An Experimental Study of CO$_2$-low Salinity Water Alternating Gas Injection in Sandstone Heavy Oil Reservoirs

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Abstract

Several studies have shown that oil recovery significantly increases by low salinity water flooding (LSWF) in sandstones. However, the mechanism of oil recovery improvement is still controversial. CO$_2$ that develops buffer in the presence of water is expected as a deterrent factor in LSWF efficiency based on the mechanism of interfacial tension reduction due to pH uprising. No bright evidence in literature supports this idea. Herein, a set of core floods including a pair of CO$_2$ water alternating gas (WAG) and a pair of water injection tests were conducted and the efficiency of LSWF and high salinity water flooding (HSWF) was compared for each pair. HSWF was followed by LSWF in tertiary mode. The results showed that not only did not CO$_2$ deteriorate LSWF recovery efficiency, it improved recovery, because CO$_2$-low salinity WAG showed the best performance among the other types at a constant pore volume injected. The positive results in both secondary and tertiary modes with Kaolinite free samples used herein showed that Kaolinite release was not the critical phenomenon in LSWF brisk performance. In addition, different pressure behaviors of CO$_2$ WAG processes in comparison with the reported behavior of LSWF proves that LSWF performance may not depend on how pressure changes through flooding.

Keywords: Low Salinity, Carbon Dioxide, WAG, Heavy Oil, Sand Stones

1. Introduction

Low salinity water flooding (LSWF) is a newly developed EOR technique which has shown significant oil recovery enhancement in both secondary and tertiary modes from 5% to 40%. On both laboratory and field scales, several positive results of improving oil recovery either on outcrop or reservoir sandstones have been reported in literature. Recently Zahid (Zahid et al., 2012) obtained evidence that a substantial increase in oil recovery occurred using carbonate reservoir core plugs. Maybe Bernard (Bernard, 1958) was the first who found out that oil recovery was improved by using fresh water instead of high salinity water. In 1990s, understanding of oil recovery improvement by low salinity water injection was broadened by researches of Jadhunandan and Morrow, Yildiz and Morrow, and Morrow et al. (Jadhunandan and Morrow, 1995; Morrow et al., 1998). Zhang (Zhang et al., 2007) showed that oil recovery improved in both secondary and tertiary modes by LSWF. Webb (Webb et al., 2004) conducted log-inject-log tests; to this end, a production or injection well logging technique, in which the zones were logged for water saturation, oil saturation, or temperature, then they were fluid-injected, and they were finally logged again, was used to examine the effect of low

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salinity water on field scale. Their results showed an oil recovery improvement of 25-50%. Lager (Lager et al., 2008) observed a significant increase in oil recovery and reduction in water oil ratio in an Alaskan reservoir. They also observed that oil production rate was doubled during 12 months of production.

Since 1990, some mechanisms for LSWF efficiency have been proposed. Among these mechanisms, three mechanisms are more acknowledged which are as follows:

1. Tang and Morrow (Tang and Morrow, 1999) claimed that particle release during low salinity injection occurred. These released particles are mixed-wet and, by their migration out of the core, they can transport the attached oil drops and improve the recovery. As these mixed-wet particles separate from the pore surface, the water-wet underlying surface is exposed to the fluids. This will in turn increase the rock water wetness.

2. Mc Guire (Mc Guire et al., 2005) claimed that a pH increase during LSWF was the main reason of oil recovery improvement. They presented that as low salinity water was injected, hydroxyl ions were generated through reactions with native minerals of the reservoir and thus pH increased from 7 to 8; it might rise up to a pH of 9 or even more. As a result, they compared low salinity water behavior with alkaline flooding. Like alkaline flooding, low salinity water reduced the interfacial tension between the reservoir oil and water and pH elevation tended to make the rock more water-wet and hence improved oil recovery. Furthermore, low salinity water resulted in the alteration of crude oil properties. When oil contacted high pH low salinity water, the acid or polar components in the oil were saponified, which was basically an in-situ surfactant generation.

