

Carbonated Smart Water Injection for Optimized Oil Recovery in Chalk at High Temperature

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Abstract. Finding cost-efficient ways of increasing oil production with a low carbon footprint is the new challenge for the petroleum industry that wants to meet the net-zero emission goals by 2050. Smart water injection is an EOR process that increases oil production and delays water breakthrough by wettability alteration. Seawater is a smart water in chalk reservoirs, being especially effective at high temperatures. Different studies have shown that the effectiveness of seawater can be further improved by modifying the ion composition before injection.

Carbonated water (CW) has been proposed as a potential EOR fluid. In addition to producing extra oil, the reduction of greenhouse gas (CO₂) in the atmosphere can be achieved by using carbonated smart water as an injection fluid. The main mechanism behind increased oil recovery by injecting carbonated water is believed to be oil viscosity reduction and swelling, as the CO₂ is transferred from the aqueous phase to the oil phase. Wettability alteration has also been proposed as a possible mechanism, and this hypothesis is further investigated in this study along with other proposed mechanisms.

Stevens Klint outcrop chalk was used in this study, this material is recognized as an excellent analogue for North Sea chalk reservoirs. Optimized oil recovery by carbonated water in chalk was investigated at a high temperature (130°C) by flooding carbonated formation water (CFW) and carbonated seawater (CSW), to be compared with high saline formation water (FW) and seawater (SW) flooding. The oil/brine/rock/CO₂ interactions were tracked by measuring the pH of the produced water (PW) and by identifying any mineralogical changes by SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray) analyses. The solubility of CO₂ in different brines was measured and compared with simulation data performed by PHREEQC. The diffusion of CO₂ from the aqueous phase to the oil phase was analysed to check if enough CO₂ can be diffused from the carbonated water into the oil phase.

By flooding CSW in both secondary and tertiary modes, a slight increase in the oil recovery was observed and was found to be the best performing brine. The oil recovery was also slightly increased using CFW in tertiary mode after FW which does not behave like smart water for carbonates.

The solubility of CO₂ was low and increased by increasing pressure and decreasing brine salinity. The acidity of CW did not increase by increasing pressure. No changes in pore surface minerals were observed after CW flooding, confirming limited mineral dissolution. A mass transfer of CO₂ from the brine phase to the oil phase was confirmed in the experimental work, but a significant amount of CO₂ remained in the brine phase.

The main mechanism behind this extra oil observed using CW is most likely not linked to oil swelling and viscosity reduction or mineral dissolution which could affect the porosity and the permeability of the rock system. Wettability alteration is a more likely explanation but needs to be looked further into for confirmation.

1 Introduction

The global energy demand is increasing by more than 1% every year because of the growth of the population and the increase in per capita energy consumption in developing countries. Although energy production from renewable sources is showing strong growth in recent years, oil is still the biggest source of energy production [1]. Therefore, to meet the net zero carbon emission goal by 2050, it is important to find a better way to produce oil in an environmentally friendly manner. Carbon capture, utilization, and storage (CCUS) might be a solution where CO₂ will be captured and used as a product to produce more oil, and

therefore, CO₂ will be stored permanently in the reservoir after permanent plug and abandonment.

Previous lab experiments and field trials have shown that injection of CO₂ can increase oil recovery by reducing oil viscosity and increasing sweep efficiency [2]. The injected CO₂ was not fully recovered and thus shows storage possibility. However, direct CO₂ injection shows gravity segregation and viscous fingering effect that causes early CO₂ breakthrough along with technical difficulties in handling CO₂. These problems can be minimized by injecting carbonated water (CW) without sacrificing CO₂ storage potential [3].

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Several mechanisms for CW EOR have been proposed in different literature [4]. The main mechanism behind extra oil recovery is believed to be the mass transfer of CO₂ from the water phase to the oil phase as the solubility of CO₂ is much higher in oil than in water [5-7]. This leads to oil swelling, reduction of interfacial tension (IFT) between oil and rock, and reduction of oil viscosity resulting in reconnection of isolated oil droplets, increases relative permeability of oil, and enhances the oil mobilization, thus increases sweep efficiency [3]. Wettability alteration due to CO₂ mass transfer was also proposed by Sohrabi et al. (2015). CO₂ dissolution into the oil phase destabilises the polar organic components of the oil attached to the rock surface and helps them to move. Decreases in the aqueous phase pH (in CW) also change the surface charges on the water/oil and water/rock interfaces which leads to subsequent changes in the wettability of the system and thus produces more oil [8].

The evolution of solution gas from the heavy oil caused by CO₂ dissolution is also considered one of the mechanisms for oil recovery by injecting CW [9]. The reaction between rock and CW resulting in rock dissolution and increase permeability by creating new a path to mobilize oil might also help to increase oil recovery [10].

Previously, our research has shown seawater (SW) works as smart water at high temperatures by changing the wettability of the reservoir. The effectiveness of SW can be further improved by removing NaCl from SW and spiking it with additional sulphate ions [11]. However, the preparation of this water demands additional energy to treat the water and obtain the desired compositions. Moreover, adding extra chemicals makes the injection less cost efficient. At high temperatures, non-stable sulphate concentration can lead to precipitation, affecting the porosity and permeability of the reservoir. Additionally, both the injection and the production facilities can experience severe scaling problems.

Therefore, there is a need for more environmentally friendly injection water that not only increases the oil recovery but also reduces the risk of precipitation. Injection of carbonated water can be a good alternative for the carbonate reservoir [4]. Many researchers reported extra oil recovery in carbonates by injecting carbonated water along with CO₂ storage possibilities [2].

Initial research done on carbonated water injection (CWI) in the 1940s by the Oil Recovery Corporation reported an extra 15% oil production when CW was injected after conventional water flooding [12]. Lake et al. (1984) have reported additional oil recovery of 26% in the tertiary mode by injecting CW in case of light oil. Recently, extensive research was conducted by Herriot Watt Institute of Petroleum Engineering Centre on CWI for oil recovery by core flooding and micro model which showed extra oil recovery both in the secondary and the tertiary mode [8]. Kilybay et al. (2016) performed a comparative oil recovery experiment by flooding different smart waters and carbonated smart water in carbonate reservoir core plugs and experienced extra oil recovery (~14%) for carbonated smart water injection. This extra oil recovery was attributed to the impact of CO₂ mass transfer from brine to oil inducing a viscosity drop, local flow diversion and trapped oil swelling. Carbonate dissolution and

pore enlargement were also proven through NMR porosity and ICP-MS studies [14]. Sand pack flooding experiments conducted by Mosavat (2014) showed it is possible to store CO₂ by injecting CW. Kechut et al. (2011) showed about 47 - 51% of total CO₂ injected can be stored by carbonated water injection through numerical simulations and laboratory experiments.

