Comparison of Oil Recovery by Low Salinity Waterflooding in Secondary and Tertiary Recovery Modes
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Abstract
Oil recovery by low salinity waterflooding in secondary and tertiary modes was investigated in the present study. Cores from Berea outcrop sandstone and Minnelusa reservoir sandstone were used in the single phase and two phase experiments. Two types of Minnelusa crude oils were used in the two phase experiments. The single phase experiments provided the baseline for pH and pressure changes in the two phase experiments.

Set of experiments were performed by using low salinity brine for the tertiary waterflood recovery method where oil saturated cores were first flooded with high salinity brine to simulate the secondary recovery method. In the second set of experiments, oil saturated cores were directly flooded with the low salinity brine. Conductivity and pH analysis of effluent brines were performed in all the single phase and two phase experiments.

Increase in oil recovery with low salinity brine as the invading brine was observed in both secondary and tertiary modes (2-8% OOIP) with Berea sandstone. However, higher oil recoveries (5-8% OOIP) were observed when low salinity waterflooding was implemented as a secondary recovery method. Minnelusa reservoir cores had little to no response to low salinity brine when it was used as a tertiary recovery method. However, Minnelusa cores showed an increase in oil recovery (10-22 % OOIP) with both types of crude oils when it was used as a secondary recovery method. An increase in pH of the effluent brine was observed during the low salinity brine injection in both Minnelusa and Berea cores. However, magnitude of the pH increase was smaller with the Minnelusa cores compared to Berea cores.

The level of investigation into the mechanism of low salinity incremental production has sharply increased in the past two years. Most of the studies focus on core floods using the tertiary mode. Our work contributes systematic coupled secondary and tertiary mode experiments that offer an expanded dataset for all researchers to use in investigation of the mechanisms.

Introduction
Waterflooding has been used since late 1800’s as an oil recovery method after primary depletion of an oil reservoir. In earlier days, the amount of water injected was considered as the most important factor in recovering oil using a waterflood. However, researchers had later pointed out that the composition and quality of the water are more important factors in obtaining optimizing oil recovery by waterflooding. The injected brine in the earlier waterfloods was the formation brine. Increase in oil recovery by decrease in injected water salinity was first observed by Bernard (1967) in an experimental study. Morrow and coworkers (Jadhunanadan and Morrow, 1995; Tang and Morrow, 1997; Morrow et al., 1998; Tang and Morrow, 1999a; Tang and Morrow, 1999b) broadly studied the effect of low salinity brine injection on oil recovery in the mid to late 90’s. BP then investigated the effect of low salinity brine injection on oil recovery in field scale (Webb et al., 2003). Since then many researchers have studied low salinity brine injection because it is one of the most inexpensive and environmentally friendly oil recovery methods (Lager et al., 2008; Patil et al., 2008; Pu et al., 2008; Webb et al., 2008; Alotaibi and Nasr_el_Din, 2009; Boussour et al., 2009; Cissokho et al., 2009; Austad et al., 2010; Kumar et al., 2010; Rivet et al., 2010; Gamage and Thyne, 2011). There are other advantages to injection of low salinity brine, such as reduction in scaling and corrosion of the equipment used in the field (Collins, 2011). This method can also reduce the potential for reservoir souring. All of these factors contribute in a positive manner to project economics.

Many studies on low salinity brine injection confirm that this method can improve oil recovery by 2-42% depending on the brine composition, crude oil composition and rock type. However, there are some laboratory and field studies which do not show any increase in oil recovery by low salinity brine injection. Some researchers have studied the effect of oil recovery by
low salinity brine injection in secondary or tertiary recovery modes (Ashraf, 2010). In the following study, we performed a comparison of oil recovery by low salinity brine injection in secondary and tertiary recovery modes for outcrop and reservoir sandstones.

