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Chemical Engineering Research and Design

Enhanced oil recovery through synergy of the interfacial mechanisms by low salinity water alternating carbon dioxide injection

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Enhanced oil recovery through synergy of the interfacial mechanisms by low salinity water alternating carbon dioxide injection

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Abstract

During this study, a comprehensive investigation of low salinity water alternating CO₂ injection was performed for enhanced oil recovery in oil-wet carbonate reservoirs. A synergy of interfacial mechanisms such as IFT, wettability alteration, CO₂ solubility, oil swelling, water shielding effect, and rock dissolution was considered in two and three-phase systems. Results showed that the monovalent ions, such as NaCl or KCl, inhibit the dissolution of carbon dioxide in brine in excess of divalent salt solutions, e.g. CaCl₂ or MgCl₂ due to the salting-out effect. In addition, more water shielding effect was observed in low salinity formation water than it in low salinity seawater. The significant change in the reservoir wettability of oil/brine/CO₂ system compared to oil/brine referred to the CO₂ solubility in brine which could cause stronger carbonated water in the reservoir. Consequently, the low salinity alternating CO₂ injection overpowers the late-production problem that occurred commonly in conventional WAG injection.

Keywords: Low salinity water, Wettability alteration, CO₂ solubility, Water shielding effect, Oil swelling.

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Introduction

Water alternating gas injection (WAG) is considered one of the enhanced oil recovery, EOR, techniques. In other words, WAG is classified as a tertiary recovery method involving the injection of different slugs of water and gas into the reservoir to enhance the recovery of the residual oil that is left behind by water flooding. The WAG injection was first introduced to improve the sweep efficiency of the gas flooding process by controlling the mobility of the displacing gas and stabilising the front. WAG has the potential to boost displacement efficiency because gas flooding leaves less bypass oil than water injection, and three-phase zones may have smaller residual oil saturation ([Motealleh et al. 2013](#); [Afzali et al. 2018](#); [Nematzadeh, et al. 2012](#)). Consequently, the WAG injection provides both increased microscopic displacement efficiency and improved macroscopic sweep because of gas flooding and water injection. A complicated saturation pattern is exhibited during the WAG process due to alternate water and gas cycles ([Christensen et al. 2001](#)). This is due to the two saturations' cyclic increase and reduction throughout injection cycles. Also, AlRassas et al. ([2022](#)) indicated that the higher values of the anisotropy ratio in CO₂-WAG can yield greater oil recovery and more CO₂ storage; also, hysteresis has great impact on residual trapping. Minssieux and Duquerroix ([1994](#)) have described the WAG process at the microscopic level that causes the alternating rise and reduction of the gas and water saturations. The pressure gradient increases intermittently throughout the imbibition sequence after a gas slug, which is the first significant aspect of the WAG process. It is since only a small percentage of the gas at reservoir conditions can be substituted by water during imbibition. It leads to a limited increase in water saturation while the gas relative permeability declines to zero at the waterfront. The "stop-and-go" feature of gas and water production is caused by such hysteresis in the gas flow ([Minssieux and Duquerroix, 1994](#)). When

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4 compared to single-slug CO₂ flooding, the WAG procedure frequently results in a delay in oil
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6 output. Although the WAG method is expected to yield more oil, the financial wise may be
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8 unfavourable due to the delayed production. This challenge can be overcome by using low
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10 salinity water alternating CO₂ injection (LSWAG), wherein the oil-recovery factor could be
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12 maximized. Consequently, oil is produced much quicker as opposed to the conventional WAG
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14 process at the initial stages of WAG cycles. LSWAG can increase the oil production rate at the
15
16 beginning by promoting the interfacial interaction, and the exchange of ion and geochemical
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18 reactions. These changes are favourable conditions for low salinity waterflooding (LSW).
19
20 Injecting low-salinity brine into carbonate and sandstone reservoirs has been shown to improve
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22 waterflood efficiency in the laboratory and the field ([Chaturvedi et al. 2021](#); [Tetteh et al. 2020](#);
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24 [Firoozabadi et al. 2015](#); [Mahani et al. 2015](#); [Romero et al. 2013](#); [Austad et al. 2011](#)). The impact
25
26 of low salinity water flooding is mostly determined by rock mineralogy. Several mechanisms
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28 have been suggested to further understand low salinity waterflooding in sandstone oil fields,
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30 including the followings:
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- 40 ❖ IFT drop and pH rise by McGuire et al. ([2005](#))
- 41
42 ❖ The migration of sand grains by Tang and Morrow ([1999](#))
- 43
44 ❖ Multi-component ionic exchange by Lager et al. ([2006](#))
- 45
46 ❖ Salt-in implications by RezaeiDoust et al. ([2009](#))
- 47
48
49 ❖ Wettability alteration and osmotic pressure by Buckley and Morrow ([2014](#)).
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52

53 Furthermore, numerous researches investigated the relationship between oil recovery
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55 enhancement and wettability alterations on carbonate rock through the low salinity water
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57 injection scenarios ([Mehraban et al, 2021](#); [Moradpour et al. 2021](#); [Wang et al, 2020](#); [Gandomkar](#)

and Rahimpour 2015; Sohrabi et al. 2015). Austad et al. (2011) discovered that low salinity oil recovery was relatively limited, ranging between 1 and 5 percent of the original oil in place. This occurred when flooded first with high salinity connate water, and subsequently with 100 times diluted formation water or 10 times diluted seawater. Javadi et al. (2022) investigated the effect of salinity on fluid/rock interactions during hybrid low salinity water and surfactant flooding in carbonate reservoir. Based on their results the effectiveness of this mechanism is dependent on both the concentration of the surfactant and concentration of the ions in brine. Shehata et al. (2014) investigated the influence of low salinity water flooding of an Indian limestone field. Their findings revealed that after injecting high salinity seawater as a secondary recovery method, injection of 20 times diluted seawater did not diminish residual oil saturation in the tertiary recovery. However, after injecting saltwater and deionized water, 50 times diluted seawater boosted oil recovery from 1% to 3% in the tertiary mode. Low salinity waterflooding is still a contentious topic, despite extensive research. The governing mechanisms of low salinity waterflooding are not fully explained and it is not straightforward to reproduce the results reported by other scholars. Moreover, the technology's field scalability is questioned. In addition, compared to tertiary recovery, low salinity water flooding is more effective in secondary recovery (Austad et al. 2011; Nasralla et al. 2014; Jiang et al. 2014; Gandomkar and Rahimpour 2015). Therefore, the LSW-CO₂ process can be a promising EOR technique in secondary and tertiary recovery. Because it does combine not only the benefits of continuous gas injection and LSW. Additionally, it boosts synergy between these procedures through the interactions between geochemical reactions resulting from CO₂ injection, such as the multi-component ionic exchange process, wettability alteration, rock dissolution, and oil trapping reduction. The LSW-CO₂ process overwhelms the late-production issue that comes across frequently in conventional WAG

