

Water-Based Enhanced Oil Recovery (EOR) by “Smart Water”: Optimal Ionic Composition for EOR in Carbonates

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ABSTRACT: The composition of the injecting brine has a profound effect on the efficiency of water-based enhanced oil recovery (EOR) methods. Recently, we observed that not only is the concentration of the active ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} important for wettability alteration in carbonates but also the amount of non-active salt, NaCl, has an impact on the oil recovery process. Removing NaCl from the synthetic seawater improved the oil recovery by about 10% of original oil in place (OOIP) compared to ordinary seawater. The results were discussed in terms of electrical double-layer effects. In this work, we have modified the seawater depleted in NaCl by adjusting the concentration of active ions, Ca^{2+} and SO_4^{2-} . Oil displacement studies in outcrop chalk samples by spontaneous imbibition were performed at temperature ranges of 70–120 °C using different oils and imbibing fluids. When the concentration of SO_4^{2-} in the seawater depleted in NaCl was increased 4 times, the ultimate oil recovery increased by about 5–18% of OOIP compared to the seawater depleted in NaCl. The amount of Ca^{2+} in the seawater depleted in NaCl had no significant effect on the oil recovery at 100 °C, but significant improvements were observed at 120 °C. Chromatographic wettability analysis confirmed that the water-wet area of the rock surface increased as the oil recovery increased, emphasizing the importance of the ionic composition and the ion concentration of the injecting brine in the water-based EOR methods.

INTRODUCTION

Wettability is one of the major parameters that control the efficiency of enhanced oil recovery (EOR) methods. The wettability of a rock surface is determined by the thickness of the water film between the rock surface and the crude oil. For a very thick film, the system is stable and remains water-wet. If it is unstable, the film will break, resulting in the adsorption of polar components onto the rock surface.¹ The stability of the water film is dependent upon the magnitude of the disjoining pressure, which results from the intermolecular or inter-ionic forces.^{2,3} The main categories of crude oil/brine/solid (COBS) interactions are identified as polar interactions, surface precipitation, acid/base interactions, and ion-binding or specific interactions between charged sites and higher valency ions.^{4,5} For the ion-bonding mechanism, di- and multivalent ions can bind at both oil and solid/water interfaces and/or bridge between them.⁶

The potential of seawater to act as a wettability modifier at high temperatures is investigated in details previously. The wettability alteration mechanism is described as a symbiotic interaction between the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} and the adsorbed carboxylic material on the carbonate surface.^{7,8} It is suggested that sulfate present in seawater will adsorb onto the positively charged water-wet sites on the chalk surface and lower the positive surface charge. Because of less electrostatic repulsion, excess of Ca^{2+} will be localized close to the chalk surface. Then, Ca^{2+} can react with adsorbed carboxylic groups bonded to the chalk surface and release some of the organic carboxylic material. At high temperatures, Mg^{2+} can substitute Ca^{2+} and also Ca^{2+} linked to carboxylic groups on the chalk surface.⁷ Recently, we observed that not only is the concentration of the active ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} important for wettability alteration to take place but also the amount of non-active salt, NaCl, has an impact on the wettability alteration process.

Removing NaCl from the seawater improved the oil recovery dramatically compared to ordinary seawater.⁹ The increase in the oil recovery is attributed to the concentration of the active ions in the double layer.

The concentration of the active ions is a very crucial parameter for the wettability alteration by seawater. In this work, an attempt was made to optimize the concentration of the active ions, especially Ca^{2+} and SO_4^{2-} , in seawater depleted in NaCl. The effect of the ionic composition and concentration was studied by spontaneous imbibition of the optimized seawater into chalk cores.

MATERIALS AND METHODS

Rock Materials. Outcrop Stevns Klint chalk nearby Copenhagen, Denmark, was used as the porous medium, with a porosity and permeability in the range of ~45% and 1–2 mD, respectively. The specific surface area is approximately 2 m²/g.^{10,11} The properties of this coccolithic material are quite similar to the North Sea chalk oil reservoirs. The cores were drilled from the same block and shaved in a lathe to similar dimensions, as shown in Table 1.

Brine. Artificial formation water (VB) similar to the Valhall field was used. Synthetic seawater (SW) was used as the base displacing brine. The SW was modified by changing the composition and salinity, and the following terminology was used: (i) SW0NaCl, SW depleted in NaCl; (ii) SW0NaCl–4 SO_4^{2-} , SW0NaCl with 4× SO_4^{2-} compared to ordinary SW; (iii) SW0NaCl–4 Ca^{2+} , SW0NaCl with 4× Ca^{2+} compared to ordinary SW.

