs, average values were determined for the reservoir characteristics of these fields and are listed in Table 6-4.[8]

Primary recovery averages 11% of the original oil in place (OOIP).[8] Because of the dead oil and low gas/oil ratios, recovery because of solution gas drive is limited. The primary production mechanism is fluid expansion. Original oil-in-place is usually difficult to estimate and experience in determining this value shows the estimate to be low in many cases.[9]

Table 6-4. Average reservoir characteristics of Minnelusa reservoirs[a]

Average reservoir permeability (md)	50 - 657
Porosity (%)	16.2
Dykstra-Parsons permeability coefficient	0.75
Connate water saturation (%)	25.5
Pay thickness (ft)	29.3
API gravity	18° to 40°API
Initial formation volume factor (bbl/STB)	1.087
Solution gas/oil ratio (ft^3/bbl)	61.5
Oil viscosity at reservoir temperature (cp)	3.6 to 38 (average 15.2 cp)
Produced water chloride content (mg/L)	2000 to 200,000

a. After Mack and Duvall, 1984.[8]

Secondary recovery operations are usually initiated early in reservoir life and are very successful because reservoir fill-up is small caused by low primary recoveries. Response to injection usually occurs soon after the initiation of water injection. Because of reservoir heterogeneity and fairly viscous crude oils (average mobility ratio of 9.9), polymer-augmented waterflooding technology is a natural fit for improving ultimate recoveries from these reservoirs through sweep improvement technology. Polymer-augmented waterflooding technology has been accepted and incorporated in the exploitation profile of most Minnelusa reservoirs to maximize ultimate recoveries.[9]

6.6 The Schuricht Lease

Of the three fields that were initially considered for focus of the MEOR research, the Schuricht Lease is in the earliest stages of exploitation. Schuricht Well 21-24, completed in December 1983, is the only well in the reservoir and is presently under primary recovery. Schuricht Well 21-24 produces from the Minnelusa A sand at 6500 to 6508 ft subsurface. The

Schuricht is about 15 mi north of Moorcroft, WY and is in the northeastern corner of the Minnelusa trend.

The Schuricht Lease has potential for additional well locations and to date, primary production has been low. No associated gas or active water drive is present in this reservoir and to date, no water has been produced. Reservoir temperature is estimated at 130°F. The Schuricht is presently being pumped 2 to 3 d/week and is producing about 90 BOPM (barrels oil per month). Existing reservoir data on this field is limited and the full reservoir potential has not been defined.

The Schuricht Lease provides an ideal opportunity to drill a well in an effort to obtain reservoir rock and indigenous microbes from the reservoir. This would be the second well in the reservoir and would make it possible to sample a previously unperturbed region of the reservoir.

6.7 The Moorcroft West Unit

The Moorcroft West Unit was discovered in February 1983 and is located in Crook County, WY south (3-4 mi) of the Schuricht Lease. There is one producing well and one injection well in the reservoir. Water injection began in April of 1989 and a polymer-augmented waterflood was initiated in November of that year. Production is 40 BOPD from the Minnelusa A sand at 5890 ft subsurface with an average thickness of 8.43 ft. Injection is into the Evans 1 at 60 bpd water/polymer with a surface injection pressure of 1000 psig. Primary production from this reservoir was low (about 6% of the original oil in place) and field production had dropped to about 3 BOPD before initiation of water injection. There is very little associated gas and no apparent active water drive in this reservoir. Water has been produced from the Moorcroft West Unit (trace) but, so far there is no evidence of injection fluid breakthrough. There is potential for drilling an additional production well in the Moorcroft West Unit.

The primary producing mechanism in the Moorcroft West Unit is rock and fluid

expansion and the original oil in place (OOIP) has been estimated at 508,485 stock tank barrels of oil (STBO). No water/oil contact is evident in either well. The porosity and water saturation for the reservoir as determined from log calculations is 15.2 and 28.1%, respectively.[10] Permeability for the field is 114 md and reservoir temperature is 120°F.

Ultimate recovery from the polymer-augmented waterflood has been estimated to be 109,112 STBO or 21.5% OOIP. Alkaline-Surfactant-Polymer (A-S-P) technology is planned at the conclusion of the polymer-augmented water flood. The A-S-P technology is predicted to increase ultimate recovery to 117,096 STBO or 23.0% OOIP.[10]

The reservoir trends northeast-southwest and the hydrocarbon trapping mechanism is controlled by stratigraphy. It appears that the reservoir is bounded to the northeast and southwest by truncation of the permeable sand and subsequent in-filling by the Opeche Shale.[10] The sand pinches out to the southeast and is also thought to pinch out to the northwest.

6.8 Future Work

The Moorcroft West Unit or the Schuricht Lease will be chosen as the target reservoir for research and field application of MEOR technology unless they are found to be unacceptable for technical or other reasons. Operator cooperation and willingness is critical to the application of MEOR technology through a field demonstration project.

Geological, biological, chemical, and engineering data will be analyzed for the target reservoir. Characterization and quantification of reservoir heterogeneity and permeability variation will be determined. This will provide the basis for design of the anticipated MEOR pilot field test.

