Improving Water-oil Relative Permeability Parameters Using New Synthesized Calcium Oxide and Commercial Silica Nanofluids

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Received: May 19, 2019; revised: June 10, 2019; accepted: June 18, 2019

Abstract

This paper addressed the application of new hydrophobic synthesized calcium oxide (CaO) and silicon dioxide (SiO₂) nanofluids to low permeability carbonate porous media. Crude oil and plugs were selected from one of oil reservoirs in the west of Iran. The main goal of this paper is comparing the results of improving water-oil relative permeability parameters in low permeability plugs of carbonate cores in the presence of new synthesized CaO and SiO₂ nanofluids. All the experiments were performed at a temperature of 40 °C and at a nanoparticle concentration of 45 ppm. The experimental approaches were designed into two main steps: 1) the effects of both nanoparticles on the changes in interfacial tension (between oil and brine) and oil viscosity 2) the effects of both nanoparticles on wettability (qualitatively) and relative permeability parameters. SiO₂ and CaO decreased interfacial tension from 46.414 mN/m to 41.772 mN/m and 32.860 mN/m respectively. Moreover, SiO₂ and CaO decreased oil viscosity from 9.90 cP to 8.61 cP and 8.01 cP respectively. Based on the obtained results in the core flood experiments, although CaO and SiO₂ nanofluids decreased effective water permeability, effective oil permeability and ultimate oil recovery increased. Moreover, it was seen that the CaO nanofluid improved oil flow in carbonate cores more than the commercial SiO₂ flooding. Finally, it was seen that both nanoparticles change the wettability from oil-wet to water-wet (qualitatively).

Keywords: Silicon Dioxide, Calcium Oxide, Relative Permeability, Interfacial Tension, Nanofluid

1. Introduction

Carbonate reservoirs are known to be oil-wet, to have low permeability, and to contain fractured rocks (Salehi et al., 2008; Roehl et al., 1985). Extracting oil which was trapped in low permeable formations is the main method to recover more oil in these formations (Zhang et al., 2007; Strand et al., 2006; Santanna et al., 2009). Due to the low amount of efficiency and the large amount of oil in place in carbonate reservoirs, many researchers have been interested in studying improving oil recovery from these reservoirs (Anderson et al., 1986; Buckley et al., 1998). Adding chemicals such as surfactants and solvents to systems has been used for lowering the interfacial tension between oil and water and increasing capillary force; polymers have been used for improving sweep efficiency in these formations.

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as well (Skauge et al., 1989; Flaaten et al., 2008). Due to the high cost of these methods and the special characteristics of nanoparticles, nanotechnology has been employed for improving oil recovery in these formations by changing effective parameters such as viscosity, interfacial tension, and contact angle (Ehtesabi et al., 2014; Holm et al., 1987; Haroun et al., 2012; Ju et al., 2012; Karimi et al., 2012; Kaminsky et al., 2007; Liu et al., 2012; Onyekonwu et al., 2010; Ogolo et al., 2012; Shahrabadi et al., 2012; Veerabhadrapa et al., 2011).

The commercial SiO$_2$ nanoparticle has been addressed in many researches, and it has been found out that silica improves oil recovery and changes wettability from oil-wet to water-wet (Ju et al., 2009; Maghzi et al., 2013; Hendraninggra, 2013; Carpenter et al., 2015; Magda et al., 2017; Sheshdeh et al., 2015). Changes in wettability, interfacial tension, viscosity, and permeability were the main factors that affected the nanofluid positive performance in porous media in the presence of silica nanofluid (Ju et al., 2009; Daniel et al., 2017; Bayat et al., 2014; Teng et al., 2017; Hendraningrat et al., 2014; Amedi et al., 2016; Tajmiri et al., 2016; Mortazavi et al., 2016; Moradi et al., 2015; Joonaki et al., 2012; Hendraningrat et al., 2012; Wasan et al., 2002; Chengara et al., 2004; Wasan et al., 2011; Shamsi et al., 2014).

