

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. Laboratory imbibition tests show that imbibition rate is not very sensitive to the surfactant concentration (in the range of 0.05 –0.2 wt%) and small amounts of trapped gas saturation. It is however very sensitive to oil permeability and water-oil-ratio. Less than 0.5 M Na₂CO₃ is needed for in situ soap generation and low adsorption; NaCl can be added to reach the necessary total salinity. The simulation result matches the laboratory imbibition experimental data. Small fracture spacing and high permeability would be needed for high rate of recovery.

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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. Laboratory imbibition tests show that imbibition rate is not very sensitive to the surfactant concentration (in the range of 0.05 –0.2 wt%) and small amounts of trapped gas saturation. It is however very sensitive to oil permeability and water-oil-ratio. Less than 0.5 M Na_2CO_3 is needed for in situ soap generation and low adsorption; NaCl can be added to reach the necessary total salinity. The simulation result matches the laboratory imbibition experimental data. Small fracture spacing and high permeability would be needed for high rate of recovery.

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 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 (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 January, 2005 through April, 2005. 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 parametric study of imbibition is highlighted in this report.

Experimental

The surfactants Alfoterra 35 (good wettability altering surfactants from contact angle and earlier imbibition experiments) was used for imbibition parametric studies. The cores were saturated with 100% field brine and then displaced with crude oil to residual water saturation (27.5%). The cores were then aged in oil bath for a period of 18 days (or more), to make it oil wet in nature. The cores were then used in imbibition cells filled with appropriate brine. For the base case (Experiment 1), 0.05 wt % Alfoterra 35 with 0.3 M Na₂CO₃ was used, the core permeability was about 150 md, and the initial oil saturation was about 72.5%. The ratio of the total amount of water in the imbibition cell and core to the amount of oil is approximately 10. This experiment was reported before.

In experiment 2, the surfactant concentration was increased to 0.2wt%; all other parameters were kept the same as in the base case. This experiment tests the effect of surfactant concentration. In experiment 3, the core permeability was 7 md, the surfactant brine composition was the same as the base case. In experiment 4, water-to-oil ratio in the imbibition cell is decreased to 3. The effect of water-to-oil ratio is tested in this experiment. In experiment 5, some gas was injected into the core at the residual water saturation condition. The gas percolated through the oil. Then oil was injected to reach residual gas saturation of about 5-10%. The effect of initial trapped gas saturation is studied in this experiment.

Results and Discussion

The effect of surfactant concentration on surfactant solution imbibition is shown in Fig. 1. As the surfactant solution imbibes into the core, oil is produced from the core. The oil production is shown as a fraction of the original oil in place. The oil production for 0.05wt% (Experiment 1) and 0.2wt% (Experiment 2) surfactant solutions is very similar. Experiment 2 has been run for only 76 days, but it is tracking the production curve of experiment 1. Recovery is 42% at 76 days and is expected to reach about 58% eventually. Thus surfactant concentration has little effect in the concentration range studied.

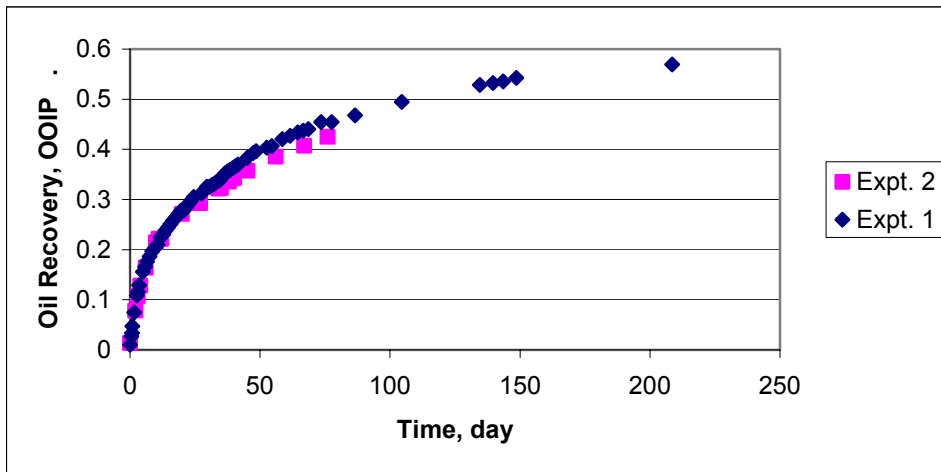


Fig. 1 – Effect of surfactant concentration (Expt. 1: 0.05wt%, Expt. 2: 0.2wt%)

The effect of core permeability is shown in Fig. 2. The recovery rate for 7 md core (Experiment 3) is much lower than that of the 150 md core. About 8.5% of the oil is recovered in 76 days for the low permeability core compared to about 45% for the high permeability core. The surfactant imbibition is driven by the gravitational force where as the viscous force opposes it. As the permeability decreases, the viscous force increases, thus slowing down imbibition. Simulation results have also shown that imbibition time increases as the permeability decreases.