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4 injection. In this matter, Kulkarni and Rao (2005) investigated the combination of LSW and
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6 WAG for the first time. On Berea sandstone cores, they performed miscible and immiscible
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8 WAG with various brine concentrations. They discovered that decreasing the salinity of the
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10 injected water lowered oil recovery by increasing CO₂ solubility in brine. Jiang et al. (2010)
11
12 studied the influence of the injection brine salinity on CO₂-WAG usefulness in tertiary recovery
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14 on Berea sandstone cores by raising the injected brine salinity to 32,000 ppm. The results
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16 demonstrated that as the salinity of the injection brine increases, the WAG recovery increases.
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18 This was explained by a salting-out effect since the solubility of CO₂ in water reduces with a rise
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20 in salinity. As a result, there is more CO₂ available for displacing oil, leading to increased oil
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22 recovery. It is also worth mentioning that the sandstone core samples which were employed in
23
24 this research were water-wet and contained a minimal amount of clay. This is a bad environment
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26 for achieving wettability change, which is required to gain the LSW advantage (Rivet, 2009;
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28 Dang et al. 2015). Zolfaghari et al. (2013) completed one of the noteworthy studies in this field.
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30 According to a set of core flood experiments conducted in LSW-friendly conditions, they found
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32 that LSW-CO₂ increased oil recovery by up to 18% OOIP. According to their data LSW-CO₂ is
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34 likewise performed effectively in heavy oil fields. These encouraging findings support the
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36 expansion of LSW and LSW-CO₂, which are now only used in the oil reservoirs with lighter to
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38 medium oil, other than heavy oil reservoirs. Through six core flood experiments, Ramanathan et
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40 al. (2015) evaluated the impact of salinity on water flooding and water alternating CO₂ injection
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42 procedure. They discovered that changing the wettability of LSW to a more water-wet state
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44 boosted oil recovery and that the CO₂ solubility owing to water composition had a significant
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46 impact on LSW-CO₂ performance. Teklu et al. (2016) discovered that larger CO₂ solubility in
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48 low salinity water in comparison to high salinity water is the primary factor for improved
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residual oil mobilisation when compared to conventional WAG. They also noted that larger CO₂ solubility in brine can result in more robust carbonated water in the reservoir condition to modify wettability and reduce interfacial tension and viscosity even further. Their conclusions are in conflict with those of Kulkarni and Rao (2005) and Jiang et al. (2010). It is possible that it is referring to rock mineralogy, which is important in evaluating the influence of LSW-CO₂. Furthermore, Aleidan and Mamora (2010) found that increasing CO₂ solubility in water (reducing water salinity) resulted in greater oil recovery during the water alternating CO₂ injection and simultaneous CO₂-water injection processes. Low salinity floods could boost oil recovery by up to 18%, according to the researchers. They attributed this to the CO₂-water mixture's higher displacement effectiveness when it comes into contact with the bypassed oil after the CO₂ slug. To investigate the effect of water salinity on the CO₂ tertiary WAG process, Jiang et al. (2010) investigated two oils: crude oil from Cottonwood Creek oil field and model oil made by blending n-decane with similar molecular weight to that of n-hexadecane. They came to the conclusion that the oil recovery during waterflood operation is independent of brine salinity in the case of model oil. Likewise, they reported that divalent ion in the injection of the brine does not affect the outcome as well. In studies with Cottonwood Creek crude oil, however, the secondary recovery of water flooding reduces as the injection brine salinity rises. Dang et al. (2016) used a compositional simulator to examine the benefits of LSW-CO₂ utilising a complete ion exchange model coupled to multiphase compositional flow equations. During the field scale simulation, their findings show that the WAG ratio has a significant impact on the eventual oil recovery. In addition, compared to CO₂-HSWAG, LSW-CO₂ delivers an additional oil recovery of 4.5 to 9% OOIP. The success of LSW-CO₂ is determined by the following factors (Rendel et

al. 2022; Al-Bayati et al. 2022; Farhadi et al. 2022; Chen et al. 2022; Austad et al. 2011; Sheng 2014):

- (1) clay type and quantity
- (2) initial reservoir wettability condition
- (3) the heterogeneity of the reservoir
- (4) calcite and dolomite as the minerals
- (5) formation water and injected brine composition
- (6) reservoir condition for attaining CO₂ miscible condition
- (7) WAG pertinent parameters

The impact of the salinity of the injected brine on the displacement performance of low salinity flooding was explored by Zekri et al. (2015). According to their findings, the LSW-CO₂ flooding (with a WAG ratio of 1:2) resulted in a 29 percent increase in displacement performance over the high salinity system. Their findings also revealed that oil recovery is a function of WAG ratios during various CO₂-WAG cycles. Dang et al. (2015) developed an innovative concept of CO₂-miscible-displacement low-salinity-water alternating gas injection using CO₂. The findings support the LSW-CO₂ process's effectiveness in oil recovery. Geochemical processes are very important during the CO₂ LSWAG injection scenarios. Furthermore, their findings revealed that calcite dissolution can enhance wettability alteration by providing a Ca²⁺ source for the ion-exchange mechanism. As a result, the total efficiency of any EOR process is affected by sweep efficiency at the microscopic and macroscopic scales. While reservoir critical characteristics such as wettability, surface tension, initial water saturation, gravity impact, and the reservoir heterogeneity may complicate the design of a successful LSW-CO₂ process, they also can simplify it. There has been no experimental evidence to indicate the intraction of oil/brine/CO₂

for a three-phase system. Therefore, in this study, a synergy of interfacial mechanisms such as IFT, wettability alteration, CO₂ solubility, oil swelling, water shielding effect, and rock dissolution was considered in three-phase systems during LSW-CO₂ injection. The LSW-CO₂ is a promising enhanced oil recovery technique as it not only combines the benefits of low salinity water and CO₂ flooding but also promotes the synergy between these scenarios.

