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Conditions for a Low-Salinity Enhanced Oil Recovery (EOR) Effect in Carbonate Oil Reservoirs

T. Austad,[†] S. F. Shariatpanahi,[†] S. Strand,^{*,†} C. J. J. Black,[‡] and K. J. Webb[‡]

[†]University of Stavanger, 4306 Stavanger, Norway

[‡]BP Exploration Limited, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, United Kingdom

ABSTRACT: Low-salinity enhanced oil recovery (EOR) effects have for a long time been associated with sandstone reservoirs containing clay minerals. Recently, a laboratory study showing low-salinity EOR effects from composite carbonate core material was reported. In the present paper, the results of oil recovery by low-salinity water flooding from core material sampled from the aqueous zone of a limestone reservoir are reported. Tertiary low-salinity effects, 2–5% of original oil in place (OOIP), were observed by first flooding the cores with high-saline formation water (208 940 ppm) and then with 100× diluted formation water or 10× diluted Gulf seawater at 110 °C. It was verified by flooding the core material with distilled water that the core samples contained small amounts of anhydrite, $\text{CaSO}_4(\text{s})$. The oil recovery was tested under forced displacement using different injection brines and oils with different acid numbers, 0.08, 0.34, and 0.70 mg of KOH/g. The low-salinity effect depended upon mixed wet conditions, and the effect increased as the acid number of the oil increased. No low-salinity effect was observed using a chalk core free from anhydrite. The chemical mechanism for the low-salinity effect is discussed, and in principle, it is similar to the wettability modification taking place by seawater described previously. In field developments, the oil reservoir is normally flooded with the most available water source. For offshore reservoirs, this means seawater or modified seawater. Thus, a relevant question addressed in this paper is can diluted seawater act as a low-saline EOR fluid after a secondary flood with seawater? Previous experiments have shown that both spontaneous imbibition and forced displacement tests using chalk cores, which were free from sulfate, did not show a low-salinity EOR effect when exposed to diluted seawater. This paper shows that, if anhydrite is present in the rock formation, diluted seawater or diluted produced water can act as an EOR injectant to improve recovery over that achieved with high-salinity brines.

■ INTRODUCTION

Large carbonate oil reservoirs, in both the North Sea and the Middle East, are today flooded with seawater to achieve sufficient recovery to justify the substantial development costs. Seawater is used to maintain reservoir pressure and sweep oil to the producing wells. Historically, microscopic displacement efficiency has not been routinely optimized in the development stage. It is well-documented in the literature that laboratory studies show that seawater can modify the wetting condition in a favorable way to increase the oil recovery from high-temperature oil reservoirs, $T_{\text{res}} > 70\text{--}80\text{ °C}$.^{1–4} The chemical mechanism for the increase in water wetness using seawater has been discussed, and the sulfate in seawater appeared to act as a catalyst for desorbing carboxylic material from the carbonate surface.⁴ Recently, it has been shown that seawater can be modified to even act as a “smarter” enhanced oil recovery (EOR) fluid than ordinary seawater: (1) Seawater depleted in NaCl was able to increase the oil recovery by 10% of original oil in place (OOIP) compared to ordinary seawater.⁵ (2) Seawater depleted in NaCl and spiked with sulfate increased the oil recovery by 15–20% of OOIP compared to seawater depleted in NaCl.⁶

The improved oil recovery observed by decreasing the NaCl concentration in seawater is related to a decrease in the non-active ions in the ionic double layer at the carbonate surface, which allows for better access of the active ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) to the surface. Both the imbibing rate and the ultimate oil recovery from displacement tests increased.

In a recent paper, we also showed how small amounts of sulfate present in the formation water (FW) could affect the initial wetting properties of carbonate rock material.⁷ The wetting properties with and without sulfate present in the formation were discussed in relation to the effect of temperatures (50, 90, and 130 °C). For all temperatures, the water wetness increased when small amounts of sulfate were present in the FW, but for a given amount of sulfate, the water wetness decreased as the temperature increased.

The amount of sulfate in the different forms, CaSO_4 solid (s), SO_4^{2-} aqueous (aq), and SO_4^{2-} adsorbed (ad), was quantified. The results indicated that sulfate dissolved in the FW and $\text{SO}_4^{2-}(\text{aq})$ appeared to be the active species dictating the wetting properties.⁷ In carbonate reservoirs, the concentration of Ca^{2+} in the FW is usually high. Therefore, sulfate is often present as anhydrite, $\text{CaSO}_4(\text{s})$, and because of a decrease in the solubility of anhydrite at high temperatures, the concentration of sulfate dissolved in the FW, $\text{SO}_4^{2-}(\text{aq})$, is usually low.

