

## “Smart Water” as a Wettability Modifier in Chalk: The Effect of Salinity and Ionic Composition

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Seawater can improve the water wetness of chalk at high temperatures, which improves the oil displacement by spontaneous imbibition of water. It is experimentally verified that the interaction between  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  at the chalk surface will displace adsorbed carboxylic acids and increase the water wetness. In this work, the effect of salinity and ionic composition of smart water on oil recovery was studied at different temperatures, 100, 110, and 120 °C. The ultimate oil recovery was compared using seawater as the base fluid. When NaCl was removed from seawater, both the imbibition rate and oil recovery increased in comparison to seawater at the temperatures tested. At 110 and 120 °C, the oil recovery from seawater depleted in NaCl increased by about 10% of original oil in place (OOIP) compared to seawater. A decrease in oil recovery of about 5% of OOIP was observed when increasing the amount of NaCl in seawater 4 times. A systematic decrease in oil recovery was observed when using seawater diluted with distilled water as imbibing fluid. Imbibition tests at 110 °C showed that the water-wet fraction increased 29% for seawater depleted in NaCl compared to 11% for ordinary seawater. Diluted seawater to 10 000 ppm did not change wetting conditions at 110 °C. The results confirmed that not only is the concentration of the active ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  important for wettability alteration to take place but also the amount of non-active salt, such as NaCl, has an impact on the wettability alteration process, which is discussed as a double-layer effect at the chalk surface. No significant improvement in the ultimate oil recovery was observed during forced displacement by modified seawater.

### Introduction

It is well-documented that seawater increases the water wetness of mixed wet chalk at high temperatures.<sup>1–4</sup> Improvement in oil recovery has been reported both by spontaneous imbibition and during forced displacement. It is experimentally verified that the interactions between the active components,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ , in seawater and the rock surface are responsible for the improvement in water wetness, and a chemical mechanism has been suggested.<sup>5</sup> It was experimentally documented that adsorption of  $\text{SO}_4^{2-}$  onto the positively charged chalk also increased the excess of  $\text{Ca}^{2+}$  close to the surface, which probably reacted with the adsorbed carboxylic material and released it from the surface. A similar combined effect with  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$  can also remove organic material. The suggested mechanism is illustrated in Figure 1. The reactivity of these ions toward the carbonate surface is dependent upon the chemical activity in the double layer close to the surface. Both the size and the nature of the double layer are related to salinity and composition of the aqueous phase.

The chemical mechanism for wettability alteration in carbonates and sandstones using “smart water” is different, as

discussed in a recent paper.<sup>6</sup> In carbonates, seawater with salinity of about 33 000 ppm acts as a wettability modifier, while in sandstones, a low-saline water, > 2000 ppm, can act as a wettability modifier and improve oil recovery in a tertiary water flood. To further document the difference in the chemical mechanisms, the oil recovery from chalk by spontaneous imbibition and forced imbibition was studied by comparing the oil recovery using modified seawater and ordinary seawater. Synthetic seawater (SW) as “smart water” was changed by adjusting the concentration of NaCl (0, 1, and 4× SW salinity), while keeping the concentration of the active potential determining ions,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ , constant and equal to the concentration in seawater. Furthermore, seawater was diluted to reduce the salinity to a low salinity range, ~1600 ppm.

### Materials and Methods

**Core Materials.** Outcrop Stevns Klint chalk nearby Copenhagen, Denmark, was used as the porous medium, with porosity and permeability in the range of ~45% and 1–2 mD, respectively. The specific surface area is approximately 2 m<sup>2</sup>/g.<sup>7,8</sup> 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, FW, similar to the Valhall field was used. As displacing fluid, SW was used as the base brine. The SW was modified by changing the composition and salinity. For the fluid termed SW0NaCl, NaCl was removed

