

PRESERVING INITIAL CORE WETTABILITY DURING CORE RESTORATION OF CARBONATE CORES

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ABSTRACT

A correct restoration of carbonate cores is very important because the wettability will influence the results of relative permeability, capillary pressure and oil recovery tests. The acidic polar components in the crude oil are the main wetting parameter for carbonates, and will dictate the wettability of the rock surface. This work aims to determine the suitability of using mild core cleaning with kerosene and heptane during core restoration to preserve the initial reservoir wettability in the reservoir cores during core restoration. Initially a water-wet outcrop chalk core with S_{wi} was flooded with crude oil. Effluent samples of produced oil were collected and the acid number (AN) was measured as a function of pore volume injected. The results showed that the Acidic polar components in the crude oil were adsorbed onto the rock surface, and gradually an equilibrium between the AN in the injected oil and AN in the effluent oil was achieved. A wettability test confirmed that the water-wetness of the core was drastically reduced. The chalk core was then put for restoration. First, the core was mildly cleaned by flooding with kerosene to displace the crude oil, followed by heptane for removal of kerosene. During the second crude oil saturation and flooding, the adsorption of acidic organic polar components onto the rock surface was drastically reduced, confirming that the rock surface had maintained approximately 3/4ths of the initially adsorbed acidic polar components during the mild core cleaning process.

INTRODUCTION

In carbonate reservoirs, the success of an oil recovery is primarily linked to the initial wetting conditions of the rock. In an oil reservoir, the initial wettability is established by a chemical equilibrium between oil, brine and rock over millions of years of interaction. The properties of the initial wetting state will decide physical parameters such as the capillary pressure, the relative permeabilities and fluid distribution. The AN, acid number, is a measure of the content of surface-active components, and is regarded as one of the most important parameters dictating the initial wetting of a carbonate rock. The AN is related to the amount of carboxylic groups that are present in the oil. It may be measured and quantified by titration and has the unit mg KOH/g oil. When analysing reservoir core material it is essential that the initial wetting is preserved, so that the wettability of the core may be investigated in the most representable state. Therefore, in a laboratory, it is crucial that steps are taken during preparation to preserve the initial core

wettability. Core material is often cleaned to a completely water-wet state and the core is aged with the formation water and reservoir oil to build up the initial conditions [1]. In practice, it is common to clean core material with Toluene followed by methanol. Toluene should remove hydrocarbons including asphaltenes and adsorbed polar components. Methanol displaces both water and toluene. The questions asked in this paper are: Will a more representative wettability be achieved by using mild cleaning, and can we perform wettability tests to validate that polar components have been preserved on the surface?

The wettability will be determined by a chromatographic wettability test at S_{or} (residual oil saturation) [2]. In this chromatographic wettability test, a separation of ions will only take place on the water-wet areas of the pore surface. The area between a non-adsorbing tracer and sulphate is proportional to the water-wet area. The ratio of this area against the area of a completely water-wet core will determine a wettability index in chalk, ranging from 0-1.

EXPERIMENTAL

Materials

Outcrop chalk from Stvens Klint, Copenhagen, Denmark, was used as model rock. The chalk has high porosity (45-50%) and low permeability (2-3 mD) and is relatively homogeneous. The outcrop chalk core consists of 98% pure biogenic CaCO_3 and is considered similar to North Sea chalk reservoirs. The properties of the core are given in Table 1.

Brine Composition

Synthetic formation water, VB0S, modelled on the Valhall field, was the brine used as the formation water in the experiments. SW0T and SW $\frac{1}{2}$ T are brines used for the chromatographic wettability test. Brine compositions are reported in Table 2.

Oil Properties

A crude oil was diluted with heptane in the ratio of 60/40 respectively. The oil was centrifuged and filtered through a 5 μm Millipore filter. An acid number (AN) of 1.7 mgKOH/g oil was measured. A part of this oil was treated with silica gel to remove surface active polar components and thereafter filtered, giving an AN of ~0.0 mgKOH/g oil.

