Geochemical Investigation of the Combined Effect of Injecting Low Salinity Water and Carbon Dioxide on Carbonate Reservoirs

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Abstract

This paper uses geochemical modeling to investigate the combined effect of low salinity water injection (LSWI) and CO2 on carbonate oil reservoirs. The geochemical modeling of recently published corefloods was performed using the PHREEQC simulator. Geochemical analysis show that the change in surface charge of carbonates by varying pH is more pronounced using LSWI only than is the combined effect of LSWI and CO2 injection. The combined effect of LSWI and CO2 is most prominent on carbonates with high dolomite composition, whereas carbonates with high anhydrite composition are most affected by LSWI only.

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1. Introduction

Low salinity water injection (LSWI) is one of the emerging improved oil recovery (IOR) techniques for wettability alteration in carbonate reservoirs. This technique has the potential of being cost effective compared to other IOR techniques. Carbon dioxide (CO2) injection is a commonly used and favorable enhanced oil recovery (EOR) technique especially when a gas source is available along with high API crude oil and low permeability formations as in carbonates. A brief description of low salinity water injection (LSW) technique, its experimental and simulation studies, and the potential of LSWI and CO2 in carbonate rocks is presented.

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Several studies have been performed on carbonates using LSWI at laboratory scale [1 – 8]. These studies have confirmed a positive response to low salinity injection upon which additional oil recovery has been obtained in both secondary and tertiary injection modes. The first ever LSWI application in carbonate reservoirs was reported by Yousef et al. [9] in the form of two single well chemical tracer tests (SWCTT). The tests resulted in about 7 saturation units reduction in the residual oil beyond conventional seawater injection.

The main reason underlying the LSWI effect on oil recovery from carbonate rocks is less complicated compared to sandstone rocks. Most of researchers agree on wettability alteration as the main contributor to LSWI effect on carbonate rocks, Austad et al. and other co-workers [1, 10 – 12]. Wettability alteration in carbonate rocks using LSWI can be achieved by injecting water containing SO₄²⁻ and either Ca²⁺ or Mg²⁺ or both of them at high temperatures (>90 °C) [11]. Yousef et al. [6] demonstrated that wettability alteration is the reason behind LSWI through NMR, contact angle, and zeta potential studies. Nevertheless, work is progressing on understanding the chemical interactions between crude oil/brine/rock (COBR) system.

There are few proposed LSWI models in the literature and especially for carbonates. One main reason is reluctance to investigate the effect of LSWI on carbonate rocks due to the need to relate the wettability alteration effect to the presence of clay [13, 14]. Another reason is complex chemical interaction between rock-oil-brine and heterogeneity of carbonate rocks, which complicate oil recovery predications by LSWI. Also, the clash in some of the published results regarding the effect of LSWI on carbonate rocks shifted the focus to laboratory work and understanding the controlling phenomena rather than on modeling. It should be noticed that all the proposed LSWI models in the literature treated water and oil phases similarly; $P_e$ and $k_r$ for both phases are shifted using similar weighting factor [15 – 22].

In our previous studies, we showed that oil relative permeability is more sensitive to LSWI compared to water relative permeability and hence water and oil phases should be treated separately [23 – 26]. Based on the latter finding, we proposed several models for the LSWI effect on oil recovery from carbonates [27, 28]. Moreover, we proposed that both dissolution and changing surface charge of the rock are the reasons for wettability alteration and incremental oil recovery by LSWI for corefloods of Yousef et al. [5, 6] from a geochemical point of view [29].

Studies have been performed to extend the applicability of LSWI and investigate its contribution to other IOR techniques. Combing LSWI and CO₂ injection is one of these applications. Fjelde et al. [30] investigated wettability alteration during water flooding and CO₂ flooding on reservoir chalk rocks from the North Sea at different temperatures (50 and 130 °C). The results showed that wettability alteration towards more water-wet was observed after the WAG slug resulting in residual oil saturation between 3 - 5%. Aleidan et al. [31] studied the effect of different CO₂ injection modes on oil recovery by conducting coreflooding experiments including continuous gas injection (CGI), water alternating gas (WAG), and simultaneous water and gas injection (SWAG). The experiments were conducted at 120 °F and 1900 psi which is 100 psi more than the MMP using outcrop limestone carbonate cores. The salinity of the injected water was varied between 0, 6 and 20 wt%. The results showed that waterflooding recovery alone was not affected by salinity; this indicates that wettability alteration is not affecting oil recovery and the only controlling parameter is CO₂ solubility in water.