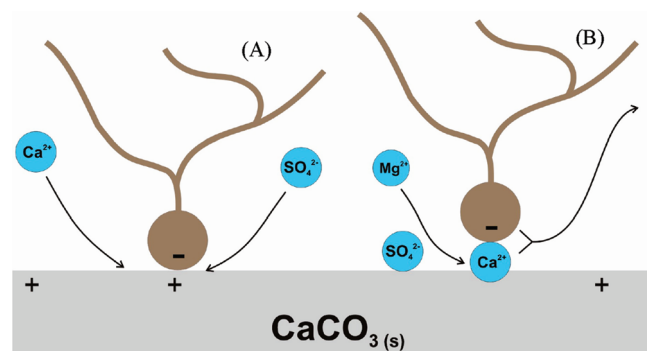
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**Figure 1.** Schematic model of the suggested mechanism for the wettability alteration induced by seawater. (A) Proposed mechanism when  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are the active species. (B) Proposed mechanism when  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are the active species.<sup>5</sup>

from the composition, and the fluid termed SW4NaCl contained  $4\times$  NaCl compared to SW. The fluids where SW was diluted with distilled water to 1600, 10 000, and 20 000 ppm were termed dSW1600, dSW10000, and dSW20000, respectively. The composition of the different brines is listed in Table 2. For the chromatographic wettability test, the core was first flooded with SW without  $\text{SO}_4^{2-}$ , the fluid termed SW0T, to remove  $\text{SO}_4^{2-}$  from the core. Then, the core was flooded with the fluid termed SW1T or SW1/2T, which contained  $\text{SCN}^-$  as a tracer and also  $\text{SO}_4^{2-}$ .

**Oil.** An acidic-reservoir-stabilized crude oil was diluted with 40 vol % *n*-heptane. The mixture was centrifuged and filtered through a  $5\ \mu\text{m}$  Millipore filter, and no precipitation of asphaltic materials was observed during storage. The acid number of the oil was determined to be  $\text{AN} = 1.90\ \text{mg of KOH/g}$  using the modified ASTM D664 method. The density was measured to be  $0.8115\ \text{g/cm}^3$ , and the viscosity of the oil was  $3.38\ \text{cP}$ .

**Core Preparation.** The chalk cores were prepared according to the method described by Puntervold et al.<sup>9</sup> The properties of the cores are given in Table 1. 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  $50\ ^\circ\text{C}$ . After drying at  $90\ ^\circ\text{C}$  to a constant weight, the cores were evacuated and saturated with formation brine to measure the pore volume. The porous plate technique using water-saturated  $\text{N}_2$  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  $50\ ^\circ\text{C}$  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 on the surface during aging in the actual oil in a closed steel container at  $90\ ^\circ\text{C}$  for 4 weeks.

**Spontaneous Imbibition.** The aged cores were immersed in the imbibing fluid in sealed steel cells. The spontaneous imbibition tests were performed at specified temperatures, 100, 110, and  $120\ ^\circ\text{C}$ , 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 the original oil in place (% of OOIP).

**Forced Displacement.** A Hassler core holder was used for the forced displacement tests. The core was placed in a rubber sleeve and mounted in the core holder with a confining pressure of  $\sim 25$  bar and back pressure of 10 bar. The injection rate was 1 PV/day, and the temperature during the forced displacement was  $120\ ^\circ\text{C}$ . The produced fluid was collected in a buret, and oil recovery was determined as a percentage of OOIP versus injected pore volumes (PVs). When combining spontaneous

imbibition and forced displacement in the same diagram, the oil recovery was determined versus the time by transforming the flooding volume rate to the time scale. The core was removed from the imbibition cell and placed in the flooding core holder, and the forced displacement took place after the temperature was stabilized similar to the temperature for the imbibition process.

**Chromatographic Wettability Test.** The chromatographic wettability test for carbonates developed by Strand et al.<sup>10</sup> was used to determine the increase in the water-wet area after spontaneous imbibition by the different fluids. After spontaneous imbibition, the core was placed in a core holder with a confining pressure of 25 bar and then flooded with at least 2.0 PVs of the brine without  $\text{SO}_4^{2-}$  and tracers, 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 (or SW1T) brine (containing  $\text{SO}_4^{2-}$  and the tracers  $\text{SCN}^-$  and  $\text{Li}^+$ ) 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  $\text{SO}_4^{2-}$  and tracer,  $\text{SCN}^-$ , 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,  $A_{\text{wet}}$ , and a reference cleaned water-wet core,  $A_{\text{ref}}$ , is a measure of the water-wet fraction of the sample, WI

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

where  $\text{WI} = 0$  is completely oil-wet,  $\text{WI} = 0.5$  is neutral wettability, and  $\text{WI} = 1$  is completely water-wet.

## Results and Discussion

The effect of salinity and composition of the displacing fluid was studied by both spontaneous and forced imbibition and also a combination of the two processes. Furthermore, the wettability changes were monitored using the chromatographic wettability test after wettability modification during spontaneous imbibition by the different brine types. The results will be discussed separately.

