Experimental Investigation of Interfacial Tension Measurement and Oil Recovery by Carbonated Water Injection: A Case Study Using Core Samples from an Iranian Carbonate Oil Reservoir

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ABSTRACT: Low volumetric sweep efficiency, early breakthrough of injected fluid, and high risk of gas leakage from the reservoir are the major technical challenges associated with direct gas and water injection into oil reservoirs. Injection of carbonated water (CW) into oil reservoirs is a carbon dioxide-augmented water injection technique, which results in improved oil recovery and possible CO2 storage in the reservoir. In this paper, the potential of carbonated water injection (CWI) into an Iranian carbonate reservoir for the purpose of improving oil recovery was investigated. In addition, the interfacial tension (IFT) of crude oil and two different carbonated brines (carbonated formation brine and carbonated seawater) as well as CO2 solubility in these two carbonated brines was determined. Experimental results showed that CO2 solubility in both brines increases with pressure and decreases with temperature. However, CO2 solubility was more promising in seawater compared to formation brine because of the lower salinity. The IFT results showed that increasing the temperature from 40 to 100 °C and increasing the pressure from 1000 to 2500 psi had a positive impact on reducing the IFT between carbonated brines and oil. In addition, coreflooding experiments showed that oil recovery increased with CWI as compared to conventional water flooding (WF). However, secondary carbonated water injection (SCWI) resulted in higher oil recovery compared to tertiary carbonated water injection (TCWI). A maximum oil recovery of 21.75%, 61.63%, and 52.58% was achieved with conventional WF, SCWI, and TCWI, respectively.

1. INTRODUCTION

The demand for energy is increasing day by day, and fossil fuels as the main energy sources in the world play an important role in energy management scenarios.1–4 The days of easy oil are over, and the expense of drilling and exploration continues to increase. Thus, an emphasis has been placed on maximizing recovery of in place oil. Hence methods to enhance oil recovery (EOR) from oil reservoirs are becoming increasingly important. Gas injection into reservoirs is one of the most attractive EOR methods. Among different gases injected to the reservoir, CO2 has received the most attention. Due to its lower solubility pressure and higher solubility in brine it is the most widely injected EOR gas.5–11 This has the additional benefit of mitigating climate effects, which CO2 would otherwise produce.12–16 CO2 injection into oil and gas reservoirs improve oil and gas recovery from these reservoirs as well as securing CO2 from the atmosphere, however the technical challenges still.17–19

One of the critical challenges associated with any CO2 flooding is the high velocity of the injected CO2, which causes viscous fingering and poor sweep.18,19 In addition, because of high mobility of injected CO2 and the risk of CO2 leakage from the reservoir, the efficiency of CO2 sequestration could be affected.18,20–24 The use of water to reduce and control the mobility of injected gas has been proposed to improve the performance of gas injection; however, technical challenges are still present. The presence of water reduces the rate of CO2 mass transfer, oil swelling, and viscosity reduction and, thus, lowers the oil recovery.25–29

Interfacial tension (IFT) between oil and water plays an important role in controlling the amount of recovered oil. IFT reduction leads to an increase in capillary number (Nc) by orders of magnitude, which enhances the oil recovery significantly. Conventional methods of IFT reduction involves the use of chemicals, most importantly surfactants and alkalis. However, other mechanisms including wettability alteration and emulsification also occurs in the presence of chemicals.30–32 Carbonated water injection (CWI) has received significant attention recently for improving oil recovery. In this method, CO2 is dissolved in the water before injection and then injected to the reservoir. In this method, the adverse effect of water shielding to reduce the effectiveness of CO2 gas is minimized. Thus, oil mobility and sweep efficiency is significantly improved through CWI. Several mechanisms including oil viscosity reduction, IFT reduction, wettability alteration, oil swelling, and coalescence of the trapped oil ganglia are proposed for improving oil recovery through CWI.33–42