The objective of this work is to determine if CW can induce EOR effects in chalk and to determine which mechanisms may be behind such effects. Thus, we compared the oil recovery performance of different core floods by injecting different carbonated brines at high temperatures in equally restored chalk cores. The reasons behind the extra oil observed were discussed. The solubility of CO₂ in different brine was studied by experimental work and simulations. The mass transfer of CO₂ from the brine phase to the oil phase was also confirmed through experimental work.

2 Experimental sections

2.1. Core Material

Outcrop Chalk collected from Stevns Klint (SK) quarry, near Copenhagen, Denmark, was used in this experiment. Cores were drilled from the same chalk block in the same direction and cut and shaped to the desired diameter of 3.8 cm and the desired length of 7 cm. All cores were inspected visually, and no visible fractures and distinct heterogeneities were found. These outcrop chalk cores consisted of 98% pure biogenic CaCO₃ and are similar to North Sea chalk reservoir cores. SEM (Scanning Electron Microscope) and EDX (Energy Dispersive X-Ray) analyses were done to see the changes in the minerals before and after the exposure to different carbonated brines. The specific surface area, (BET), porosity, and permeability of the cores were measured, and the values measured were found to be similar to previously published data [11, 16-21]. The properties of the cores are given in Table 1.

Table 1. Physical properties of the SK cores.

Core #	BET m ² /g	Porosity (%)	Water Permeability k _w (mD)	Pore volume (mL)
SK-3	2.0	48.5	3.7	38.7
SK-4		49.5	3.8	40.9
SK-6		45.4	4.1	36.3
SK-11		47.2	3.8	38.3

2.2 Crude Oil

A low asphaltenic stock tank oil with an acid number (AN) of 2.90 mg KOH/g and a base number (BN) of 0.95 mg KOH/g was used as base oil. This base oil was diluted with 40 weights % of heptane, centrifuged, and filtrated through a 5 µm Millipore filter. The AN of that diluted oil is found to be

~2.1 mg KOH/g and no precipitation of asphaltenic material was observed during storage after filtration. The surface active polar organic components were removed from a batch of the base oil using silica gel that provided an oil of ~0 AN. When the diluted oil and silica-treated oil were mixed, an oil (Oil A) with AN of 0.58 mg KOH/g and BN of 0.30 mg KOH/g was obtained which was used in the experiments. AN and BN of the oil samples were analysed by potentiometric titration. The density and viscosity of the prepared oil were determined to be 0.81 g/cm³ and 2.4 cP, respectively.

2.3 Brines

Brines used in this experiment were made by mixing deionized water (DI) and reagent-grade salts. All the brines were mixed overnight by magnetic rotation and filtered through a 0.22 µm Millipore filter. SW composition is based on the seawater composition from the North Sea and the FW composition is based on the formation water from a North Sea Chalk reservoir. The properties of the brines are given in table 2.

Table 2. Properties of brines.

Ions(mM)/ Properties	SW	FW
[Na ⁺]	450.1	997.0
[K ⁺]	10.1	5.0
[Ca ⁺]	13.0	29.0
[Mg ²⁺]	44.5	8.0
[Cl ⁻]	525.1	1066.0
[HCO ₃ ⁻]	2.0	9.0
[SO ₄ ²⁻]	24.0	0.0
TDS (g/L)	33.34	62.83
Density (g/cm ³)	1.02	1.04
Bulk-pH	7.8	7.3

Carbonated seawater (CSW) and carbonated formation water (CFW) were prepared by equilibrating access CO₂ (g) with the respective brine in a pressure cylinder at 6-7 bar and 23 °C. The equilibrated carbonated brine was then moved to a separate cylinder at a higher pressure, so no gas cap was formed.

2.4 Core restoration

2.4.1 Establishing initial water saturation (*S_{wi}*)

All cores were initially cleaned by flooding 5 PV of deionized (DI) water at room temperature to remove easily dissolvable salts, especially sulphate salts as described by Puntervold et al. (2007). The cores were then dried at 90°C to a constant weight. The initial formation water saturation (*S_{wi}*) of 10% was established by using the desiccator technique [22]. After they had reached 10% initial water saturation with formation water, the cores were stored in a sealed container for 3 days to allow an even ion distribution within the cores.

2.4.2 Oil exposure

The cores were then flooded with 4 PV of Oil (1.5 PV in each direction) at 50°C. Finally, the cores were wrapped in Teflon tape to avoid unrepresentative wetting on the outer surface and aged in the same oil for 2 weeks at 90°C to achieve a more homogeneous core wetting.

2.5 Oil Recovery by Spontaneous Imbibition

Spontaneous imbibition (SI) experiment was performed on a restored core to evaluate the degree of water wetness after core restoration. The experiment was performed at 110°C and 10 bar using formation water as the imbibing brine to avoid any chemically induced wettability alteration. The produced oil was collected in a glass burette that has a resolution of 0.1 ml. The volume of oil produced was calculated as % original oil in place (OOIP) versus time. The experimental setup is depicted in the following figure 1.

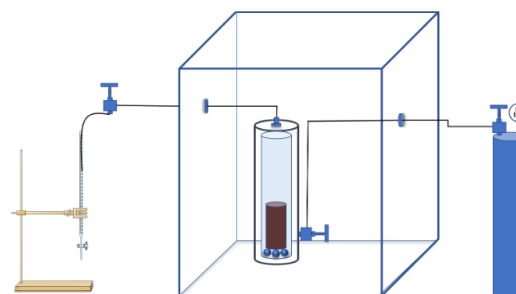


Fig. 1. Schematic of the setup used for spontaneous imbibition experiment.

