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# Evaluation of Water-Based Enhanced Oil Recovery (EOR) by Wettability Alteration in a Low-Permeable Fractured Limestone Oil Reservoir

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This paper introduces a comprehensive method on how to evaluate wetting properties and oil recovery potential by spontaneous imbibition of “smart water” into a low-permeable limestone reservoir ( $\approx 1 \text{ mD}$ ). The reservoir temperature was  $110^\circ\text{C}$ , and the salinity of the formation water was high ( $\sim 208\,000 \text{ ppm}$ ). Crude oils from different possible source rocks were characterized for acid and base numbers, asphaltene, viscosity, and density. The potential of water-based enhanced oil recovery (EOR) was evaluated on the basis of the following studies: (1) The wetting potential of crude oils toward carbonate surface was investigated. (2) The presence of capillary forces in the core material was tested by spontaneous imbibition. (3) The initial wetting condition was determined by the chromatographic wettability test on mildly cleaned cores. (4) The surface reactivity of limestone core toward  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  was evaluated, when exposed to seawater at different temperatures ( $70$ – $150^\circ\text{C}$ ). (5) The presence of anhydrite,  $\text{CaSO}_4(\text{s})$ , in the limestone core material was confirmed, which will affect the initial wetting conditions. (6) The potential of “smart water” to enhance oil recovery from limestone cores containing crude oil and formation water at  $110^\circ\text{C}$  was evaluated by imbibition of seawater and modified seawater. Because of the low content of acidic material in the crude oils and the presence of anhydrite in core material, the limestone cores were expected to be preferentially water-wet, which was confirmed by the chromatographic wettability test. About 40% of original oil in place (OOIP) was recovered in a spontaneous imbibition process at  $110^\circ\text{C}$  using formation water. In a tertiary imbibition process with seawater and modified seawater, the oil recovery increased to  $\sim 50\%$  of OOIP.

## Introduction

More than 50% of the proven oil resources are trapped in carbonate rocks, i.e., limestones, dolomites, or chalks.<sup>1</sup> Oil recovery from carbonates can be a great challenge because of structural heterogeneity in the porous media, low permeability, natural fractures, and low water-wetness. Water injection for both pressure maintenance and oil displacement is the most important secondary recovery method in sandstones but has also been implemented with great success in some carbonate reservoirs. The great success of seawater injection into the Ekofisk field, which is a mixed-wet and low-permeable naturally fractured chalk formation, is a good example.<sup>2</sup>

Recent laboratory studies have shown that seawater is able to improve the water-wetness of chalk at high temperatures.<sup>3,4</sup> It is well-documented that the reactivity between  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  at the chalk surface is the main reason for removing the strongly adsorbed carboxylic material from the rock

surface.<sup>4,5</sup> North Sea chalk is pure biogenic  $\text{CaCO}_3$ , with a high surface reactivity. The criteria for seawater to act as a wettability modifier is that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  must have strong affinity toward the carbonate surface. The reactivity increases as the temperature increases, and it has been observed that  $\text{Mg}^{2+}$  is able to substitute  $\text{Ca}^{2+}$  on the chalk surface at temperatures above  $90^\circ\text{C}$ .<sup>3</sup> Recently, it has been observed that a reservoir limestone rock reacts chemically in the same way as chalk toward the potential determining ions, although the reactivity was lower than for chalk.<sup>1</sup>

In this paper, high-salinity seawater and modified seawater are evaluated as possible enhanced oil recovery (EOR) fluids to improve oil recovery by wettability alteration in a fractured limestone oil reservoir with low matrix permeability ( $\approx 1 \text{ mD}$ ). Using crude oils from different possible source rocks and core samples from five different zones in the same well, the following test program was performed: (1) characterize the oil properties and their potential to promote wettability alterations in carbonates, (2) characterize rock properties regarding permeability, porosity, pore connectivity, and rock mineralogy, (3) characterize initial wetting conditions and the potential to change wetting properties, when exposed to seawater at high temperature, and (4) determine oil recovery by spontaneous imbibition (SI) using formation water (FW) and high-salinity seawater/modified seawater in both secondary and tertiary processes.

## Experimental Section

**Outcrop Chalk Cores.** The potential of different crude oils to wet the carbonate rock surface was tested using outcrop Stevns Klint (SK) chalk from a quarry nearby Copenhagen, Denmark. The cores were drilled from the same chalk block in the same

\*To whom correspondence should be addressed. E-mail: seyed.f.shariatpanahi@uis.no.

(1) Strand, S.; Austad, T.; Puntervold, T.; Høgnesen, E. J.; Olsen, M.; Barstad, S. M. F. “Smart water” for oil recovery from fractured limestone—A preliminary study. *Energy Fuels* 2008, 22, 3126–3133.

(2) Thomas, L. K.; Dixon, T. N.; Evans, C. E.; Vienot, M. E. Ekofisk waterflow pilot. *J. Pet. Technol.* 1987, No. February, 221–232.

(3) Zhang, P.; Austad, T. Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloids Surf., A* 2006, 279, 179–187.

(4) Zhang, P.; Tweheyo, M. T.; Austad, T. Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ . *Colloids Surf., A* 2007, 301, 199–208.

(5) Strand, S.; Høgnesen, E. J.; Austad, T. Wettability alteration of carbonates—Effects of potential determining ions ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) and temperature. *Colloids Surf., A* 2006, 275, 1–10.

**Table 1. Chalk Outcrop Core Properties<sup>a</sup>**

core	<i>L</i> (cm)	<i>D</i> (cm)	$\Phi$ (%)
SK01	7.77	3.8	46
SK02	7.73	3.8	44
SK03	7.74	3.8	49
SK04	7.61	3.8	46
SK05	7.00	3.8	46
SK06	7.93	3.8	45
SK07	8.00	3.8	45
SK08	6.97	3.8	47

<sup>a</sup> The permeability varied between 2 and 5 mD.

**Table 2. Limestone Core Characterization Summary**

zone	core	<i>L</i> (cm)	<i>D</i> (cm)	$\Phi$ (%)	<i>k</i> (mD)
1	C1-2	7.94	3.80	16	1.0
2	C2-5	8.17	3.80	13	1.0
3	C3-9	8.31	3.81	3	0.03
4	C4-11	8.22	3.79	15	0.3
4	C4-13	8.11	3.80	16	0.6
4	C4-14	8.08	3.80	16	0.4
5	C5-15	8.25	3.79	17	1.0
5	C5-16	7.11	3.80	17	1.0
5	C5-17	5.52	3.80	17	0.5
5	C5-18	3.816	3.77	17	NN

direction. Chalk cores have high porosity (45–50%) and low permeability (2–5 mD). The properties of chalk cores are shown in Table 1.

**Reservoir Limestone Cores.** Reservoir limestone cores from five different sections of a well were used. The core plugs have a diameter of 3.80 cm and lengths ranging from 5.22 to 8.31 cm. The permeability is low (0.3–1 mD), and the porosity ranges from 13 to 17%, except core C3-9, which has the measured porosity and permeability of 3% and 0.03 mD, respectively. Table 2 summarizes the limestone core data.

**Brunauer–Emmett–Teller (BET) Analysis.** The BET specific surface area for both chalk and limestone fractions was performed by MCA Service, U.K.

**Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectrometry (EDS) Microanalysis.** SEM was used to study grain size distribution and particle shape, together with chemical identification of both chalk and limestone samples. The SEM sample were prepared by placing a small piece of rock on the carbon adhesive disk mounted on the aluminum stub. A thin platinum layer was applied to avoid charging of the samples. Investigations were carried out on a Zeiss Supra 35VP field emission microscope equipped with EDS, using accelerating voltages down to 0.2 kV for optimum surface detail.

**Crude Oils.** A total of 12 different stock tank oils have been evaluated as possible reservoir crude oils. The oils were centrifuged and filtered through a 5  $\mu\text{m}$  Millipore filter to remove water and solids prior to testing. Wax or other deposits were not observed in the oils.

**Acid and Base Numbers (AN and BN).** A Mettler Toledo DL55 autotitrator was used to measure AN and BN by potentiometric titrations using an internal standard. The methods used were developed by Fan and Buckley<sup>6</sup> and are modified versions of the standard methods ASTM D2896 for BN titration

(6) Fan, T.; Buckley, J. Acid number measurements revisited. *Proceedings of the 2006 Society of Petroleum Engineers (SPE) Improved Oil Recovery (IOR) Symposium*; Tulsa, OK, 2006; SPE Paper 99884.

(7) American Society for Testing Materials (ASTM). ASTM2896-88, standard test method for base number of petroleum products by potentiometric perchloric acid titration. *Annual Book of ASTM Standards*; ASTM International: West Conshohocken, PA, 1988.

(8) American Society for Testing Materials (ASTM). ASTM664-89, standard test method for acid number of petroleum products by potentiometric titration. *Annual Book of ASTM Standards*; ASTM International: West Conshohocken, PA, 1989.

and ASTM D664 for AN titration.<sup>7,8</sup> On the basis of the measured AN and BN, three oils were selected for further studies. Oil 1.2 had the highest BN, and oil 12.2 had the highest AN, while oil 6.2 had medium AN and BN. Oil N, which was used in core experiments, was made by mixing four different oils of quite similar properties. The AN and BN values were determined to be 0.08 and 0.35 mg of KOH/g of oil, respectively.

