

# Adsorption of Crude Oil Components onto Carbonate and Sandstone Outcrop Rocks and Its Effect on Wettability

Tina Puntervold,\* Aleksandr Mamonov, Iván Darío Piñerez Torrijos, and Skule Strand



Cite This: *Energy Fuels* 2021, 35, 5738–5747



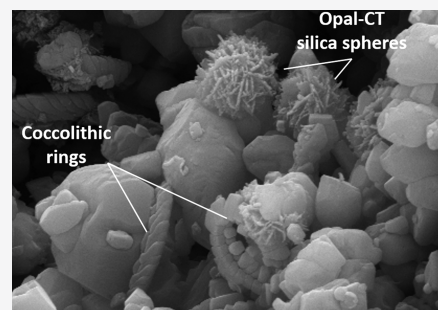
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** The processes of establishing and altering reservoir wettability are still subjects of discussion due to the complexity of the underlying crude oil–brine–rock interactions. This study was aimed at investigating the interrelationship between acidic and basic crude oil components and wetting tendencies on core samples of various mineralogies. Core flooding tests with light crude oils were performed to determine whether acidic or basic polar organic components (POC) showed the highest surface reactivity, adsorbing more readily onto the rock surfaces. The influence of this adsorption on wettability and capillary forces was then identified by performing spontaneous imbibition tests. The core materials used were a rather pure Stevns Klint outcrop chalk, a silica-containing Aalborg outcrop chalk, and an outcrop sandstone with silica minerals of quartz, clays, and feldspars. The results of this work showed a correlation between core mineralogy and the type of predominantly adsorbing POC. Pure chalk showed preference for organic acid adsorption over base adsorption, while the sandstone showed opposite preference. Because of the presence of negatively charged silica minerals, the silica-containing chalk showed increased affinity toward basic components and reduced affinity toward the acids compared to that observed for pure chalk. Oil recovery tests by spontaneous imbibition showed that for all cores, the adsorption of oil components significantly reduced water wetness. Thus, the types of minerals that make up the rock surface have a profound influence on the adsorption of POC and on the generation of wettability, and this should be kept in mind when using crude oil to restore core material wettability in the laboratory.



## INTRODUCTION

Reservoir wettability is a complex property of crude oil–brine–rock (COBR) systems, which is determined by interactions between reservoir fluids and rock surfaces in their contact zones. The main contacting elements are polar components of crude oil, ions in formation of brine, and charged surfaces of rock minerals. Accordingly, when changing the parameters of COBR systems such as crude oil/brine composition or rock mineralogy, the wettability can also change. Based on these principles, the possibility of wettability alteration to a more water-wet state during water injection is widely studied around the globe in terms of enhanced oil recovery (EOR) methods. These EOR methods are based on the modification of the ionic composition of injection brine, known as Smart Water EOR or low salinity injection for specific systems. The successful implementation of Smart Water EOR requires a good understanding and reasonable assessment of the wettability at a certain stage of reservoir development, hereafter called initial wettability.

To observe EOR by wettability alteration, the reservoir rock needs to be of an initial mixed wettability, thus not be completely water-wet. Reservoir wettability is dependent on the properties of all phases in the reservoir, that is, the reservoir crude oil composition, the reservoir rock mineralogy, the salinity and composition of the formation water, and the temperature of the reservoir. A low wettability alteration potential was observed in a

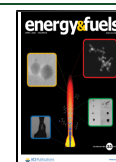
reservoir sandstone system in which high formation water salinity (>200,000 ppm) combined with high reservoir temperature (>120 °C) rendered the sandstone core too water-wet.<sup>1</sup> In another reservoir sandstone system, the low formation water salinity in combination with rock mineralogy, containing high content of feldspars, also rendered the core too water-wet for observing any wettability alteration potential by injection of a low salinity brine.<sup>2</sup> In carbonates, using Stevns Klint chalk, it was observed that the wettability was dependent not only on the salinity of the formation water phase but most importantly on the composition of the formation water.<sup>3</sup> The results in that study showed that the lowest water wetness was obtained in the core containing deionized water as formation water.

The degree of initial wetting is mainly determined by the adsorption of polar organic components (POC) from the crude oil phase onto charged mineral surfaces of the rocks.<sup>4,5</sup> POC are naturally present in crude oils and are normally divided into

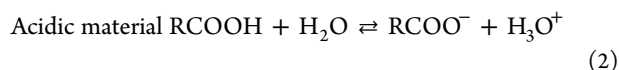
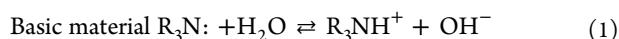
Received: September 5, 2020

Revised: February 19, 2021

Published: March 17, 2021



acidic and basic components, quantified by the acid number (AN) and base number (BN).<sup>6</sup> AN and BN can be determined in the laboratory by potentiometric titration, and both characteristics have the unit mg KOH/g.<sup>7,8</sup> The acidic components in crude oils are mainly carboxylic acids, RCOOH, while the basic material is present as nitrogen-containing aromatic molecules, R<sub>3</sub>N:. Both basic and acidic POC are polar components, and therefore an excess concentration of these components is present at the oil–water interface and can undergo acid–base reactions, i.e., accept or release protons, H<sup>+</sup>, as seen in eqs 1 and 2:



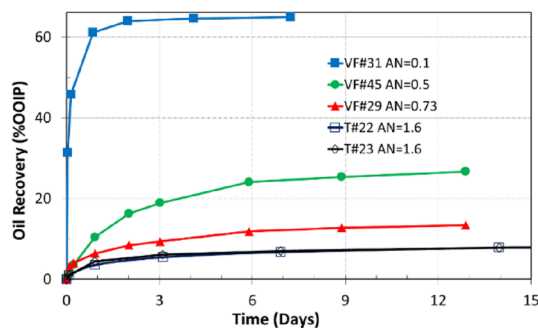
POC are present both in the liquid phase of crude oils and in the resin and asphaltene fractions. To generate a mixed wettability, oil components must adsorb or deposit on the initially water-wet grains of the sedimentary rock. The surface charges of mineral grains differ depending on the type of rock, which leads to differences in the adsorption preferences of polar crude oil molecules. Sandstone minerals are mainly silicates with negative surface charges at the initial acidic pH. Carbonate minerals are normally positively charged at slightly alkaline pH due to the dissolution of carbonate in formation water (FW).

**Adsorption of Crude Oil Components on Sandstone Minerals.** Strand et al.<sup>9</sup> illustrated and explained the establishment of initial wettability in sandstone rock as a result of the competition between polar crude oil components and inorganic ions from the water phase for balancing the surface charge of the sandstone minerals, all influenced by the pH of the system. At slightly acidic pH (<7), it was suggested that the positively charged nitrogen-containing bases electrostatically adsorbed to the rock surface to balance the negative charges of silica surfaces.<sup>10,11</sup> Experimental data also showed that protonated carboxylic acids adsorbed onto the surfaces,<sup>12</sup> which was suggested to be through hydrogen bonds with the surface.<sup>10,11,13</sup> Interpretation of the chemical model provided by Strand et al.<sup>9</sup> suggests that adsorption of POC onto rock minerals and the resulting wettability are influenced by the salinity and composition of the FW phase, the rock mineral properties, the amount and properties of the POC, and pH and temperature of the system.

Several researchers have confirmed that basic crude oils, i.e., with the predominance of the basic POC over acidic, tend to adsorb and wet silicate mineral surfaces. Dynamic adsorption studies performed by Reed<sup>14</sup> showed that nitrogen-based POC were actively adsorbing on mineral surfaces during crude oil flooding through the sandstone reservoir cores. Spontaneous imbibition (SI) tests published by Tong et al.<sup>15</sup> confirmed the establishment of mixed-wet conditions by basic crude oil adsorption on Berea sandstone cores. Recently published studies by Mamonov et al.<sup>16</sup> showed a more pronounced adsorption of bases over acids from nonasphaltic crude oil onto outcrop sandstone cores during oil flooding tests. Similar observations were obtained in the static adsorption test using individual sandstone minerals. A series of experiments using quinoline (C<sub>9</sub>H<sub>7</sub>N) as the model basic POC showed a high tendency of quinoline adsorption on all types of clays.<sup>11,17–20</sup> The results of these static studies showed that the largest amount of quinoline was adsorbed from the aqueous phase at pH ≈ pK<sub>a</sub> ≈ 5, which is a typical value for the initial pH in sandstone reservoirs.<sup>9</sup> Static

adsorption tests on clean silica sand performed by Dubey and Doe<sup>21</sup> also showed the dependence of crude oil adsorption on pH, as well as the increased isoelectric point and the wetting-reversal pH with the increasing crude oil base/acid ratio.