A mixture of treated and untreated oil was prepared at a specific ratio and analysed. The designed oil, RES40-0.35, had an AN of 0.35 mg KOH/g and a base number (BN) of 0.25mg KOH/g. The oil properties are given in Table 3.

Analyses Of Acid And Base Numbers In Crude Oil Samples

The acid and base numbers, AN and BN, of the crude oil samples were analysed by potentiometric titration. The methods used are modified versions of ASTM 665 and

ASTM 2898 [3]. The reproducibility of the acid number titration tests is presented in Table 4.

Preparation Of Chalk Core

The cores were prepared following a procedure set by Puntervold et al.[4]. All cores used were initially flooded with 5 pore volumes (PV) of de-ionized water (DI) for a removal of easily dissolvable salts and sulphate. The cores were dried to a constant weight at 90 °C.

Establishing Initial Water Saturation

The initial water saturation, S_{wi} , was established using the desiccator technique [5]. After the core had achieved a S_{wi} of 10%, the core was equilibrated in a sealed container for 4 days to allow the even distribution of salts within the core.

Oil Saturation And Establishing Core Wetting

The chalk core with $S_{wi} = 0.1$ was mounted in a Hassler core holder with an overburden pressure of 20 bar and with a back pressure of 6 bar. The core was oil flooded at 50 °C at a rate of 0.1 ml/min. Effluent samples of produced oil were collected in sealed vials using a fraction-collector.

The core was flooded with oil until the AN in the effluent samples reached the same concentration as initially present in the oil, AN = 0.35 mg KOH/g. A total of 15 PV of oil was flooded through the core. By plotting the AN against PV of oil injected, the adsorption of acidic oil components onto the rock surface can be expressed.

Core Aging

Once the core had been flooded with 15 PV of crude oil, it was wrapped in Teflon tape. The wrapped core was placed in an aging cell surrounded by oil, and aged at 50 °C for two weeks to achieve a homogeneous core wetting.

Core Wettability By Chromatographic Wettability Test

The chromatographic wettability test was designed by Strand et al.[2] and is based on the chromatographic separation between sulphate and a non-adsorbing tracer. The test is performed at S_{or} at ambient temperature. The chromatographic separation of the sulphate and the tracer is proportional to the water-wet area of the chalk core surface.

The core is flooded with the brine SW0T. SW0T is depleted in sulphate and is used to displace the remaining fluid in the core to bring the sample to S_{or} , as well as to establish a stable flow. Then the SW $\frac{1}{2}$ T brine, containing SCN^- and SO_4^{2-} , is injected and effluent samples are collected into sealed vials. SO_4^{2-} ions have an affinity towards the water-wet chalk surface, and the chromatographic separation area, A_{wet} , between SCN^- and SO_4^{2-} eluent curves gives a relative measure of the water-wet rock surface. Compared with the area determined from a completely water-wet chalk core, A_{ww} , the wettability index I_{CW} describing the water-wet fraction of the chalk surface can be calculated according to equation 1 below.

$$I_{CW} = \frac{A_{wet}}{A_{WW}} \quad (1)$$

Ionic Concentration Analyses

The ionic concentrations of the effluent samples from the chromatographic wettability test were analysed using an ion chromatograph, ICS 3000, delivered by Dionex Corporation, USA. The samples were diluted 1:200 times prior to the analysis. The anionic concentrations in the effluent were calculated using an external standard method.

Core Restoration

After the first polar component adsorption test, the core was restored. A mild core cleaning procedure with low aromatic kerosene and heptane was performed to remove the residual oil. The first step of the procedure is a miscible fluid displacement using kerosene. When the core is clean and the effluent is clear or consistent in colour, the second step of the procedure is to displace the kerosene with n-heptane. As the final step, the core was flooded with DI water to remove heptane and easily dissolvable salts. The water and heptane was afterwards removed by evaporation in a standard heating chamber, at 90°C, until constant weight. The procedure was then repeated, establishment of initial water saturation and core saturation with oil, ageing, water flooding to S_{or} , and wettability determination.

