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EFFECTS OF CHEMICAL ADDITIVES ON MICROBIAL ENHANCED OIL RECOVERY PROCESSES

TOPICAL REPORT

By
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December 1989

Performed Under Cooperative Agreement No. FC22-83FE60149

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

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U. S. DEPARTMENT OF ENERGY
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ABSTRACT

The mechanisms of oil mobilization by injection of microbial cells and nutrient have been studied to further develop an engineering methodology for optimizing formulations for oil recovery applications. An extensive laboratory study has been conducted to determine (1) the role of the microbial cells and products in oil displacement, (2) the relative rates of transport of microbial cells and chemical products from the metabolism of nutrient in porous media, and (3) the effects of chemical additives on the oil recovery efficiency of microbial formulations. This report describes experiments relating to the effects of additives on oil recovery efficiency of microbial formulations.

The effects of additives on the oil recovery efficiency of microbial formulations were determined by conducting oil displacement experiments in 1-foot-long Berea sandstone cores. Sodium tripolyphosphate (STPP), a low-molecular-weight polyacrylamide polymer, a lignosulfonate surfactant, and sodium bicarbonate were added to a microbial formulation at a concentration of 1%. The effects of using these additives in a preflush prior to injection of the microbial formulation were also evaluated. Adding polymer, surfactant, or sodium bicarbonate increased the oil recovery efficiency of the microbial formulation, while STPP had a minimal effect. Injecting preflush formulations containing the additives also increased the oil recovery efficiency of the microbial flood.

Oil-displacement experiments with and without a sodium bicarbonate preflush were conducted in 4-foot-long Berea sandstone cores, and samples of in situ fluids were collected at various times at four intermediate points along the core. The concentrations of metabolic products and microbes in the fluid samples were determined. The results showed that sodium bicarbonate had a positive effect on oil recovery efficiency and slightly improved the transport of microbial metabolites through the core.

INTRODUCTION

Microbial methods for increasing oil recovery are potentially cost-effective even at relatively low crude oil prices. Prior work in FY88 has identified the mechanisms of oil mobilization by certain microbial formulations. Mechanisms that have been shown to be important include wettability alteration, emulsification, solubilization, and alteration in interfacial forces. Recent experiments[1-2] using corefloods and micromodels have demonstrated that oil mobilization by microbial formulations is not merely the result of effects of metabolic products from in situ fermentation of nutrient, but that the production of high, localized concentrations of chemicals by the cells in situ at the oil-water interface is critical. One research

objective, addressed by Tasks 1, 4, 6, and 7 of the NIPER FY89 Annual Research Plan, was to identify chemical additives that may improve oil recovery efficiencies of in situ microbial flooding formulations while still being cost effective. The additives included cosurfactants, surfactants, polymers, inorganic and organic salts, used in small quantities (less than 1 to 2 wt %).

The additives and injection strategies for oil-displacement studies with a microbial formulation were designed either to facilitate the transport of microbial cells and products or to stimulate the microbial population and alter their metabolism. A patent by Clark[3] describes the use of sacrificial agents as a preflush for microbial injection in a petroleum reservoir. The patent claims that sacrificial agents that are strongly adsorbed on reservoir rock can facilitate the transport of microbial cells. Yen[4] has reported improved bacterial transport in simulated porous media (packed glass beads) by using pyrophosphate. The additives in this study were used as a preflush or added directly to the microbial formulation. The use of a preflush chemical additive may increase rates of transport of microbial cells and metabolites by adsorbing to the rock surface. When certain chemicals are added directly to a microbial formulation, a synergistic effect may occur. Some chemical additives can stimulate microorganisms to produce a greater amount of a certain metabolite or, alternately, produce a different metabolite by altering the cell's metabolic pathway.[5] Isoamyl and isopropyl alcohols were chosen as additives to determine if they could act as cosurfactants for microbially produced surfactants and improve microbial oil recovery efficiency. It has been previously determined that these alcohols were effective cosurfactants for other commercial surfactants. The additive 2,3 butanediol was chosen because it is a metabolic product from the microbial formulation used in these experiments.

Flask testing of the chemical additives was first conducted to determine if the additives had any inhibitory growth effects on the microbial formulation. The effects of additives on oil recovery efficiencies of microbial formulations were then determined by conducting oil-displacement experiments in 1-foot-long Berea sandstone cores. Several injection strategies were investigated using various additives: (1) using the additive as a preflush prior to injection of the microbial formulation; (2) adding the chemicals directly to the microbial formulation; and (3) injecting 2 PV of brine through the core after the additive and before microbial injection. Additional microbial coreflooding experiments were conducted using 0.5, 5.0, and 8.0% sodium chloride to determine if changes in salinity affected the performance of a selected microbial formulation, consisting of two microorganisms, NIPER 1 and NIPER 6. This work completed milestone 8 of project BE3 as stated in the FY89 Annual Research Plan.

EXPERIMENTAL APPARATUS AND PROCEDURES

Materials and Equipment

Crude Oil and Brine

Crude oil samples were obtained from the Bartlesville sand formation in Delaware-Childers field in northeastern Oklahoma. Delaware-Childers oil has a gravity of 31° API (0.87 g/cm^3). Brine with a concentration of 0.5% sodium chloride by weight was used in all oil-displacement experiments.

Nutrient

The molasses used in these experiments was obtained from Pacific Molasses Co. in Oklahoma City, and its composition is as follows: total ash, 8.1%; calcium, 0.8%; phosphorous, 0.08%; magnesium, 0.35%; potassium, 2.4%; sulfur, 0.8%; and sodium, 0.2%. The amount of total suspended solids is 74%, of which 3% is total protein, 48% is total sugar (sucrose), and the remaining 23% is fiber. The concentration of molasses used in the experiments was 4% by weight in tap water with 0.1% of ammonium phosphate added to facilitate microbial metabolism.

Microorganisms

A combination of *Bacillus licheniformis* (NIPER 1) and a *Clostridium* species (NIPER 6) was chosen as the most effective formulation for the recovery of residual oil. *Bacillus licheniformis* is a facultatively anaerobic, spore-forming rod that produces organic acids and surfactant when fermenting sucrose. The anaerobic spore-forming *Clostridium* is a member of the butyric acid group that produce acetone, butanol, ethanol, isopropanol, butyric acid, acetic acid, propionic acid, carbon dioxide, and hydrogen gas when fermenting sucrose. All coreflood and micromodel tests were performed with anaerobic cultures of NIPER 1 and 6 (approximately 1 x 10^6 cells/mL) that had incubated for 24 hours in trypticase-soy broth. The solution containing only the metabolic products was prepared by filtering the 24-hour anaerobic culture in trypticase-soy broth through a 0.45-micron syringe filter.

Coreflood Additives

The following chemicals did not appear to inhibit the growth of microorganisms NIPER 1 and 6 and were selected as additives for corefloods either as a preflush agent or as a direct additive to the microbial formulation: sodium tripolyphosphate (STPP); sodium bicarbonate (Bicarb); Cyanagel, a low-molecular-weight polyacrylamide; Petrolig-ERA, a lignosulfonate surfactant; 2,3 butanediol; isoamyl and isopropyl alcohols; and Tronacarb™, a commercial product containing 96 wt % sodium bicarbonate, 2 wt % sodium carbonate, and 1 wt % sesquicarbonate. A 1% by weight solution of each additive was prepared in deionized water for injection, with the exception of Petrolig-ERA. A previously described preflush[6] of Petrolig-ERA at a concentration of 2%, was used for the additive experiments.

Coreflood Apparatus

The experimental equipment has been previously described.[7] The fluid separators are piston devices used to inject microbial solutions and other fluids into cores and were designed to prevent corrosive fluids from contacting the pumps. Cores were encased in rubber sleeves and placed inside stainless steel Hassler coreholders, and a hydrostatic net confining pressure of 250 psi (1,723.7 kPa) was maintained throughout the tests. Sampling ports were used along the length of the core. Ports 1 through 4 corresponded to the length as follows: port 1, 0.5 ft; port 2, 2.5 ft; port 3, 2.5 ft; and port 4 was 3.5 ft from the injection end. The frontal advance rate for the waterflood was 1 ft/d.

Core Preparation

Blocks of Berea sandstone were obtained from Cleveland Quarries (Amherst, Ohio) and cut into cylindrical cores of 12 in. (25.4 cm) in length and 1.5 in. (3.8 cm) in diameter. Four-foot-long cylindrical cores that were 2 in. (5.1 cm) in diameter were also received from Cleveland Quarries. The cores were evacuated, then flushed with brine, and the absolute permeability to brine was determined using Darcy's law. Crude oil was then injected into the cores until no additional water was produced. Finally, the cores were waterflooded with brine to establish a residual oil saturation (S_{orwf}).

Gas Chromatography

Compositional analyses were performed using a Hewlett Packard 5980A gas chromatograph equipped with a flame ionization detector. A 6-ft (1.83 m) glass column packed with Poropak QS (800-100 mesh) was used for all analyses. A temperature program of 95° to 195° F (35° to 90.6° C) gave the best separation of compounds. Standards used were 0.1 or 1% alcohols or fatty acids.

Methodology

Flask Tests

Screw-capped Erlenmeyer flasks were used to evaluate the microbial growth and metabolite production in batch cultures. Twenty-four hour-old cultures were inoculated into trypticase soy broth containing 1% sodium bicarbonate, or 1% Tronacarb™. All flasks were incubated at ambient temperature in an anaerobic glovebox. A control without bicarbonate was always measured at the same time. Samples were taken from these flasks at 24-hr intervals and measured for microbial aerobic and anaerobic counts, pH, viscosity, and metabolites detectable by gas chromatography .

Additive Tests

The 12-in. cores that had been waterflooded to residual oil saturation, S_{orwf}, were prepared for injection of additives either as preflush agents or as additives to the microbial formulation. A 0.1-PV slug was used for the preflush additives, followed by 0.2-PV of the nutrient. After a 3-day incubation period,

each core was injected with a second 0.2-PV slug of the nutrient and shut-in for a second 3-day incubation period. The cores were then flooded with brine. For the direct additives, a 1:1 ratio of the additive and the microbial formulation was used, and the same coreflood procedures were followed. Another test system was used in which the core was injected with a 0.1-PV slug of the additive, shut-in for 3 days, then the core was waterflooded with 2 PV of brine. After the waterflood, the core was injected with the microbial formulation and nutrient. Flask testing with the microbial formulation and additives indicated that the direct injection of a 1:1 mixture of alcohol and microbes would not be as effective because the microorganisms would metabolize the alcohol. The alcohols were added as a postflush after the microbial formulation. A 0.1-PV slug of the microbial formulation was followed with a 0.05-PV slug of the alcohol solution.

