TITLE:

AUGMENTING A MICROBIAL SELECTIVE PLUGGING TECHNIQUE WITH POLYMER FLOODING TO INCREASE THE EFFICIENCY OF OIL RECOVERY - A SEARCH FOR SYNERGY

FIRST SEMI-ANNUAL PROGRESS REPORT

REPORTING PERIOD START DATE:
1 June 1999

REPORTING PERIOD END DATE:
31 November 1999

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DATE OF REPORT:
December 1999

DOE AWARD NUMBER:
DE-AC26-99BC15210--01

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ABSTRACT

The overall objective of this project is to improve the effectiveness of a microbial selective plugging technique (MPPM) of improving oil recovery through the use of polymer floods. More specifically, the intent is to increase the total amount of oil recovered and to reduce the cost per barrel of incremental oil recovered. In order to accomplish these objectives, six tasks will be carried out. These tasks are designed to chemically characterize the polymers, determine their biodegradeability and inhibitory impact on microorganisms, and test their ability to enhance a MPPM in sandpacks, Berea cores, and live cores from newly drilled wells. A cost/benefit evaluation of the developed MPPM-Polymer process will be conducted. To date, chemical characterization of eight polymers is in progress. None of the six polymers tested thus far are inhibitory to any of the five microbial cultures obtained from petroleum reservoirs and none support growth of these cultures as a sole carbon and energy source. Thirty sandpack devices have been fabricated and testing of Berea sandstone for permeability has begun.

INTRODUCTION

Over two thirds of all of the oil discovered in this country is still in the ground and cannot be recovered economically with present day technology. Only 27 billion barrels of the approximately 345 billion barrels remaining in known reservoirs is economically recoverable. When primary production becomes uneconomical, secondary and tertiary methods, such as waterflooding, chemical flooding, CO_2 or N_2 flooding, and microbial enhanced oil recovery (MEOR) are employed. Recently, a microbial permeability profile modification (MPPM) procedure was shown to be a cost effective means of enhancing oil recovery.[1] In fact, aside from waterflooding alone, MPPM is the least expensive of the enhanced oil recovery procedures. Since MPPM and permeability modification via polymers are similar in mode of action, it was reasoned that coupling those two technologies may result in a synergy that is not only cost effective but also results in more efficient oil recovery.

RESULTS AND DISCUSSION

Objective

The overall objective of this project is to improve the effectiveness of a microbial selective plugging technique of improving oil recovery through the use of polymer floods. More specifically, the intent is to increase the total amount of oil recovered and to reduce the cost per barrel of incremental oil recovered. In order to accomplish these objectives, the following six tasks will be carried out.

Task 1. Select, characterize, and test various polymers for their impact on the microflora indigenous to petroleum reservoirs in terms of their inhibitory capabilities and their biodegradability.

Task 2. Determine the ability of selected polymers to increase the aerial extent (aerial sweep efficiency) of stratal material colonized by microorganisms in sandpacks.

Task 3. Determine the ability of selected polymer flooding protocols in combination with microbial selective plugging techniques to increase oil recovery from Berea sandstone core plugs prepared to mimic a depleted oil sand.

Task 4. Determine the ability of a microbial selective plugging technique in combination with selected polymer flooding protocols to increase oil recovery from live cores obtained from newly drilled wells.

Task 5. Prepare a cost/benefit evaluation of adding a polymer-flooding procedure to a microbial enhanced oil recovery process using a selective plugging technique.

Task 6. Final report preparation.

To facilitate presentation of accomplishments on this project, results will be set forth by task.

Results

Task 1. **Select, characterize, and test various polymers for their impact on the microflora indigenous to petroleum reservoirs in terms of their inhibitory capabilities and their biodegradabiltiy.**

Chemical Characterization

The polyacrylamides selected for use in this project are all approximately 25% hydrolyzed to the acrylic acid moieties. Molecular weights (MW) of three of the polyacrylamides have been characterized at 9-11 million (lowest) to over 20 million. These MW are so high and the dn/dc values in water so low that light scattering has not been able to be used to define the hydrodynamic radii (R_H) or the overlap concentration. These three mobility control polymers operate by enhancing water viscosity as does the xanthan. MW data on the xanthan polymer selected for this project has been obtained, its structure is known, and its hydrodynamic radius versus brine content has been established along with viscosity vs. concentration data in water and several levels of brine.

Of the six ALCOFLOOD samples obrtained thus far, ALCOFLOOD 25ls is a polyacrylamide, while the rest (254s, 1135, 1235, 1275A, and 1285) are copolymers of acrylamide and sodium acrylate.

ALCOFLOOD 251s and 254s are used with cross-linking agents. Their MW are lower than the very high MW mobility control polymers, ALCOFLOOD 1135, 1235, 127A, and 1285, which work by increasing water viscosity. The typical working solution concentration is in the 1000s ppm range. Solution viscosities range from 4-60 cps.

ALCOFLOOD 1235 is applied in low to medium permeability reservoirs; ALCOFLOOD 175A is applied in medium to high permeability reservoirs; and ALCOFLOOD 1285 is applied in very high permeability reservoirs. The molecular weights of these polymers are in the order 1285>1275A>1235.