Calcium oxide nanoparticles can be used as catalysts, in biomedical applications, in adsorption, in water purification, and as antibacterial agents (Madhusudhana et al., 2012; Roy et al., 2013; Hai et al., 2009). To the best of our knowledge, introducing CaO to carbonate reservoirs was performed for the first time, and no attempt has been made to use CaO nanofluids in porous media yet. The main goals of this study are introducing new synthesized CaO nanoparticles for using in carbonate porous media and comparing them with commercial SiO$_2$ nanoparticles, which are more addressed in literature. The main steps of the experiments are 1) comparing the changes of interfacial tension between crude oil (containing nanofluid) and brine in the presence of both nanoparticles, 2) comparing changes of oil viscosity in the presence of both nanoparticles, 3) designing core flood tests to obtain the effects of both nanoparticles on tertiary oil recovery and relative permeability parameters at selected nanofluid concentrations, and 4) surveying wettability changes (qualitatively).

2. Materials and methodology

2.1. Materials

Crude oil was selected from a field in the west of Iran. The density and viscosity of oil are 0.864 g/cm$^3$ and 9.9 cP at 40 °C respectively. Other properties of the crude oil are listed in Table 1. The source of asphaltene came from the mentioned crude oil, so asphaltene was extracted by the IP143 method. For the extraction of asphaltene, n-heptane solvent was first added to the crude oil at a volume ratio of 40/1. Second, the mixture was left to rest for 24 hours, and asphaltene was filtered by Whatman’s paper as shown in Figures 1a and 1b. Then, Whatman’s paper was put in IP143 set up for the extraction of pure asphaltene with relevant solvents as displayed in Figure 1c. Pure asphaltene extracted from the IP143 test is shown in Figure 1d. Further information can be found in the study by Nassar et al. (Nassar et al., 2010). As the next step, the FTIR spectroscopy of the asphaltene sample was obtained to see the structural characterization of asphaltene (Figure 2). Table 2 also illustrates the interpretation of all the peaks with relevant interpretation. O–H, N–H, C–H, C=O, and C=C bonds were seen in asphaltene’s structure (Derrick et al., 1999; Mayo et al., 2003; Stuart et al., 2004; Silverstein et al., 2005; Field et al., 2008; Pavia et al., 2009; Ekholm et al., 2002). One carbonate core was extracted from one of the fields in the west of Iran, and two plugs (Plug 1 [length: 4.985 cm, diameter: 3.847 cm] and Plug 2 [length: 4.820 cm, diameter: 3.844 cm]) were prepared for the porous media displacement tests. Two plugs were cleaned according to ASTM D2172 using different solvents in a Soxhlet extraction setup. Then, the
pore volumes, porosities, and permeabilities of gas and brine were measured as listed in Table 3. n-heptane, toluene (99%, Merck, Germany) was used for the extraction of asphaltene in the IP143 test. Ethanol (99%, Merck, Germany) was employed to clean the needle valve of high pressure, high temperature interfacial tension apparatus after each test (to prevent needle valve to be oil-wet). The density and viscosity of brine are 1.025 g/cc and 0.880 cP respectively at 40 °C. Commercial silicon dioxide (SiO$_2$) nanopowder (average particle size: 20 nm, purity: 99.5%, and specific surface area: 160 m$^2$/g) was supplied by Leaf Lane, Houston Brand, and calcium oxide (CaO) nanopowder (average particle size: 20 nm and purity: 99.5%) was synthesized based on the study by Singh et al., 2007. Briefly, 10 g of calcium carbonate was mixed with 5 mL succinic acid, tartaric acid, and citric acids and was allowed to dry at 100 °C for 2 hrs (Singh et al., 2007). Then, the mixture was heated for 2 hrs at 900 °C, and CaO nanoparticles were obtained. Figure 3 shows the SEM of these two nanoparticles (A: CaO, B: SiO$_2$). For the preparation of nanofluids, certain amounts of silicon dioxide (SiO$_2$) and calcium oxide (CaO) were stirred in crude oil solutions for 3 hrs, where the nanoparticles remained stable in the solution.

![Figure 1](image)

**Figure 1**
Asphaltene extraction protocol, a) and b): the extraction of asphaltene with Whatman’s paper; c): IP143 setup; and d): pure asphaltene.
Figure 2
The FTIR spectrum of asphaltene in crude oil.

