# Dilute Surfactant Methods for Carbonate Formations

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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. Simulation studies indicate that both wettability alteration and gravity-driven flow play significant role in oil recovery from fractured carbonates. Anionic surfactants (Alfoterra 35, 38) recover about 55% 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 40% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Cationic surfactant, DTAB recovers about 35% of the oil. Plans for the next quarter include conducting simulation and imbibition studies.

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## 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. Simulation studies indicate that both wettability alteration and gravity-driven flow play significant role in oil recovery from fractured carbonates. Anionic surfactants (Alfoterra 35, 38) recover about 55% 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 40% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Cationic surfactant, DTAB recovers about 35% of the oil. Plans for the next quarter include conducting simulation 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 fourth and fifth tasks were worked on this quarter. The results of imbibition and modeling 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. 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.

### Numerical Simulation

In order to better understand the process of surfactant-aided imbibition into an initially oil-wet matrix block using surfactant, a mechanistic, numerical model is being developed. For an oil-wet reservoir, introduction of surfactant into the brine phase can improve oil production by lowering the interfacial tension (IFT) between the oil phase and brine phase and by altering the wettability of the rock to water-wet. A 3-D, finite-difference, numerical simulator is being developed which can incorporate both wettability alteration and IFT lowering mechanisms. The capillary pressure, the relative permeability and the residual saturation of both phases are considered as continuous functions of IFT between oil and brine and the rock wettability, which are correlated to the surfactant and salt concentrations. The mass balance equations are discretized on a finite difference grid and solved with a fully implicit scheme.

## 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 $Na_2CO_3$ brine. Cell 2 had 0.05 wt% Alfoterra 38 and 0.3 M $Na_2CO_3$ brine. Cell 3 had 0.05 wt% Alfoterra 68 and 0.3 M $Na_2CO_3$ 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.

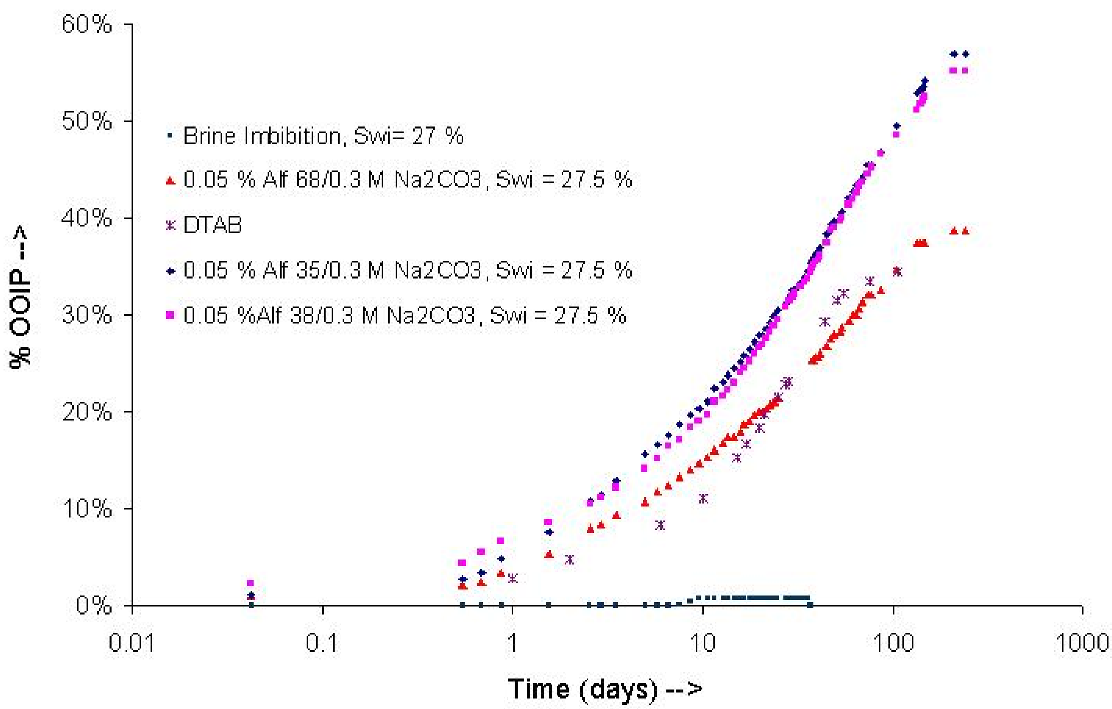


Figure 1. Spontaneous imbibition of different brines into oil-wet limestone core with Swi=27.5%

