Dilute Surfactant Methods for Carbonate Formations

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Kishore K. Mohanty

Department of Chemical Engineering

University of Houston

4800 Calhoun Road

Houston, Texas 77204-4004

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Abstract

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally fractured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. Anionic surfactants (Alfoterra 35, 38) recover about 54% of the oil in about 150 days by imbibition driven by wettability alteration and low tension in the core-scale. Anionic surfactant, Alfoterra-68, recovers about 38% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Surfactant concentration and brine composition affect wettability alteration. Plans for the next quarter include conducting simulation, mobilization, and imbibition studies.

TABLE OF CONTENTS

List of Graphical Materials

Executive Summary

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally fractured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope, yet it was developed for sandstone reservoirs in the past. The goal of this research is to evaluate dilute (hence relatively inexpensive) surfactant methods for carbonate formations and identify conditions under which they can be effective. Anionic surfactants (Alfoterra 35, 38) recover about 54% of the oil in about 150 days by imbibition driven by wettability alteration and low tension in the core-scale. Anionic surfactant, Alfoterra-68, recovers about 38% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Surfactant concentration and brine composition affect wettability alteration. Plans for the next quarter include conducting simulation, mobilization, and imbibition studies.

Introduction

There are many carbonate reservoirs in US (and the world) with light oil and fracture pressure below its minimum miscibility pressure (or reservoir may be naturally factured). Many carbonate reservoirs are naturally fractured. Waterflooding is effective in fractured reservoirs, if the formation is water-wet. Many fractured carbonate reservoirs, however, are mixed-wet and recoveries with conventional methods are low (less than 10%). Thermal and miscible tertiary recovery techniques are not effective in these reservoirs. Surfactant flooding (or huff-n-puff) is the only hope (Spinler et al., 2000), yet it was developed for sandstone reservoirs in the past (Bragg et al., 1982).

The goal of this research is to evaluate dilute surfactant methods for carbonate formations and identify conditions under which they can be effective. Adsorption, phase behavior, wettability alteration, IFT gradient driven imbibition, blob mobilization at high capillary and Bond numbers will be quantified. An existing laboratory simulator will be modified to incorporate the mechanisms of surfactant transport and effective parameters will be developed to model this process in a dual porosity reservoir simulator. Field-scale simulations will be conducted to identify criteria under which dilute surfactant methods are feasible without active mobility control.

This report summarizes our results for the period of April, 2004 through June, 2004. The five tasks for the project are: (1) Adsorption, (2) Wettability alteration, (3) Gravity and viscous mobilization, (4) Imbibition, and (5) Simulation. The third and fourth tasks were worked on this quarter. An SPE/DOE paper (Seethepalli et al., 2004) was presented summarizing the results of this work at the 14th Symposium on Improved Oil Recovery. The results of imbibition and wettability are highlighted in this report.

Experimental

Material

Imbibition studies were conducted with four surfactants: DTAB, Alfoterra 35, 38 and 68. Our studies (described in previous reports) show that DTAB, Alfoterra 35 and 38 are good wettability altering agents. Alfoterra 68 lowers the IFT considerably. Surfactants were used as supplied without further purification.

Calcite (Iceland spar) were supplied by Scientific Ward. The oil was from a West Texas fractured carbonate field (supplied by Marathon Oil Company). It was 28.2 °API, 19.1 cp viscosity, 0.2 acid number and 1.17 base number. It was similar to the oil MY3 used by Hirasaki and Zhang (2003). Synthetic brine composed of Na_2CO_3 was used for the anionic surfactants to lower adsorption and surfactant requirement. A limestone, Texas Cordova Cream was obtained from a quarry near Austin.

Imbibition Study

Outcrop limestone 1.5 inch diameter and 6 inch long cores were used. Air permeability of these cores were about 120 md. Porosity was 22.5%. Each core was first completely saturated with a 0.1 N NaCl brine. 5 PV of crude oil was injected to drive the core to connate water saturation. Oil saturation at the end of this oil flood was 72%. The core was immersed in the crude oil and aged for 18 days at 80 °C. The imbibition cell was filled with the surfactant-Na2CO3 solution. The aged core was placed in an imbibition cell and the oil production was monitored.