In sandstone reservoirs, EOR effects by low-salinity water flooding have been well-documented both in the laboratory and by field tests.^{8,9} Even though it is in general agreement that the increased oil recovery by low-saline water flooding is related to wettability modification toward a more water-wet system, the

Received: September 21, 2011

Revised: December 5, 2011

Published: December 13, 2011



detailed mechanism is still under debate.^{10–12} Recent studies have indicated that organic material adsorbed onto clay minerals is desorbed because an increase in pH as active ions, especially Ca^{2+} , is desorbed from the clay as the low-saline water invades the porous medium.^{13,14}

Up to very recently, low-salinity EOR effects have not been detected in carbonates. Yousef et al.³ showed, however, that improved oil recovery was achieved when successively flooding composite carbonate cores with diluted seawater, 2X, 10X, and 20X. The authors pointed out that the mechanism for the improved oil recovery was probably different from previous published work on carbonate and sandstone.³ Pu et al.¹⁵ also observed tertiary low-salinity effects ranging from 3 to 9.5% of OOIP in sandstones with very low clay content but with significant amounts of dolomite and anhydrite.

On the basis of the chemical knowledge of the impact of sulfate on the wetting properties of carbonates as discussed in the above cited references, the chemical condition for observing low-salinity EOR effects in carbonates is discussed. Core material from the water zone of a low-permeable homogeneous carbonate reservoir containing small amounts of anhydrite was used as the porous medium.

EXPERIMENTAL SECTION

Limestone Core. Low-permeable limestone cores were sampled from the aqueous zone of an oil reservoir. Prior to delivery, all of the cores were flooded and saturated with kerosene. The properties of the cores are listed in Table 1.

Table 1. Core Characterization

core number	length, <i>L</i> (cm)	diameter, <i>D</i> (cm)	porosity, Φ (%)	permeability, <i>k</i> (mD)	S_{wi} (%)	oil
16A	7.1	3.8	17	1.2	10	oil A
11B	8.0	3.8	18	0.2	10	oil C
5B	8.1	3.8	18	1.2	7	oil C
6B	8.4	3.8	18	NM	8	oil C
18C	8.1	3.8	16	1.2	8	oil C
12C	8.1	3.8	17	1.2	10	oil B
4B	8.3	3.8	17	0.4	8	oil A
F1	7.0	3.8	42	4.2	10	oil C

Outcrop Chalk. Outcrop chalk from Stevns Klint was used as a reference core material without the presence of anhydrite. The chalk material is very homogeneous and consists of pure CaCO_3 (>99%). The properties of the core are summarized in Table 1.

Crude Oils. Oil A was centrifuged and filtered through a 0.65 μm Millipore filter to remove water and solid particles. The acid number (AN) and base number (BN) were measured by potentiometric titration. The methods used were developed by Fan and Buckley as modified versions of the standard methods: American Society for Testing Materials (ASTM) D2896 for BN and ASTM D664 for AN.^{16–18} Oils B and C were prepared by mixing oil A (low AN) and oil D (high AN) in different volume ratios. The oil properties (AN, BN, density, and viscosity) are listed in Table 2.

Table 2. Oil Properties

oil	AN (mg of KOH/g)	BN (mg of KOH/g)	density at 20 °C (g/cm ³)	viscosity at 20 °C (cP)
oil A	0.08	0.34	0.824	4.3
oil B	0.34	0.45	0.821	4.2
oil C	0.70	0.42	0.818	3.8
oil D	1.8	0.50	0.806	3.1

Brines. Synthetic brines were made from deionized (DI) water and

reagent salts. The composition of the brines is listed in Table 3. The

Table 3. Composition and Properties of the Brines

ions	FW (mol/L)	GSW (mol/L)
HCO_3^-	0.003	0.003
Cl^-	3.643	0.662
SO_4^{2-}	0.000	0.032
Mg^{2+}	0.076	0.059
Ca^{2+}	0.437	0.010
Na^+	2.620	0.594
TDS (g/L)	208.94	42.22
IS (mol/L)	4.158	0.829

terminology is as follows: FW is formation water, and GSW is Gulf seawater.

Core Cleaning. The limestone core was flooded with toluene to remove initial crude oil until clear/transparent effluent solution. The toluene was displaced by flooding 3 pore volumes (PV) with heptane. DI water was injected to remove FW. To minimize dissolution of anhydrite from the rock surface, the injection rate was high and keeping the injection volume as low as possible (~3 PV). The core was dried at 90 °C to a constant weight.

The outcrop chalk core was initially flooded with 5 PV of DI water to remove precipitated salts, especially sulfate. The effluent was confirmed sulfate-free using a Ba^{2+} ion batch test, confirming no precipitation of $\text{BaSO}_4(\text{s})$. The core was dried at 90 °C to a constant weight.

Core Saturation. The initial water saturation, $S_{wi} \approx 10\%$, was established by a porous plate technique using water-saturated nitrogen.¹⁹ Then, the core was evacuated, saturated, and flooded with 2 PV of crude oil in each direction at 50 °C. Finally, the core was aged in the selected crude oil for 2 weeks at 90 °C.