**Spontaneous Imbibition.** Wettability alteration by seawater is very sensitive to the temperature and initial content of sulfate in the core material. Previous experiments have shown that the temperature should be above  $90\ ^\circ\text{C}$  to observe wettability modification by seawater in a spontaneous imbibition process.<sup>4</sup>

The results from the spontaneous imbibition tests at 100, 110, and  $120\ ^\circ\text{C}$  are shown in Figures 2–4, respectively. Neither  $\text{Na}^+$  nor  $\text{Cl}^-$  is regarded as a potential determining ion toward the chalk surface, which means that these ions are not part of the inner Stern layer.<sup>11</sup> The ions are, however, active in the double layer and may have influence on the access of the active ions,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ , to the chalk surface. This was studied by comparing the imbibition of modified SW, i.e., SW depleted in NaCl (SW0NaCl) and SW spiked 4 times with NaCl (SW4NaCl), with original SW at the different temperatures. Thus, the concentration of the active ions was kept constant. At  $100\ ^\circ\text{C}$  (Figure 2), the

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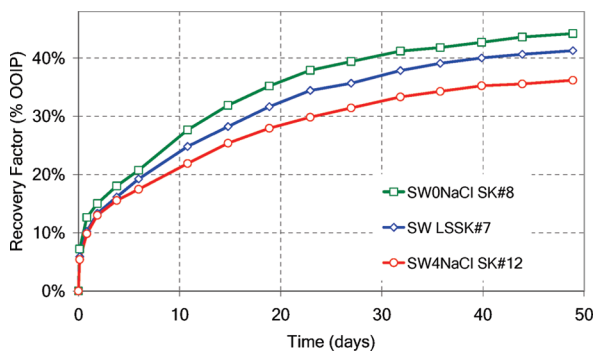
(9) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007**, *21* (6), 3425–3430.

**Table 1. Core Properties**

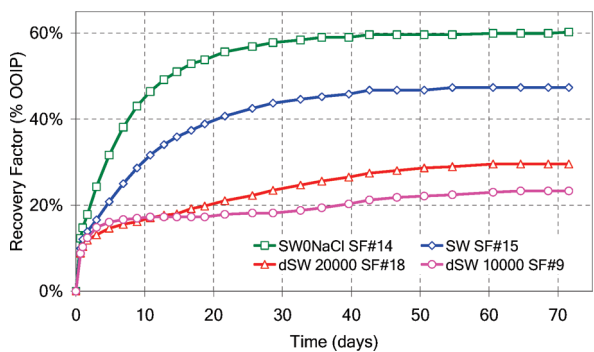
core ID	L (mm)	D (mm)	PV (mL)	$\Phi$ (%)	$S_{wi}$ (%)	$S_{oi}$ (%)	remarks
LSSK#5	70	38.1	37	46	10	90	initial wettability test
SCC#1	70	38.1	36	45	0	0	reference core
SCC#2	70	38	36	45	0	0	reference core
SK#8	69.9	38.1	37	47	9	91	SI at 100 °C
LSSK#7	70	38.1	36	45	9	91	SI at 100 °C
SK#12	69.8	37.8	35	45	9	91	SI at 100 °C
SF#14	70	38.1	36	45	8	92	SI at 110 °C and wettability test
SF#15	70	38.1	37	46	9	91	SI at 110 °C and wettability test
SF#18	70	38.1	36	46	8	92	SI at 110 °C
SF#9	70	38.1	37	46	9	91	SI at 110 °C and wettability test
LSSK#3	70	38.1	36	45	9	91	SI at 120 °C
SK#13	69.2	38.1	36	45	8	92	SI at 120 °C
LSSK#1	70	38.1	37	46	8	92	SI at 120 °C
LSSK#2	70	38.1	37	46	8	92	SI at 120 °C
LSSK#4	70	38.1	37	46	8	92	SI at 120 °C
SF#20	70	38.1	36	45	8	92	forced displacement
SF#16	70	38.1	36	45	10	90	forced displacement
SF#17	70	38.1	36	46	8	92	forced displacement

