



Core wettability reproduction: A new solvent cleaning and core restoration strategy for chalk cores

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ABSTRACT

Laboratory core restoration procedures include different core cleaning solvents, establishment of initial water saturation (S_{wi}) by diverse techniques and processes of crude oil exposure that influence the final core wetting properties. In carbonate reservoirs, the acidic Polar Organic Components (POC) in crude oil are the main components dictating the wettability of the carbonate surface. Negatively charged carboxylates strongly attach to the positively charged CaCO_3 surface, thus acting as anchor molecules for the oil phase. During core cleaning with organic solvents, some of the adsorbed POC will be detached from the mineral surfaces, thereby changing the wetting conditions. However, cores are not expected to become completely water-wet even when using strong solvents. The main aim of this paper is to develop core cleaning and core restoration procedures to reproduce initial core wettability. Fractional-wet outcrop chalk cores were exposed to two different core cleaning procedures, (1) mild kerosene-heptane cleaning, or (2) standard toluene-methanol cleaning. Chromatographic wettability tests showed that both cleaning methods increased the fraction of water-wet surface area to a similar extent, but neither of them removed all adsorbed POC from the rock surface. Wettability tests by spontaneous imbibition showed that the kerosene-heptane cleaned core behaved slightly water-wet, while the toluene-methanol cleaned core behaved very water-wet, even though the cores had similar fractions of water-wet surface areas. Increased amount of crude oil exposure during core restoration reduced the water wetness below the initial fractional core wetting. Initial core wettability was successfully reproduced by combining mild cleaning solvents preserving initial adsorbed POC, and minimizing the amount of crude oil exposure during core restoration. Only a 1.5–3.6 %OOIP variation in ultimate recovery during spontaneous imbibition in four different core systems was observed.

1. Introduction

To this date, there are no available measuring techniques for determining in-situ reservoir wettabilities. Thus, the best practice is Special Core Analyses (SCAL) performed on representative, preserved core samples (Maas et al., 2014; McPhee et al., 2015).

Reservoir zones are cored during well drilling, and at atmospheric conditions at the rig site, individual peals are sealed to reduce contamination during transportation and storage. During these operations, the core material can be exposed to drilling mud and reservoir fluid expansion due to reduction in pressure and temperature.

Representative 1½ inch reservoir core samples are drilled from seal peals prior to the SCAL analyses. Before any of these analyses can be performed, each individual core goes through a core-cleaning program, followed by a core restoration program to build up initial formation water (FW) saturation and crude oil saturation. SCAL analyses give resistivity data, capillary pressures, and pressure drop data as water saturation increases during fluid displacement processes. All these

measurements are wettability dependent and will have significant effects on the interpreted capillary pressure and relative permeability curves. Core cleaning and core restoration programs able to reproduce core wettability close to reservoir conditions are of high importance.

The reservoir wettability determines the oil and water distribution within a porous network, and it affects the fluid flow in oil recovery processes, especially during waterflooding. Positive capillary forces are an important recovery mechanism in heterogeneous pore systems with large permeability differences at various reservoir sections, i.e., layered reservoirs, or at zones of high permeability contrast, as it occurs in the adjacent area of a fracture.

Standard core restoration to its original reservoir wettability is done by: (1) solvent cleaning to a completely water-wet state, (2) formation water (FW) saturation, (3) displacement of FW to residual water saturation (S_{wr}) with the reservoir crude oil, and (4) core aging at reservoir temperature to establish initial wetting.

In the past, core cleaning procedures involving a combination of solvents have been reported to be more efficient than single solvents

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(Cuiec, 1975). Today, common core cleaning processes are hot and cold Soxhlet extraction (Kovalev et al., 2016), constant or total immersion, and solvent flushing (McPhee et al., 2015). All these methods attempt to remove hydrocarbons from the porous media and minimizing damage to mineral structures. The standard solvent system used is toluene-methanol (T/M), but also other solvents and combination of solvent systems have been proposed, like hexane, cyclohexane, kerosene, acetone, chloroform, ethylene chloride and tetrachloroethylene among others (McPhee et al., 2015). Recent research has shown that different multiple solvent systems used in core floods have led to different effects on the restored core wettability (Shariatpanahi et al., 2012). Therefore, the choice of solvent systems used to clean reservoir cores is of utmost importance, when preserved reservoir cores should be restored to a representative wettability.

Recent research has shown that the standard core cleaning/core restoration approach has weaknesses (Hopkins et al., 2017). The classical core cleaning approach aims to remove mud filtrates (Fjelde et al., 2015), evaporated salts and native crude oil to obtain strongly water-wet cores. By removing the initially adsorbed POC dictating the pore surface wetting, important information on initial core wettability is lost, and then it could be difficult to restore the core to native wetting state in the laboratory. It is important to highlight that the produced reservoir crude oil used in core restoration has not necessarily the same chemical composition as the oil that initially migrated into the reservoir and wetted the rock (Puntervold, 2008). The composition may have changed because POC both adsorb onto the reservoir rock, and are decomposed over geological time, as it has been suggested for carboxylates in presence of calcite (Jurg and Eisma, 1964; Shimoyama and Johns, 1972; Zhang and Austad, 2005).

Another challenging issue is oil saturation/flooding during core restoration. Crude oil flooding will expose mineral surfaces to surface-active POC. Research has shown that the POC adsorption take place instantaneously and increasing volumes of crude oil will result in less water-wet restored cores (Fulcher et al., 1985; Abeyasinghe et al., 2012; Guo et al., 2015; Hopkins et al., 2016; Mjos et al., 2018; Klewiah et al., 2019). The above-mentioned weaknesses of the standard protocols can lead to unrepresentative wetting states on restored carbonate cores, which could have dramatic effects on the results obtained in SCAL experiments.

In carbonate reservoirs, it has been experimentally verified that the acidic POC present in crude oil is the most important wetting parameter (Madsen et al., 1996; Madsen and Lind, 1998; Graue et al., 1999; Standal et al., 1999; Standnes and Austad, 2000a; Zhang and Austad, 2005; Karoussi et al., 2008). Carboxylic groups (R-COOH) are found in both the liquid phase and in the heavy end fractions (resins and asphaltenes) of the crude oil. Basic POC have lower impact on the wetting properties in carbonates (Puntervold et al., 2007b). The 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. It has been verified that POC instantly adsorbed onto water-wet outcrop chalk surfaces during crude oil flooding, which immediately decreased the water wetness (Hopkins et al., 2016); In addition, the degree of water wetness decreased with increasing acid number of the crude oil (Standnes and Austad, 2000a). Due to the very strong affinity of negatively charged carboxylic groups, R-COO⁻, toward the positively charged calcite surfaces at slightly alkaline conditions, it will be difficult to remove all the POC from the carbonate surface by using different solvent systems (Masalmeh and Jing, 2007; Austad et al., 2008b; Agbalaka et al., 2009).

In this present work the efficiencies of two different solvent systems in cleaning of initially fractional-wet (restored) outcrop chalk cores have been compared; (1) kerosene-heptane (K/H) (mild cleaning solvents), and (2) toluene-methanol (T/M) (standard cleaning solvents). The cores' wetting states before and after solvent cleaning were quantified by spontaneous imbibition (SI) and chromatographic wettability (CW) tests. Based on the observed data, the wettability results have been discussed in relation to the solvents' efficiency in removing adsorbed

acidic POC that are the crude oil anchor molecules to the chalk surface.

The effect of crude oil exposure in a second core restoration on reproduced core wettability was investigated. The results have been discussed in relation to the effect of solvent cleaning and optimized oil exposure for reproducing core wettability in initially fractional-wet chalk cores.

The proposed cleaning and restoration method for wettability reproduction that is offered in this work, can potentially be used in carbonates with similar mineralogical characteristics as the outcrop used, i.e., carbonates with a high purity of calcite (CaCO₃). Previously, similar surface reactivity, wettability and crude oil brine (COBR) interactions studied on pure chalk (Austad et al. 2005, 2008a; Strand et al., 2006), have been observed in calcite-rich limestone and reservoir cores (Austad et al., 2008b; Ravari, 2011; Shariatpanahi et al., 2012; Al-Shalabi and Sepehrnoori, 2016; Song et al., 2020; Tetteh et al., 2020).

However, it is important to mention that for carbonates with significant different mineralogical composition, e.g., dolomites, with different surface reactivity and wetting behaviour (Romanuka et al., 2012; Shariatpanahi et al., 2016), the suggested restoration protocols must be experimentally tested to expand such application.