Wettability Test

The wettability tests were done on mineral plates (2 cm x 1 cm x 0.2 cm). The plates were polished on a 600 mesh diamond lap and equilibrated with synthetic brine for a day. The initial wettability state of the plate was determined by measuring the advancing and recently receded contact angle of oil with the plate immersed in brine. The plate was removed from brine and aged with oil at an elevated temperature (~80 °C) in the oven for about two days to make it oil-wet. The reservoir temperature is close to the room temperature (~30 °C), but the elevated temperature aging is done to compensate for the short aging time (compared with the geological time). After removing from the oven, the plate (with oil stuck around it) was contacted with synthetic (sodium carbonate) brine for an hour and the advancing contact angle was measured. The contact angle measurements were made with the help of a Kruss goniometer. Thereafter, the synthetic brine was replaced by the surfactant-brine solution and the evolution of contact angle was studied for a period of two days by imaging the drops attached to the plate. In the cases where the drops were too small (<<0.1 mm), it was difficult to measure an accurate contact angle and a post-wettability test was performed. In the post-wettability test, the plate was washed with brine following the surfactant treatment. This plate was then placed in the brine solution and an oil drop was deposited on the bottom of the surface with the help of an inverted needle (oil drops did not attach to the top of the plate in these cases). The contact angle was then measured. This gave the final wettability state of the plate. Drops were deposited on several parts of the plate and the range of the contact angles was noted.

We are developing a method to investigate the wettability alteration at a nanometer scale using an atomic force microscope (AFM). An AFM can be used to measure the topography of a solid surface with adsorbed materials immersed in water. This is done by a relatively new technique called tapping mode scanning in water and indicates the amount of adsorption. AFM can also be used to measure the force of adhesion between a surface and a spherical tip; this force of adhesion can be used to study the nature of adsorbed materials on any surface. For using AFM, one needs a mineral surface that is close to molecularly smooth before adsorption of materials. Calcite plates are not molecularly smooth. Silica or mica plates are smooth, but carry a negative zeta potential. Thus we treated a mica plate with a chemical that bonds uniformly and changes its zeta potential to positive (similar to calcite's). This modified mica plate was aged first in brine and then a drop of crude oil was deposited at its bottom surface. The plate was aged for 14 days. Then the oil drop was washed off the plate surface by a jet of brine and the surface of the plate was probed by an AFM under water. Then the plate was washed by a surfactant solution and again probed by the AFM under water. Comparison of the measurements before and after surfactant treatment indicates molecular alterations during wettability alterations.

Results and Discussion

Imbibition

Each oil-wet core was placed in an imbibition cell filled with a different brine. Cell 1 had 0.05 wt% Alfoterra 35 and 0.3 M Na2CO3 brine. Cell 2 had 0.05 wt% Alfoterra 38 and 0.3 M Na2CO3 brine. Cell 3 had 0.05 wt% Alfoterra 68 and 0.3 M Na2CO3 brine. Cell 4 had 0.1 M NaCl brine. Finally, cell 5 had 0.1 wt% DTAB in the field brine. DTAB and Alfoterra 35, 38 are good wettability altering surfactants from contact angle experiments. Alfoterra 68 is a low IFT agent from phase behavior studies.