Figure 3
The SEM of two nanoparticles (left: Hydrophobic SiO$_2$; right: Hydrophobic CaO).

Table 1
SARA test result.

<table>
<thead>
<tr>
<th>Saturate (wt.%)</th>
<th>Aromatic (wt.%)</th>
<th>Resin (wt.%)</th>
<th>Asphaltene (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.2</td>
<td>34.1</td>
<td>7.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Table 2

Interpretation of all the peaks in the FTIR test of crude oil.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Interpretations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3424.42</td>
<td>O–H and N–H stretching</td>
</tr>
<tr>
<td>3064.34</td>
<td>C–H stretching (in CH$_2$, CH$_3$)</td>
</tr>
<tr>
<td>2821.76</td>
<td>C–H in aldehyde hydrogen</td>
</tr>
<tr>
<td>2651.31</td>
<td>C=O bond in secondary amides</td>
</tr>
<tr>
<td>1719.51</td>
<td>C=C bond</td>
</tr>
<tr>
<td>1432.21</td>
<td>C–H bond (CH$_3$)</td>
</tr>
</tbody>
</table>

Table 3

Plug specification as a candidate for the porous media tests.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Plug 1</th>
<th>Plug 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (cm)</td>
<td>4.985</td>
<td>4.820</td>
</tr>
<tr>
<td>Diameter (cm)</td>
<td>3.847</td>
<td>3.844</td>
</tr>
<tr>
<td>Gas pore volume (cc)</td>
<td>10.780</td>
<td>10.590</td>
</tr>
<tr>
<td>Gas permeability (cc)</td>
<td>9.630</td>
<td>9.770</td>
</tr>
<tr>
<td>Gas porosity (%)</td>
<td>18.600</td>
<td>18.970</td>
</tr>
<tr>
<td>Brine pore volume (cc)</td>
<td>11.350</td>
<td>11.430</td>
</tr>
<tr>
<td>Brine porosity (%)</td>
<td>19.570</td>
<td>20.450</td>
</tr>
<tr>
<td>Brine permeability (mD)</td>
<td>0.160</td>
<td>0.180</td>
</tr>
</tbody>
</table>

2.2. Interfacial tension (IFT) test

Figure 4 illustrates the setup and a schematic of the high pressure, high temperature interfacial tension apparatus used for measuring the interfacial tension between crude oil and brine (NaCl 50000 ppm). All the experiments were carried out at 40 °C. As can be seen, the setup contains a high pressure, high temperature vessel, which is coated with a heating jacket for applying the desired temperature. Also, a digital display window reported the temperature. The temperature should be constant while measuring IFT. The apparatus had two pumps for pumping nanofluid and crude oil, and there were two gauges to monitor pressures as well. First, the aqueous fluid (NaCl, 50000 ppm) was transferred to the aqueous vessel, and then the main vessel was filled with the fluid. The air of the vessel was completely removed through the upper parts. Then, crude oil was transferred through the lines and needle valves. The system was equipped with data acquisition and a camera system, which took high quality pictures; the results were analyzed by the software to obtain IFT. In the current work, the experiments were repeated three times, and the average results were reported. The reduction in IFT changed the shape of oil droplets. Equation 1 was used for measuring interfacial tension (Than et al., 1988; Hendraningrat et al., 2014).
Figure 4

\[
\sigma = \frac{\Delta \rho \cdot \Omega^2 \cdot (D_{app})^3}{8n^3 J_D \left( \frac{L}{D} \right)}
\]

where, \(\sigma\) is interfacial tension (dyne/cm), \(\Delta \rho\) represents density difference (g/cc); \(\Omega\) is rotational rate of cylinder (1/s), and \(D_{app}\) stands for measured drop diameter (cm); \(n\), \(D\), and \(J_D\) represent refractive index of fluid, the diameter of drop, and the correction factor respectively; the correction factor is a function of aspect ratio (\(L/D\)).