**Density and Viscosity.** Density and viscosity of the oils were measured at 20 °C by an Anton Parr DMA 4500 density meter and a Physica Parr UDS 200 spectrometer, respectively.

**Asphaltene Content.** A modified version of ASTM D2007-80 proposed by Wang and Buckley was used for measuring asphaltene content in crude oils.<sup>9</sup> All values are low, in the range of 0.1–0.3 g/100 mL of oil.

Table 3 summarizes the chemical and physical properties of crude oils used in this study.

**Brines.** Brines are made in the laboratory from deionized water (DIW) and the available reagent-grade salts. The brine solutions were filtered through a 0.22  $\mu\text{m}$  Millipore filter. Two types of formation water, VB and FW, were used as initial formation waters in chalk and limestone, respectively. During SI tests in limestone cores, formation brine, synthetic high-salinity seawater (HSSW), and manipulated HSSW (HSSW0NaCl and HSSW4S0NaCl) were used as imbibing fluids. Artificial seawater without  $\text{SO}_4^{2-}$  (SW0T) was used as imbibing brine in chalk cores. Artificial seawaters with and without tracer (SW1T and SW0T), respectively, were used during the chromatographic wettability test in chalk cores, as described later in this paper. In limestone cores, instead of SW1T, SW1/2T was used as seawater with tracer. Artificial seawater (SW) was also used to evaluate the surface reactivity of the limestone cores by substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$ , described later in this section. The composition of the various brines used is given in Table 4.

**Chemical Analysis.** The ionic concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{SCN}^-$  were analyzed by an ion-exchange chromatograph, ICS-3000 reagent-free, produced by Dionex Corporation, Sunnyvale, CA. The fraction samples were diluted 50 times and filtrated through a 0.2  $\mu\text{m}$  syringe filter into 2 mL standard high-performance liquid chromatography (HPLC) glasses. External standard samples with relevant ion composition and concentration were prepared. The selected set of samples were analyzed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{SCN}^-$ , and the concentration was calculated on the basis of the external standard.

**Chalk Core Preparation.** The outcrop chalk core was initially flooded with about 5 pore volumes (PV) of DIW to remove initially precipitated salt. Then, the core was dried at 90 °C to a constant weight.

**Oil-Saturated Core (100%).** The dried core was evacuated and saturated by surrounding the specified oil. The core remained immersed in the oil for at least 2 h. The porosity and pore volume were also calculated from the weight difference, bulk volume, and oil density. Then, the core was flooded with 2 PV of oil in each direction at 50 °C.

**Core with  $S_{wi} \approx 12\%$ .** The dry core sample was vacuumed and saturated with degassed VB. The saturated core was left immersed in brine for at least 2 h. Porosity and pore volume were determined from the change in weight. After that, the initial water saturation of  $\approx 12\%$  was stabilized using a porous plate. Finally, the core was flooded with 2 PV of oil in each direction at 50 °C.

**Core Aging.** The core was removed from the core holder, immersed in oil, and aged in a stainless-steel aging cell. In the case of a 100% oil-saturated core, the core was aged for 3 days, while the core with 12% initial water saturation was aged for 4 weeks, both at 90 °C. In the case of reference oil (*n*-decane), the core was not aged.

(9) Wang, J.; Buckley, J. S. Asphaltene stability in crude oil and aromatic solvents—The influence of oil composition. *Energy Fuels* 2003, 17 (6), 1445–1451.

**Table 3. Oil Properties**

oil name	AN (mg of KOH/g of oil)	BN (mg of KOH/g of oil)	asphaltene content (g/100 mL)	density (g/cm <sup>3</sup> , at 20 °C)	viscosity (cP, at 20 °C)
oil 1.2	~0	0.54	0.3	0.824	4.3
oil 6.2	0.10	0.48	0.3	0.827	5.0
oil 12.2	0.26	0.29	0.1	0.822	4.2
oil N	0.08	0.35	NN	0.8376	5.8

**Table 4. Composition and Properties of the Brines Used**

ions	VB (mol/L)	FW (mol/L)	SW (mol/L)	HSSW (mol/L)	SW0T (mol/L)	SW1T (mol/L)	SW1/2T (mol/L)	HSSW0NaCl (mol/L)	HSSW4S0NaCl (mol/L)
HCO <sub>3</sub> <sup>-</sup>	0.009	0.003	0.002	0.003	0.002	0.002	0.002	0.003	0.003
Cl <sup>-</sup>	1.066	3.643	0.525	0.662	0.583	0.492	0.583	0.136	0.117
SO <sub>4</sub> <sup>2-</sup>	0.000	0.000	0.024	0.032	0.000	0.024	0.012	0.032	0.130
SCN <sup>-</sup>	0.000	0.000	0.000	0.000	0.000	0.024	0.012	0.000	0.000
Mg <sup>2+</sup>	0.008	0.076	0.045	0.059	0.045	0.045	0.045	0.059	0.059
Ca <sup>2+</sup>	0.029	0.437	0.013	0.010	0.013	0.013	0.013	0.010	0.000
Na <sup>+</sup>	0.997	2.620	0.450	0.594	0.460	0.393	0.427	0.068	0.262
K <sup>+</sup>	0.005	0.000	0.010	0.000	0.000	0.034	0.022	0.000	0.003
TDS (g/L)	62.83	208.94	33.39	42.22	33.39	33.39	33.39	11.48	24.25
IS (mol/L)	1.112	4.158	0.657	0.829	0.643	0.647	0.645	0.303	0.567

**Reservoir Limestone Core Preparation.** The reservoir limestone cores were preflooded and stored in kerosene prior to delivery. Mildly cleaning of the core was performed by injecting *n*-heptane to displace the kerosene and finally with DIW, keeping the injection volume of DIW as low as possible to minimize the dissolution of limestone rock. The core was then dried at 90 °C to a constant weight.

**Core with  $S_{wi} \approx 10\%$ .** Initial water saturation was stabilized using a desiccator with a drying agent (silica gel). The dry core sample was vacuumed and saturated with 10 times diluted degassed FW. The core was left immersed in the brine for about 12 h, because of the low permeability of limestone rock. The porosity and pore volume were determined from the change in weight. Then, the initial water saturation of 10% was stabilized using a desiccator. This method works based on evaporation of the water. By evaporation or adsorption of water using silica gel, water is removed from the diluted brine in the sample until the brine has been up-concentrated 10 times. The core was then equilibrated in a sealed container for 3 days to obtain a uniform water saturation inside the cores.<sup>10</sup> The core with  $S_{wi} \approx 10\%$  was placed in a Hassler core holder, vacuumed, saturated, and flooded with 2 PV of oil in each direction at 50 °C.

**Core Aging.** After an initial water saturation of 10% was established, the core was removed from the core holder, immersed in oil, and aged in a stainless-steel aging cell for 2 weeks at 90 °C. In the case of using *n*-heptane as reference oil, the core was not aged.

**Wettability Modification by Hot Seawater.** Seawater at a high temperature is able to remove carboxylic material from the carbonate surface and improve the water-wetness of the rock.<sup>4–11</sup> Seawater was injected at a rate of 3 PV/day at 130 °C for 1 day into mildly cleaned limestone cores and the cores containing oil and brine after SI test to evaluate the potential of seawater to improve the water-wetness. Any improvement in the water-wet area was verified by the chromatographic wettability test.

**Chromatographic Wettability Test.** The wettability test is based on the chromatographic separation of a tracer, SCN<sup>-</sup>,

and SO<sub>4</sub><sup>2-</sup>, as described by Strand et al.<sup>12</sup> The area between the effluent curves for SCN<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> is proportional to the water-wet surface area in the core. The chromatographic wettability test can be performed both on 100% water-saturated cores and at residual oil saturation with a reproducibility of 5%.<sup>12</sup> The core is equilibrated by flooding with SW0T at a constant rate, and then the effluent curves for SCN<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were determined using SW1T or SW1/2T as flooding fluids for chalk and limestone cores, respectively. As long as we stick to the same type of core material, it is a documented correlation between Amott water index,  $I_w$ , and the chromatographic wetting index, WI.<sup>13</sup> If, however, the carbonate rock contains significant amounts of silica in the porous medium, similar to the Aalborg chalk, the relationship between  $I_w$  and WI fails.<sup>14</sup>

**Surface Reactivity.** The reactivity of surface-active ions, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>, toward the limestone surface, which is crucial for wettability alteration, was studied in the following way: (1) The adsorption of SO<sub>4</sub><sup>2-</sup> onto the limestone surface was measured by performing the chromatographic wettability tests at room temperature. (2) The substitution of Ca<sup>2+</sup> from the limestone surface by Mg<sup>2+</sup> was studied in the temperature range of 70–150 °C by injection of SW with a rate of 1 PV/day.

The effluent was analyzed for the surface-active ions, and the concentration relative to the initial concentration in SW was plotted against PV.