Gathering of additional field and reservoir data and characterization of the candidate reservoirs will continue. A testing and evaluation program developed in cooperation with the operators of the candidate reservoirs will

be designed and implemented to supplement the existing geological profile. Additional reservoir evaluation testing programs will be designed and implemented as necessary to obtain needed data for the selection of a target reservoir for application of the developed MEOR process design.

In a cost-sharing arrangement with the operator, a new well will be drilled in the target reservoir to obtain reservoir rock and indigenous microbes from a previously unperturbed area of the reservoir. The reservoir core will be used to test, optimize, and scale developed MEOR systems through the use of laboratory core floods at reservoir conditions. Samples of reservoir fluids from an un-swept region of the reservoir can possibly be collected from this new wellbore. Core analysis work will provide needed rock and fluid properties of the target reservoir and will be used in the field process design of the pilot and demonstration field tests.

A study to determine the MEOR potential for the target reservoir type and region will be performed. This study will provide an evaluation of potential MEOR reserves and an economic evaluation of the developed MEOR process design and EOR potential for fields of the target reservoir type. This may require that a limited number of laboratory experiments with other applicable EOR techniques be performed for comparison purposes unless such data can be obtained from other sources. The investigation of the potential use of MEOR processes in combination with other EOR techniques may lead to the application with or following existing EOR field projects.

6.9 Summary and Conclusions

Waterflooding is a common and long-standing successful practice for increasing oil recovery in the Powder River Basin and especially in the Minnelusa formation. Polymer-augmented waterflooding is the most common EOR technology in use in the Minnelusa. The Powder River Basin is an area that has a significant and successful history of EOR technology application and is primarily operated by independent producers who appear willing and eager to cooperate in the application of EOR technology.

It was determined that the Minnelusa formation in the Powder River Basin of Northeastern WY contained many good candidates for EOR processes.[8] The primary recovery in these reservoirs is generally low because of heterogeneity of reservoirs and the oil viscosity. Operators (mostly independents) in the area are familiar with the application of polymer technology in conjunction with or following waterflooding and are, therefore, receptive to EOR technology.[9]

The Moorcroft West Unit and the Schuricht Lease have been chosen for focus of laboratory MEOR research at the INEL based on known reservoir characteristics, field availability and accessibility, field fluid sample analysis, and operator cooperation. These fields will also be considered as possible candidates for field application of an MEOR process. Both produce from the Minnelusa formation (A sand) and are located in the Powder River Basin, WY. From available reservoir, field, and fluid data, both fit the published criteria of reservoir selection for MEOR processes.[1] These reservoirs are small confined reservoirs that provide ideal pilot testing opportunities because there would be minimal opportunity for off pattern operations to influence interpretation of results.

The MEOR research using Upper Minnelusa Reservoirs (Lower Permian - Pennsylvanian age) should be easily transferred to application in other sands of the same age and character such as the Tensleep and Leo sands of the Powder River and Big Horn Basins of WY.[2,3,5] With cross-cutting technology such as MEOR, transition of the technology to other sandstone reservoirs that fit the criteria for MEOR application should be achievable.

