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Water-Based Enhanced Oil Recovery (EOR) by "Smart Water" in Carbonate Reservoirs

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ABSTRACT

Water chemistry has a profound effect on the stability of the water film and desorption of organic oil components from the mineral surfaces in a water-based enhanced oil recovery (EOR) process. By knowing the chemical mechanism for the symbiotic interaction between the active ions in seawater; Ca^{2+} , Mg^{2+} , and SO_4^{2-} , "Smart Water" can be designed and optimized in terms of salinity and ionic composition as an EOR—fluid. In the present study, the efficiency of "Smart Water" on oil recovery in carbonate rock is summarized and discussed in the temperature range of 70–120 °C. By removing non-active salt, NaCl, from the composition of the injected seawater, the oil recovery by spontaneous imbibition was improved by about 5–10% of OOIP compared to seawater. On the other hand, an increase in the concentration of NaCl in the imbibing fluid resulted in reduced oil recovery of 5% of OOIP. A systematic decrease in oil recovery was observed when diluting seawater with distilled water to obtain a low salinity brine, 1000–2000 ppm. The decrease in the oil recovery was attributed to the reduced concentration of the active ions. When seawater depleted in NaCl was spiked by SO_4^{2-} , the oil recovery increased by about 5 to 18% of OOIP compared to seawater depleted in NaCl. The amount of Ca^{2+} in the seawater depleted in NaCl had no significant effect on the oil recovery at low temperatures, ≤ 100 °C, but improvements were observed at higher temperatures. The wetting condition after spontaneous imbibition of seawater, seawater depleted in NaCl, and seawater depleted in NaCl spiked with sulfate was monitored using a chromatographic wettability test, and it showed an increasing order in the water-wet fraction, in line with increased oil recovery. The results were discussed in terms of the previously suggested mechanism and the effect of the ionic double layer at the rock-brine interface.

Keyword: Water-Based Enhanced Oil Recovery (EOR), "Smart Water", Low Salinity, Carbonate Reservoirs, Wettability Alteration, Initial Wetting Condition

INTRODUCTION

Understanding the wetting condition is crucial for optimizing oil recovery from carbonate reservoirs. The wetting preference influences many aspects of reservoir performance, particularly in water flooding and enhanced oil recovery (EOR)

processes. Carbonate reservoirs are generally characterized as mixed-wet to preferentially oil-wet systems with wetting heterogeneity (Chilingar and Yen, 1983; Treiber et al., 1972). This wetting characteristic along with fractures results in poor displacement efficiency and low ultimate oil recovery (Allan and Sun, 2003; Manrique et al., 2007). Enhanced oil recovery techniques by wettability alteration are designed to overcome the capillary forces that trap the oil in the reservoir (Gupta and Mohanty, 2011; Puntervold, 2008). The focus is either to alter the wetting preference of the formation or to decrease the interfacial tension between the fluids, which can change the capillary forces in a favorable way (Hammond and Unsal, 2009; Morrow, 1990; Salehi et al., 2008).

Several publications have reported the role of the initial wetting condition on many aspects of reservoir performance, particularly in water flooding and enhanced oil recovery techniques. Extensive measurements from a wide spectrum of wetting conditions have indicated that optimum wetting condition for oil recovery by water flooding is neutral-wet to weakly water-wet condition (Austad et al., 2011b; Fernø et al., 2011; Fernø et al., 2010; Jadhunandan and Morrow, 1995; Jerauld and Rathmell, 1997; Morrow and Buckley, 2011; Skrettingland et al., 2011). The adsorption of polar crude oil components on mineral surfaces has a profound effect on its wetting behavior. The mechanisms by which crude oil components may adsorb on high energy mineral surfaces include polar, acid/base, and ion-binding interactions. Surface precipitation of asphaltic material can further alter surface wetting (Buckley, 1996; Buckley and Liu, 1998; Buckley et al., 1998). The mixed-wet or oil-wet character of the carbonate reservoir can be ascribed to the adsorption of negatively charged carboxylic materials from the crude oil onto the positive sites of a calcite surface (Legens et al., 1999; Thomas et al., 1993). Therefore, the carboxylic material, quantified as the total acid number, AN, is an important wetting parameter for carbonates (Standal et al., 1999a; Standnes and Austad, 2000; Xie et al., 2010; Zhang and Austad, 2005). The basic material in crude oils has a minor effect on wetting properties, but it was observed that the presence of natural basic material increased the water wetness of chalk, probably due to the formation of acid-base complexes in the crude oil, which prevents the acid from adsorbing onto the carbonate surface (Puntervold et al., 2007). The acidic components extracted from crude oils with different total acid numbers are compared based on interfacial activity and potential to alter wetting on silicate surfaces (Akhlaq et al., 1996; Barth T., 2004; Hoeiland et al., 2001; Standal et al., 1999b). The results of interfacial tension, contact angle experiments, and wettability analyses indicate that the acid structures or types may be more important than the concentrations of acid in the oils (Fathi et al., 2011a; Fathi et al., 2010b).

