# Experimental Reproduction of Wettability for Core Analysis

by

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*Μακριά ή κοντά.*

*Στη γη ή στον ουρανό.*

*Ό,τι αγαπάς βρίσκεται μέσα σου…*

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*Panos*

# Summary

The ideal scenario when core samples are retrieved from the field to the lab is to start the experiment immediately without any treatment. Due to a decrease in pressure and temperature from reservoir to standard conditions, fluid expansion occurs. The depressurized cores will not have a correct fluid saturation and need to be restored prior to laboratory core experiments. To achieve representative reservoir data from these tests, the restored core wettability needs to be close to reservoir conditions.

Wettability dictates the fluid flow in porous media, and the restored wettability will dramatically influence the results on capillary pressure, relative permeability, and oil recovery tests in laboratory experiments. Therefore, wettability should be preserved in-between restoration processes.

The wettability of a core retrieved in the lab can be affected during cleaning and restoration procedures. A wide range of cleaning techniques are followed in laboratories including different solvents, experimental set-ups, methods, etc. The same applies in core restoration, where the restoring protocol differs from one lab to another including establishing initial water saturation, crude oil exposure, the aging process, etc.

In this project, several reservoir sandstone and outcrop carbonate cores, underwent a series of experiments in regard to wettability. The solvents utilized during core cleaning and the amount of crude oil exposed to the core during core restoration were the study's major emphasis. In this work, two cleaning procedures were compared: a mild approach (kerosene and heptane) and a more rigorous industrial standard used (toluene/methanol). Amount of, 1, 5, and 11 pore volumes (PV) of crude oil was utilized to evaluate the effect of crude oil exposure in the wettability of a system. Finally, an adsorption test on a sandstone reservoir core was performed to provide more thorough monitoring of the influence of crude oil in the sandstone rock surface.

The findings indicated that mild cleaning followed by an uncontrolled quantity of crude oil exposure might have a substantial influence on the wettability of the system, causing it to become less water-wet. A more comprehensive adsorption test on the reservoir sandstone core demonstrated that polar organic components (POC) continue to adsorb on the mineral surface even after many PV injections. However, the use of more rigorous solvents resulted in the reverse situation, resulting in more water-wet conditions. Finally, the use of mild solvents with just 1 PV of crude had no effect on the wettability of the systems between restorations.

In conclusion, this doctoral thesis proposes an efficient core cleaning and restoration process in which the wettability of the cores is replicated from one restoration to the next.

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doi:https://doi.org/10.3997/2214-4609.202113237

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# Nomenclature

| | |
|---|---|
| *FW* | *Formation Water* |
| *SW* | *Seawater* |
| *COBR* | *Crude oil-Brine-Rock* |
| *POC* | *Polar Organic Compounds* |
| *PV* | *Pore Volume* |
| $S_{or}$ | *Irreducible oil saturation* |
| *IFT* | *Interfacial tension* |
| $S$ | *Entropy* |
| $V$ | *Volume* |
| $U$ | *Energy* |
| $P_c$ | *Capillary pressure* |
| $\sigma$ | *Interfacial tension* |
| $\theta$ | *Contact angle* |
| $r$ | *Radius of the capillary tube* |
| $P_{OA}$ | *Pressure at point A for oil* |
| $P_{WA}$ | *Pressure at point A for water* |
| $P_{OB}$ | *Pressure at point B for oil* |
| $P_{WB}$ | *Pressure at point B for water* |
| $\rho_{water}$ | *Density of water* |
| $g$ | *Gravitational acceleration constant* |
| $h$ | *Height of the column* |
| $\rho_{oil}$ | *Density of oil* |
| $\delta^+$ | *Partial positive end of hydrogen atoms* |
| $\delta^-$ | *Partial negative end of hydrogen atoms* |
| $WI_{New}$ | *Wettability index* |

| | |
|---|---|
| $A_{Wett}$ | *Area between the curves of the ionic concentration of sulfate and thiocyanate* |
| $A_{Heptane}$ | *Reference area* |
| $\gamma_{go}$ | *Contact angle in a gas-oil interface* |
| $\gamma_{wo}$ | *Contact angle in a water-oil interface* |
| $\gamma_{gw}$ | *Contact angle in a gas-water interface* |
| $\gamma_{os}$ | *Contact angle in a oil-solid interface* |
| $\gamma_{gs}$ | *Contact angle in a gas-solid interface* |
| $\gamma_{ws}$ | *Contact angle in a water-solid interface* |
| *NMR* | *Nuclear Magnetic Resonance* |
| *NSO* | *Nitrogen, Sulfur, Oxygen* |
| *AN* | *Acidic number* |
| *BN* | *Base number* |
| *API* | *American Petroleum Institute* |
| $f$ | *Opposite force to the liquid film* |
| $dA$ | *Area increase* |
| $\gamma$ | *Gibbs energy* |
| $dx$ | *Distance* |
| $A$ | *Area* |
| $E$ | *Total energy of a system* |
| $E_u$ | *Energy per unit volume* |
| $E_s$ | *Energy per unit area* |
| *NCS* | *Norwegian Continental Shelf* |
| *PDO* | *Plan for Development and Operation* |
| *XRD* | *X-Ray Diffraction analysis* |
| $S_{wi}$ | *Initial water saturation* |
| *SEM* | *Scanning Electron Microscopy* |
| *CT* | *Computed Tomography* |
| $V_b$ | *Bulk volume* |
| $m_o$ | *Dry weight* |
| $m_{sat}$ | *Saturated weight* |
| $\rho_{sat}$ | *Density* |
| $\Phi$ | *Porosity* |
| *SI* | *Spontaneous Imbibition* |

# 1 Introduction

Our world is changing rapidly towards a greener future, gradually leaving behind the dependency on fossil fuels. According to the Paris Agreement in 2015, 196 parties agreed to maintain the upsurge of the mean global temperature to below 2 °C by reducing the greenhouse gases. Progressively, this temperature rise stabilization will noticeably moderate the effects of climate change. The target that was set was to cut the emissions in half by 2030 to a net-zero moving in the first half of the $21^{st}$ century. This ambitious commitment has brought many new challenges to the industries including the switch from the well-established fossil fuels resources to renewable energy.

Oil and gas contribute to more than half of the global energy consumption. That means that the transition to the renewable sector will take time, while the oil will keep leading the market in the energy supply for the next at least 30 years.

What can be done in the oil industry to align with the future goals of a greener future, is to find ways to optimize oil recovery in an environmentally friendly way.

## 1.1 Enhanced Oil Recovery (EOR) by Smart Water

‘’Smart Water’’ injection is an Enhanced Oil Recovery (EOR) method the principles of which rely on wettability alteration processes. It is an environmentally friendly method, where the ultimate oil recovery is increased compared to the conventional water-flooding by wettability alteration towards more water-wet conditions inducing more positive capillary forces and increasing the sweep efficiency of the system.

What differentiates a Smart Water brine from a standard formation water (FW), or seawater (SW) is the modified ionic composition. The brines are designed in a way to disrupt the chemical equilibria of the crude oil-brine-rock system (COBR) and alter the wettability towards more water-wet conditions. This wettability alteration mechanism is different in carbonates and sandstones. Silicate surfaces are negatively charged while carbonates are positively charged.

From past studies, it was observed that wettability alteration in sandstones is a phenomenon closely related to the pH of the system which depends on the COBR interactions (Austad et al., 2010). In carbonates, wettability alteration is dependent on the presence of potential determining ions like $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$.

A major role in the wettability of a rock surface are the polar organic compounds (POC) in the crude oil phase present. They could be either positively (protonated N-containing bases) or negatively (carboxylates) charged. Either way, these compounds could interact with charged rock surfaces affecting the wettability.

This work is a continuation of past work performed in the Smart Water EOR group at the University of Stavanger. Hopkins (2017) in his doctorate thesis, measured the adsorption of acids and bases on chalk material and their effect on wettability. The water-wetness of chalk cores was decreased by increasing the amount of crude oil (pore volumes (PV) injected into the cores). Based on this evidence, Mamonov (2019) continued the work by studying the effect of adsorbed POC on sandstone minerals and their effect on wettability. The outcome of this study confirmed again the high affinity of POC towards sandstone minerals surfaces by extended crude oil exposure. Since polar organic compounds are adsorbing onto the mineral surfaces and change the wetting, a question arises:

*How could representative wettability be obtained during core restoration for special core analysis (SCA) and wettability-dependent oil recovery studies?*

## 1.2 Objectives

The ultimate goal when restoring a core is to create a representative sample close to the reservoir conditions. Core cleaning, establishing initial water saturation, crude oil exposure, and aging are the major factors that control the initial wettability conditions that will be created in the core. This project focuses on optimizing two of those parameters: core cleaning and crude oil exposure.

Following the evidence from the past work, this study comes to extend the understanding of core restoration processes. In experimental wettability studies, the core wettability should be able to be reproduced from one restoration to another. This will ensure a clear observation of any possible effect when altering a different parameter of the system e.g. brine composition, temperature, flooding rate, brine sequence, etc.

In the next chapters, two different cleaning approaches will be compared: a harsh (toluene/methanol) and a mild (kerosene/heptane). Several reservoir sandstone and outcrop carbonate cores were exposed to various crude oil amounts, and the wettability of the systems was evaluated through spontaneous imbibition tests. Furthermore, crude oil adsorption tests were performed on one sandstone reservoir core to verify that POC adsorb also in this system.

This work comes to provide some additional information on core restoration strategy by recommending an optimized core restoration strategy where the wettability of a COBR system is preserved. This newly proposed method suggests the usage of mild solvents during the cleaning process followed by the optimum amount of 1 PV of crude oil exposure. In this way, the wettability of the core samples can be reproduced as a representative core wettability in successive restoration operations.

# 2 Theory

In this chapter, the fundamental theories that govern wettability will be described. This includes the formation of the initial wettability in reservoir conditions, the connection between Smart Water and wettability, the factors that influence wettability, and the methods by which wettability can be assessed.

## *2.1 Oil formation and entrapment*

Deposition of organic matter along with fine-grained sediments through water and wind marks the start of oil creation. Oxygen is depleted in these lower zones of deposition where anaerobic bacteria begin the conversion of the organic matter into precursors of petroleum hydrocarbons (Donaldson and Alam, 2008).

This organic matter is buried for thousands-millions of years until it transforms into kerogen under mild conditions of pressure and temperature (less than 50 °C). Kerogen is a solid, insoluble organic matter with a high molecular weight that can yield oil upon heating. This compaction of sediments that causes physical, chemical, or biological alteration is called diagenesis. Hydrocarbon generation begins during **diagenesis** (Schlumberger, 1998).

When kerogen reaches the conditions of pressure and temperature needed (100-150 °C for oil and 150-200 °C for gas) will form the first hydrocarbons. The generation of gas and liquid hydrocarbons within the kerogen-clay mass increases the volume, and thus the internal pressure acting on the fluids (together with the temperature and overburden stress) creates fractures in the matrix that initiate primary migration of the fluids to adjacent porous structures (Donaldson and Alam, 2008). The above described physical and chemical alteration of sediments and pore fluids at temperatures and pressure higher than those of diagenesis is called

**catagenesis** glossary (Schlumberger, 1998). The process is also known as primary migration.

The last stage of maturation and conversion of organic matter to hydrocarbons is called **metagenesis** (Schlumberger, 1998). Continued changes in fluid pressure and fracturing of the host sediments by mechanical stress from tectonic changes, together with the formation of porous and permeable pathways for movement of the water and hydrocarbons through an inclined porous structure, result in secondary migration. During secondary migration from the source rock to the trap, the hydrocarbons become associated with brine and wettability (Donaldson and Alam, 2008). A flow chart display of the processes described is depicted in **Figure 1**.

The fluids move from the source rocks to geologic traps and areas at or near the surface. There are two general classifications of petroleum traps: **structural** (folding of the sediments, up-dip sealing of anticlines by faults, and intrusion of salt diapers) and **stratigraphic** (cessation of the accumulation of sediments, burial because of subsidence or other local environmental changes and uplift and erosion of porous sediment) (Donaldson and Alam, 2008). Often, the top layer of this trap is a relatively impermeable rock, commonly shale, anhydrite, or salt that forms a barrier or seal above and around reservoir rock so that fluids cannot migrate beyond the reservoir (cap rock) (Schlumberger, 1998). Some of the accumulations might reach the surface and form tars.

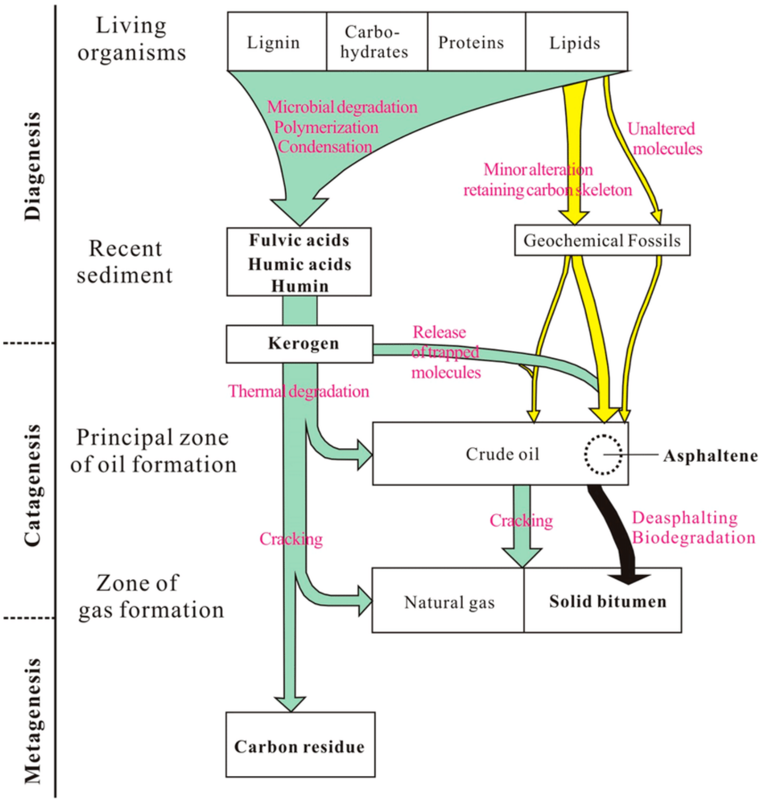


**Figure 1:** Oil formation process.
(source: https://personal.ems.psu.edu/~pisupati/ACSOutreach/Petroleum_2.html)

## 2.2 The formation of the initial wettability

While oil accumulates, it interacts with the rock surface, finally establishing an equilibrium condition of wettability. Water and the effects of wettability are present throughout the formation during migration and accumulation of gas and oil (Donaldson and Alam, 2008). Several phenomena take place until the establishment of the initial wettability in the reservoir rock.

Starting with the phenomenon of the buoyant force, which is the upward force acting on an object placed in a fluid (Schlumberger, 1998). When oil starts to accumulate, it enters the largest pores of the reservoir. In most cases, the smaller pores are filled with water because the threshold capillary pressure is too high for entry into the oil. Therefore, in this stage, pore-size distribution plays an important role to establish wettability in the system e.g. majority of large pores will lead to a more oil-wet state whereas a few large pores might lead to a more water-wet state. Subsequently, different oil distribution will alter oil properties as well (density, composition, viscosity, etc). Change of oil properties will have an effect on phenomena like adsorption of polar components, asphaltenes precipitation, etc. Thus, oil production from different zones might give significantly different results. Water breakthrough will occur earlier in the oil-wet zone and the oil production rate will be low; in the water-wet zone, water breakthrough will occur after considerable production of oil at a rapid rate, but then the rate of production will rapidly decrease along with an increase in the water/oil production ratio (Donaldson and Alam, 2008).

## 2.3 Definition of wettability

The term wettability describes the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. Wettability is a major factor controlling the location, flow, and distribution of fluids in a reservoir (Anderson, 1986). When there are two or more immiscible fluids in porous rock, each fluid will occupy a place on the mineral surface of each pore. The distribution of each fluid onto this surface depends on the fluid-rock interactions, mineralogy of the rock, gravity, and capillary forces present in the system.

An oil-water-rock system could be generally described based on wettability as:

a) Water-wet: Water occupies all small pores and most of the surface and the middle of the larger pores. In this case, oil can be found as droplets attached to the rock surface where its components have a higher affinity to some minerals rather than others.
b) Fractionally-wet: Heterogeneous wetting randomly distributed on the mineral surface.
c) Mixed-wet: Water occupies the smaller pores, whereas oil spreads to most of the surface of the larger pores.
d) Oil-wet: The inverse phenomenon of water-wet state. Oil occupies the smaller pores and most of the surface and middle part of the larger pores.

Historically, all petroleum reservoirs were believed to be strongly water-wet. This was based on two main factors. First, almost all clean sedimentary rocks are strongly water-wet. Second, sandstone reservoirs were deposited in aqueous environments into which oil later migrated. It was assumed that the connate water would prevent the oil from touching the rock surfaces (Anderson, 1986).

## 2.4 Capillary forces

As capillary pressure is defined as the pressure difference ($P_c$) between two immiscible fluids in a thin tube, resulting from the interactions of forces between the fluids and solid walls of the tube (Wikipedia, 2001). When the contact among immiscible fluids is curved, the pressure differential across the contact will be larger on the convex side in order to balance the forces that cause interfacial tension.

Capillary forces are one of the main mechanisms for oil mobilization in water-wet fractured, low permeable matrix reservoirs. Fluid velocity could influence the oil mobilization in a core experiment. At higher velocities, the displacement front is moving faster through the core. An increased amount of isolated or less mobile oil could be easily left behind after the displacement front has passed, increasing the irreducible oil saturation ($S_{or}$). To allow for capillary forces and spontaneous imbibition the flooding rate should be lowered.

When the injection brine is introduced to the heterogeneous pore system, the brine flows through the pathways with the lowest restrictions. In the presence of positive capillary forces, the brine flowing in the higher permeable pathways will imbibe and expel oil from other, smaller pores of lower permeability, as illustrated in **Figure 2** by Aghaeifar et al. (2019). In water-wet pore systems, little or no oil is attached to the mineral surfaces, and the residual oil ($S_{or}$) is trapped in the pore body. Interfacial tension (IFT) and pore heterogeneity will affect the residual oil saturation. In the same system, a reduced IFT could reduce the $S_{or}$.

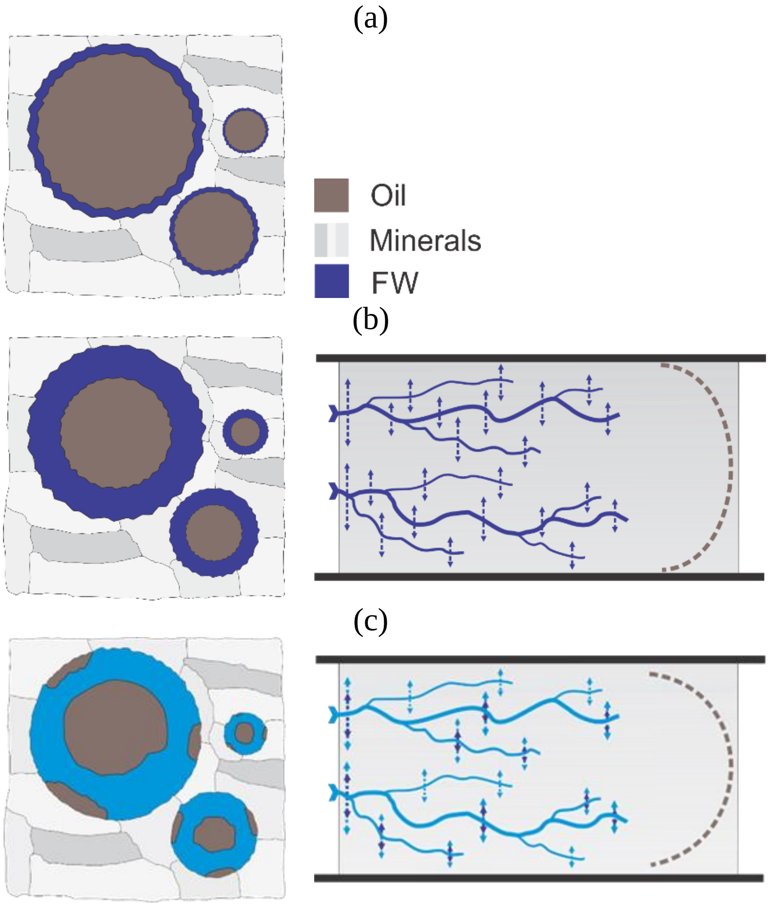


**Figure 2:** Very water-wet heterogeneous porous rock system at initial oil saturation (a). Larger pores are pathways for water and oil transport (b left). Capillary mobilized oil from smaller pores secure stable oil displacement and low $S_{or}$ (b right). $S_{or}$ after wettability alteration with Smart Water where oil displacement is controlled mainly by capillary forces (c) (Aghaeifar et al., 2019).

### 2.4.1 Capillary pressure

For a capillary tube, the capillary forces could be described as a capillary pressure phenomenon.

**Equation 1** describes the capillary pressure as a function of the radius of the capillary tube $r$, the contact angle $\theta$ and the interfacial tension $\sigma$. This is a simplified version to describe the capillary forces assuming that the entropy (S) and the volume (V) are constant ($dS=0$, $dV=0$) which brings the energy to minimum levels ($dU=0$).

**Figure 3** illustrates the case of a wetting phase (water) and a non-wetting phase (oil).

$$P_c = \frac{2\sigma\cos(\theta)}{r} \tag{1}$$

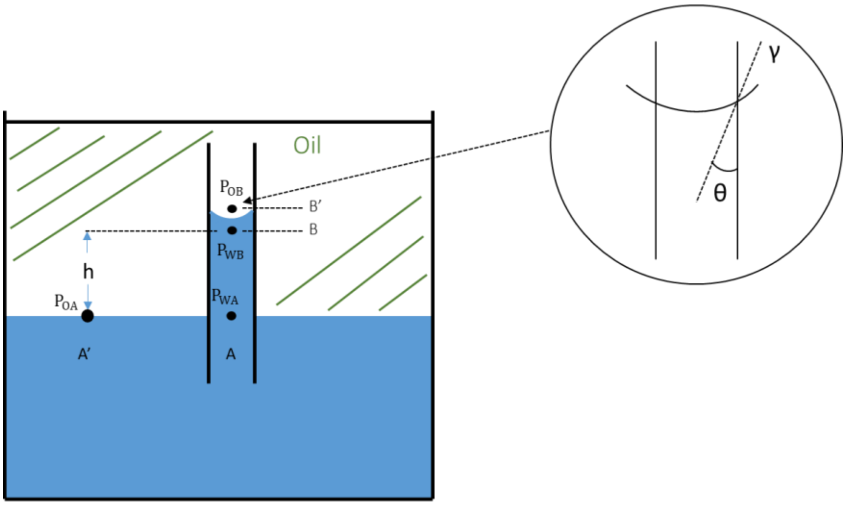


**Figure 3:** Graphical example of a capillary tube. The container is filled with water, and the surrounding phase is crude oil.

At point A, there is a pressure equilibrium between the points $P_{OA}$ and $P_{WA}$ so:

$$P_{OA} = P_{WA} \tag{2}$$

At point B the corresponding pressures $P_{WB}$ and $P_{OB}$ will be described as:

$$\mathrm{P_{WB}} = \mathrm{P_{WA}} - \rho_{\mathrm{water}} \cdot gh \tag{3}$$

$$\mathrm{P_{OB}} = \mathrm{P_{OA}} - \rho_{\mathrm{oil}} \cdot gh \tag{4}$$

By combining **Equations 2, 3** and **4**, a new **Equation 5** is derived which describes the pressure differential at the contact point:

$$\mathrm{P_{WB}} + \rho_{\mathrm{water}} gh = \mathrm{P_{OB}} + \rho_{\mathrm{oil}} gh \Longrightarrow$$

$$\mathrm{P_{OB}} - \mathrm{P_{WB}} = (\rho_{\mathrm{water}} - \rho_{\mathrm{oil}}) gh \tag{5}$$

As derived from the latest formula (**Equation 5**), the capillary pressure of a system is strongly dependent on the density $\rho$ of the fluids and the height $h$ of the tube column. The next chapter explains the capillary pressure phenomena in-depth, by looking into the actions taking place on a micro-scale.

### 2.4.2 Capillary forces in micro-scale

Depending on the shape of the meniscus formed in a capillary tube, it can be called concave or convex (**Figure 4**). In the case where a capillary tube is filled up with water and the tube is made of silica material, then a concave shape is observed. In the case where the tube is filled with mercury, a convex shape is noticed.

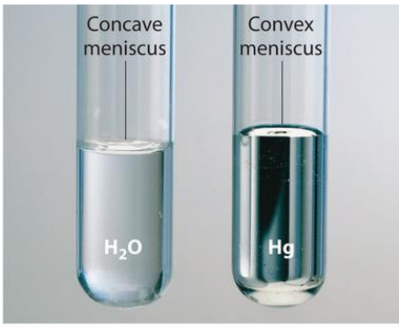


**Figure 4:** Concave and convex meniscus shape
(Source: modified from source:
https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_Matter/Properties_of_Liquids/Surface_Tension)

Each water molecule has partially negative and positive ends at the hydrogens ($\delta^+$, $\delta^-$). This is helping the hydrogen bonding to form. The polarity of the molecules of the glass made from silicon oxide lattice (two oxygen atoms per silicon atom) facilitates this attraction. The electronegativity difference between oxygen and silicon is even higher than the one between oxygen and hydrogen. Therefore, the oxygen molecules are able to get silicon's electrons, especially the ones involved in the bonding. At the water-tube interface, the kinetic energy of the water molecules will cause water molecules to move close to the glass molecules. The partially positive end of the hydrogen end of the water molecule at the hydrogen would be attracted to the partially negative ends of the oxygen in the glass. This will result in a stronger partial charge than what you see in the water due to the big electronegativity difference. This phenomenon of the water molecules ‘’sticking’’ on the glass is called adhesion. This is the reason why the concave shape is observed in a capillary tube. In **Figure 5** the whole process is schematically illustrated.

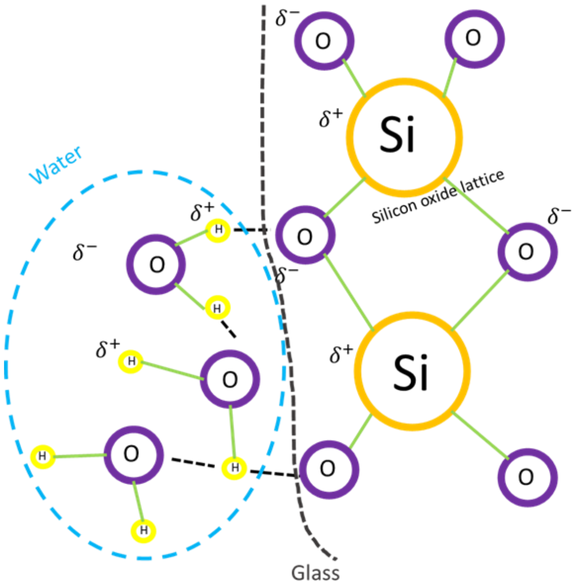


**Figure 5:** Water-glass interface of a capillary tube. Water molecules are attracted more to the partially negative ends of the oxide lattice than of those in the water, forming a meniscus shape.

## 2.5 Methods for evaluating wettability

### 2.5.1 Spontaneous Imbibition

Spontaneous imbibition is an experimental process where the wettability of porous rock is measured as a function of the displacement characteristics of the COBR system. It is controlled mainly by the action of capillary forces, which are proportional to the interfacial tension of the fluids present and to the wettability. The rate of imbibition and the total amount of the fluid displaced lead to a qualitative evaluation of the wettability of the system.

As it is shown in **Figure 6** (a) from Hodder and Nychka (2019), the apparatus consists of an Amott cell (Amott, 1959) a rock sample saturated with the displaced phase (oil) and the fluid used as the imbibing phase (water).

In (a) a water-wet case is examined by collecting the produced oil to the graded upper part of the burette. On the other hand, for an oil-wet case, the apparatus would be inverted, and the expelled water would be collected by gravity segregation at the bottom of the Amott cell. Preferentially water-wet cores are characterized by a positive displacement-by-water ratio and a value of zero for the displacement-by-oil ratio (Amott, 1959).

In **Figure 6** (b), a graphical representation of the results obtained from a spontaneous imbibition test is shown where oil production is monitored with time. The test was performed on the reservoir sandstone core using as the imbibing phase a high salinity formation water (over 200000 ppm). At the initial production phase, there was rapid water imbibition by strong capillary action. The effect of capillary forces weakens over time as the gravity forces are taking place and finally dominate the system reaching to recovery plateau at the final part of the experiment.

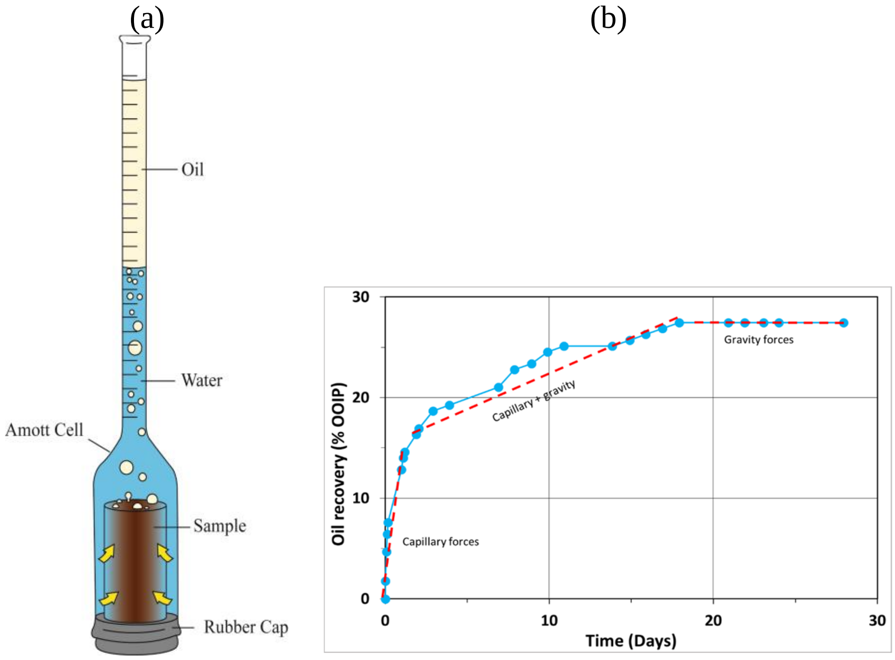


**Figure 6:** (a) Spontaneous imbibition apparatus, *Source:(Hodder and Nychka, 2019)* (b) Graphic representation of spontaneous imbibition results.