Transport Tests

Two 4-ft cores were used to compare the bicarbonate preflush with a microbial core without a preflush. Samples of the core effluent were taken at ports 1 through 4 along the core (fig. 1) and at 24-hour intervals for determination of microbial products (gas chromatograph analyses), microbial counts [aerobic and anaerobic colony forming units per milliliter(CFU)/mL], and nutrient concentration (anthrone-sucrose determination using spectrophotometry).

RESULTS AND DISCUSSION

Flask Tests

Flask tests were performed to compare microbial counts and products, surface tension, and pH of NIPER 1 and 6 when fermenting molasses with the addition of 1% Tronacarb™ in one flask (flask 3) and 1% sodium bicarbonate in a second flask (flask 2; table 1, figures 2 through 5). The microbial counts with Tronacarb™ were slightly higher. In flask experiment no. 1, the Tronacarb™ and the sodium bicarbonate did not buffer effectively, since the difference in pH values at 0 hours and at 168 hours was almost identical for all three flasks, including the control without Tronacarb™ or sodium bicarbonate (table 1). Gas chromatography showed that the total amount of microbial metabolites was greater in both flasks with sodium bicarbonate and Tronacarb™ (fig. 5). In the Tronacarb™ flask, the amount of products increased over that of the sodium bicarbonate at 120 hr. The primary metabolite responsible for this increase was ethanol, although all flasks showed an increase in propionic and butyric acids with time.

A second flask test (flask experiment no. 2) was conducted with some minor modifications: (1) a sample from each flask was frozen for future biosurfactant analyses by high-pressure liquid chromatography; (2) surface tensions were not measured because the tensiometer malfunctioned; and (3) viscosity measurements were also taken during the flask test to determine if addition of bicarbonate affected the viscosity of the microbial formulation. Particular attention was given to the types of products

detectable by gas chromatography that the microorganisms produced in each flask. The data from both flask experiments no. 1 and no. 2 illustrates how consistently the pH drops in each flask from the 24 hr to the 48 hr sample (figs. 4 and 8). This may be the optimal incubation time for production of short-chained fatty acids by NIPER 1 and NIPER 6. The surface tensions were lower for the Tronacarb™ flask, but the values were not low enough to conclude if surfactant production was being stimulated by the Tronacarb™. Results from gas chromatographic analyses of the flask samples showed again that the amount of microbial metabolites produced was much higher with Tronacarb™. In both flask experiments, the Tronacarb™ flasks showed an increase in alcohols produced, with a maximum value at 120 hr, a drop at 144 hr, and then increasing again at 168 hr. In both acid and alcohol production, changes occur somewhere between 24 and 72 hr incubation, and, with Tronacarb™, a change also occurs at 144 hr incubation. Biological calorimetry experiments would be extremely useful to assist in the interpretation of these metabolic data, and may define the mechanisms by which the sodium bicarbonate and Tronacarb™ are altering the cell's metabolic activity, as well as provide insights into the oil recovery improvement by these additives.

Additive Coreflooding Tests

Previous experiments showed that chemical additives sodium tripolyphosphate (STPP), a low-molecular-weight polyacrylamide (Cyanagel), a lignosulfonate (Petrolig-ERA), and sodium bicarbonate solutions (Bicarb and Tronacarb™) did not inhibit the growth of microorganisms NIPER 1 and 6 or their metabolite production. Coreflood experiments were performed using these additives as a preflush before microbial injection, adding the chemical directly to the microbial formulation before injection, and using the additive as a preflush followed by a waterflood before microbial injection. The results of these corefloods are summarized in tables 3 through 6, and figures 11 through 13. Berea sandstone cores injected with 1% Tronacarb™; both as a preflush and added directly to the microbial formulation, did not show a significant improvement in oil recovery over that of the coreflood using sodium bicarbonate (table 3). Figure 11 shows the Tronacarb™ coreflood compared with a coreflood using sodium bicarbonate as the preflush. A repeat of this coreflood series is being conducted to verify the difference in oil recovery with the different sodium bicarbonate preflushes. Most of the additives, when used as preflushes, improved oil recovery efficiency (E_r) over the average of the control corefloods (fig. 12). One of the Cyanagel corefloods (core 28) differed significantly in E_r. A repeat coreflood (core 31), showed a more consistent result when compared to that of core 12. The average E_r of the Cyanagel corefloods was 28.4% at 1 PV and 34.9% at 2 PV. The sodium bicarbonate coreflood recovery efficiencies were much more consistent, and the average E_r of these corefloods was 33.5% at 1 PV and 36.2% at 2 PV. A preflush of STPP improved E_r after 1 PV of brine had been injected, but no more oil was recovered after 2 PV of brine injection. Only Cyanagel, isoamyl, and isopropyl alcohols improved E_r over the control corefloods when

used as direct additives (fig. 13). The results from corefloods where the core was waterflooded after the chemical preflush and before the microbial injection indicated that there were really no synergistic effects by this injection strategy. The bicarbonate coreflood (core 23) was the only one that showed an oil recovery efficiency even comparable to that of the control corefloods.

The improved E_r by sodium bicarbonate may be attributed to increased microbial growth, changes in composition or amounts of microbial metabolites, or by the chemical facilitating the transport of microbial cells and/or metabolites through the core. The improved E_r with Cyanagel, Petrolig-ERA, and STPP may be due to a direct synergism with the microbial formulation, or they may be acting as sacrificial agents to facilitate transport. The shape of the oil recovery curves indicated that the additives assisted in the formation of an oil bank. Use of the chemical additives as a preflush proved to be slightly better in recovering oil than adding the chemical directly to the microbial formulation. Corefloods were also performed using the additives without the microbial formulation. These tests showed that the additives alone at these concentrations did not recover oil.

Use of sodium chloride at 0.5, 5.0 and 8.0% for microbial coreflooding experiments (corefloods MEOR-1, MEOR-2, and MEOR-3) indicated that NIPER 1 and 6 had an optimal salinity range at which the oil recovery efficiency was better (table 7, fig. 14). Until 1 PV of brine was flushed through the core, the oil recovery was about the same for 0.5% and 5.0% sodium chloride; however, after 1 PV of brine, the 5.0% sodium chloride core showed more improvement in residual oil recovery. The 8.0% sodium chloride core still showed microbial oil recovery, but not as much as the 0.5 or 5.0% sodium chloride.

4-Ft Additive Corefloods

4-ft cores MEOR-26 and MEOR-37 compared oil recovery efficiencies of the microbial formulation with and without a 1% sodium bicarbonate preflush (0.1 PV) (table 8, fig. 15). Additive data from corefloods in 1-ft-long cores had indicated that sodium bicarbonate improved the microbial oil recovery efficiency when used as a preflush. MEOR-26 had an E_r of 10%, which was about half that of the E_r observed from other 4-ft microbial corefloods. This was expected since the amount of microbes and nutrient that was injected was about half what was usually injected into 4-ft cores, and the core was not shut-in for a second time. MEOR-37 showed an E_r of 40%, and the only difference between the two corefloods was the preflush of sodium bicarbonate. The permeabilities of the two cores were nearly equal (385 and 353 millidarcies). A preflush of sodium bicarbonate alone did not recover additional crude oil; thus, the bicarbonate must have had a synergistic effect on the microbial formulation to significantly improve oil recovery. It is not known whether the bicarbonate improved the transport of the cells and/or products so that the oil recovery was greater, or whether the bicarbonate improved the transport of a microbial product such as a biosurfactant that was not detected by gas chromatography.

Three-dimensional graphs of microbial products detectable by gas chromatography, microbial counts (CFU/mL), fluorescein, and molasses concentration as a function of brine pore volumes throughput along the length of cores MEOR-26 (no bicarbonate) and MEOR-37 (with bicarbonate) are shown in figures 16 through 22. The concentration of products was greater at the beginning of the waterflood in the core with bicarbonate. At sampling ports 3 and 4 (2.5 and 3.5 ft from the inlet), the products peaked after 0.3 PV of fluid had been injected into core MEOR-37, and at about 0.6-PV in core MEOR-26. These data indicate that the preflush did indeed allow the microbial products to transport more effectively through the core. The microbial cell population was consistently 100 times greater at the start of the waterflood in all ports of core MEOR-37. After about 0.5-PV of brine had been injected, the cell population actually began to decrease slightly in the bicarbonate core when compared to the control. It is unclear whether the bicarbonate preflush significantly affected the microbial cell transport in the core since the microbial populations remained relatively equal except at the initiation of the waterflood.

Fluorescein has been used successfully as a tracer in a microbial-enhanced waterflood experiment.[9-10] At the concentrations used, it had no deleterious effects on the injected microorganisms and appeared to transport through porous media without a great amount of retention. Figure 20 illustrates the transport of fluorescein through a 4-ft-long Berea sandstone core that had been waterflooded to residual oil saturation (MEOR-37). Figure 21 shows the concentration of fluorescein detected in the effluent during the waterflood. Approximately 83% of the fluorescein was recovered in the effluent from the core. The fluorescein moved through the core at an interstitial velocity approximately equal to that of the injected water. The fluorescein transported through the core at a rate of 1.48 ft/d, while the waterflood rate was 1.45 ft/d.

After tracer was injected, the core was injected with a sodium bicarbonate preflush followed by microorganisms and nutrient. The core effluent samples were assayed for unmetabolized sugar, and the values were converted to total molasses concentration. The results from these samples showed that the molasses rate of transport was 1.14 ft/d, which was slower than that of the fluorescein (1.48 ft/d) and the injected brine (1.45 ft/D) (fig. 22). The lower rate of transport for molasses was expected, probably because it was being metabolized by the microorganisms along the length of the core. The amount of molasses that was consumed by microbial metabolism, or lost by adsorption or trapping by the rock, in coreflood MEOR-37 was approximately 74% of the injected molasses. After injection of 1.2 PV of water injection, the molasses concentration at all ports was 0; the microorganisms had apparently metabolized all of the nutrient.

CONCLUSIONS

The results from flask testing of the microbial formulation NIPER 1 and 6 clearly showed that both bicarbonates, sodium bicarbonate and the Tronacarb,™ did not effectively buffer the amount of acid being produced by the microorganisms. It appears that between 24 and 48 hours of incubation, the microoganisms produce the greatest amount of acid. The sodium bicarbonate and Tronacarb™ stimulated microbial growth by a factor of 10 to 100 times. The increased growth appeared to correlate with the production of metabolites detectable by gas chromatography. The total volume percent of products for the Tronacarb™ flask was much higher and the growth was also higher by a factor of 10 (tables 1 and 2) than that of the sodium bicarbonate flask. The surface tension values were not significantly low enough to warrant any conclusions regarding surfactant production by the microorganisms with the different bicarbonates. Quantitation of surfactant production during these tests will improve critical interpretation of these results. The observation of increased ethanol production with Tronacarb™ is significant, particularly since Tronacarb™ was not an effective preflush additive in the microbial coreflood. Based on only one coreflood comparison, the Tronacarb™ preflush did not appear to be nearly as effective as the 1% sodium bicarbonate, while in flask tests, the Tronacarb™ additive was better for microbial growth and gas chromatographically detectable metabolite production. Although the total amount of products detectable by gas chromatography was higher with Tronacarb™, these products may inhibit the production of the biosurfactant, which may be responsible for improved oil mobilization.