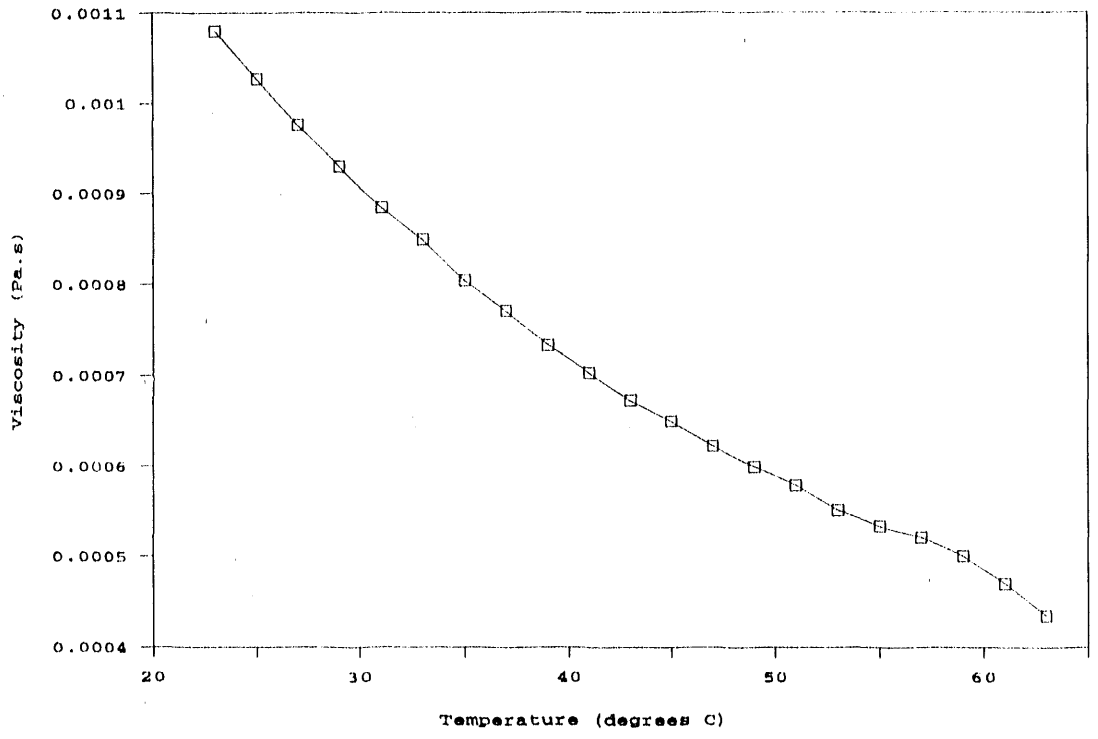

Figure 6-1. Produced brine viscosity - Moorcroft West Unit.

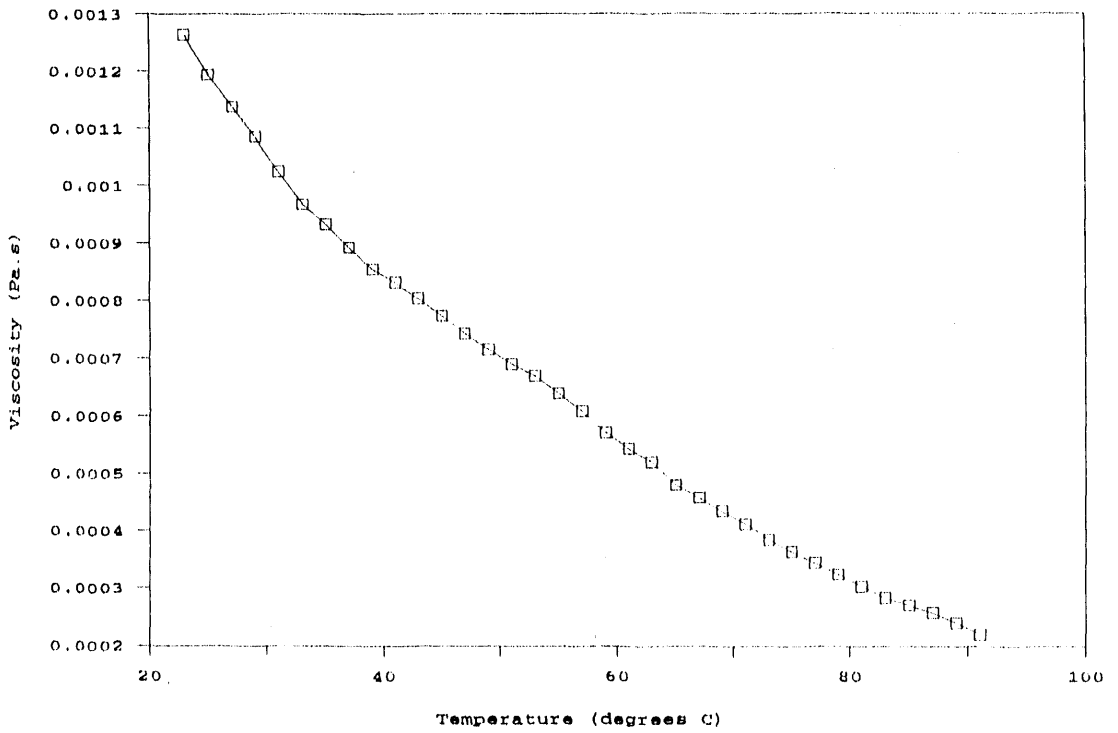

Figure 6-2. Produced brine viscosity - South Rozet Unit.