### 2.5.2 Chromatographic wettability test for carbonates

This wettability test method relies on the chromatographic separation of sulfate ions, ($SO_4^{2-}$) and thiocyanate, ($SCN^-$), as a tracer (Strand, 2005). According to this method, a carbonate core is flooded to $S_{or}$ with the selected brine without tracer and sulfate. Afterward, a brine with an equal molar concentration of $SCN^-$ and $SO_4^{2-}$ is flooded into the core. Then, the effluents are analyzed through an ionic chromatographer. The ion concentrations are plotted against the pore volume injected and the area between the two curves is calculated. The wetting index, thus the level of wettability, can be derived as shown in **Equation 6**:

$$\mathrm{WI_{New}} = \frac{\mathrm{A_{Wett}}}{\mathrm{A_{Heptane}}} \qquad (6)$$

Where:

$WI_{New}$ = wettability index, ranges from 0 (completely oil-wet) to 1(completely water-wet)

$A_{Wett}$ = area calculated between the curves of the ionic concentration of sulfate and thiocyanate

$A_{Heptane}$ = reference area which indicates a completely water-wet state

In conclusion, the above-calculated area $A_{Wett}$ must be directly proportional to the water-wet surface in the porous medium, because the water-soluble components, $SCN^-$ and $SO_4^{2-}$, contacted the same water-wet area (Strand, 2005).

An example of the method is illustrated in **Figure 7.** When sulfate ions find a lot of pore surface available to adsorb, the $A_{wett}$ will increase indicating a strongly water-wet behaviour. Likewise, as the amount of sulfate adsorb reduces, the level of water-wetness in the system is decreased.

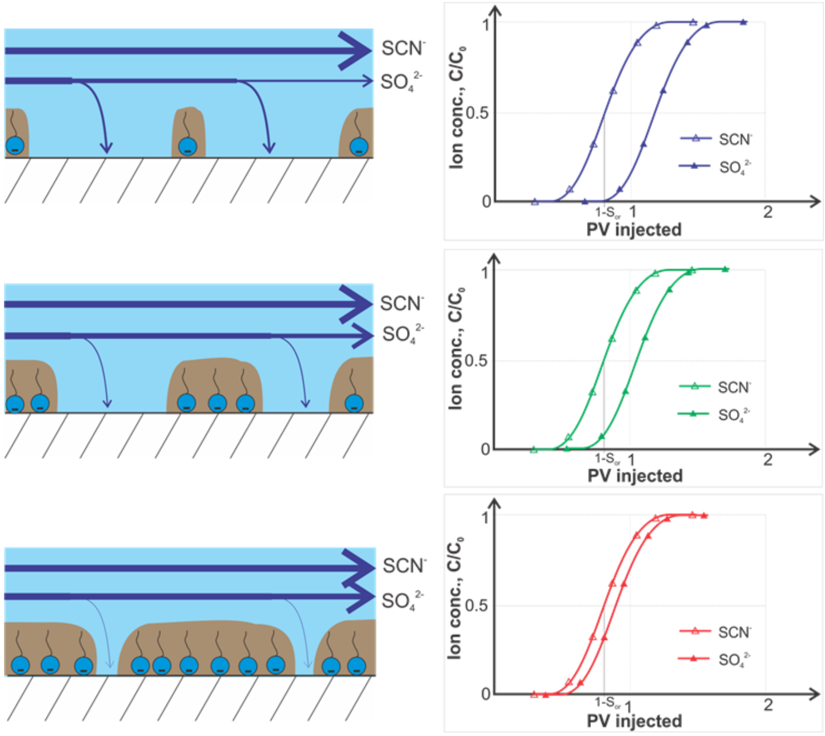


**Figure 7:** From top to bottom: completely water wet-state, completely oil-wet state and mixed wet state.

### 2.5.3 Contact angle

Contact angle measurements have been used quite extensively in the last decades. According to this method, a droplet of fluid (e.g. water) is placed on a flat solid surface. This solid afterwards is submerged in a different fluid than the previously wetting phase (e.g. oil). The droplet of water will stay in contact with the solid at a specific angle. The value of this angle ranges between $0^o$ (infinitely water-wet) and $180^o$ (infinitely oil-wet). For contact angles of about $90^o$ the wetting is characterized as neutral-wet.

An example of a contact-angle measurement is shown in **Figure 8**. In **Figure 8** (a) a strongly water-wet case is presented, where the contact angle between the water and the solid is equal to zero, and thus there is the formation of a thin water film on the solid surface. In **Figure 8** (b) a strongly oil-wet with oil-film is illustrated, and in **Figure 8** (c), a weakly water-wet case with water-film. Finally, in **Figure 8** (d), a weakly oil-wet case without an oil-film is depicted.

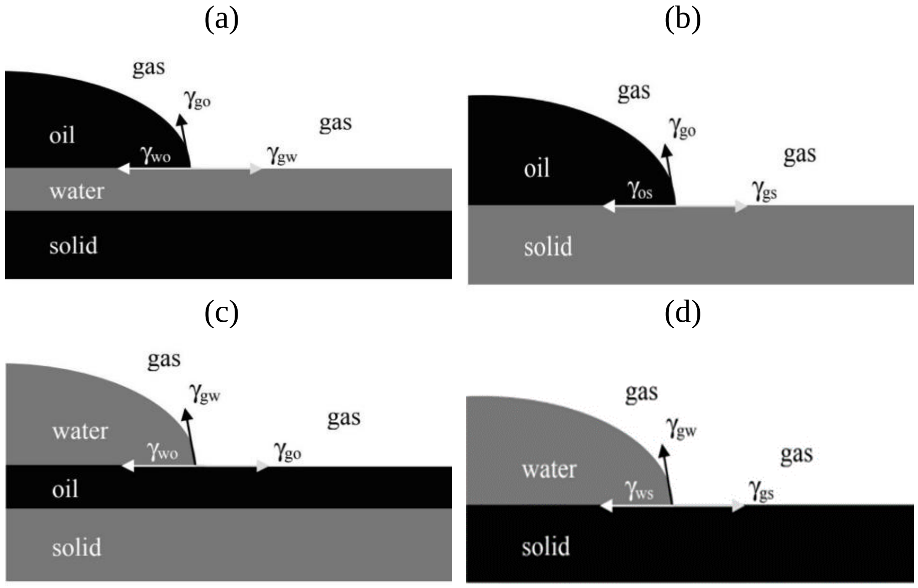


**Figure 8:** Contact angle measurements for strongly water-wet with water film (a), weakly water-wet with no water-film (b), strongly oil-wet with oil-film (c) and weakly oil-wet with no oil-film (d)
(Source: (Donaldson and Alam, 2008))

## 2.5.4 Other methods

Besides the above-mentioned methods, several other methods have been proposed for evaluating the wettability. Some of them are based on the:

- Thermodynamic definition of wetting

Relates to the physicochemical reaction caused by intermolecular forces of attraction. An example of this method can be found in the literature (Jiang et al., 2020; Xie et al., 2015).

- Interfacial tension and displacement-pressure measurements

Considering that wettability can be measured quantitatively by defined contact angle measurements using interfacial-tension and displacement-pressure measurements.

- Shape of relative permeability curves

Investigates the influence of wettability on the shape of relative-permeability curves. (Anderson, 1987; Fatemi et al., 2012; Jahanbakhsh et al., 2016).

- Shape of recovery curves

Relates the shape of recovery curves as a function of the volume of water injected in the waterflooding of a natural sample, using low viscosity fluids.

- Permeability and saturation measurements

It is based on saturation frequency distributions of samples as a function of their permeabilities.

- Nuclear magnetic relaxation measurements

In this technique varying proportions of two sand packs are mixed and treated so that one was strongly water-wet and the other strongly oil-wet (Newgord et al., 2019).

- Dye adsorption

This method had the advantage of not requiring any complicated equipment and of not altering the samples prior to the test.

- Flotation experiments

They can be used for unconsolidated rocks but are not very sensitive and are affected by parameters other than wettability (particle size, particle density, etc.).

- X-ray photoelectron spectroscopy

This technique is used for the qualitative determination of the wettability of rocks from an evaluation of the amounts of organic carbon and sulfur present on the solid surface.

- Use of well logs

It is a method based on the fact that the electrical resistivity index of an oil-wet rock is known to be greater than that of a water-wet rock so this property can be used to evaluate wettability in-situ.

- Use of capillary pressure curve

A method that combines the use of the correlation existing between the degree of wetting and the areas under the capillary-pressure curves as well as the speed with which these curves are determined by using centrifuging (Morrow, 1990).

## 2.6 Factors influencing wettability

### 2.6.1 Crude oil

The crude oil phase is the major factor that dictates wettability in a rock system. Due to the chemical complexity and variation of its components, it is not an easy fluid to characterize, thus many different studies are needed to evaluate its physical and chemical properties (chromatography, NMR, rheological, etc).

The key to altered wettability appears to be exposure of the rock surface to crude oil (Buckley and Morrow, 1990). The oil contains interfacially active species that can alter wetting. Whether and when these species actually do affect wetting depends, in part, on the composition of the rest of the oil phase (Buckley et al., 1989).

Surface-active components of crude oil are more prevalent in the heavier fractions of crude, such as resins and asphaltenes. These surfactants are believed to be polar compounds that contain oxygen (Anderson, 1986). Therefore, several studies took place in the past years in an attempt of explaining the effect of asphaltenes and resins on rock surfaces (Buckley, 1995). **Asphaltenes** are molecular substances that are found in crude oil and they consist primarily of carbon, hydrogen, nitrogen, oxygen, and sulphur, as well as trace amounts of vanadium and nickel (Speight, 1999) (**Figure 9**). They are highly polar heterocyclic compounds which are insoluble in saturated alkanes (Donaldson and Alam, 2008). **Resins** are smaller molecules than asphaltenes but have in general higher content of the polar elements nitrogen, sulfur, and oxygen (NSO-compounds), and they are in general more polar than the asphaltenes (Speight, 1999) (**Figure 9**).

Precipitates that form as the result of interactions between an asphaltic crude oil and low molecular weight paraffin solvents can remain suspended in the oil phase, rather than being adsorbed onto solid surfaces. Adsorption may be restricted to surfaces made oil-wet by COBR interactions prior to precipitation. Visual observations show that the waterflood displacement mechanisms after asphaltene precipitation are similar to the mechanisms of displacement of the unprecipitated crude oil (Buckley, 1995).

Strong interactions between asphaltenes and solids, especially clays, have been documented in many studies. These can be divided into two subgroups: studies of asphaltenes and solids with water excluded from the system, and studies that include consideration of the influence of water (Buckley, 1995).

(Buckley et al., 1998) found that the tendency of crude oils to alter wettability toward a more oil-wet condition can be attributed to the solvent properties of the oils with respect to the asphaltene content. They conducted measurements of spontaneous imbibition, adsorption of polar compounds and contact angles, and found that alteration of wettability to more oil-wet conditions was more pronounced as the crude oil solvency for asphaltenes decreased. In addition, when glass surfaces were treated with de-asphalted crude oils, wettability alteration did not take place, but when the glass surfaces were treated with crude oils, more oil-wet conditions developed immediately (Buckley and Morrow, 1990).

(Johansen and Dunning, 1959) found that asphaltenes were responsible for changing some crude-oil/water/glass systems from water-wet to oil-wet. The system was oil-wet when the crude was used but water-wet when the de-asphalted crude was used (Anderson, 1986).

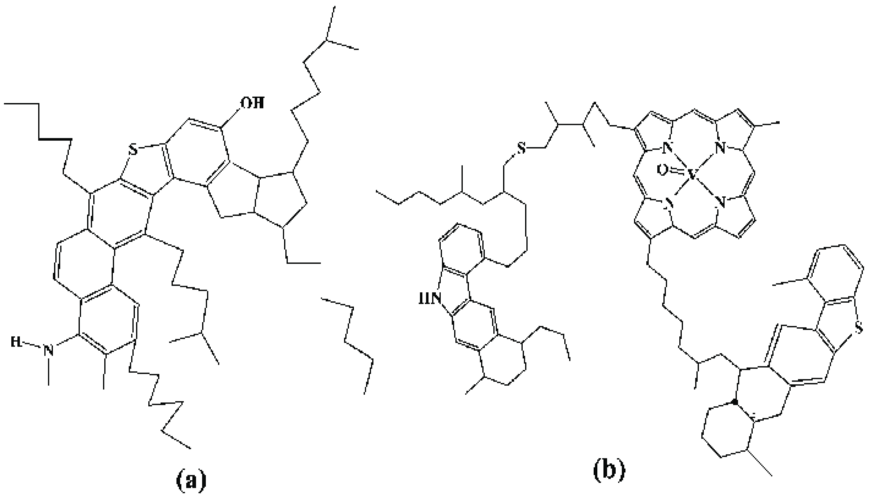


**Figure 9:** Molecular structures of (a) resins and (b) asphaltenes (He et al., 2015).

Experimental observations have pointed towards a smaller group of components from the asphaltene/resin fractions as more important regarding wettability alteration (Strand, 2005). These components are more specifically acidic- and basic by nature (Anderson, 1986), (Crocker and Marchin, 1988), (Cuiec, 1984). Transport of these polar components through the aqueous phase can also determine the stability of water films, causing wettability alteration or intensifying the oil wetness of a system (Kaminsky and Radke, 1997), (Fathi et al., 2011).

### 2.6.2 Formation water

Different brine properties are of high importance in the wetting processes, being the chemical composition, salinity, and the pH of brine are the most dominating factors (Anderson, 1986).

Formation water contains several inorganic compounds such as $Mg^{2+}$, $Ca^{2+}$, $Na^{+}$, $K^{+}$, $Cl^{-}$, $Ba^{2+}$, and $Sr^{2+}$. From past laboratory studies on carbonates (Zhang et al., 2007), it was observed that divalent cations of $Mg^{2+}$ and $Ca^{2+}$ contribute significantly to wettability alteration processes.

The salinity and pH of brine are very important in determining wettability because they strongly affect the surface charge on the rock surface and fluid interfaces, which in turn can affect the adsorption of surfactants and POC (RezaeiDoust et al., 2011; Stumm, 1970). Changes in salinity and the type of salt (therefore changes in salt concentration) can cause changes to the COBR system by disrupting the balance of forces causing rupture of a water film separating oil from contact with a surface (Donaldson and Alam, 2008).

Finally, several studies presented that pH has a relevant role in the processes of protonation and deprotonation of polar components in the oil phase, which can also affect their affinity towards the sandstone surface, regulating the initial wetting of a system (Austad et al., 2010; Brady et al., 2015; Buckley et al., 1989).

### 2.6.3 Rock minerals

The mineralogy of a reservoir rock plays a role of utmost importance in wettability and petroleum engineering studies. COBR interactions vary significantly considering the big variation in minerals contained in a rock. The ion exchange process is affected and thus changes in wettability occur. Sandstones, carbonate, and shale rock are the main formations in which oil is trapped and are therefore the main topic of interest in wettability.

Sandstone is a clastic sedimentary rock whose grains are predominantly sand-sized (Schlumberger, 1998). They consist mainly of silicates (quartz or feldspar) with lithic fragments to be also common. Their grains' mesh sizes range from coarse sand (1 to 2 mm in diameter) to fine (0.25 mm), silt (0.05 to 0.005 mm), and clay minerals (<0.005 mm) (Donaldson and Alam, 2008). If a sandstone rock consists of more than 90% of quartz clasts then it is called **quartzose,** while if it contains more than 25% of feldspar minerals (albite, anorthite, orthoclase, microcline, etc) it is called **arkose**. They have enough porous space to ''host'' fluids and interconnected porous media to allow them to flow.

Carbonate is a class of sedimentary rock whose chief mineral constituents (95% or more) are calcite and aragonite (both $CaCO_3$) and dolomite [$CaMg(CO_3)_2$], a mineral that can replace calcite during the process of dolomitization. Limestone, dolostone or dolomite, and chalk are carbonate rocks. Although carbonate rocks can be clastic in origin, they are more commonly formed through processes of precipitation or the activity of organisms such as coral and algae. Carbonates form in shallow and deep marine settings, evaporitic basins, lakes, and windy deserts. Carbonate rocks can serve as hydrocarbon reservoir rocks, particularly if their porosity has been enhanced through dissolution. They rely on fractures for permeability (Schlumberger, 1998).

Shale is a fine-graded, clastic sedimentary rock formed from mud that is a mix of flakes of clay minerals and tiny fragments of other minerals, especially quartz and calcite (Blatt, 2001). It exists in abundance within the sedimentary rocks and has a large potential of being a rich hydrocarbon source rock, even though a typical shale contains just 1% organic matter (Schlumberger, 1998).

Trying to understand wettability phenomena in sandstone rocks is a challenging task due to their geochemical and mineralogical complexity. Silica minerals normally have negative surface charges and weakly acidic pH. That is why silica tends to adsorb simple organic bases. The wettability of silica will be more affected by the organic bases since these surfaces will preferentially adsorb compounds of the opposite polarity (Anderson, 1986). It was observed by (Gaudin and Fuerstenau, 1955) (Gaudin and Chang, 1952) that the acidic compounds had very little effect on silica. However, most of the adsorbed compounds changed the wettability only from strongly to mildly water-wet, rather than to oil-wet (Anderson, 1986) An example of basic compounds that adsorbed on the acidic silica surfaces included iso-quinoline and octadecylamine (Block, 1967), (McCaffery, 1970).

### 2.6.4 Pressure and temperature

It has been observed that the solubility of polar active components in crude oil is increased as pressure and temperature are increased (Anderson, 1986). Other studies have demonstrated that the pressure effect is not very significant, for example, Wang and Gupta (1995) carried out a set of experiments where it was found that the pressure effect on wettability measurements was not very sensitive.

According to Rao (1999), the quartz surface tends to become more oil-wet as the temperature increases and the opposite result was found in carbonates where the calcite surface tends to get more water-wet.

## 2.7 Crude oil-brine-rock interactions

Four mechanisms by which the polar compounds can adsorb onto the rock surface have been identified (Al-Maamari and Buckley, 2000; Buckley et al., 1998; Buckley and Liu, 1998):

- Polar interactions between the oil and solid predominate in the absence of a water film, resulting in adsorption of the polar oil components onto the polar surface sites.
- Surface precipitation is dependent on the ability of the oil to solvate the asphaltenes.
- Acid/Base interactions in the presence of water control the surface charges of the oil/water and solid/water interfaces. The net charge affects the stability of the water film, and the ionized acidic/basic sites influence adsorption.
- Ion-binding is an interaction between charged sites at the mineral surface and higher valency ions in the brine, creating bridges between like charges.

By assessing the rock type and the characteristic properties of the crude oil, such as the API gravity, acid number (AN), and base number (BN), the so-called G-AB parameters, the mechanism by which the crude oil is likely to alter the rock wettability, can be evaluated (Buckley and Liu, 1998).

Other factors, than the above described, that have an effect on the wettability alteration of the COBR system are (Puntervold et al., 2007).

- Capillary pressure and thin-film forces, disjoining pressure
- Water solubility of polar oil components and diffusion through water films
- Stabilization of heavy components by oil
- Temperature
- Pressure
- Initial water saturation

The main physical and chemical principles that govern wettability and wettability alteration are the surface phenomena. Basic principles of surface energy and tension, adsorption/desorption, precipitation/dissolution, and COBR interactions will be briefly analyzed in this section.

### 2.7.1 Surface energy/surface tension

**Surface energy** quantifies the disruption of intermolecular bonds that occurs when a surface is created. That means that the energy of a surface molecule is therefore higher than that of a molecule in the interior of the solid and energy must be expended to move a molecule from the interior to the surface of a solid (Castellan, 1979). This change in energy can be described also from **Equation 7** as:

$$f \cdot dx = \gamma \cdot dA \qquad (7)$$

Where we assume that a liquid film is stretched on a wireframe. When increasing its area by $dA$ by using the surface Gibbs energy $\gamma$, an opposite force *f* will be opposed by the wire if it moves a distance *dx*. **Figure 10** is an illustration of the above-described phenomenon.

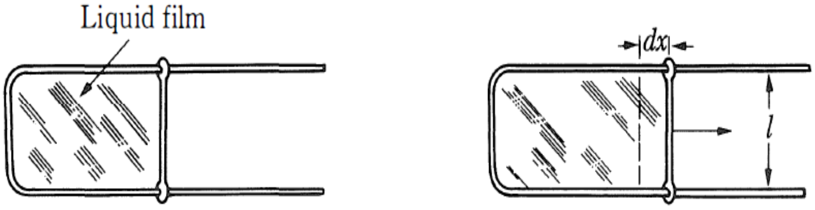


**Figure 10:** Stretched film *(Source: Physical chemistry, Castellan, 1983)*

**Surface tension** is the consequence of the above theory. It is the tendency of fluid surfaces to shrink into the minimum surface area possible (Wikipedia, 2001). In this case, the energy of the system can be described from **Equation 8**:

$$E = E_u V + E_s A \qquad (8)$$

Where V and A are the volume and area, $E_u$ and $E_s$ are the energy per unit volume and the energy per unit area.

### 2.7.2 Adsorption/desorption

**Adsorption** is the property of some solids and liquids to attract a liquid or a gas to their surfaces. Some solids, such as activated charcoal or silica gel, are used as surfaces of adhesion to gather liquid hydrocarbons from a natural gas stream. To complete the process, the solids are treated with steam to recover the liquid hydrocarbons glossary. This effect depends on the temperature, the nature of the adsorbed substance (the adsorbate), the nature and the state of subdivision of the adsorbent (the finely divided solid), and the concentration of the dye or pressure of the gas (Castellan, 1979).

Four general mechanisms control the rate of adsorption on reservoir rocks (Donaldson and Alam, 2008):

a) Diffusion of the compounds from the bulk solution to the interface
b) Transfer to the surface
c) Physical adsorption on the surface
d) Chemical interaction, if bonding criteria are present

The heats of adsorption for the compounds and rock that were used were less than 10kCal/g-mol; therefore, the conclusion was that only physical adsorption took place. Physical adsorption occurs rapidly when the molecules contact the surface. Therefore, the rates of adsorption were controlled by the first two mechanisms: diffusion to the surface and transfer across the interface to the solid (Clayfield and Smith, 1970).

The opposite process of adsorption is called **desorption** according to which, an adsorbed substance is removed from a surface. Desorption is as well a temperature-dependent phenomenon.

## 2.8 Smart Water EOR method

The proposed Smart Water EOR method disturbs the established chemical equilibrium between crude oil, brine and rock, by injecting a modified ionic composition brine. After several experimental studies performed over the past few decades, it was observed that improved oil recovery can be obtained by altering the ionic composition of the injected brine.

In sandstone rocks, desorption processes and pH are the key factors that control wettability alteration (Austad et al., 2010). When a modified ionic composition brine is injected into a sandstone core, desorption of active cations like $Ca^{2+}$ and $Mg^{2+}$ occurs due to diffusion. This effect creates negative charges on the clay surface that must be charge-balanced (RezaeiDoust, 2011). At reservoir conditions, the $H^+$ ion has the largest affinity towards clay minerals, and by adsorption of an $H^+$ ion, the negative site located at the clay surface becomes charged balanced. The adsorbed $H^+$ ion is up taken from water molecules, creating a local pH rise (Pinerez, 2017). Acid-base reactions that include these H+ exchanges are described in **Equations 9** for basic material and in **Equation 10** for acidic.

$$R_3N\!: + H_2O \leftrightarrow R_3NH^+ + OH^+ \qquad (9)$$

$$R - COOH + H_2O \leftrightarrow RCOO^- + H_3O^+ \qquad (10)$$

The wettability alteration with Smart Water in carbonates is a result of a combined effect among the determining ions $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, temperature and carboxylic acids (Gupta and Mohanty, 2008; Strand et al., 2006; Zhang and Austad, 2005).

The proposed mechanism for the wettability alteration processes for sandstone rocks is illustrated in **Figure 11** (Austad et al., 2010) and for carbonates rocks in **Figure 12** (Zhang et al., 2007).

The basic requirement to observe a Smart Water EOR effect, is for the reservoir to be either in mixed-wet or fractional wet conditions. In the case of a very water-wet system, the potential of Smart Water is low or non-existing. Therefore, the understanding of the initial wettability of the reservoir is of utmost importance.

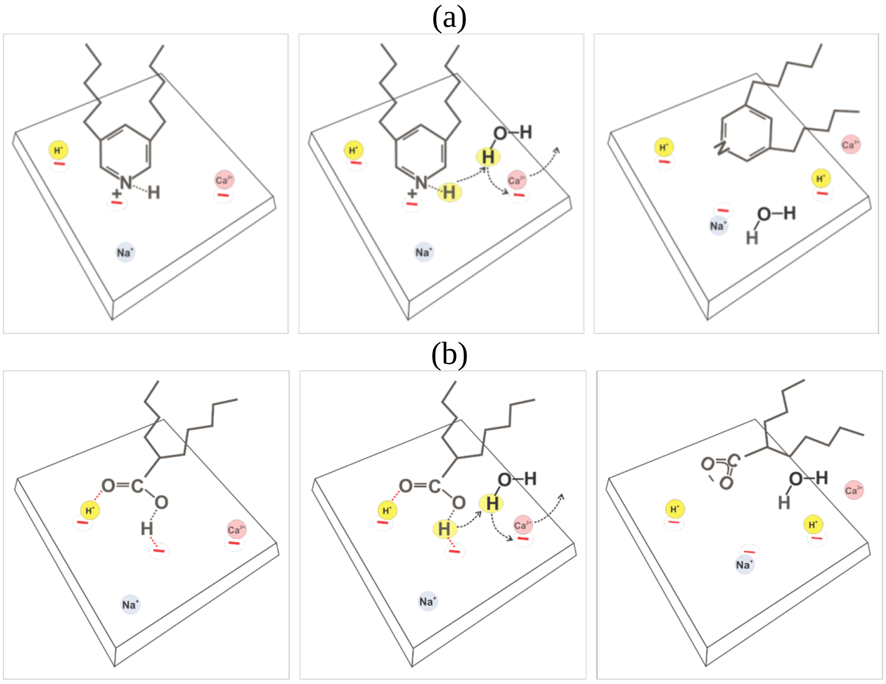


**Figure 11:** Illustrated wettability alteration in sandstones by ionic exchange. Desoprtion of basic (a) and acidic (b) material (Austad et al., 2010).

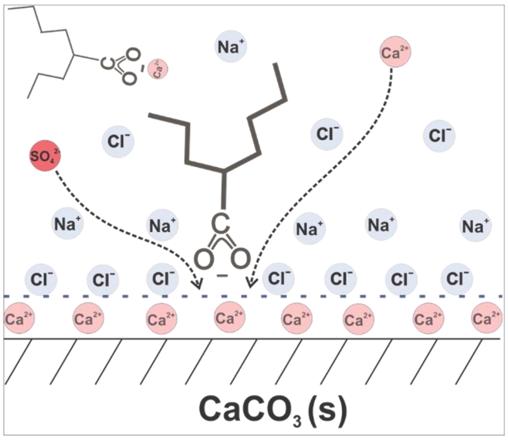


**Figure 12:** Wettability alteration mechanism by Smart Water in carbonate rocks (modified from (Zhang et al., 2007)).

Two examples of the Smart Water mechanism are presented below.

In **Figure 13** an example of wettability alteration by Smart Water in chalk material is depicted from the study of (Fathi et al., 2011). Firstly, usage formation water (VB0S), indicate mixed/slightly water-wet conditions. Usage of seawater resulted in a higher oil recovery since it behaves as a Smart Water brine, inducing the wettability alteration processes. A further increase in oil recovery was observed when the SW0Na (seawater depleted in NaCl) was used, acting as a better wettability-modifier brine. The most efficient brine for wettability alteration and thus the highest oil recovery in this study was achieved when using the SW0Na4S brine (seawater depleted in NaCl and spiked with 4 times sulfate).

In **Figure 14** Pinerez (2017) performed viscous flooding experiments on sandstone reservoir cores. In this study, two reservoir sandstone cores were selected for spontaneous imbibition tests. In the case of the core B21, wettability alteration was observed when the imbibition brine was switched to low salinity (LS) at the tertiary mode. In the case of core B26, the LS brine was more effective than the normal seawater in ultimate recovery.

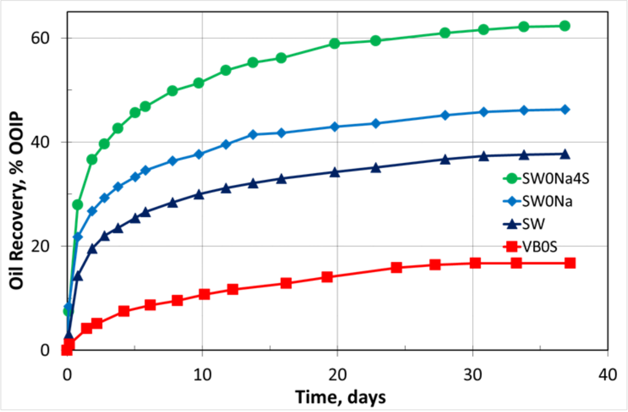


**Figure 13:** Spontaneous imbibition experiments on chalk outcrop material. Highest recoveries were obtained with the usage of Smart Water brines (Fathi et al., 2011).

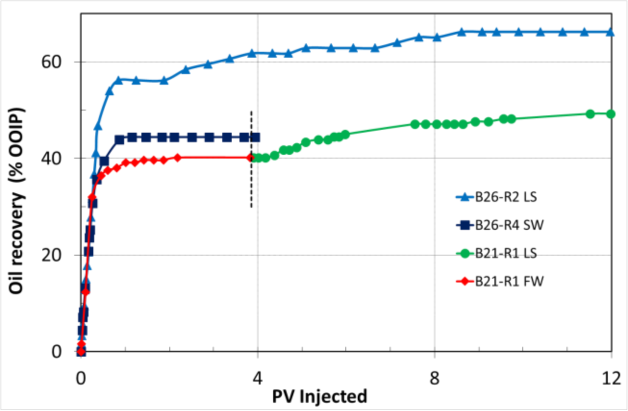


**Figure 14:** Wettability alteration example in sandstone reservoir cores (Pinerez, 2017).

Parametric studies on how to effectively obtain a representative initial wettability are extremely important in core analysis. Thus, emphasis should be given in finding the optimal procedure for treating a core in the lab.

# 3 State-of-the-art background

The fluid restoration procedure, which includes generating a proper water saturation with formation water (FW) and initial oil saturation by reservoir crude oil exposure on cores in the laboratory, is a significant aspect of the whole wettability restoration process.

Polar organic components (POC) present in crude oils are of utmost importance to surface wettability (Buckley and Morrow, 1990; Standnes and Austad, 2003). According to previous experimental studies on sandstone core material, polar organic bases of the crude oil phase tend to adsorb promptly onto the mineral surface way more than the polar organic acids, affecting this way the core wettability (Mamonov et al., 2019). Similarly, in chalk observations (Hopkins et al., 2016), a large amount of crude oil exposure to the rock affects the wettability towards a less water-wet state. However, in chalk, it is the polar organic acids that have the highest affinity for the calcite surfaces and that dictate the wettability (Puntervold et al., 2021).