A detailed evaluation of CO₂ LSWAG from a one-dimensional heterogeneous model into full field simulation was represented by Dang et al. [32]. They highlighted through simulations the combined benefits of gas and low salinity water floods by including geochemical reactions associated with CO₂ injection, ion exchange process, and wettability alteration. A scaled ion-exchange equivalent fraction based on calcium adsorption on clay was used to interpolate between two sets of relative permeability representing water-wet and oil-wet systems. The authors concluded that CO₂ LSWAG overcomes the late production problem frequently encountered in conventional WAG processes. CO₂ LSWAG resulted in incremental oil recovery of 4.5 – 9 % OOIP.

In this paper, we investigate from a geochemical point of view, the combined effect of injecting low salinity water and carbon dioxide on oil recovery from carbonates. We mainly compare our previous geochemical analysis results of LSWI only [29] with the findings of both CO₂ injection only and the combined LSWI and CO₂ injection. The methodology, combined LSWI and CO₂ effects on calcite, dolomite, and anhydrite, experimental data,
2. Methodology

In this work, the PHREEQC simulator was used to run different simulations. PHREEQC is a computer program developed by United States Geological Survey (USGS) which is capable of simulating different aqueous phase geochemical species at low temperatures. PHREEQC has capabilities for speciation and saturation-index calculations, batch-reaction and one dimensional transport calculations with reversible and irreversible reactions including aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, kinetically controlled reactions, multi-component diffusion and dispersion, mixing of solutions, and inverse modeling [33].

The phase equilibrium option in the PHREEQC simulator was used to simulate both CO2 injection only and the combined effect of injection low salinity water and CO2 by considering a certain maximum amount of CO2 in moles to react at the reservoir pressure condition. The work of Yousef et al. [5] including the first coreflood was chosen for simulating the effect that the combined low salinity water and CO2 might have on oil recovery from carbonate by considering the related geochemical reactions. The seawater was injected as a secondary injection mode followed by three tertiary injection modes: LSWI only, CO2 injection only, and the combined LSWI and CO2 injection. In both tertiary LSWI modes, the salinity of the injected water was varied by considering different seawater dilutions (twice, 10 times, 20 times, and 100 times diluted seawater).

Next, we compare the findings of this study with our previous findings for the LSWI only [29] on the same case study to investigate the contribution of injecting CO2 to LSWI. The phreeqc.dat database was used for considering the needed reactions for the different simulations. The same database was used earlier for the case of LSWI only; however, some of these reactions have a more pronounced effect in the presence of CO2 gas which is discussed next.

3. Combined LSWI and CO2 Effects on Calcite, Dolomite, and Anhydrite

The most abundant acid in natural water systems that is responsible for rock weathering is carbonic acid. The carbonic acid forms as a result of CO2 dissolution in water upon which CO2(g) becomes aqueous CO2(aq) and associates with water molecules as follows [34]:

\[
CO_{2(g)} \rightarrow CO_{2(aq)} ,
\]

\[
CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 .
\]

By convention, the two species of CO2(aq) and H2CO3 are summed up as H2CO3* which is given by

\[
CO_{2(g)} + H_2O \leftrightarrow H_2CO_3^* .
\]

Then, the formed carbonic acid affects both calcite and dolomite directly, and anhydrite indirectly depending on the pH of the formation. The first stage of carbonic acid dissociation is as the following [33]:

\[
H_2CO_3^* \leftrightarrow H^+ + HCO_3^- .
\]

The second stage of dissociation is given by

\[
HCO_3^- \leftrightarrow H^+ + CO_3^{2-} .
\]
For calcite, the equation of calcite dissolution is
\[ \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}. \] (6)

