Effect of wettability on oil recovery in Chalk.

Skule Strand\textsuperscript{a,b} and Tina Puntervold\textsuperscript{a,b}
\textsuperscript{a} University of Stavanger, \textsuperscript{b} The National IOR Centre of Norway

Introduction

Smart Water injection with optimized ionic composition is a low cost EOR technique with huge EOR potential in both carbonate and sandstone reservoirs. Compared to classical chemical EOR involving polymer or surfactants, Smart Water is low cost, environmentally friendly, and easily implementable.

The Ekofisk North Sea chalk reservoir is highly fractured with low matrix permeability, and are classified as mixed-wet and close to neutral. Primary production started in 1971. Pressure drawdown with increasing GOR and low ultimate oil recovery resulted in a change in the production strategy by the operator. A seawater (SW) pilot injection was introduced in 1984, and continued by full field implementation have with a tremendous success. The expected recovery factor is now estimated to be above 52% when the production ends sometimes after 2050.

Oil drainage from porous media is dictated by gravity, capillary, and viscous forces. Darcy’s law describes the mobility of water and oil by relative permeabilities as the water saturation increases in an viscous flooding process. Capillary pressure curves account for the contribution of capillary forces. Both capillary forces and relative permeabilities are wettability dependent, and wettability needs to be properly understood when laboratory experiments are performed. The wettability of porous rocks can easily be determined by spontaneous imbibition (SI) experiments. The capillary forces are dependent on the heterogenous fluid distribution of formation water (FW) and crude oil at the pore surfaces.

In order to restore carbonate cores, and to mimic initial reservoir conditions, a detailed understanding of the crude-oil-brine-rock (COBR) interactions is important (Masalmeh et al. 2004, Masalmeh and Jing 2007). Slightly alkaline FW in carbonate reservoirs contains higher concentrations of Ca\textsuperscript{2+} ions, giving a positive surface charge at pH<9.5 (Pierre et al. 1990, Strand et al. 2006). Negatively charged acidic polar organic components (POC) in the crude oil, mostly carboxylates, R-COO\textsuperscript{-}, have strong affinity towards positive charged calcite surfaces, and is regarded as the most important wetting parameter in Chalk reservoirs (Thomas et al. 1993, Standnes and Austad 2000). The amount of acid POC in crude oil could be express by the acid number (AN) with the unit mgKOH/g. The effect of increased AN in crude oil on Stevn Klint (SK) chalk wettability could be observed in Fig.1 (left) (Puntervold 2008).

![Figure 1. Oil recovery tests on SK cores with Swi=10% FW and exposed to oil before imbibition with FW (left) All cores exposed to crude oil with increasing AN; 0.1, 0.5, 0.73, or 1.6 mgKOH/g oil before aging (Puntervold 2008) and SI at 90 °C. (right) core exposed to heptane and SI at 23 °C](image)

The cores were spontaneously imbibed with FW as imbibing brine to avoid any chemically induced wettability alteration during the experiments. As observed, the restored core wettability was significantly affected by the amount of acidic POC present in the crude oil. The amount of acids controls both the rate of imbibition and ultimate recoveries, in line with the wettability evaluation by Anderson (1986, 1987). The adsorption of acidic material present in the crude oil onto chalk is fast during a dynamic crude oil flooding process at 50 °C (Hopkins et al. 2015), and aging of the core in crude oil is actually not required to observe a mixed core wettability, but a slightly lower water wetness was observed after aging (Hopkins et al. 2016b). However, while carboxylic acid is the main parameter responsible for the wetting in carbonates, the polar organic bases appeared to have only a minor effect (Puntervold et al. 2007b). At constant AN, and by increasing BN in the crude oil the water wetness slightly increased. It was suggested that the basic POC interacted with the acidic POC and reduced the adsorption of acids onto calcite surfaces.
A SI experiment was performed on a virgin outcrop SK core P8, Fig 1 (right), which had not seen any crude oil containing POC. The core with Swi=10%, was saturated with heptane, before SI with FW at 23 °C. Ultimate recovery plateau of 75 %OOIP was reached after only 30 minutes, confirming very strong positive capillary forces, and very water-wet core behaviour.

SW behave as Smart Water in mixed-wet chalk cores and significantly improving oil recoveries during both SI and viscous flooding processes, as seen in Fig. 2 (Strand et al. 2008b).