**SI.** Imbibition tests at room temperature and 50 °C were performed using standard Amott cells. The volume of oil produced was recorded as a function of time. At high temperatures, sealed steel imbibition cells were used, which were connected to a supporting pressure cell (~10 bar). The amount of oil produced [% original oil in place (OOIP)] was collected in a buret and recorded as a function of time.

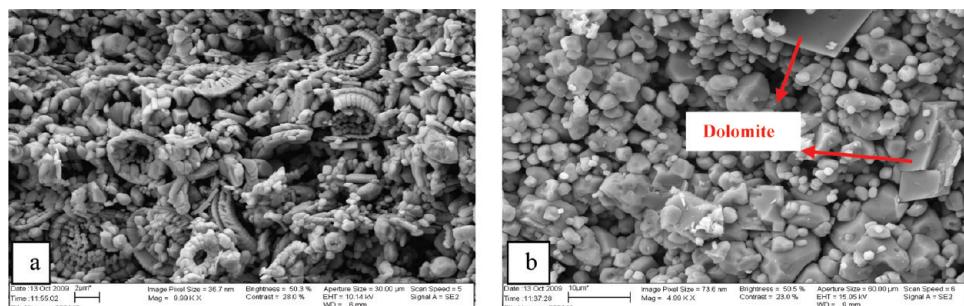
## Results and Discussion

**Rock Properties.** Specific surface area of chalk is 1.70 m<sup>2</sup>/g, while the specific surface area of a limestone sample showed a lower value (0.29 m<sup>2</sup>/g).

(12) Strand, S.; Standnes, D. C.; Austad, T. New wettability test for chalk based on chromatographic separation of SCN<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. *J. Pet. Sci. Eng.* **2006**, 52, 187–197.

(13) Zhang, P.; Austad, T. The relative effects of acid number and temperature on chalk wettability. *Proceedings of the Society of Petroleum Engineers (SPE) International Symposium on Oilfield Chemistry*; Houston, TX, 2005; SPE Paper 92999, pp 185–191.

(14) Strand, S.; Hjuler, M. L.; Torsvik, R.; Pedersen, J. I.; Madland, M. V.; Austad, T. Wettability of chalk: Impact of silica, clay content, and mechanical properties. *Pet. Geosci.* **2007**, 13, 69–80.



**Figure 1.** SEM images: (a) chalk sample with 10000 $\times$  magnification and (b) limestone sample with 5000 $\times$  magnification.

**Table 5. EDS Analyses of Chalk and Limestone Samples at Low Magnification**

element	limestone (at %)	SK chalk (at %)
Mg	7.32	1.45
Al	0.44	0.41
Si	0.36	0.91
Ca	91.88	97.23
total	100.00	100.00

Typical SEM pictures of the two carbonate rocks used, chalk and reservoir limestone, are shown in Figure 1. Fragments of coccolithes are visible in the chalk material. The EDS analysis of SK chalk and reservoir limestone is given in Table 5. SK chalk mainly consists of  $\text{CaCO}_3$ . Limestone contains 7.3 atomic percent (at %) Mg, which is far higher than chalk cores. A high amount of Mg is due to the presence of dolomite, which is observed as well block-shaped particles in the SEM image (Figure 1b). The small amount of Si and Al indicates low clay content in both chalk and limestone samples.

**Wetting Potential of the Oils.** It is noticed from Table 3 that the amount of polar components, quantified as AN and BN, in the received oil samples is low,  $\leq 0.26$  and  $0.29 - 0.54$  mg of KOH/g of oil, respectively. The amount of carboxylic material present in the crude oil is the most important wetting parameter for carbonates,<sup>15</sup> and it is a question whether these oils are able to cause changes in the wetting condition of any carbonates. The potential of the three oils, oils 6.2, 1.2, and 12.2, to impose wetting on carbonates was tested using water-wet homogeneous outcrop chalk as a porous medium. Two sets of SI tests were performed, i.e., (1) without initial formation water and (2) with VB initial formation water ( $S_{wi} \approx 12\%$ ). Normal decane was used as a reference oil representing a completely water-wet system, and in all cases, SWOT was used as the imbibing fluid.

The imbibition rate at room temperature for all of the tested oils was very high on 100% oil-saturated cores and similar to the 100% *n*-decane-saturated core. Ultimate oil recovery approached 80% OOIP within 1 day in all cases (Figure 2a). In the presence of formation water, the imbibition rate at room temperature was quite different. The lowest imbibition rate was observed for the core containing the oil with the highest BN. After 1 day, the temperature was increased to 50 °C and the oil recovery reached between 64 and 71% OOIP (Figure 2b). As shown in Figure 2b, SI into a

strongly water-wet system using *n*-decane, as reference oil, resulted in an oil recovery of 70%. Thus, even though the imbibition rate is quite different for the cores containing the different oils, all of the cores appeared to be quite water-wet.

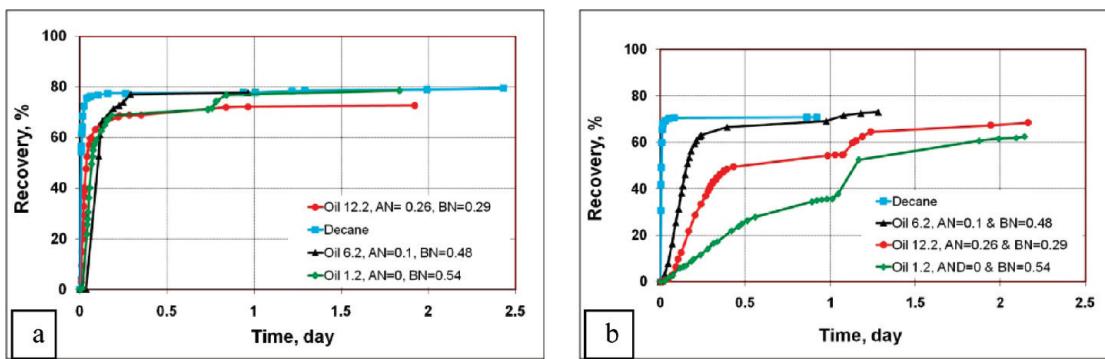
Figure 3a shows the chromatographic separation between the two components ( $\text{SCN}^-$  and  $\text{SO}_4^{2-}$ ) for a cleaned water-wet reference core. The wetting condition was also evaluated after SI of SWOT into the core containing the oil 1.2, with the highest BN, that appeared to be less water-wet, as judged from the imbibition rate (Figure 3b). The area between the tracer and the sulfate curve is quite similar (0.154 and 0.165), with a difference of 7%, i.e., slightly greater than the uncertainty of 5%, indicating a very small change in the water-wet surface area. The distinct difference in the symmetry of the sulfate curve in the two case points, however, shows some changes in wetting properties (panels a and b of Figure 3). The type of asymmetry in the sulfate curve indicates that the larger pores are less water-wet than the smaller pores because of faster breakthrough of  $\text{SO}_4^{2-}$  in the latter case. Thus, even though the AN and BN values are low for all of the oils, some difference in wetting properties may be expected but the ultimate oil recovery appears to be quite similar.

**Limestone Core Treatments.** Because of the low values of AN and BN of the oil samples, it was expected that the reservoir limestone rock should behave preferentially water-wet, as observed for the chalk cores. This is, however, no guarantee for a similar behavior for the reservoir rock. The oil may be partly stripped of polar components because of adsorption onto the carbonate rock, even by different crude oils during geological time. Therefore, it is important to obtain confirmation of the initial wetting properties of the reservoir rock. Because the core materials from the well were flooded with kerosene to displace the reservoir crude oil, it was decided to perform a very mild cleaning of the cores to maintain the initial wetting condition: (1) The cores were flooded with *n*-heptane to remove kerosene. (2) Then, DIW was injected into the cores to remove salt. (3) Finally, the cores were dried at 90 °C to a constant weight.

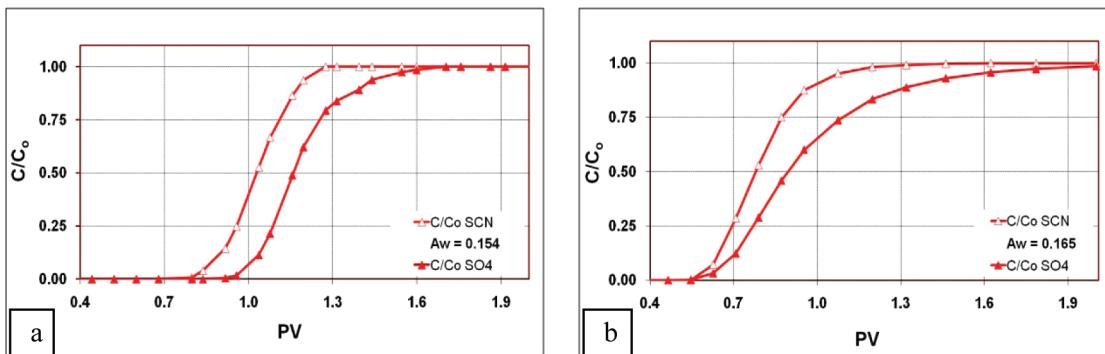
Because the crude oil had been removed by preflooding with kerosene, no precipitation of asphaltic material is expected when flooding the cores with *n*-heptane. It is assumed that the cores are not contaminated by other production or mud chemicals. To obtain the initial wetting condition and also to find the effect of seawater on the wetting condition of the reservoir core, one core was selected from each zone.