EXPERIMENTAL RESULTS

A correct initial wetting condition is crucial for achieving reliable experimental results from core analyses. The initial wetting conditions in the core dictates capillary pressure measurements and are very important for relative permeability calculations which is an important parameter in most reservoir modelling and simulations. Oil recovery tests and “Smart Water” effects are also dictated by the initial wetting properties of the restored cores. An optimized core restoration laboratory procedure that preserves the initial reservoir wetting during core cleaning is of great interest for the industry.

In this work, a water-wet outcrop chalk core was used. The effect of core cleaning and core restorations on rock wettability is discussed.

Initial Wetting of the Outcrop Chalk Core

The outcrop chalk cores used in these experiments are initially completely water-wet. Cores saturated with oils without polar components, like mineral oils, will not change the initial wettability. Restored cores imbibe water very rapidly giving oil recoveries above 70 % OOIP. The chromatographic wettability test was performed at ambient temperature on an outcrop core at 100% initial water saturation, Figure 1. The core details are presented under reference core on Table 1. The results show a large separation between the non-adsorbing tracer thiocyanate and sulphate which adsorbs to water-wet chalk surfaces. The calculated area between the tracer and sulphate eluent curves is $A_{ww} = 0.254$, represents a very water-wet rock surface area.

Initial Adsorption of Carboxylic Material Onto Water-Wet Chalk Surface

The chalk core used was initially very water-wet. After establishing $S_{wi} = 0.1$, the core was mounted in a core holder with a confining pressure of 20 bar and with a back pressure of 6 bar. The core was flooded at 50 °C with the oil containing polar components with an AN=0.35 mg KOH/g oil. Effluent samples of the produced oil were collected and analysed for the content of acidic polar components, AN. Figure 2 shows the AN in the effluent with increasing PV injected.

The results confirm adsorption of polar acidic components towards the pore surface in the chalk core. The initial measurements, the first 2 PV, show that the effluent oil has a very low AN, Figure 2. This shows that the acidic polar material in the oil adsorbs onto the surface of the chalk core, which results in an effluent oil with minimal acidic components. As more oil is flooded into the chalk core the surface becomes more saturated with acidic polar material. There is less ability for the acidic polar groups to adsorb on to the surface, due to the lack of available surface sites. As a consequence, the AN in the oil effluent increases. After 13PV of injected oil, the system establishes an equilibrium, where the AN in the effluent samples is equal to the AN of the injected oil, 0.35 KOH/g oil.

Core Wetting Of The Outcrop Chalk Core After Oil Flooding

A new chromatographic wettability test was performed on the oil flooded core. The core was successively flooded with SWOT to S_{or} , 0.25, at ambient temperature, and the chromatographic test was performed by switching to SW $\frac{1}{2}$ T at ambient temperature. The results from the chromatographic wettability test is presented in Figure 3.

The chromatographic separation between SCN^- and SO_4^{2-} is given in Figure 3. The calculated area between the tracer curve and sulphate curve is now dramatically lower compared to the initially water-wet core, in Figure 1. The calculated area is now $A_{wet} = 0.055$, confirming a dramatic reduction in water-wet sites on the pore surface after flooding 15 PV with an acidic oil.

Adsorption Of Acidic Organic Compounds In A Second Oil Flood

The Core#1 was then prepared for a second oil flooding test. The core, at S_{or} , was first mildly cleaned by kerosene, heptane and then flooded with DI water and dried. Initial $S_{wi}=0.1$ was established and the core#1 was mounted in a core holder. The core was once again flooded at 50 °C with a RES40-0.35 oil containing polar components. Effluent samples of produced oil were collected and then analysed for the content of acidic polar components. The results of the adsorption of acidic components on a chalk surface that has previously seen oil are shown in Figure 4. Unlike the first adsorption test, the AN in the effluent samples starts relatively high, 0.13 mg KOH/g. This indicates that there is something preventing a full adsorption of the carboxylic material onto the chalk surface as seen in the first adsorption test on a water-wet sample. This further implies that the pore surface already has acidic organic components adsorbed to the pore surface, and

reduces the adsorption of more acidic organic material. The slope of the AN curve is relatively sharp, and is brought to a new equilibrium within 6 PV of oil flooded.