**Experimental Procedure**

Crude oils from two Minnelusa fields, Raven Creek (RC) and Gibbs (GBS), were used this study. The Raven Creek reservoir bottomhole temperature is about 75°C while Gibbs is about 68°C. The two oils represent the lighter end of the range of oil gravities in Minnelusa fields. Crude oil properties are listed in Table 1. Crude oil was centrifuged at 6000 rpm for 2 hours and filtered to remove water and sediments, vacuumed for 4 hours to remove the light ends. This process can increase water wetness in the system benefiting the low-salinity effect (Tang and Morrow, 1997). Crude oil was stored in amber colored bottles in the dark to avoid photochemical dissociation of the crude oil components.

Outcrop Berea sandstones, and reservoir cores from the Minnelusa Donkey Creek Field were used in the core flooding experiments. Core plugs (1.5 x 3.0 inches) were drilled from either slabbed core or a block (Berea) and dried in the oven at 100°C for 48 hours. The outside of the core plugs were cleaned by a brush before measuring air permeability. Permeability of the cores was measured using nitrogen gas flow (confining pressure, 500 psi). Petrophysical properties of the Berea core plugs are listed in Table 3. Core plugs were stored in a desiccator until use. Reservoir core plugs were drilled from a Donkey Creek Field Minnelusa whole core. The core plugs were cleaned by a Soxhlet for a week with toluene and acetone. Finally, core plugs were dried in an oven at 100°C for 48 hours. Air permeability was measured (confining pressure, 500 psi) and mineral compositions were determined by XRD and thin section petrography. The composition and properties of the core plugs are listed in Table 2. Berea core plugs are quartz rich sandstones with minor amount of calcite and dolomite (Fig. 1 and Fig. 3). Minnelusa lithology is quartz-rich sandstone with minor amounts of anhydrite and dolomite (Figure 2 and Figure 4). There are very small amounts of clay, identified in XRD as illite (Fig. 2).

Synthetic brine representing average Minnelusa formation water composition was made from ACS grade chemicals and distilled water. Brine compositions are listed in Table 3. Synthetic brines were vacuumed for two hours to remove dissolved gas before the experiments.

Both single and two phase experiments were performed. The single phase experiments provide a baseline to evaluate the two phase experiments. First, core plugs were saturated with formation brine under vacuum then aged at room temperature for 7 days. Porosity was calculated by subtracting dry weight of the core from the weight of the brine saturated core. Next, the core plug was mounted in a Hassler core holder and high-salinity brine (2-3 PV) was injected to establish a constant pressure drop across the core (Fig. 5). Pressure drop at different flow rates (0.1, 0.2, 0.3 and 0.4 ml/min) was used to calculate the brine permeability (Kb). In the single phase experiments brine saturated cores were flooded directly with the high salinity brine at 0.2 ml/min for more than 10 pore volumes. During the high salinity brine injection pressure drop across the core was measured continuously. Effluent brine was collected in 8 ml samples, pH and the conductivity of the collected samples were measured immediately.

For the tertiary mode two phase experiments, cores were aged with brine, then brine permeability was measured by the same procedure used in single phase experiments. To establish the initial water saturation (Swi) the core plug was flooded with the crude oil (5 PV) (Tang and Morrow, 1997). Volume of brine displaced by the oil was used to calculate the original oil in place (OOIP) and Swi. Oil permeability was measured at Swi by using the same method as brine permeability. Cores were removed from the core holder and placed in an aging cell for 10 days at 60°C (Tang and Morrow, 1997). After aging, core plugs were re-mounted in the Hassler core holder and flooded with fresh crude oil for about 5 PV (same direction used to establish the Swi). After preparation, core plugs were flooded with the high-salinity brine (formation brine) at 0.2 ml/min for about 10 PV. Pressure drop across the core was measured continuously during the experiment; oil production was measured at set time intervals. Effluent brine was collected in 8 ml samples by using a fraction collector. Therefore, the discrete samples represent an average of dissolved properties for the sampled interval.