In the literature are mentioned several cleaning methods regarding hydrocarbons and cleaning extraction (Borre and Coffey, 2014; Conley and Burrows, 1956; Cuiec, 1975; Gant and Anderson, 1988; Grist et al., 1975; Guedez et al., 2020; Gupta et al., 2017; Jennings, 1957). In addition to that, many scientists have proposed different experimental assemblies like centrifuge cleaning and the distillation extraction method (Conley and Burrows, 1956; Dean and Stark, 1920). The American Petroleum Institute (API) has proposed several solvents for core cleaning purposes and their solubilization (**Table 1**).

**Table 1:** Selected solvents for core cleaning and their use.

| Solvents | Boiling Point, °C | Solubilizing |
|---|---|---|
| Acetone | 56.5 | oil, water, salt |
| Chloroform/methanol azeotrope (65/35) | 53.5 | oil, water, salt |
| Cyclohexane | 81.4 | oil |
| Ethylene Chloride | 83.5 | oil, limited water |
| Hexane | 49.7–68.7 | oil |
| Methanol | 64.7 | water, salt |
| Methylene chloride | 40.1 | oil, limited water |
| Naphtha | 160.0 | oil |
| Tetrachloroethylene | 121.0 | oil |
| Tetrahydrofuran | 65.0 | oil, water, salt |
| Toluene | 110.6 | oil |
| Trichloroethylene | 87.0 | oil, limited water |
| Xylene | 138.0–144.4 | oil |

## 3.1 Core cleaning and restoration methods

Core restoration methods may have a significant effect on wettability tests. Even before the cores arrive at the lab several factors may affect the later test results. Some of the factors could be e.g. the use of synthetic formation water when cutting the cores or the usage of a “clean” oil without any polar components or low aromatic. After the cores arrive at the lab, the treatment of the samples before starting each test has a tremendous effect on wettability.

Starting with the cleaning process, there are at least four schools of thought regarding how core samples should be cleaned (Morrow, 1990):

a) No solvents

According to this method, the usage of solvents might wash away components naturally existing in the porous media. This interference with the initial wetting conditions would influence the later wettability studies.

Typical ‘’no solvents’’ preparation includes water-base ‘’bland’’ fluid when cutting the cores and flushing the cores with synthetic brine followed by reservoir crude oil. A disadvantage of this approach is that pore volume and saturation cannot be known until the conclusion of the measurements (Morrow, 1990).

b) Avoid hysteresis

These procedures are designed to maintain the history of fluid displacements in the sample. So, this procedure preferably begins with a sample that was cut with an oil-based drilling fluid so that no new water had been introduced.

c) Clean without restoring

A convenient and cheap method and it is not a serious attempt to maintain wettability, although it is frequently used. It will be effective only if the natural wettability happens to be similar to the wettability after cleaning (Morrow, 1990).
According to some of those methods, cores will be dried in order to calculate their pore volume later. Exposure to very high temperatures might cause hot extraction as a result making them more water-wet by removing naturally absorbed organics or more oil-wet by removing water but not the heavy ends of crude oil (Morrow, 1990).

d) Clean and restore

This procedure suggests that the core should be thoroughly cleaned before the experiments start due to the effect of the drilling fluid invasion, pressure and temperature changes, oxidation, evaporation, or contamination (Morrow, 1990).
The restoration processes, in this case, include flushing of the core at low flooding rates and room temperature with the usage of several solvents like kerosene, heptane, methanol, toluene chloroform, acetone. Afterward, the cores are dried (or not) and saturated with formation water

up to irreducible water saturation. Then, crude oil is injected into the core followed by aging at a specific temperature and pressure. Values of days of aging, aging temperature, and pressure could vary.

## 3.2 *Effect of POC on wettability*

The effect of POC present in the crude has been studied in the past years. Standnes and Austad (2000) found that the adsorption of polar components onto a chalk surface is a fast process. They pointed out that the higher the acid number in the crude oil, the less water-wet a chalk surface can become (**Figure 15**).

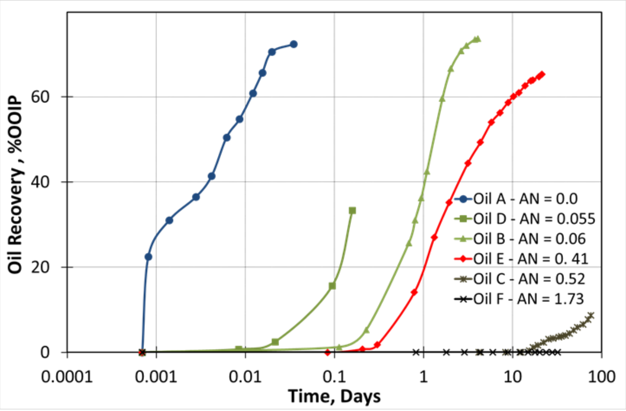


**Figure 15:** Spontaneous imbibition on chalk cores using crude oils that differ in AN number (Standnes and Austad, 2000).

Following these observations, Puntervold et al (2007) examined further the effect of AN components on chalk mineral surface presented as an AN/BN ratio (**Figure 16**). They indicated that co-adsorption of strong and small organic bases could affect the wettability of a chalk COBR system towards less water-wet state.

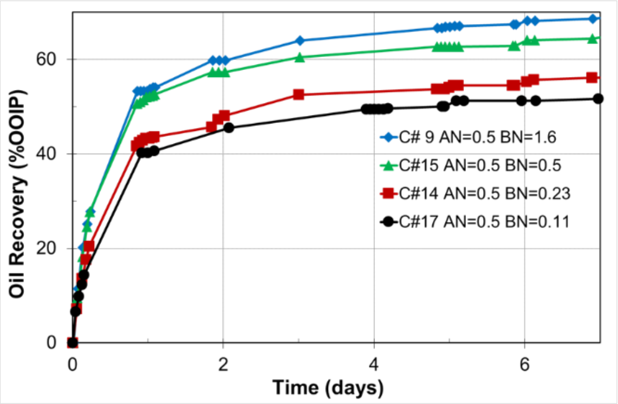


**Figure 16:** Spontaneous imbibition with crude oils containing different AN/BN ratios (replotted from (Puntervold et al., 2007)).

Hopkins et al (2016), investigated the effect of temperature on crude oil adsorption. It was observed that the adsorption of polar acids decreased as the temperature rises.

In addition, studies on sandstone cores showed that the minerals present in a sandstone core (clays, feldspars) interact significantly with the POC present in the crude oil phase (Mamonov et al., 2020; Puntervold et al., 2018).

Finally, Mamonov et al (2019) studied the effect of POC on a sandstone mineral surface. This study showed that polar organic bases have the highest affinity toward the sandstone minerals. In **Figure 17** is it shown that the basic POC have a higher affinity towards a sandstone mineral surface. More precisely, in this study, POC continue adsorbing onto the sandstone mineral surface even after 10 PV of crude oil injection. On the other hand, acidic POC had a small affinity toward the mineral surface.

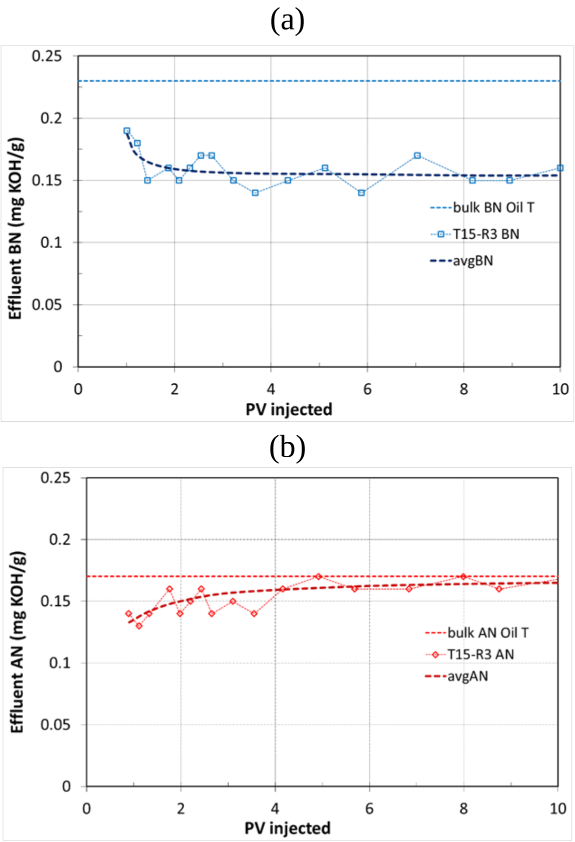


**Figure 17:** Adsorption of polar organic bases (a) and polar organic acids (b) onto a sandstone mineral surface (Mamonov et al., 2019).

Shariatpanahi et al. (2012) investigated the effect of different cleaning methods, introducing the "mild" cleaning method. According to this method, kerosene and heptane are used as non-aggressive cleaning agents. The low aromatic but highly miscible with oil kerosene can effectively displace the oil phase from the pore space and not interfere further with the wettability. Heptane is injected to displace kerosene and avoid contact with oil. In **Figure 18** a forced imbibition experiment is presented of one reservoir limestone core restored twice. Before the first restoration, the "mild" cleaning scheme was followed while the standard toluene/methanol cleaning was used before the second restoration.

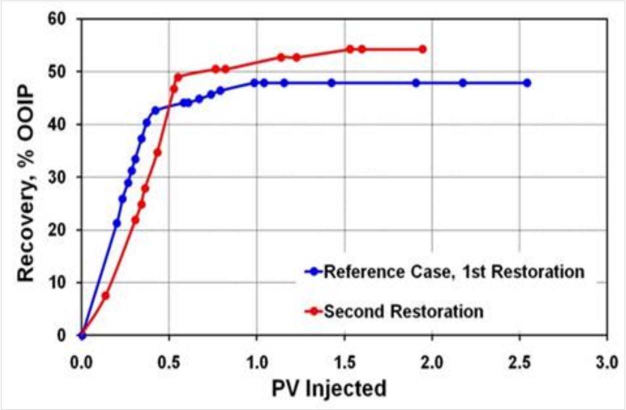


**Figure 18:** Effect of toluene/methanol solvents in oil recovery on a limestone reservoir core (Shariatpanahi et al., 2012).

The results showed an increase in the ultimate recovery after the toluene/methanol solvents were used indicating that a more aggressive approach to treating the cores while cleaning can affect the wettability towards more water-wet

In their study on chalk outcrop material, Strand and Puntervold (2019) observed that acidic polar components affect the core wettability. As shown in **Figure 19** the acidic POC present in the crude oil are retained by the core after several PV injected. An equilibrium was reached after 8PV of crude oil injection.

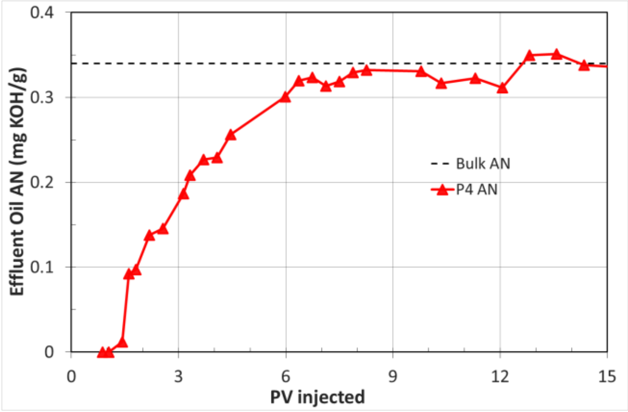


**Figure 19:** Acid number (AN) in effluent oil samples during crude oil flooding (Strand and Puntervold, 2019).

## 3.3 Effect of crude oil amount in core restoration

After all the past studies conducted on POC adsorption, it is reasonable to conclude that POC affect the wettability of a COBR in restoration processes when trying to establish initial wettability conditions similar to the reservoir.

Hopkins et al (2017) observed that adsorption of POC was to some extent proportional to the crude oil injected into the rock. An increased amount of pore volumes injected into the core resulted in a less water-wet state. As shown in **Figure 20**, the wettability of the studied core was less water-wet after the second restoration and thus a higher amount of crude oil exposure. So an increased amount of crude oil flooded through the core during core restoration reduces the water-wetness of the system (Hopkins et al., 2017).

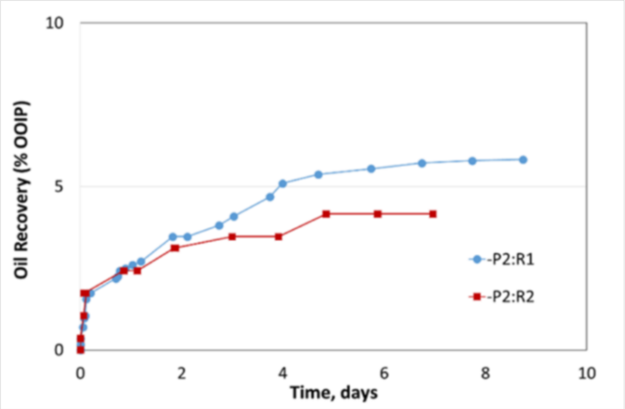


**Figure 20:** Effect of crude oil amount during core restoration after using kerosene and heptane as cleaning solvents, when the core is firstly exposed to 15 PV of crude oil (Hopkins et al., 2017).

Adsorption studies during the crude oil exposure process of the core P2 showed that the acidic components keep adsorbing for several PV injected even during the second restoration (**Figure 21**). This fact confirms that polar organic acids have a strong effect on reducing the water-wetness of the system.

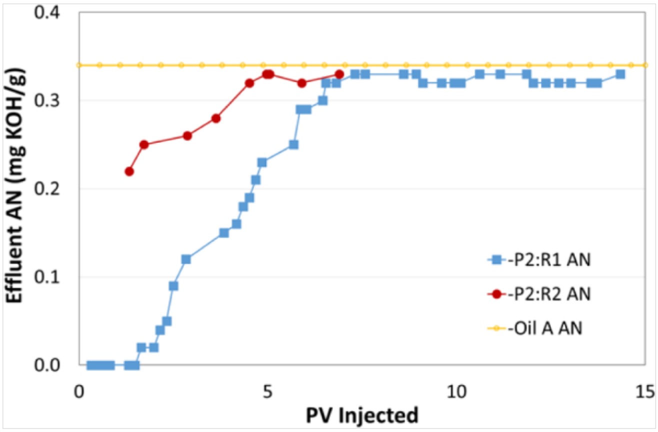


**Figure 21:** Crude oil adsorption analysis of the chalk core P2 (Hopkins et al., 2017).

The primary goal of this research was to determine the best restoration procedure for reservoir sandstone and outcrop carbonate cores in order to provide consistent core wettability from one restoration to the next. A new cleaning and fluid restoration technique for recovering the original wettability of preserved reservoir sandstone core samples has been developed that takes into consideration both optimum solvent cleaning and crude oil exposure. A Hassler core holder was utilized in this work to flush various solvents through the core throughout the core cleaning procedure. Flooding solvents via a core in a Hassler core holder provides for precise control of solvent volumes (PV injected). Two distinctly different core cleaning solvent systems involving mild (kerosene/heptane) and rigorous (toluene/methanol) solvents were used. The first solvent approach is designed to maintain wettability, while the second uses industry-standard core cleaning solvents to clean a core to fully water-wet conditions before restoring wettability. Initial water saturation (Swi) was in front of crude oil exposure using the desiccator approach (Springer et al., 2003) before the core was subjected to various PVs of crude oil (1 PV, 5 PV, or 11 PV). Spontaneous imbibition oil recovery experiments were used to assess the restored core wettability after aging.

# 4 Experimental

## *4.1 Materials*

### *4.1.1 Core material*

In this study, both reservoir sandstone and outcrop carbonate core material were used with more emphasis on sandstones.

#### 4.1.1.1 Sandstones

Sandstone reservoir core material retrieved from the Varg field of the Norwegian Continental Shelf (NCS) was mainly used in the following study. With a sea depth of 84 meters, the Varg field is located in the center section of the North Sea, in the southwest part of the (NCS) (**Figure 22**). In 1984, the field was discovered, and in 1996, the plan for development and operation (PDO) was established. By the end of 2018, it was producing under the management of Chrysaor Norge AS (60 %) and OKEA ASA (40 %). Varg produced oil mainly from the sandstone of the Late Jurassic age in the Ula Formation. The reservoir is located at a depth of 2700 meters. The structure is segmented and comprises several isolated substructures with varying reservoir properties. The field was produced with pressure support from water and gas injection. The smaller structures were produced with pressure relief while all the wells were produced by gas lift. The samples were obtained from two wells, 9S and A5T2, at depths less than 3479.50m (upper sequence) and over 3493.75m (lower sequence) respectively.

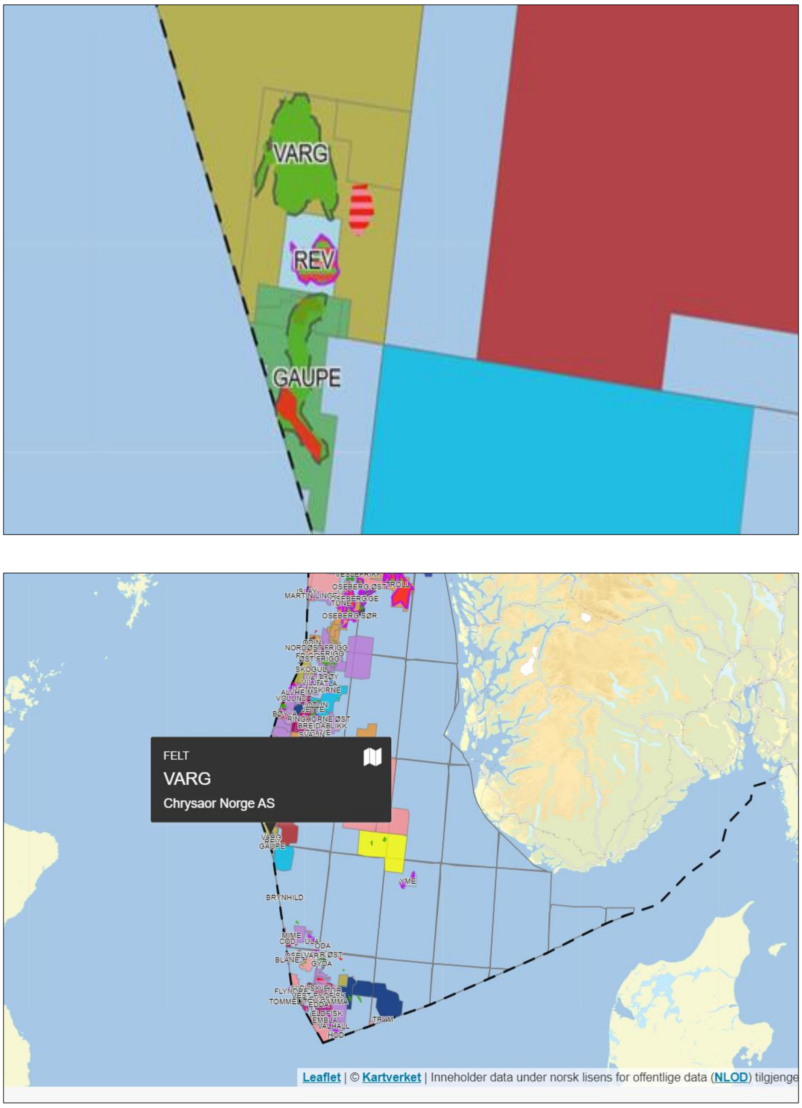


**Figure 22:** The location of the Varg field in the Norwegian Continental Shelf (*source: Norwegian Petroleum Directorate*)

The mineralogical composition was evaluated through XRD analysis by the operating company at the time and is presented in **Table 2** while the physical properties were measured in-house and are presented in **Table 3**.

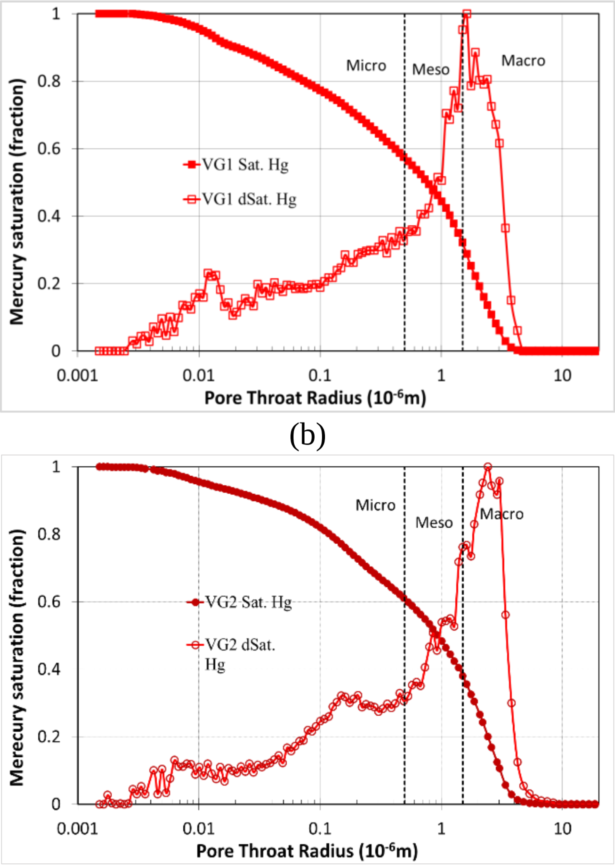
**Table 2:** Mineralogical composition of the sandstone core material.

| **Minerals** | **Well** | |
|---|---|---|
| | **9S (wt%)** | **A5T2 (wt%)** |
| Illite+Mica | 15.4 | 9.5 |
| Kaolinite | 1.1 | 1.1 |
| Chlorite/Smectite | 0.1 | 0 |
| Chlorite | 2.4 | 3.4 |
| Quartz | 62.3 | 67.6 |
| K Feldspar | 4.5 | 5.6 |
| Plagioclase | 8.4 | 8.7 |
| Calcite | 0 | 0.6 |
| Dolomite | 3.9 | 2.8 |
| Siderite | 1.1 | 0 |
| Pyrite | 0.8 | 0.8 |
| **Total** | 100 | 100 |

**Table 3:** Physical properties of the sandstone core material.

| **Core** | V1 | V2 | V5 | V6 | V7 | V9 | V10 |
|---|---|---|---|---|---|---|---|
| **Well** | 9S | | A5T2 | | | | |
| **Depth, m** | 3404.83 | 3404.88 | 3507.82 | 3507.87 | 3507.92 | 3528.82 | 3528.87 |
| **Cleaning** | Kerosene/ Heptane | Toluene/ Methanol | Kerosene/ Heptane | | | | Toluene/ Methanol |
| **Length (cm)** | 8.85 | 8.18 | 7.39 | 7.53 | 6.75 | 8.22 | 8.18 |
| **Diameter (cm)** | 3.80 | 3.80 | 3.8 | 3.8 | 3.8 | 3.80 | 3.80 |
| **Bulk volume (cm$^3$)** | 100.4 | 92.8 | 83.53 | 85.01 | 76.15 | 93.2 | 92.8 |
| **Dry weight (g)** | 203.52 | 188.47 | 168.18 | 171.82 | 152.2 | 179.65 | 167.62 |
| **PV (ml)** | 21.27 | 21.40 | 17.82 | 18.01 | 17.18 | 21.58 | 24.97 |
| **Porosity (%)** | 21.2 | 23.1 | 21.3 | 21.2 | 22.6 | 23.2 | 26.9 |
| **Permeability (md)** | 11.3 | 10.9 | 4.5 | 3.1 | 11.1 | 3.5 | 22.4 |

The fluid used for the permeability measurements was a low salinity (LS) brine and was injected at the residual oil saturation ($S_{or}$) after the cleaning process (analytically described later). The cores were low permeable with permeability values ranging from 2-22 mD for the A5T2 cores and 5-17 mD for the 9S cores. A mercury injection analysis was performed by Stratum Reservoir, in order to determine the pore size distribution of the core plugs (**Figure 23**).


(a)

(b)

**Figure 23:** Pore size distribution of the plugs V1(a) retrieved from the 9S and V9 (b) retrieved from the A5–T2 well.

In addition, a Scanning Electron Microscopy (SEM) analysis was performed on one core of each well, and the images are shown in **Figure 24**.

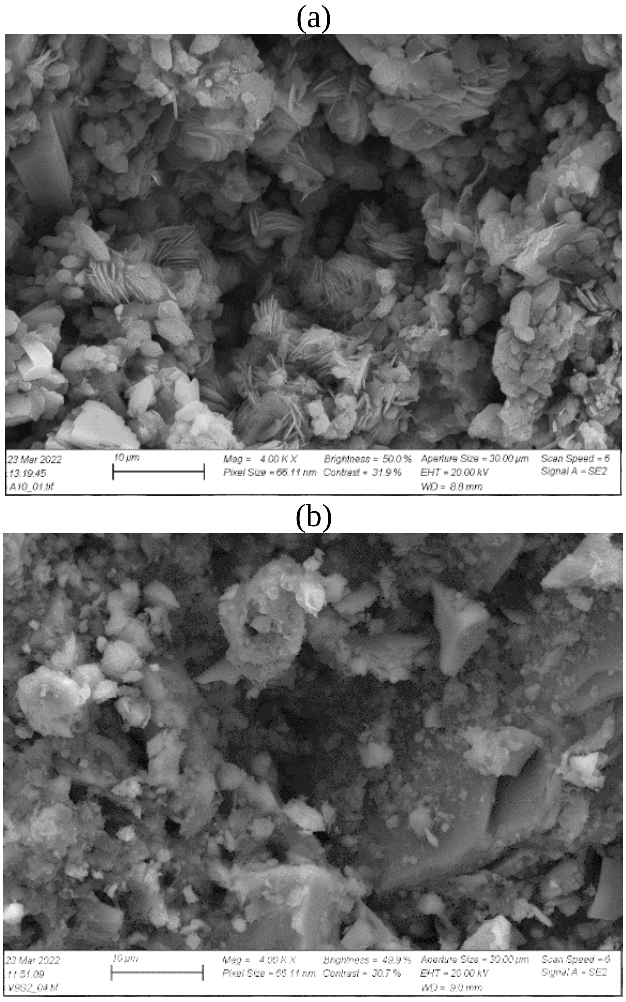


**Figure 24:** SEM images from the cores V10 (a) and V2 (b).

Finally, a Computed Tomography (CT) scanning was carried out on the sandstone cores to observe any heterogeneities or impurities in the cores. This process was carried out during the mobility stay at DTU Offshore-Danish Offshore Technology Centre. The CT scanning images are shown in **Figure 25**.

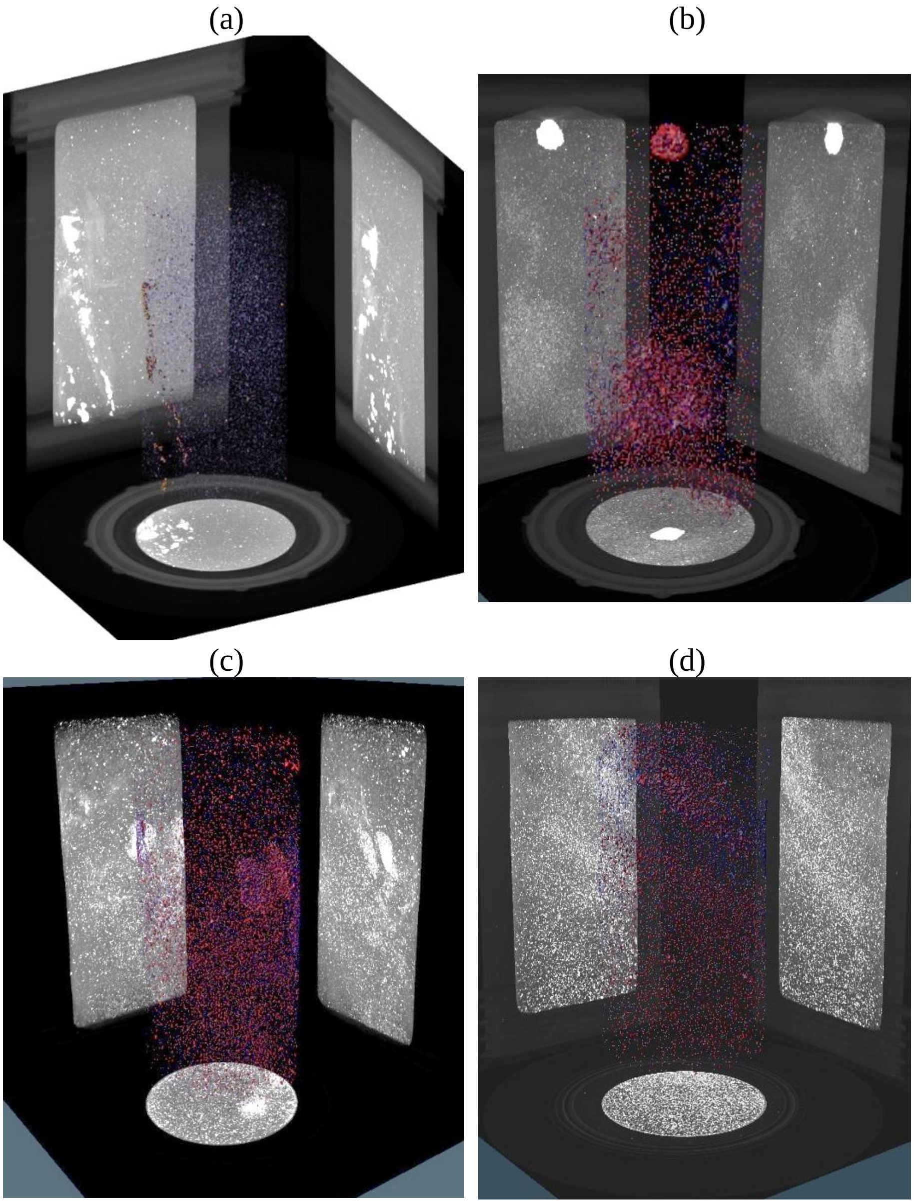


**Figure 25:** CT scanning images from the cores V1(a), V5(b), V9(c) and V10(d).

#### 4.1.1.2 Carbonates

For this part of the thesis, outcrop chalk was retrieved from the Stevns Klint quarry in Denmark. The mineralogical features of this material include a high amount of $CaCO_3$ (>98%) and a small amount of silicates (Bertolino et al., 2013; Fabricius and Borre, 2007; Hjuler and Fabricius, 2009; Skovbjerg et al., 2012). In the literature review (Andersen et al., 2018; Andersson et al., 2014; Bovet et al., 2015; Fernø et al., 2011; Megawati et al., 2015; Røgen and Fabricius, 2002; Skovbjerg et al., 2013; Strand et al., 2007) a higher amount of silicates was observed. The presence of other minerals (quartz, clays, polysaccharides) in significant amounts could affect several properties of the core (surface reactivity, mechanical) (Frykman, 2001; Røgen and Fabricius, 2002). Stevns Klint is a highly porous (41-50%), low permeable (1-5 mD) systems and are representative as a North Sea chalk reservoir (Frykman, 2001; Røgen and Fabricius, 2002). The previous studies performed in the Smart Water group, showed that the cores retrieved from the same bock could reproduce the results from an oil recovery test fact that facilitates their use in parametric studies (Fathi et al., 2010; Hopkins et al., 2017; Puntervold et al., 2007; Standnes and Austad, 2000; Strand et al., 2006; Zhang and Austad, 2005). Pore size distribution analysis was performed by Stratum reservoir and the results are shown in **Figure 26**. An optical representation of the pore structure of Stevns Klint material is depicted in **Figure 27** from SEM analysis. in