Materials and Methods

• Rock and fluid properties

All laboratory experiments employed reservoir crude oil with an API of 29.8 from one of the Middle Eastern oil fields. The oil filtration was performed to separate particles and impurities from the oil to reduce any experimental complications. Saturates, Aromatics, Resins, and Asphaltenes (SARA) analysis findings are shown in [Table 1](#). The colloidal instability index was developed to examine the instability of oil (CII). The CII is the proportion of saturates and asphaltenes to resins and aromatics. If the CII number exceeds 0.9, the crude oil is considered unstable ([Gandomkar and Nasriani, 2020](#)). From the SARA analysis, the CII value is 0.62 for crude oil and indicates that the asphaltene precipitation is not possible for this case during WAG injection. In addition, both low salinity formation and seawater were made by the addition of the designed volume of deionized water to the original salinity of formation (220000 ppm) and seawater (34000 ppm). The properties of both low salinity waters are reported in [Table 2](#). Also, the carbonate reservoir rock was used for core flooding and contact angle measurements. The chemical composition of carbonate rock was determined using the XRD (X-Ray Diffraction) technique. According to the findings, the crushed material contains roughly 78 percent calcite (CaCO₃), 14 % dolomite (CaMg(CO₃)₂), 6 % anhydrate (CaSO₄) and 2% quartz (SiO₂).

Moreover, the substrates were prepared for contact angle tests. These are polished by different sizes of sandpapers to avoid any hysteresis issues.

Table 1

Table 2

• IFT measurements and wettability alteration

The wettability and IFT of three systems, including oil/CO₂, oil/water, and oil/water/CO₂, were measured using the HPHT IFT 700 equipment. The pendant drop technique is a state of the art and precise method for determining contact angle and IFT. During IFT measurements, a drop of oil is formed from the capillary needle's tip, which is bounded by gas or water at the desired temperature. Furthermore, the IFT error was computed using the standard deviation of four repeat measurements of each mixture and was found to be around 0.1 mN/m ([Hassan et al. 2022](#); [Gandomkar and Sharif, 2020](#); [Azizkhani et al. 2020](#)). Furthermore, contact angle experiments were used to look into the effects of salinity and CO₂ solubility on wettability alteration. To begin, the carbonate substrates were aged in an oven for three weeks at 50° C in a steel cell loaded with crude oil. After that, it was placed on the top of the vessel which was loaded with the stated brine/CO₂ and then a droplet of oil is set at the bottom of the substrate. Different runs were conducted to assess the impact of salinity and CO₂ solubility on the contact angle of the carbonate rock. An average of left and right angles was reported after several repetitions ([Zhang et al. 2021](#); [Aminian et al. 2019](#); [Strand et al. 2006](#); [Ghorbani et al. 2019](#)). All the IFTs and contact angle tests were conducted at the reservoir conditions ($P_{res}=2300$ psia and $T_{res} = 150$ °F).

• CO₂ solubility and oil swelling

To capture the effect of salinity on CO₂ solubility in the sea and formation waters, an experimental setup was utilised. The details of the CO₂ solubility procedure were provided in Yan et al. work (2011). In addition, during the oil swelling test, a live oil sample is entered into a visual PVT cell at the temperature of 150 °F (i.e., reservoir temperature). After that, through the constant mass expansion (CME) method, the initial bubble point pressure (P_b) is calculated. Then, a prearranged amount of gas is entered into the cell. Following that the pressure is raised until the resulting mixture has just one phase again; the new bubble point pressure is measured through the CME method (Heagle et al. 2022; Sohrabi et al. 2011; Yang et al. 2006). The swelling factor (SF) is simply defined as:

$$SF = \frac{\text{Volume of oil at new bubble point pressure}}{\text{volume of oil at initial bubble point pressure}}$$

The previous step is repeated up to the point that new P_b reaches to the favourable pressure. Moreover, the carbonated water (prepared from the CO₂ solubility tests) was used to perform the oil swelling tests due to investigate the water shielding effect.

• Coreflooding procedure

The high-pressure high temperature (HPHT) core flooding experiments was considered to investigate the low salinity water alternating gas injection. The system is comprised of two HPLC pumps, an air bath with constant temperature, a core holder (high pressure) with an inner diameter of 1.5 in, vessels for fluid transfer, a BPR (backpressure regulator), a DP (differential pressure) transducer to record the pressure gradient across the core sample, an overburden pressure pump, and a visual separator by which the effluent fluids are collected. The reservoir cores are prepared based on the idea that the saturation state (connate water saturation) and

wettability of the core (aging process) are restored to their original state. Details of the core flooding procedure were provided in our previous works (Zahedany et al. 2022; Khayati et al. 2020; Goodyear et al. 2003; Gandomkar and Kharrat, 2013; Gandomkar et al. 2013). At reservoir conditions, the core flood tests were conducted at a frontal advance rate of 0.4 cc/min for low salinity water and 0.15 cc/min for CO₂ (i.e. 2300 psi and 150 °F). The rates of oil, gas, and water production, as well as pressure drop during core flooding experimentations, were measured. To study the various processes, samples of the effluent water were obtained by means of a fraction gatherer and were sent for ion chromatography and inductively coupled plasma (ICP) analysis. Table 3 lists the characteristics of carbonate cores. The core plugs employed in this investigation have porosity and permeability ranging from 13-17 percent and 3-6 mD, respectively. The cylindrical core plugs have a diameter of 1.5 inches and a length of 7 to 8 cm.

Table 3

Results and discussion

During this study, a comprehensive investigation of low salinity water alternating CO₂ injection was performed for enhanced oil recovery in oil-wet carbonate reservoirs. Therefore, the CO₂ solubility (in the sea and formation brines), oil swelling, IFTs measurement and wettability alteration in two and three-phase systems, water shielding effect, and rock dissolution were considered to synergy the interfacial mechanisms for enhanced oil recovery. The vanishing interfacial tension technique was also utilised to determine the minimum miscibility pressure. It was 3115 psi which immiscible low salinity water alternating CO₂ injection is occurred at reservoir conditions. These results have been presented as follows.

