University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/Specialization:

Master study in Reservoir Technology

Spring semester, 2018

Open

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Title of thesis:

Optimizing carbonate core restoration procedures – Effect of crude oil saturation and mild cleaning

Credits (ECTS): 30

Key words:
Core cleaning, wettability, restoration, chalk, EOR, spontaneous imbibition, ion chromatography, saturation process

Pages: 67
+ enclosure: 12

Stavanger, June 15, 2018

Abstract

Wettability has a big impact on how much we can recover by water flooding a reservoir, and there is a commercial potential for improvement done through alteration of the wettability. Studies have been conducted and shown that Smart Water can enhance the recovery significantly by manipulating the composition in the injected water. Optimized core restoration procedures reproducing reservoir wettability are important when core experiments are performed in the laboratory.

A Stevns Klint outcrops chalk core with S_{wi} = 0.1 has initially gone through a restoration with a crude oil containing polar acidic components. Spontaneous and forced imbibition experiments together with chromatographic wettability test have been used to give a basis for discussion of initial rock wettability.

The effect of mild core cleaning and a second core restoration on wettability have then been evaluated. The experiment shows that mild cleaning did not influence the wettability significantly conserving the polar components that have been established on the surface of the carbonate. The results confirm that the amount crude oil the core is exposed to during core restoration is the dominant factor regarding the establishment of core wettability. The spontaneous imbibition gave a much lower and slower oil recovery after the core had been exposed to oil a second time.

Acknowledgements

I want to thank Dr. Tina Puntervold and Dr. Skule Strand for giving me the opportunity to do research on a very interesting topic that has been fun and challenging to study. It has been a great help having such engaged and kind teachers as supervisors.

I also want to thank Dr. Ivan Dario Pinerez Torrijos for dedicating so much time and effort into supervision on the experimental part in the lab, but also for giving good advice in the writing. This has really been crucial, as many of the machines and tools are difficult to use without any experience.

The other students doing similar experiments in the lab have made this experience very pleasant and have been a great help.

My family has been supporting me through this five-year journey. Thank you all.

I also acknowledge The National IOR Centre of Norway for my collaboration.

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1 Introduction

Oil and gas have become more and more important resources the last decades and the demand is growing continuously. As the limited fields do not produce in accord to the growing demand, new ways of improving the production from these fields have to be found and implemented if they turn out to be commercially viable and environment friendly. Instead of being short term oriented when it comes to production, the industry now looks at the long-term recovery, also called the “ultimate recovery”. This way of approach will ultimately result in more oil being produced; and the methods of enhancing the oil recovery can be relatively simple.

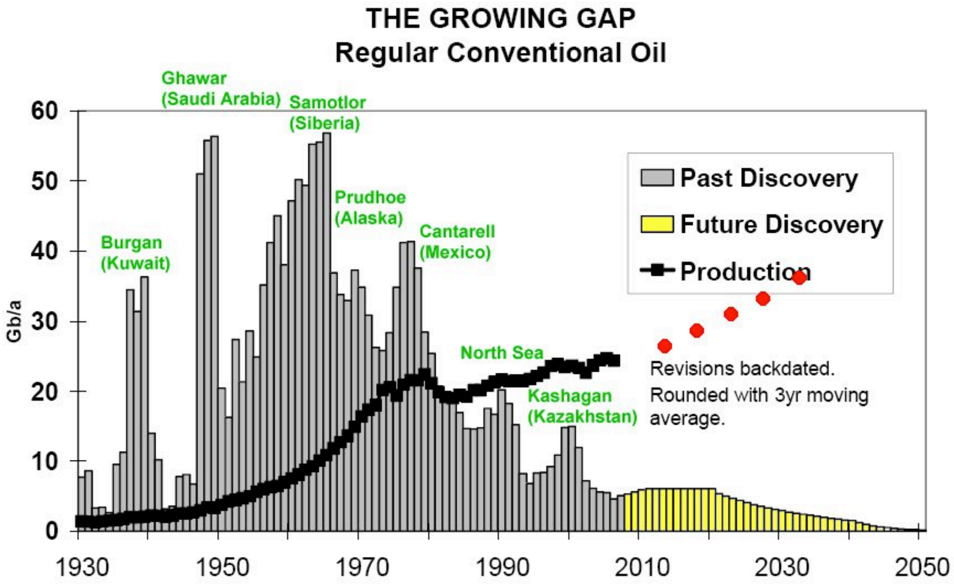


Figure 1: Production demand, historical supplies dating from 1930 and estimated future supplies (Campbell, Hill, Ballydehob, & Co, 2009).

As big countries like China and India are getting more developed and grow economically, the demand for oil is increasing. Figure 1 shows how the demand is expected to grow the next years.

1.1 Enhanced oil recovery

Enhanced Oil Recovery (EOR) can be defined as all recovery that is made due to injection of not primarily existing materials into the reservoir (Lake, 2010). Improving the recovery is an increasingly important aspect of hydrocarbon production as the demand is rising contra what is considered amount recoverable reserves. By developing new more cost efficient and environmentally friendly methods of enhancing the production, the estimated reserves will grow.

EOR can be introduced at all stages of production, even the primary phase. We intuitively think of EOR as something that is introduced in the secondary and tertiary stages, but this does not mean that recovery can´t be enhanced from the start of production.

1.1.1 Primary recovery

Primary recovery is that what is recovered by the drive mechanisms that naturally occur in the reservoir. Water influx from the aquifer, gravity drainage and gas drive are natural energy sources that will displace the oil in the first stage of a producing reservoir. We can also expect expulsive forces from compaction in the rock due to poor consolidation in the reservoir (Donaldson, 1989). These forces do sometimes co-exist, but it is expected that one of them is dominant as a driving mechanism. This is all dependent characteristics in the reservoir. Secondary stage is reached when the pressure is depleted to a degree were it no longer produces an economically efficient amount of hydrocarbons. It is expected to reach a recovery factor of 10-15% (average) of the original oil in place (OOIP) at this stage, which is low considering a much higher target factor with EOR. This leaves a significant amount of oil to be recovered in the two next stages (Green & Willhite, 1998).

1.1.2 Secondary recovery

Secondary recovery is a stage where injection of gas and/or water is introduced to maintain the pressure in the reservoir and/or to affect the displacement of the hydrocarbons. You essentially help the system to maintain its flow of hydrocarbons towards the producing well. The effectiveness of this stage may vary a lot, as this is greatly dependent on the quality (heterogeneity, fracturing etc.) of the reservoir.

1.1.3 Tertiary recovery

The last stage (Tertiary recovery) is where Enhanced Oil Recovery (EOR) methods are implemented. The methods are many and are grouped into thermal and non-thermal methods (S, 2008; Taber, Martin, & Seright, 1997) and further improved/expanded by Hopkins (Hopkins, 2017) by adding a non-thermal group; wettability alteration. Wettability is an important property because it effects relative permeability curves and capillary pressure curves that are used when describing reservoirs in reservoir simulation.

Thermal	Hot Water Steam In-Situ Combustion Electrical Heating
Miscible	Slug Process Enriched Gas Drive Vaporizing Gas Drive CO2 Miscible N2 Miscible Alcohol
Chemical	Polymer Surfactant Alkaline Micellar ASP Emulsion
Immiscible gas drives	CO2 Flue Gas Inert Gas
Other	Microbial Enhanced Oil Recovery Foam Water Alternating Gas Low Salinity water injection

Table 1: Categories of approaches to EOR (Taber et al. 1997, Thomas 2008)

Wettability alteration	Smart Water Low Salinity (in Sandstone) Seawater/modified Seawater (in Carbonates)

Table 2: Wettability alteration (Hopkins 2017)

Wettability alteration gives the ability to affect and increase the capillary forces which again will increase the microscopic sweep efficiency. The recovery is not only restricted in the fraction of area it is sweeping (macroscopic), but also in the efficiency of microscopic sweeping. By modifying the composition of the water that is flooded through the core, a change in polar components on the surface of the rock will alter the wettability.

1.2 Objectives

This experimental thesis starts with restoring an initially very water-wet chalk core, with S_{wi} = 0.1 and expose it to 5 PV crude oil and aged it. This will establish the wetting condition (reduced water wetness) and represents a preserved reservoir outcrop core. Measurements are done on the core; spontaneous imbibition, forced imbibition and chromatographic wettability test.

A mild cleaning is then executed on the same core using kerosene/heptane and DI-water to preserve adsorbed polar components from the crude oil saturation process.

The last step is to perform a new core restoration, going through the same steps as for the initial restoration; exposing the core for additional 5 PV of crude oil. Wettability measurements will be done again to observe the change in wetting. Results and data from this thesis will be supporting the Smart Water Group at the University of Stavanger.

1.3 EOR in carbonates

Carbonates hold a significant amount of the remaining hydrocarbons. The reservoirs that have been exploit to production have typically an approximate of 40 to 50 % of the original oil in place (OOIP) as remains. The method that is the dominant EOR method in the United States is CO2 flooding, which has been economically viable (Manrique, Gurfinkel, & Muci, 2004). The application of processes other than carbon dioxide and polymer flooding is not very common - yet.

Wettability alteration as a driving mechanism is believed to be the new big thing in enhancing oil recovery in carbonate reservoirs. The method is kind of a mixture between secondary recovery and tertiary EOR, which is still a form of water flooding. It is achieved by optimizing the ionic composition of the water that is being injected into the rock (Yousef, Liu, Blanchard, & Al-Mulhim, 2012).

1.4 Carbonates classified

Carbonates are formed by deposition of organic material (mostly reefs) and sedimentation. This usually occurs at shallow depth with low salinity at relatively high temperature (Wilson, 1975). The deposition is commonly taking place by transport of loose sediments through ocean currents. The result of this is a structure that is very homogeneous is terms of minerology, and a particle mixture of a wide range of shapes and sizes. Porosity ranges normally from 40 % to 75 % and the permeability from 0.2 Darcy to 30 Darcy (Lucia, Kerans, & Jr., 1998). Carbonates consist of anionic complexes of carbonate (CO_3^{2-}) and different metallic cations like Mg^{2+}, Ca^{2+} and Fe^{2+} (Ahr, 2008). The trivial examples of carbonate mineral are Calcite and Dolomite ($Ca(CO)_3$ and $CaMg(CO_3)_2$) and they make up for the vast amount of minerals found in carbonates.

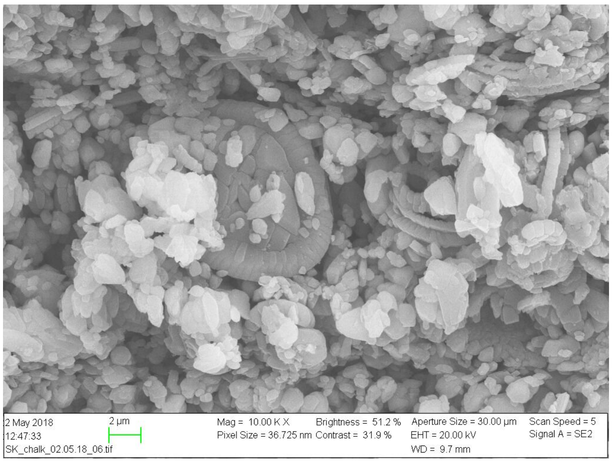


Figure 2: Photo taken with SEM of a Stevns Klint chalk sample at University of Stavanger.

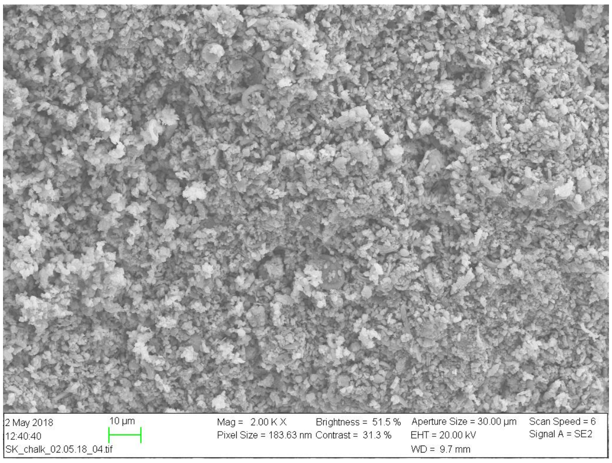


Figure 3: Same source and sample as Figure 1, only zoomed out 5 times.

1.4.1 Core outcrops

Cores used in experimental studies at The University of Stavanger are normally shaped to have a diameter of 1.5 inches (or 3.8 cm) and a length of 7 cm. A core is just a small part of the rock (or reservoir) and will therefore not necessarily represent the reservoir in a sufficient way, as a rock´s homogeneity varies. The wettability may be changed going through processes as cleaning and drying (Schön, 2015).

Figure 4: Illustration of Stevns Klint chalk cores.

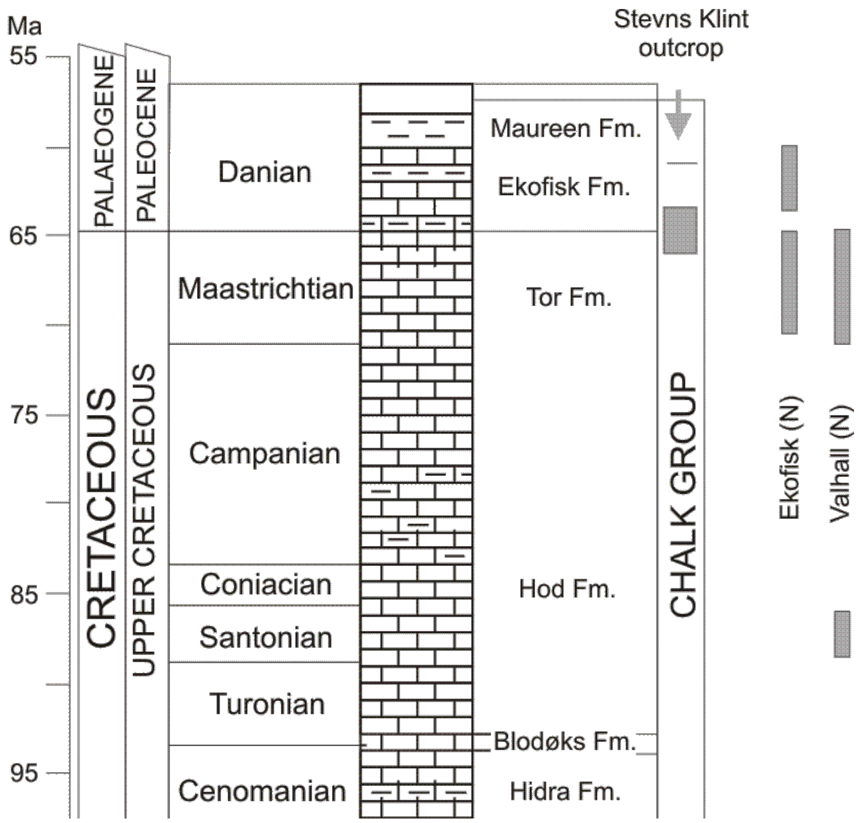


Figure 5: Stevns Klint, geological timeline (Frykman, 2001).

The Stevns Klint outcrop cores are a good analog to the reservoirs in the North Sea area. As seen from Figure 5, it matches the depositional sequence of the fields Ekofisk and Valhall.