2.3. Water-oil relative permeability tests
Figure 5 shows the schematic of the set up used for performing water-oil relative permeability tests. All the experiments were performed at 40 °C. The set up was mainly equipped with three transfer vessels (crude oil, NaCl: 50000 ppm, and crude oil containing the nanofluids solution), two Vinci pumps, core holder, oven, pressure gauges, hydraulic pump for applying overburden pressure, differential pressure gauges, and the data acquisition system.

The procedure for oil and water permeability and the experimental work is summarized as follows:

A. Gas porosity and permeability were measured, and then brine porosity and permeability were measured by Darcy’s law (ASTM Standard D2434-68).

B. Crude oil was injected into the core to reach residual water saturation, and volume and pressure drop were recorded along the core at each step.

C. The core was in –reservoir pressure and temperature for at least three weeks, then core which is saturated with oil displaced with formation brine (initial imbibition).

D. The core was flooded by crude oil at two pore volumes, at 40 °C, and at a confining pressure of 1500 psi; the system was then remained for 24 hrs in this condition.

E. The second imbibition test was performed.

F. The data were analyzed using Toth method.

3. Results and discussion

3.1. IFT and viscosity tests

Figure 6 displays the interfacial tension (IFT) between oil and brine (NaCl, 50000 ppm) as a base and the effects of SiO$_2$ and CaO nanoparticles on IFT and oil viscosity at a nanoparticle concentration of 45 ppm and a temperature of 40 °C. Based on the results, the calcium oxide nanoparticle decreased IFT much more than the silicon dioxide nanoparticle. The IFT between oil and brine (NaCl, 50000 ppm) was 46.414 mN/m, and SiO$_2$ and CaO in oil solution decreased the IFT to 44.414 mN/m and 32.860 mN/m respectively at a nanofluid concentration of 45 ppm. The main mechanism of IFT reduction in
the presence of nanoparticle is capillary force (Shahrabadi et al., 2012; Onyekonwu et al., 2010; Zaid et al., 2013; Roustaei et al., 2013; Teng et al., 2017). Moreover, SiO$_2$ and CaO decreased oil viscosity from 9.90 cP to 8.61 cP and 8.01 cP respectively at a nanoparticle concentration of 45 ppm.

![Figure 6](image-url)

The effects of CaO and SiO$_2$ nanofluids on IFT and oil viscosity.

### 3.2. Water-oil relative permeability

An unsteady-state approach was employed in which the method of Toth et al. was applied to the recovery data points (Toth et al., 2002). Figures 7 illustrates the effects of SiO$_2$ nanofluid on relative permeability and ultimate oil recovery at a concentration of 10 ppm respectively. According to the results, the intersection shifted from the left side to the right side. On the other hand, in the presence of silica, residual oil saturation dropped from 30 to 20%, but residual water saturation increased from 21 to 32%. Moreover, it was seen that the effective oil permeability increased from 0.081 to 0.131 mD while the effective water permeability decreased from 0.0729 to 0.0.0446 mD in the presence of SiO$_2$ nanofluid. Also, the ultimate oil recovery increased from 62.02 to 70.6% (an improvement of 8.58%) when flooded by SiO$_2$. Teng et al. performed the same experiments, and based on their results on silica flooding, residual water saturation rose significantly from 0.351 to 0.459% (Teng et al., 2017). The same trend was observed in the relative permeability curve, and the intersection shifted to the right. Accordingly, based on their work and our results, silica improved the ability of oil to flow in porous media. Amedi et al. investigated the effects of nanosilica on water-oil relative permeability (Amedi et al., 2016). Although they did not study the optimum nanoparticle concentration, they found out a similar trend in water-oil relative permeability, and the intersection shifted to the right during nanosilica flooding. To the best of our knowledge, although some papers have addressed silica flooding in porous media, no study has been reported on the use of CaO nanofluids in porous media. Hence, this paper
investigated the effects of this nanofluid on water-oil relative permeability parameters at 40 °C and a selected nanoparticle concentration of 45 ppm. Figures 8 depicts relative permeability and ultimate recovery before and after nanoflooding in the carbonate plug in the presence of CaO nanoparticle. According to the results, although the trend of the graph is similar to nanosilica flooding, CaO showed better applications in the improvement of oil flow in porous media. The water-oil relative permeability intersection moved further to the right side in comparison to when silica nanofluid was used. The main flowing parameters are listed in Table 4. As can be seen, residual oil saturation dropped from 30 to 20%, but residual water saturation increased from 21 to 32%. Ultimate oil recovery improved from 54.4 to 65.30% (tertiary oil recovery is 10.9%). Another result from the calcium oxide flooding was that effective oil permeability increased from 0.081 to 0.131 mD while the effective water permeability decreased from 0.0729 to 0.0446 mD. Finally, it was concluded that CaO nanofluid improved oil flow in carbonate cores even more than commercial silica nanofluid, and the main mechanisms were wettability alteration and IFT reduction.