Oil Displacement. Forced displacement tests were performed at reservoir temperature, 110 °C, using an injection rate of 0.01 cm^3/min (~1 PV/day) with a constant back pressure of 10 bar. Spontaneous imbibition tests were performed at the same temperature, 110 °C, in sealed steel imbibition cells connected to a supporting pressure cell of ~10 bar.

Verification of Anhydrite. The presence of anhydrite in the rock material was confirmed after the oil displacement tests. The core was cleaned by flooding with toluene and methanol, dried, saturated 100% with FW, and aged in the core holder at 110 °C to establish equilibrium between FW and the rock surface. DI water was then injected through the core at the same temperature with a rate of 0.01 cm^3/min , and effluent samples were analyzed for Ca^{2+} and SO_4^{2-} .

Chemical Analysis. The ionic concentrations of Ca^{2+} and SO_4^{2-} were analyzed by an ion-exchange chromatograph, ICS-3000 Reagent-free produced by Dionex Corporation, Sunnyvale, CA.

RESULTS

The limestone core material used was sampled from the aqueous zone of an oil reservoir. The cores appeared very homogeneous, with permeability in the range of 0.5–1.0 mD and porosity of about 17%. The FW was of high salinity, 208 940 ppm, and the low-AN crude oil A appeared to have relevant properties of the oil present in the reservoir. In our parametric studies, oil A was mixed with a crude oil D of higher AN to obtain oils B and C. The viscosities of the three oils were quite similar, about 4 cP at 20 °C, and the BNs varied between 0.34 and 0.45 mg of KOH/g. The AN in the crude is regarded as the most important parameter determining the wetting properties of carbonates, and the AN varied from 0.08 to 0.70 mg of KOH/g for oils A and C, respectively (Table 2). The difference in the wetting behavior between the low AN crude

oil A and the high AN crude oil C is clearly illustrated by Figure 1, showing spontaneous imbibitions of FW into the cores

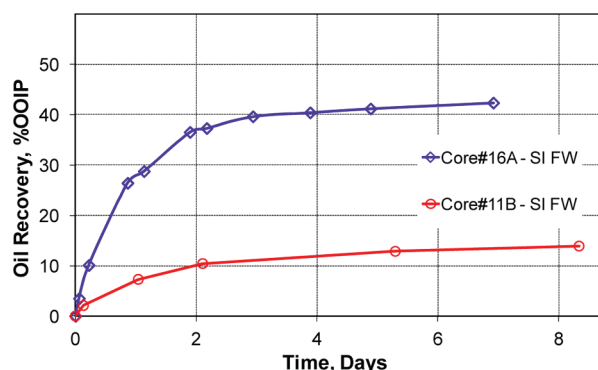


Figure 1. Spontaneous imbibition with FW into limestone cores with $S_{wi} \sim 0.1$ at $110\text{ }^{\circ}\text{C}$. Core 16A was saturated and aged with oil A (AN = 0.08), and core 11B was saturated and aged with oil C (AN = 0.70).

saturated with oil of low and high AN, cores 16A and 11B, respectively. Thus, the limestone cores became less water-wet as the AN present in the crude oil increased.

Tertiary Low-Salinity EOR Effect Using Diluted FW.

Usually, the low-salinity EOR effect in sandstone is demonstrated by flooding the core with high-saline FW in a secondary oil displacement mode, and after reaching the plateau for oil recovery, the flooding fluid is switched to low-salinity brine in a tertiary process. The same flooding sequence was applied in the present study.

Core 5B. The core was saturated with oil C with AN = 0.70 mg of KOH/g, and according to Figure 1, low water wetness was expected. The core was flooded at $110\text{ }^{\circ}\text{C}$ with FW, and about 65% of OOIP was recovered in the secondary process (Figure 2a). When the core was switching to 100× diluted FW, the oil recovery increased by 5% of OOIP and the differential pressure over the core dropped, as indicated by Figure 2b. After water break through, the concentration of sulfate in the effluent was monitored, as shown in Figure 2c. Notice that the FW did not contain any sulfate, and the sulfate must be released from the rock, probably because of dissolution of anhydrite, $\text{CaSO}_4(\text{s})$. The concentration decreased rapidly during the flooding with FW, from ≈ 0.7 to ≈ 0.2 mM. The concentration decreased further to about 0.1 mM during the low-saline flood. After about 8 days, the flooding was stopped for 1 day to establish ionic equilibrium between the formation and injected fluid. An increase in the concentration of sulfate, to ≈ 0.15 mM, was noticed as the flooding was restarted with diluted FW, but the concentration dropped again to 0.1 mM. After about 11 PV, the temperature was reduced to $70\text{ }^{\circ}\text{C}$ and the flooding was again stopped for 1 day. The concentration of sulfate in the effluent increased again to ≈ 0.2 mM as the flooding was continued. Later, the concentration of sulfate dropped to 0.1 mM, which is quite low. No significant extra oil was produced during this sequence of flooding.