Mosavat and Torabi43,44 studied the performance of CWI in a light oil system. Their experiments were conducted in an
artificially unconsolidated sand-pack, and the effect of different operating conditions on the overall performance of CWI was investigated. Results of flooding experiments showed that ultimate recovery is higher when CW is injected as compared to conventional water injection. In their experiments, a maximum oil recovery of 78.76% was achieved, while a maximum oil recovery of 59.74% was achieved with conventional waterflooding. They also concluded that the process is efficient from a CO2 storage point of view since 40.7%–61.1% of the total injected CO2 was stored at the end of CWI. They stated that CWI provides a great potential to permanently store a significant portion of the injected CO2 in light oil reservoirs while improving oil recovery. Alizadeh et al. investigated the effectiveness of CWI in both macro- and microscale flooding experiments. They found out recovery factor is increased with CWI in both systems as compared to conventional waterflooding. In the microscale, the recovery factor increased from 35% to 75.4% with CWI. Similarly, in the macroscale core flooding experiments, the recovery factor increased from 40.1% to about 74.47% with CWI. In another study by Mosavat and Torabi, the wettability alteration and thus, improving oil recovery by CWI in a microscale system were explored. Their experiments showed that the wettability of micromodels changed from mixed and oil-wet to water-wet as the CWI proceeds. Their experiments showed that recovery factor is increased with CWI as compared to conventional waterflooding. However, the increase in recovery factor was 9.4% and 7.3% for secondary and tertiary scenarios, respectively.

Hasanvand et al. performed a case study in one of Iran’s southern reservoirs. The performance of CWI was compared with natural depletion of the reservoir and conventional waterflooding. In addition, the effectiveness of the process for sequestering CO2 was also investigated. Their results showed that CWI could increase ultimate recovery by up to 20% compared to water injection and 71% compared to when the reservoir is naturally depleted. Moreover, nearly 75% of the injected CO2 was safely stored and sequestered. In another case study by Shakiba et al., the oil recovery and CO2 storage during secondary and tertiary injection of CW in an Iranian carbonate oil reservoir were investigated. They concluded that the recovery factor in both cases (secondary and tertiary CWI) was higher than for conventional waterflooding. However, oil recovery was higher when CW was applied as secondary recovery rather than tertiary recovery. The decrease in oil recovery with tertiary CWI was because the critical amount of oil remained in the system after the initial waterflood stage.

Sohrabi et al. investigated the effect of oil viscosity on the overall performance of CW injection. Three different oils with different viscosities including a light oil with the viscosity of 0.82 cP, a refined oil with the viscosity of 81 cP and a stock tank crude oil with the viscosity of 145 cP were used. Their experiments showed that oil recovery is indirectly related to oil viscosity where oil recovery was higher for lighter oil. They concluded that mobility ratio and oil swelling are the major mechanisms for increasing oil recovery with lighter oil. They found that mobility ratio was more favorable when lighter oil was used as compared to heavier oils. Apart from that, CO2 diffusion from carbonated water into the oil found to be important, which resulted in unlimited oil swelling and enhanced oil recovery. On the other hand, viscosity reduction is also one of the oil recovery mechanisms with CW injection. Viscosity reduction is more significant with heavier oils than the light oils. However, it seems that oil swelling and mobility ratio are dominant over the oil viscosity reduction, which resulted in higher oil recovery with light oil than the heavy oil. This statement is also in good agreement with results of Mosavat and Torabi.

In this study, the feasibility of CWI into core samples of a carbonated oil reservoir in Iran was investigated. Initially, CO2 solubility in formation brine and seawater under different pressures (500–4000 psi) and temperatures (25–100 °C) was investigated. Then, the effect of different pressure (1000–2500 psi) and temperatures (40–100 °C) on IFT of crude oil and carbonated brine was investigated. After exploring the results of CO2 solubility and IFT, a series of coreflood experiments were designed and implemented. A carbonated core sample and crude oil from a carbonated oil reservoir in Iran were used for this purpose. Three main flooding scenarios including conventional WF, SCWI, and TCWI were designed and conducted at constant temperature and pressure of 80 °C and 1000 psi, respectively. Finally, oil recovery under each scenario was calculated and analyzed, respectively.

2. EXPERIMENTAL SECTION

2.1. Fluids. Crude oil in this study was taken from a carbonated oil reservoir in Iran. The physical and chemical properties of crude sample including density, viscosity, and composition analysis were measured and presented in Tables 1–3. As shown in Table 1, the API of crude oil is 32.56. In addition, saturated, asphaltene, resin, and aromatic percentage is 51.35, 8.59, 9.78 and 30.28%, respectively. Table 2 represents the compositional analysis of crude oil used in this study. As shown in this table, the crude oil used in this study is rich in C1 (47.66%) and C7+ (25.49%) with no presence of CO2 and H2S. Table 3 represents the density and viscosity of crude oil at different temperatures. As shown in this table, the viscosity of the crude oil is in the range of 0.848 to 0.883 g/cm3. On the other hand, the measured crude oil viscosity is in the range of 4.62–24.94 cP.

