A Mechanistic Study of Wettability Alterations in Sandstone by Low Salinity Water Injection (LSWI) and CO$_2$ Low Salinity Water-Alternating-Gas (WAG) Injection

Shijia Ma$^1$ and L.A. James$^{1,*}$

$^1$Hibernia EOR Research Group, Department of Process Engineering, Memorial University of Newfoundland, St. John’s, NL, Canada, A1B 3X5

Abstract. Low salinity water injection (LSWI), an emerging Enhanced Oil Recovery (EOR) method, has proven to be effective in increasing oil recovery by wettability alteration. As low salinity water is injected into the reservoir, the pre-established equilibrium is disturbed. The chemical reactions among the oil-brine/rock system alters the existing wettability, resulting in enhanced oil recovery. Water-alternating-gas (WAG) injection is also a leading EOR flooding process in light to medium oil sandstone and carbonate reservoirs. A recently proposed hybrid EOR method, CO$_2$ low salinity (LS) WAG injection, shows promise based on experimental and simulation studies, compared to LSWI or CO$_2$ injection alone. Wettability alteration is considered as the dominant mechanism for CO$_2$ LSWAG injection. In this study, a new displacement contact angle measurement which better mimics the actual displacement process taking place in a reservoir is used, aiming to investigate the effect of monovalent and divalent cations, CO$_2$, and injection schemes. It is found that the injection of NaCl low salinity water alters the wettability towards slightly water-wet, and the injection of CaCl$_2$ low salinity water alters the wettability towards slightly oil-wet. The injection of CO$_2$ promotes water-wetness and geochemical reactions between oil and brine. Injection scheme of CO$_2$ and NaCl low salinity water is more efficient than WAG cycle of CO$_2$/NaCl in wettability alteration towards more water-wet. However, the opposite trend is observed with CaCl$_2$ low salinity water, of which WAG cycle of CO$_2$/CaCl$_2$ is more efficient in altering wettability towards water-wet. The oil drop deformation process during LSWI resembles the process of oil removal using surfactant. As CO$_2$ is introduced, due to the acidic effect of CO$_2$ and ion exchange, it acts to wet the rock surface, leading to a more water-wet state. With introduction of CO$_2$, the oil drop deformation resembles the “roll-up” oil removal process.

1 Introduction

Low salinity water injection (LSWI) has been widely investigated and recognized as an effective enhanced oil recovery (EOR) method in both secondary and tertiary mode [1-3]. Compared to other chemical EOR methods, such as polymer or surfactant flooding, LSWI is advantageous due to its lower cost and reduced impact on the environment. Another advantage for LSWI is that it can be combined with other EOR methods to further improve oil recovery [4-6]. According to economic evaluations on chemical EOR methods by Al-Murayyi et al. [7] and Muriel et al. [8], LSWI and CO$_2$ injection generate the highest net present value (NPV) and both methods are effective in increasing oil recovery. Therefore, a hybrid technique termed CO$_2$ low salinity water-alternating-gas (LSWAG) injection, which combines the EOR effect of both methods, has been developed over the last 15 years. CO$_2$ LSWAG injection has been studied through core flooding experiments, contact angle and interfacial tension (IFT) measurements, primarily with sandstone, at ambient or reservoir conditions. Most results confirm improved oil recovery using this hybrid technique, in both secondary and tertiary modes, with some exceptions [9-11]. Studies with negative or neutral outcomes are mainly due to the fact that the cores are strongly water-wet or contain very small amount of clay minerals. Clean water-wet sandstones may not be the most favourable reservoir conditions for CO$_2$ LSWAG injection [12, 13].

The proposed mechanisms of CO$_2$ LSWAG injection are a combination of LSWI and CO$_2$ WAG injection. Al-Abri et al. [14] proposed that the improved oil recovery by immiscible CO$_2$ LSWAG injection is due to mobility control and wettability alteration. The IFT between high salinity brine and oil reduces as CO$_2$ is introduced. However, changes in the IFT of low salinity brine and oil are not noticeable, indicating that IFT reduction is not a dominant mechanism in this process. They also suggest multi-component ionic exchange (MIE) in which Na$^+$ substitutes the divalent cations (Mg$^{2+}$) accounts for the higher oil recovery when injecting monovalent NaCl brine compared to injection of MgCl$_2$ brine. Teklu et al. [15] claimed that CO$_2$ LSWAG injection improved oil recovery of conventional CO$_2$ WAG injection by forming in-situ Carbonated Water of higher CO$_2$ saturation in the brine phase due to the higher CO$_2$ solubility in low salinity water. This in-situ Carbonated Water promotes wettability alteration towards more water-wet and CO$_2$-brine IFT reduction, hence improved oil recovery. They also
compared the CO$_2$–brine solubility model developed by Enick and Klara [16] and Li and Nghiem [17] with fresh water and 100,000 ppm NaCl at 71°C from 0 to 41 MPa. Both models show that CO$_2$ solubility in brine increases with pressure and CO$_2$ solubility is higher in fresh water. Chaturvedi et al. [18] and AlQuraishi et al. [11] suggest that fines migration and wettability alteration, mechanisms of LSWI, might be the dominant mechanisms for increased oil recovery by CO$_2$ LSWAG injection. The presence of clay minerals, especially kaolinite, is considered essential. However, this proposed mechanism is questioned by Zolfaghari et al. [19] as they achieved oil recovery in sandstone without kaolinite. Wettability alteration towards more water-wet was suggested by Al-Saedi et al. [20-22]. Based on the proposed mechanisms, wettability alteration and mobility control may be considered the dominant mechanisms in CO$_2$ LSWAG injection.