**Table 2. Brine Compositions (mol/L)**

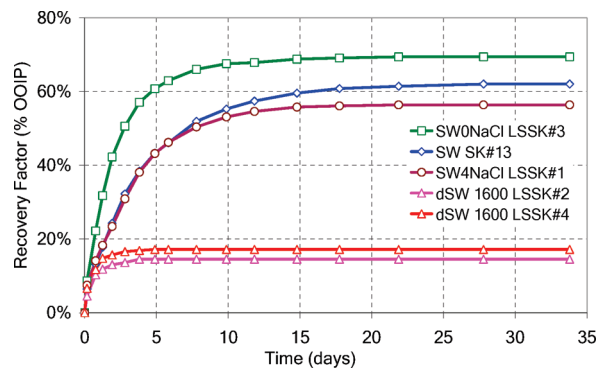
salt	FW (mol/L)	SW (mol/L)	SW0NaCl (mol/L)	SW4NaCl (mol/L)	dSW 1600 (mol/L)	dSW 10000 (mol/L)	dSW 20000 (mol/L)	SW0T (mol/L)	SW1/2T (mol/L)	SW1T (mol/L)
ions										
HCO <sub>3</sub> <sup>-</sup>	0.009	0.002	0.002	0.002	0.000	0.001	0.001	0.002	0.002	0.002
Cl <sup>-</sup>	1.07	0.525	0.126	1.726	0.027	0.158	0.314	0.583	0.538	0.492
SO <sub>4</sub> <sup>2-</sup>	0.00	0.024	0.024	0.024	0.001	0.007	0.014	0.000	0.012	0.024
SCN <sup>-</sup>	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.024
Mg <sup>2+</sup>	0.008	0.045	0.045	0.045	0.002	0.013	0.027	0.045	0.045	0.045
Ca <sup>2+</sup>	0.029	0.013	0.013	0.013	0.001	0.004	0.008	0.013	0.013	0.013
Na <sup>+</sup>	1.00	0.450	0.050	1.650	0.023	0.135	0.269	0.460	0.427	0.393
K <sup>+</sup>	0.005	0.010	0.010	0.010	0.001	0.003	0.006	0.010	0.022	0.034
Li <sup>+</sup>	0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.024
ionic strength	1.112	0.657	0.257	1.857	0.033	0.197	0.393	0.644	0.647	0.649
TDS (g/L)	62.80	33.39	10.01	103.53	1.67	10.02	20.00	33.39	33.39	33.39



**Figure 2.** Spontaneous imbibition into oil-saturated chalk cores using SW, SW0NaCl, and SW4NaCl at 100 °C.  $S_{wi} = 10\%$ .



**Figure 3.** Spontaneous imbibition into oil-saturated chalk cores at 110 °C using SW, SW0NaCl, dSW10000, and dSW20000.  $S_{wi} = 10\%$ .



**Figure 4.** Spontaneous imbibition into oil-saturated chalk cores at 120 °C using different imbibing fluids with different salinities and ionic composition: SW, SW0NaCl, SW4NaCl, and dSW1600.  $S_{wi} = 10\%$ .

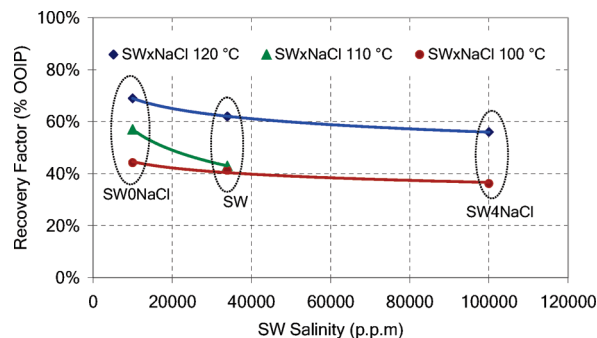
imbibition rate is low and the oil recovery after 30 days is in the range of 32–40%. The oil recovery increases as the concentration of NaCl in the seawater decreases. At 110 °C (Figure 3), the difference in oil recovery between SW and SW0NaCl is more pronounced. After 30 days, the difference is about 15%. The plateau recovery for the fluid depleted in NaCl was 60%, which is the recovery factor normally obtained for a completely water-wet core. No imbibition was performed using SW4NaCl at 110 °C. The same trend in recovery was observed at 120 °C; i.e., the recovery increased as the concentration of NaCl decreased (Figure 4). Note that 70% of OOIP was recovered using seawater without NaCl present. This is a very high recovery by spontaneous

