Introduction
Low salinity waterflooding (LSWF) is a worldwide growing enhanced oil recovery technique since it is economically feasible and environmentally friendly. Low salinity effect has not been well studied in carbonate reservoirs compared to sandstone reservoirs. To shed light on the effect of the salinity of the injection brine, both rock-fluid and fluid-fluid interactions should be understood. The interfacial tension of oil-brine is an important criterion to characterize the fluid-fluid interactions. The IFT reduction enhances the oil recovery by lowering capillary forces and dragging residual oil into an emulsion form with aqueous fluid. Also, contact angle (CA) of crude oil-brine-rock (CBR) system is an index of wettability and rock-fluid interactions. In a waterflooding process, CBR system is in contact for a period of time. Both the oil-brine IFT and CA, are influenced by the presence of active ions in brine, and could change by time [1,2]. Hence, analyzing the dynamic behavior of IFT is as important as that of equilibrium behavior [3,4].

Many works have attributed oil recovery variation to wettability alteration through multi ion exchange, mineral dissolution, and electrical double layer expansion [5-7]. However, Wang et al [8] showed that rock-fluid interactions can even negatively affect other involved mechanisms proposed to enhance oil recovery. Also, Sohrabi et al [9] performed a number of coreflooding tests using oils with different potentials to generate micro-dispersions. They observed that the fluid-fluid interactions were superior compared to rock-fluid interactions.

According to the provided literature, the objective of this work is to examine both rock-fluid and fluid-fluid interaction to shed light on the share of each interaction in LSWF. For this purpose, the dynamic interfacial tension (DIFT) and dynamic contact angle (DCA) were measured for different brines. Finally, a coreflooding test with sequence of formation water−sea water−diluted sea water is performed to investigate the low salinity effect of sea water and its diluted counterpart.

Experimental

Materials:

Brines. Different brines including formation water (FW), sea water (SW) and 10-time diluted sea water (SW10D) were used in this work. The compositions of these brines are summarized in Table 1. The Diluted level of sea water was prepared by adding appropriate volumes of deionized water to sea water.

<table>
<thead>
<tr>
<th>Salts</th>
<th>Formation Water (mg/lit)</th>
<th>Persian Gulf brine (mg/lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>150.446</td>
<td>28.400</td>
</tr>
<tr>
<td>CaCl₂.2H₂O</td>
<td>69.841</td>
<td>1.828</td>
</tr>
<tr>
<td>MgCl₂.6H₂O</td>
<td>20.396</td>
<td>13.730</td>
</tr>
<tr>
<td>KCl</td>
<td>0.000</td>
<td>0.800</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.518</td>
<td>4.490</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.487</td>
<td>0.1000</td>
</tr>
</tbody>
</table>

Rock. To mimic the reservoir rock for core flooding tests, pure calcium carbonate powder with the mesh between 325 and 400 (between 44 and 37 μm) was packed. The basic properties of the synthetic cores are listed in table 2.

Table 2. Basic physical properties of synthetic cores.

<table>
<thead>
<tr>
<th>Core number</th>
<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>
<th>Initial Oil in Place (IOIP) (cm³)</th>
<th>Irreducible Water saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.10</td>
<td>2.95</td>
<td>89.47</td>
<td>30.10</td>
<td>32.52</td>
<td>3.06</td>
<td>27.1</td>
<td>6.87</td>
</tr>
<tr>
<td>2</td>
<td>13.60</td>
<td>2.95</td>
<td>92.89</td>
<td>31.53</td>
<td>33.95</td>
<td>8.01</td>
<td>29.55</td>
<td>6.46</td>
</tr>
</tbody>
</table>
Crude Oil. Reservoir oil sample from a southwestern Iranian oil field was used in this study.

Methods

IFT measurement. Pendant drop method was used for IFT measurement in this study. The pendant oil drop was injected from bottom into a cell filled with the desired brine. The pendant drop images were monitored and recorded through a camera, then analyzed by drop shape analysis software. As soon as the pendant drop reached to appropriate volume, the injection valve was closed and the online software program began to calculate and record the IFT with time.