The wettability alteration by seawater is described as a symbiotic interaction between the potential determining ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} and the adsorbed carboxylic material on the carbonate surface (Strand et al., 2008; Zhang et al., 2007). It is suggested that sulfate present in seawater will adsorb onto the positively charged water-wet sites on the chalk surface and lower the positive surface charge. Due to less electrostatic repulsion, excess of Ca^{2+} will be localized close to the chalk surface. Then, Ca^{2+} can react with adsorbed carboxylic groups bonded to the chalk surface and release some of the organic carboxylic material (Zhang and Austad, 2006; Zhang et al., 2007). At high temperatures, Mg^{2+} can substitute Ca^{2+} and also Ca^{2+} linked to carboxylic groups on the chalk surface (Strand et al., 2006a; Zhang and Austad, 2006; Zhang et al., 2006; Zhang et al., 2007). The reactivity of these ions towards the carbonate surface is depending on the chemical activity in the double layer close to the surface. Both the size and the nature of the double layer are related to salinity and composition of the aqueous phase.

Wettability alteration by water-based enhanced oil recovery (EOR) controls desorption of the crude oil from the rock surface through ionic interactions at the rock surface in the molecular level. In the present study, “Smart Water” is defined as an enhanced oil recovery fluid with an optimal ionic composition and salinity, which can act as a wettability modifier in carbonate reservoirs. Several critical parameters can influence the wettability alteration process including ionic composition

of the injected brine, the chemistry of crude oil, temperature, the mineralogy of the rock surface, and initial wetting state. The present study discusses the following objectives with regard to “Smart Water”: a) effect of mono—valents (NaCl) and salinity, b) effect of divalents, c) optimal ionic composition and optimal salinity, d) the effect of temperature, and e) effect of total acid number (AN) or initial wetting state.

EFFECT OF MONO-VALENTS AND SALINITY

The effect of mono—valents (NaCl) was investigated by adjusting the concentration of NaCl (0, 1, and 4× SW salinity), while keeping the concentration of the active potential determining ions, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , constant and equal to the concentration in seawater (Fathi et al., 2010a; Fathi et al., 2011b). Neither Na^+ nor Cl^- is regarded as potential determining ions toward the chalk surface, which means that these ions are not part of the inner Stern layer (Pierre et al., 1990). The ions are, however, active in the double layer and may have influence on the access of the active ions, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , to the chalk surface. This was studied by comparing the imbibition of modified SW, i.e. SW depleted in NaCl (SW0NaCl) and SW spiked 4 times with NaCl (SW4NaCl), with original SW at the different temperatures. Thus, the concentration of the active ions was kept constant. The results from the spontaneous imbibition tests at 100, 110 and 120 °C are shown in Figures 1–3, respectively. Spontaneous imbibition experiments indicate the oil recovery increases as the concentration of NaCl in the seawater decreases. At 100 °C, Figure 1, the imbibition rate was low, and the oil recovery after 50 days was in the range of 35–45%. While the oil recovery by SW0NaCl was about 45% of OOIP, the imbibition of SW4NaCl gave an ultimate recovery of 35% of OOIP.

At 110 °C after 80 days, the difference in oil recovery between SW and SW0NaCl was about 15%, Figure 2. The plateau recovery for the fluid depleted in NaCl (SW0NaCl) was 60%.

The same trend in recovery was observed at 120 °C, Figure 3. Note that 70% of OOIP was recovered by using seawater without NaCl present, which is a very high recovery by spontaneous imbibition for a Stevns Klint core. The imbibition rate was also very fast, and plateau recovery was reached within 15 days. SW spiked 4 times with NaCl (SW4NaCl) resulted in about 7% low ultimate oil recovery compared to SW.

The surface reactivity of Ca^{2+} , Mg^{2+} and SO_4^{2-} increases as the temperature increases as discussed in detail in previous papers (Strand et al., 2006a; Zhang and Austad, 2006). As the affinity of SO_4^{2-} toward the chalk surface increases, more Ca^{2+} is adsorbed due to less electrostatic repulsion. Mg^{2+} is even able to displace Ca^{2+} from the rock. Thus, increased concentration of NaCl will probably decrease the ability of the active ions, Ca^{2+} , Mg^{2+} , and SO_4^{2-} , to get in contact with the positively charged chalk surface to release the adsorbed carboxylic material due to the double layer effect. The effect of NaCl is illustrated with respect to the previously suggested mechanism (Zhang et al., 2007) in Figure 4. Due to the positive charge of the chalk surface in the presence of high saline formation water containing potential determining ions like Ca^{2+} and Mg^{2+} , a lot of Na^+ and Cl^- will be present in the double layer due to the high concentration of NaCl. If the cations in the double layer mainly consisted of Ca^{2+} and Mg^{2+} , they would have much better access to the rock surface. The same is the case for SO_4^{2-} . If the concentration of Cl^- in the double layer is decreased, SO_4^{2-} would have better access to the surface. Thus, due to the change in the composition of the double layer by depleting the seawater for NaCl, both imbibition rate and oil recovery are increased.

The chemical mechanism for wettability modification is different for the carbonate and sandstone reservoirs (Austad et al., 2011a; RezaeiDoust et al., 2009; Yousef et al., 2011). This is also confirmed in the present study. In two parallel tests, SW was diluted by distilled water to 1600 ppm (dSW1600) and imbibed into mixed wet chalk cores at 120 °C as shown by Figure 3. The oil recovery was very low, around 15 % of OOIP. The reason for the low recovery is the decrease in the concentration

of the active ions, which change the wetting properties. Similarly, oil recovery also decreased when diluting SW to 10000 and 20000 ppm (dSW10000 and dSW 20000) by distilled water as shown by Figure 2. A summary of the oil recovery by spontaneous imbibition of modified SW at different salinities and ionic compositions at 100, 110 and 120 °C is shown in Figures 5 and 6. Removing NaCl from the composition improves the oil recovery factor while diluting seawater to obtain lower salinities brines has a negative impact, and it decreases the recovery factor significantly.