2. Experimental

2.1. Core material

A model rock, outcrop chalk from the Stevns Klint quarry (SK) was used in this work. SK chalk mostly consists of the calcite mineral with CaCO₃ >98 wt %, and contains a low amount of silicate impurities, in comparison to other chalks with higher amount of silicates (Fabricius and Borre, 2007; Hjuler and Fabricius, 2009; Skovbjerg et al., 2012; Bertolino et al., 2013). Having impurities like quartz, clays, or polysaccharides can impact surface reactivity and mechanical properties (Røgen and Fabricius, 2002; Strand et al., 2007; Fernø et al., 2011; Skovbjerg et al., 2013; Andersson et al., 2014; Bovet et al., 2015; Megawati et al., 2015; Andersen et al., 2018).

SK chalk has a high porosity with typical values ranging from (41–50%), and a low permeability (1–5 md), and is regarded as a North Sea chalk reservoirs analogue (Frykman, 2001; Røgen and Fabricius, 2002). Cores drilled from the same block has shown good reproducibility in oil recovery and wettability experiments, which makes SK chalk useful in parametric studies (Standnes and Austad, 2000b; Zhang and Austad, 2005; Strand et al., 2006; Puntervold et al., 2007b; Fathi et al., 2010; Hopkins et al., 2017). SK chalk matrix is composed of coccolithic remnants, Fig. 1.

The pore size distribution of SK chalk was measured by mercury

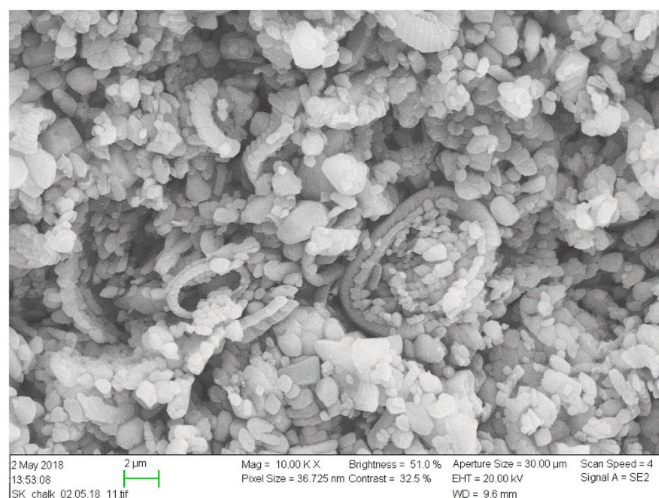


Fig. 1. Image of Stevns Klint outcrop chalk. SEM magnification 10000 X.

capillary injection (MICP) on a representative core sample; the external service provider Stratum laboratories performed the analyses. The pore size distribution is presented in Fig. 2; and it can be observed that the majority of the pores are located in the micro pore region (0.1–0.5 μm).

The cores used were drilled from two different blocks and equally prepared as suggested by Puntervold et al. (2007a). The cores were cleaned with 5 pore volumes (PV) of de-ionized (DI) water to clear away easily dissolvable salts, e.g., sulphate bearing salts, which can affect the core initial wettability (Puntervold et al., 2007a). Thereafter, the cores were dried at 90 °C until achieving constant weight. The main core properties are displayed in Table 1.

2.2. Brines

The synthetic formation water termed FW, is a brine based on the composition of a North Sea chalk reservoir, and it was used as formation water in core restorations and as imbibing fluid during the spontaneous imbibition tests. This brine is depleted in sulphate to not induce wettability alteration. SWOT and SW $\frac{1}{2}$ T were used in the chromatographic wettability experiments, (CW), (Strand et al., 2006). These tests are performed at room temperature to hinder sulphate reactivity and wettability alteration. All brine compositions are presented in Table 2.

2.2.1. Ion chromatography analyses

Effluent brine samples were analyzed for ion chromatography; these analyses were performed on a Dionex IC 3000. External standards of each analyzed ion were used for the concentration calculations.

2.3. Oils and solvents

2.3.1. Core cleaning solvents

During core cleaning and core restorations two different types of solvent systems were used, the mild kerosene-heptane and the standard toluene-methanol systems. In the standard solvent system with toluene and methanol, toluene is a strong solvent for heavier oil components. Methanol dissolves both, oil components and water. The mild core cleaning solvents are kerosene and heptane; both have reduced solubility of larger oil components due to their low aromaticity. The main aim of mild core cleaning is to displace the residual oil in the core without attaining substantial removal of POC adsorbed to the rock surface, which dictate rock wettability (Hopkins et al., 2015). All chemicals were purchased from Merck and their quality was reagent grade.

2.3.2. Crude oil

A stock solution of crude oil was prepared by diluting a reservoir crude oil with heptane in a 60/40 vol ratio, respectively. No asphaltene

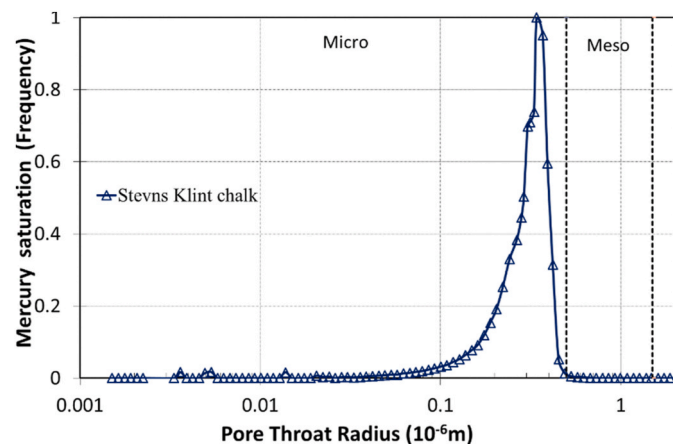


Fig. 2. Distribution of pore sizes in SK outcrop chalk by mercury capillary injection (MICP).

precipitation was observed due to initial low asphaltene content in the original crude oil. Then, this model oil was centrifuged and filtered using a 5 μm Millipore filter. The model crude oil had an acid number (AN) of 1.8 mgKOH/g and a base number (BN) of 0.74 mgKOH/g. Then, 10 wt % of silica gel was added to a batch of the crude oil-heptane mixture to remove surface-active components, and it was left stirring for 4 days, this step was repeated once, obtaining an oil with an and BN of ~ 0 and 0.03 mgKOH/g, respectively. By mixing these two crude oils in different proportions, three crude oils were prepared; Oil A, Oil B and Oil C. The oil properties are shown in Table 3. No precipitation of crude oil components was seen during storage and preparation of the crude oil samples.

The acid and base numbers, (AN) and (BN), were quantified by potentiometric titration. The methods used are versions of ASTM 664 and ASTM 2898 (Fan and Buckley, 2007). The reproducibility of the modified methods is better than ± 0.02 mgKOH/g for both AN and BN analyses.

2.4. Core preparation

2.4.1. Initial core preparation

The chalk cores were first flooded with 5 PV of DI water; this was done to get rid of easily dissolvable salts. Effluent samples were evaluated to discard the presence of sulphate at the end of this step. All cores were dried to constant bulk weight at 90 °C.

2.4.2. Core restoration

Initial water saturation, was established at, (S_{wi}) = 0.1, with FW by using the desiccator technique (Springer et al., 2003). After achieving the target weight, the cores were left in a closed container for a minimum of 72 h to obtain an even distribution of ions within the core plugs.

Crude oil saturations were performed by mounting the cores with established water saturation, $S_{wi} = 0.1$, in a Hassler core holder with 25 bars of confining pressure and 10 bars of backpressure. The cores were then oil saturated at 50 °C with their respective oil at the rate of 0.1 ml/min, 2.5 PVs were injected in each direction to assure an even oil distribution.

In addition, in some of the second restoration experiments performed to minimize the crude oil exposure, an alternative crude oil exposure routine was used. This procedure was implemented by a short-time vacuum saturation of only 1 PV of crude oil after establishing $S_{wi} = 0.1$.

Core aging was performed for 2 weeks at 50 °C. Cores exposed to crude oil were wrapped in Teflon tape and placed on marble balls in a closed aging cell surrounded by the same crude oil. The Teflon tape wrapping was used to avoid unrepresentative adsorption of active POC on the outer core surface, which could influence the spontaneous imbibition (Standnes and Austad, 2000a). Static aging was selected over dynamic aging due the fact that additional exposure of crude oil increases POC adsorption and hence affecting wettability (Hopkins et al. 2015, 2016). All cores were aged with the same procedure to minimize deviations caused by the aging process parameters, such as oil injected, aging time or temperature.

2.4.3. Core cleaning

The cores exposed to crude oils were prior to the second core restoration cleaned by using one of the two different solvent systems studied; mild cleaning with kerosene-heptane, or standard cleaning with toluene-methanol. The cleaning process was initiated at S_{or} /high water saturation.

Core C11 was mildly cleaned by flooding 5 PV of low aromatic kerosene, followed by 5 PV of heptane, repeated 3 times with a total of 30 PV of solvent flooding.

Core C12, was cleaned in the same way as core C11, but with standard cleaning solvents, i.e. toluene and methanol, for a total of 30 PV of solvents.

All cores from block 2 were mildly cleaned by using 10 PV of low

Table 1
Physical core properties of the SK outcrop material.