**Adsorption of Crude Oil Components on Carbonate Minerals.** Carbonate rocks are usually positively charged, which can lead to a more active adsorption of acids over bases. Previously, SI tests were performed on several Stevns Klint (SK) chalk cores restored with crude oils with increasing AN. As shown in the results in Figure 1, the chalk cores containing crude



**Figure 1.** Oil recovery tests by SI at 90 °C on restored SK cores using FW as imbibing brine. The cores were restored with  $S_{wi} = 10\%$  FW and exposed to crude oil with increasing AN: 0.1, 0.5, 0.73, or 1.6 mg KOH/g oil before aging.<sup>23</sup>

oil with a higher AN showed less water-wet behavior both with respect to the rate of imbibition and the level of ultimate oil recovery.<sup>22,23</sup> The influence of crude oil bases on core wettability in SK chalk has also been tested in a previous study by Puntervold et al.<sup>24</sup> In that study, SK chalk cores were exposed to crude oils with a constant AN but with a varying BN. It was observed that the water wetness of the cores slightly increased with the increasing BN, confirming that the acids are the main wetting parameter in chalk.

Dynamic adsorption studies by Hopkins et al.<sup>25</sup> showed that the adsorption of acidic POC was more pronounced than that of basic POC onto the SK chalk during crude oil flooding tests. The acidic components mainly represented by dissociated carboxylic acids, RCOO<sup>-</sup>, were instantly adsorbed on mineral surfaces upon contact of crude oil with the core samples. Similar adsorption tendencies have also been demonstrated in static studies with carbonate minerals using long-chain fatty carboxylic acids as model acidic POC.<sup>26,27</sup> In addition, in a recently published paper by Al-Balushi et al.,<sup>28</sup> they investigated the effect of BN to AN ratios on the wetting properties of calcite surfaces. Basic POC were represented by quinoline, and acidic POC were represented by stearic acid. The results showed that the wettability of calcite surfaces was shifting toward a less water-wet state even at relatively low concentrations of stearic acid. The adsorption of quinoline could also change the wettability of the calcite surface toward the neutral state but only at relatively high concentrations. In the work by Puntervold et al.,<sup>24</sup> different behaviors from natural crude oil bases and a model base were observed. An increased amount of natural crude oil bases in the crude oil leads to a lower decrease in water-wet behavior or a slightly more water-wet behavior after crude oil exposure. This was explained by steric hindrance in that the large basic molecules formed acid–base complexes with the carboxylates, thus preventing them from adsorbing to the same extent. When a model base, the small molecule benzyl amine, was added to the

crude oil, the water wetness decreased somewhat, which was explained by the possibility of the small molecule being able to co-adsorb with the acid onto the carbonate surface.

Carbonate reservoirs do not always consist of pure calcite ( $\text{CaCO}_3$ ) but may also contain impurities of other minerals like silicates. The question is whether silica minerals, which usually have negative surface charges, affect the adsorption of POC from crude oil and the resulting wettability. Will the presence of negatively charged minerals decrease the amount of adsorbed acidic POC in crude oil, i.e., the negatively charged carboxylates (deprotonated carboxylic acids), and could it increase the amount of adsorbed organic bases? Answering these questions can improve initial wettability estimation and ultimately help developing a better understanding of COBR interactions involved in the wettability generation. Especially, it is important to understand which crude oil components wet the mineral surfaces and which crude oil to use when establishing wettability in the laboratory. Thus, the objective of this work was to alter the wettability of water-wet outcrop rock to a mixed-wet state by crude oil flooding and observe the effect of the mineral surface composition on adsorption of crude oil components, type and amount, and the resulting wettability.

Outcrop SK chalk and sandstone cores were used as representatives for carbonate and silicate rocks, respectively. In addition, a silica-containing outcrop chalk was used as an intermediate case with mixed mineralogy. The amounts of adsorbed/retained acidic and basic components were measured by mass balance of influent and effluent POC during core flooding with modified crude oils. Finally, the obtained wettability after the crude oil flooding adsorption tests was investigated by SI oil recovery tests.

## EXPERIMENTAL SECTION

**Core Material.** Pure SK outcrop chalk, collected from a quarry near Copenhagen, Denmark, and a silica-containing outcrop chalk (AA) from a quarry near Aalborg, Denmark, were used in the experimental work as chalk material. Chalk mineralogy from EDS analyses is given in Table 1. SK outcrop cores have been previously used in various core flooding experiments and showed very good reproducibility.<sup>25,29,30</sup>

**Table 1. Composition of Stevns Klint (SK) and Aalborg (AA) Chalk Material in Atomic % (at %)**

outcrop	calcite (at %)	silica (at %)	sum (at %)
Stevns Klint (SK)	99	1	100
Aalborg (AA)	94	6	100

The sandstone outcrop cores of unknown origin were provided by Total E&P, France, and contained approximately 10 wt % clay minerals (mostly illite) and 30 wt % feldspar minerals in the form of albite (Na-feldspar). The sandstone mineralogy was obtained by X-ray diffraction measured on a rock piece sampled nearby the core T15 used in this work, Table 2. The outcrop sandstone material has previously shown very good reproducibility in wettability studies linked to low salinity/Smart Water EOR.<sup>11,13,31</sup> The physical properties of both sandstone and chalk cores used in this study are given in Table 3.

**Table 2. Mineralogical Composition of the Outcrop Sandstone Core Material**

core	mineral composition (wt %)						sum
	quartz	albite	illite	chlorite	calcite	others	
T15	56.7	31.9	8.4	1.9	0.3	0.8	100

**Table 3. Physical Core Properties**

core	diameter (cm)	length (cm)	PV (ml)	porosity (%)	permeability (mD)	BET ( $\text{m}^2/\text{g}$ )
SK1	3.75	6.40	31.7	44.8	1–10	2.0
SK3	3.80	5.59	30.6	48.5	1–10	
T15	3.79	7.04	15.6	19.6	20–100	1.8
T29	3.79	7.04	16.2	20.5	20–100	
AA1	3.80	6.60	35.5	48.0	3.7	4.0
AA3	3.80	6.40	34.1	47.0	3.1	

**Crude Oil.** Negatively charged carboxylates ( $\text{RCOO}^-$ ) have strong affinity to positively charged calcite surfaces, while positively charged basic materials ( $\text{R}_3\text{NH}^+$ ) have strong affinity to negatively charged silica surfaces. To compare adsorption affinity, crude oils with a similar content of acidic and basic POC (i.e., similar AN and BN) were prepared for the core flooding tests. Due to different batches of oil, the absolute POC content was not identical. The preparation of the oils involved mixing calculated amounts of three low-asphaltene crude oils with a known AN and BN, resulting in oils of desired and similar AN and BN values in the range of 0.17–0.40 mg KOH/g oil. The amount of acids and bases was set low enough to detect adsorption during core flooding and high enough to minimize analytical uncertainties. The properties of the oils used are given in Table 4. Crude oil S was used in SK chalk cores, crude oil T was used in sandstone core (T15), and crude oil A was used in AA chalk cores.

**Table 4. Crude Oil Properties**

oil	density at 20 °C (g/ $\text{cm}^3$ )	asphaltene (wt %)	AN	BN	absolute error
				mg KOH/g	
S	0.803	< 1	0.40	0.24	$\pm 0.01$
T	0.800	< 1	0.17	0.23	
A	0.810	< 1	0.35	0.35	

**Brines.** The FW brines were synthesized by dissolving reagent grade salts in deionized (DI) water and filtered through a 0.22  $\mu\text{m}$  Millipore filter.  $\text{FW}_\text{S}$  and  $\text{FW}_\text{A}$  brines were identical and used for establishing initial water saturation ( $S_{\text{wi}}$ ) and as imbibing brine in SK and Aalborg chalk cores, respectively. The composition of the  $\text{FW}_\text{S}/\text{FW}_\text{A}$  brine is similar to that of the FW of a North Sea chalk reservoir but depleted in sulfate ions. Sulfate ions can influence the adsorption of crude oil components during crude oil flooding and wettability establishment and were therefore removed.<sup>32</sup> Using the same FW composition for  $S_{\text{wi}}$  and as imbibing brine minimizes any water-based wettability alteration during the SI test, since the imbibing brine is already in equilibrium with the COBR system. For the sandstone core material, 50,000 ppm  $\text{FW}_\text{T}$  was used for establishing  $S_{\text{wi}}$  and as imbibing brine. The brine compositions are listed in Table 5.