![Figure 7](image)

**Figure 7**

Effects of silicon dioxide nanofluid on water-oil relative permeability at a concentration of 45 ppm.
Figure 8
Effects of calcium oxide nanofluid on water-oil relative permeability at a concentration of 45 ppm.

Table 4
Information of water-oil relative permeability for the two nanofluids.

<table>
<thead>
<tr>
<th>Property</th>
<th>Plug 1, CaO</th>
<th>Plug 2, SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil effective permeability (mD)</td>
<td>0.072</td>
<td>0.122</td>
</tr>
<tr>
<td>Water effective permeability (mD)</td>
<td>0.0526</td>
<td>0.0407</td>
</tr>
<tr>
<td>Recovery factor (%)</td>
<td>54.40</td>
<td>65.30</td>
</tr>
<tr>
<td>Saturation of oil residual (%)</td>
<td>36</td>
<td>25</td>
</tr>
<tr>
<td>Saturation of water residual (%)</td>
<td>21</td>
<td>28</td>
</tr>
</tbody>
</table>

4. Conclusions
This paper presents the application of new synthesized CaO and commercial SiO₂ nanoparticles in improving fluid transport in low permeable carbonate reservoirs. After comparing the changes of oil viscosity and interfacial tension between crude oil (containing nanofluid) and brine, a core flood test was designed to obtain the effects of nanofluid on tertiary oil recovery and two-phase relative permeability parameters. All the experiments were performed at a temperature of 40 °C and a nanoparticle concentration of 45 ppm. The CaO nanoparticle decreased IFT and oil viscosity more than SiO₂ nanoparticle. Moreover, CaO and SiO₂ nanofluids reduced effective water permeability, but raised effective oil permeability and ultimate oil recovery. Also, it was seen that CaO nanofluid improved oil flow in carbonate cores more than commercial SiO₂ nanoparticles. Finally, it was qualitatively seen that both nanoparticles changed wettability from oil-wet to water-wet.
Acknowledgments

The author would like to thank Amirkabir Laboratory Research Center for preparing the core flood and the high pressure, high temperature apparatus for performing the static/dynamic tests.

Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>cP</td>
<td>Centipoise</td>
</tr>
<tr>
<td>°C</td>
<td>Centigrade</td>
</tr>
<tr>
<td>cc</td>
<td>Cubic centimeter</td>
</tr>
<tr>
<td>D</td>
<td>Diameter of drop</td>
</tr>
<tr>
<td>Dapp</td>
<td>Drop diameter [cm]</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>HP-HT</td>
<td>High pressure-high temperature</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial tension [mN/m]</td>
</tr>
<tr>
<td>J_D</td>
<td>Correction factor as a function of L/D</td>
</tr>
<tr>
<td>L/D</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>mD</td>
<td>Millidarcy</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index of fluid</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>R.F.</td>
<td>Recovery factor (%)</td>
</tr>
<tr>
<td>SARA</td>
<td>Saturate-aromatic-resin-asphaltene</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>Δρ</td>
<td>Density difference [g/cc]</td>
</tr>
<tr>
<td>Ω</td>
<td>Rotational rate of cylinder [1/s]</td>
</tr>
<tr>
<td>σ</td>
<td>Interfacial tension [dyne/cm]</td>
</tr>
</tbody>
</table>

References


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