**Table 4** the physical properties of the cores are presented.

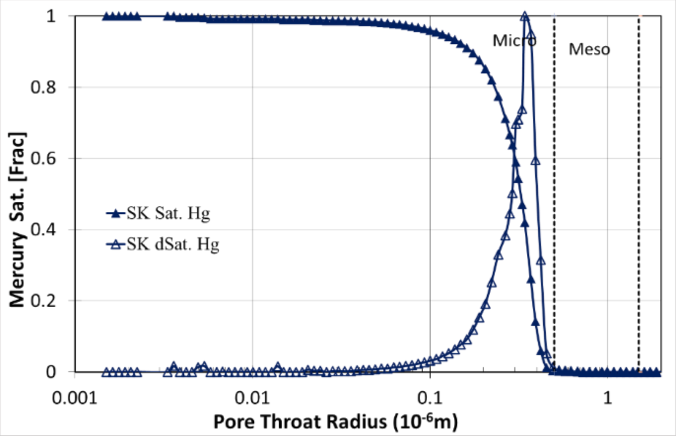
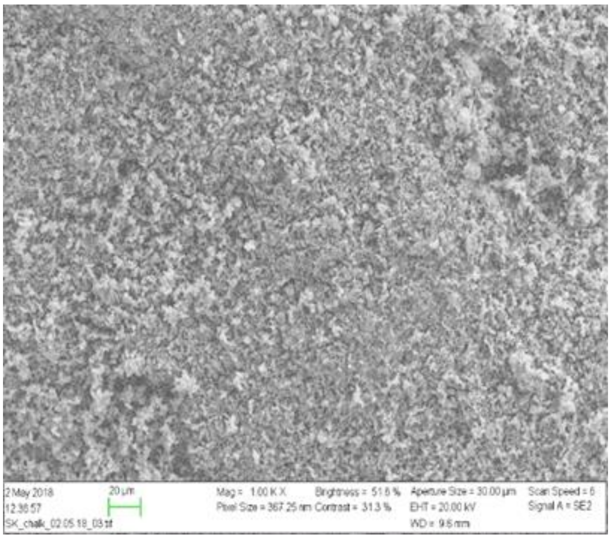


**Figure 26:** Pore size distribution from the carbonate cores.



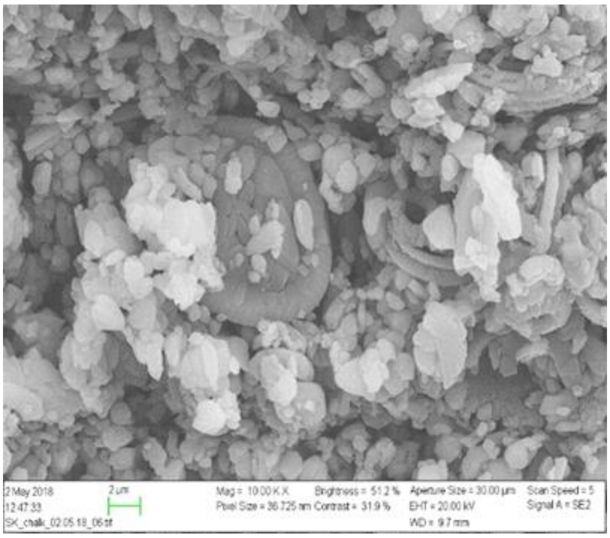


**Figure 27:** SEM images from the carbonate cores.

**Table 4:** Physical properties of the carbonate core material.

| **Core** | **C4** | **C5** | **C6** | **C7** | **C8** | **C9** |
|---|---|---|---|---|---|---|
| **Length, cm** | 6.94 | 6.94 | 6.92 | 7.00 | 7.00 | 7.04 |
| **Diameter, cm** | 3.80 | 3.80 | 3.82 | 3.80 | 3.80 | 3.79 |
| **Bulk volume, $V_b$, cm3** | 78.8 | 78.8 | 79.3 | 79.5 | 79.5 | 79.4 |
| **Dry weight, $m_0$, g** | 108.5 | 107.2 | 108.7 | 111.8 | 110.2 | 110.1 |
| **Sat. weight, $m_{sat}$, g** | 146.9 | 147.1 | 146.5 | 149.1 | 149.1 | 148.1 |
| **Density, $\rho_{sat}$ , d10FW, g/cm3** | 1.002 | 1.002 | 1.002 | 1.002 | 1.002 | 1.002 |
| **Pore volume, PV, ml** | 38.3 | 39.9 | 37.7 | 37.3 | 38.8 | 38.5 |
| **Porosity, Φ, %** | 49 | 50 | 48 | 47 | 48 | 49 |
| **Permeability, md** | 2.5 | 1.0 | 0.8 | 1.6 | 2.0 | 1.2 |

### 4.1.2 Brines

In-house prepared synthetic brines were used for all the experiments. Different brines were used in each of the three sets of experiments of this work (reproducing wettability on sandstones, reproducing wettability in carbonates, adsorption of polar components). In **Table 5** the ionic composition and the properties of the brines are given.

**Table 5:** Ionic brine composition and properties of the brines used per experiment.

| **Experiment** | **Reproducing wettability (sandstones)** | | **Reproducing wettability (carbonates)** | **Adsorption test** |
|---|---|---|---|---|
| Ions | LS (mM) | | $FW_V$ (mM) | $FW_{VOS}$ (mM) |
| $Na^+$ | 17.1 | 2086.0 | 997 | 817.6 |
| $K^+$ | - | 51.0 | 5 | - |
| $Li^+$ | - | - | 0 | 20 |
| $Ca^{2+}$ | - | 536.0 | 29 | - |
| $Mg^{2+}$ | - | 144.0 | 8 | - |
| $Cl^-$ | 17.1 | 3526.0 | 1066 | 857.6 |
| $Ba^{2+}$ | - | 7.0 | - | - |
| $Sr^{2+}$ | - | 8.0 | - | - |
| $HCO_3^-$ | - | - | 9 | - |
| $SO_4^{2-}$ | - | - | 0 | - |
| $SCN^-$ | - | - | 0 | - |
| Density ($g/cm^3$) | 0.999 | 1.139 | 1.041 | 1.035 |
| Bulk pH | 5.7 | 5.9 | 6.7 | 5.8 |
| Viscosity (cP) | 0.95 | 1.45 | - | - |
| TDS (mg/L) | 1000 | 201600 | 62830 | 50000 |

### 4.1.3 Crude Oils

Partial distilled Oil V1 from the Varg field was used in reproducing the wettability in sandstone oil recovery tests. The density and viscosity of Oil V1 were measured at atmospheric conditions with the usage of Anton Paar densitometer and MCR 302 rheometer respectively.

In the case of the carbonate experiments, a modified version of a RES40 crude oil (mixture of Heidrun crude oil and heptane in a volume ratio of 60/40) was used. Initially, for the removal of polar organic components present in RES40 crude oil, silica gel was added and mixed for approximately 6 days. Subsequently, the oil was filtered through a 5μm Millipore filter. This resulted in the oil RES40-0 with acid number (AN) and base number (BN) values of 0 and 0.03 mgKOH/g, respectively. By mixing RES40 and RES40-0 in appropriate ratios, Oils A, B and C were created.

Similarly, for the adsorption tests, crude oils with similar content of acidic and basic POC were prepared for the core flooding experiments. The preparation of the oils involved mixing calculated amounts of three low-asphaltene crude oils with known AN and BN, resulting in oils of desired and similar AN and BN of 0.23 mg KOH/g oil. The amount of acids and bases was set low enough to detect adsorption during core flooding and high enough to minimize analytical uncertainties.

The AN and BN for all the experiments were analyzed by potentiometric titration according to the procedures described by Fan and Buckley (2007), procedures that are modified from the standard methods ASTM664–89 and ASTM2896–88 for AN and BN measurements, respectively. The properties of all the oils used are listed in **Table 6**.

**Table 6:** Crude oil properties at each set of experiments.

| Oil | Test | Density at 20 °C (g/cm3) | Viscosity at 25° C (cP) | Asphaltene (wt %) | AN | BN | Used in Cores |
|---|---|---|---|---|---|---|---|
| | | | | | mg KOH/g | | |
| V1 | **Reproducing wettability (sandstones)** | 0.845 | 11.3 | < 1 | 0.13 | 1.25 | V1<br>V2<br>V5<br>V6<br>V7<br>V9<br>V10 |
| A | **Reproducing wettability (carbonates)** | 0.808 | 3.25 | <1 | 0.34 | 0.24 | C1<br>C2<br>C4<br>C5<br>C6<br>C7 |
| B | | 0.807 | 2.52 | < 1 | 0.36 | 0.30 | |
| C | | 0.807 | 2.36 | < 1 | 0.5 | 0.23 | |
| V2 | **Adsorption tests** | | | < 1 | 0.23 | 0.23 | V2 |

### 4.1.4 Other chemicals

In the core cleaning procedures, several chemical solvents purchased from Merck laboratories were used; low aromatic kerosene, n–heptane (hereafter referred to as heptane) both having reduced solubilization of large oil components, toluene, which is a strong solvent that efficiently removes heavy oil components and methanol, which can dissolve both oil and water.

## 4.2 Core cleaning

In this project, the area of focus is the comparison between two different cleaning methods: (a) ‘’mild cleaning’’ using kerosene/heptane and (b) ‘’harsh cleaning’’ using toluene/methanol. For the removal of the latest solvent present in the core during cleaning (heptane or methanol) a 1000ppm NaCl brine was used for the sandstone cores. In this way, the clays are prevented from swelling and the easily dissolvable salts are removed. The effluents of the 1000ppm NaCl brine were collected, and the pH was monitored. In the case of the carbonate cores, pure deionised water was injected. The apparatus used was a Hassler core holder with a confining pressure at 20 bars. while the operating conditions were atmospheric (room temperature and atmospheric pressure). The flooding rate was constant at 0.1ml/min and the pressure differential (ΔP) values were monitored at all times to observe any changes in core permeability between restorations. The effluent samples from the cleaning procedures were collected for visual inspection of the core's cleaned state (API, 1998) **Figure 28**. In **Figure 29** an illustration of the core flooding apparatus is shown. Cleaning with kerosene/heptane is an in-house procedure developed for maintaining the original wettability of the core by removing the mobile oil phase while minimizing the desorption of adsorbed organic material at the rock surface (Shariatpanahi et al., 2012). Past work performed on outcrop chalk showed that most organic material (75%) stays adsorbed after the ''mild cleaning'' approach (Hopkins et al., 2016). On the other hand, usage of high aromatic solvents like toluene tends to remove any adsorbed organic components leading to a more water-wet state.

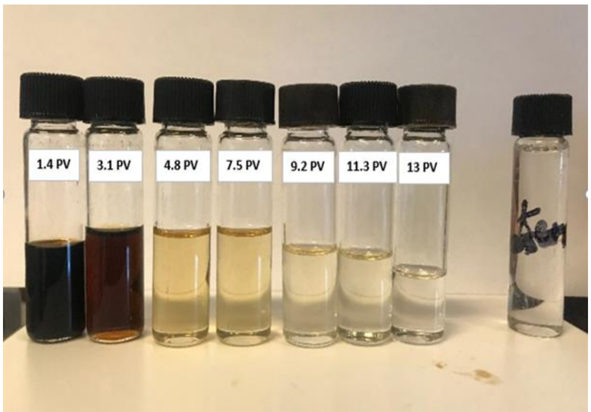


**Figure 28:** Visual inspection of the cleaning state of reservoir sandstone cores from the effluents of the kerosene injection.

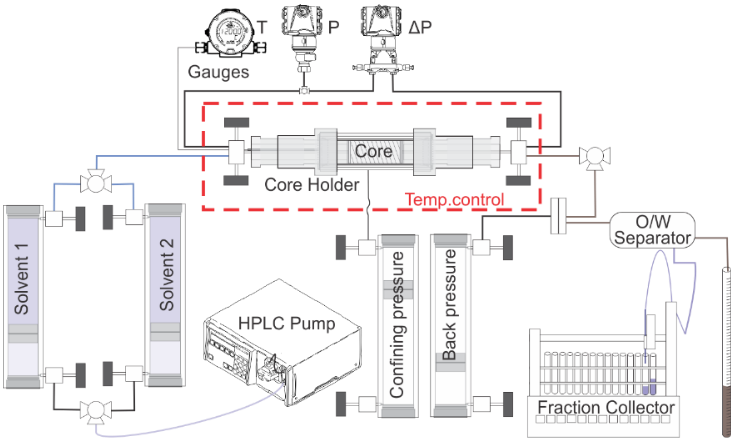


**Figure 29:** Core cleaning apparatus.

### 4.2.1 Cleaning using kerosene/heptane

Kerosene is a low-aromatic solvent that is used to remove the mobile oil phase, whilst heptane is used to displace kerosene without causing any salts to dissolve. Residual oil is dissolved by low aromatic kerosene, although bitumenic solids are not. Finally, a LS brine is flushed through the core to remove the easily dissolvable salts and to prevent clays from swelling. The amount of kerosene flushed into the cores V1, V5, V6, V7 and V9 was approximately 10 PV until a clear effluent was collected (API, 1998), followed by 5PV of heptane and 10 PV of LS brine (or deionised water for chalk).

### 4.2.2 Cleaning using toluene/methanol

The toluene/methanol cleaning process is a well-known and widely utilized hydrocarbon extraction procedure. This vigorous technique, in comparison to the kerosene/heptane strategy, tends to eliminate elements that contribute to the rock's inherent wettability. Methanol dissolves polar compounds, water, and precipitated salts, while toluene removes the oil phase, including polar organic components, asphaltenes, and bitumenic precipitates. The cores V2 and V10 were cleaned according to this protocol with 5PV and 5PV of toluene and methanol in two cycles followed by 10PV of the LS brine (or deionised water for chalk).

## 4.3 Core fluid restoration

### 4.3.1 Establishing initial water saturation $S_{wi}$

For establishing the initial water saturation ($S_{wi}$), the desiccator technique was implanted as suggested by (Springer et al., 2003). After each core cleaning protocol, the cores were placed for drying at 90 °C, until constant weight, before they were vacuum–saturated with fivefold diluted FW (d5FW). The silica gel present in the desiccator will gradually dry the cores to reach the desired 20% and 10% $S_{wi}$ for sandstones and carbonates respectively. At this stage, the remaining brine will have the original formation water composition. To ensure an even brine distribution along the pore network of the core, each core was stored for three days.

### 4.3.2 Crude oil exposure and aging

The cores used for the reproduction of wettability studies were exposed to various amounts of Oils V1, A, B, and C; 1 PV (more accurately (1–$S_{wi}$) PV), 5 PV, or 11 PV.

The cores with an $S_{wi} = 0.2$ and 0.1 for sandstones and carbonates respectively, were placed in the Hassler core holder at $50^{o}$ C and exposed to vacuum from both sides for a short period of time prior to oil exposure. Depending on the amount of oil introduced into the core the oil exposure process took place in a different way:

- Cores saturated with 1 PV: vacuum saturation from both sides at a rate of 0.5ml/min

- Cores saturated with 5 PV: vacuum saturation from both sides at a rate of 0.5ml/min, 2 PV oil in both directions at a rate of 0.1 ml/min
- Core saturated with 11 PV: vacuum saturation from both sides at a rate of 0.5ml/min, 5 PV oil in both directions at a rate of 0.1 ml/min

Finally, the oil exposure process ceased with the aging process. The cores were placed in the aging cells surrounded by the corresponding oil (see **Table 6**) for 14 days at 60 °C and 1 atm pressure. A thermal expansion of the oil phase due to temperature increase should be expected.

## 4.4 Spontaneous imbibition

One of the methods for evaluating the core wettability after COBR interactions is the spontaneous imbibition (SI) oil recovery test. After the core is restored, is placed into an Amott cell (Amott, 1959) submerged in water or oil (**Figure 6**). If the surrounding fluid manages to imbibe into the pores of the core and displace the mobile oil, then it is the wetting phase of the system. The displaced fluid is collected in a graded burette, while the imbibition is monitored with time. The ultimate recovery and the rate of imbibition of the wetting phase will finally dictate the level of wettability. All the cores from reproducing wettability experiments containing their corresponding oil were placed on top of marbles inside the Amott imbibition cell and surrounded by the imbibition brine. No wettability alteration should be expected during the imbibition process since the FW is in chemical equilibrium with the COBR-system. The calculated oil recovery in %OOIP is derived from the collected crude oil and plotted against the time of imbibition.

## 4.5 Crude oil adsorption test

The crude oil adsorption test is a method to evaluate the chemical interactions between the crude oil and the rock phase. After the establishment of $S_{wi}$ the cores were placed in a Hassler core holder with a 20bar confining pressure and 10bar backpressure. Crude oil with known AN and BN numbers is injected through the core at a rate of 0.1 ml/min. Produced oil samples are collected by a fraction collector and analysed for the presence of POC. Adsorbed POC were then calculated as the difference between the AN and BN of the influent and effluent crude oil samples (Puntervold et al., 2021). The adsorbed POC AN and BN are plotted versus PV injected. The experimental apparatus is presented in **Figure 30**.

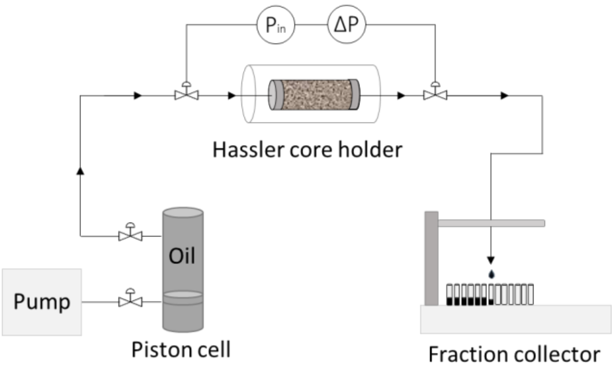


**Figure 30:** Crude oil core flooding set-up.

## 4.6 Fluid and rock characterization

Below is a quick explanation of the analyses performed throughout this project.

### 4.6.1 Potentiometric titration

The quantity of acidic and basic polar components, in mg KOH/g of oil, was measured in samples of stabilized reservoir crude oils by potentiometric titration samples. Buckley and Fan (2007) modified versions of ASTM 664 and ASTM 2895 were utilized for the procedures. The Mettler Toledo DL55 auto-titrator was used to quantify AN and BN.

### 4.6.2 Ionic composition analysis

During several core tests, samples of effluent brine were obtained. The trilutionTM LH system from Gilson was used to dilute the brine samples prior to the analysis. An ion chromatograph, the DIONEX ICS-3000, was used to undertake chemical analyses of both anions and cations. The concentrations of ions were determined using an external standard technique.

### 4.6.3 pH measurement

Mettler Toledo's pH meter seven easy $^{TM}$ was used to determine the pH of brines and effluent water samples. The semi-micro-pH electrode was utilized. The reproducibility of the measurements was within the range of +/- 0.01 pH units.

### 4.6.4 Viscosity

The viscosities of brine and crude oil were measured with an Anton Paar Physica MCR 302 rotating rheometer.

### 4.6.5 Density

A density meter DMA-4500 from Anton Paar was used to test the density of brines, oils, and produced water samples.

### 4.6.6 Scanning Electron Microscopy (SEM), EDAX

Images of rock surfaces were collected from rock samples collected from reservoir cores using a ZEISS SUPRA 35VP Environmental Scanning Electron Microscope. An EDAX detector was used to perform basic analyses on the same rock sample.

# 5 Results and discussion

The main goal of this work has been to optimize the workflow in the laboratory for reproducing the core wettability of preserved reservoir cores. The level of wettability of reservoir sandstone and outcrop carbonate cores was evaluated, by following two different cleaning protocols. In addition, the aim was to reproduce the wettability of a system using the optimum restoration process. The two cleaning strategies compared in this study were the kerosene/heptane and toluene/methanol schemes. Furthermore, the change in core wettability between restorations provided important information regarding the effect of crude oil exposure in these two differently cleaned sandstone rock systems. Charged POC might have a higher affinity onto mineral surfaces with opposite charges, especially in the water-wet case. An increased amount of crude oil exposure during a core restoration process, or in successive core restorations could increase the accumulation of these surface–active components and result in a less water-wet behavior of the restored core, observable in spontaneous imbibition tests (Aslanidis et al., 2021). Industry uses aggressive solvents to achieve a water-wet state during core cleaning before the fluid restoration process. Apart from the solubilization of the solvents with the residual oil and the POC, this aggressive approach might interact with parts of the mineral surface that contribute to the natural initial wettability of the rock like asphalts/bitumen and salt minerals. The milder approach of kerosene will solubilize and remove the residual oil but minimize the removal of POC along with the solid organics and salt precipitates that consist of a part of the rock.

In this study, a combination of using the kerosene/heptane scheme combined with an optimum amount of crude oil exposure that will fill the pores sufficiently without altering the wettability is proposed. All the cleaning procedures were performed using a Hassler core holder, and no Soxhlet extraction method has been implemented. Finally, a crude oil adsorption test was performed to observe the effect of POC onto the sandstone mineral surface.

## 5.1 Evaluation of core wettability

Smart Water is a wettability alteration EOR method that results in more water-wet conditions (Aghaeifar et al., 2015; Mamonov et al., 2019; Puntervold et al., 2021). To predict the EOR-potential by either method for a given reservoir, a reliable estimate of the reservoir wettability is needed. For strongly water-wet reservoirs the EOR-potential by wettability alteration will be very low and Smart Water or low salinity water injection are not recommended (Aghaeifar et al., 2015). Realistic predictions of reservoir wettability can be achieved through precise laboratory core experiments. To maximize the accuracy of the results produced in the lab, the cleaning and restoration procedures need to be optimized in a way that will duplicate the reservoir conditions in front of wettability tests, permeability measurements, etc. This work is particularly important in regard to this aspect of special core analysis.

A comparison of the core wettability after the first core cleaning and core restoration of SI experiments in the reproducing wettability experiment of sandstones is presented in **Figure 31**. The ultimate recovery of the cores varied from 27 %OOIP to 45 %OOIP confirming the water-wet behavior of these reservoir sandstone cores. Apart from the difference in the ultimate recovery, a difference in the rate of imbibition was observed as well after 7-30 days. ‘’Sister’’ cores that were retrieved from the same seal peel behaved in a different way. This may be explained by mineralogy and pore size distribution heterogeneity, as seen in **Figure 31**, where the pore throat radii of the sandstone core material vary dramatically and nonuniformly. Cores cleaned mildly (kerosene/heptane) should show a less water-wet behavior in contrast with the cores cleaned with more rigorous solvents (toluene/methanol) where a more water-wet state should be expected.

The big variation in ultimate recovery results confirms the difference in the initial wettability of the cores. Thus, direct comparison and analysis based on the ultimate recovery results is a very difficult task. Pore heterogeneity in sandstone cores seems to be an important factor in core laboratory studies.

Laboratory protocols for replicating core wettability in repeated core experiments on the same core might be improved with a better understanding of the parameters impacting core wettability during core cleaning and fluid restoration.

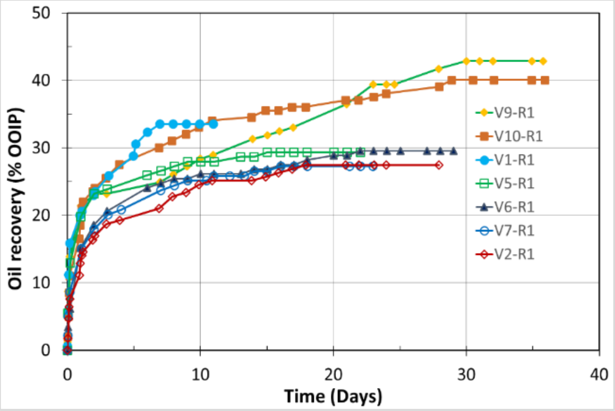


**Figure 31:** SI tests performed at 60 °C on 7 preserved Varg cores after the first core cleaning and core restoration. All cores were restored with $S_{wi}$ = 20% of $FW_V$ and exposed to 5PV of oil V before aging. The cores were imbibed with $FW_V$.

## 5.2 Effect of crude oil exposure on core wettability

The wettability of mildly cleaned reservoir sandstone cores due to the crude oil exposure after multiple restorations were investigated. Spontaneous imbibition (SI) tests were performed on the cores using $FW_V$ as imbibing fluid. As already explained, no chemical-induced wettability alteration should be expected from the imbibing fluid, since $FW_V$ is used for establishing $S_{wi}$. The spontaneous imbibition rate and ultimate recovery plateau will therefore indicate the core wettability

(Anderson, 1987). Core V6 was mildly cleaned (kerosene/heptane) and restored with $S_{wi}$=20% as described in chapter 4. The amount of oil exposure in this core was 11 PV during the first restoration (R1). SI with $FW_V$ at 60 °C was performed to evaluate the wettability of the system at R1. When the ultimate oil recovery was reached, the core was restored again with the same amount of 11PV introduced into the core. The results of both tests are presented in **Figure 32**.

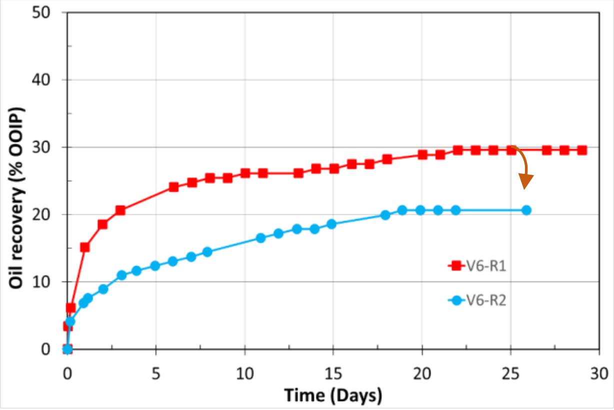


**Figure 32:** Oil recovery by spontaneous imbibition at 60 °C from core V6 at $S_{wi}$=0.2, which was cleaned with kerosene/heptane and exposed to 11 PV of crude oil in both restorations R1 and R2.

After the first core restoration with 11 PV of crude oil exposure (Oil V1), core V6 at R1 reached a recovery of 21 %OOIP rapidly after 3 days of production and ultimate recovery of 30 %OOIP after 22 days. During the second restoration process (R2), core V6 behaved significantly less water-wet reaching to ultimate recovery of 21 %OOIP after 19 days. The reduction in the water-wetness of the system, in this case, is at 30% compared to V6 at R1. The dramatic change in core V6 wettability designates that the 11 PV of the Oil V exposed into the core in between the restoration processes was not the optimum amount for a wettability reproduction. Thus, an optimized amount of crude oil should be introduced into the core when designing a core restoration procedure in sandstone reservoir cores. The findings also revealed that mild core cleaning with kerosene/heptane was ineffective in eliminating POC adhering to mineral surfaces, resulting in increased POC build-up on pore surfaces and decreased core V6 water-wetness during subsequent core restorations. Emphasis should be given to the fact that mild solvents aimed for wettability preservation by reducing the amount of POC removed from the rock surface. Mild core cleaning in outcrop chalk has shown that approximately 75% of the adsorbed POC remained adsorbed on the outcrop chalk surface after kerosene/heptane cleaning (Hopkins et al., 2017). Therefore, the crude oil amount should be optimized in order to achieve wettability reproduction.

## 5.3 Crude oil adsorption on sandstones

This change in the wettability of the system towards less water-wet could be explained by the successive adsorption of polar components onto the sandstone mineral surface.

Core V2 was previously used in wettability tests and it was shown that the reservoir rock was quite water-wet initially. After cleaning the core with toluene/methanol to a preferentially water-wet condition, the core wettability was assessed using a SI test on the restored core with a $S_{wi}$ of 20% and mineral oil (C7) as the oil phase, as shown in **Figure 33**. The results showed that the toluene/methanol cleaning was successful. After the toluene/methanol cleaning, the oil production reported, reached an ultimate recovery of 50 %OOIP after 2 hours and 54% after 1 day, demonstrating significant capillary forces and a water-wet behavior of the rock pore surfaces.

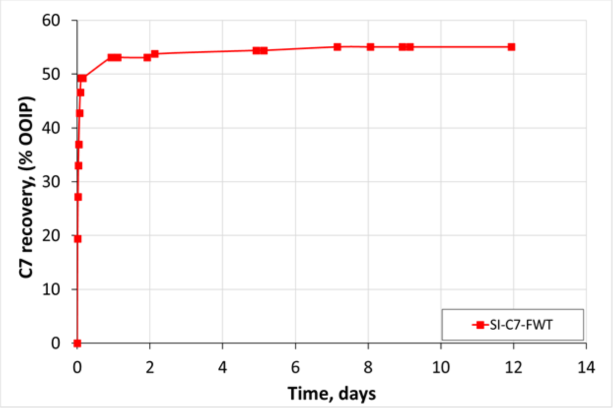


**Figure 33:** SI test on reservoir sandstone core V2 at T=60 °C. The core with established with $S_{wi}$= 20% was saturated with mineral oil (C7) and spontaneously imbibed with FW until reaching recovery plateau.

### 5.3.1 Surface reactivity test

Because of dissolved acidic gases such as $CO_2$ and $H_2S$, the pH of formation water, in general, is low (around 5) under reservoir conditions. At this pH, the clay minerals, which operate as cation exchange material, are adsorbed by acidic and protonated basic components of crude oil, as well as cations, particularly divalent cations from formation water, such as $Ca^{2+}$. Injection of a low saline fluid, which facilitates $Ca^{2+}$ desorption, causes a local elevation in pH along with the brine-clay interface because $Ca^{2+}$ is substituted by $H^+$ from the water. Desorption of organic material from clay will occur as a result of a rapid interaction between $OH^-$ and the adsorbed acidic and protonated basic substance. The water wetness of the rock improves, and oil recovery improves.

A surface reactivity test was conducted by successfully flooding a 100% water-saturated core V2 with $FW_T$ – LS brine to analyze the chemical reactivity of the surface minerals. **Figure 34** depicts the end outcome.

The effluent pH was 7.7 at the start of the $FW_T$ injection and thereafter the pH was stabilized just below 8. The injection brine was changed to

LS after 8 PV. The pH of the effluent steadily rose, indicating that the chemical compositions of the injection brines had an impact on Brine–Rock interactions. A decrease of one pH unit in the effluent brine corresponds to a tenfold rise in proton concentration ([H+]). These results indicate that low salinity effect could be observed in this material using these brines.