Wettability alteration taking place during CO$_2$ LSWAG injection could be ascribed to LSWI or the acidic effect of CO$_2$ [23, 24] or a combination of both. Drummond and Israelachvili [25] demonstrate wettability alteration indicated by contact angle measurements at ambient conditions for low salinity water varying from oil-wet to water-wet as pH is lower than 9 and from water-wet to intermediate-wet as pH is greater than 9. The pH during a LSWI is mostly below 9 [26], indicating the wettability alteration is more likely to be from water-wet to intermediate-wet [27]. The main functions of injecting CO$_2$ are oil swelling and viscosity reduction due to CO$_2$ solubility in oil, miscibility with oil if pressure is above minimum miscible pressure and wettability modification [21]. Since low salinity water and CO$_2$ both impact wettability, the question remains as to whether the introduction of CO$_2$ in low salinity water will assist in promoting the geochemical reactions and low salinity effect. Generally, monovalent cations (Na$^+$) and divalent cations (Ca$^{2+}$ or Mg$^{2+}$) have different impacts on the rock surface. The MIE mechanism by LSWI proposed by Lager et al. [28] demonstrates that multivalent cations, such as Ca$^{2+}$, act as bridges between the oil polar components and the negatively charged rock surface, promoting oil-wetness. The mechanism of electrical double layer expansion by LSWI suggested by Ligthelm et al. [29] indicates that lowering the electrolyte content, especially reducing the content of multivalent cations, yields expansion of the electrical double layer surrounding the clay and oil, and an increase in zeta potential. This leads to wettability modification of the rock surface towards more water-wet. Wettability characterization is uncertain for CO$_2$ introduced with low salinity water in the sandstone/oil/brine/rock system since previous experimental data is limited.

To investigate wettability of the rock and fluid systems, direct or indirect and qualitative or quantitative methods can be used. Indirect and qualitative methods for characterizing rock wettability are capillaryimeter method [30], spontaneous imbibition [31, 32], capillary pressure curves, and relative permeability method [33, 34]. Indirect and quantitative methods include the Amott and Amott-Harvey index method, USBM (U.S. Bureau of Mines) method, and the combined Amott/USBM method, which measure the average wettability of the rock samples, i.e., a macroscopic mean value of the rock wettability to a given fluid. Direct and quantitative method for characterizing the wettability of a specific surface is the contact angle measurement [35, 36], as well as the new SEM-MLA method introduced [37, 38]. Contact angle measurement works the best with pure fluids and well-prepared surfaces [39]. It can also be used to determine the effect of crude oil, brine chemistry, temperature and pressure on wettability. According to Arif et al. [40], direct contact angle measurements is a widely recognized technique for wettability characterization of rock/CO$_2$/brine or rock/oil/CO$_2$-enriched-brine systems. In this research we used contact angle measurement as a method to evaluate wettability alteration. Our particular interest is understanding the ion exchange and chemical reactions of the rock/oil/brine/ and rock/oil/brine/CO$_2$ systems by comparing the effect of monovalent and divalent ions and the effect of CO$_2$ on water-wet and oil-wet sandstone under different injection sequences. Contact angle measurements may indeed be the best choice to differentiate any wettability changes as we are able to 1) conduct measurements with high temperature and pressure, under which the commonly used Amott or USBM method is not applicable [40, 41] and 2) still appreciate the core scale aspects of rock mineralogy and some differences in water-wet and oil-wet “real” surfaces [42].