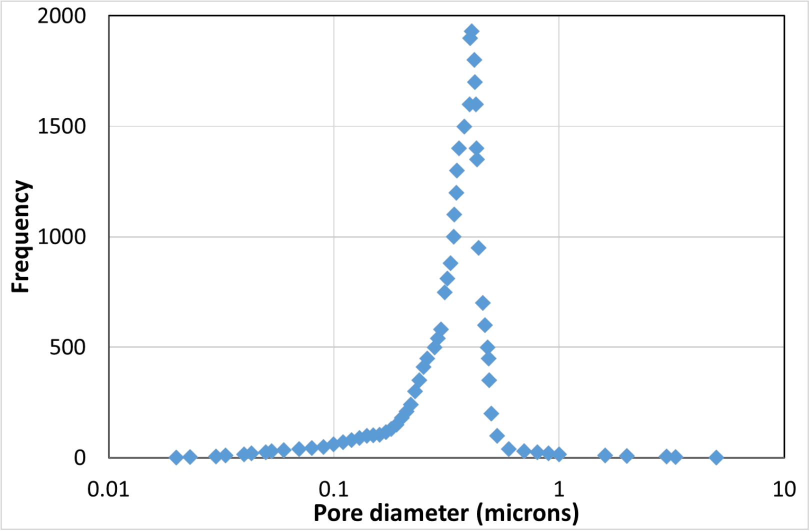


Figure 6: Pore size distribution in Stevns Klint chalk determined by mercury injection. Redrawn after Milter (1996).

The pore distribution in the Stevns Klint cores is shows in Figure 6 and confirms the heterogeneity of the pore size. The results are given by mercury injection method.

2 Theory

2.1 Wettability

One property that is fundamental for other parameters in a reservoir rock is the wettability. The wettability is connected to the important parameter capillary pressure (P_c) that is directly connected to the microscopic sweep efficiency (E_D) but does not necessarily correlate directly. The relationship between wettability and capillary pressure is complicated by the following (Morrow, 1990):

- Complex pore structures of the reservoir rocks
- Mineralogy of the reservoir rocks
- Effects of the adsorbed organic components from the crude oil

Wettability can be measured in different ways but is most frequently measured by using the contact angle (Morrow, 1990). A 100 % water repellent surface will have a contact angle (θ) of 0°. Designing an umbrella, this would be a desired property as is would keep both the fabric and the person using it from getting wet (droplets would roll off of the fabric). In a crude-oil/brine system, the reservoir will be either water-wet, oil-wet or mixed-wet. The wetness is in this way determined by the contact angle with a range of 0 to 180.

Looking at an oil droplet surrounded by water and its contact with a solid surface, we can further understand how to classify wettability. For a water-wet reservoir, the contact angle would be everything from 0° to 90°. An oil-wet reservoir would have a contact angle between 90° and 180°. Mixed-wet is a term that is relative, also called fractional, and basically means that there will be presence of both water-wet and oil-wet areas on a surface.

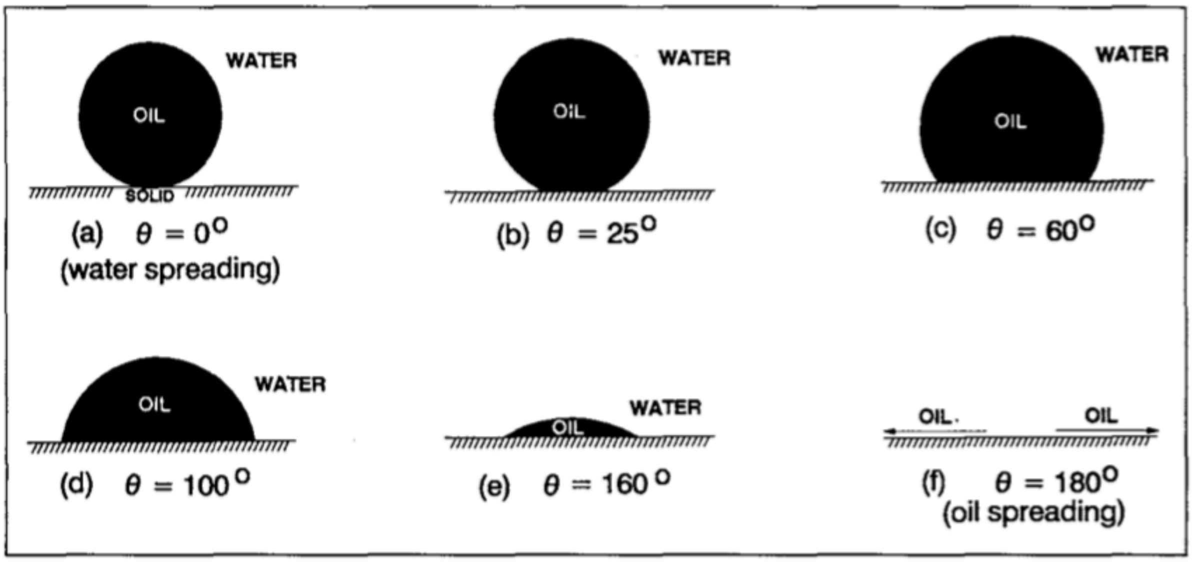


Figure 7: Contact angles and spreading (Morrow 1990).

In a porous media that is water-wet, water will be continuously connected covering the surface in the pores. The water will occupy the smaller pores while the non-wetting phase mainly will be found in the larger pores, still surrounded by the wetting water.

2.2 Wettability measurement

There are several ways of measuring the wettability of a reservoir, and the methods are categorized into two categories which are qualitative and quantitative methods. The qualitative methods are indirect methods of measurements. Imbibition is commonly used for qualitative measuring, and other qualitative methods are relative permeability methods, microscopic examination, flotation method, reservoir logs, capillary pressure curves, displacement capillary pressure, capillarimetric method, nuclear magnetic relaxation, dye adsorption and glass slide method. The direct methods (quantitative) consist of angle measurements, United States Bureau of Mining wettability method (USBM) and spontaneous and forced imbibition (Amott test) (Anderson, 1986).

2.2.1 Contact angle

Contact angle is optimal when dealing with artificial cores and pure fluids. This is because surfactants and other “impurities”/compounds that may alter wettability are neglected. The measurement is categorized into methods like the tilting plate method, vertical rod method, sessile drops or bubbles, tensiometric method, capillary rise method and cylinder method (Anderson, 1986). Crude has surface-active agents that makes the contact angle reach equilibrium slower, and therefore a lot of time is needed when executing these experimental methods. Amongst the methods mentioned above, the most common one in the petroleum industry is sessile drops.

The contact angle is obtained using Young´s equation:

$$\sigma_{OS} = \sigma_{OW} * \cos(\theta_c) + \sigma_{WS} \tag{2.1}$$

Here σ_{OS} is the interfacial tension between the solid and the oil, σ_{OW} the interfacial tension between water and the oil, σ_{WS} the interfacial tension between solid and water and θ_c the contact angle, the angle of the water/oil/solid interface line.

This method is economically desired compared to the previously mentioned ones. When doing this measurement, it is assumed that it is a rather smooth mineral surface and that its representing a homogeneous wetting. It is not suitable for wettability measurement for inhomogeneous, porous rocks that will have different surface properties caused by an inconsistent surface mineralogy (Strand, 2005). The heterogeneity is due to difference in pore size, surface roughness and surface mineralogy. The distribution and location of the wetted spots could have a significant effect on the oil recovery process. Figure 8 shows the definition of the contact angle for a water droplet on a surface, surrounded by oil.

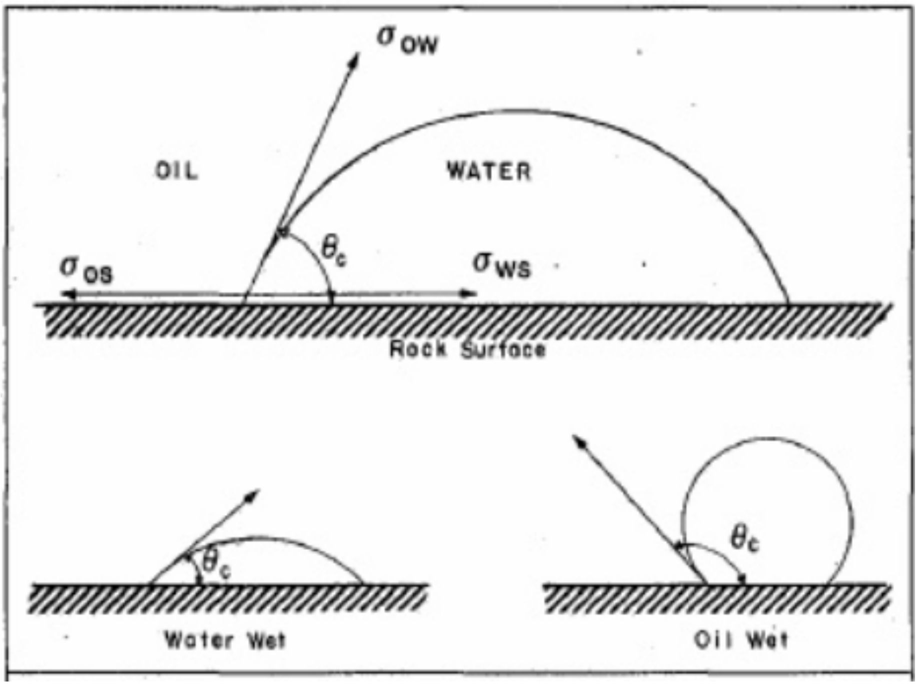


Figure 8: Equilibrium in tensions between liquids and the solid (Anderson, 1986).

Below is a table that suggests a description of wettability preferences by giving the contact angle ranges to categorize them. Given a contact angle, you can express the preferred wetting fluid (Zolotukhin and Ursin, 2000).

Contact angle range	Wettability preference
0-30	Strongly water-wet
30-90	Preferentially water-wet
90	Neutral wettability
90-150	Preferentially oil-wet
150-180	Strongly oil-wet

Table 3: Wettability preference sorted by contact angle ranges

2.2.2 Amott wettability index

The Amott test that measures the average wettability of the core consists of two methods of recovering the oil from the core; spontaneous imbibition and forced imbibition (Amott, 1959). This method is based on the principle that the wetting fluid, in this case the water, will imbibe spontaneously into the core that is saturated with the non-wetting phase (Anderson, 1986a). The test has four steps which are as follows:

1. Saturate a core with oil, then measure the amount of water that is displacing oil when executing a spontaneous imbibition (SI) of the core.
2. The amount of imbibed water introduced by force is measured from a forced imbibition of the core.
3. Spontaneous drainage of oil, where the volume of produced water is measured.
4. The last step is to force an imbibition of oil into the core and measure the volume displaced. This is called forced drainage.

Figure 9 illustrates the different steps done to the core. The initial state of the core is expressed by the point X, and from this point the four steps are executed. Step 1 expresses stage AB, step 2 expresses BC, and so on. Two indexes are combined to get the Amott-Harvey wettability index (I_{AH}); water wetting index and oil wetting index. The I_{AH} ranges from -1 to 1 where -1 is strongly oil wet, whilst 1 is strongly water wet (Glover, 2007).

$$Wetting\ index, water = I_W = \frac{AB}{AC} \tag{2.2}$$

$$Wetting\ index, oil = I_O = \frac{CD}{CA} \tag{2.3}$$

$$Amott\ Harvey\ index = I_{AH} = I_W - I_O \tag{2.4}$$

The water index gives a measure of positive capillary forces that are very important when heterogeneous pore systems are produced and could improve the microscopic sweep efficiency.

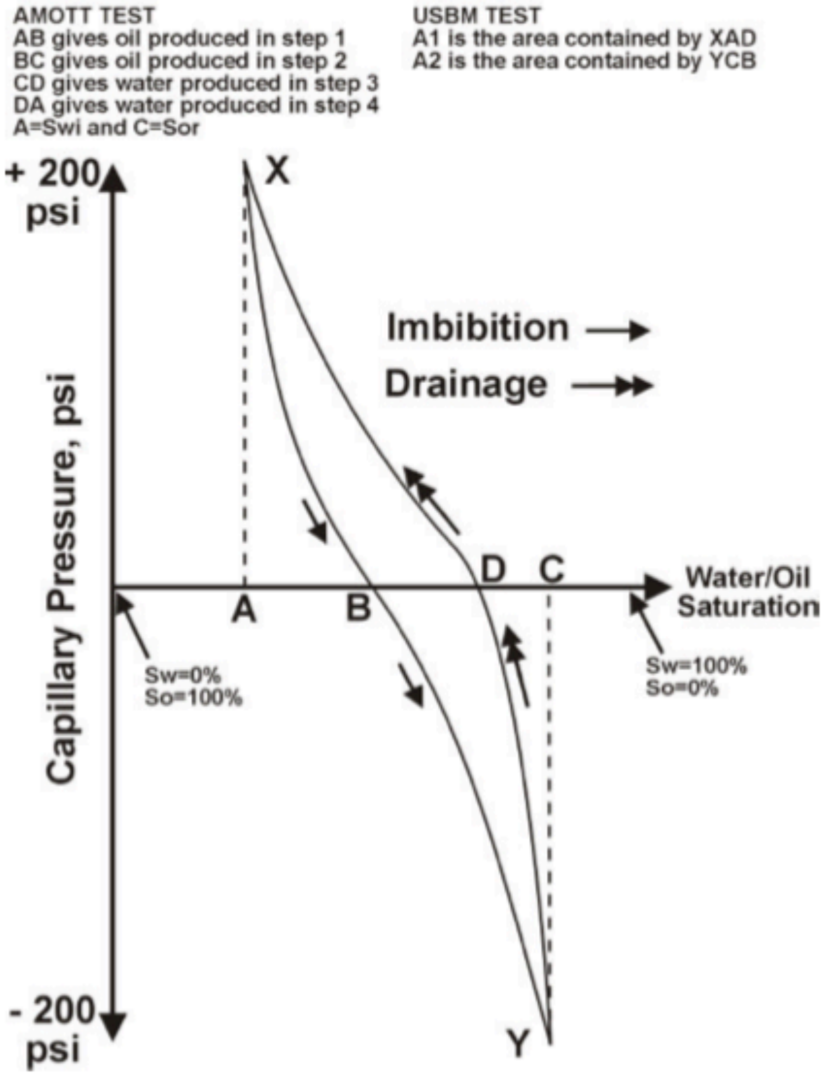


Figure 9: Amott and USBM techniques in measuring wettability (Glover, 2007).

2.2.3 United States Bureau of Mining (USBM)

Being very similar to the Amott method, this method differs with regards to imbibition. The index is calculated using the areas under the curves shown in Figure 9; A1 and A2. The samples are centrifuged, and a requirement is therefore that they are plug-sized (Abdallah et al., 2007). This method is believed not to be as reliable as the Amott method especially in the neutral part of the spectrum (Glover, 2007).

$$W = \log\frac{A1}{A2} \tag{2.5}$$

A1 is the spontaneous drainage curve area and A2 is the forced imbibition curve area. USBM, Amott and contact angles are compared (Glover, 2007) in Table 4.

Index	Oil-wet	Neutral-wet	Water-wet
Amott wettability index water ratio	0	0	>0
Amott wettability index oil ratio	>0	0	0
Amott-Harvey wettability index	-1.0 to -0.3	-0.3 to 0.3	0.3 to 1.0
USBM wettability index	about -1	about 0	about 1
Minimum contact angle	105° to 120°	60° to 75°	0°
Maximum contact angle	180°	105° to 120°	60° to 75°

Table 4: Comparison of wettability tests

2.2.4 Chromatographic wettability test

A new test for measuring wettability was presented in a paper by Skule Strand et al. (2006) on chalk, based on chromatographic separation of SCN^- and SO_4^{2-}; a water-soluble tracer (non-adsorbing) and the potential determining sulphate ion respectively. This test in conducted at residual oil saturation condition and the separation measured is due to sulphate reacting with the water-wet surface areas and giving a delay in the concentration found in the effluent. The tracer on the other hand does not react with the surface and will therefore be detected earlier in the effluent. The range between the two curves in the effluent concentration will be proportional to the area that (during the process of flooding) was in contact with water. Comparing this area to the area of a reference sample of completely water-wet surface will give a desired ratio. The ratio is between 0 and 1, and is the proposed wettability index:

$$WI_{New} = \frac{A_{Wett}}{A_{Heptane}} \tag{2.6}$$

In this equation A_{Wett} is the area between SCN^- (thiocyanate) and the SO_4^{2-} curves, and the $A_{Heptane}$ is a reference area that is measured by flooding a strongly/completely water-wet core. The first area is from a core that is aged in crude oil, while the reference core is saturated with heptane (Strand et al., 2006). Figure 10 illustrates the separation between the sulfate and the thiocyanate with a concentration vs pore volume plot (Aksulu, 2010).