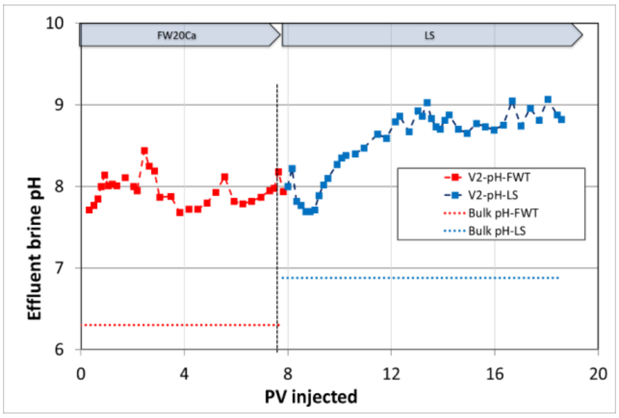


**Figure 34**: Surface reactivity test of the core V2 at T=60 °C using a brine sequence of $FW_T$-LS brine

## 5.3.2 Crude oil adsorption test

The core was dried and restored with an initial water saturation of 20% with $FW_T$ after the SI and surface reactivity tests on the quite water wet core V2, before a crude oil adsorption test was performed. The 20% $S_{wi}$ core was placed in a Hassler core holder and flooded with crude oil V2 at a rate of 0.1 ml/min, with an AN=BN=0.23 mg KOH/g.

Potentiometric titration of the generated oil samples was used to measure the levels of AN and BN in the oil. The findings are shown in **Figure 35**.

As can be seen, both acidic and basic POC components adsorb in the first contact of oil with the brine-rock system. It's also worth noting that adsorption to mineral surfaces happens quite quickly. During the first 6 PV of Oil V2 injection, substantial adsorption of basic polar components was detected (**Figure 35** (a)), but only 35% of the bases contained in Oil V2 had an affinity for the mineral surfaces. The BN of the produced oil was equal to the bulk value of Oil V2 after 8 PV of Oil V2 injection.

On the other hand, there was no evidence of continued adsorption of acidic components (**Figure 35** (b)). The bulk AN = 0.23 mg KOH/g was attained quickly. This observation is in line with the concept of positively/neutral charged bases having a higher affinity to the mineral surface than neutral/negative acids at slightly acidic pH.

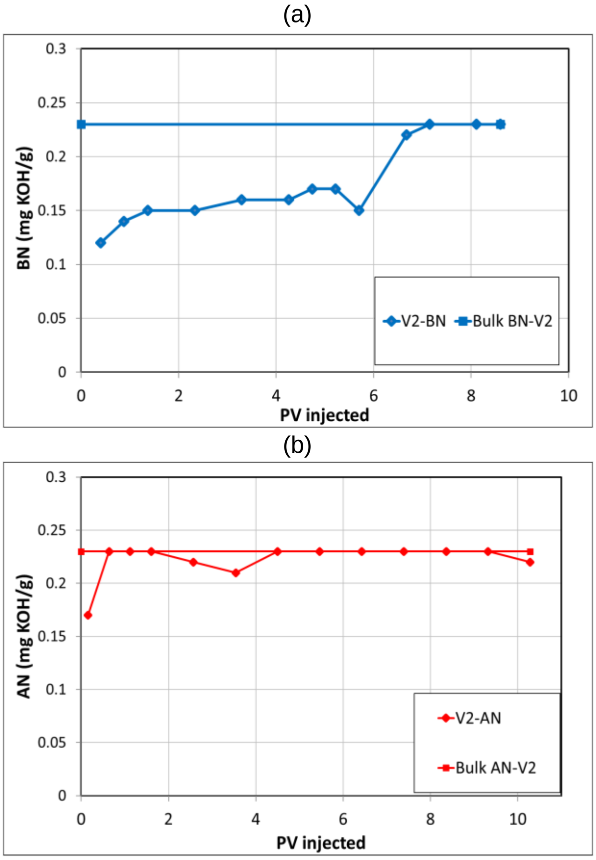


**Figure 35:** Adsorption of acidic and basic POC onto reservoir V2 sandstone during crude oil flooding. 10 PV of modified crude oil (AN=BN=0.23 mg KOH/g) were injected into core V2 with Swi = 19% at 60 °C and at a rate of 0.1 mL/min. Effluent oil samples were analysed for (a) BN and (b) AN and plotted against PV of crude oil injected.

A spontaneous imbibition test was performed on core V2 to determine the wettability response after Oil V2 exposure. At 60 °C, $FW_T$ was employed as the imbibing brine. **Figure 36** shows a considerable difference in core wettability when compared to the completely water-wet core cleaned with toluene-methanol and saturated with heptane.

After an exposure of 10 PV of Oil V2, the water wetness of the core was dramatically reduced, and adsorption of basic polar components was observed. After 23 days, an ultimate oil recovery of 47% was attained, showing that the capillary forces and oil mobilization were dramatically reduced as a result of the exposure to Oil V2 and the observed adsorption of basic components, indicating reduced water wetness. It's also worth noting that no aging was done prior to the imbibition test, indicating that the observed decrease in core water wetness is not the product of a long-term aging process. This demonstrates that during core restoration, core aging is not required to turn a reservoir sandstone core to less water-wet conditions.

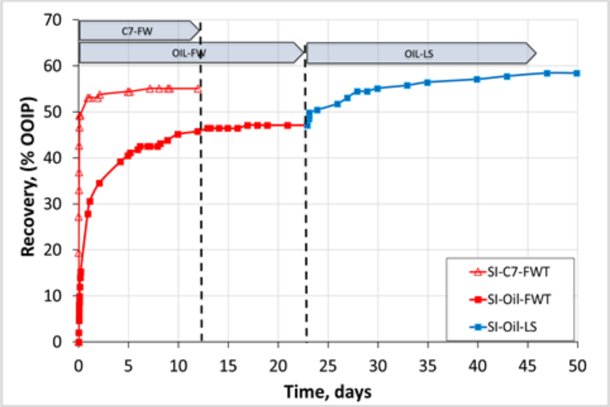


**Figure 36:** SI oil recovery test at T=60 °C on reservoir sandstone core V2 exposed to 10 PV of crude oil. FW and LS were used as the imbibing brines.

After reaching the ultimate oil recovery plateau with the 50 000 ppm $FW_T$ brine with 20 mM $Ca^{2+}$ ions, the imbibition brine was changed to LS after 23 days to disturb the chemical equilibrium during the test. A change in ion composition and salinity led to a radically altered brine rock equilibrium, encouraging an elevated pH, as seen in the surface reactivity test. The oil mobilization from the core V2 was greatly enhanced using 1000 ppm NaCl as LS brine. After 47 days, a further 11 %OOIP recovery was discovered, bringing the total oil recovery to 58 %OOIP.

In conclusion, even a crude oil with a low amount of POC seems to interact with the mineral surface of the reservoir sandstone cores. Mainly basic POC keep adsorbing on the mineral surface after several amounts of PV injected altering the wettability of the system towards a less water-wet state.

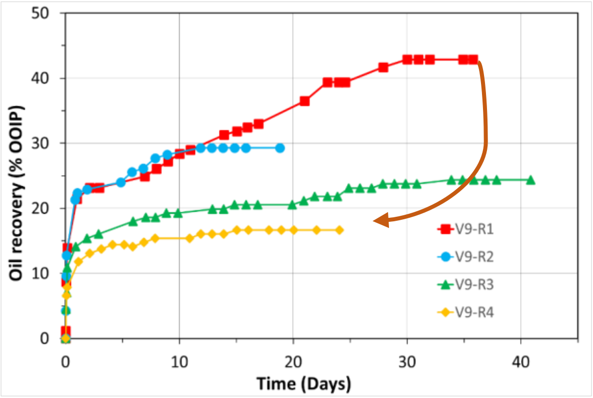
## 5.4 Effect of kerosene/heptane cleaning solvents on core wettability

The primary idea at the earliest stages of this study was to implement a method that will not interfere with the natural characteristic of the rock system but preserve the initial wettability. The low aromatic content of the kerosene and high miscibility with the organic compounds made kerosene a good candidate to be included in a new optimized restoration strategy.

### 5.4.1 Sandstones

To examine the effect of core cleaning on sandstone wettability after multiple restorations in further detail, the cores V9 and V1, derived from two different wells (see **Table 3**) were restored four times each. In this case, the amount of Oil V1 exposed to the cores was reduced to 5 PV during each restoration procedure. Likewise, with core V6, SI oil recovery tests were performed at 60 °C using $FW_V$ as the imbibing fluid to evaluate the wettability of the system. The results of this experiment are presented in **Figure 37**. As shown, both cores V9 and V1 were slightly water-wet producing a total amount of 43 %OOIP after 30 days and 34 %OOIP after 7 days respectively after the first restoration. This water-wet behavior is in line with what was observed previously in core V6 in R1. In the following restorations for core V9, **Figure 37** (a), the ultimate oil recoveries systematically declined, V9–R2 reached an ultimate recovery of 29 %OOIP, V9–R3 declined to 24 %OOIP, and V9–R4 only reached 17 %OOIP. Core V1 behaved similarly, **Figure 37** (b), with the oil recovery declining from 33 %OOIP in V1-R1 to 25 %OOIP in V1–R3, and to 14 %OOIP in V1–R4. The SI experiment from the second restoration failed and is so skipped. These findings demonstrate that mild cleaning can retain POC adsorbed on a rock mineral surface. The combination of mild core cleaning and just 5 PV of Oil V exposure during fluid restoration resulted in considerably less water-wet cores in subsequent core restorations and is thus not an effective method for duplicating core wettability in subsequent core experiments. The resulted accumulation of POC reduced the water-wetness of the system as a result of the extensive (5PV) crude oil exposure.

(a)



(b)

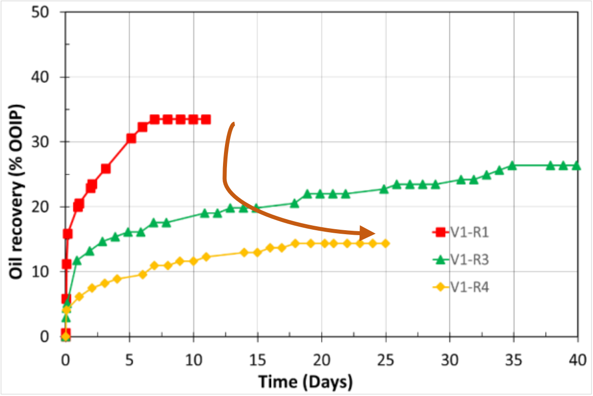


**Figure 37:** Spontaneous imbibition at 60 °C of the cores V9 (a) and V1 (b) cleaned with kerosene and heptane and exposed to 5 PV of crude oil.

### 5.4.2 Carbonates

Previous studies of the effect of mild solvents on carbonate outcrop core material have confirmed the preservation of POC on the mineral surface (Hopkins et al., 2017). In this case, outcrop chalk core C9 was restored twice. The core was cleaned with mild solvents followed by deionized water. The core saturated with the $FW_{V0S}$ at initial water saturation of $S_{wi}$ =0.1 was exposed to 5 PV of Oil B with AN=0.36 mgKOH/g at both R1 and R2 and restored as described in chapter 4. A SI oil recovery test was performed at 50° C with $FW_{V0S}$ as the imbibing fluid and the results are presented in **Figure 38**. As shown, core C9 produced an amount of 41 %OOIP in R1 which was dramatically reduced to 20 %OOIP in R2.

These results bring to a conclusion the fact that mild solvents preserve the POC present in the mineral surface and can preserve the initial wettability dictated from previous use in both carbonate and sandstone rock systems but it seems that mild cleaning and 5 PV of this crude oil do not satisfactorily reproduce wettability in multiple restorations.

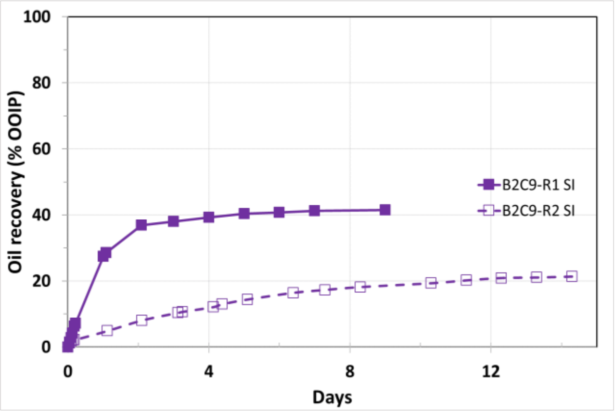


**Figure 38:** SI tests performed at 50 °C after the initial restoration (R1) and the second restoration (R2) in core C9. During R1 the core was exposed to 5 PV Oil B with AN = 0.36 mgKOH/g. After mild cleaning the core was exposed to another 5 PV of Oil B in R2.

So, the question raised from the above results was: could a more rigorous solvent approach minimize the changes in core wettability after multiple restorations? The answer to this question can be found in the next chapter.

## *5.5 Effect of toluene/methanol cleaning solvents on core wettability*

### 5.5.1 Sandstones

The mild cleaning seemed to not reproduce the wettability in multiple restorations and therefore a more rigorous approach was selected. Cores V10 and V2 were cleaned with toluene and methanol. The cores were restored three times, same as all the previous cores, and the amount of Oil V exposure of 5 PV was kept the same as well. The SI oil recovery tests are presented in **Figure 39**. At the first restoration R1, core V10 produced an amount of 40 %OOIP, recovery which increased to 43 % OOIP in R2 and to 45 %OOIP in V3. The same trend was observed in core V2 where in restoration R1, the core produced 27 %OOIP, 33 %OOIP in R2 and finally 34 %OOIP in R3. In contrast with the previous case presented in chapter **5.2** where it was observed that mild solvents preserved the POC adsorption and decreased the water-wetness, here we observed higher recovery and a more water-wet case. In addition, toluene/methanol may have also removed components attached to the mineral surfaces that govern core wettability, such as bitumenic or salt precipitates that are part of the rock phase and cannot be properly restored in cores via core restoration techniques. Although the wettability change between restorations was smaller than in the kerosene/heptane case, the amount of crude oil exposure needed for the wettability to be reproduced under this scheme is unknown. Therefore, this is not an optimal cleaning procedure either.

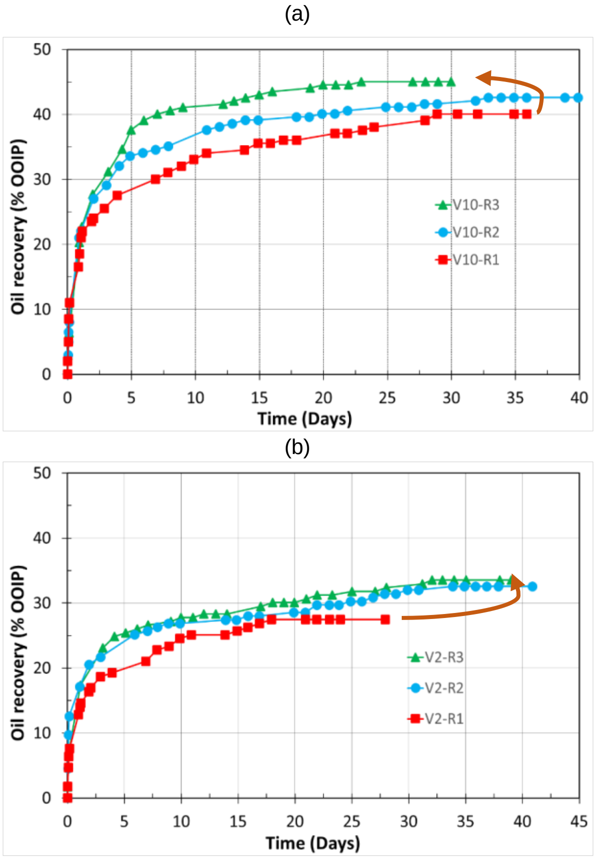


**Figure 39:** Spontaneous imbibition at 60 °C of the cores V10 (a) and V2 (b) cleaned with toluene and methanol and exposed to 5 PV of crude oil in every restoration.

## 5.6 Reproducing wettability in sandstone reservoir cores

### 5.6.1 Sandstones

As it has been shown so far, the two attempts of reproducing the core wettability failed. The mild solvents combined with 5 PV of crude oil exposure are not adequate to remove effectively all the POC while the more rigorous solvents tend to remove more components than desired resulting in a non-representative and non-reproducible wettability.

The two scenarios that could be followed in order to get a step closer to a reproducible wettability are the following:

a) Restoring the core with aggressive solvents and increasing the amount of crude oil exposure or
b) Preserving the initial wettability using mild solvents and decreasing the amount of crude oil exposure

This work addresses case (b) where the oil exposure is limited while mild solvents are used during the core cleaning process. An attempt to keep most of the POC initially in place and conclude to a reproducible initial reservoir wettability was targeted.

The reservoir cores V5 and V7 were mildly cleaned using kerosene and heptane before they were restored. The cores were exposed to only 1 PV, i.e. (1-$S_{wi}$) PV of Oil V before they were put for aging. The results from the SI experiments are presented in **Figure 40**. As seen in **Figure 40** (a), the SI of the core V7 reached an ultimate recovery of 27% and 28 %OOIP after the first (R1) and second (R2) restorations respectively with a very similar rate of imbibition. Similarly, the core V5 (**Figure 40** (b)) produced an amount of 29 %OOIP in all three restorations R1, R2 and R3 with a slight difference in the imbibition rate. These two experiments confirm that no significant changes occurred to the wettability of the cores during the cleaning and restoration process. This suggested procedure can be a more optimal way of reproducing representative wettability in core plugs used for laboratory testing.

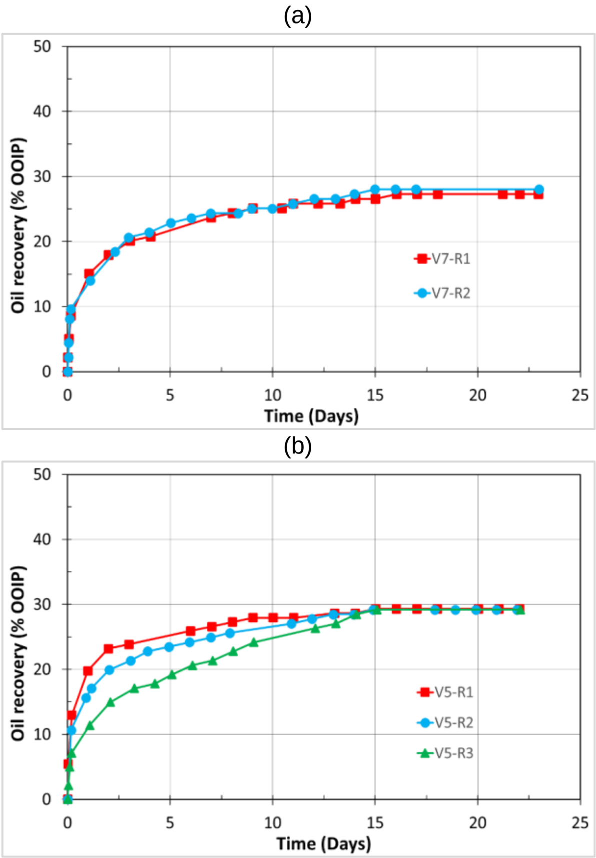


**Figure 40:** Spontaneous imbibition at 60 °C of the cores V7 (left) exposed to and V5 (right) cleaned with kerosene and heptane and exposed to 1 PV of crude oil.

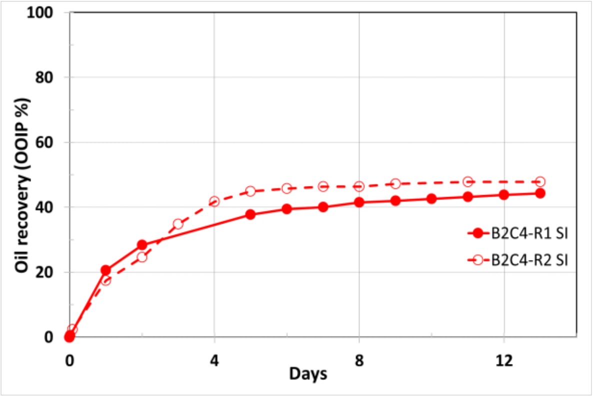
## 5.6.2 Carbonates

In this work, similarly to the previous results, it was suggested that the kerosene/heptane cleaning strategy followed by 1 PV of crude oil can maintain the original POC attached to the mineral surface and thus preserve the initial wettability of the system. In this case, four outcrop chalk cores were restored twice, and their wettability was evaluated by

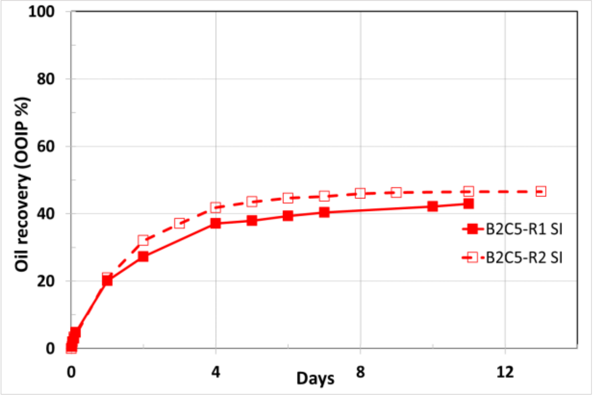
SI experiments at 50° C. All the results from the reproduction of wettability on carbonate cores are gathered in **Figure 41**.

As can be seen in **Figure 41**a, core C4 and C5 exposed to Oil B gave reproducible results from the SI experiments reaching an ultimate recovery of 44 %OOIP and 43% respectively in R1 (**Figure 41** (a) and (b)). Cores C6 and C7 exposed to Oil C reached an ultimate recovery of 25% and 37% in R1 respectively. In all four cases, the wettability was successfully reproduced. The difference in oil recovery in the second restoration for all the cores varied from +1.5% to 3.5 %OOIP **Figure 41** (c) and (d)).

(a)



(b)



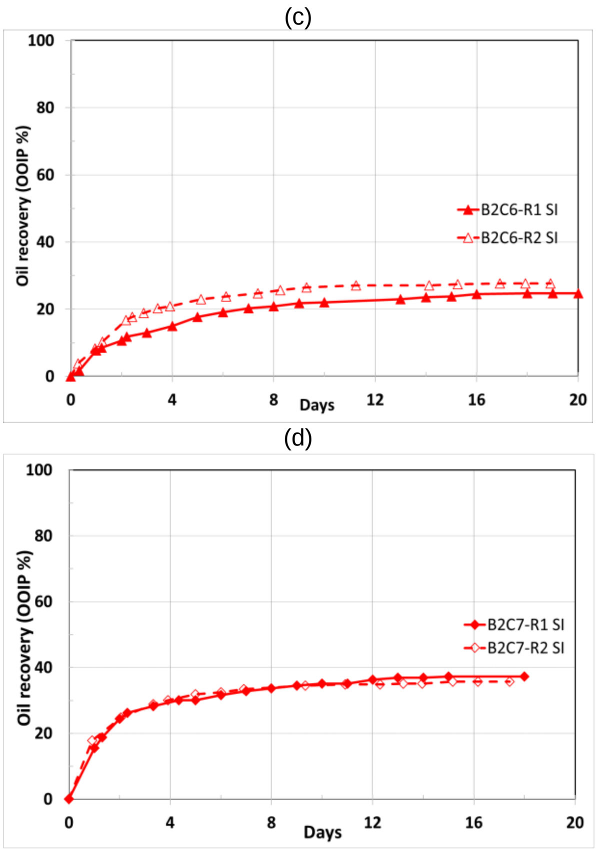


**Figure 41:** SI tests performed at 50 °C after initial restoration (R1) and a second restoration (R2) on cores with $S_{wi} = 0.1$. (a) Core C4 and (b) Core C5 exposed to Oil B (AN = 0.36 mgKOH/g). (c) Core C6 and (d) Core C7 exposed to Oil C (AN = 0.5 mgKOH/g).

As final remarks of the experimental part, the wettability of both carbonate and sandstone cores was successfully reproduced after multiple restorations. Uncontrolled volumes of crude exposure and usage of rigorous solvents proved to have a tremendous effect on core wettability. On the other hand, mild solvents combined with only 1 PV of crude oil seemed to be a more effective core restoration strategy in regard to wettability preservation.

# 6 Concluding remarks

## *6.1 Conclusions*

The study focused on the reproduction of the wettability in reservoir sandstone cores from the NCS and outcrop carbonate cores from Stevns Klint in Denmark. Two different cleaning approaches were compared, the mild cleaning (kerosene/heptane) and the more rigorous cleaning (toluene/methanol). Furthermore, the effect of crude oil exposure was examined in various amounts of 11 PV, 5 PV and 1 PV. Finally, an adsorption analysis was performed on the sandstone outcrop core material in order to explain this change in wettability when oil gets in contact with the mineral surface. The conclusion drawn from this project can be summarized as follows:

- Crude oil exposure of 5 PV or greater in repeated core restorations utilizing the mild solvents kerosene and heptane resulted in a reduction in oil recovery and water-wetness after each restoration operation in sandstone cores V1, V6, and V9.
- Crude oil exposure of 5 PV of crude oil in successive core restorations using the mild solvents kerosene and heptane resulted in a decrease in oil recovery and thus in water-wetness between restoration R1 and R2 in outcrop carbonate core C9.
- Cleaning using more rigorous solvents, toluene and methanol, resulted in higher oil recovery after each restoration from cores V2 and V10 when exposed to 5 PV of crude oil during core restoration. This gradual increase in oil recovery may imply that strong solvents might harm the rock surface by dissolving/removing material that contributes to the rock's initial wettability.
- Reservoir core wettability was successfully reproduced on the preserved sandstone cores V7 and V5 after mild cleaning and 1 PV exposure of crude oil with a small decrease in the rate of

imbibition but not in the ultimate oil recovery. Reservoir core wettability was successfully reproduced on the outcrop carbonate cores C4, C5, C6 and C7 after mild cleaning and 1 PV exposure of crude oil.

- An approximate amount of 35% of basic polar organic components of a low AN and BN oil adsorbed onto the reservoir sandstone mineral surface after 5 PV of crude oil injection. Adsorption of acid components was observed to be very low.

## *6.2 Future work*

The presented work is an additional step in optimizing the core preparation process for wettability studies. Additional work could further improve the understanding of core restoration. Some recommendations are provided below.

The efficiency of reproducing the wettability should be tested. A parallel set of experiments should be ran using the proposed core restoration method and a standard industry restored protocol. These experiments should include two or more restorations with the identical oil recovery test each time. The goal of this work would be to observe any changes in ultimate oil recovery due to changes in core wettability during the cleaning and restoration procedure.

- Test wettability reproduction with different methods e.g. NMR, contact angle, etc
- Advanced analysis on POC adsorption on sandstone mineral surface/which components have a higher affinity towards the surface.
- Compare against industry standards by other means of cleaning and restoring the cores in laboratories.

# 7 References

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# Paper I

## Reproducing Wettability in Sandstone Reservoir Core Material in Laboratory Core Restorations

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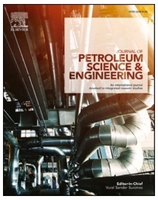

# Reproducing wettability in sandstone reservoir core material in laboratory core restorations

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ABSTRACT

Replicating initial reservoir wettability conditions in core restoration by core cleaning and fluid restoration in the laboratory is of great importance. There are several core cleaning and restoration protocols used in the oil industry and academia that include the usage of different equipment, techniques, and materials. Strong solvents used in core cleaning can remove material that is part of the rock phase leading to more water–wet behavior. Large volumes of crude oil exposure in core restorations can result in high adsorption of polar organic components onto the mineral surfaces giving less water–wet behavior. Therefore, sufficient core cleaning should be targeted, involving no physical damage to the solid rock phase and effective crude oil exposure securing realistic water saturations, avoiding overexposure of crude oil.

The objective of this study was to establish an optimum core restoration process in terms of cleaning solvents and the amount of crude oil exposure, to re-establish the same core wettability from one core restoration to the next. Seven sandstone cores from a reservoir on the Norwegian Continental Shelf underwent a series of core restorations. Two different core cleaning procedures were used, in which mild (kerosene/heptane) and strong (toluene/methanol) solvents were involved, and furthermore, the cores were exposed to various volumes of crude oil.

Spontaneous imbibition experiments showed that mild core cleaning in combination with 5 pore volumes or more crude oil exposure rendered the cores less water-wet in successive core restorations. More rigorous cleaning with 5 pore volumes of crude oil exposure rendered the cores more water-wet in successive core restorations. From spontaneous imbibition results it was concluded that an optimum core restoration procedure involving mild cleaning and only 1 pore volume of crude oil exposure successfully reproduced core wettability in successive experiments.

## 1. Introduction

Predictions of reservoir performance are usually based on laboratory measurements of core properties (Jennings, 1957). Capillary forces during waterflooding are related to the wettability of rock surfaces, and reservoir wettability is recognized to be a critical issue in many types of oil recovery processes (Morrow et al., 1994). To have trustworthy results, it is important to mimic and reproduce the initial core wettability in laboratory experiments.

Laboratory restoration of preserved reservoir cores consists of two main operations, core cleaning and fluid restoration, both dependent on each other and affecting the final core wettability. There are various core cleaning strategies mentioned in the literature regarding hydrocarbons and brines extraction (Borre and Coffey, 2014; Conley and Burrows, 1956; Cuiec, 1975; Gant and Anderson, 1988; Grist et al., 1975; Guedez et al., 2020; Gupta et al., 2017; Jennings, 1957). Some solvents used for cleaning purposes are listed in Table 1 (Institute, 1998). In addition, several techniques and experimental assemblies have been suggested in the past decades, like cleaning by centrifuge (Conley and Burrows, 1956), distillation extraction method (Dean and Stark, 1920). Since there is a large variety of crude oil-brine-rock (COBR) systems, a different approach could be used in every case. Many solvents are not complete solvents for all types of oils and a clean extract may reflect oil solubility and not complete extraction (Institute, 1998).