The data for contact angle measurements on sandstone/crude oil/CO$_2$-enriched brine system is very limited. Jaeger et al. [43] performed captive bubble contact angle measurements with sandstone samples which were previously aged at room temperature with 1.5 wt% cyclohexanepentanoic acid in decane for two months. They reported a strongly water-wet condition, contact angle of 46º, of such system under 50°C and 20.7 MPa with 32,000 ppm synthetic seawater. Ameri et al. [44] conducted contact angle measurements on Bentheimer sandstones that are initially water-wet and oil-wet at elevated pressure from 0.2 to 14 MPa and with NaCl brine salinity ranging from 5000 to 35,000 ppm. They found that in initially water-wet sandstones, contact angle increases with pressure, and decreases with increasing NaCl brine concentration. The overall contact angle for using NaCl brine salinity ranging from 20,000 to 35,000 ppm is very low, less than 20º. The average contact angle for using 5000 ppm NaCl brine is 40º and the value when distilled water is used is 57º. This indicates that decreasing salinity of NaCl brine leads to a less water-wet state, which differs from the results obtained by Espinoza et al. [45]. For initially oil-wet sandstone, samples were aged for 22 months with crude oil at 60°C. In the sub-critical and near-critical state region of CO$_2$ (0-9 MPa), contact angle increases is slightly higher with 35,000 ppm brine than with distilled water. However, the opposite is observed for super-critical state region of CO$_2$ (9-13 MPa), Seyyedi et al. [46] reported that contact angle values of the quartz with CO$_2$-enriched brine are slightly higher than that with brine phase alone, indicating that injection of CO$_2$ alters wettability towards slightly less water-wet. However, Al-Abri et al. [14] reported contradictory results, showing that the contact angle was reduced with the addition of CO$_2$, indicating a wettability alteration towards more water-wet. They conducted their contact angle measurements with Berea sandstone discs aged with crude oil at 60º for three weeks. They also found that changes in wettability are greater with divalent ions (Mg$^{2+}$) than monovalent ions (Na$^+$ and K$^+$).

It is worth mentioning that there are limitations on these contact angle measurements that would result in misleading
interpretations on the effect of CO₂ and low salinity water, and the working mechanisms of CO₂ LSWAG injection. In these measurements, the oil drop is introduced after the rock surface has been in contact with injection brine and CO₂, which is not representative of the actual displacement in a reservoir, where oil exists before the injection fluids. Therefore, in order to better capture and mimic the real displacement procedure taking place in a reservoir to investigate what triggers the wettability alteration during LSWI and CO₂ LSWAG injection, a displacement method developed by Sofla et al. [42] for measuring contact angle was employed in this study. We investigated the dynamic contact angle changes during the displacement process of LSWI, continuous CO₂ and LSWI, and CO₂ LSWAG injection, respectively. With this method, the interactions among crude oil, brine and CO₂ were investigated without the additional effect of capillary imbibition and drainage [47]. The objective is to compare the resulting wettability alteration (through contact angle measurements) due to multicomponent ion exchange (MIE), chemical reactions, and injection sequence of low salinity water methods. This paper addresses the question as to whether or not the ionic charge and injection scheme play a role in differentiating LSWI and CO₂ LSWAG injection at the fluid-rock interaction level.

3 Methods

Figure 1 illustrates the experimental setup used to perform contact angle measurements in this study. All experiments are conducted at ambient conditions. In order to mimic the actual displacement taking place in a reservoir, the cell is initially filled with formation brine. Subsequently, an oil drop with radius ranging from 1.8 to 2.0 mm is introduced through the needle at the bottom of the cell and adheres onto the rock surface. The initial contact angles are measured after the system reached equilibrium, which is 1 hour after it is introduced into the system. This indicates the initial wettability of the rock surface and initial condition of an oil droplet in a reservoir.

2 Materials

Fluids. The oil phase used in this experiment is an offshore Newfoundland and Labrador (NL) light crude oil. Synthetic brines were prepared to mimic the Hibernia formation water and Grand Banks seawater. The two low salinity brines are 2000 mg/L NaCl and 2000 mg/L CaCl₂. Their chemical compositions and basic properties are presented in Table 1.

Table 1. Compositions and properties of synthetic brines and oil

<table>
<thead>
<tr>
<th>Component</th>
<th>FB</th>
<th>SW</th>
<th>NaCl</th>
<th>CaCl₂</th>
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</thead>
<tbody>
<tr>
<td>Na⁺, mg/L</td>
<td>35,671</td>
<td>10,974</td>
<td>786</td>
<td>/</td>
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<tr>
<td>Mg²⁺, mg/L</td>
<td>330</td>
<td>1,310</td>
<td>/</td>
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<tr>
<td>Ca²⁺, mg/L</td>
<td>3,599</td>
<td>420</td>
<td>/</td>
<td>721</td>
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<td>K⁺, mg/L</td>
<td>255</td>
<td>407</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Cl⁻, mg/L</td>
<td>62,371</td>
<td>19,740</td>
<td>1,214</td>
<td>1,279</td>
</tr>
<tr>
<td>SO₄²⁻, mg/L</td>
<td>233</td>
<td>2,766</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>HCO₃⁻, mg/L</td>
<td>/</td>
<td>129</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Total</td>
<td>102,430</td>
<td>35,746</td>
<td>2,000</td>
<td>2,000</td>
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<tr>
<td>pH@22°C</td>
<td>5.9</td>
<td>7.9</td>
<td>6.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1.074</td>
<td>1.023</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Oil Viscosity, cP</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil Density, g/cm³</td>
<td>0.878</td>
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</tr>
</tbody>
</table>