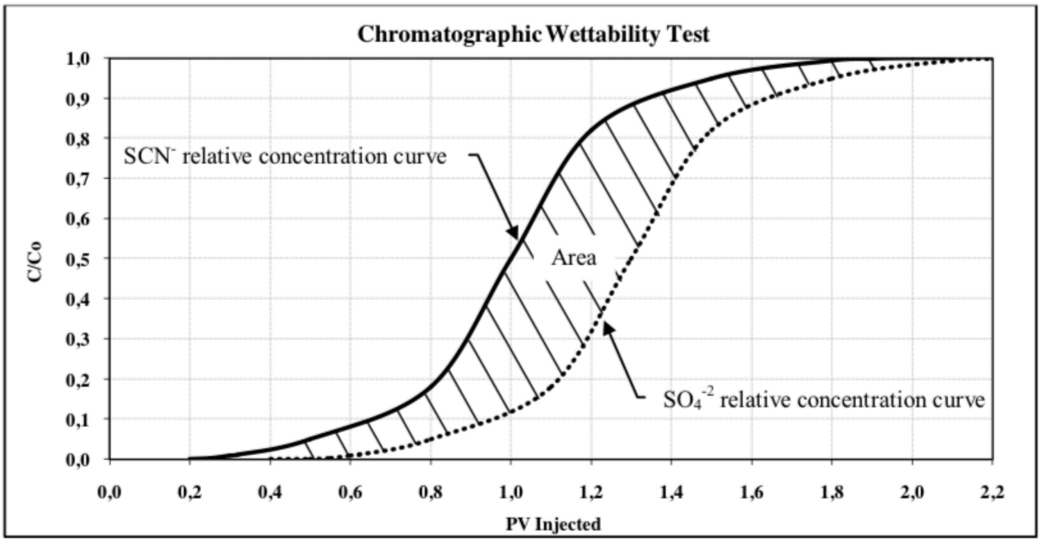


Figure 10: Schematic illustration of separation, chromatographic wettability test (Aksulu, 2010).

2.3 Alteration of wettability

Wettability alteration happens when ions react with the surface, changing the preferred wetting substance. Simply put; when a surface is exposed to a fluid (ex. water or oil), it will chemically react with it and alter the wettability to prefer this fluid in a larger extent than previously.

The electrical potential or zeta potential between crude-oil/brine and rock/brine interface is an important factor in determining the wettability of a crude-oil/brine/rock system. The system can be expected to be nonwater-wet where the two interfaces have opposite charge. (Hirasaki & Zhang, 2004). Alteration is therefore achieved by changing the surface chemistry.

2.3.1 Wetting alteration: Crude oil in carbonate reservoirs

Reservoirs containing oil will have a change in wetting when the components from the crude oil become adsorbed onto the mineral surfaces (Buckley, 1996). Acidic and basic groups of surface active components are prone to react both physically and chemically with the surface of carbonates, and research has shown a positive correlation between increase in acidic number (AN) and decrease in water wetness (Standnes & Austad, 2000). Crude oil can consist of a very large number of components that often are divided into the following groups; saturates, aromatics, resins and asphaltenes (Buckley, 1996). The resins and asphaltenes are the groups focused on when considering the wetting properties, as these groups have very long chemical chains that are a lot more stable and less soluble than lighter components. Carboxylic acid is an example of surface-active components which are present in these heavier components; resins and asphaltenes (Shimoyama & Johns, 1972).

Research done on several petroleum reservoirs sampled randomly has shown a tendency of the reservoir rock being oil-wet. In a research done on 55 reservoirs in Amoco operations areas, 66 % were oil-wet and the rest in either the water-wet or intermediate wettability category. 84 % of all the carbonate reservoirs in this survey were oil-wet (Treiber et al., 1972).

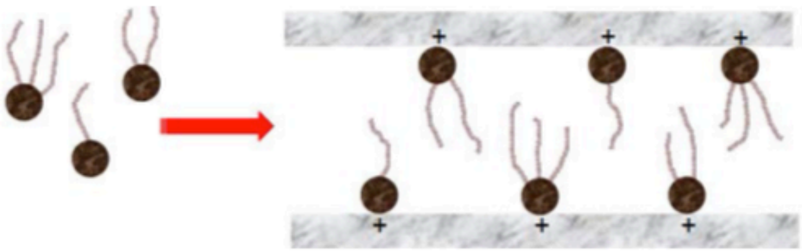
A study on how oil behaves when introduced onto a calcite surface that is water wet has been done by Jess Milters (1996) where dimples of oil are observed as they form a connection through the thinnest parts of the water filter and on to the calcite surface. Adsorption of polar active components will be a fact if the water film is uneven and not consistently thick throughout the surface, which is due to opposite charges. The significance of an oil alternating a core sample's wettability is determined by how much of the rock that was previously occupied by water, in other words; the initial water saturation.

2.3.2 Adsorption of oil components

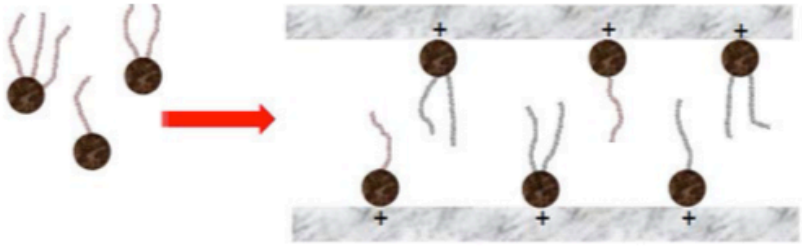
There are four modes of establishing oil-wet condition according to Buckley (1996) and they are described as;

I. Adsorption from the oil phase
II. Adsorption through the water phase
III. Oil/brine interface formed insoluble monolayer deposition
IV. Precipitation of oil-wet solid materials

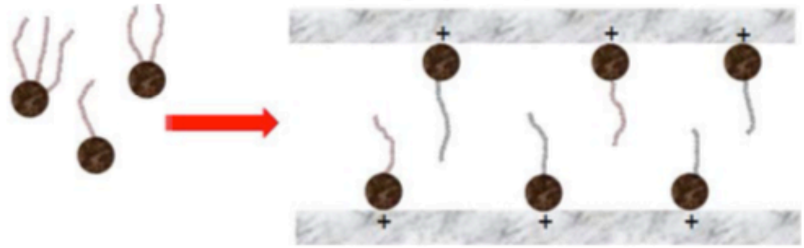
The wettability change done by crude oil on chalk surfaces is much related to the acidic number, i. e. the amount of acid components in the oil phase will be significant in terms of how the oil will change wetting conditions. When not saturated with water, the process of adsorption will be independent of temperature, thus considered irreversible and relatively rapid (Wong et al. 1993; Kaminsky & Radke, 1998; Buckley, 1998). The adsorption is limited to the chalk-material's adsorption sites which is determined by the effective surface area (Standnes & Austad 2000; Rouquerol 2013). Adsorption isotherms are often used to understand adsorption processes expressed by amount absorbed as a function of its concentration or pressure, done at a constant temperature (vlab.amrita.edu, 2011). Oil components that are negatively charged attach to the available sites. But as soon as the limited sites are occupied, the highest affinity acidic components will be preferred to attach to the surface. A suggested illustration of the adsorption process, in steps, during oil saturation is made by Wakwaya (2016):



(a) Initial phase of adsorption.



(b) seconadry stage of adsorption.



(c) tertiary stage of adsorption.

Figure 11: Adsorption of different carboxylic groups (Wakwaya 2016).

Yan et al. (1997) investigated the effect of increasing cationic valences and the effect of decreasing the initial water saturation. Results indicated increased oil-wetting, but also how water was preventing access to the surface and that ions bound to the double layer could make a bridge-connection to the surface (Spiecker, 2003; Puntervold, 2008).

2.3.3 Wetting alteration by modified sea water

Enhancing the recovery from carbonates has proven to be a challenge as the formation tends to be rather oil-wet. Wettability tests have been carried out on carbonate formation cores, and it has been found that even small amounts of sulfates in the formation water will affect the initial wettability of the core. It is also observed that the mineral anhydrite (calcium sulfate) will dissolve and form free sulfate ions when reacting with lower salinity water (Brady et al., 2015; Puntervold et al., 2007).

Several studies have been performed with SW, where it has revealed its ability to change carbonates wetness into a more water-wet rock. Figure 12 shows the increase in oil recovery done by SW after FW through spontaneous imbibition of a limestone core with $S_{oi} = 0.9$ (RES 40-0.57), performed at 130 °C (Ravari, 2011; Austad et al., 2010).

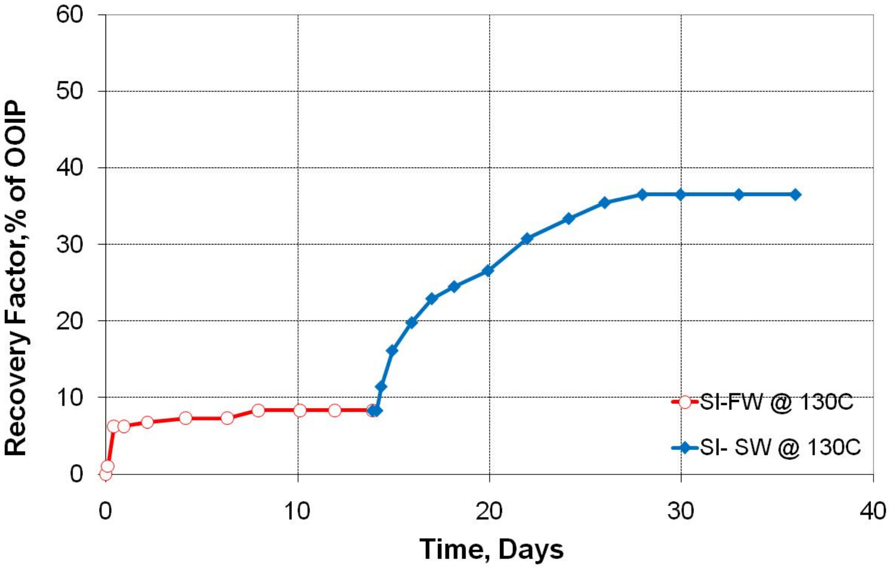


Figure 12: Spontaneous imbibition test; FW imbibition followed by SW imbibition (Ravari, 2011).

By further modifying the ionic composition of the injected brine, we get a commercial EOR method that should be implemented at the very start of the water flooding (Austad, 2012). The result is called “Smart Water”, which is a method of improving recovery has been proven to work (Strand et al., 2006; Fathi et al., 2010). The Smart Water wettability alteration is illustrated with a chemical mechanism (Hopkins, 2017; Zhang et al., 2007) in Figure 13.

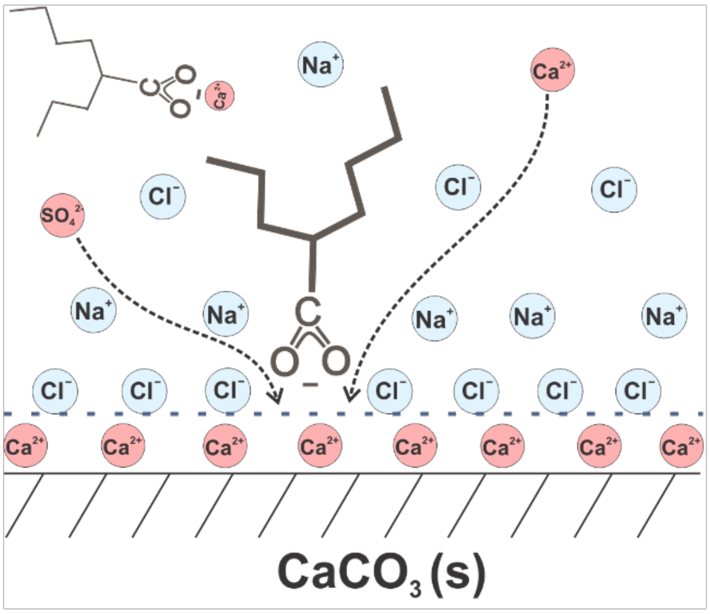


Figure 13: Illustration of Smart Water wettability alteration (Hopkins, 2017).

The modifying ions in this case are Ca^{2+} and SO_4^{2-}, and the SO_4^{2-} will in this case adsorb onto the chalk surface which is positively charged, making it less positively charged. This will result in more Ca^{2+} attraction to the surface, due to less electrostatic repulsion (Austad et al., 2009). The concentration of calcium ions near the surface of the chalk is this way increased by adding sulphate ions. The calcium ions are now able react with the carboxylic acidic material and help displacing it:

$$RCOO^- - CaCO_3(s) + Ca^{2+} + SO_4^{2-} = RCOOCa^+ + CaCO_3(s) + SO_4^{2-} \tag{2.7}$$

It is also experimentally shown that Mg^{2+} can substitute Ca^{2+} at higher temperatures through chemical analysis. At 130°C Mg^{2+} concentration is decreasing in the effluent while Ca^{2+} is increasing (Madland et al., 2011).

2.3.4 Initial wetting: Carbonates

The initial wetting properties of a carbonate reservoir dictates several of the reservoir parameters like fluid distribution, capillary pressure and relative permeability of the fluids. These parameters are very important as they are connected to the oil displacement efficiency. The sedimentation and deposition of carbonate reservoirs takes place in an aqueous state and oil is later introduced by migration from source rock. This is when the chemical equilibrium is slowly establishing over a geologically significant timespan. Most frequently the carbonate reservoirs turn out to be preferentially oil-wet (Treiber et al., 1972).

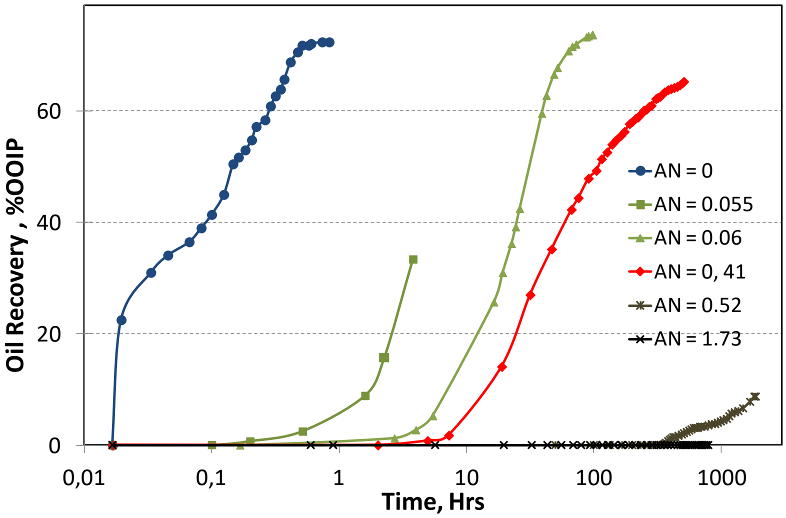


Figure 14: Spontaneous imbibition of chalk cores with crude oils that have various AN (Standnes & Austad, 2000)

Figure 14 shows that the acidic number of the crude oil that is present in the reservoir will affect the amount recovered from a spontaneous imbibition (Standnes & Austad, 2000). An increase in AN will decrease the oil recovery significantly and the chalk will have an initially more oil-wet surface.