Use of certain chemical additives in low concentrations, particularly as a preflush prior to injection, can improve residual oil recovery of the microbial formulation NIPER 1 and 6. The same chemicals, when added directly to the microbial formulation, did not increase the oil recovery efficiency over that of the control corefloods. The alcohols isoamyl and isopropyl added as post-flushes with the microbial formulation did show some synergistic activity. It has not been determined whether they are acting as cosurfactants with the microbial surfactant, but more corefloods and flask testing are recommended with these two alcohols.

The products of microorganisms, primarily acids, alcohols, and surfactants, transport ahead of microbial cells in porous media. The cells do transport through Berea sandstone, and eventually a microbial population is present throughout the core. Once we are able to quantitate biosurfactant production by the microorganisms, then we can determine whether the sodium bicarbonate preflush is assisting in its transport through the core, and whether this transport is the key reason for the greatly improved oil recovery efficiency of the microbial formulation when following a bicarbonate preflush.

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TABLE 1. - Flask experiment no. 1 with sodium bicarbonate and Tronacarb™

Time, hr	pH	Surface tension, dynes/cm	Aerobic, cfu/mL[1]	Anaerobic, cfu/mL	TGC[2], vol %
			Flask 1 Control - No bicarbonate		
0	6.7	44.0	3.0×10^3	3.0×10^3	0.000
24	6.4	47.5	2.4×10^7	2.1×10^7	0.133
48	5.0	45.2	3.6×10^7	4.2×10^7	0.166
72	4.8	45.8	2.9×10^7	4.8×10^7	0.103
96	4.7	47.0	3.4×10^7	2.9×10^7	0.129
120	4.6	46.5	1.9×10^7	2.9×10^7	0.122
144	4.4	47.0	2.0×10^7	2.6×10^7	0.132
168	4.2	45.8	1.7×10^7	2.9×10^7	0.218
			Flask 2 Sodium bicarbonate		
0	8.0	47.5	9.0×10^3	9.0×10^3	0.000
24	7.6	49.5	1.9×10^7	2.2×10^7	0.186
48	7.3	52.5	3.6×10^8	4.2×10^8	0.191
72	5.6	48.5	4.6×10^8	4.6×10^8	0.201
96	5.4	44.5	2.3×10^8	2.1×10^8	0.189
120	5.2	45.8	4.2×10^8	2.9×10^8	0.154
144	4.9	45.0	2.4×10^8	1.7×10^8	0.194
168	4.9	46.5	7.9×10^8	7.6×10^8	0.180
			Flask 3 Tronacarb™		
0	8.4	47.0	3.0×10^3	3.0×10^3	0.000
24	8.3	52.2	1.4×10^7	1.6×10^7	0.181
48	6.9	48.2	2.0×10^9	2.4×10^9	0.114
72	6.6	48.0	6.6×10^9	1.3×10^{10}	0.195
96	6.3	48.5	3.5×10^9	2.3×10^9	0.200
120	6.2	45.5	8.4×10^9	4.4×10^9	0.301
144	6.1	48.0	6.1×10^9	8.2×10^9	0.262
168	5.8	48.0	6.3×10^9	5.5×10^9	0.285

[1]cfu - colony forming units/mL.

[2]Total products detected by gas chromatography, vol %.

TABLE 2. - Flask experiment no. 2 with sodium bicarbonate and Tronacarb™

Time, hr	pH	Viscosity, cP	Aerobic, cfu/mL[1]	Anaerobic, cfu/mL	TGC[2], vol %
Flask 1 Control - No bicarbonate					
0	6.70	1.30	7.65×10^3	1.00×10^0	0.053
24	6.40	1.31	5.60×10^7	3.70×10^7	0.052
48	4.95	1.25	8.60×10^7	5.60×10^7	0.137
72	4.95	1.36	1.65×10^8	9.00×10^7	0.125
96	4.75	1.30	9.05×10^7	1.33×10^8	0.139
120	4.45	1.24	5.70×10^7	5.30×10^7	0.192
144	4.25	1.48	2.10×10^7	6.70×10^7	0.173
168	4.15	1.25	4.00×10^5	9.85×10^6	0.184
Flask 2 Sodium bicarbonate					
0	7.95	1.30	5.75×10^3	1.00×10^0	0.056
24	7.80	1.23	3.60×10^7	3.55×10^7	0.042
48	6.35	1.10	8.90×10^7	1.30×10^8	0.048
72	6.40	1.34	3.35×10^7	1.03×10^8	0.140
96	6.55	1.19	5.30×10^8	1.85×10^8	0.122
120	6.35	1.35	7.60×10^8	8.60×10^7	0.143
144	6.15	1.34	7.50×10^7	1.20×10^8	0.138
168	6.40	1.27	7.50×10^7	8.80×10^7	0.142
Flask 3 Tronacarb™					
0	8.2	1.20	5.20×10^3	1.00×10^0	0.063
24	8.10	1.17	7.15×10^7	3.30×10^7	0.060
48	6.65	1.05	7.70×10^8	7.40×10^8	0.146
72	6.25	1.16	5.15×10^8	6.90×10^8	0.353
96	6.45	1.39	2.80×10^8	8.70×10^8	0.385
120	6.60	1.66	8.55×10^8	7.85×10^7	0.394
144	6.55	1.72	7.25×10^8	1.10×10^8	0.405
168	6.60	1.44	3.95×10^8	5.15×10^8	0.470

[1]cfu - colony forming units/mL.

[2]Total products detected by gas chromatography, vol %.

TABLE 3. - 1-ft Berea sandstone cores with bicarbonate and Tronacarb™

Core	Treatment	S_{orwf}[3]	S_{orcf}[4]	S_{orcf}[5]	E_r[6]	ΔS_{orcf}[7]	ΔS_{orcf}[8]	E_r[9]	k[10]
CONTROL	[1]0.5	35.3	28.1	24.0	20.4	7.2	11.3	32.0	925
BICARB	[2]0.6	33.4	21.2	19.1	36.5	12.2	14.3	42.8	830
TRONACARB	[2]0.6	40.3	30.5	28.5	24.3	9.8	11.8	29.3	828

[1]Core was injected with 0.1 PV microbes, 0.2 PV molasses, shut-in 3 days, re-fed with 0.2 PV molasses, shut-in 3 days, and waterflooded.

[2]Core was injected with 0.1 PV of additive preflush (1%), then injected with 0.1 PV microbes, 0.2 PV molasses, shut-in 3 days, re-fed with 0.2 PV molasses, shut-in 3 days, and waterflooded.

[3]S_{orwf} = Oil saturation after waterflooding.

[4]S_{orcf} = Oil saturation after microbial treatment and 1 PV waterflood.

[5]S_{orcf} = Oil saturation after microbial treatment and 2 PV waterflood.

[6]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[7]$\Delta S_{orcf} = S_{orwf} - S_{orcf}$, after 1 PV waterflood.

[8]$\Delta S_{orcf} = S_{orwf} - S_{orcf}$, after 2 PV waterflood.

[9]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[10]k = absolute permeability to brine in millidarcies.

TABLE 4. - Preflush/microbial corefloods

Core	Treatment[1]	S_{orwf}[2]	S_{orcf}[3]	S_{orcf}[4]	E_r[5]	ΔS_{orcf}[6]	ΔS_{orcf}[7]	E_r[8]	k[9]
4	Control	38.7	27.6	25.2	28.7	11.1	13.5	34.9	804
10	Control	35.3	28.1	24.1	20.4	7.2	11.2	31.7	925
11	Bicarb	33.4	21.2	19.1	36.8	12.3	14.3	42.8	830
27	Bicarb	36.0	24.5	23.9	31.9	11.5	12.1	33.6	773
12	Cyanagel	36.2	22.7	18.9	37.0	13.4	17.3	47.8	1007
28	Cyanagel	31.6	26.3	25.7	16.9	5.3	5.9	18.9	753
31	Cyanagel	36.0	24.7	22.3	31.3	11.3	13.7	38.0	833
13	Petrolig	36.2	23.6	22.7	34.8	12.6	13.5	37.3	905
8	STPP	36.9	24.4	24.4	33.9	12.5	12.5	33.9	1020

[1]All cores used 0.1 PV of additive as a preflush. All cores were injected with 0.1 PV NIPER 1 & 6; 0.2 PV 4% molasses, shut-in 3 days, re-fed 0.2 PV 4% molasses, shut-in 3 days, then waterflooded. Additives:
Control - only microbes, no additives
Bicarb - 1% sodium bicarbonate
Cyanagel - 1% polyacrylamide (low molecular weight)
Petrolig - 2% lignosulfonate
STPP - 1% sodium tripolyphosphate

[2]Oil saturation after waterflooding (%).

[3]Oil saturation after microbial treatment and 1 PV waterflood (%).

[4]Oil saturation after microbial treatment and 2 PV waterflood (%).

[5]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[6]Difference in residual oil saturation after 1 PV waterflood.

[7]Difference in residual oil saturation after 2 PV waterflood.

[8]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[9]Absolute permeability to brine in millidarcies (md).

TABLE 5. - Direct additive/microbial corefloods

Core	Treatment[1]	S_{orwf}[2]	S_{orcf}[3]	S_{orcf}[4]	E_r[5]	ΔS_{orcf}[6]	ΔS_{orcf}[7]	E_r[8]	k[9]
4	Control	38.7	27.6	25.2	28.7	11.1	13.5	34.9	804
10	Control	35.3	28.1	24.1	20.4	7.2	11.2	31.7	925
18	Bicarb	33.1	24.4	23.9	26.3	8.6	9.2	27.8	942
15	Cyanagel	35.2	23.3	21.0	33.8	11.9	14.1	40.3	1017
16	Petrolig	32.8	23.5	22.2	28.4	9.3	10.6	32.3	982
17	STPP	37.6	28.3	26.4	24.7	9.3	11.2	29.8	1019
33	Isoamyl	35.1	23.4	22.3	33.3	11.6	12.8	36.5	791
40	Butanediol	34.6	26.5	25.7	23.4	8.1	8.9	25.7	804
49	Isopropyl	37.0	27.0	25.0	27.0	10.0	12.0	32.4	788

[1]All cores were injected with 0.1 PV of the additive and 0.1 PV NIPER 1 & 6; 0.2 PV 4% molasses, shut-in 3 days, re-fed with 0.2 PV 4% molasses, shut-in 3 days, then waterflooded. Additives: all in wt %.
Control - only microbes, no additives
STPP - 1% sodium tripolyphosphate
Bicarb - 1% sodium bicarbonate
Cyanagel - 1% polyacrylamide (low molecular weight)
Petrolig - 2% lignosulfonate
Butanediol - 1%
Isoamyl alcohol - 1%
Isopropyl alcohol - 1%

[2]Oil saturation after waterflooding (%).