The composition of the different brines is listed in Table 2. For the chromatographic wettability test, the core was first flooded with SW without SO_4^{2-} , with the fluid termed SW0T, to remove SO_4^{2-} from the

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Table 1. Core Properties

core ID	L (cm)	D (cm)	pore volume (mL)	Φ (%)	S_{wi} (%)	S_{oi} (%)	remarks	crude oil
SWK#1	7.0	3.8	37.9	48	10	90	SI by VB at 90 °C	
SWK#3	7.0	3.8	36.3	46	11	89	SI by SW0NaCl at 90 °C	
SWK#5	7.0	3.8	37.1	47	9	91	SI by SW0NaCl–4SO ₄ ²⁻ at 90 °C	cores saturated and aged with oil B (AN = 0.5 mg of KOH/g)
SWK#6	7.0	3.8	36.7	46	9	91	SI by SW at 90 °C	
SWK#7	7.0	3.8	37.0	46	11	89	SI by SW0NaCl–4SO ₄ ²⁻ at 70 °C	
SWK#8	7.0	3.8	35.4	44	11	89	SI by SW0NaCl at 70 °C	
SWK#9	7.0	3.8	35.5	44	10	90	SI by SW at 70 °C	
SK#1	7.0	3.8	36.7	46	9	91	SI by SW0NaCl at 100 °C	
SK#2	7.0	3.8	38.5	48	10	90	SI by SW0NaCl–4Ca ²⁺ at 100 °C	
SK#3	7.0	3.8	37.9	47	10	90	SI by SW0NaCl–4SO ₄ ²⁻ at 100 °C	cores saturated and aged with oil A (AN = 2.0 mg of KOH/g)
SK#4	7.0	3.8	36.0	45	10	90	SI by SW0NaCl at 120 °C	
SK#5	7.0	3.8	38.3	48	9	91	SI by SW0NaCl–4SO ₄ ²⁻ at 120 °C	
SK#6	7.0	3.8	36.5	46	10	89	SI by SW0NaCl–4Ca ²⁺ at 120 °C	
SWK#10	7.0	3.8	36.0	45			clean reference core for wettability test	

Table 2. Brine Compositions (mol/L)

ions	VB (mol/L)	SW (mol/L)	SW0NaCl (mol/L)	SW0NaCl–4SO ₄ ²⁻ (mol/L)	SW0NaCl–4Ca ²⁺ (mol/L)	SW0T (mol/L)	SW1/2T (mol/L)
HCO ₃ ⁻	0.009	0.002	0.002	0.002	0.002	0.002	0.002
Cl ⁻	1.07	0.525	0.126	0.126	0.193	0.583	0.538
SO ₄ ²⁻	0.00	0.024	0.024	0.096	0.024	0.000	0.012
SCN ⁻	0.00	0.000	0.000	0.000	0.000	0.000	0.012
Mg ²⁺	0.008	0.045	0.045	0.045	0.045	0.045	0.045
Ca ²⁺	0.029	0.013	0.013	0.013	0.052	0.013	0.013
Na ⁺	1.00	0.450	0.050	0.194	0.050	0.460	0.427
K ⁺	0.005	0.010	0.010	0.010	0.010	0.010	0.022
Li ⁺	0	0.000	0.000	0.000	0.000	0.000	0.012
ionic strength	1.112	0.657	0.257	0.473	0.368	0.644	0.647
TDS (g/L)	62.80	33.39	10.01	16.79	11.43	33.39	33.39

core and to establish equilibrium at room temperature. Then, the core was flooded with the fluid termed SW1/2T, which contained a similar concentration of the tracer SCN⁻ and SO₄²⁻, equal to 0.012 mol/L.

Oil. Two test oils with different concentrations of acidic components were prepared. Oil A was made by diluting an acidic stabilized crude oil, base oil, with 40 vol % heptane. The mixture was centrifuged and filtered through a 5 μ m Millipore filter. No precipitation of asphaltenic material was observed during storage. Oil B was prepared by adding oil A into a crude oil sample depleted in polar components. The crude oil depleted in polar components was prepared by adsorbing the polar components onto an active silica gel and termed oil C.¹² About 10 wt % of silica gel was added to oil A, and the mixture was stirred at room temperature for 3 days. Then, a similar amount of silica gel was added to the mixture and stirred for 2 more days. The oil was then centrifuged and filtered through a 0.65 Millipore filter, and it was confirmed that the acid number (AN) and base number (BN) were <0.01 mg of KOH/g. The density of the crude oils was measured at room temperature using a DMA 4500 density meter, and the viscosity was measured using a Physica Parr UDS 200 viscometer. The properties of the crude oils are given in Table 3.

