

# Influence of Sandstone Mineralogy on the Adsorption of Polar Crude Oil Components and Its Effect on Wettability

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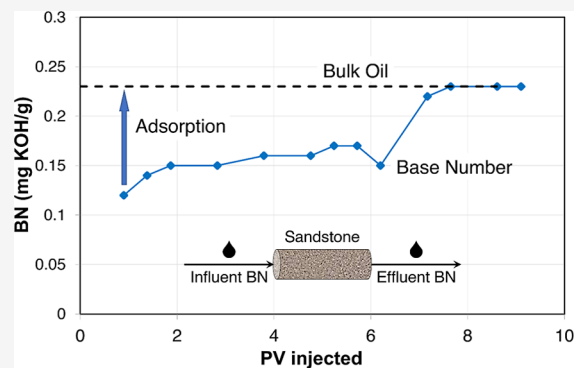
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**ABSTRACT:** The crude oil–brine–rock (COBR) system is a combination of contacting phases where polar organic molecules in crude oil, inorganic ions from the brine phase, and charged mineral surfaces participate in complex interactions. One of the surface phenomena that occur in the COBR system is the adsorption of polar crude oil components, which can directly affect the capillary forces and wettability of the rock. The purpose of this research work was to determine polar organic component (POC) adsorption trends for sandstones of different origins and mineralogical compositions. Adsorption preferences for acidic and basic POCs were quantified by potentiometric titration during dynamic core flooding tests using modified crude oil. The influence of POC adsorption on wettability was investigated by evaluating capillary forces during the displacement of oil in a spontaneous imbibition (SI) process. The results of this work showed a clear relationship between the intensity of POC adsorption and sandstone mineralogy. Greater adsorption capacity and a predominant affinity for bases compared to that for acids were found in the sandstone material containing a sufficient amount of reactive illite clay minerals. On the other hand, the sandstone material consisting mainly of quartz with an insignificant content of kaolinite clay did not show a pronounced tendency to adsorb POCs. All the studied rock materials have also shown a significant impact of POC adsorption on capillary forces and wettability, confirmed during SI tests. As a result, a detailed mineralogical analysis along with crude oil chemistry is required to properly evaluate sandstone wettability and competently plan core flooding laboratory studies.



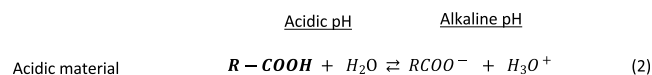
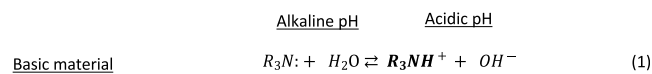
## INTRODUCTION

Wettability dictates the location of fluids in the reservoir and influences fluid flow during water injection. For an improved oil recovery (IOR) method, such as Smart Water or low-salinity water injection, relying on wettability alteration, the initial wettability of the reservoir is an important characteristic. To observe wettability alteration to more water-wet conditions, the reservoir must be of an initial less water-wet state.

The initial wettability of a crude oil–brine–rock system (COBR) is mainly dictated by the interactions between active polar organic components (POCs) and the rock minerals in presence of brine. POCs present in the crude oil adsorb onto the mineral surfaces of the rocks, creating the wetting conditions. Crude oils are complex mixtures consisting of thousands of different chemical compounds, including groups of saturates, aromatics, resins, and asphaltenes. The two latter groups contain the heavier components, of which the “NSO compounds”, those containing nitrogen (N), sulfur (S), and oxygen (O), are part. The crude oil components that have affinity for a charged mineral surface are the polar organic acids and bases, represented by O-containing carboxylic acids and N-containing aromatic compounds, respectively. Experimental work related to the basic content in crude oils from the

Norwegian continental shelf (NCS) has suggested that the bases are part of the maltenes, present in the resin fraction.<sup>1,2</sup> Additionally, a previous adsorption work by Mamonov et al.<sup>3</sup> has shown substantial adsorption of bases onto sandstone surfaces from a low-asphaltene crude oil.

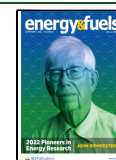
The charges of polar organic acids and bases in contact with water depend on the pH of the water phase according to eqs 1 and 2



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At an acidic pH ( $\text{pH} < 7$  at  $25\text{ }^\circ\text{C}$ ), the polar organic bases are positively charged, while at an increased alkalinity ( $\text{pH} > 7$  at  $25\text{ }^\circ\text{C}$ ), they are neutrally charged. In the case of the polar organic acids, they are protonated and have a neutral charge at a low pH and become deprotonated and negatively charged at an alkaline pH. Therefore, the wettability of a charged mineral surface is dependent on the formation brine pH. Nenningsland et al.<sup>2</sup> studied the interfacial activity of crude oils and found that it was at its highest around a pH of 5. Basic oil components dominated the interfacial reactivity at a pH below 5, when the protonated fraction is higher, as shown in eq 1, while non-bases were more dominant at a higher pH, when, for example, carboxylic acids are deprotonated, as shown in eq 2. The influence of pH on adsorption of polar organic material onto various clay mineral surfaces has been reported previously.<sup>4–7</sup>