3. This mechanism considers bridging negatively-charged oil to the clay minerals by multivalent cations (Buckley et al., 1989; Liu et al., 2005). Lager (Lager et al., 2006) provided evidence that multicomponent ion exchange (MIE) occurred during LSWF and improved oil recovery. They revealed that MIE occurred between rock, oil, and brine and by some procedure detached the oil from rock surface which resulted in oil recovery improvement.

The second mechanism called alkaline water flooding has some discrepancies. Based on the alkaline water flooding model, several studies on the pH of effluent have been conducted. These researches resulted in a fluctuated trend in pH alteration instead of incremental trend (Rivet et al., 2010; Lager et al., 2006). Some researchers observed an incremental trend in pH at the beginning, but pH reduction began after a while in LSWF (Zhang and Morrow, 2006). Since there is no common consensus on how exactly pH affects LSWF, more elaborate experimental investigation is still needed. Despite numerous studies, there has been little investigation on how alternating injection of CO\textsubscript{2} affects LSWF oil recovery performance. CO\textsubscript{2} develops a buffer ambition which prevents pH from uprising in an in-situ manner. This in-situ prevention acts as a controlling factor on alkaline water flooding mechanism.

Water flooding has been a common method for secondary production. After that, gas injection has been applied to produce the residual oil. Water alternating gas injection has originally been recommended as a method to reduce mobility in gas injections to delay breakthrough while maintaining high gas microscopic efficiency (Caudle and Dyes, 1958). Although different factors are involved in the efficiency of a WAG process (Christensen et al., 2001), there is no insight into a challenging liquid phase such as low salinity water. Herein, WAG process is used for simulating an intermittent contact of low salinity water, crude oil phase, and carbon dioxide as what occurs in reservoir conditions.

In this work, the efficiency of a pair of carbon dioxide WAG and a pair of water injection tests for low and high salinity brine as the injected fluid was compared through a set of core flood experiments, and
the controversial role of CO$_2$ in oil recovery during low salinity water floods was investigated. CO$_2$ is considered as the probable cause of carbonates neutrality to LSWF, for it interrupts pH uprising. Therefore, the results of these experiments will clarify the CO$_2$ challenging role in LSWF oil recovery performance.

2. Experimental

2.1. Experimental setup

The core displacement tests were performed in a core flooding apparatus. The main components of the system are illustrated in Figure 1. Two high accuracy displacement pumps were used for the injection of working fluids in constant rate mode. The working fluids (brine, oil, and gas) were in thermal equilibrium before the tests. The core effluent fluids flashed into atmospheric pressure through a back pressure regulator (BPR) and were collected in a partial collector. For recovery measurement, the volume of the total liquid gathered in collector was monitored and recorded for several steps. XRD analysis has been also applied to the core material to evaluate the key mineral presence.

![Figure 1](image_url)

Core flood apparatus

2.2. Rock and fluids

In this study, four sandstone core samples plugged from one core were used. Table 1 shows the physical and geometrical properties of the core sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>Porosity</th>
<th>Permeability (mD)</th>
<th>$S_{wc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.45</td>
<td>3.81</td>
<td>0.31</td>
<td>341</td>
<td>0.29</td>
</tr>
<tr>
<td>B</td>
<td>7.58</td>
<td>3.81</td>
<td>0.32</td>
<td>357</td>
<td>0.30</td>
</tr>
<tr>
<td>C</td>
<td>7.52</td>
<td>3.81</td>
<td>0.29</td>
<td>333</td>
<td>0.27</td>
</tr>
<tr>
<td>D</td>
<td>7.34</td>
<td>3.81</td>
<td>0.31</td>
<td>340</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Synthetic brine with low (1000 ppm) and high (50,000 ppm) concentrations of NaCl and CaCl$_2$ was prepared for the experiments. The brines composition and properties are shown in Table 2.