Legends: FB – formation brine; SW – seawater; / - not included

Rock sample. Berea sandstone with 80% quartz content and <2% clay content [37] was used in this study. The core samples with an approximate diameter of 2 cm were cut into 5-mm thin slices using MK-370EXP Tile Saw. The dust was blown off with pressurized nitrogen and the core slices were dried in oven overnight. The water-wet samples were immersed in formation brine for one day prior to conducting contact angle measurements. To obtain an oil-wet initial wettability, the core slices initially immersed in formation brine were removed to a beaker containing NL crude oil and aged at 98°C in the oven for six weeks as suggested by Sripal et al. [37] to obtain oil-wet conditions. Subsequently, the surface of the oil-wet samples was cleaned and immersed in formation water for one day before contact angle measurements.

A total of 13 experiments were completed, using the injection schemes outlined in Table 2. Each scenario was completed twice, once using NaCl as the LSW and again using CaCl₂ as the LSW.

Table 2. Injection scheme of experiment

<table>
<thead>
<tr>
<th>Scenario #</th>
<th>Injection Scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1 (60 mL)</td>
</tr>
<tr>
<td>1</td>
<td>SW</td>
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<tr>
<td>2</td>
<td>SW</td>
</tr>
<tr>
<td>3</td>
<td>LSW</td>
</tr>
<tr>
<td>4</td>
<td>SW</td>
</tr>
<tr>
<td>5</td>
<td>SW</td>
</tr>
<tr>
<td>6</td>
<td>LSW</td>
</tr>
<tr>
<td>7</td>
<td>LSW</td>
</tr>
</tbody>
</table>

Scenario 1 represents seawater injection. Scenario #2 and #3 represent LSWI. Scenarios #4 and #6 represents seawater or low salinity water injection, followed by continuous CO₂
injection and LSWI. Scenario #5 and #7 represent seawater or low salinity water injection, followed by LSWAG injection. Brines and CO\textsubscript{2} were injected through the injection inlet into the cell to displace the existing fluid. The injection speed was controlled so that the oil drop remains attached on the rock surface throughout the experiment.

The total volume of the cell is 20 mL. In cycle 1, 60 mL of seawater or low salinity water is injected to ensure that the initial formation brine is fully displaced. The system is allowed to set for equilibrium for half an hour after every 20 mL of injection fluid and the reading at equilibrium state is taken. Figure 2, as an example, shows the contact angle changes during the half-an-hour equilibrium time of scenario #1, indicating that an equilibrium was gradually established.

\[ \Delta \theta [\%] = (\theta - \theta_{\text{initial}}) / \theta_{\text{initial}} \times 100 \quad (1) \]

where $\Delta \theta$ refers to the change in contact angle, $\theta$ is the value of contact angle measured after each injection cycle, and $\theta_{\text{initial}}$ is the initial contact angle measured with the presence of formation water. The reason for comparing changes instead of absolute contact angles is to avoid the influence of the samples and each scenario starts from the same point. Initial contact angle is also reported.

To calculate the uncertainty, or error propagation of $\Delta \theta$, the root-sum square method proposed by Kline and McClintock is used [48]. The effect of uncertainty $\sigma_{\Delta \theta}$ on the calculated $\Delta \theta$ can be expressed as follow:

\[ \sigma_{\Delta \theta} = \sqrt{\sigma_{\theta}^2 + \left( \frac{\partial \Delta \theta}{\partial \theta} \right)^2 + \sigma_{\theta_{\text{initial}}}^2 \left( \frac{\partial \Delta \theta}{\partial \theta_{\text{initial}}} \right)^2} \quad (2) \]

Subsequently, changes in contact angle with calculated uncertainty are plotted against injected volume to investigate the effect of low salinity water, injection of CO\textsubscript{2} and WAG injection schemes.

Moreover, in order to validate that the measured contact angle changes are mainly due to the chemical reactions (intermolecular forces) in the oil/brine/rock system, rather than gravitational force, we have estimated the Bond number ($B_o$) of the oil/seawater/brine system using equation from Li et al. [49].

\[ B_o = \frac{\Delta \rho g l^2}{\gamma} \quad (3) \]

where $\Delta \rho$ is the density difference of oil and brine (kg/m\textsuperscript{3}), $g$ is gravitational acceleration (m/s\textsuperscript{2}), $L$ refers to the radius of curvature of oil drop (m), $\gamma$ is surface tension (N/m). With the measured surface tension (31.5 mN/m), and oil drop radius in seawater (1.86 mm), Bond number is calculated to be 0.154, which is lower than 1, indicating that surface tension dominates.