**Core Restoration. Core Cleaning.** The chalk cores were initially mounted in a Hassler core holder and flooded by 5 PV of DI at room temperature (23 °C) to remove any easily dissolvable salts including sulfate salts, which may influence the adsorption of polar organic components and thus impact the chalk wettability after exposure to crude oil.<sup>32</sup> The cores were thereafter dried at 90 °C to constant weight.

The sandstone core had previously been used in other oil recovery tests and thus was cleaned differently before use. Crude oil was displaced by low-aromatic kerosene until clear effluent and kerosene was displaced by heptane. Finally, heptane and any soluble salts were displaced by a 1000 ppm NaCl brine. The NaCl was needed to avoid any swelling of clays during core cleaning. The remaining heptane and water were removed by drying at 90 °C to constant weight.

**Initial Water Saturation ( $S_{\text{wi}}$ ).** After core cleaning,  $S_{\text{wi}}$  was established using a desiccator, according to the procedure described by Springer et al.<sup>33</sup> A desired initial water saturation was established by saturation and flooding of a diluted FW followed by evaporation of water until the target weight of the core and the desired  $S_{\text{wi}}$  (10 or 20%)



Table 5. Brine Compositions

ions	$FW_S/FW_A$ mM	$FW_T$ mM
Na <sup>+</sup>	997.0	817.6
Li <sup>+</sup>	0.0	
K <sup>+</sup>	5.0	
Ca <sup>2+</sup>	29.0	20.0
Mg <sup>2+</sup>	8.0	
SO <sub>4</sub> <sup>2-</sup>	0.0	
SCN <sup>-</sup>	0.0	
HCO <sub>3</sub> <sup>2-</sup>	9.0	
Cl <sup>-</sup>	1066.0	857.6
density (g/cm <sup>3</sup> )	1.041	1.035
TDS (g/L)	62.83	50.00
pH	6.7	5.8
ionic strength	1.112	0.877

were reached. The remaining water inside the core has increased its salt concentrations to the original FW values. After evaporation, the core was left to equilibrate for 3 days. In the sandstone core, initial pH was measured during FW flooding prior to crude oil flooding. Previous research has shown that pH is related to the charges of the crude oil components and may influence the adsorption of POC onto sandstone and the resulting wettability.<sup>6,11,34</sup>

**Oil Exposure.** After establishing  $S_{wi}$ , the core was mounted in a Hassler core holder with a confining pressure and back pressure of 20 and 10 bar, respectively. The oil was flooded through the core at 50 °C at a rate of 0.1 mL/min. The AN and BN of the effluent crude oil samples were determined, and the results are presented versus pore volume (PV crude oil injected). Adsorbed POC were then calculated as the difference between the AN and BN of the influent and effluent crude oil samples. The experimental setup is shown schematically in Figure 2.

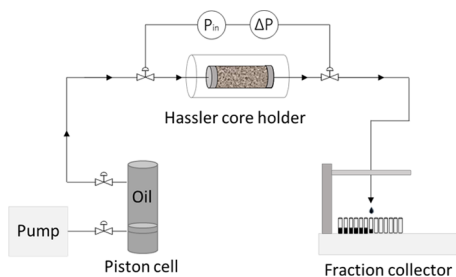


Figure 2. Crude oil core flooding setup.

**Oil Recovery by SI.** The restored cores were placed in an Amott cell and submerged in FW for an SI oil recovery test. The cumulative oil produced was registered with time. The chalk cores were placed in aging cells surrounded by the same crude oil as was inside the cores and aged for 14 days at 50 °C prior to the SI test at 50 °C. To avoid unrepresentative adsorption of POC on the chalk surface during aging, the cores were wrapped in Teflon tape. The sandstone core sample did not experience any aging after the crude oil flooding and prior to the SI test at 60 °C.

**Chemical Analyses. AN and BN Measurements.** The AN and BN of influent and effluent crude oil samples were measured by potentiometric titration using a Mettler Toledo T50 auto-titrator. The methods used were developed by Fan and Buckley<sup>35</sup> and are modified versions of the standard methods ASTM D664 for AN titration and ASTM D2896 for BN titration.<sup>7,8</sup> The reproducibility of both AN and BN measurements was  $\pm 0.01$  mg KOH/g.

## RESULTS AND DISCUSSION

The initial wettability of a rock is a result of chemical interactions between all phases in the COBR system: the crude oil, rock, and the initial brine phase. Interactions between the aqueous and solid phases, such as mineral dissolution, salt precipitation, ion exchanges, etc., determine the initial pH in the reservoir before the invasion of the crude oil. Thus, the adsorption of crude oil components from the crude oil is likely to be influenced by the pH of the reservoir prior to the invasion. Since chalk rocks are mainly composed of CaCO<sub>3</sub>, which is partially soluble in water, the initial pH in chalk reservoirs is slightly alkaline. Sandstones on the other hand possess a slightly acidic pH. Additionally, chalk surfaces are positively charged at pH < ~9, while sandstones are generally negatively charged at pH > ~2.<sup>36</sup> However, exceptions are possible when chalk contains impurities. In addition, a sandstone is composed mainly of various amounts of different silica containing minerals such as quartz, clays, and feldspars, to name the most abundant. Therefore, a series of experiments was conducted to study the tendencies of acidic and basic POC to adsorb on three different mineral surfaces: pure chalk, sandstone, and silica-containing chalk. Pure chalk (99% calcite) and silica-containing sandstone are extreme cases, while silica-containing chalk has a mineralogical composition between the other two. The difference between the influent and effluent AN and BN was used as a quantitative measure of acidic or basic components' tendencies to adsorb on certain mineral surfaces. The resulting wettability was estimated by comparing SI oil recovery tests with FW as imbibing fluid, performed before and after the cores' exposure to crude oil. The parameters for comparison were the rate of imbibition and the total amount of oil displaced.

**Crude Oil Component Adsorption and Wettability in Pure SK Chalk.** SK is a very pure chalk composed of CaCO<sub>3</sub> > 98 wt %. The porosity is quite high, 45–50%, and as shown in the image obtained by scanning electron microscopy (SEM) in Figure 3, coccolithic rings are still intact due to limited

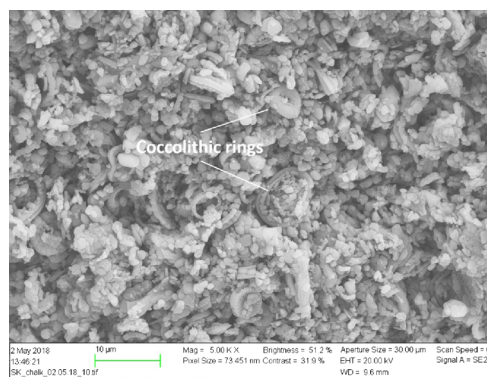
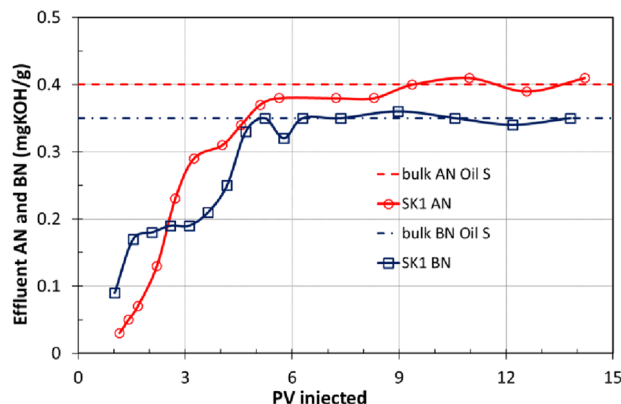


Figure 3. SEM image of SK outcrop chalk with 5000 times magnification.

diagenesis over time. This outcrop is often referred to as an analog to the chalk reservoirs on the Norwegian continental shelf.<sup>37</sup>

SK chalk has a specific surface area of 2.0 m<sup>2</sup>/g and is mainly composed of calcite mineral. For this rock material, zeta potential measurements have confirmed that typical FW brines, FW<sub>S</sub> and FW<sub>A</sub> in Table 5, with high salinity and high concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions will promote positive surface charge.<sup>30</sup> Therefore, negatively charged acidic POC

(carboxylates) from crude oil are more likely to be attracted to the surface of this carbonate rock. To study the affinity of acidic and basic POC to chalk mineral surfaces, core SK1 with  $S_{wi} = 10\%$  FW<sub>S</sub> was flooded with Oil S. The effluent AN and BN were measured and plotted as a function of PV of Oil S injected, Figure 4.