2.4 Core cleaning and restoration

There are two main reasons for why you would clean a core. Number one is to remove all the liquids in the rock so that proper measurements of porosity, permeability and the fluid saturation can be obtained. The other reason for cleaning a core would be if the core was altered in wetting, and restoration of the initial wettability of this core is desirable (Gant & Anderson, 1988). To preserve the wettability of a core that is taken from a reservoir, you would have to take special precautions when choosing the mud. No mud like this is known to be commercially available.

There is often wettability alteration happening to a core due to either oxygen exposure (and/or drying of the core), or due to the core being cut with a mud containing surfactants (Gant &

Anderson, 1988). The procedure of restoring is then to remove all surface components, flow reservoir crude into the core, and then finally age the core with reservoir temperature until adsorption has established the state of equilibrium. It is possible to leave some of the surface components by changing the cleaning solvents used to get a milder cleaning of the core. In this way, it is possible to get a more direct approach to the desired wetting state.

2.4.1 Distillation/Extraction method

The distillation/extraction method is a commonly used method and can be performed with a Soxhlet extractor, an apparatus invented by Franz von Soxhlet in 1879 (Soxhlet, 1879). The extractor consists of a percolator (boiler) that is circulating the chosen solvent for this process, a thimble that will hold the sample and the solvent that is to be cleaned, and finally a siphon that will empty the thimble and make sure that the dirty solvent will be replaced by "fresh" solvent. The oil is dissolved in the thimble, and the process continues until the core is cleaned. This method is not bullet proof, as it may leave the center of the core contaminated when dealing with low permeable rocks and cause unwanted wetting changes as well (more oil-wet) (Soxhlet, 1879).

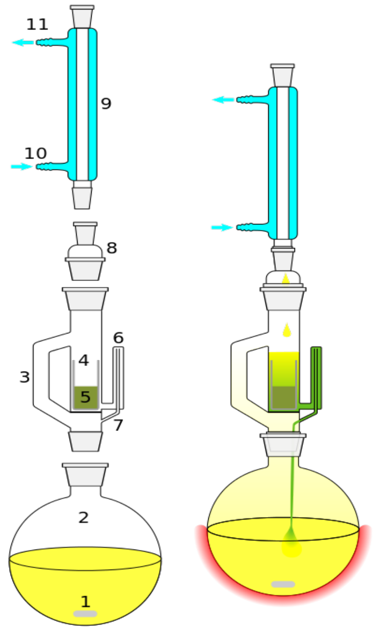


Figure 15: Soxhlet extractor, illustrated (Wikipedia).

2.4.2 Flow-Through Core method

The flow-through core method is performed with a core holder setup. The core is placed in a sleeve that is then placed into a core holder. Confining pressure (overburden pressure) is applied to the outer of the sleeve to prevent any fluid from flowing outside of the core instead of through it. A pump will pressurize the fluid to flow through the core and out into a collecting beaker. The effluent will be observed visually as it will be increasingly clear in color. Even low permeable cores will be properly cleaned by the use of this method, as you can control the flow by increasing the pressure from the pump and even apply backpressure (Gant & Anderson, 1988).

2.4.3 Kerosene and Heptane as solvents

Kerosene is a result of fractional distillation of hydrocarbons and has a density of close to 0.8 g/cm^3. It generally consists of components that are straight/branched alkanes and naphthenes (American institute of Petroleum, 2014). Kerosene is also known as lamp oil, or lighter fluid.

Heptane is also obtained by fractional distillation and is the zero point on scale of octane rating when it is pure. Since this liquid is non-polar, it is therefore used in laboratories as a solvent of heavier oils.

A mild cleaning of a core will involve flooding with kerosene, and then heptane and distilled water. The kerosene in this cleaning method is used to displace the oil and water that is present in the core, while preserving the adsorbed polar components. Heptane is introduced to displace the kerosene, and then DI water is introduced to displace the heptane and to remove the initial water. These solvents have low solubility of larger oil components.

2.4.4 Core aging

In order to imitate a reservoir through a core that has just been exposed to crude oil after being cleaned, it is necessary to age it at reservoir temperature long enough to establish an equilibrated crude/brine/rock system. Studies have shown that aging has an effect on the wettability (Puntervold et al., 2007).

2.5 Displacement forces

There are different forces acting on a petroleum reservoir, and they will affect how the hydrocarbons and water are distributed and how these fluids and gases may move through the formation. The three most important forces are the capillary forces, viscous forces and simple gravitational segregation.

2.5.1 Capillary pressure

When two immiscible fluids are in contact in capillary sized pores, there will be a pressure difference between them. The difference can be used to calculate the capillary pressure, which is obtained by subtracting the pressure of the non-wetting phase from the wetting phase's pressure (Dandekar, 2013; Zolotukhin, 2000). This difference is a product of pore sizes, interfacial tension (IFT) and the wetting characteristics.

Most of the water that is injected into a reservoir will follow the structure of the fractures that are present in the formation, thus resulting in a very low recovery. The goal is to force the fluid into the matrix by overcoming the threshold, which is expressed by the Leverett J-function (Al-Hadhrami & Blunt, 2001):

$$P_C = \sigma\sqrt{\frac{\phi}{k}}J \tag{2.8}$$

Here P_C is the capillary pressure, σ the interfacial tension, ϕ is the porosity, k the permeability and J the dimensionless Leverett value (normal value is around 0.25). As seen from the equation, you will get a reduction in entry pressure by lowering the interfacial tension between the fluids. Another way to get a better intrusion is to alter the wettability.

Cylindrical tube model is used as an idealization method as it simplifies the pores to cylindrical tubes (Mørk, 1997). This model expresses the capillary pressure by the radius of the cylinder (r), the contact angle (θ) and the interfacial tension (σ_{OW}) between the two fluids (oil and water). In the following equation where water is the wetting phase, and oil as the non-wetting phase, capillary pressure follows (Strand, 2005):

$$P_C = \frac{2\sigma_{OW} * \cos\theta}{r} \tag{2.9}$$

Figure 16 shows the cylindrical tube model:

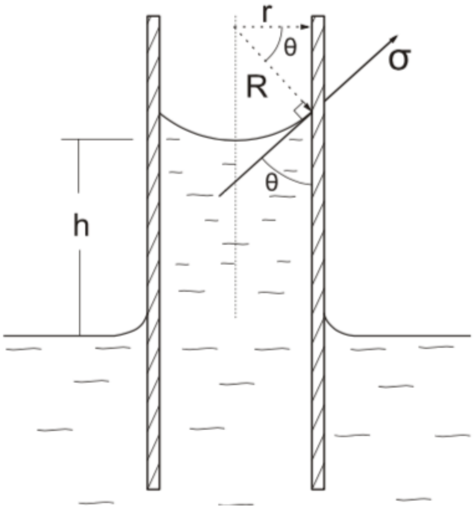


Figure 16: Cylindrical tube model (Strand, 2005).

2.5.2 Viscous forces

Viscous forces are forces which occur internally in the fluid due to different relative motion of the layers in a fluid that is flowing. This friction amount will differ from space to space in the fluid and cause varying viscosity. Viscosity may be viewed as the fluids internal resistance to shear stress (Finnemore & Franzini, 2001). Poiseulle's law can be used to determine the viscosity by using a simplified model of the system. The model consists of capillary tubes, and the delta pressure is given as follows:

$$\Delta P = \frac{8\mu L\bar{v}}{r^2 g_c} \tag{2.10}$$

Where ΔP is the difference in pressure across the tube, μ is the viscosity of the fluid, L is the length of the tube, r is the radius of the tube, $\bar{v}$ is the average velocity of the flowing fluid in the tube and g_c is a factor of conversion.

2.5.3 Gravity forces

The fluid that is inside a porous rock will be influenced by the gravitational force that is determined by the liquids density. Oil is lighter than oil and will therefore experience an upwards force due to this density difference (Lake, 2010). As capillary forces are reduced in an imbibition cell, the segregation done by gravity will partake in a larger scale (Schechter, 1994). The equation for this gravitational pressure difference is given by:

$$G = \Delta\rho g h \tag{2.11}$$

The small g is the gravity acceleration constant, the $\Delta\rho$ is the density difference and the h is the column of fluid height. High permeable reservoirs with a great difference in densities and low interfacial tension will have a greater dominant force of gravity segregation (Chen et al., 2000).

2.6 Scanning Electron Microscopy

A scanning electron microscopy is used to obtain microscopically sized images of a surface, but also to get information about surface topography and mineral composition. The machine is sending a beam onto the surface of a sample and detectors collect the electrons that are emitting from it. These electrons are used when imaging, and they are sorted into secondary electrons (SE) and backscattered electrons (BSE). When adding a sample to the machine, it is important to pre-coat the specimen with a conductive material like Palladium to increase the electrical conductivity (Nanoscience, 2018).

2.7 Brunauer-Emmett-Teller

The BET analysis gives a measurement of the specific surface area of a rock sample in powder form. The specific surface area is defined as the surface area of the material divided by the volume of the material or the mass of the material. The basics of the method is to use non-corrosive gasses as physical multilayer adsorbents onto the solid material (Hellack, 2016). The experimental part is normally conducted at the boiling temperature of liquid Nitrogen (N_2), which is -196°C.

3 Experimental Materials and Methods

3.1 Risk assessment

Before using any of the equipment, a risk assessment was filled out and signed. These documents included all precautions that had to be followed when using the different stations in the laboratory. There are a lot of security equipment in a lab that have to be used, the basics being googles, lab coat and rubber gloves. Masks were available when dealing with chemicals (especially solvents).

3.2 Chalk cores

The rock samples that were used in this experiment are taken from Stevns Klint in Sjælland, Denmark. The cores were prepared by using a drill to cut out samples (all in the same direction) from bigger chunks of rock. Before further use of the cores, they were dried, shaved and cut into properly dimensioned cores. The final measurements desired in this experiment were 38.0 mm in diameter and 7 cm in length. A standard diameter is usually 38.1 mm, but in this experiment 38.0 mm is preferred because of the relatively tight membrane sleeve used later on. The cores had a porosity of close to 50 % and are similar to North Sea chalk properties. Here are the core data:

Chalk core name	unit	S2	S1
Length	[mm]	69.8	70.09
Diameter	[mm]	38.0	38.0
Pore volume	[ml]	38.55	38.79
Porosity	[%]	48.64	48.83
Permeability	[mD]	1.2293	2.1302

Table 5:Measurements and properties of the oil saturated core, S2, and the reference core S1.

The Stevns Klink chalk consist of a coccolithic matrix that is mostly fine-grained, but also some larger bioclasts (Milter, 1996). The porosity is calculated using Equation (3.1), which is the pore volume divided by the bulk volume, multiplied by 100 to get percent as unit. The weight of the core was measured after cleaning it. After shaping them, the cores were put to dry in a 90 degrees Celsius oven until a stable weight was reached.

$$Porosity = \frac{Pore\ Volume}{Bulk\ Volume} * 100\ \% = \frac{V_{pore}}{V_{bulk}} * 100\ \% \qquad (3.1)$$

3.3 Brine compositions

Brines were prepared synthetically in the laboratory, using chemicals produced by the company Merck. The chemicals were pre-diluted into separate beakers (200 ml) in a special order before mixing; first the chlorides, then the sulfates and carbonates. Now the chemicals were mixed into 1-liter bottle batches and diluted to 1 liter using deionized water (DI). The formation water (VB0S) had some precipitation of particles and was therefore filtered through 0.22 µm membrane filters. The other brines that were made did not precipitate and did not need filtering.

Brine	Description
VB0S	Valhall brine, synthetic formation water without any sulfate.
SW	Synthetic sea water.
SW0T	Synthetic sea water made for chromatographic wettability test, without any sulfate.
SW1/2T	Synthetic sea water made for chromatographic wettability test, with both sulfate and thiocyanate (SCN-).

Table 6: The different brines that were used.

Density and pH was measured when the brines had reached a stable state after about 1 day of stirring. The density was measured 3 times for each brine and the mean was calculated based on these measurements. All of these measurements were taken at ambient temperature.

Chemistry of the Brines that where prepared. Numbers expressed in mM.				
Ions (mM)	VB0S	SW	SW0T	SW1/2T
HCO3-	9	2	2	2
Cl-	1066	525	583	538
SO42-	0	24	0	12
SCN-	0	0	0	12
Mg2+	8	45	45	45
Ca2+	29	13	13	13
Na+	997	450	460	427
Li+	0	0	0	12
K+	5	10	10	22
pH (measured)	7.41	7.74	7.86	7.79
Density (measured)	1.0414	1.0225	1.0215	1.0216

Table 7: Chemistry of brines.

3.3.1 Diluted brine for initial water saturation

A 10 times diluted brine was made through mixing 100 ml brine (VB0S) with 900 ml DI water to create a batch of 1 liter. This diluted brine was prepared with the intent of later using it to establish the initial water saturation (S_{wi}) in the chalk cores.

3.4 Crude Oil preparation

3.4.1 RES 40 preparation

Crude oil (Heidrun) and n-heptane was mixed in a 60/40 fashion and thereafter centrifuged for about 30 minutes. Filtering without centrifuging was executed once without success as it did not flow through the filter. After centrifuging the oil mixture, it was filtered with a 5 µm Millipore filter. The product was a model oil called RES 40. Acidic and Basic Numbers (AN and BN) were measured and are shown in Table 9. Half of the RES 40 oil was used to prepare the oil called RES 40-0. By diluting the heavier Heidrun oil with heptane, the mixture will be less viscous and therefore less pressure required during displacement. The Stevns Klint chalk is very fragile, and the risk of fracturing the core it will be reduced.

3.4.2 RES 40-0 preparation

RES 40-0 has AN and BN of the value ~0 and is used as a mixing ingredient to easily obtain the desired composition of AN for oil.

This oil was made by adding 10 weight percent active silica gel into the RES 40 and stirring it for 3 days. Now, additional 10 percent were added. After 3 new days, the oil had lot of precipitates which was a result of adsorption of polar components into the gel. The precipitates formed a thick mass that was separated from the rest of the oil manually. By centrifuging it for about 50 minutes and filtering (5 µm) the remaining oil, we got the desired RES 40-0 crude oil. The centrifuge also heats the oil sufficiently to make it flow better through the filter.

3.4.3 AN and BN measurement

The method used for measuring the acid and base number is developed by Buckley and Fan (Fan & Buckley, 2006) using potentiometric titration. The equipment used for this was a Mettler Toledo DL55 auto-titrator. The goal was to make a third crude oil with a AN of close to 0.35 (RES 40-0.35) by mixing the two previously mentioned crude oils. The purpose of the mixing was to obtain the target acid number.

Fraction RES 40	0.183
Fraction RES 40-0	0.817
Calculated **AN** for RES 40-0.35 (mmol)	0.35136

Table 8: Mixing ratio for oils.

Crude oil	Acid number	Base number	Density	Viscosity (23°C), cp	Viscosity (50°C), cp
Heidrun	2.8	0.74	0.886	N/A	N/A
RES 40	1.925	0.840	0.81341	N/A	N/A
RES 40-0	0.000	0.100	0.80716	N/A	N/A
RES 40-0.35	0.350	0.365	0.80640	1.72	1.03

Table 9: Measured oil properties.

The measuring was done by running a standard and a blank test before doing the actual oil samples. Values that were in an acceptable range, had to be close to equal when executing the test three times consecutively, and the average was calculated as seen in the table above. Viscosity and density was measured a minimum of three times and the average was calculated.