Gant and Anderson (1988) did an extended investigation of the solubilization efficiency of several solvents (toluene, methanol, 2–butoxyethanol etc.) in a Dean–Stark apparatus on sandstone and dolomite cores after these had been contaminated with surfactants from

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**Table 1**
Selected solvents and their use.

| Solvents | Boiling Point, °C | Solubilizing |
|---|---|---|
| Acetone | 56.5 | oil, water, salt |
| Chloroform/methanol azeotrope (65/35) | 53.5 | oil, water, salt |
| Cyclohexane | 81.4 | oil |
| Ethylene Chloride | 83.5 | oil, limited water |
| Hexane | 49.7–68.7 | oil |
| Methanol | 64.7 | water, salt |
| Methylene chloride | 40.1 | oil, limited water |
| Naphtha | 160.0 | oil |
| Tetrachloroethylene | 121.0 | oil |
| Tetrahydrofuran | 65.0 | oil, water, salt |
| Toluene | 110.6 | oil |
| Trichloroethylene | 87.0 | oil, limited water |
| Xylene | 138.0–144.4 | oil |

invert–oil–emulsion drilling muds. The results of this study showed that a 50/50 toluene/methanol mixture removed the surfactants slightly more efficiently than the three-step method involving three Dean–Stark extractions using different solvents every time. On the other hand, Dean–Stark extraction with toluene, 2–butoxyethanol, 2–methoxytetrahydrofuran and 1, 1, 1–trichloroethane gave unsatisfactory results. Guedez et al. (2020) investigated the effect of the huff-and-puff supercritical $CO_2$-based cleaning process on ultra–low permeable rocks. According to the outcome of that study, no precipitation of minerals and minimal dissolution of minerals occurred after mineralogy tests and scanning electron microscope (SEM) images. Jennings (1957) presented results of toluene extraction procedures on water–oil relative permeability. In that study it was observed that toluene significantly increased the permeability of the core material. In addition, it was stated that the analysed effluents showed removal of mostly paraffinic and aromatic hydrocarbons. Gupta et al. (2017) used high-pressure extractor and Soxhlet techniques to observe the effect of cleaning methods on petrophysical properties. It was concluded that the Soxhlet apparatus was more efficient due to the low solvent consumption compared to a high–pressure extractor. Furthermore, a higher cleaning efficiency of toluene, dichloromethane and chloroform was observed compared to that of n–heptane. Borre and Coffey (2014) used a new multi-step core cleaning procedure on carbonate core material that included two cycles of Soxhlet cleaning with pentane and methyl azeotrope with drying in-between. This process included an initial Soxhlet cleaning with pentane and drying at 60 °C. Subsequently, a second Soxhlet cleaning took place, but this time with methyl azeotrope for removing the remaining heavy oil and salts. Cuiec (1975) reported reproducible results in plugs that had been restored once, in spontaneous imbibition (SI) and forced displacement experiments using chloroform, ethanol, pyridine and hydrogen peroxide as cleaning agents as well as hydrochloric and acetic acids. He reported that the usage of toluene and chloroform regarding crude oil pollution was not recommended after observing that polluted samples could not be restored to initial conditions even after large amounts of solvents used. Grist et al. (1975) observed that toluene extraction did not affect the wettability as long as the process was not followed by methanol extraction and brine soaking. It was suggested that extraction with toluene/methanol or with chloroform/methanol especially for asphaltic crude oils was the optimum solution, since according to their remarks, methanol removes polar organic components and precipitated salts. From the core cleaning literature review, the main aim has been to bring the core back to water-wet conditions. During these operations strong solvents have been proposed which also affect bitumenic and salt precipitations that are part of the solid phase. These solid pore surface materials are not easily restored during the core and fluid restoration process.

The fluid restoration process, including establishing a correct water saturation with formation water (FW) and initial oil saturation by reservoir crude oil exposure, is an important part of the total wettability restoration process performed on cores in the laboratory. The importance of the polar organic components (POC) present in crude oils and their effect on surface wettability is well-known (Buckley and Morrow, 1990; Standnes and Austad, 2003). Previous experimental studies on outcrop sandstone cores have shown that polar organic bases present in crude oil instantly adsorbed onto the mineral surface at a larger extent than the polar organic acids, significantly affecting the core wettability (Mamonov et al., 2019). It was also observed that increased crude oil exposure further reduced the water wetness of the core. Similar observations have been confirmed on outcrop chalk, where increased crude oil exposure reduced the water wetness of chalk cores (Hopkins et al., 2016). However, in chalk it is the polar organic acids that have highest affinity for the calcite surfaces and that dictate the wettability (Puntervold et al., 2021).

In a recent core restoration study on chalk, it was observed that wettability in multiple restorations could be reproduced if the core was mildly cleaned with kerosene/heptane in front of a new fluid restoration (Piñerez et al., 2020), after initial water saturation ($S_{wi}$) of $S_{wi} = 0.1$ was established by the desiccator technique (Springer et al., 2003). The amount of crude oil exposure, in pore volumes (PV), needed to reproduce the wettability was limited to (1–$S_{wi}$)PV (Piñerez et al., 2020). Larger volumes of crude oil gave significantly less water-wet cores.

The main objective of this study was to develop an optimum restoration process for reservoir sandstone cores to restore reproducible core wettability from one core restoration to the next. Both optimized solvent cleaning and crude oil exposure have been taken into account in a new, proposed cleaning and fluid restoration strategy for restoring the initial wettability of preserved reservoir sandstone core samples. In the present study, a Hassler core holder was used for flooding various solvents through the core in the core cleaning process. Flooding solvents through a core mounted in a Hassler core holder allows for easy control of the amounts of solvents used. Two distinctly different core cleaning solvent systems were applied involving mild (kerosene/heptane) and strong (toluene/methanol) solvents. The first solvent system aims to preserve wettability, while the latter consists of standard core cleaning solvents used by the industry to clean a core to completely water-wet conditions before restoring wettability. In every fluid restoration process $S_{wi} = 0.2$ was established by the desiccator technique (Springer et al., 2003), before the core was exposed to various PVs of crude oil (1 PV, 5PV or 11PV). After aging, the restored core wettability was evaluated by spontaneous imbibition oil recovery tests.

## 2. Experimental

### *2.1. Materials*

### *2.1.1. Core material*

Preserved reservoir sandstone cores were retrieved from two wells on the Varg field on the Norwegian Continental Shelf (NCS). The cores from the 9 S well were obtained from the upper sequence at depths less than 3479.50 m while the cores from the A5T2 well were taken from the lower sequence, at depths over 3493.75 m. Mineralogical composition at the respective depths was provided by the operating company and the mineralogical composition in wt% (weight per cent) representative of the cores used from each well is given in Table 2. The physical core properties are given in Table 3. Note that the permeability was measured at residual oil saturation ($S_{or}$) during the low salinity (LS) brine flooding in the core cleaning process (described later). Permeability varied between 2 and 22 mD in the A5T2 cores and between 5 and 17 mD in the 9 S cores. Pore size distributions of core plugs from the 9 S and A5T2 wells were determined by mercury injection at Stratum Reservoir, and the results are shown in Fig. 1.

### *2.1.2. Brines*

The three brines used for the experiments are synthetic and were prepared in the laboratory; Varg formation water (FW) had total dissolved solids (TDS) or salinity of 201,600 ppm (mg/L), the low salinity

**Table 2**
Core mineralogy by XRD.

| Minerals | Cores | |
|---|---|---|
| | P1–P2 | P5–P10 |
| Well | 9 S | A5T2 |
| Illite + Mica (wt%) | 15.4 | 9.5 |
| Kaolinite (wt%) | 1.1 | 1.1 |
| Chlorite/Smectite (wt%) | 0.1 | 0 |
| Chlorite (wt%) | 2.4 | 3.4 |
| Quartz (wt%) | 62.3 | 67.6 |
| K Feldspar (wt%) | 4.5 | 5.6 |
| Plagioclase (wt%) | 8.4 | 8.7 |
| Calcite (wt%) | 0 | 0.6 |
| Dolomite (wt%) | 3.9 | 2.8 |
| Siderite (wt%) | 1.1 | 0 |
| Pyrite (wt%) | 0.8 | 0.8 |
| Total (wt%) | 100 | 100 |

brine (LS) consisted of 1000 ppm NaCl, and a fivefold diluted Varg FW ($d_5FW$) was used in the establishment of $S_{wi}$ using the desiccator technique (described later). Brine compositions and properties are given in Table 4.

### 2.1.3. *Crude oil*

Stabilized stock tank oil from the Varg field, Oil V, was used in the oil recovery tests. The acid number (AN) and base number (BN) were analysed by potentiometric titration according to the procedures described by Fan and Buckley (2007), procedures that are modified from the standard methods ASTM664–89 and ASTM2896–88 for AN and BN measurements, respectively. Oil V density was measured at ambient conditions using an Anton Paar densitometer, and viscosity at 23 and 60 °C was measured by an Anton Paar MCR 302 rheometer. The Oil V properties are presented in Table 5.

### 2.1.4. *Other chemicals*

In the two core cleaning procedures, several chemical solvents purchased from Merck laboratories were used; low aromatic kerosene,

**Table 4**
Brine properties.

| Ions | LS (mM) | FW (mM) | $d_5FW$ (mM) |
|---|---|---|---|
| $Na^+$ | 17.1 | 2086.0 | 417.2 |
| $K^+$ | – | 51.0 | 10.2 |
| $Ca^{2+}$ | – | 536.0 | 107.2 |
| $Mg^{2+}$ | – | 144.0 | 28.8 |
| $Cl^-$ | 17.1 | 3526.0 | 705.2 |
| $Ba^{2+}$ | – | 7.0 | 1.4 |
| $Sr^{2+}$ | – | 8.0 | 1.6 |
| Density (g/cm$^3$) | 0.999 | 1.139 | 1.027 |
| Bulk pH | 5.7 | 5.9 | 5.8 |
| Viscosity (cP) | 0.95 | 1.45 | 1.01 |
| TDS (mg/L) | 1000 | 201,600 | 40,300 |

**Table 5**
Crude oil properties.

| | Oil V |
|---|---|
| AN (mgKOH/g) | 0.13 |
| BN (mgKOH/g) | 1.25 |
| Viscosity at 60 °C (cP) | 4.3 |
| Viscosity at 23 °C (cP) | 11.3 |
| Density at 23 °C (g/cm$^3$) | 0.845 |

**Table 3**
Core properties.

| Core | P1 | P2 | P5 | P6 | P7 | P9 | P10 |
|---|---|---|---|---|---|---|---|
| Well | 9 S | | A5T2 | | | | |
| Depth, m | 3404.83 | 3404.88 | 3507.82 | 3507.87 | 3507.92 | 3528.82 | 3528.87 |
| Cleaning | Kerosene/Heptane | Toluene/Methanol | Kerosene/Heptane | | | | Toluene Methanol |
| Length (cm) | 8.85 | 8.18 | 7.39 | 7.53 | 6.75 | 8.22 | 8.18 |
| Diameter (cm) | 3.80 | 3.80 | 3.8 | 3.8 | 3.8 | 3.80 | 3.80 |
| Bulk volume (cm$^3$) | 100.4 | 92.8 | 83.53 | 85.01 | 76.15 | 93.2 | 92.8 |
| Dry weight (g) | 203.52 | 188.47 | 168.18 | 171.82 | 152.2 | 179.65 | 167.62 |
| PV (ml) | 21.27 | 21.40 | 17.82 | 18.01 | 17.18 | 21.58 | 24.97 |
| Porosity (%) | 21.2 | 23.1 | 21.3 | 21.2 | 22.6 | 23.2 | 26.9 |
| Permeability (md) | 11.3 | 10.9 | 4.5 | 3.1 | 11.1 | 3.5 | 22.4 |

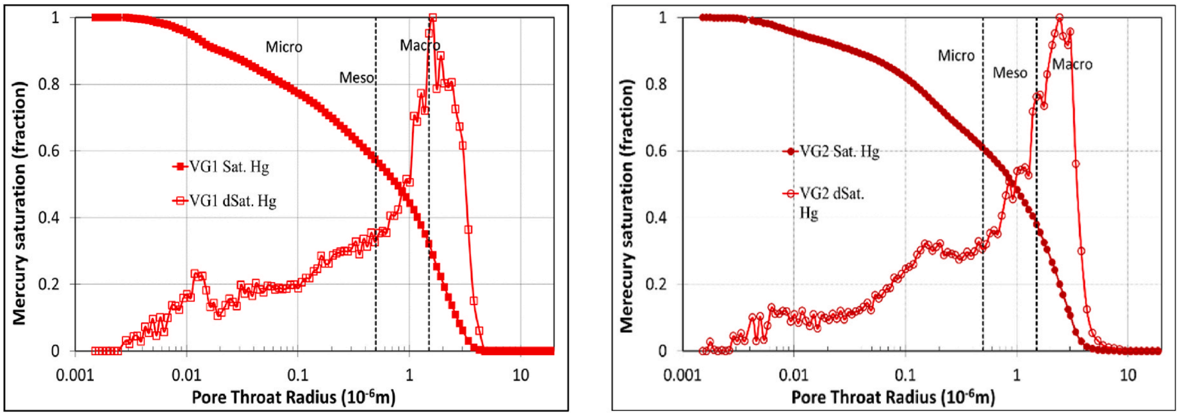

**Fig. 1.** Pore size distributions of the core plugs P1 (left) retrieved from the 9 S well and P9 (right) retrieved from the A5–T2 well.

n–heptane (hereafter referred to as heptane) both having reduced solubilization of large oil components, toluene, which is a strong solvent that efficiently removes heavy oil components and methanol, which can dissolve both polar oil components and water.

### 2.2. Core cleaning

In this study, two different approaches were used to clean the core material: (1) kerosene/heptane and (2) toluene/methanol. After cleaning with the various chemical solvents, 1000 ppm NaCl (LS) brine was injected to displace heptane or methanol while at the same time preventing any clay swelling. The cores were cleaned in a Hassler core holder at room temperature with a confining pressure of 20 bars. The solvents were injected at a flooding rate of 0.1 ml/min $\Delta P$ was monitored during each cleaning process to detect if any changes in core permeability had occurred between restorations. During the core cleaning process effluent samples were collected for visual inspection of the core's cleaned state (Institute, 1998). The core flooding setup for solvent cleaning can be seen in Fig. 2.

Cleaning with kerosene/heptane is an in-house procedure developed for maintaining the original wettability of the core by removing the mobile oil phase while minimizing desorption of adsorbed organic material at the rock surface (Shariatpanahi et al., 2012). Previous work on outcrop chalk has shown that approximately 75% of the adsorbed organic material remained adsorbed after the kerosene/heptane cleaning procedure (Hopkins et al., 2016). Cleaning by toluene/methanol, on the other hand, aims to clean the core to a very water–wet state by removing adsorbed organic material. Wettability is afterwards restored by crude oil exposure and subsequent aging.

#### 2.2.1. Cleaning using kerosene/heptane

Low–aromatic kerosene is used to remove the mobile oil phase and non–polar oil constituents, whereas heptane displaces the kerosene fraction. LS brine is injected to displace the FW and any easily dissolvable salts and at the same time reduce the potential of clay swelling. The cores P1, P5, P6, P7 and P9 were initially flushed with approximately 10 PV of kerosene until a visually clear effluent was collected (Institute, 1998), followed by 5 PV of heptane and 10 PV of LS brine.

#### 2.2.2. Cleaning using toluene/methanol

Toluene/methanol cleaning is a well-known method, which, in contrast to kerosene/heptane cleaning, tends to remove most of the material that contribute to the natural wettability of the rock. Toluene removes the oil phase, including polar organic components, asphaltenes and bitumenic precipitates, while methanol dissolves polar compounds, water and precipitated salts. The cores P2 and P10 were flooded with 5 PV of toluene followed by 5 PV of methanol, after which the cycle was repeated. Finally, the cleaning process was completed after injecting 10 PV of LS brine.

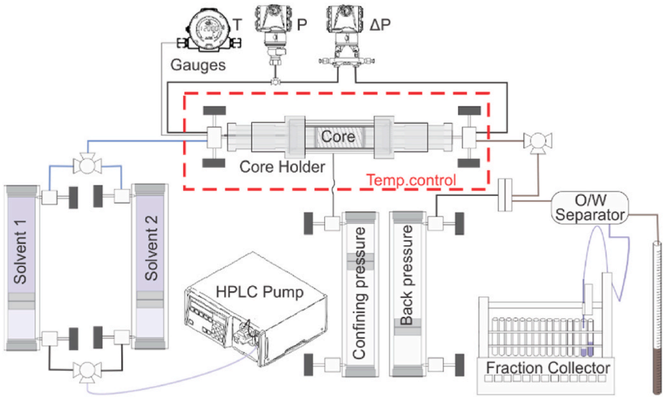

**Fig. 2.** Solvent cleaning setup.

### 2.3. Core fluid restoration

#### 2.3.1. Establishing initial water saturation, $S_{wi}$

After the core cleaning procedure described above, the cores were dried at 90 °C, until constant weight, $S_{wi}$ was established using the desiccator procedure described by (Springer et al., 2003). The dried cores were vacuum–saturated with fivefold diluted FW ($d_5$FW). A desiccator was used to gradually dry the cores to the predetermined weight corresponding to 20% $S_{wi}$. Finally, the cores were stored for 3 days to ensure even brine distribution inside the core. Note that the residual brine inside the core had attained its original FW composition after desiccation.

#### 2.3.2. Crude oil exposure and aging

The Varg cores were exposed to various amounts of Oil V; 1 PV (more accurately $(1–S_{wi})$PV), 5 PV or 11 PV. The cores with $S_{wi} = 0.2$ were first shortly evacuated above water vapor pressure for less than 10 min in the Hassler core holder prior to oil exposure. The cores exposed to only 1 PV of Oil V were vacuum-saturated from both sides, and oil was injected at a rate of 0.5 ml/min to quickly fill the void space after evacuation. The cores exposed to 5 PV were vacuum-saturated with oil, and then flooded with 2 PV oil in both directions at a rate of 0.1 ml/min. The core exposed to 11 PV oil was first vacuum-saturated, before 5 PV oil was flooded in each direction at a rate of 0.1 ml/min. All oil floods were performed at 50 °C until the pressure reached 5 bar. To finish the oil exposure process, the cores were placed in aging cells surrounded by Oil V for 14 days at 60 °C. No pressure support was applied during aging, but a small increase in pressure inside the aging cell due to thermal expansion inside the aging cell is to be expected.

### 2.4. Oil recovery by spontaneous imbibition

A spontaneous imbibition (SI) oil recovery test is a method for evaluating the core wettability established after COBR interactions. The restored core is submerged in water or oil in an Amott cell (Amott, 1959). If the fluid that surrounds the core is the wetting phase of the system, then the surrounding fluid imbibes into the pores of the core and the mobile in-situ fluid is displaced. Fluid imbibition is monitored with time, by collecting the displaced fluid in a graded burette. Evaluation of wettability with this method can be done by observing the ultimate recovery of the fluid displaced and the rate of imbibition of the wetting phase.

After aging, the core containing $S_{wi} = 0.20$ and Oil V was placed on top of marble balls inside the Amott imbibition cell and surrounded by the imbibition brine. Since the FW is already in chemical equilibrium with the COBR–system, it was used as imbibing fluid, securing no chemically–induced wettability alteration in the imbibition process. The produced crude oil was collected in a graded burette, and the recovery in %OOIP (oil originally in place), was determined versus time of imbibition.

## 3. Results and discussion

The purpose of this study was to evaluate the wettability of reservoir sandstone cores restored using two different core cleaning procedures. Additionally, the aim was to find the optimum restoration process after which a reproducible wettability could be obtained. To achieve this, two distinctly different core cleaning methods were applied using kerosene/heptane and toluene/methanol. Furthermore, the effect of crude oil exposure in two differently cleaned sandstone rock systems was evaluated with respect to the core wettability generated.

When water wet-core material is exposed to crude oil, charged POC may adsorb onto oppositely charged mineral pore surfaces. Increased amount of crude oil exposure during a core restoration process, or in successive core restorations could increase the accumulation of these surface–active components, and result in a less water-wet behavior of the restored core, observable in spontaneous imbibition tests.

Strong solvents are used by the industry to achieve water-wet cores during core cleaning prior to fluid restoration. The solvents solubilize the residual oil together with POC attached to the mineral surfaces, but they also interact with the solid part of the rock surface, especially asphalts/bitumen and salt minerals. Mild core cleaning solvents will remove the residual oil but reduce the removal of POC, solid organics and salts that belong to the rock phase.

A combination of a mild but effective cleaning method, with sufficient crude oil exposure to fill the pores without creating a less water-–wet surface is presented at this study. All cleaning processes described have been performed by core flooding through a Hassler core holder. No Soxhlet extraction has been used in any of the experiments.

### 3.1. *Effect of crude oil exposure on core wettability*

The effect of crude oil exposure on core wettability was investigated on reservoir cores after successive core restorations. Oil recovery by spontaneous imbibition (SI) was performed on the restored cores using FW as imbibing fluid. FW is already in equilibrium with the crude oil and rock surface and will therefore not generate any wettability alteration in the imbibition process. The spontaneous imbibition rate and ultimate recovery plateau will therefore indicate the core wettability (Anderson, 1986).

After a mild cleaning with kerosene/heptane and LS brine to remove easily dissolvable salts, fluid restoration was performed on the dried core P6 by establishing $S_{wi} = 0.2$ with FW using desiccator as described above. Then the core was exposed to 11 PV with Oil V before aging for 2 weeks at 60 °C. SI of FW at 60 °C was performed to evaluate the mobilization of oil by positive capillary forces after the first core restoration (R1). When oil production ceased, core cleaning, fluid restoration, aging and spontaneous imbibition were repeated in a second core restoration process (R2), and the results of both tests are presented in Fig. 3.

After the first restoration (R1) with 11 PV of Oil V exposure, core P6–R1 behaved quite water-wet reaching 21 %OOIP after 3 days and an ultimate recovery of 30 %OOIP after 22 days. However, after the second core restoration, core P6–R2 behaved significantly less water-wet. Only 11 %OOIP was produced after 3 days and reaching the ultimate recovery plateau of 21 %OOIP after 19 days. This represents a reduction of 30% in water-wetness compared to P6–R1. Core P6–R1 had been exposed to 11 PV of Oil V and produced 30 %OOIP, whereas after the second restoration the core P6–R2 had been exposed to a total of 22 PV of Oil V and produced only 21 %OOIP. This dramatic difference indicates that the injected volume of Oil V into core P6 affected the core wettability and needs to be considered when optimized core restoration procedures are designed for reservoir sandstone cores. The results also confirmed that mild core cleaning with kerosene/heptane was not efficient in removing POC attached to mineral surfaces, resulting in increased POC accumulation on pore surfaces and reduced water wetness of core P6 during successive core restorations. It should, however, be emphasized that the mild core cleaning procedure aims to preserve wettability by reduced removal of adsorbed POC from the rock surface. Mild core cleaning on outcrop chalk has shown that approximately 75% of the adsorbed POC remained adsorbed on the outcrop chalk surface after kerosene/heptane cleaning (Hopkins et al., 2017). The results on reservoir sandstone cores confirm trends observed previously in outcrop chalk (Piñerez et al., 2020), that increased crude oil exposure after mild core cleaning and restoration leads to a less water-wet core. Thus, the crude oil amount needs to be optimized for establishing a reproducible wettability.

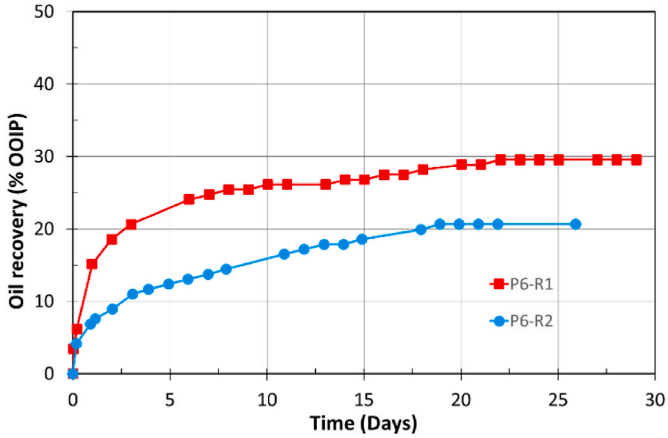

**Fig. 3.** Oil recovery by spontaneous imbibition at 60 °C from core P6, which was cleaned with kerosene/heptane and exposed to 11 PV of crude oil in both restorations R1 and R2.

### 3.2. *Effect of kerosene/heptane cleaning solvents on core wettability*

The main aim of using mild solvents kerosene and heptane in the restoration process, is preserving wettability. To examine the effect of mild core cleaning on core wettability in multiple restorations in further detail, the reservoir cores P9 and P1, originating from two different wells, were restored four times. In these experiments the amount of Oil V injected into the cores during each fluid restoration process was reduced to 5 PV. SI experiments were performed at 60 °C, using FW as the imbibing fluid, to evaluate core wettability after every cleaning and restoration process. As seen in Fig. 4, both cores P9 and P1 behaved quite water-wet after the first core restoration (R1).

Core P9 reached an ultimate recovery of 43 %OOIP after 30 days, while P1 reached an ultimate recovery of 34 %OOIP after 7 days. The quite water-wet behavior of cores P9 and P1 agree with that observed for core P6, which was restored with 11 PV of Oil V, Fig. 3. In the following restorations for core P9, Fig. 4 (left), the ultimate oil recoveries systematically declined, P9–R2 reached an ultimate recovery of 29 %OOIP, P9–R3 declined to 24 %OOIP, and P9–R4 only reached 17 %OOIP. Core P1 behaved similarly, Fig. 4 (right), with the oil recovery declining from 33 %OOIP in P1-R1 to 25 %OOIP in P1–R3, and to 14 %OOIP in P1–R4. The SI experiment after R2 failed and is therefore omitted.

The aim of the kerosene/heptane approach is to preserve the initial wettability of the cores during cleaning processes. The results on core P9 and P1 confirm this. The combination of mild core cleaning and only 5 PV of Oil V exposure during fluid restoration gave significantly less water-wet cores in successive core restorations and is thus not an optimal solution for reproducing core wettability in successive core experiments. 5 PV of Oil V exposure was too extensive, and increased accumulation of POC and reduced water wetness was observed. The question then asked was: could more rigorous cleaning solvents minimize changes in core wettability in successive core restorations?

### 3.3. *Effect of toluene/methanol cleaning solvents on core wettability*

Since the mild cleaning approach seemed to accumulate adsorbed POC and did not give reproducible results, a more rigorous method was selected. Toluene and methanol were used as cleaning agents in cores P10 and P2. The cores were restored three times each, and the amount of Oil V exposure remained the same at 5 PV in every fluid restoration. The SI results after each core restoration are shown in Fig. 5.

The ultimate oil recovery for P10–R1 was 40 %OOIP and increased to 43 %OOIP for P10–R2 and reached an ultimate recovery plateau of 45 % OOIP after P10–R3. The same behavior was also observed for P2. The ultimate oil recovery plateaus increased from 27 %OOIP to 33 %OOIP and 34 %OOIP in restorations R1, R2 and R3 respectively.

In the previous section it was seen that 5 PV Oil V exposure increased adsorption of POC and decreased water wetness after mild core cleaning.

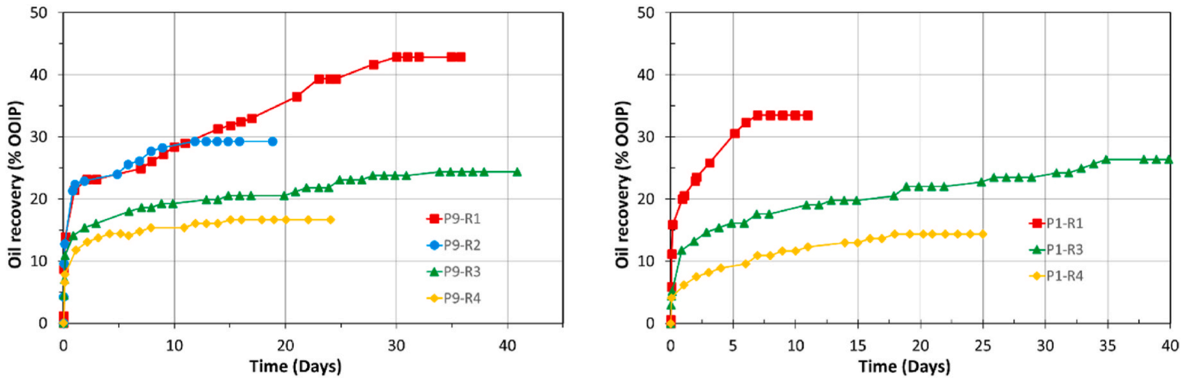

**Fig. 4.** Spontaneous imbibition of FW at 60 °C in the cores P9 (left) and P1 (right) cleaned with kerosene and heptane and exposed to 5 PV of crude oil.

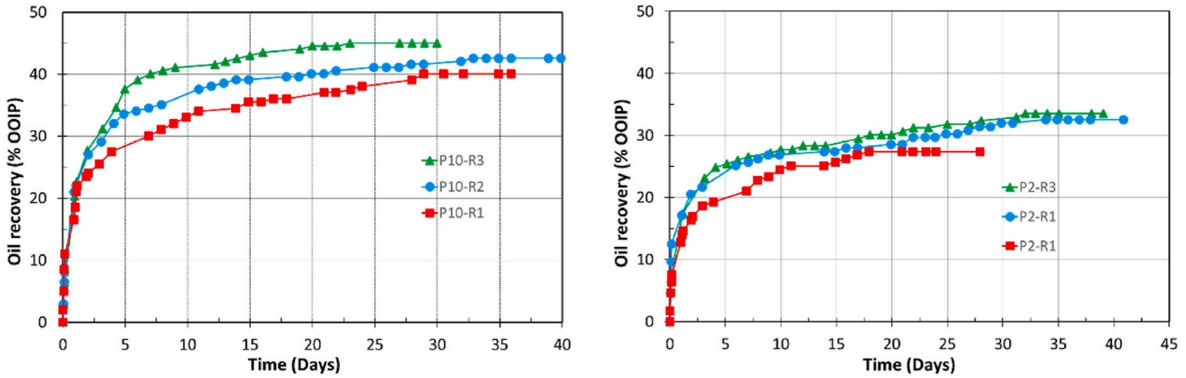

**Fig. 5.** Spontaneous imbibition of FW at 60 °C in the cores P10 (left) and P2 (right) cleaned with toluene and methanol and exposed to 5 PV of crude oil in every restoration.

Here the results show that the strong cleaning solvents used during fluid restorations promoted a gradual *increase* in the water wetness of the cores in successive core restorations. These results confirm efficient removal of adsorbed POC during core cleaning by toluene/methanol. Toluene/methanol potentially also removed components attached to the mineral surfaces controlling the total core wettability, such as bitumenic or salt precipitates that belong to the rock phase. These components cannot be easily and correctly restored in the cores during core restoration processes. However, these results can also indicate that the cores were not sufficiently cleaned before the first restoration, or that toluene/methanol is not able to remove all adsorbed POC from the reservoir sandstone surface.

### 3.4. *Reproducing wettability in sandstone reservoir cores*

The conclusions from the above attempts of reproducing the reservoir sandstone core wettability were that using mild solvents was not adequate to remove the POC adsorbed after 5 PV of Oil V exposure, but that a more rigorous approach removed more POC components after each restoration. Both methods proved to not be the best practice for restoring the core to its previous conditions. The challenge with core restoration after a rigorous approach with toluene/methanol is not knowing how many PVs of crude oil the core should be exposed to obtain a representative core wettability. As shown in Figs. 3 and 4, the extent of crude oil exposure affects the resulting wettability.

The better approach could be to maintain most of the POC controlling the initial core wettability in the preserved core, as done in the kerosene/heptane approach in Fig. 4, and afterwards limit the crude oil exposure in the fluid restoration process. This has been addressed in the final part of this work. The preserved reservoir cores P5 and P7 were cleaned by the mild cleaning solvents kerosene and heptane. Low aromatic kerosene solubilizes residual oil but not bitumenic solids. Heptane easily removes kerosene but will not dissolve salts as does methanol. After mild cleaning, core P5 and P7 were only exposed to 1 PV with Oil V, or (1-$S_{wi}$)PV to be more precise, since $S_{wi}$ was already established in the cores.