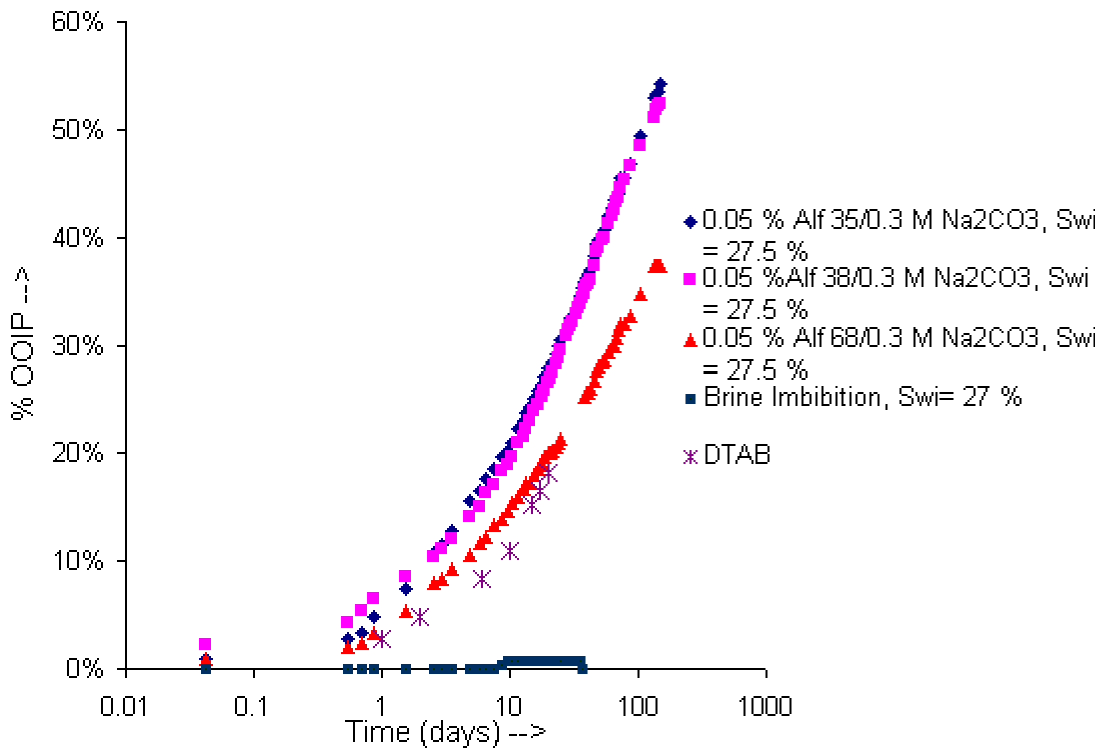

Figure 1. Spontaneous imbibition of different brines into oil-wet limestone core with Swi=27.5%

The oil production in each cell due to spontaneous imbibition is shown in Figure 1. The spontaneous imbibition volumes in cells 1 and 2 are about the same and higher than the other two. About 54% of the oil has been produced in about 150 days of spontaneous imbibition with Alfoterra 35 and 38. These two surfactants were good wettability altering agents in the calcite plate wettability study. The production in cell 3 is about 38% in 150 days. Alfoterra 68 induces spontaneous imbibition, but to a lower extent compared to the first two cases. There was very little imbibition in cell 4. This indicates that the core is oil-wet and brine without any surfactant does not imbibe. The oil production in cell 5 is substantial, about 20% in 30 days. This (DTAB) experiment started later than the other imbibition experiments. But the production curve is following that of cell 3 so far.

The imbibition obtained with these surfactants can be compared to literature values. Austad & Standness (2003) obtained about 15% OOIP recovery at 40 C and about 45% OOIP recovery at 70 C from spontaneous imbibition with 1 wt% DTAB for chalks with Swi=26%. Xie et al. (2004) have used nonionic surfactants to enhance oil recovery from dolomitic Class II reservoirs. They observed about 5-10% recovery. This indicates that the anionic surfactants have performed well in the laboratory-scale.

It is observed that initially the oil left in thin streams from sides of the core in the imbibition experiments of Alfoterra 35 and 38. In case of DTAB and Alfoterra 68 at all times oil is seen to be leaving from the top of the core, indicating a gravity driven process. The same was observed for Alfoterra 35 and 38 at later times. The pictures of the cores during the imbibition experiments are shown in Figure 2. All these processes are gravity driven due to low interfacial tension. If the wettability is altered, then capillarity driven flow sets in first, but eventually gravity driven flow controls the movement of the fluids. We have done a few numerical simulations of water imbibition into water-wet and oil-wet rocks in the absence of surfactants. Even in water-wet rocks, gravity driven cocurrent imbibition dominates after a few hours of capillarity-driven counter-current flow. We are currently developing a simulator with surfactant transport and wettability alterations to understand the laboratory experiments.

Figure 2a. Imbibition experiments: the picture on the left for the case of Alfoterra 38 shows oil leaving from sides, where as on the right for the case of Alfoterra 68 oil is found to leave from the top.

Figure 2b. Imbibition experiments: oil leaves from the top in the case of DTAB

At the end of the imbibition, the oil saturation in a water-wet rock tends towards the residual oil saturation at the existing microscopic Bond number. In an oil-wet rock, however, the final state is of nonuniform saturation distribution controlled by the capillary pressure distribution which, in turn, is governed by the fluid densities. The top of the core (or fracture block) would be at the initial oil saturation. The oil saturation would decrease with depth and approach the residual oil saturation at the existing microscopic Bond number. If the macroscopic gravity to capillary force ratio is large, most of the core would be at the residual oil saturation. If that ratio is small, then a capillary end effect would exist and the oil saturation would be higher. The total recovery possible in the case of a water-wet core with surfactant-aided gravity drainage is the difference between the initial oil saturation and the residual oil saturation. In cores being studied, that would amount to ~58% OOIP. With surfactants Alfoterra 38 and Alfoterra 35, we have a recovery of around 54 % OOIP in the imbibition experiments.