**Figure 4.** Retention/adsorption of acidic and basic POC onto SK chalk during crude oil flooding. 15 PV of Oil S (AN = 0.4 and BN = 0.24 mg KOH/g) was injected into core SK1 with  $S_{wi} = 10\%$  FW<sub>S</sub> at 50 °C and at a rate of 0.1 mL/min. The effluent AN and BN were measured and plotted as a function of PV of Oil S injected.

It can be seen that the first oil eluted from the core was depleted in acidic POC, resulting in an AN  $\sim 0$  mg KOH/g. The eluted oil was also reduced in basic POC. In Figure 4, the influent AN and BN are shown by the dotted lines. Immediate adsorption of POC during crude oil flooding of SK chalk has previously been reported in several studies.<sup>25,38–40</sup> It has also been observed that aging of the core material was not required to obtain a mixed-wet core after crude oil exposure.<sup>39</sup> The acid adsorption equilibrium was reached at 9 PV of crude oil injected, as seen in Figure 4. The base adsorption equilibrium however was reached much earlier, after injection of only 5 PV.

The adsorption of acids and bases can be quantified by calculating the area between the influent and effluent AN and BN curves using the trapezoidal method. The area ( $AN_{ads}$ ) between the adsorption curve and the equilibrium value is a quantitative measure of the amount of acidic functional groups adsorbed onto the chalk surface. The area is calculated by numerical integration using eq 3:

$$AN_{ads} = (AN_i)(PV_n) - \sum_{x=0}^n \frac{AN_x + AN_{x+1}}{2} (PV_{x+1} - PV_x), \quad (3)$$

where  $PV_n$  is the number of PV injected for the eluted crude oil to reach  $AN_i$  (influent AN).  $PV_x$  and  $PV_{x+1}$  are injected pore volumes in integration steps  $x$  and  $x+1$ ;  $AN_x$  and  $AN_{x+1}$  are the values of AN in the eluted oil after injecting the pore volumes  $PV_x$  and  $PV_{x+1}$ .

Similarly, a measure of basic POC adsorption can be obtained by calculating  $BN_{ads}$ , using eq 3 and replacing all AN with BN, giving eq 4:

$$BN_{ads} = (BN_i)(PV_n) - \sum_{x=0}^n \frac{BN_x + BN_{x+1}}{2} (PV_{x+1} - PV_x), \quad (4)$$

where again  $PV_n$  is the number of PV injected for the eluted crude oil to reach  $BN_i$  (influent BN).  $PV_x$  and  $PV_{x+1}$  are injected pore volumes in integration steps  $x$  and  $x+1$ ;  $BN_x$  and  $BN_{x+1}$  are the values of BN in the eluted oil after injecting the pore volumes  $PV_x$  and  $PV_{x+1}$ .

Note, that eqs 3 and 4 are based on the PV injected, meaning that at the end of the adsorption test, the core sample will contain 1 PV of crude oil with unmeasured AN and BN values. Thus, the term “adsorption” accounts for acidic and basic POC retained inside the core, i.e., adsorbed on mineral surfaces and present in the crude oil phase. This assumption, however, does not affect the comparative analysis between different cores and general conclusions.

The calculated retention/adsorption of POC is presented in Table 6. According to these adsorption results, acids have 43% higher retention in SK chalk compared to the bases.

**Table 6.** Adsorption of Acidic and Basic Crude Oil Components on SK Chalk

core	SK1
$S_{wi}$ (%)	10
$AN_{ads}$ (PV*mg KOH/g)	1.33
$BN_{ads}$ (PV*mg KOH/g)	0.93

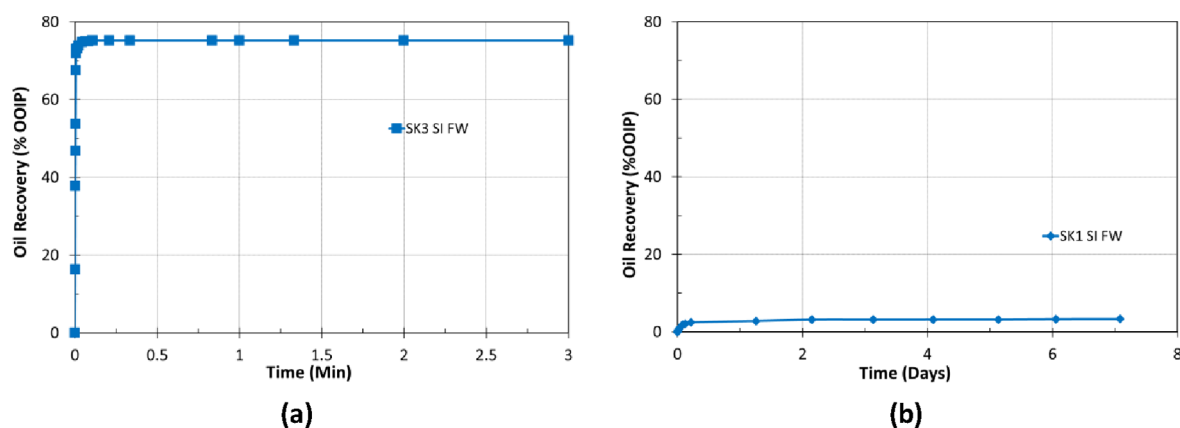
Upon completion of the adsorption test, core SK1 was placed for 14 days aging. Thereafter, a SI test using FW<sub>S</sub> as imbibing brine was performed at 50 °C to evaluate the wettability of the core. For comparison, a similar SI test was performed on a completely water-wet virgin core SK3 with properties analogous to the SK1 core properties, Table 3. The SI results from both tests with cores SK1 and SK3 are shown in Figure 5.

The virgin core SK3 reached a maximum oil recovery plateau of 75% of OOIP after only 90 s of imbibition, confirming strong positive capillary forces and very water-wet behavior, Figure 5a. The core SK1 exposed to 15 PV of Oil S produced only 6% of OOIP, showing mixed-wet behavior, Figure 5b. The results indicate that the adsorption of POC, predominantly acidic, in pure chalk cores significantly affected capillary forces and altered the wettability of a virgin initially very water-wet core toward a less water-wet state. Alteration of virgin chalk core wettability to a less water-wet state by introduction of crude oil has been observed also in previous studies on SK chalk.<sup>38,39</sup>

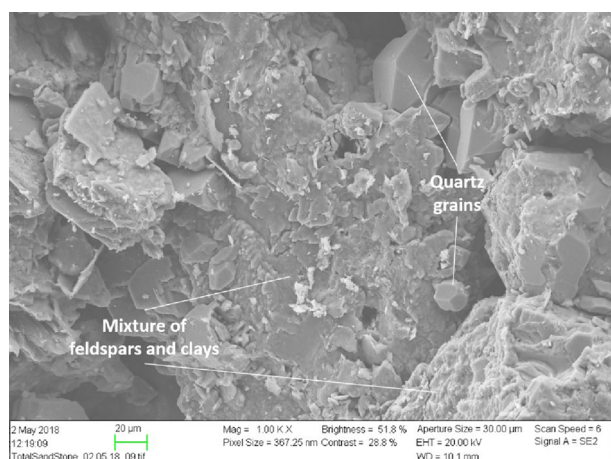
**Crude Oil Component Adsorption and Wettability in Sandstone.** The outcrop sandstone core T15 used in this study was mainly composed of silica minerals, primarily quartz, approximately 10 wt % illite clay, and 30 wt % feldspar minerals. A detailed mineralogical composition is given in Table 2. A SEM picture of the sandstone material similar to that used in the adsorption tests is shown in Figure 6.