AN and BN Measurements. A Mettler Toledo DL55 autotitrator was used to measure the AN and BN for the different crude oils. The methods involve potentiometric titrations using an internal standard. The methods used were developed by Fan and Buckley,^{13,14} which are modified variations of American Society for Testing Materials

(ASTM) D2896 for BN titration and ASTM D664 for AN titration^{15,16} (Table 3).

Core Preparation. The chalk cores were prepared according to the method described by Puntervold et al.¹⁷ The cores were drilled from the same chalk block in the same direction with an oversized bit and shaped to the correct dimension using a lathe. To remove initial soluble salts, especially sulfate, which could affect the wetting properties significantly, the cores were flooded with 250 mL of distilled water at 50 °C. After the cores were dried at 90 °C to a constant weight, they were evacuated and saturated with formation brine to measure the pore volume (PV). The porous plate technique using water-saturated N₂ gas was used to drain the cores to the initial water saturation of about 10%. To establish uniform oil saturation, the cores were flooded with 2 PV of oil in both directions at 50 °C using a Hassler core holder with a confining pressure not exceeding 25 bar. The cores were wrapped with Teflon tape to avoid unrepresentative adsorption of polar components onto the surface during aging at 90 °C. To establish a wide range of the initial wetting conditions, two types of crude oils with different concentrations of polar components, AN and BN, were used. Variation of aging time of a core in crude oil is a viable parameter of obtaining systematic change in wettability.^{18,19} To study the oil displacement efficiency at 100–120 °C, the cores were saturated with oil A, high AN, and aged for 8 weeks. For the displacement studies at 70–90 °C, the cores were saturated with oil B, low AN, and aged for 4 weeks. The reproducibility of the chalk cores in

Table 3. Crude Oil Properties

oil type	density ^a (g/cm ³)	AN (mg of KOH/g)	BN (mg of KOH/g)	viscosity ^a (cP)	remarks
base oil	0.886	2.82	1.13	20.47	recently sampled crude oil
oil A	0.815	2.0	0.5	3.38	diluting base oil with 40 vol % <i>n</i> -heptanes
oil B	0.798	0.5	0.3	2.60	diluting oil A with oil C
oil C	0.801	<0.01	<0.01	2.44	depleted in polar components by active silica gel

^a Density and viscosity were determined at room temperature.

the spontaneous imbibition and chromatographic wettability test is previously well-demonstrated.^{17,20}

Spontaneous Imbibition. The aged cores were immersed in the imbibing fluid in sealed steel cells. The spontaneous imbibition tests were performed at specified temperatures, 70–120 °C, with a back pressure of 10 bar to avoid boiling of the fluids. The produced oil during the test was collected in a buret, and oil recovery was determined versus time as a percentage of original oil in place (% OOIP).

Chromatographic Wettability Test. The chromatographic wettability test for carbonates developed by Strand et al.²⁰ was used to determine the increase in the water-wet surface area after spontaneous imbibition by different imbibing brines. The core was placed in a core holder with a confining pressure of 25 bar and flooded at room temperature with at least 2.0 PVs of the brine without SO₄²⁻ and tracer, SW0T, at a rate of 0.20 mL/min, followed by another 1.0 PV of the brine at a rate of 0.40 mL/min to establish residual oil saturation. Next, the core was flooded with at least 2.0 PV of SW1/2T brine (containing SO₄²⁻ and the tracer SCN⁻) at a rate of 0.20 mL/min. The effluent was collected in fractions of 1–4 mL using a fraction collector. The fractions were analyzed for the concentration of SO₄²⁻ and SCN⁻, using a Dionex ICS-3000 ion chromatograph. The concentration relative to the initial concentration was plotted against the injected pore volume. The area between the tracer curve and the sulfate curve is directly proportional to the water-wet area inside the core because the chromatographic separation only takes place at the water-wet sites. The area ratio between the tracer and sulfate curves of the sample, A_{wet} , and a reference cleaned water-wet core, A_{ref} is a measure of the water-wet fraction of the sample, WI

$$WI = \frac{A_{wet}}{A_{ref}}$$

where WI = 0 is completely oil-wet, WI = 0.5 is neutral wettability, and WI = 1 is completely water-wet.