Core	Block 1			Block 2					
	C11	C12	C13	C24	C25	C26	C27	C28	C29
Length, cm	6.17	6.17	5.91	6.94	6.94	6.92	7.00	7.00	7.04
Diameter, cm	3.70	3.70	3.75	3.80	3.80	3.82	3.80	3.80	3.79
Bulk volume, V_b , cm ³	66.3	66.3	65.0	78.8	78.8	79.3	79.5	79.5	79.4
Dry weight, m_0 , g	96.3	93.7	89.6	108.5	107.2	108.7	111.8	110.2	110.1
Sat. weight, m_{sat} , g	127.1	120.3	117.0	146.9	147.1	146.5	149.1	149.1	148.1
Density, ρ_{sat} , $d_{10}FW$, g/cm ³	1.003	1.003	1.003	1.002	1.002	1.002	1.002	1.002	1.002
Pore volume, PV, ml	30.8	26.5	27.3	38.3	39.9	37.7	37.3	38.8	38.5
Porosity, Φ , %	46	41	42	49	50	48	47	48	49
Permeability, md	2.0	1.4	1.3	2.5	1.0	0.8	1.6	2.0	1.2

Table 2
Brine properties and compositions.

Brines Ions	FW mM	SW0T mM	SW½T 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

Table 3
Chemical and physical crude oil properties.

Crude Oil	AN mgKOH/g	BN mgKOH/g	Viscosity at 25 °C cP	Density at 25 °C g/cm ³	Used in cores
Oil A	0.34	0.24	3.25	0.808	C11, C12
Oil B	0.36	0.30	2.52	0.807	C24, C25
Oil C	0.50	0.23	2.36	0.807	C26, C27

aromatic kerosene, followed by 5 PV of heptane, summing up to 15 PV of solvent flooding.

DI water was injected to remove the resident solvents and dissolvable salts; 5 PV of DI water were used in each core. Right after, the cores were put into an oven at 90 °C to evaporate the water and solvents left inside, this process finalized when the core achieved a constant weight.

2.5. Core experiments

2.5.1. Oil recovery by spontaneous imbibition (SI)

Oil recovery tests were carried out on the restored cores by using spontaneous imbibition (SI). The imbibition tests were performed in glass Amott cells at 50 °C; the imbibing fluid was FW to avoid any chemically induced wettability alteration. Oil recovery, as percentage of original oil in place (%OOIP), was logged vs. time until the recovery ceased. The precision of the volumetric measurements is ± 0.1 ml.

2.5.2. Chromatographic wettability test (CW)

Chromatographic wettability tests (CW) were implemented in this study as an additional way of assessing wettability, the test was developed by Strand and co-workers (Strand et al., 2006). The tested cores were mounted into a Hassler core holder at room temperature with a confining pressure of 25 bars and a back pressure of 10 bars. The cores flooded at an injection rate of 0.2 ml/min with the brine termed, SW0T, until achieving residual oil saturation, S_{orw} . Then, the brine containing

the tracer, SCN⁻, and sulphate, SO₄²⁻, was injected, this brine is termed, SW½T. Effluent brine samples were collected with an autosampler, and then analyzed for ion chromatography.

The tests consist in the evaluation of the water-wet areas of the porous media by the chromatographic separation the non-adsorbing tracer and the adsorbing sulphate ion, the area in between the two elution curves, A_w , is proportional to the water-wet surface area of the carbonate core plug. Experiments reproducibility is ~5% (Strand et al., 2006). An utterly water-wet reference core was used as main reference, and the area in between the elution curves (A_{ww}) was calculated to be, $A_{ww} = 0.256$. The wettability index (I_{CW}), that describes the water-wet fraction of the chalk surface, is estimated according to equation (1):

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

A wetting index of $I_{CW} = 0$, exhibits a completely oil-wet surface area, whereas a $I_{CW} = 1$ represents a strongly water-wet surface area.

2.5.3. Wettability by spontaneous imbibition (SI)

The presence of capillary forces and the core wettability were evaluated by spontaneous imbibition (SI). The cores were 100% saturated with heptane and imbibed with DI water in a glass Amott cell at 23 °C. Oil recovery was measured and logged against time.

A practical way of quantifying wettability of porous systems is by SI (Anderson, 1986). Both the imbibition rate and ultimate recovery gives valuable information to describe the core wettability. SI experiments can be performed at reservoir temperature, which will reduce uncertainties regarding physical fluid properties of oil and brine and temperature effects of core wettability.

When the oil recovery (%OOIP) by SI from a strongly water-wet reference core, SI_{WWC} , is available, a simplified wetting index, I_{W-SI} , only based on SI experiments can be calculated, Eq. (2):

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

SI_C is the oil recovery (%OOIP) from the tested core. I_{W-SI} approaches 1 for a strongly water-wet core, and 0 for a fractional/neutral wet core (Schlumberger, 2016).

3. Results and discussion

In this work, the effect of crude oil exposure on core wettability, and how different core cleaning solvent systems affects the core wettability during laboratory core restorations, have been studied. Stevns Klint outcrop chalk is a rock type that has been regarded as an analogue for most chalk oil reservoirs in the North Sea area, for this reason it was used in this study. The outcrop chalk has also been reported to show similar behaviour as reservoir limestone regarding wettability and wettability alteration processes (Ravari, 2011; Austad et al., 2015).

The experimental work is divided into two main parts; (1) the effect of solvent cleaning on core wettability, and (2) the effect of crude oil exposure on mildly cleaned carbonate cores.

3.1. Effect of solvent cleaning on core restoration wettability

Solvent cleaning is an important part of the core restoration procedures used on preserved reservoir cores prior to Special Core Analyses (SCAL) in the laboratories. Relative permeability measurements, capillary pressure curves and resistivity measurements are wettability dependent, and representative wettability is needed for obtaining correct SCAL representative of the reservoir. Two cleaning procedures; kerosene-heptane and toluene-methanol, were evaluated based on their ability to clean crude oil-wetted chalk cores, and their influence on a repeated second core restoration.

3.1.1. Water-wet outcrop chalk

The initial wettability of a clean outcrop chalk core was tested by SI, and the area between the non-adsorbing tracer and the sulphate curves was determined with a CW test. The results from the SI and CW tests for core C13 are presented in Fig. 3.

The SI results from the heptane-saturated core C13 in Fig. 3a, shows very strong capillary forces, and an ultimate recovery by SI of 78 %OOIP after less than 30 min, confirming that the outcrop chalk behaves strongly water-wet. The area between the sulphate and tracer curves measured with the CW test for a completely water-wet chalk core was $A_{ww} = 0.251$ Fig. 3b. Both SI and CW results for the completely water-wet core will be used for further calculations of water-wet surface area and wettability indexes below. $I_{CW} = 1$ for the water-wet core.

3.1.2. Establishing initial wetting conditions

The cores C11 and C12 from block 1 were initially restored with $S_{wi} = 0.1$ and exposed to an equal amount of crude oil by flooding a total of 5 PV of Oil A, before aging. Oil recovery tests were carried out by SI at 50 °C using FW as imbibing fluid, the results are shown in Fig. 4. The oil recovery plateau for core C11 and C12 was reached after 8–10 days, with an ultimate recovery of 8 and 10 %OOIP respectively, confirming reproducible initial wetting properties of the two cores.

Right after the SI experiments, both cores achieved S_{or} at 23 °C by injecting SWOT brine, and CW tests were performed on both cores to evaluate the water-wet fraction of the cores' surface area, Fig. 5.

The water-wet surface areas were nearly the same in both cores, i.e. the areas between the effluent tracer (SCN^-) and SO_4^{2-} curves, A_w , were calculated to $A_w = 0.118$ and $A_w = 0.124$ for C11 and C12 respectively, Fig. 5. The water-wet surface area for the strongly water-wet reference core C13 was $A_{ww} = 0.251$, Fig. 3b. Thus, the water-wet fraction of the surface area, Eq.(1), was $I_{CW} = (0.118/0.251) = 0.47$ for core C11, and $I_{CW} = (0.124/0.251) = 0.49$ for core C12. The values correspond to a fractional/neutral wetting according to the CW method (Strand et al., 2006). The CW tests agree with the SI test results, confirming that the

equally restored cores C11 and C12 possess similar core wetting.

Comparing the SI results for core C11 and C12 with the results from the strongly water-wet core C13, the modified water index I_{W-SI} (Eq.(2)) was calculated to 0.10 for core C11, and 0.13 for core C12. In these cores 5 PV of crude Oil A was injected, and both behaved slightly water-wet.

Measured and calculated data are summarized in Table 4.

3.1.3. Efficiency of mild kerosene-heptane cleaning vs. standard toluene-methanol cleaning

After confirming fractional, close to neutral initial wetting properties in SI and CW, the two cores with high initial water saturation went through core cleaning prior to a new core restoration.

