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# Managing Injected Water Composition To Improve Oil Recovery: A Case Study of North Sea Chalk Reservoirs

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**ABSTRACT:** In recent years, many core displacement experiments of oil by seawater performed on chalk rock samples have reported  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  as potential determining ions for improving oil recovery. Most of these studies were carried out with outcrop chalk core plugs. The objective of this study is to investigate the potential of the advanced waterflooding process by carrying out experiments with reservoir chalk samples. The study results in a better understanding of the mechanisms involved in increasing the oil recovery with potential determining ions. We carried out waterflooding instead of spontaneous imbibition, which has been applied in most of the previous studies. Two different flooding schemes (with and without aging) were used for flooding North Sea reservoir chalk samples. For comparison, two tests were also carried out with Stevns Klint core plugs. The flooding tests were carried out with the following injecting fluids: distilled water, brine with and without sulfate, and brine containing only magnesium ions. The total oil recovery, recovery rate, and interaction mechanisms of ions with rock were studied for different injecting fluids at different temperatures and wettability conditions. Studies of the temperature dependence of the oil recovery indicated that the interaction of the ions contained in brine with the rock cannot be the only determining mechanism of enhanced recovery. We observed no substitution of  $\text{Ca}^{2+}$  ions with  $\text{Mg}^{2+}$  ions at high temperatures for both rocks. Not only the injection brine composition but also the formation water composition affected the oil recovery at high temperatures from the Stevns Klint chalk rock.

## 1. INTRODUCTION

Waterflooding has been the most widely used oil recovery method for many decades. Historically, the injected brine salinity was not considered as an important factor influencing the amount of oil recovered. However, over the past decade many studies have shown that waterflooding can be significantly improved by manipulating the injected brine chemistry for both sandstone and carbonate reservoirs.<sup>1–5</sup> The exceptional success of seawater injection in the Ekofisk chalk reservoir<sup>6</sup> has been the motivation for a number of experimental studies to understand complex crude oil/water/rock chemical interactions for carbonate reservoirs.

Several laboratory experimental studies of water injection were carried out by Austad and co-workers, who used different core plugs and studied recovery as a function of brine composition and temperature.<sup>5,7–10</sup> It was observed that  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  are the potential determining ions for improving the oil recovery in chalk reservoirs at high temperatures (above 90 °C). It was also reported that these ions must act together, because none of them alone had an effect on spontaneous imbibition. On the basis of these experimental results, wettability alteration was proposed to be a key reason for the improvement of oil recovery. A schematic model of the chemical mechanism for wettability modification was suggested. According to this model, the ions adsorb to the rock surface, which changes the surface charge, so that the adsorbed crude oil may be removed from the rock.

Webb et al.<sup>11</sup> presented a comparative study of the oil recovery from a North Sea carbonate core sample with simulated  $\text{SO}_4^{2-}$ -free brine and seawater containing  $\text{SO}_4^{2-}$  under reservoir conditions. The imbibition tests were

performed with live oil. It was concluded that the wettability alteration of the carbonate rock with the  $\text{SO}_4^{2-}$  ion is responsible for the saturation changes.

Fjelde et al.<sup>12</sup> carried out spontaneous imbibition experiments using seawater and formation brine with core plugs from two fractured chalk fields at reservoir temperature. Only a small increase in oil recovery was observed with the seawater compared to the formation brine (containing no  $\text{SO}_4^{2-}$ ) for reservoir core plugs compared to Stevns Klint outcrop chalk core plugs. Karoussi et al.<sup>13</sup> investigated extreme cases of waterflooding of Stevns Klint core plugs with ion-free water and water containing just  $\text{Mg}^{2+}$  or  $\text{SO}_4^{2-}$  ions. Water saturated with  $\text{Mg}^{2+}$  ions alone showed the highest oil recovery in the spontaneous imbibition experiments. Madland et al.<sup>14</sup> studied the effect of aqueous chemistry on the mechanical strength of chalk. Hydrostatic creep tests were carried out with continuous flooding of seawater, distilled water, NaCl, and  $\text{MgCl}_2$ . It was shown that the presence of only  $\text{Mg}^{2+}$  in the injected brine can deform the rock. Bagci et al.<sup>15</sup> also studied the effect of brine composition on oil recovery by waterflooding. Experiments were carried out with different brine compositions (NaCl, KCl,  $\text{CaCl}_2$ , and mixed brines, such as 2 wt % KCl + 2 wt % NaCl, 2 wt % KCl + 5 wt %  $\text{CaCl}_2$ , etc.). The highest oil recovery (18.8% higher than under distilled water injection) was observed for the 2 wt % KCl brine. No analysis of the reasons for such a recovery variation was presented.

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In most of the studies discussed above, outcrop chalk core plugs were used. Very few studies have been carried out using reservoir chalk core plugs. To our knowledge, no single study has yet been reported in the literature about the interaction of potential determining ions with the reservoir rock at different temperatures and under different wetting conditions with regard to oil recovery.

The objectives of this study are (1) to experimentally investigate the oil recovery potential of the advanced waterflooding process for reservoir chalk samples at different wettability and temperature conditions, (2) to investigate reactivity of the potential determining ions toward the reservoir chalk surface, and (3) to compare the reservoir chalk and the Stevns Klint outcrop core plugs with respect to oil recovery and reactivity of the potential determining ions under the same experimental conditions.

The flooding tests with North Sea chalk samples were carried out both with and without aging at different temperatures and using different injected brine solutions. For comparison, similar experiments were performed with the Stevns Klint outcrop chalk cores. All of the flooding experiments were designed so that we could study both the oil recovery and the affinity of the potential determining ions with the chalk surface.

We carried out waterflooding instead of spontaneous imbibition, which was applied in most of the previous studies. Skauge et al.<sup>16</sup> reported high oil recovery for a carbonate core sample that showed no spontaneous water imbibition. The study of the forced injection is important, because viscous and gravity forces usually prevail over capillary forces at characteristic reservoir scales.

