

NEW METHOD TO PREPARE OUTCROP CHALK CORES FOR WETTABILITY AND OIL RECOVERY STUDIES AT LOW INITIAL WATER SATURATION

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ABSTRACT

The initial water saturation in North Sea chalk reservoirs is extremely low, often in the range of 5-7%. Outcrop material is often used to perform parametric studies on wettability and secondary oil recovery by water injection. In order to relate the experiments to a certain reservoir, it is desirable to mimic the reservoir conditions as closely as possible. This is done using outcrop cores. The cores are usually drilled in the same direction from the same block, dried at 120 °C, evacuated and saturated with the actual brine. Homogeneous water saturation can be obtained by draining the initial brine to a saturation less than 10% by using water-saturated nitrogen gas and a porous plate. During this process, the water saturation is decreased from 100% to less than 10%. Potential determining ions like Mg^{2+} , Ca^{2+} , CO_3^{2-} and SO_4^{2-} present in the brine or as salt initially present in the core, will adsorb onto the chalk surface. Thus, during the drainage process, the potential determining ions are up-concentrated in the core, and the apparent concentration in the residual water becomes different from the initial brine. The wetting condition obtained during an aging period at 90 °C is very sensitive to the concentration of SO_4^{2-} in the initial brine. Outcrop chalk cores that were pre-flushed with 4 PV of distilled water to remove SO_4^{2-} , appeared to be much less water-wet compared to cores not pre-cleaned in the same way. The amount of SO_4^{2-} present before and after cleaning was quantified. A new standard procedure to prepare outcrop chalk cores for wettability studies is suggested:

- The cores must be flooded with distilled water or formation brine without SO_4^{2-} to remove SO_4^{2-} that may be present initially.
- The initial saturation brine must not contain SO_4^{2-} .

INTRODUCTION

Even though nearly half of the world's proven petroleum reserves are present in carbonates, only a very small part of these is found in chalk. The naturally fractured coccolithic chalk reservoirs in the North Sea are characterized by high porosity of 40-50%, low permeability, 1-3 mD, and very low initial water saturation, 5-7%

(Frykman, 2001; Røgen and Fabricius, 2002). Thus, each volume unit of a chalk reservoir contains about twice the amount of oil compared to a sandstone reservoir. The biogenic chalk has a large specific surface area, about $2 \text{ m}^2/\text{g}$, and it is extremely pure, 98% CaCO_3 . The high porosity was preserved due to an early invasion of hydrocarbons and creation of overpressure. The absence of normal diagenetic processes has resulted in a very small degree of cementation. The pure chalk surface is reactive, which affects the interaction between the rock surface and the pore fluid. The SEM-picture in Figure 1 shows chalk on pore scale, and coccolithic rings, ring fragments and pore space is easily observed.

Seawater appears to be an excellent injection fluid in the Ekofisk chalk field where the expected oil recovery is approaching 50%. It was documented by laboratory studies that seawater contained potential determining ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}) towards the chalk surface, which were able to improve the water-wetting nature of chalk (Austad et al. 2005; Strand et al., 2006a; Zhang et al., 2007). Parametric EOR-studies in the laboratory require a large number of cores with similar properties. Fortunately, outcrop sources are available with similar properties as the reservoir chalk formations. The question is: “What is the optimal way to prepare outcrop cores in order to mimic the reservoir conditions regarding wettability and initial water saturation and composition?”

It is impossible to flood the low permeable chalk to residual water saturation below 10% using viscous oil. The use of a centrifuge is an alternative method, but due to the weak mechanical strength of the high porosity material, the core often experiences mechanical damage during this process. However, chalk cores saturated with formation water can be drained to very low water saturation by a gradual increase in pressure using water-saturated nitrogen gas (N_2) and a porous plate. The formation brine of chalk reservoirs contains potential determining cations, Ca^{2+} and Mg^{2+} , but only negligible amounts of potential determining anions like CO_3^{2-} and SO_4^{2-} . The potential determining ions will adsorb onto the chalk surface, and due to the low residual water saturation, <10%, they will be up-concentrated in the residual water relative to the composition of the initial brine during the drainage process. This will especially be a problem if the brine prior to drainage contains even a small amount of SO_4^{2-} , because the adsorption of SO_4^{2-} increases as the temperature and concentration of Ca^{2+} increases (Strand et al. 2006a). It is further known that the final wetting properties will be strongly dictated by the amount of SO_4^{2-} (Zhang et al., 2006).

In the present paper we will demonstrate that small amounts of SO_4^{2-} present in the outcrop chalk can affect the wetting conditions after aging in crude oil if precautions are not taken. A lesson learned from this work is that chalk cores should be pre-flushed with the actual fluid to remove traces of SO_4^{2-} that could be present in the outcrop material due to its strong affinity for the chalk surface.

EXPERIMENTAL

Core material

The core material used is outcrop Stevns Klint chalk from a quarry nearby Copenhagen, Denmark. This chalk is high in porosity (45-50%), low in permeability (2-5 mD) and it has a specific surface area of about 2.0 m²/g (Frykman, 2001; Røgen and Fabricius, 2002). The amount of clay is very small.

Oils

Oils with desired acid numbers (AN) and base numbers (BN) were obtained by mixing **Oil A** (AN~1.9 mgKOH/g oil, BN~0.50 mgKOH/g oil), **Oil B** (AN~0.20 mgKOH/g oil, BN~0.10 mgKOH/g oil) and **Oil C** (AN~0.20 mgKOH/g oil, BN~2.4 mgKOH/g oil) in **Table 1** in different ratios.

Brines

Artificial brines were used, and the compositions are listed in **Table 2**.

Core preparation procedure to achieve low initial water saturation ~10%

The method that has been used so far regarding core preparation is based on the method developed by Standnes and Austad (2000), but the method has been modified in order to achieve low initial water saturation in the 5-10% range. The cores were drilled from the same chalk block in the same direction with an oversized bit and shaped to the correct dimension using a lathe and saw. Afterwards, the cores were dried at 120 °C until a constant weight was obtained. Air was removed from the cores in an evacuator, and the specific brine was introduced. Once the cores were saturated with brine, they were placed on a porous plate and drained to an initial water saturation of about 10% by using water-saturated N₂ and gradually increasing the pressure up to 10 bar. After drainage, the core was placed in a Hassler core holder and flooded at 50 °C with 1.5 PV of crude oil at a rate of 0.4 ml/min in each direction with a 15 bar confining pressure. Finally, the cores were aged in crude oil at 90 °C for 4 weeks. Due to the up-concentration of negatively charged potential determining ions like SO₄²⁻ during drainage by the porous plate technique, it was decided to pre-flood the core with distilled water or initial formation water without SO₄²⁻ present.

Chromatographic wettability test method

A chromatographic method was developed by Strand et al. (2006b), which can be used to determine the wettability of chalk. After aging, the core was again placed inside the Hassler core holder, with a confining pressure not exceeding 25 bar, and flooded with 1.0 PV SSW-U brine at a rate of 0.2 ml/min followed by another 1.0 PV at rate of 0.4 ml/min

using the same brine to obtain residual oil saturation, S_{or} . The SSW-U brine (see **Table 2**) contained neither SO_4^{2-} nor the tracer thiocyanate (SCN^-). Next, the core was flooded with at least 2.0 PVs of SSW-M brine (containing both SO_4^{2-} and tracer) at a rate of 0.2 ml/min. The effluent was collected in fractions of 1-3 ml by use of a fraction collector. The fractions were analyzed for concentrations of SO_4^{2-} and SCN^- , and the concentration relative to the initial concentration was plotted against injected PV. Chromatographic separation between the non-adsorbing tracer SCN^- and the adsorbing SO_4^{2-} takes place at the water-wet sites of the chalk surface, and the area between the elution curves of the two components is directly proportional to the water-wet area inside the core. A completely water-wet condition is assumed when using heptane as the oil phase. A wetting index, WI, describing the fraction of water-wet area was calculated according to the following equation:

$$WI = \frac{A_{Wett}}{A_{Heptane}} \quad (1)$$

Where:

$A_{Heptane}$ and A_{Wett} are the areas between the SCN^- and the SO_4^{2-} curve for a complete water-wet system using heptane as oil and the actual crude oil system, respectively. All areas were calculated using the trapezoidal method. According to the definition of WI:

- WI = 1.0 represents a completely water-wet system
- WI = 0.5 represents neutral wetting conditions
- WI = 0.0 represents a completely oil-wet system

RESULTS AND DISCUSSION

The impact of acid and base numbers of the crude oil on the wetting condition of chalk has been studied previously, (Punternold et al., 2007) and during that work it was found, when using crude oils with constant AN=0.5 mgKOH/g oil and various BN, that the cores were unusually water-wet. Spontaneous imbibition of initial reservoir brine at 90 °C and with a 10 bar backpressure resulted in approximately 70% oil recovery, Figure 2. In that study, two new blocks of outcrop chalk from Stevns Klint were used. Since Stevns Klint is situated close to sea, the blocks may have been contaminated by some influx of seawater. It is well known that seawater will act as a wettability modifier to increase the water-wetness of chalk, the reason being the presence of SO_4^{2-} together with Ca^{2+} and Mg^{2+} (Zhang et al., 2007). Usually, the salinity of the reservoir brine is much higher than the expected dissolved salt in the outcrop chalk, and therefore, direct saturation of chalk by the reservoir brine should give a representative composition of the initial water in the core. If, however, the core contains a small amount of SO_4^{2-} , which is absent in the initial formation brine, the final wetting properties of the core can be changed drastically. It was therefore decided to investigate if SO_4^{2-} was already present in the chalk matrix.

SO₄²⁻-content inside the core determined by core flooding and core drainage

Two dried cores (with PV ~34 ml) were flooded with 4 PV of distilled water, DW, to remove all dissolvable SO₄²⁻ from the core. The amount of SO₄²⁻ in the effluent was analyzed and is plotted in Figure 3. DW could be used because the chalk contained only minor amounts of clay, which did not cause any problems regarding permeability change due to clay swelling. If the cores contain significant amounts of clay, instead of DW it is suggested to use reservoir brine without SO₄²⁻. The total amount of SO₄²⁻ eluted from each core by core flooding was on average 5.3 mg.

Fifteen dried cores of similar size were saturated with reservoir brine, VB/US (without SO₄²⁻), placed on a porous plate, and drained with water-saturated N₂ stepwise increased in pressure. The amount of SO₄²⁻ in the drained water was analyzed frequently, and the average amount of SO₄²⁻ drained from each core was calculated and is plotted as a function of PV in Figure 4. For comparison, the amount of SO₄²⁻ eluted from a DW-flooded core was plotted in the same figure. The average amount of SO₄²⁻ drained from each core by the porous plate technique was determined to be 2.2 mg. Thus, the amount of SO₄²⁻ left in each core should be: 5.3- 2.2 mg = 3.1 mg. The residual water saturation for each core was on average 10.4%. With an average PV of 34 ml, the apparent concentration of SO₄²⁻ in the residual water was determined to be 0.74 g/l, which corresponds to as much as one-third of the concentration present in seawater.

Wettability determination by spontaneous imbibition and chromatographic test

Having determined that the initial water inside the core is up-concentrated in SO₄²⁻, new experiments were performed in order to demonstrate the effect of core cleaning on wettability. Two cores were prepared for spontaneous imbibition. After drying, one core was pre-flooded with 4 PV of DW in order to remove dissolvable salt, possibly containing SO₄²⁻. Both cores were saturated with VB formation brine under vacuum and then drained to residual water saturation, S_{wi} ~10%, using water-saturated N₂ and a porous plate. The cores were flooded with 2 PV of crude oil, AN = 0.5 mgKOH/g oil and BN = 0.2 mgKOH/g oil, in each direction, and after flooding, the cores were aged in the actual crude oil for 4 weeks at 90 °C. Prior to the spontaneous imbibition tests, 2 mm of the cores were shaved off on all sides to remove unrepresentative adsorbed crude oil components on the chalk surface (Standnes and Austad, 2000). The cores were imbibed in sealed steel containers at 90 °C with a 10 bar backpressure using the same formation water, Figure 5. The cores showed great difference in wetting properties. The core that had been cleaned with DW appeared to be much less water-wet than the non-cleaned core. About 70% of the oil was recovered within 4 days for the non-cleaned core, while only 30% of the oil was recovered after 13 days for the cleaned core.

The water-wet fraction of the chalk surface was determined by using the chromatographic wettability test method developed by Strand et al. (2006b). The test was performed on three cores, of which one was saturated with heptane, to represent a completely water-wet

system. The second and third core were saturated with the same oil AN = 0.5 mgKOH/g oil, BN = 0.2 mgKOH/g oil. One of the cores was cleaned beforehand with DW, while the other was not. The chromatographic separation curves between the tracer, SCN^- , and SO_4^{2-} for the three cores are given in Figure 6. The calculated values for the water-wet fractions using this method were 0.84 and 0.65 for the non-cleaned and cleaned core, respectively, which agrees well with the respective response from the spontaneous imbibition experiments. There is a significant decrease in water-wetness by cleaning the core.

Effect of temperature

Previously, it has been shown by spontaneous imbibition experiments with SSW that increased temperature enhanced oil recovery at constant AN (Strand et al., 2006a). In order to observe the effect of temperature on cleaned cores, two cores were cleaned with DW and treated in the same way as described earlier. In this case, an oil with AN = 0.73 mgKOH/ g oil and BN = 0.3 mgKOH/g oil was used. Higher AN, and lower BN will create a less water-wet condition according to the previous tests performed by Puntervold et al. (2007). The cleaned cores imbibed VB spontaneously at 90 and 110 °C, Figure 7. The oil recovery at 90 °C approached 15% after 20 days, and at 110 °C, the oil recovery plateau at 17% was reached within 5 days. After 7 days, the imbibing fluid at 110 °C was exchanged with synthetic seawater, SSW, and 50% of the oil was recovered after 40 days, while the increased recovery at 90 °C was only a few percents after exchanging the imbibing fluid to SSW after 13 days. In the case of the cleaned cores, temperature was still able to enhance recovery when the cores were imbibed with SSW, which is due to a wettability alteration toward a more water-wet condition caused by the increased affinity of SO_4^{2-} for the chalk surface at higher temperatures. The same effect of temperature can be seen in Figure 8, where increasing temperature from 90 °C to 130 °C. When imbibing with SSW, the recovery was enhanced by 40%. These results documents again, what has been stated before, (Zhang et al., 2007) that seawater is an excellent EOR-fluid for chalk at high temperature due to the presence of the potential determining ions, Ca^{2+} , Mg^{2+} , and SO_4^{2-} .

Effect of initial water saturation

The effect of initial water saturation on the wetting conditions in cleaned cores was also tested. Two cores washed with DW were drained to different residual water saturation, $S_{wi} = 22\%$ and 10% , and thereafter saturated with an oil with AN = 1.6 mgKOH/g oil and BN = 0.5 mgKOH/g oil. Regardless of the initial water saturation, the cores behaved similarly, Figure 8, i.e. spontaneous imbibition of VB/US and SSW was limited at 90 °C and stabilized at 10%, but it increased dramatically at 130 °C, resulting in 50% recovery for both cores. Thus, the initial water saturation appeared to play a minor role regarding spontaneous imbibition into chalk with wettability modification. Normally, the water wetness is observed to decrease as the initial water saturation decreases, (Jadhunandan

and Morrow, 1991; Xie and Morrow, 2001) which was also experienced in our previous study (Punternold et al., 2007).

Wettability alteration inside the core

Previous work has shown that seawater is an excellent EOR-fluid for high temperature chalk reservoirs, and the chemical mechanism behind the wettability modification towards more water-wet conditions has been studied in detail (Zhang et al., 2006; Zhang et al., 2007). Adsorption of SO_4^{2-} onto the positively charged chalk surface and the presence of Ca^{2+} and Mg^{2+} appeared to be the key factors in this process. The efficiency of the wettability modification increases with temperature due to enhanced affinity of SO_4^{2-} to the chalk surface (Strand et al., 2006a). Thus, if the water film inside the core contains a small amount of SO_4^{2-} in the presence of significant amounts of Ca^{2+} and Mg^{2+} , the water-wetness will increase as the aging temperature increases or if the imbibition was performed at a higher temperature than the aging temperature. If, however, the imbibition is performed at a lower temperature than the aging temperature, a less water-wet nature could be obtained if SO_4^{2-} was present. Thus, the wetting conditions may change depending on the imbibing temperature. This will be prevented if the core was pre-flushed with SO_4^{2-} -free water. A lesson learned from this work is to be aware of the great influence that even small amounts of SO_4^{2-} could have on the wetting conditions during the preparation of core material for further oil recovery studies. It is therefore recommended that chalk cores be flushed with at least 4 PVs of SO_4^{2-} -free brine before saturating the core with the actual fluids, which must be free from negatively charged potential determining ions.

CONCLUSIONS

- It was found that even small amounts of SO_4^{2-} in a non-flushed core or in the initial brine, had a major impact on the initial wetting state of the chalk core, due to an up-concentration of SO_4^{2-} in the remaining water film inside the core after drainage by the porous plate method to establish low S_{wi} .
- Spontaneous imbibition data showed a significant reduction in the water-wetness after the cores had been cleaned with 4 PVs of distilled water prior to core saturation. A reduction of the water-wet area inside the core was also verified by the chromatographic wettability test method.
- Higher temperature in combination with SO_4^{2-} from SSW increased spontaneous imbibition dramatically. This shows that seawater can be an excellent EOR-fluid for chalk.
- An initial water saturation variation between 10 and 20% in cleaned cores did not seem to affect the wetting condition noticeably.
- Outcrop chalk material must be flushed before use with at least 4 PVs of distilled water to remove negatively charged potential determining ions, i.e. SO_4^{2-} , that can have a major impact on the wetting condition of chalk.

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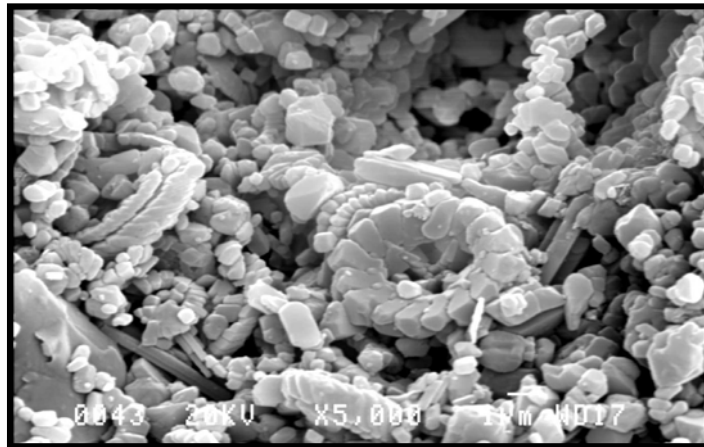
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Table 1. Oils

Oil	AN (mgKOH/g oil)	BN (mgKOH/g oil)	Density g/cm ³
A	1.9	0.50	0.808
B	0.20	0.10	0.801
C	0.20	2.4	0.856

Table 2. Molar (mol/l) composition of brines

	VB	SSW	SSW-U	SSW-M	VB/US
HCO ₃ ⁻	0.009	0.002	0.002	0.002	0.009
Cl ⁻	1.065	0.525	0.623	0.525	1.066
SO ₄ ²⁻	0.001	0.024	-	0.024	-
SCN ⁻	-	-	-	0.024	-
Mg ²⁺	0.008	0.045	0.045	0.045	0.008
Ca ²⁺	0.029	0.013	0.013	0.013	0.029
Na ⁺	0.996	0.450	0.500	0.450	0.996
K ⁺	0.005	0.010	0.010	0.034	0.005
Ionic strength	1.112	0.657	0.683	0.681	1.112
TDS (g/l)	62.8	33.4	35.7	35.7	62.8

**Figure 1** SEM picture of chalk showing the coccolithic rings, ring fragments and pore space

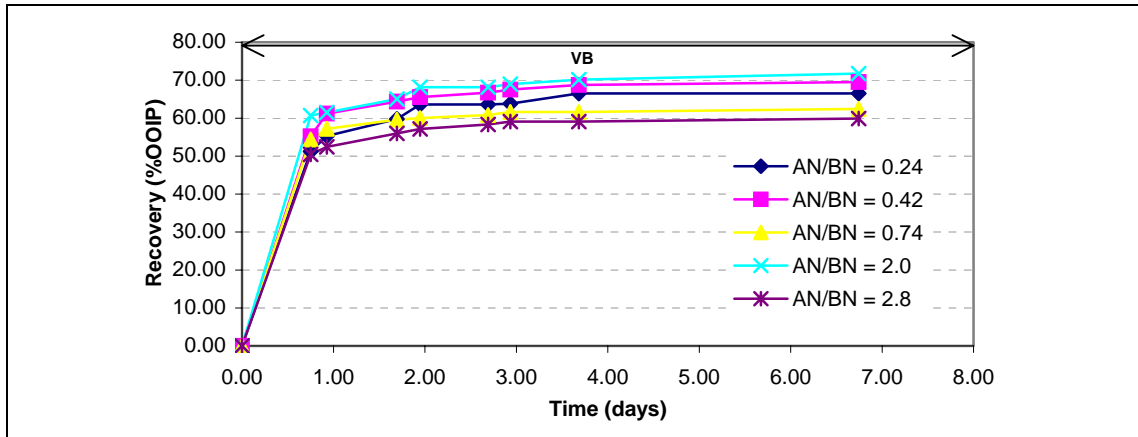


Figure 2 Imbibition of VB-brine at 90 °C in non-cleaned cores saturated with various AN/BN-ratio oils. The AN = 0.5 mgKOH/g oil and constant.

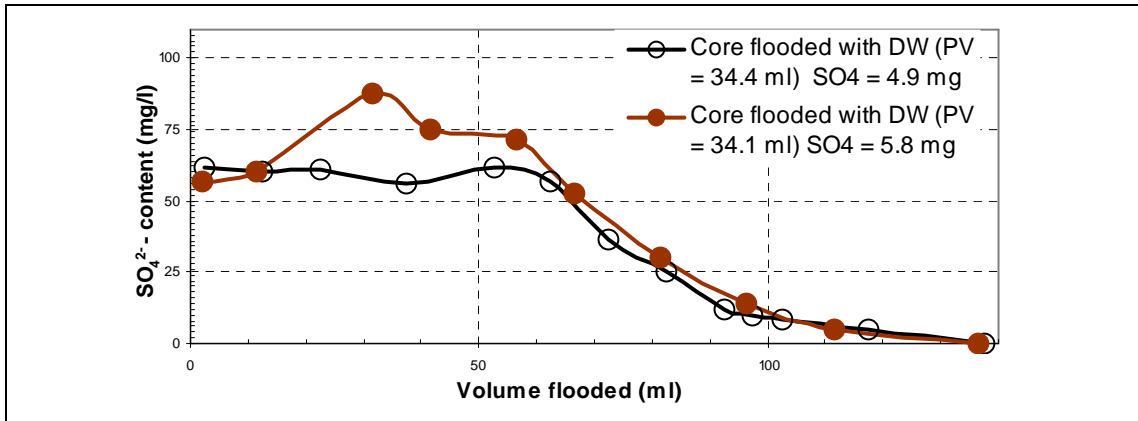


Figure 3 Effluent sulfate content from two cores flooded with distilled water at 50 °C.

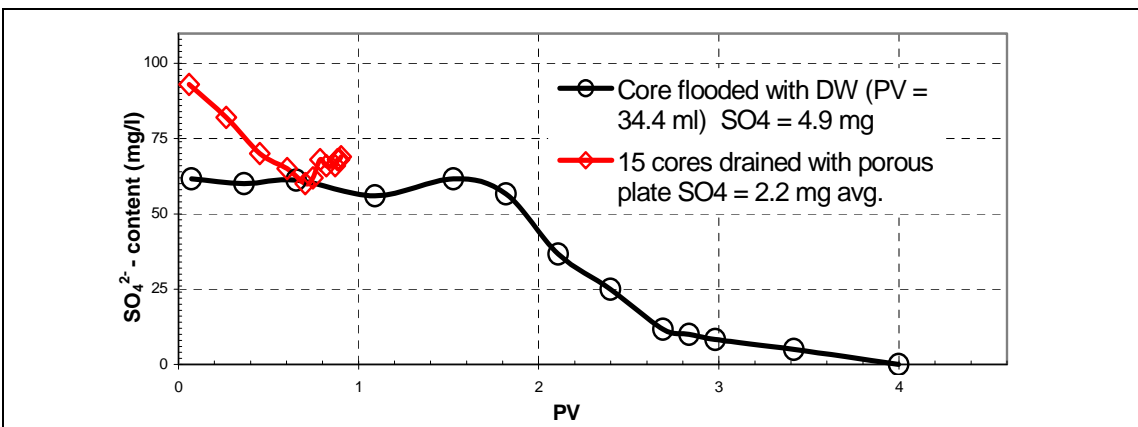


Figure 4 Difference in effluent sulfate content from core flooding and core drainage.

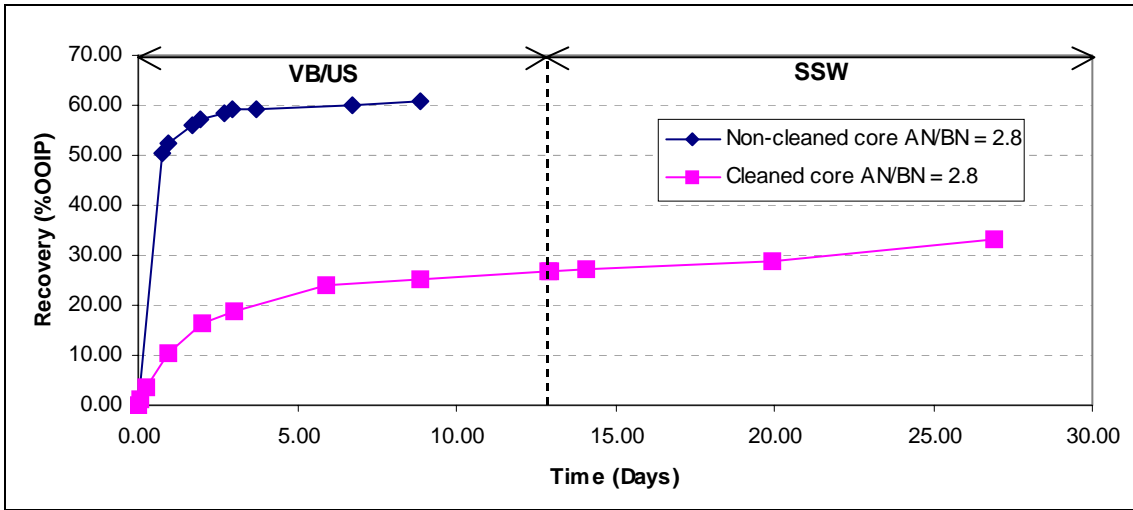


Figure 5 Imbibition at 90 °C into non-cleaned and cleaned cores. The cores were first imbibed with VB without any sulfate. The cleaned core appeared to be much less water-wet than the non-cleaned core.

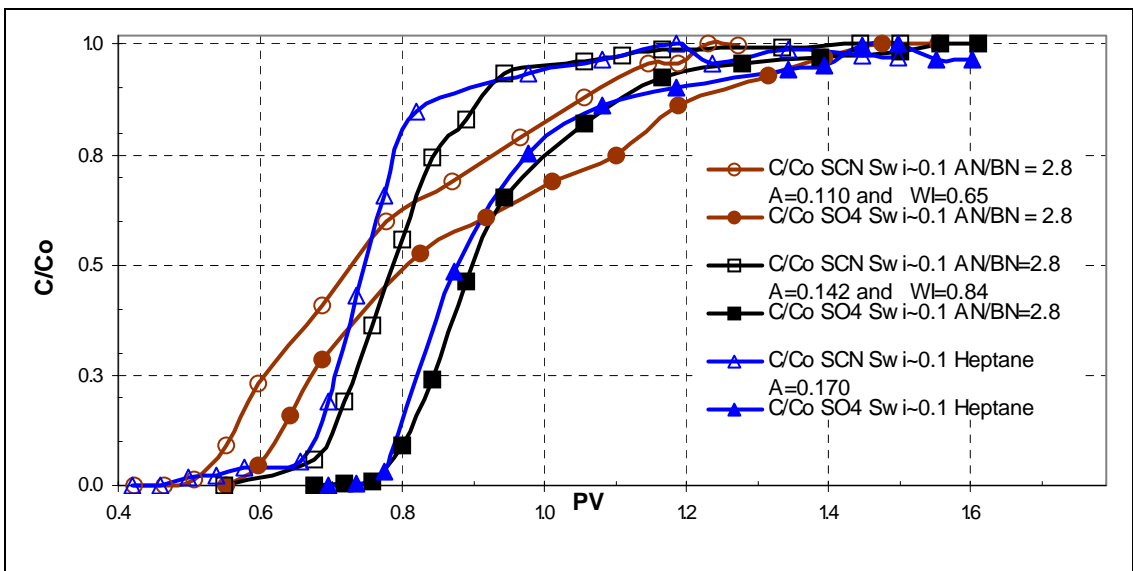


Figure 6 Comparable wettability indices for cleaned and non-cleaned cores

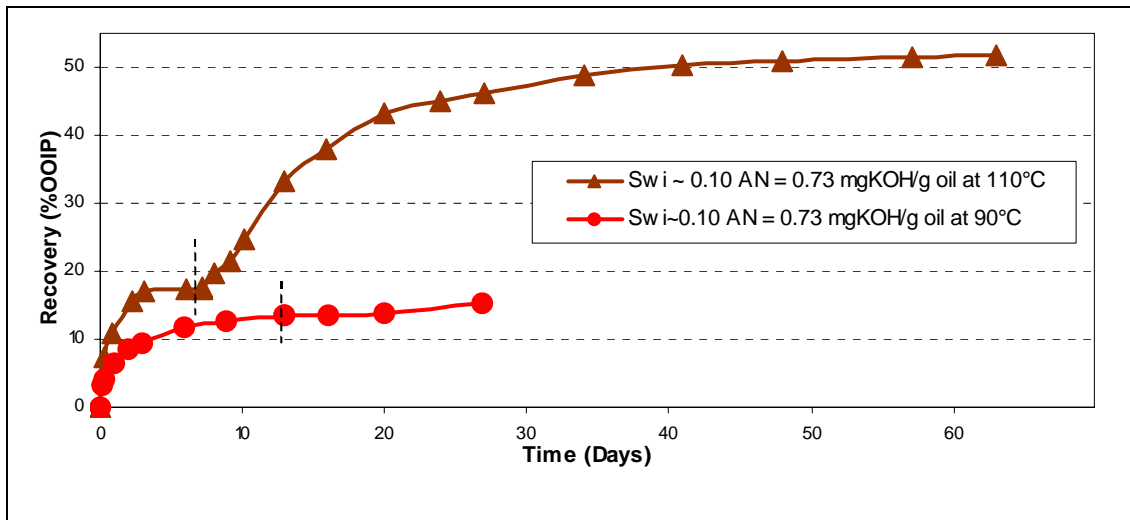


Figure 7 The effect of temperature on spontaneous imbibition of cleaned cores. The dashed lines mark the time when imbibition fluid was changed from VB/US to SSW.

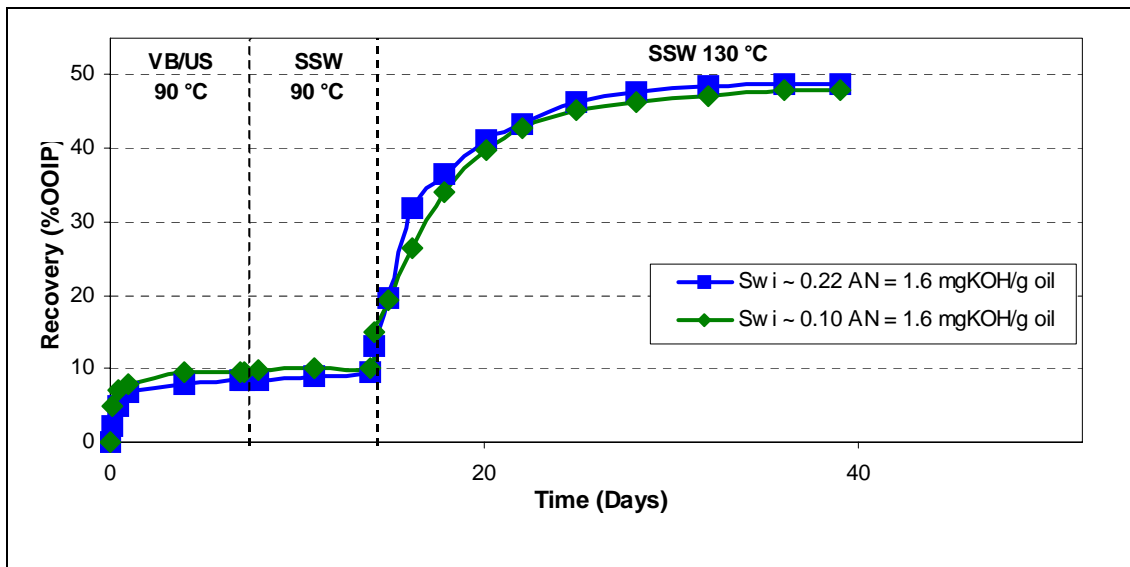


Figure 8 The effect of S_{wi} on spontaneous imbibition of SSW in cleaned cores.