Core 6B. This core was also saturated with oil C, but in this case, the core was flooded first with FW and then with diluted FW at $90\text{ }^{\circ}\text{C}$, i.e., the same as the aging temperature. The flooding temperature was decreased to increase the dissolution of anhydrite present in the matrix. The dissolution of anhydrite increases as the temperature decreases. Sulfate is a catalyst for the wettability alteration process, and it is important to have a maximum concentration of sulfate dissolved in the brine. As

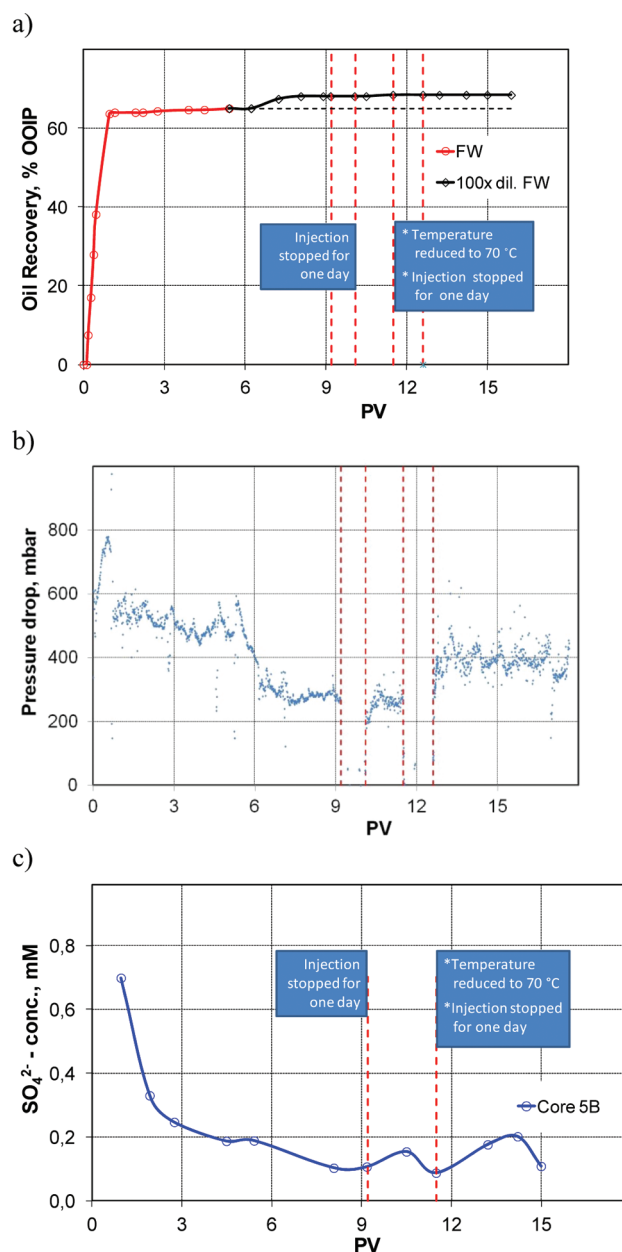


Figure 2. (a) Core 5B with $S_{wi} \sim 0.1$, saturated and aged in oil C (AN ≈ 0.70 mg of KOH/g), was flooded at a rate of $0.01\text{ cm}^3/\text{min}$, first with FW at $110\text{ }^{\circ}\text{C}$ and continued with 100× diluted FW at 110 and $70\text{ }^{\circ}\text{C}$. (b) Differential pressure over core 6B decreased as the diluted FW remobilized oil. (c) Concentration of SO_4^{2-} in the effluent versus injected PV.

noticed by Figure 3a, the amount of oil produced in the secondary flood with FW was very comparable to the first test at $110\text{ }^{\circ}\text{C}$. The tertiary low-salinity response was also in the same range. The differential pressure over the core also decreased as the low-salinity brine mobilized more oil (Figure 3b).

Both tests confirmed that limestone cores containing anhydrite will respond to a low-saline flood in a similar way as sandstones containing clay minerals. To verify that the increased recovery is linked to carbonate cores containing anhydrite, a similar test was performed on an outcrop chalk core, which was carefully depleted in sulfate prior to core preparation, by flooding the core with distilled water.