Core C11 was mildly cleaned by flooding 5 PV kerosene (K) followed by 5 PV heptane (C_7/H). This flooding sequence was executed 3 times. The same core cleaning procedure was also applied to core C12, but this time using the standard cleaning solvents toluene (T) and methanol (M). After the core cleaning was completed, new chromatographic wettability tests and spontaneous imbibition tests were carried out on both cores C11 and C12, to evaluate the change in wetting properties due to the core cleaning method. The CW tests results are shown in Fig. 6.

After mild core cleaning with kerosene and heptane, the water-wet fraction of the surface area in core C11 increased from $I_{CW} = 0.47$ to $I_{CW} = (0.150/0.251) = 0.60$. After standard core cleaning with toluene and methanol on core C12, the water-wet fraction increased from $I_{CW} = 0.49$ to $I_{CW} = (0.165/0.251) = 0.66$. The experimental results confirmed that both solvent systems removed POC from the chalk surface and increased the fraction of water-wet surface area. However, mild kerosene-heptane core cleaning increased I_{CW} by 13%, while the I_{CW} increased with 17% after toluene and methanol cleaning. Still, after an extensive solvent flooding, 40% and 34% of the rock surfaces in the cores were still covered by oil components, preventing SO_4^{2-} ions from interacting with the carbonate surface. Thus, completely water-wet carbonate mineral surfaces in the cores after solvent cleaning were not obtained.

The effect of the different cleaning solvents on the wettability and capillary forces was investigated by SI tests. In both cores, 5 PV of DI water were injected to displace the CW brines, then they were dried, and vacuum-saturated with 100% heptane. The heptane-saturated cores were spontaneously imbibed at 23 °C with DI as imbibing fluid, and the test results are shown in Fig. 7.

The kerosene and heptane cleaned core, Fig. 7a, reached a heptane recovery plateau of 27 %OOIP after 9 days. By comparing the result with the SI test on the initially restored C11 core in Fig. 4a, the capillary forces had increased, indicating that the core had become slightly more water-wet after kerosene and heptane cleaning. The results are in line with those from the CW tests, Figs.5an and 6a, showing that the mild

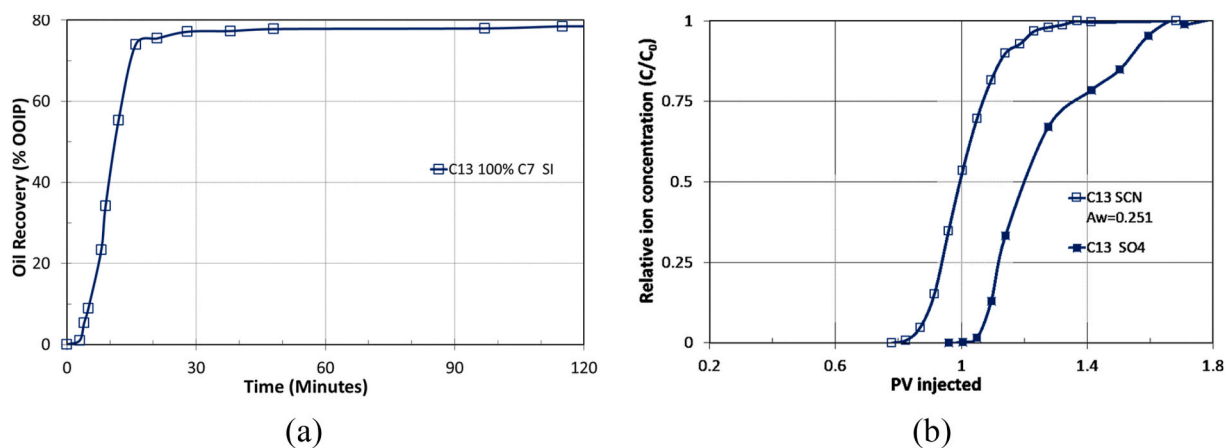


Fig. 3. Initial core wettability of outcrop chalk core C13. (a) The core was 100% heptane saturated and spontaneously imbibed with DI water at 23 °C. (b) CW test performed on a 100% brine saturated core C13 at 23 °C.

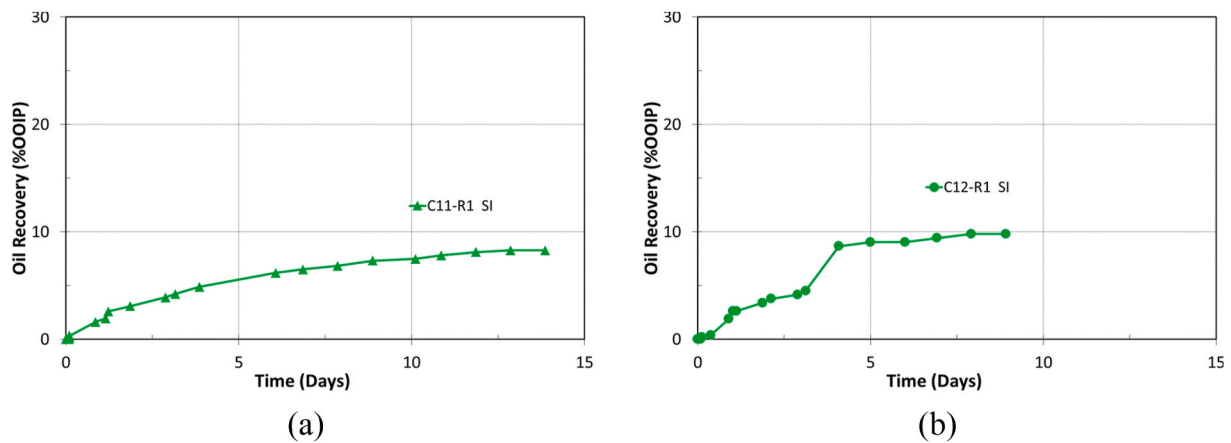


Fig. 4. Oil recovery tests by SI at 50 °C, FW used as imbibing brine for the cores C11 and C12, both equally restored with $S_{wi} = 0.1$ and exposed to 5 PV Oil A (first restoration – R1), before aging. (a) Core C11-R1 and (b) Core C12-R1.

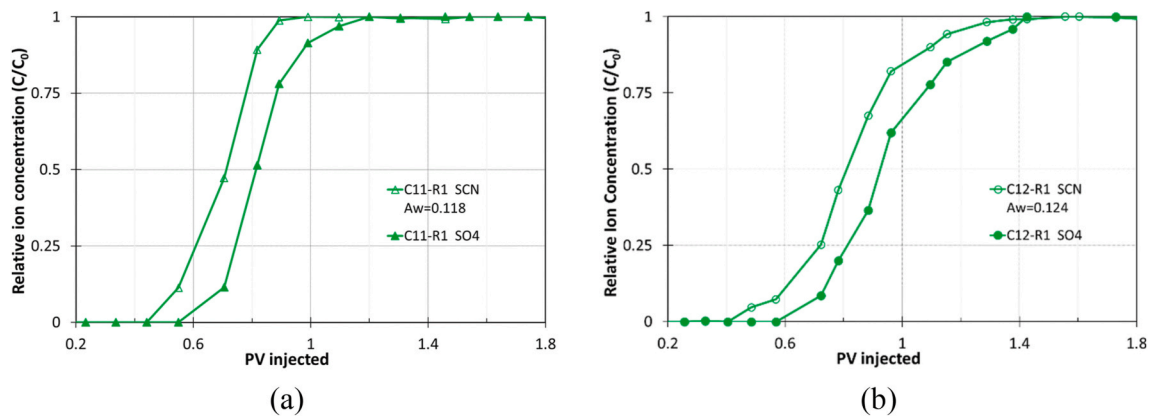


Fig. 5. CW test performed on initially restored core C11 and C12 after the SI tests. The figures show the relative concentrations of the tracer, SCN^- , and SO_4^{2-} in the effluent samples versus PV injected (a) Effluent curves for core C11, and (b) Effluent curves for core C12.

Table 4
SI and CW results summary.

Core	Solvent	SI			CW			
		SI-R1 (%OOIP)	SI _{C7-AS^a} (%OOIP)	SI-R2 (%OOIP)	A _w -R1	I _{CW} -R1	A _w -AS ^a	I _{CW} -AS ^a
C11	K/H	8	27	3	0.118	0.47	0.150	0.60
C12	T/M	10	62	12	0.124	0.49	0.165	0.66
C13	-	75	-	-	0.251	1	-	-

^a AS - After-solvent cleaning.

kerosene and heptane core cleaning resulted in a slightly higher fraction of water-wet surface area.

As expected, the pair toluene and methanol is a more efficient solvent combination with higher ability to solvate more complex oil components. The toluene and methanol cleaned core, Fig. 7b, reached a heptane recovery of 62 %OOIP within only 5 h, showing very water-wet behaviour with high imbibition rate and high ultimate recovery (Anderson, 1986), despite the fact that 34% of the rock surface is still protected from interactions with water due to adsorbed organic material.