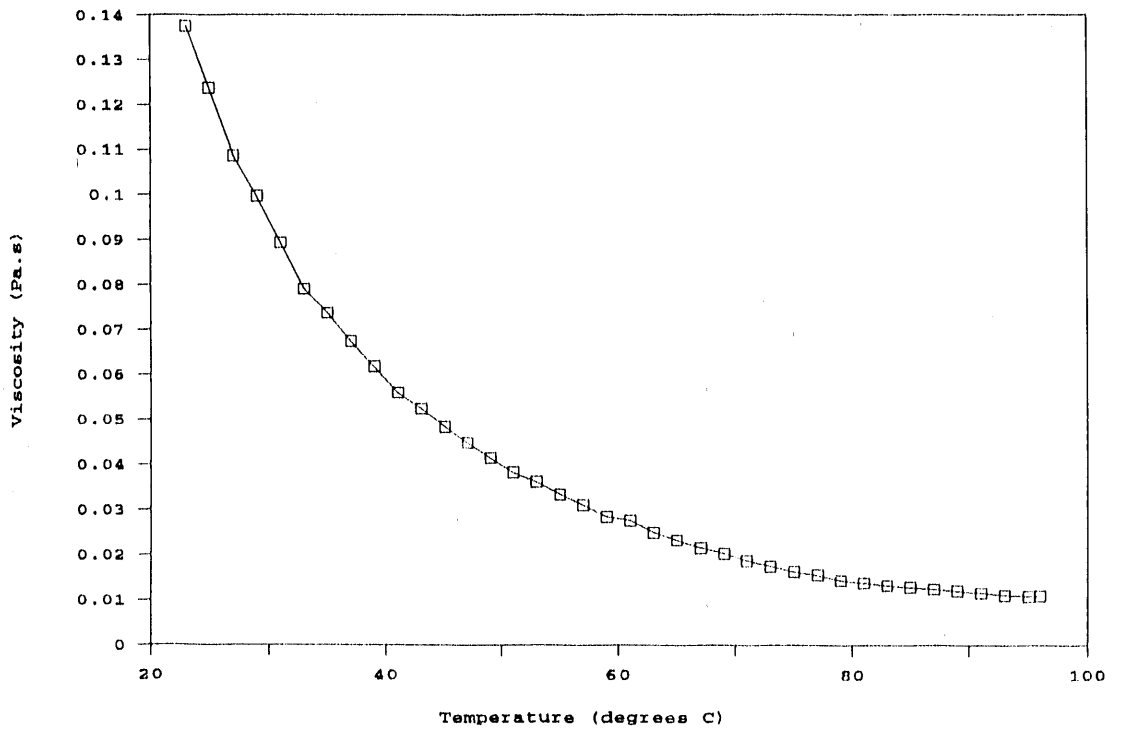

Figure 6-3. Crude oil viscosity - South Rozet Unit, 22.1° API @ 60°F.

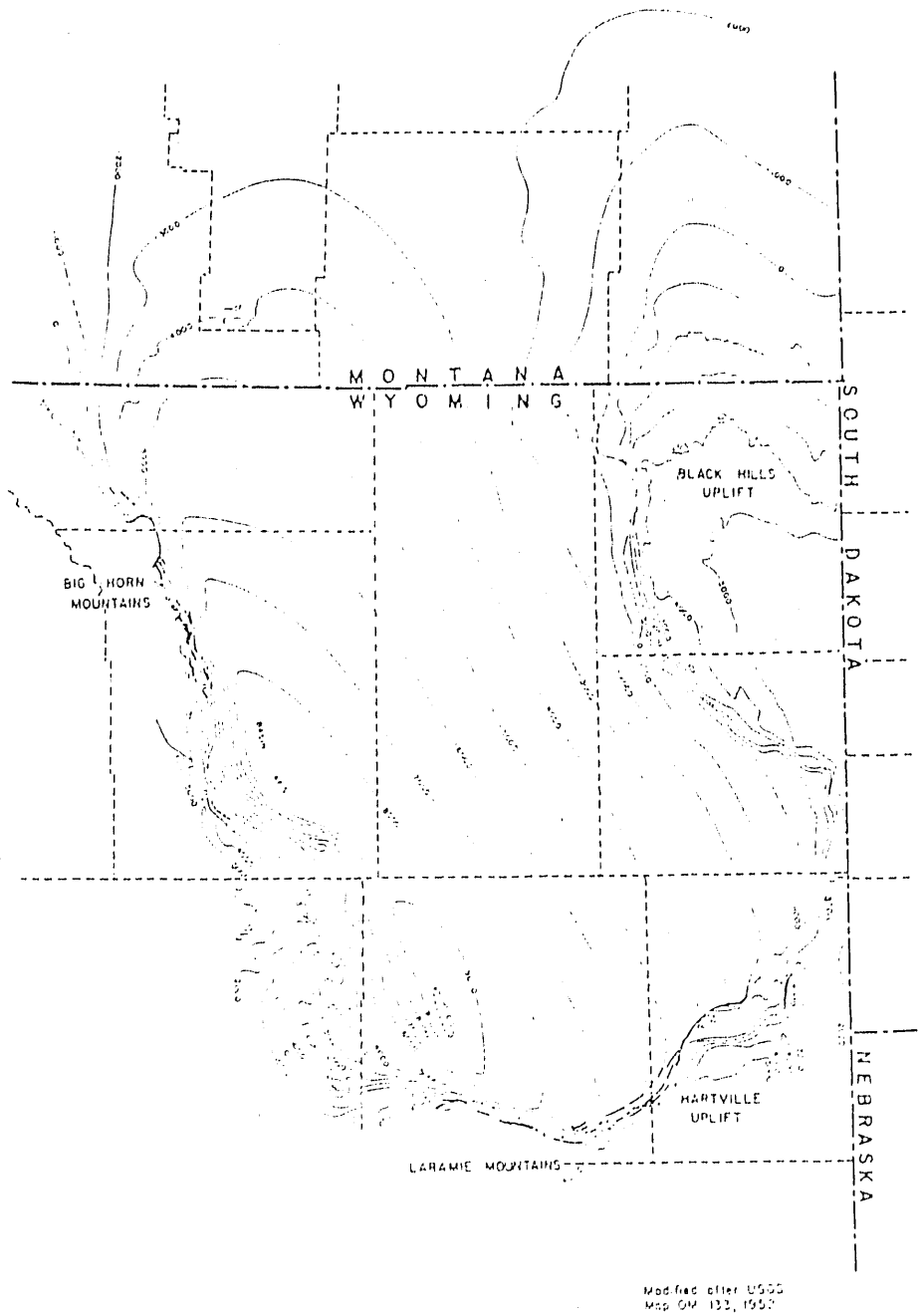

Figure 6-4. Structure contour map - Powder River Basin, from Strickland, 1958.[2]