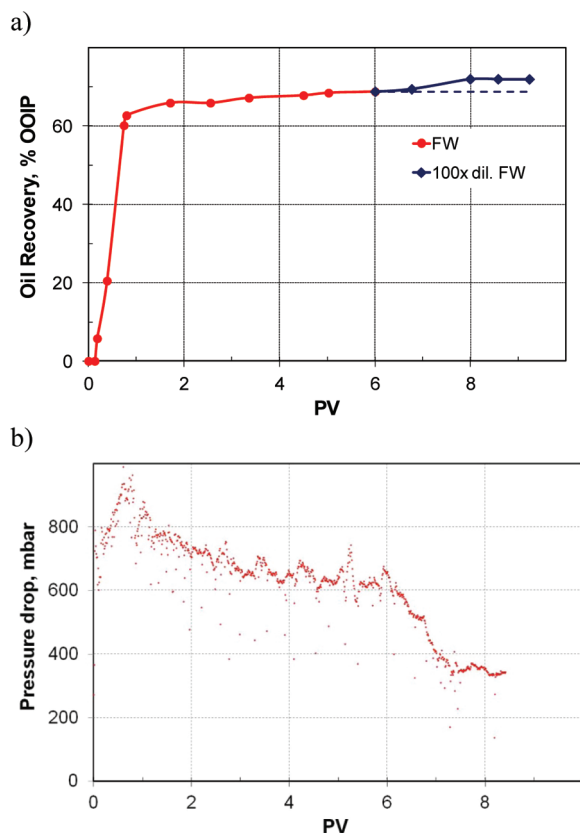


Figure 3. (a) Core 6B with $S_{wi} \sim 0.1$, saturated and aged in oil C (AN ≈ 0.70 mg of KOH/g), was flooded at a rate of $0.01 \text{ cm}^3/\text{min}$, first with FW and then continued with 100 \times diluted FW at 90°C . (b) Differential pressure over core 6B decreased as the diluted FW remobilized oil.

Outcrop Chalk Core F1. The chalk core was saturated with the high-AN crude oil C, and the test procedure was exactly the same as for core 5B. The secondary oil recovery using FW was about 57% of OOIP, and no extra oil was recovered during the flood with 100 \times diluted FW (Figure 4). Thus, carbonates

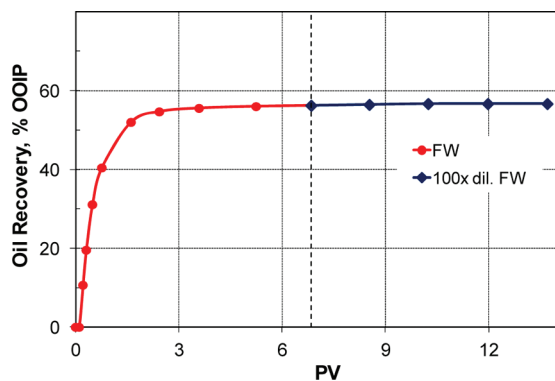


Figure 4. Chalk core F1 with $S_{wi} \sim 0.1$, saturated and aged in oil C (AN ≈ 0.70 mg of KOH/g), was flooded at a rate of $0.01 \text{ cm}^3/\text{min}$, first with FW and then continued with 100 \times diluted FW at 110°C .

without sulfate initially present in the formation, usually as anhydrite, do not show improved oil recovery in response to a salinity gradient in the injected fluid.

Tertiary Low-Salinity EOR Effect Using Diluted GSW.

In actual field developments, the oil reservoir is not normally

flooded with FW but with the most available water source. For offshore reservoirs, this means seawater or modified seawater. Thus, a relevant question is can diluted seawater act as a low-saline EOR fluid after a secondary flood with seawater? Previous experiments have shown that both spontaneous imbibition and forced displacement tests using chalk cores, which were free from sulfate, did not show a low-salinity EOR effect when exposed to diluted seawater.⁵

Core 18C. The core was saturated with oil C, AN = 0.70 mg of KOH/g, and flooded first with FW and then with 10 \times diluted GSW in a tertiary process at 110°C (Figure 5). The oil

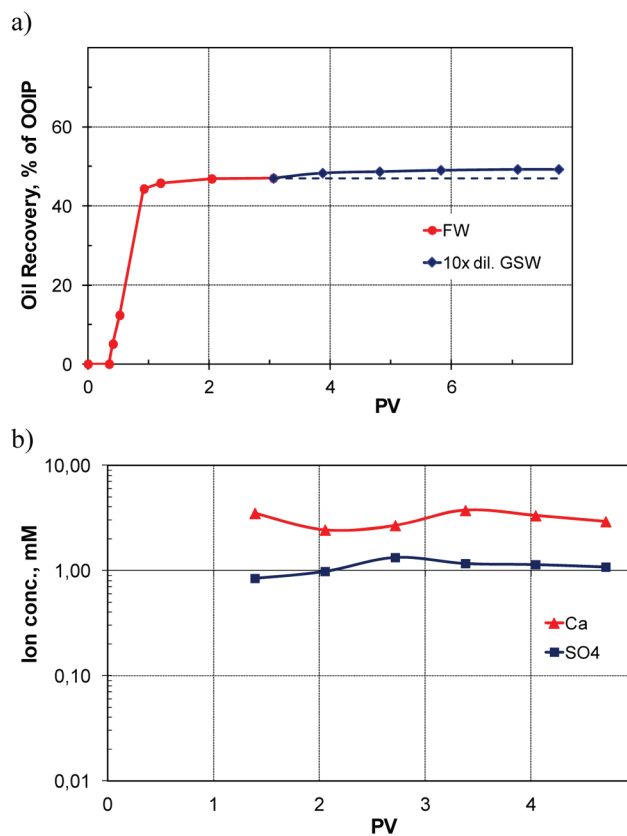


Figure 5. (a) Limestone core 18C with $S_{wi} \sim 0.1$, saturated and aged in oil C (AN ≈ 0.70 mg of KOH/g), was flooded at a rate of $0.01 \text{ cm}^3/\text{min}$, first with FW and then continued with 10 \times diluted GSW at 110°C . (b) Presence of anhydrite in core 18C was confirmed by injecting $0.01 \text{ cm}^3/\text{min}$ with DI water at 110°C into the core saturated with FW.

recovery using FW was 46% of OOIP, and the diluted GSW increased the recovery to 50%, i.e., a low-salinity effect of 4% of OOIP, which is comparable to the effect using 100 \times diluted FW (Figure 2a).