The oil production in each cell due to spontaneous imbibition is shown in Figure 1. Oil production has ceased in all the cells. The spontaneous imbibition volumes in cells 1 and 2 are about the same and higher than the other two. About 55% of the oil has been produced in about

200 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 40% in 200 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 35% in 100 days. This (DTAB) experiment started later than the other imbibition experiments.

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. 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.

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 55 % OOIP in the imbibition experiments.

Gravity-driven, one-dimensional oil recovery can be plotted (Hagoort, 1980) in terms of dimensionless time ($t_{Dg}$) and fractional recovery ($E_R$), where

$$t_{Dg} = \frac{k\, k^{o}{}_{ro} \Delta\rho}{(S_{oi} - S_{or}) \phi \mu_o L} \tag{1}$$

The fractional recovery is given by

$$E_R = \begin{cases} t_{Dg} & t < t_{BT} \\ 1 - \dfrac{(1 - 1/n)}{(n t_{Dg})^{\frac{1}{n-1}}} & t > t_{BT} \end{cases} \tag{2}$$

$$t_{Dg,BT} = 1/n$$

Figure 2 shows the experimental data plotted as the dimensionless variables. The theoretical prediction is shown as the solid line. The theoretical line exceeds the experimental recovery between the dimensionless time of 0.5 and 5. Outside this range, the theoretical line underpredicts. Possibly, mechanisms other than gravity drainage are important.

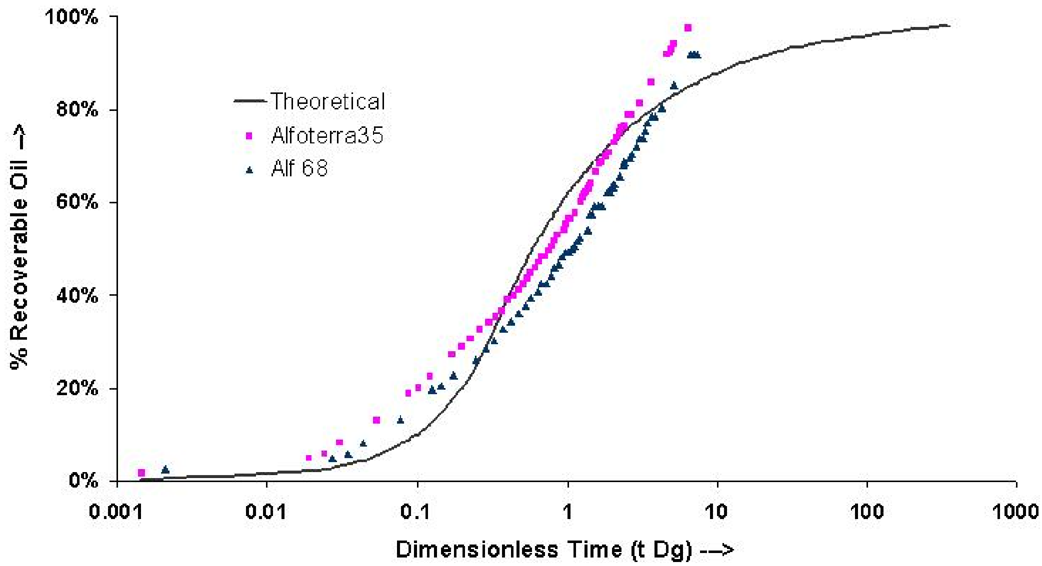


Figure 2. Comparison of experimental results with theoretically predicted curve for gravity drainage