2.6 Oil Recovery by Viscous Flooding (Forced Imbibition)

All experiments were performed at 130°C. The restored cores were mounted in the Hassler core holder with a confining pressure of 20 bar and a back pressure of 10 bar to prevent boiling. The cores were then successively flooded with different injection brines in secondary and tertiary mode at a constant injection rate of 1 PV/Day. When the recovery plateau was reached, the injection rate of the tertiary injection fluid was increased 4 times (4 PV/Day) to observe any end effects. The pressure drop was recorded during the experiment. Samples of produced water were collected during the experiment, and the pH of produced water were measured to catch any chemical reactions during the brine injections. The oil recovery, pressure drop, and the pH of the produced water was plotted against the PV brine injected. The experimental setup is illustrated in figure 2.

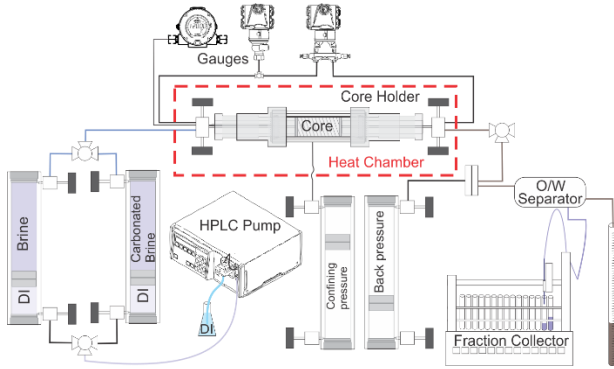


Fig. 2. Schematic of flooding setup.

2.7 Solubility of CO₂ in brines

The solubility of CO₂ in brines at 60°C was measured in the pressure range from 10 to 200 bar. 150 ml of a specific brine (DI, SW, FW) was mixed with 150 ml of CO₂ (g) at 10 bar in a pressured cylinder. The 2-phase system with a CO₂ gas cap above the brine was then temperature equilibrated overnight at 60°C. At each pressure stage the CO₂ – brine systems were mixed and allowed to equilibrate into 2 phases before a single flash of the equilibrated carbonated brine phase was performed. A small volume of the carbonated brine was flashed to standard conditions (SC). The pressure was maintained in the sample cylinder during the flash experiment. The mass of brine collected in the flash apparatus and liberated gas volume at SC was measured by a gasometer. The GOR as mg CO₂ per gram of brine was calculated based on the average of 3 flash experiments at each pressure stage. The pH of the carbonated brine was also measured in freshly taken samples after each flash experiment at ambient conditions.

2.8 Simulation of CO₂ solubility using PHREEQC

PHREEQC (version 3) software was used to simulate the solubility of CO₂ in different brines. The pH of the brines equilibrated with CO₂ was also simulated at specific pressure points at 60°C. The simulated data were then compared with the experimentally obtained data.

3 Results and discussion

3.1. Solubility of CO₂

To understand the potential of carbonated brine in EOR and the storage capacity of CO₂ in aquifers, it is important to understand the solubility of CO₂ in brines at pressure and temperature. Therefore, flash experiments were conducted to measure how much CO₂ is soluble in different brines at 60°C at a wide range of pressures. The amount of dissolved CO₂ in FW, SW, and DI water is presented in figure 3, as an average of the result from 3 flash experiments. The experimental data is also compared with simulated data obtained from PHREEQC.

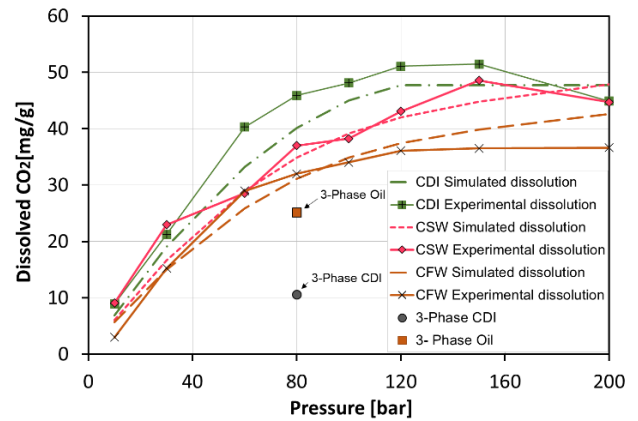


Fig. 3. Solubility of CO₂ in different brines at 60°C was plotted against pressure. Continuous lines are representing experimental data and dotted lines are representing the simulated data. 2 single points are representing the solubility of CO₂ in the water phase and the oil phase when both phases are present.

The experimental results show that the solubility of CO₂ gradually increases with the increase in pressure, but no significant increases are observed at pressures above 100 bar. CO₂ becomes a supercritical fluid when temperature and pressure exceed 31°C and 73 bar, without affecting the solubility of CO₂ in the brine phase. The solubility of CO₂ also depends on the salinity. The highest solubility is observed in DI water, and it decreases with increasing salinity. Thus, the formation water having the highest salinity (62830 ppm) showed the lowest solubility. However, the solubility difference was not more than 40% for FW and DI water at any pressure stages above the critical CO₂ pressure. The solubility of CO₂ in brines is low with maximum values of 50 mg/g in DI water. The solubility is less than 10 mg/g in all the brines at 10 bar which is the injection pressure for all the flooding experiments that will be presented in the next section.

The solubility of CO₂ in DI, SW, and FW has also been simulated using PHREEQC. The results from the simulations are presented in figure 3 and are in line with the experimental data, confirming the low CO₂ solubility at any pressure. This confirms that PHREEQC could be used to estimate CO₂ solubility in other brines or at other process temperatures.

The experimental data is aligned with simulated data and previously published experimental data by Duan et al. (2006) and Spycher and Pruess (2004).

The main mechanism behind extra oil recovery by carbonated water is the mass transfer of CO₂ from the water phase to the oil phase as the solubility of CO₂ is much higher in oil than in water. This phenomenon has been investigated in a 2-phase flash experiment at 80 bar and 60°C. CDI water at 80 bar and 60°C was equilibrated with the same amount of stabilized Oil A. Single flash experiments were performed from both equilibrated phases to SC.

