Condition for Low Salinity EOR-Effect in Carbonate Oil Reservoirs

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ABSTRACT

Low salinity EOR-effects have for a long time been associated with sandstone reservoirs containing clay minerals. Recently, a laboratory study showing low salinity EOR-effects from composite carbonate core material was reported. In the present paper, the results of oil recovery by low salinity water flooding from core material sampled from the aqueous zone of a limestone reservoir are reported. Tertiary low salinity effects, 2-5\% of OOIP, were observed by first flooding the cores with high saline formation water (208 940 ppm) and then with 100x diluted formation water or with 10x diluted Gulf seawater at 110 °C. It was verified by flooding the core material with distilled water that the core samples contained small amounts of anhydrite, CaSO\textsubscript{4}(s). The oil recovery was tested under forced displacement using different injection brines and oils with different acid number, 0.08, 0.34, and 0.70 mgKOH/g. The low salinity effect depended on mixed wet conditions, and the effect increased as the acid number of the oil increased. No low salinity effect was observed using a chalk core free from anhydrite. The chemical mechanism for the low salinity effect is discussed, and in principle, it is similar to the wettability modification taking place by seawater described previously.

In field developments, the oil reservoir is normally flooded with the most available water source. For offshore reservoirs, this means seawater or modified seawater. Thus, a relevant question addressed in this paper is: “Can diluted seawater act as a low saline EOR-fluid after a secondary flood with seawater?” Previous experiments have shown that both spontaneous imbibition and forced displacement tests using chalk cores, which were free from sulfate, did not show low salinity EOR-effect when exposed to diluted seawater. This paper shows that if anhydrite is present in the rock formation that diluted sea water or diluted produced water can act as an EOR injectant to improve recovery over that achieved with high salinity brines.

INTRODUCTION

Large carbonate oil reservoirs, both in the North Sea and in the Middle East, are today flooded with seawater to achieve sufficient recovery to justify the substantial developments costs. Sea water is used to maintain reservoir pressure and sweep oil to the producing wells. Historically, microscopic displacement efficiency has not been routinely optimized in the development stage. It is well documented in the literature, that laboratory studies show that seawater can modify the wetting condition in a favorable way to increase the oil recovery from high temperature oil reservoirs, T\textsubscript{res}>70-80 °C.\textsuperscript{1-4} The chemical mechanism for the increase in water wetness using seawater has been discussed, and the sulfate in seawater appeared to act as a catalyst for desorbing carboxylic material from the carbonate surface.\textsuperscript{1}
Recently, it has been shown that seawater can be modified to act as an even “smarter” EOR-fluid than ordinary seawater:

- Seawater depleted in NaCl was able to increase the oil recovery by 10% of original oil in place, OOIP, compared to ordinary seawater.\(^5\)
- Seawater depleted in NaCl and spiked with sulfate increased the oil recovery by 15-20% of OOIP compared to seawater depleted in NaCl.\(^5\)

The improved oil recovery observed by decreasing the NaCl concentration in seawater is related to a decrease in the non-active ions in the ionic double layer at the carbonate surface, which allow better access of the active ions (Ca\(^{2+}\), Mg\(^{2+}\), and SO\(_4^{2-}\)) to the surface. Both the imbibing rate and the ultimate oil recovery from displacement tests, increased.

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

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

In sandstone reservoirs, EOR-effects by low salinity water flooding have been well documented both in the laboratory and by field tests.\(^8,9\) Even though, it is in general agreement that the increased oil recovery by low saline waterflooding is related to wettability modification towards a more water-wet system, the detailed mechanism is still under debate.\(^10-12\) Recent studies have indicated that organic material adsorbed onto clay minerals are desorbed due to an increase in pH as active ions, especially Ca\(^{2+}\), are desorbed from the clay as the low saline water invades the porous medium.\(^13,14\)

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

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

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

Outcrop chalk: Outcrop chalk from Stevns Klint was used as a reference core material without presence of anhydrite. The chalk material is very homogeneous and consists of pure CaCO$_3$ (>99%). The properties of the core used are summarized in Table 1.

Crude Oils: Stock tank crude oil was centrifuged at room temperature to remove water and solid particles and then filtered through a 0.65 µm Millipore filter. The acid and base numbers, AN and BN, of the filtrated oil, termed Oil A, were determined by a modified version of ASTM D664 and ASTM D2896. The Oils B and C were prepared by mixing Oil A with crude Oil D of high AN, ≈ 1.8 mg KOH/g. The properties (AN, BN, density, and viscosity) of all the oils used are listed in Table 2.

Brines: Synthetic brines were made from DI water and reagent salts. The composition of the brines is listed in Table 3. The terminology is as follows: FW is formation water, and GSW is Gulf seawater.