When oil recovery is dominated by capillarity-driven flow as in a strongly water-wet rock, Zhang et al. (1995) have shown that the following dimensionless time controls the oil recovery. All their experimental data collapse onto one single curve with these dimensionless groups.

$$t_{DP_c} = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_o \mu_w} L_c^2} \qquad L_c = \frac{Ld}{2\sqrt{d^2 + 2L^2}} \tag{3}$$

The dimensionless curve developed by Morrow et al. (1995) is plotted along with our experimental data in Figure 3. Again the capillarity-driven dimensionless recovery does not match our experimental data.

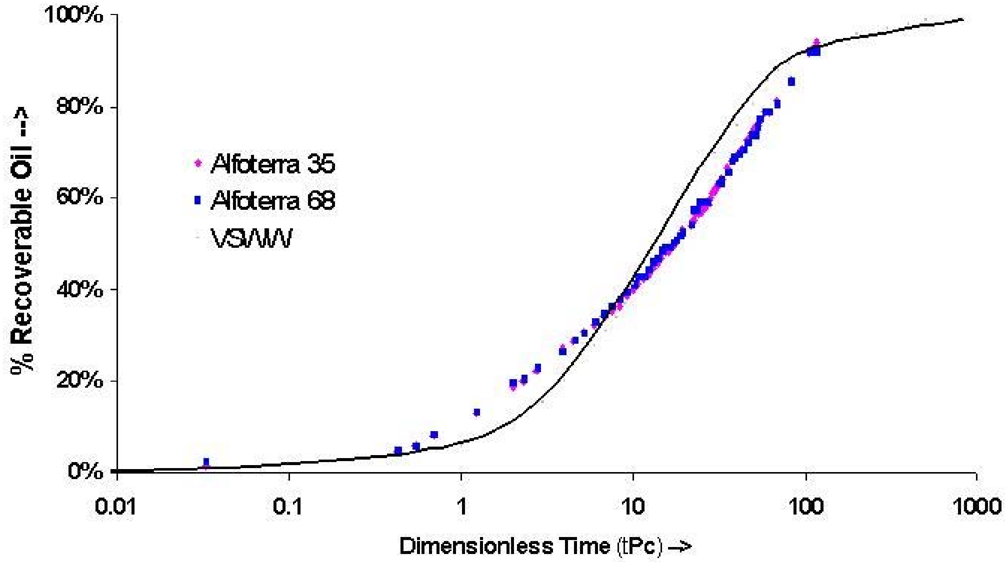


Figure 3. Comparison of the experimental results with theoretically predicted capillary dominated strongly water-wet rock curve

**Simulation**

Simulations were carried out initially for a completely oil-wet and completely water-wet matrix block without any change in wettability. The single fracture block was taken to be cylindrical with 10 m in height and 10 m in diameter. The block and the process were assumed to be axisymmetric. The entry capillary pressure is taken to be 1.4 psi, porosity 22 %, and permeability 120 mD. Common relative permeability and capillary pressure models are used. The results of the simulations for various cases are shown in Figure 4. 50 grid blocks are used in the vertical directions and 20 in radial directions for the results shown here. The top curve shows the oil recovery for a completely water-wet rock at typical oil-water interfacial tension (without surfactants). Oil is recovered the fastest in this case. The second curve from the top shows the recovery from a water-wet rock in the absence of gravitational forces. The recovery is similar to the last case in the first 50 days, but much lower thereafter. This comparison demonstrates that gravity plays an important role in capillarity-driven flow after the initial phase. In the simulations, it was seen that the majority of the oil was recovered from the top (76%) of the rock matrix as compared to the sides (24%), indicating the important role of gravity. In case of water-wet rocks, the initial capillarity-driven mechanism of imbibition changes to a gravity-driven mechanism at the later stage.