The SI water index, I_{W-SI} , increased from 0.10 to 0.36 for core C11 by kerosene and heptane cleaning, and from 0.13 to 0.82 for core C12 by toluene and methanol cleaning, confirming dramatic changes in positive capillary forces after toluene and methanol cleaning.

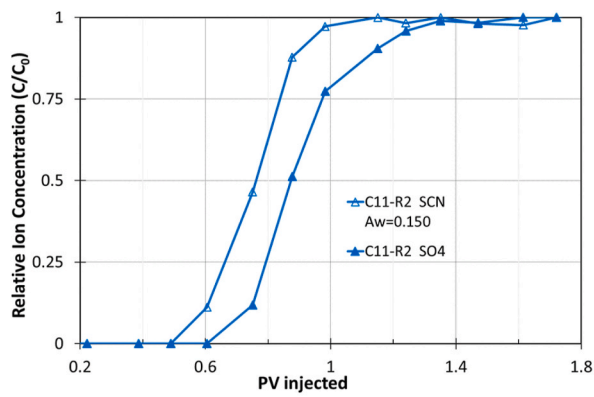
It is important to highlight from the results that not only the amount of POC adsorbed onto the rock surface dictates the core wettability, but

also the distribution of POC at the pore surfaces seems to be important. POC adsorbed at pore throats will influence capillary forces more than components adsorbed onto pore bodies. Spontaneous imbibition results confirm that extensive toluene and methanol flooding is removing POC at strategic places that affects capillary forces, resulting in dramatically increased imbibition rate and ultimate oil recovery, even though only slight changes in the fraction of water-wet surface area were observed.

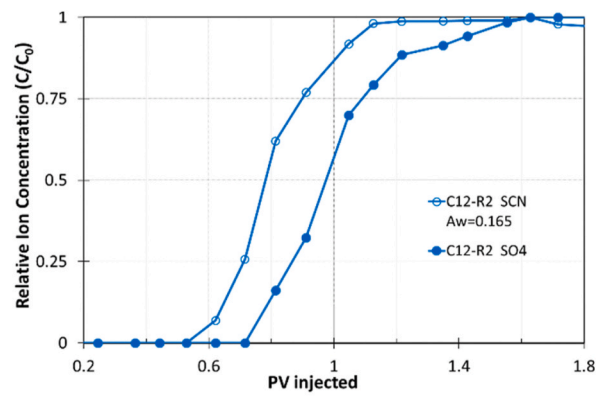
In optimal carbonate reservoir core restoration procedures, both the total amount of POC adsorbed and the distribution at the mineral surfaces dictates capillary forces and core wettability. The mild kerosene and heptane core cleaning method removed less initially adsorbed POC and only slight changes in the positive capillary forces were observed.

3.1.4. Effect of cleaning procedure on a second core restoration

The effect of the two different core cleaning methods on core wettability in a second core restoration was studied in two initially

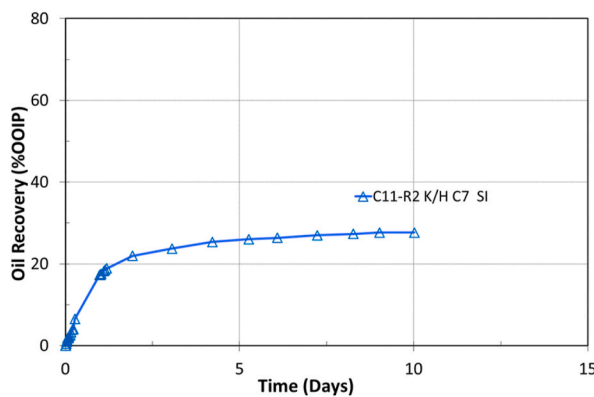


(a) Kerosene-heptane cleaned core C11

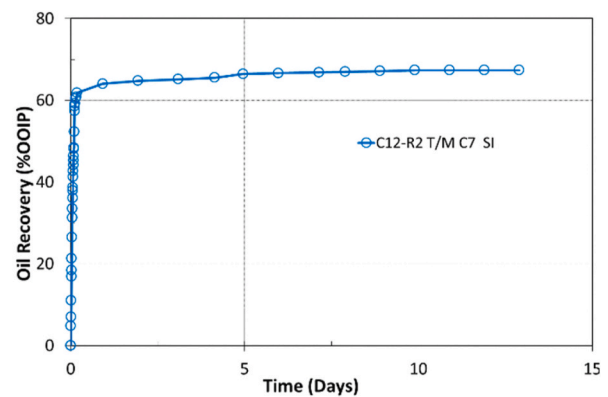


(b) Toluene-methanol cleaned core C12

Fig. 6. CW test performed on (a) Kerosene-heptane cleaned core C11 and on (b) Toluene-methanol cleaned core C12.



(a)



(b)

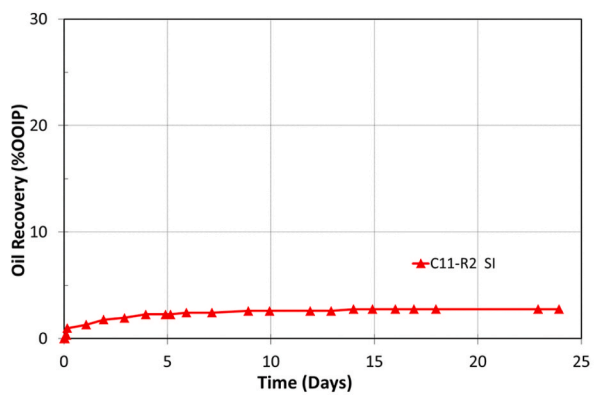
Fig. 7. SI at 23 °C on the solvent cleaned cores, saturated 100% with heptane, DI was the imbibing fluid. (a) Heptane recovery (%OOIP) from the kerosene-heptane cleaned core C11. (b) Heptane recovery (%OOIP) from the toluene-methanol cleaned core C12.

equally restored cores, C11 and C12. $S_{wi} = 0.1$ with FW was established before both cores were exposed to 5 PV Oil A before aging. Oil recovery tests by SI at 50 °C were carried out with FW as the imbibing brine, Fig. 8.

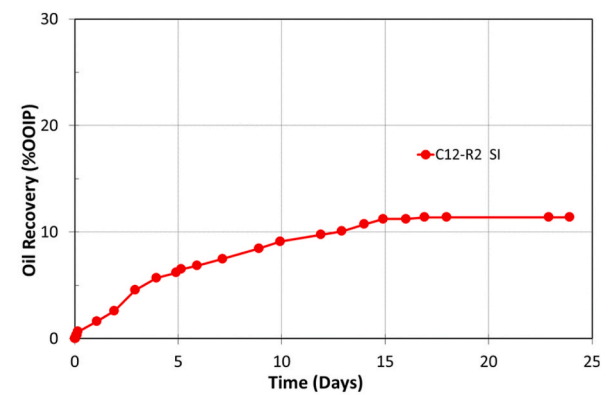
The ultimate recoveries by SI after 15 days was 3 and 12 %OOIP respectively, compared to 8 and 10 %OOIP after the initial restoration, Fig. 4. The kerosene-heptane cleaned core C11 became less water wet

than the toluene-methanol cleaned C12 core. The water indexes, I_{W-SI} , were reduced from 0.10 to 0.04 for core C11 and increased slightly from 0.13 to 0.16 for core C12.

When an already fractionally wetted core is exposed to more crude oil with surface-active components, more POC could adsorb, reducing the water wetness. This effect of the amount of crude oil exposure during core restoration on wettability has previously been reported (Hopkins



(a)



(b)

Fig. 8. Oil recovery tests by SI at 50 °C with FW as imbibing brine. After solvent cleaning, both cores were restored with $S_{wi} = 0.10$ with FW and exposed to 5 PV of Oil A. (a) Oil recovery (%OOIP) for kerosene-heptane cleaned core C11-R2, and (b) Oil Recovery (%OOIP) for toluene-methanol cleaned core C12-R2.

et al., 2015).

The more water wet core C12, also exposed to 5 PV of Oil A, became significantly more water wet than core C11, with I_{W-SI} of 0.16 and 0.04 respectively.

Both initial wetting, the distribution of POC on mineral surfaces, and the amount of crude oil exposure affects the core wettability during core restoration processes.

For real reservoir systems a toluene methanol cleaning will remove more of the POC from the rock surface that dictates the core wettability. The produced reservoir crude used in core restoration can differ from the invading oil dictating the initial reservoir wettability. (Puntervold, 2008). Optimized core restoration could then be obtained preserving most of the POC on the rock surface during core cleaning, and reducing the amount of crude oil exposure during the process of core restoration.

A data summary for the experiments carried out on the cores of block 1 is presented below in Table 4.