Formation brine and seawater were used to represent brine in this study. The components and total dissolved solids (TDS) of both were determined as shown in Table 4. The TDS of formation brine was measured to be 97645 ppm, while the value was 35079 ppm for seawater. In addition, the physical properties of formation brine including total hardness, conductivity, density, turbidity, and pH were measured, and the results are shown in Table 5.

Analytical grade CO2 (purity >99.9%) was used to prepare the CW sample. In order to differentiate between different liquid phases in flooding tests, blue and red dyes were used for brine and oil, respectively.

2.2. Core Samples. The core samples used in this study were taken from outcrops of an Iranian carbonate oil reservoir. Porosity of the core samples were measured using helium porosity test and brine was used to determine the permeability of the cores. Also, the dimensions of core samples were measured accordingly. Table 6 represents the dimensions and properties of carbonate core samples used in this study. The average porosity and permeability of core samples are 11.28% and 14.91 mD, respectively.

2.3. Apparatus. The experimental setup presented by Mohamadian et al. was used to measure CO2 solubility in brine under different pressures and temperatures. The solubility measurement setup consists of an ISCO pump (Teledyne, 100 DX), a 100 mL autoclave reactor equipped with a stirrer, CO2 cylinder, an electric heater, and a 1/8 in. dip tube, which was connected to a floating piston sampler fabricated locally. The sampler was controlled by a syringe
pump manufactured by KD scientific (model 53100). The dynamic IFT of different oil and water samples was measured using pendant drop method, as this method is one of the best methods for determining the IFT at reservoir conditions. In this study, IFT400 with a maximum operating pressure of 3000 psi and temperature of 400°F was used to determine the IFT. The system has a 50 cm³ stainless steel chamber along with a glass window, which allows for taking photographs of the drops. Eventually, IFT was measured using an image processing code written by LabVIEW. In this method, the dynamic IFT is determined using drop shape analysis, commonly known as axisymmetric drop shape analysis (ADSA) technique. Figure 1 represents the schematic diagram of the IFT400 used in this study.

Table 2. Compositional Analysis of Crude Oil Used in This Study

<table>
<thead>
<tr>
<th>Component</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅</th>
<th>C₆</th>
<th>C₇+</th>
<th>H₂S</th>
<th>CO₂</th>
</tr>
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<tbody>
<tr>
<td>mole %</td>
<td>47.66</td>
<td>11.32</td>
<td>6.48</td>
<td>1.08</td>
<td>2.89</td>
<td>1.21</td>
<td>1.49</td>
<td>2.38</td>
<td>25.49</td>
<td>0</td>
<td>0</td>
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</table>

Table 3. Density and Viscosity of Crude Oil Used in This Study

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>density (g/cm³)</th>
<th>viscosity (cP)</th>
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<tr>
<td>20</td>
<td>0.883</td>
<td>24.94</td>
</tr>
<tr>
<td>40</td>
<td>0.871</td>
<td>12.14</td>
</tr>
<tr>
<td>60</td>
<td>0.858</td>
<td>7.04</td>
</tr>
<tr>
<td>80</td>
<td>0.848</td>
<td>4.62</td>
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</table>

Table 4. Composition of Brines Used in This Study

<table>
<thead>
<tr>
<th>ion</th>
<th>seawater (ppm)</th>
<th>formation brine (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>419</td>
<td>3800</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1304</td>
<td>1944</td>
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<tr>
<td>Na⁺</td>
<td>11100</td>
<td>38406</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>146</td>
<td>45</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2690</td>
<td>1200</td>
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<tr>
<td>Cl⁻</td>
<td>19350</td>
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<td>Br⁻</td>
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<tr>
<td>TDS</td>
<td>35079</td>
<td>97645</td>
</tr>
</tbody>
</table>

Table 5. Physical Properties of Formation Brine from a Carbonate Oil Reservoir in Iran