The other cases shown in Figure 4 are for an oil-wet matrix with different interfacial tension reductions. It is assumed that IFT is reduced instantaneously everywhere. The macroscopic inverse bond number is given as

$$(N_b)^{-1} = P_c^{*} / [\Delta\rho\ g\ L] = [C\ \sigma\ (\varphi/\kappa)^{1/2}] / [\Delta\rho\ g\ L] \tag{4}$$

C is generally a constant value ~ 0.4. In case 1, the macroscopic inverse bond number, $N_b^{-1}$, is 1 and no water is imbibed in this case. In case of oil-wet rocks, there is no oil recovery for the cases where the macroscopic inverse bond number $N_b^{-1}$, which is ratio of capillary to gravity forces, is greater than one. Water does not imbibe in these cases because the capillary pressure between oil and water does not exceed the entry capillary pressure of the porous medium. The macroscopic inverse bond number can be reduced by lowering the interfacial tension. In case 2, the macroscopic inverse bond number, $N_b^{-1}$, is 0.292 and about 30% of the original oil is recovered by water imbibition. The unrecovered oil corresponds to the capillary end effect and residual oil saturation. In case 3, the macroscopic inverse bond number, $N_b^{-1}$, is 0.0292 and oil recovery increases to 50%; the capillary end effect is reduced. In case 4, the macroscopic inverse bond number, $N_b^{-1}$, is decreased to $0.292 \times 10^{-4}$ but the oil recovery does not increase further. The capillary end effect is reduced to zero and cannot be reduced further.

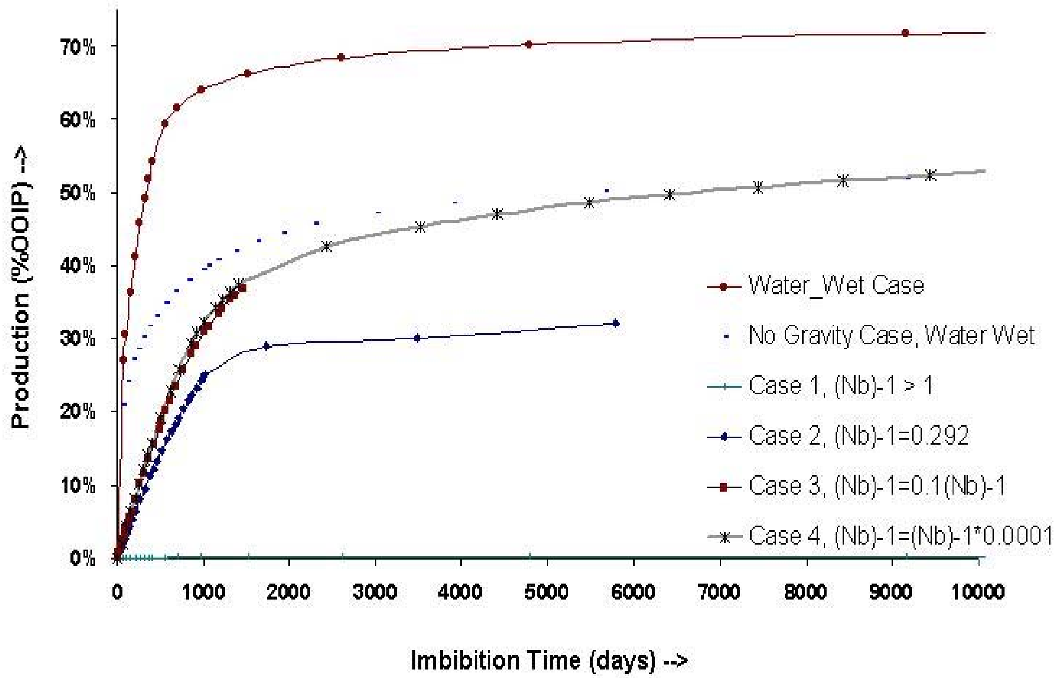


Figure 4. Spontaneous imbibition curves of oil-wet and water-wet blocks

A second set of simulations were performed including the surfactant transport and associated IFT and wettability alteration. The matrix block size was 1 m in height and 1 m in diameter, with the same physical and chemical properties as before. 20 grid blocks were used in the z-direction and 10 grid blocks in axial direction in the results shown. The brine solution outside the matrix block contained 0.01 wt % surfactant in these simulations.