At 80 bar and 60 °C, the CDI is able to dissolve 45 mg CO₂/g DI. After equilibrating with the same amount of crude oil, the amount of CO₂ in DI water was reduced 4 times down to 11

mg/g, while the amount of CO₂ transferred to the Crude oil Phase was 25 mg/g, giving a gas/oil ratio about 2.5 times higher than the gas/water ratio. Thus, this experiment confirms that CO₂ in carbonated water could be transferred to the oil phase as claimed by several researchers [5-7]. This transportation of CO₂ is because of the chemical potential difference between the two phases. But the amount of CO₂ that could be transported from carbonated water is very limited, so it is hard to believe that swelling and viscosity reduction of the oil phase could be the main mechanisms for enhancing oil recovery.

The brine phase collected from the single flash of carbonated water was collected, and the measured pH values for the individual brines at ambient conditions are presented in figure 4.

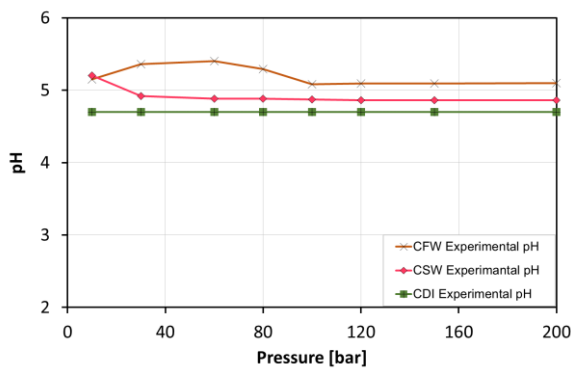
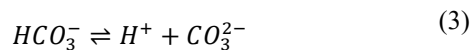
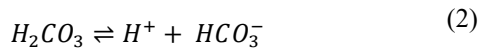
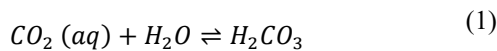


Fig. 4. The pH of different carbonated brines at different pressure and constant temperature (60°C). pH was measured at ambient conditions.

The pH was in the range of 4.7 to 5.2 for all brines and independent on the equilibrating pressure. CFW showed a slightly higher pH (~5) while CDI showed the lowest pH (~4.7).

Carbonic acid (H₂CO₃) is formed by dissolving CO₂ into different brine which is a weak acid (eq. 1). Carbonic acid is then rapidly separated into carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) (eq. 2 and 3) which provide hydrogen ions that give lower pH values (~5).



The constant pH values at different pressure points prove that the concentration of protons (H⁺) cannot be increased by increasing the amount of CO₂ in the brine phase as we observed by increased pressure. Simulation of the pH of different carbonated brine using PHREEQC confirmed the same trend, figure 5. The simulated pH is lower than the measured because the pH was measured in ambient

conditions.

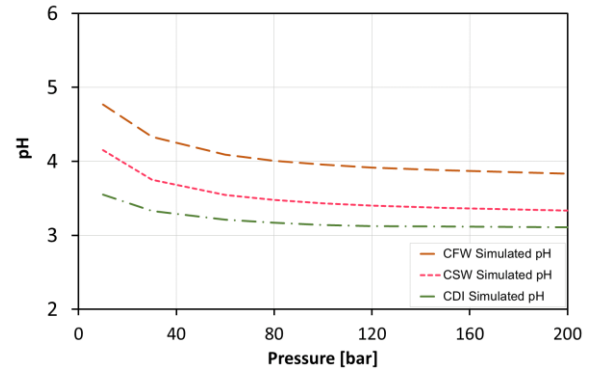


Fig. 5. Simulated pH of different carbonated brines at different pressure and constant temperature (60°C).

As the concentration of protons (H⁺) cannot be increased with an increase in pressure, the chemical effect of carbonated water in EOR cannot be increased by increasing pressure.

3.2. Initial wetting of the restored cores

All oil recovery studies performed on equally restored SK chalk cores were taken from the same block to minimize the variation in physical core properties. Spontaneous imbibition (SI) is a practical way to approach and quantify the wettability of oil/brine/rock systems [25]. Both the speed of imbibition and the ultimate recovery gives valuable information to describe the core wettability after the core restoration. SI experiments could easily be performed at reservoir temperature, to reduce uncertainties regarding physical fluid properties and temperature effects. A spontaneous imbibition test was performed on the restored core SK-3 at 10 bar at 110°C. FW was used as the imbibing brine to exclude the effect of chemical induced wettability alteration during the test. The result is presented in figure 6.

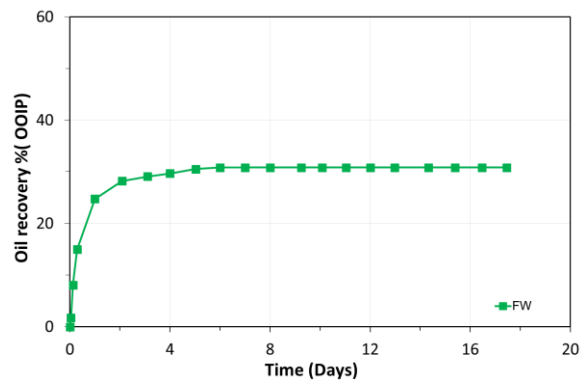


Fig. 6. Spontaneous imbibition into oil (AN=0.58 mgKOH/g) saturated (Swi=10%) chalk core at 110°C using FW as imbibing brine with a constant pressure of 10 bar. Oil recovery (% OOIP) was plotted against time (Days).

The Oil recovery reached its plateau at around 31% of OOIP on the 7th day, confirming positive capillary forces and that the core wettability is clearly on the water wet side.

A simplified wetting index only based on SI experiments can be used to calculate the wettability [26]. The degree of water-

wetness can be quantified by a modified Amott water index (I_{W-SI}^*) (eq. 4) using a very water-wet core as a reference core.

$$I_{W-SI}^* = \frac{SI_C}{SI_{WWC}} \quad (4)$$

SI_{WWC} is the oil recovery (% OOIP) by spontaneous imbibition from a strongly water-wet SK reference core which have not been exposed to any crude oil. The value of the modified Amott water index is 1 for a strongly water wet core and 0 for a neutral to strongly oil wet core.