When using formation water as the imbibing fluid, the oil recovery from the cores was systematically low, about 10% of OOIP, Figure 2 and 3. Due to the lack of SO_4^{2-} in the formation water, it is not able to induce wettability modification during the imbibing process (Zhang et al., 2007). The oil recovery is therefore related to capillary forces and initial wettability conditions resulting from the polar components in the crude oil.

The main conclusion from these observations is that not only the concentration of the active ions Ca^{2+} , Mg^{2+} and SO_4^{2-} is important for wettability alteration to take place, but also the amount of non-active salt like NaCl has an impact on the wettability alteration, which is discussed as a double layer effect at the chalk surface. The temperature plays a very important role for the chemical reactions taking place at the chalk surface and for the diffusion of active ions (Ca^{2+} , Mg^{2+} and SO_4^{2-}) into the chalk matrix. At high temperatures, the effect of wettability modification using seawater and modified seawater became even more significant with regard to oil recovery.

The change in the wetting condition by using modified SW as imbibing fluid was verified by the chromatographic wettability test (Strand et al., 2006b). The initial wetting condition of the cores saturated with the crude oil was determined, WI, to be 0.53, which is a neutral condition. Chromatographic wettability tests for the cores after spontaneous imbibition at 110 °C using dSW10000, SW, and SW0NaCl were determined accordingly. The corresponding water-wet fractions were 0.64, 0.52 and 0.82, respectively, Figure 7. Using SW as the imbibing fluid, the water-wet area was increased by 11%. The diluted seawater (dSW10000) did not increase the water-wet area at all. Seawater depleted in NaCl (SW0NaCl) appeared to have the greatest effect on the wetting properties by increasing the water-wet area by 29%.

EFFECT OF DIVALENTS AND OPTIMAL IONIC COMPOSITION

The concentration of the active ions is a very crucial parameter for the wettability alteration by “Smart Water”. In a new set of experiments the effect of the active ions, especially SO_4^{2-} and Ca^{2+} , on the displacement efficiency of the imbibing fluid was investigated. The non-active salt, NaCl, was initially removed from the seawater, and the objective was to optimize the concentration of Ca^{2+} and SO_4^{2-} . The amount of carboxylic materials in crude oil, AN and BN, influences the wetting condition of the carbonate reservoir (Fernø et al., 2010; Xie et al., 2010; Zhang and Austad, 2005). To study a wide range of the initial wetting conditions, two types of crude oils with different concentration of polar components, AN and BN, were used: a) Oil-A with AN=2.0, BN=0.5 mgKOH/g, b) Oil-B with AN=0.5, BN=0.3 mgKOH/g. Variation of aging time of a core in crude oil is a viable parameter of obtaining systematic change in wettability (Zhou et al., 1995; Zhou et al., 2000). For the displacement studies at high temperatures, 100–120 °C, the cores were saturated with Oil-A and aged for 8 weeks. To study the displacement efficiency at lower temperatures, 70–90 °C, the cores were saturated with Oil-B and aged for 4 weeks. Oil displacement studies in outcrop chalk samples by spontaneous imbibition were performed at temperature ranges of 70 to 120 °C using different imbibing fluids. The results are discussed in terms of the displacement efficiency during spontaneous imbibition and wetting alteration.

The results from the spontaneous imbibition studies using Oil-B at 70 and 90 °C are shown in Figures 8 and 9, respectively. At 70 °C, the oil recovery by spontaneous imbibition of SW into the chalk core was about 38 % of OOIP,

Figure 8. The recovery increased to 45% of OOIP when SW0NaCl was used as the imbibing fluid. When the concentration of sulfate in SW0NaCl increased (SW0NaCl-4SO₄²⁻) the oil recovery at the production plateau was increased to 50 % of OOIP.

At 90 °C, the oil recovery by spontaneous imbibition of the formation brine, FB, into the core was about 17% of OOIP, indicating mixed-wet condition, Figure 9. The oil recovery increased to 38% of OOIP when using SW as the imbibing fluid. Seawater depleted in NaCl (SW0NaCl) resulted in the oil recovery of 47% of OOIP at the plateau. When SW0NaCl was spiked by sulfate (SW0NaCl-4SO₄²⁻), the oil recovery increased to 62% of OOIP. Compared to ordinary SW, the rate of imbibition was improved when removing NaCl and spiking the fluid with sulfate, which is in line with increased concentration of active ions in the double layer at the chalk surface.

The results of the spontaneous imbibition tests using Oil-A after 60 days at 100 and 120 °C are shown in Figure 10 and 11, respectively. The cores were saturated with Oil-A with AN=2.0 mg KOH/g, and aged for 8 weeks to establish a neutral to preferentially oil-wet condition. This was also reflected in the lower oil recovery by spontaneous imbibition.

At 100 °C, spontaneous imbibition by SW0NaCl-4SO₄²⁻ increased the oil recovery by 18% of OOIP compared to the seawater depleted in NaCl, SW0NaCl. The amount of Ca²⁺ in the seawater depleted in NaCl (SW0NaCl-4Ca²⁺) had no significant effect on the oil recovery at 100 °C, Figure 10. The oil recovery, either by SW0NaCl or SW0NaCl-4Ca²⁺, was very low, about 11% of OOIP, which is in line with very low water wetness.