The paper is structured in the following way: The experimental methodology is described in the next section. The subsequent sections provide the results of the laboratory core flooding study and detailed discussion. Finally, the conclusions are drawn.

## 2. EXPERIMENTAL SECTION

**2.1. Core Plugs.** Outcrop Stevns Klint core plugs and core plugs from two different North Sea chalk reservoirs were used in the experiments.

The outcrop chalk is of Maastrichtian age and has a large specific surface area of around 2 m<sup>2</sup>/g, as determined by nitrogen adsorption.<sup>17</sup> The porosity is about 46–48%, and the permeability is about 6–7 mD. The core plugs are very homogeneous with regard to permeability and porosity, which makes them suitable for parametric studies. The Stevns Klint core plugs were 3.6–3.8 cm in diameter and 7–8 cm in length. The core plugs were provided by the Danish Geotechnical Institute (GEO).

The core plugs from two different North Sea chalk reservoirs (1L and RE05) have a specific surface area of 2.06 and 2.10 m<sup>2</sup>/g, respectively, as determined by Brunauer–Emmett–Teller (BET). The detailed properties of all of the core plugs used in this study are given in Table 1. To confirm the homogeneity of the cores and absence of fissures, X-ray computer tomography (CT) scan analysis was performed on each core plug.

**2.2. Crude Oil.** We used North Sea dead crude oil for this study. No model oil was used, because the goal was to provide more realistic fluid–fluid and fluid–rock interactions. Puntervold et al.<sup>18</sup> observed that natural and model oils behave differently during displacement. Our studies<sup>19</sup> also indicated that the results of the recovery by waterflooding are strongly oil-dependent.

Acid and base numbers of the crude oil were measured using Metrohm 702 SM Titrino by the methods developed by Fan and Buckley<sup>20</sup> [modified versions of American Society for Testing and Materials (ASTM) D2896 for the base number titration and ASTM

**Table 1. Core Plug Properties**

name of plug	length (cm)	diameter (cm)	porosity (%)	permeability (mD)
North Sea (1L)	5.79	2.57	31.74	0.97
North Sea (RE05)	7.47	3.72	37.87	0.83
Stevns Klint-1	7.70	3.69	47–50	6.48
Stevns Klint-2	7.86	3.82	47–50	6.96

D664 for the acid number titration]. Density, acid number, base number, and viscosity of the crude oil are given in Table 2.

**Table 2. Crude Oil Properties**

	SW0S (ppm)	SW3S (ppm)	FW (ppm)
Na <sup>+</sup>	8471.18	7758.46	31022.62
K <sup>+</sup>	390.98	390.98	521.84
Mg <sup>2+</sup>	1093.73	1093.73	664.95
Ca <sup>2+</sup>	521.01	521.01	5667.24
Cl <sup>-</sup>	17459.61	11255.33	60272.08
HCO <sub>3</sub> <sup>-</sup>	122.03	122.03	13.07
SO <sub>4</sub> <sup>2-</sup>	0.000	6916.32	0.000
TDS (g/L)	33.39	33.39	98.158

**2.3. Brine Solutions.** The synthetic brine solutions were prepared by adding different amounts of NaCl, NaHCO<sub>3</sub>, KCl, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>·2H<sub>2</sub>O, and Na<sub>2</sub>SO<sub>4</sub> to distilled water. Three different brine solutions were prepared for injection: (1) synthetic seawater without sulfate ions (SW0S), (2) sulfate concentration 3 times larger than in the synthetic seawater (SW3S), and (3) 0.1 M MgCl<sub>2</sub> (0.1 M Mg). The total dissolved solid for the first two brine solutions was made similar by adjusting the amount of NaCl. North Sea synthetic formation water (FW) was also prepared for use as initial water in the tests. The detailed compositions of all of the brine solutions are given in Table 3.

**2.4. Core Preparation.** Prior to any flooding experiment, the core plugs from the North Sea reservoirs were cleaned. They were put into a Hassler core holder, flooded with toluene until the effluent was colorless, and then flooded with ethanol. After cleaning, the core plugs were dried in an oven at 90 °C to a constant weight and then evacuated. The dried core plugs were flooded with distilled water at 40 °C. The pore volume was calculated by comparing the weights of the dry and saturated cores. We established initial water saturation (IWS) by flooding the confined core by 5–7 pore volumes (pv) of crude oil at an injection rate of 0.2 cm<sup>3</sup>/min at 70 °C. Afterward, the two different flooding sequences were applied, as shown in Figure 1. Flooding sequence 1 was without aging of the plug in crude oil, while flooding sequence 2 involved aging. For aging in flooding sequence 2, three pore volumes of crude oil were flooded from both sides of the core plug. The saturated core was then aged for 3 days at 80 °C. Flooding sequence 2 was not applied to the second North Sea chalk sample RE05. We assumed that solvent-cleaned reservoir cores are water-wet and remain so during flooding sequence 1 and that it changes to more oil-wet during sequence 2.

The drilled core plugs from Stevns Klint were dried in the oven at 90 °C overnight. Then, they were saturated with a brine solution for 3 h under vacuum, after which the pore volume was calculated for each core plug. The IWS was established in the same way as for the reservoir core plug. No aging was carried out with the Stevns Klint plugs.