<table>
<thead>
<tr>
<th>properties</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity (μS/cm)</td>
<td>184100</td>
</tr>
<tr>
<td>total hardness (mg/L)</td>
<td>17500</td>
</tr>
<tr>
<td>density at 20 °C (g/cm³)</td>
<td>1.1005</td>
</tr>
<tr>
<td>turbidity (NTU)</td>
<td>0.40</td>
</tr>
<tr>
<td>pH</td>
<td>7.01</td>
</tr>
</tbody>
</table>

Table 6. Dimensions and Properties of the Reservoir Core Used in the Study

<table>
<thead>
<tr>
<th>length (cm)</th>
<th>diameter (cm)</th>
<th>bulk volume (cm³)</th>
<th>pore volume (cm³)</th>
<th>porosity (%)</th>
<th>permeability (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.14</td>
<td>3.78</td>
<td>91.35</td>
<td>10.30</td>
<td>11.28</td>
<td>14.91</td>
</tr>
</tbody>
</table>

gas. All experiments were conducted at constant temperatures using an air bath system.

2.4. Experimental Procedure. CO₂ solubility in formation brine and seawater was determined using the method explained by Mohammadian et al. In this method, brine is injected into the reactor and then heated to the desired temperature. CO₂ is injected to the reactor at the desired pressure and then the equilibrium is achieved by stirring the solution between 3 and 24 h. After that, a sample of CO₂ saturated brine (half of chamber size) was taken and poured into the sampling chamber to react with NaOH. This is to dissolve all carbon species in NaOH and convert them to CO₃²⁻. The other half of the sampling chamber was filled with distilled brine, which was gradually withdrawn (using a syringe pump) to allow the CO₂ saturated brine reacting with the NaOH. The reaction of NaOH and solution was given 30 min time before withdrawal. Then HCl was used to analyze the preserved NaOH samples using potentiometric method. HCl addition to analyte (NaOH and CO₃²⁻ mixture) was continued until the equivalence point was achieved. Finally, CO₂ solubility in brine was calculated in molar units (mol/kg).

The procedure given by Shu et al. was followed for preparing the carbonated water. A syringe pump and a high pressure transfer vessel (made of stainless steel) were utilized to prepare the carbonated water. Initially, the transfer vessel was filled with brine (either formation brine or seawater). The vessel was connected to the syringe pump under the pressure setting of 2000 psi. Then, the transfer vessel was placed in an air bath of room temperature and rocked for 24 h to achieve complete
phase equilibrium between CO\textsubscript{2} and brine. Finally, the prepared carbonated water was utilized for IFT measurements and flooding experiments.

In order to measure the IFT, initially the whole system was checked for leakage with deionized water. Then, it was cleaned with acetone and deionized water, flushed with nitrogen, and finally evacuated. To determine the IFT of carbonated water and crude oil, a total of 15 cm\textsuperscript{3} of brine (either formation brine or seawater) was injected to the high pressure cell. Then, CO\textsubscript{2} was slowly injected to the cell to provide the desired pressure. Then, adequate time (10–12 h) was given to each solution to reach equilibrium conditions. An upward oil drop was introduced from the bottom of the cell by installing the syringe needle at the bottom of the pressure cell. In order to confirm the reproducibility of IFT data, the measurements were repeated three times and, then, the average was taken and reported.

In order to perform the flooding experiments, the core sample was dried and weighed. Then, the core was washed by injecting toluene, methanol, and formation brine. The brine permeability was determined using the recorded pressure data in this step. The core was dried again and evacuated by a vacuum pump. In the next step, the core was flooded with the formation brine until complete saturation with water was achieved. After this, the core was flooded with oil until an irreducible water saturation was achieved. After this step, three main experiments including water flooding (WF), secondary carbonated water injection (SCWI), and tertiary carbonated water injection (TCWI) were designed and implemented. For conventional waterflooding, the maximum of three pore volumes (PV) of formation brine was injected into the core after establishing the irreducible water saturation. Three PV were chosen to make sure that all the recoverable oil is produced under conventional WF. For the TCWI, after establishing the irreducible water saturation, the first WF was performed using formation brine. Then, CW with the maximum of 5 PV was injected into the core sample. For the SCWI, 5 PV of CW was injected after establishing the irreducible water saturation. At the end, an oil recovery factor of WF, SCWI, and TCWI was calculated. All these flooding experiments were carried out at 1000 psi and 80 °C. A constant displacement rate of 0.1 cm\textsuperscript{3}/min was used in all flooding experiments in this study.