At 120 °C, the seawater depleted in NaCl spiked by sulfate (SW0NaCl-4SO₄²⁻) resulted in an extra oil recovery of 14% of OOIP compared to SW0NaCl, Figure 11. The oil recovery at the plateau using SW0NaCl as the imbibing fluid was about 33% of OOIP. Increasing the Ca²⁺ concentration in the imbibing fluid had a marginal effect on oil recovery, about 4% of OOIP, confirming that Ca²⁺ also is active in the wettability alteration process. In all the experiments, the rate of imbibition was improved when spiking the fluid with sulfate.

The potential of the different imbibing fluids, FB, SW, SW0NaCl, and SW0NaCl-4SO₄²⁻, to change the wetting properties of chalk was quantified by determining the water-wet fraction of the rock surface after the spontaneous imbibition process at 90 °C. The water-wet fraction of the core after the imbibition by formation brine at 90 °C was calculated to be, WI=0.44. No wettability alteration is supposed to take place during the oil displacement process by formation brine and the water-wet fraction is directly related to the initial wetting condition resulting from the adsorption of the polar components on the positively charged rock surface. Considering the wetting index of the neutral wetting condition is 0.5, the value of 0.44 corresponds to a preferentially oil-wet condition. Similarly, the water-wet fraction of the rock surface after imbibition by SW, SW0NaCl and SW0NaCl-4SO₄²⁻ was calculated to be 0.52, 0.56, and 0.6, respectively. The wetting indexes, WI, and the oil recovery after spontaneous imbibitions with the different fluid are shown in Figure 12. It is seen that the oil recovery correlates very well with the water-wet fraction. As the water-wet fraction of the rock surface increases from 0.44 to 0.6, the oil recovery increases from 17% to 62% of OOIP.

CONCLUSIONS

- “Smart Water” can be designed and optimized both with regard to salinity and ionic composition to act as an improved wettability modifier in a water-based EOR process in carbonates.
- The imbibition rate and the ultimate oil recovery increased relative to seawater when seawater was depleted in NaCl. The effect was more significant at high temperatures. A decrease in oil recovery was observed when increasing the NaCl concentration.

- Using diluted seawater as the imbibing fluid, the oil recovery decreased drastically. The oil recovery by seawater diluted to 1600 ppm at 120 °C was in the range of 15%, while the recovery by seawater was about 60% of OOIP. Thus, the wettability alteration is not a low salinity effect.
- The concentration of sulfate had the largest effect on oil recovery. When the concentration of SO_4^{2-} was increased four times in the seawater depleted in NaCl, the ultimate oil recovery increased 5 to 18% of OOIP compared to the seawater depleted in NaCl at the temperature range of 70–120°C.
- The oil recovery by spontaneous imbibitions increased in the order $\text{FB} < \text{SW} < \text{SW0NaCl} < \text{SW0NaCl-4SO}_4^{2-}$, which also corresponded to the order of increased water–wet fraction after the imbibitions process.

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NOMENCLATURES

A	Adsorption area
AN	Acid number, mgKOH/g
BN	Base number, mgKOH/g
C/Co	Relative concentration of ions
dSW1600	Diluted seawater with distilled water to 1600 p.p.m
dSW10000	Diluted seawater with distilled water to 10000 p.p.m
dSW20000	Diluted seawater with distilled water to 20000 p.p.m
FB	Formation brine
OOIP	Original oil in place
Swi	Initial water saturation, %
SI	Spontaneous imbibition
SW	Synthetic seawater
SW0NaCl	Seawater depleted in NaCl
SW0NaCl-4 SO_4^{2-}	Seawater depleted in NaCl with 4 times the concentration of SO_4^{2-}
SW0NaCl-4 Ca^{2+}	Seawater depleted in NaCl with 4 times the concentration of Ca^{2+}
SW4NaCl	Seawater with 4 times the concentration of NaCl
WI	Water–wet surface fraction

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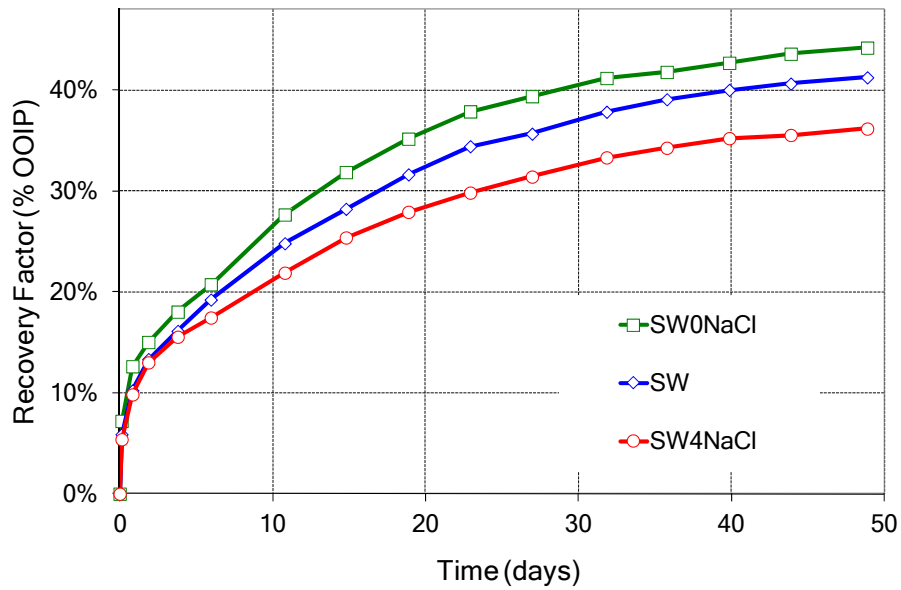