Two different categories of simulations were considered, one for a water-wet rock and the second for an oil-wet rock with surfactant solution imbibition. In the case of water-wet rock, the surfactant transport is through both diffusion and convection. In the case of oil-wet rock, the surfactant transport is initially through only diffusion, which in turn leads to a lower interfacial tension, making the $N_b^{-1} < 1$. This then leads to gravity-driven water imbibition. Presence of high enough surfactant concentration leads to wettability alteration, which in turn induces water imbibition by capillarity.

The following dependence of IFT on surfactant concentration ($C_{SW}$) was considered. If $C_{SW}$ < 0.04 wt %, then IFT=30.0 dyne/cm. If $C_{SW}$ >0.05 wt %, then IFT=0.01 dyne/cm. In between, the IFT is linearly interpolated. The capillary pressure is altered in a continuous manner depending on the concentration of the surfactant in that particular grid block, from an initial oil-wet state to final water-wet state as a function of the surfactant concentration.

Figure 5 shows the simulation results for the water-wet matrix. Cases 1-3 represent the imbibition of a brine with no surfactant. In Case 1, both (usual) capillary and gravitational forces are present; this was also shown as the top curve in Figure 4. In Case 2, the capillary pressure is set to zero; hence oil recovery is by gravitational forces alone. In Case 3, the gravitational forces are set to zero; hence oil recovery is by capillary forces alone. In Case 4, the brine solution outside the matrix block contains 0.01 wt% surfactant, which leads to the lowering of IFT and capillary pressure.

The oil recovery is the highest and the fastest in Case 1. Case 2 has the lowest recovery at early times (< 5 days), because imbibition is driven by only gravity. Once sufficient amount of water is in the matrix, the gravitational mechanism is strong and the imbibition rates are high. Case 3 has the high imbibition rate at the beginning, but the lowest rate at the later stage (>5 days). This is because the gravitational forces were artificially suppressed. The recovery in Case 4 almost tracks the recovery in Case 2, but significantly higher at the early stage. The capillary pressure is significant in the beginning because the surfactant takes some time to diffuse into the matrix and lower the tension in Case 4. Thus capillarity driven imbibition is higher for case 4 than for case 2 in the beginning. At a later stage, the gravitational forces are important and lower tension aides this mechanism. The recovery in the initial stage in Case 4 is lower than that of cases 1 and 3 where high capillary pressure drives the imbibition. It can be seen from these cases that gravity plays a very important and positive role in oil recovery for water-wet rocks and presence of surfactant in the imbibing fluid slows the process of oil recovery for water wet rocks by reducing the capillary driving force by reduction of IFT.