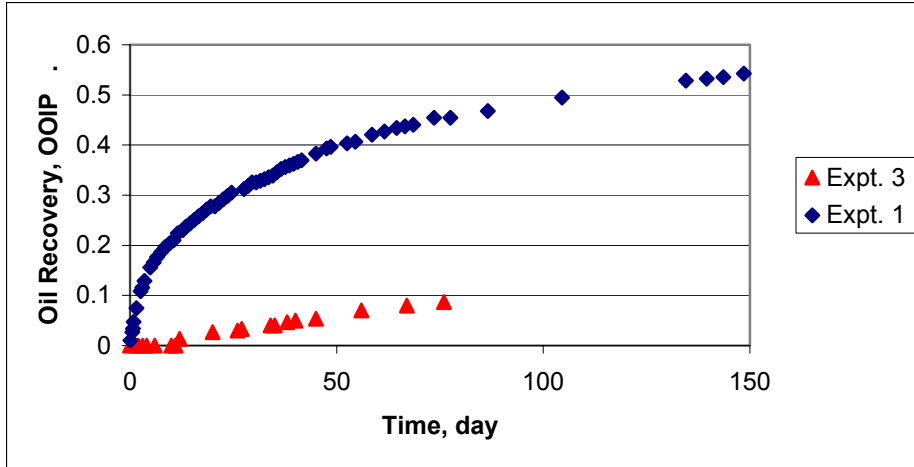


Fig. 2 – Effect of core permeability (Expt. 1: 150md, Expt. 3: 7md)

The effect of water-oil-ratio (WOR) in the imbibition cell is shown in Fig. 3. In Experiment 1, the overall water-oil-ratio is about 10. This ratio is decreased to 3 in Experiment 4 by filling the cell with empty closed glass bottles. The oil recovery decreases as the water-oil-ratio decreases (from 45% to 32% in 76 days). As the WOR decreases, the ratio of synthetic surfactant to the soap made from crude oil by Na_2CO_3 decreases. This ratio can affect the optimal salinity and thus the interfacial tensions. It is not clear how the WOR ratio seen by the pores at the imbibition front would be different from the overall WOR in the imbibition cell.

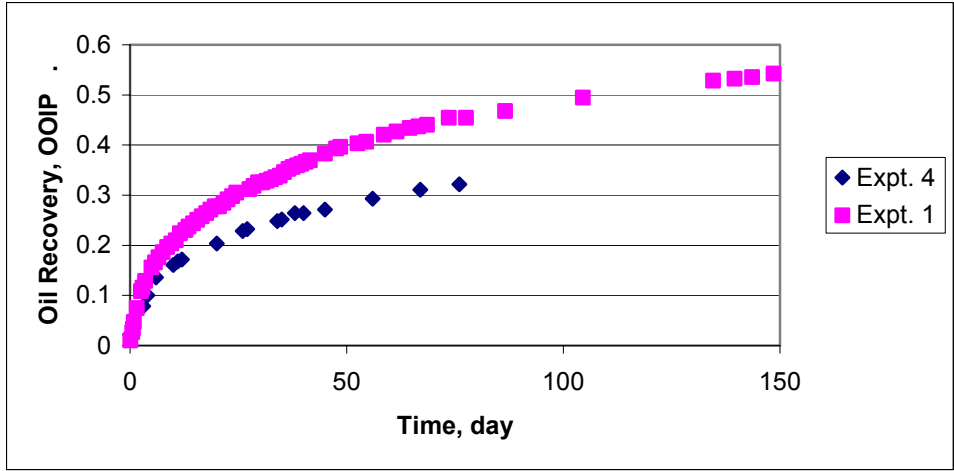


Fig. 3 – Effect of water-oil ratio (Expt. 1: 10, Expt. 4: 3)

The effect of trapped gas saturation is studied in Fig. 4. The gas saturation is zero in Experiment 1 and nonzero in Experiment 5. The oil recovery is slightly higher in Experiment 5 (49% vs. 45% in 76 days). The difference may be due to the variation from core to core. The presence of gas can decrease the effective oil permeability to the core and thus reduce the oil production rate. No such reduction was seen in this experiment, perhaps due to a very low trapped gas saturation.

