Sensitivity Analysis of Different Parameters on Dissolution and Precipitation in Low Salinity Water Injection

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Abstract
Low Salinity Water injection (LSW) is a promising EOR method to improve the oil recovery for both sandstone and carbonate reservoirs. It has been observed that changing injection water composition (engineered water) and lowering water salinity are considered to improve the performance of water flood for carbonate reservoirs, by changing formation rock properties such as wettability alteration. Wettability alteration from oil wet to water wet is proven to be the main contributor to the incremental oil recovery when the salinity of the injection fluid is lowered. In this study, experiments are performed with diluted seawater and seawater contained different sulphate concentration to investigate the effect of changing injection brine physicochemical properties. Afterwards, it was history matched with the use of PHREEQC geochemical simulation software. The matched model was used to sensitivity analysis of different parameters such as calcium ion and magnesium ion concentration, alkalinity, salinity, temperature and the amount of carbonate material.

Keywords: Low Salinity Water Flooding LSW, Wettability Alteration, Geochemical Simulation, EOR, Equilibrium Concentration.

Introduction
Low salinity flooding (LSF) is proven to be a sufficient method to create an incremental oil recovery in or after secondary recovery. LSF might improve the performance of water flood for carbonate reservoirs, by wettability alteration. Since 60% of the proven oil reserves are present in Carbonate reservoirs, it is interesting to investigate the potential of LSF in carbonates. Several experimental and modelling studies are performed on LSF in carbonate rock. However, there are still a lot of uncertainties and challenges about the LSF effects and how this can contribute to the oil recovery. The recovery mechanisms of LSF in carbonates differ from LSF in sandstone, because of the difference in initial wettability and the lack of clay in carbonates.

A multi-ion exchange mechanism that explained many of the Austad group’s findings was proposed in Zhang et al. (2007). Seawater contains ions like Ca$^{2+}$, Mg$^{2+}$ and SO$^{2-}$ which are reactive towards carbonate rock surface. According to zeta potential measurements, these ions can act as potential determining ions as This is explained in Zhang et al. (2007) by the
substitution process of Ca\(^{2+}\) by Mg\(^{2+}\) at the rock surface. This substitution process is very sensitive to the temperature [1,2].

Previous studies showed that anhydrite is formed at critical temperature, due to the bonding of injection water sulfate ion with carbonate rock. As a result, the concentration of sulfate ion concentration of the solution decreases. As a consequence, sulphate ion can’t contribute in wettability modification by adsorption on rock surface. When Magnesium is added to the solution, the limiting temperature for CaSO\(_4\) precipitation is raised [4]. This is because SO\(_4^{2-}\) and Mg\(^{2+}\) form an ion pair in an aqueous solution, which increases with temperature. Substitution of ions can also occur between Calcium and Magnesium at chalk surfaces at high temperatures [5].

Wettability alteration as an effect of LSF in carbonate rock is proven by Yousef et al. at Saudi Aramco Oil Company conducted different laboratory studies to investigate the potential of LSF in carbonates. They performed oil/brine/rock interaction tests and coreflood experiments with different composition and salinity [6,7].

The surface charge is strongly pH dependent, because H\(^+\) and OH\(^-\) are potential determining ions in many solids. An increase in pH creates a more negative surface charge for both oil and calcite. The surface charge of an oil phase is in general negative. So, the sign of the rock surface charge equals the sign of fluid's surface charge, which results in repulsion forces between the oil and rock surface, which means rock surface changed to water-wet.

The rock surface charge was lower for the same pH if Calcium was removed from the brine, while Na\(^+\) had an insignificant effect. Increasing the temperature created a more negative surface charge. This effect was mainly present for the limestone particles. Lowering the salinity of the brine created a more negative surface charge as well.

Hiroth et al. developed a thermodynamics model based on aqueous phase chemistry, surface adsorption and mineral dissolution/precipitation in order to discuss how the water chemistry may impact on rock surface charge [8].

One of the most important problems in water injection projects to oil reservoir is the incompatibility problems of injection and formation water and scale deposition. As stated earlier about low salinity flooding (LSF) as a sufficient EOR method, it is essential to investigate water incompatibility alongside with LSF mechanisms such as ion exchange, surface potential alteration and wettability alteration. To do the objective previously mentioned, the experimental data was history matched through using the simulation technique by the aid of Phreeqc as a pioneer geochemical modeling software, to build the model. The matched model was used to sensitivity analysis of different parameters such as calcium ion and magnesium ion concentration, alkalinity, salinity, temperature and the amount of carbonate material. Sharma and Mohanty performed experiments including brines equilibrated with crushed limestone were compared with brines equilibrated without limestone to understand rock-brine interactions [9]. Table 1 shows chemical compositions of various brines including formation brine (FB), seawater (SW), diluted seawaters and 4xSO4 SW (4S-SW) brine that were tested. Crushed lime stone core was composed of 97.7% calcite, 0.1% dolomite, 1.2% fluorapatite, 0.3% quartz, and 0.6% Chlorite.