The error in the reproducibility of the calculated area between the tracer and sulfate curve was less than 0.5% between different cores, as reported by Strand et al.²⁰

RESULTS

Wettability alteration in carbonate reservoirs by modified seawater is sensitive to the ionic composition and the concentration of the ions in the injecting brine as well as the temperature. The mixed-wet or oil-wet character of the carbonate reservoir can be ascribed to the adsorption of carboxylic materials from the crude oil onto the positive sites of a calcite surface.^{21,22} Therefore, the carboxylic material, quantified as the total AN, is an important wetting parameter for carbonates.^{12,23} In this study, two types of crude oils with different concentrations of polar components, AN and BN, were used: (a) oil A with AN = 2.0 mg of KOH/g and BN = 0.5 mg of KOH/g and (b) oil B with AN = 0.5 mg of KOH/g and BN = 0.3 mg of KOH/g. For the displacement studies at high temperatures, 100–120 °C, the cores were saturated with oil A and aged for 8 weeks. To study the

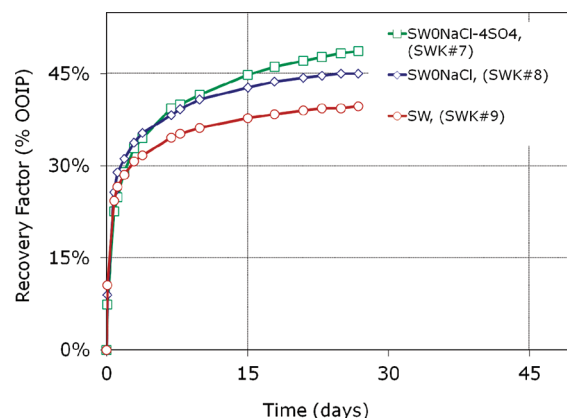


Figure 1. Spontaneous imbibition into oil-saturated chalk cores at 70 °C using different imbibing fluids with different salinities and ionic compositions: SW, SW0NaCl, and SW0NaCl–4SO₄²⁻, respectively. S_{wi} = 10%, oil B, and AN = 0.5 mg of KOH/g.

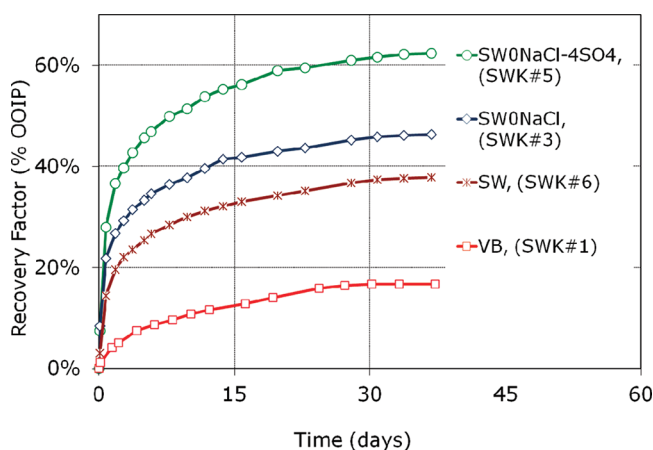


Figure 2. Spontaneous imbibition into oil-saturated chalk cores at 90 °C using VB, SW, and modified seawater: SW0NaCl and SW0NaCl–4SO₄²⁻. S_{wi} = 10%, oil B, and AN = 0.5 mg of KOH/g.

displacement efficiency at lower temperatures, 70–90 °C, the cores were saturated with oil B and aged for 4 weeks. The results are discussed in terms of the displacement efficiency during spontaneous imbibition and wetting alteration.

Spontaneous Imbibition Using Oil B. The results from the spontaneous imbibition studies at 70 and 90 °C are shown in Figures 1 and 2, respectively. At 70 °C, the oil recovery by spontaneous imbibition of SW into the chalk core was about 38% of OOIP (Figure 1). The recovery increased to 45% of OOIP when SW0NaCl was used as the imbibing fluid. When the concentration of sulfate in SW0NaCl increased, SW0NaCl–4SO₄²⁻, the oil recovery at the production plateau was increased to 50% of OOIP.