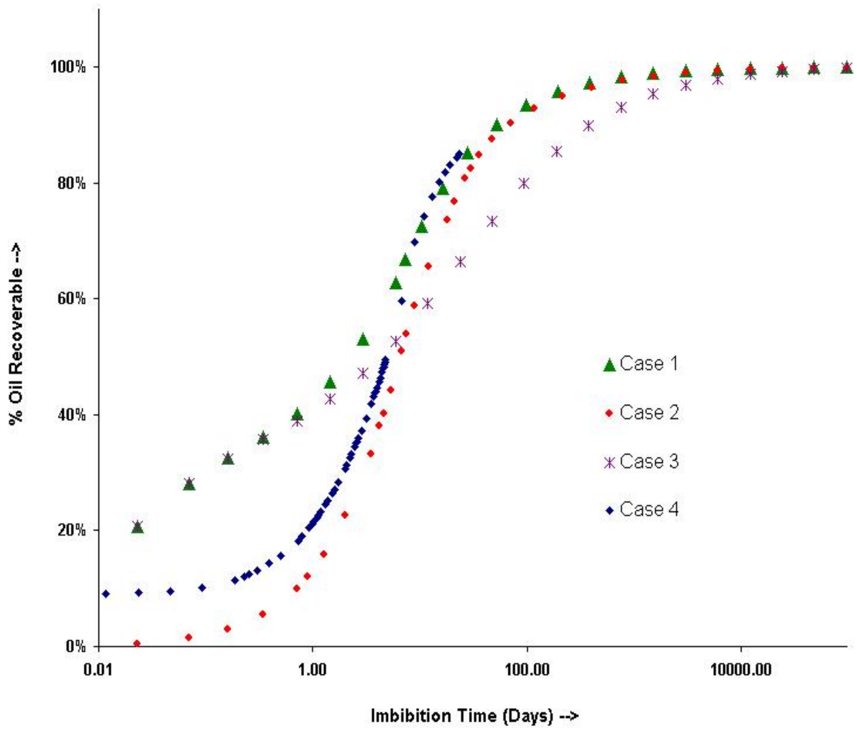


Figure 5. Spontaneous imbibition curves of water-wet blocks

Figure 6 shows the simulation results for an oil-wet rock except for Case 1, which is the water-wet case (shown as Case 1 in Figure 5 also) included for comparison. In cases 2-4, an oil-wet matrix is surrounded with a 0.1 wt% surfactant solution. In Case 2, both wettability alteration and IFT reduction is accounted for as a result of surfactant concentration. As shown in Figure 6, the imbibition is minimal in the first 10 days. Surfactant takes a long time to diffuse in and change the wettability and IFT. After the initial period, imbibition rate is high and the final recovery is as good as the initially water-wet case (Case 1).