The pH and conductivity of the samples were measured immediately. Finally, the core plug was flooded with the low-salinity brine at 0.2 ml/min for another 10 PV. Oil production, pressure drop across the cores, pH and the conductivity were measured as described in the high salinity brine flood. In secondary mode experiments, cores were saturated with brine, flooded and aged with the oil as described under tertiary mode experiments. The core plugs were flooded directly with low-salinity brine for about 10 PV. Oil production, pressure drop across the core, pH and the conductivity were measured during the low salinity brine injection.

**Results and Discussion**

**Single Phase Experiments**

A Berea core plug was flooded with about 12 PV of high salinity brine followed by about 10 PV of low salinity brine (Fig. 6). Pressure across the core plug was nearly constant during the high salinity brine flood. Pressure drop started to increase after high salinity brine is switched with the low salinity brine. The pressure drop reached the maximum value (23 psi) over 5-6 pore volumes and then slowly declined as the injection continued. Fines were observed in the effluent during the low salinity brine injection.
salinity brine injection. During the high salinity brine flood pH of the effluent brine was stabilized around 7.8, during the low salinity brine flood pH increases to about 8.8 and slightly decreased upon continuation of the low salinity flood.

Next, the single phase experiment was performed with a Minnelusa reservoir core plug. The core plug was flooded sequentially with approximately 25 pore volumes of high salinity brine and low-salinity brine to represent tertiary mode application (Fig. 7). Pressure across the core plug increased rapidly at the start of the high salinity brine flood and then decreased during the entire high salinity brine flood. The abrupt pressure change coincident with change in salinity is an experimental artifact and not related to salinity of injected water. Low-salinity brine injection resulted in continued pressure decline along a similar slope compared to the high salinity brine flood. The single phase experiments show that the initial pH value of about 7.8 changed after injection of low-salinity brine to about 8. Fines were not observed in the effluent during high salinity or low-salinity brine flood with the Minnelusa core.

The change in pH and brine salinity, as measured by conductivity, takes place over about 2 pore volumes in both high salinity or low-salinity brine flood with the Minnelusa core. The simultaneous change of pH and brine salinity indicates that pH is controlled by water-rock reactions.

**Two Phase Experiments**

Tertiary mode and secondary mode experiments were performed with both RC and GBS oils using Berea and Minnelusa cores. Results of each core flooding experiment are summarized in table 3. About 40% oil was recovered during high salinity brine flood of an experiment with Berea core plug and RC crude oil (Fig. 8). Pressure drop across the core plug increased during the injection of first one and half pore volumes, then dropped and stabilized around 6-7 psi. Conductivity and the pH of the effluent brine were remains constant during the high salinity brine injection. About 4% additional oil was produced upon the injection of low salinity brine. Pressure drop across the core increased for about 4-5 pore volumes, then gradually decreased after reaching the highest pressure (30 psi). Conductivity decrease and the pH increase took place within 2-3 pore volumes. The pH of the effluent brine increased from 7.6 to 9.1 during the low salinity brine injection. The duplicate experiment produced about 41% oil recovery during the high salinity brine injection and about 3.5% more oil upon the injection of low salinity brine (Table 3). Secondary mode experiments performed with the same rock and crude oils (Fig. 9) produced about 51% total oil recovery. The total oil recovery in the secondary mode experiment is about 6% higher than the total oil recovery of the tertiary mode experiment with the same crude oil and rock type. However, conductivity and pH variation of the effluent brine are very similar to pH and conductivity change during the low salinity brine injection of tertiary mode experiment.

Duplicate tertiary mode core flooding experiments were performed with Berea core plugs and GBS crude oil. About 46.5% oil was recovered during the high salinity brine injection (Fig. 10). Low salinity brine flood was resulted another 5.5% oil recovery. The duplicate experiment produced about 51.5% oil recovery during the high salinity brine flood did not produce measurable oil during the low saline brine injection. However, total oil recovery of the both experiments was essentially the same (52% and 53%). About 59% (Figure 10) and 62% oil was recovered in the secondary mode experiment with the same crude oil type and the rock type. Average total oil recovery in the secondary mode experiments is about 60.5 while the average oil recovery of tertiary mode experiments is about 52.5%. Again, secondary mode experiments produce more oil (about 8%) compared to tertiary mode experiment.