As well as, a Phreeqc model build based on experiments condition. Table 2 shows the experimental data together with the PHREEQC modelling data.

As shown in table 2, simulation results are matched with experimental data. The small difference between our model result and Sharma and Mohanty’s likelihood depends on an unknown parameter which is solution mass to crushed rock mass ratio. This ratio has a significant effect on simulator output. We assumed 1 kg water equilibrated with 9.77 moles calcite, 0.01 moles dolomite, 0.03 moles quartz and 0.06 moles chlorite. Their experimental
results showed that surface dolomitization was more dominant in increasing the concentration of calcium ions than calcite dissolution. Although, No attempt was made to analyze the rock surface. The matched model was used to sensitivity analysis of different parameters such as divalent cations concentration, pH, TDS, temperature and pressure in equilibration with 4S-SW and SW50.

Table 1: Composition of various brines used in static test by Sharma and Mohanty [9].

<table>
<thead>
<tr>
<th></th>
<th>FB</th>
<th>SW</th>
<th>SW/50</th>
<th>4*SO4-SW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>41,411</td>
<td>12,891</td>
<td>239</td>
<td>9700</td>
</tr>
<tr>
<td>Ca</td>
<td>11,686</td>
<td>510</td>
<td>10.2</td>
<td>510</td>
</tr>
<tr>
<td>Mg</td>
<td>2763</td>
<td>1600</td>
<td>29</td>
<td>1600</td>
</tr>
<tr>
<td>SO4</td>
<td>215</td>
<td>3485</td>
<td>67</td>
<td>13,940</td>
</tr>
<tr>
<td>Cl</td>
<td>103,002</td>
<td>26,578</td>
<td>501</td>
<td>13,428</td>
</tr>
<tr>
<td>TDS</td>
<td>149,160</td>
<td>41,127</td>
<td>822</td>
<td>41,237</td>
</tr>
</tbody>
</table>

Table 2: experimental data and the PHREEQC modelling data for Single-phase static experiments data and of crushed limestone particles with brines at 120 0C

<table>
<thead>
<tr>
<th></th>
<th>Formation Water</th>
<th>SW</th>
<th>(SW/50)</th>
<th>(4*SO4-SW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca+2</td>
<td>Experiment</td>
<td>Simulation</td>
<td>Experiment</td>
<td>Simulation</td>
</tr>
<tr>
<td></td>
<td>11334</td>
<td>11339</td>
<td>894</td>
<td>896</td>
</tr>
<tr>
<td>Mg+2</td>
<td>2804</td>
<td>2754</td>
<td>1362</td>
<td>1371</td>
</tr>
<tr>
<td>SO4-2</td>
<td>200</td>
<td>214</td>
<td>3482</td>
<td>3588</td>
</tr>
</tbody>
</table>

Sensitivity analysis of SW50 and 4S-SW equilibrated with carbonate rock

Divalent Cations Concentration

Figures 1 and 2 illustrate the effect of initial calcium and magnesium concentration ion in the final concentration of dissolved ions (after equilibrium) for the SW50 and 4S-SW waters. As illustrated in Figure 1, the increase in calcium ion initially dissolves more calcite and dolomite, when the sea water is diluted by 50 times. Calcium concentration in SW50 is 61 and concentration equilibrium is more than 90 in this initial concentration. Therfore can be dissolved in solution. The concentration of magnesium ion also increases, while it is not significant. This issue is also true for 4S-SW water, but it's effect is not very visible. In other words, it indicates the effect of reduction in salinity in this dissolution.

As shown in figure 2, the increase in magnesium ion initially dissolves more calcite and dolomite, when the sea water is diluted by 50 times. Hence, the concentration of magnesium ion also increases, while it is not very sensitive. This issue is also true for 4S-SW water that is very efficient for magnesium and not effective for other ions.

pH Change

Figure 3 illustrate the effect of pH change on the final concentration of dissolved ions (after equilibrium) for SW50 and 4S-SW waters. An increase in pH is associated with a reduction in calcium concentration and an increase in calcium scales. Thus, based on Figure 3, the concentration of calcium in the solution will increase as pH decreases. However, decrease in pH does not have much effect on the concentration of magnesium and sulfate (very low dissolution of dolomite). Also a decreasing of not visible for 4S-SW water is illustrated in Figure 3 with larger zoom. In other words, with reducing salinity, the effects of pH change are
quite clear. However, merely sulfate changes in the sample of injection water cannot clearly show the effects of pH change.