During the flooding of core C1-2 with DIW, it was observed that the effluent water contained significant amounts of sulfate, which should be removed prior to a chromatographic wettability test. With the rate of 0.2 mL/min, the concentration of sulfate decreased steadily, but when the

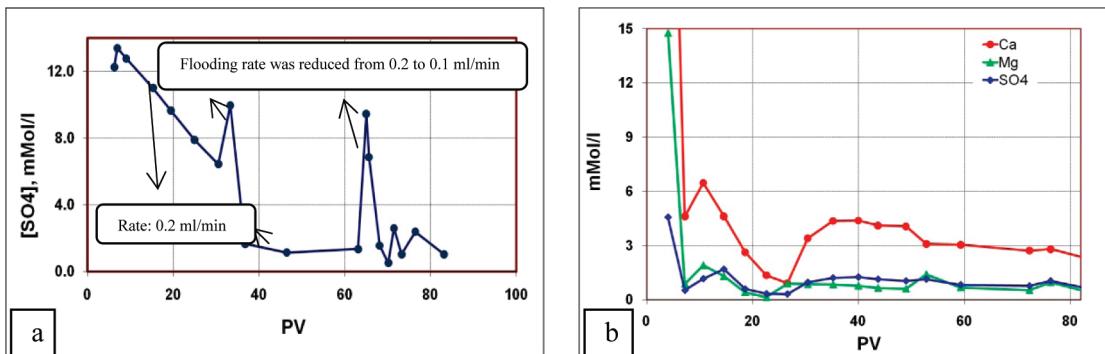
(15) Strand, S.; Standnes, D. C.; Austad, T. Spontaneous imbibition of aqueous surfactant solutions into neutral to oil-wet carbonate cores: Effects of brine salinity and composition. *Energy Fuels* 2003, 17 (5), 1133–1144.



**Figure 2.** Oil recovery by SI of SW0T into chalk cores (a) without initial water saturation ( $S_{wi} \sim 0\%$ ) and (b) with initial water saturation ( $S_{wi} \sim 12\%$ ).



**Figure 3.** Wetting condition of chalk cores: (a) clean water-wet reference core and (b) after SI of SW0T into the core containing oil. Chromatographic brines, SW0T and SW1T; tests at room temperature;  $C/C_o$ , relative concentration of  $SCN^-$  and  $SO_4^{2-}$ .



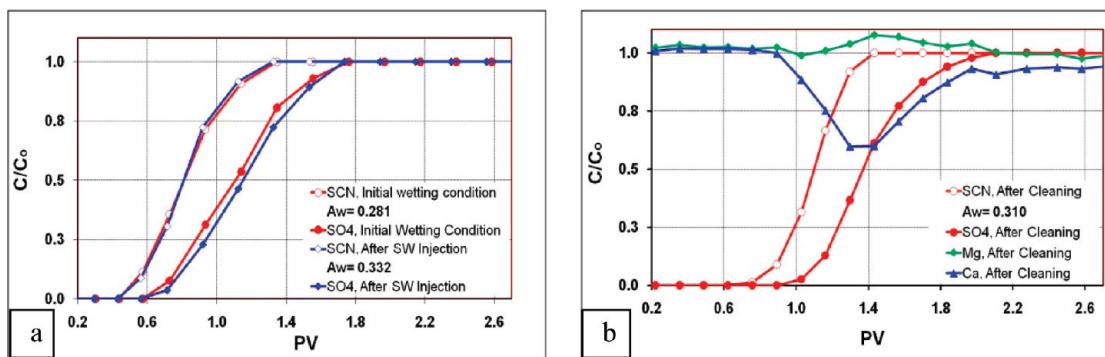
**Figure 4.** Dissolution of  $CaSO_4$  when DIW was injected through the cores: (a) concentration of  $SO_4^{2-}$  in the outlet of core C1-2 and (b) concentration of  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $SO_4^{2-}$  in the outlet of core C2-5.

flooding rate was reduced to 0.1 mL/min, the concentration of sulfate immediately increased, indicating dissolution of anhydrite,  $CaSO_4(s)$  (Figure 4a). This was confirmed by the test on core C2-5, showing that the variation in  $Ca^{2+}$  and  $SO_4^{2-}$  in the effluent was harmonized when changing the flow rate (Figure 4b). The impact of anhydrite as part of the porous medium will be discussed in more detail later in the last part of the paper.

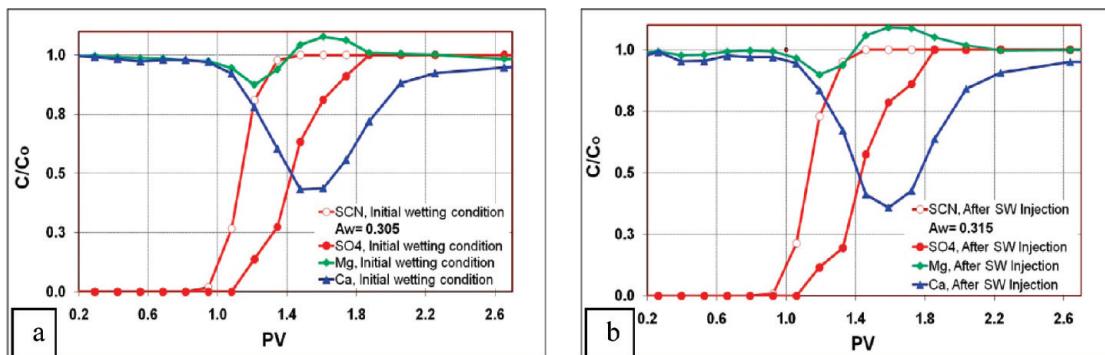
**Initial Wetting Properties.** The area between the effluent curves ( $SCN^-$  and  $SO_4^{2-}$ ) for the core C1-2 after the mild cleaning was 0.281 (Figure 5a). The chromatographic separation between the two curves was surprisingly high, indicating a large water-wet area with high surface reactivity. To study the potential of SW to improve the water-wetness, the core was flooded with SW at 130 °C at 3 PV/day for 1 day.

Thereafter, a new wettability test was performed. As confirmed by Figure 5a, an increase in the chromatographic separation of  $SCN^-$  and  $SO_4^{2-}$  occurred (area of 0.332), corresponding to an increase in the water-wet area of 18%. Thus, SW at high temperatures is able to increase the water-wet area significantly, which of course will depend upon the initial wetting condition. Thereafter, the core was flooded at room temperature with DIW to remove SW and then with toluene and methanol alternately until the toluene effluent was colorless. A new wettability test was performed, and the area between the tracer and sulfate curve decreased to 0.310 ( $\approx 6\%$ ), which is very close to the reproducibility of the test (Figure 5b).

When the elution curves for  $SO_4^{2-}$  are compared in panels a and b of Figure 5, it is noticed that the breakthrough of



**Figure 5.** Chromatographic wettability test on core C1-2 (a) after mild cleaning and after hot SW injection, with the presence of *n*-heptane, and (b) after cleaning the core with toluene and methanol. Chromatographic brines, SW0T and SW1/2T; tests at room temperature;  $C/C_o$ , relative concentration of SCN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>.



**Figure 6.** Chromatographic wettability test on core C4-13 (a) after mild cleaning and (b) after hot SW injection. Chromatographic brines, SW0T and SW1/2T; tests at room temperature;  $C/C_o$ , relative concentration of SCN<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>.

SO<sub>4</sub><sup>2-</sup> relative to SCN<sup>-</sup> is later when the core has been cleaned by toluene and methanol. This indicates that the larger pores have become more water-wet when flooded with toluene and methanol, even though the water-wet surface area is nearly the same. It appears that some redistribution of adsorbed organic material took place during the flooding with toluene and methanol, which may have impact on the capillary forces and SI. This phenomenon will be discussed in a forthcoming paper.

Similar wettability tests were performed on a core from zone 4 (core C4-13). As shown by panels a and b of Figure 6, the water-wet surface area is quite similar before and after flooding the core with SW at 130 °C,  $A_w = 0.305$  and 0.315, respectively.

The increase in the water-wet surface area after flooding the cores with SW at 130 °C for mildly cleaned cores from the zones 1, 2, 4, and 5 is shown in Table 6. It was only the core from zone 1 (C1-2) that showed a significant increase in water-wetness when it was exposed to SW at 130 °C. Thus, these preliminary results indicate that the core materials are preferentially water-wet, and it is expected that the oil recovery by SI of seawater would not be considerable.

**Presence of Capillary Forces.** Because the actual oil reservoir is naturally fractured with low matrix permeability, the driving force for oil recovery by water injection must be related to a positive capillary pressure; i.e., the injected water must imbibe spontaneously from the fractures into the matrix blocks and displace the oil into the fracture network.