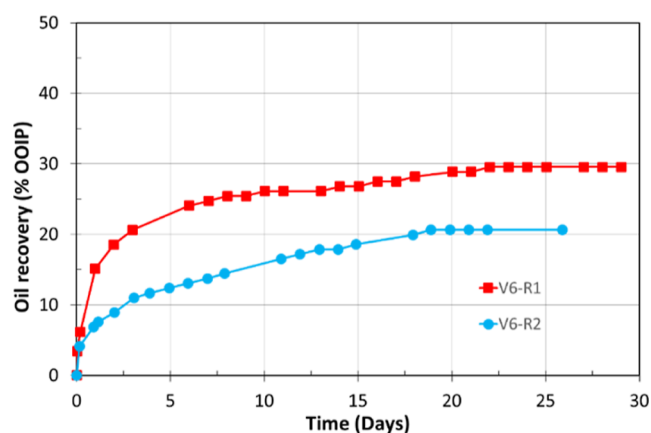
It is reported that polar organic acids, quantified by the acid number (AN) in crude oil, dictate the wettability in chalk,<sup>8,9</sup> a positively charged  $\text{CaCO}_3$  rock having an alkaline pH in the presence of brine. However, Fathi et al.<sup>10,11</sup> found that water-extractable acids from crude oil seemed to influence the chalk wettability more than the non-extractable acids. The water-extractable acids were also found to be more difficult to desorb in wettability alteration processes. Polar organic bases present in crude oil, quantified by the base number (BN), were found to only play a minor role for chalk wettability.<sup>12</sup> However, Puntervold et al.<sup>12</sup> also observed that the small model base, benzyl amine, influenced chalk wettability by co-adsorption with crude oil acids to the chalk surface. Interfacial activities of different crude oil naphthenic acids and bases at low and high molecular weights were studied by Bertheussen et al.<sup>13</sup> They found that the acids partitioned into the water phase to a higher degree than the bases and that the low-molecular-weight acid partitioned to a higher degree than the higher-molecular-weight acid, regardless of pH. The higher molecular weight base did not partition into the water phase at the pH range studied. Hence, individual components in the crude oil acid and base fractions are expected to have varying reactivity toward water and rock surfaces based on, for example, their size, steric hindrance, number of functional groups, and so on. Thus, it should be emphasized that there is not a direct link between the AN, BN, and molecular reactivity.

The adsorption preference of acids over bases has been identified and quantified for pure chalk.<sup>14</sup> In a silica-containing chalk, it was observed that although its preference for acidic components was maintained, increasing adsorption of basic components was observed.<sup>15</sup> This was attributed to the presence of negatively charged silica minerals, which preferably adsorbed neutrally charged basic molecules over negatively charged acidic molecules in an alkaline pH environment.

The presence and distribution of clay minerals in the pore network of sandstone rock can have a significant influence on the crude oil adsorption processes. Due to an unbalanced negative surface charge, clay minerals can adsorb/desorb charged crude oil molecules and react with the aqueous phase through ion exchange.<sup>16</sup> Clay minerals have a layered structure and a larger cation exchange capacity (CEC) and surface area than other sandstone minerals.<sup>17</sup> It has been shown that the adsorption of POCs onto quartz and the feldspar mineral albite was low,<sup>18</sup> both of which possess lower CEC and surface area than clay minerals.<sup>17</sup> Recently, Mamonov et al.<sup>3</sup> performed an adsorption study on an outcrop sandstone containing approximately 60 weight per cent (wt %) quartz, ~30 wt %

albite feldspar, and ~9 wt % of illite clay mineral. It was shown that the negatively charged silicate surfaces had a stronger affinity to positively charged basic POCs, while adsorbing less negatively charged carboxylates (dissociated carboxylic acids).<sup>3</sup> The adsorption was quantified, and only about 30% of the crude oil bases adsorbed to the rock surface, while only ~10% of the acids were found to adsorb. A spontaneous imbibition (SI) test performed after the crude oil flooding and adsorption proved that the core had become mixed-wet after the adsorption of polar organic bases from the crude oil.

In many laboratories, to establish the initial core wettability, the core sample is flooded with a crude oil to displace the formation water (FW) to initial water saturation. In this process, many and inconsistent pore volumes (PVs) of crude oil can be used depending on the rock properties. Recently, Aslanidis et al.<sup>19</sup> investigated the wettability changes of reservoir sandstone material after crude oil exposure in several core restorations using mild solvents (kerosene/heptane). SI tests were performed to evaluate the level of wettability after each restoration step. The results in Figure 1 demonstrate the



**Figure 1.** Effect of 11 PVs of crude oil exposure on core wettability in two core restorations using mild solvents (kerosene/heptane). Modified with permission from Aslanidis et al.<sup>19</sup> Copyright 2022 Elsevier.

effect of 11 PVs of crude oil exposure in each restoration process on core wettability. The apparent decrease in the rate of imbibition and the difference in ultimate oil recovery of 10% of the original oil in place (OOIP) between core restorations indicate that the exposure of uncontrolled amounts of crude oil into a core could have a detrimental effect on wettability. Thus, an optimized amount of crude oil should be injected into the core to establish the initial oil saturation and representative wettability, and more work is needed to further understand the process of initial crude oil adsorption in sandstone rocks.

The main goal of this experimental work was to study the influence of the sandstone mineralogical composition on the adsorption of POCs and the subsequent change in wettability. Two sandstone rock materials of different mineralogical compositions and origins (reservoir and outcrop) were used in adsorption tests. The Varg reservoir core used had a similar mineralogy to the outcrop used by Mamonov et al.,<sup>3</sup> while the Leopard outcrop core had a low clay content and consisted mainly of the quartz mineral. The effect of POC adsorption on wettability was determined by comparing the obtained SI results to those from a water-wet reference case. The research questions asked were the following: (1) Does reservoir

Table 1. Mineralogical Composition

sandstone	quartz	mineral composition (wt %)							sum
		feldspars		clays			carbonate	others	
		albite	microcline	kaolinite	illite	chlorite			
V	62.3	8.4	4.5	1.1	15.4	2.5	5.0	0.8	100
L	93.9	0.5		2.5			0.1	3	100

sandstone with a similar mineralogy behave the same as the outcrop sandstone regarding POC adsorption and effect on wettability? (2) How does an outcrop sandstone of low clay/feldspar content adsorb POCs compared to the other two rock materials?