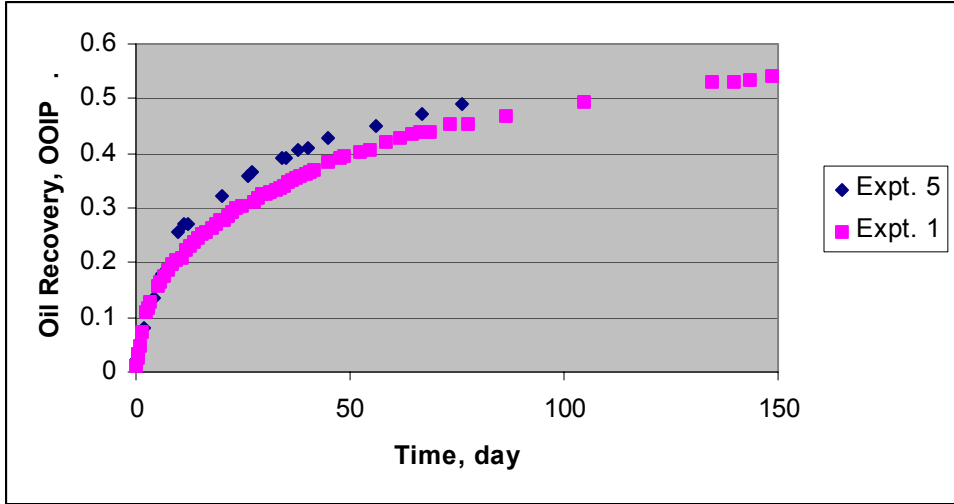


Fig. 4 - Effect of trapped gas saturation (Expt. 1: no trapped gas, Expt. 5: trapped gas)

The effect of NaCl salt substitution is shown in Fig. 5. The base case (Experiment 1) surfactant solution had 0.3M Na₂CO₃. Only small part of that Na₂CO₃ reacts with the acids in the oil and forms in situ surfactant; the rest of the Na₂CO₃ behaves like a salt. Experiment 6 has 0.05M Na₂CO₃ and 0.25M NaCl. The oil recovery in Experiment 6 tracks that of the Experiment 1. This experiment shows that the extra Na₂CO₃ behaves like the salt NaCl and can be replaced by the salt.

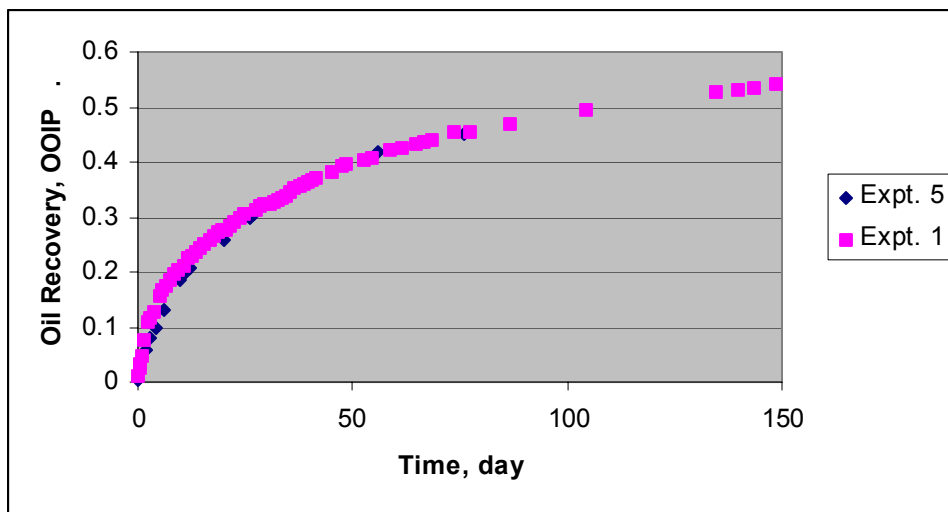


Fig. 5 - Effect of salt (Expt. 1: 0.3M Na₂CO₃, Expt. 5: 0.05M Na₂CO₃+0.25M NaCl)

Laboratory scale simulation results are compared with the experimental results in Fig. 6. The experimental values are the volume of coalesced oil collected at the top of the cell. In addition to that oil, there is a certain amount of oil in the macro-emulsion form in the surfactant solution surrounding and above the core. A simple calculation estimates this amount to be around 2ml, which results in the error bars in the experimental values in Fig. 6. Thus, there is a good match between the experimental data and simulation results. The simulation of the oil production from the lab-scale core also generates the saturation profile and various other parameters like IFT,

contact angle, capillary pressure, etc. at various locations. Simulation results indicate that both capillarity and gravity help to improve oil production: in the early stage of the production, capillarity is found to be the major driving force, and in the late stage, gravity dominates the production behavior. Wettability varies with the surfactant concentration; this is taken as a ramp function from initial wettability to final wettability in the model. Experimentally, we know that the initial wettability is oil-wet, and the initial contact angle is taken by measure the contact angle of water droplet placed on top of the core. A more thorough wettability index needs to be used for quantifying the initial wettability of the system.