4 Results and Discussion

As shown in Table 3, section 4.1 investigates the effect of seawater injection on wettability alteration of water-wet and oil-wet Berea sandstone samples. Section 4.2 discusses the effect of CO\textsubscript{2} by comparing scenario #2 and #4, and #3 and #6. Subsequently, the deformation process of the oil drops during the injection of low salinity water and CO\textsubscript{2} is investigated in section 4.3. In the end, section 4.4 studies the effect of different injection schemes by comparing CO\textsubscript{2} + LSW injection scheme to CO\textsubscript{2}/LS WAG injection scheme (#4 and #5, and #6 and #7). The effect of monovalent and divalent cations is discussed and compared in all sections.

<table>
<thead>
<tr>
<th>Section</th>
<th>Comparison of different scenarios</th>
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<tr>
<td>4.1 Effect of Low Salinity Water</td>
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<tr>
<td></td>
<td>#2 SW + LSW (NaCl and CaCl\textsubscript{2})</td>
</tr>
<tr>
<td></td>
<td>#3 LSW + LSW (NaCl and CaCl\textsubscript{2})</td>
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<tr>
<td>4.2 Effect of CO\textsubscript{2}</td>
<td>#2 SW + LSW</td>
</tr>
<tr>
<td></td>
<td>#4 SW + CO\textsubscript{2} + LSW</td>
</tr>
<tr>
<td></td>
<td>#3 LSW + LSW</td>
</tr>
<tr>
<td></td>
<td>#6 LSW + CO\textsubscript{2} + LSW</td>
</tr>
<tr>
<td>4.4 Effect of Injection Scheme</td>
<td>#4 SW + CO\textsubscript{2} + LSW</td>
</tr>
<tr>
<td></td>
<td>#5 SW + CO\textsubscript{2}/LS WAG</td>
</tr>
<tr>
<td></td>
<td>#6 LSW + CO\textsubscript{2} + LSW</td>
</tr>
<tr>
<td></td>
<td>#7 LSW + CO\textsubscript{2}/LS WAG</td>
</tr>
</tbody>
</table>

4.1 Effect of Low Salinity Water

Contact angle changes due to the injection of seawater alone, low salinity waters alone, and combinations of seawater and low salinity water are shown in Figures 3 and 4 for water-wet and oil-wet sandstones, respectively. These injection schemes mimic the displacement process of (1) seawater injection, (2)
secondary seawater and tertiary LSWI, and (3) LSWI. Overall, changes in contact angle in the oil-wet samples are not as significant as in water-wet samples. However, it is worth comparing and understanding the changing trend after each injection cycle, which could be an estimation for the potential changes in a core scale experiment.

In Figure 3, the initial wettability of the rock sample is water-wet, with measured contact angles varying from 34° to 50° (average: 40.6°±5.0°). Contact angle changes due to the injection of seawater are within 5%, which is not very significant. This indicates that the injection of seawater has negligible effect on the rock wettability. The trend of using NaCl and CaCl₂ in LSWI shows different impacts on wettability. The red arrow in Figure 2 indicates changing towards more oil-wet, and the blue arrow suggests changing towards more water-wet. It is seen that NaCl alters the wettability towards more water-wet, around 10% less compared to initial contact angle, whereas CaCl₂ results in wettability alteration moving to less water-wet. A similar trend is also observed in the combined seawater and LSWI process.

In Figure 4, the initial wettability of the rock sample is oil-wet, with measured contact angle varying from 117° to 155° (average: 133.0°±13.5°). For seawater injection (SW + SW), the contact angle remains almost constant throughout the process. The injection of NaCl LSW alters the rock wettability towards slightly less oil-wet (SW + NaCl, NaCl + NaCl) and use of CaCl₂ (SW + CaCl₂, CaCl₂ + CaCl₂) and use of CaCl₂ (SW + CaCl₂, CaCl₂ + CaCl₂) alters the wettability towards more oil-wet. This observation agrees with that in the water-wet samples where NaCl promotes water-wetness and CaCl₂ promotes oil-wetness.

Generally, the configuration of water on rock mineral surfaces exist in two ways: (1) pendular-ring on contact points of grains; and (2) thin film on the mineral surfaces [50]. In this study, the oil drop is introduced after formation water and is kept attached to the surface throughout the experiment. Therefore, the model proposed is as shown in Figure 5, where a thin water film is formed between the rock and oil drop. A similar model was also proposed by Lee et al. [51]. They manufactured sand/clay like silica particles using simple anionic surface similar to sand grain and measured the thickness of this water film to be roughly 9-15 nm. According to their measurements on the simple wet system (fabricated simple anionic surface, similar to a sand grain) [51], the thickness of the water film on the silica/clay (sandstone-like) surface is thicker in brines with lower salinities (except for pure water). Therefore, in a system where the substrate is initially oil-wet, in order alter the wettability from oil-wet to intermediate-wet or water-wet, a thicker water film along the pore wall is needed.