imbibition for a Stevns Klint core. The imbibition rate was also very fast, and the plateau recovery was reached within 15 days. The surface reactivity of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  increases as the temperature increases, as discussed in detail in previous papers.<sup>1,12</sup> As the affinity of  $\text{SO}_4^{2-}$  toward the chalk surface increases, more  $\text{Ca}^{2+}$  is adsorbed because of less electrostatic repulsion.  $\text{Mg}^{2+}$  is even able to displace  $\text{Ca}^{2+}$  from the rock. Thus, an increased concentration of NaCl will probably decrease the ability of the active ions,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ , to become in contact with the positively charged chalk surface to release the adsorbed carboxylic material because of the double-layer effect. Because of the positive charge of the chalk surface in the presence of high saline formation water containing potential determining ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , a lot of  $\text{Na}^+$  and  $\text{Cl}^-$  will be present in the double layer because of the high concentration of NaCl. If the cations in the double layer mainly consisted of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , they would have much better access to the rock surface. The same is the case for  $\text{SO}_4^{2-}$ . If the concentration of  $\text{Cl}^-$  in the double layer is decreased,  $\text{SO}_4^{2-}$  would have better access to the surface. Thus, because of the change in the composition of the double layer by depleting the seawater for NaCl, both the imbibition rate and oil recovery are increased.

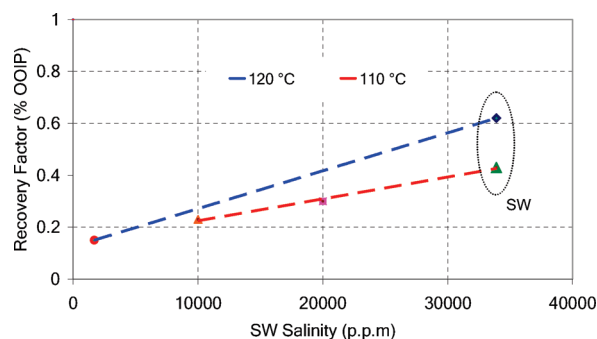
It has been stated that improved oil recovery by low-salinity flooding is not possible for carbonates because the chemical mechanism for wettability modification is different for the two reservoir rocks.<sup>6</sup> This is also confirmed in the present study. In two parallel tests, SW was diluted by distilled water to 1600 ppm and imbibed into mixed wet chalk cores at 120 °C, as shown by Figure 4. The oil recovery was very low, around 15% of OOIP. The reason for the low recovery is the decrease in the concentration of the active ions, which change the wetting properties. Similarly, oil recovery also decreased when diluting SW to 20000 and 10000 ppm by distilled water, as shown by Figure 3. A summary of the oil recovery by spontaneous imbibition of modified SW at different salinities and composition at 100, 110, and 120 °C is shown in Figures 5 and 6. Removing NaCl from the composition improves the oil recovery factor, while diluting seawater to lower salinities has a negative impact and decreases the recovery factor significantly. It was determined that not only is the concentration of the active ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  important for wettability alteration to take place but also the amount of non-active salt, such as NaCl, has an impact on the wettability alteration, which is discussed as a double-layer effect at the chalk surface. The temperature plays a very important role for the chemical reactions taking place at the chalk surface and the diffusion of active ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ ) into the chalk matrix. At high temperatures, the effect of wettability modification using seawater and modified seawater became even more significant regarding oil recovery.

**Wettability Monitoring by the Chromatographic Wettability Method.** The change in wetting conditions using modified SW as imbibing fluid was verified by the chromatographic wettability test described previously.<sup>10</sup> A chalk core flooded with SW at 130 °C at the rate of 3 PV/day for 1 day was used as a reference core for a completely water-wet system.

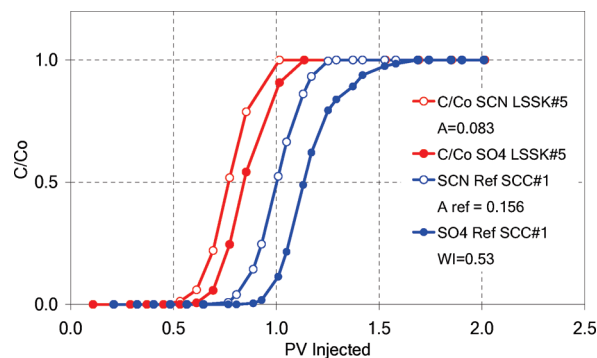
The initial wetting condition of the cores saturated with the crude oil was determined from the test shown in Figure 7.



**Figure 5.** Summary of oil recovery during spontaneous imbibition. The effect of salinity and composition of seawater with different concentrations of NaCl on the oil recovery factor at specified temperatures.