Contact angle measurement. Sessile drop technique was used in this study to determine the wettability alteration of the pure calcite rock. The same apparatus of pendant drop was used; however, the oil drop is released and adheres to rock surface and then CA is measured accurately with time. To minimize the roughness of thin sections, they were polished carefully. To prepare the rock substrate, appropriate thin section of calcite rock was aged in the crude oil under temperature of 80 °C for 2 weeks. Then, it was immersed and washed in toluene/heptane solution for 15 minutes to prevent any oil film on the rock surface during contact angle measurement. Finally, the aged rock was placed in brine for 30 minutes to form a water film on the surface.

Coreflooding. A coreflooding test with sequence of FW-SW-SW10D is conducted to study the effectiveness of sea water and dilute SW oil recovery. After packing the synthetic calcite core, the permeability of the core to the FW was measured. In the next step, the core was flooded by the crude oil sample in the horizontal direction to establish irreducible water saturation (S_{irr}). The core outlet was kept at atmospheric pressure. Then, it was aged with oil injection rate of 0.01 cc/min for two weeks under temperature of 80 °C. In addition to CA tests, an increase in pressure drop across the core and additional water production was considered as a demonstration of wettability alteration toward oil-wetness. The secondary and tertiary water flooding tests were conducted at temperature of 30 °C. For each flooding stage, the injection rate was set to 0.2 cc/min and once core reached to the residual oil saturation, the rate increased to 0.4 cc/min to eliminate the possible capillary end effect at low rates. Throughout the experiment the oil recovery and the pressure drop across the core were measured and recorded. This experiment has been repeated in core #2 to confirm the repeatability.

Results

The results of the coreflooding test are shown in Figure 1 and Figure 2. FW as high salinity water recovered 67.4% of IOIP. SW has recovered 2.8% additional oil, which shows it has small low salinity effect. SW10D has insignificant additional oil recovery and change in pressure drop (Figure 2). To find out the reason behind this behavior, a series of dynamic IFT and CA tests are conducted.

![Figure 1. Recovery factor during FW-SW-SW10D sequence of injection versus injected pore volume (PVI)](image-url)
Dynamic IFT tests. The tertiary waterflooding is replicated through IFT measurement tests using pendent drop apparatus. At the beginning, an oil drop was formed in the bulk of formation water in IFT cell. The oil drop was aged in the bulk for an hour, which resembles the water/oil IFT during secondary water flooding. To simulate tertiary waterflooding, the FW was then replaced with SW by injection of SW gently into the cell to alleviate motion of the drop oil. The conductivity of effluent brine is monitored during this process to make sure that the FW is completely replaced with SW. In the case of SW10D flooding, SW is replaced with SW10D. The results of SW and SW10D tertiary flooding are presented in Figure 3. Replacement of FW by SW leads to significant decrease in IFT (~5mN/m) (Figure 3-Left), which might be the reason for additional oil recovery of SW tertiary flooding. However, as shown in Figure 3-Right, SW10D injection leads to significant increase in IFT (~6mN/m). The result is in agreement with insignificant additional oil recovery in tertiary SW10D injection. To obtain more insights into effect of LSWF, rock-fluid interaction should be studied as well.

Dynamic CA. The result of dynamic contact angle is presented in Figure 4. As shown in Figure 4-left, the CA of the oil drops has no change with time. Also, CA change is insensitive to the salinity of aqueous phase. Therefore, one can conclude that fluid-fluid interaction dominated the oil recovery mechanisms of pure calcite/crude oil/brine system under investigation.
Conclusion

Coreflooding tests with sequence of FW-SW-SW10D is conducted on oil-wet pure calcite systems. Although the additional oil recovery is low (~%3 of IOIP), more investigation was performed to understand the effect of water film with different salinities on fluid-rock and fluid-fluid interactions. Dynamic contact angle measurement show that wettability alteration is negligible during these coreflooding tests. Tertiary water flooding was also replicated through dynamic IFT measurements. The results show that tertiary SW flooding leads to reduction in IFT (~5 mN/m). However, the diluted counterpart leads to the increase in IFT by about 6 mN/m, which is in line with the observed results of tertiary oil recovery test. Therefore, fluid-fluid interactions seem to effectively dominate the low salinity effect in pure calcite/crude oil/brine system under investigation here.

References