By adding equations (3-6), the effect of CO\(_2\) injection on calcite can be summarized as follows:
\[ \text{CO}_2(g) + \text{H}_2\text{O} + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- . \] (7)

Hence, more dissolution of calcite occurs with CO\(_2\) injection. Similarly, the dissolution reaction for dolomite can be written as
\[ 2\text{CO}_2(g) + 2\text{H}_2\text{O} + \text{CaMg(}\text{CO}_3\text{)}_2 \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 4\text{HCO}_3^- . \] (8)

For anhydrite, the effect of CO\(_2\) is considered indirectly through the changes in calcium ion which affects the dissolution of anhydrites which is given by
\[ \text{CaSO}_4 \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}. \] (9)

Nevertheless, by including the LSWI effect on the reactions in the presence of CO\(_2\) along with the different conditions of temperature, pressure, and pH, the trends for dissolution/precipitation of calcite, dolomite, and anhydrite change.

4. Experimental Data

The first coreflood of Yousef et al. [5] was considered for geochemical modeling using PHREEQC. Carbonate reservoir core plugs were used with average porosity of 25.1%, and average brine permeability of 39.6 mD for the first coreflood. The fluids used included field oil sample (API = 30 °API @ 60 °F and IFT = 39 dynes/cm @ 212 °F), field formation brine, and seawater with different dilution versions. In this coreflood, the core was saturated with live reservoir oil at the irreducible water saturation, and then field seawater was injected at reservoir conditions of 212 °F and 3000 psig, followed by the injection of various seawater dilutions for the tertiary recovery. Both oil recovery and pressure drop were provided for both experiments. More details about the experimental work are described elsewhere [5].

5. Simulation Model

A 1D simulation model was developed for the first coreflood using PHREEQC. The composite core was composed of four core plugs of slightly different permeability. Five gridblocks were used to represent each core plug, thus a total of 20 grid blocks. A Cartesian grid system was used for the first coreflood with dimensions of 20 x 1 x 1. In the simulation model, the length of the gridblock varies to match the length dimensions of the core plugs used in the experiment (Table 1).

Table 1. Composite core simulation model data (First Coreflood)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Gridblocks</td>
<td>20</td>
<td>1D (20 x 1 x 1)</td>
</tr>
<tr>
<td>Gridblock Lengths (Dx)</td>
<td>1-5, Dx is 0.0085 m</td>
<td>Variable gridblock length for the x direction.</td>
</tr>
<tr>
<td></td>
<td>6-10, Dx is 0.00786 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11-15, Dx is 0.00804 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16-20, Dx is 0.00808 m</td>
<td></td>
</tr>
</tbody>
</table>
6. Results and Discussion

6.1. Solid Species Comparison

Geochemical modeling of the first coreflood of Yousef et al. [5] was performed using PHREEQC. Comparisons between the three tertiary injection modes (LSWI, CO$_2$, LSWI+CO$_2$) in terms of solid species including calcite, dolomite, and anhydrite are shown in Figures 1, 2, and 3, respectively. The comparison results are shown at the end of each injection cycle for the first gridblock where the dissolution/precipitation effect is more pronounced due to the slow dissolution/precipitation wave. The latter figures show that there are discrepancies between the three tertiary injection modes in terms of solid species analysis.

Figure 1 shows a comparison of calcite concentration at the end of each injection cycle between the three tertiary injection modes. For LSWI only, calcite precipitation is the general trend with decreasing the salinity of the injected water, whereas a slight dissolution of calcite is pronounced for CO$_2$ injection only. For the case of combined LSWI and CO$_2$ injection, the effect of LSWI dominates the CO$_2$ injection effect, which results in calcite precipitation. Nevertheless, the rate of calcite precipitation for the combined LSWI and CO$_2$ injection is slightly lower than is LSWI only. Calcite precipitation with decreasing the injected water salinity might be related to the decrease in calcite solubility as salinity decreases.

![Calcite Concentration](image)

Fig. 1. Calcite concentration at different injection cycles.

