Surfactant-aided Low-salinity Waterflooding for Low Temperature Carbonate Reservoirs

Yue Shi, Chammi Miller, and Kishore Mohanty*, The University of Texas at Austin

Abstract

Carbonate reservoirs tend to be oil-wet/mixed-wet and heterogeneous due to mineralogy and diagenesis. The objective of this study is to improve oil recovery in low-temperature dolomite reservoirs using low salinity and surfactant-aided spontaneous imbibition. The low-salinity brine composition was optimized using zeta potential measurements, contact angle experiments, and a novel wettability alteration measure. Significant wettability alteration was observed on dolomite rocks at a salinity of 2,500 ppm. Thirty-seven surfactants were evaluated by performing contact angle, IFT and spontaneous imbibition experiments. Three (quaternary ammonium) cationic and one (sulfonate) anionic surfactants showed significant wettability alteration and produced 43% - 63% OOIP by spontaneous imbibition. At a low temperature (35°C), oil recovery by low salinity effect is small compared to that by wettability altering surfactants. Core flood tests were performed with a selected low-salinity cationic surfactant solution. A novel core flood was proposed that modeled heterogeneity and dynamic imbibition into low permeability regions. The results of the "heterogeneous" core flood were consistent with that of spontaneous imbibition tests. These experiments demonstrated that a combination of low salinity brine and surfactants can make originally oil-wet dolomite rocks more water-wet and improve oil recovery from regions bypassed by waterflood at a low temperature of 35°C.

Keywords: Wettability alteration, Low salinity effect, Surfactant, Spontaneous imbibition, Dynamic imbibition

*Corresponding Author: Kishore K. Mohanty, Hildebrand Department of Petroleum & Geosystems Engineering, The University of Texas at Austin, Austin, TX 78712, mohanty@mail.utexas.edu.

Introduction

Carbonate reservoirs hold more than half of the world's oil (Roehl and Choquette 2012). Around 60%-80% of the original oil in place (OOIP) is left behind in carbonate reservoirs after primary recovery and water flooding. Most carbonate rocks are heterogeneous at multiple scales due to diagenesis. Dolomites have microporosity, vugs and often fractures. Carbonate rocks are also oil-wet/mixed-wet rock due to positive mineral surface charge and presence of acidic oils. Wettability and heterogeneity (i.e., existence of vugs and natural fractures) are two main factors that result in low oil recovery (Manrique et al. 2007). The injected fluid is likely to flow through the fractures and bypass the oil in matrix due to the high permeability of fractures and negative capillary pressure of the oil-wet matrix.

Wettability alteration has been considered to enhance oil recovery in such reservoirs by triggering the spontaneous imbibition of injected fluids into the matrix (Zhang et al., 2006b). Low salinity injection brine can affect wettability of rock surface and in turn influence oil recovery. Extensive laboratory and field scale tests have been conducted in sandstone reservoirs (Tang and Morrow 1999, McGuire et al. 2005, Lager et al. 2008, RezaeiDoust et al. 2009). However, the low salinity EOR in carbonates is less documented (Austad et al. 2005, Yousef et al. 2011). Vijapurapu and Rao (2003, 2004) studied the effect of brine dilution by measuring oil-brine IFT and contact angle for oil-brine-dolomite system and identified a critical interfacial tension for oil spreading. The results show that only certain dilution can change the wettability and the contact angle is negatively correlated to IFT. Pu et al. (2010) performed low salinity water flooding with Phosphoria dolomite and observed additional oil recovery of 8.1% OOIP after switching from formation brine to diluted brine. The authors attributed the enhanced oil recovery to anhydrite dissolution as evidenced by increase sulfate ions in the effluent. Austad et al. (2012) conducted similar low salinity flooding with limestone and confirmed the importance of anhydrite in low salinity effect. Mahani et al. (2015) presented that diluted sea water can alter the wettability of carbonates to more water-wet even in absence of mineral dissolution. The low salinity effect was explained by a weaker electrostatic adhesion between the oil-brine and rock-brine interfaces based on zeta potential data. Strand et al. (2006) showed that adding sulfate in injection brine can change the wetting state of chalk from oil-wet to preferential water-wet conditions and effect of sulfate increased as temperature and calcium ion increased. Effect of sulfate and magnesium ions on wettability alteration was also investigated by Karoussi and Hamouda (2008). Chandrasekhar et al. (2018) demonstrated the effect of ion-exchanges reactions in carbonate cores experimentally and Sharma and Mohanty (2018) modeled the mechanisms through a geochemical simulator, IPHREEQC. But most of the wettability alterations in carbonates through ion modification have been demonstrated at high temperatures, greater than 60 ºC.

An alternate way to modify wettability is by treatment with surfactants. Cationic surfactant has demonstrated to be an effective agent in wettability alteration (Standnes et al. 2000, Standnes et al. 2002, Rostami Ravari et al. 2011, Jarrahian et al. 2012, Sharma and Mohanty 2013). Standnes et al. (2000) performed spontaneous imbibition tests with a group of quaternary ammonium cationic surfactants on calcite cores. C_{10}TAB and C_{12}TAB are found to show excellent performance in oil recovery (>60% OOIP). The contact angle measurements indicate that C_nTAB can significantly change the oil-wet surface to preferentially more water-wet. The proposed mechanism of wettability alteration is the desorption of adsorbed organic acids by the formation of strong ion-pair between cationic surfactant and adsorbed organic acids (Standnes et al. 2000). Standnes and Austad (2003) showed that the wettability alteration process stopped at cationic surfactant concentration below critical micelle concentration, which revealed the importance of micelles in storing the detached organic acids and maintaining wettability alteration process. Standnes et al. (2002) found the longer cores give higher oil recovery by CTAB imbibition compared to the shorter cores and contributed this observation to gravity effect. This observation suggests although interfacial tension (IFT) is not reduced to ultra-low by cationic surfactants, gravity still assists in surfactant invasion and would be more important at the field scale.

Anionic surfactants, although more efficient in reducing IFT to ultra-low, have also been extensively studied in wettability alteration (Standnes et al. 2000, Standnes et al. 2002, Zhang et al. 2006a, Gupta and Mohanty 2011). Standnes et al. (2000) found ethoxylated sulfonates can alter oil-wet calcite surface to less oil-wet and the surfactant with highest degree of ethoxylation tends to be most effective. The authors explained wettability alteration by anionic surfactants as the formation of a double layer by hydrophobic-hydrophobic interaction between surfactant and adsorbed organic acids. Micelles solubilization of adsorbed acids was proposed as another explanation for anionic surfactant wettability alteration (Kumar et al. 2005). There is a positive correlation between the extent of wettability alteration and number of EO groups. High salinity, especially high divalent ion concentration, can be detrimental to the effectiveness of anionic surfactants (Ahmadall et al. 1993). Divalent ion scavengers or sequestration agent (e.g., EDTA, sodium polyacrylate) were used to avoid the precipitation and sequester divalent ions for anionic surfactant solutions (Chen and Mohanty 2013). Wang and Mohanty (2014) showed that the propoxylated sulfate together with EDTA can change the calcite to preferentially water-wet and produce more than 50% OOIP by spontaneous imbibition. Adsorption of anionic surfactant in carbonate rocks is significantly higher than that of cationic surfactants. This high adsorption would limit the surfactant performance in wettability alteration. Alkali, such as sodium carbonate, can be used to suppress adsorption (Hirasaki and Zhang 2003). Propoxy sulfate surfactants can be excellent wettability altering agents for calcite surface in presence of sodium carbonate. Alpha olefin sulfonate (AOS) was also found to be effective in wettability alteration when suitable amount of sodium carbonate is added. Gravity plays an important role in anionic surfactant treatments because the interfacial tension can be ultralow (Seethepalli et al. 2004).

Wettability alteration in carbonates has also been studied with nonionic surfactants (Vijapurapu and Rao 2003, 2004, Xie et al. 2005). Several mechanisms of wettability alteration by nonionic surfactants have been proposed, including formation of a second layer over adsorbed organic layer (Standnes et al. 2002), adsorption of surfactant onto rock surface and release of organic acids (Jarrahian et al. 2012) and removal of organic acids triggered by hydrophobic interactions between surfactant and acids (Das et al. 2018). Gupta and Mohanty (2010) showed that the contact angle on initially oil-wet calcite decreases when nonionic surfactants were added and high temperature can further reduce the contact angle. Sharma and Mohanty (2013) showed that the addition of cationic surfactant into nonionic surfactants can increase its temperature tolerance by the salting in effect. The mixture of a nonionic surfactant and a cationic surfactant can change the calcite to more water-wet under harsh condition (high salinity, high temperature) and give high oil recovery (>70% OOIP) in spontaneous imbibition tests. The wettability alteration ability of nonionic surfactants does not necessarily increase with its concentration.

In this study, the combined effect of surfactants and low salinity water is investigated on the wettability of a dolomite rock at a low temperature (35 °C). The initial formation brine salinity is considered high (~110,000 ppm), but waterflood brine (produced water or PW) salinity is lower (~40,000 ppm). In order to study low salinity effect, PW was mixed with deionized (DI) water in various proportions. Zeta potential and contact angle analysis was performed to identify optimum salinity of diluted PW. Thirty-seven surfactants were tested in this study, which consist of cationic, nonionic and anionic surfactants. Contact angle, IFT and spontaneous imbibition tests have been carried out to identify effective chemical formulations. Core flood tests were performed to study the EOR potential of the selected chemical formulation.

Materials and Methods

Materials

A total of 37 surfactant candidates (5 cationic, 10 anionic and 22 nonionic) were tested in this study. Cationic surfactants were received from Fisher Scientific, Stepan and BASF. Anionic surfactants were received from Sasol, Pilot Chemicals, and BASF. Nonionic surfactants were obtained from Sasol, BASF and Harcros. All ACS grade salts were purchases from Fisher Scientific. Silurian Dolomite outcrop cores used in this study were purchased from Kocurek Industries. Reservoir rock and fluid samples were obtained from a West Texas reservoir. This is a dolomite-rich reservoir with a temperature of 35 °C (95 °F). Average porosity and permeability of this reservoir are 10% and 14 mD, respectively.

Reservoir rock and SD outcrop cores were analyzed for mineralogy by Premier Oilfield Laboratories. **Table 1** shows the XRD analysis of the two rocks. Both rocks are predominantly dolomite (about 94 wt%). Anhydride content in the reservoir rock is 1.4 wt% whereas that of the outcrop is 2 wt%. Quartz content in the outcrop is about 2 wt%. Clay content in both rocks appeared to be less than 2 wt%. Both rocks have similar mineralogy. In this study, the majority of the tests were conducted with SD cores (to optimize the chemical formula before using more valuable and limited reservoir cores).

Table 1 XRD analysis for rocks

Sample ID	**Reservoir rock**	**Outcrop**
Tectosilicates (wt%)		
Quartz	<0.5	2.0
Plagioclase	<0.5	0.0
K-spar	<0.5	0.0
Carbonates (wt%)		
Calcite	1.1	1.0
Dolomite	94.4	94.0

Aragonite	<0.5	0.0
Siderite	<0.5	0.0
Phyllosilicates (wt%)		
Chlorite	0.5	<0.5
Kaolinite	<0.5	0.0
Illite/Mica	0.6	<0.5
Other (wt%)		
Pyrite	<0.5	0.0
Marcasite	<0.5	0.0
Gypsum	<0.5	0.0
Fluorite	<0.5	0.0
Anhydrite	1.4	2.0

Complete oil analysis including acid number, base number, molecular weights, and SARA (Saturate, Aromatic, Resin and Asphaltene) analysis is shown in **Table 2**; it was conducted by SGC North America Inc. The acid number is 0.25 mg KOH/g whereas the base number is 1.0 mg KOH/g. This oil contains a high number of nitrogen-containing compounds. SARA analysis shows that saturates are 50.8%, aromatics are 16.5%, resins are 32.5%, and asphaltenes are 0.1%. Higher resin content is another indication that this oil is rich in compounds with long aliphatic chains containing atoms such as oxygen, nitrogen, and sulfur. The oil density is 0.84 g/cc at the room temperature. Oil viscosity is 7.46 cP at 35ºC.