<table>
<thead>
<tr>
<th>Brine Type</th>
<th>Ingredient Cations</th>
<th>CaCl$_2$ Concentration (ppm)</th>
<th>NaCl Concentration (ppm)</th>
<th>Density (gr/cm$^3$)</th>
<th>Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Salinity Brine(A)</td>
<td>Ca$^{2+}$, Na$^+$</td>
<td>200</td>
<td>800</td>
<td>1.0005</td>
<td>0.864</td>
</tr>
<tr>
<td>High Salinity Brine(B)</td>
<td>Ca$^{2+}$, Na$^+$</td>
<td>10000</td>
<td>40000</td>
<td>1.0275</td>
<td>0.969</td>
</tr>
</tbody>
</table>

The hydrocarbon fluid used in the experiments is a filtrated stock tank heavy crude oil the properties of which are given in Table 3.

<table>
<thead>
<tr>
<th>Hydrocarbon Fluid</th>
<th>Asphaltene Content</th>
<th>Density (gr/cc)</th>
<th>Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>6.5%</td>
<td>0.8845</td>
<td>10.07</td>
</tr>
</tbody>
</table>

2.3. Test procedures

Prior to performing each test, core samples were cleaned with toluene and ethanol. Then, they were completely dried in an oven at a temperature of 110 °C for 12 hours. After the saturation of the core samples with the brine type B, each test began with the injection of brine at different flow rates and the measurement of the resulting pressure drops to calculate absolute permeability.

To establish irreducible water saturation, oil was injected into the core at a low rate of 2 cc/min to overcome capillary forces. The oil injection was stopped when the volume of the produced water remained stable. Then, temperature was increased to 70 °C to perform aging. Two days of aging was performed on the core samples to restore the wettability after cleaning. The heavy crude oil, which had a high content of huge polar components, was used for this purpose.

Displacement in both continuous and alternating schemes was vertically downward to avoid gravity override. The pressure drop in core was measured by a pressure transducer and was recorded in a computer file. The following tests were designed to monitor the effect of the buffer obtained by the contact of carbon dioxide with the injected low salinity brine on oil recovery in the case of LSWF. Carbon dioxide in contact with water makes carbonic acid, a weak acid which could act as buffer in the solution. This generated buffer inhibits pH increase in the system.

The test configurations are tabulated in Table 4. In all the tests, the gas slug size was 2.5cc; WAG ratio was one and the first injected slug was gas. PVT calculations with a commercial simulator showed that the MMP of CO$_2$ with the oil phase was around 3000 psia; therefore, at the test pressure of 800 psia, carbon dioxide WAG injection was in immiscible mode. Total injection volume was two pore volumes in both WAG experiments.

All the tests were performed at 800 psia and the overburden pressure was selected to be 1300 psia. The tests were all carried out at a temperature of 50 °C.

Four core flood experiments were conducted on similar Berea sandstone cores. The summarized configurations of the tests are tabulated in Table 4. The brine and gas injection rates in all the tests were 0.3 cc/min.
Table 4
Experiments configurations and results

<table>
<thead>
<tr>
<th>EXP#</th>
<th>Description</th>
<th>Mode</th>
<th>Water Breakthrough (PV)</th>
<th>Recovery at Water Breakthrough (%)</th>
<th>Reaching to Ultimate Recovery (PV)</th>
<th>Ultimate Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ordinary HiSal+Tertiary LoSal</td>
<td>Secondary+ Tertiary</td>
<td>0.55</td>
<td>58</td>
<td>Secondary:1.90</td>
<td>Secondary:79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tertiary: 2.84</td>
<td>Tertiary: 84</td>
</tr>
<tr>
<td>2</td>
<td>Ordinary LoSal</td>
<td>Secondary</td>
<td>0.41</td>
<td>48</td>
<td>1.59</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>WAG LoSal</td>
<td>Secondary</td>
<td>0.78</td>
<td>31</td>
<td>1.66</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>WAG HiSal</td>
<td>Secondary</td>
<td>0.8</td>
<td>33</td>
<td>2.0</td>
<td>74</td>
</tr>
</tbody>
</table>

a. Water flooding: secondary injection of high and low salinity and also tertiary injection of low salinity brine after high salinity secondary brine injection