Figure 1: The effect of change in the calcium ion in the final concentration of dissolved ions (after equilibrium) for the SW50 water (Right) and 4S-SW water (Left)

Figure 2: The effect of change in the magnesium ion in the final concentration of dissolved ions (after equilibrium) for the SW50 water (Left) and 4S-SW water (Right)

Figure 3: The effect of pH change on the final concentration of dissolved ions (after equilibrium) for SW50 water (Left) and 4S-SW water (Right)

**TDS Change**

Figures 4 illustrate the effect of TDS change on the final concentration of dissolved ions (after equilibrium) for SW50 and 4S-SW waters. As illustrated in Figure 4, an increase in TDS leads into dissolution of calcite. Thus, the calcium concentration in the solution increases for SW50. In other words, the equilibrium concentration of calcium in the solution decreases with decreasing the salinity. It can be stated that the tendency to form deposit increases with calcium changes. When TDS increases, the solution tends to dissolve the calcite and this dissolution increases the concentration of carbonate ions in the solution and can result in
dolomite deposition (magnesium ion reduction). These cases can be examined in experiments. Figure 4 shows this phenomenon with larger zoom for 4S-SW water.

**Figure 4:** The effect of TDS change on the final concentration of dissolved ions (after equilibrium) for SW50 water (left) and for 4S-SW water (Right).

**Rock Type Change**
As illustrated in Figure 5, at very low calcite masses (near zero), where there is not sufficient calcite to dissolve, calcium is deposited and its concentration in the solution decreases and the magnesium concentration increases (dolomite dissolution). However, no change in equilibrium concentration is observed at a point where calcite or dolomite increases. This phenomenon is illustrated in Figure 4 with larger zoom for 4S-SW water.

**Figure 5:** The effect of calcite phase mass change on the final concentration of the dissolved ions (after equilibrium) for the SW50 water (Left) for the 4S-SW water (Right)

Figures 6 illustrate the effect of dolomite phase mass change on the final concentration of the dissolved ions (after equilibrium) for the SW50 and 4S-SW waters. As dolomite is always deposited in both of the cases, its mass change at the final concentration of dissolved ions has no effect. Also the results illustrate the effect of Quartz phase mass and chlorite phase mass change on the final concentration of dissolved ions (after equilibrium) for SW50 and 4S-SW waters. The results have shown that presence of these phases has no effect on the results.

**Temperature Change**
The calcium equilibrium concentration decreases for SW50 with increasing the temperature but the magnesium equilibrium concentration increases as show in figure 7. It suggests that there is a possibility of deposit formation when the desired water is exposed to temperatures above 120 °C, given the initial concentration of calcium. Additionally, the possibility of dissolution of the magnesium compounds such as dolomite can be increased since the equilibrium concentration of magnesium increases at high temperatures. It is also true for 4S-SW, but due to the low initial calcium concentration and high calcium equilibrium concentration in the solution, calcium can initially be dissolved to reach equilibrium
concentration, but the calcium deposition increases and the dolomite compounds dissolve with increasing the temperature.

![Figure 6: The effect of dolomite phase mass change on the final concentration of the dissolved ions (after equilibrium) for the SW50 water (Left) for the 4S-SW water (Right)](image)

![Figure 22: the effect of temperature change on the final concentration of dissolved ions (after equilibrium) for the SW50 water (Left) and the 4S-SW water (Right)](image)

**Pressure Change**
The results revealed that the pressure did not have a significant impact on the simulation.

**Conclusions**
The results of the investigations on ionic changes of injectable water suggest that by diluting the sea water up to 50 times, the tendency for calcite dissolution increases due to the higher equilibrium concentration of calcium compared to its initial concentration. It is also true for magnesium or dolomite. It is not clear for calcium in the 4S-SW water, but it is much clearer for magnesium.

With regard to SW50 water, the effect of pH changes on the changes in equilibrium concentration of calcium is greater than that of magnesium, so that equilibrium concentration decreases with increasing pH and the tendency to form the deposit increases. This issue is not clearly seen for 4S-SW water. The simulation results suggest that the equilibrium concentration of calcium for higher TDS increases for SW50 water. In other words, the solubility of calcite rock increases with increasing dissolved salts. In contrast, the magnesium equilibrium concentration does not change significantly. These effects can be also observed for the 4S-SW, while with a lower impact ratio.

The results suggest that the dissolution and deposition mechanism is associated with the value of rock samples. In other words, a critical point can be defined for the value of rock. At low values of calcite rock (less than 3 moles per 1 kg of injectable water), a decrease in the equilibrium concentration for calcium and an increase in the equilibrium concentration for
magnesium will be seen. In other words, by decreasing the value of rock, there will be an increase in deposition for calcite. This issue is non-significant for the 4S-SW due to the high initial concentration of magnesium and calcium. The changes in rock value have no effect on equilibrium concentration in the dolomite.

The values of other phases, such as quartz or chlorite, did not show any effect on equilibrium concentration of calcium or magnesium.

Temperature has a significant effect on the dissolution and deposition mechanisms, so that increasing the water temperature for the water that its salinity has been reduced can intensify the calcite deposition phenomenon and dissolve the dolomite.

The results revealed that the pressure did not have a significant impact on the simulation.

References