3. RESULTS AND DISCUSSION

3.1. CO\textsubscript{2}–Brine Solubility. In this study, CO\textsubscript{2} solubility in formation brine and seawater was determined at different pressures and temperatures. Figure 3 presents the solubility of CO\textsubscript{2} in formation brine and seawater with respect to pressure changes at constant temperature of 80 °C. Also, Figure 4 presents the effect of temperature on CO\textsubscript{2} solubility at constant pressure of 1000 psi.

As shown in Figure 3, CO\textsubscript{2} solubility in brine increases with pressure regardless of the brine type. For both solutions, the minimum CO\textsubscript{2} solubility is achieved at the lowest pressure (500 psi) and the maximum value is achieved at the highest pressure (4000 psi). However, CO\textsubscript{2} solubility becomes less sensitive to pressure at higher pressures (for example at pressures above 2500 psi). This could be because the highest CO\textsubscript{2} saturation of brine is achieved at higher pressures. The increase in CO\textsubscript{2} solubility can be explained by Henry’s law as stated by Duan and Sun.\textsuperscript{50} Another observation from this figure is that CO\textsubscript{2} solubility in seawater is always higher than CO\textsubscript{2} solubility in formation brine, regardless of the pressure. At constant pressure and temperature, CO\textsubscript{2} solubility is affected by brine salinity in which the higher the salinity, the lower the solubility. In this study, salinity of the formation brine is higher than the salinity of the seawater, thus a lower CO\textsubscript{2} solubility is expected in formation brine rather than the seawater. This can be explained by a salting out effect where some fraction of water becomes unavailable for the CO\textsubscript{2} when the salt ions are dissolved. Thus, CO\textsubscript{2} solubility is reduced by increasing the brine salinity.\textsuperscript{48,51}

On the other hand, increasing temperature decreases CO\textsubscript{2} solubility in the formation brine and seawater, as shown in Figure 4. In addition, CO\textsubscript{2} solubility is always higher in seawater as compared to formation brine, which is due to lower salinity of seawater. The kinetic energy is increased by increasing the temperature, and this results in more rapid motion between the molecules and, hence, breakage of intermolecular bonds. This enables molecules to escape to the gas phase.\textsuperscript{48,52,53} Thus, CO\textsubscript{2} solubility is reduced by increasing the temperature regardless of the brine’s salinity and pressure as the results presented here confirm.

3.2. Effect of CO\textsubscript{2} on IFT. The effect of CO\textsubscript{2} on IFT was determined by measuring the IFT of carbonated brines and oil. Formation brine and seawater were used to prepare CW and then IFTs were measured at 178 °F and 1000 psi and at equilibrium state. Table 7 presents the results of IFTs of

<table>
<thead>
<tr>
<th>solution</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>formation brine/oil</td>
<td>22.54</td>
</tr>
<tr>
<td>seawater/oil</td>
<td>17.12</td>
</tr>
<tr>
<td>carbonated formation brine/oil</td>
<td>15.18</td>
</tr>
<tr>
<td>carbonated seawater/oil</td>
<td>12.72</td>
</tr>
</tbody>
</table>

Figure 3. CO\textsubscript{2} solubility in formation brine and seawater at 80 °C versus pressure.
carbonated and normal brines with oil. The presence of CO₂ in brine was found to be promising in reducing the IFT of oil and water, where carbonated brines (both formation brine and seawater) had lower IFTs as compared to normal brines. The IFT of formation brine/oil was 22.54 mN/m, while the value was reduced to 15.18 mN/m for carbonated formation brine and oil. On the other hand, the IFT of seawater and oil was 17.12 mN/m and the value was reduced to 12.72 mN/m for carbonated seawater and oil.