Core Wetting of the Outcrop Chalk Core after Oil Flooding

The core wetting after the secondary Oil Flooding was tested by using the chromatographic wettability test. The core was flooded with SWOT to $S_{or, 0.2}$ at ambient temperature, and the chromatographic test was performed flooding $SW\frac{1}{2}T$ at ambient temperature. The results from the chromatographic wettability test are presented in Figure 5. This result shows a very low separation between the tracer and sulphate curve. The calculated area, $A_{wet} = 0,008$, is dramatically reduced compared with the previous wettability tests for water wet core, the core that has been injected 15 PV of crude oil. The test shows that the wettability of the core has become even less water-wet.

DISCUSSION

In this experimental work, we started with an initially water-wet core sample. This could simulate the initial situation in a reservoir before crude oil accumulates into the water filled reservoir trap. The first oil flooding we performed on a water-wet core sample could represent the process when the crude oil migrates from source rock into a water saturated reservoir trap. This oil-flooded core could represent the initial situation inside the reservoir regarding adsorption of acidic polar components and the initial reservoir wetting properties that could be established. Initial content of acidic polar components in the crude oil that migrates into the reservoir, and number of crude oil reservoir refilling during geological time will definitely contribute with large uncertainties to a correct wettability description.

Results show that the initial adsorption of acidic organic compounds increases with increasing PV of acidic oil injected, Figure 2, and that the adsorption at the end reaches an equilibrium. The adsorption of polar components onto the rock surface, reduced the water-wet surface area of the core dramatically, which is clearly seen when we compare Figure 1 and 3. The area between these curves in the water-wet core is $A_{ww} = 0.254$ and for the core flooded with crude oil, the area is $A_{wet}=0.055$ which corresponds to a fraction of water-wet surface area:

$$I_{CW} = \frac{A_{wet}}{A_{WW}} = \frac{0.055}{0.254} = 0.22 \quad (2)$$

The mild core cleaning that was performed on the oil flooded core, preserved large amount of polar components that were adsorbed to the pore surface. This is clearly shown when we compare Figure 2 and 4, Figure 7.

During the second oil flooding far less acidic polar components was adsorbed compared to the first oil flooding. The area above the adsorption curves represent the total amount of acidic organic material adsorbed onto the surface, AA_T . The Acid Adsorption (AA) was determined for both adsorption tests, before and after mild cleaning.

$$AA = \frac{AN_{plateau} - AN_x}{AN_{plateau}} \quad (3)$$

AN plateau is the average highest acid number when the oil reaches equilibrium with the surface. AN_x is the acid number value of a given sample number. Giving the total acid adsorption, AA_T:

$$AA_T = \sum \Delta PV \cdot AA \quad (4)$$

The calculated area above the curve shown in Figure 2 was $AA_T = 1.47$. The corresponding area in Figure 4 was $AA_T = 0.37$. This partly represents the amount of acidic organic components removed from the pore surface during the mild core cleaning, and partly the amount of acidic components that could be re-adsorbed during the second core restoration. Approximately 75% of the initial adsorbed material was still present on the pore surface. An increased number of PV injected with oil, will reduce the water-wet surface area inside the core. This could have dramatic effects on initial wetting and on the capillary pressure.

There is not a direct link between the AA_T and the water-wet surface area measured by the chromatographic wettability test when we compare wettability tests from 1st restoration, Figure 3, and the 2nd restoration, Figure 5, shown in Figure 8.

The separation area between these curves are now $A_{wet} = 0.055$, 1st restoration, and $A_{wet} = 0.008$, 2nd restoration, which corresponds to the water-wet fraction of $I_{cw} = 0.22$ and $I_{cw} = 0.03$ respectively.