**Figure 6.** Summary of oil recovery during spontaneous imbibition. The effect of diluting seawater as imbibing fluid on oil recovery at different temperatures.



**Figure 7.** Initial wetting condition of a core saturated with the crude oil. WI, 0.53; chromatographic brines, SW0T and SW1T; test at room temperature;  $C/C_0$ , relative concentration of  $\text{SCN}^-$  and  $\text{SO}_4^{2-}$ .

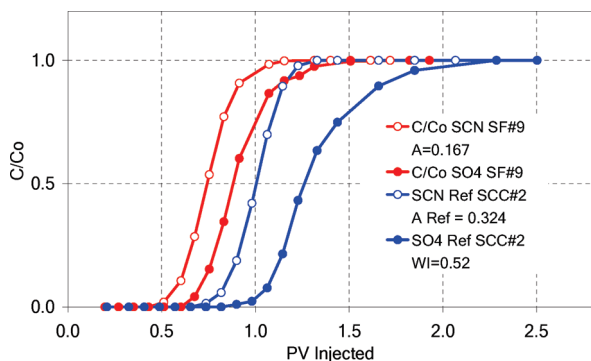
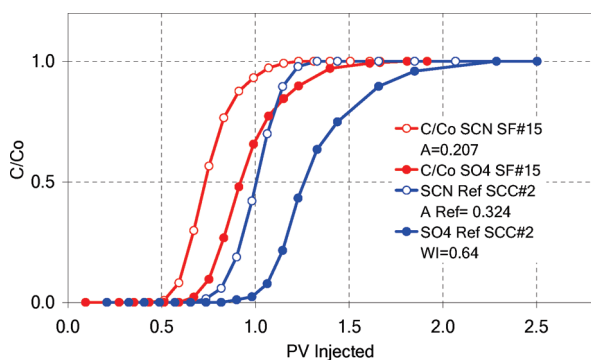
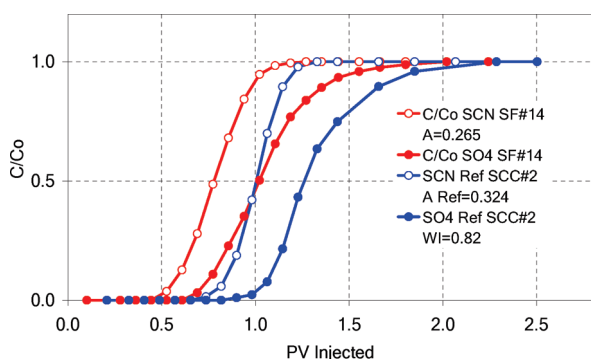
The reference core and the core aged in crude oil with initial Valhall brine were flooded at room temperature with SW0T to remove  $\text{SO}_4^{2-}$  and to establish residual oil saturation. Afterward, the cores were flooded with SW1T (containing  $\text{SO}_4^{2-}$  and the tracers  $\text{SCN}^-$  and  $\text{Li}^+$ ) at the rate of 0.2 mL/min, and the effluent was collected using a fraction collector. The calculated area between the elution curves was 0.156 and 0.083 for the complete water-wet core and the core aged in crude oil, respectively. The initial water-wet fraction, WI, was calculated as  $0.083/0.156 = 0.53$  (Table 3).

Chromatographic wettability tests for the cores after spontaneous imbibition using dSW10000, SW, and SW0NaCl are shown in the Figures 8–10, respectively. In these cases, the brines SW0T and SW1/2T were used during the

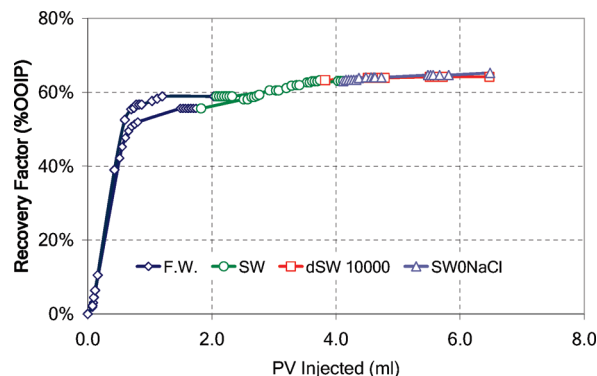
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**Table 3. Water-Wet Fraction (WI) and Increase in Water-Wet Fraction ( $\Delta$ WI %) Initial Condition and after Spontaneous Imbibition with Seawater and Modified Seawater at 110 °C**

system	core ID	WI	$\Delta$ WI (%)
initial condition	LSSK#5	0.53	
dSW10000	SF#9	0.52	$\approx 0$
SW	SF#15	0.64	11
SW0NaCl	SF#14	0.82	29