IWS is high in the core plugs compared to average saturation in reservoirs. Tang et al.<sup>21</sup> conducted a study on the effect of IWS on oil recovery with Kansas outcrop chalk samples (Kansas outcrop chalk is very similar to the rock matrix of the North Sea fractured chalk reservoirs). They concluded that the effect of IWS on oil recovery depends upon wettability. IWS has a significant effect on water injection in an intermediate-wet chalk. This effect is much less

Table 3. Different Brine Compositions

	density at 20 °C (g/cm <sup>3</sup> )	acid number (mg of KOH/g)	base number (mg of KOH/g)	asphaltene (%)	viscosity (cp)
North Sea	0.847	0.095	2.442	0.302	8.837

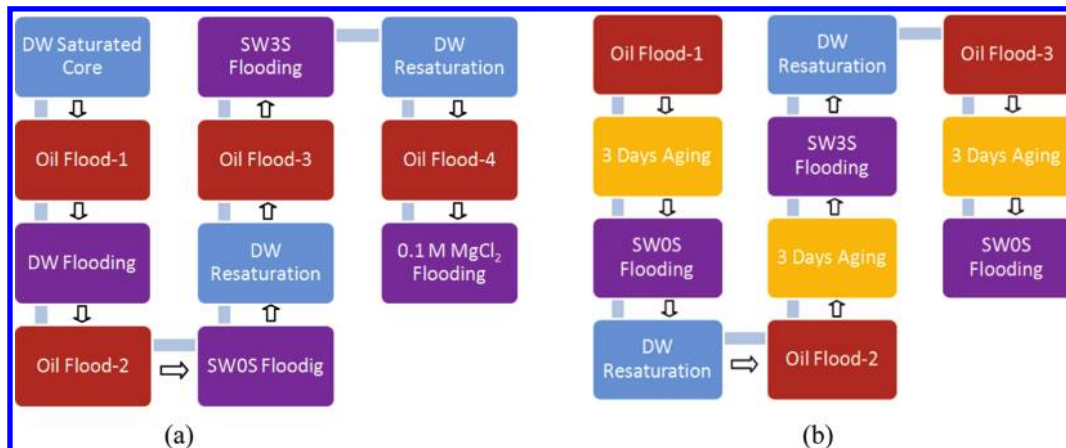


Figure 1. (a) Flooding sequence 1 without aging and (b) flooding sequence 2 with aging: DW, distilled water; SW0S, synthetic seawater without sulfate ions; and SW3S, sulfate concentration 3 times larger than in the synthetic seawater.

pronounced for a water-wet chalk. In our study, flooding sequence 1 with reservoir chalks and tests with Stevns Klint are at water-wetting conditions (without aging). Therefore, in these cases, possibly the effect is less pronounced. It could affect the two tests in flooding sequence 2 with reservoir chalk core plug (1L).

**2.5. Flooding Schemes.** In all of the experiments, flooding was initially carried out at 40 °C. When no more oil came out, the temperature was increased to 70 °C and finally to 120 °C. The flooding tests were carried out with a sleeve pressure of 70 bar for the reservoir core plugs and 30 bar for the outcrop core plugs. A back pressure of 12 bar was used for all of the experiments to avoid boiling of the liquids. The volume of produced oil was measured as a function of pore volumes injected. All flooding tests are listed in Table 4.

Table 4. Summary of Flooding Tests

core plugs	cycle number	injected fluid	initial water	IWS (%)	oil recovery (% OOIP)
Flooding Sequence 1, without Aging					
North Sea (1L)	1	DW	DW	32.3	53.1
	2	SW0S	DW	34.4	54.4
	3	SW3S	DW	33.4	56.1
	4	0.1 MgCl <sub>2</sub>	DW	32.3	53.8
Flooding Sequence 2, with Aging					
North Sea (1L)	1	SW0S	DW	34.4	50.7
	2	SW3S	DW	36.4	53.4
	3	SW0S	DW	35.1	50.9
Flooding Sequence 1, without Aging					
North Sea (1L)	1	SW3S	FW	27.4	58.4
North Sea (RE05)	1	SW0S	DW	13.1	53.1
	2	SW3S	DW	14.2	54.2
Stevns Klint-1	1	SW3S	DW	31.2	37.9
Stevns Klint-2	1	SW3S	FW	20.2	43.5

**2.6. Chemical Analysis.** Effluent was collected by means of a fractional collector at different time intervals and analyzed for potential determining ions (SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>). The SO<sub>4</sub><sup>2-</sup> ion was detected with the ion chromatograph DX-120 produced by Dionex, Sunnyvale, CA. The Ca<sup>2+</sup> and Mg<sup>2+</sup> ions were analyzed with the inductive coupled plasma (ICP) Varian 720-ES. The effluent samples

were diluted with deionized water before the analysis to meet the concentration limits of the equipment.

3. RESULTS

3.1. North Sea Chalk Reservoir Core Plug (1L).

**3.1.1. Flooding Sequence 1.** In flooding sequence 1, a preliminary flooding test was carried out at 40 °C with a plug initially saturated by oil and distilled water. First, distilled water was injected at a relatively slow injection rate of 2 pv/day. When the production stopped, the temperature of the system was increased to 70 °C and finally to 120 °C. As shown in Figure 2, 53.1% original oil in place (OOIP) was recovered after injection of the distilled water at 40 °C. The oil was produced only before the water breakthrough, so that the displacement looked piston-like. Increasing the temperature to 70 and 120 °C produced no additional oil.

After completion of the first cycle, the core was resaturated with distilled water and, afterward, 7 pv of crude oil was injected to establish the IWS. In the second cycle, the core was flooded with SW0S brine at 40, 70, and 120 °C, in the same way as for the first cycle. Also, in this case, no oil was produced after water breakthrough, and an increase in the temperature to 70 and 120 °C did not result in additional production, as shown in Figure 2a. The total amount of oil produced was 54.4% OOIP. The effluent was analyzed for Ca<sup>2+</sup> and Mg<sup>2+</sup> ions at different temperatures. The results, plotted in Figure 2b, indicate that the concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the effluent increases with time at 40 °C. This is because, at the initial stage of flooding, the distilled water, which was initially in the core, comes out of it. The concentration for both ions remains constant at 70 °C, and the concentration of Ca<sup>2+</sup> increases, while the Mg<sup>2+</sup> concentration decreases in the effluent at 120 °C.