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4 **• The solubility of CO₂ in brine (SW and FW) and oil swelling**
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7 Enlarged solubility of carbon dioxide in low saline water is one of the key reasons for improving
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9 the mobility of the residual oil in comparison to traditional WAG. Also, increased CO₂ solubility
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11 in brine can result in more profound carbonated water in situ, lowering the interfacial tension.
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13 Despite various studies on CO₂ solubility in brine solutions, data on CO₂ solubility in low
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15 salinity brine is still limited. As a result, the impacts of salinity and salt composition on CO₂
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17 solubility at reservoir conditions were captured in this work, i.e. 2300 psi and 150 °F. **Figure 1**
18
19 illustrates the CO₂ solubility in the sea and formation waters at different salinities. It clearly
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21 shows that the CO₂ solubility increases once seawater salinity and formation waters decreased.
22
23 The decrease in the salinity of the brine caused an increase in CO₂ solubility, irrespective of the
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25 pressure and temperature. The solubility of carbon dioxide was increased from 0.73 mol.kg⁻¹ to
26
27 1.5 mol.kg⁻¹ when the seawater salinity decreased from 34000 ppm to 1000 ppm. It showed that
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29 approximately a 100 % improvement in the CO₂ solubility once the concentration of the seawater
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31 was decreased by 34 folds (from 34000 ppm to 1000 ppm). However, a different behaviour was
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33 observed in the CO₂ solubility in formation water compared to the seawater. The solubility of
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35 CO₂ in formation water was increased from 0.26 mol.kg⁻¹ to 1.3 mol.kg⁻¹. 5 times increase was
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37 observed when the formation water salinity decreased by 220 folds (from 220000 ppm to 1000
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39 ppm). In addition, the CO₂ solubility in low salinity sea and formation waters was 1.5 and 1.3
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41 mol.kg⁻¹ respectively, for 1000 ppm concentration. It showed that the affinity of CO₂ molecules
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43 to low salinity seawater is more than that for low salinity formation water. Furthermore, adding
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45 salt to the solution decreases the solubility of CO₂. The strength of this impact is governed by the
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47 salt's composition; monovalent salts, such as NaCl or KCl, block CO₂ dissolving more than
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49 divalent salts, such as CaCl₂ or MgCl₂. It should be noted that among the monovalent salts, NaCl
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seems to inhibit CO₂ solubility more than KCl. This discrepancy is not observed between different divalent chloride salts and sulphate salts. Therefore, in this study, the concentrations of Na⁺ are about 293 and 325.3 ppm for low salinity seawaters as well as formation waters (1000 ppm) respectively. Also, when salt is added to water, the ions attract the water molecules to solvate; hence, less water is attracted by CO₂. To be specific, the participation of water molecules in ions solvation reduces CO₂ molecules' weak affinity for water and forces dissolved CO₂ out of polar water. The addition of other solutes, such as NaCl, has a major impact on CO₂ solubility in water. Because of the increasing salting-out phenomenon, solubility reduces as salinity rises. The salting-out effect is the decrease in CO₂ solubility as the concentration of solid particles in the brine rises. It is critical to comprehend this effect to calculate the drop in solubility as salinity rises. According to Mohammadian et al. (2015), the salting-out effect is minimal in brines with small dissolved solids, but it becomes more pronounced as the solid concentration of the brine increases. Therefore, when the solubility of CO₂ in low salinity seawater is raised it can enhance the recovery of the oil in comparison to conventional WAG due to stronger carbonated water in situ (Teklu et al. 2016). Furthermore, during immiscible gas-based flooding, oil swelling has a significant compositional impact. It increases the effectiveness of the gas-oil displacement procedure by causing oil to swell. Figure 2 showed the variation of oil swelling factor versus CO₂ molar percentage. It can be seen that with an increase in CO₂ molar percentage, the swelling factor increases. This result implies that there is a direct correlation between the oil swelling factor and CO₂ molar percentage. During the CO₂ injection process, the oil swelling can happen on account of the mass transfer between CO₂ and oil. Heagle et al. (2022) indicated that during the oil swelling process, light and intermediate hydrocarbons moved from the oil to the surrounding phase even at pressures below the MMPs,

which may impact the performance of a CO₂ injection by leaving the heavier fractions of oil in the reservoir. The swelling phenomenon can reduce the capillary force, and thus lead to an increase in the CO₂ capillary trapping. Besides, the high oil swelling factor can change the endpoints of oil and gas relative permeability and increase the CO₂ capillary trapping. If the capillary number is less than 10⁻⁵, the flow processes are dominated by the capillary forces. In contrast, when the capillary number is above its critical point (i.e., 10⁻⁵ to 10⁻⁴) the decrease rate of S_{or} will be extremely fast. Therefore, it can be deduced that as the capillary number goes up (IFT decline), meaning lower resistance against oil flow, and eventually enhanced oil recovery ([Gandomkar and Sharif, 2020](#); [Yang et al, 2006](#)). In addition, more enhancements of oil swelling and CO₂ solubility lead to reducing the gas relative permeability in the immiscible displacement. The reduced relative permeability of the gas reduces the water shielding effect, which improves oil recovery. Also, the CO₂ mass transfer from carbonated waters in oil was investigated and showed that the oil swelling factor for low salinity carbonated sea and formation water were 1.09 and 1.05, respectively. Therefore, more water shielding effect is observed in low salinity formation water than it in low salinity seawater. However, increasing oil swelling and CO₂ solubility during low salinity water alternating CO₂ displacement could lead to a substantial enhancement of oil recovery. This is attributed to the decrease in the impact of water shielding. As a result, optimised conditions for efficient LSWAG displacements must be identified in order to reduce the water shielding effect ([Kamali et al. 2017](#)).

Figure 1

Figure 2

• IFT measurements in two and three-phase systems

Chemical interactions between crude oil, brine, and gas can cause significant differences in the microscopic displacement proficiency of low salinity water alternating CO₂ injection. Therefore, thermo-physical properties such as IFTs of any hydrocarbon/brine/gas system take a leading role in oil recovery. It decreases the capillary forces, mobilises oil further, and consequently increases oil recovery. However, the IFTs between oil and low salinity waters were investigated (two-phase flow) and then the CO₂ was added to the system (three-phase flow) for illustrating its impact on IFTs. **Table 4** indicates the interfacial tensions of two and three-phase systems in the different low salinity sea and formation waters at reservoir conditions. In the case of two-phase flow, the IFTs of the FW (220000 ppm), diluted FW (15000 ppm) by a factor of 15, and diluted FW (1000 ppm) by a factor of 220 are 10.7, 21.5, and 23.1 mN/m, respectively. In addition, the IFTs for seawater increased with diluting 2.2 and 34 times and changed from 18.6 to 23 and 25.7 mN/m for 34000, 15000, and 1000 ppm low salinity sea waters, respectively. The 220000 ppm FW displayed a lesser IFT result than others and the presence of bicarbonate ion (HCO₃⁻), which is the main source of alkalinity in the formation water, might induce it. Because low salinity brine can cause a pH rise, so, low salinity waterflooding works as an alkaline/surfactant process. As a result, when crude oil fatty acids contact with alkali at the oil-water interface, they are transformed into the surfactant (Gandomkar and Rahimpour 2015; McGuire et al. 2005). Lashkarbolooki et al. (2016) showed that the equilibrium IFT of crude oils/sea water increases due to reduction of surface excess concentration of natural surfactants at the fluid/fluid interface as a dominant mechanism. Moreover, in the case of the three-phase system (oil/brine/CO₂), results showed that the IFTs decreased compared to the two-phase systems. The IFT for oil/low salinity SW (1000 ppm)/CO₂ were 20.3 mN/m and it was lower than that for oil/low salinity SW

(1000 ppm), 25.7 mN/m. Also, the interfacial tensions of oil/FW/CO₂ showed a similar trend compared to the case of oil/SW/CO₂, but a slight change in its IFTs was observed. However, the increase in CO₂ solubility with low salinity brine could result in a decrease in the interfacial tensions of oil/brine/CO₂ in a three-phase system. Consequently, the IFT drop can have two effects on imbibition and oil mobilisation. Depending on the magnitude of the IFT reduction, also the capillary pressure is decreased. In addition, oil mobilisation is another result of IFT lowering. Reduced residual oil saturation allows more oil to be mobilised, which can lead to higher oil recovery. These findings suggest that IFT can improve oil recovery and, as a result, should be considered when using low salinity water for alternating CO₂ injection.