3.2. Reproducing initial core wettability in mildly cleaned cores

By limiting the kerosene-heptane solvent injection to a minimum volume during core cleaning and restoration procedures in the laboratory, a smaller amount of adsorbed POC dictating the reservoir wettability will be removed. In that case also a minimum reservoir crude oil volume would be needed for reproducing the reservoir wettability. In the next part of this experimental work the focus was on optimizing the amount of crude oil needed to reproduce the initial core wettability after a mild solvent cleaning.

Mild core cleaning using the kerosene-heptane solvent system is displacing the residing crude oil without severely affecting the initial core wettability. A core restoration program preserving the POC adsorbed at the mineral surface responsible for the core wetting, reduces the amount of crude oil needed during core restoration. The reservoir crude oil available for laboratory tests is most likely different from the initial oil responsible for generating the original reservoir wettability. Thus, it could be important to keep the original crude oil adsorbed onto the core, for generating a representative core wettability. The main objective in this part was to reproduce the initial core wettability after mild core cleaning with kerosene and heptane solvents.

3.2.1. Water-wet outcrop chalk behaviour

For this section, the core material used was the same SK outcrop chalk, but it was taken from block 2. The water-wet reference core from block 2 was termed C28. $S_{wi} = 0.1$ was established and heptane was used as the oil phase to verify water-wet behaviour by SI. A CW test was carried out on a 100% water saturated core. The SI and CW results are presented in Fig. 9.

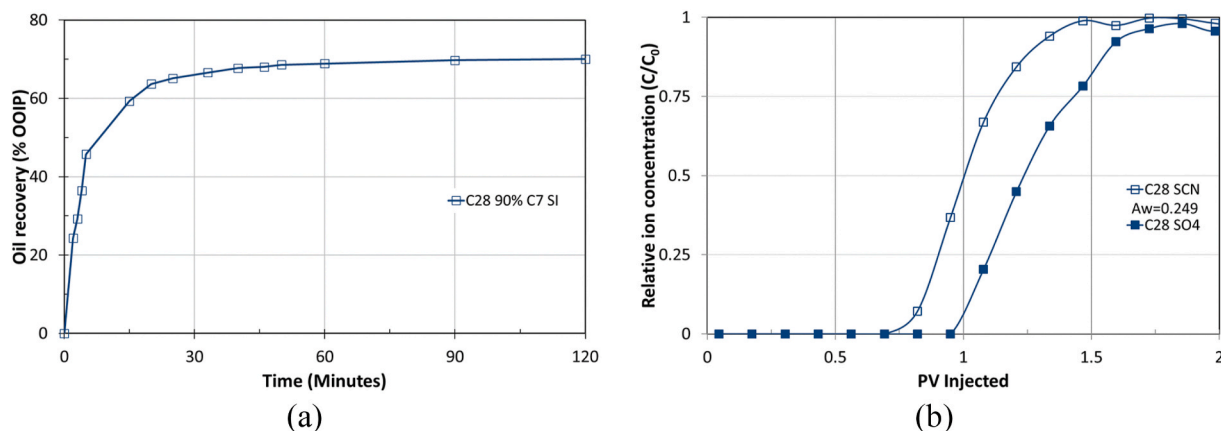


Fig. 9. Initial wettability of water-wet core C28 from block 2. (a) SI test performed at 23 °C using DI water as FW. Core C28 with $S_{wi} = 0.1$ and heptane saturated (b) CW test on the 100% water saturated C28 core.

The spontaneous imbibition results confirm very strong capillary forces for core C28, with high rate of imbibition and reaching the heptane recovery plateau of 70 %OOIP after 60 min, as seen in Fig. 9a. The CW test resulted in an area between the tracer and sulphate curves of $A_{ww} = 0.249$, Fig. 9b, corresponding to a fraction of water-wet surface area of $I_{CW} = 1$, that is, the entire rock surface is water-wet in the core that has not been exposed to crude oil. These results are comparable in terms of imbibition rate and profile shapes with the strongly water-wet reference core from block 1, Fig. 3, Table 4.

3.2.2. Establishing initial wettability

Two chalk cores from block 2, C24 and C25 were restored with $S_{wi} = 0.1$ FW, and exposed to 5 PV Oil B, before aging. The initial wettability established during core restoration was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test to verify reduction in water-wet mineral surface. The results are shown in Fig. 10.

The oil recovery plateaus were reached for cores C24 and C25 after 7–10 days, with ultimate recoveries of 44 and 43 %OOIP, respectively, indicating a high reproducibility of the induced initial wettability of these two cores. The CW test gave slightly different areas of separation between the tracer and sulphate curves, $A_w = 0.230$ and $A_w = 0.188$ for C24 and C25 respectively, however both areas were considerably lower than $A_{ww} = 0.249$ from the water-wet core, confirming significant reduction in water-wet surface area in both cores.

A second set of cores, C26 and C27, were restored using the same core restoration procedure. This time Oil C with $AN = 0.50$ and $BN = 0.23$ mgKOH/g was used. A higher amount of acidic components should reduce the initial wettability, as previously shown by Standnes and Austad, (2000a). The results from SI and CW tests are presented in Fig. 11.

The oil recovery plateaus were reached in both cores after 15 days, with ultimate recoveries of 25 and 37 %OOIP from cores C26 and C27, respectively. In this case, the established wettabilities of the two cores were slightly different, but both behaved slightly less water-wet than the cores exposed to Oil B, which has a lower AN (0.36 mgKOH/g), as expected. The water-wet fractions surface areas were nearly the same in the cores, as seen by similar separation areas between the curves of the non-adsorbing tracer and adsorbing sulphate, which were determined to $A_w = 0.203$ and $A_w = 0.205$ for C26 and C27, respectively. The calculated fractions of water-wet surface area were 0.81 and 0.82, which correspond to a water-wet state.

Comparing the SI results of the cores from block 2 (C24–C27), all cores achieved a fractional wetting after being exposed to 5 PV of the respective Oil B and Oil C, but some inconsistencies were observed. These could be due to differences in pore distribution, fractures, and variation in rock mineralogy and surface reactivity. The cores saturated

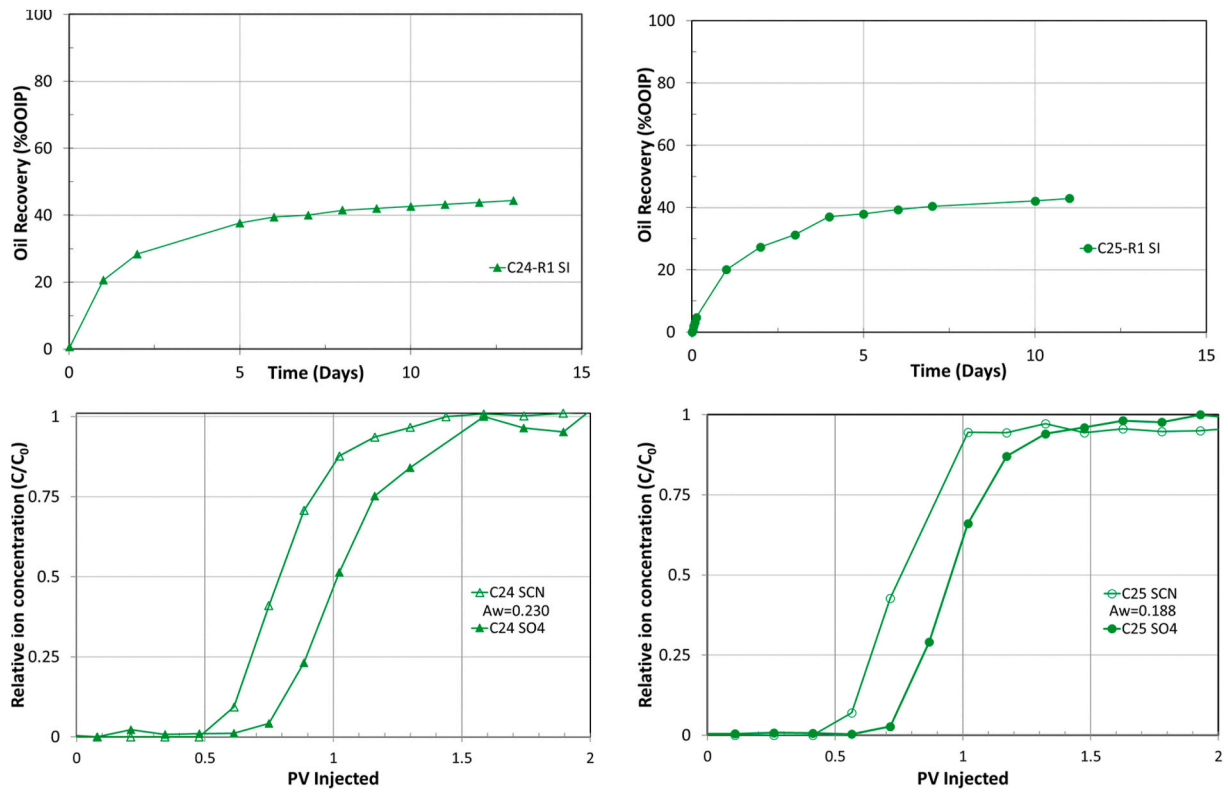


Fig. 10. Initial wettability was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test. (Left) Core C24 and (Right) core C25. Both cores were restored with $S_{wi} = 0.1$ (FW) and exposed to 5 PV Oil B before aging.