**Table 6. Increase in Water-Wet Area by Flooding the Smoothly Cleaned Limestone Cores by SW at 130 °C**

core	$A_w$ (after smooth cleaning)	$A_w$ (after flooding with SW at 130 °C)	increase in the water-wet surface area (%)
C1-2	0.281	0.332	18
C4-13	0.305	0.315	3.3
C2-5	0.470	0.487	3.6
C5-17	0.311	0.335	7.7

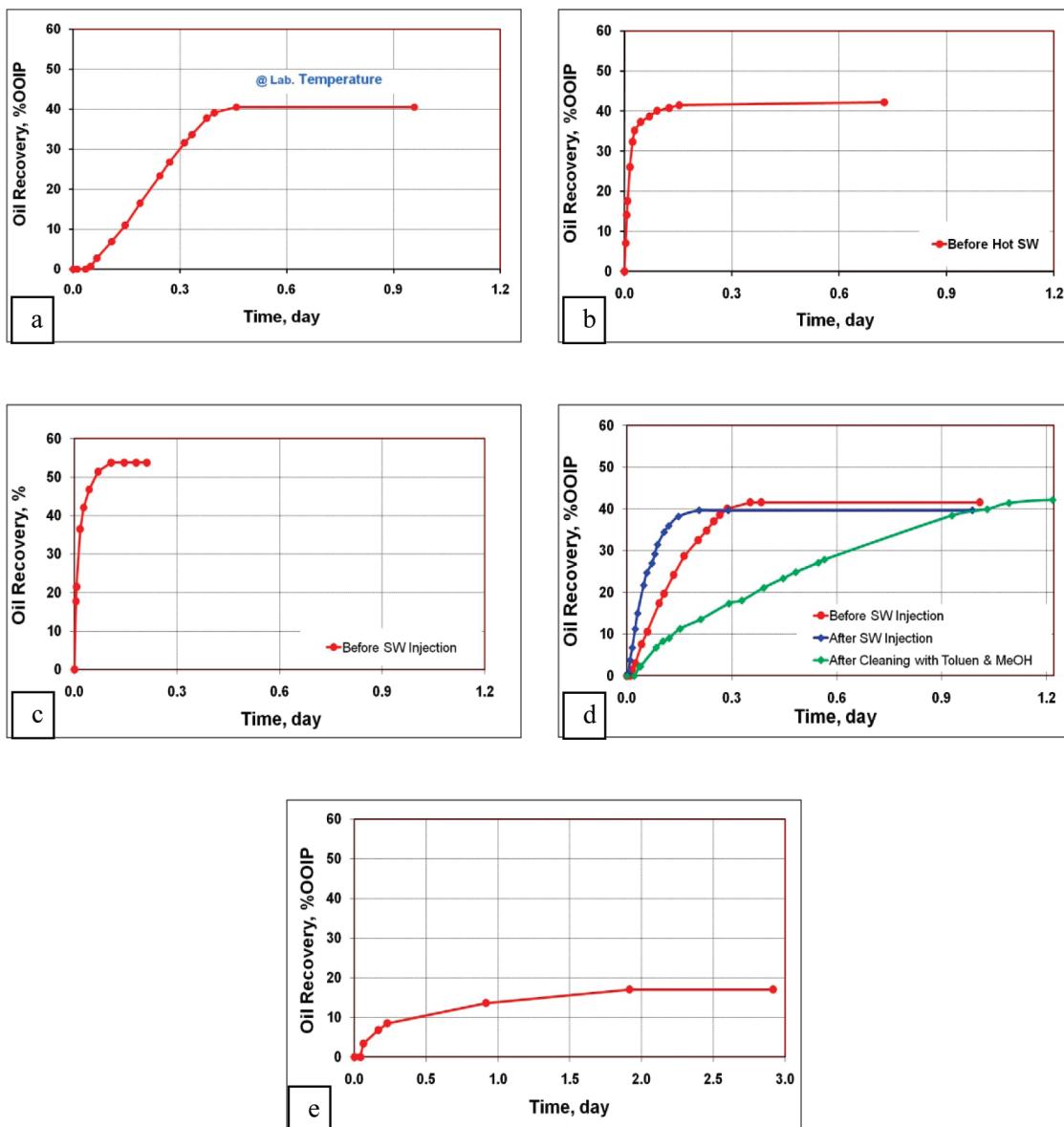
It is well-established that homogeneous water-wet low permeable carbonates can have strong capillary forces, which is excellent for oil recovery by SI, similar to the Tor formation in the Ekofisk field.<sup>16</sup>

According to the chromatographic wettability tests, the different cores appeared to be quite water-wet after the mild cleaning. It was decided to test the capillary forces by performing SI of SW0T into 100% *n*-heptane-saturated cores at room temperature. When the model oil (*n*-heptane) is introduced into the core material, no further wettability alteration is expected to occur. SI of SW0T into mildly cleaned cores was performed. For core C2-5, which was exposed to SW at 130 °C, another SI test was also conducted.

Two mildly cleaned cores from zone 4 (C4-13 and C4-12) imbibed SW0T very fast, and ultimate recovery was about 40% in both cases (panels a and b of Figure 7). Ultimate recovery from the core C5-17, from zone 5, was significantly higher than from cores C4-12 and C4-13, in the range of 57% (Figure 7c).

A small difference in the imbibition rate and ultimate recovery was observed after the core C2-5 had been flooded with SW at 130 °C, indicating negligible changes in wetting

(16) Torsaeter, O. An experimental study of water imbibition in chalk from the Ekofisk field. *Proceedings of the Society of Petroleum Engineers (SPE)/Department of Energy (DOE) Fourth Symposium on Enhanced Oil Recovery*; Tulsa, OK, April 15–18, 1984; SPE Paper 12688.



**Figure 7.** SI on 100% *n*-heptane-saturated cores using SW0T as imbibing fluid: (a) core C4-13, (b) core C4-12, (c) core C5-17, (d) core C2-5, and (e) core C3-9.

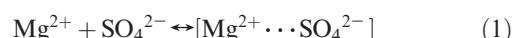
conditions after treatment with SW (Figure 7d). This is also in line with the chromatographic wettability tests. In both cases, ultimate recovery was in the range of 40%, within 0.3 day. However, it is very interesting to note that, after cleaning with toluene and methanol, the imbibition rate decreased significantly and the same oil recovery was obtained after 1.2 days. In line with the wettability test discussed above, it appears that, during the toluene–methanol flooding, some redistribution of adsorbed organic material has taken place; i.e., some organic material may adsorb onto the surface of the smaller pores, which initially were water-wet because of strong capillary forces. This will be discussed in more detail in a later paper.

The oil recovery from the low-permeability and low-porosity core C3-9 was low, about 17% after mild cleaning (Figure 7e). Thus, core material from zone 3 appears to be from a low-quality reservoir.

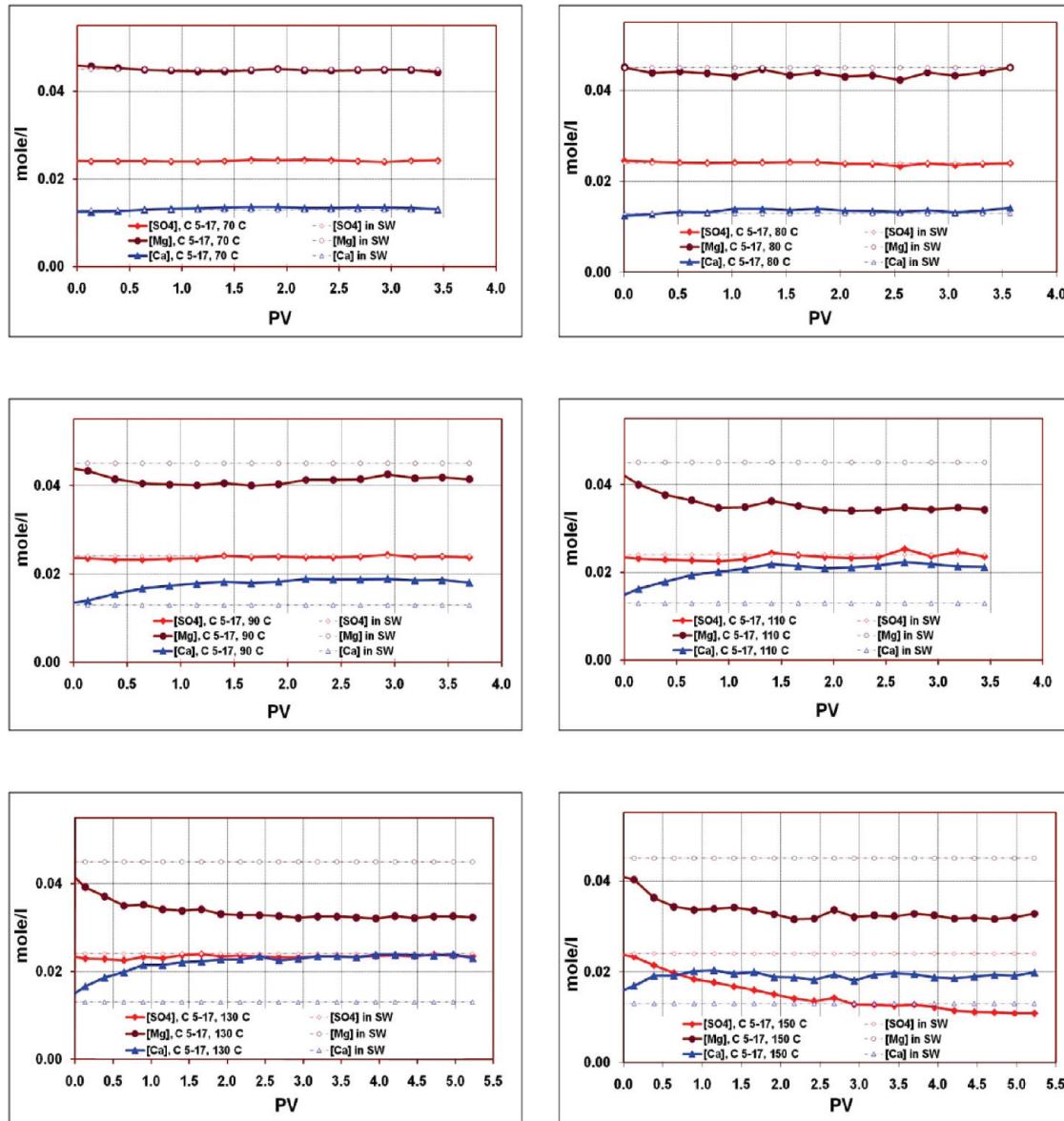
**Surface Reactivity.** The reactivity of potential determining ions toward the limestone surface was investigated by performing the chromatographic wettability test at room