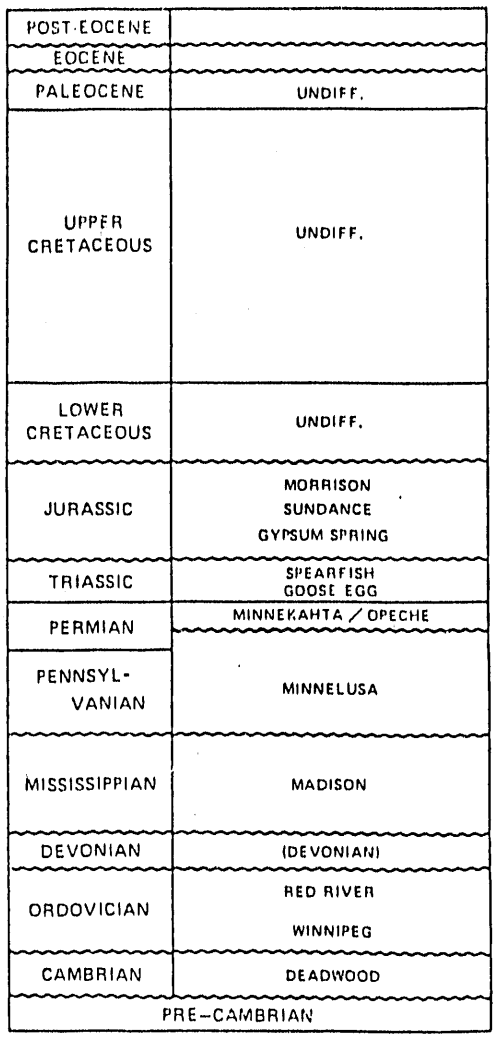

Figure 6-5. Generalized stratigraphic column - NE Powder River Basin, from Van West, 1972.[4]

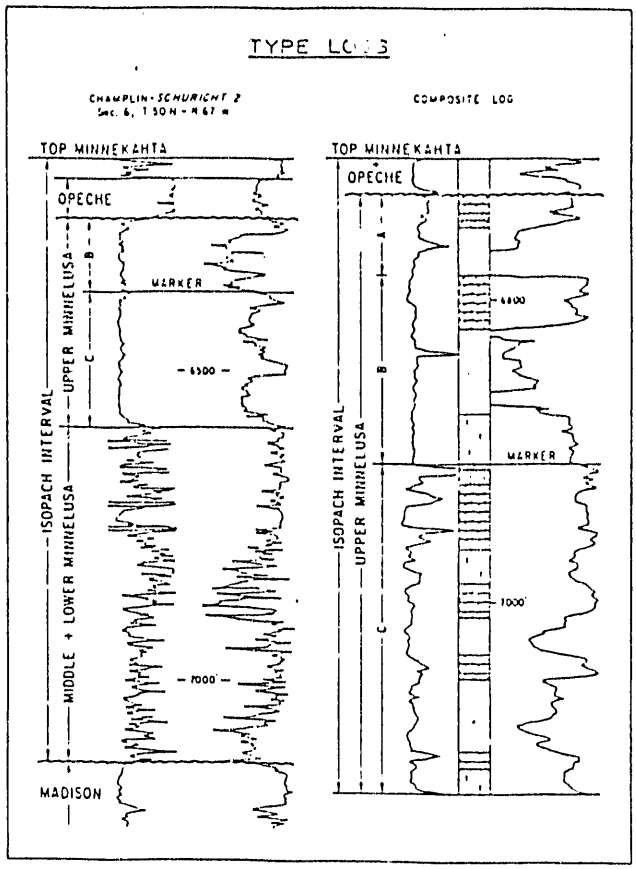

Figure 6-6. Minnelusa type logs, from Van West, 1972.[4]