Four experiments were performed with RC and GBS crude oils with Minnelusa core plugs. Fig. 11 shows the tertiary mode experiment with RC crude oil. About 46% oil was recovered during the initial high salinity brine injection. During the high salinity brine injection pressure drop across the core was increased for about 3 pore volumes. Then pressure drop was gradually decreased for about next 10 PV and stabilized around 65 psi. Low salinity brine injection does not produce any incremental oil recovery. Pressure across the core was decreased during the entire low salinity brine flood. The pH of the effluent brine changed slightly during the low saline brine injection. The pH change was small with compared to the pH change of the effluent brine in the Berea core experiments. Fig. 12 shows the results of secondary mode experiment with RC crude oil and Minnelusa rock. About 68% oil was produced during the low salinity brine injection, which is about 22% more oil with compared to the tertiary mode experiment with same crude oil and rock type. Again, pH of the effluent brine was stabilized around 7.2 which is lower than the effluent brine pH of the secondary mode experiment with Berea core plugs.

Fig. 13 depicts the results of tertiary mode experiment with GBS oil and Minnelusa core. During the high saline brine injection about 49% oil was recovered. Low salinity brine injection resulted an additional 1% oil recovery. However, secondary mode experiment with the same crude oil and rock type produced about 60.5% OOIP, which is about 10% more total oil recovery than the tertiary mode experiment with the same oil and rock type.

**Conclusions**

Single phase core flooding experiments were performed with the Berea and Minnelusa core plugs. The experiment with Berea core plug shows a pH increase from 7.7 to 8.8 during the low saline brine injection. Fines were observed in the effluent brine during the low salinity brine flood. Pressure across the core increased for about 4-5 pore volumes during the low salinity brine flood then declined. The single phase experiment with Minnelusa core plug shows a smaller increase in pH during the low salinity brine injection. Fines were not observed in the single phase Minnelusa core flooding experiment.
Secondary mode and tertiary mode core flooding experiments were performed using two Minnelusa formation crude oils and two rock types (Minnelusa and Berea). Incremental oil recovery from low-salinity brine injection was observed in most of the tertiary mode experiments. The incremental recovery is coincident with the decrease in salinity and increase in pH in Berea sandstone core flooding experiments. However, similar pH increases was not observed during the low salinity brine injection in Minnelusa core flooding (single and two phase) experiments. Fines were observed in the effluent of some Berea core flooding experiments.

Among each rock type and oil combination, secondary mode experiments produced more oil than the tertiary mode experiments. In the experiments with RC crude oil and Berea core plugs secondary mode experiments produced about 6% more oil than the tertiary mode experiments. Core flooding experiments of Berea core plugs and GBS oil shows about 8% higher oil recovery in the secondary mode experiments with compared to tertiary mode experiments. The highest oil recovery (68%) was observed in the secondary mode experiments with RC oil and Minnelusa rock system. In the secondary mode experiment with Minnelusa rock and RC oil system, about 22% more oil was produced than the tertiary mode experiment. In the experiments with Minnelusa rock and GBS oil, secondary mode low-salinity flooding produced about 10% more than the tertiary mode flooding.

**Abbreviations**

- MNB: Synthetic Minnelusa brine
- 1%MNB: Low salinity brine
- RC: Raven Creek oil
- GBS: Gibbs oil
- OOIP: Original Oil in Place
- Swi: Initial water saturation, %
- Sor: Residual oil saturation, %
- Ka: Air permeability
- Kb: Brine Permeability
- Ro: Oil recovery, % OOIP
- Rot: Tertiary oil recovery, % OOIP
- Rt: Total oil recovery, % OOIP

**References**


Bernard, G.G., 1967, Effect of Floodwater Salinity on Recovery of Oil from Cores Containing Clays, SPE 1725-MS

Boussour, S., Cissokho, M., Cordier, P., Bertin, H. and Hamon, G., 2009, Oil Recovery by Low Salinity Brine Injection: Laboratory Results on Outcrop and Reservoir Cores. SPE 124277.