To calculate the modified Amott water index for SK cores, we have used a strongly water-wet SK core as the reference core described by Piñerez Torrijos et al. (2019). The reference core was restored with FW, $S_{wi}=10\%$, heptane as oil phase, and FW was used as imbibing fluid at 23°C. A rapid oil production occurred, reaching a recovery of 68% OOIP after 40 minutes and an ultimate recovery of 71% OOIP after 4 hours. Therefore, the value of SI_{WWC} is 71. SI_C for the assessed SK-3 core is 31. I_{W-SI}^* for core SK-3 calculated by eq. 4 is then equal to 0.44 which suggests that the core has intermediate water wetness.

3.3. Flooding experiment

To evaluate the effectiveness of different types of injection brines on oil production, we have used equally restored sister cores of core SK-11, SK-6, and SK-4.

After core restoration, the cores were flooded at 130°C with different injection brines in both secondary and tertiary modes. The experiments were maintained by 20 bar confining pressure and 10 bar back pressure. The injection rate was constant and was 1 PV/D in all experiments performed. In the end, the injection rate was increased four times to evaluate any end effects. 4 different injection brines were used, formation water (FW), seawater (SW), carbonated formation water (CFW), and carbonated seawater (CSW). The carbonated brines were equilibrated with CO₂ gas at 6-7 bar, before the carbonated brine phase was transferred to a separate cylinder. The amount of CO₂ dissolved in the carbonated brines used for injection was then close to 5 mg CO₂/g of liquid. All injection brines were pressurized to 10 bar to match the back pressure of the system before injection.

In the first flooding experiment on core SK-11, FW was injected in secondary mode at a rate of 1 PV/D. The pressure difference between the inlet and outlet of the core was monitored. An ultimate oil recovery plateau of 68 %OOIP was reached after 2 PV was injected, figure 7a. The pressure drop (ΔP) gradually increased and reached the maximum value of 450 mbar after 0.5 PV was injected before it declined and stabilized at 150 mbar.

The pH in produced water samples was measured and compared with %OOIP in figure 7b. The first produced water was observed after 0.5 PV was injected (60 %OOIP). The produced water pH was close to 6.5, slightly lower than the bulk FW pH of 7.2.

After 3.5 PV injection, the injection brine was switched to CFW, figure 7. During the next 5 days (5 PV), 5% extra oil

was mobilized. The ΔP immediately increased from 150 mbar to 800 mbar which could not be explained by a change in the viscosity of CFW. With 4 times increase in ΔP it is difficult to pinpoint if the extra oil mobilized is a result of the CFW or increased viscous forces.

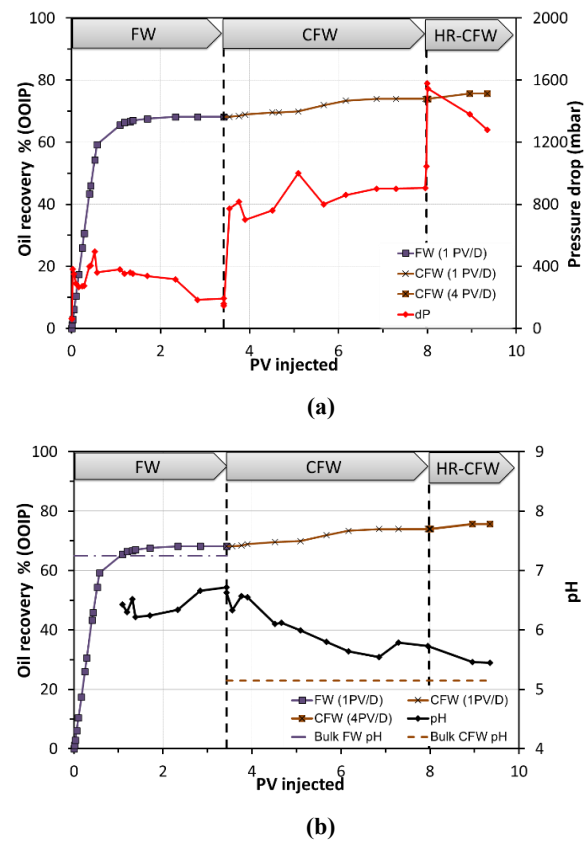


Fig. 7. Oil recovery tests on SK-11 core at 130°C. The flooding sequence was FW-CFW at a flooding rate of 1 PV/D. Oil recovery (%OOIP) was plotted against the PV injected and (a) average ΔP over the core, (b) pH of the produced water samples. At the end the injection rate was increased 4 times to 4 PV/D. Black dotted vertical lines are representing the change of injection fluid or change of injection rate. Coloured dotted horizontal lines represents the bulk pH of the injected fluids.

During CFW injection the pH in produced water samples went down below 6, confirming the presence of CFW which have a bulk pH of 5.2.

Since the chalk cores used in this experiment are mainly composed of calcite minerals, CaCO₃ dissolution could happen in presence of water, and CaCO₃ breaks into Ca²⁺ and CO₃²⁻ ions. CO₃²⁻ that take up a proton (H⁺) from water and becomes HCO₃⁻ leaving OH⁻ behind. On the other hand, CO₂ dissolved in water will form a weak Carbonic acid, H₂CO₃ which turns to H⁺ and HCO₃⁻. Then Ca²⁺ can take two ions of HCO₃⁻ and becomes soluble Ca(HCO₃)₂ while OH⁻ and H⁺ combine and become H₂O. Thus, the weak carbonic acid system is buffered in the porous media. This chemical process is illustrated simply in figure 8. The chemical equilibrium depicted in the figure does not change too much regardless of which brine (FW, SW, or DI) is being used.

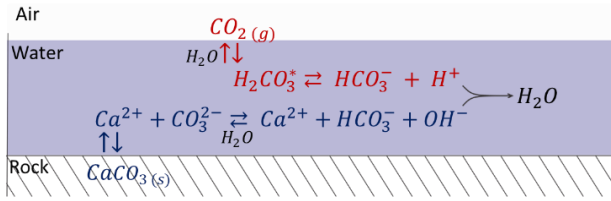
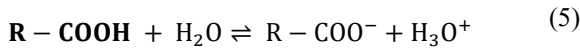


Fig. 8. Simple illustration of chemical processes happening inside the core in presence of both CaCO_3 (s) and CO_2 .