ALCOFLOOD 1235, 1275A and 1285 contain 12.2-99% of water. Their densities are all 0.8g/ml.

Dynamic light scatter (DLS) analysis give negative results in the MW determinations of the ALCOFLOOD samples. ALCOFLOOD 1235 and 251s were examined. The suspect factor is the low dn/dc value coupled with the very low solution concentrations which must be used with such high molecular weight polymers. The reported dn/dc value for polyacrylamide was found to be 0.1869 (at 25C, 632.8nm).

Dialysis was tried to see if much salt existed in the as-received polymer. Recovery of the sample after purification was around 93%. The 7% missing was mainly from experimental lost. The samples are almost all polymer. Atomic absorption showed negligible Cl or S. Therefore, chloride or sulfate salts were not present. The MW and molecular weight distributions (MWD) of polyacrylamides have been measured by evaporative light scattering, gel permeation chromatography (GPC), an ultra centrifugation method, electron microscopy in a solvent mixture, and turbidometric titration. However, the polymers used in this work test the limits of these methods so good MWD or good $\overline{M}_Z$ values (e.g. the Z-averaged MW values which correlate well with viscosity) cannot be obtained. Therefore, only viscosity measurements will be employed in the future.

Liquid xanthan, FLOCON 4800, has a MW of between 1-2 million. The active content ranges from 3% to 5% and >2000 ppm of formaldehyde was added in the polymer liquid. The density of FLOCON 4800 is 0.95-1.00 g/ml. The cross-linking agent, Cr(III), is usually used in oil field applications. This trivalent cation gels the ALCOFLOODS 251s and 254s by the reaction where -COO- groups complex Cr(III). These are used with polyacrylamides. The working viscosities of FLOCON 4800 range from 5 to 40 cps.

The viscosity of these polymer does not change in the pH range of 5-12 and is slightly decreased by adding salts. A sandpack measurement procedure is given in the menu.

Liquid KUSP1, a biological by-product polymer was obtained for testing. This polymer can be dissolved in water at pH>9.5. No other detailed information was collected on its structure. It was produced

from a biological source at Kansas State University. If it is pumped at a pH>9.5, it will flow nicely while dissolved in water. After the pH is lowered, it sets up a complex gel structure which blocks further flow.

The xanthan polymer is more rod-like and less random coil-like than the ALCOFLOOD polyacrylamides. Therefore, its Mark Houwink relation dependence (=KM) has a higher value of the exponent where is the intrinsic viscosity, K is a constant, M is molecular weight, and is a constant. Therefore, it gives a greater value of [n] per given MW than the polyacrylamides. Furthermore, since it is more rod-like, it does not have as large a change in its hydrodynamic radius as the polyacrylamides do when the ionic strength (e.g. brine content) goes up.

Microbiological Evaluation of Polymers

Tests were conducted to determine if a polymer was (1) inhibitory to microbial cultures obtained from petroleum reservoirs or (2) would serve as a carbon and energy source for these cultures. Five cultures were selected for the initial testing. The cultures and some of their characteristics were as follows:

Culture #1 is a gram positive bacillus, non-acid fast, non-spore forming, obligate anaerobe isolated from the Mabe oil field situated in Andrews Co., Tx.

Culture #3 is a gram negative bacillus, non-acid fast, non-sporeforming, microaerophile isolated from the Mabee oil field situated in Andrews Co., Tx.

Culture #10 is a gram positive coccobacillus, acid fast, obligate anaerobe isolated from the Kern river Oil field situated in Kern Co. LA.

Culture #16 is a gram positive coccobacillus, acid fast, microaerophile isolated from the Kern River Oil field situated in Kern Co., CA.

Culture #17 is a gram positive bacillus, non-acid fast, facultative anaerobe isolated from the Kern River oil field situated in Kern Co., CA.

All media employed were prepared using simulated production water in place of distilled water, and

were composed of 10.9 g $CaCl_2$, 2.71 g $MgCl_2$, 4.57g, $BaCl_2$, 1.84g Na_2SO_4, and 147.8g NaCl in 50 l of distilled water.

In preparing media, this simulated production water was supplemented with 1g KNO_3 and 0.26g NaH_2PO_4 per l and hereinafter will be referred to as PWB (production water broth).

Test for Inhibitory Properties of Polymers

The protocol to determine if a polymer is inhibitory to cultures obtained from oil reservoirs was the disc assay procedure. Tests were conducted using both Bacto-Plate Count Agar (PCA) and Oil Agar (OA) prepared as follows. The crude oil employed was obtained from the North Blowhorn Creek Oil Field situated in Lamar Co., AL. PWB was saturated with oil by vigorously mixing for one hour. Granulated agar (1.7%, w/v) was added to the oil-saturated PWB and dispensed in 18 ml amounts into 20 x 145 mm screw-capped test tubes. Crude oil (0.18 ml/tube) was added and the medium sterilized in the autoclave at 121C for 15 min. The PCA was prepared in 18 ml amounts in 20 x 145 mm screw-capped test tubes and sterilized as above.