3.5 Chalk core preparation

A chalk core will contain anhydrate to some extent, and this molecule will dissolve and release ions of sulfate. This is basically a Smart Water made in situ (in the original place). A flushing is therefore appropriate to avoid this effect when doing experiments with Smart Water on chalk cores. An experiment done by Tina Puntervold (2008) shows the importance of core cleaning when reproducible wetting conditions are crucial.

3.5.1 Pre-flush saturation

Before flushing the core, it was saturated with DI water. By pre-saturating the core, we got a much quicker process when flushing it. The saturation was done through a vacuum-chamber, by first lowering the pressure in the pores of the core, and then letting the water flow into it. The weight of the core was measured before and after saturating it, in order to know the amount of DI to flush it with.

Core	Weight, dry (grams)	Weight, wet (grams)
S2	110.05	148.68
S1	110.20	149.08

Table 10: Weight of the chalk cores after cleaning and when saturated with diluted brine.

3.5.2 Flushing of cores

The cores were washed with about 5 times the pore volume of the cores, which was about 200 ml for our chalk cores. Samples were taken during the flushing procedure to observe the presence of sulfate, $SO4^{2-}$, and its removal. The first samples were taken in the early stage of effluent, then some after about 130 ml, and in the end one sample to compare the precipitation of the particle $BaSO_4$ that was formed by adding Ba^{2+} to the effluent. The flushing of the core was done in a cell with a pump rate of 0.100 ml pr. minute. The observed rate of effluent was measured to be 0.103 ml pr. minute (uncertainty in equipment). This process lasted for about 33 hours (displacement mode with 200 ml) pr. core at ambient temperature. To be sure, another 1 PV was injected after the core had been idle in the closed cell for more than 1 hour, just to get out any remaining salts that would have dissolved in this idle period.

$$Ba^{2+} + (aq) + SO_4^{2-}\ (aq) \rightleftharpoons BaSO_4\ (s) \tag{3.2}$$

The cores were now “clean” from the flushing and put into an oven set to 90 degrees Celsius and stored there for at least 3 days, until a constant weight was obtained.

3.5.3 Delta pressure and permeability

The delta pressure was measured with the same setup as for the flushing of the core, just by modifying the setup by opening the valves that are connected to the measuring equipment. The difference in pressure is calculated by the pressure tool, based on inlet and outlet pressure of the system. The cores got the following measurements:

Core	$Pressure,\ \Delta P$ (mBar)	Permeability, k (mD)
S2	848	1.2293
S1	490	1.9976

Table 11: Cores delta pressure and permeability.

The permeability, k, for these cores was calculated using Darcy's equation:

$$q = -\frac{kA}{\mu}\frac{\Delta P}{\Delta x} \tag{3.3}$$

3.5.4 Establishing the initial water saturation

The initial water saturation (S_{wi}) in the cores was created using 10 times diluted brine (VB0S). The core was saturated 100 % with this brine using a vacuum chamber and letting it stay in the chamber for about 30 minutes after the whole core was submerged in the brine, in order to get a best possible saturation (accessing as close as possible to all of the effective porosity).

Thereafter, it was put into a desiccator (Springer et al. 2003) to vaporize the saturation down to 10 %. In this way, we get a correct composition in the water saturating the core, as the salts will not vaporize during the process. The target weight was calculated using the characteristics of the core and the saturating fluid, and then color-changing silica gel was used to adsorb the moisture in the desiccator. Below is a figure illustrating the setup used (Layti, 2015).

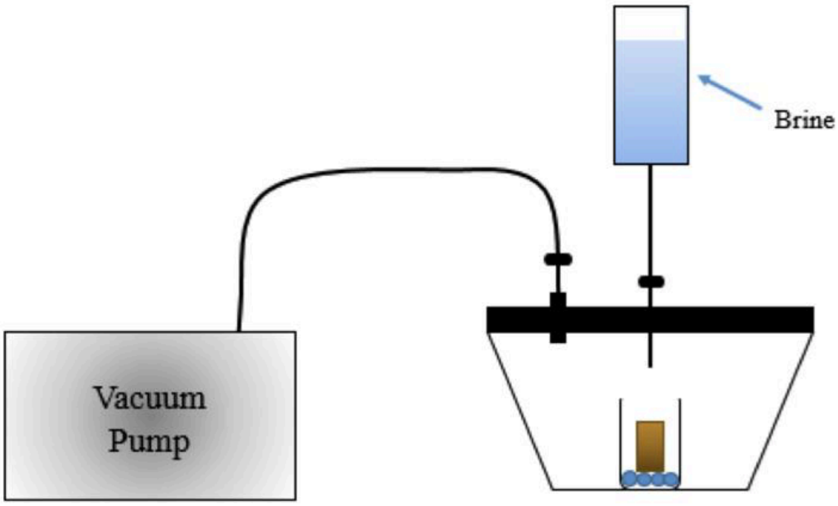


Figure 17: Vacuum pump illustration by Frida Layti (BSc, 2015)

After the target weight was reached, the core was put into a container with a lid that was moisturized lightly on the inside to keep the atmosphere in the container saturated. The core was then left in this container for 3 days to get an even distribution of the brine inside the core.

3.5.5 Saturation of core with oil and ageing

The core was placed inside a core holder (Hassler) inside an oven that was set to 50°C. Before doing anything further, the lines were carefully cleaned using heptane and DI water. Thereafter, the system was mounted properly with all lines involved, and vacuumed (using a pump). Now the core was saturated with 1 PV of crude oil plus about 5 ml to account for the empty (vacuumed) lines. The outlet was closed during this stage, and the flooding continued until the pressure gauge (mounted to outlet) displayed a pressure between 5-8 bar.

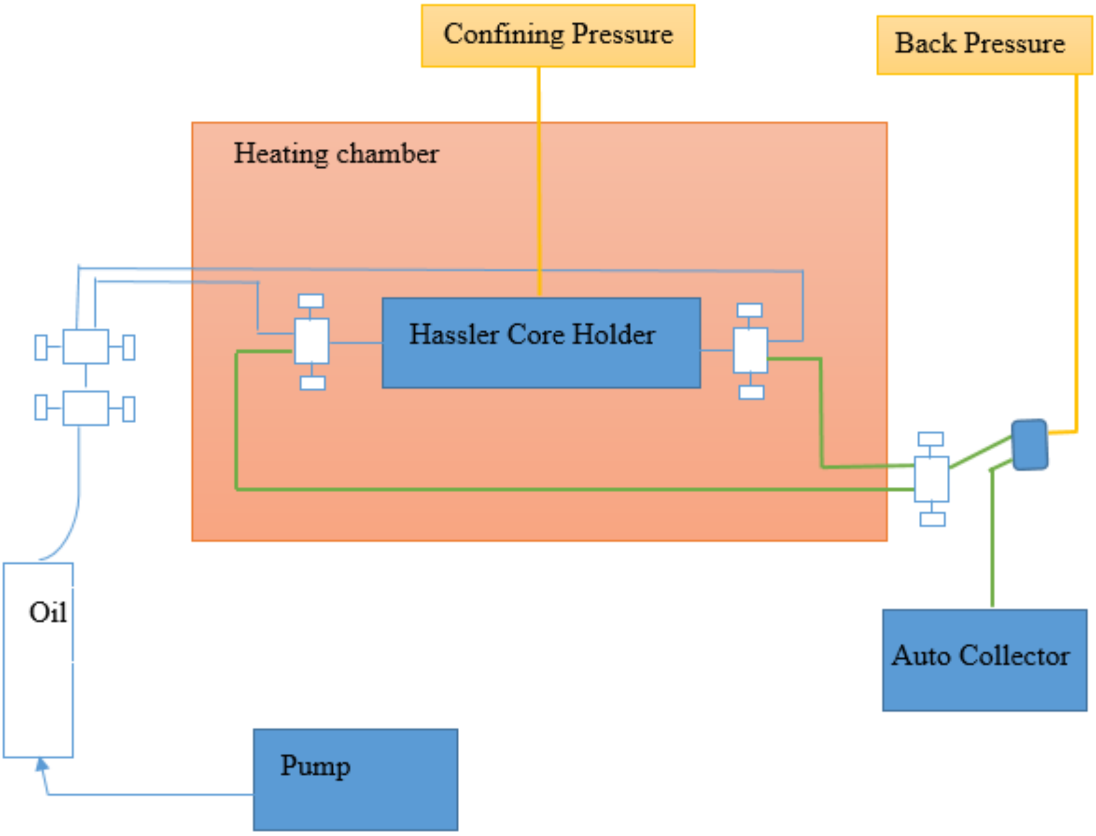


Figure 18: Setup for initial oil saturation, illustrated by Magnus Kinn (BSc, 2015).

The core was then flooded with 2 PV in each direction by opening and closing the paired inlets and outlets. All flooding was done with a confining pressure of about 20 bars, with no back pressure and with a constant temperature of 50°C. The core was thereafter wrapped in Teflon tape to avoid any unrepresentative active polar components to adsorb and then placed in an ageing cell with 4 marbles in the bottom of the cell. The ageing cell was filled with the same oil (RES 40-0.35) to cover the core. The cell was then properly sealed and stored for 14 days, at 50°C, to get an evenly distribution of the acidic components in the core.

3.6 Spontaneous imbibition

Spontaneous imbibition was performed on the core after the aging was complete. The imbibition was done at 50°C in a standard Amott glass cell. The condition of the cell (leakage, cracks etc.) was examined and grease was applied as a sealing agent on the contact surface between the two parts of the cell. The aged core was placed into the cell with the formation brine VB0S as displacing fluid. The displacement was recorded with an accuracy of about ± 0,1 ml over time, until the process had reached equilibrium. Oil recovery plateaued after 4-6 days. The SI-process was again executed after the core was restored. The reference core (S1) was also put through this process, but with DI water instead of the VB0S as formation brine, and the process had to be logged in a much denser matter as it happened rather quickly.

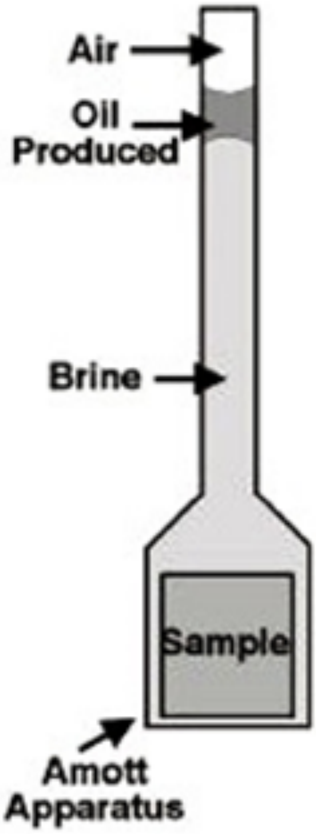


Figure 19: Principle of Amott cell and spontaneous imbibition.

3.7 Forced imbibition

After the spontaneous imbibition reached a plateau, the core was set to forced imbibition. By forcing the displacement with a rate of 1 PV pr. day, the core got to a condition of having residual oil saturation (S_{or}). The rate was calculated by using the pore volume (ml) of the core divided by one day (in seconds), to be 0.026 ml pr. minute. The Hassler core holder was mounted into an oven that held 50°C and samples were taken throughout the experiment. After plateau was reached with 0.026 ml. pr. minute, the rate was increased to 4 times PV pr. day until a new plateau was reached.

The recovery was not expected to be very high, as the spontaneous imbibition recovered 41 % of the oil in place. This flooding was done with a backpressure of ~7 bars and 19 bars as confining pressure. Differential pressure was observed and logged with the same interval as volume of recovery was measured.

3.8 Chromatographic wettability test

When the forced imbibition was completed successfully, the oven was turned off to make the system reach room temperature. Two racks with glass containers were prepared and all glasses were weighed and given a number. This was important because it later was used to calculate the weight of the effluent pr. glass, which is necessary to know where the points are to be referred to in the process. The injecting fluid was changed from VB0S to SW0T and SW1/2T; connected to the inlet through two separate cells (Figure 20). SW0T was flooded for 4 PV's at a rate of 0,3 ml/min and then decreased to 0,2 for ca. 1 PV. The last two hours of SW0T flooding was sampled by using the auto-sampler, and then the injection was switched to SW1/2T at the same rate of 0,2 ml/min for about 1 day with auto-sampling. Before switching to SW1/2T, a Batch test was conducted on the effluent to check if the core was sulfate-free. The auto-sampling was done by filling 6 ml pr. glass container.

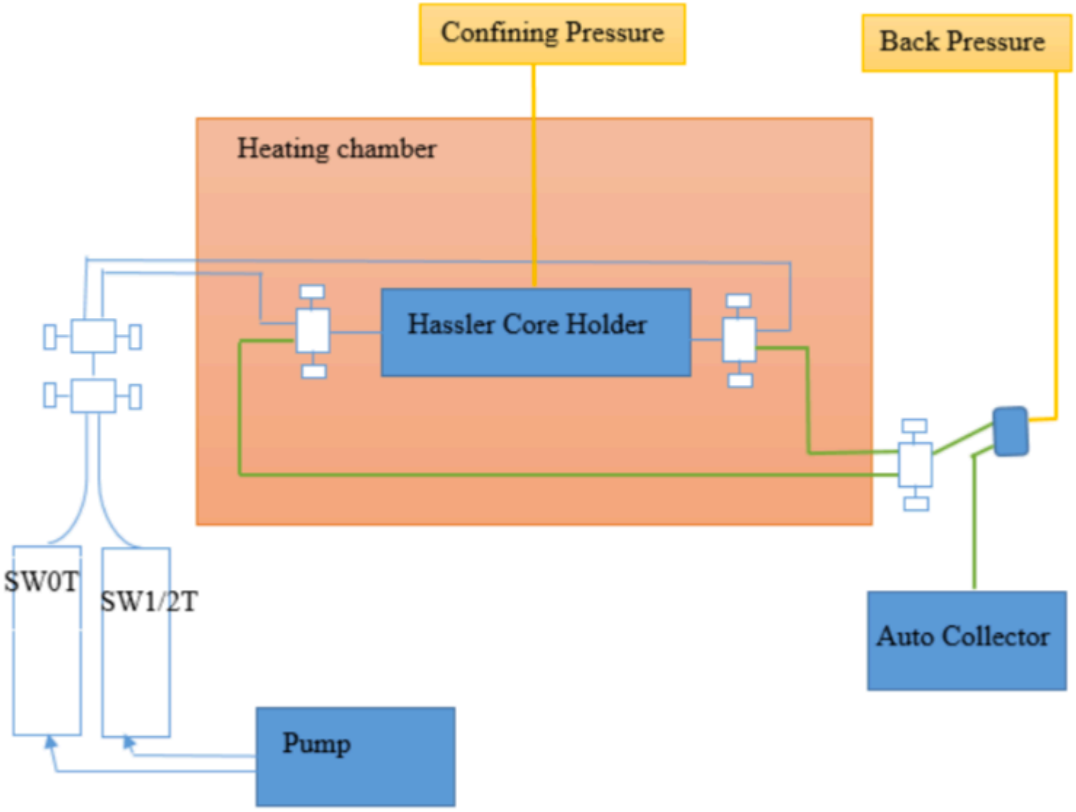


Figure 20: Overview of the setup that was used to get samples for chromatographic wettability test (Kinn, BSc 2015)

Small plastic containers were filled with the 1000 times diluted SW1/2T effluent brine taken from the auto-sample samples and inserted into the IC-machine. It was necessary to prepare reference-samples in this part of the experiment to get a correlation between values from the effluent samples and the supposed saturated value (that are to be reached after completed adsorption). The references were SW, SW0T and SW1/2T brine and DI-water and these were diluted is the same manner as previously.