temperature and also the substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$  at different temperatures (70–150 °C).

In the chromatographic wettability test, initially, the core contained SW without sulfate (SW0T). When the chromatographic fluid containing the equal concentration tracer and sulfate (SW1/2T) was injected, a sudden change in the equilibrium took place. The sensitivity of the sulfate ion regarding the surface charge on reservoir limestone is clearly shown in panels a and b of Figure 6. As the sulfate concentration increases, sulfate adsorbs onto the rock surface. The equilibrium condition for the  $\text{Ca}^{2+}$  ion is then changed, and  $\text{Ca}^{2+}$  co-adsorbs onto the surface, causing a decrease in the equilibrium concentration, while  $\text{Mg}^{2+}$  releases from the rock surface. This has been explained by the ion-pair formation between  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$ , which lowers the activity of  $\text{Mg}^{2+}$ , as shown by eq 1.<sup>17</sup>



It is verified that the equilibrium is moved to the right as the temperature is increased.<sup>18</sup>



**Figure 8.** Changes in molar concentrations of  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $SO_4^{2-}$  when flooding SW through the reservoir limestone core C5-17 at different temperatures ( $70\text{--}150\text{ }^\circ\text{C}$ ). Flow rate = 1 PV/day.

As observed for chalk, both the affinity of  $SO_4^{2-}$  and the substitution of  $Ca^{2+}$  by  $Mg^{2+}$  increase as the temperature increases.<sup>4,5</sup> A previous observation of limestone reservoir cores indicated that the surface reactivity was lower than for chalk; i.e., the substitution rate of  $Ca^{2+}$  by  $Mg^{2+}$  was significantly slower.<sup>1</sup>

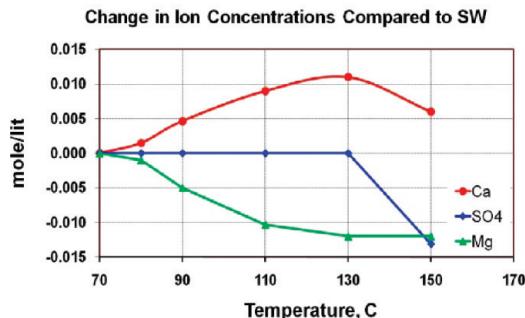
In line with studies on chalk, no significant substitution of  $Ca^{2+}$  by  $Mg^{2+}$  was observed at temperatures below  $80\text{ }^\circ\text{C}$  (Figure 8). The substitution of  $Ca^{2+}$  by  $Mg^{2+}$  at the carbonate surface increases as the temperature increases ( $90$ ,  $110$ , and  $130\text{ }^\circ\text{C}$ ), which is confirmed by a similar molar decrease in  $Mg^{2+}$  and increase in the  $Ca^{2+}$  concentrations; i.e., it is a 1:1 substitution. No change in the sulfate concentration was

observed at temperatures below  $130\text{ }^\circ\text{C}$ , indicating no precipitation of anhydrite,  $CaSO_4(s)$ , in the porous medium. The decrease in the sulfate concentration and the difference in the decrease of  $Mg^{2+}$  and increase in  $Ca^{2+}$  concentrations are a strong indication of precipitation of  $CaSO_4$  at  $150\text{ }^\circ\text{C}$ . Figure 9 shows the changes in the  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$  concentrations compared to the injected seawater at different temperatures. A 1:1 substitution occurs at temperatures lower than  $130\text{ }^\circ\text{C}$ , and  $CaSO_4$  precipitation occurs at  $150\text{ }^\circ\text{C}$ . It is interesting to note that the present limestone reservoir rock appears to have a reactive surface, which is comparable to the pure biogenic chalk studied previously.<sup>4,5</sup>

**Oil Recovery.** According to the previous experiments confirming strong adsorption of sulfate and also substitution of  $Ca^{2+}$  by  $Mg^{2+}$  at the chalk surface at temperatures above  $90\text{ }^\circ\text{C}$ , it is expected that SW could act as a wettability modifier, causing improved oil recovery in a SI process, provided that the rock behaves mixed-wet. Because of the low AN of the crude oil used for the tests, it is hard to believe any of the crude oils, which are listed in Table 3, are able to

(17) Puntervold, T.; Austad, T. Injection of seawater and mixtures with produced water into North Sea chalk formation: Impact of fluid–rock interactions on wettability and scale formation. *J. Pet. Sci. Eng.*, **2008**, *63*, 23–33.

(18) Carleberg, B. L.; Matthews, R. R. Solubility of calcium sulfate in brine. *Proceedings of the Oilfield Chemistry Symposium of the Society of Petroleum Engineers of American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME)*; Denver, CO, 1973.



**Figure 9.** Substitution (1:1) of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$  at temperatures lower than  $130\text{ }^{\circ}\text{C}$  and precipitation of  $\text{CaSO}_4$  at  $150\text{ }^{\circ}\text{C}$ .

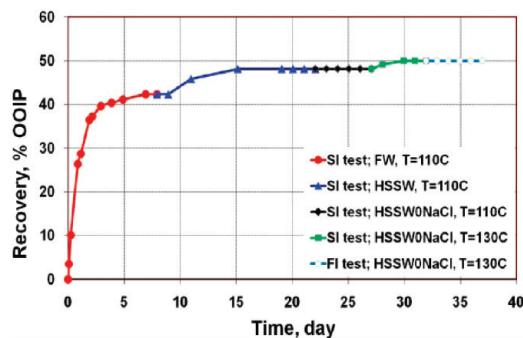
change the wetting properties of a preferential water-wet reservoir limestone core significantly, as also confirmed by the SI tests performed on the outcrop chalks (Figure 2). It is therefore important to maintain the initial wetting properties of the reservoir core material. The selected cores for the oil recovery studies (C1-3, C4-11, C4-14, C5-15, and C5-16) were initially cleaned mildly with *n*-heptane and DIW as described previously. The initial wetting condition of the cores was determined, except core C1-3, as shown in panels a–d of Figure 13. The nice S-shaped curve of the tracer ( $\text{SCN}^-$ ) is an indication of homogeneous cores with good pore connectivity. After the cores were saturated and aged using oil N and FW ( $S_{wi} \approx 10\%$ ), the cores were first imbibed with FW at  $110\text{ }^{\circ}\text{C}$  in a secondary process, and after the oil recovery plateau was reached, FW was substituted by HSSW or modified HSSW in a tertiary SI process, except cores C1-3 and C4-11, which were used in secondary imbibition by HSSW. No wettability alteration will take place in the secondary imbibition process with FW because no sulfate is present.

**Secondary Imbibition of FW.** According to Figures 10–12, the oil recovery by SI of FW reached a maximum in the range of 40% recovery within 7–15 days. The difference in the imbibition rate may be reflected in somewhat different wetting properties.

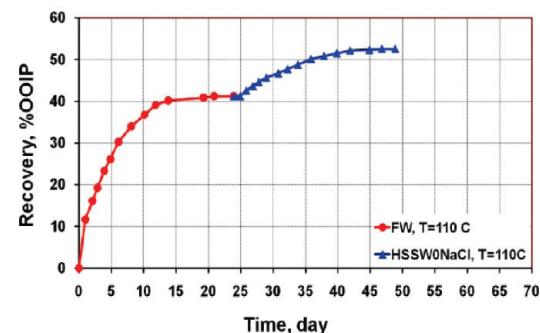
After we switched to HSSW, the oil recovery from core C5-16 increased from 43% to slightly below 50%. No significant extra oil was recovered when HSSW was substituted by HSSW0NaCl, at both  $110\text{ and }130\text{ }^{\circ}\text{C}$  and even by forced imbibition at  $130\text{ }^{\circ}\text{C}$  (Figure 10).