Table 2 Oil analysis

Property	**Value**
Density @25℃	0.84 ± 0.0040 g/cc
Viscosity @35℃	7.46 ± 0.0154 cP
Molecular Weight	213 g/mol
Acid Number	0.26 mg KOH/g
Base Number	1.0 mg KOH/g
Saturate	50.8 wt%
Aromatic	16.5 wt%
Resin	32.5 wt%
Asphaltene	0.1 wt%

Brine samples were analyzed for ion composition by Premier Oilfield Laboratories; the composition is shown in **Table 3**. The initial formation water (FW) of the target reservoir is a high salinity brine with total dissolved solids (TDS) of 112,668 ppm. As the reservoir has been water flooded for years, the salinity of recent produced water (PW) has dropped to 40,393 ppm. The divalent cation (Ca^{2+} and Mg^{2+}) concentration has also decreased from 4,040 ppm for FW to 2,240 ppm for PW. The pH of both brine samples was in a range of 7.5-7.7.

Table 3 Brine composition

Composition	**Formation Water (FW)**	**Produced Water (PW)**

Na^{+}	37.88 g/L	11.14 g/L
K^{+}	0 g/L	0.52 g/L
Ca^{2+}	3.28 g/L	1.61 g/L
Mg^{2+}	0.76 g/L	0.63 g/L
Cl^{-}	67.58 g/L	22.02 g/L
SO_4^{2-}	3.17 g/L	4.13 g/L
TDS	112,668 ppm	40,393 ppm
pH	7.50	7.74

Aqueous Stability Test

Aqueous stability of the surfactants was tested in PW. 0.5 wt% surfactant solutions were prepared in the brine and aged in an oven at 35℃ for 2 weeks. The test solutions were visually inspected to determine the aqueous stability. Any precipitation, haziness or color change in the solutions was considered as unstable and the clear solutions were considered to be stable.

Contact Angle Measurement

Contact angle measurements were performed using the end cuttings of the reservoir rocks. First, the rock samples were polished using a 600-mesh grinding plate (CrystalMaster 8) to obtain a relatively flat surface. The synthetic FW was used to clean the polishing mud on the rock samples. The cleaned samples were aged in FW at the reservoir temperature. Then the samples were transferred into crude oil (oil-rock volume ratio ~ 10:1) and aged for 3 weeks at 85 °C. Oil-wet rock samples were then placed in visualization cells filled with different testing solutions. The samples were equilibrated for 5 days in an oven at the reservoir temperature (35 °C). The fate of the surface oil was observed after the equilibration. The shape of the oil droplets was evaluated to estimate the contact angles. Samples with no visible oil on the surface were analyzed for wettability change by introducing an external oil droplet to the bottom of the rock samples. Several oil droplets were placed on random locations and the contact angle was measured with a Ramé-Hart Goniometer.

Interfacial Tension (IFT) Measurement

For the oil-brine system, IFT was measured by the Ramé-Hart Goniometer using the pendant-drop method since the IFT is relatively high. A drop of oil was injected into a brine solution through a U-shaped hypodermic needle. The droplet was equilibrated in a vibration-free condition for about 10 minutes. Then, the IFT was measured using DROPimage Advanced software. IFT of the oil-surfactant system was measured by the KRÜSS Spinning Drop Tensiometer (SDT). First, the surfactant solution (0.5 wt%) was equilibrated with the crude oil for 48 hours at 35℃. Then the equilibrated aqueous solution was inserted into the SDT tube along with the oil phase drop; the tube was spun and IFT was measured by SDT at 35℃.

Wettability Alteration Test

In this study, wettability alteration test was performed to optimize brine salinity and to screen surfactant candidates. PW was mixed with DI water to prepare diluted PW solutions. The diluted PW is denoted as ‘PW/n’, where n represents the extent of dilution. Oil-wet samples were submerged in PW/2, PW/4, PW/8, PW/16, and PW/32 dilutions and equilibrated for five days at 35 °C. The shape of the oil droplets on the rock surface was evaluated for contact angles as described above. 0.5 wt% surfactant solutions were prepared in diluted PW (PW/16) for surfactant screening. Oil-wet rock samples were immersed in the surfactant solution and contact angle was evaluated after five days of equilibration.

Zeta Potential Measurement

Two series of zeta potential measurements were carried out. The first series of measurements were performed on brine-rock system without introduction of oil. The following procedure was used.

a. 60 g of the SD rock were pulverized using a Ball Mill and sieved through sieves to have particles of diameter between 20 µm and 38 µm.
b. 25g of pulverized sample was mixed with 225 g of PW and equilibrated for 24 hours at 35 °C with continuous stirring.
c. Zeta potential was measured using a Zeta Probe by Colloidal Dynamics, assuming the density of the solid as the density of dolomite and the dielectric constant of the liquid phase as the dielectric constant of water. The measurement was performed at the room temperature (23.5 °C).
d. The sample was centrifuged at 3000 rpm for 2 hours, and the sand-free liquid phase was separated. The liquid was used for the background correction in the Zeta Potential measurements.
e. The same sample was diluted with DI water to obtain PW/2 diluted brine. The Zeta Potential of new equlibrated sample was measured by repeating steps c-d.
f. The same sample was then further diluted, and zeta potential was measured for dilution PW/4, PW/8, PW/16, and PW/32.

The second series of measurements were conducted on brine-oil-rock system. 40 g of particles were soaked in 200 g of a model oil (95 wt% hexadecane + 5 wt% naphthenic acid) for 7 days under 85 °C. The particles were then filtered out of the oil and dried at 85 °C. The oil-aged powder was mixed with a series of diluted PW to obtain 1 wt% suspension samples. The samples were then equilibrated for 24 hours at 35 °C with continuous stirring. Zeta potential was measured by following steps c - d as presented for the first series.

Spontaneous Imbibition

SD cores were used for spontaneous imbibition tests. First, the cores were dried in an 85 °C oven for 48 hours. The initial mass was measured before the saturation process. The cores were assembled in a Hassler-type core holder with 800 psi confining pressure. The system was vacuumed and then saturated with CO_2 under 400 psi. Three cycles of vacuum and CO_2 saturation were performed to purge all the air. The vacuumed cores were saturated with 100% crude oil (filtered through 0.5-µm in-line oil filter). Around two PV of crude oil was then injected through the core (injection rate < 0.5 mL/min) and the permeability of the rock to oil was measured during this step. The cores were aged at 85 °C for more than one month to obtain oil-wetness. Finally, the oil-saturated cores were placed in Amott cells filled with test solutions. The Amott cells were placed in an oven at 35 °C. As the water imbibed into the core, oil came out and collected in the neck of the cell. The volume of the collected oil was monitored periodically.

Core flood Test

SD cores were used in core flood tests. The cores were saturated with oil as in the previous spontaneous imbibition section. The core flood experimental setup is shown in **Figure 1**. The oil saturated cores were mounted vertically in a Hassler-type core holder. Two ISCO pumps were used. The confining pump was running in a constant pressure mode to provide 1000 psi confining pressure. The injection pump was working in a constant injection rate mode. The core holder and accumulator were placed in an oven with a constant temperature of 35 °C. A back-pressure regulator (BPR) was connected to the outlet of the core holder to maintain 50 psi downstream pressure for the test. Pressure drop across the core was measured by Rosemount pressure transducers. The pressure data was automatically recorded by the data acquisition system.

Two core floods were carried out in this study. In the first core flood, a 1-ft long SD core was used; it was called the "homogeneous core flood". In the second core flood, a heterogeneous core was used. A 1-ft long SD core was split in half longitudinally. A layer of crushed SD rock powder was placed between the two core halves to form a heterogeneous core in a Hassler-type coreholder. The middle part of the core was unconsolidated and had a permeability much higher than that of the core matrix. This flood is called the "heterogeneous core flood." In both the core floods, produced water was injected first to mimic a waterflood followed by the surfactant solution (0.5 wt%) in the PW/16 water. Oil recovery, oil cut and pressure drops are monitored.

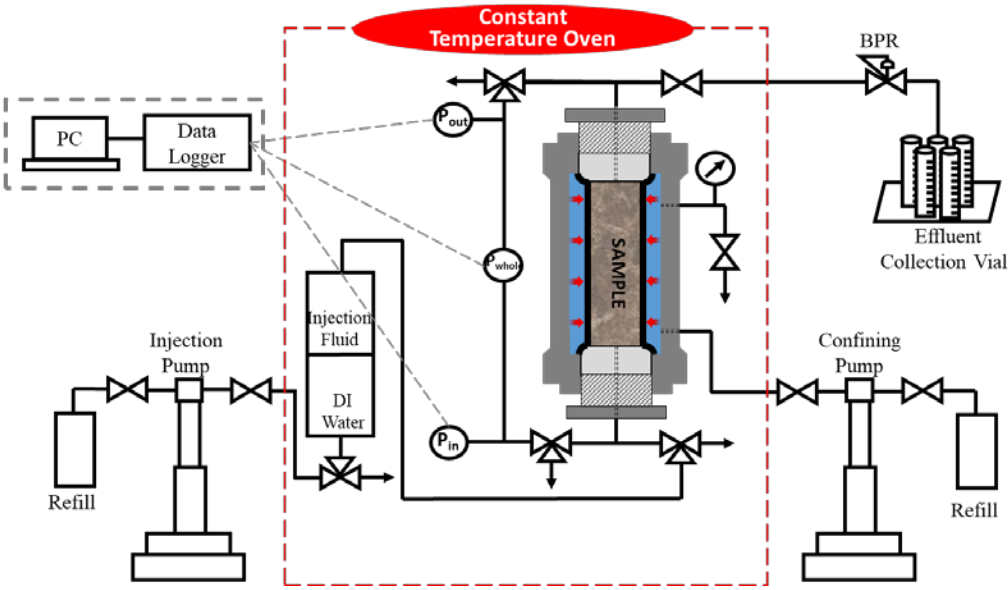


Figure 1 Experimental setup of core flood tests

Results and Discussion

The objective of this study is to develop a low salinity surfactant formulation for enhanced oil recovery. First, salinity optimization was performed by conducting zeta potential, IFT and contact angle measurements. Then, aqueous stability, IFT, contact angle and spontaneous imbibition tests were carried out to identify effective surfactant formulations. Finally, the optimal formulation was used in core flood tests to study the EOR potential of surfactant-aided low-salinity waterflooding in oil-wet carbonate cores.

Salinity Optimization

The first series of zeta potential measurements were performed on brine-rock system to evaluate the low salinity effect on mineral chemistry. As presented in methodology section, the SD sample was mixed with different dilutions of PW and zeta potential was measured. To assure the reproducibility of the measurement, two SD samples were tested by following exact same procedure. According to data shown in **Table 4**, pH of the solution increased slightly with increasing dilution. Zeta potential was slightly positive and also increased with dilution. In diluted brine, the double layer adjacent to the solid surface expands and exposes the surface charge. Zeta potential as well as pH did not change much after PW/16 dilution.