This outcrop sandstone material has a specific surface area of  $\sim 1.8$  m<sup>2</sup>/g. A surface reactivity test with FW<sub>T</sub> conducted prior to the establishment of  $S_{wi}$  showed that the initial pH in the core sample is expected to be slightly acidic, pH  $\sim 7$ .<sup>16</sup> At this pH level, silicate mineral surfaces are negatively charged and thus more likely to attract positively charged basic POC (protonated nitrogen-containing compounds) from crude oil. To determine the affinity of acidic and basic POC with silicate mineral surfaces, the sandstone core T15 with initial  $S_{wi} = 20\%$  FW<sub>T</sub> was flooded with Oil T.<sup>16</sup> The effluent AN and BN were measured and plotted as a function of PV of Oil T injected, Figure 7.

In accordance with the results in Figure 7, both crude oil acids and bases have affinity to sandstone silica surfaces. Nevertheless,



**Figure 5.** SI oil recovery tests performed on two similar chalk cores with  $S_{wi} = 10\%$  FW<sub>S</sub>. (a) SI at 23 °C on a water-wet virgin core SK3 exposed to mineral oil (heptane, C<sub>7</sub>H<sub>16</sub>). (b) SI test at 50 °C on core SK1 exposed to 15 PV of Oil S. FW<sub>S</sub> was used as an imbibing brine in both tests.

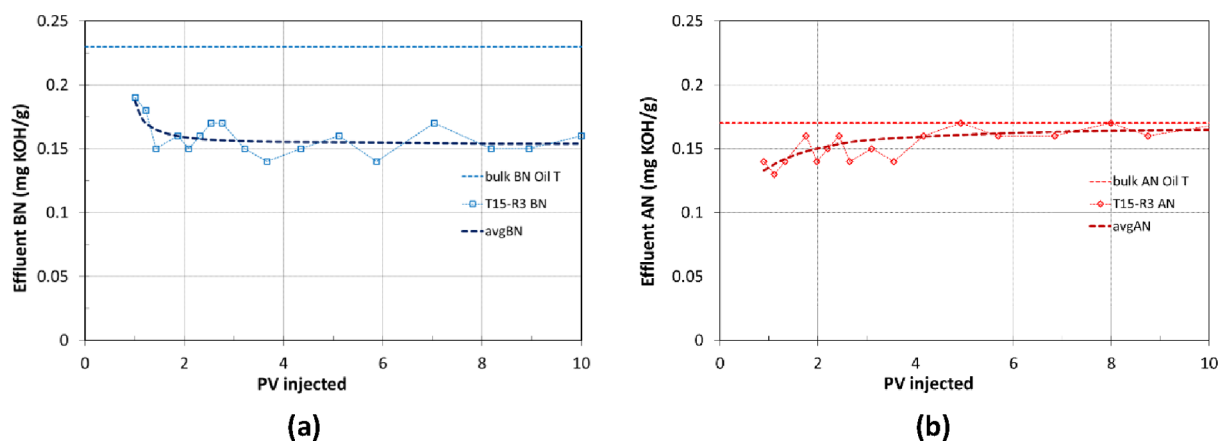


**Figure 6.** SEM image of the outcrop sandstone material with 1000 times magnification.

it can be noted that the crude oil bases have a prominently higher affinity than the acids. With an influent BN = 0.23 mg KOH/g, the effluent BN stabilized at ~0.15 mg KOH/g, and no affinity/adsorption equilibrium was reached after 10 PV injection, Figure 7a. The total amount of bases retained was calculated to be >0.66 PV\*mg KOH/g. The retention of acidic POC was

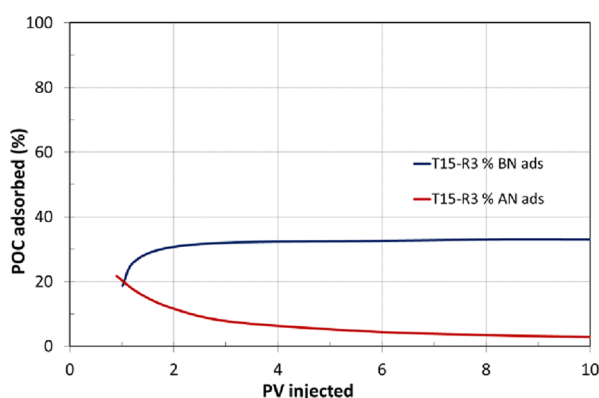
noticeably less, and equilibrium was reached after ~7–8 PV injection, Figure 7b. The total amount of acids retained was calculated to be 0.10 PV\*mg KOH/g. In an attempt to reach base adsorption equilibrium, Mamonov et al.<sup>16</sup> flooded 40 PV of crude oil through the same sandstone material, but still the equilibrium could not be reached. The rather large surface area of sandstone is mainly formed by clays, which carry a permanent negative surface charge. Thus, with the relatively low BN of the crude oil, there are a large number of still available adsorption sites after 1 PV injection of crude oil, which leads to the continuous base adsorption trend observed over the entire injection period.

Mass balance calculations between the influent and effluent AN and BN showed that during 10 PV of Oil T injection, 31.9% of the bases and 6.6% of the acids adsorbed on the rock surfaces, Figure 8. It is also important to highlight that the retention of POC is an immediate process and only a fraction of the acidic and basic components in Oil T were retained in the core and thus have affinity to the silica surfaces. Additionally, an initial decreasing trend of the effluent BN and thus an increasing base adsorption trend were observed in the sandstone core but not in the carbonate core. It is believed that the adsorption increases as the relative amount of the more reactive species (R<sub>3</sub>NH<sup>+</sup>) increases in the crude oil because of a decrease in the brine pH occurring when the crude oil is injected into the sandstone



**Figure 7.** Retention/adsorption of acidic and basic POC onto T sandstone during crude oil flooding. 10 PV of Oil T (AN = 0.17 and BN = 0.23 mg KOH/g) was injected into core T15 with  $S_{wi} = 20\%$  FW<sub>T</sub> at 50 °C and at a rate of 0.1 mL/min. Effluent oil samples were analyzed for (a) BN and (b) AN and plotted against PV of Oil T injected.



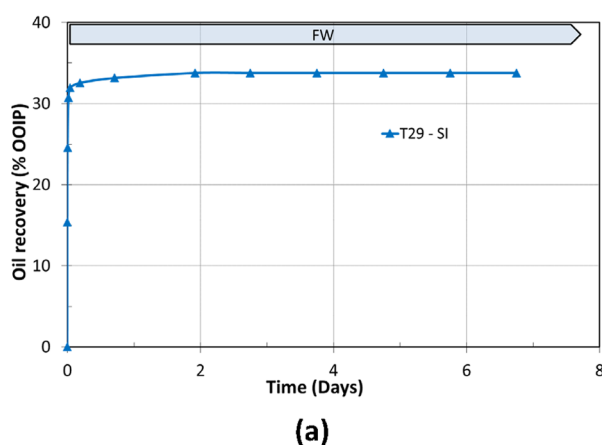


**Figure 8.** POC adsorbed (%) during the Oil T flooding at 60 °C through the core T15. The calculated total amount of POC adsorbed was 31.9% of the bases and 6.6% of the acids after 10 PV injection of Oil T.

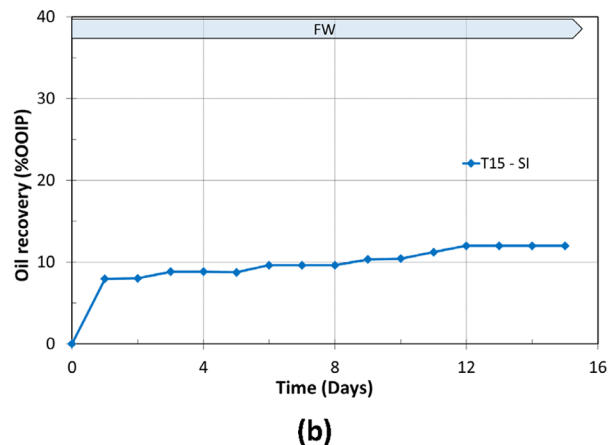
core.<sup>11,31</sup> Carbonate brine pH is alkaline and buffered by the carbonate system, and thus, the relative amount of the more reactive species ( $\text{RCOO}^-$ ) is high and stable, and therefore, a decreasing adsorption trend is observed.