[3]Oil saturation after microbial treatment and 1 PV waterflood (%).

[4]Oil saturation after microbial treatment and 2 PV waterflood (%).

[5]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[6]Difference in residual oil saturation after 1 PV waterflood.

[7]Difference in residual oil saturation after 2 PV waterflood.

[8]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[9]Absolute permeability to brine in millidarcies (md).

TABLE 6. - Corefloods using an additive preflush, followed by 2 PV waterflood

Core	Treatment[1]	S_{orwf}[2]	S_{orcf}[3]	S_{orcf}[4]	E_r[5]	ΔS_{orcf}[6]	ΔS_{orcf}[7]	E_r[8]	k[9]
4	Control	38.7	27.6	25.2	28.7	11.1	13.5	34.9	804
10	Control	35.3	28.1	24.1	20.4	7.2	11.2	31.7	925
20	Petrolig	37.2	31.1	30.2	16.4	6.1	7.0	18.8	999
21	STPP	43.7	38.1	37.9	12.8	5.6	5.8	13.3	815
22	Cyanagel	34.0	30.1	29.6	11.5	3.9	4.4	12.9	961
23	Bicarb	38.1	30.5	28.8	20.0	7.6	9.3	24.4	952

[1]All cores were injected with 0.3 PV of the additive, waterflooded with 2 PV of brine, and injected with 0.1 PV NIPER 1 & 6; 0.2 PV 4% molasses, shut-in 3 days, re-fed 0.2 PV 4% molasses, shut-in 3 days, then waterflooded. Additives:

Control - only microbes, no additives
Petrolig - 2% lignosulfonate
STPP - 1% sodium tripolyphosphate
Cyanagel - 1% polyacrylamide (low molecular weight)
Bicarb - 1% sodium bicarbonate

[2]Oil saturation after waterflooding (%).
[3]Oil saturation after microbial treatment and 1 PV waterflood (%).
[4]Oil saturation after microbial treatment and 2 PV waterflood (%).

[5]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[6]Difference in residual oil saturation after 1 PV waterflood.
[7]Difference in residual oil saturation after 2 PV waterflood.

[8]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[9]Absolute permeability to brine in millidarcies (md).

TABLE 7. - Effects of sodium chloride on microbial oil recovery efficiency

Core	Treatment[1]	S_{orwf}[2]	S_{orcf}[3]	S_{orcf}[4]	E_r[5]	ΔS_{orcf}[6]	ΔS_{orcf}[7]	E_r[8]	k[9]
MEOR1	0.5%	31.0	25.3	25.3	22.0	5.7	5.7	22.0	512
MEOR2	5.0%	28.4	23.8	19.9	18.4	4.6	8.5	31.9	348
MEOR3	8.0%	35.3	30.8	28.7	12.8	4.5	6.6	18.9	603

[1]All cores were injected with 0.1 PV NIPER 1 & 6; 0.2 PV 4% molasses, shut-in 3 days, re-fed 0.2 PV 4% molasses, shut-in 3 days, then waterflooded. Brine used:
0.5% NaCl
5.0% NaCl
8.0% NaCl

[2]Oil saturation after waterflooding (%).

[3]Oil saturation after microbial treatment and 1 PV waterflood (%).

[4]Oil saturation after microbial treatment and 2 PV waterflood (%).

[5]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[6]Difference in residual oil saturation after 1 PV waterflood.

[7]Difference in residual oil saturation after 2 PV waterflood.

[8]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[9]Absolute permeability to brine in millidarcies (md).

TABLE 8. - 4-ft core experiments with microbes and sodium bicarbonate

Core	Treatment[1]	Sorwf[2]	Sorcf[3]	Sorcf[4]	Er[5]	ΔSorcf[6]	ΔSorcf[7]	Er[8]	k[9]
MEOR-26	0.35	32.9	30.1	29.5	8.5	2.8	3.4	10.3	385
MEOR-37	0.45	30.9	24.6	19.5	20.4	6.3	11.4	36.9	353

[1]MEOR-26 - 0.05 PV NIPER 1 & 6, 0.1 PV 4% molasses, shut-in 3 days, fed 0.1 PV 4% molasses, then waterflooded.
MEOR-37 - same as above, with a preflush of 0.1 PV of 1% sodium bicarbonate.
[2]Oil saturation after waterflooding (%).
[3]Oil saturation after microbial treatment and 1 PV waterflood (%).
[4]Oil saturation after microbial treatment and 2 PV waterflood (%).

[5]E_r - Oil recovery efficiency after 1 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[6]Difference in residual oil saturation after 1 PV waterflood.
[7]Difference in residual oil saturation after 2 PV waterflood.

[8]E_r - Oil recovery efficiency after 2 PV waterflood, $\frac{S_{orwf} - S_{orcf}}{S_{orwf}} \times 100\%$.

[9]Absolute permeability to brine in millidarcies (md).

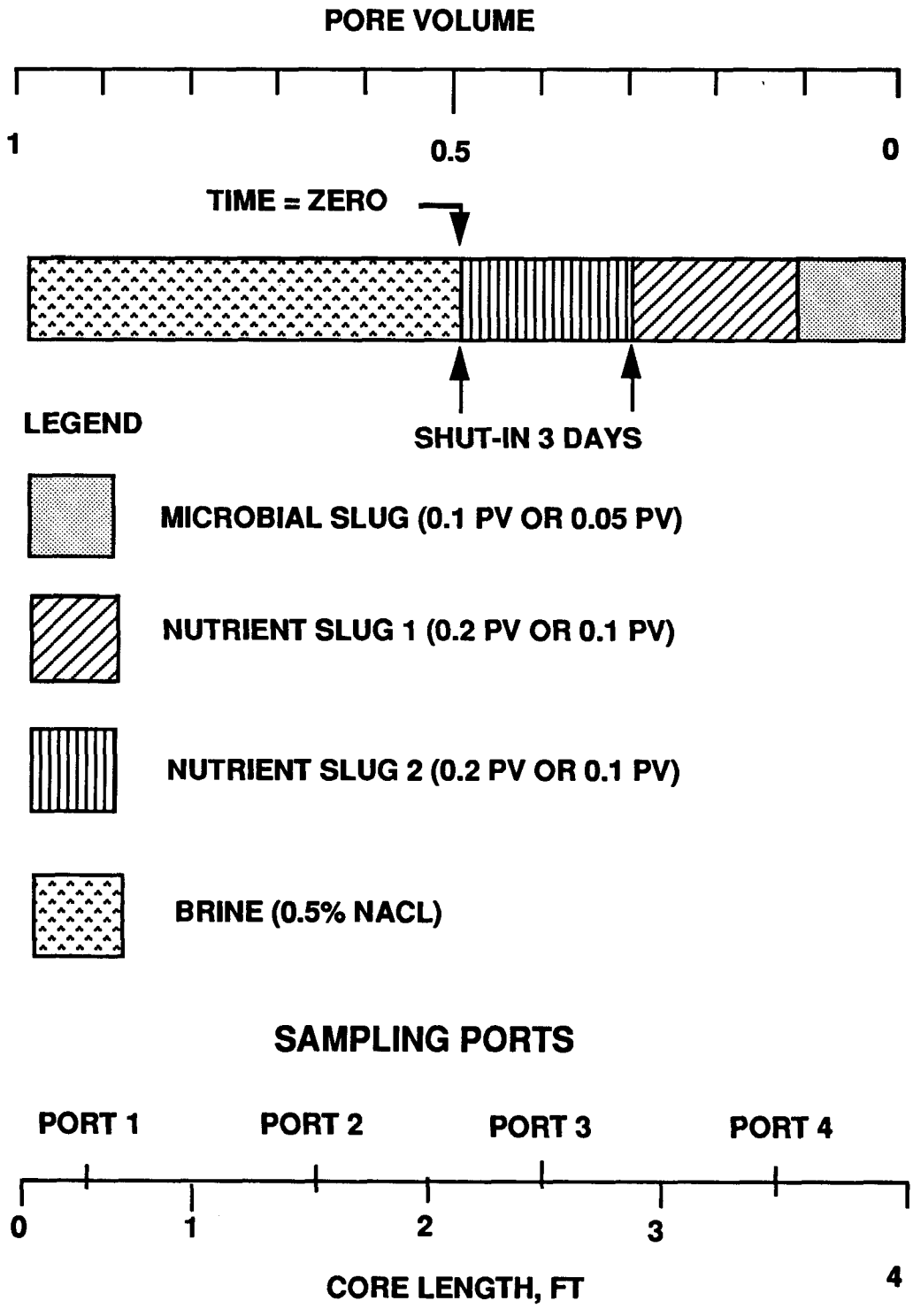

FIGURE 1. - Diagram of 4-ft coreflood apparatus showing injection strategies and sampling port positions.

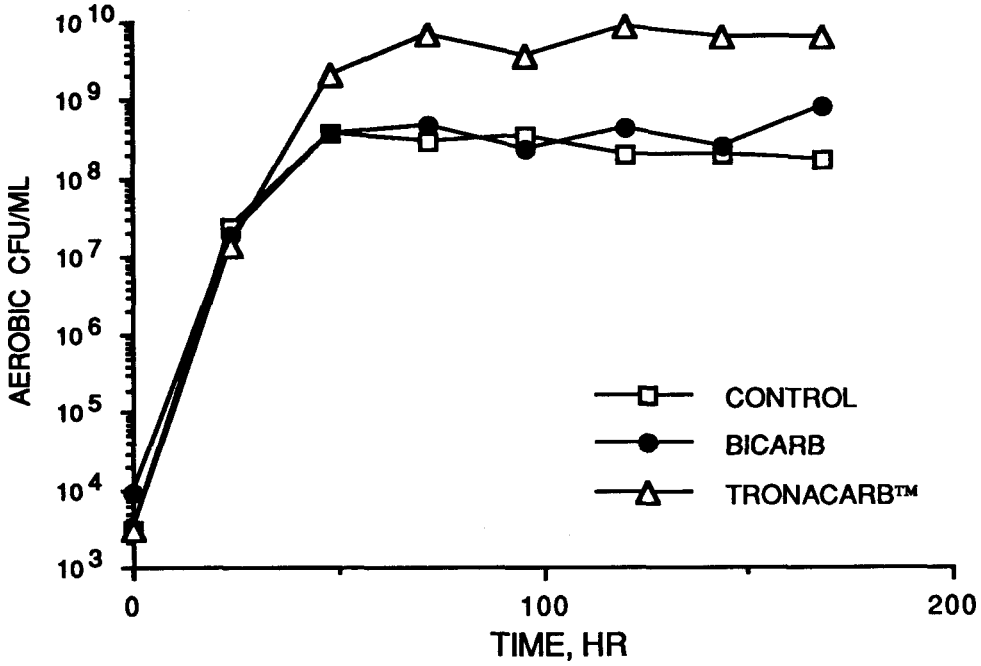

FIGURE 2. - Aerobic microbial counts from flask experiment no. 1.