Table 4

- **The wettability alteration during LSWAG injection**

The solubility of CO₂ in low salinity water can cause stronger carbonated water in the reservoir to change the wettability towards an intermediate and water-wet condition, leading to larger oil recovery. Therefore, the wettability alteration was investigated for oil/brine and oil/brine/CO₂ systems. **Table 5** presents the average contact angles of the seawater and formation brines on aged carbonate rock substrates after 24 hours for two and three-phase systems. It is noted that as the water salinity declines, the water wetting characteristic of the rock becomes more pronounced. In the case of a two-phase system with original seawater and formation water (34000 and 220000 ppm, respectively), the values for contact angle are roughly 124° and 141°, correspondingly; this highlights the oil-wetting characteristic of the carbonate rock. Also, a lower alteration has been noticed with 15 and 220 folds diluted formation water (15000 and 1000 ppm); and the contact angle values decreased from 141° to 130° and 114°, respectively. In contrast, a noticeable reduction in the contact angles was noted with 2.2 (15000 ppm) and 34

times diluted (1000 ppm) seawater and led to alter reservoir wettability towards an intermediate (96°) and water-wet (50°) state, respectively. The water wetness in limestone and dolomite can be improved using cationic surfactants of the type alkyl trimethyl ammonium, $R-N(CH_3)_3^+$, dissolved in seawater. The change in the wettability is thought to be caused by interaction among cationic surfactant monomers and adsorbed negatively charged carboxylic material, resulting in the formation of a cationic-anionic complex that is discharged from the surface. Based on the published research works ([Gandomkar et al. 2017](#); [Amiri et al. 2019](#); [Strand et al. 2006](#)), it is hypothesised that when seawater is absorbed into a rock sample, the sulphate ion (SO_4^{2-}) will adsorb on a positively charged surface, weakening the connection between a negative oil component and the rock surface. More Ca^{2+} ions will be able to bond to the rock surface as the positive surface charge decreases, allowing negative oil components to be released. The relative interaction of Ca^{2+} and Mg^{2+} toward limestone is determined by the amount of SO_4^{2-} in seawater. Ca^{2+} appeared to adsorb more strongly than Mg^{2+} due to the formation of ion pairs between Mg^{2+} and SO_4^{2-} and the considerable adsorption of SO_4^{2-} onto the rock ([Gandomkar et al. 2015](#); [2017](#); [Strand et al. 2006](#)). In addition, in the case of a three-phase system, it was shown that the carbonate rock was more water-wet while CO_2 was injected into the system. The contact angle values were 71° and 112° for low salinity sea and formation waters (15000 ppm), indicating intermediate and oil-wet states, respectively. A strong water-wet condition (28°) has been observed for low salinity seawater (1000 ppm) compared to its two-phase system. The wetting films swell ahead of the displacement front in the smaller pore during the strongly water-wet condition, causing oil trapping in bigger portions. Despite the scale of the negative electric charge at both the rock/brine and oil/brine interfaces being larger in the strongly water-wet condition than in the intermediate water-wet condition, the incremental oil recovery in the

intermediate water-wet condition causes compared to the strongly water-wet condition. Different pore structures and snap-off processes could cause it (Gandomkar and Rahimpour 2015). Consequently, the significant change in reservoir wettability of the three-phase system compared to the two-phase system was due to the solubility of CO₂ in brine which causes a more intense carbonated water in the reservoir conditions. Furthermore, the persistence of the water film between the rock and oil affects rock wettability. The electrical double-layer repulsion caused by surface charges at the solid/water and water/oil interfaces determines the stability of the water film. If the charges on these two interfaces are identical, an electrostatic repulsive force is developed, which maintains the large disjoining pressure and keeps a thick water film, resulting in a water-wet surface layer. Also, the pictures that are taken from a droplet of oil on rock surfaces in two and three-phase systems were shown in Figure 3 after 24 hours with the salinity of 15000 ppm. Ion binding between the oil and the rock is reduced as a result of the LSWAG-induced multi-component ionic exchange. When contacted by low salinity brine, the oil-rock bond serves to maintain the oil films in oil-wet pores, but it is eliminated. The oil films get unstable after the bonds are destroyed, and the brine contacts the rock surface.

Table 5

Figure 3

- **Enhanced oil recovery during LSWAG injection**

In this study, a comprehensive investigation was performed to present the interfacial mechanisms such as wettability alteration, IFT reduction, oil swelling, CO₂ solubility in brine, and water shielding effect using low salinity water alternating CO₂ injection. In addition, the effect of all of these mechanisms was illustrated on oil recovery separately. Moreover, the synergy of these mechanisms on oil recovery was investigated by several core flooding tests in oil-wet carbonate

reservoirs through low salinity water alternating CO₂ injection. Therefore, based on the above results, six core flooding tests were designed to perform the low salinity sea and formation waters alternating CO₂ injection in different WAG cycles (1, 3, and 5 cycles) at reservoir conditions, [Table 6](#). In the first set of core flooding tests, the cores were flooded by low salinity sea and formation waters (15000 ppm) alternating CO₂ injection at 1 cycle WAG. Also, the second and third sets of LSWAG were performed similarly to the first set of tests with 3 and 5 cycles of WAG, respectively. All the LSWAG were injected by 1 PV of low salinity brine and 1 PV CO₂ with the same WAG ratio (1:1). The 1 cycle LSWAG flooding was performed on C1 and C2 uses low salinity sea and formation waters (15000 ppm), respectively. The immiscible LSWAG produced 47 and 31 percent of OOIP for low salinity sea and formation water alternating CO₂ injection. Also, from the second set of LSWAG, the total oil recovery factor increased to 63 and 40 percent by increasing the WAG cycle from 1 to 3 for low salinity sea and formation waters CO₂ injection, respectively. Khather et al. ([2022](#)) indicated that low permeable core slows down the WAG fluid flow and give more time for CO₂-carbonate rock interactions and reactions because of the tightness of the pore spaces. In the case of low salinity seawater CO₂ injection (WAG cycle 3), the oil recovery factor is about 31 percent during the first cycle and 20 percent of the oil was recovered during the second cycle and finally 12 percent additional oil was produced during the third cycle. In addition, the third set of core flooding scenarios was performed on core C5 and C6 by flooding immiscible LSWAG at 5 cycles WAG. The total oil recovery is about 52 and 34 percent for low salinity sea and formation waters CO₂ injection, respectively. It can be argued that the increased oil recovery is due to the higher CO₂ solubility and foam generation in low salinity water when compared to traditional WAG. Li et al. ([2015](#)) was achieved a high resistance factor in WAG process which is attributed to the CO₂ foams and