SW as a Smart Water could be further improved by modifying the salinity and/or the ion composition, especially Ca²⁺ and SO₄²⁻, which are the ions needed for the wettability alteration process (Strand et al. 2006, Zhang et al. 2007). Smart Water EOR effects have been reported in chalks, limestone, dolomitic limestones at temperatures ranging from 65–130 °C (Strand et al. 2008a, Austad et al. 2012, Romanuka et al. 2012, Austad et al. 2015, Puntervold et al. 2018).

Viscous processes are controlled by mobility ratio (M), expressed in Eq. 1:

\[ M = \frac{\lambda_D}{\lambda_d} = \frac{\lambda_w}{\lambda_o} = \frac{k_{rw}}{\mu_w} \frac{S_{or}}{k_{ro}} \frac{\mu_o}{S_{wi}} \]

Eq. (1)

A small and unfavourable change in the mobility ratio due to brine viscosity (\(\mu_w\)) cannot explain the huge EOR response of 75 % extra oil, as observed in Fig. 2. The EOR response is also not in line with the generally accepted understanding of highest oil recovery (lowest S or) observed at slightly water-wet conditions, due to lower capillary entrapment of oil (Anderson 1987, Jadhunandan and Morrow 1995).

Porous rocks are by definition capillary systems, and a generalized expression describing capillary pressure (Pc) resulting from interfacial forces in a capillary tube is given in Eq. 2:

\[ P_c = \frac{2\sigma_{ow} \cos \theta}{r} \]

Eq. (2)

where \(\sigma_{ow}\) is the interfacial tension between oil and water, \(\theta\) is wettability, and \(r\) represent the pore radius/distribution and could be expressed as a constant working with the same core. The interfacial tension between oil and brine (\(\sigma_{ow}\))will not change significantly by small change in salinity from 68 000 ppm for FW to 33 000 ppm for SW. The main parameter that could affect capillary forces is the wettability (\(\theta\)). Wettability alteration toward more water-wet conditions will increase capillary forces, and promote increased recovery by...
SI during the viscous flooding.

In this paper, very water-wet outcrop chalk – coccolithic limestone - cores were restored to different initial core wettabilities in the laboratory. Spontaneous imbibition (SI) and viscous flooding (FI) oil recovery experiments were performed to evaluate the effect of initial wettability on ultimate oil recoveries. The results were discussed in relation to wettability alteration processes by Smart Water.

**Experimental**

**Core material.** Outcrop coccolithic chalk from Stevns Klint (SK) in Denmark was used in this study. SK cores can be used as fair representative for the North Sea chalk reservoirs (Frykman 2001), and in wettability studies this material has shown reproducible results. Core properties are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Properties of the Stevns Klint outcrop cores</th>
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<tbody>
<tr>
<td><strong>Core name</strong></td>
</tr>
<tr>
<td>Length, cm</td>
</tr>
<tr>
<td>Diameter, cm</td>
</tr>
<tr>
<td>Bulk Volume, cm³</td>
</tr>
<tr>
<td>Dry weight, g</td>
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<tr>
<td>Sat. weight, g</td>
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<tr>
<td>Pore Volume, ml</td>
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<td>Porosity %</td>
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**Brines.** The FW composition is similar to an offshore north sea chalk field. A typical north sea SW is used, Table 2.

<table>
<thead>
<tr>
<th>Table 2. Brine properties and compositions</th>
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<tr>
<td><strong>Brines</strong></td>
</tr>
<tr>
<td>Ions</td>
</tr>
<tr>
<td>Na⁺</td>
</tr>
<tr>
<td>K⁺</td>
</tr>
<tr>
<td>Li⁺</td>
</tr>
<tr>
<td>Ca²⁺</td>
</tr>
<tr>
<td>Mg²⁺</td>
</tr>
<tr>
<td>Cl⁻</td>
</tr>
<tr>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>Ionic strength</td>
</tr>
<tr>
<td>TDS g/l</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Viscosity at 20 °C</td>
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**Crude oil.** A stabilized crude oil containing similar amounts of acids and bases, that is having similar AN and BN, was used in the tests. No precipitation of asphaltenes was observed during storage prior to analyses and core saturation. The crude oil properties are given in Table 3. AN and BN of the crude oil samples were analysed by potentiometric titration according to methods developed by Fan and Buckley, and which are modified versions of ASTM 665 and ASTM 2898 (Fan and Buckley 2007).