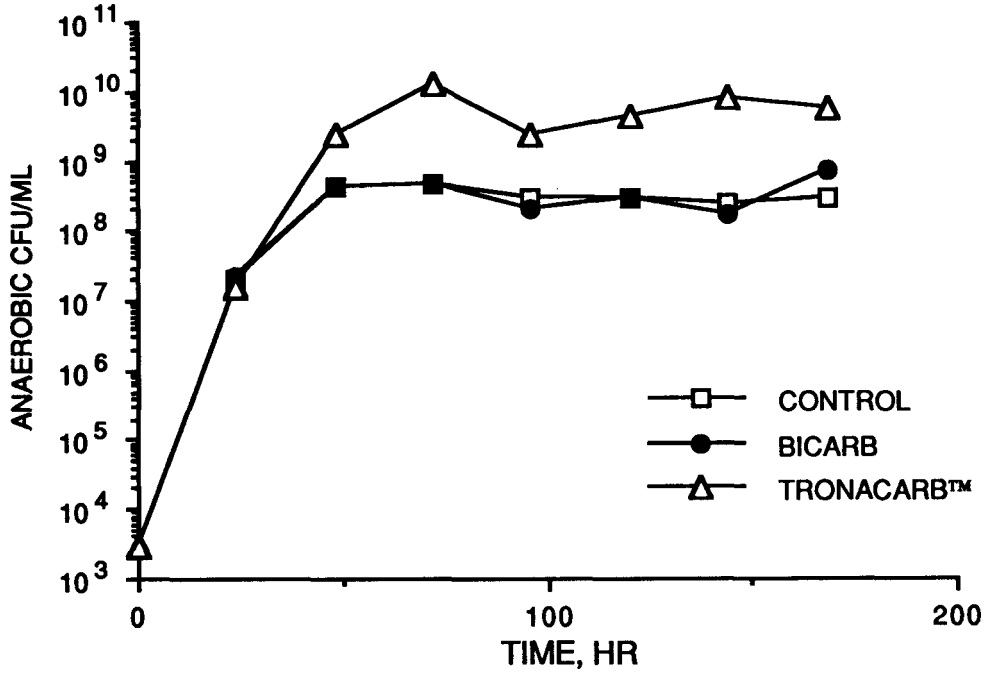

FIGURE 3. - Anaerobic microbial counts from flask experiment no. 1.

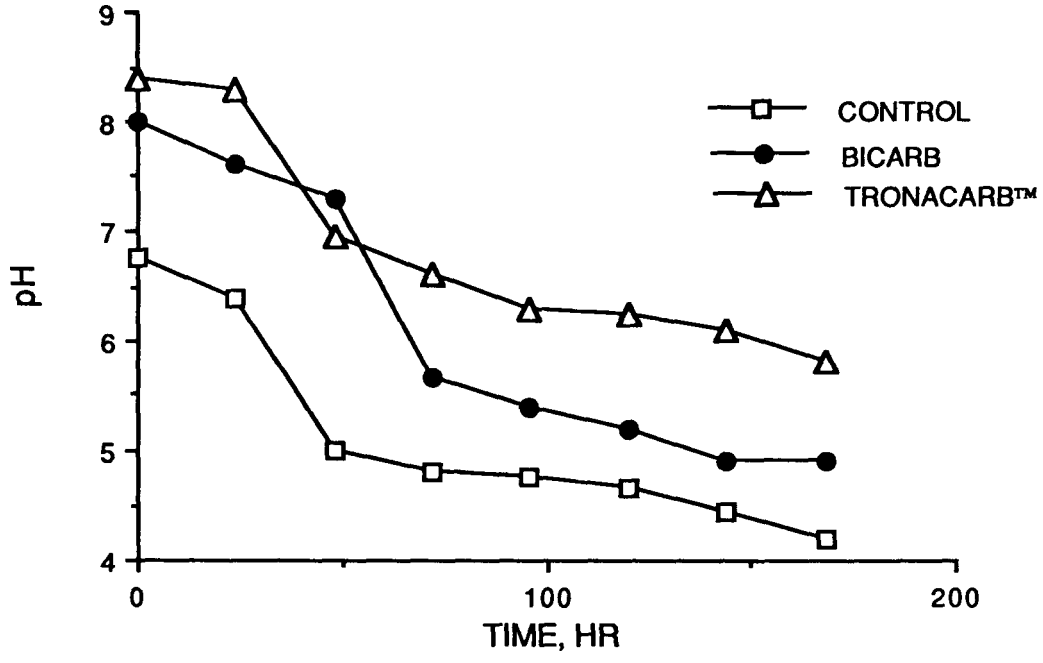

FIGURE 4. - pH from flask experiment no. 1.

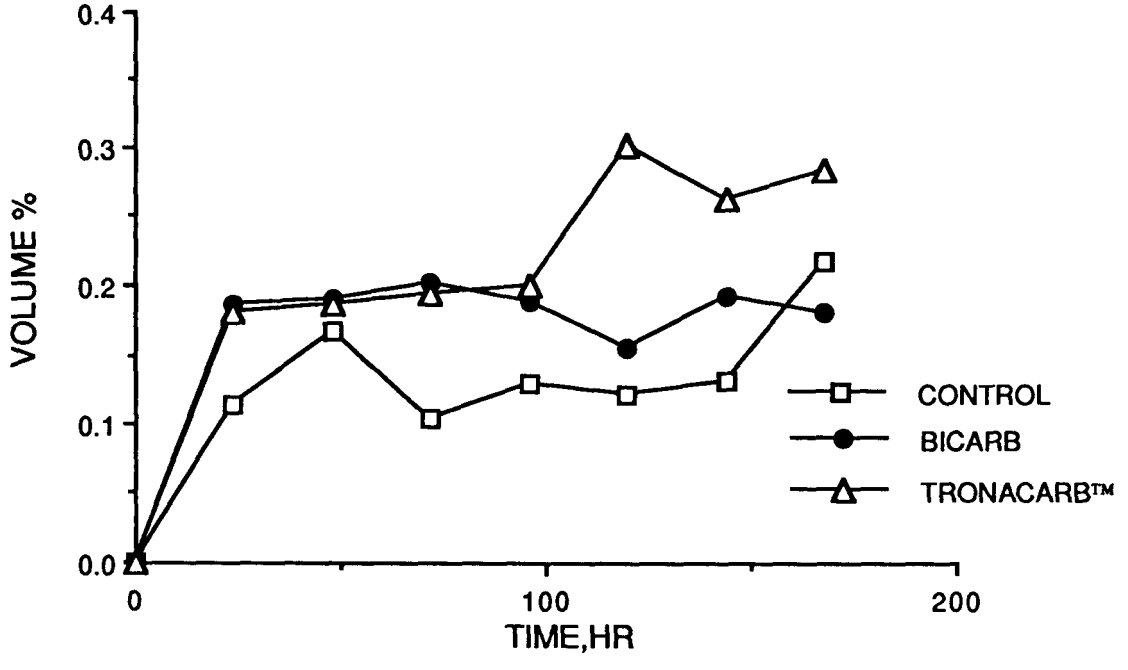

FIGURE 5. - Microbial products detected by gas chromatography from flask experiment no. 1.

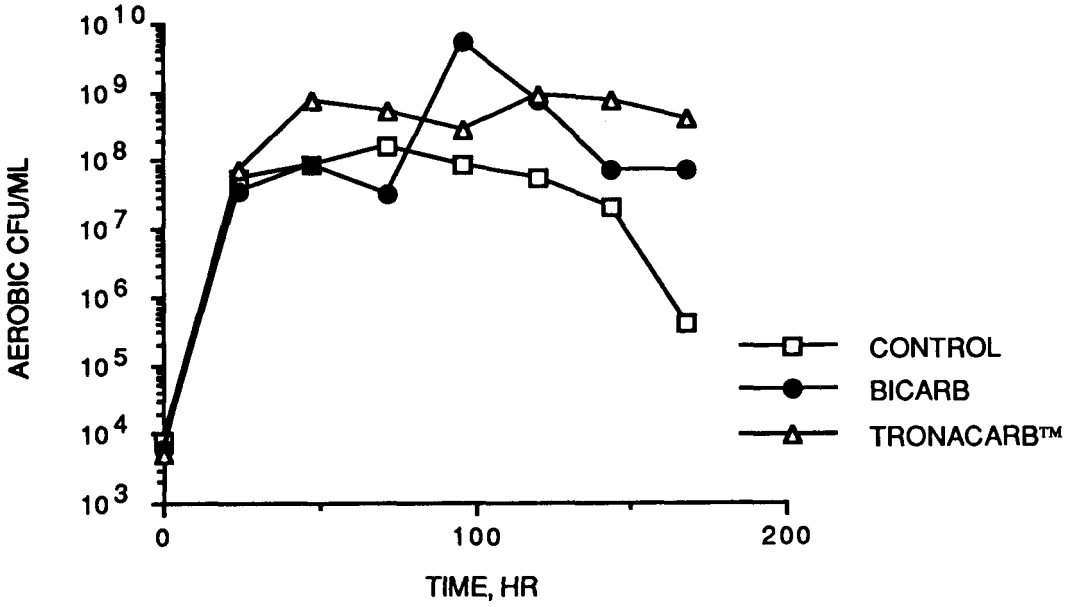

FIGURE 6. - Aerobic microbial counts from flask experiment no. 2.

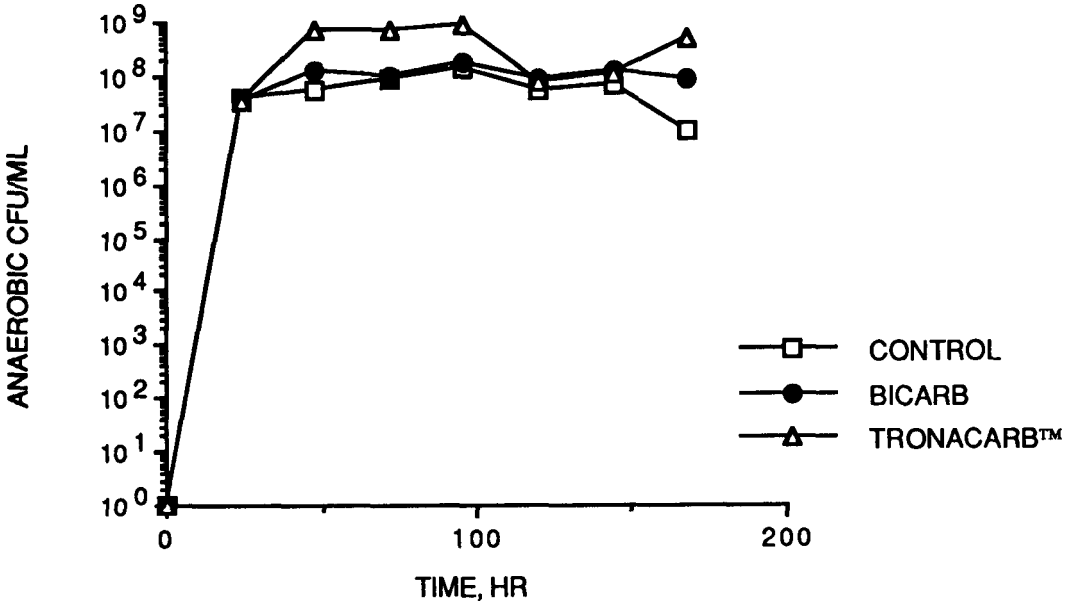

FIGURE 7. - Anaerobic microbial counts from flask experiment no. 2.