As seen from Fig. 6 (left), SI of core P7 reached ultimate oil recovery plateaus of 27 and 28 %OOIP in the first (R1) and second (R2) restorations respectively, at very similar imbibition rates, confirming a very close reproduction of core wettability.

In Fig. 6 (right), a successful reproduction of wettability was achieved after restorations R1 and R2 for core P5 with the exact same amount of oil produced, 29 %OOIP, and with similar imbibition rates. In restoration R3, the core P5 had been exposed to a total of 3 PV of Oil V, which might explain the observed decrease in the rate of imbibition. Nonetheless, the same ultimate oil recovery of 29 %OOIP was reached, indicating that no significant changes in the core wettability had taken place.

### 3.5. *Evaluation of reservoir wettability*

Smart Water or low salinity EOR are described as results of wettability alteration toward more water-wet conditions (Aghaeifar et al., 2015; Mamonov et al., 2019; Puntervold et al., 2021). To predict the EOR-potential by either method for a given reservoir, a reliable estimate of the reservoir wettability is needed. For strongly water-wet reservoirs the EOR-potential by wettability alteration will be very low and Smart Water or low salinity water injection are not recommended (Aghaeifar et al., 2015).

Reliable estimates of the reservoir wettability can be done through accurate core experiments in the laboratory. Improved laboratory procedures are needed, involving optimized cleaning procedures for

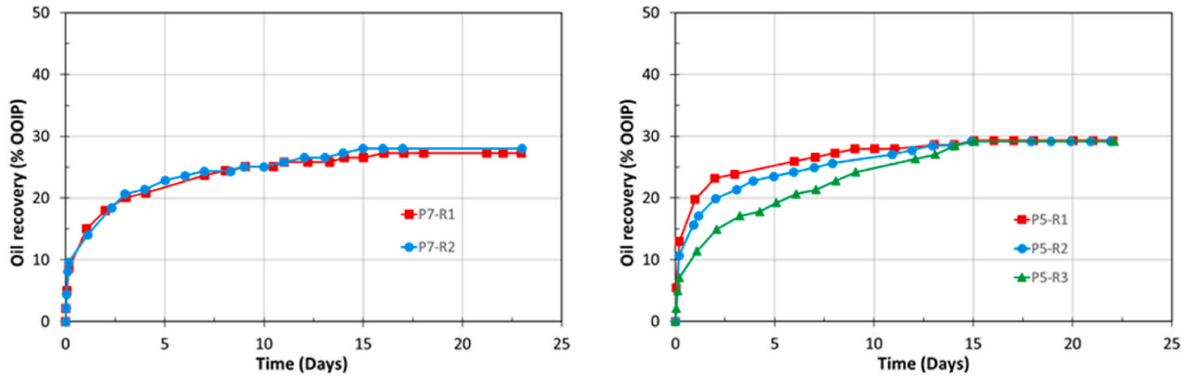

**Fig. 6.** Spontaneous imbibition at 60 °C of the cores P7 (left) exposed to and P5 (right) cleaned with kerosene and heptane and exposed to 1 PV of crude oil.

preserved reservoir cores, and reliable fluid restoration protocols in front of oil recovery tests, capillary pressure, and relative permeability measurements. This addresses the importance of this work.

In Fig. 7, the oil recovery results from the SI experiments performed after the first core restorations are compared. It can be observed that all cores clearly were on the water-wet side, giving ultimate recovery plateaus from 27 %OOIP to 45 %OOIP. Differences in the imbibition rates were also observed, with the various cores reaching recovery plateaus after 7–30 days of imbibition.

Even ‘‘sister’’ cores drilled from the same seal peel behaved differently. This can be explained by effects of heterogeneity in the mineralogy and pore size distribution, supported by Fig. 1, in which the pore throat radii of the sandstone core material vary significantly and non-uniformly from approximately 50 nm to 10 μm.

As seen in this work, a less water–wet state could be expected when mild solvents (kerosene/heptane) are used in combination with a large volume of crude oil exposure during fluid restorations. When more rigorous solvents (toluene/methanol) are applied, slightly more water-wet cores are expected even at large oil volume exposure. All SI results are summarized in Table 6.

The overall summary of the spontaneous imbibition tests shows that all the restored reservoir cores were clearly on the water wet side, spontaneously imbibing water, and that the capillary forces mobilized and produced 27–45 %OOIP of the oil. These results confirm that capillary forces are important and need to be accounted for when ultimate recovery potential from reservoirs with heterogenous pore size distribution are to be evaluated in laboratory experiments, or in modelling and simulations of fluid flow in reservoirs.

The core wettability has a huge impact on the experimental results for capillary pressure, relative permeability, oil recovery, Smart Water and any other water-based chemical EOR methods. The large variation in initial wettability results confirms that it will be very difficult to compare and discuss core analysis results from one core to the next. With improved understanding of parameters affecting core wettability during core cleaning and fluid restorations, laboratory procedures for reproducing the core wettability in successive core experiments on the same core could be developed. For this preserved reservoir core system, reproduction of core wettability in successive core experiments was successfully obtained by mild core cleaning with kerosene and heptane, followed by a minimum exposure of crude oil during fluid restoration.

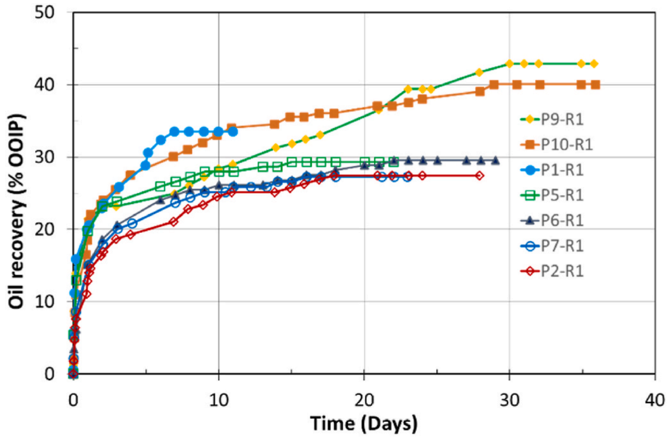

**Fig. 7.** Spontaneous imbibition results of all cores after the first restoration.

**Table 6**
Summary of all SI results from preserved reservoir cores.

| Core | Solvent cleaning system | Oil V exposure in fluid restorations (PV) | SI (%OOIP) | | | |
|---|---|---|---|---|---|---|
| | | | R1 | R2 | R3 | R4 |
| P1 | Kerosene/ | 5 | 34 | –[a] | 25 | 14 |
| P9 | Heptane | 5 | 43 | 29 | 24 | 17 |
| P5 | | 1 | 29 | 29 | 29 | – |
| P6 | | 11 | 30 | 20 | – | – |
| P7 | | 1 | 27 | 28 | – | – |
| P2 | Toluene/ | 5 | 27 | 33 | 34 | – |
| P10 | Methanol | 5 | 40 | 43 | 45 | – |

[a] Experiment failed.

## 4. Conclusions

The effect of core cleaning procedures and crude oil exposure in fluid restorations on the wettability of preserved reservoir sandstone cores retrieved from the NCS were examined in this study. Kerosene/heptane and toluene/methanol cleaning were used in the experimental procedures while the amount of crude oil exposure was 11 PV, 5 PV and 1 PV. The conclusions drawn from this work were the following:

1. Crude oil exposure of 5 PV and above in successive core restorations using the mild solvents kerosene and heptane, resulted in a decrease in oil recovery after each restoration process in cores P1, P6 and P9.
2. Cleaning with stronger solvents, toluene and methanol, showed an increase in oil recovery from cores P2 and P10 when these were exposed to 5 PV of crude oil during core restoration. This progressive increment in oil recovery might indicate that strong solvents can damage the rock surface by dissolving/removing material that contribute to the initial wettability of the rock.
3. Reservoir core wettability was successfully reproduced when cleaning with kerosene and heptane followed by 1 PV of crude oil exposure. A slight difference in imbibition rate was observed, although this difference did not have any impact on the ultimate oil recovery, which was similar in several repeated experiments.

## Credit author statement

**Panagiotis Aslanidis:** Methodology, Experimental, Data Processing, Writing, Reviewing, Editing. **Ivan D. Pinerez Torrijos:** Experimental, Reviewing. **Skule Strand:** Conceptualization, Writing, Reviewing, Editing. **Tina Puntervold:** Conceptualization, Writing, Reviewing, Editing.

## 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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# Paper II

# Core Wettability Reproduction: A new Solvent Cleaning and Core Restoration Strategy for Chalk Cores

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# 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; Abeysinghe 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 ($CaCO_3$). 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 $CaCO_3$ >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

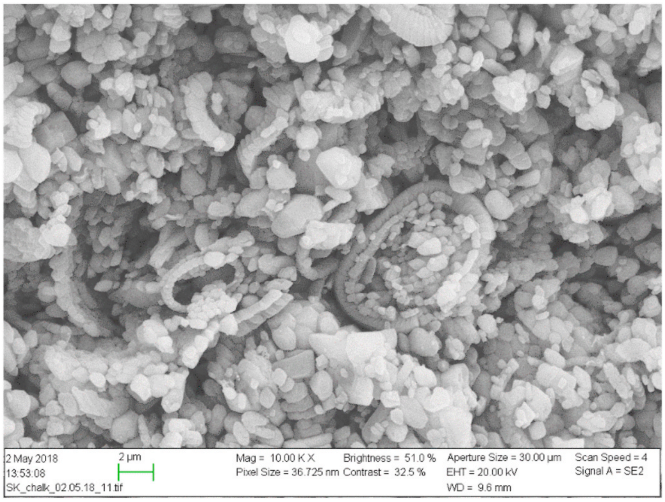


**Fig. 1.** Image of Stevns Klint outcrop chalk. SEM magnification 10000 X.

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. SW0T and SW½T 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 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.

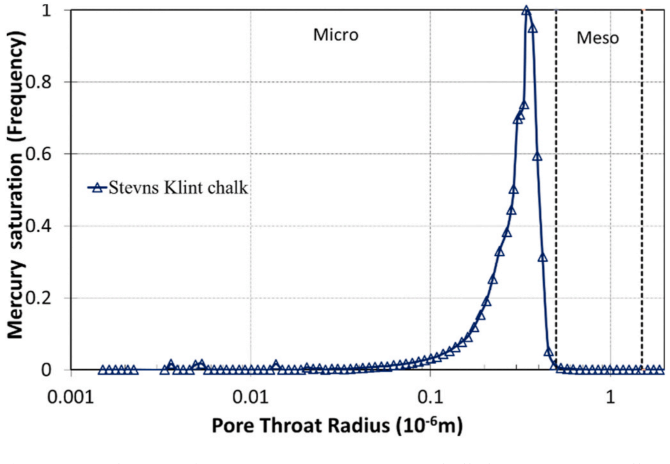


**Fig. 2.** Distribution of pore sizes in SK outcrop chalk by mercury capillary injection (MICP).

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.

| | Block 1 | | | Block 2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Core | 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, $\rho_{sat}$, $d_{10}$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, $SO_4^{2-}$, 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):

$$I_{CW} = \frac{A_w}{A_{ww}} \tag{1}$$

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, $I_{W\text{-}SI}$, only based on SI experiments can be calculated, **Eq. (2)**:

$$I_{W-SI} = \frac{SI_C}{SI_{WWC}} \tag{2}$$

$SI_C$ is the oil recovery (%OOIP) from the tested core. $I_{W\text{-}SI}$ 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 SW0T 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 $I_{W\text{-}SI}$ (**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*

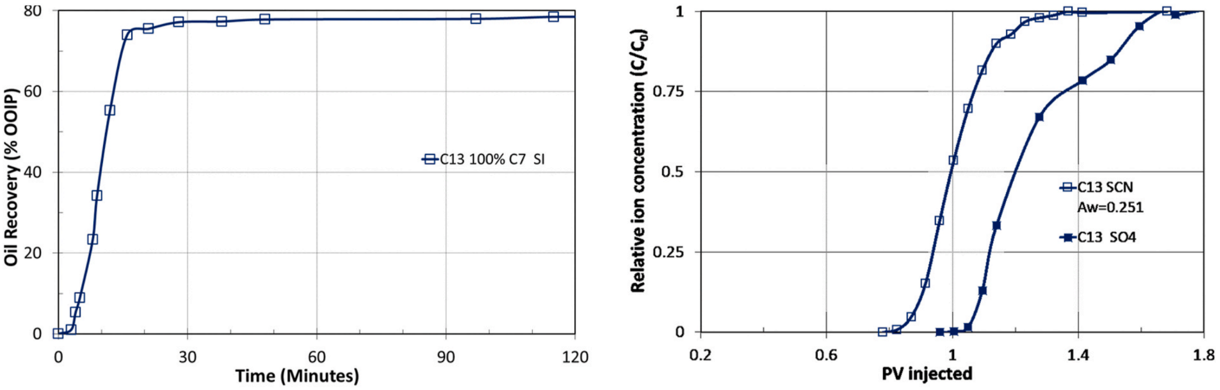
After confirming fractional, close to neutral initial wetting properties in SI and CW, the two cores with high initial water saturation went through core cleaning prior to a new core restoration.

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.

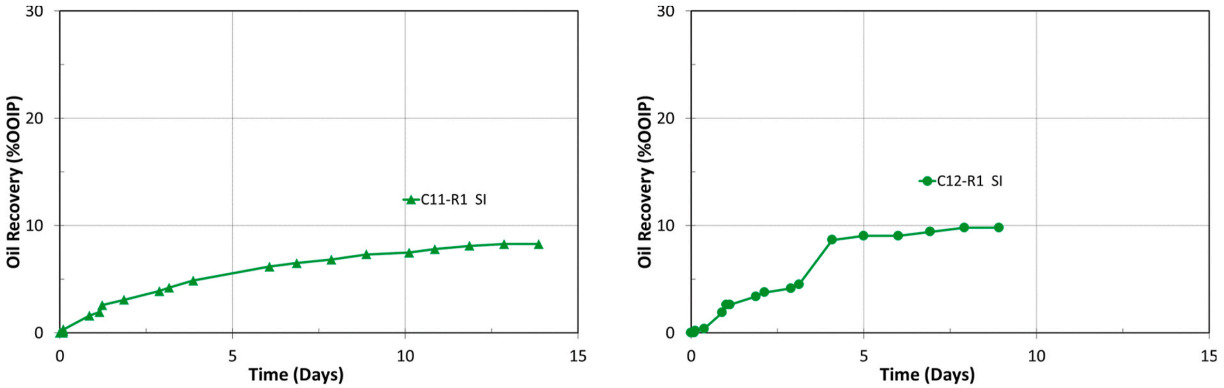
The effect of the different cleaning solvents on the wettability and capillary forces was investigated by SI tests. In both cores, 5 PV of DI water were injected to displace the CW brines, then they were dried, and vacuum-saturated with 100% heptane. The heptane-saturated cores were spontaneously imbibed 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



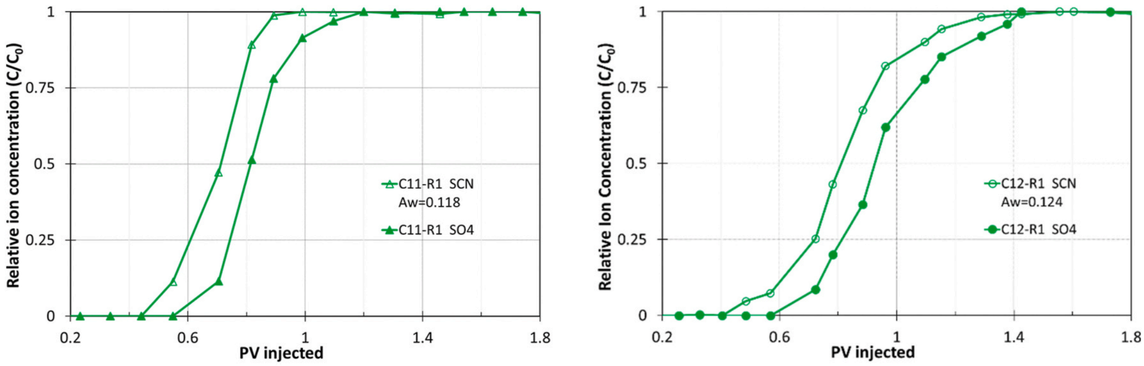
(a) (b)

**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.



(a) (b)

**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.



(a) (b)

**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.

| | Solvent | SI | | | CW | | | |
|---|---|---|---|---|---|---|---|---|
| Core | | 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.

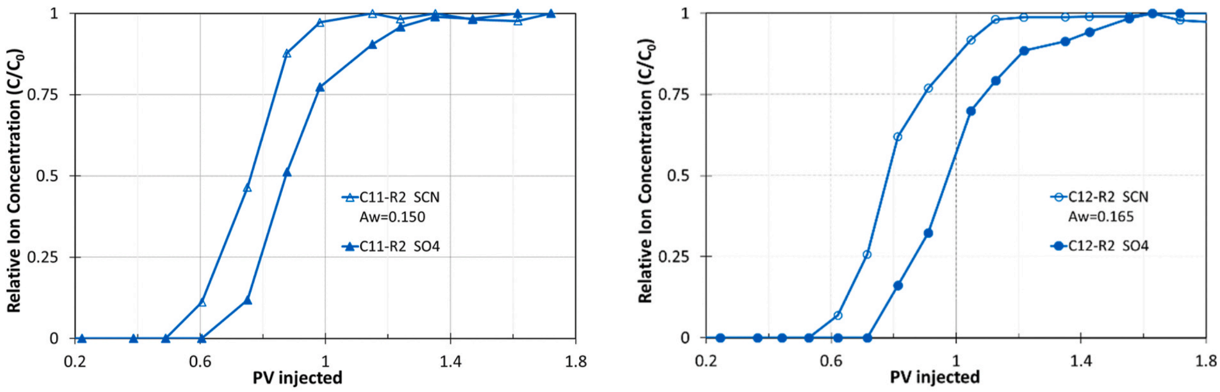
The SI water index, $I_{W\text{-}SI}$, increased from 0.10 to 0.36 for core C11 by kerosene and heptane cleaning, and from 0.13 to 0.82 for core C12 by toluene and methanol cleaning, confirming dramatic changes in positive capillary forces after toluene and methanol cleaning.

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*

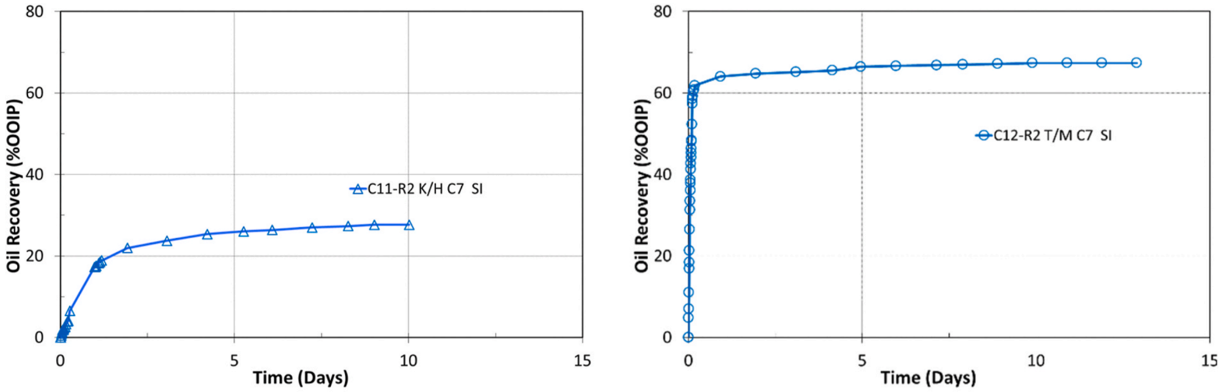
The effect of the two different core cleaning methods on core wettability in a second core restoration was studied in two initially



(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)

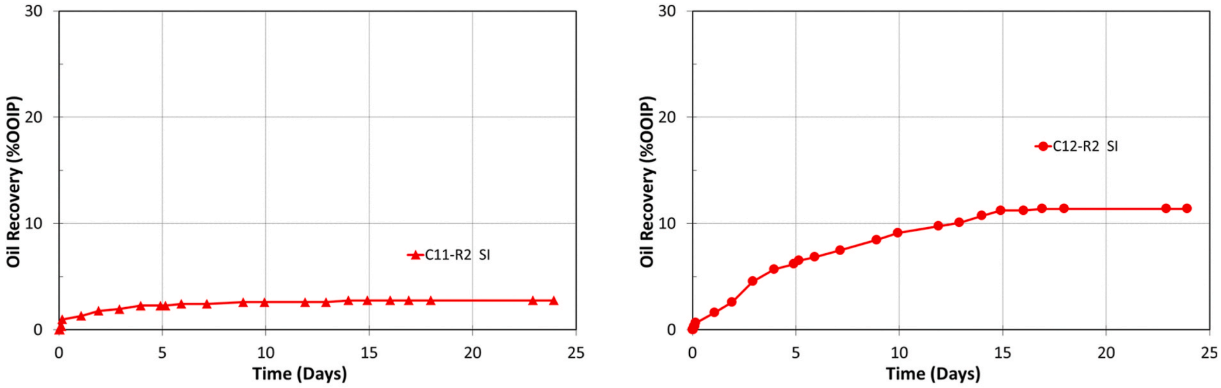
(b)

**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, $I_{W\text{-}SI}$, 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 $I_{W\text{-}SI}$ 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.

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*

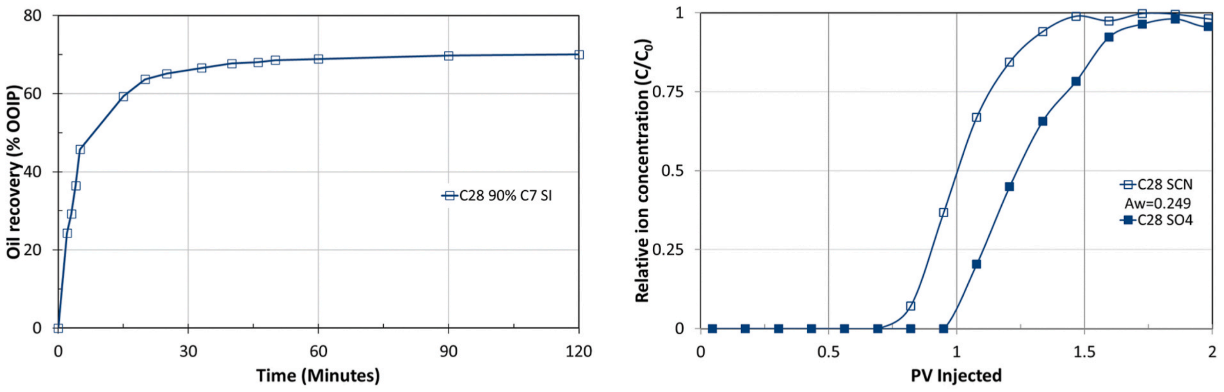
Two chalk cores from block 2, C24 and C25 were restored with $S_{wi} = 0.1$ FW, and exposed to 5 PV Oil B, before aging. The initial wettability established during core restoration was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test to verify reduction in water-wet mineral surface.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



(a)

(b)

**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.

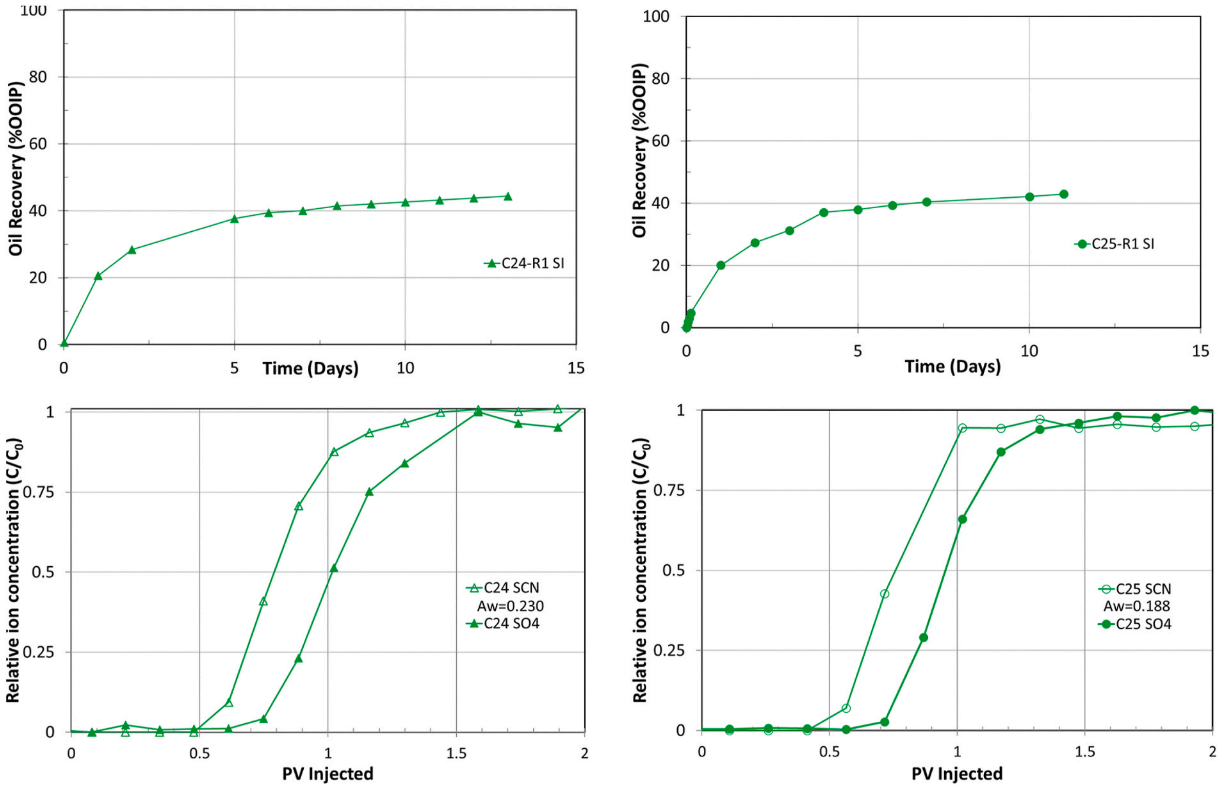


**Fig. 10.** Initial wettability was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test. (Left) Core C24 and (Right) core C25. Both cores were restored with $S_{wi}$ = 0.1 (FW) and exposed to 5 PV Oil B before aging.

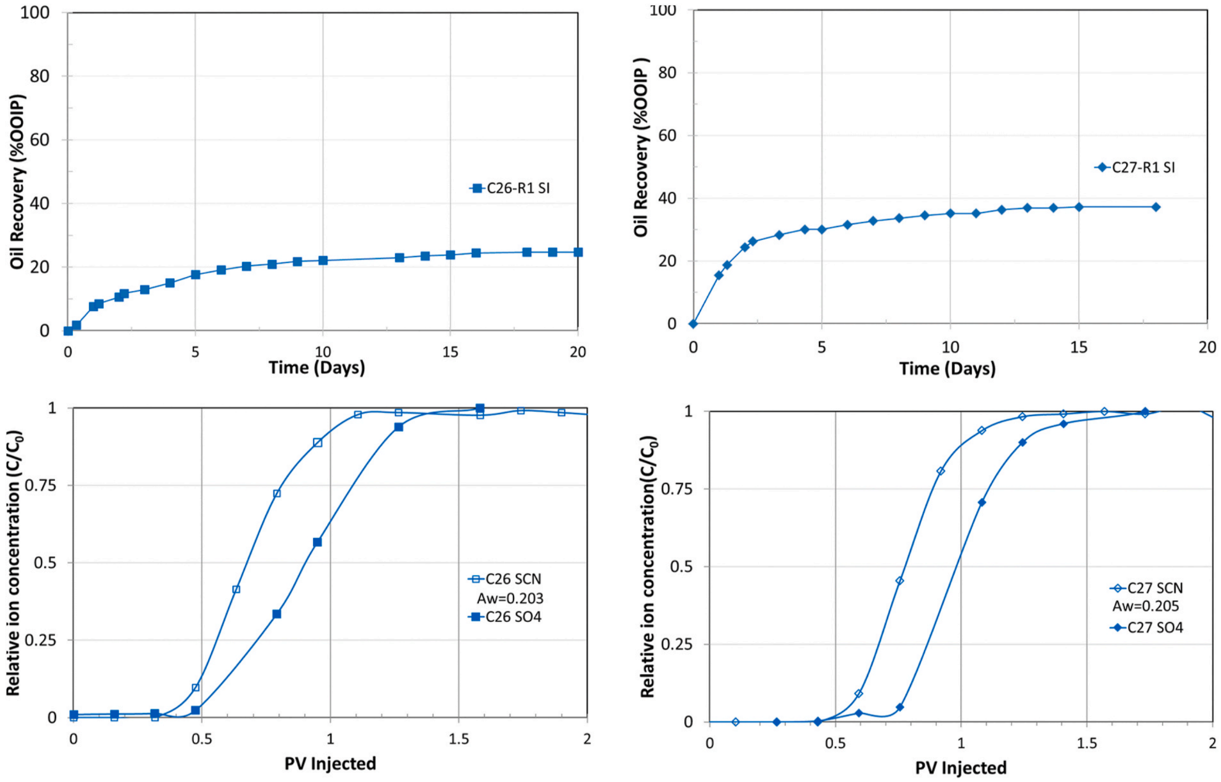


**Fig. 11.** Initial wettability was measured by SI at 50 °C using FW as imbibing fluid, followed by CW test. (Left) Core C26 and (Right) core C27. Both cores were restored with $S_{wi}$ = 0.1 FW and exposed to 5 PV Oil C before aging.