## EXPERIMENTAL SECTION

**Core Material.** Leopard outcrop sandstone, abbreviated L, and reservoir sandstone from the Varg field on the NCS, abbreviated V, were used in the experimental work. The core material was represented by well-consolidated samples. No change in permeability or particle migration was observed in any of the experimental stages. Mineralogical compositions obtained by X-ray diffraction (XRD) analysis are presented in Table 1. The physical properties of the cores are presented in Table 2.

Table 2. Core Properties

core	diameter (cm)	length (cm)	PV (mL)	porosity (%)	permeability (mD)	BET (m <sup>2</sup> /g)
V9S2	3.8	7.73	18.7	21	11	3
L1	3.8	6.27	14	19.6	220	2

**Brines.** Synthetic formation water (FW20Ca) containing 20 mM Ca<sup>2+</sup> in a NaCl brine with a salinity of 50,000 ppm was prepared in the laboratory by dissolving reagent-grade salts in deionized water, followed by filtration through a Millipore 0.22 μm filter. FW20Ca was used for establishing the initial water saturation,  $S_{wi}$ , before exposure to crude oil and as an imbibing brine in SI tests. Brine composition and properties are given in Table 3.

Table 3. Brine Composition and Properties

brine	ion composition, (mM)			salinity, ppm	bulk pH
	Na <sup>+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>		
FW20Ca	817.6	20	857.6	50 000	6.3

**Crude Oil.** A modified crude oil, oil A, with a similar content of acidic and basic POCs was prepared for the adsorption tests by mixing three low-asphaltene crude oils of known AN and BN in certain proportions so that the resulting AN and BN values were close to 0.2 mg KOH/g. The target value was chosen to be able to detect the adsorbed POC during core flooding with minimal uncertainty in the chemical analyses. As a result of the modification, oil A contained similar amounts of acidic and basic POCs, which are naturally present in low-asphaltene crude oils and exhibit typical surface reactivity. The properties of the modified crude oil are given in Table 4.

**Core Cleaning.** The reservoir core V9S2 was rigorously cleaned to bring the initial wettability conditions close to the water-wet state.

Table 4. Crude Oil Properties

crude oil	density at 20 °C (g/cm <sup>3</sup> )	asphaltene (wt %)	AN	BN	absolute error
			mg KOH/g		
A	0.8	≪1	0.23	0.23	±0.02

Crude oil was displaced by toluene until a clear effluent was obtained, and then, toluene was displaced by methanol. The cleaning cycle was completed by flooding 1000 ppm NaCl brine to remove any easily dissolvable salts while at the same time avoiding potential clay swelling, although the latter is not expected due to the absence of swelling clays such as smectite and montmorillonite. The outcrop core L1 has not been previously exposed to crude oil and thus was only cleaned by 1000 ppm NaCl brine injection. After cleaning, both cores were dried to a constant weight at 90 °C.

**Initial Water Saturation.** Prior to crude oil exposure, the cleaned and dried cores were flooded with five times diluted FW20Ca to measure the absolute permeability and establish the initial water saturation ( $S_{wi}$ ) using the desiccator method introduced by Springer et al.<sup>20</sup> The saturated core samples were placed in a desiccator for water evaporation, and the weight of the cores was monitored until it reached the predetermined, calculated value. The dilution rate of the FW was chosen to achieve the initial composition of FW20Ca at  $S_{wi} \sim 20\%$  after water evaporation. Upon reaching the desired weight, the cores were placed in a closed container for 3 days for equilibration.

**Crude Oil Adsorption Test.** After  $S_{wi}$  had been established, the core was mounted in a Hassler core holder for crude oil exposure in the adsorption test. The experimental setup is shown in Figure 2. A

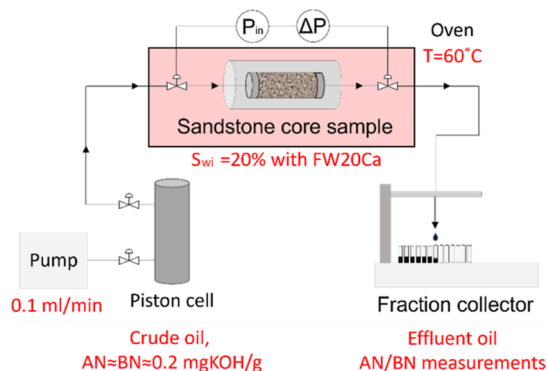


Figure 2. Crude oil flooding setup.

confining pressure of 20 bar, a back pressure of 10 bar, and a temperature of 60 °C were used. Oil A was injected into the core at a rate of 0.1 mL/min. The produced crude oil was collected using a fraction collector, and the AN and BN were measured by potentiometric titration. The adsorption of polar organic acids and bases was evaluated by plotting effluent AN and BN values against the PV injected.

**Acid and Base Number Measurements.** Potentiometric titration using a Mettler Toledo T50 auto-titrator was performed to measure the AN and BN of the influent and effluent oil samples. The methods used were developed by Fan and Buckley<sup>21</sup> and are modified versions of the standard methods ASTM D664 and ASTM D2896 for AN and BN titration, respectively.<sup>22,23</sup> The reproducibility values of both AN and BN measurements were ±0.02 mg KOH/g.