Table 4 Zeta potential in diluted PW for brine-rock system

Dilution Series	**Salinity (ppm)**	**Sample #1**		**Sample #2**	
		pH	**Zeta P (mV)**	**pH**	**Zeta P (mV)**
PW	40,393	7.75	4.97±0.40	7.78	4.27±0.24
PW/2	20,147	8.25	5.98±0.24	8.23	5.98±0.18
PW/4	10,074	8.39	6.79±0.14	8.45	6.52±0.10
PW/8	5,037	8.68	7.63±0.06	8.73	7.53±0.04
PW/16	2,517	8.71	8.18±0.05	8.94	8.36±0.04
PW/32	1,259	8.72	8.08±0.02	8.93	8.38±0.03

The second series of zeta potential measurements were performed on the brine-oil-rock system to study the low salinity effect on oil-aged rock surface. **Table 5** summarizes the zeta potential of the oil-aged samples equilibrated in a series of diluted PW brines. Due to the adsorbed organic acids on the sample surface, zeta potential values were slightly negative. As dilution increased from PW/2 to PW/32, surface charge increased from -5.28 mV to -2.14 mV. This indicates that fewer organic acids remained on rock surface as brine was diluted. The increase in zeta potential was similar to the case of no oil. Zeta potential did not change much below the salinity of 2,500 ppm; PW/16 was selected as the low salinity brine for potential enhancing oil recovery.

Table 5 Zeta potential in diluted PW for brine-oil-rock system

Dilution Series	**Salinity (ppm)**	**pH**	**Zeta P (mV)**
PW	40,393	7.51	-5.11 ±0.45
PW/2	20,147	7.32	-5.28 ±0.15
PW/4	10,074	8.05	-3.50 ±0.10
PW/8	5,037	8.25	-2.32 ±0.02
PW/16	2,517	8.55	-2.21 ±0.05
PW/32	1,259	8.12	-2.14 ±0.08

Interfacial Tension (IFT) between oil and diluted PW was measured by the Ramé-Hart goniometer at the room temperature, as shown in **Figure 2**. The IFT between oil and DI water (0 ppm) was also measured as a base case. All brine samples show high IFT values that range between 22.7 – 29 mN/m. The IFT in this range is not expected to significantly affect the capillary number or oil recovery.

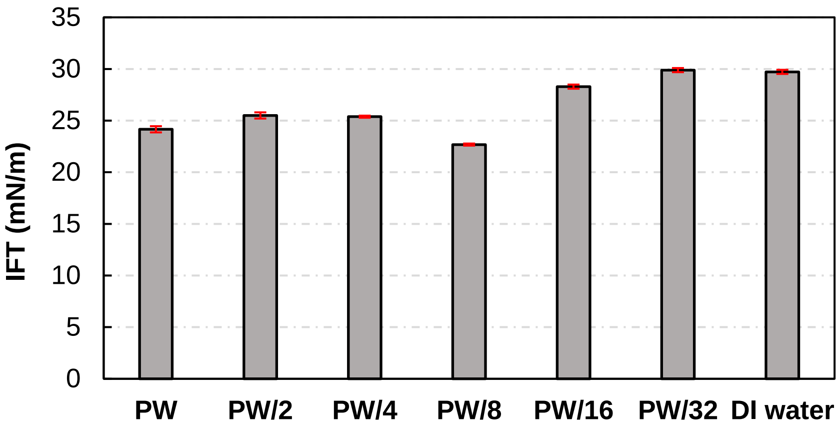
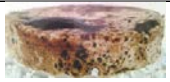


Figure 2 IFT between oil and diluted PW

To further investigate the wettability altering potential of low salinity brine, oil aged rock samples were placed in diluted PW brines. Changes to the surface oil were monitored over time. **Figure 3** shows the side view and the top view of the samples after 14 days in brine solutions. Oil is smeared in all cases and contact angles are greater than 160º. This indicates that low salinity brine did not change the contact angle of oil-wet rocks at this low temperature. However, when brine salinity decreased, some parts of the sample surface got clear and free of dark oil. For instance, the sample surface was completely covered by oil in the PW case, whereas around 70% of the sample surface was clear in the PW/16 case. Therefore, the effect of low salinity brine can be quantified based on the 'surface cleanliness' of rock samples.

To confirm the wetting changes of the oily areas and the cleaned areas of the sample surface, a post contact angle test was conducted. In the post contact angle test, the rock samples were immersed in a brine solution. Additional oil droplets were introduced at the bottom side of the samples using a U-shaped hypodermic needle. For each sample, several oil droplets were introduced on oily areas and cleaned areas. **Figure 3** shows the shape of oil droplets in the post contact angle test. The average value of the contact angles is tabulated in **Table 6**. In dark areas, oil droplets were smeared for all cases, which indicates a strong oil-wet surface. In contrast, on cleaned areas the contact angle ranged from 50° to 60°, which suggest the area to be water-wet. The post contact angle test measures the receding contact angles, which are expected to be lower than the advancing contact angles (Seethepalli et al. 2004).

Dilution	PW	PW/2	PW/4	PW/8	PW/16	PW/32
CA test side view						

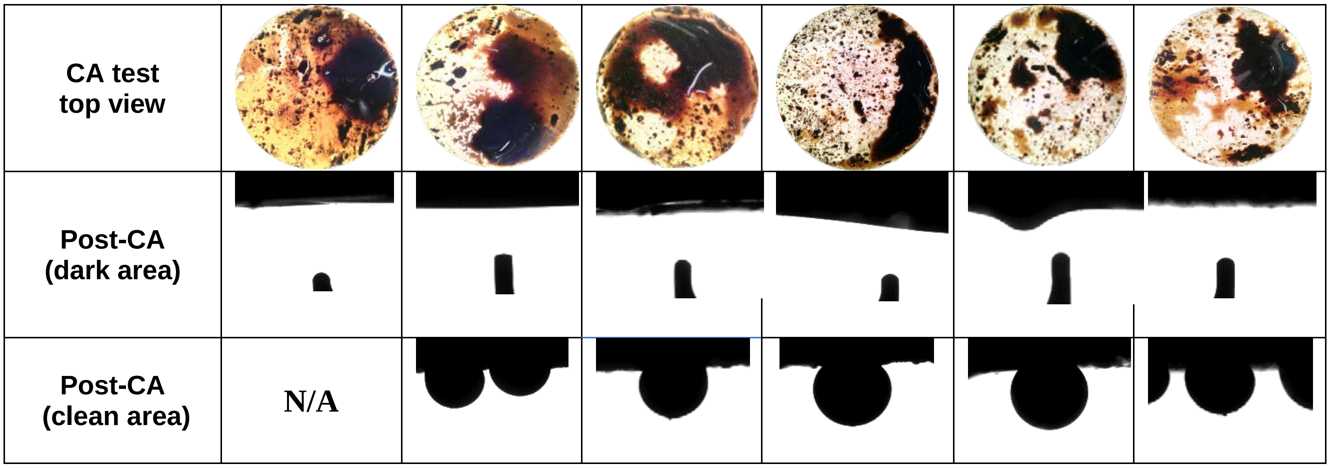


Figure 3 Images of contact angle (CA) tests and post contact angle (post-CA) tests in produced water (PW) dilution series

To quantify the 'surface cleanliness' of rock samples in low salinity brine, an Area-weighted Contact Angle (ACA) was defined as:

$$ACA = (CA_o \times AF_o) + (CA_w \times AF_w) \tag{1}$$

where CA_o and CA_w denote average receding contact angles on oil-wet and water-wet areas, respectively. AF_o is the oil-wet surface area as a fraction of the total surface area; AF_w is the water-wet surface area as a fraction of the total surface area. ACA is obtained by analyzing rock surfaces in the contact angle test and can vary in the range of 0° to 180°.

The ACA can be used to evaluate the low salinity effect. The lower ACA reflects a more water-wet surface. As shown in **Table 6**, the calculated ACA mostly decreased with increased dilution. The minimum ACA appeared at 2,517 ppm, which corresponding to PW/16 dilution, as shown in Test #1 of **Figure 4**. To eliminate the effect of rock heterogeneity on 'surface cleanliness' and ACA, the CA test was repeated with a different group of rock samples. The ACA of the repeat test was calculated, as shown in Test #2 of **Figure 4**. Although the ACA data from two tests are not exactly the same, the ACA in Test #2 also decreased with increasing of dilution and reached minimum value at PW/16 dilution. According to ACA and zeta potential analysis, PW/16 dilution is the effective salinity to use in low salinity waterflood experiments. It is worth mentioning that PW/8 and PW/32 are not that different from PW/16 in terms of zeta potential and ACA. Especially, PW/8 can also be considered for field application, since less dilution is needed.

Table 6 Area-Weighted Contact Angle (ACA) in diluted PW (Test #1)

Dilution series	Salinity (ppm)	Oil-wet Area		Water-wet Area		ACA (°)
		Fraction	CA (°)	Fraction	CA (°)	
PW	40,393	1	180°	0	N/A	180.0
PW/2	20,147	0.65	180°	0.35	80°	129.6
PW/4	10,074	0.75	180°	0.25	75°	147.5
PW/8	5,037	0.28	180°	0.72	50°	86.4

PW/16	2,517	0.25	170°	0.75	50°	80.0
PW/32	1,259	0.48	180°	0.52	50°	112.4

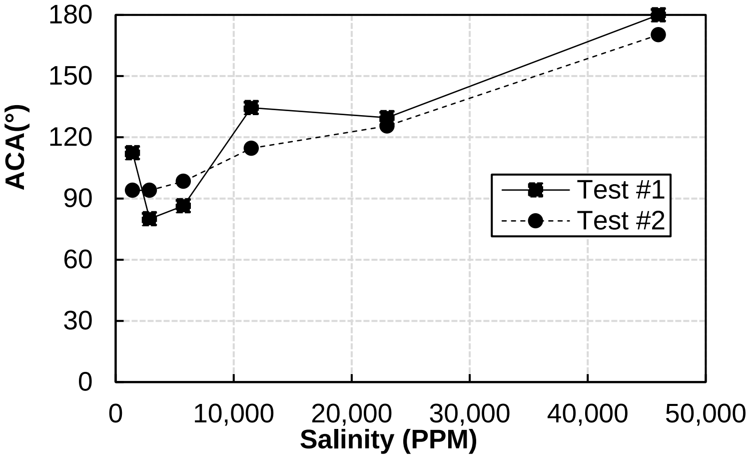


Figure 4 ACA as a function of brine salinity

Aqueous Stability of Surfactants

37 surfactants, including 5 cationic, 10 anionic and 22 nonionic surfactants, were tested in this study. All 5 cationic candidates are quaternary ammonium surfactants and named from C-1 to C-5, as listed in **Table 7**. Anionic surfactants are named as A-1 to A-11. Soloterra series are carboxylates surfactants with various EO and PO groups. Calfax series are diphenyl oxide disulfonate anionic surfactants. Calimulse AOS is a C14-16 alpha olefin sulfonate anionic surfactant. Nonionic surfactants are named from N-1 to N-22, including Aspiro S series provided by BASF and Phenol-4PO-nEO series provided by Harcros.

All the surfactants were prepared in the PW at a concentration of 0.5 wt% to test the aqueous stability. Three anionic surfactants (A-1, A-2, and A-4) and four nonionic surfactants (N-13, N-14, N-15, and N-16) showed haziness in the solution at the room temperature, indicating intolerance to the high salinity. Such haziness persisted when the temperature was raised to 35℃, as shown in **Figure 5**. The remaining 30 surfactants were stable in PW at 35℃. **Table 7** summarizes the aqueous stability results for all 37 surfactants. The 30 surfactants that passed the aqueous stability test were further screened based on contact angle and IFT analysis.