Even though the total acidic adsorption capacity, AA_T , was reached in both experiments, the wettability test showed a reduction in available water-wet surface area, I_{CW} , from 22% to 3% after the second oil flood. This could be explained by the presence of acidic organic components in the crude oil with different surface reactivity. The more PV of oil flooded through the core, the more higher reactive acidic components will be concentrated at the rock surface, compared to what is initially present in the crude oil [6, 7]. Injection of 15 PV of crude oil in the second restoration was too large to reproduce the initial wetting achieved in the first restoration.

CONCLUSIONS

In this work, a water-wet outcrop chalk core was used. The effect of core cleaning and core restorations on rock wettability is discussed.

- The results showed that the adsorption of acidic organic compounds onto the pore surface increases with increasing PV of acidic oil injected.
- The adsorption of acidic organic compounds reached an equilibrium after 13 PVs of crude oil flooded in the first restoration.

- The adsorption of polar components to the pore surface reduced the water-wet core surface.
- Mild core cleaning preserved approximately 3/4 of the polar components that were adsorbed to the pore surface.
- In the second restoration acidic the adsorption equilibrium was reached after only 8 PVs of crude oil.
- After 15 PV crude oil injected in the second restoration, the water surface area had been reduced from 22% to 3%, giving a less water wet core compared to the first restoration.

The mild core cleaning procedure preserved most of the adsorbed acidic components. Lower crude oil volume was needed to restore the initial core wetting.

NOMENCLATURE

AN	Acid number
BN	Base number
ASTM	American Society for Testing and Materials
D	Core diameter
L	Core length
Φ	Core porosity
PV	Pore volume
S_{wi}	Initial water saturation
K_{ro}	Relative permeability of oil
K_{rw}	Relative permeability of water
A_{wet}	The area between the thiocyanate and sulphate curve of a sample
A_{ww}	The area between the thiocyanate and sulphate curve of a water-wet sample
VB0S	Valhall brine with no sulphate
TDS	Total dissolved salt
SW0T	Seawater without thiocyanate tracer
SW $\frac{1}{2}$ T	Seawater that contains thiocyanate tracer
C/Co	Relative concentration of ion in effluent fractions
I _{cw}	Chromatographic wettability index

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Table 1. Core data for chalk cores used.

	Core material		
	A1	A1b	Reference core
Stvens Klint Chalk	A1	A1b	Reference core
Dry weight, g	96,78	92,28	84,27
Length, cm	6,21	6,21	5,43
Diameter, cm	3,74	3,74	3,70
Bulk Volume, cm ³	68,22	68,22	58,33
Sat. Weight, g	128,56	119,79	112,01
Density of FW 10xD g/cm ³	1,00	1,00	1,02
Pore Volume, ml	31,69	27,43	27,14
Porosity %	46 %	40 %	47 %

Table 2. Compositions of the brines used.

Brine Reference	VBOS	SWOT	SW1/2T
Salt	mole/l	mole/l	mole/l
HCO ₃ ⁻	0,009	0,002	0,002
Cl ⁻	1,066	0,583	0,583
SO ₄ ²⁻	0	0	0,012
SCN	0	0	0,012
Mg ²⁺	0,008	0,045	0,045
Ca ²⁺	0,029	0,013	0,013
Na ⁺	0,997	0,460	0,427
K ⁺	0,005	0,01	0,022
Li ⁺	0	0	0,012
Density g/cm ³	-	1,022	1,022

Table 3. Properties of the oil used.

Crude oil	
AN mgKOH/g	0,33-0,35
BN mgKOH/g	0,24
Viscosity cP 25°C	3,25
Density g/cm ³ 25°C	0,808

Table 4. The reproducibility of Acid Number titration tests.