**Oil Recovery by Spontaneous Imbibition.** For determining the wettability state of the core, SI experiments were performed. After the cores had been exposed to crude oil, they were placed in an Amott cell and submerged in FW20Ca at a test temperature of 60 °C. The oil produced by brine imbibition was collected in a graded burette and monitored over time. No aging prior to the SI test was performed. SI of a completely water-wet sample was performed using *n*-heptane

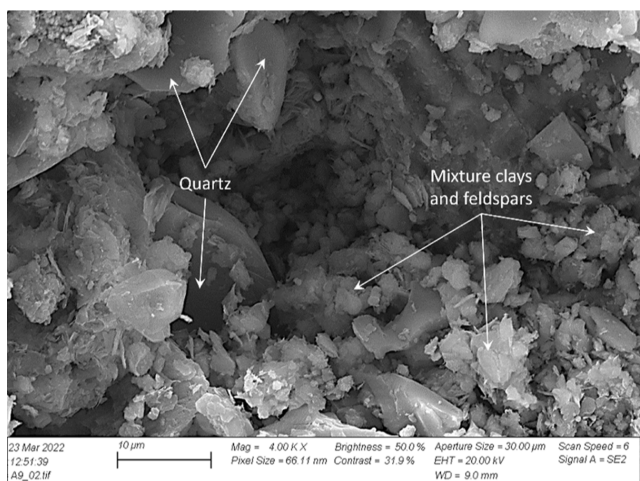


(C7) as the oil phase and FW20Ca as the imbibing brine. The tests were performed on cleaned cores with an established  $S_{wi} = 20\%$  and at a test temperature of  $60\text{ }^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

The work aimed to investigate relationships between the mineralogical composition of the sandstone material, its origin, and the adsorption preference for the organic crude oil components. For adsorption studies, two sandstone cores of different origins (reservoir and outcrop) and with significantly different quantitative and qualitative mineralogical compositions were used. The influence of POC adsorption on capillary forces and wettability was determined by comparing SI curves before and after exposure to crude oil. Finally, the results were compared with previously published data from POC adsorption on another outcrop sandstone.<sup>15</sup>

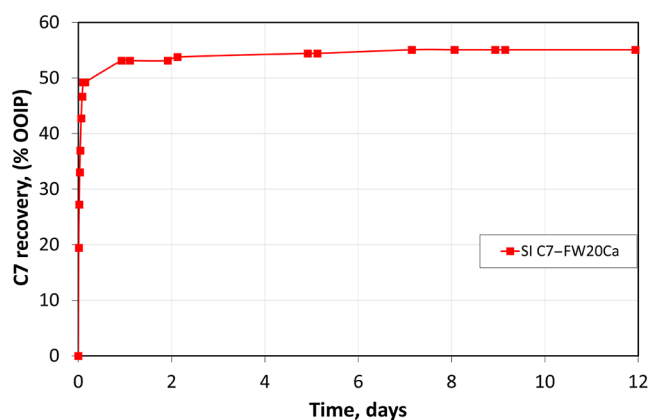
**Adsorption of Crude Oil Components on Reservoir Sandstone and Its Impact on Wettability.** To obtain detailed mineralogical information, a rock sample from the V9S2 core was studied using scanning electron microscopy (SEM) combined with energy-dispersive spectroscopy (EDS). An SEM image of the material is shown in Figure 3.



**Figure 3.** SEM image of the reservoir V-sandstone at a 4000 times magnification.

Approximate identification of minerals in the SEM image was carried out by comparative analysis of the EDS and XRD data. As can be seen from Figure 3, the mixture of reactive sandstone minerals (clays and feldspars) covers the quartz minerals and hence defines a significant part of the rock–fluid contact surfaces in the pore structure. With this distribution, reactive minerals can serve as a surface for adsorption/desorption of polar crude oil components, as well as react with the surrounding water phase through ion exchange.

V-sandstone reservoir cores obtained from the Varg field on the NCS have previously been used in wettability studies that indicated that the reservoir rock was initially slightly water-wet.<sup>19</sup> Therefore, prior to POC adsorption studies, the reservoir core V9S2 was cleaned with toluene and methanol to bring the initial rock wetting state closer to strongly water-wet conditions. The initial wetting was then confirmed by a SI test using *n*-heptane (C7) as the oil phase and  $S_{wi}$  of 20% FW20Ca. The SI test was conducted at  $60\text{ }^{\circ}\text{C}$  with FW20Ca as the imbibing brine. The results are shown in Figure 4. A strongly water-wet behavior was indicated by a rapid initial C7