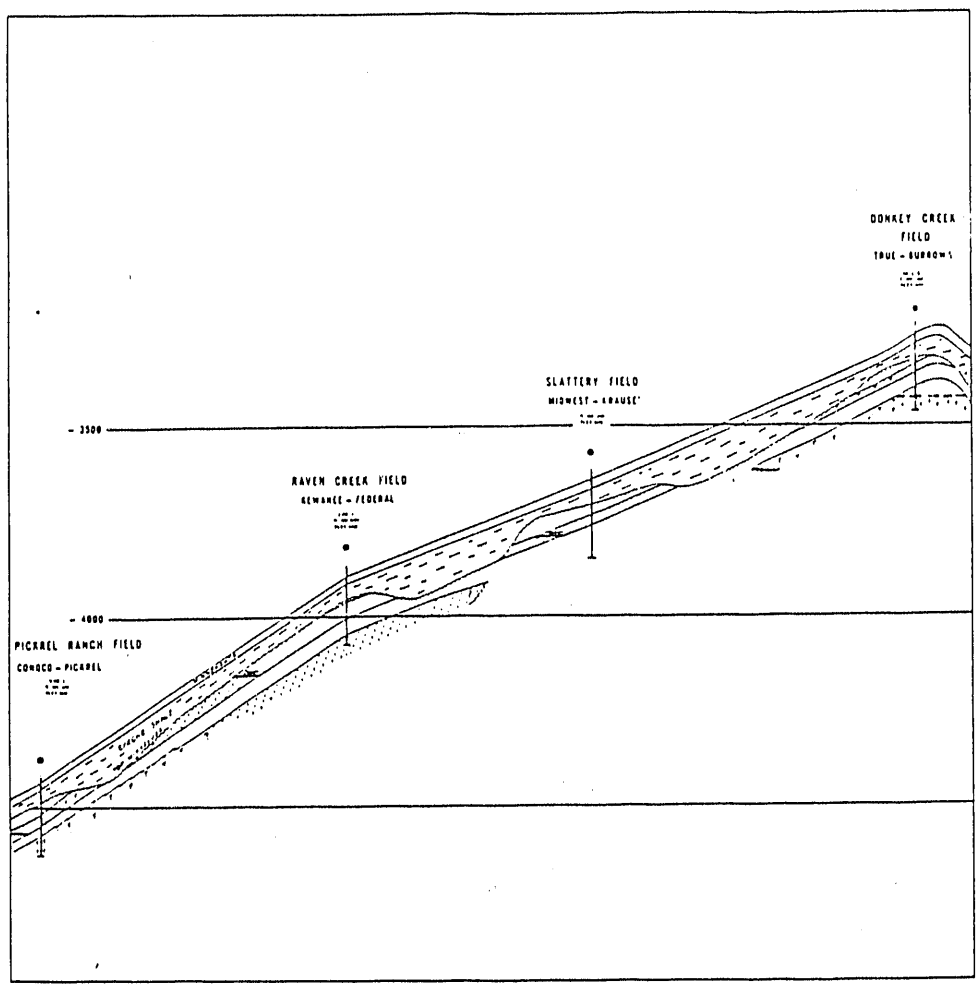

Figure 6-7. SW-NE cross section - east flank Powder River Basin, Campbell County, Wyoming, from Van West, 1972.[4]

6.10 References

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7. K. V. Tholstrom, "Performance History and Operations of Two Minnelusa Reservoirs - West Semlek Field, Crook County, Wyoming," Society of Petroleum Engineers Annual Fall Technical Conference, New Orleans, Louisiana, October 3-6, 1976, SPE 6164.

8. J. C. Mack and M. L. Duvall, "Performance and Economics of Minnelusa Polymer Floods," Society of Petroleum Engineers Rocky Mountain Regional Meeting, Casper, Wyoming, May 21-23, 1984, SPE 12929.

9. S. M. Hochanadel, M. L. Lunceford, and C. W. Farmer, "A Comparison of 31 Minnelusa Polymer Floods with 24 Minnelusa Waterfloods," Society of Petroleum Engineers/Department of Energy Seventh Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 22-25, 1990, SPE/DOE 20234.

10. J. A. McCartney, Waterflood Feasibility Study - Moorcroft West Field, Crook County, Wyoming, June, 1988.

7. RESERVOIR WETTABILITY AND ITS EFFECT ON OIL RECOVERY

This section contains a summary of the reports, publications, and presentations resulting from research performed under the INEL Contract C89-102443 at the New Mexico Petroleum Recovery Research Center (NMPRRC) in Socorro, NM for the period October 1, 1989 to September 30, 1990. The principal investigators for the research project are Dr. N. R. Morrow and Dr. J. S. Buckley. Contributors at NMPRRC are Nouraddine Benalil, Martha Cather, Mary Graham, Pudji Jadhunandan, Duo Jia, Xuan Lu, Shouxiang Ma, Yiping Xuan, and Xiaoyun Zhang.

7.1 Background

Study of reservoir wettability and its effect on oil recovery concerns the interactions between crude oil and mineral surfaces. The problem is being approached from a number of directions. These fall under two main tasks such as surface phenomena studies and oil displacement studies.

Task 1 focuses on surface phenomena including simple observations of adhesion or lack of adhesion when a drop of crude oil contacts a smooth solid surface covered with brine. Changes in surfaces because of adsorption from crude oil, as well as the persistence of such changes under various cleaning conditions are observed. The effect of changing crude oil composition, either by dilution with solvents, fractionation, or evaporation of the lighter components has also been investigated. Studies of the surface charge at crude oil/brine and solid/brine interfaces have been made using electrophoresis techniques.

The emphasis in Task 2 was to relate flow behavior and oil recovery to the wetting conditions prevailing in a porous medium. This task was attacked on several fronts. The work included determination of core wettability, extrapolation of laboratory tests to in situ conditions, and preparation of

cores of known and reproducible wetting properties over the range of intermediate and mixed-wet conditions for study of displacement mechanisms. Displacements were studied through flow visualization in glass micromodels and laboratory flow tests in cores with cores exposed to crude oil to alter wettability.