Immediately after crude oil flooding, i.e., without additional aging, the core sample was placed for the SI test with  $\text{FW}_T$  for assessing the initial wettability of the core. When using  $\text{FW}_T$  as the  $S_{wi}$  brine and the imbibing brine, any wettability alteration of the system is diminished, since  $\text{FW}_T$  is already equilibrated with the mineral surfaces and oil. The results of the SI test are given in Figure 9a. For comparison, the results of a similar SI test performed on a completely water-wet (previously not exposed to crude oil with POC) sister core T29 with similar mineralogy (Table 3) are shown in Figure 9b. In the T29 core sample,  $S_{wi} = 20\%$  was established using  $\text{FW}_T$  and nonpolar heptane was used as the oil phase.

Core T29, which has been exposed to mineral oil without POC, reached 30% of OOIP after only 25 min, Figure 9a. An ultimate recovery plateau of 34% of OOIP was reached after 2 days, confirming strong water-wet initial conditions. Core T15, exposed to 10 PV of Oil T and not aged prior to the SI test, reached the recovery plateau of 12% of OOIP after 12 days, Figure 9b. The results indicate that the adsorption/retention of POC significantly reduced the water wetness of the core and the established core wettability was not an effect of a long-term



(a)

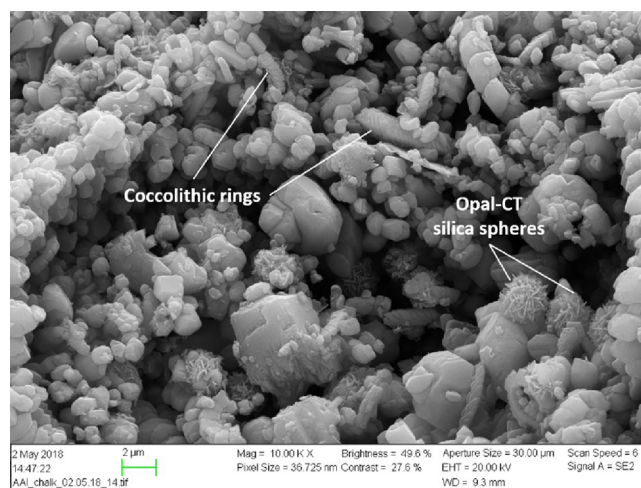


(b)

**Figure 9.** SI oil recovery tests performed on two sandstone sister cores with  $S_{wi} = 20\%$   $\text{FW}_T$ . (a) SI test at 50 °C on core T29 exposed to heptane. (b) SI test at  $T = 60$  °C on core T15 exposed to 10 PV of Oil T.  $\text{FW}_T$  was used as an imbibing brine in both tests.

aging process. In a previously published study, similar results were observed, i.e., adsorption of polar organic bases continued beyond 10 PV of crude oil injected, and wettability of the sandstone core was altered from completely water-wet to less water-wet.<sup>16</sup>

**Crude Oil Component Adsorption and Wettability in Silica-Containing Chalk.** AA chalk is a coccolithic chalk containing silica minerals as shown in Table 1. The silica is present in the chalk material in the form of opal-CT.<sup>41</sup> An SEM image of the AA chalk depicting coccolithic rings and opal-CT structures is shown in Figure 10. Due to the presence of opal-



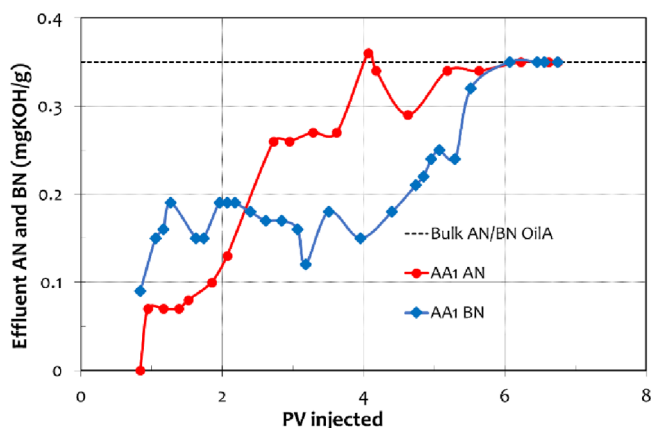
**Figure 10.** SEM image of the AA chalk with 10,000 times magnification.

CT, the specific surface area of the AA chalk ( $4.0 \text{ m}^2/\text{g}$ ) is twice the surface area measured for the SK chalk ( $2.0 \text{ m}^2/\text{g}$ ), Table 3. The mechanisms for the transformation of diatoms via opal-A to opal-CT and finally quartz have been described by Williams and Crerar.<sup>42</sup> Opal-CT is not normally found in reservoir chalk because it dissolves and later recrystallizes as quartz at high temperatures during diagenesis.

Opal-CT is silica-based and therefore negatively charged because of the associated external silanol group  $-\text{Si}-\text{OH}$ . The point of zero charge (PZC) for silica is at  $\text{pH} \sim 2$ , suggesting that the silica surface is negatively charged in the entire pH range observed under reservoir conditions. Chalk has predominantly

positively charged  $\text{CaCO}_3$  mineral surfaces with PZC at pH  $\sim 8-9$ .<sup>36</sup> To determine the effect of the opal-CT silica presence in chalk on POC adsorption and wettability, a series of tests were carried out similarly to those performed on SK chalk and sandstone.

A crude oil flooding adsorption test was performed on core AA1 with  $S_{wi} = 10\% \text{FW}_A$ . Oil A with equal amounts of acidic and basic POC, Table 4, was flooded through the core at  $50^\circ\text{C}$ . Effluent oil samples were analyzed for AN and BN values, and the adsorption test results are shown in Figure 11.



**Figure 11.** Retention/adsorption of acidic and basic POC onto AA chalk during crude oil flooding. 7 PV of Oil A was injected at  $50^\circ\text{C}$  into core AA1 with  $S_{wi} = 10\% \text{FW}_A$  at a rate of  $0.1 \text{ mL/min}$ . The effluent AN and BN were measured and plotted as a function of PV of Oil A injected.

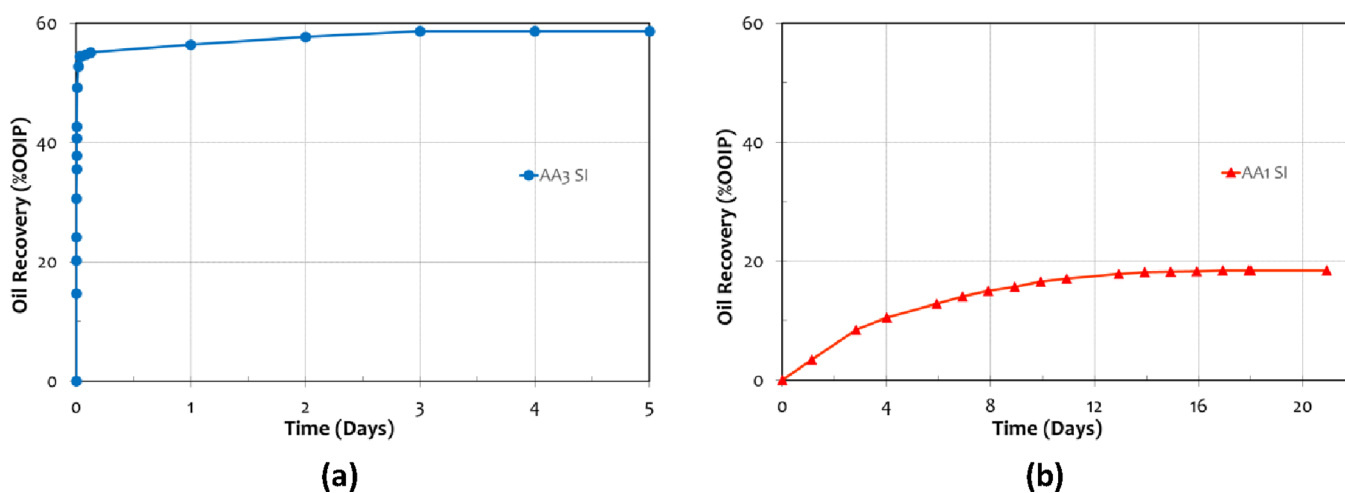
The results show that the first effluent oil sample from core AA1 was completely depleted in acids, which was also observed in the pure SK chalk. As the Oil A flooding continued, the AN in the effluent oil samples gradually increased, reaching equilibrium after 4 PV injection of Oil A. Basic POC were also reduced in concentration in the first effluent oil samples, however, not to the same extent as for acids. The retention/adsorption equilibrium for the bases was reached at 6 PV of Oil A injected, which is an extra 2 PV of crude oil injected compared

to what was injected to reach the acid adsorption equilibrium. This indicates that the opal-CT lepispheres contribute with a large amount of negatively charged silica surfaces available for adsorption, primarily of the basic POC. Mass balance calculations of the influent and effluent AN and BN were performed, and the adsorption of acids and bases was determined. The total amount of acids and bases retained was calculated to be  $0.83$  and  $1.02 \text{ PV}\cdot\text{mg KOH/g}$  respectively, indicating more pronounced adsorption of basic POC onto this rock material.