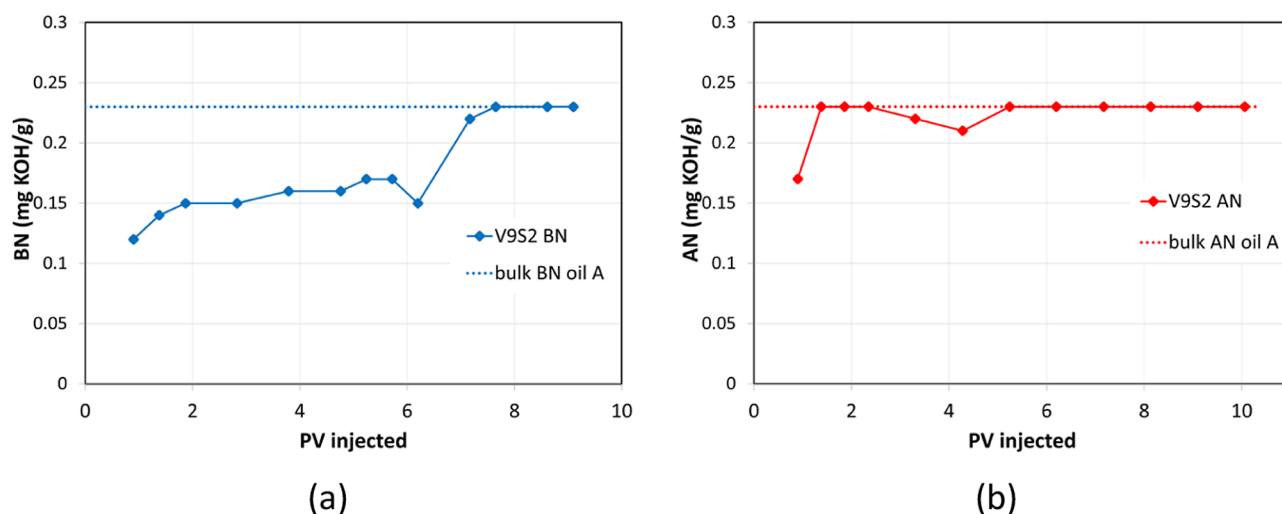
**Figure 4.** Oil recovery test performed on a strongly water-wet core V9S2 by SI with FW20Ca at  $60\text{ }^{\circ}\text{C}$ . Prior to the test, the core was cleaned with toluene and methanol and restored with  $S_{wi} = 20\%$  FW20Ca and mineral oil (C7).

recovery of 50% of OOIP after 2 h with an ultimate value of 54% of OOIP reached after  $\sim 7$  days. The steep oil recovery profile corresponds to strong capillary forces that allow for rapid water imbibition and displacement of the oil phase. The results of this SI test were further used as a reference case for the strongly water-wet behavior of the V9S2 core.

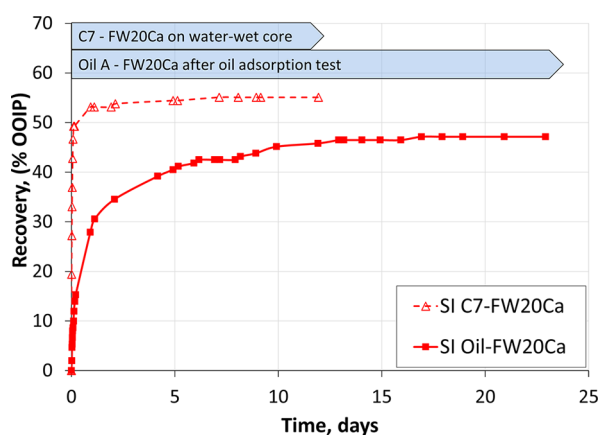
After the SI test, the V9S2 core was dried and restored with  $S_{wi} = 20\%$  FW20Ca. Then, the crude oil adsorption test was performed by flooding oil A with a similar content of acidic and basic POCs through the core at a rate of 0.1 mL/min at  $60\text{ }^{\circ}\text{C}$ . Knowing the influent AN and BN values (0.23 mg KOH/g), the adsorption of POCs was determined by monitoring the AN and BN in the produced oil samples, measured by potentiometric titration. The BN and AN of effluent and influent (bulk) oil A samples are presented in Figure 5.

Instant adsorption of both acidic and basic POCs was observed at the first contact of oil A with the brine–rock system and resulted in the largest reduction in the effluent AN (0.17 mg KOH/g) and BN (0.12 mg KOH/g) compared to their bulk values (0.23 mg KOH/g). Further flooding of oil A through the V9S2 core led to extensive adsorption of basic polar components, which continued throughout  $\sim 6$  PVs injected, with subsequent achievement of the adsorption equilibrium, that is,  $BN_{\text{effluent}} \approx BN_{\text{influent}}$  (Figure 5a). The acidic POC, on the other hand, did not show a high affinity for V-sandstone mineral surfaces, confirmed by the absence of continuous adsorption and the rapid achievement of adsorption equilibrium, as shown in Figure 5b.

To determine the effect of POC adsorption on wettability, the V9S2 core was placed for the SI test after the exposure to 10 PVs of oil A without additional aging. The SI test was performed at  $60\text{ }^{\circ}\text{C}$  using FW20Ca as the imbibing brine. The results of the SI test are presented in comparison with the reference case of the strongly water-wet behavior of the V9S2 core, as shown in Figure 6. A comparison of the SI test results shows a significant reduction in water wetness of the core after exposure to crude oil. The more gradual production of crude oil A, together with the longer time needed to reach the ultimate oil recovery plateau (47% of OOIP achieved in 23 days), indicates that the observed adsorption of the basic POC significantly reduced the capillary forces. Moreover, the instant effect of POC adsorption on wettability is observed despite the absence of an additional aging process prior to the SI test.



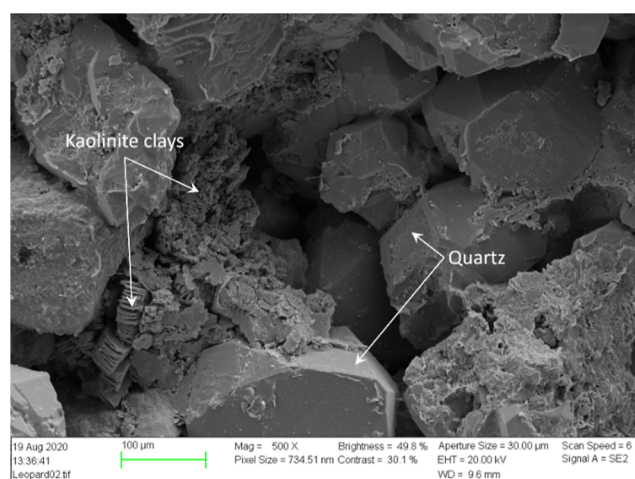
**Figure 5.** Adsorption of basic and acidic POCs onto reservoir V-sandstone during crude oil flooding at 60 °C. 10 PVs of oil A (AN = BN = 0.23 mg KOH/g) were injected into core V9S2 with  $S_{wi} = 20\%$  FW20Ca and at a rate of 0.1 mL/min. Produced oil samples were analyzed for (a) BN and (b) AN and plotted against the PV of crude oil injected.