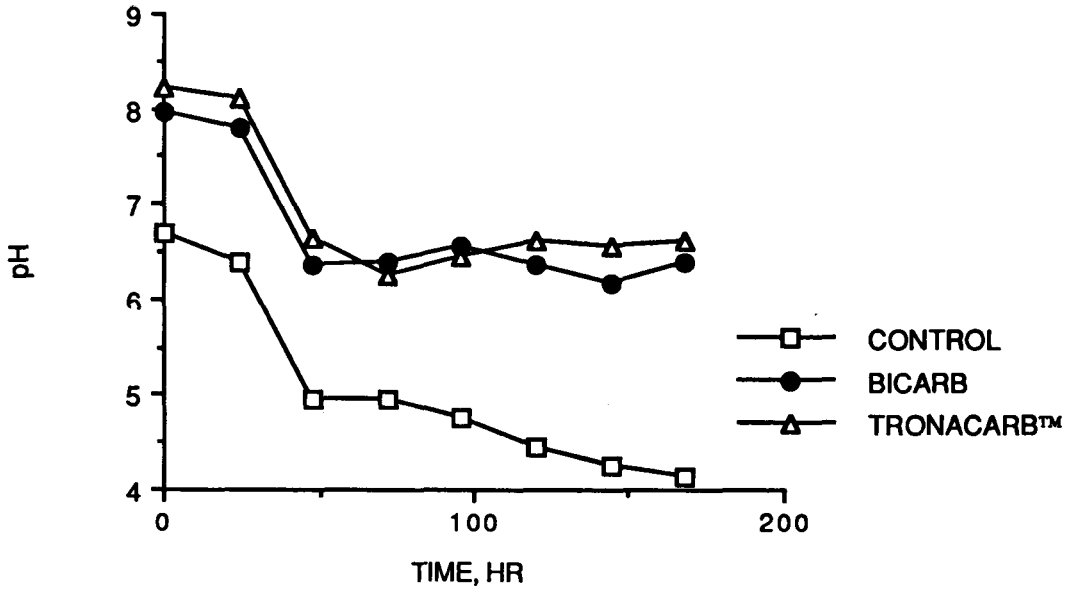

FIGURE 8. - pH from flask experiment no. 2.

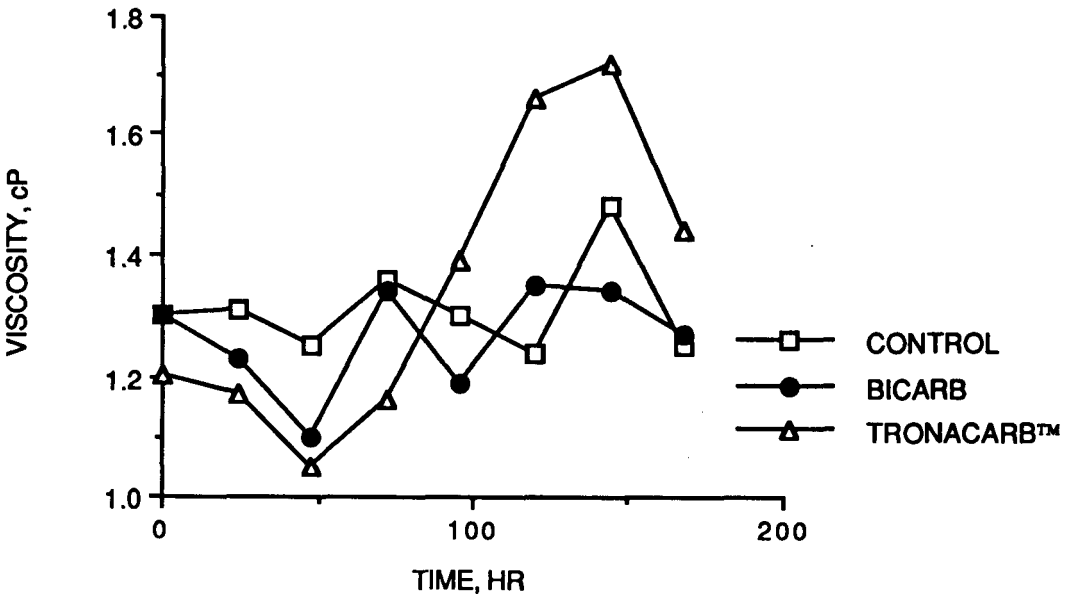

FIGURE 9. - Viscosity values from flask experiment no. 2.

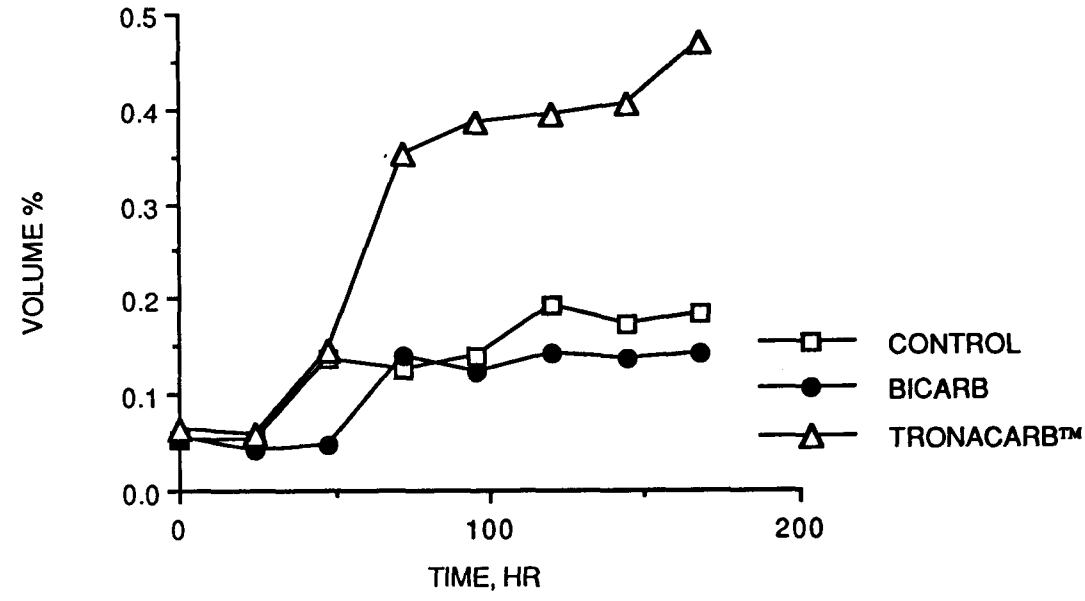

FIGURE 10. - Microbial products detected by gas chromatography from flask experiment no. 2.

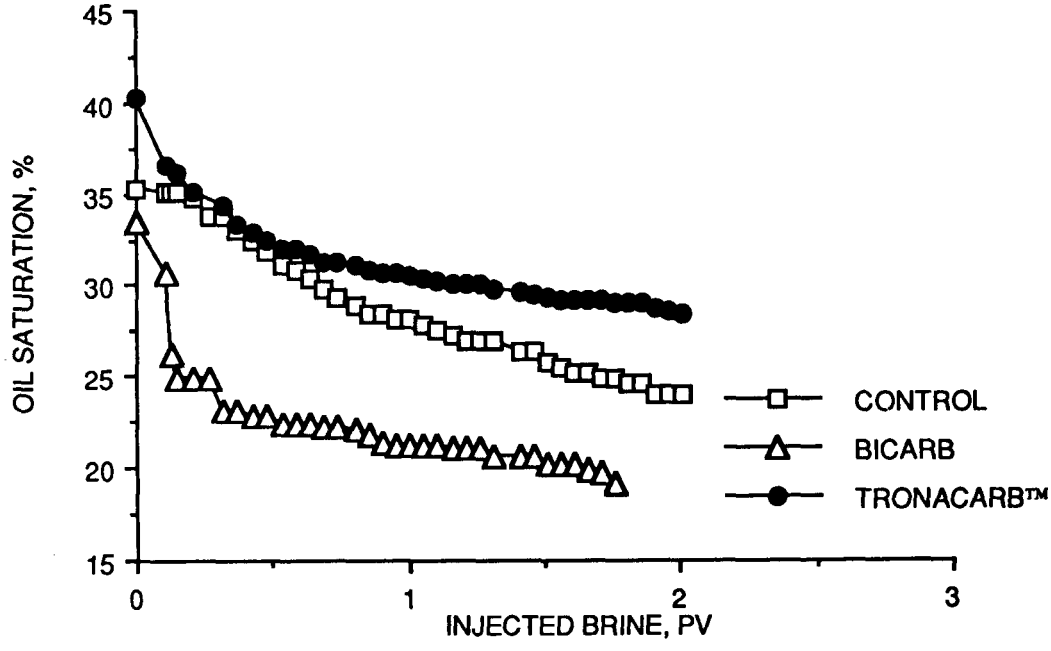

FIGURE 11. - Oil recovery from sodium bicarbonate and microbial corefloods.