In the third cycle, the core was resaturated with distilled water and then IWS was established in the same way as for the second cycle. In this case, the core was flooded with brine SW3S with the same injection rate of 2 pv/day. This relatively slow injection rate was used to allow for the different potential determining ions to interact with the chalk matrix. The oil recovery at 40 °C was 56.1% OOIP, which is 1.7% higher than

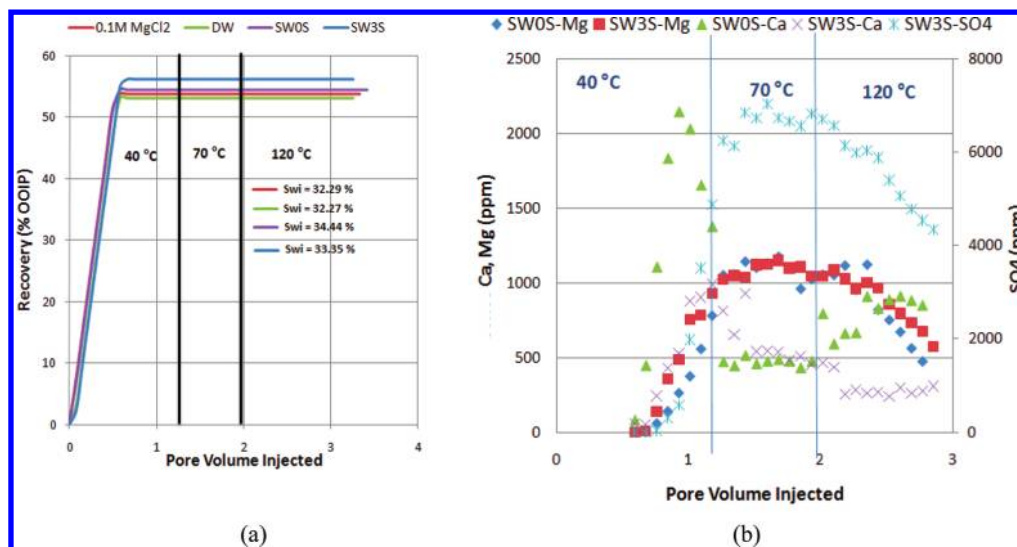


Figure 2. (a) Waterflooding in North Sea chalk core plug (1L) without aging, with oil recovery (% OOIP) as a function of the pore volume injected. (b) Effluent ion concentrations as a function of the pore volume injected.

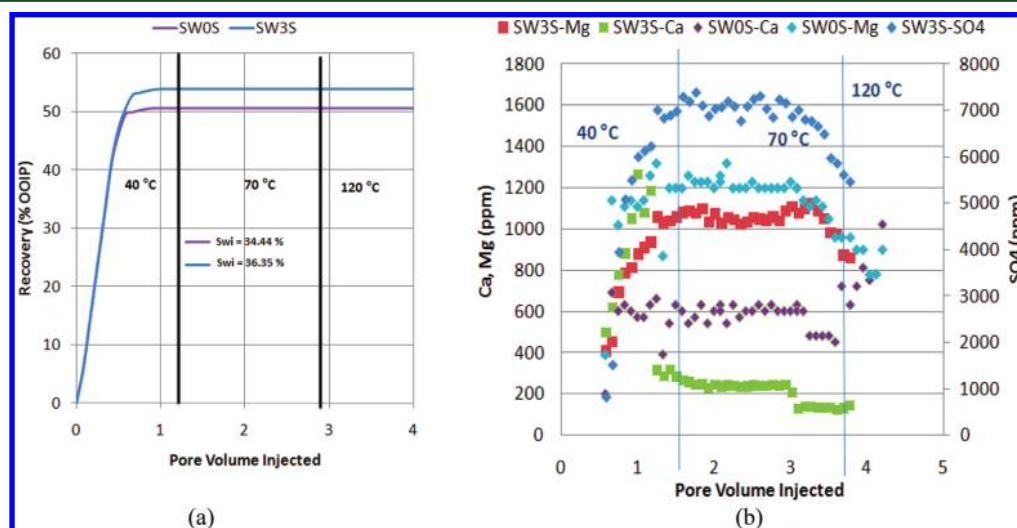


Figure 3. (a) Waterflooding in North Sea chalk (1L) core plug with aging, with oil recovery (% OOIP) as a function of the pore volume injected. (b) Effluent ion concentrations as a function of the pore volume injected.

for the SW0S injection. Increasing the temperature to 70 and 120 °C did not improve the oil recovery. The concentration of the different potential determining ions increased with time at 40 °C and remained constant at 70 °C, but at 120 °C, the concentration of all of the ions decreased in the effluent.

In the fourth cycle, the core was flooded with the 0.1 M MgCl<sub>2</sub> brine solution in the same sequence as above, to check the effect of Mg<sup>2+</sup> ions on the reservoir chalk core plug. A total of 53.8% OOIP of oil was produced in this case, which is less than for the SW3S flooding. Thus, in this case, Mg<sup>2+</sup> ions did not help to give high oil recovery compared to SO<sub>4</sub><sup>2-</sup> ions. The effluent was also analyzed for Ca<sup>2+</sup> and Mg<sup>2+</sup> ions, and the trend in the Mg<sup>2+</sup> ion concentration was the same as for the SW3S case.