A 10% suspension (w/v) of each polymer was prepared by adding 1.0 g of polymer to 9.0 ml of sterile distilled water. BBL 1/2 inch paper discs were placed aseptically in the 10% polymer solution and allowed to remain for 24 h. The discs then were taken out of the suspension and allowed to air dry. Under anaerobic conditions, 0.2 ml of the test microbial culture was added to 18 ml of melted and cooled (45C) OA and mixed. Approximately 3.5 ml of the inoculated agar were poured into 20, 35x10 mm plastic petri dishes. After the agar solidified, a polymer-saturated disc was placed on the surface of the agar. Duplicates were done for each polymer. Plates of inoculated PCA were prepared and treated as above. PCA-inoculated and OA-inoculated plates also were prepared using cultures #3, 10, 16, and 17. Plates prepared as above but without polymer-saturated discs were employed as controls.

The petri plates were incubated in BBL® anaerobic chambers for 20 d at 30 C. After incubation, plates were examined for zones of inhibition around the discs which would indicate inhibition of the culture by the polymer.

The following six polymers have been tested - ALCOFLOOD 1235, ALCOFLOOD 1135, ALCOFLOOD 1275A, ALCOFLOOD 1285, ALCOFLOOD 254S, and KUSPI.

Tests for the Ability of Polymers to Support Microbial Growth

Tests of the ability of microbial cultures from oil reservoirs to grow on polymer and/or degrade the polymer are being conducted using three different media - (1) polymer in PWB, (2) polymer in PWB supplemental with 1% (v/v) oil, and (3) polymer in PWB supplemented with 1% (v/v) molasses were sterilized by autoclaving for 15 min at 121C. A 1.8% polymer suspension (w/v) was prepared by placing 1.8 g of polymer in 100 ml of distilled water. One ml of the 1.8% polymer suspension was added to 17 ml of each of the three media listed above to make a 0.1% polymer medium. Under anaerobic conditions, 10 μl of each of the five microbial cultures were added to two tubes of each of the three media. Controls were prepared with (1) no cells added to medium plus polymer and with (2) only medium with no cells and no polymer. All the cultures were allowed to incubate at 30C. The cultures are monitored weekly.

After two weeks, growth was examined only in cultures containing molasses plus polymer (ALCOFLOOD 1235, ALCOFLOOD 1135, ALCOFLOOD 1275A, ALCOFLOOD 1285, and 254S). After 3 weeks of incubation one culture showed slight growth in molasses plus polymer KUSP1. Culture #16 was growing in oil medium plus polymer after 3 weeks (ALCOFLOOD 1135, ALCOFLOOD 1275A, ALCOFLOOD 1285, and KUSP1). No growth was obtained in samples containing polymer as the sole source of carbon and energy.

Task 2. **Determine the ability of selected polymers to increase the aerial extent (aerial sweep efficiency) of stratal material colonized by microorganisms in sandpacks.**

Fabrication of 30 sandpacks is complete. Each Plexiglas sandpack is 6" x 6" by 0.25" and has a total internal volume of 41.49 ml. The sandpacks are fitted with a No. 17 needle in each of two opposite corners to serve as a means of introducing liquids into the sandpacks and collecting the effluent. On one side of each sandpack 100 holes were drilled, 1/4" in diameter. One layer of thin “see through” plastic was placed beneath the side with 100 holes to contain formation materials inside the sandpack. A 1" diameter plug was glued on to a 1 1/2" x 1 1/2" plexiglas baseplate to close the sandpack (secured using methylene chloride) following filling with formation materials.

Task 3. **Determine the ability of selected polymer flooding protocols in combination with microbial selective plugging techniques to increase oil recovery from Berea sandstone core plugs prepared to mimic a depleted oil sand.**

One Hassler type core holder has been put in a model and the system is in running condition. Numerous runs have been conducted to: a) test the reliability of the model and, b) to measure gas and liquid permeability of 2 blocks of Berea sandstone available in house. Other Berea sandstone blocks of moderate to high permeability are being ordered.

Porosity and permeability of two blocks of Berea sandstone have been measured by the Ruska type and by Hassler types. This is to verify that we have access to a reliable system to measure porosity and permeability of Berea sandstone and other core materials as, it is believed, porosity and permeability may play a major role in upcoming experiment in the projects.

Task4. **Determine the ability of a microbial selective plugging technique in combination with selected polymer flooding protocols to increase oil recovery from live cores obtained from newly drilled wells.**

Not scheduled.

Task 5. **Prepare a cost/benefit evaluation of adding a polymer-flooding procedure to a microbial enhanced oil recovery process using a selective plugging technique.**

Not scheduled.

Task 6. **Final report preparation.**

Not scheduled.

CONCLUSION

Preliminary tests on five polyacrylamides and one biological by-product polymer (KUSPI) have not demonstrated any inhibitory characteristics toward five microbial cultures isolated from petroleum reservoirs and will not serve as a sole source of carbon and energy for these cultures.

REFERENCES

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