7.2 Reporting

The results of this research effort have been reported in detailed quarterly reports that have been summarized and included in the quarterly progress reviews published by the U.S. DOE, Office of Oil, Gas, and Shale Technology and Bartlesville Project Office (BPO), and in several presentations and contributions to the permanant technical literature as listed below.

7.2.1 Quarterly Reports

Work has been reported in detail in a series of four quarterly reports to the INEL and to BPO and included in the INEL quarterly technical progress reports. Each report describes general progress and includes a detailed thematic report as outlined below. The quarterly reports are also distributed to corporate sponsors of the NMPRRC research program.

7.2.1.1 October Through December 1989: Surface Phenomena. Maps of adhesion of crude oil to glass as a function of brine composition were reviewed in detail in the report for the previous quarter ending in September 1989. This quarter adhesion results were presented for Moutray crude oil with the oil altered by both dilution and evaporation to simulate possible effects of exposure of oil to microorganisms. The effects on adhesion of evaporation of about 20% of the lighter crude oil components and of dilution of the oil by toluene to as much as 1:1 oil to toluene were minor, as evaluated by the adhesion test. Electrophoresis measurement conditions for 12 oils (including evaporated and diluted Moutray) were outlined, as were drilling fluid additives and filtrates prepared for use in a study of the effects of water-based drilling fluids on wettability.

7.2.1.2 January Through March 1990: Surface Phenomena. Adhesion of Schuricht crude oil, supplied by INEL was reported. Electrophoretic mobilities as a function of oil type, ionic composition of brine, emulsion age, temperature, and emulsion concentration were reported in detail.

7.2.1.3 April Through June 1990: Oil Recovery. The report for this quarter focused on a study entitled "Crude Oil Recovery in Laboratory Waterfloods." Imbibition rate and extent were reported for two crude oils (Moutray and an oil from the North Sea), with varying conditions of brine composition, aging temperature, and initial water saturation. Imbibition is used as a measure of wetting for cores after exposure to crude oil and is correlated to oil recovery in subsequent waterflood tests. These data provide the most extensive set of experimental work available yet that relates recovery of crude oil to wettability.

7.2.1.4 July Through September 1990: Wettability Control. A study of the use of crude oils to produce cores of altered wettability from strongly water-wet to intermediate in wetting as measured by the Amott imbibition test was reported. This method is being developed as part of the study of drilling fluid filtrates. Crude oils are used to produce Berea sandstone cores of altered wettability in a reasonably reproducible fashion, so that the effect of exposure to drilling fluids and their component chemicals can be assessed for non-water-wet cores.

7.2.2 General Communication of Project Results in the Public Domain

Communication of results of the Petrophysics and Surface Chemistry Group in the public domain through presentations and contributions to the permanent literature are listed below.

7.2.2.1 Publications.

1. J. S. Buckley and N. R. Morrow, "Characterization of Crude Oil Wetting Behavior by Adhesion Tests," Society of Petroleum Engineers/Department of Energy Seventh Symposium on Enhanced Oil Recovery, Tulsa, Oklahoma, April 22-25, 1990, SPE/DOE 20263, to be published, Society of Petroleum Engineers Formation Evaluation.

2. N. R. Morrow, "Introduction to Interfacial Phenomena in Oil Recovery," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekker, 1990, pp. 1-21.

3. J. S. Buckley, "Multiphase Displacements in Micromodels," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekker, 1990, pp. 157-189.

4. N. R. Morrow and J. C. Melrose, "Application of Capillary Pressure Data to the Determination of Connate Water Saturation," Interfacial Phenomena in Oil Recovery, Ed. N. R. Morrow, Marcel Dekkar, 1990, pp. 257-287.

5. D. Jia, J. S. Buckley, and N. R. Morrow, "Control of Core Wettability with Crude Oil," Society of Petroleum Engineers International Symposium on Oilfield Chemistry, Anaheim, California, February 20-22, 1991, SPE 21041.

6. S. Ma and N. R. Morrow, "Effect of Firing on Fluid Flow Properties in Berea Sandstone," Society of Petroleum Engineers International Symposium on Oilfield Chemistry, Anaheim, California, February 20-22, 1991, SPE 21045.

7. N. R. Morrow, "Wettability and Its Effect on Oil Recovery," Society of Petroleum Engineers Distinguished Author Series, Journal of Petroleum Technology, 42, 12, 1990, pp. 1476-1484.

8. G. Mason and N. R. Morrow, "Capillary Behavior of a Wetting Liquid in Irregular Triangular Tubes," to be published, Journal of Colloid and Interface Science.

7.2.2.2 Presentations

1. N. R. Morrow, "Surfaces and Interfaces," keynote address, Fifth IFP Research Conference on Exploration and Production, Fundamentals of Fluid Transport in Porous Media, Arles, May 14-18, 1990.

2. P. Jadhunandan and N. R. Morrow, "Crude Oil Recovery in Laboratory Water Floods," Fifth IFP Research Conference on Exploration and Production, Fundamentals of Fluid Transport in Porous Media, Arles, May 14-18, 1990.