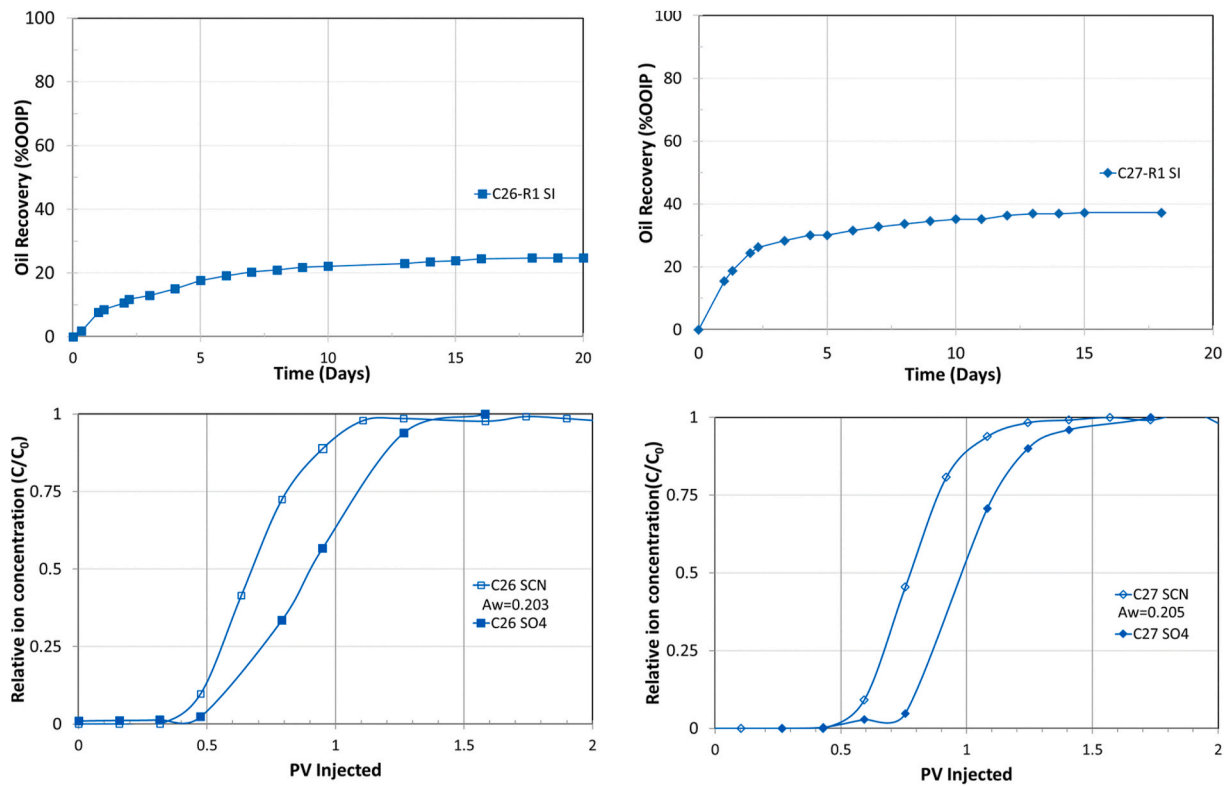


Fig. 11. Initial wettability was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test. (Left) Core C26 and (Right) core C27. Both cores were restored with $S_{wi} = 0.1$ FW and exposed to 5 PV Oil C before aging.

with Oil C with higher AN behaved slightly less water-wet than the cores saturated with Oil B.

3.2.3. Optimal core restoration for reproduction of core wettability

In the first part of the paper, it was observed that mild cleaning with kerosene-heptane solvents preserved some of the initially adsorbed POC on the mineral surface. However, the wettability established in a second core restoration process was impacted by the amount of crude oil injected in the second restoration process, as observed previously by Hopkins et al., (2017). It was also observed that the harsher cleaning method, toluene-methanol, was able to better clean and reproduce wettability in the second restoration. However, a very important point to make is that although, toluene and methanol successfully reproduced the first restoration-wettability after the second restoration, as seen in Figs. 2b and 6b, the restored wettability is not necessarily representative and correct, because the crude oil used in the laboratory may be depleted in the surface-active POC due to their adsorption onto the reservoir rock. Therefore, it is hypothesized that a more representative core wettability can be achieved by preserving initially adsorbed POC during mild cleaning, and completing the restoration process by optimal exposure to crude oil. To test this hypothesis, the four initially restored outcrop cores (C24–C27) underwent the following procedure:

- 1 Mild cleaning with kerosene-heptane solvent injection, this time only 10 PV kerosene, 5 PV heptane, 5 PV DI water, and drying to constant weight.
- 2 Establishing S_{wi} of 10% with FW by using the desiccator technique.
- 3 Vacuum-saturating the core at $S_{wi} = 0.1$, with 0.9 PV of the same crude oil used in the initial restoration, followed by aging.
- 4 SI of FW at the same temperature (50 °C).

The SI results after the second core restorations (R2) are compared with the initial core wettability (R1) results in Fig. 12.

By comparing the oil recoveries by SI after the initial (R1) and second (R2) core restorations (before and after kerosene-heptane cleaning), it is evident that a very good reproduction of wettability was achieved in the second restoration (R2). The difference in oil recoveries by SI between initial and second restoration, ΔSI , varied only between +1.5 and +3.5 %OOIP. The degree of water-wetness was quantified by the wettability index based on SI, I_{W-SI} , Eq. (2).

The ultimate oil recoveries from of initially restored cores C24 and C25 exposed to Oil B were very similar, with a 44.4% and 42.9 %OOIP, giving a similar wetting index, I_{W-SI} , of 0.63 and 0.61 respectively. After the second restoration, the oil recovery only slightly increased and I_{W-SI} of 0.68 and 0.67 was calculated.

In the case of C26 and C27 exposed to Oil C, ultimate recoveries of 24.7 and 37.2 %OOIP was observed, respectively. This rather large difference in recovery and initial wettability was not expected, as explained above. Nevertheless, the second restorations (R2) were successful for both cores, despite the differences in initial wettability. For core C26 I_{W-SI} slightly increased from 0.35 to 0.40, while for core C27, I_{W-SI} slightly decreased from 0.53 to 0.51.

A new core C29 was thereafter used to test the effect on SI of exposing a core to 5 PV of Oil B with AN = 0.36 mgKOH/g during the second restoration after mild cleaning with 10 PV of kerosene and 5 PV of heptane, the rest of the procedure being the same as for the cores C24 and C25. In Fig. 13 the oil recoveries from core C29 after R1 and R2 have been compared. SI from the initially restored core (R1) gave a recovery of 41.5 %OOIP, which was similar to the recoveries from C24 and C25, seen in Fig. 10.