Based on the results from Figure 3 and Figure 4, it is observed that the use of monovalent cations as injection brine alters the wettability towards more water-wet, which agrees with the finding from Xie et al. [52] that monovalent cations (Na⁺) give rise to positive disjoining pressure; however, divalent cations (Ca²⁺) lead to negative disjoining pressure at the same concentration. Negative disjoining pressure between rock surface and oil droplet indicates the attractive force is dominant; thus, more oil-wet is expected for the rock surface. On the other hand, positive disjoining pressure suggests the repulsive force between the rock surface and oil droplet, leading to more water-wet.

4.2 Effect of CO₂

The wettability changes caused by CO₂ after seawater injection and LSWI (NaCl or CaCl₂) were investigated by comparing the contact angle changes in scenarios with CO₂ (#4 and #6) and without CO₂ (#2 and #3). Contact angle changes during cycle 2 – 4 are studied. For LSWI (#2 and #3), cycle 2-4 are injection of LSW. For CO₂ + LSW (#4 and #6), cycle 2 is injection of CO₂, cycle 3-4 are injection of LSW. To calculate the changes, \( \theta_{initial} \) in Eq. (1) is not the initial value in cycle 1, but the equilibrium contact angle measured after cycle 1 (\( \theta_{cycle 1 eq} \)). Hence, Eq. (4) was used to calculate
contact angle changes (Δθ) and uncertainty was calculated according to Eq. (2).

\[ Δθ [\%] = \left( \frac{θ - θ_{\text{cycle 1,eq}}}{θ_{\text{cycle 1,eq}}} \right) × 100 \]  

(4)

Based on this, all the scenarios investigated in this section will start from the same point in cycle 2 with respect to contact angle change.

Figures 6 and 7 show the results of LSWI and CO\(_2\) + LSWI after seawater injection in water-wet and oil-wet samples respectively. When comparing scenario #2 (SW + LSW) and #4 (SW + CO\(_2\) + LSW), the addition of CO\(_2\) after seawater promotes water-wetness for both water-wet and oil-wet samples. After CO\(_2\) injection, further injection of CaCl\(_2\) changes the wettability towards more oil-wet, and the injection of NaCl changes further more towards water-wet.

![Fig. 6 Comparison of contact angle changes during LSWI and CO\(_2\) + LSWI in water-wet sandstone after 1st cycle of seawater injection (scenario #2 and #4).](image6)

![Fig. 7 Comparison of contact angle changes during LSWI and CO\(_2\) + LSWI in oil-wet sandstone after 1st cycle of seawater injection (scenario #2 and #4).](image7)

The contact angle changes of LSWI (scenario #3) and CO\(_2\) + LSWI (scenario #6) after LSWI in cycle 1 are shown in Figure 8 and Figure 9. Injection of LSW in cycle 2-4 has no significant impact on contact angle after the 1st cycle of LSWI. However, with the injection of CO\(_2\) in cycle 2 and NaCl in cycle 3-4, CO\(_2\) + NaCl alters wettability towards more water-wet in both water-wet and oil-wet samples (Figure 8 and Figure 9). For scenario #6 (CO\(_2\) + CaCl\(_2\)), CO\(_2\) alters wettability towards more water-wet, whereas further injection of CaCl\(_2\) changes the wettability to more oil-wet.

![Fig. 8 Comparison of contact angle changes during LSWI and CO\(_2\) + LSWI in water-wet sandstone after 1st cycle of LSWI (scenario #3 and #6).](image8)

![Fig. 9 Comparison of contact angle changes during LSWI and CO\(_2\) + LSWI in oil-wet sandstone after 1st cycle of LSWI (scenario #3 and #6).](image9)

It is also observed from Figure 8 and 9 that CO\(_2\) injected after CaCl\(_2\) low salinity water alters wettability towards more water-wet compared to that injected after NaCl low salinity water. As suggested by Lager et al. [53], it is possible that divalent cations are exchanged for monovalent cations during LSWI. Therefore, in our case, more Ca\(^{2+}\) on the rock surface is expected in scenario #6 with CaCl\(_2\).