Table 7. Aqueous stability of surfactants in produced water (PW) at 35°C

Surfactant Trade Name	**Surfactant ID**	**Source**	**Stability in PW**	**Surfactant Trade Name**	**Surfactant ID**	**Source**	**Stability in PW**
Domiphen Bromide	C-1	Fisher Sci.	Stable	Aspiro S 1420X	N-4	BASF	Stable
STEPANQUAT 3712W	C-2	Stepan	Stable	Aspiro S 1425 01	N-5	BASF	Stable
CTAC	C-3	Fisher Sci.	Stable	Aspiro S 1510X	N-6	BASF	Stable
DTAB	C-4	Fisher Sci.	Stable	Aspiro S 1610X	N-7	BASF	Stable
Aspiro 6420	C-5	BASF	Stable	Aspiro S 1651X	N-8	BASF	Stable

Soloterra 938	A-1	Sasol	Unstable
Soloterra 939	A-2	Sasol	Unstable
Soloterra 982	A-3	Sasol	Stable
Soloterra 983	A-4	Sasol	Unstable
Calfax 10L-45	A-5	Pilot	Stable
Calfax 16L-35	A-6	Pilot	Stable
Calimulse AOS	A-7	Pilot	Stable
Aspiro S 2425X	A-8	BASF	Stable
Aspiro S 2850X	A-9	BASF	Stable
RD 219591	A-10	BASF	Stable
Aspiro 1265X	N-1	BASF	Stable
Aspiro 1275X	N-2	BASF	Stable
Aspiro S 1415X	N-3	BASF	Stable
Aspiro S 1661X	N-9	BASF	Stable
Aspiro S 2410	N-10	BASF	Stable
Aspiro S 2420	N-11	BASF	Stable
Aspiro S 2430X	N-12	BASF	Stable
Aspiro S 2455X	N-13	BASF	Unstable
Aspiro S 2465X	N-14	BASF	Unstable
Phenol-4PO-5EO	N-15	Harcros	Unstable
Phenol-4PO-7.5EO	N-16	Harcros	Unstable
Phenol-4PO-15EO	N-17	Harcros	Stable
Phenol-4PO-20EO	N-18	Harcros	Stable
Phenol-4PO-25EO	N-19	Harcros	Stable
Phenol-4PO-30EO	N-20	Harcros	Stable
Phenol-4PO-40EO	N-21	Harcros	Stable
Phenol-4PO-50EO	N-22	Harcros	Stable

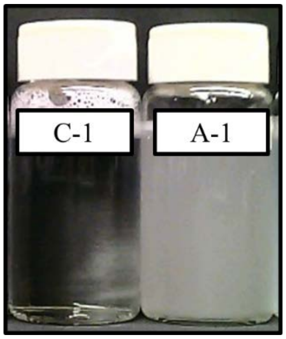


Figure 5 Comparison of a stable surfactant solution (C-1) and an unstable surfactant solution (A-1)

Contact Angle and IFT

Contact angle and IFT measurements were conducted to evaluate the wettability alteration performance of the stable surfactants. All surfactants were prepared in optimized low salinity brine (PW/16) at a concentration of 0.5 wt%. **Table 8** shows the contact angles and IFT data for the surfactant solutions. The control sample in PW/16 (without surfactant) gave a contact angle range of 160° - 170° in oil-wet areas. IFT between oil and PW/16 is 28.3 mN/m. Four cationic surfactants C-2, C-3, C-4, and C-5 showed significant wettability alteration effects with a contact angle range of 80° - 120°. According to the post contact angle test, cationic surfactants, C-3 and C-5 showed water-wet conditions with a contact angle range of 40° - 60°. **Figure 6** shows contact angle results of C-5. The cationic surfactants are known to be effective in removing the adsorbed organic acids by forming strong ion-pair between surfactants and acids (Standnes et al. 2000). Four cationic surfactants, including C-2 to C-5, were selected for spontaneous imbibition tests due to their significant wettability altering performance.

No oil droplets were observed on the rock surface for most anionic surfactants except A-3 and A-8. A-3 reduced the contact angle to 105° - 120°, indicating an intermediate-wet surface. Post contact angle test was performed to evaluate the samples with no oil droplets on the surface. A-7 and A-10 showed high 'surface cleanliness' with a post contact angle range of 120° - 145°. Among all the anionic surfactants, A-7 and A-10 also have relatively low IFT. Thus, A-3, A-7 and A-10 were selected for further analysis in spontaneous imbibition. For the remaining anionic surfactants, the rock surfaces remained oil-wet. As shown in **Figure 6**, for instance, A-6 created a preferentially oil-wet surface.

For nonionic surfactants, the rock surface was free of oil for N-1, N-2, N-8, and N-9. According to post contact angle test, N-2, N-4 and N-8 changed the solid surface to preferentially intermediate-wet resulting contact angle range of 100° - 130°. For the remaining nonionic surfactants, contact angle ranged from 130° - 180°, indicating poor effectiveness in wettability alteration. Phenol-4Po-nEO series (N-17 to N-22) were not effective in wettability alteration or in IFT reduction.

Table 8 pH, CA and IFT for 0.5 wt% surfactant solution in PW/16

Surfactant ID	pH	CA (°)	Post-CA (°)	IFT (mN/m)	
				Mean	SD
C-1	7.45	120-130	145-155	1.14	0.03
C-2	7.90	95-120	130-135	1.94	0.01
C-3	7.93	80-115	40-60	0.86	0.04
C-4	8.38	85-115	90-130	1.70	0.06
C-5	3.92	80-110	40-60	0.21	0.04
A-3	7.70	105-120	125-145	2.60	0.02
A-5	7.82	N/A	170-172	1.13	0.01
A-6	8.56	N/A	170-177	1.27	0.02
A-7	8.60	N/A	122-141	0.87	0.01
A-8	8.69	140-160	-	1.08	0.00
A-9	7.25	N/A	165-170	0.67	0.01
A-10	7.25	N/A	125-145	0.19	0.02
N-1	7.80	N/A	180	4.58	0.02
N-2	7.64	N/A	130-135	3.59	0.00
N-3	7.56	120-130	172-175	1.72	0.02
N-4	8.37	105-140	100-110	1.53	0.00
N-5	7.71	130-155	128-130	3.03	0.00
N-6	7.92	122-130	170-175	0.98	0.01

N-7	8.37	155-165	-	5.41	0.01
N-8	7.46	N/A	125-130	1.75	0.00
N-9	7.66	N/A	170-178	0.36	0.00
N-10	8.33	135-152	165	0.40	0.00
N-11	8.34	125-160	160-165	0.52	0.02
N-12	7.80	130-162	165-170	1.09	0.01
N-17	9.04	162-170	-	10.68	0.03
N-18	8.69	150-172	-	8.74	0.07
N-19	8.79	170-180	-	5.00	0.01
N-20	8.19	140-175	-	6.21	0.04
N-21	8.54	140-165	-	10.10	0.05
N-22	7.82	180	-	6.83	0.07

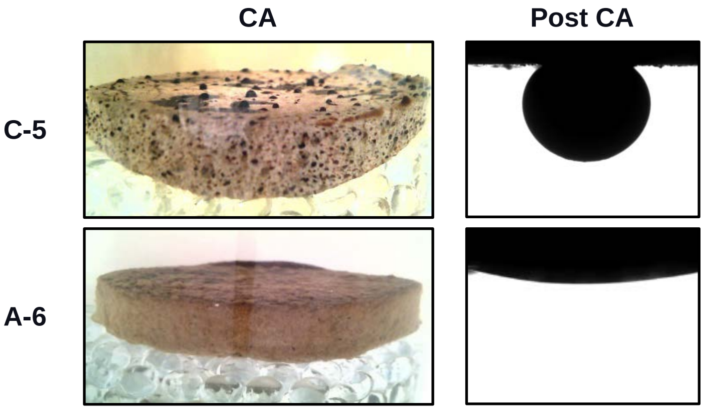


Figure 6 Comparison of contact angle (CA) and post contact angle (post-CA) in a cationic surfactant (C-5) and an anionic surfactant (A-6)

Spontaneous Imbibition

After evaluating contact angles and IFT, ten surfactant candidates including four cationic, three anionic, and three nonionic were selected for spontaneous imbibition, as listed in **Table 9**. This table also shows the properties of Silurian Dolomite cores used in these experiments. All the core plugs were 100% saturated with oil initially. The porosity of the core plugs ranged from 10% - 14% and permeability ranged from 12.88 – 40.51 mD. The core plugs were immersed in corresponding surfactant solutions in Amott cells and produced oil was monitored over time. For reference, Core #11 and Core #12 were placed in PW and PW/16 brines, respectively.

Table 9 Properties of Silurian Dolomite cores used in spontaneous imbibition tests

Core ID	**Surfactant ID**	**Diameter (cm)**	**Length (cm)**	**Porosity (fraction)**	**Permeability (mD)**	**Final oil recovery (%OOIP)**
1	C-2	3.78	2.89	0.12	20.68	34.3
2	C-3	3.78	2.87	0.12	20.68	46.7
3	C-4	3.78	2.87	0.12	20.68	63.0

4	C-5	3.78	3.22	0.10	16.55	43.0
5	A-3	3.78	2.64	0.13	40.51	14.3
6	A-7	3.78	2.97	0.14	12.88	50.5
7	A-10	3.78	2.97	0.13	40.51	36.3
8	N-2	3.78	3.01	0.13	40.51	10.7
9	N-4	3.78	2.49	014	12.88	25.1
10	N-8	3.78	2.97	0.13	40.51	27.2
11	PW	3.78	2.55	0.14	12.88	8.2
12	PW/16	3.78	2.88	0.14	12.88	4.8

Figure 7 shows the oil recovery for all the samples up to 110 days. In general, recovery rates of cationic surfactants (in PW/16 brine) were significantly higher than that of anionic and nonionic surfactants. Among cationic surfactants, C-4 showed the highest oil recovery rate and maximum final oil recovery, 63.0% OOIP. C-3 and C-5 recovered 46.7% and 43.0% OOIP. As shown in **Table 8**, C-3 and C-5 displayed lower contact angles than C-4 , but C-4 has the higher oil recovery. It may be explained by the relatively higher IFT of C-4 and thus a higher capillary pressure. Spontaneous imbibition is affected by many factors including contact angles, IFT, capillary pressure, residual oil saturation, relative permeability, and heterogeneity. C-2 showed the lowest oil recovery among four cationic surfactants with 24.22% OOIP. This is consistent with the fact that C-2 can only change the oil-wet rock sample into intermediate-wet, as shown in **Table 8**. A-7 showed the highest oil recovery among three anionic surfactants with a recovery of 50.5% OOIP. The recovery for three nonionic surfactants N-2, N-4 and N-8 were relatively low. N-2 showed the lowest oil recovery among all surfactants with only 10.7% OOIP after 110 days.