3.9 Mild Cleaning with Kerosene and Heptane

After the samples for IC were finished, the mild cleaning was executed using the same setup as previously. Both before and after flooding with the solvents, DI-water was flooded through the core, until no sulphate was observed in the effluent. Kerosene was flooded through the core until the effluent was transparent/clear, this took about 1 day and was done at a rate of 0.2 ml/min. The kerosene flooding was stopped at 280 ml effluent. Backpressure was not needed during this cleaning, and the oven was still shut off during this process.

Heptane was then flooded with the same rate as the kerosene with the purpose of displacing the kerosene. Around 4-5 PV is sufficient to get a good displacement and did in this case result in clear effluent. The last flooding with DI-water was executed and then the core was taken out of the core holder and placed in a 90°C oven to dry.

3.10 Core restoration after mild cleaning

When the core had reached a stable dry weight after the cleaning process, the restoration of the core was performed. This included all previous steps, starting from the establishing of initial water saturation with VB0S. The weight of the core had decreased by a very small amount, which was caused by wear and tear during the different stages in the experiment.

Core	New Weight, dry (grams)	New Weight, wet (grams)	New 10 % FW Weight (grams)
S2	109.88	148.15	113.08

Table 12: New measured values for S2.

The steps are summarized in short as follows as they are equal to the steps in the initial restoration:

- Establishing of the initial water saturation, 10 % VB0S, using the desiccator to reach the target weight.
- Saturation of the core with crude oil, RES40-0.35, by flooding the core from both directions.
- Ageing of the core for 14 days to simulate the reservoir distribution of acid components.
- Spontaneous imbibition with VB0S. The core was left in the spontaneous imbibition cell so that further work could be executed on it later.
- The experiments were stopped after SI of the core, because of insufficient time.

3.11 Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS) analysis

Additional pieces of chalk were cut from the same block as core S1 and S2 to be used for SEM and EDS analysis. The pieces that were used in this analysis were coated with Palladium before the high magnification images could be taken. Grain size and element analysis is obtained from this machine.

3.12 Brunauer-Emmett-Teller (BET) Analysis

Additional pieces of chalk were cut from the same block as core S1 and S2 to be used for BET analysis of the chalk to obtain the specific surface area. The samples were put into the sample holder (formed like a bulb) and mounted onto the machine. The container which the samples were descended into was carefully filled with liquid nitrogen before performing the analysis.

Figure 21: Photography of BET equipment.

4 Results

In this chapter the results are presented. The objective has been to investigate how a mild core cleaning followed by a restoration will affect the wettability of an initially restored core (which represents a preserved reservoir outcrop). Does this process result in a recreated representative core wetting?

4.1 Core properties

4.1.1 Scanning Electron Microscopy pictures & Elementary analysis

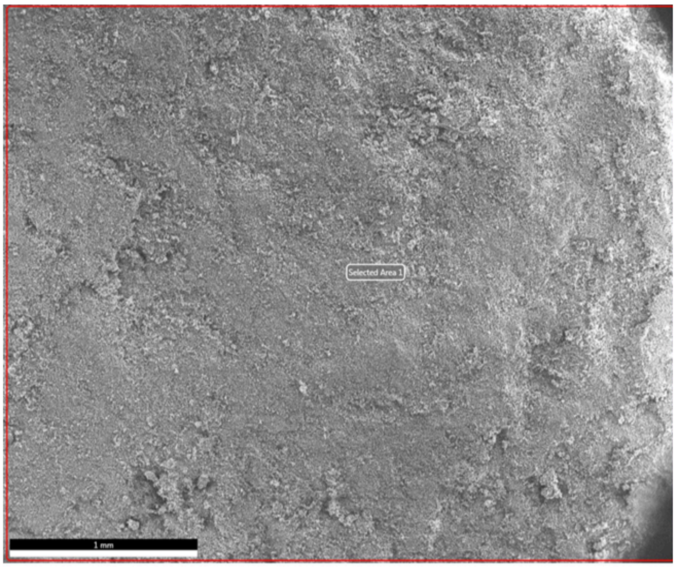


Figure 22: Area of investigation when doing the analysis of a SK chalk sample. The scale down to the left shows the length of 1 mm.

Figure 22 shows the surface of investigation when doing a compositional scan of the chalk sample. From Table 13 the results of the scan are given, and it is observed that the sample is close to pure Calcium carbonate in content. There are very small amounts of Silica present as well.

Element	Weight %	Atomic %
Ca	99.93	99.9
Si	0.06	0.09
S	0.01	0.01

Table 13: EDS results from a sample of Stevns Klint chalk.

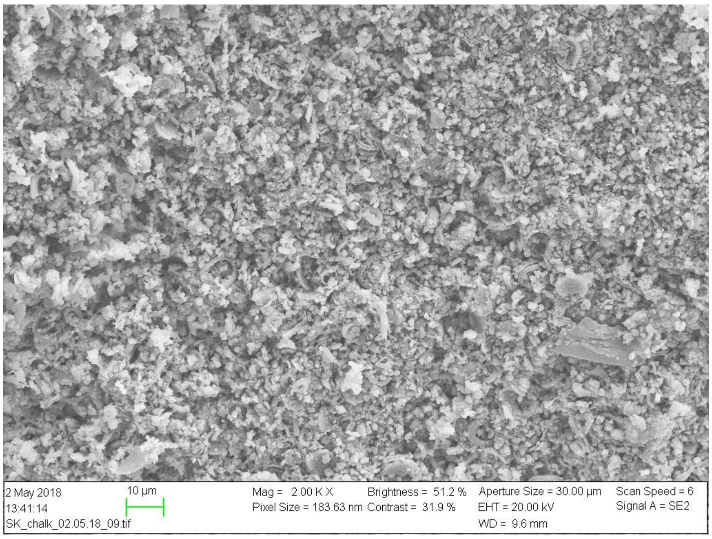


Figure 23: SK outcrop sample with a scale of 10 µm.

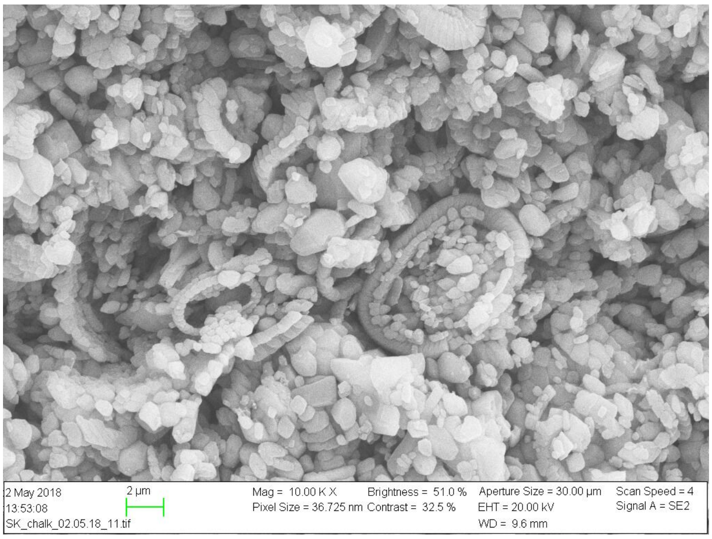


Figure 24: SK outcrop sample with scale of 2 µm with visible coccolith ring.

The SEM pictures gave high resolution images of the chalk samples. Figure 23 shows a bigger area of the chalk with a green scale reference in the lower left corner, while Figure 24 is the same picture but magnified 5 times. It is possible to see single chalk grains which have about 1 μm in diameter in general. Organic material is easy to observe and often formed in ring-like structures (coccolith rings). It is also possible to see the pore space between grains, spotted as the darker parts of the images. The cores used in this experiment had a porosity of 48 % which is consistent with this highly porous structure observed from the SEM images.

4.1.2 Brunauer-Emmett-Teller analysis results

A Brunauer-Emmett-Teller instrument was used to measure the specific surface area of the Stevns Klint chalk. It was measured to be 2.18 m^2/g. The large surface area is due to the grain size of chalk (1 µm) (Røgen & Fabricius 2002).

4.2 Core S1 – Initial core wettability

The S1 core is what is used as a reference in this experiment. Instead of saturating the core with initial water and crude oil, this core was completely saturated with heptane. The spontaneous imbibition was then performed at 23°C with DI water as imbibing fluid, and the volumes had to be measured quickly in a dense matter, because the low viscosity in heptane increases the displacement velocity as the capillary forces are very strong. The recovery had a plateau at 71 % of OOIP after about 4 hours. The oil recovery is plotted in Figure 25:

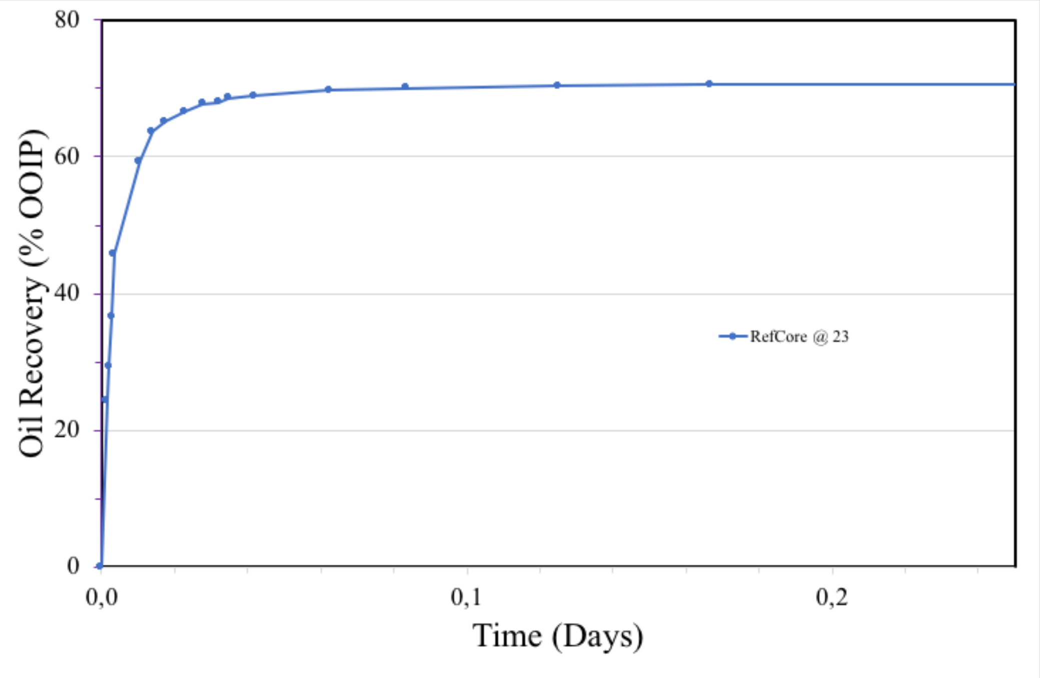


Figure 25: Spontaneous imbibition with 100 % heptane saturated core.

The results from the spontaneous imbibition with the reference core S1 show that the core is completely water-wet. The heptane that was saturating the core has no acidic components (AN=0) and is this way not changing the wetting of the core.

4.2.1 Chromatographic wettability test (S1)

The chromatographic wettability test is normally conducted after residual oil saturation has been reached, and SW0T (zero sulfate) has been flooded through the core to reach dynamic equilibrium. Then sea water containing tracer (SW1/2T) is flooded through the core. The effluent ion concentration relative to the brine concentration (C/Co) is then plotted versus pore volume (PV) injected. The chromatographic wettability test gave a significant separation between the thiocyanate (tracer) and the sulfate. This is a clear indicator of sulfate being adsorbed by the water-wet surface sites of the chalk. The area was calculated to be $A_{Heptane}$ = 0.2920 and is used as the denominator in the wettability index equation (2.6). Hopkins (2017) had a similar value for the area between the two curves when doing a chromatographic wettability test on his reference core, which was $A_{Heptane}$ = 0.256.

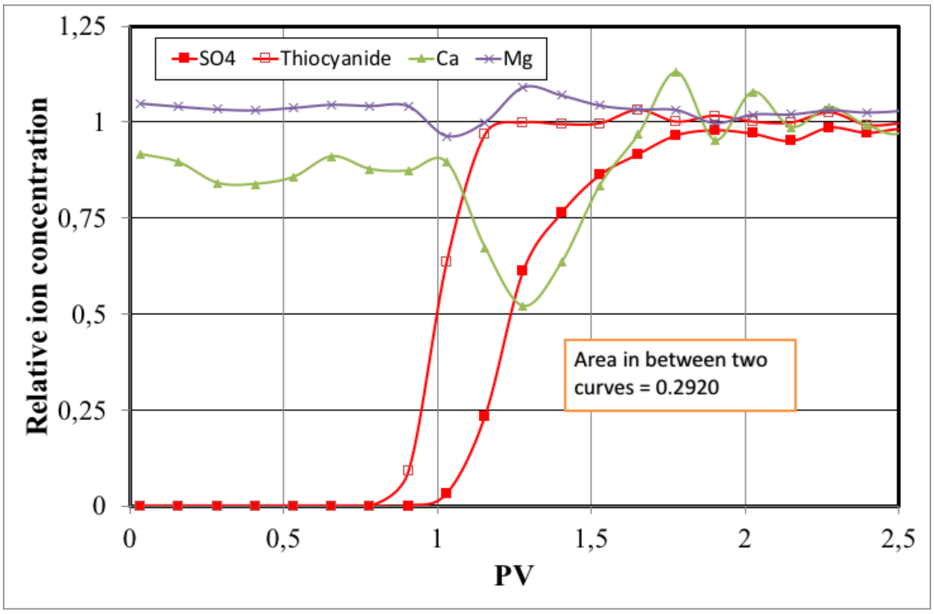


Figure 26: Ion Chromatographic wettability test for S1, reference core. The relative concentrations of SCN^- and SO_4^{2-} that is present in the effluent samples are plotted versus PV injected.

The wettability index of this core is WI = 1 as it represents a completely water-wet rock surface. A completely oil-wet rock surface would in contrast have WI = 0. From the chromatographic wettability test, one can detect several ions. As seen in Figure 26, calcium and magnesium are plotted in addition to sulfate and thiocyanate to observe how these ions adsorb during the experiment. Calcium has an adsorption reaction that peaks at the sulfate front.

4.3 Core S2 – Core wettability after initial core restoration (R1)

The S2 core was saturated to have an initial water saturation of 10 %, with the formation brine VB0S. The remaining 90 % of the effective porosity was then filled with the crude oil, RES 40-0.35, and the core was aged for 14 days, and the first spontaneous imbibition test was carried out.