The adsorption test was completed at 7 PV injection of Oil A, and after this, sample AA1 was placed for 14 days of aging at  $50^\circ\text{C}$ . The core was afterward spontaneously imbibed with  $\text{FW}_A$  to evaluate the initial core wettability. A virgin AA chalk core, AA3, was restored with  $S_{wi} = 10\% \text{FW}_A$  and saturated with mineral oil (heptane), before a SI test was performed to evaluate the wettability of a completely water-wet AA chalk prior to POC exposure. The results from both tests with cores AA1 and AA3 are displayed in Figure 12.

The results in Figure 12a show that core AA3, which was not exposed to POC, behaved strongly water-wet reaching a recovery of 54% of OOIP after 60 min and reaching an ultimate oil recovery plateau of 59% of OOIP within 3 days. Core AA1 exposed to 7 PV of Oil A behaved much less water-wet confirmed by significant reduction in the imbibition rate compared to that of core AA3 and an ultimate oil recovery plateau of only 19% of OOIP reached within 13 days of SI, Figure 12b.

**Summary of POC Adsorption Trends.** The acidic and basic POC adsorption/retention trends on various mineral surfaces were analyzed by flooding modified crude oils through three different outcrop cores: pure chalk, sandstone, and silica-containing chalk. The highest acidic POC retention was observed in pure SK chalk, where the pore surface minerals are composed of calcite. With the presence of silica minerals in the chalk structure, the amount of adsorbed basic POC components increased, which was observed for AA chalk. For the sandstone outcrop material, which consists mainly of silicate minerals, the highest adsorption was observed for the basic POC. The results of adsorption/retention tests are summarized in Table 7.



**Figure 12.** SI oil recovery tests performed on two silica-containing AA chalk cores with  $S_{wi} = 10\% \text{FW}_A$ . (a) SI test at  $23^\circ\text{C}$  on core AA3 exposed to mineral oil (heptane). (b) SI at  $50^\circ\text{C}$  on restored core AA1 exposed to 7 PV of Oil A (AN =  $0.35$  and BN =  $0.35 \text{ mg KOH/g}$ ) and aged for 14 days.  $\text{FW}_A$  was used as an imbibing brine in both tests.



**Table 7. Summary of the Acidic and Basic POC Retained in Cores during Crude Oil Flooding**

core sample	surface minerals	BET	AN <sub>ads</sub>	BN <sub>ads</sub>	BN <sub>ads</sub> / AN <sub>ads</sub>
		m <sup>2</sup> /g	PV*mg KOH/g		
SK chalk, SK10	mainly calcite	2.2	1.33	0.93	0.70
AA chalk, AA1	calcite and silica	4.0	0.83	1.02	1.22
sandstone, T15	mainly silica	1.8	0.10	0.66	6.5

The effect of retention of POC on core wettability could be quantified based on SI experiments by a modified Amott water index ( $I_{W-SI}^*$ ) when a very water-wet core is used as a reference, eq 5.

$$I_{W-SI}^* = \frac{SI_C}{SI_{WWC}}, \quad (5)$$

where  $SI_{WWC}$  is the oil recovery (% of OOIP) by SI from the reference strongly water-wet core and  $SI_C$  is the oil recovery (% of OOIP) by SI from the core exposed to crude oil with POC. The degree of water wetness,  $I_{W-SI}^*$ , approaches 1, for a strongly water-wet core, and 0 for a mixed-wet core.

The wettability indices ( $I_{W-SI}^*$ ) calculated for the outcrop core systems used in this study are presented in Table 8.

**Table 8. POC Adsorption onto Various Mineral Surfaces and its Effect on Wettability**

core	surface minerals	oil – PV injected	AN <sub>ads</sub>	BN <sub>ads</sub>	BN <sub>ads</sub> / AN <sub>ads</sub>	SI (% of OOIP)	$I_{W-SI}^*$
SK3	mainly calcite	heptane (C <sub>7</sub> )				75	1
SK1		Oil S – 15PV	1.33	0.93	0.70	3	0.04
AA3	calcite and silica	heptane (C <sub>7</sub> )				59	1
AA1		Oil A – 7PV	0.83	1.02	1.22	19	0.32
T29	mainly silica	heptane (C <sub>7</sub> )				34	1
T15		Oil T – 10PV	0.10	0.66	6.5	12	0.35

The results show that the adsorption of POC significantly reduced the water wetness of the exposed cores. For the chalk core SK1, water wetness reduced from 1 to 0.04 after the injection of 15 PV of Oil S and predominant adsorption of acidic POC. The injection of 7 PV of Oil A through the core AA1 with a substantial amount of silica surfaces resulted in increased adsorption of bases compared to the SK chalk and reduced water wetness to 0.32. For the T15 sandstone core, adsorption of mostly basic POC during 10 PV of Oil T injection reduced water wetness from 1 to 0.35 without additional core aging.

The results confirm the action of the basic electrostatic principles; i.e., negatively charged silicates attract basic POC, while acidic POC more actively react with positively charged carbonate surfaces. In carbonate COBR systems, pH is maintained at an alkaline level due to the dissolution of CaCO<sub>3</sub> promoting positive mineral surface charges. Alkaline conditions also lead to the formation of negatively charged carboxylates, R-COO<sup>-</sup>, which will have a greater affinity for carbonate surfaces than the neutrally charged basic components, R<sub>3</sub>N<sup>+</sup>. In the case of sandstones, the pH is slightly acidic, which contributes to increased concentration of protonated bases, R<sub>3</sub>NH<sup>+</sup>, and their adsorption on negatively charged silicate

surfaces. With mixed mineralogy, such as in the AA chalk, significant activity of both acidic and basic components is observed, and because of the opal-CT presence, the affinity for basic POC is significantly increased.

POC adsorption on all studied mineral surfaces contributed to a significant decrease in capillary forces and a change in wettability toward a less water-wet state as compared to virgin cores. However, in real reservoir conditions, the process of establishing initial wettability is expected to be more complex due to potential influence of reservoir temperature, FW brine composition/salinity, the presence of sour gases in crude oil, and so on. All these parameters are important and are subjects for further research.

## CONCLUSIONS

This research work is a fundamental study aimed to improve the understanding of surface chemistry in COBR systems. The used experimental design allowed for the observation of adsorption/retention of POC on various mineral surfaces during dynamic crude oil flooding tests and its effect on capillary forces and wettability. The various mineralogies were represented by three different outcrops: pure chalk, sandstone, and silica-containing chalk.

The main conclusions from the work can be summarized as follows:

1. The types of POC that interact with mineral surfaces depend on the type of mineral on pore surfaces. Thus, the retention of acidic POC was more pronounced in pure chalk, while basic POC components were more retained in the sandstone core. Silica-containing chalk adsorbed similar amounts of acidic and basic POC with slightly more pronounced adsorption of basic components.
2. In all crude oil flooding tests, the adsorption of acids and bases occurred immediately from the first pore volumes of oil injection. For carbonate rocks, adsorption equilibrium for acidic and basic POC occurred after injection of about 6 PV of modified crude oil. For the sandstone rock, acidic components reached adsorption equilibrium after injection of about 5 PV of modified crude oil, while basic components were continuously adsorbing even when the test was terminated.
3. SI oil recovery tests performed after adsorption/retention tests show a significant change in capillary forces compared to the completely water-wet scenario for all studied core samples. In the case of the sandstone core, mixed-wet conditions were achieved by flooding of a basic POC-rich crude oil without additional aging.