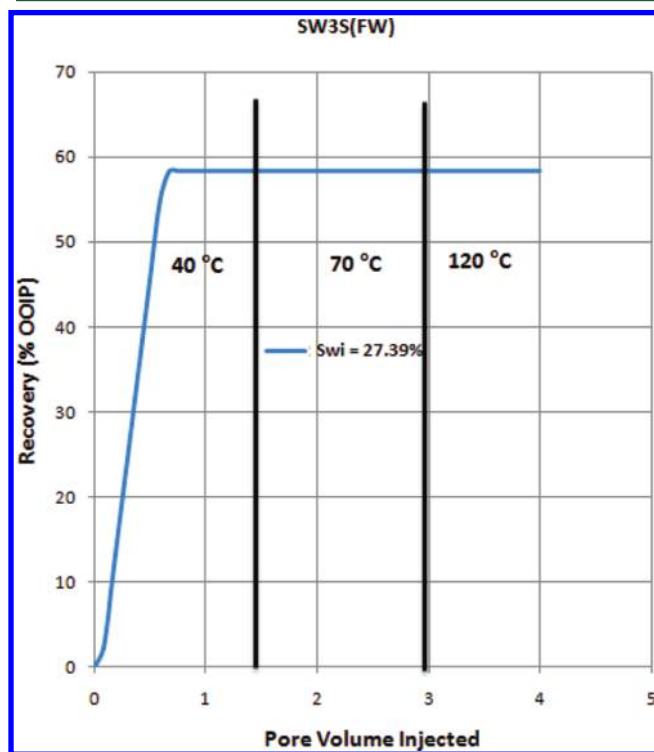
**3.1.2. Flooding Sequence 2.** After completion of flooding sequence 1, the core was resaturated with distilled water and IWS was established by flooding 3 pv of crude oil from both sides of the core plug. After IWS was established, the core was aged at 90 °C for 3 days. In the first cycle of this flooding sequence, the core was flooded with brine SW0S in the same

way as in flooding sequence 1. This resulted in a final oil recovery of 50.7% OOIP. As shown in Figure 3a, most of the oil was produced before the water breakthrough but some oil was also produced after the breakthrough. For comparison, no oil was produced after breakthrough in flooding sequence 1. Increasing the temperature to 70 and 120 °C did not improve the oil recovery. The effluent was also analyzed for Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations, which are plotted in Figure 3b. The reactivity trend of these ions with the rock is the same as in flooding sequence 1. The concentration of Ca<sup>2+</sup> in the effluent increases, while the concentration of Mg<sup>2+</sup> decreases with time at 120 °C. In cycle 2 of flooding sequence 2, the core was flooded with brine SW3S, which resulted in an oil recovery of 53.4% OOIP. This is around 2.7% higher than for cycle 1. No more oil was produced with the increase in the temperature even in this case. The effluent ion profile of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> is plotted in Figure 3b.

In cycle 3, we flooded the core plug (Swi = 35.1%) with SW0S brine again to check for the repeatability of the tests. A

total of 50.9% OOIP oil was produced, which is very much similar to the previous test (not plotted).

**3.1.3. Formation Brine Composition.** In all of the flooding tests and flooding sequences described until now, distilled water was used to establish IWS in the cores. One more test was carried out with the North Sea formation brine as initial water to check if this could affect the oil recovery mechanism. After the completion of flooding sequence 2, the core was cleaned with toluene and ethanol and was dried in an oven until constant weight was achieved. The core plug saturated with the North Sea formation brine and crude oil was flooded with the SW3S brine at different temperatures. As in the previous cases, in this case, an increase of the temperature did not result in a recovery increase, as shown in Figure 4. The effluent was



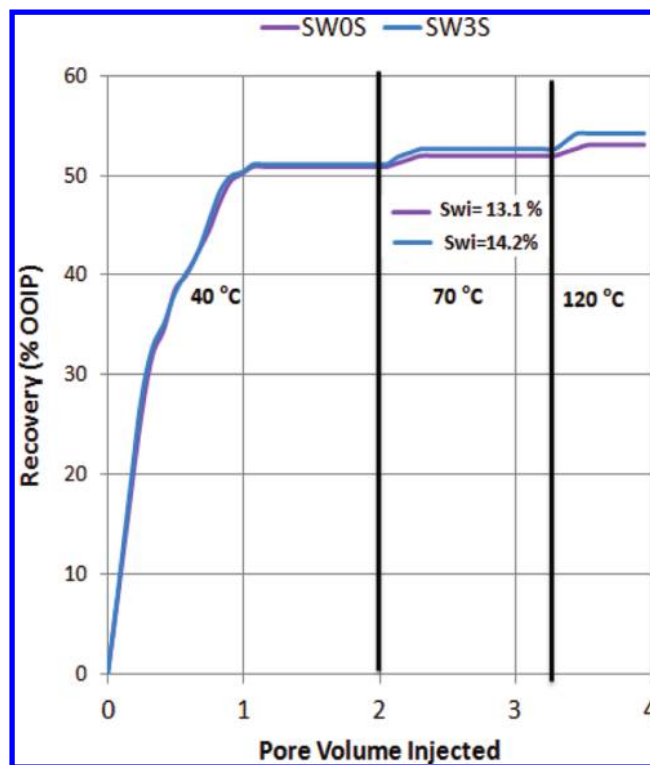
**Figure 4.** SW3S brine injection in North Sea chalk (1L) core plug without aging with North Sea formation brine as initial water.

analyzed for potential determining ions (not plotted). The reactivity trend of the ions remained the same as in the case of SW3S injection in flooding sequences 1 and 2.

### 3.2. North Sea Chalk Reservoir Core Plug (RE05).

**3.2.1. Flooding Sequence 1.** Another coreflood experiment was conducted using a different reservoir chalk core plug RE05 to see especially the effect of the temperature on oil recovery. The core was first flooded with brine SW0S in the same way as in flooding sequence 1 for the first North Sea chalk sample (1L) at different temperatures. As shown in Figure 5, 50.9% OOIP was recovered after injection of SW0S at 40 °C. A significant amount of oil was produced after water breakthrough. Increasing the temperature to 70 and 120 °C resulted in an additional production of 2.2% OOIP.