Figure 1 Spontaneous imbibition into oil saturated chalk cores at 100 °C using different imbibing fluids: SW, SW0NaCl, and SW4NaCl, $S_{wi}=10\%$

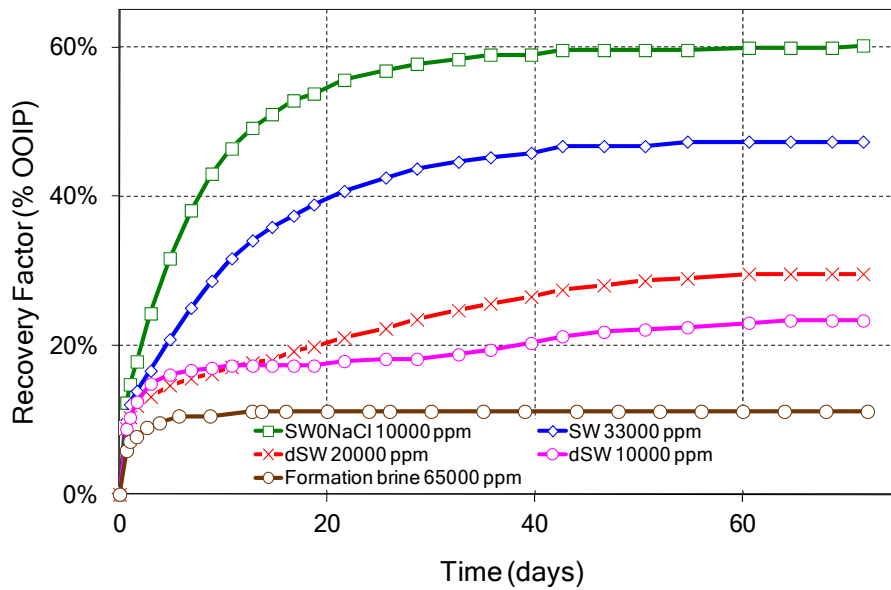


Figure 2 Spontaneous imbibition into oil saturated chalk cores at 110 °C using seawater, SW, and modified seawater: SW0NaCl, dSW10000, dSW20000, and formation brine, $S_{wi}=10\%$

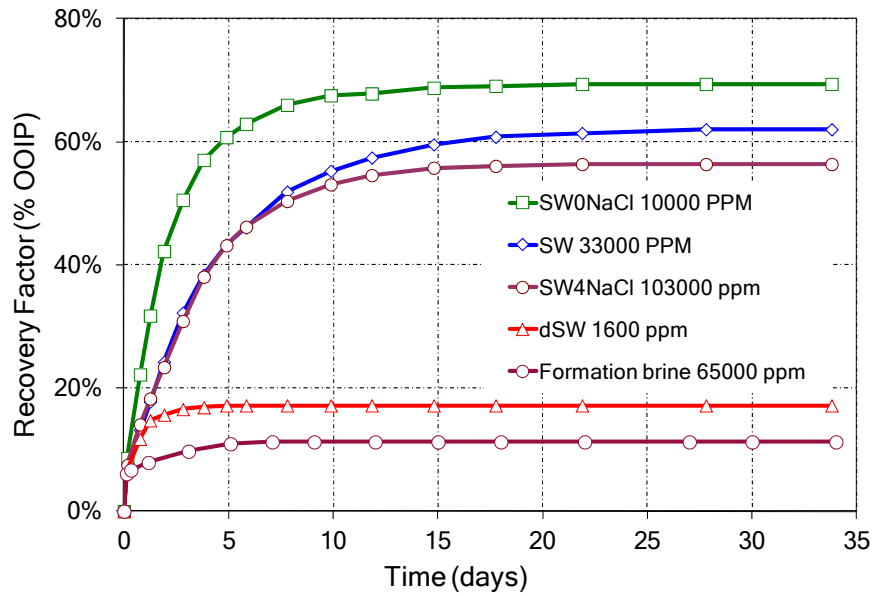


Figure 3 Spontaneous imbibition into oil saturated chalk cores at 120 °C using different imbibing fluids with different salinities and ionic composition: SW, SW0NaCl, SW4NaCl, dSW1600, and formation brine, $S_{wi}=10\%$

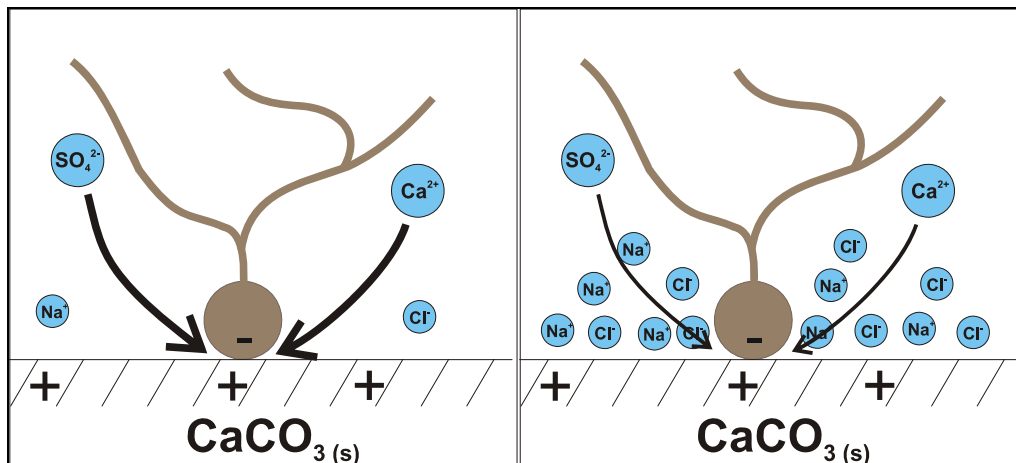


Figure 4 Schematic diagram of the effect of NaCl based on the interaction of the ions at the rock surface