The presence of anhydrite in core 18C was verified after the oil displacement test, according to the method described in the Experimental Section. The concentration of Ca^{2+} and SO_4^{2-} (Figure 5b) became constant after displacing the FW with DI water. The concentration of Ca^{2+} was significantly higher than the concentration of SO_4^{2-} , which can be related to the dissolution of calcite in addition to anhydrite.

Core 12C. This core was subjected to a similar test as core 18C, but in this case, oil B with lower AN, AN = 0.34 mg of KOH/g, was used. As expected, the core became more water-wet and the secondary recovery by FW was 63% of OOIP

(Figure 6). The low-salinity response on the oil recovery was very small. Obviously, the initial wetting condition will have an

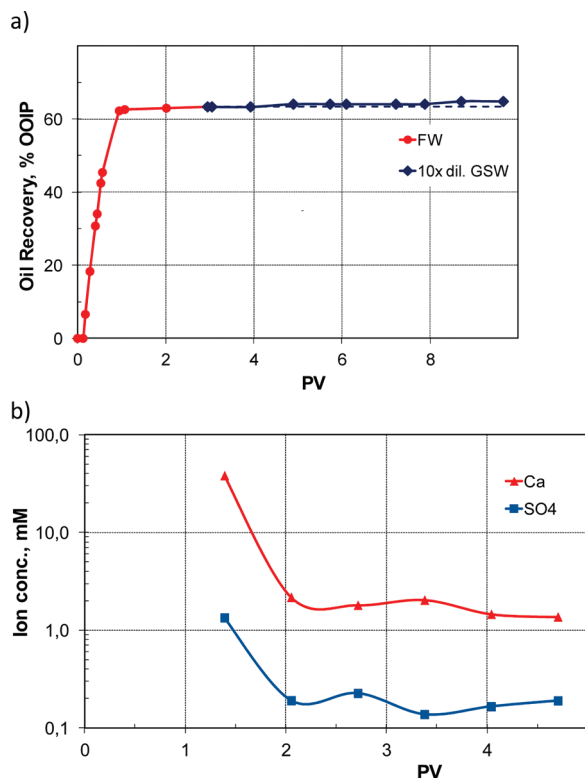


Figure 6. (a) Limestone core 12C with $S_{wi} \sim 0.1$, saturated and aged in oil B (AN ≈ 0.34 mg of KOH/g), was flooded at a rate of $0.01 \text{ cm}^3/\text{min}$, first with FW and then continued with 10 \times diluted GSW at 110°C . (b) Presence of anhydrite was tested by injecting DI water at 110°C with a rate of $0.01 \text{ cm}^3/\text{min}$ into core 12C saturated with FW.

impact on the potential of extra oil using a low-saline fluid. The presence of dissolvable anhydrite appeared to be small, as indicated by the low concentration of sulfate in the effluent, nearly 10 times lower than for core 18C (Figure 6b).

Core 4B. The core was saturated by oil A with a very low amount of acidic material, AN = 0.08 mg of KOH/g. The core was flooded at 110°C , first with GSW and then with 10 \times diluted GSW. A completely piston-like displacement was observed with GSW, and the recovery was 53% of OOIP (Figure 7). A strongly water-wet core does not give optimal oil recovery by water flooding because of capillary trapped oil by “snap-off”.²⁰ The low-salinity response with diluted GSW was, as expected, very small.

DISCUSSION

The observed tertiary low-salinity EOR effect was rather small probably because of the small amount of dissolvable anhydrite initially present in the core material. During the core preparation, the cores were initially flooded with a few pore volumes of DI water to remove FW. Some anhydrite may be lost during this operation. Furthermore, the concentration of sulfate in the effluent decreased rapidly when flooding with FW, from 0.7 to 0.2 mM, even though the flooding rate was low (Figure 2c). At a higher concentration of dissolvable anhydrite in the rock material, equilibrium between ions and rock would be established and the concentration of sulfate in the effluent should be constant. Among the cores tested for anhydrite, core