In the second cycle, the core was flooded with the SW3S brine solution with the same injection rate and temperature sequence as was adopted for the first cycle. The oil recovery at 40 °C was 51.1% OOIP. Increasing the temperature to 70 °C and then to 120 °C resulted in an additional production of



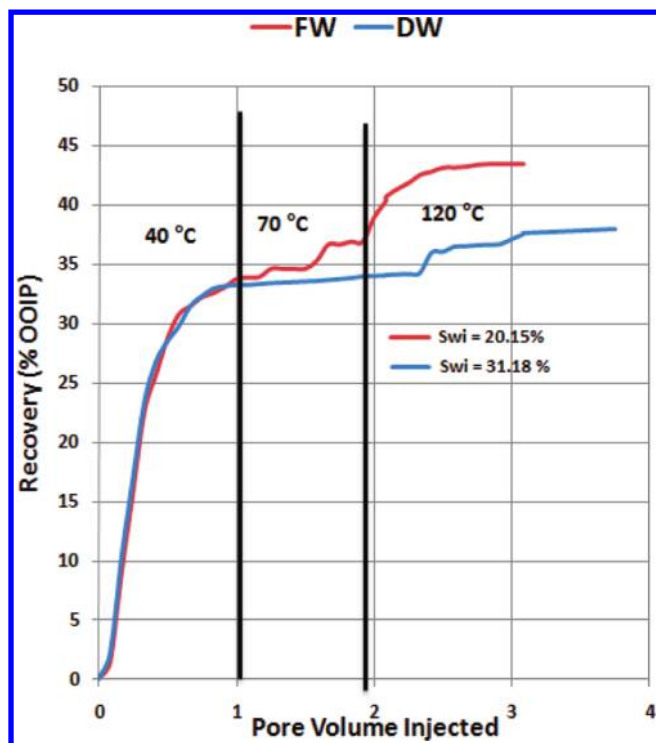
**Figure 5.** Waterflooding in North Sea chalk (RE05) core plug without aging, with oil recovery (% OOIP) as a function of the pore volume injected.

3.1% OOIP. For both cycles, oil production at 40 °C is approximately the same, as shown in Figure 5. However, at 70 and 120 °C, the core plug flooded by SW3S brine produced approximately 0.7 and 1.2% OOIP more oil, respectively, compared to the core plug flooded with SW0S brine.

**3.3. Stevns Klint Chalk Plugs.** For comparison, two flooding tests were carried out with the Stevns Klint chalk cores. Both tests were carried out with the same injected fluid SW3S but with different compositions of water forming IWS. In the first test, the core was saturated with distilled water, after which IWS was established by flooding 7 pv of crude oil. The saturated core plug was then flooded with SW3S at 40 °C. This resulted in an oil recovery of 33.8% OOIP. As shown in Figure 6, the oil production at water breakthrough was 26.1% OOIP, and after water breakthrough, an additional 7.7% OOIP was produced. Increasing the temperature to 70 and 120 °C resulted in an additional production of 0.4 and 3.7% OOIP, respectively. Thus, the temperature played an important role in recovering more oil after water breakthrough in the Stevns Klint case, which is in accordance with most of the previous studies.<sup>5,22</sup>

In the second test, a core plug was saturated with the North Sea reservoir formation brine and then IWS was established by flooding with crude oil. Flooding was carried out with brine SW3S at 40 °C and resulted in an oil recovery of 34.6% OOIP. As shown in Figure 6, 8.9% OOIP was produced after water breakthrough. Increasing the temperature to 70 °C and then to 120 °C resulted in an additional production of 2.3 and 6.6% OOIP, respectively.

The effluent was analyzed for the three potential determining ions for both tests, and the concentration profiles are presented in Figure 7. In Figure 7a, at 40 °C, the concentration of all of the ions increases with time (because initial formation water is



**Figure 6.** SW3S brine injection in two Stevns Klint chalk core plugs without aging with distilled water and North Sea formation brine as initial water.

distilled), remains constant at 70 °C, and decreases at 120 °C. In Figure 7b, the calcium ion concentration decreases at 40 °C because the formation water already has a high calcium concentration compared to the injected brine SW3S. The reactivity trend of the rest of the ions at different temperatures is the same as for the first test.

#### 4. DISCUSSION

##### 4.1. Effect of Reactivity of Potential Determining Ions.

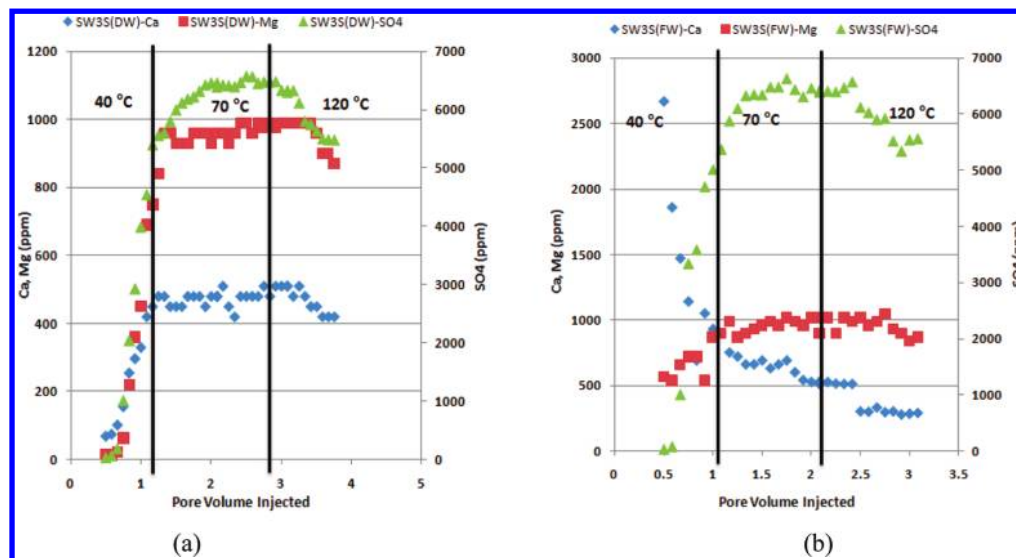
It has been established that seawater is an excellent injection

fluid for high-temperature chalk reservoirs because of the presence of potential determining ions  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ .<sup>22</sup> We have carried out all of the experiments at both low and high temperatures to investigate the potential of seawater flooding. We observed no increment in oil recovery with an increase in the temperature for both flooding sequences (with and without aging) for reservoir chalk sample 1L. On the contrary, experiments with the Stevns Klint outcrop chalk showed a very clear effect of the temperature. Increasing the temperature produced additional 4.1 and 5.2% OOIP oil for the first and second tests, respectively (see Figure 6). For another reservoir rock sample RE05, increasing the temperature resulted in an additional oil recovery of 2.2 and 3.1% OOIP during SW0S and SW3S brine flooding, respectively.