CO₂ solubility is a governing mechanism in controlling the IFT of carbonated brine and oil. At constant pressure and temperature, CO₂ solubility is affected by brine salinity in which the higher the salinity the lower the solubility. In this study, the salinity of seawater is lower than the salinity of formation brine. Thus, it is expected to have a higher IFT with formation brine solutions as compared to seawater solutions as it happened in this study. Riazi and Golkari determined the IFT of carbonated and noncarbonated brine with oil. Their investigation showed that IFT of carbonated brine and oil is lower than the IFT of noncarbonated brine and oil. This is because CO₂ dissolves in both brine and oil, which leads to IFT reduction. In addition, in the absence of CO₂, water molecules are oriented across the surface via strong hydrogen bonds, forming a strong interface between water and oil. However, in the presence of CO₂, due to low reactivity toward polar water molecules, they tend to move toward the surface (oil/water interface). As CO₂ molecules reach the surface, they reduce the space available for water molecules, imposing some spatial (conformational) constraints onto water molecules. In response, hydrogen bonds among water molecules are weakened, which results in IFT reduction. Thus, IFT of carbonated brine and oil is lower than the IFT of brine and oil.

Another observation from drop analysis is the shape and volume of analyzed oil drops. Figure 5 represents typical images of the pendant drops of different solutions. Figure 5a represents oil drop in the presence of formation brine, b represents oil drop with carbonated formation brine, c represents oil drop with seawater, and d represents oil drop with carbonated seawater. The increase in shape and volumes are clearly shown in these images, which is because of IFT reduction and oil swelling. This oil swelling is the result of dissolved CO₂ in the CW phase and its partitioning at the CW and oil interface and subsequently its diffusion and dissolution into the oil phase.

3.3. Effect of Temperature on the Carbonated Brine/Oil IFT. The dynamic IFT of CFW/oil and CSW/oil systems was determined at different temperatures (40–100 °C), and the results are shown in Figures 6 and 7, respectively. As shown in these figures, the dynamic IFT is decreased with temperature, regardless of brine type. The minimum value of IFT is achieved at 100 °C, and the maximum value is achieved at 40 °C. The CFW/oil IFT decreased from 16.80 to 14.02 mN/m by increasing the temperature from 40 to 100 °C. On the other hand, the dynamic IFT of CSW/oil decreased from 16.59 to 10.37 mN/m by increasing the temperature to 100 °C.

The IFT is affected by CO₂ solubility in which the higher the solubility, the lower the IFT. An example is IFT reduction with increasing the pressure where CO₂ solubility is increased, thus IFT is reduced. However, another mechanism that controls the IFT is the total entropy of the two phase surface. When it comes to temperature impact on IFT, the dominant mechanism is entropy change rather than the CO₂ solubility. The kinetic
energy and mobility of the molecules are increased with temperature, which inherently increases the total entropy of two phase surface and consequently, reduces the free energy ($\Delta G$), resulting in lower IFT with temperature.$^{34,57,58}$

Another observation from the IFT data was that the minimum value of IFT for CSW/oil was lower than the IFT of CFW/oil. As was explained earlier, at constant temperature and pressure, IFT is affected by the brine salinity. The higher the brine salinity, the lower the $CO_2$ solubility and consequently the higher the IFT.$^{48,50,52}$ The total salinity of the formation brine is higher than the salinity of the seawater, thus it is expected to have a lower IFT with solutions made by seawater, as confirmed in this study. The minimum value of IFT CFW/oil was 14.02 mN/m while it was 10.37 mN/m for CSW/oil.

3.4. Effect of Pressure on the Carbonated Brine/Oil IFT. The dynamic IFT of CFW/oil and CSW/oil was determined with respect to pressure changes from 1000 to 2500 psi as shown in Figures 8 and 9, respectively. Increasing pressure was found to be favorable in reducing the IFT in which the minimum value of IFT was achieved under 2500 psi and the maximum value of IFT was achieved under 1000 psi. This trend was true for both CFW/oil and CSW/oil. However, the IFT of CSW/oil was lower than the IFT of CFW/oil. The IFT of CFW/oil reduced 15.17 to 13.67 mN/m by increasing the pressure from 1000 to 2500 psi. On the other hand, the IFT of CSW/oil reduced from 12.71 to 10.64 mN/m by increasing the pressure to 2500 psi.