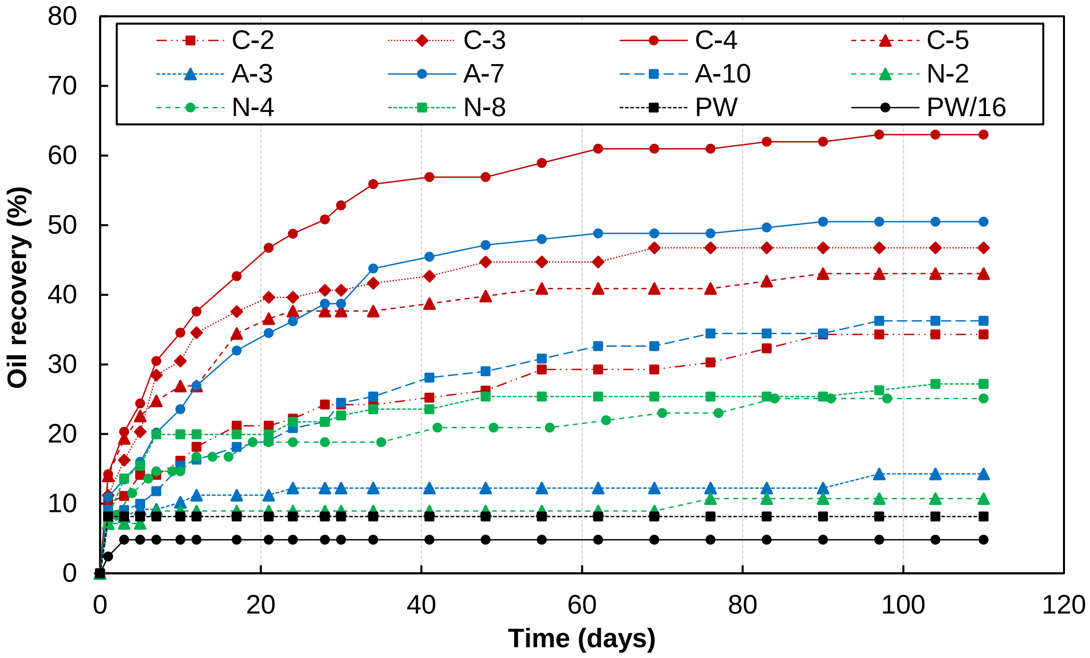


Figure 7 Oil recovery results from spontaneous imbibition test

Spontaneous imbibition is known to be affected by petrophysical properties of rock, such as porosity and permeability, fluid properties as well as fluid-rock interactions (Mattax and Kyte 1962; Parsons and Chaney 1966). To eliminate the effect of rock dimension and properties on imbibition results, a dimensionless scaling group introduced by Ma et al. (1997) is used here:

$$t_D = \sqrt{\frac{K}{\emptyset}} \frac{\sigma}{\sqrt{\mu_o \mu_w}} \frac{1}{L_c^2} t \tag{2}$$

K and $\emptyset$ are permeability and porosity, respectively. σ is interfacial tension. μ_o and μ_w denote viscosity of oleic and aqueous phase, respectively. L_c is the core characteristic length. For a cylindrical core, L_c can be computed as (Kazemi et al. 1992):

$$L_c = \frac{Ld}{2\sqrt{d^2 + 2L^2}} \tag{3}$$

where L is core length and d is core diameter. In this study, μ_w is assumed to be 1 cP for all the surfactant solutions and values of the rest of the parameters in Eqs. (2) and (3) are provided in previous tables. **Figure 8** shows the oil recovery ratio versus the dimensionless time calculated by Eq. (2). Three cationic surfactants (C-3, C-4 and C-5) and one anionic surfactant (A-7) fall in the top-left area of the figure, as highlighted in **Figure 8**. Compared with the remaining surfactants, the highlighted four surfactants have higher oil recovery within relatively shorter time. This indicates that C-3, C-4, C-5 and A-7 have relatively better performance in wettability alteration.

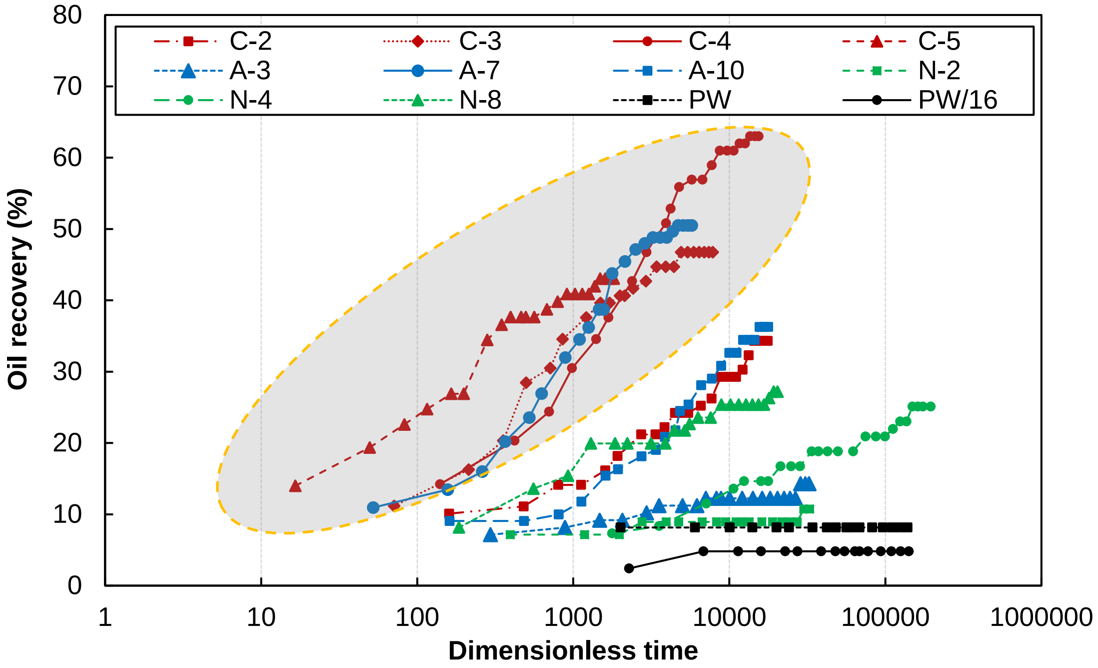
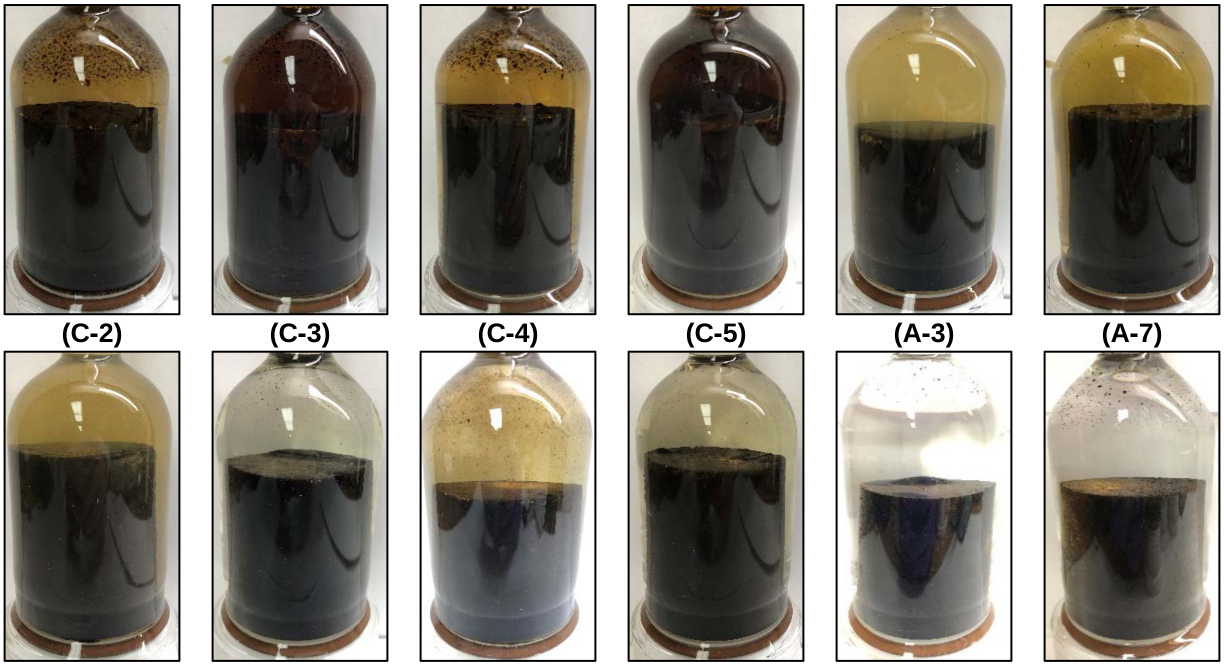


Figure 8 Oil recovery ratio versus dimensionless time

Figure 9 shows images of the core plugs in the imbibition test after 110 days. For cationic surfactants, the aqueous phase in all experiments developed a brownish color, which indicates that the oil produced from the core plug is solubilized by micelles in the solution. The solutions of C-3 and C-5 turned to dark brown. This is consistent with the fact that C-3 and C-5 have relatively lower IFT compared with C-2 and C-4, as shown in **Table 8**. The solutions of anionic surfactants also developed light brownish color after 110 days of imbibition. Nonionic surfactants (N-2 and N-8 especially) showed relatively clear solutions, which is related to their higher IFT (>1.5 mN/m) compared with most cationic and anionic surfactants. Two reference solutions, PW and PW/16, remained clear indicating no oil solubilization.


(C-2) (C-3) (C-4) (C-5) (A-3) (A-7)

(A-10) (N-2) (N-40) (N-8) (PW) (PW/16)

Figure 9 Core plugs in spontaneous imbibition test after 12 days

Figure 10 shows the oil droplets on core surfaces for C-3 and A-7 at 2 and 12 days during the spontaneous imbibition tests. Contact angles decreased for both surfactants, which indicates gradual wettability alteration with time. Specifically, contact angle in C-3 changed from 130° - 150° at day 2 (**Figure 10a**) to 85° - 110° at day 12 (**Figure 10b**) and the contact angle in A-7 changed from 140° - 150° at day 2 (**Figure 10c**) to 110° at day 12 (**Figure 10d**). The spontaneous imbibition experiments demonstrated that a combination of low water salinity and surfactants can make the originally oil-wet dolomite rocks more water-wet and improve oil recovery by imbibition at a low temperature of 35°C.

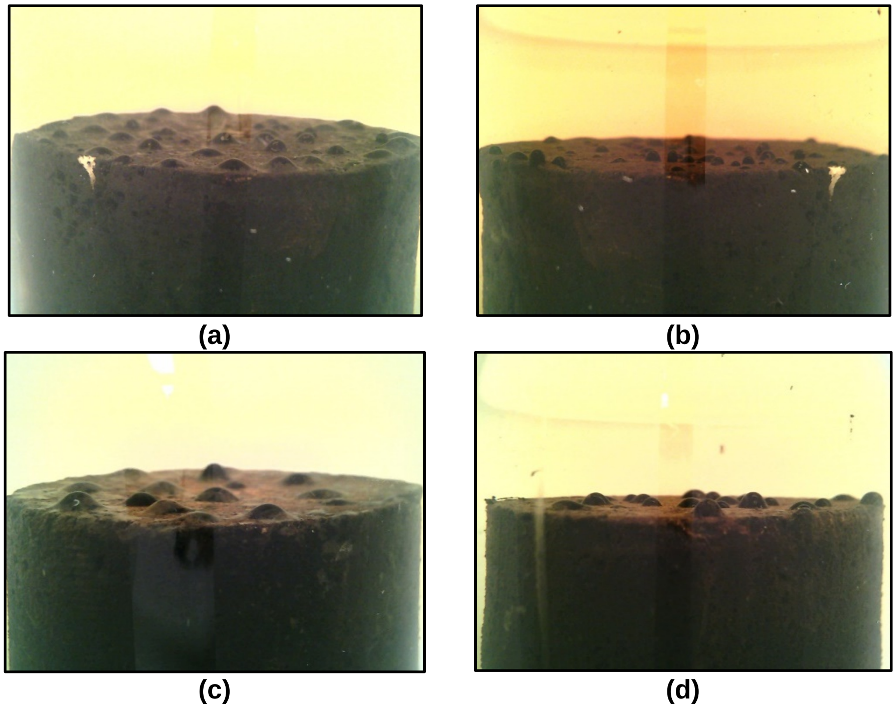


Figure 10 Top side of the core plug in C-3 after (a) 2 days and (b) 12 days; Top side of the core plug in A-7 after (c) 2 days and (d) 12 days

In the original test, PW produced 8.15% OOIP while PW/16 produced 4.81% OOIP, as shown in **Figure 7**. To test the reproducibility of this result, one pair of twin SD core plugs were used to repeat the brine imbibition test. **Figure 11** compares oil recovery by imbibition of PW and PW/16 for both original and repeat tests. Similar to the original test, PW reached a plateau with a recovery of 9.92% while PW/16 recovered only 4.02% OOIP. It is important to note that the core plugs in imbibition tests were not conditioned in FW before oil saturation. Thus, there was no connate high salinity brine in the rock. Instead, the rock surface is covered by oil and the low salinity brine could not displace oil films and interact with the rock surface. In case of surfactants, solubilization of oil gave access to the surfactant solution to the solid surface.