Therefore, the carbonate is working as a buffer to the injected CFW and increases its pH. Nevertheless, a change in pH can change the reactivity of the polar organic components (POC) towards the positively charged calcite rock surface as seen in the equations below.



Negative charged POC ($\text{R}-\text{COO}^-$) has the strongest affinity towards the positively charged calcite surface [28]. A reduction in pH could theoretically reduce the amount of $\text{R}-\text{COO}^-$ species and affect wettability, but the pK_a values for Naphthenic Acids described in Eq. 5 are typically below 4.5 [29] and will not significantly change the amount of non-protonated carboxylic acids.

However, the pressure difference during CFW was four times higher than FW. If viscous forces are important in the oil mobilization this could also cause higher oil recovery.

According to Wiebe and Gaddy (1940), the solubility of CO_2 reduces with an increase in temperature. In our experiment, the injection fluid was prepared at room temperature and then injected into the core at high temperature. The significant increase in pressure drop development is most likely linked to gas liberation and a third fluid phase in the pore system.

Many researchers have claimed that when carbonated water (CW) is injected into the carbonate reservoir, the acidic nature increases the dissolution of carbonate minerals which could promote an increase in porosity and permeability [31-34]. These changes in petrophysical properties help to increase oil recovery by creating a new flow path. CaCO_3 and MgCO_3 are carbonate minerals that can easily react with carbonated water. FW has a high concentration of both Ca^{2+} and Mg^{2+} ions which will limit the dissolution of carbonates even though the pH is somewhat reduced, as illustrated in figure 8. If there was a new flow path created during the oil recovery experiment in figure 7, the pressure drop should have been reduced.

After the oil production reached its plateau during CFW injection, the injection rate was increased from 1 PV/D to 4 PV/D to observe the effect of viscous forces and any end effects. A marginal extra oil mobilization of 1.5 %OOIP. The pH of the produced water was somewhat lower than at 1 PV/day, which could be explained by that the injection fluid has less time to interact with the minerals.

In the second oil recovery experiment on core SK-6, CSW was flooded in secondary mode followed by SW in tertiary

mode. Injection of CSW gave an ultimate oil recovery of 79 %OOIP which was reached after 2.5 PV injected, figure 9.

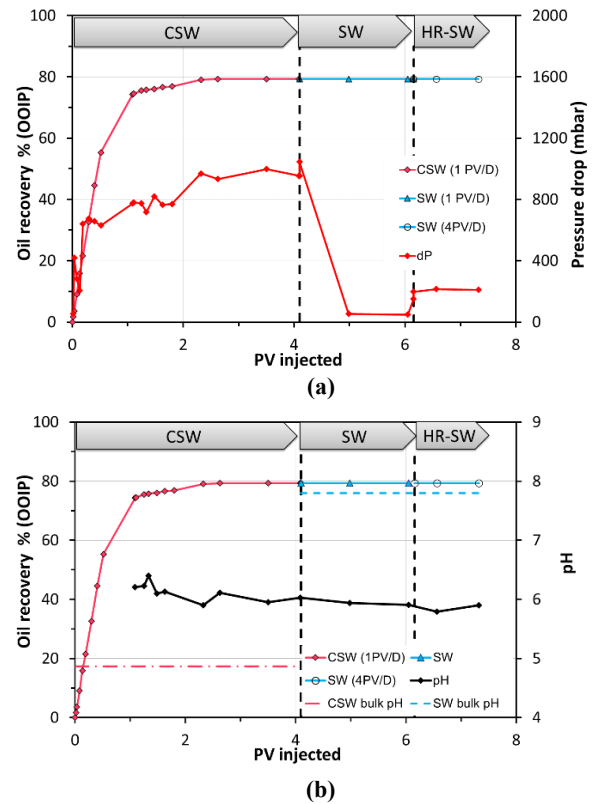


Fig. 9. Oil recovery tests on SK-6 core at 130°C with a back pressure of 10 bar. The flooding sequence was CSW-SW-HRSW. The flooding rate was 1 PV/D followed by a higher rate (HR) of 4 PV/D at the end. Oil recovery % (OOIP) was plotted against the PV injected of respective brine and (a) the average ΔP around the inlet and the outlet of the core, (b) the pH of the produced water. Black dotted lines are representing the change of injection fluid or change of injection rate. Colored dotted lines are representing the bulk pH of the injected fluid.

The ΔP was gradually increased during the hole CSW injection of 4 PV, even though water breakthrough took place after 0.5 PV injected. As previously discussed, the solubility of CO_2 reduces in higher temperatures and free CO_2 gas may promote the increase in ΔP .

After switching to SW, no extra oil mobilization was observed, but a significant decline in ΔP developed. This clearly indicates that free CO_2 liberated during CSW injection is taken up by SW and a new 2-phase flow system of Oil A and brine reestablished a more normal ΔP of 80 mbar. The results clearly indicate that CO_2 liberated from the brine phase trapped in the pore system is not easily diffusing into the residual oil but is being taken up in SW when that is passing through.

Increasing the injection rate 4 times did not mobilize any extra oil, but the ΔP increased to 200 mbar confirming typical pressure drop performance for a 2-phase fluid system in a heterogenous core. The pH of produced water is slightly acidic with a pH close to 6 during injection of both CSW and SW injection. This is slightly above the bulk pH of CSW and significantly below the bulk pH of SW.

Comparing the recovery results from FW-CFW injection (figure 7), and CSW- SW injection (figure 9), the CSW is significantly more efficient than FW in secondary mode. We know that SW behaves as a Smart Water and is able to change wettability and improve the sweep by inducing more positive capillary forces [11, 35]. To be able to evaluate if the significant improvement in the oil recovery during CSW injection is a result of wettability alteration by the ions present in the SW, or if the CO₂ present in the aqueous phase also contributes to the extra mobilized oil, a third core flooding experiment was performed on core SK-4 by injecting SW followed by CSW.

SW injection in secondary mode gave an ultimate oil recovery of 74 %OOIP after 2 PV injected. The water breakthrough was observed after 0.5 PV injected when 65 %OOIP was recovered. The experimental result is presented in figure 10.