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, $\Delta$ *SI,* varied only between + 1.5 and + 3.5 %OOIP. The degree of water-wetness was quantified by the wettability index based on SI, $I_{W\text{-}SI}$, 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, $I_{W\text{-}SI}$, of 0.63 and 0.61 respectively. After the second restoration, the oil recovery only slightly increased and $I_{W\text{-}SI}$ 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 $I_{W\text{-}SI}$ slightly increased from 0.35 to 0.40, while for core C27, $I_{W\text{-}SI}$ 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

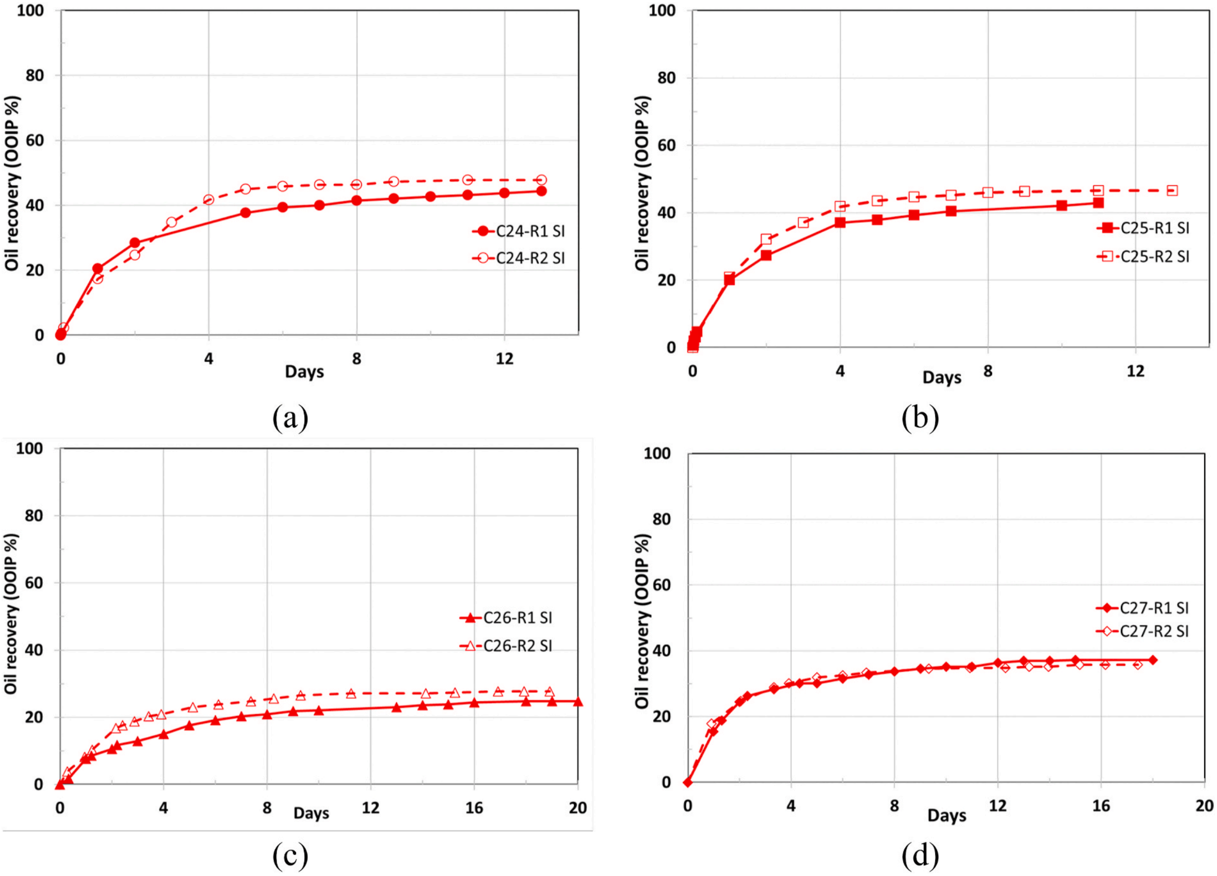


**Fig. 12.** Oil recovery tests by SI performed at 50 °C after initial restoration (R1) and a second restoration (R2) on cores with $S_{wi} = 0.1$. (a) Core C24 and (b) Core C25 exposed to Oil B (AN = 0.36 mgKOH/g). (c) Core C26 and (d) Core C27 exposed to Oil C (AN = 0.5 mgKOH/g).

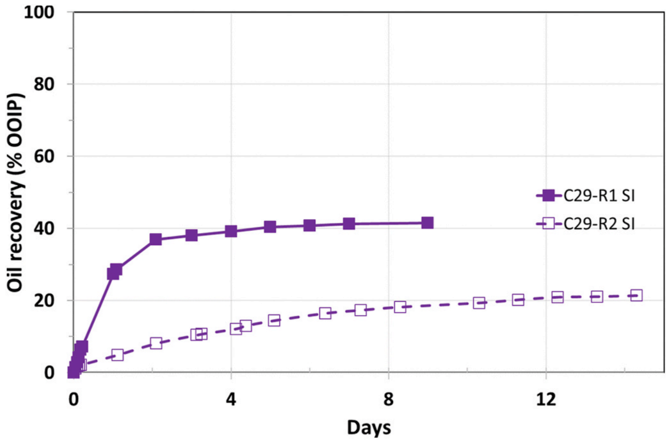


**Fig. 13.** SI tests performed at 50 °C after the initial restoration (R1) and the second restoration (R2) of core C29. During R1 the core was exposed to 5 PV Oil B with AN = 0.36 mgKOH/g. After mild cleaning the core was exposed to another 5 PV of Oil B in R2.

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, $I_{W\text{-}SI}$, 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 | $I_{W\text{-}SI\text{-}R1}$ | $I_{CW\text{-}R1}$ | $SI_{R2}$ % OOIP | $I_{W\text{-}SI\text{-}R2}$ | Δ SI % OOIP | Δ $I_{W\text{-}SI}$ |
|---|---|---|---|---|---|---|---|
| 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 $mol^{-3}$/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 |
| 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 |
| $\rho_{sat}$ | 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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## Paper III

# Core Restoration and its Effect on Initial Wetting of NCS Sandstone Reservoir Cores

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*Peer reviewed conference paper presented at the 35th International Symposium of the Society of Core Analysts, TX, US, SCA2021-032*

## Paper IV

# Influence of Sandstone Mineralogy on the Adsorption of Polar Crude oil Components and its Effect on Wettability

A. Mamonov, P. Aslanidis, N. Fazilani, T. Puntervold, S. Strand

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

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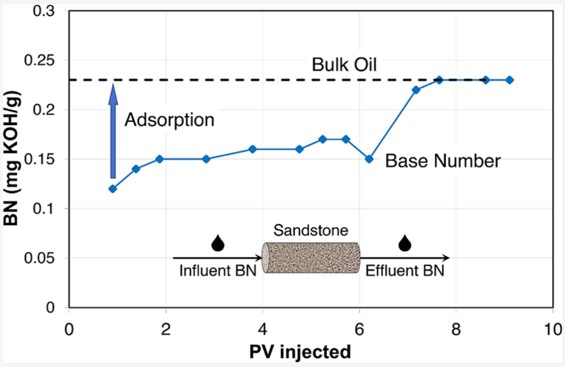
**ABSTRACT:** The crude oil−brine−rock (COBR) system is a combination of contacting phases where polar organic molecules in crude oil, inorganic ions from the brine phase, and charged mineral surfaces participate in complex interactions. One of the surface phenomena that occur in the COBR system is the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



## ■ INTRODUCTION

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

The initial wettability of a crude oil−brine−rock system (COBR) is mainly dictated by the interactions between active polar organic components (POCs) and the rock minerals in presence of brine. POCs present in the crude oil adsorb onto the mineral surfaces of the rocks, creating the wetting conditions. Crude oils are complex mixtures consisting of thousands of different chemical compounds, including groups of saturates, aromatics, resins, and asphaltenes. The two latter groups contain the heavier components, of which the "NSO compounds", those containing nitrogen (N), sulfur (S), and oxygen (O), are part. The crude oil components that have affinity for a charged mineral surface are the polar organic acids and bases, represented by O-containing carboxylic acids and N-containing aromatic compounds, respectively. Experimental work related to the basic content in crude oils from the Norwegian continental shelf (NCS) has suggested that the bases are part of the maltenes, present in the resin fraction.[1,2] Additionally, a previous adsorption work by Mamonov et al.[3] has shown substantial adsorption of bases onto sandstone surfaces from a low-asphaltene crude oil.

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

Basic material

$$R_3N: + H_2O \underset{\text{Acidic pH}}{\overset{\text{Alkaline pH}}{\rightleftarrows}} \boldsymbol{R_3NH^+} + OH^- \quad (1)$$

Acidic material

$$\boldsymbol{R-COOH} + H_2O \underset{\text{Alkaline pH}}{\overset{\text{Acidic pH}}{\rightleftarrows}} RCOO^- + H_3O^+ \quad (2)$$

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

It is reported that polar organic acids, quantified by the acid number (AN) in crude oil, dictate the wettability in chalk,[8,9] a positively charged $CaCO_3$ rock having an alkaline pH in the presence of brine. However, Fathi et al.[10,11] found that water-extractable acids from crude oil seemed to influence the chalk wettability more than the non-extractable acids. The water-extractable acids were also found to be more difficult to desorb in wettability alteration processes. Polar organic bases present in crude oil, quantified by the base number (BN), were found to only play a minor role for chalk wettability.[12] However, Puntervold et al.[12] also observed that the small model base, benzyl amine, influenced chalk wettability by co-adsorption with crude oil acids to the chalk surface. Interfacial activities of different crude oil naphthenic acids and bases at low and high molecular weights were studied by Bertheussen et al.[13] They found that the acids partitioned into the water phase to a higher degree than the bases and that the low-molecular-weight acid partitioned to a higher degree than the higher-molecular-weight acid, regardless of pH. The higher molecular weight base did not partition into the water phase at the pH range studied. Hence, individual components in the crude oil acid and base fractions are expected to have varying reactivity toward water and rock surfaces based on, for example, their size, steric hindrance, number of functional groups, and so on. Thus, it should be emphasized that there is not a direct link between the AN, BN, and molecular reactivity.

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

The presence and distribution of clay minerals in the pore network of sandstone rock can have a significant influence on the crude oil adsorption processes. Due to an unbalanced negative surface charge, clay minerals can adsorb/desorb charged crude oil molecules and react with the aqueous phase through ion exchange.[16] Clay minerals have a layered structure and a larger cation exchange capacity (CEC) and surface area than other sandstone minerals.[17] It has been shown that the adsorption of POCs onto quartz and the feldspar mineral albite was low,[18] both of which possess lower CEC and surface area than clay minerals.[17] Recently, Mamonov et al.[3] performed an adsorption study on an outcrop sandstone containing approximately 60 weight per cent (wt %) quartz, ∼30 wt % albite feldspar, and ∼9 wt % of illite clay mineral. It was shown that the negatively charged silicate surfaces had a stronger affinity to positively charged basic POCs, while adsorbing less negatively charged carboxylates (dissociated carboxylic acids).[3] The adsorption was quantified, and only about 30% of the crude oil bases adsorbed to the rock surface, while only ∼10% of the acids were found to adsorb. A spontaneous imbibition (SI) test performed after the crude oil flooding and adsorption proved that the core had become mixed-wet after the adsorption of polar organic bases from the crude oil.

In many laboratories, to establish the initial core wettability, the core sample is flooded with a crude oil to displace the formation water (FW) to initial water saturation. In this process, many and inconsistent pore volumes (PVs) of crude oil can be used depending on the rock properties. Recently, Aslanidis et al.[19] investigated the wettability changes of reservoir sandstone material after crude oil exposure in several core restorations using mild solvents (kerosene/heptane). SI tests were performed to evaluate the level of wettability after each restoration step. The results in Figure 1 demonstrate the effect of 11 PVs of crude oil exposure in each restoration process on core wettability. The apparent decrease in the rate of imbibition and the difference in ultimate oil recovery of 10% of the original oil in place (OOIP) between core restorations indicate that the exposure of uncontrolled amounts of crude oil into a core could have a detrimental effect on wettability. Thus, an optimized amount of crude oil should be injected into the core to establish the initial oil saturation and representative wettability, and more work is needed to further understand the process of initial crude oil adsorption in sandstone rocks.

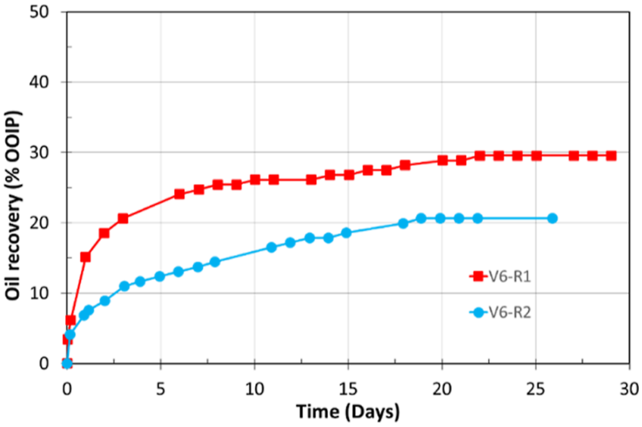

**Figure 1.** Effect of 11 PVs of crude oil exposure on core wettability in two core restorations using mild solvents (kerosene/heptane). Modified with permission from Aslanidis et al.[19] Copyright 2022 Elsevier.

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

**Table 1. Mineralogical Composition**

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

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

## EXPERIMENTAL SECTION

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

**Table 2. Core Properties**

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

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

**Table 3. Brine Composition and Properties**

| | ion composition, (mM) | | | | |
|---|---|---|---|---|---|
| brine | $Na^+$ | $Ca^{2+}$ | $Cl^-$ | salinity, ppm | bulk pH |
| FW20Ca | 817.6 | 20 | 857.6 | 50 000 | 6.3 |

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

**Table 4. Crude Oil Properties**

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

**Core Cleaning.** The reservoir core V9S2 was rigorously cleaned to bring the initial wettability conditions close to the water-wet state. Crude oil was displaced by toluene until a clear effluent was obtained, and then, toluene was displaced by methanol. The cleaning cycle was completed by flooding 1000 ppm NaCl brine to remove any easily dissolvable salts while at the same time avoiding potential clay swelling, although the latter is not expected due to the absence of swelling clays such as smectite and montmorillonite. The outcrop core L1 has not been previously exposed to crude oil and thus was only cleaned by 1000 ppm NaCl brine injection. After cleaning, both cores were dried to a constant weight at 90 °C.

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

**Crude Oil Adsorption Test.** After $S_{wi}$ had been established, the core was mounted in a Hassler core holder for crude oil exposure in the adsorption test. The experimental setup is shown in Figure 2. A confining pressure of 20 bar, a back pressure of 10 bar, and a temperature of 60 °C were used. Oil A was injected into the core at a rate of 0.1 mL/min. The produced crude oil was collected using a fraction collector, and the AN and BN were measured by potentiometric titration. The adsorption of polar organic acids and bases was evaluated by plotting effluent AN and BN values against the PV injected.

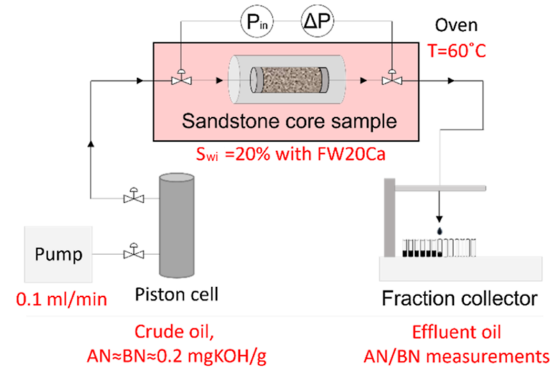

**Figure 2.** Crude oil flooding setup.

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

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

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

## ■ RESULTS AND DISCUSSION

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

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

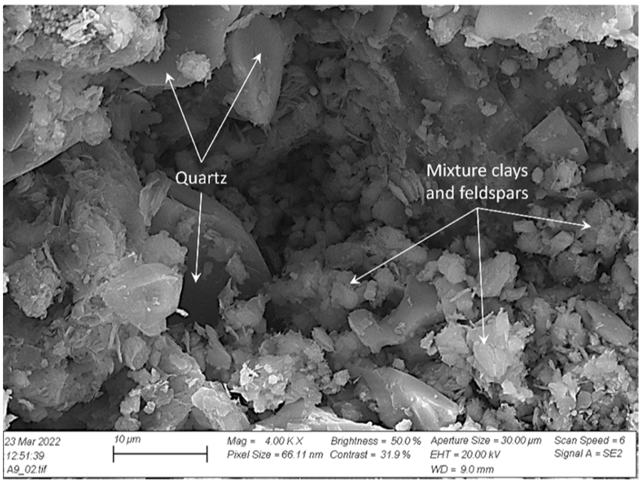

**Figure 3.** SEM image of the reservoir V-sandstone at a 4000 times magnification.

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

V-sandstone reservoir cores obtained from the Varg field on the NCS have previously been used in wettability studies that indicated that the reservoir rock was initially slightly water-wet.[19] Therefore, prior to POC adsorption studies, the reservoir core V9S2 was cleaned with toluene and methanol to bring the initial rock wetting state closer to strongly water-wet conditions. The initial wetting was then confirmed by a SI test using *n*-heptane (C7) as the oil phase and $S_{wi}$ of 20% FW20Ca. The SI test was conducted at 60 °C with FW20Ca as the imbibing brine. The results are shown in Figure 4. A strongly water-wet behavior was indicated by a rapid initial C7 recovery of 50% of OOIP after 2 h with an ultimate value of 54% of OOIP reached after ∼7 days. The steep oil recovery profile corresponds to strong capillary forces that allow for rapid water imbibition and displacement of the oil phase. The results of this SI test were further used as a reference case for the strongly water-wet behavior of the V9S2 core.

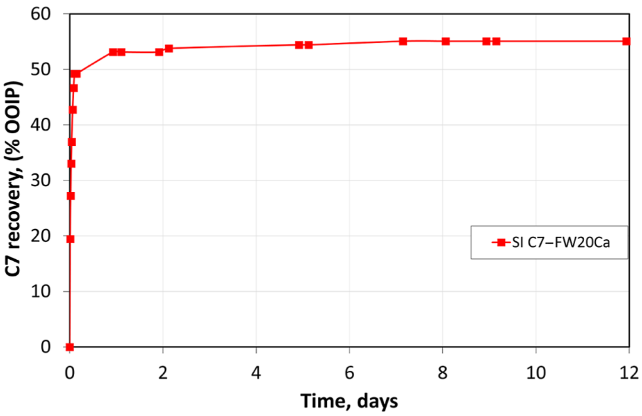

**Figure 4.** Oil recovery test performed on a strongly water-wet core V9S2 by SI with FW20Ca at 60 °C. Prior to the test, the core was cleaned with toluene and methanol and restored with $S_{wi}$ = 20% FW20Ca and mineral oil (C7).

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

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

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

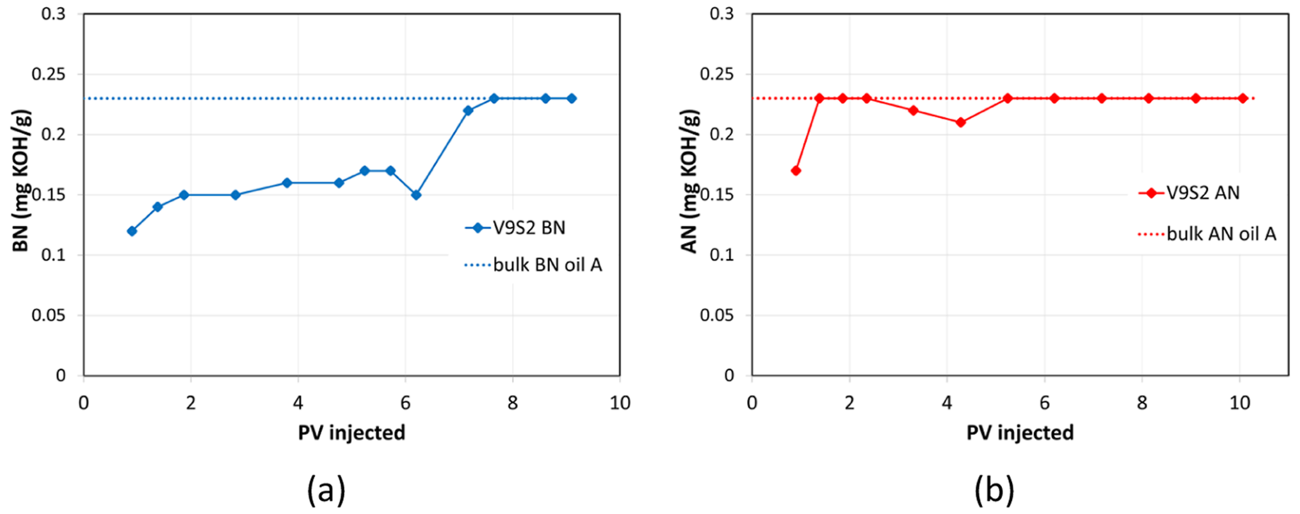

**Figure 5.** Adsorption of basic and acidic POCs onto reservoir V-sandstone during crude oil flooding at 60 °C. 10 PVs of oil A (AN = BN = 0.23 mg KOH/g) were injected into core V9S2 with $S_{wi}$ = 20% FW20Ca and at a rate of 0.1 mL/min. Produced oil samples were analyzed for (a) BN and (b) AN and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

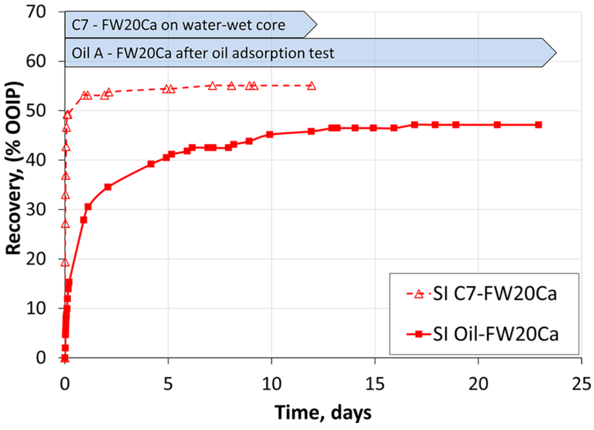

**Figure 6.** Comparison between SI oil recovery tests performed on the strongly water-wet reservoir core V9S2 and on the same core after exposure to 10 PVs of oil A. Both tests were carried at 60 °C using FW20Ca as an imbibing brine.

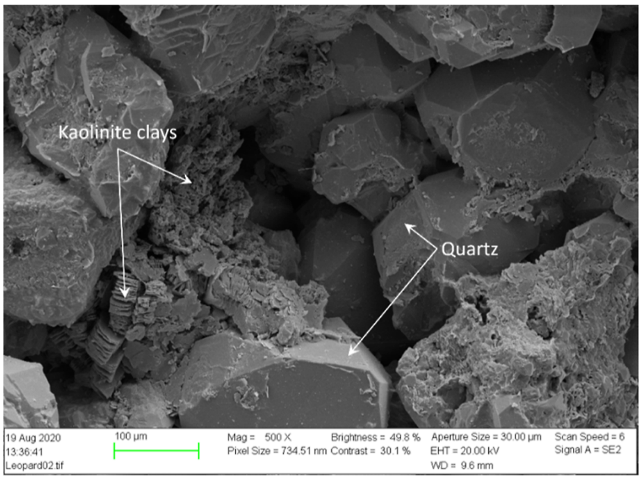

**Figure 7.** SEM image of the outcrop L-sandstone material with a 500 times magnification.

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

The outcrop core L1 had not been previously exposed to crude oil and was therefore in a completely water-wet state. To assess the action of capillary forces, core L1 was tested by SI using *n*-heptane (C7) as the oil phase and $S_{wi}$ = 23% FW20Ca. The SI test was conducted at 60 °C with FW20Ca as the imbibing brine. The results are shown in Figure 8. During the first few hours of the SI test, the FW20Ca brine was rapidly imbibing, resulting in the oil recovery reaching 35% of OOIP. After 2 days, the system reached an oil recovery plateau of 37% of OOIP, confirming a strongly water-wet behavior. The results of this SI test were further used to assess the change in wettability after crude oil adsorption.

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

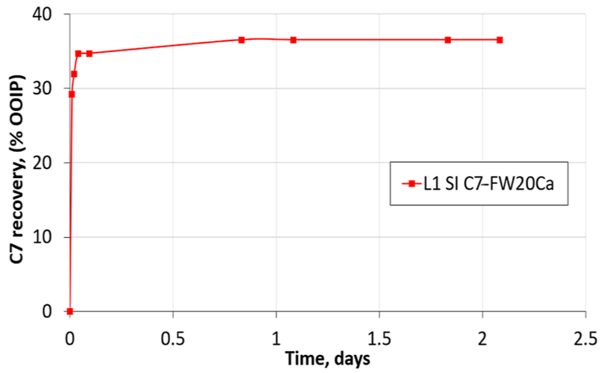

**Figure 8.** SI test on the completely water-wet outcrop sandstone core L1 at $T$ = 60 °C. The core with an established $S_{wi}$ = 23% was saturated with mineral oil (C7) and spontaneously imbibed with FW20Ca until a recovery plateau was reached.

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

Upon completion of the oil adsorption test, the L1 core sample was directly placed for an SI experiment without additional aging. The SI test was conducted at 60 °C using FW20Ca as the imbibing brine. Comparison between SI experiments performed on a completely water-wet core L1 and after crude oil adsorption is presented in Figure 10. The results show a significant reduction in the speed of imbibition after oil A exposure compared to that in the completely water-wet reference case. A recovery plateau of 34% of OOIP (oil A) was reached after 13 days, while the initial wettability test with mineral oil resulted in a recovery plateau of 37% of OOIP (C7) after only 1 day. It is important to note that the primary indicator of the wettability change is the imbibition rate and not the ultimate oil recovery as this will also depend on the oil/brine interfacial tension (IFT). Thus, a comparison of the SI test results shows that despite the absence of a clear POC adsorption trend on the L-sandstone material (Figure 9), the exposure to crude oil distinctly affected the capillary forces required to mobilize the oil.

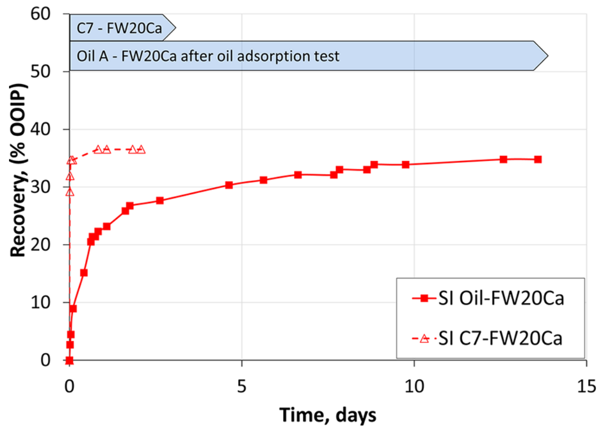

**Figure 10.** Comparison between SI oil recovery tests performed on a completely water-wet outcrop core L1 and on the same core after exposure to 10 PVs of oil A. Both tests were carried out at 60 °C using FW20Ca as the imbibing brine.

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

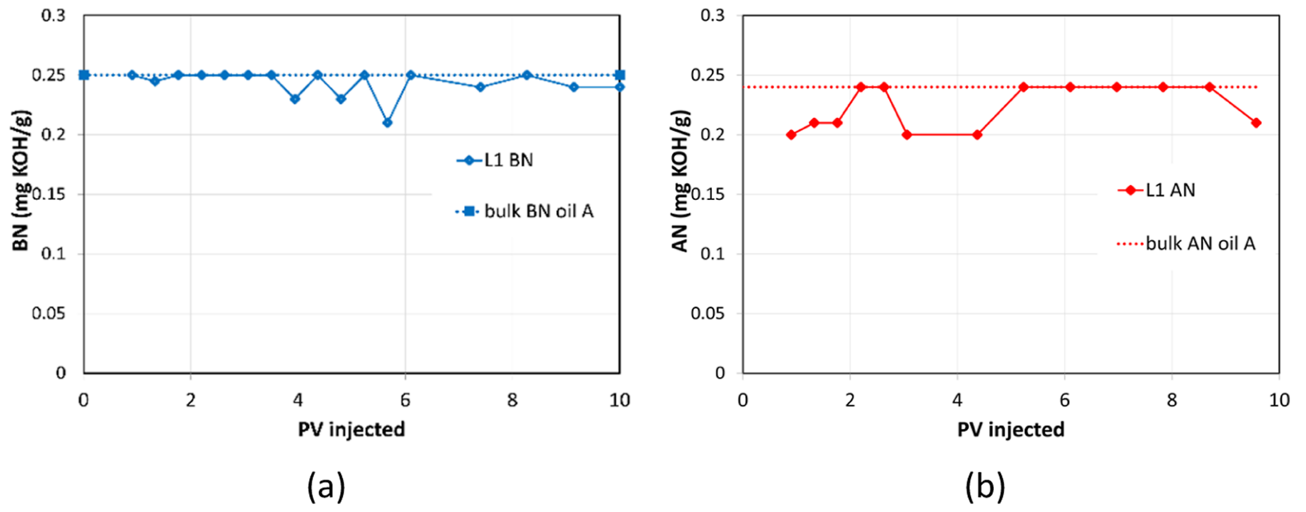

**Figure 9.** Adsorption of acidic and basic POCs onto L-sandstone during crude oil flooding. 10 PVs of modified crude oil (AN ≈ BN ≈ 0.25 mg KOH/g) were injected into core L1 with $S_{wi}$ = 21% at 60 °C and at a rate of 0.1 mL/min. Effluent oil samples were analyzed for (a) BN and (b) AN and plotted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

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

| sandstone material | origin | dominant clay type | BET, $m^2/g$ | $AN_{ads}$ | $BN_{ads}$ | $AN_{ads} + BN_{ads}$ | $BN_{ads}/AN_{ads}$ |
|---|---|---|---|---|---|---|---|
| | | | | PV*mg KOH/g | | | |
| V | reservoir | Illite−15.4 wt % | 3 | 0.04 | 0.45 | 0.49 | 10.3 |
| L | outcrop | Kaolinite−2.5 wt % | 2 | 0.12 | 0.06 | 0.18 | 0.5 |
| T | outcrop | Illite−8.4 wt % | 1.8 | 0.10 | 0.66 | 0.76 | 6.5 |

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

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

**Factors Affecting Adsorption of Crude Oil Components and Wettability.** The main factors affecting the intensity of POC adsorption in the COBR system are the presence and distribution of reactive minerals in the rock structure, the chemical composition of crude oil, salinity and pH of FW, and temperature. The above parametric studies were focused on determining the adsorption propensity for acidic and basic POCs onto V- and L-sandstone materials with significant differences in the mineralogical composition. The trapezoidal method was then used to quantify the amount of adsorbed acidic and basic organic components during crude oil injection. The principle of this method is based on the calculation of the area between the influent and effluent AN or BN curves using numerical integration. An example of calculating the adsorption area for the AN is shown in eq 3.

$$AN_{ads} = (AN_i)(PV_n) - \sum_{x=0}^{n} \frac{AN_x + AN_{x+1}}{2}(PV_{x+1} - PV_x) \tag{3}$$

where $PV_n$ is the number of PVs injected for the eluted crude oil to reach $AN_i$ (influent AN); $PV_x$ and $PV_{x+1}$ are the injected pore volumes in integration steps x and $x + 1$, respectively; and $AN_x$ and $AN_{x+1}$ are the values of the AN in the eluted oil after injecting the pore volumes $PV_x$ and $PV_{x+1}$, respectively.

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

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

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

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

## CONCLUSIONS

The influence of sandstone mineralogical composition on the adsorption of polar crude oil components has been studied in a dynamic oil flooding process. A COBR system was chosen with (a) modified crude oil containing similar amounts of acids and bases, AN ≈ BN, (b) FW of medium salinity containing divalent calcium ions ($Ca^{2+}$), and (c) reservoir and outcrop sandstone core materials with different mineralogical compositions. With the crude oil, rock material, and brines used in this study, the following conclusions could be drawn

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

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### Notes

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