**Figure 6.** Comparison between SI oil recovery tests performed on the strongly water-wet reservoir core V9S2 and on the same core after exposure to 10 PVs of oil A. Both tests were carried at 60 °C using FW20Ca as an imbibing brine.

**Adsorption of Crude Oil Components on Outcrop Sandstone and Its Impact on Wettability.** The V-sandstone reservoir core material contained a relatively large amount of reactive minerals, namely,  $\sim 8$  wt % albite feldspars and  $\sim 15$  wt % illite clay minerals, distributed as a mixture in the rock matrix, as shown in Table 2 and Figure 3. As the opposite case, an outcrop L-sandstone core with a significantly smaller amount of clay and feldspar minerals was selected for identical crude oil adsorption studies. The L-sandstone outcrop core was mainly composed of  $\sim 94$  wt % quartz minerals, with a small content,  $\sim 2.5$  wt %, of kaolinite clay and  $\sim 0.5$  wt % of albite feldspar, as shown in Table 2. The distribution of minerals in the pore structure of the rock was studied using SEM/EDS/XRD analyses and is presented in Figure 7. Despite the relatively small amount of clay minerals quantified by XRD analysis, SEM/EDS results show that kaolinite clays occupy a certain part of the pore space and thus can react with the contacting oil phase, hence adsorbing the POC.

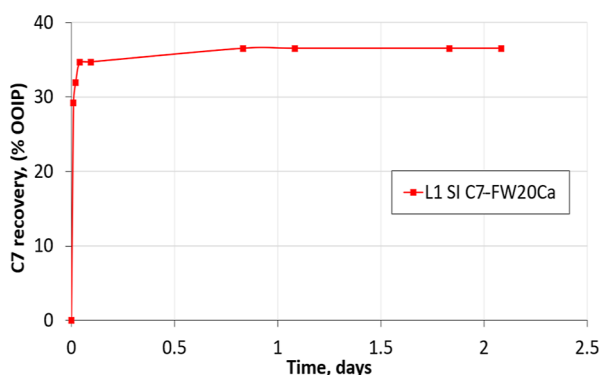
The outcrop core L1 had not been previously exposed to crude oil and was therefore in a completely water-wet state. To



**Figure 7.** SEM image of the outcrop L-sandstone material with a 500 times magnification.

assess the action of capillary forces, core L1 was tested by SI using *n*-heptane (C7) as the oil phase and  $S_{wi} = 23\%$  FW20Ca. The SI test was conducted at 60 °C with FW20Ca as the imbibing brine. The results are shown in Figure 8. During the first few hours of the SI test, the FW20Ca brine was rapidly imbibing, resulting in the oil recovery reaching 35% of OOIP. After 2 days, the system reached an oil recovery plateau of 37% of OOIP, confirming a strongly water-wet behavior. The results of this SI test were further used to assess the change in wettability after crude oil adsorption.

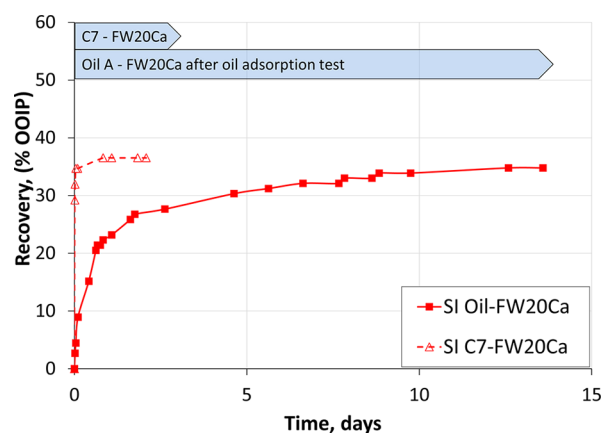
After the SI test, the L1 core was dried and again restored with  $S_{wi} = 21\%$  FW20Ca. The ability of L-sandstone mineral surfaces to adsorb POCs was then examined by performing an oil exposure test at 60 °C and at an injection rate of 0.1 mL/min. Produced oil samples were analyzed by potentiometric titration to identify any deviations in the effluent AN and BN compared to the influent bulk values. The results are presented in Figure 9. During the first 4 PVs injected, the eluted oil samples had a BN of 0.25 mg KOH/g, which is identical to the influent BN values and indicates the absence of retained basic components, as shown in Figure 9a. Further injection of oil A



**Figure 8.** SI test on the completely water-wet outcrop sandstone core L1 at  $T = 60\text{ }^{\circ}\text{C}$ . The core with an established  $S_{wi} = 23\%$  was saturated with mineral oil (C7) and spontaneously imbibed with FW20Ca until a recovery plateau was reached.

showed a slight reduction of the effluent BNs compared to bulk values; however, a pronounced BN adsorption trend, similar to that of the V9S2 reservoir core, was not observed. Acidic components seemingly had higher affinity toward L-sandstone mineral surfaces, which was reflected in the reduced effluent ANs during the first 5 PVs injected, followed by the achievement of the adsorption equilibrium, as shown in Figure 9b. Nevertheless, no significant and continued adsorption of acidic components was observed, and with the uncertainty of the chemical analysis of  $\pm 0.02\text{ mg KOH/g}$  in mind, it was concluded that the overall adsorption of POCs onto L-sandstone was rather low.