**Figure 8.** Wettability test after spontaneous imbibition with dSW10000 at 110 °C. WI, 0.52; chromatographic brines, SW0T and SW1/2T; test at room temperature;  $C/C_o$ , relative concentration of  $SCN^-$  and  $SO_4^{2-}$ .**Figure 9.** Wettability test after spontaneous imbibition with SW at 110 °C. WI, 0.64; chromatographic brines, SW0T and SW1/2T; test at room temperature;  $C/C_o$ , relative concentration of  $SCN^-$  and  $SO_4^{2-}$ .**Figure 10.** Wettability test after spontaneous imbibition with SW0NaCl at 110 °C. WI, 0.82; chromatographic brines, SW0T and SW1/2T; test at room temperature;  $C/C_o$ , relative concentration of  $SCN^-$  and  $SO_4^{2-}$ .

chromatography test. First, the cores were flooded with SW0T to achieve the residual oil saturation. Next, the cores were flooded with SW1/2T, and the effluent was collected in

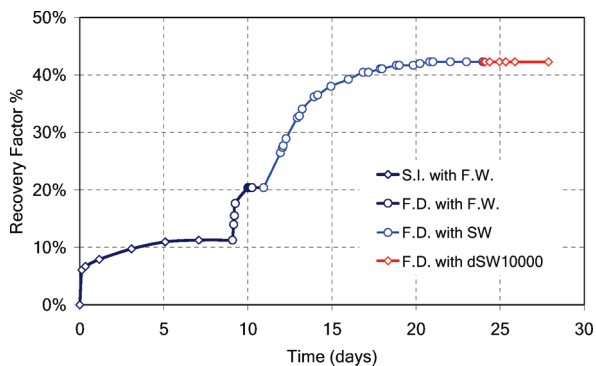
**Figure 11.** Forced displacement by successive injection of formation brine, seawater, and modified seawaters, dSW or SW0NaCl. Rate of injection, 1 PV/day;  $T$ , 120 °C; core, SF#20.

the fractions using a fraction collector. The area for the chromatographic separation between the tracer and the sulfate curve for the reference core was determined to be 0.324. After spontaneous imbibition of SW, dSW10000, and SW0NaCl at 110 °C, the area between the tracer and the sulfate curve was calculated to be 0.207, 0.167, and 0.265, respectively. The corresponding water-wet fractions were 0.64, 0.52, and 0.82, respectively, as shown in Table 3. Thus, using SW as the imbibing fluid, the water-wet area was increased by 11%. The diluted seawater, dSW10000, did not increase the water-wet area at all. Seawater depleted in NaCl, SW0NaCl, appeared to have the greatest effect on the wetting properties by increasing the water-wet area by 29%. The change in wetting properties is completely in line with the imbibition tests shown in Figure 3.

**Forced Displacement.** The effect of salinity and composition was also studied during a forced displacement process. In the first two experiments, the forced displacement was performed by successive injection of FW, SW, and modified SW. The objective was to verify if modified seawater could enhance oil recovery after a tertiary flood by seawater. The motivation for doing this test was to create a different concentration ratio between the actual ions,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$ , when injecting modified seawater compared to ordinary seawater because of the adsorption of  $SO_4^{2-}$  onto the rock surface. Thus, because of desorption of  $SO_4^{2-}$ , it was expected that the concentration of  $SO_4^{2-}$  relative to  $Ca^{2+}$  and  $Mg^{2+}$  became somewhat higher in the diluted seawater at the same time that the salinity was decreased. In the first case, the modified seawater was dSW10000. The recovery by FW was about 56% and was increased to 63% by SW (Figure 11). No extra oil was recovered using dSW10000.

A similar forced displacement was performed by SW depleted in NaCl, SW0NaCl (Figure 11). In this case, the secondary recovery by FW was about 59%, and the tertiary injection of SW increased the recovery to 64%. No significant increase in recovery was noticed when flooding with SW depleted in NaCl. Thus, in both cases, the oil recovery after the tertiary flood with SW is quite high and SW0NaCl or dSW10000 was not able to mobilize more oil.