As it was explained earlier, at constant temperature, pressure, and brine salinity are the governing factors in controlling the IFT. Increasing pressure enhances the solubility of $CO_2$ which creates a favorable condition for reducing the IFT. Again, this was confirmed in the current study. Riazi and Golakri$^{54}$ determined the IFT of carbonated brine and oil under variable pressure. Their results showed that the IFT is reduced by increasing the pressure from 2.76 to 13.79 MPa. They concluded that the IFT is affected by the solubility of $CO_2$ in which the higher pressure is more favorable in reducing the IFT. Another observation from experimental results in this study was the effect of brine salinity on the IFT, which was explained earlier. Under 2500 psi, the IFT of CFW/oil was 13.67 mN/m while the value reduced to 10.64 mN/m for CSW and oil.

3.5. Effect of Aging Time on the Carbonated Brine/Oil IFT. As shown in Figures 6–9, the IFT of oil and carbonated brines (both carbonated formation brine and carbonated seawater) decreases with time, regardless of pressure and temperature. As shown in these figures, IFT decreased with time initially, followed by a relatively constant trend where it was at equilibrium state. No significant changes occurred in IFT after the equilibrium point was achieved. An observation based on these figures is that the pressure had stronger effect on equilibrium IFT compared to temperature. In other words, IFT reduced with a slower rate with temperature as compared to pressure. This is because the equilibrium IFT was achieved faster when different pressures were used as compared to the experiments where different temperatures were used. The equilibrium IFT was achieved after 840–1560 s when different temperatures were applied while the value was found to be 360–1020 s when different pressures were applied.

$CO_2$ absorption along carbonated water and oil interface is promoted with time. In addition, $CO_2$ tends to leave the water phase and move into the oil phase, which results in IFT reduction. However, beyond a certain time (equilibrium point), the same amount of $CO_2$ absorbed along the interface is transferred into the oil phase, maintaining a relatively constant IFT. Meanwhile, increasing the temperature increases the molecular movements, causing $CO_2$ molecules to exhibit further affinity toward leaving the water phase and move toward the oil phase. Thus, postponing the time by which IFT reaches an equilibrium state, i.e., IFT reduces at a slower rate. On the other hand, IFT reduction with pressure experienced a faster rate. As was explained earlier, as little as 360 s was required for the IFT to reach equilibrium under 2500 psi. The reason for this phenomenon is that $CO_2$ solubility is greatly increased at higher pressure, which promotes IFT reduction. In other words, the reason for fast convergence of IFT to equilibrium state at higher pressures is the rapid saturation of $CO_2$ along the interface, which results in achieving the equilibrium state at a faster rate.$^{56,62}$

3.6. Oil Recovery. In order to investigate the effect of CW on oil recovery, conventional WF and SCWI were implemented at 80 °C and 1000 psi. Figure 10 represents the oil recovery of both conventional WF and SCWI in terms of injected PV.

As shown in this figure, oil recovery increased with increasing injected PV for both conventional WF and SCWI. However, CW was shown to be more efficient than conventional WF. Oil recovery of conventional WF gradually increases from its lowest value of 8.41% under 0.1 PV of injected brine to its maximum
value of 21.75% under 1 PV of injected brine. The oil recovery remained unchanged with further increasing the injected brine to about 3 PV as can be seen from Figure 10. On the other hand, oil recovery with CW revealed a slightly different behavior. Oil recovery increment found to be stage wise with CW injection. Initially, oil recovery increased from 9.11% (under 0.1 PV) to about 27.38% (under 0.6 PV) and then it remained almost unchanged with further increasing the PV to about 1.1 PV. In the next step, oil recovery again started to increase to about 39.26% (under 1.5 PV) and then remained almost unchanged with further increasing the PV to about 2.5 PV. In the final step, oil recovery again increased to about 51.84% under 3 PV of injected CW. In general, it seems that oil recovery is more favorable with CW injection as compared to conventional WF.

The efficiency of SCWI and TCWI was compared and the results are shown in Figure 11. TCWI with the maximum of 5 PV of injected CW was implemented after conducting 3 PV of conventional WF. And, SCWI was continued as much as 5 PV with CW injected to the core. All the flooding experiments were conducted at 80 °C and 1000 psi.