When CO\(_2\) is in contact with water, it first dissolves according to reaction (5):

\[ CO_2(g) \rightleftharpoons CO_2(aq) \]  

(5)

At room temperature, solubility of CO\(_2\)(g) is 0.034 mol/L. Subsequently, reaction (6) takes place to form H\(_2\)CO\(_3\). This reaction is kinetically slow and only a small fraction (0.2 – 1.0%) of dissolved CO\(_2\), CO\(_2\)(aq), is converted to H\(_2\)CO\(_3\).

\[ CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \]  

(6)

However, this carbonic acid dissociates very rapidly at ambient conditions to bicarbonate [54], as shown in reaction (7). The bicarbonate electrolyte in the solution can also form CO\(_3^{2-}\) as shown by reaction (8).
\[ H_2CO_3(aq) \rightleftharpoons HCO_3^- + H^+ \]  \hspace{1cm} (7)

\[ HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \]  \hspace{1cm} (8)

With the injection of CO₂, some of the produced CO₃²⁻ would potentially react with the existing Ca²⁺ ions, forming CaCO₃, which results in equation (8) to move to the right direction, leading to slight increase in H⁺. Based on the selectivity of cation affinity to negatively charged surfaces from Velde [55], as shown below, the proton H⁺ has the strongest affinity to be adsorbed onto a negatively charged surface.

\[ \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{H}^+ \]

Therefore, the generated H⁺ is likely to replace the pre-attached divalent cations, resulting in more water-wetness. In this way, the injection of CO₂ after CaCl₂ low salinity water alters wettability towards more water-wetness after NaCl low salinity water.

### 4.3 Surfactant-Like Behavior of Oil Drops

During the injection of LSW and a combination of CO₂ and LSW in the water-wet and oil-wet samples, a surfactant-like deformation process of the oil drop is constantly observed when the initial equilibrium of the system is disturbed. The oil drop deformation with and without CO₂ is discussed respectively in the subsections.

#### 4.3.1 Deformation in the absence of CO₂

Figure 10 and Figure 11 illustrate the deformation process during the injection of NaCl LSW in water-wet and CaCl₂ LSW in oil-wet sandstones, respectively. For NaCl LSWI in water-wet sample, the contact angle varies from water-wet to intermediate-wet and then back to more water-wet while reaching equilibrium. For CaCl₂ LSWI in oil-wet sample, contact angle changes from oil-wet to intermediate-wet and then back to more oil-wet in the end.

Based on Figures 10 and 11, the deformation process during LSWI resembles a surfactant-like behaviour. The potential removal of the droplet exhibits a “necking” or emulsification mechanism. One mechanism for LSWI proposed by McGuire et al. [56] suggests that the changes in wettability during low salinity water injection appear to be similar to the observations from alkaline and surfactant flooding. In this study, the interactions between the oil drop and injection fluids are more dominant due to the presence of just one oil drop. As listed in Table 1, the pH of the injection fluids is higher compared to that of the initial formation water. During the injection of low salinity water, in-situ “surfactants” are generated, as shown in Eq. (9), when the oil drop is in contact with the elevated pH fluid near the rock and oil surfaces. This improves oil recovery [56]. In this way, low salinity water injection is similar to micellar or surfactant flooding.

\[(R_3COO)_3R_2 + 3NaOH \rightleftharpoons 3(R_3COONa) + R_2(OH)_3 \]  \hspace{1cm} (9)

where \( R_1 \) and \( R_2 \) represent the R group, which consists of a group of carbon and hydrogen atoms.

According to the study of oil removal from soil surfaces by Miller and Raney [57], two approaches are proposed as mechanisms for oil removal from hydrophobic surfaces using surfactants: (1) roll-up resulting from wetting; and (2) emulsification resulting from reduction in interfacial tension (Figure 12).
4.3.2 Deformation with CO\textsubscript{2} present

The top two pictures shown in Figure 13 are the oil drop deformation during injection of CO\textsubscript{2} + CaCl\textsubscript{2}, (scenario #4) and the bottom two pictures are during CaCl\textsubscript{2} LSWI (scenario #2). These two deformation processes resemble the two approaches in Figure 12. Without addition of CO\textsubscript{2}, the detachment of the oil drop is a saponification or emulsification process. However, the roll-up process is expected with CO\textsubscript{2} due to the geochemical reactions that change the wetting state of the contact point on the rock surface.

4.4 Effect of Injection Scheme

The impact of different injection schemes with respect to CO\textsubscript{2} is explored by comparing the scenarios of SW + CO\textsubscript{2} + LSW (#4) and SW + LSWAG (#5), and scenarios of LSW + CO\textsubscript{2} + LSW (#6) and LSW + LSWAG (#7).