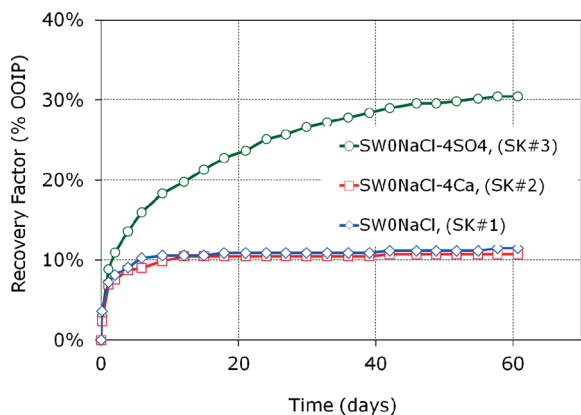


Figure 3. Spontaneous imbibition into oil-saturated chalk cores at 100 °C using different imbibing fluids with different salinities and ionic compositions: SW0NaCl, SW0NaCl–4SO₄²⁻, and SW0NaCl–4Ca²⁺. S_{wi} = 10%, oil A, and AN = 2.0 mg of KOH/g.

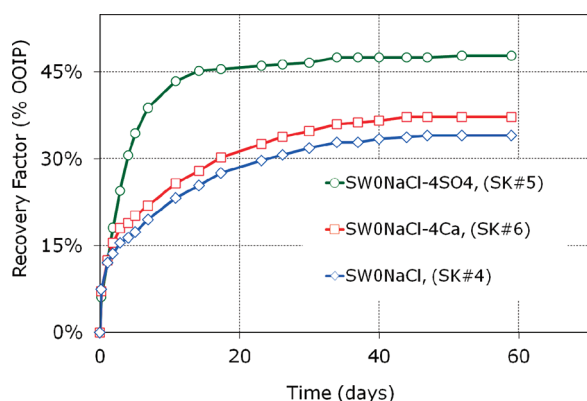


Figure 4. Spontaneous imbibition into oil-saturated chalk cores at 120 °C using different imbibing fluids with different salinities and ionic compositions: SW0NaCl, SW0NaCl–4SO₄²⁻, and SW0NaCl–4Ca²⁺. S_{wi} = 10%, oil A, and AN = 2.0 mg of KOH/g.

At 90 °C, the oil recovery by spontaneous imbibition of VB into the core was about 17% of OOIP, indicating mixed-wet conditions (Figure 2). The oil recovery increased to 38% of OOIP when using SW as the imbibing fluid. Seawater depleted in NaCl, SW0NaCl, resulted in the oil recovery of 47% of OOIP at the plateau. When SW0NaCl was spiked by sulfate, SW0NaCl–4SO₄²⁻, the oil recovery increased to 62% of OOIP, a similar result that is obtained in a water-wet chalk core.^{24,25}

In comparison to ordinary SW, the rate of imbibition was improved when removing NaCl and spiking the fluid with sulfate, which is in line with increased concentrations of active ions in the double layer at the chalk surface. Neither Na⁺ nor Cl⁻ are regarded as potential determining ions toward the chalk surface, which means that these ions are not part of the inner Stern layer.²⁶ The ions are, however, active in the double layer and may have influence on the access of the active ions, Ca²⁺, Mg²⁺, and SO₄²⁻, to the chalk surface. The surface reactivity of Ca²⁺, Mg²⁺, and SO₄²⁻ increases as the temperature increases, as discussed in detail in previous papers.^{9,27}

Spontaneous Imbibition Using Oil A. The results of the spontaneous imbibition tests after 60 days at 100 and 120 °C are shown in Figures 3 and 4, respectively. The cores were saturated

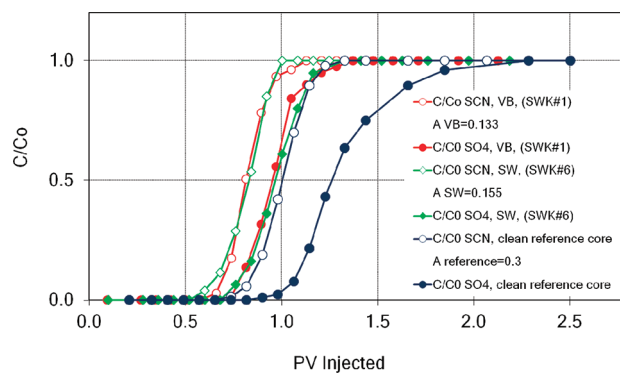


Figure 5. Chromatographic wettability analysis after spontaneous imbibition at 90 °C using formation brine and seawater. The cores were saturated with oil B with AN of 0.5 mg of KOH/g and chromatographic brines of SW0T and SW1/2T at room temperature. C/C_0 = relative concentration of SCN⁻ and SO₄²⁻. The wettability analyses are summarized in Table 4.