Dolomite concentration is shown in Figure 2 for the three tertiary injection modes. Dissolution of dolomite is the common trend in the three injection modes; however, the highest rate of dolomite dissolution is achieved by the combined LSWI and CO$_2$ injection.
Figure 3 shows the anhydrite concentration for the three tertiary modes of injection. The figure shows that CO$_2$ injection only, results in precipitation of anhydrite, whereas both LSWI only and the combined LSWI and CO$_2$ injection cause dissolution of anhydrite. This might again indicate that the LSWI effect dominates the CO$_2$ injection effect, leading to anhydrite dissolution instead of precipitation. Nevertheless, LSWI only has higher rate of anhydrite dissolution compared to the combined LSWI and CO$_2$ injection. Anhydrite reaction in equation (9) is related to calcite reaction in equation (7) as for the case of CO$_2$ injection only, the dissolution of calcite increases calcium ion concentration according to equation (7), and hence precipitation of anhydrite according to equation (9). The situation is just the opposite for LSWI only and combined LSWI and CO$_2$ upon which the precipitation of calcite leads to a decrease in calcium ion concentration and hence dissolution of anhydrite.

![Anhydrite Concentration at Different Injection Cycles](image)

**Fig. 3.** Anhydrite concentration at different injection cycles.
6.2. Fluid Species Comparison

Comparisons of different fluid species between the three tertiary injection modes are shown in Figures 4 – 13. Figures 4 and 5 show the concentration of sodium and chloride ions, respectively for the three injection modes upon which LSWI only and the combined LSWI and CO₂ injection have similar results because CO₂ injection does not affect these fluid species. For CO₂ injection only, concentrations of sodium and chloride ions are similar to the seawater cycle injection conditions, which as expected.

Calcium ion concentration, which is shown in Figure 6 for the three injection modes, is mainly controlled by calcite dissolution and precipitation (Figure 1). Calcium concentration is the highest for CO₂ injection only due to
calcium dissolution, followed by calcium concentration for the combined LSWI and CO₂ injection because of the lower rate of calcite precipitation compared to the LSWI only.

![Calcium Ion Concentration](image1.png)

Fig. 6. Calcium ion concentration using PHREEQC-Fluid Specie.

Figure 7 shows that the combined LSWI and CO₂ injection has slightly higher magnesium concentration compared to LSWI only which is due to the higher rate of dolomite dissolution (Figure 2). The trend of magnesium ion for CO₂ injection only, reflects the dissolution; however, this is not the case for the combined LSWI and CO₂ injection, and LSWI only upon which the overall trend is decreasing.

![Magnesium Ion Concentration](image2.png)

Fig. 7. Magnesium ion concentration using PHREEQC-Fluid Specie.
Sulfate ion concentration is shown in Figure 8 upon which the combined LSWI and CO₂ injection has lower concentration compared to LSWI only. This is due to the lower rate of anhydrite dissolution for combined LSWI and CO₂ compared to LSWI only (Figure 3). Moreover, the lower sulfate concentration for CO₂ injection only, compared to the seawater injection cycle can be probably explained by anhydrite precipitation.

![Figure 8. Sulfate ion concentration using PHREEQC-Fluid Specie.](image)

The concentration of alkalinity ions including carbonate, bicarbonate, hydroxide, and hydrogen, shown in Figures 9 – 12, are related to each other and results in pH number as shown in Figure 13. The figure shows that pH increases as results of LSWI only; however, pH decreases by CO₂ injection only, which can be justified by equations 1 – 5. For the case of the combined LSWI and CO₂ injection, a slight increase in pH is observed as a result of diluting seawater compared to CO₂ injection only.

![Figure 9. Carbonate ion concentration using PHREEQC-Fluid Specie.](image)
Fig. 10. Bicarbonate ion concentration using PHREEQC-Fluid Specie.

Fig. 11. Hydroxide ion concentration using PHREEQC-Fluid Specie.
Fig. 12. Hydrogen ion concentration using PHREEQC-Fluid Specie.