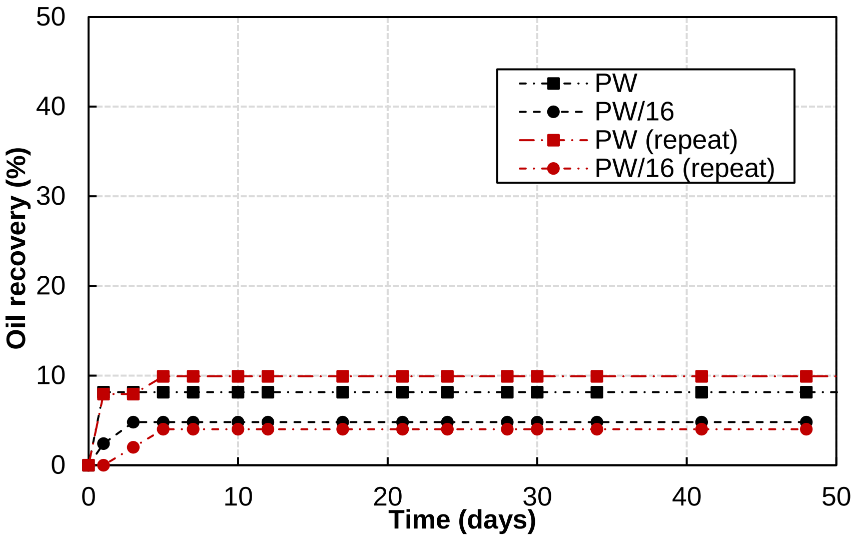


Figure 11 Comparison of original and repeat tests for PW and PW/16 spontaneous imbibition

Sequential Spontaneous Imbibition

To evaluate the effect of connate (high salinity) water on low salinity EOR, a series of sequential spontaneous imbibition tests were performed. The same rock sample was sequentially immersed into a different brine once the equilibrium was reached in the first step. The information of SD cores used in this test is summarized in **Table 10**. SD_1 and SD_2 were 100% oil saturated without connate water (S_{wc}=0). SD_3 and SD_4 were initially 100% saturated with FW, then connate water saturation (S_{wc}=40.9%) was achieved by displacing FW with oil. All four cores were aged in oil for one month, under 85ºC to induce oil-wetness. Longer cores were used in test #3 and test #4 to guarantee reasonable amount of OOIP.

Figure 12 shows the sequential spontaneous imbibition results for Test #1 and Test #2. Two cores were first immersed in PW for 30 days. Plateau oil recovery was reached within 5 days for both the cores, with 8.1% OOIP for SD_1 and 9.9% OOIP for SD_2. At day 30, the PW was replaced by PW/16 for both cores. No additional oil was produced by PW/16 over 25 days of immersion. This observation indicates that there is no low salinity effect for the cores that do not have connate water. At day 55, PW/16 in Tests #1 and #2 were switched to C-3 and C-5 surfactant solutions, respectively. All the surfactant solutions were prepared in PW/16 at concentration of 0.5 wt%. Oil production restarted right after switching to surfactant solutions. After around 100 days of surfactant imbibition, C-3 recovered additional 43.5% OOIP after brine imbibition. C-5 showed excellent performance in wettability alteration with additional 59.5% OOIP (after brine imbibition).

Figure 13 shows the sequential spontaneous imbibition results for Tests #3 and #4 with a non-zero initial connate water saturation. Initially, SD_3 was immersed in PW and SD_4 was immersed in PW/16. Up to day 44, SD_4 recovered 18.6% OOIP and oil was still produced slowly. However, SD_3 already reached equilibrium with a recovery of 11.3%. At day 44, PW was switched to PW/16 for SD_3 while SD_4 remained in PW/16. As shown in **Figure 13**, oil production was resumed for SD_3 and oil recovery reached 18.5% at day 73, which is similar to the oil recovery of SD_4 (20.8%). In other words, PW/16 produced 7.2% additional oil from SD_3 after PW imbibition reached equilibrium. Compared with the fact that no additional oil recovery by PW/16 in Test #1 and #2, the result of Test #3 proved that the presence of high salinity connate water is required for the low salinity effect. In addition, brine imbibition recovered 18-20% in Test #3 and #4 while only recovered less than 10% in Test #1 and #2. This observation may suggest that connate water can assist low salinity water imbibition. Zhang and Morrow (2006) also observed that oil recovery by low salinity brine injection increased with increasing of initial water saturation. However, it should be noted that the pores that were filled with the connate water remained water-wet (even after aging), which results in less oil-wetness of the rock sample. This may contribute to a higher oil recovery. Thus, higher oil recovery from the core with higher initial water saturation could be due to wetting affinity of the rock sample rather than the low salinity effect.

At day 73, PW/16 was switched to surfactant solution in Tests #3 and #4. SD_3 was immersed in the C-5 surfactant solution and SD_4 was immersed in the C-3 surfactant solution, as shown in **Figure 13**. Similar to the results in **Figure 12**, additional 34.5% OOIP and 54.1% OOIP oil was produced by C-3 and C-5, respectively. It is worth noticing that, in Test #3, PW/16 recovered additional 7.2% OOIP. Compared to the additional 54% oil recovery achieved by C-5 surfactant, the oil recovery by low salinity effect is small for these cores. Sheng (2014) also commented that the incremental oil recovery from low salinity effect is small compared with that from chemical flooding.

Table 10 Properties of Silurian Dolomite cores used in sequential spontaneous imbibition tests

Test #	**Core #**	**Diameter (cm)**	**Length (cm)**	**Porosity**	**Permeability (mD)**	**S_{wc}**	**OOIP (cc)**	**Testing Solution**
1	SD_1	3.78	6.40	14.0%	12.88	0%	10.08	PW → PW/16 → C-3 +PW/16
2	SD_2	3.78	6.48	10.1%	16.55	0%	7.36	PW → PW/16 → C-5 +PW/16
3	SD_3	3.78	13.67	10.7%	1.85	40.9%	9.71	PW → PW/16 → C-5 +PW/16
4	SD_4	3.78	14.30	10.7%	1.85	40.9%	10.16	PW/16 → C-3 +PW/16

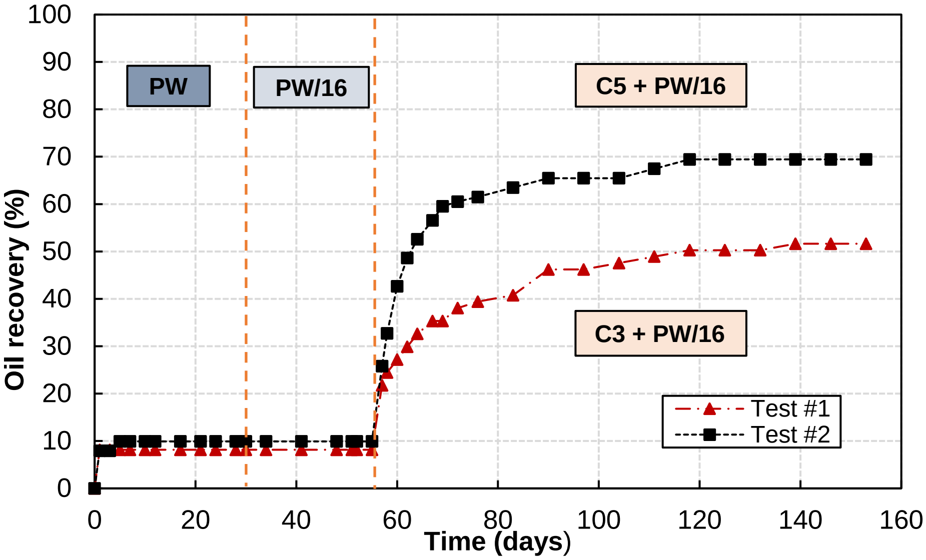


Figure 12 Sequential spontaneous imbibition on SD cores (S_{wc}=0)

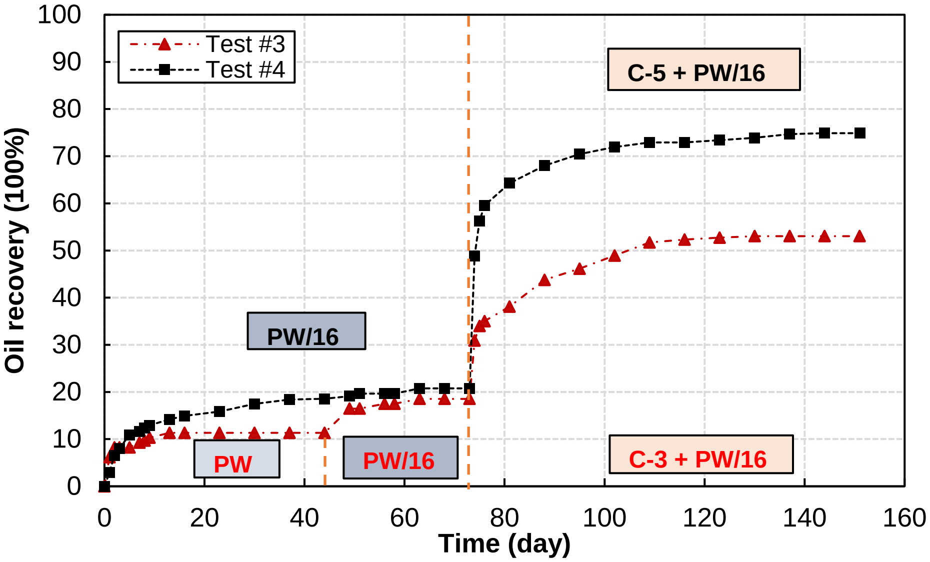


Figure 13 Sequential spontaneous imbibition on SD cores (S_{wc}=40.9%)

Core flood Tests

Two core flood tests were conducted to evaluate the potential of EOR by selected chemical formulations in initially oil-wet carbonate rocks. In the first test, a relatively homogeneous core was used, whereas the second test used a heterogeneous core.

Homogeneous Core flood

Table 11 summarizes the properties of the "homogeneous" SD core used in the test. The core was 100% oil saturated and aged with oil at 85°C for a month. The water injection rate was kept constant at 0.03 mL/min, which is equivalent to 1.13 ft/day, throughout the test. **Figure 14** shows the injection procedure, cumulative oil recovery, oil cut and saturation, as well as surfactant concentration of effluent water. PW was first injected at 1.13 ft/day to simulate the waterflood at a typical field rate. 53.6% OOIP was produced during 2 PV of water injection. Oil saturation of the core was reduced to 46.4% OOIP. Then injection fluid was switched to PW/16 to study the low salinity effect. No oil was produced during 2.1 PV of PW/16 injection. This result is consistent with the wettability and spontaneous imbibition tests. PW/16 injection was followed by the surfactant injection. C-5 cationic surfactant was selected due to its excellent wettability altering performance and relatively low IFT. 0.5 wt% of C-5 surfactant was prepared in PW/16 and injected into the core at 1.13 ft/day. The injection was continued for about 3.2 PV. Additional oil recovery over surfactant injection was only 3.6% OOIP. On the contrary, as discussed in **Figure 12**, C-5 achieved additional 60% oil recovery in spontaneous imbibition test. The surfactant imbibition test started with a high oil saturation (90.1%), whereas the starting oil saturation for surfactant flood was low (46.4%). This experiment shows that this wettability altering surfactant does not improve oil recovery significantly in well swept regions after waterflood. We think, wettability was altered inside the core. Oil was detached from pore walls, mobilized, but was re-trapped in pores. The residual oil saturation does not decrease monotonically as the core becomes more water-wet, as demonstrated by Jadhunandan and Morrow (1995). The S_{orw} may decrease by a small amount in some cases (~5%) due to more water-wet conditions; it may also increase in some cases (resulting in no incremental production). Also, the extra oil is produced at a low rate (and takes many PV) because the oil relative permeability is low at saturations close to S_{orw}.