with oil A with AN = 2.0 mg KOH/g and aged for 8 weeks to establish a neutral to preferentially oil-wet condition. This was also reflected in the lower oil recovery by spontaneous imbibitions. The experiments were performed to study the effect of the active ions, especially SO₄²⁻ and Ca²⁺, on the displacement efficiency of the imbibing fluid. The non-active salt, NaCl, was initially removed from the seawater, and the objective was to optimize the concentration of Ca²⁺ and SO₄²⁻. The seawater depleted in NaCl was modified by separately increasing the concentration of active ions, Ca²⁺ and SO₄²⁻, 4 times compared to ordinary seawater. The results indicate that the concentration of SO₄²⁻ in the imbibing brine had the largest effect on the oil recovery.

At 100 °C, spontaneous imbibition by SW0NaCl–4SO₄²⁻ increased the oil recovery by 18% of OOIP compared to the seawater depleted in NaCl, SW0NaCl. The amount of Ca²⁺ in the seawater depleted in NaCl had no significant effect on the oil recovery at 100 °C (Figure 3). The oil recovery, by either SW0NaCl or SW0NaCl–4Ca²⁺, was very low, about 11% of OOIP, which is in line with very low water wetness.

At 120 °C, the seawater depleted in NaCl spiked by sulfate, SW0NaCl–4SO₄²⁻, resulted in an extra oil recovery of 14% of OOIP compared to SW0NaCl (Figure 4). The oil recovery at the plateau using SW0NaCl as the imbibing fluid was about 33% of OOIP. Increasing the Ca²⁺ concentration in the imbibing fluid had a marginal effect on oil recovery, about 4% of OOIP, confirming that Ca²⁺ is also active in the wettability alteration process. In all of the experiments, the rate of imbibition was improved when spiking the fluid with sulfate.

Chromatographic Wettability Test. The potential of the different imbibing fluids, VB, SW, SW0NaCl, and SW0NaCl–4SO₄²⁻, to change the wetting properties of chalk was quantified by determining the water-wet fraction of the rock surface after the spontaneous imbibition process at 90 °C. The water-wet fraction is the ratio of the chromatographic separation area between the effluent curves, SCN⁻ and SO₄²⁻, at the residual oil saturation divided by the chromatographic separation area for a completely water-wet reference core.¹⁸ To obtain a water-wet reference core, a clean chalk core was flooded with seawater at 130 °C at the rate of 3 PV/day for 1 day, which will remove possible adsorbed organic material.²⁸

The chromatographic wettability test after the imbibition of VB into the core at 90 °C is shown in Figure 5. The area between

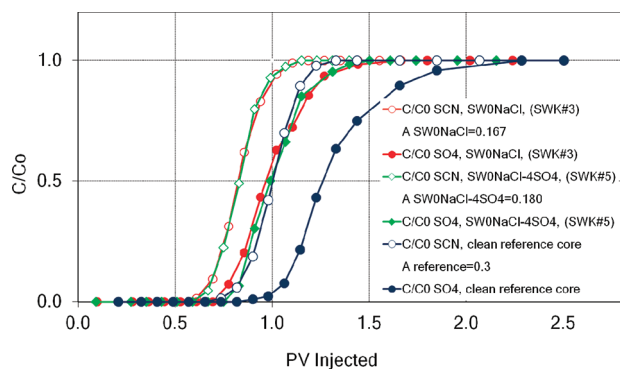


Figure 6. Chromatographic wettability analysis after spontaneous imbibition at 90 °C using modified seawater: SW0NaCl and SW0NaCl–4SO₄²⁻. The cores were saturated with oil B with AN of 0.5 mg of KOH/g and chromatographic brines of SW0T and SW1/2T at room temperature. C/C_0 = relative concentration of SCN⁻ and SO₄²⁻. The wettability analyses are summarized in Table 4.

Table 4. Actual Data from the Chromatographic Wettability Test Performed on Cores Imbibed at 90 °C Using Oil B

imbibing fluid	A_{wet}	WI
VB	0.133	0.44
SW	0.155	0.52
SW0NaCl	0.67	0.56
SW0NaCl–4SO ₄ ²⁻	0.180	0.60
clean reference core	0.300	

the tracer, SCN⁻, and sulfate elution curves was determined to be 0.133. The chromatographic separation area between the corresponding curves for the water-wet reference core was 0.300. The water-wet fraction of the core after the imbibition by formation brine was calculated to be $WI = 0.133/0.300 = 0.44$. No wettability alteration is supposed to take place during the oil displacement process by formation brine, and the water-wet fraction is directly related to the initial wetting condition resulting from the adsorption of the polar components on the positively charged rock surface. Considering that the wetting index of the neutral wetting condition is 0.5, the value of 0.44 corresponds to a preferentially oil-wet condition. Similarly, the water-wet fraction of the rock surface after imbibition by SW, SW0NaCl, and SW0NaCl–4SO₄²⁻ was calculated to be 0.52, 0.56, and 0.6, respectively (Figures 5 and 6). The calculated wetting indexes for all of the imbibing fluids are listed in Table 4.