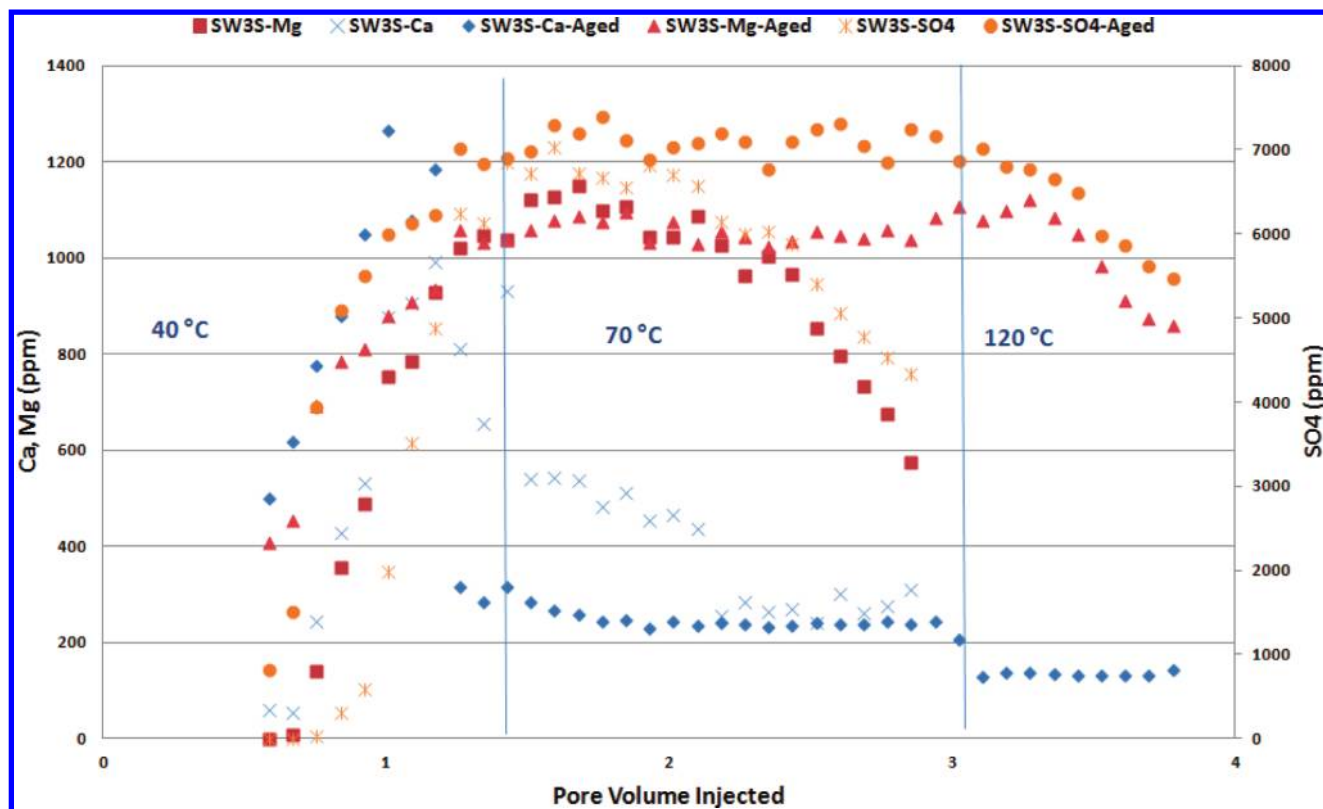
Strand et al.<sup>9</sup> mentioned reactivity of potential determining ions (rock–fluid interactions and symbiotic interactions between the three ions:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  or mutual affinity of the ions toward the rock) with the chalk surface as a necessary condition for improving the oil recovery. This reactivity increases with an increase in the temperature for reservoir (1L) and outcrop rock. Meanwhile, recovery in our experiments increased with the temperature only for reservoir rock RE05 and the outcrop chalk samples. The effect for the reservoir rock RE05 was considerably lower than for the outcrop chalk. No effect of the temperature on oil recovery was observed in the case of reservoir rock 1L.

One explanation of the observed difference might be that potential determining ions did not react in the same way with the reservoir chalk (1L) as with the Stevns Klint rock. However, Figures 2b, 3b, 7a, and 7b show that the reactivity trend of potential determining ions at different temperatures is the same for both rocks (1L and Stevns Klint). Thus, it is possible that, in some rock, the potential determining ions react with the internal porous surface, but this has no effect on the recovery. For such reservoir rocks, it is not the ion interaction that controls the oil recovery process. However, for other reservoir rocks, such as RE05, it could be the controlling mechanism of the oil recovery process.

In general, the concentration of all potential determining ions at high temperature decreases in the effluent. This decrease in



**Figure 7.** (a) Effluent ion concentrations during SW3S brine injection in Stevns Klint chalk core plugs with distilled water as initial water. (b) Effluent ion concentrations during SW3S brine injection in Stevns Klint chalk core plugs with North Sea formation brine as initial water.



**Figure 8.** Effluent ion concentrations during SW3S brine injection at different wetting conditions in North Sea chalk core plug (1L). Comparatively, a lesser loss of ions is observed in the case of aging.

the concentration could be because of high adsorption (Austad et al.<sup>7</sup> reported high adsorption of sulfate at high temperatures) or *in situ* precipitation of  $\text{CaSO}_4$ .