viscous micelles generated in situ during CO₂ injection. Additionally, in low salinity brines, increasing CO₂ solubility will cause more robust carbonated water in the reservoir condition, which can change wettability and reduce interfacial tension. Moreover, the higher CO₂ solubility may cause rock dissolution during LSWAG injection. It can change the reservoir permeability, pH, and residual oil trapping. Therefore, the effluent brine concentration (Mg²⁺ and Ca²⁺) was measured for all core flooding scenarios due to investigating the dissolution of minerals and surface reactions. Ion concentrations were illustrated in [Figure 4](#). Results showed that the calcium and magnesium ions effluent concentrations were increased during all LSWAG injections in limestone cores. Most probably, the significant cause of high Ca²⁺ and Mg²⁺ concentrations in runoff low salinity seawater were calcite, dolomite, and anhydrate and desorption effects, that is because the cores that were used in this research work contained 78 % calcite (CaCO₃), 14 % dolomite (CaMg(CO₃)₂), and 6 % anhydrate (CaSO₄). Rock dissolution may be the primary factor for enhancing absolute permeability during LSWAG injection, as evidenced by high quantities of calcium and magnesium ions in effluent brine. However, in the case of low salinity formation water CO₂ injection, Ca²⁺ and Mg²⁺ effluent concentrations displayed a small variation throughout LSWAG injection compared to effluent low salinity seawater cases. For example, the effluent concentration of Mg²⁺ was increased from 188 (initial concentration) to 236 ppm in the case of low salinity formation water CO₂ injection; whereas, it was increased from 690 (initial concentration) to 751 ppm in the case of low salinity seawater CO₂ injection. Maybe it referred to the high solubility of CO₂ in seawater compared to formation water. This is also consistent with the small permeability improvement seen in the LSWAG injection scenarios, as evidenced by the reduced pressure drops. They all agreed that any effects observed could be accounted for by the dissolution of CO₂ and the resulting acidity in the water,

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4 which accelerated dissolution. However, excess carbon dioxide will strongly influence this
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6 equilibrium and when the acidity is too high, calcite will dissolve.
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10 **Table 6**

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12 **Figure 4**

13 14 15 16 17 **Conclusion**

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20 This study shows a comprehensive investigation of LSW-CO₂ in oil-wet carbonate reservoirs. It
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22 showed that LSW-CO₂ is a promising enhanced oil recovery technique as it not only combines
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24 the benefits of low salinity water and CO₂ flooding but also promotes the synergy between these
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26 processes. In addition, LSW-CO₂ overcomes the late production problem frequently encountered
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28 in the conventional WAG in field scale. Also, it could be effective in conventional and
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30 unconventional reservoirs under miscible and immiscible conditions, which can improve the oil
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32 recovery. Based on the results of this study the following conclusions can be drawn:
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38 • The low salinity alternating CO₂ injection mitigates the late-production issue that occurs
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40 recurrently during conventional WAG injection.
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44 • The affinity of CO₂ molecules to low salinity seawater is more than that for low salinity
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46 formation water due to the salting-out effect.
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50 • Monovalent ions, such as NaCl or KCl, are more effective at inhibiting CO₂ dissolution than
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52 divalent salt solutions, such as CaCl₂ or MgCl₂.
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56 • The IFT for the three-phase system (oil/brine/CO₂) decreased compared to the two-phase
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58 systems while CO₂ was introduced to the system.
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- The more water shielding effect was observed in low salinity formation water than it in low salinity seawater.
- The significant change in reservoir wettability of oil/brine/CO₂ system compared to oil/brine referred to the solubility of CO₂ in brine, which can result in more robust carbonated water in the reservoir condition.
- The higher CO₂ solubility in low salinity seawater plays a key role in the enhancement of the oil recovery in comparison to the conventional WAG process.
- The dissolution of CO₂ increased the acidity which accelerated calcite dissolution and leads to high Ca²⁺ and Mg²⁺ concentrations in effluent.

Abbreviations

WAG	Water alternating gas injection
LWAG	Low salinity water alternating gas injection
LSW-CO ₂	Low salinity water alternating CO ₂ injection
HSW-CO ₂	High salinity water alternating CO ₂ injection
LSW	Low salinity water flooding
LSFW	Low salinity formation water
LSSW	Low salinity sea water
SARA	Saturates, Aromatics, Resins, and Asphaltenes
CII	Colloidal instability index

CME	Constant mass expansion
SF	Swelling factor
OOIP	Original oil in place (STB)
HPHT	High pressure-high temperature
HPLC	High pressure liquid chromatography
DP	Differential pressure
MIE	Multicomponent ionic exchange
XRD	X-Ray diffraction
EDL	Electrical double layer expansion
FW	Formation water (ppm)
SW	Sea water (ppm)
CA	Contact angle (degree)
IFT	Interfacial tension (mN/m)
EOR	Enhanced oil recovery
ICP	Inductively coupled plasma
T	Temperature, °F
θ	Contact angle (degree)

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List of Figures

Figure 1: CO₂ solubility in; 1: SW (34000 ppm), 2: SW (15000 ppm), 3: SW (10000 ppm), 4: SW (1000 ppm), 5: FW (220000 ppm), 6: FW (100000 ppm), 7: FW (34000 ppm), 8: FW (15000 ppm), 9: FW (10000 ppm), 10: FW (1000 ppm); at 150 °F and 2300 psi, i.e. reservoir conditions

Figure 2: Oil swelling factor

Figure 3: Contact angles for two and three phase fluid systems

Figure 4: Effluent concentrations (ppm) during coreflooding tests, 1: initial concentrations, 2: C1 and C2 coreflooding tests, 3: C3 and C4 coreflooding tests, 4: C5 and C6 coreflooding tests