In these two tests, two pore volumes of high salinity and low salinity brine were injected in secondary mode to verify whether low salinity brine injection had a positive effect on this type of rock. Furthermore, one pore volume of low salinity brine was injected in the first test after the secondary injection of high salinity brine to monitor the effect of low salinity brine injection on oil recovery in tertiary mode.

b. CO$_2$ WAG experiment: the secondary injection of high and low salinity brine as liquid phase

In the first WAG injection test, one pore volume of high salinity brine was injected in secondary mode alternated by a total one pore volume of CO$_2$ gas slugs; however, in the second WAG injection test the same volume of low salinity brine was alternated by the same amount of gas slugs to investigate the effect of low salinity brine on oil recovery in the presence of a buffer preventing the increase of pH.

3. Results and discussion

3.1. Water flooding: the secondary injection of high salinity brine followed by tertiary low salinity brine injection

Oil recovery versus the pore volume of the injected fluids for the injection of high salinity brine followed by tertiary low salinity brine injection is demonstrated in Figure 2. The results for this test show a water breakthrough after the injection of 0.55 PV fluids. The recovery at breakthrough time was 58%. While the oil production already stopped at 1.9PV, the injection was continued to ensure an ultimate recovery after a total of two pore volumes of the injected fluids. At the end of this flooding period, oil recovery approached 79%.

In tertiary mode, the injection of low salinity brine caused the start oil flow again to recover more of the trapped oil. The trapped oil required the injection of 0.5 PV of low salinity brine to start to recover after secondary injection. This oil recovery was significant only for a 0.3 PV more injection of low salinity brine. The oil recovery after a total 3 PV of secondary and tertiary injection was 84%.
3.2. Water flooding: the secondary injection of low salinity brine

Figure 2 also shows the oil recovery versus the pore volume of the injected fluids for the injection of low salinity brine. In this test, water breakthrough occurred at an earlier time of 0.41 PV injection and 48% of oil was recovered. The low salinity water injection stopped at two pore volumes of the injected fluids, while the oil production had already stopped after the injection of 1.6 pore volumes of the fluids. The oil recovery reached an ultimate value of 87%.

By comparing this experiment with experiment number 1, the sensitivity of rock sample to the salinity of injection water could be inferred. Experiments characteristics are tabulated in Table 4.

3.3. CO₂ WAG experiment: the secondary injection of low salinity brine as liquid phase

Oil recovery versus the pore volume of the injected fluids for the CO₂ WAG experiment with low salinity brine as liquid phase is demonstrated in Figure 3. In this test, water breakthrough occurred when 0.92 PV was injected with an oil recovery of 40%. At the beginning of the test, during liquid injection phase of each WAG cycle, the oil recovery showed a more obvious response to the injection, while this was diminished during gas injection in each cycle. The ultimate oil recovery reached a value of 92% once a total fluid volume of 1.66 PV was injected.

3.4. CO₂ WAG experiment: the secondary injection of high salinity brine as liquid phase

Figure 3 also shows the oil recovery versus the pore volume of the injected fluids for CO₂ WAG experiment with high salinity brine as liquid phase. In this test, water breakthrough occurred after the injection of 0.96 PV of fluids with a recovery of 38%. Similar to the third experiment, a step like increase in oil recovery at the beginning was observed. The fluctuations continued up to one pore volume of the total injection and gradually disappeared to form a linear trend. This linear recovery trend continued for an additional one pore volume of the total fluids until there was no significant oil production. The injection was continued and stopped after the injection of a total of 2.2 pore volumes to ensure an ultimate recovery of 74%. The summary of the results is presented in Table 4.
The comparison of oil recovery results in the first and second tests proved the better performance of LSWF in the provided sandstone samples. The higher mobility of low salinity brine due to lower viscosity resulted in an earlier water breakthrough. However, the LSWF more than compensated for this to give a higher final oil recovery compared to the high salinity case. The first experiment additionally showed the capability of low salinity brine to mobilize the trapped oil in tertiary mode. In third and fourth experiments, while the buffer solution developed by contact of carbon dioxide with brine prevented pH increase, it did not reduce the positive effect of low salinity brine injection on the efficiency of oil recovery. This refutes the hypothesis of alkaline water flooding as the main cause of additional oil recovery in LSWF. According to the results of the second and third tests, an increase of 5% in oil recovery was observed in low salinity WAG compared to LSWF at the same pore volume of the injected fluids. This shows the positive effect of low pH buffer solution developed by carbon dioxide.