Core Preparation: All the limestone cores were first flooded with toluene and then with heptane. DI water was then injected to remove FW. To minimize the dissolution of anhydrite, DI water was injected at high rate, keeping the injection volume as low as possible, ≈3 PVs. All the cores were dried at 90°C to constant weight. The chalk core was initially flooded with DI water to remove precipitated salts, especially sulfate (about 5 PVs). The effluent was tested with BaCl$_2$ solution. Then, the core was dried at 90°C to a constant weight.

Core Saturation: The initial water saturation, $S_{wi}$, ≈10%, was established by the porous plate technique using water saturated nitrogen. Then, the cores were evacuated, saturated and flooded with 2PVs of oil in each direction at 50°C. Finally, the cores were aged in the selected crude oil for 2 weeks at 90°C.

Oil Displacement: Forced displacements were performed at 110°C (the reservoir temperature for the sourced limestone core material) with a back pressure of 10 bars. The injection rate was kept constant in all the tests, 0.01 ml/min or about 1 PV/day. Spontaneous imbibition tests were performed at the same temperature, 110°C, in a sealed steel cell. The cell was connected to a supporting pressure cell of ~10 bars.

Verification of Anhydrite: The presence of anhydrite was confirmed after the oil displacement tests. The core was cleaned by flushing with toluene and methanol, dried, saturated with FW, and aged in the core holder for one day at 110°C. DI water was then injected through the core at the same temperature with a rate of 0.01 ml/min, and samples from the effluent were analysed for Ca$^{2+}$ and SO$_4^{2-}$.

Chemical Analysis: The ionic concentrations of Ca$^{2+}$ and SO$_4^{2-}$ were analyzed by an ion-exchange chromatograph, ICS-3000 Reagent-free™ produced by Dionex Corporation, USA.

RESULTS
The limestone core material used was sampled from the aqueous zone of an oil reservoir. The cores appeared very homogenous with a permeability in the range of 0.5-1.0 mD and porosity of about 17%. The formation water was of high salinity, 208940 ppm, and the low acid number crude Oil A appeared to have relevant properties of the oil present in the reservoir. In our parametric studies, Oil A was mixed with a crude Oil D of higher acid number to obtain Oil B and C. The viscosity of the three oils was quite similar, about 4 cP at 20 °C, and the base number varied between 0.34 to 0.45 mg KOH/g. The AN of the crude is regarded as the most important parameter determining the wetting properties of carbonates, and the AN is varied from 0.08 to 0.70 mg KOH/g for Oil A and C, respectively. **Table 2.** The difference in the wetting behavior between the low AN crude Oil A and the high AN crude Oil C is clearly illustrated by **Fig. 1** showing spontaneous imbibitions of formation water, FW, into the cores saturated with oil of low and high AN, core 16A and 11B, respectively. Thus, the limestone cores became less water wet as the AN of the crude oil present in the core increased.

**Tertiary low salinity EOR-effect using diluted FW.**

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

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

**Core 6B:** This core was also saturated with Oil C, but in this case, the core was flooded first with FW and then diluted FW at 90 °C, i. e. the same as the aging temperature. The flooding temperature was decreased in order to increase the dissolution of anhydrite present in the matrix. The dissolution of anhydrite increases as the temperature decreases. Sulfate is a catalyst for the wettability alteration process, and it is important to have a maximum concentration of sulfate dissolved in the brine. As noticed by **Fig. 3a,** the amount of oil produced in the secondary flood with FW was very comparable to the first test at 110 °C. The tertiary low salinity response was also in the same range. The differential pressure over the core also decreased as the low salinity brine mobilized more oil, **Fig. 3b.**
Both tests confirmed that limestone cores containing anhydrite will respond to a low saline flood in a similar way to clay containing sandstones. In order to verify that the carbonate core contained anhydrite, a similar test was performed using an outcrop chalk sample, which was carefully depleted in sulfate by flooding the core with distilled water prior to core preparation.

**Outcrop Chalk Core F1:** The chalk core was saturated with the high AN crude Oil C, and the test procedure was exactly the same as for Core 5B. The secondary oil recovery by FW was about 57% of OOIP, and no extra oil was recovered during the flood with 100x diluted FW, Fig. 4. Thus, carbonates without sulfate initially present in the formation, usually as anhydrite, do not show improved oil recovery in response to a salinity gradient in the injected fluid.

**Tertiary low salinity EOR-effect using diluted GSW.**

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

**Core 18C:** The core was saturated with Oil C, AN=0.70 mg KOH/g, and flooded first with FW and then with 10x diluted GSW in a tertiary process at 110 °C, Fig. 5. The oil recovery by FW was 46% of OOIP, and the diluted GSW increased the recovery to 50%, i.e. a low salinity effect of about 4% of OOIP, which was comparable to the effect using 100x diluted FW, Fig. 2a.