The lack of extra recovery at high temperatures in reservoir rock (1L) is not because of the low acid number of crude oil (see Table 2) because the same crude oil was used for all rock types (North Sea chalk samples and Stevns Klint). We think the reason belongs to the rock, but right now, it is difficult to explain the exact mechanism; therefore, we just reported this interesting observation.

Thus, according to the above analysis, the different temperature effect on the different rock samples cannot be explained by the reasons commonly discussed in the literature and needs further study.

**4.2. Reactivity of Potential Determining Ions and Effect of Aging.** Verification of the aging effect on recovery is achieved by a comparison of the flooding experiments with and without aging (see section 3.1.2). The concentrations of the effluent ions are plotted in Figure 8 for both flooding schemes. As shown in the figure, for injection of the SW3S brine, the ion interaction behavior is similar with and without aging but a lesser loss of ions is observed in the case of aging. This could be because the oil layer formed on the rock surface by aging hinders or prevents reaction. The results are similar for injection of SW0S (not plotted).

**4.3. Substitution Reaction.** Zhang et al.<sup>10</sup> reported an increase in the effluent calcium concentration during seawater flooding in Stevns Klint at temperatures above 100 °C. This effect was interpreted as a result of substitution of  $\text{Ca}^{2+}$  by  $\text{Mg}^{2+}$  ions on the internal rock surface. This substitution reaction is reported as a possible reason for an increment in oil recovery.

In our experiments, we did not observe this substitution reaction during SW3S flooding, with either Stevns Klint rock or the reservoir chalk (1L). Unexpectedly, an increase in the  $\text{Ca}^{2+}$  ion concentration was observed above 100 °C during SW0S flooding in reservoir chalk (1L) for both flooding sequences, but the mechanism of this is not clear.

#### 4.4. Effect of the Composition of Formation Brine.

The effect of the composition of the formation brine was studied and tested in the two experiments with the Stevns Klint core plugs. The IWS was formed by the distilled water for the first plug ( $\text{Sw}_i = 31.18\%$ ) and the reservoir brine for the second plug ( $\text{Sw}_i = 20.15\%$ ), as described in section 3.2. This significant difference in IWS shows that initial water composition also affect the displacement with crude oil. This was also observed in the case of reservoir core 1L (5% difference). For both tests with Stevns Klint plugs, the oil production at 40 °C is approximately the same, as shown in Figure 6. However, at 70 and 120 °C, the core plug initially saturated by formation brine produced approximately 2 and 3.2% OOIP more oil, respectively, compared to the core plug saturated with distilled water. This indicates that not only the injection brine composition but also different ions in the formation brine can increase the oil recovery at high temperatures. This difference in oil recovery may not be attributed to the difference in IWS, because if this was the reason, then there should be a difference in oil recovery at 40 °C also. At high temperatures, some ions in the formation water take part in improving the recovery, but how the different ions in formation brine affect the oil recovery is not yet clear. In the reservoir chalk (1L) case, high temperatures did not help to improve the oil recovery for the different compositions of the formation brine.



#### 4.5. Outcrop Chalk as a Substitute in Flooding Tests.

The outcrop rock was used in many studies as a model for reservoir rock because of easy availability and good rock characterization. We used both the reservoir and outcrop rocks for this study. Experimental results demonstrate that the oil recovery mechanism at high temperatures is different for the different rocks, although they have similar surface area and reactivity of potential determining ions. Enrichment of the brine by sulfate ions increased oil recovery under water-wetting conditions, but the comparatively less recovery increment was observed for the reservoir core plugs than for the Stevns Klint outcrop chalk. Recovery in the experiments with the outcrop chalk is strongly temperature-dependent.<sup>9</sup> Meanwhile, the experiments with the reservoir chalk rocks showed relatively less effect of the temperature compared to Stevns Klint in one case (RE05) and no effect of the temperature in another case (1L). This indicates that the rock may also determine whether the effect of the temperature on the recovery is observed. We also acknowledged that the much lower recovery at 40 °C for the outcrop (less than 35% OOIP) could contribute to its increased scope for further recovery at the higher temperatures compared to the reservoir core plugs (which had already established quite high recovery >50% at 40 °C). From many years, reservoir rock stayed with crude oil, temperature, and pressure, and this is not the case with outcrop rock. This could be the reason for the different responses of reservoir rock, especially with regard to temperature, compared to outcrop. Thus, care should be taken in using outcrop chalk as a model of reservoir chalk and, in particular, for the water-based improved oil recovery (IOR).

#### 5. CONCLUSION

(1) The temperature did not affect oil recovery in experiments with one reservoir rock sample and showed relatively less effect for another reservoir rock sample, while flooding of the Stevns Klint outcrop chalk rock was strongly affected by the temperature. (2) The interaction of different ions with rock depends upon the temperature; meanwhile, for the recovery, this is not always the case. This indicates that, in some rocks, the interaction of the ions with rock is not the main controlling factor for the oil recovery process. However, for other reservoir rocks, it could be the controlling parameter. (3) In two different flooding schemes (with and without aging of the core plug), the trend of the interaction of ions with reservoir rock remains the same but a comparatively smaller loss of ions was observed in the aged core. (4) Enrichment of the brine by sulfate ions increased oil recovery under water-wetting conditions, but the comparative recovery increment was less for the reservoir core plugs than for the Stevns Klint outcrop chalk. (5) No substitution of  $\text{Ca}^{2+}$  ions by  $\text{Mg}^{2+}$  ions was observed at high temperature for the Stevns Klint cores. (6) The initial brine composition showed an effect on oil recovery at high temperature for the outcrop chalk but not for the reservoir rock. (7) Care should be taken in using outcrop chalk as a model of reservoir chalk and, in particular, for the water-based IOR. Salinity-based enhanced oil recovery (EOR) needs to be checked in each particular case of rock.

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#### Notes

The authors declare no competing financial interest.

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