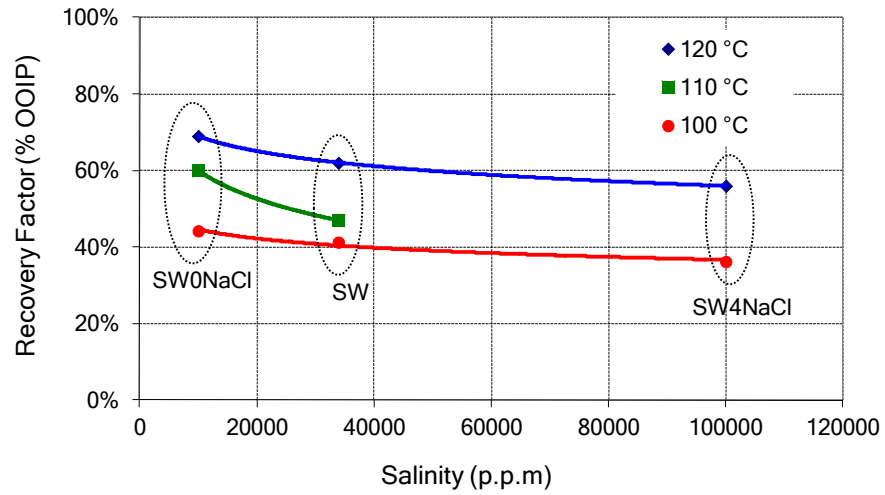


Figure 5 The effect of different concentration of NaCl in seawater on the oil recovery factor at specified temperatures

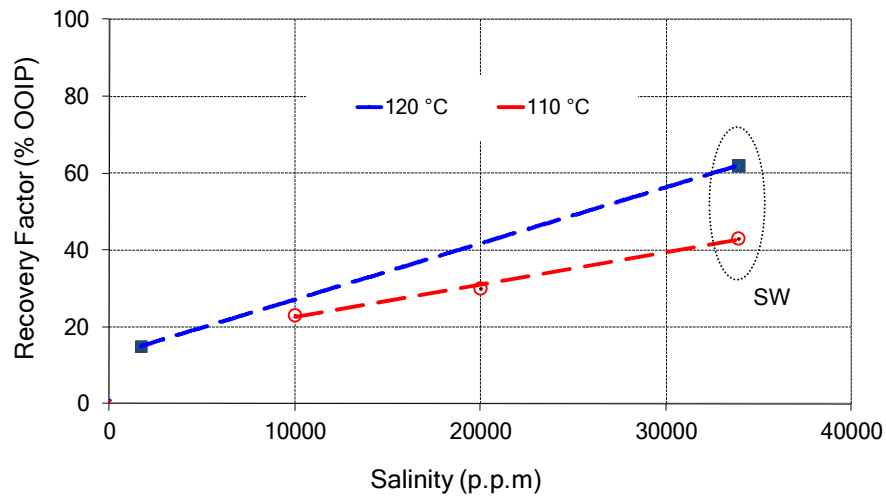


Figure 6 The effect of diluting seawater as the imbibing fluid on oil recovery at different temperatures

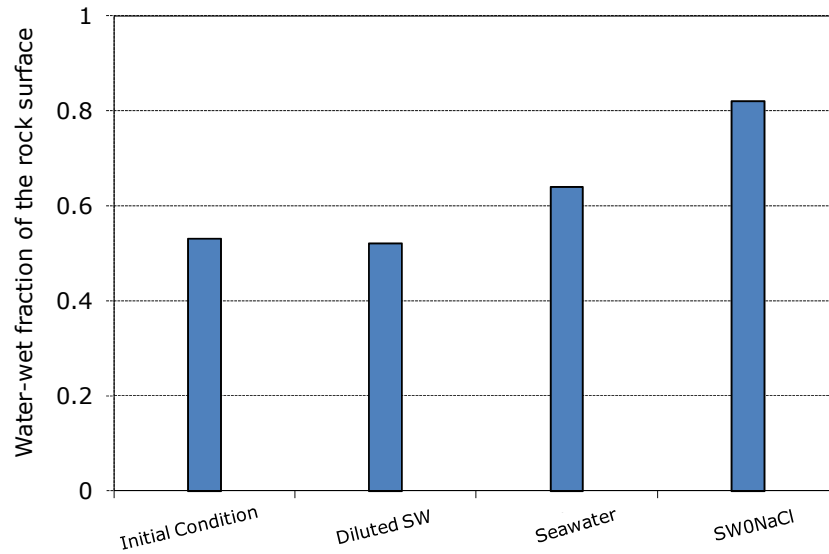


Figure 7 Water-wet fraction of rock surface (WI): initial condition and after spontaneous imbibition with seawater and modified seawater at 110 °C.