After a mild cleaning with kerosene and heptane, core C29 was

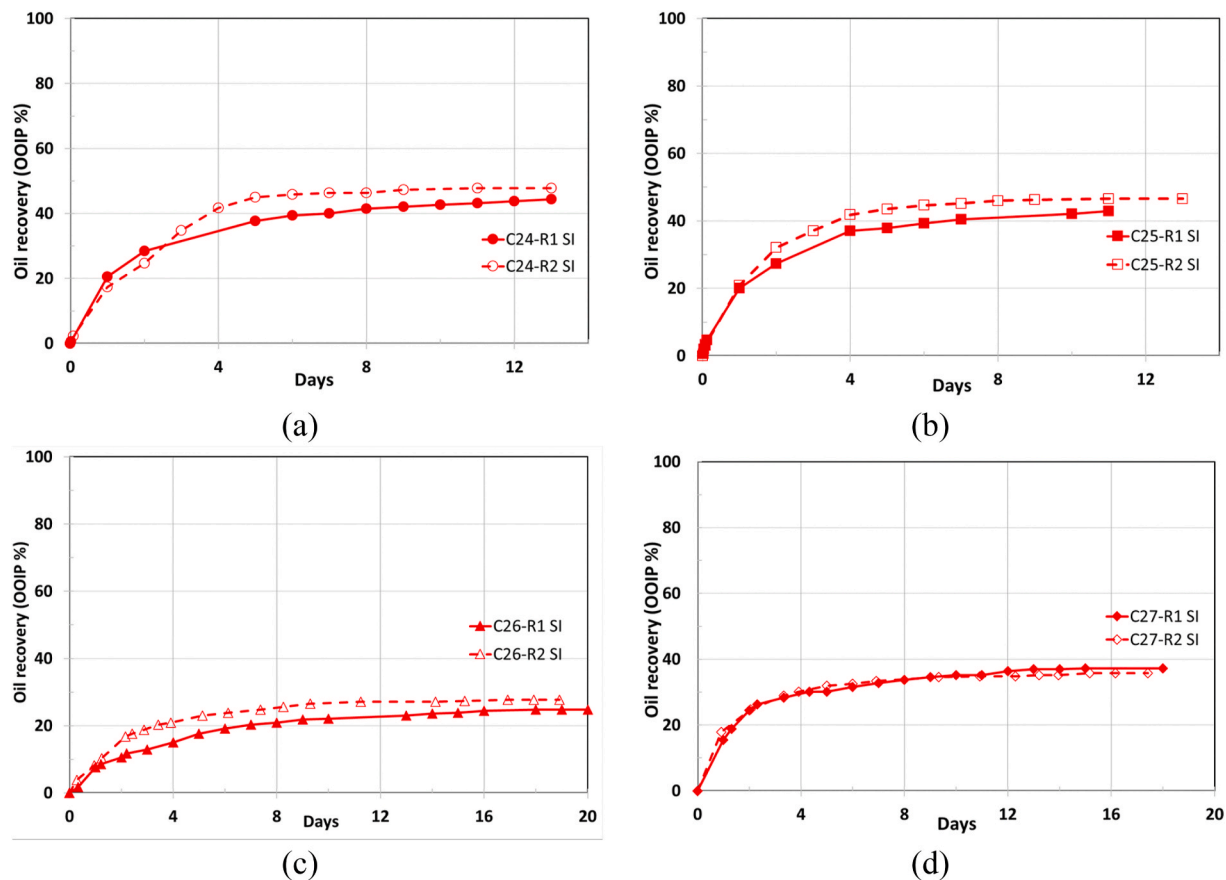


Fig. 12. Oil recovery tests by SI performed at 50 °C after initial restoration (R1) and a second restoration (R2) on cores with $S_{wi} = 0.1$. (a) Core C24 and (b) Core C25 exposed to Oil B (AN = 0.36 mgKOH/g). (c) Core C26 and (d) Core C27 exposed to Oil C (AN = 0.5 mgKOH/g).

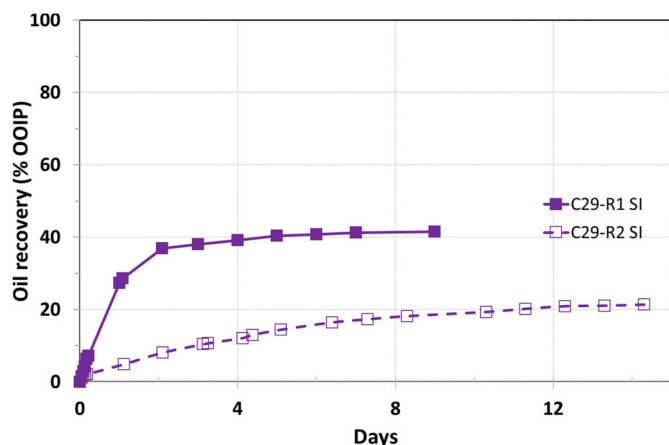


Fig. 13. SI tests performed at 50 °C after the initial restoration (R1) and the second restoration (R2) of core C29. During R1 the core was exposed to 5 PV Oil B with AN = 0.36 mgKOH/g. After mild cleaning the core was exposed to another 5 PV of Oil B in R2.

restored in a second restoration (R2) with $S_{wi} = 10\%$, and another 5 PV of Oil B. In the following SI test, the ultimate recovery was reduced to 21.0 %OOIP. A reduction in oil recovery of 20.5% OOIP confirmed a significant drop in the water-wetness of the core due to the increased exposure to Oil B. The wetting index, I_{W-SI} , dropped dramatically from 0.59 to 0.30. These results confirm previous observations by Hopkins et al., (2017).

The mild core cleaning process carried out with reduced volumes of kerosene and heptane preserves a larger amount of adsorbed POC on the mineral surfaces. Thus, in the core restoration process, less POC are needed for reproducing the initial core wettability. In the mild core cleaning procedure with kerosene-heptane, the residual crude oil was efficiently removed with 10 PV kerosene injection and a clear effluent oil was observed. The kerosene was then displaced by heptane. After building initial water saturation with desiccator, vacuum saturation of crude oil (0.9 PV) successfully reproduced the initial core wettability. A summary of SI and CW data before and after mild core cleaning is presented in Table 5. The suggested methodology for wettability reproduction can potentially be applied in core materials with similar mineralogy as SK chalk, that is on calcite surfaces with a low content of silicate impurities.

4. Concluding remarks

The efficiencies of two different cleaning solvent systems, toluene-methanol (standard cleaning) and kerosene-heptane (mild cleaning), in cleaning crude oil-wetted outcrop chalk cores were tested. The wetting of the cores was evaluated by spontaneous imbibition and chromatographic wettability tests.

The results showed that spontaneous imbibition and capillary forces had increased after cleaning by both solvent systems. The toluene-methanol cleaned core behaved more water-wet than the kerosene-heptane cleaned core in spontaneous imbibition tests, resulting in higher ultimate oil recoveries. A larger water-wet surface area in the toluene-methanol cleaned core was confirmed by the chromatographic wettability test.

Increased imbibition rates and ultimate oil recovery were reported in cases when only small changes in the fraction of water-wet surface area were measured, suggesting that the distribution of POC at the pore surfaces is important.

After a second restoration, with an injection of 5 PV of crude oil through the mildly cleaned cores, new spontaneous imbibition tests showed reduced ultimate oil recovery compared to the first restoration, thus the initial wettability was not completely reproduced.

Table 5

Data summary after initial (R1) and second core restorations (R2).

Core	SI_{R1} % OOIP	I_{W-SI} $R1$	I_{CW} $R1$	SI_{R2} % OOIP	I_{W-SI} $R2$	ΔSI % OOIP	ΔI_{W-SI}
C24	44.4	0.63	0.92	47.8	0.68	+3.5	+0.05
C25	42.9	0.61	0.75	46.6	0.67	+3.6	+0.05
C26	24.7	0.35	0.81	27.7	0.40	+3.0	+0.04
C27	37.2	0.53	0.82	35.8	0.51	+1.5	+0.02
C28	70.0	1.0	1.0	-	-	-	-
C29	41.5	0.59	-	21.0	0.30	-20.5	-0.29

Reproduction of initial wettability after mild cleaning with kerosene-heptane was attempted by only introducing (1- S_{wi}) PV crude oil by vacuum-saturation. Spontaneous imbibition tests at 50 °C showed a very good match between the production profiles before and after cleaning. Reproduction of the initial wettability was successful, showing a difference of +1.5–3.6% OOIP between the first and second restorations in all cores.

Consequently, by limiting the kerosene-heptane injection during core cleaning, desorption of the specific POC dictating the initial reservoir wettability is minimized. By this procedure, only a minimum volume of crude oil is therefore needed to reproduce the wettability. The crude oil that originally created the reservoir wetting might be different in composition to the in-situ reservoir oil today, thus this proposed procedure could result in a more representative reservoir core wettability than that obtained in standard routine SCAL analyses.

CRedit authorship contribution statement

Iván Piñerez: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration. **Tina Puntervold:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing - original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Skule Strand:** Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Paul Hopkins:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Panagiotis Aslanidis:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Hae Sol Yang:** Validation, Formal analysis, Investigation, Data curation, Visualization. **Magnus Sundby Kinn:** Validation, Formal analysis, Investigation, Data curation, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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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
D	Core Diameter
DI	Deionized water
d ₁₀ FW	Ten times diluted formation water
FW	Formation water
H	Heptane
I_{CW}	The fraction of water-wet surface area of a core sample
K	Kerosene
k_{ro}	Relative permeability to oil
k_{rw}	Relative permeability to water
L	Core length
M	Methanol
mM	Milli-molar (10^{-3} mol/L)
m_{sat}	Weight of saturated core
m_0	Weight of dry core
OOIP	Original oil in place
P_c	Capillary pressure
PV	Pore volume, mL
V_b	Bulk volume, cm ³
R-COO	Carboxylate
SCA	Special core analysis
SK	Stevns Klint
S_{orw}	Residual oil saturation after waterflood
S_w	Initial water saturation, % PV
S_{wr}	Residual water saturation, % PV
SWOT	Sea water without thiocyanate tracer and sulphate
SW ^{1/2} T	Seawater that contains thiocyanate tracer and sulphate
T Toluene	TDS Total Dissolved Salt, mg/L
Φ	Core Porosity
ρ_{sat}	Density of saturation fluid, g/cm ³

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2020.107654>.

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