After the oil displacement test, the presence of anhydrite in core 18C was verified according to the method described in experimental section, Fig. 5b. The concentration of Ca^{2+} and SO_{4}^{2-} became constant after displacing the FW with DI-water. The concentration of Ca^{2+} was significantly higher than the concentration of SO_{4}^{2-}, which can be related to dissolution of calcite in addition to anhydrite.

**Core 12C:** This core was subjected to a similar test, but in this case, Oil B with lower acid number, AN=0.34 mg KOH/g, was used. As expected, the core became more water wet, and the secondary recovery by FW was about 63% of OOIP, Fig. 6. The low salinity response on the oil recovery was very small. Obviously, the initial wetting condition will have impact on the potential of extra oil by using a low saline fluid. The presence of dissolvable anhydrite appeared to be small as indicated by the low concentration of sulfate in the effluent, nearly 10 times lower that for Core 18C, Fig. 6b.

**Core 4B:** The core was saturated by Oil A with a very small amount of acidic material, AN=0.08 mg KOH/g. The core was flooded at 110 °C, first with GSW, and then with 10x diluted GSW. A completely piston like displacement was observed with GSW, and the recovery was about 53% of OOIP, Fig. 7. A strongly water-wet core does not give optimal oil recovery by water flooding due to capillary trapped oil by “snap-off”. The low salinity response with diluted GSW was, as expected, very small.
DISCUSSION
The observed tertiary low salinity EOR-effect was rather small probably due to the small amount of dissolvable anhydrite initially present in the core material. During the core preparation, the cores were flooded with a few pore volumes of DI-water to remove formation water. Some anhydrite may be lost during this operation. Furthermore, the concentration of sulfate in the effluent decreased rapidly when flooding with FW, from 0.7 to 0.2 mM, even though the flooding rate was slow, Fig. 2c. At a higher concentration of dissolvable anhydrite in the rock material, equilibrium between ions and rock would be established, and the concentration of sulfate in the effluent should be constant. Among the cores tested for anhydrite, core 18C appeared to contain most anhydrite. The concentration of sulfate in the effluent when flooding with DI-water at 110 °C stabilized at 1.0 mMole/l, Fig. 5b. To test the potential of low salinity effect in cases with low content of anhydrite present in the rock matrix, it is recommended not to flood the cores with DI-water prior to core preparation.

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

\[
\text{CaSO}_4(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \leftrightarrow \text{Ca}^{2+}(ad) + \text{SO}_4^{2-}(ad) \quad (1)
\]

\text{Ca}^{2+}(aq) \text{ and } \text{SO}_4^{2-}(aq) \text{ are ions dissolved in the pore water, and } \text{Ca}^{2+}(ad) \text{ and } \text{SO}_4^{2-}(ad) \text{ are ion adsorbed onto the carbonate surface. According to the previously reported study, where the impact of sulfate on the initial wetting conditions was studied, the concentration of } \text{SO}_4^{2-}(aq) \text{ appeared to be the key factor determining the wetting properties.}^7 \text{ Dissolution of anhydrite, } \text{CaSO}_4(s), \text{ which is the source for } \text{SO}_4^{2-}(aq), \text{ is dependent on the salinity/composition of the brine and the temperature in the following way:}

- The solubility increases as the concentration of Ca\(^{2+}\) in FW decreases (common ion effect).
- The solubility decreases as the concentration of NaCl decreases.
- The solubility normally decreases as the temperature increases.
- The concentration of \(\text{SO}_4^{2-}(aq)\) may also decrease as the temperature is increased due to increased adsorption onto the carbonate surface, i.e. the concentration of \(\text{SO}_4^{2-}(ad)\) increases.

The efficiency of the wettability alteration process is also dependent on the temperature and the concentration of non-active salt, NaCl in the following way:

- Imbibition rate and ultimate oil recovery increase as the temperature increases.
- Imbibition rate and ultimate oil recovery increase as the concentration of non-active salt, NaCl, in the imbibing brine decreases.