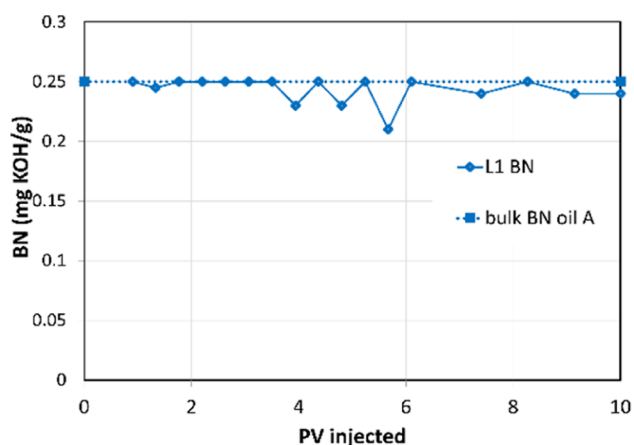
Upon completion of the oil adsorption test, the L1 core sample was directly placed for an SI experiment without additional aging. The SI test was conducted at  $60\text{ }^{\circ}\text{C}$  using FW20Ca as the imbibing brine. Comparison between SI experiments performed on a completely water-wet core L1 and after crude oil adsorption is presented in Figure 10. The results show a significant reduction in the speed of imbibition after oil A exposure compared to that in the completely water-wet reference case. A recovery plateau of 34% of OOIP (oil A) was reached after 13 days, while the initial wettability test with mineral oil resulted in a recovery plateau of 37% of OOIP



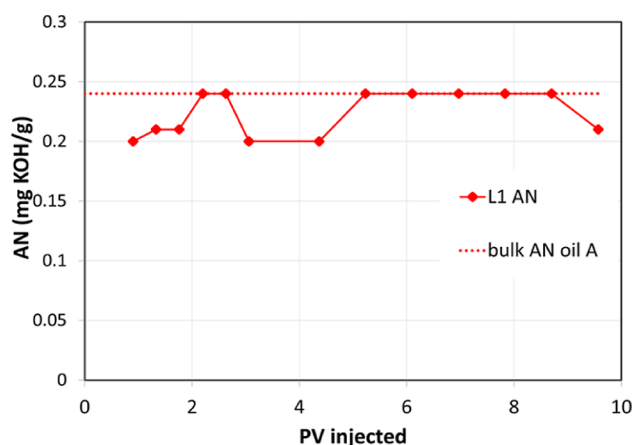
**Figure 10.** Comparison between SI oil recovery tests performed on a completely water-wet outcrop core L1 and on the same core after exposure to 10 PVs of oil A. Both tests were carried out at  $60\text{ }^{\circ}\text{C}$  using FW20Ca as the imbibing brine.

(C7) after only 1 day. It is important to note that the primary indicator of the wettability change is the imbibition rate and not the ultimate oil recovery as this will also depend on the oil/brine interfacial tension (IFT). Thus, a comparison of the SI test results shows that despite the absence of a clear POC adsorption trend on the L-sandstone material (Figure 9), the exposure to crude oil distinctly affected the capillary forces required to mobilize the oil.

A direct comparison of SI results for the two sandstone cores shown in Figures 6 and 10 would be incorrect due to, for example, differences in the pore structure, mineralogical composition, and amount of adsorbed crude oil components. However, ultimate recovery was used as a proxy for the core wettability before and after the adsorption test. The significant difference between crude oil and C7 ultimate recovery in V-sandstone in Figure 6 indicates a less water-wet state achieved by crude oil flooding. On the contrary, with a low adsorption of crude oil acids and bases onto L-sandstone, it is expected that the resulting wettability state will be close to a completely water-wet scenario, as observed by the small difference in the ultimate recovery of crude oil and C7 in Figure 10.



(a)



(b)

**Figure 9.** Adsorption of acidic and basic POCs onto L-sandstone during crude oil flooding. 10 PVs of modified crude oil ( $AN \approx BN \approx 0.25\text{ mg KOH/g}$ ) were injected into core L1 with  $S_{wi} = 21\%$  at  $60\text{ }^{\circ}\text{C}$  and at a rate of  $0.1\text{ mL/min}$ . Effluent oil samples were analyzed for (a) BN and (b) AN and plotted against PVs of crude oil injected.



Table 5. Quantitative Assessment of POC Adsorption onto Various Sandstone Material during Crude Oil Flooding

sandstone material	origin	dominant clay type	BET, m <sup>2</sup> /g	AN <sub>ads</sub>	BN <sub>ads</sub>	AN <sub>ads</sub> + BN <sub>ads</sub>	BN <sub>ads</sub> /AN <sub>ads</sub>
				PV*mg KOH/g			
V	reservoir	Illite–15.4 wt %	3	0.04	0.45	0.49	10.3
L	outcrop	Kaolinite–2.5 wt %	2	0.12	0.06	0.18	0.5
T	outcrop	Illite–8.4 wt %	1.8	0.10	0.66	0.76	6.5