In a newly published paper, we have shown experimentally that more oil is recovered when NaCl was removed from SW; i.e., SW without NaCl acts as a better “smart water”. The oil recovery in an imbibition process using chalk core increased 10% of OOIP compared to SW as imbibing fluid.<sup>19</sup> Therefore, after the oil recovery plateau was reached with FW for the core C5-15, the imbibing fluid was switched to seawater depleted in NaCl (HSSW0NaCl) in a tertiary imbibition process. The oil recovery increased from 41 to 54% (Figure 11), i.e., an increase of 13% of OOIP, which is significantly higher than the increase in oil recovery by just using HSSW after first imbibing with FW, about 7% of OOIP (Figure 10). Thus, in line with the previous results, HSSW depleted in NaCl appears to be a better wettability modifier than HSSW, which was previously discussed in terms of double-layer effects at the carbonate surface.<sup>19</sup>

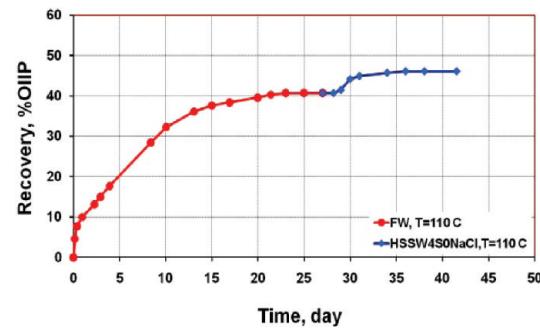
(19) Fathi, S. J.; Austad, T.; Strand, S. “Smart water” as wettability modifier in chalk: The effect of salinity and ionic composition. *Energy Fuels* 2010, 24 (4), 2514–2519.



**Figure 10.** Oil recovery from oil-saturated reservoir limestone core C5-16. Test sequence: (1) SI test with FW followed by HSSW and HSSW0NaCl at  $110\text{ }^{\circ}\text{C}$ , (2) SI test with HSSW0NaCl at  $130\text{ }^{\circ}\text{C}$ , and (3) forced imbibition with HSSW0NaCl at  $130\text{ }^{\circ}\text{C}$ .  $S_{wi} \approx 10\%$ .



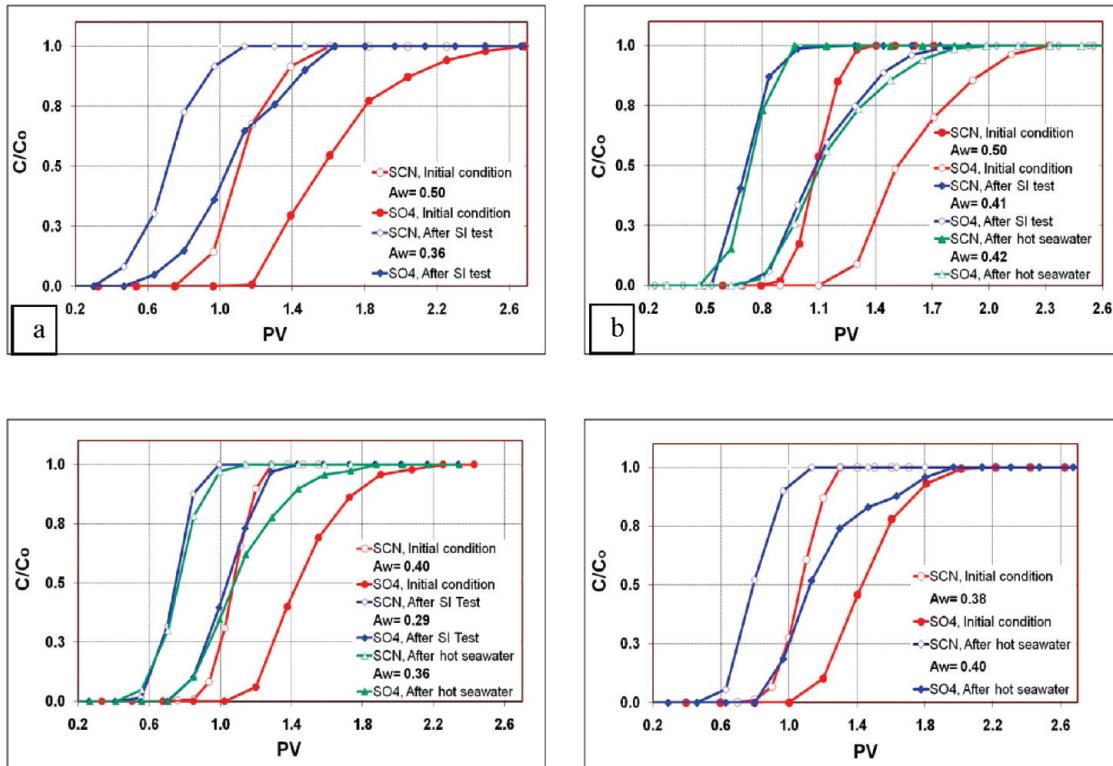
**Figure 11.** SI on oil-saturated reservoir limestone core C5-15 with FW followed by HSSW0NaCl at  $110\text{ }^{\circ}\text{C}$ .  $S_{wi} = 10\%$ .



**Figure 12.** SI on oil-saturated reservoir limestone core C4-14 with FW followed by HSSW4S0NaCl at  $110\text{ }^{\circ}\text{C}$ .  $S_{wi} = 10\%$ .

A third attempt to modify HSSW for improving oil recovery by wettability alteration is shown in Figure 12. In this case, the concentration of  $\text{SO}_4^{2-}$  was increased to 4 times the concentration in ordinary HSSW. To avoid precipitation of anhydrite,  $\text{CaSO}_4(s)$ , at  $110\text{ }^{\circ}\text{C}$ ,  $\text{CaCl}_2$  was removed from HSSW as well as NaCl. The oil recovery from core C4-14 increased by 6%, which is significantly smaller compared to HSSW0NaCl as smart seawater.

Besides the wetting data for the cores after mild cleaning, chromatographic wettability tests were also performed on the cores after the SI tests and after flooding the core with HSSW at  $130\text{ }^{\circ}\text{C}$  for the cores C4-14, C5-15, and C5-16 (panels a–d of Figure 13). As a general trend, the water-wetness of the cores decreased after the SI process, as compared to the initial wetting, after mild cleaning (Table 7). Thus, introducing oil N into the limestone cores made them less water-wet even after SI tests, but after the cores were



**Figure 13.** Chromatographic wettability tests conducted on (a) core C4-11, (b) core C4-14, (c) core C5-15, and (d) core C5-16 to observe possible changes in wetting properties after SI test and after HSSW injection at 130 °C, which are compared to the initial wetting area.

**Table 7. Results of Chromatographic Wettability Test, Initial, after SI Test, and after Hot SW**

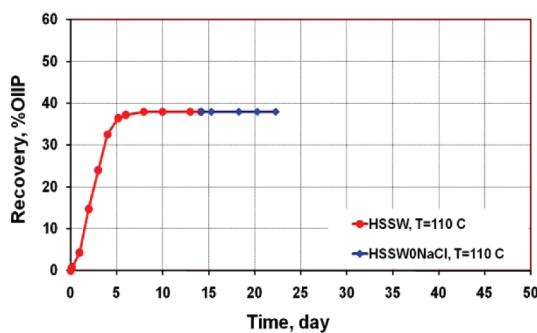
core	$A_w$ (initial wetting condition)	$A_w$ (after SI test)	$A_w$ (after flooding with HSSW at 130 °C)
C4-11	0.5	0.36	
C4-14	0.5	0.41	0.42
C5-15	0.4	0.29	0.36
C5-16	0.38		0.40

flooded with HSSW at 130 °C, it appears that the wetting condition of the cores approached the initial condition.

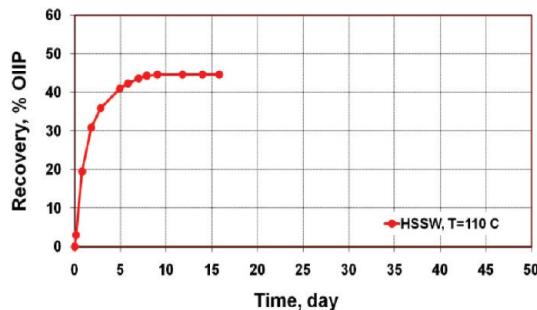
**Secondary Imbibition by HSSW.** Two cores from zones 1 and 4 (C1-3 and C4-11) were tested using HSSW as the first imbibing fluid in a secondary process, and the maximum oil recovery of 38–45% of OOIP was reached within less than 10 days (Figures 14 and 15). Even though only two cores were imbibed with HSSW in a secondary process, the oil recovery is in the same range as observed before, when FW was used as the imbibing fluid in the secondary recovery (Figures 14 and 15). Opposite to FW, no extra oil was recovered when HSSW0NaCl was introduced as the imbibing fluid in a tertiary process (Figure 14). Thus, with the wetting conditions of the reservoir cores, obtained with oil N and the given FW, HSSW does not act as a wettability modifier, which can increase oil recovery compared to injection of FW, but can act as an EOR fluid in a tertiary process. It would be of interest to use HSSW0NaCl as the imbibing fluid in a secondary process, but because of the limited number of cores, no such test was performed.