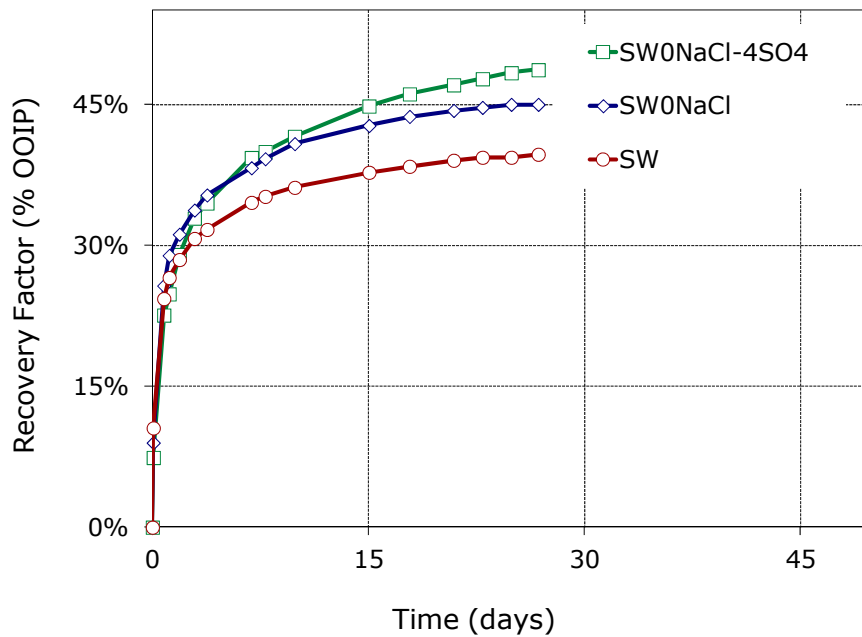


Figure 8 Spontaneous imbibition into oil saturated chalk cores at 70 °C using different imbibing fluids with different salinities and ionic composition: SW, SW0NaCl, and SW0NaCl-4SO₄²⁻, respectively. $S_{wi}=10\%$, Oil-B, AN=0.5 mgKOH/g.

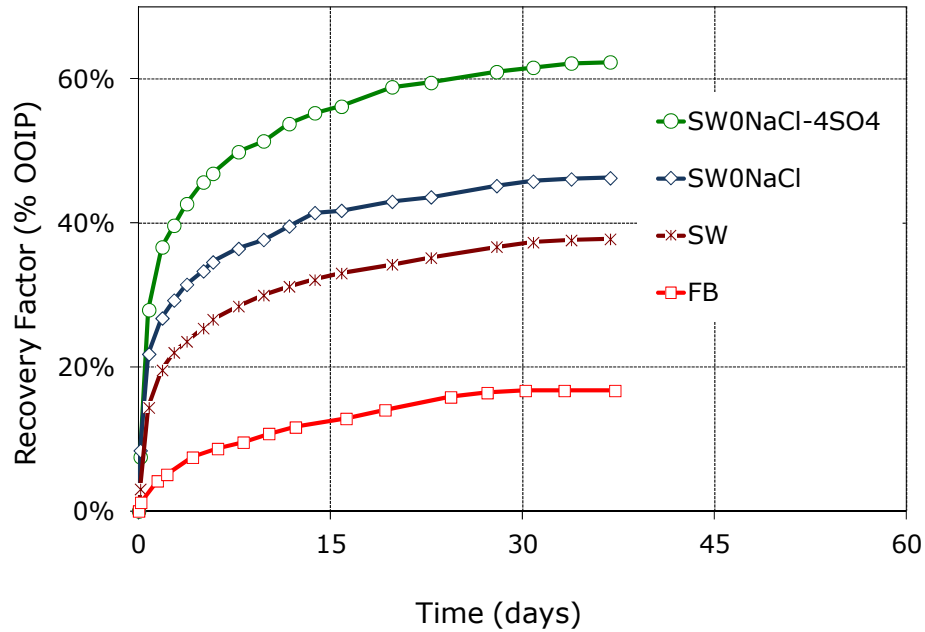


Figure 9 Spontaneous imbibition into oil saturated chalk cores at 90 °C using FB, SW, and modified seawater: SW0NaCl, and SW0NaCl-4SO₄²⁻, $S_{wi}=10\%$, Oil-B, AN=0.5 mgKOH/g.