3. N. R. Morrow and J. C. Melrose, "Application of Capillary Pressure Data to the Determination of Connate Water Saturation," keynote address, European Core Analysis Symposium, London, May, 1990.

4. M. E. Cather, N. R. Morrow, and I. Klich, "Characterization of Porosity and Pore Quality in Sedimentary Rocks," Second IUPAC Symposium on Characterization of Porous Solids, Alicante, May, 1990.

5. J. S. Buckley, "Wettability Effects of Crude Oils," American Geophysical Union Spring Meeting, Baltimore, Maryland, May 29-June 1, 1990.

6. J. S. Buckley and N. R. Morrow, "Crude Oil Wetting," poster, International Symposium on Contact Angles and Wetting Phenomena, Society of Chemical Industry, Toronto, Canada, June 21-23, 1990.

7. J. S. Buckley, "Prediction of Crude Oil/Rock Wettability," Society of Core Analysts Fourth Annual Technical Conference, Dallas, Texas, August 14-16, 1990.

(See Table 7-1 for additional presentations made at the First International Symposium on the Effect of Wettability on Oil Recovery.)

7.2.3 First International Symposium on the Effect of Wettability on Oil Recovery

The First International Symposium on the Effect of Wettability on Oil Recovery was sponsored by the New Mexico Petroleum Recovery Research Center (NMPRRC) and held at the New Mexico Institute of Mining and Technology in Socorro New Mexico on September 18 to 21, 1990. Ninety participants from 6 countries and 32 different organizations including 17 major oil companies participated in the symposium. The program included presentations on work by the Petrophysics and Surface Chemistry Group at NMPRRC.

Table 7-1. Presentation program for the First International Symposium on the Effect of Wettability on Oil Recovery held September 18 to 21, 1990 in Socorro, NM

Measurement of Wettability and its Effect on Oil Recovery[a]	**Norman Morrow** NMPRRC, New Mexico Tech
The Role of Surface Structural Forces in Wettability	**George Hirasaki** Shell Development Co. Houston, TX
Wetting Behavior of Crude Oil/Brine/Solid Surfaces from Adhesion Tests and Electrophoretic Mobilities[a]	**Jill Buckley** NMPRRC, New Mexico Tech
Effect of Microbial Activity on the Wettability of Surfaces by Water and Oil	**Norman Wardlaw** Univ. of Calgary, Canada
Control of Core Wettability with Crude Oil[a]	**Jill Buckley** NMPRRC, New Mexico Tech
Wettability Alteration by Asphaltine Deposition	**Sheila Yeh** Chevron Oil Field Research Corp. La Habra, Calif.
Using Cryomicroscopy to Visualize Oil and Brine in Porous Media	**Michel Robin** Institut Français du Pétrole Paris, France

Table 7-1. (continued)

Fluid Distribution in Mixed Wettability Rock	**Gary Jerauld** ARCO Oil and Gas Plano, Texas
Pore Level Trapping of Oil in Single Pores, Pore Doublets, and Pore Networks	**Norman Wardlaw** Univ. of Calgary, Canada
Capillary Phenomena in Foam Flow Through Porous Media	**Clay Radke** Univ. of Calif., Berkeley
Results of in situ Measurements of Residual Oil After Waterflood	**Harry Deans** Univ. of Wyoming, Laramie
Diagenesis, Pore Structure, and Surface Properties of Reservoir Rocks[a]	**Martha Cather** NMPRRC, New Mexico Tech
Capillary Properties of Single Pores[a]	**Norman Morrow** NMPRRC, New Mexico Tech
Obtaining Samples with Preserved Wettability	**Robert Wunderlich** Chevron Oil Field Research Corp. La Habra, Calif.
Effect of Drilling Mud Filtrates on Mixed Wettability Rock[a]	**Jia Duo** NMPRRC - Visiting Scientist (Drilling & Exploitation Research Inst. of Dagang Oil Field, PRC)
Core Analysis Procedures for Evaluation of Reservoir Wettability	**Louis Cuiec** Institut Français du Pétrole Paris, France
Measurement of Relative Permeabilities	**Cliff Black** British Petroleum Glasgow, United Kingdom
Laboratory Measurement of Relative Permeability with Reservoir Fluids	**Jon Ringen** Statoil Stavanger, Norway
Observations on Slow Rate Displacements for Mixed Wettability Systems	**Gerard Glotin/** **Alaine Labastie** Elf Aquitaine Pau, France
Numerical Simulation of Core Floods[a]	**Ahmed Ouenes** NMPRRC - Visiting Scientist (Elf Aquitaine)

Table 7-1. (continued)

Relative Permeability Measurements on Ninety Samples from Oil-Bearing Formations of a Single Well	**Ase Scheie** Norsk Hydro Bergen, Norway
Effect of Brine Composition, Crude Oil, and Aging Conditions on Wettability and Oil Recovery[a]	**Pudji Jadhunandan** NMPRRC, New Mexico Tech

a. Presentations on work by the Petrophysics and Surface Chemistry Group at NMPRRC.

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