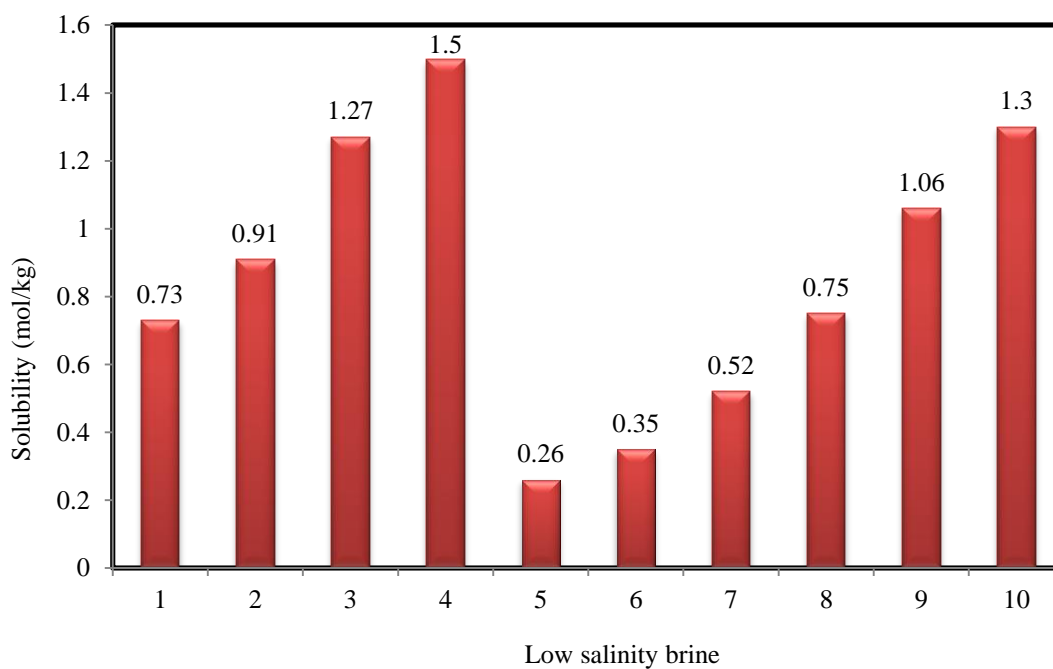


Figure 1

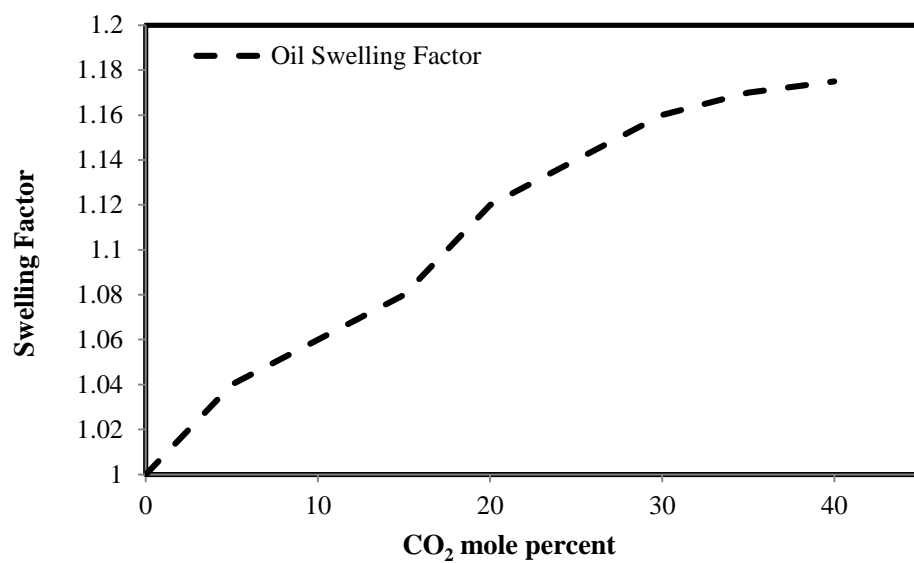


Figure 2

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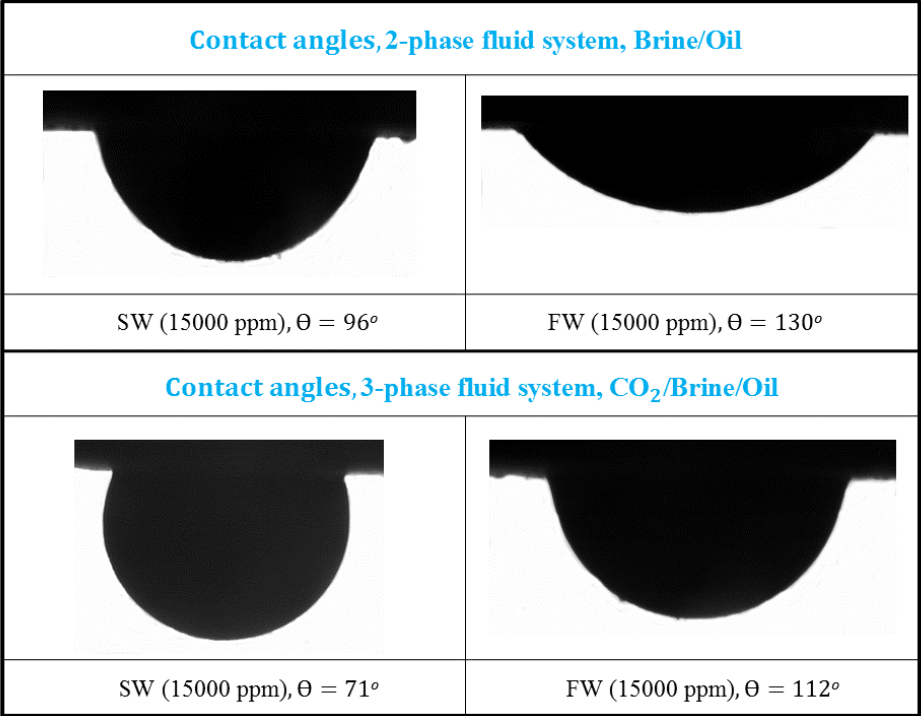