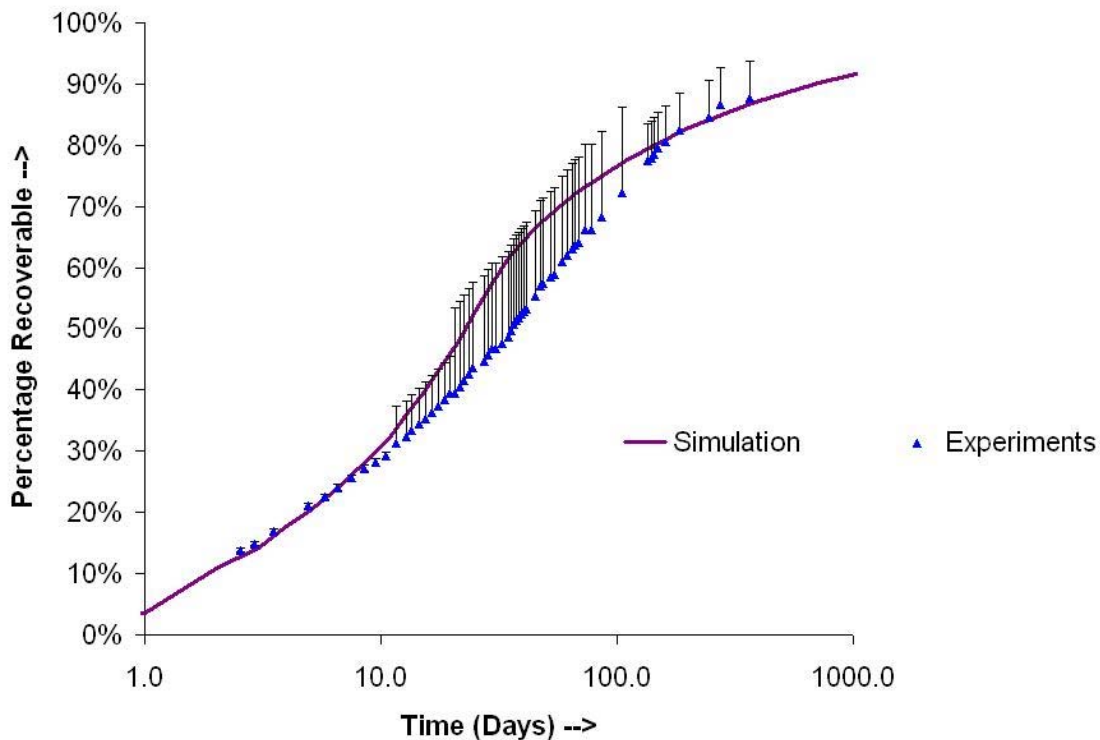


Fig. 6 - Experimental and numerical simulation comparison for 0.05wt% Alf-35 system

The time of simulation on a 1 GB RAM, 1.6 MHz processor for a lab simulator is 240 mins, and for 10mX 10m field-scale simulation is 6 days. The number of grid blocks used is 10x 40, with radial symmetry. The code is also run in a Unix machine where the simulations are at least 4

times faster. The grid structure is being modified to include 3-D Cartesian coordinate system and also inclusion of fracture. This numerical simulator is also being used to simulate surfactant imbibition in field-scale fracture blocks.

Technology Transfer

We have written an abstract, SPE 93009, for presentation in Fall 2005. We have collaborated with Oil Chem, Stepan, and Sasol for surfactants.

Conclusions

Dilute anionic surfactant solutions (Alfoterra 35) recover oil by imbibition driven by wettability alteration and gravity in the core-scale. The imbibition rate is not very sensitive to the surfactant concentration (in the range of 0.05 –0.2 wt%) and small amounts of trapped gas saturation. It is however very sensitive to oil permeability and water-oil-ratio. Less than 0.5 M Na₂CO₃ is needed for in situ soap generation and low adsorption; NaCl can be added to reach the necessary total salinity. (Task 4) The simulation result matches the laboratory imbibition experimental data. Small fracture spacing and high permeability would be needed for high rate of recovery. (Task 5)

Plans for Next Reporting Period

- Simulation (Task 5)

References

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.

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.