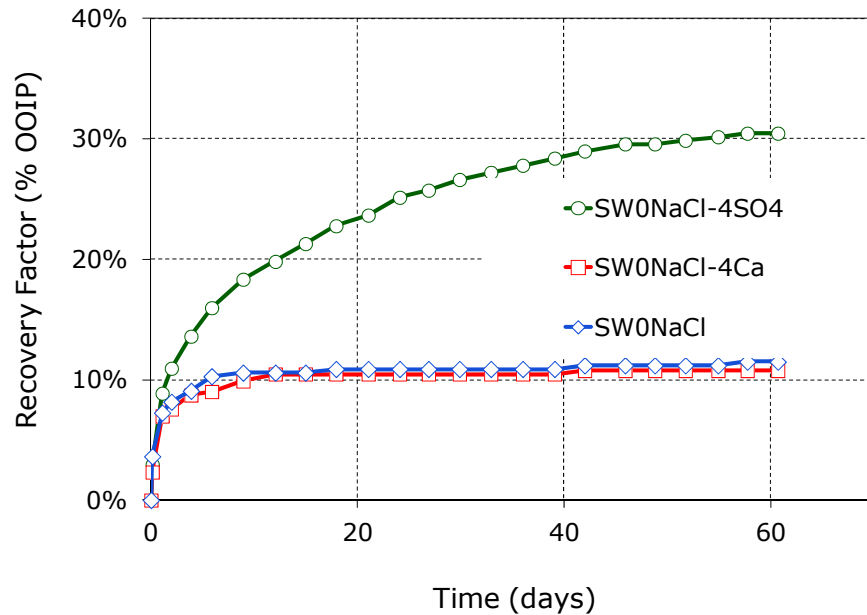


Figure 10 Spontaneous imbibition into oil saturated chalk cores at 100 °C using different imbibing fluids with different salinities and ionic composition: SW0NaCl, SW0NaCl-4SO₄²⁻, and SW0NaCl-4Ca²⁺, $S_{wi}=10\%$, Oil-A, AN=2.0 mgKOH/g.

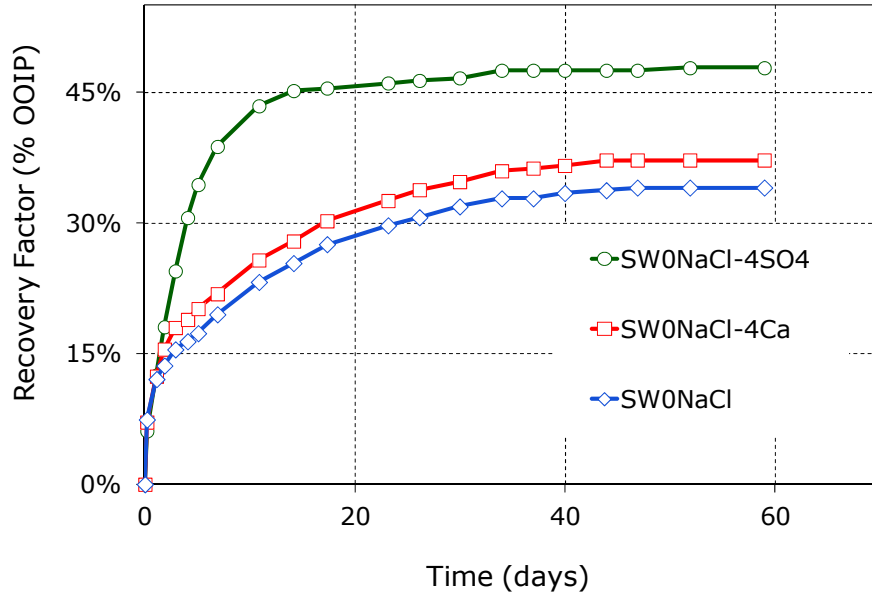


Figure 11 Spontaneous imbibition into oil saturated chalk cores at 120 °C using different imbibing fluids with different salinities and ionic composition: SW0NaCl, SW0NaCl-4SO₄²⁻, and SW0NaCl-4Ca²⁺, $S_{wi}=10\%$, Oil-A, AN=2.0 mgKOH/g.

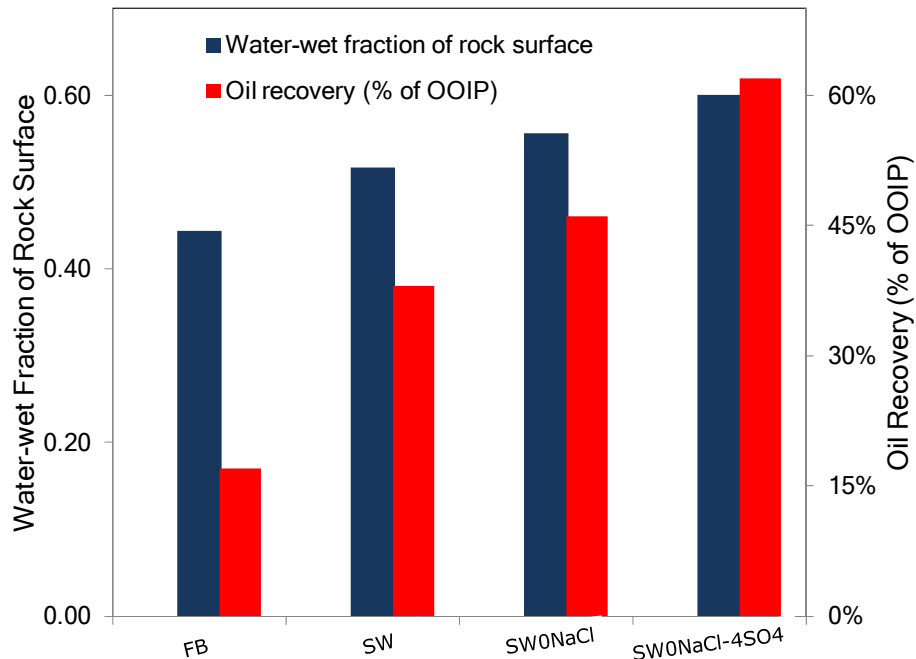


Figure 12 Relationship between oil recovery and water-wet fraction of the rock surface after spontaneous imbibition with FB, SW, SW0NaCl, and SW0NaCl-4SO₄²⁻ at 90 °C, Oil-B. As the water-wet fraction of the rock surface increases from 0.44 to 0.6, the oil recovery increases from 17% to 62% of OOIP.