Table 11 Properties of Silurian Dolomite core used in the “homogeneous” core flood

Sample	**Mass (g)**	**Length (cm)**	**Diameter (cm)**	**Porosity**	**Perm (mD)**	**Oil Saturation**	**Injection Rate (mL/min)**	**Surfactant Retention (mg-surf/g-rock)**
SD	849.5	28.75	3.81	11.05%	6.70	100%	0.03	0.073

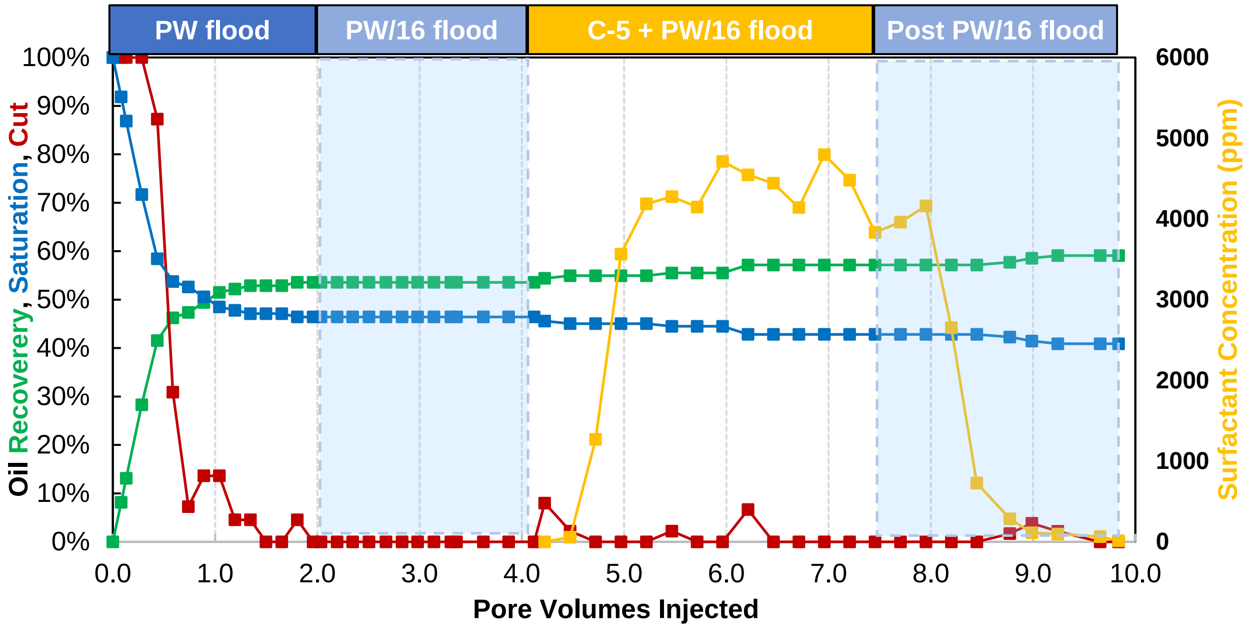


Figure 14 Oil recovery, oil cut, oil saturation and effluent surfactant concentration profile for core flood test

The surfactant injection was followed by a brine flood to quantify surfactant retention. **Figure 14** shows the surfactant concentration in the effluent samples during surfactant and post-brine injection. A two-phase titration method proposed by Miller et al. (2020) was adopted to quantify surfactant concentration. The retained surfactant was calculated by subtracting the produced surfactant from the injected surfactant. As shown in **Table 11**, surfactant retention is 0.073 mg-surf/g-rock, which is considered to be small (and economically feasible, < 0.3 mg-surf/g-rock) for field applications.

Heterogeneous Core flood

Reservoirs are heterogeneous and waterflood in oil-wet reservoirs bypasses oil in many low permeability regions. To simulate this bypassing, a heterogeneous core was constructed. A Silurian Dolomite core was initially 100% saturated with oil. Then the oil-saturated core was cut along its length, as shown in **Figure 15a**. The core was aged in oil at 85 °C for one month to obtain oil-wet rock surface before assembling. Next, SD powder with particle sizes between 1 – 2 mm was placed between the core halves to create a high permeability layer of width 2.27 mm, as shown in **Figure 15b**. The powder layer and the matrix mimic a heterogenous carbonate rock. The heterogeneous core was assembled in a Hassler-type core holder. Oil was injected at 0.005 mL/min from the bottom side of core to saturate void volume of the powder layer. The volume of injected oil was recorded to obtain pore volume and porosity of the powder layer. **Table 12** summarizes the heterogeneous core characteristics. Before the test, the whole system was placed in 35 °C oven for 2 days to equilibrate.

Table 12 Properties of core used in the heterogeneous core flood test

Core	Length (cm)	Cross-sectional Area (cm^2)	Bulk volume (cm^3)	Pore Volume (cm^3)	Porosity	Perm (mD)	Oil Saturation
Matrix (SD core)	30.16	11.40	343.85	47.07	13.69%	1.63	100%
Powder Layer	30.16	0.86	26.08	7.27	27.88%	7592	100%

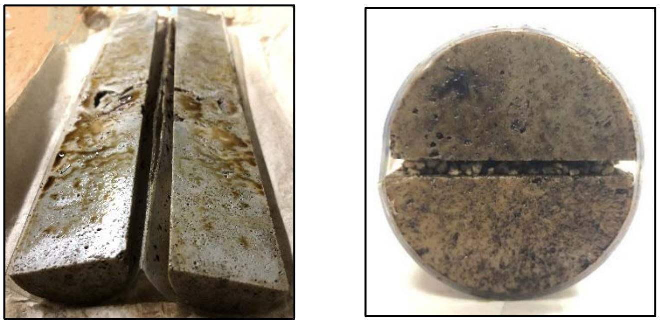

(a) (b)

Figure 15 Views of the oil-aged SD core (a) before packing and (b) after packing

Figure 16 shows the testing procedure, cumulative oil recovery, oil saturation and oil cut profiles for this heterogeneous core flood. The injected volume was normalized by total pore volume (pore volume of matrix and powder regions). PW was first injected at 0.05 mL/min, which is equivalent to 1.5 ft/day, for around 1.2 days until oil production ceased. 21.2% OOIP was produced over 1.6 PV of injection in this heterogeneous core. In comparison, PW flood recovered 53.6% OOIP in the homogeneous core, as shown in **Figure 14**. Oil was recovered mainly from the powder layer. Presumably, oil saturation was high in the tight matrix at this stage of the core flood because oil-wetness prevented PW imbibition. Oil recovery by PW flood in this test is reasonably close to the typical oil recovery in heterogenous tight carbonate reservoirs. A high degree of heterogeneity in oil-wet cores results in low oil recovery by PW. Pressure drop across the core increased first due to multiphase flow, then decreased, and stabilized at 0.75 psi after one PV of PW injection.

After PW injection, surfactant solution was injected at 1.5 ft/day for 2.5 hours, as shown in **Figure 16**. The surfactant solution included 0.5 wt% C-5 in PW/16. The purpose of this step was to quickly replace the PW by the surfactant solution in the powder layer. 2.5 hours of injection was designed according to the pore volume of the powder layer, as shown in **Table 12**. The pressure drop remained at 0.75 psi during this step. Then, the injection rate of surfactant solution was reduced to 0.004 mL/min, which is equivalent to 0.12 ft/day, and core flood continued at a low rate. The pressure difference along the core was low (~0.25 psi) during this step. It should be noted that the pressure transducer system in this study was not designed for measuring accurately such a low pressure drop. The effluent sample was collected in collection vials and the volume of fluid was recorded on a daily basis. **Figure 16** shows that oil production restarted at day 1 of slow rate flood and continued for at least a month. In general, oil cut fluctuated, but kept decreasing slowly with time. After 2 weeks, discontinuous oil production was observed with zero oil intervals getting longer with time. This indicates that surfactant solution imbibed into the matrix further from the high permeability layer to recover oil. Oil recovery reached 42.7% OOIP over one PV of C-5 injection and 54.1% OOIP over two PV of C-5 injection. After 4 weeks of test, 58.3% OOIP was produced over three PV of injection. Over 38% OOIP incremental oil recovery was achieved by the surfactant flood in this test, which is consistent with the spontaneous imbibition result in **Figure 12**. This result reveals that the oil recovery from the bypassed low permeability matrix depends more on the time (as in spontaneous imbibition) than the injection rate. A significant amount of incremental oil (21.5% OOIP) was recovered within 1 PV of surfactant injection, which is a high rate compared to those produced by low salinity floods (Yousef et al., 2011).

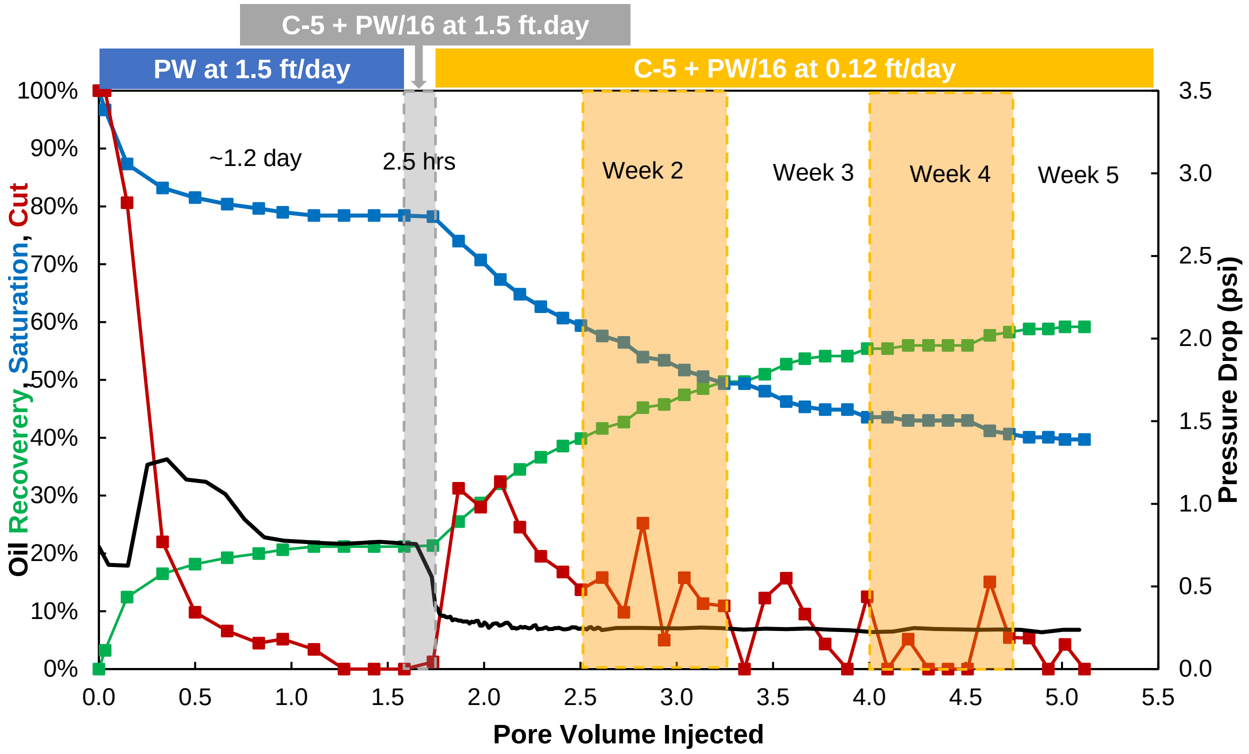


Figure 16 Oil recovery, oil cut and oil saturation evolution for the core flood test

This "heterogeneous" core flood showed that the wettability altering surfactant can recover additional oil after waterflood if the core is heterogeneous (and oil-wet) and oil is bypassed in low permeability regions at a high oil saturation. The surfactant imbibition into the bypassed layer reduced the oil saturation from near-S_{oi} values to near-S_{orw} values. The "homogeneous" core flood recovered little additional oil because the oil saturation was reduced close to S_{orw} values. This implies that if the oil-wet carbonate reservoirs are well-swept by water flood, these wettability-altering surfactants will not improve oil recovery significantly. However, if the oil-wet reservoirs have unswept regions after waterflood, the wettability-altering surfactant floods can improve oil recovery significantly if enough time is given.