Wettability

In this phase, we did experiments to study the effectiveness of surfactants on wettability reversal at different concentrations and with the field brine. In our previous study, we found that the surfactant Alfoterra-38 gave good wettability reversal at 0.05 wt% surfactant concentration as observed by its post wettability contact angle of around 40^0.

To study the effect of surfactant concentration on wettability reversal, the surfactant concentration (Alfoterra-38) was varied from 0.05 wt% to 0.5 wt %. The contact angle was monitored for a period of 48 hrs. It was seen that the contact angle was intermediate to oil-wet regime at higher surfactant concentrations. At 0.05 wt% surfactant concentration the post wettability contact angles were 40- 60^0. With 0.1-wt % surfactant concentration, the post wettability contact angles were 105- 160^0 and with 0.5-wt % surfactant the contact angles were 108- 130^0. The pictures of the calcite plate are shown in Figure 3.

Figure 3a. Slab after 48 hrs, in 0.05 wt % Alfoterra 38 and 0.3 M Na_2CO_3 in field brine solution. The oil left the slab because of low IFT but the contact angle showed oil wet slab.

Figure 3b. Slab after 48 hrs, in 0.1 wt % Alfoterra 38 and 0.3 M Na_2CO_3 in synthetic brine solution. The oil left the slab because of low IFT but the contact angle showed oil wet slab.

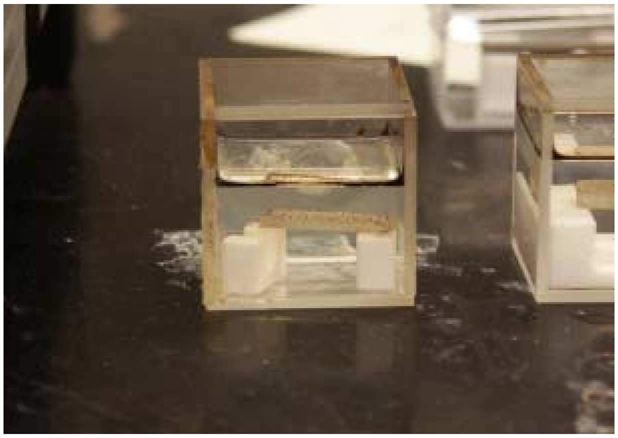

Figure 3c. Slab after 48 hrs, in 0.5 wt % Alfoterra 38 and 0.3 M Na_2CO_3 in synthetic brine solution. The oil left the slab because of low IFT but the contact angle showed oil wet slab.

To study the effect of field brine surfactant interactions on wettability reversal, the previous procedure was altered to include the field brine for contact angle measurements. The procedure followed was as follows: The calcite slab was aged in the field brine for a period of 1 day, followed by aging in the crude oil at an elevated temperature for a period of 48 hrs. The slab was then placed in a cuvette and the field brine was introduced to study the contact angle of oil on the slab in the field brine. It was found that the slab was oil-wet (contact angle of 180^0). To the field brine solution, surfactant (Alfoterra-38) was added in such a quantity as to make the final concentration 0.05 wt %. The contact angle was monitored for a period of 48 hrs. The oil left the slab because of low IFT, but the post wettability test gave a contact angle of $106\text{-}120^0$. This indicated that the interaction of field brine with surfactant plays a pivotal role in surfactants ability to alter wettability. The slab was then placed in 0.05 wt % Alfoterra–38 surfactant solution prepared in 0.1 N NaCl brine for period of 2 days and the contact angle between oil and water was measured. This measurement gave contact angles of 61^0-101^0. Thus, the presence of the field brine has a significant effect on the wettability.

Figure 4 shows the AFM topography of the adsorbed organic material on top of a modified mica in water. It shows a very small area (25 μm x 25 μm) at the boundary of the surface whose wettability was altered by aging with a crude oil drop. Approximately, the left half of the plate is oil-wet and the right half is water-wet. On the left half, patches of organic adsorption of ~ 1 μm scale can be seen. The maximum height scale is 700 nm. Figure 5 shows the AFM topography of the same surface after the surfactant Alfoterra 38 treatment. The left half of the plate has lost most of the adsorbed organic material. The maximum height scale of the adsorbtion is 100 nm in this figure.