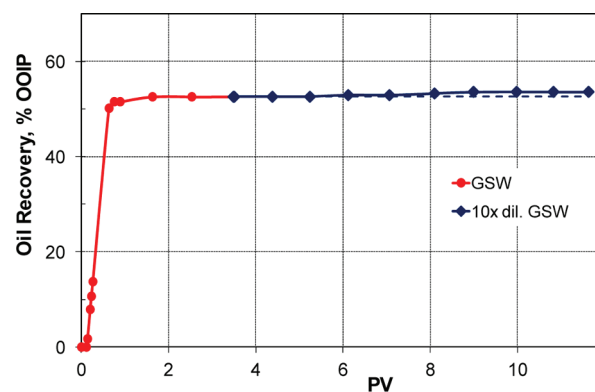
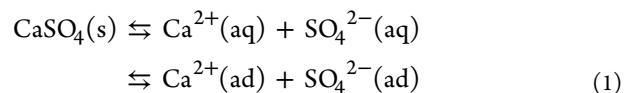


Figure 7. Limestone core 4B with $S_{wi} \sim 0.1$, saturated and aged in oil A (AN = 0.08 mg of KOH/g), was flooded at a rate of $0.01 \text{ cm}^3/\text{min}$, first with GSW and then continued with 10 \times diluted GSW at 110°C .

18C appeared to contain the most anhydrite. The concentration of sulfate in the effluent when flooding with DI water at 110°C stabilized at 1.0 mM (Figure 5b). To test the potential of the low-salinity effect in cases with a low content of anhydrite present in the rock matrix, it is recommended not to flood the cores with DI water prior to core preparation.

To discuss the chemical mechanism for the observed low-salinity effect in carbonates, the impact of the temperature and brine composition on the following equilibrium must be understood:



$\text{Ca}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ are ions dissolved in the pore water, and $\text{Ca}^{2+}(\text{ad})$ and $\text{SO}_4^{2-}(\text{ad})$ are ions adsorbed onto the carbonate surface. According to the previously reported study, where the impact of sulfate on the initial wetting conditions was studied, the concentration of $\text{SO}_4^{2-}(\text{aq})$ appeared to be the key factor determining the wetting properties.⁷ Dissolution of anhydrite, $\text{CaSO}_4(\text{s})$, which is the source for $\text{SO}_4^{2-}(\text{aq})$, is dependent upon the salinity/composition of the brine and the temperature in the following way: (1) The solubility increases as the concentration of Ca^{2+} in FW decreases (common ion effect). (2) The solubility decreases as the concentration of NaCl decreases. (3) The solubility normally decreases as the temperature increases. (4) The concentration of $\text{SO}_4^{2-}(\text{aq})$ may also decrease as the temperature is increased because of the increased adsorption onto the carbonate surface; i.e., the concentration of $\text{SO}_4^{2-}(\text{ad})$ increases.

The efficiency of the wettability alteration process is also dependent upon the temperature and the concentration of non-active salt, NaCl, in the following way: (1) Imbibition rate and ultimate oil recovery increase as the temperature increases. (2) Imbibition rate and ultimate oil recovery increase as the concentration of non-active salt, NaCl, in the imbibing brine decreases.

Thus, both the effect of the temperature and concentration of NaCl are in conflict; i.e., the concentration of $\text{SO}_4^{2-}(\text{aq})$ decreases as the temperature increases, but the surface reactivity leading to the wettability alteration increases as the temperature increases. Similarly, the concentration of $\text{SO}_4^{2-}(\text{aq})$ decreases as the amount of NaCl decreases, but the surface reactivity promoting wettability alteration increases. Therefore, for a carbonate system, there appears to be an optimum temperature

window for observing the maximum low-salinity effect, probably between 90 and 110 °C.

The dissolution of $\text{CaSO}_4(\text{s})$ in FW and 10× and 100× diluted FW versus the temperature was modeled using the OLI software, which is a thermodynamic model (Figure 8). As

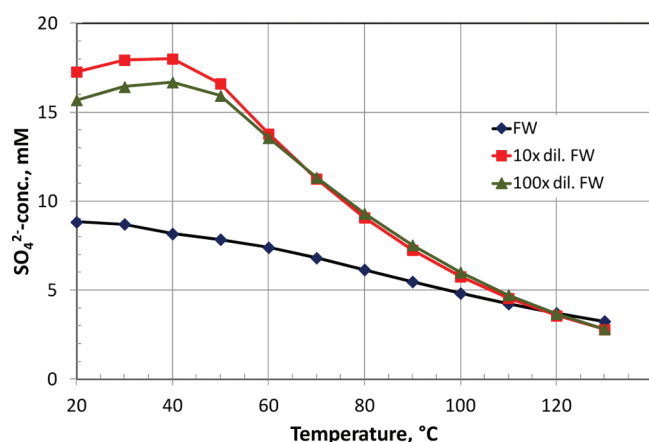


Figure 8. Concentration of sulfate in solution at different temperatures when anhydrite [$\text{CaSO}_4(\text{s})$] was exposed to FW and 10× and 100× diluted FW, as modeled by the OLI software.

expected, the solubility of anhydrite in the diluted FW is higher than in ordinary FW but the difference became smaller as the temperature is increased beyond 100 °C. The solubility of anhydrite in 100× diluted FW is lower than in 10× diluted FW. Knowing that the dissolution of anhydrite is dependent upon the concentration of Ca^{2+} (common ion effect) and the concentration of NaCl in the opposite way, it is natural that, at some stage of dilution of FW, the dissolution of anhydrite is reversed.