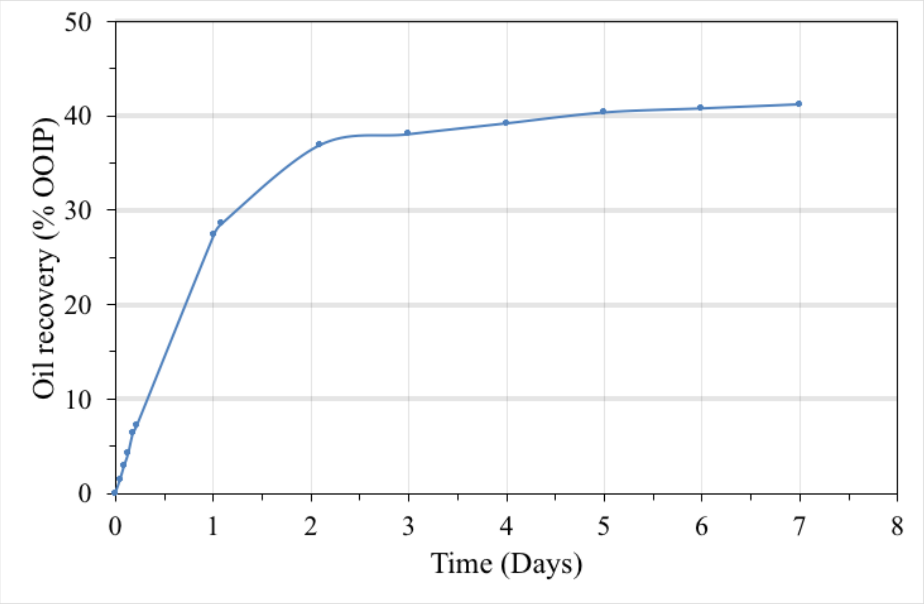


Figure 27: Before cleaning: Spontaneous imbibition with VB0S at 50°C of core S2, with S_{wi} *= 0.1 of VB0S and then saturated and aged in RES 40-0.35.*

The SI test was performed with VB0S as the imbibing formation brine, which will not react chemically with the core. The recovery reached 41 % of OOIP (Figure 27), at a temperature of 50°C. Ultimate recovery from SI was reached after 7 days and the high value indicates that the core is preferably water-wet after being initially restored and exposed to only 5 PV of crude oil.

The Amott water index I_W is calculated by dividing the recovery percentage from the spontaneous imbibition on the total imbibition recovery. S2 had I_W = 0.614 after the initial core restoration, and this puts it into the water-wet category.

$$I_W = \frac{Spontaneous\ imbibiton}{Spontaneous\ imbibiton + Forced\ imbibition} \tag{4.1}$$

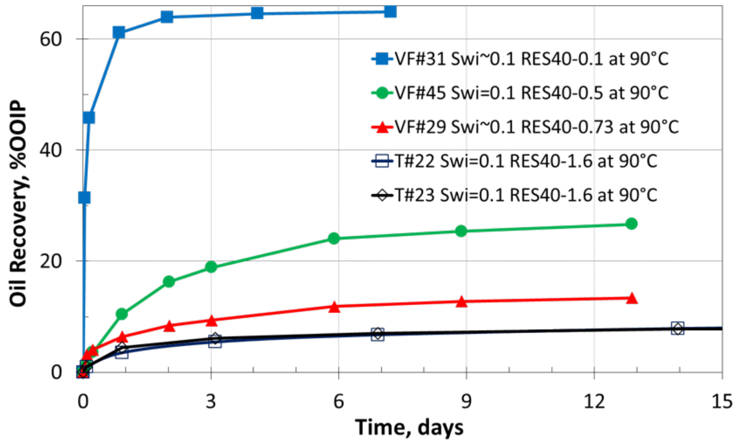


Figure 28: Spontaneous imbibition recovery results when using crude oils with different AN (Puntervold, 2008).

The oil has acidic number 0.35 which fits very well into Figure 28, which are results from earlier experiments performed by Tina Puntervold (2008). This is a good reference for this experiment, despite the difference in temperature.

After the spontaneous imbibition, there was 59 % of the OOIP left in the core. The forced imbibition was performed by flowing VB0S into the core at 50°C with a confining and backpressure of 19 and 7 bar respectively. First with a rate of 1 PV pr. day until plateau, and thereafter 4 PV pr. day until plateau. Results are shown in the Figure 29.

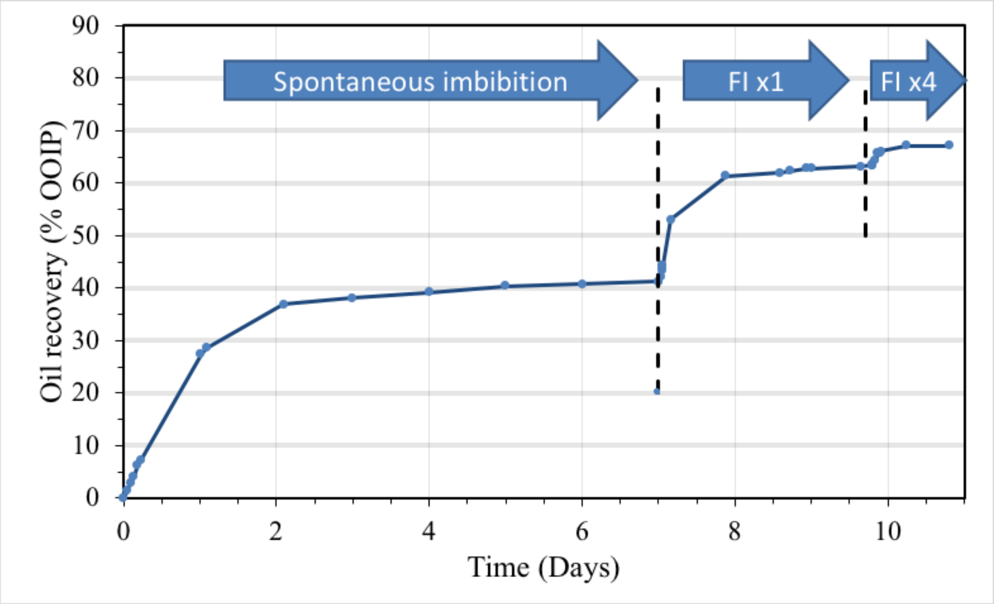


Figure 29: Before cleaning: Spontaneous and forced imbibition with VB0S at 50°C of core S2, with S_{wi} = 0.1 of VB0S and then saturated and aged in RES 40-0.35.

The additional recovery obtained by forced imbibition was 22 % of OOIP, from the rate of 1 PV pr. day, and roughly 4 % additionally from 4 PV pr. day. Viscous forces from the FI have increases the oil recovery. This increase in viscous force will overrule the capillary forces when the pressure gradient through the core is increased sufficiently. The total recovery from all steps of imbibition was now at 67 % of OOIP. This is very close to what was recovered from the S1 core without forced imbibition (71 % of OOIP). The next step was to prepare for chromatographic wettability test.

4.3.1 Chromatographic wettability test (S2-R1)

The core was flooded with SW0T at ambient temperature to get to the residual oil saturation (S_{or}) that was calculated to be 0.275. Chromatographic wettability test was now performed on the S2 core to evaluate the water-wet surface area of the core. The area between the curves was calculated to be 0.1592 for the chromatographic wettability test for this core.

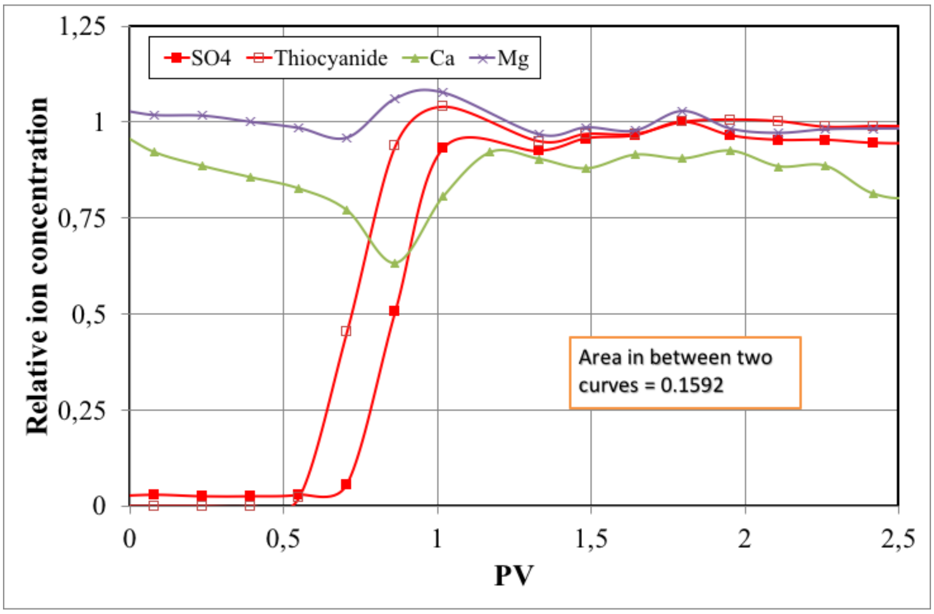


Figure 30: Ion Chromatographic wettability test for S2, before the mild cleaning. The relative concentrations of SCN^- and SO_4^{2-} that is present in the effluent samples are plotted versus PV injected.

The wettability index was calculated to be WI = 0.545 and indicates a clearly mixed wettability. Seeing such a high recovery from the spontaneous imbibition, we would expect the WI to be somewhat closer to 1. Similar experiments have been conducted by Magnus Kinn (BSc, 2015) and Paul Hopkins (PhD, 2017), which had a larger WI value despite lower recovery from the spontaneous imbibition. The reason for this difference may be due to the significantly larger value for the area between the curves for this experiments reference core.

4.4 Core S2 – Wettability after mild cleaning and a second core restoration (R2)

S2 was mildly cleaned and put through the same saturation process as previously, exposing the core for another 5 PV when saturating it. First saturated 10 % with VB0S and then 90 % with RES 40-0.35, aged for 14 days, and then inserted into the Amott glass cell for spontaneous imbibition. The result was a recovery of 21 % OOIP after 14 days. It seems like the mild cleaning did in fact preserve a significant amount of the already adsorbed acidic polar components from the initial restoration, as the second restoration has made the core less water-wet. Not only is the spontaneous recovery lower than before; it also has a different profile/shape.

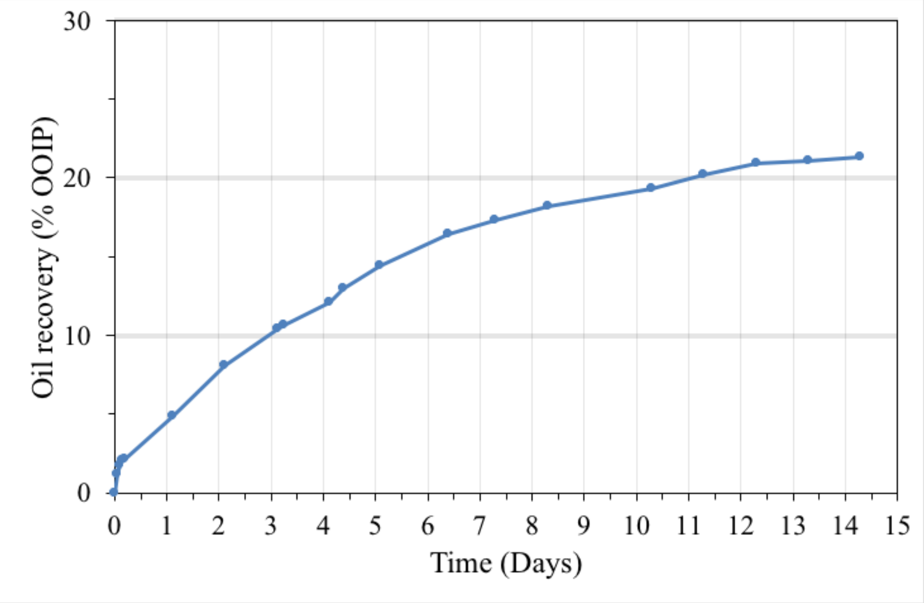


Figure 31: After cleaning and second restoration: Spontaneous imbibition with VB0S at 50°C of core S2, with S_{wi} = 0.1 of VB0S and then saturated and aged in RES 40-0.35.

4.5 Further work

- Do a Chromatographic wettability test on the S2 core (after the second restoration) after reaching residual oil saturation.
- Comparing the S2-R2 results from the chromatographic wettability test with previous work done Paul Hopkins to see if his conclusion can be confirmed.
- Do the whole experiment again but change the second restoration saturation process to only be vacuum saturation of the core (only exposed to 1 PV crude oil).

5 Discussion

- R1 – Initial restoration
- R2 – Second restoration

Core	S1	S2-R1	S2-R2
I_W	1	0.614	N/A
A_{wett}	0.2920	0.1592	N/A
WI	1	0.545	N/A

Table 14: Wettability indexes for S1 and S2. R1 and R2 represents the first and second restoration respectively.

The Amott water index ranges from 0 to 1, were 1 is completely water-wet and 0 is somewhere between neutral and oil-wet. The wettability is slightly water-wet for S2 after the initial restoration, if we are looking at the Amott water index (I_W). The chromatographic wettability index (WI) gives a more mixed-wet indication, which does not match the high recovery from the spontaneous imbibition.

No index is calculated after the second restoration (R2) of core S2 as there was not sufficient time to carry it through more than a spontaneous imbibition. These results still give a good understanding of the wettability change that has taken place.

5.1 Effect of oil saturation on chalk surface wetting

Core	S1	S2-R1	S2-R2
Volume oil seen	0	5 PV	10 PV
SI recovery	71 % OOIP	41 % OOIP	21 % OOIP

Table 15: Results from spontaneous imbibition compared to the amount of crude oil the core is exposed to.

S2 was saturated with oil twice in this experiment, thus being exposed to crude oil two times, 5 PV each time. It turns out that the second restoration process resulted in a much more oil-wet core. It is therefore questionable how much the aging actually affects the wetting, and rather more interesting to look at the saturation process itself.

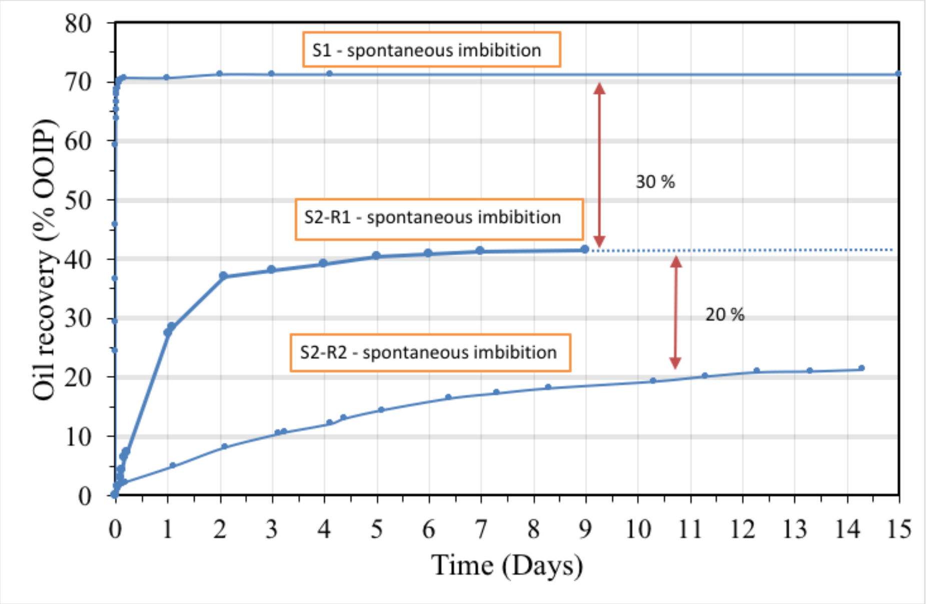


Figure 32: Comparison of spontaneous imbibition done on the two cores S1 and S2.

The initial restoration (R1) decreases the recovery (OOIP) from a spontaneous imbibition by 30 %, while a second restoration (R2) decreases it by additional 20 %. This may be a basis for claiming that the amount oil being flooded through the core is the more crucial part, when restoring a core that has been mildly cleaned.

By exposing the core to a minimal of crude oil when restoring it the second time, we would most likely obtain a better recreation of the initial wettability that S1-R1 is representing. If the experiment was executed by only vacuum saturating the core when doing the post-cleaning restoration, the results would most likely be much closer to the initial wetting.