Table 6. Percentage of Adsorbed Acidic and Basic POCs during Various Crude Oil Flooding Tests

sandstone material	modified oil used for adsorption studies	asphaltene (wt %)	AN	BN	total PVs injected	% adsorbed acidic POC	% adsorbed basic POC
			mg KOH/g				
V	oil A	<1	0.23	0.23	10	1.9	21.3
L	oil A	<1	0.24	0.25	10	5.5	2.4
T	oil T	<1	0.17	0.23	10	6.6	31.9

**Factors Affecting Adsorption of Crude Oil Components and Wettability.** The main factors affecting the intensity of POC adsorption in the COBR system are the presence and distribution of reactive minerals in the rock structure, the chemical composition of crude oil, salinity and pH of FW, and temperature. The above parametric studies were focused on determining the adsorption propensity for acidic and basic POCs onto V- and L-sandstone materials with significant differences in the mineralogical composition. The trapezoidal method was then used to quantify the amount of adsorbed acidic and basic organic components during crude oil injection. The principle of this method is based on the calculation of the area between the influent and effluent AN or BN curves using numerical integration. An example of calculating the adsorption area for the AN is shown in 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 PVs injected for the eluted crude oil to reach  $AN_i$  (influent AN);  $PV_x$  and  $PV_{x+1}$  are the injected pore volumes in integration steps  $x$  and  $x + 1$ , respectively; and  $AN_x$  and  $AN_{x+1}$  are the values of the AN in the eluted oil after injecting the pore volumes  $PV_x$  and  $PV_{x+1}$ , respectively.

Quantification of adsorbed acidic and basic POCs was performed for V- and L-sandstones and compared with previously published results for T-sandstone material, for which similar adsorption studies were carried out.<sup>15</sup> The results are shown in Table 5. The adsorption capacity of the studied rocks, determined by the total adsorption area ( $AN_{ads} + BN_{ads}$ ), showed that L-sandstone material retained 3 times less crude oil components compared to V-sandstone and 4 times less compared to T-sandstone.<sup>15</sup> This can be explained by the type of clay minerals (kaolinite) present in the composition of the L-rock and their low content (2.5 wt %). Most of the accessible surfaces in L-sandstone are composed of quartz minerals, which generally have a low POC adsorption potential, as confirmed by previously published static adsorption studies.<sup>24</sup> Similar studies have also shown that kaolinite clays only have half the adsorption capacity compared to illite clays in static tests.<sup>6</sup> V- and T-sandstones, which are similar in mineralogical composition, have shown similar adsorption trends with a predominant affinity of basic components over acidic components,  $BN_{ads}/AN_{ads} = 10.3$  and 6.5, respectively.

The highest  $BN_{ads}/AN_{ads}$  ratio and adsorption capacity ( $AN_{ads} + BN_{ads}$ ) were observed for the outcrop T-sandstone, despite the lower BET surface area and illite clay content than that of V-sandstone. This could be the result of using a different modified crude oil (oil T) for the adsorption studies on T-sandstone. Despite the identical  $BN = 0.23$  mg KOH/g in oil A and oil T, the basic components originated from different crude oils. POCs of different origins can also have different adsorption affinities on the same mineral surfaces, which is difficult to determine by potentiometric titration since this analytical method only gives a quantitative measure of the adsorbed organic material. The influence of oil type on adsorption and the identification of the most reactive components with high affinity toward mineral surfaces are topics for further research.

To estimate the fraction of polar components adsorbed during oil injection, mass balance calculations between the influent and effluent AN and BN were carried out for all the studied rocks. The resulting percentages of adsorbed acidic and basic POCs during crude oil flooding tests on V-, L-, and T-sandstone materials, along with the modified oil properties, are presented in Table 6. The results show that with a more pronounced adsorption of basic components on V- and T-sandstones, the fraction of POCs retained in the core does not exceed ~20–30%. This indicates that only the most reactive polar molecules are adsorbed, while the rest of the POCs remain in the oil phase. Compared to other studied rocks, the mineral surfaces of L-sandstone material retained a negligible amount of POCs with over 90% of acids and bases passing through the core without adsorbing.

Despite the difference in mineralogical composition and the corresponding difference in POC adsorption capacity, all studied sandstones showed reduced water-wetness after exposure to crude oil. The change in wettability toward the less water-wet state is associated with a decrease in capillary forces as a result of POC adsorption, which was mainly reflected in a slower and more gradual oil recovery in the subsequent SI process.

## CONCLUSIONS

The influence of sandstone mineralogical composition on the adsorption of polar crude oil components has been studied in a dynamic oil flooding process. A COBR system was chosen with (a) modified crude oil containing similar amounts of acids and bases,  $AN \approx BN$ , (b) FW of medium salinity containing divalent calcium ions ( $Ca^{2+}$ ), and (c) reservoir and outcrop

sandstone core materials with different mineralogical compositions. With the crude oil, rock material, and brines used in this study, the following conclusions could be drawn

1. The different mineralogical compositions of the studied sandstones had a significant effect on the intensity of POC adsorption. The outcrop material containing only a limited amount of clay minerals showed low adsorption capacity and no apparent adsorption affinity for acidic or basic components. Conversely, the reservoir sandstone material containing a larger amount of illite clay minerals showed a clear tendency to adsorb basic POCs.
2. A comparison between reservoir and outcrop sandstones with similar mineralogical compositions showed similar POC adsorption trends and a predominant affinity for bases over acids.
3. All studied rock materials showed a clear deviation from the initial strongly water-wet behavior after exposure to crude oil.
4. The amount of adsorbed POCs showed a dependence on the number of PVs of the injected crude oil. Thus, excessive exposure to crude oil during the core restoration process can significantly affect the wettability of the core and potentially lead to misinterpretation of subsequent oil recovery results.

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### Notes

The authors declare no competing financial interest.

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