Table 1. Crude oil properties.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Density</th>
<th>API</th>
<th>Viscosity (cp)</th>
<th>S. (%)</th>
<th>A. (%)</th>
<th>R. (%)</th>
<th>Asph. (%)</th>
<th>TBN</th>
<th>TAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raven Creek</td>
<td>0.8578</td>
<td>33.5</td>
<td>8.0</td>
<td>80.2</td>
<td>15.8</td>
<td>2.6</td>
<td>1.4</td>
<td>0.92</td>
<td>0.074</td>
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<td>Gibbs</td>
<td>0.8834</td>
<td>28.7</td>
<td>11.50</td>
<td>61.5</td>
<td>23.4</td>
<td>3.2</td>
<td>10.4</td>
<td>---</td>
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</tr>
</tbody>
</table>

S = saturates, A = aromatics, R = resins, Asph. = Asphaltenes

Table 2. Core properties.

<table>
<thead>
<tr>
<th>Name</th>
<th>Rock Type</th>
<th>Length (cm)</th>
<th>Diameter (cm)</th>
<th>Permeability (mD)</th>
<th>Porosity (%)</th>
<th>PV (ml)</th>
</tr>
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<tbody>
<tr>
<td>SE-01</td>
<td>Berea</td>
<td>7.854</td>
<td>3.788</td>
<td>207.64</td>
<td>20.51</td>
<td>18.15</td>
</tr>
<tr>
<td>SE-02</td>
<td>Minnelusa</td>
<td>7.795</td>
<td>3.775</td>
<td>1.74</td>
<td>7.44</td>
<td>6.40</td>
</tr>
<tr>
<td>SE-03</td>
<td>Berea</td>
<td>7.952</td>
<td>3.789</td>
<td>238.22</td>
<td>20.68</td>
<td>18.54</td>
</tr>
<tr>
<td>SE-04</td>
<td>Berea</td>
<td>7.765</td>
<td>3.788</td>
<td>218.32</td>
<td>20.62</td>
<td>18.04</td>
</tr>
<tr>
<td>SE-05</td>
<td>Berea (5)</td>
<td>7.78</td>
<td>3.786</td>
<td>242.76</td>
<td>20.68</td>
<td>18.11</td>
</tr>
<tr>
<td>SE-07</td>
<td>Berea (16)</td>
<td>7.69</td>
<td>3.783</td>
<td>238.43</td>
<td>20.53</td>
<td>17.75</td>
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<tr>
<td>SE-08</td>
<td>Berea (19)</td>
<td>7.793</td>
<td>3.798</td>
<td>372.02</td>
<td>19.89</td>
<td>17.27</td>
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<tr>
<td>SE-09</td>
<td>Berea</td>
<td>7.524</td>
<td>3.783</td>
<td>277.96</td>
<td>21.30</td>
<td>18.02</td>
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<tr>
<td>SE-10</td>
<td>Berea</td>
<td>7.657</td>
<td>3.799</td>
<td>373.13</td>
<td>19.90</td>
<td>17.28</td>
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<tr>
<td>SE-11</td>
<td>Minnelusa(26)</td>
<td>7.664</td>
<td>3.787</td>
<td>12.02</td>
<td>11.17</td>
<td>9.64</td>
</tr>
<tr>
<td>SE-12</td>
<td>Minnelusa 28</td>
<td>7.624</td>
<td>3.779</td>
<td>4.18</td>
<td>9.15</td>
<td>7.82</td>
</tr>
<tr>
<td>SE-13</td>
<td>Minnelusa 22</td>
<td>7.667</td>
<td>3.766</td>
<td>43.489</td>
<td>13.85</td>
<td>11.828</td>
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<tr>
<td>SE-14</td>
<td>Minnelusa 27</td>
<td>7.637</td>
<td>3.781</td>
<td>10.51</td>
<td>6.74</td>
<td>5.779</td>
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Table 3. Summary of experimental results.