DISCUSSION

With the chemical mechanism known for the symbiotic interaction between the active ions in SW, Ca²⁺, Mg²⁺, and SO₄²⁻, it is possible to modify the seawater to become a “smart” EOR fluid. The formation water in a carbonate reservoir always contains significant amounts of Ca²⁺ and Mg²⁺, but the concentration of SO₄²⁻ is usually very low because of the low solubility of anhydrite, CaSO₄(s). The solubility decreases as the concentration of Ca²⁺ increases (common ion effect) and as the temperature increases. Because calcium and magnesium act as potential determining ions toward calcite and the fact that they are already present in the formation brine, an equilibrium between ions dissolved in the pore water, Ca²⁺(aq) and Mg²⁺(aq), and

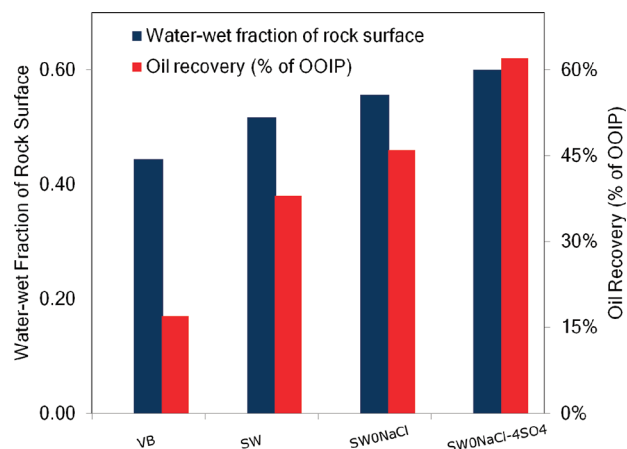


Figure 7. Relationship between the oil recovery and water-wet fraction of the rock surface after spontaneous imbibition with VB, SW, SW0NaCl, and SW0NaCl–4SO₄²⁻ at 90 °C for oil B. As the water-wet fraction of the rock surface increases from 0.44 to 0.6, the oil recovery increases from 17 to 62% of OOIP.

ions adsorbed onto calcite, Ca²⁺(ad) and Mg²⁺(ad), is established at the reservoir conditions. Because the concentration of NaCl is usually high, the ionic double layer close to the positively charged calcite surface will contain a lot of Na⁺ and Cl⁻. Sulfate in the wettability-modifying fluid also acts as a potential determining ion toward calcite and is therefore a key ion, which acts as a catalyst for the wettability alteration process. Thus, the efficiency of the wettability-modifying fluid is dependent upon the access of sulfate to the calcite surface. Obviously, if the ionic double layer close to the calcite surface is free from non-active salt, such as NaCl, the double layer will mainly consist of active cations, which are charge-balanced by mainly Cl⁻. The access of sulfate to the calcite surface will be improved, and it will be even better if the concentration of sulfate in the imbibing fluid is increased, which is in line with the experimental observations. How much sulfate that can be added to SW free from NaCl to optimize the oil recovery is dependent upon the initial concentration of Ca²⁺ in the formation brine and the temperature. It is very important to avoid precipitation of anhydrite, CaSO₄(s), as the injected fluid contacts the formation brine, which can block the pores and reduce the permeability of the rock. The solubility of anhydrite increases as the temperature decreases, and the efficiency of the wettability alteration process increases as the temperature increases. The present study shows that it is possible to compensate for the decrease in oil recovery at lower temperatures by increasing the amount of sulfate in the imbibing brine. Therefore, spiking the imbibing fluid with sulfate may be of greater benefit at lower temperatures compared to high temperatures, as illustrated by Figures 3 and 4. The increase in oil recovery when going from SW0NaCl to SW0NaCl–4SO₄²⁻ at 100 °C is about 20% of OOIP compared to 11% at 120 °C. In the latter case, there may be some precipitation of CaSO₄(s). The small difference in oil recovery between SW0NaCl and SW0NaCl–4SO₄²⁻ at 70 °C (Figure 1) compared to the greater difference shown in Figure 2 at 90 °C can be related to the temperature effect; i.e., 70 °C is expected to be at the lower temperature limit for the process to take place.