Previously, work has shown that a decrease in recovery after forced displacement by SW can be obtained by combining spontaneous imbibition and forced displacement.<sup>4</sup> Therefore, in the last test, the core was first spontaneously imbibed with FW and then a forced imbibition with FW was performed (Figure 12). Because of the lack of  $SO_4^{2-}$ , the oil



**Figure 12.** Oil recovery from core SF#17 at 120 °C. Test sequence: (1) spontaneous imbibition by FW, (2) forced displacement by FW, (3) forced displacement by SW, and (4) forced displacement by diluted SW. Temperature, 120 °C; flow rate, 1.0 PV/day. To visualize the oil recovery in the different steps, the oil recovery was plotted versus the time; i.e., the flooding rate was converted to the time scale.

recovery by spontaneous imbibition of FW was in the range of 10%, which is slightly less than that for the diluted seawater, as shown in Figure 4. This is the expected amount of oil produced if the imbibing fluid is not “smart water”, which can change wetting properties during the imbibing process. The oil recovery after the forced displacement with FW was ~20% of OOIP. After SW was switched as the displacing fluid, the oil recovery increased to 42.5% but no further oil production was noticed when SW was substituted by dSW10000. Because no time-consuming wettability alteration is taking place during forced displacement with FW, the plateau is reached much faster than using SW as the injection fluid, confirming that wettability alteration is a time-consuming process.

These preliminary studies on the effect of modifying the salinity and composition of SW on oil recovery by forced displacement indicate that diluted seawater, dSW10000, will not improve oil recovery after flooding with traditional SW. More studies are needed to verify the effect of removing NaCl from SW in a forced displacement process.

### Conclusions

Modified seawater, regarding both salinity and composition, as a wettability modifier has been compared to seawater during a spontaneous imbibition and forced displacement process at temperatures between 100 and 120 °C. The following conclusions were made: (1) The imbibition rate and ultimate oil recovery increased relative to seawater when seawater was depleted in NaCl. The effect was more significant at high temperatures. A decrease in oil recovery was observed when increasing the NaCl concentration. (2) Using diluted seawater as the imbibing fluid, the oil recovery

decreased drastically. The oil recovery by seawater diluted to 1600 ppm at 120 °C was in the range of 15%, while the recovery by seawater was about 60% of OOIP. Thus, the wettability alteration is not a low-salinity effect. (3) The order of improved water wetness by the different fluids was confirmed by separate chromatographic wettability tests, and the increase in the water-wet fraction after spontaneous imbibition at 110 °C was dSW10000 < SW < SW0NaCl. The initial water wet fraction was 0.53, which was close to neutral condition. (4) After flooding with formation water and seawater at 120 °C, the oil recovery was over 60% of OOIP. Under this condition, it was impossible to increase oil recovery by modifying the seawater by diluting to 10 000 ppm or removing the NaCl. (5) In a combined spontaneous imbibition and forced displacement by formation water flowed by forced displacement with seawater, the recovery ended at 42.5%. No incremental oil was produced by flooding with diluted seawater, dSW10000.

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### Nomenclature

- $A$  = adsorption area
- AN = acid number (mg of KOH/g)
- $C/C_o$  = relative concentration of ions
- $D$  = core diameter (cm)
- dSW1600 = diluted seawater with distilled water to 1600 ppm
- dSW10000 = diluted seawater with distilled water to 10 000 ppm
- dSW20000 = diluted seawater with distilled water to 20 000 ppm
- FW = formation brine
- $L$  = core length (cm)
- OOIP = original oil in place
- PV = pore volume
- $S_{wi}$  = initial water saturation (%)
- $S_{oi}$  = initial oil saturation (%)
- SW = synthetic seawater
- SW0T = synthetic seawater without  $SO_4^{2-}$
- SW1/2T = synthetic seawater where the concentration of  $SCN^-$  and  $SO_4^{2-}$  is 0.012 mol/L
- SW1T = synthetic seawater where the concentration of  $SCN^-$  and  $SO_4^{2-}$  is 0.024 mol/L
- SW0NaCl = seawater depleted in NaCl
- SW4NaCl = seawater with 4 times the concentration of NaCl
- TDS = total dissolved solids (g/L)
- WI = water-wet surface fraction
- $\Phi$  = porosity (%)
- $\Delta WI$  = change in the water-wet surface fraction