AN range	Trial 1	Trial 2	Trial 3	Stdev.
Sample of low AN	0,06	0,06	0,06	0,00
Sample of medium AN	0,27	0,27	0,26	0,01
Sample of high AN	0,34	0,34	0,34	0,00

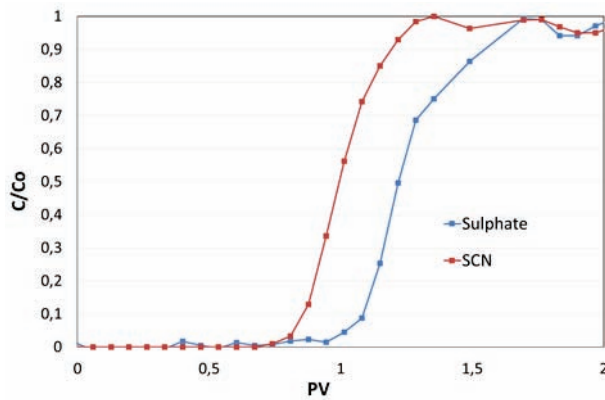


Figure 1. Chromatographic wettability test on a 100% water saturated core, Core#1. The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected.

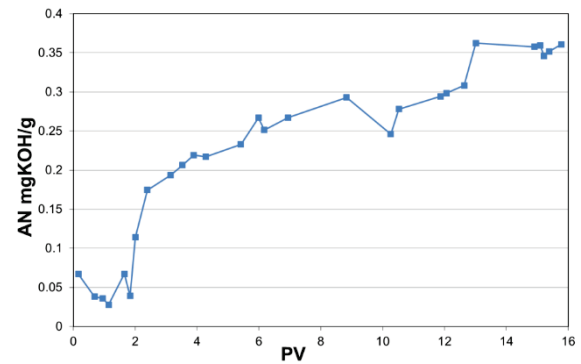


Figure 2. The adsorption of carboxylic material during flooding of an oil with $\text{AN}=0.35 \text{ mgKOH/g}$ into chalk Core#1 at 50°C , with a flow rate of 0.1 ml/min (4 PV per day). The AN in the effluent samples is presented vs. PV injected.

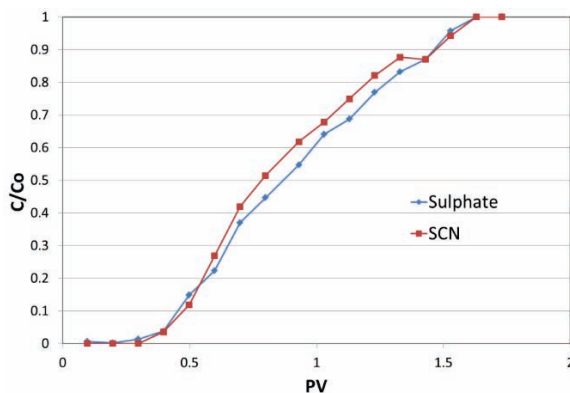


Figure 3. Chromatographic wettability test of Core#1 after the first oil flooding of 15 PV with an oil having $\text{AN} = 0.35 \text{ mgKOH/g}$ oil. The test on Core#1 was performed at S_{or} . The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected.

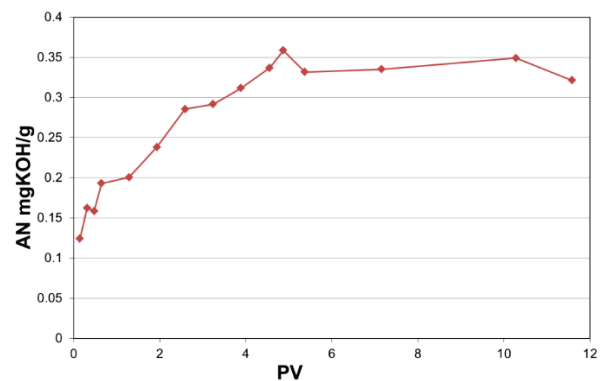


Figure 4. The adsorption of Acidic organic material during the second Oil flooding of Chalk Core#1 at 50°C with RES40-0.35 oil, with a flow rate of 0.1 ml/min (4 PV per day). The AN in effluent samples is presented vs. PV injected.