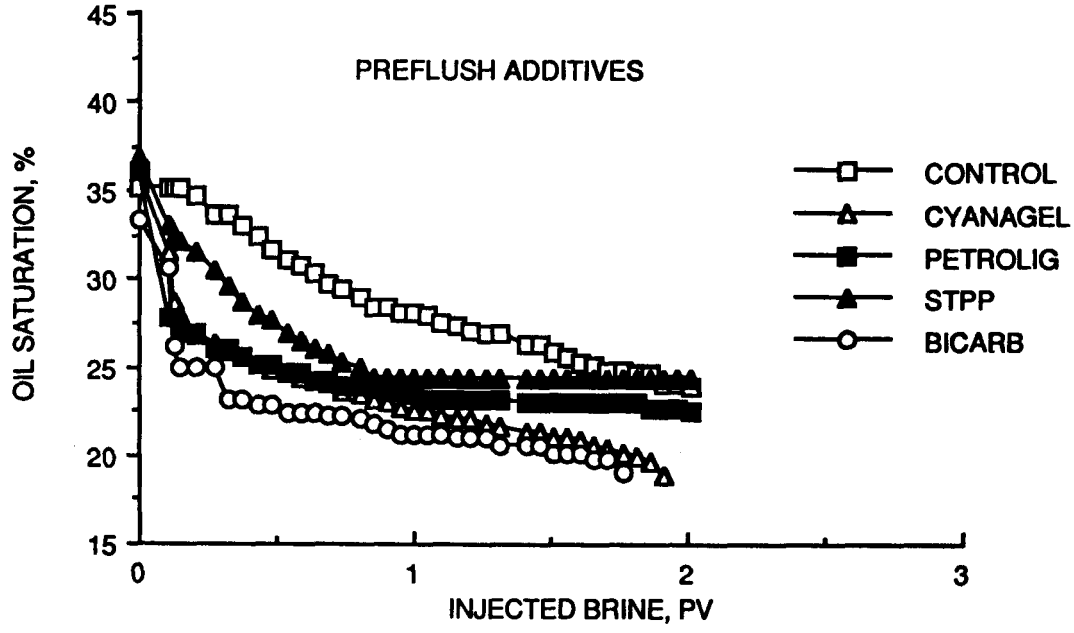

FIGURE 12. - Oil recovery from additive preflush microbial corefloods.

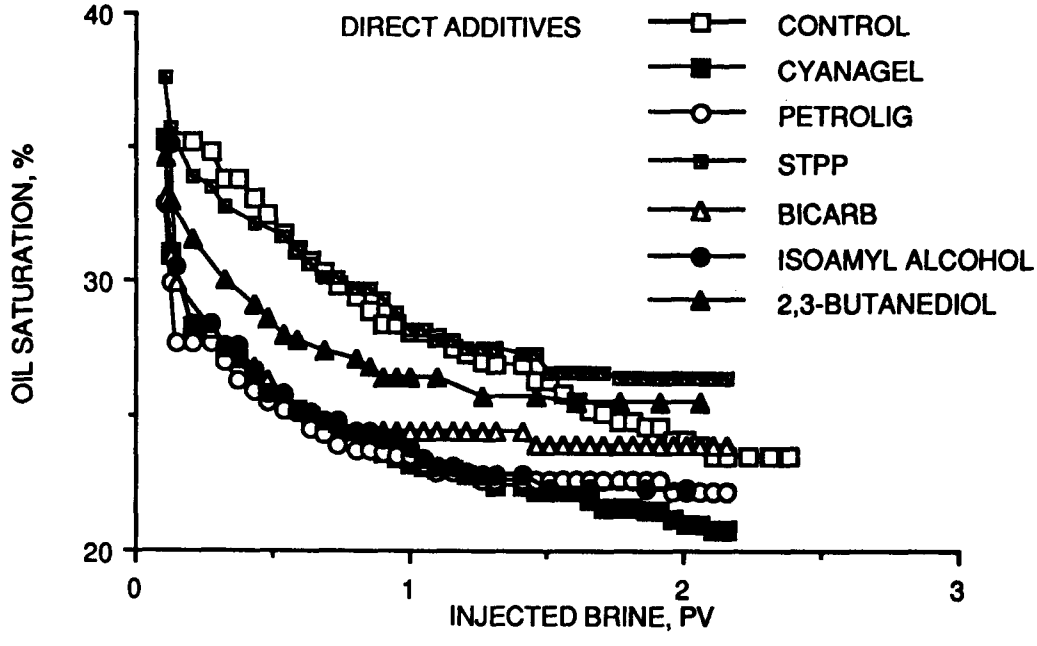

FIGURE 13. - Oil recovery from direct additive microbial corefloods.

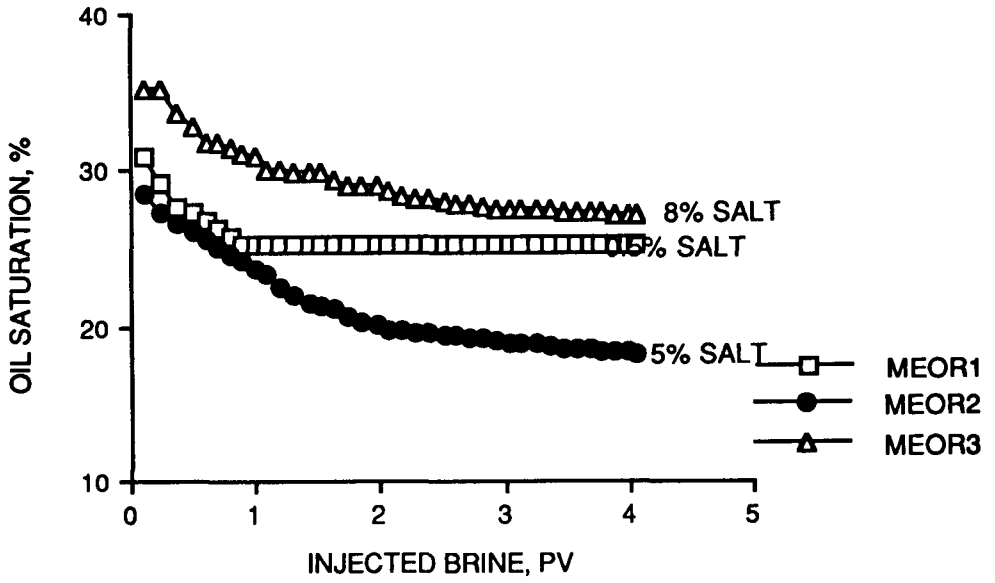

FIGURE 14. - Oil recovery from corefloods using various salt concentrations with the microbial formulation NIPER 1 and 6.

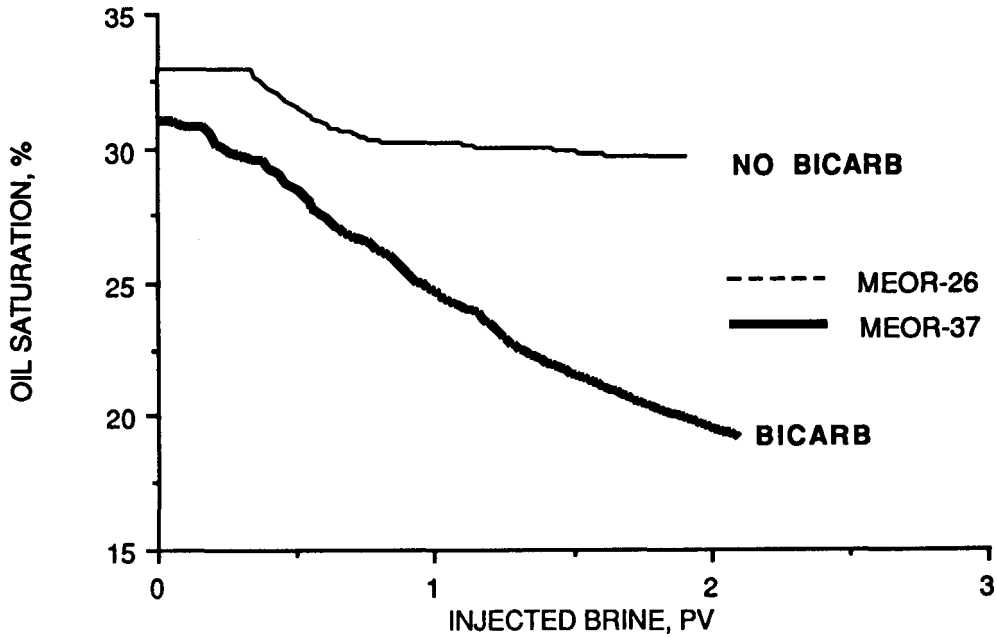

FIGURE 15. - Oil recovery from 4-ft corefloods with and without a sodium bicarbonate preflush.

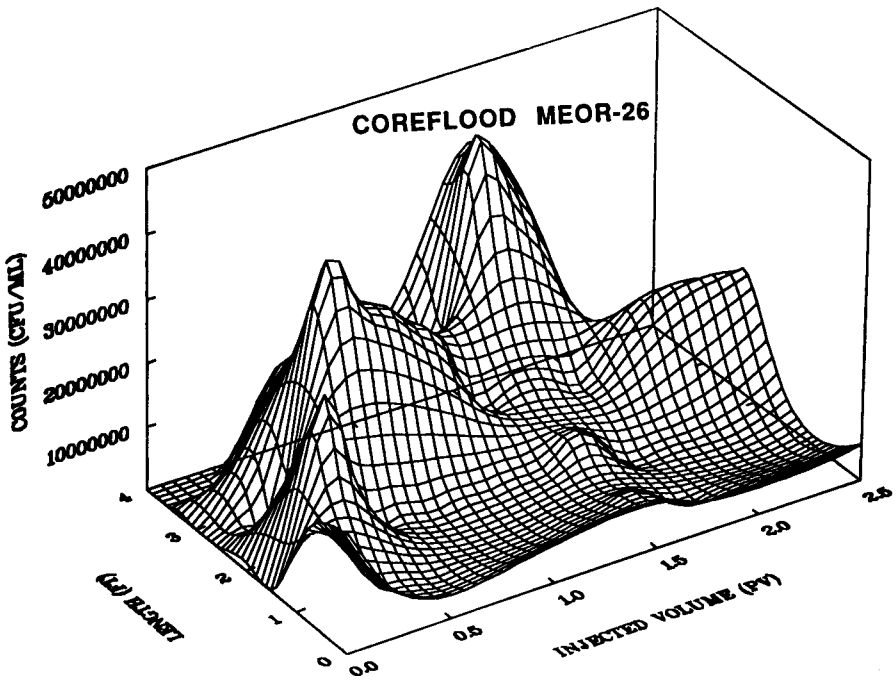

FIGURE 16. - Microbial counts from coreflood MEOR-26.

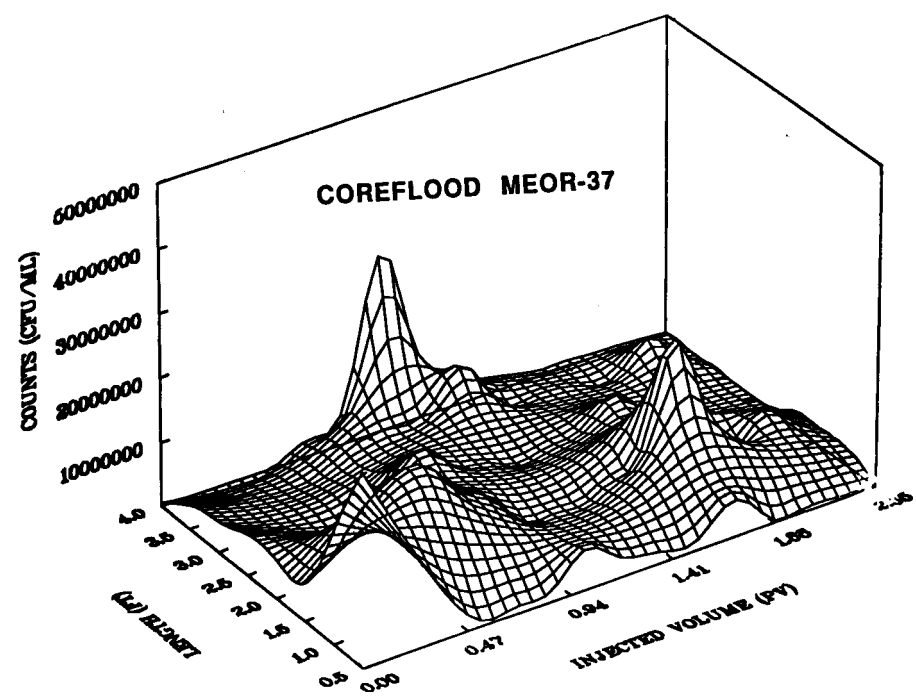

FIGURE 17. - Microbial counts from coreflood MEOR-37, with a bicarbonate preflush.