Examining the recovery trend in WAG injection showed fluctuations especially in the early injection times. Increased upstream pressure during the test decreases the gas compressibility to make it show a more liquid like behavior, resulting in a more smooth recovery curve during the later stages of each WAG test. Higher amounts of dissolved CO$_2$ in brine in the later stages of each test can also be a relevant factor. These fluctuations are more announced in high salinity WAG injection. This is because of the lower amounts of CO$_2$ dissolved in high salinity brine with higher concentrations of solids (Jiang et al., 2010; Kulkarni et al., 2004).

The XRD analysis of the applied core samples showed that they were Kaolinite free samples. The XRD spectrum is presented in Figure 4. Kaolinite is regarded as a critical particle in low salinity oil recovery improvement (Jerauld et al., 2006; Seccombe et al., 2008). The observed additional oil recovery for LSWF provides evidence that Kaolinite does not play a prominent role in the higher efficiency of low salinity oil recovery.

Figure 5 and 6 show the system pressure at the top of core through CO$_2$ WAG experiments by low and high salinity brines respectively. The severe fluctuations at the beginning of the diagram are...
related to piston friction. Since back pressure is 800 psia, the pressure drop across the core is obtainable from the system pressure. It is obvious from Figure 5 that for aqueous phase higher steps pressure drop shows an increase, then decreases to a minimum amount, and finally increases twice; however, pressure drop in LSWF does not show the incremental trend at the end of the experiments in some studies (Lager et al., 2008; Zhang and Morrow, 2006).

Figure 4
Intensity versus 2-theta as core sample XRD spectra

Figure 5
System pressure versus time in CO₂-low salinity WAG injection
4. Conclusions

Based on the results obtained the following conclusions can be drawn:

1. CO$_2$ showed a significant positive effect on oil recovery improvement in the WAG injection of low salinity brine with heavy oil; this observation was contrary to the little examined expectation that CO$_2$ deteriorated LSWF distinctive performance. This evidence may provide impetus for working further on the LSWF of carbonates;

2. The observation that CO$_2$ as a buffer in the presence of water significantly increased oil recovery showed that alkaline water flooding might not be the responsible mechanism in LSWF additional recovery performance;

3. Low salinity showed an additional recovery for the heavy oil and sandstone outcrop samples either in secondary or tertiary modes; this occurred while the sample was Kaolinite free. This observation casts doubt on considering Kaolinite release as a key mechanism in LSWF performance;

4. Pressure drop showed an increasing trend at the end of CO$_2$-low salinity WAG experiments; however, this increase has not appeared in the reports on the pressure drop of LSWF in some documented references. This increase may be due to CO$_2$ presence or it may indicate that pressure drop does not follow an identified trend for all the experiments; this weakens the dependability of LSWF mechanism on pressure drop.

Nomenclature

<table>
<thead>
<tr>
<th>EOR</th>
<th>Enhanced oil recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFA</td>
<td>Electrofacies analysis</td>
</tr>
<tr>
<td>LSWF</td>
<td>Low salinity water flooding</td>
</tr>
</tbody>
</table>
MMP : Minimum miscibility pressure
MIE : Multicomponent ion exchange
PV : Pore volume
WAG : Water alternating gas

References