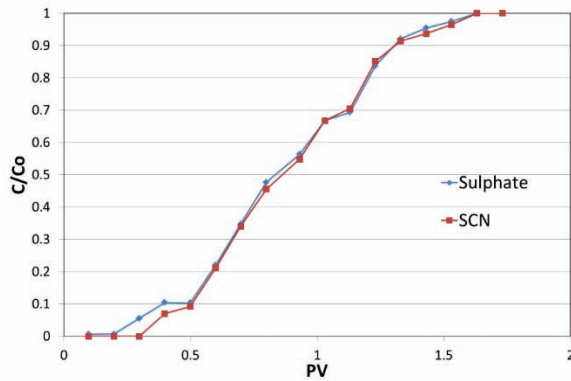


Figure 5. Chromatographic wettability test of Core#1 after the second oil flooding of 15 PV with RES40-0.35 oil. The test on Core#1 was performed at S_{or} . The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected.

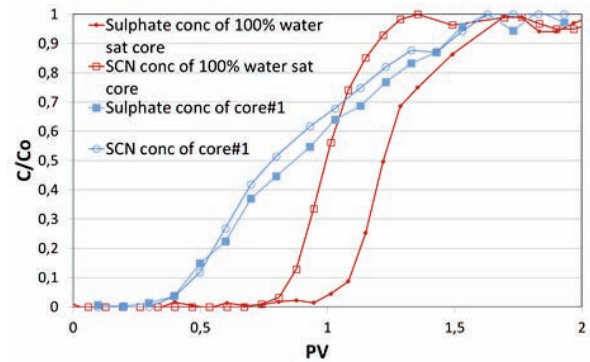


Figure 6. Chromatographic wettability test of a reference core and Core#1 after the first oil flooding of 15 PV with RES40-0.35 oil. The reference core was 100% saturated. The test on Core#1 was performed at S_{or} . The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected.

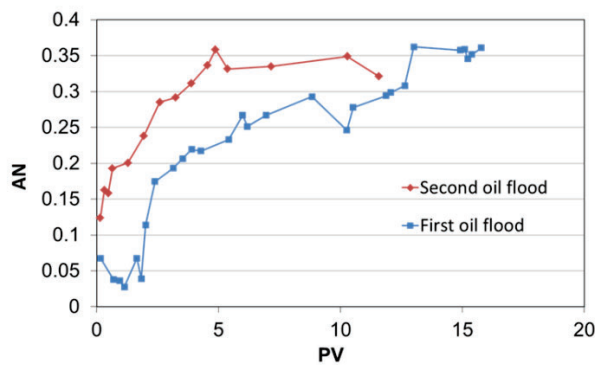


Figure 7. A comparison for the adsorption of Acidic organic material for both first and second Oil flooding of Chalk Core#1. The tests were performed at $50^\circ C$ with RES40-0.35 oil, with a flow rate of 0.1 ml/min (4 PV per day). The AN in effluent samples is presented vs. PV injected.

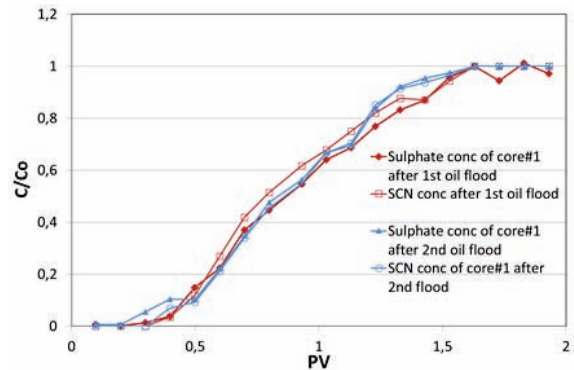


Figure 8. Chromatographic wettability test of Core#1 for both the first oil flood and second oil flood. 15 PV was flooded with RES40-0.35 oil. Both tests on Core#1 was performed at S_{or} . The relative effluent concentrations of SCN^- and SO_4^{2-} are plotted vs. PV injected.