Conclusions

Wettability alteration of dolomite rocks is studied in this work using low salinity brine and wettability altering surfactants for low temperature applications. IFT, zeta potential, and contact angle measurements were performed to optimize the salinity of injection brine. Surfactant candidates were then screened based on aqueous stability, contact angle, IFT and spontaneous imbibition tests. The selected low-salinity surfactant formulation was tested for EOR potential in oil-wet dolomite cores by conducting core flood tests. A novel core flood, named "heterogeneous core flood", was proposed in this study. The key findings of this study are summarized as follows:

- The zeta potential on dolomite mineral was positive in produced water (PW). It increased as the PW was diluted with DI water at 35°C, but equilibrated around 2,500 ppm salinity (PW/16). The zeta potential on dolomite minerals exposed to reservoir oil was negative due to adsorption of organic acidic groups and it also increased (absolute value decreased) as the salinity is decreased.
- To optimize salinity, a novel Area-weighted Contact Angle (ACA) was developed that considered the fraction of cleaned surface and the contact angles. ACA data mimicked the trend with zeta potential analysis. Diluted PW with salinity of 2,500 ppm was selected as the injection brine.
- Three (quaternary ammonium) cationic and one (sulfonate) anionic surfactants resulted in oil recovery of 43% - 63% OOIP in spontaneous imbibition tests, which indicates significant wettability alteration in the dolomite rocks with these surfactants at low salinity (PW/16).
- Sequential spontaneous imbibition revealed that the presence of high-salinity connate water is essential for the low salinity effect, but the improvement of oil recovery is small. Switching from PW (46,000 ppm) to diluted PW (2,500 ppm) resulted in 7% OOIP additional oil recovery. Sequential spontaneous imbibition also showed that surfactant imbibition can recover additional 40% - 60% OOIP after brine imbibition.
- A core flood in a "homogeneous" core showed that the tertiary wettability-altering surfactant flood produced only 3-5% OOIP incremental oil after water flood. The wettability altering surfactant does not improve oil recovery significantly in well-swept regions after waterfloods.
- A core flood in a "heterogeneous" core showed an incremental oil recovery of 38% OOIP after the waterflood. The oil production rate was slow (took one month), but consistent with the oil production in spontaneous imbibition tests. If the oil-wet reservoirs have unswept regions after waterfloods, the wettability-altering surfactant floods can improve oil recovery significantly.
- The "heterogeneous" core floods should be used to evaluate wettability-altering surfactants for oil-wet, heterogeneous carbonate reservoirs, not the "homogeneous" core floods.

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References

Ahmadall, T., Gonzalez, M. V., Harwell, J. H., & Scamehorn, J. F. (1993). Reducing surfactant adsorption in carbonate reservoirs. *SPE reservoir engineering*, 8(02), 117-122.

Austad, T., Shariatpanahi, S. F., Strand, S., Black, C. J. J., & Webb, K. J. (2012). Conditions for a low-salinity enhanced oil recovery (EOR) effect in carbonate oil reservoirs. *Energy & fuels*, 26(1), 569-575.

Austad, T., Strand, S., Høgnesen, E. J., & Zhang, P. (2005, January). Seawater as IOR Fluid in Fractured Chalk. In *SPE international symposium on oilfield chemistry*. doi:10.2118/93000-MS

Chandrasekhar, S., Sharma, H., & Mohanty, K. K. (2018). Dependence of wettability on brine composition in high temperature carbonate rocks. *Fuel*, 225, 573-587.

Chen, P., & Mohanty, K. (2013). Surfactant-mediated spontaneous imbibition in carbonate rocks at harsh reservoir conditions. *SPE Journal*, 18(01), 124-133.

Das, S., Nguyen, Q., Patil, P. D., Yu, W., & Bonnecaze, R. T. (2018). Wettability alteration of calcite by nonionic surfactants. *Langmuir*, 34(36), 10650-10658.

Gupta, R., & Mohanty, K. (2010, September). Temperature Effects on Surfactant-Aided Imbibition Into Fractured Carbonates. *SPE Journal*. doi:10.2118/110204-PA

Gupta, R. & Mohanty, K. K. (2011) Wettability Alteration Mechanism for Oil Recovery from Fractured Carbonate Rocks, *Transport in Porous Media*, 87 (2), 635. doi: 10.1007/s11242-010-9706-5.

Hirasaki, G., & Zhang, D. L. (2003, January). Surface chemistry of oil recovery from fractured, oil-wet, carbonate formation. *In International Symposium on Oilfield Chemistry*. doi: 10.2118/80988-MS

Jadhunandan, P.P., and N.R. Morrow. (1995) Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems. *SPE reservoir engineering*, 10, 40–46.

Jarrahian, K., Seiedi, O., Sheykhan, M., Sefti, M. V., & Ayatollahi, S. (2012). Wettability alteration of carbonate rocks by surfactants: a mechanistic study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 410, 1-10.

Karoussi, O., & Hamouda, A. A. (2008). Macroscopic and nanoscale study of wettability alteration of oil-wet calcite surface in presence of magnesium and sulfate ions. *Journal of colloid and interface science*, 317(1), 26-34.

Kazemi, H., Gilman, J. R., & Elsharkawy, A. M. (1992). Analytical and numerical solution of oil recovery from fractured reservoirs with empirical transfer functions (includes associated papers 25528 and 25818). *SPE Reservoir Engineering*, 7(02), 219-227.

Kumar, K., Dao, E. K., & Mohanty, K. K. (2005, January). Atomic Force Microscopy Study of Wettability Alteration. In *SPE International Symposium on Oilfield Chemistry*. doi:10.2118/93009-MS

Lager, A., Webb, K. J., Black, C. J. J., Singleton, M., & Sorbie, K. S. (2008). Low salinity oil recovery-an experimental investigation1. *Petrophysics*, 49(01).

Ma, S., Morrow, N.R., Zhang, X. (1997). Generalized scaling of spontaneous imbibition data for strongly water-wet systems. *Journal of Petroleum Science and Engineering*, 18(3-4), 165-178.

Mahani, H., Keya, A. L., Berg, S., Bartels, W. B., Nasralla, R., & Rossen, W. R. (2015). Insights into the mechanism of wettability alteration by low-salinity flooding (LSF) in carbonates. *Energy & Fuels*, 29(3), 1352-1367.

Manrique, E. J., Muci, V. E., & Gurfinkel, M. E. (2007). EOR field experiences in carbonate reservoirs in the United States. *SPE Reservoir Evaluation & Engineering*, 10(06), 667-686.

Mattax, C. C., & Kyte, J. R. (1962). Imbibition oil recovery from fractured, water-drive reservoir. *Society of Petroleum Engineers Journal*, 2(02), 177-184.

McGuire, P. L., Chatham, J. R., Paskvan, F. K., Sommer, D. M., & Carini, F. H. (2005, January). Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope. In *SPE western regional meeting*. doi:10.2118/93903-MS

Miller, C., Bageri, B. S., Zeng, T., Patil, S., & Mohanty, K. K. (2020). Modified Two-Phase Titration Methods to Quantify Surfactant Concentrations in Chemical-Enhanced Oil Recovery Applications. *J. of Surfactants & Detergents*, 23 (6), 1159-1167.

Parsons, R. W., & Chaney, P. R. (1966). Imbibition model studies on water-wet carbonate rocks. *Society of Petroleum Engineers Journal*, 6(01), 26-34.

Pu, H., Xie, X., Yin, P., & Morrow, N. R. (2010, January). Low-Salinity Waterflooding and Mineral Dissolution. In *SPE annual technical conference and exhibition.* doi:10.2118/134042-MS

RezaeiDoust, A., Puntervold, T., Strand, S., & Austad, T. (2009). Smart water as wettability modifier in carbonate and sandstone: A discussion of similarities/differences in the chemical mechanisms. *Energy & fuels*, 23(9), 4479-4485.

Roehl, P. O., & Choquette, P. W. (Eds.). (2012). Carbonate petroleum reservoirs. *Springer Science & Business Media*.

Rostami Ravari, R., Strand, S., & Austad, T. (2011). Combined surfactant-enhanced gravity drainage (SEGD) of oil and the wettability alteration in carbonates: the effect of rock permeability and interfacial tension (IFT). *Energy & fuels*, 25(5), 2083-2088.

Seethepalli, A., Adibhatla, B., & Mohanty, K. K. (2004). Physicochemical interactions during surfactant flooding of fractured carbonate reservoirs. *SPE journal*, 9(04), 411-418.

Sharma, G., & Mohanty, K. (2013). Wettability alteration in high-temperature and high-salinity carbonate reservoirs. *SPE Journal*, 18(04), 646-655.

Sharma, H., & Mohanty, K. K. (2018). An experimental and modeling study to investigate brine-rock interactions during low salinity water flooding in carbonates. *Journal of Petroleum Science and Engineering*, 165, 1021-1039.

Sheng, J. J. (2014). Critical review of low-salinity waterflooding. *Journal of Petroleum Science and Engineering*, *120*, 216-224.

Standnes, D. C., & Austad, T. (2000). Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. *Journal of Petroleum Science and Engineering*, 28(3), 123-143.

Standnes, D. C., & Austad, T. (2003). Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 216(1-3), 243-259.

Standnes, D. C., Nogaret, L. A., Chen, H. L., & Austad, T. (2002). An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a nonionic and a cationic surfactant. *Energy & Fuels*, 16(6), 1557-1564.

Strand, S., Høgnesen, E. J., & Austad, T. (2006). Wettability alteration of carbonates—Effects of potential determining ions (Ca2+ and SO42−) and temperature. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 275(1-3), 1-10.

Tang, G. Q., & Morrow, N. R. (1999). Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery. *Journal of Petroleum Science and Engineering*, 24(2-4), 99-111.

Vijapurapu, C. S., & Rao, D. N. (2003, January). Effect of brine dilution and surfactant concentration on spreading and wettability. In *International Symposium on Oilfield Chemistry*. doi: 10.2118/80273-MS

Vijapurapu, C. S., & Rao, D. N. (2004). Compositional effects of fluids on spreading, adhesion and wettability in porous media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 241(1-3), 335-342.

Wang, L., & Mohanty, K. (2014). Enhanced oil recovery in gasflooded carbonate reservoirs by wettability-altering surfactants. *SPE Journal*, 20(01), 60-69.

Xie, X., Weiss, W. W., Tong, Z. J., & Morrow, N. R. (2005). Improved oil recovery from carbonate reservoirs by chemical stimulation. *SPE Journal*, 10(03), 276-285.

Yousef, A. A., Al-Saleh, S., & Al-Jawfi, M. S. (2011, January). Smart waterFlooding for carbonate reservoirs: Salinity and role of ions. In *SPE middle east oil and gas show and conference*. doi:10.2118/141082-MS

Zhang, D. L., Liu, S., Puerto, M., Miller, C. A., & Hirasaki, G. J. (2006a). Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering*, 52(1-4), 213-226.

Zhang, P., Tweheyo, M. T., & Austad, T. (2006b). Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate. *Energy & fuels*, 20(5), 2056-2062.

Zhang, Y., & Morrow, N. R. (2006, January). Comparison of secondary and tertiary recovery with change in injection brine composition for crude-oil/sandstone combinations. In *SPE/DOE symposium on improved oil recovery*. doi:10.2118/99757-MS44