The calculated equilibrium concentration of sulfate versus the temperature, when 10× and 20× diluted GSW was exposed to anhydrite, is shown in Figure 9. The concentration of sulfate

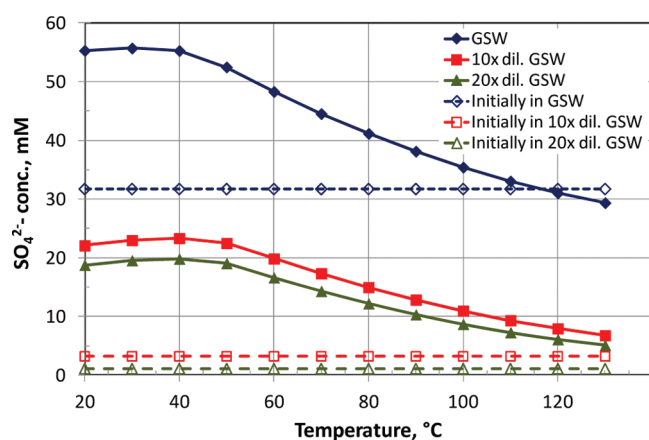


Figure 9. Concentration of sulfate in solution at different temperatures when anhydrite [$\text{CaSO}_4(\text{s})$] was exposed to GSW and 10× and 20× diluted GSW, as modeled by the OLI software.

is increased significantly because of dissolution of anhydrite. When the amount of $\text{SO}_4^{2-}(\text{aq})$ at 110 °C was compared for 100× diluted FW and 10× diluted GSW, the values are about 5 and 9 mM, respectively. According to Figures 2a and 5a, the tertiary low-saline EOR effect was quite similar for the two

cases. The reason may be the difference in the salinity. The concentration of NaCl in 100× diluted FW is 26 mM, as compared to 59 mM in 10× diluted GSW, i.e., a factor of about 2. Maybe 20× diluted GSW would be an even “smarter” low-salinity injection water?

Thus, the chemical mechanism for improved oil recovery from carbonates containing anhydrite in a tertiary low-salinity process is, in principle, the same as previously described for seawater. The only difference is that the catalytic agent sulfate is created from the matrix because of enhanced dissolution of anhydrite. A decrease in total salinity by a factor of 10–100 will improve the efficiency of the wettability alteration process, as reported previously.⁵

Provided that dolomite will respond in a similar way as calcite toward seawater as a wettability modifier, it is reasonable to believe that the low-salinity effect observed by Pu et al.¹⁵ in sandstone with a low content of clay but with significant amounts of dolomite and anhydrite was linked to a wettability alteration of dolomite. An increase in the sulfate concentration and a decrease in the salinity will activate the wettability alteration process. It was also concluded by the authors that the interstitial dolomite crystals probably play a role in the low-salinity recovery mechanism.

As for sandstones, the low-salinity effect is dependent upon a mixed wet condition; i.e., the effect will increase when more organic material is adsorbed onto the surface. This was verified by the decrease in the low-salinity effect as the AN of the crude oil decreased from 0.70 to 0.34 mg of KOH/g (Figures 5 and 6).

In a forthcoming paper, we will report greater low-salinity effects from carbonates containing much more anhydrite.

CONCLUSION

Oil recovery from core material sampled from the aqueous zone of a limestone oil reservoir was tested under forced displacement using different injection brines and oils with different ANs. It was verified by flooding the core material with distilled water that the matrix contained small amounts of anhydrite. The following conclusions are drawn: (1) Tertiary low-salinity EOR effects can be obtained in carbonates provided that anhydrite is present in the matrix. Many limestone reservoirs contain small amounts of anhydrite. (2) No low-salinity effect was detected in chalk cores that did not contain anhydrite. (3) Tertiary low-salinity oil recovery was quite small and varied between 1 and 5% of OOIP when flooding first with high-salinity FW (208 940 ppm) and then with 100× diluted FW or 10× diluted GSW because of the low concentration of anhydrite in the core material. (4) The chemical mechanism for improved oil recovery from carbonates containing anhydrite in a tertiary low-salinity process was discussed, and it is, in principle, the same as previously described for seawater. The only difference is that the catalytic agent sulfate is created in the matrix because of dissolution of anhydrite. A decrease in total salinity by a factor of 10–100 will improve the efficiency of the wettability alteration process, as reported previously.

AUTHOR INFORMATION

Corresponding Author

*E-mail: skule.strand@uis.no.

■ ACKNOWLEDGMENTS

The authors are grateful to BP in Sunbury for the financial support and providing core and oil materials.

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