Contact angle changes of scenario #4 and #5 are shown in Figure 14 and Figure 15. It is observed that after 1\textsuperscript{st} cycle of seawater injection, further injection of CO\textsubscript{2} + CaCl\textsubscript{2} alters wettability in the direction of more oil-wet, however, CO\textsubscript{2}/CaCl\textsubscript{2} WAG injection alters rock wettability towards more water-wet. Injection schemes of CO\textsubscript{2} + NaCl and CO\textsubscript{2}/NaCl WAG both change the rock wettability to more water-wet, whereas changes are more significant for CO\textsubscript{2} + NaCl. The wettability changes by CO\textsubscript{2}/LSWAG processes (for both NaCl and CaCl\textsubscript{2}) are not as significant as CO\textsubscript{2} + LSW injection when implemented after seawater injection (Figure 14 and Figure 15).
compared to CO\textsubscript{2} sandstone. However, of CO\textsubscript{2} + NaCl injection scheme is more efficient than WAG process, more interactions between injection brine, CO\textsubscript{2} and pre-existing brine are expected, and this leads to different wettability alteration trend compared to CO\textsubscript{2} + LSWI. When NaCl LSW is used, continuous CO\textsubscript{2} + NaCl injection scheme is more efficient than WAG cycle of CO\textsubscript{2}/NaCl in wettability alteration towards more water-wet. However, with CaCl\textsubscript{2}; LSW, WAG cycle of CO\textsubscript{2}/CaCl\textsubscript{2} can alter the rock wettability to more water-wet compared to continuous CO\textsubscript{2} + CaCl\textsubscript{2} injection.

The WAG process of CO\textsubscript{2} and CaCl\textsubscript{2} low salinity water leads to wettability alteration to slightly water-wet. With respect to the scenario of CO\textsubscript{2} + CaCl\textsubscript{2} (#6), even though CO\textsubscript{2} changes wettability to be more water-wet, the generated H\textsuperscript{+} is not sufficient. Thus, subsequent injection of CaCl\textsubscript{2} replaces the monovalent cations and alters the rock wettability towards more oil-wet.

Summarising, if NaCl LSW is used, the continuous CO\textsubscript{2} + NaCl injection scheme is more efficient than WAG cycle of CO\textsubscript{2}/NaCl in achieving a more water-wetness condition of sandstone. However, if CaCl\textsubscript{2}; LSW is used, WAG cycle of CO\textsubscript{2}/CaCl\textsubscript{2} can alter the rock wettability to more water-wet compared to continuous CO\textsubscript{2} + CaCl\textsubscript{2} injection.

5 Conclusion

1. In this study, a displacement method for measuring contact angle changes during the process of seawater injection, LSWI, CO\textsubscript{2} and LSWI, and CO\textsubscript{2} LSWAG injection has been conducted. Seawater, low salinity water with only monovalent and divalent cations were selected as the injection aqueous phases. The effect of these ions, oil drop deformation process, and the effect of CO\textsubscript{2} and injection scheme have been investigated. It is found that for our Berea sandstone with an initial wettability of either water-wet and oil-wet\textsuperscript{1}, the injection of 2000 ppm NaCl water alters the wettability towards slightly water-wet, and the injection of 2000 ppm CaCl\textsubscript{2} alters the wettability towards slightly oil-wet. Low salinity water with divalent cation could increase the attraction forces between the oil/rock and oil/brine interfaces, promoting oil-wetness. However, low salinity with monovalent cation reduces the attraction forces, i.e., repulsive force increases, therefore, resulting in more water-wet.

2. The deformation process during LSWI resembles the process of oil removal using surfactant. This “surfactant-like” behaviour lowers the interfacial tension and contributes to increased oil recovery. As CO\textsubscript{2} is introduced, due to the acidic effect of CO\textsubscript{2}, it acts to wet the rock surface, leading to a more water-wet state. Therefore, the oil removal or oil drop deformation resembles the “roll-up” oil removal process.

3. The injection of CO\textsubscript{2} promotes water-wetness and geochemical reactions between oil and brine. In the WAG process, more interactions between injection brine, CO\textsubscript{2} and pre-existing brine are expected, and this leads to different wettability alteration trend compared to CO\textsubscript{2} + LSWI. When NaCl LSW is used, continuous CO\textsubscript{2} + NaCl injection scheme is more efficient than WAG cycle of CO\textsubscript{2}/NaCl in wettability alteration towards more water-wet. However, with CaCl\textsubscript{2}; LSW, WAG cycle of CO\textsubscript{2}/CaCl\textsubscript{2} can alter the rock wettability to more water-wet compared to continuous CO\textsubscript{2} + CaCl\textsubscript{2} injection.

6 Future Work

In this study, all the measurements are conducted at ambient condition. The effect of temperature and pressure is not considered. As the temperature and pressure exceeds the critical point for CO\textsubscript{2}, the state of CO\textsubscript{2} will become supercritical, with properties midway between a gas and a liquid. Therefore, in order to better understand the wettability alterations with supercritical CO\textsubscript{2}, more research with respect to elevated temperature and pressure should be carried out in the future. If wettability alteration is considered as the main mechanism for LSWI or CO\textsubscript{2} LSWAG injection, this displacement contact angle measurement which mimics the real reservoir displacement process could be used as a preliminary screening for brine concentration and composition, as well as injection schemes. However, to achieve a systematic evaluation process, more experimental data with respect to temperature and pressure are required.

\textsuperscript{1} Note: wettability was inferred from the contact angle and was not independently verified by measurements like USBM or Amott.
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