## AUTHOR INFORMATION

### Corresponding Author

Tina Puntervold – University of Stavanger, 4033 Stavanger, Norway; The National IOR Centre of Norway, 4033 Stavanger, Norway; [orcid.org/0000-0002-5944-7275](https://orcid.org/0000-0002-5944-7275); Email: [tina.puntervold@uis.no](mailto:tina.puntervold@uis.no)

### Authors

Aleksandr Mamonov – University of Stavanger, 4033 Stavanger, Norway; The National IOR Centre of Norway, 4033 Stavanger, Norway; [orcid.org/0000-0002-3800-9364](https://orcid.org/0000-0002-3800-9364)

Iván Darío Piñerez Torrijos – University of Stavanger, 4033 Stavanger, Norway; The National IOR Centre of Norway, 4033 Stavanger, Norway

Skule Strand – University of Stavanger, 4033 Stavanger, Norway; The National IOR Centre of Norway, 4033 Stavanger, Norway

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.energyfuels.0c03003>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

PhD candidate Jon Endre Seljeset Mjos and the students, Isaac Klewiah, Miltiadis Konstantinopoulos, Heydar Gaybaliyev, and Ove André Kvandal, are acknowledged for their contributions to parts of the experimental work performed. The authors acknowledge the University of Stavanger, the Research Council of Norway and the industry partners, ConocoPhillips Skandinavia AS, Aker BP ASA, Vår Energi AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, and Wintershall DEA, of The National IOR Centre of Norway for support.

## REFERENCES

- (1) Aghaeifar, Z.; Strand, S.; Austad, T.; Puntervold, T.; Aksulu, H.; Navratil, K.; Storås, S.; Håmsø, D. *Energy Fuels* **2015**, *29*, 4747–4754.
- (2) Reinholdtsen, A. J.; RezaeiDoust, A.; Strand, S.; Austad, T. In *Why such a small low salinity EOR - potential from the Snorre formation?*, 16th European Symposium on Improved Oil Recovery, Cambridge, UK, 12–14 2011. DOI: 10.3997/2214-4609.201404796.
- (3) Shariatpanahi, S. F.; Hopkins, P.; Aksulu, H.; Strand, S.; Puntervold, T.; Austad, T. *Energy Fuels* **2016**, *30*, 180–187.
- (4) Buckley, J. S. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 191–196.
- (5) Anderson, W. G. Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability. *J. Petrol. Technol.* **1986**, *38*, 1125–1144.
- (6) Buckley, J. S.; Morrow, N. R. In *Characterization of Crude Oil Wetting Behavior by Adhesion Tests*, SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, 1990. DOI: 10.2118/20263-MS.
- (7) ASTM, I., ASTM2896–88 Standard test method for base number of petroleum products by potentiometric perchloric acid titration. American Society for Testing Materials: Philadelphia, 1988.
- (8) ASTM, I., ASTM664–89 Standard test method for acid number of petroleum products by potentiometric titration. American Society for Testing Materials: Philadelphia, 1989.
- (9) Strand, S.; Puntervold, T.; Austad, T. *J. Pet. Sci. Eng.* **2016**, *146*, 1079–1091.
- (10) Austad, T.; RezaeiDoust, A.; Puntervold, T. In *Chemical mechanism of low salinity water flooding in sandstone reservoirs*, Paper SPE 129767 prepared for presentation at the 2010 SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 24–28 2010. DOI: 10.2118/129767-ms.
- (11) RezaeiDoust, A.; Puntervold, T.; Austad, T. *Energy Fuels* **2011**, *25*, 2151–2162.
- (12) Madsen, L.; Ida, L. *SPE Res. Eval. Eng.* **1998**, *1*, 47–51.
- (13) Piñerez Torrijos, I. D.; Puntervold, T.; Strand, S.; Austad, T.; Tran, V. V.; Olsen, K. *J. Pet. Sci. Eng.* **2017**, *156*, 102–109.
- (14) Reed, M. G. *Clays Clay Miner.* **1968**, *16*, 173–178.
- (15) Tong, Z. X.; Morrow, N. R.; Xie, X. *J. Pet. Sci. Eng.* **2003**, *39*, 351–361.
- (16) Mamonov, A.; Kvandal, O. A.; Strand, S.; Puntervold, T. *Energy Fuels* **2019**, *33*, 5954–5960.
- (17) Puntervold, T.; Mamonov, A.; Aghaeifar, Z.; Frafjord, G. O.; Moldestad, G. M.; Strand, S.; Austad, T. *Energy Fuels* **2018**, *32*, 7374–7382.
- (18) Burgos, W. D.; Pisutpaisal, N.; Mazzaresse, M. C.; Chorover, J. *Environ. Eng. Sci.* **2002**, *19*, 59–68.
- (19) Mamonov, A.; Puntervold, T.; Strand, S. In *EOR by Smart Water Flooding in Sandstone Reservoirs - Effect of Sandstone Mineralogy on Initial Wetting and Oil Recovery*, SPE Russian Petroleum Technology Conference, Moscow, Russia, 2017/10/16/, 2017. DOI: 10.2118/187839-MS.
- (20) Fogden, A. *Colloids Surf., A* **2012**, *402*, 13–23.
- (21) Dubey, S. T.; Doe, P. H. Base Number and Wetting Properties of Crude Oils. *SPE Res. Eng.* **1993**, *8*, 195–200.
- (22) Standnes, D. C.; Austad, T. *J. Petrol. Sci. Eng.* **2000**, *28*, 111–121.
- (23) Puntervold, T. *Waterflooding of carbonate reservoirs - EOR by wettability alteration*. University of Stavanger, Norway, 2008.
- (24) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007**, *21*, 1606–1616.
- (25) Hopkins, P. A.; Strand, S.; Puntervold, T.; Austad, T.; Dizaj, S. R.; Waldeland, J. O.; Simonsen, J. C. *J. Pet. Sci. Eng.* **2016**, *147*, 381–387.
- (26) Rezaei Gomari, K. A.; Denoyel, R.; Hamouda, A. A. *J. Colloid Interface Sci.* **2006**, *297*, 470–479.
- (27) Madsen, L.; Fabricius, I. L. Adsorption of Carboxylic Acids on Reservoir Minerals From Organic and Aqueous Phase. *SPE Res. Eval. Eng.* **1998**, *1*, 47–51.
- (28) Al-Balushi, M. A.; Karimi, M.; Al-Maamari, R. S. *Energy Fuels* **2020**, *34*, 245–257.
- (29) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2009**, *23*, 2527–2536.
- (30) Zhang, P.; Tweheyo, M. T.; Austad, T. *Colloids Surf., A* **2007**, *301*, 199–208.
- (31) Piñerez Torrijos, I. D.; Puntervold, T.; Strand, S.; Austad, T.; Abdullah, H. I.; Olsen, K. *Energy Fuels* **2016**, *30*, 4733–4739.
- (32) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007**, *21* (6), 3425–3430.
- (33) Springer, N.; Korsbech, U.; Aage, H. K. In *Resistivity index measurement without the porous plate: A desaturation technique based on evaporation produces uniform water saturation profiles and more reliable results for tight North Sea chalk*, International Symposium of the Society of Core Analysts, Pau, France, 21–24 2003.
- (34) Austad, T.; Rezaeidoust, A.; Puntervold, T. In *Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs*, SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 2010. DOI: 10.2118/129767-MS.
- (35) Fan, T.; Buckley, J. S. *SPE J.* **2007**, *12*, 496–500.
- (36) Kosmulski, M. *J. Colloid Interface Sci.* **2011**, *353*, 1–15.
- (37) Frykman, P. *Marine Petrol. Geol.* **2001**, *18*, 1041–1062.
- (38) Hopkins, P. A.; Omland, I.; Layti, F.; Strand, S.; Puntervold, T.; Austad, T. *Energy Fuels* **2017**, *31*, 4663–4669.
- (39) Hopkins, P. A.; Walrond, K.; Strand, S.; Puntervold, T.; Austad, T.; Wakwaya, A. *Energy Fuels* **2016**, *30*, 7229–7235.
- (40) Mjos, J. E. S.; Strand, S.; Puntervold, T.; Gaybaliyev, H. In *Effect of Initial Wetting on Smart Water Potential in Carbonates*, SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 2018/3/26, 2018. DOI: 10.2118/190414-MS.
- (41) Strand, S.; Hjuler, M. L.; Torsvik, R.; Pedersen, J. I.; Madland, M. V.; Austad, T. *Petrol. Geosci.* **2007**, *13*, 69.
- (42) Williams, L. A.; Crerar, D. A. *J. Sediment. Res.* **1985**, *55*, 312–321.