Thus, both the effect of the temperature and the concentration of NaCl are in conflict, i.e. the concentration of \(\text{SO}_4^{2-}(aq)\) decreases as the temperature increases, but the surface reactivity leading to the wettability alteration increases as the temperature increases. Similarly, the concentration of \(\text{SO}_4^{2-}(aq)\) decreases as the amount of NaCl decreases, but the surface reactivity promoting wettability alteration increases. Therefore, for a carbonate system, there appears to be an optimum temperature window for observing maximum low salinity effect, probably between 90-110 °C.
The dissolution of CaSO$_4$(s) in FW, 10x, and 100x diluted FW versus temperature was modeled using the OLI software, which is a thermodynamic model, Fig. 8. As expected, the solubility of anhydrite in the diluted FW is higher than in ordinary FW, but the difference became smaller as the temperature is increased beyond 100 °C. The solubility of anhydrite in 100x diluted FW is lower than in 10x diluted FW. Knowing that the dissolution of anhydrite is dependent on the concentration of Ca$^{2+}$ (common ion effect) and the concentration of NaCl in the opposite way, it is natural that at some stage of dilution of FW, the dissolution of anhydrite is reversed.

The calculated equilibrium concentration of sulfate versus temperature, when 10x and 20x diluted GSW was exposed to anhydrite, is shown in Fig. 9. The concentration of sulfate is increased significantly due to dissolution of anhydrite. By comparing the amount of SO$_4^{2-}$(aq) at 110 °C for 100x diluted FW and 10x diluted GSW, the values are about 0.002 and 0.006 mole/l, respectively. According to Fig. 2a and Fig. 5a, the tertiary low saline EOR-effect was quite similar for the two cases. The reason may be the difference in the salinity. The concentration of NaCl in 100x diluted FW is 0.026 mole/l compared to 0.059 mole/l in 10x diluted GSW, i.e. a factor of about 2. May be 20x diluted GSW would be an even “smarter” low salinity injection water?

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

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

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

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

CONCLUSIONS

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

ACKNOWLEDGMENT
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REFERENCES
113976 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, OK, USA, 2008.


### Table 1. Limestone core characterization summary

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<th>Core ID</th>
<th>L (cm)</th>
<th>D (cm)</th>
<th>Φ (%)</th>
<th>k (mD)</th>
<th>S_{wi} (%)</th>
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### Table 2. Oil Properties

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<th>Oil Name</th>
<th>AN mgKOH/g</th>
<th>BN mgKOH/g</th>
<th>Density g/cm³ @20 °C</th>
<th>Viscosity cP @20 °C</th>
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### Table 3. Composition and properties of the brines used in this study

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<th>Ions</th>
<th>FW mole/l</th>
<th>GSW mole/l</th>
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<td>Cl⁻</td>
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<td>IS, mole/l</td>
<td>4.158</td>
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Fig. 1. Spontaneous imbibition on the limestone cores 16A and 11B saturated with low acidic crude Oil A and high acidic crude Oil C, respectively. Imbibing brine: FW, Test temperature: 110°C, $S_w=0.10$. 
Fig. 2a. The Core 5B was flooded by FW and 100× diluted FW at 110 and 70 °C. Injection rate: 0.01 cc/min. AN ≈ 0.70 mgKOH/g.

Fig. 2b. The differential pressure over the core decreased as the diluted FW remobilized oil.

Fig. 2c. Concentration of SO$_4^{2-}$ in the effluent vs. injected PV
Fig. 3a. Demonstration of low salinity effects in core 6B. The core was flooded by FW and 100× diluted FW at 90°C. Injection rate: 0.01 cc/min. AN≈ 0.70 mg KOH/g.

Fig. 3b. The differential pressure over the core decreased as the diluted FW remobilized oil.

Fig. 4. The chalk core F1 was flooded by FW and 100x diluted FW at 110°C. Injection rate: 0.01 ml/min. AN≈ 0.70 mg KOH/g.
Fig. 5a. Low salinity effects in limestone 18C. The core was flooded by FW and 10× diluted GSW at 110°C. Injection rate: 0.01 ml/min. AN≈ 0.70 mg KOH/g.

Fig. 5b. The presence of anhydrite was confirmed by injecting DI water at 110°C into FW saturated core. Injection rate: 0.01 ml/min.
Fig. 6a. Low salinity effects in core 12C. The core was flooded by FW and 10× diluted GSW at 110°C. Injection rate: 0.01 ml/min. AN ≈ 0.34 mg KOH/g.

Fig. 6b. The presence of anhydrite was tested by injecting DI water at 110°C into FW saturated core. Injection rate: 0.01 ml/min.

Fig. 7. A very small low-salinity effect on the core 4B flooded by GSW and 10× diluted GSW at 110°C. Injection rate: 0.01 cc/min. AN ≈ 0.08 mg KOH/g.
Fig. 8. Dissolution of CaSO₄ when exposed to FW, 10×, and 100× diluted FW at different temperatures as modeled by the OLY software. Pressure: 10 bars

Fig. 9. The concentration of sulfate when anhydrite was exposed to 10 times diluted GSW, as modeled by the OLY software. Pressure: 10 bars.