Figure 3

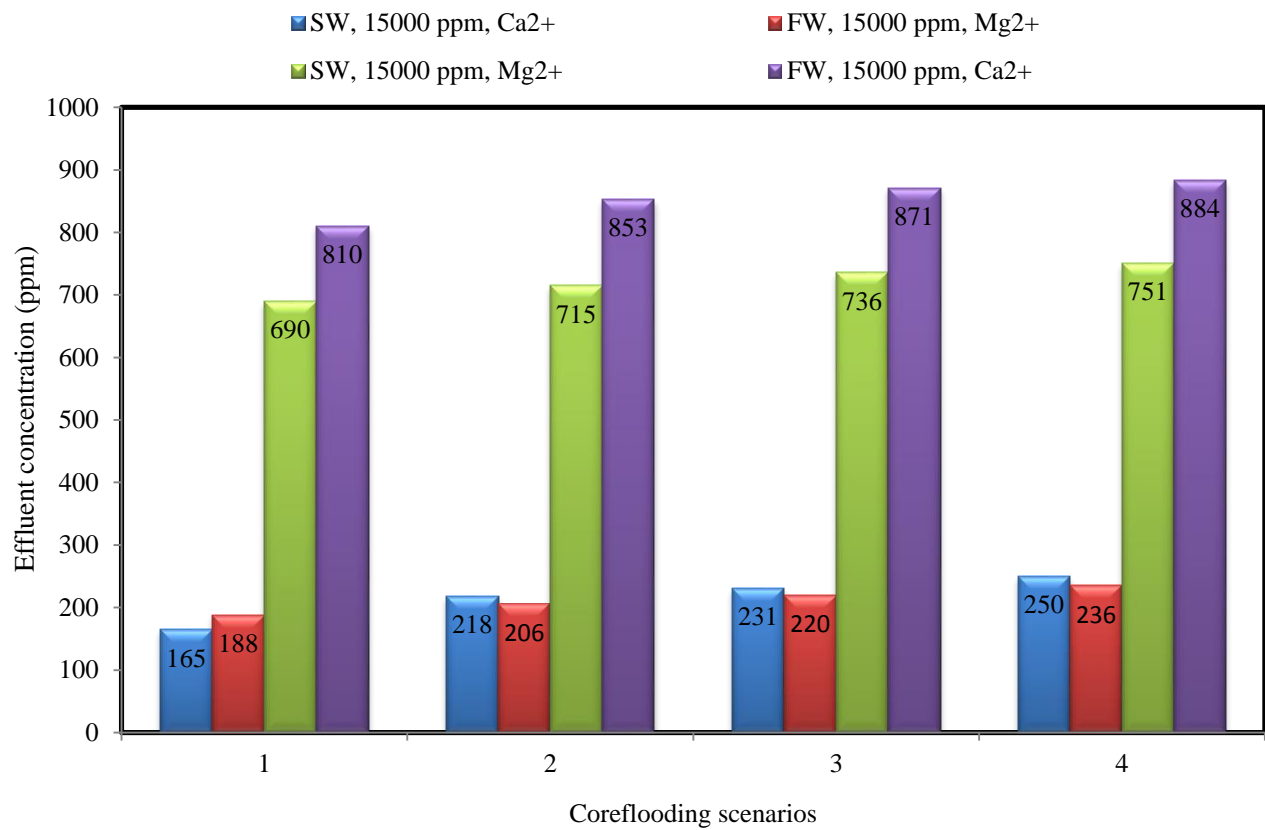


Figure 4

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Table 3: The properties of the carbonate core samples

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Table 1

SARA fraction	Weight percent
Saturates	36.7
Aromatics	56.2
Resins	5.4
Asphaltenes	1.7
Additional crude oil data	
CII	0.62
API	29.8
MW (gr/mol), IP-86	102.4
Reservoir conditions	
Tres (°F)	150
Pres (psi)	2300

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Table 2

Ions	Low salinity FW Concentrations (ppm)	Low salinity SW Concentrations (ppm)
Na ⁺	325.3	293
Mg ²⁺	12.5	46
Ca ²⁺	54	11
Cl ⁻	607.1	559
HCO ₃ ⁻	0.20	9.5
SO ₄ ²⁻	0.036	71
K ⁺	0	9
Br ⁻	0	1.5
TDS	1000	1000
Additional low salinity water properties		
Properties	Low salinity FW	Low salinity SW
pH	7.1	7.6
Density(gr/cc)	1.0016	1.0014

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Table 3

Limestone Cores No.	Length (cm)	Diameter (in)	PV (cc)	Grain Density (gr/cc)	Helium Porosity (Percent)	Permeability (md)	Connate Water (Percent)
C1	7.0	1.5	11.4	2.70	15.0	4.1	27.1
C2	7.1	1.5	12.7	2.73	14.1	3.7	26.4
C3	7.2	1.5	12.0	2.70	15.5	4. 0	28.6
C4	7.0	1.5	11.8	2.69	15.0	5.1	29.0
C5	7.5	1.5	13.8	2.74	13.8	4.6	27.3
C6	7.4	1.5	11.4	2.75	16.4	3.8	28.6

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Table 4

Fluid systems	Gas	Crude Oil	Brine	IFT (mN/m)
2-phase fluid system	CO ₂	Oil	-	53.8
	-	Oil	SW (34000 ppm)	18.6
	-	Oil	SW (15000 ppm)	23.0
	-	Oil	SW (1000 ppm)	25.7
	-	Oil	FW (220000 ppm)	10.7
	-	Oil	FW (15000 ppm)	21.5
	-	Oil	FW (1000 ppm)	23.1
3-phase fluid system	CO ₂	Oil	SW (34000 ppm)	12.6
	CO ₂	Oil	SW (15000 ppm)	18.1
	CO ₂	Oil	SW (1000 ppm)	20.3
	CO ₂	Oil	FW (220000 ppm)	9.4
	CO ₂	Oil	FW (15000 ppm)	18.0
	CO ₂	Oil	FW (1000 ppm)	19.1

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Table 5

Fluid systems	Gas	Brine	Average CA (°)
2-phase fluid system	-	SW (34000 ppm)	124
	-	SW (15000 ppm)	96
	-	SW (1000 ppm)	50
	-	FW (220000 ppm)	141
	-	FW (15000 ppm)	130
	-	FW (1000 ppm)	114
3-phase fluid system	CO ₂	SW (34000 ppm)	107
	CO ₂	SW (15000 ppm)	71
	CO ₂	SW (1000 ppm)	28
	CO ₂	FW (220000 ppm)	133
	CO ₂	FW (15000 ppm)	112
	CO ₂	FW (1000 ppm)	97

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Table 6

Core samples	WAG Cycle	Water 15000 ppm	Gas	Recovery Factor per Cycle					
				Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Total R.F
C1	1	LSSW	CO ₂	47	-	-	-	-	47
C2	1	LSFW	CO ₂	31	-	-	-	-	31
C3	3	LSSW	CO ₂	31	20	12	-	-	63
C4	3	LSFW	CO ₂	20	16	4	-	-	40
C5	5	LSSW	CO ₂	21	13	10	6	2	52
C6	5	LSFW	CO ₂	13	10	6	4	1	34

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: