Initial Wettability in Carbonates by Advanced Core Analyses: «*A Step Closer to Representative Reservoir Wettability*»

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Abstract. The cleaning and core restoration strategy proposed in this work has successfully reproduced core scale wettability under spontaneous imbibition (SI) processes in Chalk, high reproducibility of ultimate oil recovery and recovery profiles in between restorations was reported; differences were rather low and ranged from 1.5 to 3.6 %OOIP in 4 different systems. Stevns Klint (SK) outcrop chalk with a high calcium carbonate content was used in this work. The cleaning procedure consisted of a mild cleaning process using kerosene and heptane, with minimized solvent injection. During the core restoration procedure after building up initial water saturation, S_{wi}, oil saturation was performed by limiting the amount of crude oil exposure to (1-S_{wi}) pore volume (PV). A comparison at low temperature, 23 °C, between a harsh solvent cleaning method with toluene and methanol and the mild cleaning process by kerosene and heptane was carried out; the results showed that the mild cleaning solvents preserved a larger fraction of polar organic components (POC) adsorbed on the carbonate surfaces during the first restorations process, validating the mild cleaning process as more suitable for preservation of adsorbed POC on carbonate surfaces. Despite the excellent performance of the mild cleaning solvents, they also removed a small fraction of adsorbed POC, making slightly water-wet the mineral surfaces. Thus, even mild organic solvents at low temperature still affect wettability by solvating adsorbed POC. Changes in wettability were assessed by SI and chromatographic wettability (CWT) tests.

1 Introduction

Reliable estimation of in-situ reservoir wettability continues to be an elusive objective despite long-termed efforts and integration of cutting edge technologies for this purpose [1-4].

Integrating wettability measurements in reservoir engineering studies is a critical task because this single parameter has a tremendous impact on recovery factors, reserves estimation and profitability of commercial projects. Low accuracy in wettability assessments can produce erratic results that can lead to underestimation or overestimation of recoverable reserves [2].

As long as the desired goal of in-situ wettability measurements is not reached, Special Core Analyses (SCAL) will continue to serve as the standard practice to quantify reservoir wettability [5, 6]. However, its precision, reproducibility and repeatability stand out as weak points for the current accepted SCAL practices.

Reservoir core sampling is a complex work-routine that aims to preserve wettability. Wettability can be highly affected by drilling fluids, especially the ones bearing surfactants, or by fluids with different pH values than that of the formation [7, 8]. Such routines also aim to reduce native fluids loss associated to pressure and temperature changes during extraction and sampling. Such changes can potentially induce asphaltene precipitation, loss of light ends of hydrocarbons and fluid redistribution within the porous media; thus, altering core wettability.

Peal packaging is carried out to minimize contamination before sample arrival to the laboratory for routine and special core analyses. Then, typical samples of 3.8 cm of diameter are drilled from sealed peals and the samples are subjected to a core cleaning procedure. During core cleaning the solvents and fluids used can change the composition and concentration of polar organic material initially adsorbed onto the rock surface, leading to substantial changes in wettability [7-9]. The accepted protocol has the objective of shifting the wettability of the core to a strongly water-wet state to later recreate reservoir wettability. This work offers a critical stance specially on the standard procedure, with special focus on the choice of inducing a strongly water-wet state,

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while suggesting an alternative solution to the challenging task of assessing reservoir wettability.

It is well known that several critical parameters assessed in SCAL analyses are wettability dependent. Core restoration begins with core solvent cleaning and it is followed by the establishment of initial fluid saturations, i.e., water and oil.

During SCAL analyses, data related to fluid-flow characterization is collected as fluids saturation is changed, this data includes, resistivity, capillary pressure and pressure drops. From here on, the "*data*" is further processed to be assembled into reservoir simulations through relative permeability curves. Thus, core cleaning and core restoration protocols are of great importance because they have a major impact on the evaluation of field development plans, hydrocarbon productions forecasts, and economic analyses associated to hydrocarbon production.

Core cleaning and core restoration programs that can closely reproduce the native reservoir wettability can contribute to reduce uncertainty in the reservoir characterization value-chain.

Wettability controls fluid distribution on pore surfaces, giving rise to complex fluid-flow recovery processes, and the study of this phenomena has been a primary objective for understanding oil recovery processes. During waterflooding operations, capillarity plays major role in such processes, and this becomes more significant for reservoirs or reservoir zones with greater heterogeneity.

A brief description of the steps taken to restore a core are summarized as follows, (1) solvent cleaning aiming to render the cores to a completely water-wet state, (2) establishment of formation water saturation, (3) introduction of crude oil until reaching residual water saturation (S_W), (4) Maturation or aging process at reservoir temperature.

Combinations of cleaning solvents had been reported to be more adequate than cleaning process engaging single solvents [10]. Up to date, typical core cleaning units are based on high and low temperature cleaning by Soxhlet extraction [11], constant or total immersion, and solvent flooding [6].

Solvent cleaning methods are meant to efficiently remove hydrocarbons from the porous network but at the same time minimizing any possible damage onto the present minerals. Currently, the standard cleaning pair is toluene and methanol but many other options are available; simple examples are hexane, cyclohexane, kerosene, acetone, chloroform, ethylene chloride and tetrachloroethylene among others [6]. The use of different solvents can lead to different restored wettability states [12]. Thus, a correct solvent selection is crucial if preserved core samples are required to be restored to a representative reservoir wettability.

Furthermore, weaknesses of standard core restorations are coming to light [13]. Classical core cleaning methods have as objective to remove mud filtrates [14], precipitated salts and native crude oil to achieve a water-wet state.

However, by taking away the initially adsorbed polar organic components (POC) that dictate reservoir wettability with strong organic solvents, the wettability state to evaluate is simply destroyed. Then, restoring initial core wettability in the laboratory becomes an impractical and difficult task. This is mainly due to the fact that the sampled reservoir crude oil used in core restoration processes might be different in its chemical composition from the oil that initially wetted the reservoir during the first oil migration [15]. Furthermore, the oil chemical composition may have changed during geological time due to adsorption and decomposition processes[16, 17].

Other important aspect of core restoration to consider is oil saturation. The presence of crude oil will expose mineral surfaces to surface active POC. Recent investigations had shown that POC adsorption takes place rapidly as crude oil enters in contact with porous media surfaces; it has also been shown that increased oil volumes reduce the degree of water-wetness of the restored cores [18-23].

The weaknesses of core restoration protocols can promote unrepresentative wetting states in restored carbonate cores, giving rise to scattered wetting states in SCAL experiments.

Acidic and basic material in the crude oil can be quantified by the acid number (AN) and base number (BN), both having the unit mgKOH/g oil. In carbonates, the acidic POC (AN) represent the most relevant wetting parameter [24-30].

In the acidic fraction, carboxylic groups (R-COOH) appear to have a large surface activity, they are found in both resins and asphaltenes. On the other hand, basic POC have less impact on the carbonates wettability [31]. POC get adsorbed onto water-wet outcrop chalk surfaces in crude oil flooding processes, one consequence of this is that the water wetness will decrease [18]; In addition to this, increasing acid number of crude oil appears to reduce the degree in water-wetness [25]. The negatively charged carboxylic groups, R-COO⁻, adsorb strongly onto the positively charged calcite surfaces at slightly alkaline conditions, for this reason, it is challenging to remove all the POC from the carbonate surfaces by using different organic solvent combinations [32-34].

This paper discusses the implications of: (1) correct solvent selection for cleaning mixed wet carbonate cores, and (2) core restoration processes that aim to preserve wettability and reproduce the wetting state of a carbonate system at core scale. For the first topic a comparison between the harsh solvent cleaning combination of toluene and methanol and our proposed mild cleaning with kerosene and heptane is carried out.

In the first section the wetting states of the cores were measured by spontaneous imbibition and chromatographic wettability tests. The results were discussed in terms of the ability of the organic solvents to remove polar organic components adsorbed onto the carbonate surfaces of the cleaning fluids. It is important to know that POC adsorption has a direct impact on surface wettability, the solvents sets compared were toluene-methanol against kerosene-heptane.

In the second part of this work, the crude oil exposure of the restored cores was optimized to achieve wettability reproduction in carbonates at core scale.

The combination of both correct cleaning and a correct understanding of restoration processes facilitated achieving the goal of wettability reproduction at core scale. The proposed cleaning and restoration strategy can potentially be applied in core material with similar mineralogical characteristics, the outcrop material is made of high purity calcite (CaCO3), the chemical interactions that dictate wettability in this crude oil-brine-rock system (COBR), are heavily controlled by the nature of the mineral phases present, and previous studies on chalk have proved that surface reactivity and wettability can be extended to limestone reservoir cores [12, 34-41].

2 Experimental

A brief description of the materials used is found below, it covers, the outcrop core material used, the synthetic brines, crude oils, model oil and solvents used.

2.1 Materials

2.1.1 Core material

Outcrop chalk from a quarry at Stevns Klint (SK) was used in this work. SK chalk is made up of pure biogenic calcite >98 wt.%, with a minimum silicate traces compared to other types of chalk [42-45]. The presence of natural chalk impurities as quartz or clays can impact on the chemical properties of the material, i.e. surface reactivity and mechanical properties [46-53].Average porosity values are in the range of 41 to 50 %, and permeabilities varied from 1 to 5 md.

The material is well recognize as an excellent analogue to the North Sea Chalk reservoirs [48, 54], and its high reproducbility of results in laboratory tests have consolidate it as an outstanding material for parametric studies [18, 35, 54, 55]. Its biogenic origin is reflected on its structure, which is largely formed by of coccoliths fragments, **Figure 1**.
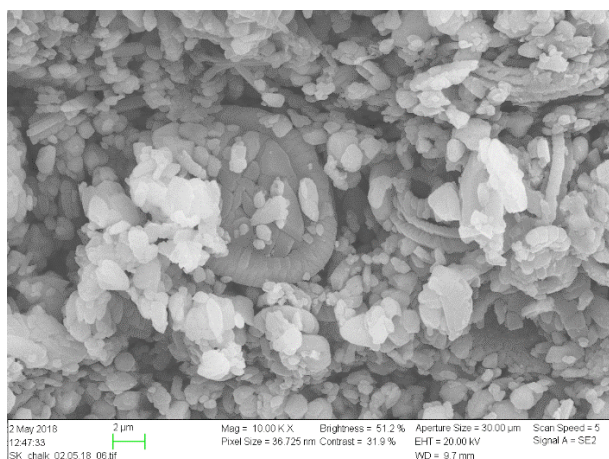

Figure 1. Image of outcrop chalk retrieved from the Stevns Klint quarry. SEM magnification 10000 X.

Mercury capillary injection pressure (MICP) tests were obtained from a representative sample; Stratum laboratories carried out the tests. Pore size distribution is shown in **Figure 2**; average pore size belongs to the micro-pore region (0.1-0.5 μm).
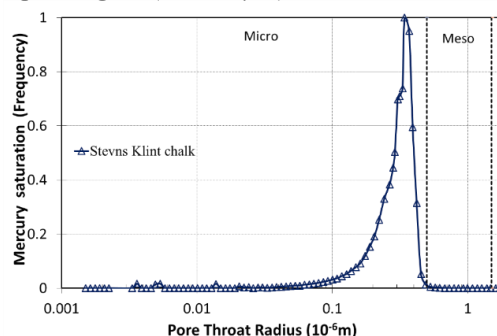

Figure 2. Pore size distribution in SK outcrop chalk.

The cores were retrieved from two blocks and were cleaned and restored as suggested by Puntervold et al [56]. They were initially cleaned with 5 pore volumes (PV) of de-ionized (DI) water to remove dissolvable salts, e.g., calcium sulphate salts that can affect initial core wettability [56]. Subsequently, all cores were dried at 90 °C until achieving constant weight. The main core properties are displayed in **Table 1**.

Table 1. Physical core properties of the SK outcrop material.

	Block 1			Block 2					
Core	B11	B12	B13	B24	B25	B26	B27	B28	B29
L (cm)	6.17	6.17	5.91	6.94	6.94	6.92	7.00	7.00	7.04
Ø(cm)	3.70	3.70	3.75	3.80	3.80	3.82	3.80	3.80	3.79
PV (ml)	30.8	26.5	27.3	38.3	39.9	37.7	37.3	38.8	38.5
Φ, %	46	41	42	49	50	48	47	48	49
K(md)	2.0	1.4	1.3	2.5	1.0	0.8	1.6	2.0	1.2

2.1.2 Brines

All brines were synthetically prepared from reagent grade chemicals purchased from Merck laboratories. Formation water (FW) composition is based on a North Sea chalk reservoir formation water. SW0T and SW½T were used in the chromatographic wettability experiments (CW) [35], these tests are performed at room temperature to minimize wettability alteration induced by sulphate on carbonate surfaces. Compositions are presented in **Table 2**.

Table 2. Brine properties and compositions.

Brines	FW	SW0T	SW½T
Ions	mM	mM	mM
Na^+	997	460	427
K^+	5	10	22
Li^+	0	0	12
Ca^{2+}	29	13	13
Mg^{2+}	8	45	45
Cl^-	1066	583	538
HCO_3^-	9	2	2
SO_4^{2-}	0	0	12
SCN^-	0	0	12
Ionic strength	1.112	0.643	0.644
TDS g/l	62.83	33.39	33.39

2.1.3 Crude oil

A crude oil stock solution was prepared by mixing reservoir crude oil and heptane in a volume ratio of 60/40, respectively; the reservoir crude oil had a low asphaltene content and no asphaltene precipitation was observed. The prepared model oil was filtered using a 5μm Millipore filter, its acid number (AN) and base number (BN) were quantified and the results shown that the AN was 1.8 mgKOH/g and the BN was 0.74 mgKOH/g. A fraction of the stock solution was treated with silica gel (10 wt. %) to remove polar organic components, this step was repeated after 4 days. The silica treated oil had an AN and BN of ~0 and 0.03 mgKOH/g, respectively. Three crude oils were prepared by mixing the model and treated oil with the objective of achieving the targeted AN and BN; Oil A, Oil B and Oil C, their crude oil properties are presented in **Table 3**.

Table 3. Chemical and physical crude oil properties

Crude Oil	AN mgKOH/g	BN mgKOH/g	μ at 25°C cP	ρ @ 25°C g/cm^3	Used in cores
Oil A	0.34	0.24	3.25	0.808	B11, B22
Oil B	0.36	0.30	2.52	0.807	B24, B25, B29
Oil C	0.50	0.23	2.36	0.807	B26, B27

The AN and BN quantification was carried out by potentiometric titration, using modified version of the ASTM 664 and ASTM 2898 [57]. The methods reproducibility is better than ± 0.02 mgKOH/g for both AN and BN analyses.

2.2 Analyses

2.2.1 Ion chromatography analyses SDR

A Dionex IC 3000 was used to analyze brine effluent samples. External standards were used for quantification of ionic concentrations.

2.3 Methods

2.3.1 Organic solvents for core cleaning

Two sets of organic solvents were used, a mild cleaning consisting of kerosene/heptane and the standard harsh cleaning with toluene/methanol. Kerosene and heptane have low aromaticity and reduced solvation power of larger oil components. On the other hand, toluene is known for being a strong solvent for heavy oil components and methanol acts as a solvent for both crude oil components and water.

The objective of using the mild core cleaning approach is to remove the residual oil in the core without inducing significant desorption of the adsorbed POC onto the rock surface, since they are the components establishing the original wetting of the core [58]. All solvents were reagent grade and purchased from Merck.

2.3.2 Core preparation

Initial core preparation

All chalk cores were initially flooded with 5 PV of distilled water (DI) with the objective of removing easily dissolvable salts. The presence of sulfate was qualitatively evaluated at the end of this cleaning stage to avoid wettability alteration of the carbonate surface by this ion. The cores were dried to constant bulk weight at 90 °C in an oven.

Core restoration

Initial water saturation, was established with FW at (S_{wi})=0.1, by using the desiccator technique [59]. After reaching the target weight, all cores were stored in a closed container for a minimum time of 72 hours to obtain a uniform distribution of ions within the porous media.

Crude oil saturations were carried out by putting the cores at S_{wi} = 0.1, in a Hassler core holder with a confining pressure of 20 bars and 10 bars of backpressure. A short vacuum was performed on the system to avoid trapped gas into the system. Then, the water-wet cores in the first restoration were oil flooded at the temperature of 50 °C and at an injection rate of 0.1 ml/min, 2.5 PVs were injected from both directions, this step helped to establish an initial wettability induced by crude oil adsorption.

With the objective of optimizing the restoration procedure and reproducing wettability, in the second restorations the crude oil exposure, was limited to (1-S_{wi}) PV of crude oil after establishing S_{wi} = 0.1.

Core aging was carried out for 2 weeks at the temperature of 50 °C. The cores were placed on marble balls in a closed aging cell containing crude oil, they were wrapped in Teflon tape to avoid adsorption of unrepresentative POC on the core surfaces [25]. The static aging process was chosen over dynamic aging to avoid additional crude oil exposure, which increases POC adsorption affecting wettability [18, 58].

2.3.3 Core cleaning

The cores flooded with crude oil were cleaned in a second restoration using two different of organic solvents. Mild cleaning uses kerosene and heptane, and the standard harsh cleaning uses toluene and methanol. The solvent cleaning process was initiated at S_{or}, i.e., at high water saturation to avoid transport of polar components to non-representative water-wet spots.

The cores from block 1 B11 and B12 were cleaned with 30 PV of solvents. B11 was mildly cleaned with 5 PV of low kerosene and 5 PV of heptane in three cycles. Core B12, was cleaned in the same way as core B11, but with toluene and methanol.

Cores from block 2 were only mildly cleaned by using 10 PV of kerosene and 5 PV of heptane, with a total amount of 15 PV of solvents injected.

To remove the last injected solvent and easily dissolvable salts; 5 PV of distilled water (DI) were flooded in each core. Then, the cores were dried to constant weight at 90°C to evaporate water and solvents.

2.3.4 Oil recovery by Spontaneous Imbibition (SI)

Spontaneous imbibition (SI) was the method chosen for oil recovery tests. The tests were carried out in glass Amott cells at 50 °C; FW was the imbibing fluid to avoid wettability alteration. Oil recovery was expressed as percentage of original oil in place (%OOIP), the values were logged against time until the recovery plateau was reached, the volumetric measurements had a precision of ± 0.05 ml. For water-wet outcrop the SI tests were carried out at 23 °C with distilled water as imbibing fluid and heptane as the organic phase.

2.3.5 Chromatographic wettability test (CW)

The chromatographic wettability tests (CW) was used as an additional way of measuring wettability, the test was

developed by Strand and co-workers [35], In this test, the cores are mounted into a Hassler core holder with a confining and back pressure of 20 and 10 bars, respectively. The test is performed at room temperature to hinder sulphate reactivity. An injection rate of 0.2 ml/min is used in the tests. A brine termed, SW0T, is injected until reaching residual oil saturation, S_{orw}. Then, a brine containing the non-reactive tracer, SCN^-, and sulphate, SO_4^{2-} is flooded, this brine is described as SW½T. Effluent samples are collected with an autosampler to be later analyzed by ion chromatography.

The CW test evaluates the water-wet surface area in the core sample by chromatographic separation of the non-adsorbing tracer, SCN^-, and the adsorbing sulphate ion. Then, the area in between the two elution curves is quantified, A_w, this area is proportional to the water-wet surface area of a carbonate core sample. Its reproducibility is ~5% [35]. A strongly water-wet reference core is used as main reference, in this core the area, (A_{ww}) was calculated to be, $A_{ww} = 0.251$. The CW tests provide a wettability index termed, I_{CW}. The index describes the water-wet fraction of a chalk surface, and is quantified with the following **Eq.1**:

$$I_{CW} = \frac{A_w}{A_{ww}} \qquad (1)$$

An index of $I_{CW} = 0$, represents a completely oil-wet surface area, whereas a, $I_{CW} = 1$ corresponds to a strongly water-wet surface area.

2.3.6 Wettability by spontaneous imbibition (SI)

Spontaneous imbibition (SI) is used to evaluate the active presence of capillary forces [60]. Description of the wetting state of the core comes from ultimate recovery and oil production profiles. An advantage of SI experiments is that they can be carried out at reservoir temperatures, reducing uncertainties associated to physical fluid properties, COBR interactions and core wettability.

When a SI test recovery from a strongly water-wet reference core is available, SI_{WWC}, in units of (%OOIP), a simplified wettability index, I_{W-SI}, can be calculated as expressed in **Eq.2**:

$$I_{W-SI} = \frac{SI_C}{SI_{WWC}} \qquad (2)$$

Where, SI_C is the oil recovery (%OOIP) from the tested core. As I_{W-SI} approaches *1* the core is categorized as strongly water-wet, and 0 for a fractional/neutral wet core [61].

3 Results and discussion

This work studies the effect of core cleaning and core restoration on carbonates core wettability. It pretends to show how different core cleaning systems may impact on core wettability. Outcrop chalk from SK is used for this purpose [54]. The outcrop chalk has also been reported to show similar behavior as reservoir limestone regarding wettability and wettability alteration processes [38, 62].

This experimental study has two main sections, the first one evaluates the effect of solvent cleaning on chalk

samples, the second one, proposes an optimized restoration method to reproduce wettability at core scale in chalk cores under spontaneous imbibition processes.

3.1 Impact of solvent selection on wettability

Two solvent cleaning methods are compared in this study: a mild cleaning procedure with kerosene-heptane against the classical harsh cleaning with toluene-methanol. Wettability was measured by SI and CW tests to quantify the cleaning effect on previously crude oil-wetted chalk cores. The effect on a second core restoration process was also tested.

3.1.1 Water-wet outcrop chalk

Initial wettability of a strongly water-wet outcrop chalk core was measured by SI; the chromatographic separation was also measured in a CW test. A strongly water-wet reference core retrieved from block 2 was termed B28. Initial water saturation, $S_{wi} = 0.1$, heptane was used in the SI test as oil phase. A CW test was carried out on a 100% water saturated core. The SI and CW results are presented in **Fig. 3**.
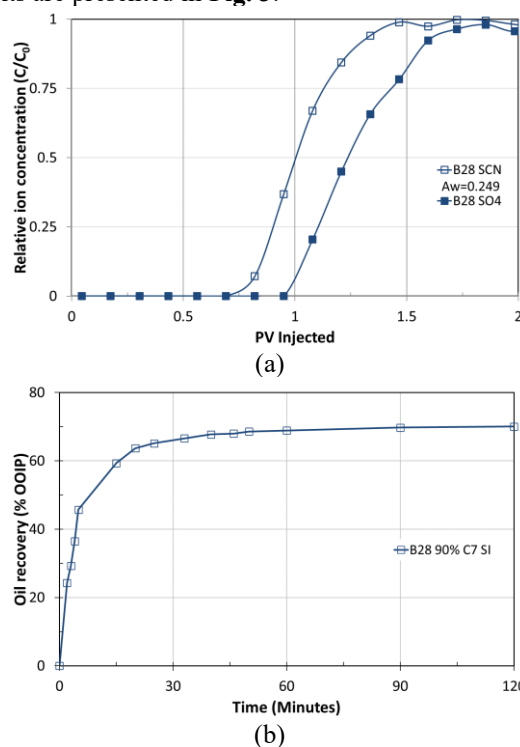

(a)

(b)

Figure 3. Wettability of water-wet core B28 (a) SI test carried out at 23°C using DI water as FW. Core B28 with $S_{wi} = 0.1$ and heptane (b) CW test on the 100 % water saturated B28 core.

Strongly water-wet behavior is confirmed by both wettability tests. SI tests showed strong positive capillary forces for core B28, the recovery plateau of 70 %OOIP was reached after 1 hour, as seen in **Fig. 3a**. The CW test resulted in an area between the tracer and sulphate curves of $A_{ww} = 0.249$, **Fig. 3b,** this correspond to a chromatographic index, $I_{CW} = 1$.

Parallel SI and CW tests were carried out in the strongly water wet core B13, this core was retrieved from block 1. The SI test performed in B13 was done with 100% heptane saturation, the experiment showed evidence of highly active capillary forces, a 75 %OOIP of oil was recovered in less than 30 minutes, validating the strongly

water-wet behavior. The test showed an area of $A_{ww}=0.251$, in line with a strongly water-wet case of block 2. Both results are used in respective wettability indexes calculations. Notice that initial water saturation was different in the cores from the different blocks, this had a consequence in the ultimate oil recovery observed for similar systems. The results are presented in **Tables 4-5**.

3.1.2 Initial wetting conditions by crude oil exposure

The cores B11 and B12 retrieved from block 1, were restored with $S_{wi} = 0.1$ and crude oil flooded with 5PV of Oil A, prior aging. SI tests were performed at 50 °C using formation water (FW) as imbibing fluid. The oil recovery plateau for cores B11 and B12 were achieved after 8 to 10 days, ultimate oil recoveries were 8 and 10 %OOIP, respectively; validating the chalk material reproducibility.

Chromatographic wettability tests were performed after the spontaneous imbibition tests to evaluate the water-wet fraction of the cores surface area. The water-wet surface areas were similar, $A_w = 0.118$ for B11 and $A_w = 0.124$ for B12. Therefore, the water-wet fraction of the surface area, **Eq.1**, was $I_{CW} = (0.118/0.251) = 0.47$ for core B11, and $I_{CW} = (0.124/0.251) = 0.49$ for core B12. The values point to a fractional/neutral wettability for the CW test [35].

By using the modified water index I_{W-SI} (**Eq.2**), the core B11 had a water index of 0.10 and 0.13 for core B12. Both cores were flooded with 5 PV of crude Oil A. Both the CW tests and the SI test results confirm similar cores wetting states.

3.1.3 Mild cleaning kerosene/heptane vs. harsh and conventional toluene/methanol cleaning.

After confirming core wettability in the previous step, both cores were solvent cleaned before undergoing a new core restoration procedure. Each core was subjected to a different solvent cleaning method. Core B11 was cleaned by injecting 5 PV of kerosene (K) and 5 PV of heptane (C_7/H), this process was executed in 3 cycles. Core B12, was cleaned in the same fashion but this time using toluene (T) and methanol (M). After completing the core cleaning stage new SI and CW tests were performed on both cores.

The mildly cleaned core, B11 increased its water-wet fraction to $I_{CW} = (0.150/0.251) = 0.60$, and the harshly cleaned core B12 increased its water wet fraction to $I_{CW} = (0.165/0.251) = 0.66$. Therefore, both solvents removed POC components from the chalk surface. However, the mildly cleaned core cleaning increased its I_{CW} by 13%, whereas the harshly cleaned core increased its I_{CW} by a 17%.

From the CW tests, it was found that after the lengthy solvent flooding, 40% and 34% of the rock surfaces were covered by oil components, hindering SO_4^{2-} ions reactivity towards the carbonate surface. The consequence was that completely water-wet carbonate surfaces in both cases were not obtained.

After the tests, active capillary forces were investigated by SI tests. The cores were flooded with 5 PV of DI water to remove the CW test brines. The cores where then dried, and vacuum-saturated with heptane without any prior initial water saturation. The SI tests were run at 23 °C with DI as imbibing fluid.

The mildly cleaned core achieved an ultimate recovery of 27 %OOIP. Thus, capillary forces in B11 core had increased after mild cleaning, showing to some extent a more water-wet state. The CW test also showed a slight increase in the water-wet surface area.

The harsh cleaning resulted in a more efficient removal of POC from the chalk surface. With a recovery plateau of 62 %OOIP reached in 5 hours, a very water-wet behavior was displayed [60]. This occurred even though 34% of the rock surface was covered with adsorbed organic material.

The spontaneous imbibition water index, I_{W-SI}, for the mildly cleaned core B11 increased to 0.36, and for the harshly cleaned core B12 the index raised to 0.82, showing major changes in positive capillary forces after the harsh cleaning with toluene and methanol.

From the experimental results it seems that the process of activation or deactivation of capillary forces is not only associated to the water-wet area of the core or by the covered areas with crude oil POCs. From the results it can be deduced that the superficial distribution of the adsorbed POC is crucial. This means that adsorption-desorption processes of POC in pore throats will have a greater influence on the activation-deactivation of capillary forces than when the process occurs onto its pore bodies. In other words, the fluid connectivity from water-wet and oil-wet spots is different due to the different cleaning processes, being B11 less even in terms of water-wet spots in comparison to B12.

SI tests confirmed that extensive toluene-methanol injection removes POC at specific places affecting capillary forces. The consequence of this, is that increased imbibition rates and ultimate oil recovery are achieved, in despite of observing minimum changes in the water-wet surface area quantified by the CW test.

The mild kerosene-heptane core cleaning appears to preserve more adsorbed POC, thus, preserving the initial wettability in a greater degree than the harsh cleaning with toluene and methanol.

3.1.4 Cleaning effect on a second core restoration

The different cleaning methods effects on wettability were compared on a second restoration. The cores B11 and B12 were equally restored for comparison purposes, initial water saturation was established at $S_{wi} = 0.1$ and 5 PV Oil A were flooded in the cores before aging. SI tests at 50 °C were performed using FW as imbibing brine.

The observed crude oil recoveries by SI, were 3 and 12 %OOIP respectively, compared to 8 and 10 %OOIP after the first restoration. The mildly cleaned core behaved this time less water wet than the harshly cleaned core B12. SI water indexes, I_{W-SI}, reduced for core B11 from 0.10 to 0.04 and increased for core B12 from 0.13 to 0.16.

Thus, further crude oil POC adsorption on a mixed wet core appears to reduce its original water-wetness degree. Effects on crude oil exposure and had been previously reported on carbonates [23, 58, 63].

On the other hand, the harshly cleaned core B12 and equally restored, behaved more water wet than core B11,

with a water index, I_{W-SI} = 0.16 in comparison to 0.04 for core B11.

In summary, the amount of crude oil exposure and polar components being adsorbed on the carbonate surfaces can significantly affect core wettability in a restoration procedure.

The results suggest that the harsh cleaning with toluene and methanol will remove in a greater extent POC from carbonate mineral surfaces, inducing a significant change in the original wettability towards the water-wet region.

However, it is of high importance to know that the sampled crude oil used in core restoration can be completely different from the one that originally wetted the reservoir as stated by Puntervold (2008).

Thereby, to improve the efficiency of a core restoration protocol to get closer to a representative reservoir wettability it is required to preserve on the mineral surfaces as much as possible of the originally adsorbed crude oil POC. Furthermore, reducing the amount of oil exposed in the restoration process can avoid reducing changing wettability towards a less water-wet state. A general summary of the experimental data is presented below in **Tables 4 and 5**.

Table 4. SI results

Core	Solvent	SI		
		SI-R1 (%OOIP)	SI$_{C7}$-AS* (%OOIP)	SI-R2 (%OOIP)
B11	K/H	8	27	3
B12	T/M	10	62	12
B13	-	75	-	-

*AS - After-solvent cleaning

Table 5. CW test results summary

Core	Solvent	CW			
		A_w-R1	I_{CW}-R1	A_w-AS*	I_{CW}-AS*
B11	K/H	0.118	0.47	0.150	0.60
B12	T/M	0.124	0.49	0.165	0.66
B13	-	0.251	1	-	-

3.2 Reproducing initial core wettability in mildly cleaned cores

The next section aims to optimize the most important restoration parameters to preserve core wettability. From the previous section it can be concluded that the mild cleaning was more efficient in retaining original POC components on the rock surfaces, and that limiting the amount of kerosene heptane flooded to a minimum injection volume can contribute to preservation of the initial wettability. Another important point is that crude oil should not be flooded extensively, otherwise wettability will also be changed.

For these reasons the proposal for improving the restoration protocol, includes a mild cleaning process with kerosene and heptane. The experimental evidence indicates that by using the mild cleaning method, a minimum amount of oil injected is then required to complete a satisfactory restoration process. As early mentioned, the crude oil available for restoration can significantly differ in composition from the initial oil responsible for generating the original reservoir

wettability. Thus, preserving original POC adsorbed is crucial for achieving a more representative core wettability.

3.2.1 Establishing initial wettability

Four chalk cores were restored with the same procedure, the first two cores were exposed to oil B and the other two to Oil C. The two first chalk cores, B24 and B25, were restored at Swi = 0.1 with FW, and flooded with 5 PV of Oil B prior aging. Their initial wettability was quantified by SI at 50 °C, FW was used as imbibing fluid. A CW test was carried out afterwards to verify crude oil adsorption. The oil recovery tests results are shown in **Fig. 4**.
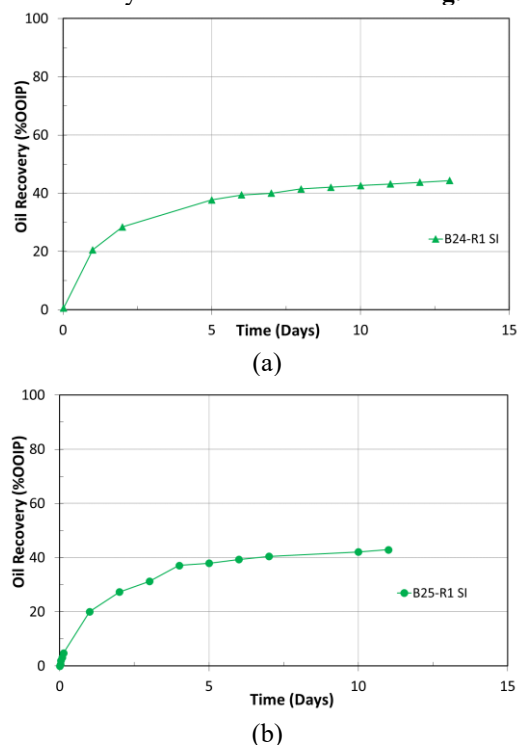

(a)

(b)

Figure 4. Initial core wetting measured by SI at 50 °C using FW as imbibing fluid (a) Core B24 and (b) core B25. Cores restored with S_{wi} = 0.1 (FW) and 5 PV of Oil B prior aging.

Ultimate oil recovery for the core plugs B24 and B25 was reached after 7 to 10 days, with 44 and 43 %OOIP, respectively. Confirming the high reproducibility of the initial core wettability and restoration protocol. The results of the CW tests showed different chromatographic separation areas, A_w = 0.230 and A_w = 0.188 for B24 and B25 respectively, **Fig. 5**. Please note that both areas were lower than strongly water wet measured areas, A_{ww} = 0.249, the results confirm a water-wet surface reduction after oil exposure.

The cores, B26 and B27, were equally restored. However, Oil C with AN=0.50 and BN=0.23 mgKOH/g was used. A higher AN number is meant to reduce the initial core wettability, as reported by Standnes and Austad [25].
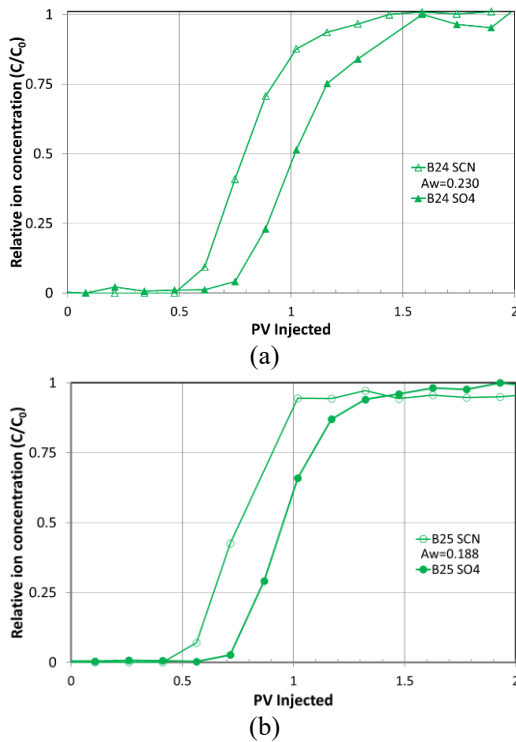
(a)

(b)

Figure 5. Chromatographic wettability tests (a) Core B24 and (b) core B25.

Ultimate recoveries of 25 and 37 (%OOIP) were reached for cores B26 and B27, respectively, **Fig. 6(a-b)**. In this case, core wettabilities were slightly different, even though a general less water-wet state was observed in comparison with the cores that were exposed to Oil B with lower AN, this is in line with the experimental expectations.
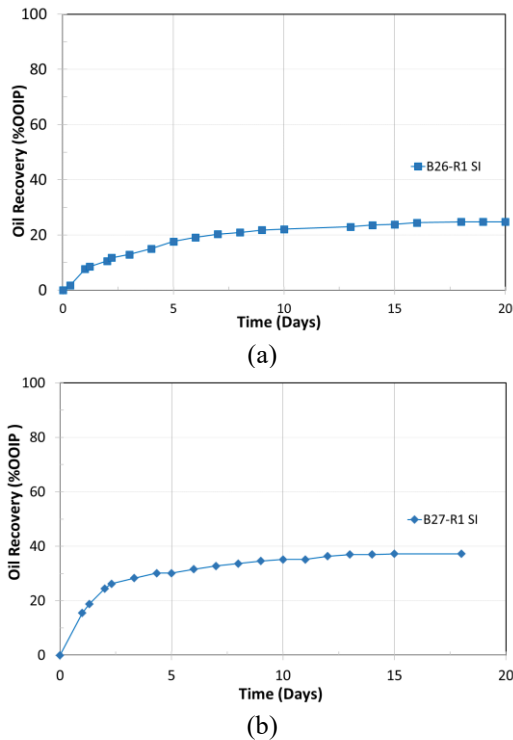

(a)

(b)

Figure 6. Initial wettability by SI at 50 °C using FW as imbibing fluid. (a) Core B26 and (b) core B27. Cores restored with S_{wi} = 0.1 FW and exposed to 5 PV Oil C before aging.

The CW tests showed similar chromatographic separation areas. The measured areas were, A_w = 0.203 and A_w = 0.205 for B26 and B27, respectively. The quantified water-wet fractions areas were 0.81 and 0.82, which is classified as a water-wet state.
The slightly different behavior in cores B26 and B27 can be possible attributed to heterogeneity associated to the core plugs structure, i.e. microfractures or slightly different porous media structure.
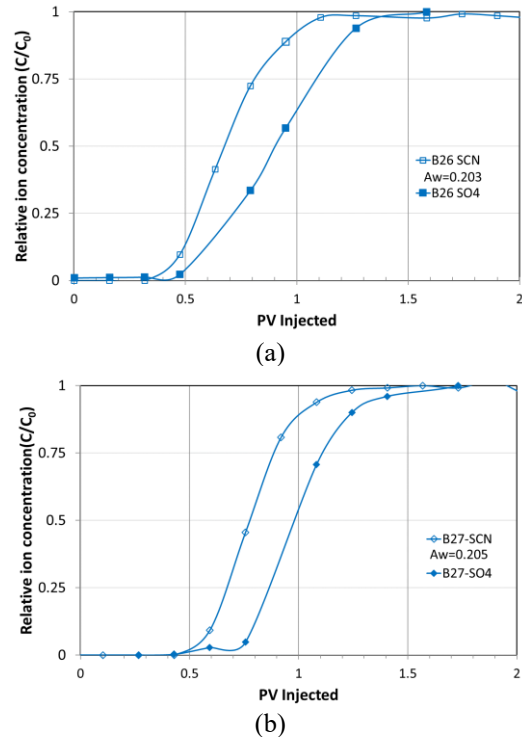

(a)

(b)

Figure 7. CW tests (a) Core B26 and (b) core B27.

All 4 cores exposed oil B or C for 5 PV altered their wettability to a fractional wet state. However, in the cores saturated with oil C differences were observed, these differences can be attributed to pore distribution, microfractures or variation in rock mineralogy and surface reactivity from core to core. In summary, the cores flooded with Oil C with higher AN, were less water-wet than the cores flooded with Oil B.

3.2.2 Optimized core restoration for wettability reproduction at core scale for chalk cores

Mild cleaning preserved more of the adsorbed POC on the mineral surface. Furthermore, the harsh toluene-methanol cleaning has a higher solvation power to remove POC, even at room temperature, the harsh cleaning method removes original polar components from the surface very effectively. As these adsorbed components dictate the original core wetting, one can assume that valuable information is lost by using this method.

In addition, the amount of crude oil injected in the second restoration process had an significant effect on wettability, as reported by Hopkins et al [13].

Taking into account these facts, our proposal to improve the restoration process in chalk cores is based on the following simple assumptions: (1) Mild cleaning is more suitable to preserve wettability, (2) Minimization of the mild solvent floods can help to preserve more

adsorbed POC on the carbonate mineral surfaces, (3) If the POC are preserved during cleaning, a minimum amount of crude oil should be required for an optimum core restoration.

To test these ideas, the four initially restored outcrop cores from block 2 (B24-B27) were subjected to the following second restoration procedure (R2):

1. The cores will undergo a mild solvent cleaning with kerosene and heptane. A limited amount of kerosene (10PV) is injected; in the same way only 5 PV of heptane are used. This step is followed by 5 PV of distilled water to evacuate the resident solvents, then the cores are dried until achieving constant weight.
2. Establishment of initial water saturation, in this case, $S_{wi} = 0.1$, with FW by using the desiccator technique.
3. Once initial water saturation is established, the core is vacuum-saturated at $S_{wi} = 0.1$, with $(1-S_{wi})$ PV of the same crude oil used in the prior restoration.
4. The core is aged at the test temperature for 2 weeks.
5. Spontaneous imbibition test is carried out with FW in the same temperature conditions as before (50 °C).

The spontaneous imbibition results of the first and second restoration using the mild cleaning with limited solvent injection and minimum crude oil exposure are presented in **Fig. 8**.

The oil recovery displayed in the SI tests, showed minimum differences between the first and second restoration with the proposed cleaning and restoration method, Δ *SI,* ranged between + 1.5 to + 3.6 %OOIP. The water-wetness degree was measured using the wettability water index based on spontaneous imbibition, I_{W-SI}, **Eq. 2**.

Cores B24 and B25 saturated with Oil B were quite similar, with a 44.4 % for B24 and 42.9 %OOIP for B25. Both resulted in similar water indexes, I_{W-SI}, of 0.63 and 0.61 respectively. After the optimized cleaning and restoration procedures, for both cores the oil recovery slightly increased and the water indexes, $I_{W-SI,}$ obtained were of 0.68 and 0.67 respectively.

For the cores exposed to Oil C, ultimate recoveries were 24.7 for B26 and 37.2 %OOIP for B27. Such differences were attributed to porous media heterogeneity. Despite the differences observed, the second restorations (R2) reproduced closely the initial wetting before cleaning, confirming that the strategy of cleaning and restoration for chalk cores is relatively effective. Core B26 slightly increased its water index by SI, $I_{W-SI,}$ from 0.35 to 0.40, whereas core B27 water index, I_{W-SI}, had a minor drop from 0.53 to 0.51.

To validate the idea that suggests that an increased oil exposure reduces the cores water-wetness. A core was exposed to 5 PV of Oil B instead of 0.9 PV or $(1-S_{wi})$ PV during the second restoration after a mild cleaning process with 10 PV of kerosene and 5 PV of heptane.
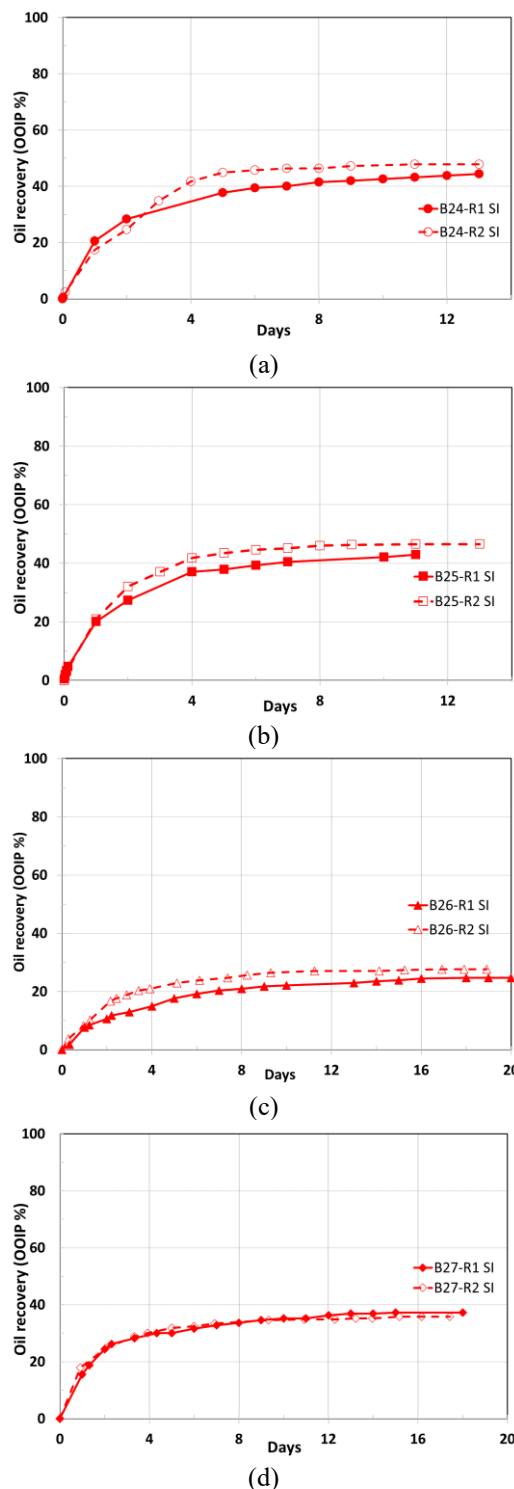

(a)

(b)

(c)

(d)

Figure 8. Oil recovery experiments by SI, $T_{tests}=50$ °C after initial restoration (R1) and a second restoration (R2) after optimized cleaning and restoration process. Cores restored with $S_{wi} = 0.1$. (a) Core B24 and (b) Core B25 exposed to Oil B (AN = 0.36 mgKOH/g). (c) Core B26 and (d) Core B27 exposed to Oil C (AN = 0.5 mgKOH/g).

Thus, the cleaning and restoration processes were equal to the rest of the cores. In **Fig. 9**, oil recovery by SI tests after R1 and R2 were compared. SI from the initially restored core (R1) gave a recovery of 41.5 %OOIP, which was similar to the recoveries observed from cores B24 and

B25 in their first restoration. Cores B24, B25 and B29 were saturated with Oil B.
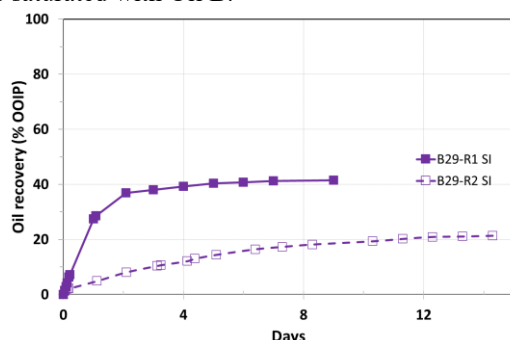

Figure 9. SI tests performed at 50 °C after the initial restoration (R1) and the second restoration (R2) o core B29. During R1 the core was exposed to 5 PV Oil B with AN = 0.36 mgKOH/g. After mild cleaning the core was exposed to another 5 PV of Oil B in R2.

After the mild cleaning with kerosene and heptane, core B29 was restored in a second restoration (R2) with S_{wi} = 10%, and 5 PV of Oil B. Ultimate oil recovery was reduced to 21.0 %OOIP after the second restoration. This represents a significant reduction of 20.5% OOIP, the result confirms a significant drop in the water-wetness of the core due to the increased exposure to Oil B in the second restoration. The water wetting index by SI, I_{W-SI}, dropped from 0.59 to 0.30. The results confirmed the results obtained by Hopkins et al [13].

A summary of SI and CW data before and after mild core cleaning is presented in **Tables 6-7**.

Table 6. Data summary after initial (R1)

Core	SI_{R1} %OOIP	$I_{W-SI-R1}$	I_{CW-R1}
B24	44.4	0.63	0.92
B25	42.9	0.61	0.75
B26	24.7	0.35	0.81
B27	37.2	0.53	0.82
B28	70.0	1.0	1.0
B29	41.5	0.59	-

Table 7. Data summary after second core restorations (R2) and changes in recovery and wettability in relation to (R1).

Core	SI_{R2} %OOIP	$I_{W-SI-R2}$	ΔSI %OOIP	ΔI_{W-SI}
B24	47.8	0.68	+ 3.5	+ 0.05
B25	46.6	0.67	+ 3.6	+ 0.05
B26	27.7	0.40	+ 3.0	+ 0.04
B27	35.8	0.51	+ 1.5	+ 0.02
B28	-	-	-	-
B29	21.0	0.30	- 20.5	- 0.29

4 Conclusion

This study compared the effect of two solvent cleaning methods on initially water wet chalk cores exposed to crude oil. The solvent systems studied were harsh cleaning with toluene and methanol, and a mild cleaning method with kerosene and heptane. The effects on wettability were measured by spontaneous imbibition and chromatographic wettability tests.

Oil recovery and capillary forces increased after cleaning the chalk cores with both systems. The harsh cleaning method resulted in higher ultimate oil recoveries than the mild cleaning. Thus, the toluene and methanol system appeared to have a greater solvation effect on the adsorbed POC on the chalk mineral surfaces.

The results suggested that the distribution of adsorbed POC on mineral surfaces is crucial in the activation or deactivation of capillary forces. Apparently, POC adsorbed at pore throats will have a greater impact on wettability than POC adsorbed onto pore bodies. Increased oil recovery together with highly efficient positive capillary forces were observed, even though minor changes were observed in the water-wet fraction measured by the CW tests. The combination of both spontaneous imbibition tests and chromatographic wettability experiments was crucial for this observation.

An injection of 5 PV of crude oil into a mildly cleaned core, showed reduced ultimate oil recovery compared to the first restoration. This effect did not allow the desired wettability reproduction to occur.

Reproduction of initial wettability after mild cleaning was successfully achieved by injecting $(1-S_{wi})$ PV of crude oil by vacuum-saturation. SI tests at 50 °C resulted in an adequate match between the oil production profiles before and after using the optimized cleaning and restoration procedure. Differences of +1.5 - 3.6% OOIP were observed.

Minimizing solvent injection by kerosene and heptane reduced POC desorption from mineral surfaces that established the initial core wettability. In consequence the crude oil required to restore and reproduce the chalk cores wettability was reduced to $(1-S_{wi})$ PV.

The suggested cleaning and restoration procedure could potentially help to get closer to reservoir wettability in carbonate cores with similar mineralogy as chalk. The method can have a positive impact for wettability dependent SCAL analyses, which is critical for reservoir characterization studies.

Nomenclature
- AN   Acid Number, mg KOH/g
- ASTM American Society for Testing and Materials
- A_w Water-wet surface area of a core sample, from chromatographic test
- A_{ww} Water-wet surface area of a completely water-wet reference core sample
- BN   Base number, mg KOH/g
- C/Co   Relative concentration of ion in effluent fractions
- C_7 Heptane
- DI   Deionized water
- FW   Formation water
- H   Heptane
- I_{CW} The fraction of water-wet surface area of a core sample
- K   Kerosene

- L Core length
- M Methanol
- mM milli-Molar ($10 \, mol^{-3}/L$)
- OOIP Original oil in place
- PV Pore volume, mL
- R-COO⁻ Carboxylate
- SCAL Special core analysis
- SK Stevns Klint
- S_{orw} Residual oil saturation after waterflood
- S_{wi} Initial water saturation, % PV
- SW0T Sea water without thiocyanate tracer and sulphate
- SW½T Seawater that contains thiocyanate tracer and sulphate
- T Toluene
- TDS Total Dissolved Salt, mg/L
- Φ Core Porosity
- Ø Diameter
- ρ_{sat} Density of saturation fluid, g/cm^3
- μ Dynamic viscosity, mPa.s

References

1. Khishvand, M., A.H. Alizadeh, and M. Piri, In-situ characterization of wettability and pore-scale displacements during two- and three-phase flow in natural porous media. Advances in Water Resources, (2016). **97**: p. 279-298.

2. Cockcroft, P.J., D.R. Guise, and I.D. Waworuntu, *The Effect of Wettability on Estimation of Reserves*, in *SPE Asia-Pacific Conference*. (1989), Society of Petroleum Engineers: Sydney, Australia. p. 10.

3. Alhammadi, A.M., et al., *In situ Wettability Measurement in a Carbonate Reservoir Rock at High Temperature and Pressure*, in *Abu Dhabi International Petroleum Exhibition & Conference*. (2017), Society of Petroleum Engineers: Abu Dhabi, UAE. p. 13.

4. Al-Hilali, M.M., et al., *A Novel Evaluation of In-Situ Wettability in IRAQi Oil Fields; Case Studies*, in *SPE Russian Petroleum Technology Conference and Exhibition*. (2016), Society of Petroleum Engineers: Moscow, Russia. p. 14.

5. Maas, J., et al., *Advanced Core Measurements "Best Practices" for Low Reservoir Quality Chalk*, in *JCR-7 LRQC Best Practices Manual 1st Edition*, SCA, Editor. (2014).

6. McPhee, C., J. Reed, and I. Zubizarreta, *Core analysis: a best practice guide*. Developments in Petroleum Science ed. J. Cubitt. **Vol. 64**. (2015), Amsterdam, Netherlands: Elsevier.

7. Anderson, W.G., *Wettability literature survey- part 1: rock/oil/brine interactions and the effects of core handling on wettability.* Journal of Petroleum Technology, (1986). **38**(10): p. 1125-1144.

8. Wendell, D.J., W.G. Anderson, and J.D. Meyers, *Restored-State Core Analysis for the Hutton Reservoir.* SPE Formation Evaluation, (1987). **2**(04): p. 509-517.

9. Soltani, P., et al., *Quantitative Monitoring of Cleaning Time and Wettability Alteration of Carbonate Rocks During Soxhlet Cleaning.* SPE Reservoir Evaluation & Engineering, (2019). **22**(04): p. 1334-1345.

10. Cuiec, L.E., *Restoration of the natural state of core samples - SPE 5634*, in *The 50th annual fall meeting of the Society of Petroleum Engineers of AIME*. (1975): Dallas, TX, USA.

11. Kovalev, K., et al., *Aged Carbonate Cores Wettability Verification*, in *SPE Russian Petroleum Technology Conference and Exhibition*. (2016), Society of Petroleum Engineers: Moscow, Russia. p. 18.

12. Shariatpanahi, S.F., et al., *Wettability restoration of limestone cores using core material from the aqueous zone.* Petroleum Science and Technology, (2012). **30**(1-9).

13. Hopkins, P.A., et al., *Crude Oil Quantity and Its Effect on Chalk Surface Wetting.* Energy & Fuels, (2017). **31**(5): p. 4663-4669.

14. Fjelde, I., A.V. Omekeh, and M. Wetrhus Minde. *Removal of mud components from reservoir sandstone rocks.* in *Symposium of the Society of Core Analysts held in St. John's Newfoundland and Labrador, Canada.* (2015). St. Jhon's Newfoundland and Labrador, Canada.: SCA.

15. Puntervold, T., *Waterflooding of carbonate reservoirs - EOR by wettability alteration.* (2008), University of Stavanger, Norway. ISBN 978-82-7644-347-9: PhD Thesis.

16. Shimoyama, A. and W.D. Johns, *Formation of alkanes from fatty acids in the presence of CaCO₃.* Geochimica et Cosmochimica Acta, (1972). **36**(1): p. 87-91.

17. Shimoyama, A. and W.D. Johns, *Catalytic Conversion of Fatty Acids to Petroleum-like Paraffins and their Maturation.* Nature Physical Science, (1971). **232**(33): p. 140-144.

18. Hopkins, P., et al., *Adsoprtion of acidic crude oil components onto outcrop chalk at different wetting conditions during both dynamic adsorption and aging processes.* Energy & Fuels, (2016). **30**(9): p. 7229-7235.

19. Guo, H., et al., *Review of capillary number in chemical enhanced oil Recovery*, in *Paper SPE 175172 presented at the 2015 Oil and Gas Show and Conference*, SPE, Editor. (2015), Society of Petroleum Engineers: Mishref, Kuwait.

20. Abeysinghe, K.P., I. Fjelde, and A. Lohne, *Dependency of remaining oil saturation on wettability and capillary number* in *Paper SPE-160883 presented at the 2012 SPE Technical symposium and Exhibition*. (2012), Society of Petroleum Engineers: Al-Khobar, Saudi Arabia.

21. Fulcher, R.A., Jr., T. Ertekin, and C.D. Stahl, *Effect of capillary number and its constituents on two-phase relative permeability curves.* Journal of Petroleum Technology, (1985). **37**(2): p. 249-260.

22. Mjos, J.E.S., et al., *Effect of Initial Wetting on Smart Water Potential in Carbonates*, in *Paper presented at the 2018 SPE EOR Conference at Oil and Gas West Asia*. (2018), Society of Petroleum Engineers: Muscat, Oman. p. 13.

23. Klewiah, I., et al., *Adsorption of Crude Oil Polar Components onto Silica-Rich Chalk and its Impact on Wetting*, in *SPE Norway One Day Seminar*. (2019), Society of Petroleum Engineers: Bergen, Norway. p. 15.

24. Zhang, P. and T. Austad, *The relative effects of acid number and temperature on chalk wettability*, in *Paper SPE 92999 presented at the SPE International Symposium on Oilfield Chemistry*. (2005), Society of Petroleum Engineers (SPE), Richardson, TX 75083-3836, United States: Houston, TX, USA. p. 185-191.

25. Standnes, D.C. and T. Austad, *Wettability alteration in chalk. 1. Preparation of core material and oil properties.* Journal of Petroleum Science and Engineering, (2000). **28**(3): p. 111-121.

26. Madsen, L. and I. Lind, *Adsorption of Carboxylic Acids on Reservoir Minerals From Organic and Aqueous Phase.* SPE Reservoir Evaluation & Engineering, (1998). **1**(01): p. 47-51.

27. Graue, A., B.G. Viksund, and B.A. Baldwin, *Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk.* SPE Reservoir Evaluation & Engineering, (1999). **2**(02): p. 134-140.

28. Standal, S., et al., *Effect of polar organic components on wettability as studied by adsorption and contact angles.* Journal of Petroleum Science and Engineering, (1999). **24**(2): p. 131-144.

29. Madsen, L., et al., *Adsorption of polar aromatic hydrocarbons on synthetic calcite.* Organic Geochemistry, (1996). **24**(12): p. 1151-1155.

30. Karoussi, O., et al., *AFM study of calcite surface exposed to stearic and heptanoic acids.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, (2008). **325**(3): p. 107-114.

31. Puntervold, T., S. Strand, and T. Austad, *Water flooding of carbonate reservoirs: effects of a model base and natural crude oil bases on chalk wettability.* Energy & Fuels, (2007). **21**(3): p. 1606-1616.

32. Masalmeh, S.K. and X.D. Jing, *Improved characterisation and modelling of carbonate reservoirs for predicting waterflood performance*, in *Paper IPTC 11722 presented at the International Petroleum Technology Conference*. (2007): Dubai U.A.E.

33. Agbalaka, C.C., et al., *Coreflooding studies to evaluate the impact of salinity and wettability on oil recovery efficiency.* Transport in Porous Media, (2009). **76**(1): p. 77-94.

34. Austad, T., et al., *New method to clean carbonate reservoir cores by seawater*, in *Paper SCA2008-15 presented at the International Symposium of the Society of Core Analysts*. (2008): Abu Dhabi, U.A.E.

35. Strand, S., D.C. Standnes, and T. Austad, *New wettability test for chalk based on chromatographic separation of SCN⁻ and SO₄²⁻.* Journal of Petroleum Science and Engineering, (2006). **52**: p. 187-197.

36. Austad, T., et al., *Seawater as IOR Fluid in Fractured Chalk*, in *SPE International Symposium on Oilfield Chemistry*. (2005), Society of Petroleum Engineers: The Woodlands, Texas. p. 10.

37. Austad, T., et al., *Seawater in Chalk: An EOR and Compaction Fluid.* SPE Reservoir Evaluation & Engineering, (2008). **11**(04): p. 648-654.

38. Ravari, R.R., *Water-Based EOR in Limestone by Smart Water*, in *Institute of Petroleum Engineering*. (2011), University of Stavanger, Norway: Stavanger, Norway.

39. Song, J., et al., *Effect of salinity, Mg2+ and SO42– on "smart water"-induced carbonate wettability alteration in a model oil system.* Journal of Colloid and Interface Science, (2020). **563**: p. 145-155.

40. Al-Shalabi, E.W. and K. Sepehrnoori, *A comprehensive review of low salinity/engineered water injections and their applications in sandstone and carbonate rocks.* Journal of Petroleum Science and Engineering, (2016). **139**: p. 137-161.

41. Tetteh, J.T., et al., *Surface Reactivity Analysis of the Crude Oil–Brine–Limestone Interface for a Comprehensive Understanding of the Low-Salinity Waterflooding Mechanism.* Energy & Fuels, (2020). **34**(3): p. 2739-2756.

42. Bertolino, S.A.R., et al. *Mineralogy, geochemistry and isotope geochemistry to reveal fluid flow process in flooded chalk under long term test conditions for EOR purposes.* in *XV International Clay Conference, Brasil.* (2013).

43. Fabricius, I.L. and M.K. Borre, *Stylolites, porosity, depositional texture, and silicates in chalk facies sediments. Ontong Java Plateau–Gorm and Tyra fields, North Sea.* Sedimentology, (2007). **54**(1): p. 183-205.

44. Hjuler, M.L. and I.L. Fabricius, *Engineering properties of chalk related to diagenetic variations of Upper Cretaceous onshore and offshore chalk in the North Sea area.* Journal of Petroleum Science and Engineering, (2009). **68**(3): p. 151-170.

45. Skovbjerg, L.L., et al., *Nano sized clay detected on chalk particle surfaces.* Geochimica et Cosmochimica Acta, (2012). **99**: p. 57-70.

46. Andersen, P.Ø., et al., *Comparative Study of Five Outcrop Chalks Flooded at Reservoir Conditions: Chemo-mechanical Behaviour and Profiles of Compositional Alteration.* Transport in Porous Media, (2018). **121**(1): p. 135-181.

47. Megawati, M., M.V. Madland, and A. Hiorth, *Mechanical and physical behavior of high-porosity chalks exposed to chemical perturbation.* Journal of Petroleum Science and Engineering, (2015). **133**: p. 313-327.

48. Røgen, B. and I.L. Fabricius, *Influence of clay and silica on permeability and capillary entry pressure of chalk reservoirs in the North Sea.* Petroleum Geoscience, (2002). **8**(3): p. 287-293.

49. Fernø, M.A., et al., *Use of Sulfate for Water Based Enhanced Oil Recovery during Spontaneous Imbibition in Chalk.* Energy & Fuels, (2011). **25**(4): p. 1697-1706.

50. Strand, S., et al., *Wettability of chalk: impact of silica, clay content and mechanical properties.* Petroleum Geoscience, (2007). **13**(1): p. 69-80.

51. Skovbjerg, L.L., et al., *Preferential Adsorption of Hydrocarbons to Nanometer-Sized Clay on Chalk Particle Surfaces.* Energy & Fuels, (2013). **27**(7): p. 3642-3652.

52. Andersson, M.P., et al., *Infrared Spectroscopy and Density Functional Theory Investigation of Calcite, Chalk, and Coccoliths—Do We Observe the Mineral Surface?* The Journal of Physical Chemistry A, (2014). **118**(45): p. 10720-10729.

53. Bovet, N., et al., *Interaction of alcohols with the calcite surface.* Physical Chemistry Chemical Physics, (2015). **17**(5): p. 3490-3496.

54. Frykman, P., *Spatial variability in petrophysical properties in Upper Maastrichtian chalk outcrops at Stevns Klint, Denmark.* Marine and Petroleum Geology, (2001). **18**(10): p. 1041-1062.

55. Fathi, S.J., T. Austad, and S. Strand, *Effect of water-extractable carboxylic acids in crude oil on wettability in carbonates.* Energy & Fuels, (2011). **25**(6): p. 2587-2592.

56. Puntervold, T., S. Strand, and T. Austad, *New method to prepare outcrop chalk cores for wettability and oil recovery studies at low initial water saturation.* Energy & Fuels (2007). **21**(6): p. 3425-3430.

57. Fan, T. and J. Buckley, *Acid number measurements revisited - SPE 99884.* SPE Journal, (2007). **12**(4).

58. Hopkins, P., T. Puntervold, and S. Strand, *Preserving initial core wettability during core restoration of carbonate cores*, in *The International Symposium of the Society of Core Analysts*. (2015): St. John's Newfoundland and Labrador, Canada.

59. Springer, N., U. Korsbech, and H.K. Aage, *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*, in *Paper presented at the International Symposium of the Society of Core Analysts* (2003): Pau, France.

60. Anderson, W., *Wettability literature survey- part 2: wettability measurement.* Journal of Petroleum Technology, (1986). **38**(11): p. 1246-1262.

61. Schlumberger *Wettability* Oilfield Review: The defining series, (2016).

62. Austad, T., et al., *Low salinity EOR effects in limestone reservoir cores containing anhydrite: a discussion of the chemical mechanism.* Energy & Fuels, (2015). **29**(11): p. 6903-6911.

63. Konstantinopoulos, M., et al., *Effect of Mineralogy on Initial Wettability and Oil Recovery from Silica-containing Chalk.* (2019). **2019**(1): p. 1-5.