<table>
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<tr>
<th>Table 3. Crude oil properties</th>
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<tr>
<td>Crude oil</td>
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<tr>
<td>Oil A</td>
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**Core restoration.** The $S_{wi}$ of 10% was established by the desiccator technique (Springer et al. 2003). The core was then mounted in a Hassler core holder with a confining and back pressure of 25 and 10 bar, respectively. Core P4 was exposed to 15 PV of oil A at 50 °C by flooded in one direction at a rate of 0.1 ml/min (4 PV/D). Core P3 was exposed to 5 PV of oil A, first saturated, then flooded 2 PV in each directions., Effluent oil samples were collected and AN analysed. The cores were aged at 50 °C for 2 weeks.

**Oil recovery tests.** SI tests were performed in Amott cells at 50 °C. Cumulative amount of capillary driven oil was monitored by time and until recovery plateau was reached. Viscous flooding experiment was performed in Hassler core holder at 50 °C with confining and back pressure of 25 and 10 bar. FW or SW was injected at a rate of 1PV/D until oil recovery plateau was reached.
Results and discussion

The presence of POC in crude oil have been highlighted as a main wetting parameter for controlling reservoir wettability both in sandstone and carbonate reservoirs (Standnes and Austad 2000, Puntervold et al. 2007b, Hopkins et al. 2016a, Mamonov et al. 2019). The result in Fig.1 confirms the importance of acidic POC regarding core wetting in chalk, and the same effect has previously also been confirmed using different types of reservoir crude oils (Standnes and Austad 2000). Keeping all core restoration procedures the same, including the volumes of crude oil exposure, the established core wettability is controlled by the amount of acidic POC present in the crude oil. SI experiments confirmed reduced water wetness with increased AN of the crude oil (Standnes and Austad 2000).

To verify the importance of crude oil exposure to the established core wettability, two SK chalk cores were exposed to different amounts of crude oil during the core restoration process. Core P4 was flooded with 15 PV of oil A and core P3 was flooded with 5 PV. Produced effluent oil samples were collected during core restoration, and AN was analysed and plotted in Fig. 3.

![Figure 3. AN in effluent oil samples during crude oil flooding of core P4 and P3 at 50°C. Both cores was restored with Swi=10% FW. (left) Core P4 was flooded with 15 PV of oil A in one direction. (right) Core P3 was flooded with 2.5 PV of oil A in both directions. Flooding rate was 4 PV/D.](image)

The stippled line at AN = 0.34 mgKOH/g oil indicates the amount of acidic POC in the influent oil A. As seen in Fig. 3, the first effluent samples from core P4 were completely depleted in acidic POC, confirming that the acids had been retained inside the core. With increasing amount of injected oil, the effluent AN gradually increased. Negatively charged carboxylates (R-COO⁻) adsorbed onto the easily available adsorption sites at the positively charged chalk surface. By time, the sites filled up, and the adsorption gradually reduced until the equilibrium between adsorbed carboxylates on the surface and in the free oil phase was reached at 8-9 PV injected, Fig. 3 (left). To secure a more even distribution of polar components in core P3, 2.5 PV of oil A was injected in each direction, Fig. 3 (right).

After aging, the restored cores were SI with FW to evaluate the degree of water wetness, Fig. 4.

![Figure 4. Oil recovery experiments by SI and viscous flooding at 50 °C The cores were restored with Swi = 10% FW. Core P4 (left) was exposed to 15 PV of oil A, while core P3 (right) was exposed to only 5 PV of oil A. FW was used as both imbibing and injection brine.](image)

Core P4 (left), exposed to 15 PV of oil A, steadily imbibed FW giving a recovery plateau of 13 %OOIP after 9 days. Both the shape of the SI curve and the ultimate recovery plateau reveal the core wettability (Ma et al. 1999), both indicated slightly water-wet conditions.