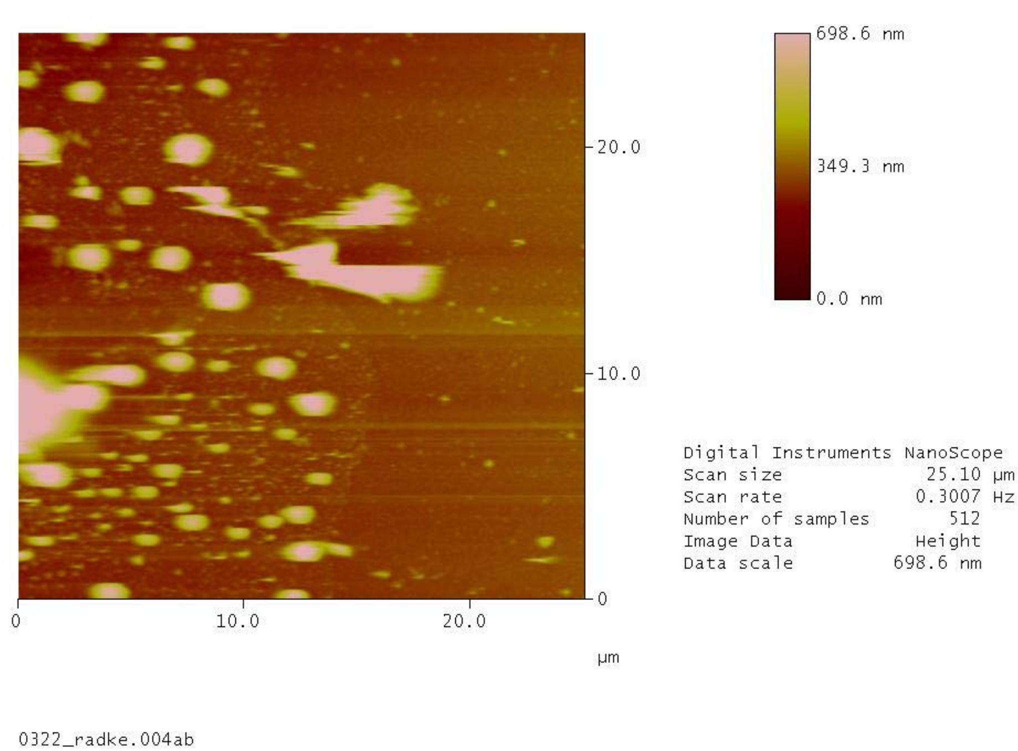

Figure 4. Adsorbed organic material topography before surfactant treatment. The left half (approximately) is oil-wet and the right half is water-wet.