Fig. 13. pH number using PHREEQC.
6.3. Justification of LSWI and CO$_2$ in Carbonates

Wettability alteration is believed to be the main reason underlying the LSWI effect on incremental oil recovery from carbonate rocks. Wettability alteration by LSWI can occur in two processes dissolution and/or changing the rock surface charge. Both these processes were highlighted in our previous findings [29] upon which anhydrite dissolution was more pronounced and changing rock surface charge was deduced from the increase in pH. This increase in pH most probably exceeds the point of zero charge (PZC), turns the rock surface charge into negative, and hence releases the adsorbed organic material rendering the rock surface to a more water-wet state.

Geochemical flow and transport simulation of solid species for Yousef et al. [5] showed that it is difficult to conclude which tertiary injection mode (LSWI only, CO$_2$ injection only, combined LSWI and CO$_2$) best fit limestone carbonates because the results are almost comparable (Figure 1). The analysis showed that the combined LSWI and CO$_2$ injection is most beneficial for carbonates with high dolomite composition such as dolostones (Figure 2). Moreover, the effect of LSWI only is most pronounced on carbonates with high anhydrite composition among other tertiary injection modes (Figure 3). The latter finding is consistent with Yousef et al. [6] findings of the pronounced anhydrite dissolution effect using LSWI. This is because the rate of anhydrite dissolution dominates the rate of dolomite dissolution for LSWI only; however, the case might be the opposite for the combined LSWI and CO$_2$ injection.

The process of changing rock surface charge is more promising compared to the dissolution process [29]. This is because the dissolution process cannot justify the incremental oil recovery obtained by LSWI at reservoir-scale [35]. For the combined LSWI and CO$_2$ injection, our analysis of Yousef et al. [5] shows that there is no clear evidence of changing rock surface charge by pH. This is because the trends of pH shown in Figure 13 are either decreasing for CO$_2$ injection only or slightly increasing by the combined effect of LSWI and CO$_2$ injection, and this slight increase is not enough for exceeding the PZC. Nevertheless, wettability alteration by the combined effect of LSWI and CO$_2$ injection was reported by Fjelde et al. [30], then multi-ion exchange could be the processes responsible for desorption of organic acid groups through the mechanism described by Zhang et al. [3]. More laboratory work should be conducted to investigate wettability alteration by multi-ion exchange using combined LSWI and CO$_2$ in carbonates.

We cannot generalize our findings as the combined effect of LSWI and CO$_2$ injection on oil recovery is a case dependent based on temperature, pressure, rock lithology, oil type, initial rock wettability state, and injected water composition.

7. Conclusions

The combined effect of LSWI and CO$_2$ injection on oil recovery from carbonates in Yousef et al. [5] was investigated from a geochemical point of view. The main findings of this work can be summarized as follows:

- Three tertiary injection modes were investigated using PHREEQC including LSWI only, CO$_2$ injection only, and the combined LSWI and CO$_2$ injection, to highlight the contribution of CO$_2$ injection to LSWI.
- Geochemical analysis of solid species showed that the combined LSWI and CO$_2$ injection has similar dissolution/precipitation trends of calcite, dolomite, and anhydrite to LSWI only. This indicates that solid species concentrations are controlled by LSWI than CO$_2$ injection.
- The combined effect of LSWI and CO$_2$ is most pronounced on carbonates with high dolomite composition, whereas carbonates with high anhydrite composition are most affected by LSWI only.
- Geochemical analysis of fluid species showed that the slight increase in pH due to the combined effect of LSWI and CO$_2$ cannot justify wettability alteration by exceeding PZC. This is because the pH is controlled by CO$_2$ injection than LSWI.
- The combined effect of LSWI and CO$_2$ on oil recovery from carbonates depends on temperature, pressure, mineralogy, oil type, initial rock wettability state, and injected water composition; hence the results in other carbonate rocks might vary.
Nomenclature

IFT  Water-oil interfacial tension  
k_r  Relative permeability curves  
LS  Low salinity  
MMP  Minimum miscibility pressure  
P_c  Capillary pressure curves

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References