Core P3 (right) which had only seen 5 PV of oil A, behaved significantly more water-wet, reaching its recovery plateau of 26 %OOIP after 7 days. This effect on wettability of crude oil exposure have been reported previously. (Hopkins et al. 2016b).
The experimental results confirmed that acidic POC in crude oil is a key wetting parameter for chalk. Both the amount of acidic POC present in the crude oil (Standnes and Austad 2000), and the volumes of crude oil the core is exposed to during core restoration will influence the wettability of the restored core. This should be borne in mind when preserved reservoir cores are restored prior to SCAL analyses in laboratories, especially when wettability dependent analyses are performed, like oil recovery tests, or when relative permeability and capillary pressure curves are measured. It should be pointed out that most reservoirs are charged with less than 1 PV (1-Swi) reservoir fluid during the accumulation. The amount of POC present in the crude oil during reservoir filling, and the ability of the reservoir fluid to wet reservoir mineral surfaces is unknown.

After the SI experiments on core P3 and P4, both cores were exposed to viscous flooding (FI) using FW as injection brine. The injection rate was 1 PV/D. When viscous forces were applied, increased oil recovery was observed, Fig. 4.

For the slightly water-wet core P4, the oil recovery increased from 13 %OOIP after SI, to a new ultimate recovery plateau of 28 %OOIP during FW flooding. But, for the more water-wet core P3, significantly higher ultimate recovery plateaus were reached: 26 %OOIP after SI, and 48 %OOIP after FW injection, corresponding to an extra 71% oil produced compared to the slightly water-wet core P4. This increased recovery happened even though the average water saturation in the core after SI was significantly higher when the FW injection started in P3.

By using both spontaneous and forced imbibition data, the Amott water index, Iw, can be calculated according to Eq. (3) (Amott 1959):

\[
I_w = \frac{\Delta S_{WS}}{\Delta S_{WS} + \Delta S_{WF}}
\]

where \(\Delta S_{WS}\) signifies increase in water saturation after spontaneous imbibition of water, and \(\Delta S_{WF}\) signifies increase in water saturation after forced imbibition of water.

The Amott water index incorporates the change in water saturation from spontaneous imbibition to the total change in water saturation from both spontaneous and forced imbibition, hence it reflects the relative importance of capillary forces in the oil recovery process. The scale goes from 0 to 1, where 0 is equal to an oil-wet system, where no spontaneous imbibition of water takes place, and 1 is equal to a very water-wet system where all oil is recovered by spontaneous imbibition. The Amott indices and the experimental results from all three cores are summarized in Tbl. 4.

Table 4. Summary of oil recovery results and Amott water indices

<table>
<thead>
<tr>
<th>Core</th>
<th>P4</th>
<th>P3</th>
<th>P8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A injected, PV</td>
<td>15</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>SI recovery, %, OOIP</td>
<td>13</td>
<td>26</td>
<td>75</td>
</tr>
<tr>
<td>FI recovery 1PV/D, %OOIP</td>
<td>28</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>FI – SI, %OOIP</td>
<td>15</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>Iw</td>
<td>0.31</td>
<td>0.35</td>
<td>-</td>
</tr>
</tbody>
</table>

The significantly increased oil recovery from the more water-wet core P3 could be explained by positive capillary forces contributing to the mobilization of oil from smaller pores, increasing the microscopic displacement efficiency. During FW injection, no change in physical properties of the brine phase takes place, and FW will not induce any chemical wettability alteration during oil recovery. The oil recovery results are in line with the Smart Water EOR observation in Fig. 2. The extra mobilized oil is a result of increased water wetness by Smart Water flooding, promoting increased positive capillary forces, and increased microscopic sweep efficiency. However, these experimental results are also contradicting the general acceptance of the highest oil recovery (lowest Sor) observed at slightly water-wet conditions due to lower capillary entrapment of oil (Anderson 1987, Jadhunandan and Morrow 1995).

Conclusions

By performing spontaneous and forced imbibition tests, the core wettabilities of two cores exposed to unequal amounts of crude oil, 5 and 15 PV, were evaluated. Based on the results from this study the following conclusions were drawn:

1. The amount of crude oil flooded through the core during core restoration affected the initial core wettability. Increased volumes of oil reduced the water wetness of initially very water-wet cores.
2. Spontaneous imbibition showed that the core exposed to 15 PV of crude oil behaved slightly water-wet. The core exposed to 5 PV crude oil behaved significantly more water-wet, confirmed by both imbibition rates and ultimate recoveries.

3. The increase in oil recovery by forced imbibition was significantly higher for the more water-wet core.

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References