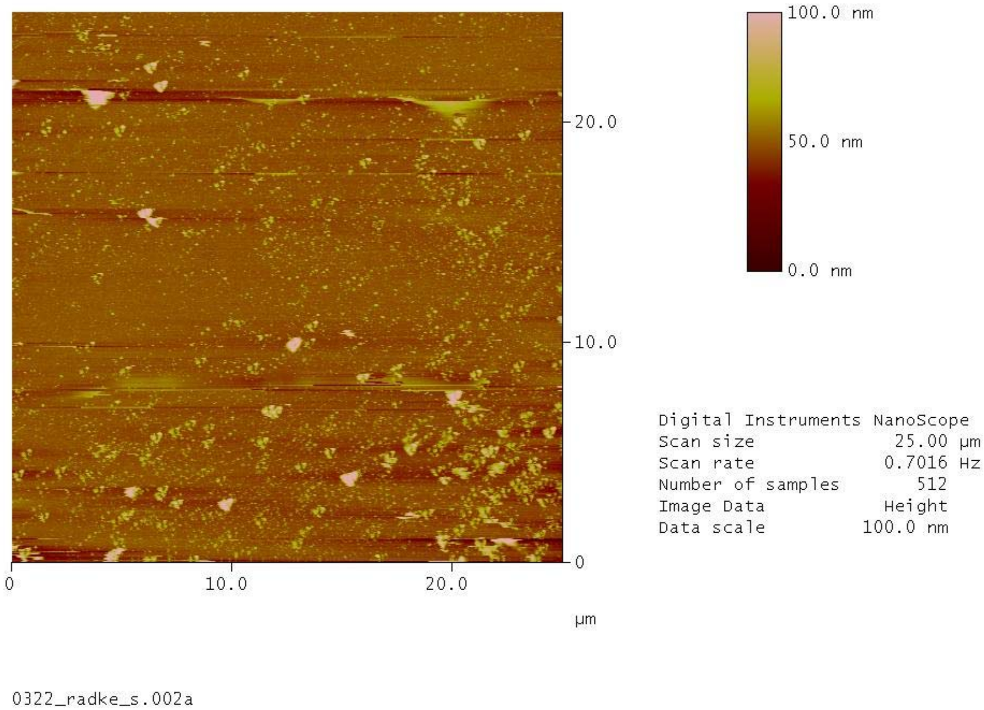

Figure 5. Adsorbed organic material topography after surfactant treatment.

Figure 6 shows the force of adhesion between a 1 μm radius COOH terminated borosilicate spherical tip and the surfaces. The force of adhesion for the modified mica plate is about 22 nN. After aging with the oil drop the oil-wet region has a force of adhesion of about 34 nN. The water-wet regions showed a force of about 19 nN, not too different from the original value. After the surfactant treatment, the regions that were oil wet showed a force of about 23 nN, close to the original value. The force of adhesion of the water-wet regions did not change much after surfactant treatment. These numbers indicate that the adsorbed organic material is removed by the surfactant and the surfactant does not adsorb significantly on the water-wet surfaces. Atomic force microscopy shows that the solubilization of adsorbed organics is the key mechanism behind wettability alteration.

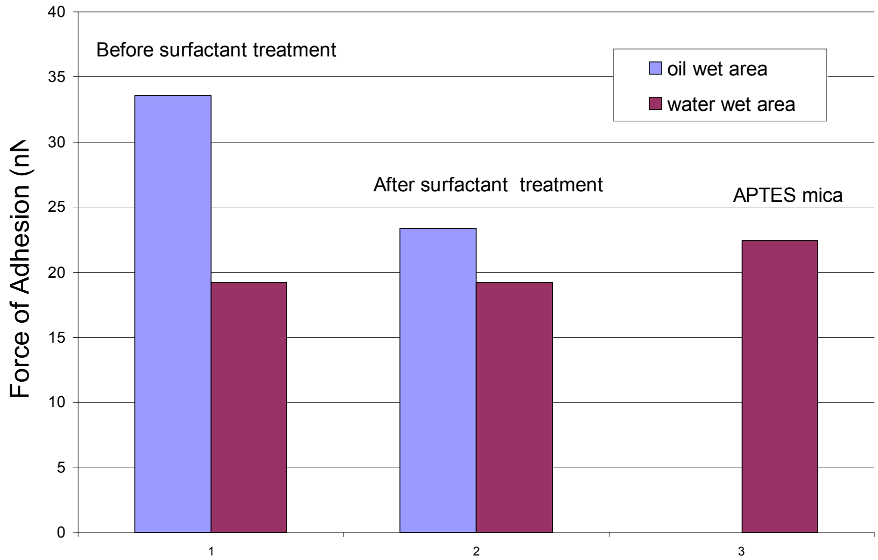

Figure 6. Force of adhesion for modified mica, after oil treatment (but before surfactant treatment), after surfactant treatment. Blue bar corresponds to the oil-wet region, red bar to water-wet regions.

Technology Transfer

Marathon oil company is one of the major producers in West Texas carbonates. We have briefed them about our project plans and have received field samples. We are working with Oil Chem Technology, Stepan and Sasol on surfactants. These collaborations are extremely important to the success of our project. We have written a paper, SPE 89423, which was presented at the 14th SPE/DOE IOR symposium in Tulsa, April, 2004.

Conclusions

Anionic surfactants (Alfoterra 35, 38) recover about 54% of the oil in about 150 days by imbibition driven by wettability alteration and gravity in the core-scale (Task 4). Anionic surfactant, Alfoterra-68, recovers about 38% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Cationic surfactant DTAB recovers about 20% of the oil in about 30 days; gravity driven flow plays an important role even though wettability alteration is present (Task 4). Surfactant concentration and brine composition play an important role in wettability alteration. Atomic force microscopy shows wettability alteration by the solubilization of adsorbed organics (Task 2).

Plans for Next Reporting Period

- Mobilization experiments (Task 3)
- Imbibition experiments (Task 4)
- Simulation (Task 5)

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