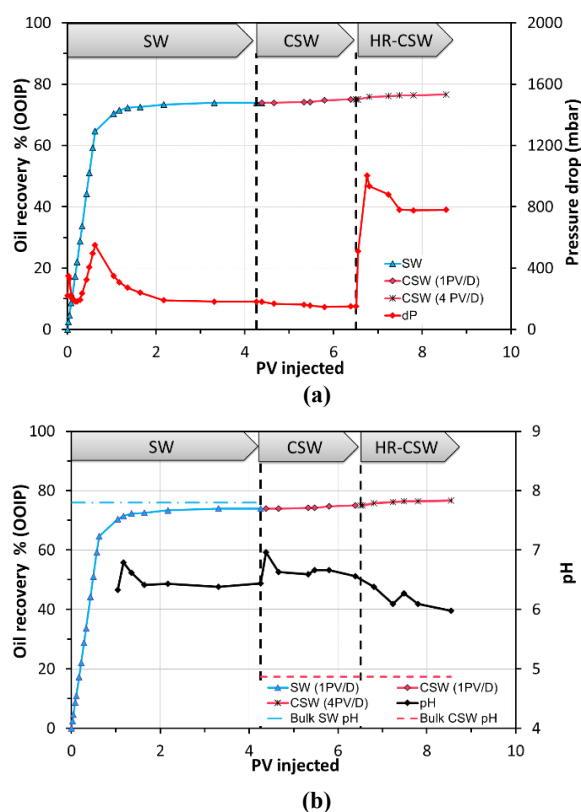


Fig. 10. Oil recovery tests on SK-4 core at 130°C with a back pressure of 10 bar. The flooding sequence was SW-CSW-HR CSW. The flooding rate was 1 PV/D followed by a higher rate (HR) of 4 PV/D at the end. Oil recovery % (OOIP) was plotted against the PV injected of respective brine, and (a) the average pressure drops around the inlet and the outlet of the core, (b) the pH of the produced water. Black dotted lines are representing the change of injection fluid or change of injection rate. Coloured dotted lines are representing the bulk pH of the injected fluid.

The ΔP profile is more normal and follows the same trend as observed during secondary FW injection when no gas phase is present, figure 7. The highest ΔP of 500 mbar was observed after 0.6 PV, gradually declining to 170 mbar when the oil recovery plateau was reached. The PW pH was almost constant and was around 6.5 during the SW injection.

After 4 PV, the injection brine was changed to CSW. During the next 3 PV, a slight increase of 1% OOIP extra oil was observed, indicating a tiny effect of the CO₂ present, supported by a slight decline in the PW pH towards 6. The ΔP during CSW injection indicated no free gas phase developing, and a low and stable ΔP of 150 mbar was observed, peaking at 1000 mbar during high-rate injection, before stabilizing again at 800 mbar. The significant increase in injection rate and ΔP had only a minor effect on oil mobilization, improving the recovery by only 2 %OOIP.

The overall recovery results confirm that by changing the chemistry of the injection brines, significant changes in ultimate oil recoveries could be observed. SW behaves as a Smart Water in mixed wet chalk, and the SW injection improved the ultimate oil recovery of 74% OOIP compared to baseline oil recovery using FW giving 68% OOIP. By adding CO₂ to the brine phase, carbonated brines could be formed. By injecting CSW in secondary mode an ultimate oil recovery of 79% OOIP was reached which is significant above SW recovery. Tertiary injection of CFW after FW and CSW after SW injection indicates smaller EOR effects.

The experimental results clearly demonstrate that the amount of CO₂ that could be dissolved in the brine phase is very limited. A significant amount of the CO₂ will still remain in the brine phase after equilibrium with the crude oil. The classical explanation linked to swelling and viscosity reduction of the oil phase is not likely the main mechanism for the extra oil mobilized during CW injection.

To evaluate the EOR mechanism of carbonated brines, we need to understand what could happen at the mineral surfaces linked to mineral dissolution processes and/or wettability alteration which we know could improve the sweep efficiency in water displacement processes in the presence of CO₂. We clearly observe a pH reduction during CW injection which due to mineral dissolution which was described in figure 8.

3.4. SEM and EDX analysis

Carbonated water will affect the mineral dissolution of calcite as described in figure 8. The effect of carbonate water exposure on mineral composition and pore surface minerals have been investigated by performing SEM and EDX analyses. In table 3, the mineral composition of SK Chalk in atomic weight % retrieved from EDX analyses before carbonated brine exposure is given in Table 3.

Table 3. Atomic weight % of SK cuttings retrieved from EDX before carbonated brine exposure.

Element	Na	Mg	Al	Si	S	K	Ca
Atomic %	0.02	0.13	0.19	0.81	0.54	0.23	98.06

The result confirms that SK chalk is very pure, consisting of more than 98% CaCO₃. The rest of the minerals are silicate minerals, Quartz, Clay, and/or Feldspars.

A Scanning Electron Microscopy (SEM) picture of the sample is given in figure 11.

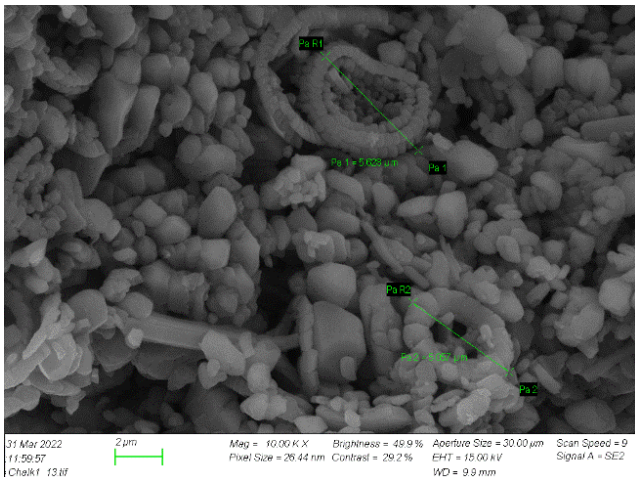


Fig. 11. SEM photo of the core sample before oil recovery test.

The presence of the intact coccolith ring confirms the biogenic origin of the Chalk.