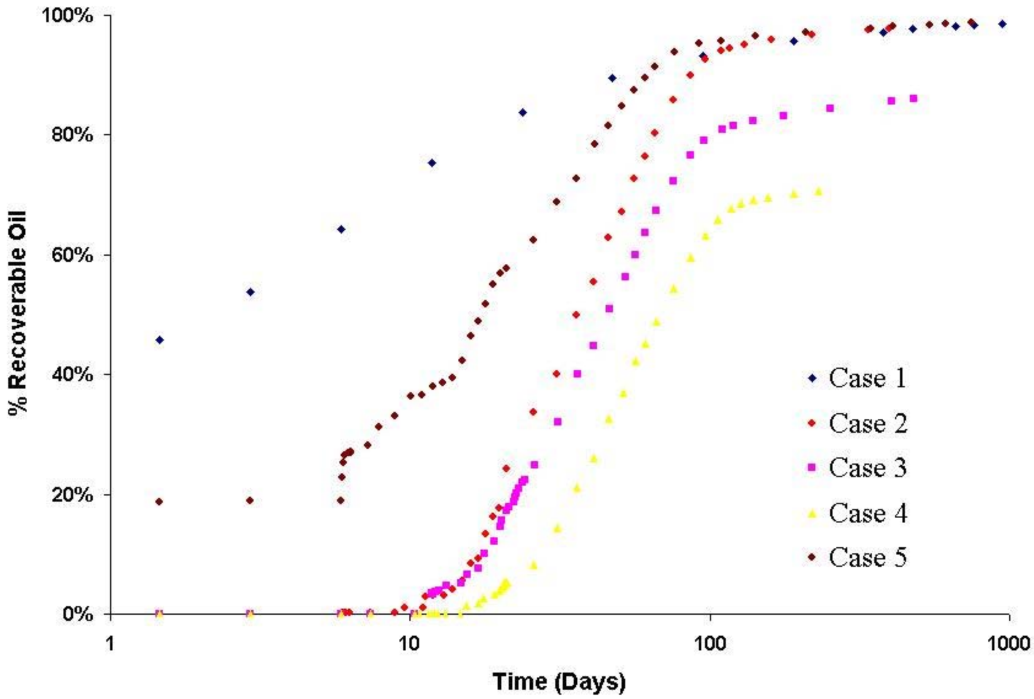


Figure 6. Spontaneous imbibition curves of oil-wet blocks

In Case 3, wettability alteration is ignored, and only the IFT reduction is considered. It can be seen that the oil recovery is less (than Case 2) with only IFT reduction as the driving force. In Case 4, the wettability alteration is ignored and IFT is lowered only to 1 mN/m instead of 0.01 mN/m. The oil recovery is lower than that of Case 3, because the end effect is higher. This is because $N_b^{-1}$ is < 1 but not as low as in Case 3. In Case 5, initially, the boundary grid blocks of the matrix are considered water-wet and the rest of the matrix is considered oil-wet. The oil recovery rate is significantly higher than that of Case 2, but lower than the completely water-wet case (Case 1). It can be seen that changing the nature of the surface makes a significant impact on the time of recovery. Water-wet boundary grids imbibe surfactant solution by capillary forces, dragging surfactant by convection into the matrix, which then leads to wettability alteration of the oil-wet matrix blocks. In Case 5, the surfactant transport is through convection instead of diffusion at the beginning, unlike cases 2-4. Simulations have shown that both wettability alteration and gravity-driven flow contribute to oil recovery in fractured carbonates. We are studying the sensitivity to relevant petrophysical parameters and evaluating the effectiveness of this process at the field-scale.

## Technology Transfer

We have written a paper, SPE 89423, which was presented at the 14$^{th}$ SPE/DOE IOR symposium in Tulsa, April, 2004. We are writing another paper for the 2005 SPE International Oilfield Chemistry Symposium. 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.

## Conclusions

Simulations show that gravity plays a very important and positive role in oil recovery even for water-wet rocks. Both wettability alteration and gravity-driven flow contribute significantly to oil recovery in fractured oil-wet carbonates (Task 5). Anionic surfactants (Alfoterra 35, 38) recover about 55% of the oil in about 200 days by imbibition driven by wettability alteration and gravity in the core-scale (Task 4). Anionic surfactant, Alfoterra-68, recovers about 40% of the oil by lower tension aided gravity–driven imbibition in the core-scale. Cationic surfactant DTAB recovers about 35% of the oil in about 150 days; gravity driven flow plays an important role even though wettability alteration is present (Task 4).

## Plans for Next Reporting Period

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

## References

Austad, T. and Standnes, D. C.: "Spontaneous Imbibition of Water into Oil-wet Carbonates," J. Pet. Sci. & Eng, 39, 363-376 (2003).

Bragg, J. R. et al.: "Loudon Surfactant Flood Pilot Test," SPE/DOE 10862, SPE/DOE 3rd Joint Symposium on EOR, Tulsa, April 4-7, 1982.

Hagoort, J., "Oil Recovery by Gravity Drainage," SPE 7424, SPE Journal, 20, 139 (1980).

Hirasaki, G. and Zhang, L., "Surface Chemistry of Oil Recovery From Fractured, Oil-wet, Carbonate Formation," SPE 80989 presented at SPE International Symposium on Oilfield Chemistry held in Houston, Texas, USA, 5-8 February, 2003.

Spinler, E. A. et al.: "Enhancement of Oil Recovery Using Low Concentration Surfactant to Improve Spontaneous or Forced Imbibition in Chalk," SPE 59290, SPE/DOE Improved Oil Recovery Symposium, Tulsa, April 3-5, 2000.

Xie, X., Weiss, W., Tong, Z., and Morrow, N. R., "Improved Oil Recovery from Carbonate Reservoirs by Chemical Stimulation," SPE 89424, SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, 17-21 April, 2004.

Zhang, X., Morrow, N. R., and Ma, S., "Experimental Verification of a Modified Scaling Group for Spontaneous Imbibition," SPE 30762, Proceedings of the ATCE of the SPE, Dallas, October 22-25, 1995.