The difference in oil recovery by the various imbibing fluids, as shown in Figure 2, could be related to their potential to act as wettability modifiers, as verified by the chromatographic wettability

tests after the imbibition tests at 90 °C. No wettability alteration is expected to take place using VB as the imbibing fluid. Therefore, the initial water-wet fraction of the cores saturated and aged with oil B is WI = 0.44, which is characterized as preferential oil-wet. The water-wet fraction of the core increased to WI = 0.60 after being imbibed with the most efficient fluid SW0NaCl–4SO₄²⁻ (Table 4). The wetting indexes, WI, and the oil recovery after spontaneous imbibitions with the different fluid are shown in Figure 7. It is seen that the oil recovery correlates very well with the water-wet fraction. As the water-wet fraction of the rock surface increases from 0.44 to 0.6, the oil recovery increases from 17 to 62% of OOIP.

Water chemistry is experimentally shown to affect the stability of the water film and desorption of organic oil components from mineral surfaces in a water-based EOR process.^{7,9} The results confirm that the wettability alteration in carbonates is dependent upon the ionic composition and the concentration of the ions in the injecting brine. Both spontaneous imbibition and chromatographic wettability tests emphasize the importance of the ionic composition and the concentration of the ions in the displacing fluid.

CONCLUSION

Seawater can be modified with regard to both salinity and ionic composition to act as an improved wettability modifier in a water-based EOR process in carbonates. The following brines have been used as the imbibing fluids: formation water, VB; seawater, SW; seawater depleted in NaCl, SW0NaCl; seawater depleted in NaCl and spiked with either 4 × SO₄²⁻ or 4 × Ca²⁺ compared to ordinary seawater, termed SW0NaCl–4SO₄²⁻ and SW0NaCl–4Ca²⁺, respectively. The following conclusions were drawn: (1) At 70 and 90 °C, the imbibition rate and ultimate oil recovery increased relative to seawater when seawater was depleted in NaCl, 5–10% of OOIP. The effect was more significant at high temperatures. Further improvement was observed when seawater depleted in NaCl was spiked by sulfate. (2) When the concentration of SO₄²⁻ was increased 4 times, the ultimate oil recovery increased 5–18% of OOIP compared to the seawater depleted in NaCl depending upon the temperature, 70–120 °C. (3) The amount of Ca²⁺ in the seawater depleted in NaCl had no significant effect on the oil recovery at 100 °C, but significant improvements were observed at 120 °C. (4) The oil recovery by spontaneous imbibitions increased in the order VB < SW < SW0NaCl < SW0NaCl–4SO₄²⁻, which also corresponded to the order of the increased water-wet fraction after the imbibition process. (5) The difference in water wetness was monitored by the chromatographic wettability test, and it was confirmed that the water wetness of the cores was in the order of SW0NaCl–4SO₄²⁻ > SW0NaCl > SW > VB. (6) Both sulfate and non-active salt, NaCl, have a great impact on the imbibing fluid to act as a wettability modifier toward carbonates. (7) Field application using optimized seawater as an EOR fluid in carbonates is dependent upon techniques for preparing the specific fluid economically.

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NOMENCLATURE

- A = adsorption area
 AN = acid number (mg of KOH/g)
 BN = base number (mg of KOH/g)
 C/C_o = relative concentration of ions
 COBS = crude oil/brine/solid
 D = core diameter (cm)
 L = core length (cm)
 OOIP = original oil in place
 PV = pore volume
 S_{wi} = initial water saturation (%)
 S_{oi} = initial oil saturation (%)
 SI = spontaneous imbibition
 SW = synthetic seawater
 SW0T = synthetic seawater without SO₄²⁻
 SW1/2T = synthetic seawater, with the concentration of SCN⁻ and SO₄²⁻ being 0.012 mol/L
 SW0NaCl = seawater depleted in NaCl
 SW0NaCl–4SO₄²⁻ = seawater depleted in NaCl with 4 times the concentration of SO₄²⁻
 SW0NaCl–4Ca²⁺ = seawater depleted in NaCl with 4 times the concentration of Ca²⁺
 TDS = total dissolved solids (g/L)
 VB = formation brine
 WI = Water-wet surface fraction
 Φ = porosity (%)
 ΔWI = change in water-wet surface fraction

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