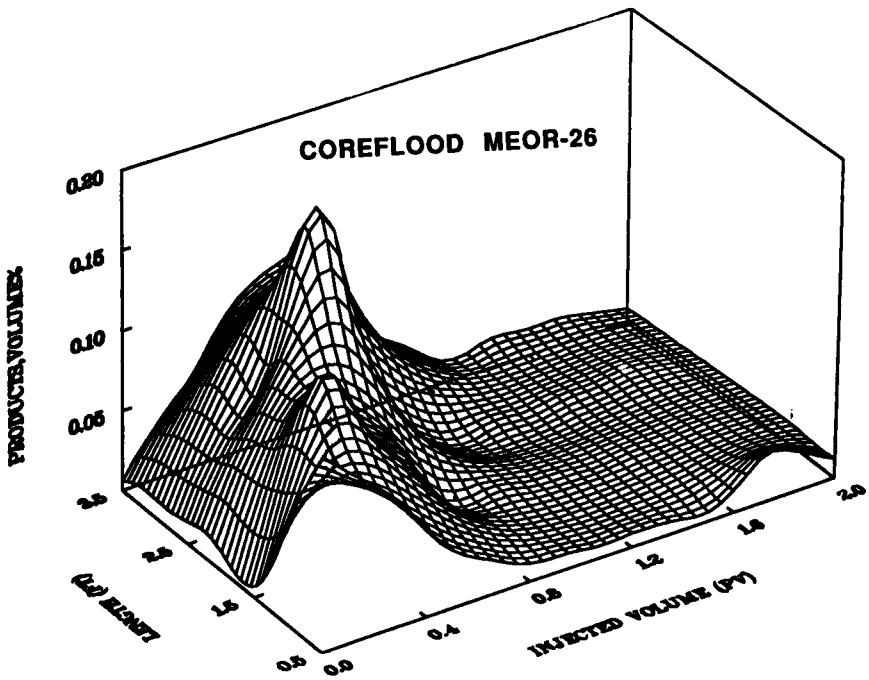

FIGURE 18. - Microbial products detected by gas chromatography from coreflood MEOR-26.

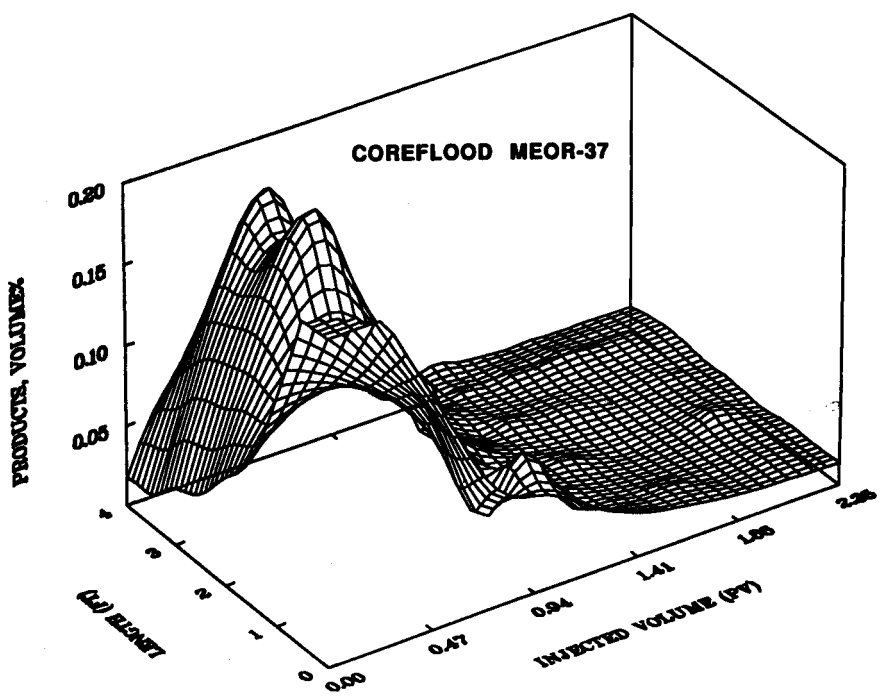

FIGURE 19. - Microbial products detected by gas chromatography from coreflood MEOR-37 with a bicarbonate preflush.

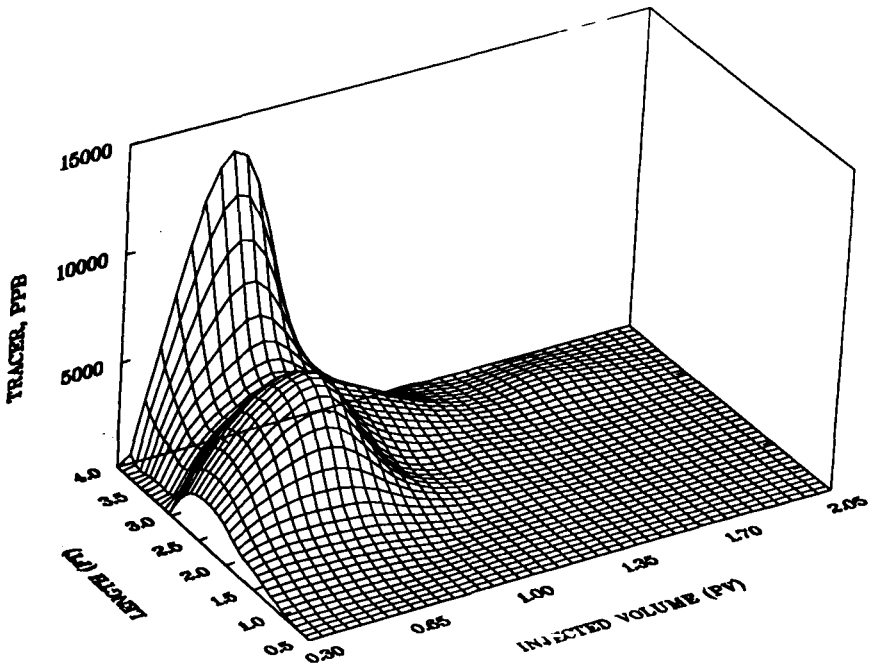

FIGURE 20. - Tracer (fluorescein) in coreflood port samples from MEOR-37.

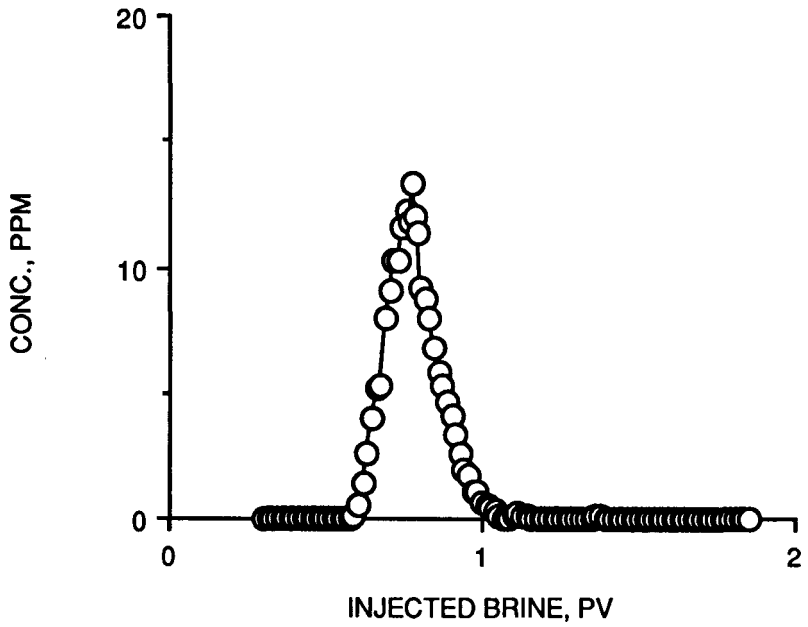

FIGURE 21. - Tracer (fluorescein) concentration from coreflood MEOR-37.

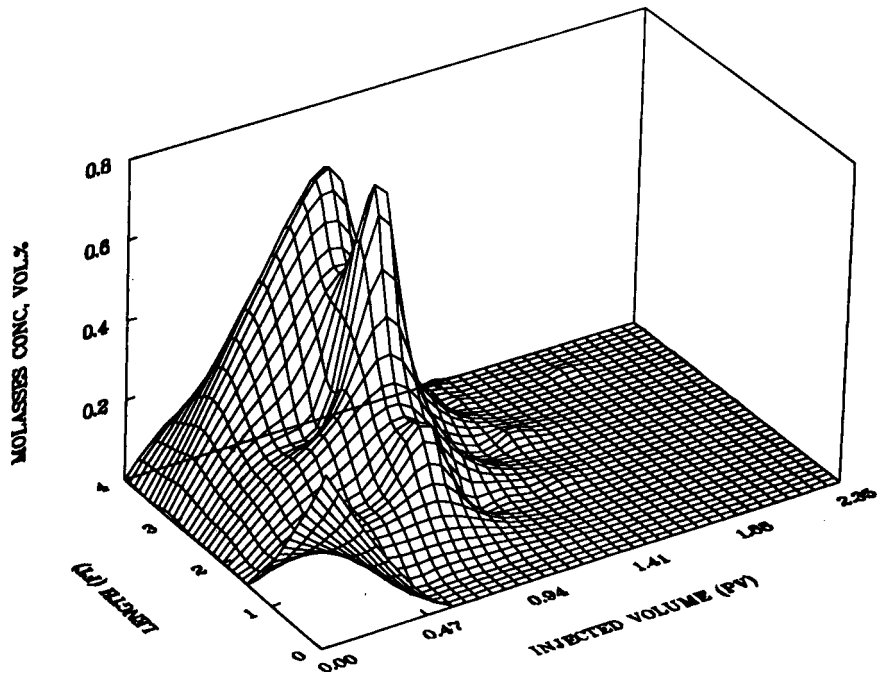

FIGURE 22. - Molasses concentration from coreflood MEOR-37.

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