### General Field Considerations

The AN of crude oil is the most important parameter when discussing wetting properties of the carbonates. The BN



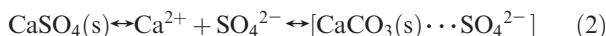
**Figure 14.** Secondary imbibition by HSSW on oil-saturated reservoir limestone core C4-11 followed by HSSW0NaCl at 110 °C.  $S_{wi} = 10\%$ .



**Figure 15.** Secondary imbibition by HSSW on oil-saturated reservoir limestone core C1-3 at 110 °C.  $S_{wi} = 10\%$ .

appears to play a minor role in this type of rock.<sup>20</sup> It is also observed that the water-wetness of carbonates increases as the reservoir temperature increases.<sup>21</sup> The AN and temperature are, however, not independent parameters because the AN

decreases as the temperature increases because of decarboxylation of acidic material during geological time.<sup>13</sup> In addition, the decarboxylation process is catalyzed by  $\text{CaCO}_3$ .<sup>13</sup> Normally, because of the high concentration of  $\text{Ca}^{2+}$  in the formation water, the concentration of anionic-potential-determining ions, such as  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , dissolved in the formation water is very low. It was verified in a previous paper that even the presence of small amounts of  $\text{SO}_4^{2-}$  in chalk had a large effect on the initial wetting properties when the core was aged at 90 °C in a crude oil with AN = 0.5 mg of KOH/g of oil.<sup>22</sup> Thus, the presence of anhydrite,  $\text{CaSO}_4(\text{s})$ , in the carbonate rock can affect the initial wetting properties. Even though the solubility of  $\text{CaSO}_4(\text{s})$  decreases as the temperature increases, the adsorption of  $\text{SO}_4^{2-}$  onto the carbonate rock increases by increasing the temperature.<sup>4</sup> This is illustrated in the following chemical equilibrium:



To verify the equilibrium, the core C5-18 was flooded with *n*-heptane to remove the kerosene, dried at 90 °C, saturated with formation water without sulfate (FW), and aged for 3 days at 110 °C. Then, the core was flooded with DIW at a rate of 0.1 mL/min, and the effluent was analyzed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ . The concentration of sulfate increased to a maximum ( $\approx 0.0028 \text{ mol/L}$ ) after 1 PV, which could be related to the dissolved and loosely adsorbed sulfate (Figure 16). Later, after injection of about 4 PVs of DIW, the concentration of  $\text{Mg}^{2+}$  dropped to a very low level, indicating that most  $\text{Mg}^{2+}$  present in solution and loosely adsorbed onto the carbonate surface has been removed; this may also be the case for  $\text{SO}_4^{2-}$ . Previous studies in chalk without anhydrite present showed that about 4 PVs of DIW must be injected to remove sulfate from the core material. Thus, after 5 PVs of DIW were injected, a constant and similar decrease in the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  was observed, which may be related to a slow dissolution of anhydrite. Thus, in the same way that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in combination with  $\text{SO}_4^{2-}$  is able to change wetting properties at high temperatures, the same ions can keep the carbonate rock preferentially water-wet when present in the initial formation water at a high reservoir temperature.

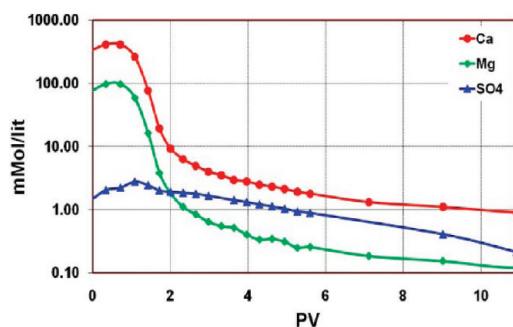
During the imbibition process into a carbonate rock, the imbibing front of the smart water will be partly stripped for sulfate because of strong adsorption. If anhydrite is present as a rock mineral and the injected fluid is seawater with a low concentration of  $\text{Ca}^{2+}$  compared to the formation water, increased dissolution of  $\text{CaSO}_4(\text{s})$  will take place at the front. Because the  $\text{Ca}^{2+}$  concentration is decreased drastically, the chemical equilibrium (eq 2) is moved to the right. Thus, sulfate, which is a very important catalyst for wettability alteration, can be created *in situ* at the water front. At certain initial wetting conditions, dissolution of  $\text{CaSO}_4(\text{s})$  at the water front can improve the water-wetness and give increased oil recovery in a SI process.

The benefit of anhydrite present in high-temperature carbonate rock is 2-fold: (1) The carbonate reservoir can act preferential to water-wetness. (2) Dissolution of anhydrite in

(20) Puntervold, T.; Strand, S.; Austad, T. Water flooding of carbonate reservoirs: Effects of a model base and natural crude oil bases on chalk wettability. *Energy Fuels* 2007, 21 (3), 1606–1616.

(21) Rao, D. N. Wettability effects in thermal recovery operations. *SPE Reservoir Eval. Eng.* 1999, 2 (5), 420–430.

(22) Puntervold, T.; Strand, S.; Austad, T. New method to prepare outcrop chalk cores for wettability and oil recovery studies at low initial water saturation. *Energy Fuels* 2007, 21 (6), 3425–3430.



**Figure 16.** Concentration profiles of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  when flooding the core C5-18 with DIW after aging with FW. Temperature, 110 °C; flooding rate, 0.1 mL/min.

the water front can improve the water-wetness and increase oil recovery in a SI process.

## Conclusions

Special core analysis was conducted to evaluate oil recovery from a low-permeable naturally fractured ( $\approx 1 \text{ mD}$ ) and high-temperature (above 100 °C) limestone reservoir by injecting high-saline seawater (42 220 ppm). Core material from five different zones in the same well, with oils from different possible source rocks, was used in the evaluation. The following tests were performed: (1) The wetting potential of three possible source rock oils toward chalk was evaluated after characterizing the oils by AN and BN. (2) The initial wetting condition as well as the potential of improving the water-wetness by smart water was studied chromatographically. (3) The presence of capillary forces in mildly cleaned core material was tested. (4) The reactivity of the limestone surface toward  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  was studied at different temperatures. (5) The oil recovery was tested at 110 °C by SI of formation water, seawater, and modified seawater.

The main results drawn from this study were as follow: (1) The reservoir rock was characterized as preferentially water-wet, and only a small increase in the water-wet area was achieved after flooding the cores with seawater at 130 °C. (2) Oil recovery by SI at 110 °C was about 40% of OOIP for both formation water and high-saline seawater. (3) High-saline seawater and modified seawater (depleted in NaCl) increased the oil recovery in a tertiary SI process after imbibing formation water from  $\approx 40$  to about 53 and 63% of OOIP, respectively. (4) No improvement in oil recovery was noticed using modified seawater in a tertiary process after a secondary imbibition with seawater. (5) A test program for special core analysis to evaluate the potential for water-based EOR in carbonates, which can serve as a “best practice”, has been demonstrated.

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## Nomenclature

$A_w$  = adsorption area (the area between the tracer and sulfate in the chromatographic wettability test)

AN = acid number (mg of KOH/g of oil)

at % = atomic percent

BET = technique for the measurement of the specific surface area of a material  
BN = base number (mg of KOH/g of oil)  
D = core diameter (cm)  
DIW = deionized water  
EDS = energy-dispersive spectrometry  
EOR = enhanced oil recovery  
FW = formation water used in reservoir limestone cores  
IS = ionic strength (mol/L)  
 $I_w$  = Amott water index  
 $k$  = permeability (mD)  
 $L$  = core length (cm)  
OOIP = original oil in place (mL)  
HSSW = synthetic high-salinity seawater  
HSSW0NaCl = HSSW without NaCl

HSSW4S0NaCl = HSSW containing 4 times sulfate and without NaCl and CaCl<sub>2</sub>  
PV = pore volume  
SEM = scanning electron microscopy  
SK = Stevns Flint  
 $S_{wi}$  = initial water saturation (%)  
SW = synthetic seawater  
SW1/2T = SW where the concentration of SCN<sup>−</sup> and SO<sub>4</sub><sup>2−</sup> is 0.012 mol/L  
SW1T = SW where the concentration of SCN<sup>−</sup> and SO<sub>4</sub><sup>2−</sup> is 0.024 mol/L  
SW0T = SW without SO<sub>4</sub><sup>2−</sup>  
TDS = total dissolved solids (g/L)  
VB = formation water used in chalk cores  
WI = chromatographic wetting index