After the core flooding experiments with carbonated brines, rock samples from the flooded cores were taken, dried, and analysed by SEM and EDX to track any mineralogical or visual changes in the mineral surfaces. Figure 12, 13, and 14 is representing the SEM photos from core SK-11, SK-4, and SK-6. Compared with figure 11, no visual changes on the mineral surfaces after carbonated brine exposure were detected. The coccolith rings are still intact and the grain sizes of the rock fragments are similar. No significant changes were found in the elements after the exposure by EDX.

The unchanged cation composition confirms negligible mineral dissolution by carbonated water. A few PV with carbonated brine is not enough to significantly affect the mineral surfaces when we have 2 m² of mineral surfaces in one gram of Chalk. At the same time, the calcite dissolution in brines with a high Ca²⁺ concentration as we have in FW and SW should be low due to the common ion effect.

However, Kono et al. (2014) observed significant dissolution of carbonate minerals by SEM. They reported smaller and smoother grains after carbonated water exposure and observed a significant increase of Ca²⁺ in the effluent brine. But in these core experiments, the total pore volume of fluid injected was several hundred, and without reporting injection rates. It is apparent that high injection volumes and rates could cause carbonate dissolution. Riazi (2011) found even sandstone is corroded by carbonated brine due to prolonged exposure to CWI for 2 weeks at the process conditions of 2000 psi and 38°C, which was a static exposure test, not a flooding experiment.

In our experiments, we have flooded SK cores with only about 4 PV which is more realistic to what could happen in the main part of the reservoir. Exposure with several PV with carbonated brines is more realistic to near wellbore effects for injection wells.

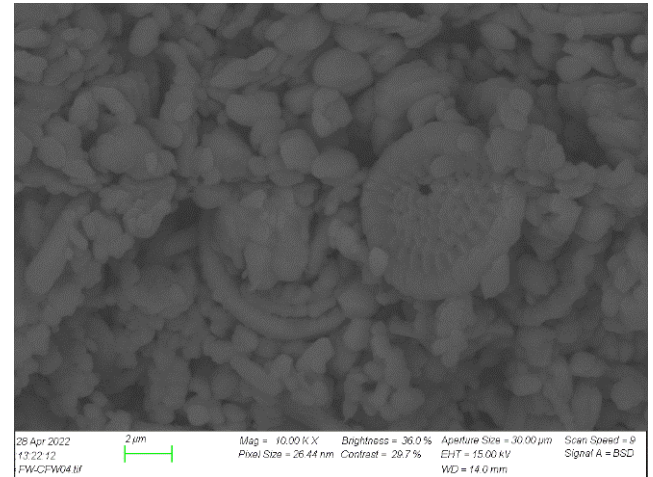


Fig. 12. SEM photo of chalk sample from core SK-11 after the oil recovery test by brine flooding (FW-CFW-HR CFW).

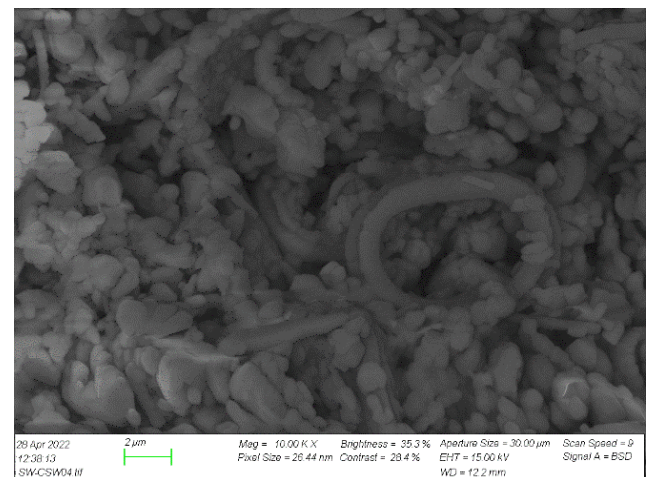


Fig. 13. SEM photo of chalk sample from core SK-4 after the oil recovery test by brine flooding (SW-CSW-HR CSW)

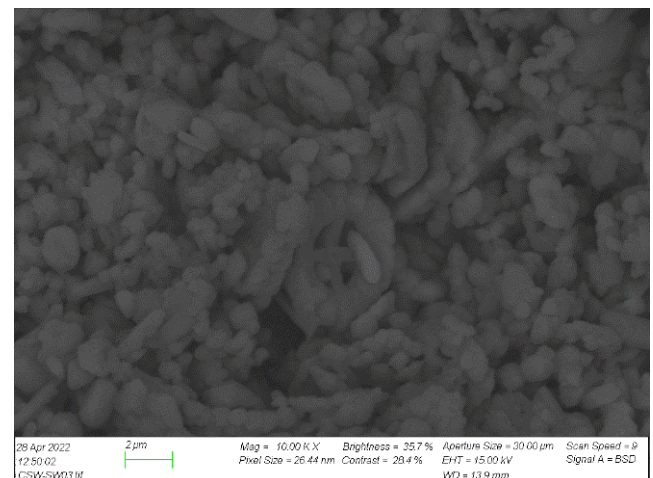


Fig. 14. SEM photo of chalk sample from core SK-6 after the oil recovery test by brine flooding (CSW-SW-HR SW)

4 Conclusions

Stevens Klint chalk was exposed to different carbonated brines at 130 °C to evaluate the effect of carbonated brines as an EOR fluid. The studies were coupled with CO₂ solubility experiments with 2 and 3 phases (CO₂, brines, and oil), as well as PHREEQC simulations. The main findings of this study were:

- The solubility of CO₂ in brine was low and depends on brine salinity. After reaching the super critical conditions of CO₂ the solubility did not increase significantly. The experimental solubility studies validated a relatively good performance of the PHREEQC simulator.
- Oil recoveries were slightly increased in chalk at high temperature both in secondary and tertiary mode. A mechanism linked to swelling and viscosity reduction of the oil phase is not likely to be a main mechanism for the extra oil.
- Dissolution of CaCO₃ in presence of carbonated brines can also contribute to change in petrophysical properties and thus produce extra oil. However, no changes on pore surface minerals after flooding with carbonated brines were observed by SEM and EDX analyses.
- Wettability alteration might play a vital role in increasing oil recovery but need further investigation.

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