As shown in Figure 11, oil recovery revealed similar trend with increasing the injected fluid. Oil recovery increased stage-wise with CWI, regardless of being secondary or tertiary oil recovery method. For both SCWI and TCWI, oil recovery increased and then it reached a plateau and remained unchanged with further increasing PV. Again, after a plateau period, oil recovery increased to a maximum value and remained unchanged with further increasing the PV. This scenario continued for both SCWI and TCWI where the maximum oil recovery of 61.63% and 52.58% was achieved under SCWI and TCWI, respectively.

Experimental results showed that CWI is more efficient than the conventional WF. Several mechanisms are behind this improvement by CWI. The main mechanisms contributing to the additional recovery in CWI was found to be IFT reduction between oil and CW and oil swelling. Continuous CO2 mass transfer into oil phase, cause the trapped oil after water flooding to swell and reconnect. Thus, oil displacement and recovery increased as the results of CWI. Moreover, oil recovery could be due to wettability alteration to a more favorable condition, i.e., water wet condition, which resulted in improving the oil recovery. Another observation form core flood experiments was that SCWI is more efficient than the TCWI. This is due to the fact that TCWI took place after conventional WF, where some fraction of original oil in place was already produced. Thus, a lower amount of oil was there to be produced through TCWI.

Mosavat and Torabi48 performed a micro-optical analysis of carbonated water injection in irregular and heterogeneous oil wet pore geometry system. Their micromodel observation revealed that, micromodel wettability is changed from oil wet to water wet with continues injection of CW. They found that CWI is capable of recovering an extra 3.1% of original oil in place. They also concluded that the extent of this recovery improvement can be correlated to CO2 solubility and mass transfer rate, which takes place in during CWI. In another study by Shakiba et al.,42 the effectiveness of SCWI and TCWI in improving the oil recovery in a coreflow system was investigated. They also concluded that CW injection is more beneficial than the conventional WF, however, SCWI found to be more efficient than the TCWI. They also concluded that oil swelling and viscosity reduction, which takes place during CW injection is the main mechanism responsible for improving the oil recovery by CWI as compared to conventional WF. An additional oil recovery of 40.54% and 56.74% was reported during tertiary and secondary carbonated water injection compared to conventional WF by the authors. In another study by Seyyedi and Sohrabi,53 the effectiveness of CWI in improving the oil recovery in carbonate and sandstone rocks was investigated. They also found that oil recovery is significantly increased with CWI compared to conventional WF. They concluded that viscosity reduction by oil swelling, IFT reduction between oil and brine, changes in wettability and mineral dissolution are the main mechanisms behind oil recovery increments with CWI. They also concluded that wettability alteration by CW injection is stronger in in carbonate rocks as compared to sandstone rocks.

4. CONCLUSION

This study investigated the effectiveness of CWI into an Iranian carbonate oil reservoir core samples for the purposes of improving oil recovery. CO2 solubility in formation brine and seawater was determined. IFT of different samples of carbonated brines and oil was determined. The following conclusions could be extracted from the studies performed:

1. CO2 solubility is increased with increasing pressure and decreasing temperature. On the other hand, CO2
solubility was higher in seawater compared to formation brine, which is due to lower salinity of seawater.

2. The presence of CO₂ on IFT of brine and oil was found to be positive. The IFT of carbonated brine and oil was lower than the IFT of normal brine and oil.

3. Increasing pressure had significant influence on IFT of carbonated brine and oil. The minimum IFT between carbonated brine and oil was achieved with 2500 psi, while the maximum value was achieved with 1000 psi.

4. IFT of carbonated brine and oil affected by temperature where the higher the temperature, the lower the IFT.

5. IFT of carbonated brine and oil decreased with increasing time, regardless of temperatures and pressures applied. CO₂ absorption along the carbonated water and oil interface is promoted with time, which thus reduces IFT between carbonated brine and oil.

6. IFT was influenced by the brine nature as well. In all experiments, a lower value of IFT was resulted for CSW and oil compared to CFB and oil, which was due to lower salinity of seawater and higher CO₂ solubility in seawater compared to formation brine.

7. CWI into carbonate core found to be very promising in improving the oil recovery compared to conventional WF. In addition, SCWI was more effective than the TCWI because more oil was available in place for recovery. Maximum oil recoveries of 21.75%, 61.63%, and 52.58% was achieved with conventional WF, SCWI, and TCWI, respectively. IFT reduction and oil swelling were found to be the main mechanisms for improving oil recovery during CWI.

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**Notes**

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