<table>
<thead>
<tr>
<th>Name</th>
<th>Oil</th>
<th>K_d (mD)</th>
<th>S_wi</th>
<th>R_o</th>
<th>R_R</th>
<th>R_T</th>
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<tbody>
<tr>
<td>SE-01</td>
<td>N/A</td>
<td>96.3268</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<td>SE-02</td>
<td>N/A</td>
<td>0.1981</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>SE-03</td>
<td>RC</td>
<td>77.80</td>
<td>40.83</td>
<td>39.54</td>
<td>4</td>
<td>43.54</td>
</tr>
<tr>
<td>SE-04</td>
<td>RC</td>
<td>88.20</td>
<td>37.28</td>
<td>41.23</td>
<td>3.5</td>
<td>44.83</td>
</tr>
<tr>
<td>SE-05</td>
<td>RC</td>
<td>71.71</td>
<td>39.11</td>
<td>50.78</td>
<td>N/A</td>
<td>50.78</td>
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<tr>
<td>SE-06</td>
<td>RC</td>
<td>105.96</td>
<td>28.50</td>
<td>51.45</td>
<td>N/A</td>
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<td>GBS</td>
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<td>trace</td>
<td>53.15</td>
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<tr>
<td>SE-08</td>
<td>GBS</td>
<td>209.17</td>
<td>32.28</td>
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<td>SE-09</td>
<td>GBS</td>
<td>101.26</td>
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<td>SE-10</td>
<td>GBS</td>
<td>227.71</td>
<td>28.19</td>
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<tr>
<td>SE-11</td>
<td>RC</td>
<td>2.78</td>
<td>30.50</td>
<td>46.23</td>
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<td>SE-12</td>
<td>RC</td>
<td>1.0218</td>
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<td>SE-13</td>
<td>GBS</td>
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<td>28.98</td>
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<tr>
<td>SE-14</td>
<td>GBS</td>
<td>1.136</td>
<td>30.50</td>
<td>61.54</td>
<td>N/A</td>
<td>61.54</td>
</tr>
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Fig. 1. XRD spectra of Berea sample from core material showing the presence of quartz, Calcite and dolomite.

Fig. 2. XRD spectra of whole rock Minnelusa sample from core material showing the presence of quartz, anhydrite and dolomite.
Fig. 3. Photomicrograph (plain light) showing pores with single dolomite rhomb (center) in Berea sandstone.

Fig. 4. Photomicrograph (plain light) showing pores lined with small dolomite rhombs (a) and pore-filling anhydrite cement (polarized light) in Minnelusa sandstone (b).
Fig. 5. Schematic diagram of core flooding experimental setup.

Fig. 6. Pressure drop, conductivity and the pH variation during a single phase experiment, tertiary mode experiment with core SE-01.
Fig. 7. Pressure drop, conductivity and the pH variation during a single phase experiment, tertiary mode experiment with core SE-02.

Fig. 8. Oil recovery, pressure drop, conductivity and the pH variation during a tertiary mode experiment with core SE-03.

Fig. 9. Oil recovery, pressure drop, conductivity and the pH variation during a secondary mode experiment with core SE-05.
Fig. 10. Oil recovery, pressure drop, conductivity and the pH variation during a tertiary mode experiment with core SE-08.

Fig. 10. Oil recovery, pressure drop, conductivity and the pH variation during a secondary mode experiment with core SE-09.

Fig. 11. Oil recovery, pressure drop, conductivity and the pH variation during a tertiary mode experiment with core SE-11.
Fig. 12. Oil recovery, pressure drop, conductivity and the pH variation during a secondary mode experiment with core SE-12.

Fig. 13. Oil recovery, pressure drop, conductivity and the pH variation during a tertiary mode experiment with core SE-13.

Fig. 14. Oil recovery, pressure drop, conductivity and the pH variation during a secondary mode experiment with core SE-14.