Acidic components are adsorbed onto the sites that are positively charged and will continue to do so until electrostatic equilibrium. Research on quantity of oil versus equilibrium in charges has been conducted and has shown that injecting 8-9 PV of crude oil is enough to measure the original AN from the effluent. It is obvious from Figure 33 that 5 PV of crude oil flooding through the core makes a significant difference in AN measured from the effluent. 1 PV on the other hand, does not affect the AN by much. Even though mild core cleaning will preserve most of the wettability-dictating components; results show that the cleaning makes the core more water-wet. So, by minimizing the cleaning solvents injected and exposure of crude oil in the saturation process, one will able to reproduce a core wettability representative of initial reservoir wetting.

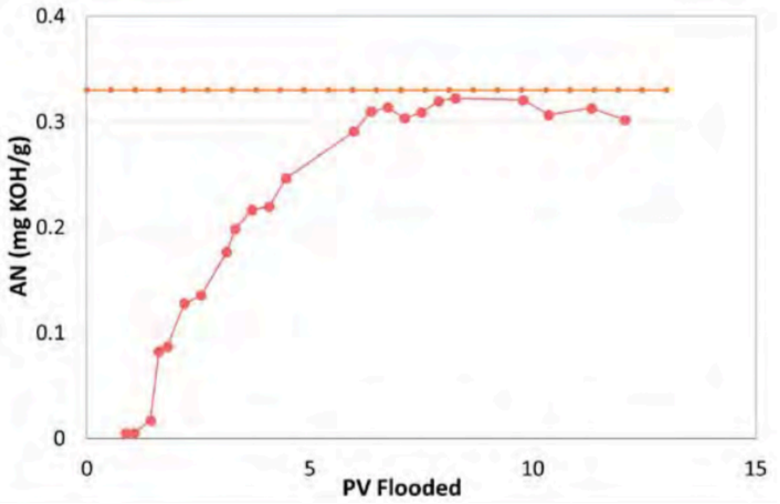


Figure 33: Acid number measurements of crude oil effluent samples during flooding of 15 PV RES40-0.34 at rate 0.1 ml/min. Swi = 0.1 SK chalk at 50°C (Hopkins, 2017).

5.2 Other Observations

Core S2 had successfully gone through two tests of displacement of the oil inside the pores of the sample. Both runs where executed in the same manner, without any observed errors occurring. Tests with barium cations were done on the effluent after the pre-cleaning of the cores. These came out clean, so there was no reason to believe that there was any sulfate left in the pores. Still, the results from the Ion Chromatographic test gave small traces of sulfate, and we know that sulfate alters the water-wetness. This may be an explanation for why the oil recovery was so high from the imbibition, and therefore why it seems to be strongly water-wet.

	S1	S2
	C/Co Sulfate	C/Co Sulfate
Sample 1	0	0.0131
Sample 2	0	0.0223
Sample 3	0	0.0275
Sample 4	0	0.0236

Table 16: Comparison between detected sulfate in the first 4 samples from the two chromatographic wettability tests.

Pure SW1/2T is the reference and has C/Co = 1, so the first few effluent samples therefore have a relative ion concentration of 2 %, for the S2 core. One could argue that the pre-flushing of the core should rather be performed at 30-50°C instead of ambient temperature, as this may give a more complete dissolution of the sulfate ions present on the chalk surface.

One parameter that could be a critical factor is the low permeability of the S2 core of 1.2293 mD, which is about 1/3 of the permeability calculated for the other cores that were cut from the very same block. Carbonate formations tend to be very heterogeneous and have permeability variations. Having relatively low permeability can be because of a small pore throat radius, and this would give a large capillary pressure force that could be a reason for high oil recovery by spontaneous imbibition.

Magnus S. Kinn (BSc, 2015) did a similar experiment with the same Stevns Klint chalk. One of his cores had similar behavior when displacing the oil with spontaneous and forced imbibition, which could mean that we both had core samples that where abnormally water-wet.

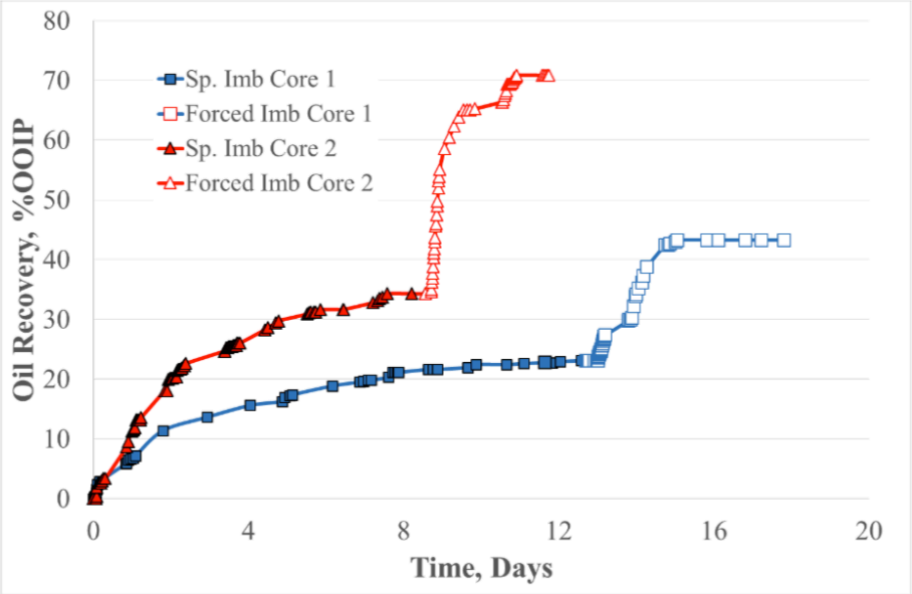


Figure 34: Imbibition tests on Stevns Klint cores, S_{wi} = 0.1 with FW, oil with AN=0.33 mgKOH/g, aged 14 days at 80°C (Kinn BSc, 2015).

Figure shows how the spontaneous imbibition on Core 2 reaches a plateau of 34 % OOIP, which is close to the 41 % of the S2 core. Hopkins (2017) did similar with nearly equal crude oils and brines, and his spontaneous imbibition results for two cores were 8 and 10 % of OOIP. This definitely confirms the heterogeneity of this type of chalk, and that we should look at trends/ratios instead of absolute values when comparing core samples.

6 Conclusion

The core wettability of core S1 and S2 was evaluated by performing spontaneous imbibition, forced imbibition and chromatographic wettability test. Core S2 went through an initial restoration followed by a mild core cleaning and a second restoration. Formation water (VB0S) was used both as initial saturated water in the core and as imbibing brine. By using formation water, we expect no chemical alteration of the wettability when performing the recovery tests. Conclusions drawn are based on the results from this study:

- The initial wettability of a chalk core is affected by the amount of crude oil that the core has been exposed to. By increasing the amount of oil that is flooded through the core you will see a reduction in the water-wetness of the core surface.
- The spontaneous imbibition experiments show a decrease in recovery for the S2 core when it has gone through the second restoration process.
- From the chromatographic wettability test, we confirm that the initial restoration (exposure to oil) gives a significant decrease in the wettability index.
- The wettability index calculated from the chromatographic test confirmed less water-wet behavior in SI after the initial restoration process of core S2.
- To recreate a representative initial wetting, it is recommended to expose the core to as little as possible crude oil after performing a mild core cleaning. One way of doing this is to only vacuum-saturate the core.

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8 Appendix

8.1 AN Solutions

A titration solution for the AN part of the measuring was prepared.

Solutions	Chemicals	Chemical formula	Description
Titrant	KOH (>85%) 2-propanol	KOH $CH_3CHOHCH_3$	2.8 g KOH dilute to 1000 ml with 2-propanol
Spiking solution	Stearic Acid Acid titration solvent	$CH_3(CH_2)_{16}COOH$	0.5 g Stearic Acid dilute to 100 ml with Acid titration solvent
Standard solution	Potassium Hydrogen Phthalate (KHP) DI-water	$HOOCC_6H_4COOK$	0.2 g KHP dilute to 500 ml with DI-water
Titration solvent	DI-water 2-propanol Toluene	$CH_3CHOHCH_3C_6H_5CH_3$	6 ml DI-water with 494 ml 2-propanol and with 500 ml Toluene
Electrode/ Electrolyte	Potassium chloride DI-water	KCl	Mettler DG-114 Electrode 3 M KCl in DI-water

8.2 BN Solutions

Solutions	Chemicals	Formula	Description
Titrant	Perchloric Acid (70%) Acetic Anhydride Acetic Acid	$HClO_4$ (70%) $(CH_3CO)_2O$ CH_3COOH	5 ml Perchloric Acid, 15 ml Acetic Anhydrite dilute to 1000 ml with Acetic Acid
Spiking solution	Quinoline Decane	C_9H_7N $CH_3(CH_2)_8CH_3$	0.5 g Quinoline dilute to 100 ml with Decane
Standard solution	Potassium Hydrogen Phthalate, KHP Acetic Acid	$HOOCC_6H_4COOK$ CH_3COOH	0.2 g KHP dilute to 250 ml with Acetic Acid
Titration solvent	Methy Isobutyl Ketone MIBK	$(CH_3)CHCH_2COCH_3$	Found in the laboratory
Electrode/ Electrolyte	Sodium Perchlorate, (solid) 2-propanol	$NaClO_4$ (S) $CH_3CHOHCH_3$	Mettler DG-113 Electrode Electrolyte: Saturated sodium perchlorate in 2-propanol

8.3 S2-R1: Displacement data

S2 OOIP (ml):		34.69
Spontaneous imbibition S2-run 1		
Time (Days)	Volume Oil (ml)	% OOIP (Cum. Prod)
0,00	0	0,000
0,05	0,5	1,441
0,09	1	2,883
0,13	1,45	4,180
0,18	2,2	6,342
0,22	2,5	7,207
1,01	9,5	27,385
1,09	9,9	28,538
2,09	12,8	36,898
3,00	13,2	38,051
4,00	13,6	39,204
5,00	14	40,357
6,00	14,15	40,790
7,00	14,3	41,222

Forced imbibition 1 PV/day S2-R1			
Time (Days)	Volume oil (ml)	% OOIP (Cum. Prod)	∆P (mbar)
7.00	14.3	41.222	690
7.03	14.6	42.087	689
7.04	15	43.240	689
7.05	15.2	43.817	686
7.06	15.35	44.249	690
7.06	15.4	44.393	657
7.16	18.4	53.041	459
7.89	21.3	61.401	417
8.59	21.5	61.978	416
8.72	21.6	62.266	411
8.93	21.8	62.842	410
9.00	21.8	62.842	410
9.66	21.9	63.131	n/a
9.80	22	63.419	n/a

Forced imbibition 4 PV/day S2-R1			
Time (Days)	Volume oil (ml)	% OOIP (Cum. Prod)	∆P (mbar)
9.80	22	63.419	n/a
9.80	22.1	63.707	n/a
9.84	22.3	64.284	892
9.87	22.8	65.725	844
9.89	22.8	65.725	829
9.89	22.8	65.725	824
9.90	22.8	65.725	844
9.91	22.9	66.013	828
10.24	23.3	67.166	730

8.4 S2-R2: Spontaneous imbibition data

OOIP (ml):	34.69	
Spontaneous imbibition S2-R2		
Time (Days)	Volume oil (ml)	% OOIP (Cum. Prod)
0.00	0	0.000
0.05	0.4	1.153
0.09	0.6	1.730
0.15	0.7	2.018
0.19	0.75	2.162
1.13	1.7	4.901
2.10	2.8	8.071
3.13	3.6	10.378
3.26	3.7	10.666
4.13	4.2	12.107
4.38	4.5	12.972
5.10	5	14.413
6.40	5.7	16.431
7.30	6	17.296
8.30	6.3	18.161
10.30	6.7	19.314
11.30	7	20.179
12.30	7.25	20.899
13.30	7.3	21.044
14.30	7.4	21.332

8.5 S1: Spontaneous imbibition data

OOIP (ml):	34.69	
Spontaneous imbibition S1, reference core		
Time (Days)	Volume oil (ml)	% OOIP (Cum. Prod)
0.00	0	0.000
0.00	8.4	24.214
0.00	10.1	29.115
0.00	12.6	36.322
0.00	15.8	45.546
0.01	20.5	59.095
0.01	22	63.419
0.02	22.5	64.860
0.02	23	66.302
0.03	23.4	67.455
0.03	23.5	67.743
0.03	23.7	68.319
0.04	23.8	68.608
0.06	24.1	69.472
0.08	24.2	1.000
0.13	24.3	70.049
0.17	24.4	70.337
1.00	24.4	70.337
2.00	24.6	70.914
3.01	24.6	70.914
4.13	24.6	70.914
15.00	24.6	70.914

8.6 S2: Chromatographic wettability test

Comment: Yellow samples were not included in the plot because they were taken before switching to the SW1/2T. The red samples are samples which were removed due to having abnormally high values from the IC-test.

Thiocyanide					
Glass number	Before [g]	After [g]	Wt fluid [g]	PV injected*	C/Co
1	9.06	15.09	6.03	-0.86	0.0000
2	8.37	14.40	6.03	-0.71	0.0000
3	8.41	14.46	6.05	-0.55	0.0000
4	8.60	14.66	6.06	-0.39	0.0000
5	8.45	14.53	6.08	-0.24	0.0000
6	8.41	14.44	6.03	-0.08	0.0000
7	8.37	14.49	6.12	0.08	0.0000
8	9.04	15.13	6.09	0.24	0.0000
9	9.01	15.04	6.03	0.39	0.0000
10	8.40	14.47	6.07	0.55	0.0208
11	8.45	14.53	6.08	0.71	0.4542
12	9.00	15.07	6.07	0.86	0.9375
13	8.49	14.49	6.00	1.02	1.0396
14	9.06	15.00	5.94	1.17	1.0938
15	8.98	15.04	6.06	1.33	0.9500
16	9.07	15.04	5.97	1.48	0.9688
17	8.40	14.51	6.11	1.64	0.9688
18	9.17	15.17	6.00	1.80	1.0000
19	8.38	14.45	6.07	1.95	1.0063
20	8.43	14.42	5.99	2.11	1.0021
21	8.51	14.45	5.94	2.26	0.9875
22	8.53	14.58	6.05	2.42	0.9896
23	9.07	15.09	6.02	2.58	0.9917
24	8.47	14.50	6.03	2.73	1.5854
25	9.05	15.17	6.12	2.89	1.0146
26	8.93	14.94	6.01	3.05	1.3792
27	9.10	15.05	5.95	3.20	1.0354
28	8.50	14.57	6.07	3.36	1.0458
29	8.43	14.42	5.99	3.51	1.0000
30	9.01	15.02	6.01	3.67	1.0042
31	8.52	14.58	6.06	3.82	1.0125
32	8.50	14.60	6.10	3.98	1.0271
33	8.44	14.37	5.93	4.14	0.9604
34	8.55	14.68	6.13	4.29	0.9479

35	8.40	14.38	5.98	4.45	1.0146
36	8.45	14.56	6.11	4.61	1.0271
37	8.37	14.27	5.90	4.76	1.0417
38	8.32	14.42	6.10	4.92	0.9250
39	8.99	15.02	6.03	5.07	0.9917
40	8.97	14.99	6.02	5.23	1.0021
41	9.08	15.11	6.03	5.39	1.0354
42	8.40	14.44	6.04	5.54	1.0042

Sulfate					
Glass number	Before [g]	After [g]	Wt fluid [g]	PV injected*	C/Co
1	9.06	15.09	6.03	-0.86	0.0000
2	8.37	14.40	6.03	-0.71	0.0000
3	8.41	14.46	6.05	-0.55	0.0000
4	8.60	14.66	6.06	-0.39	0.0000
5	8.45	14.53	6.08	-0.24	0.0131
6	8.41	14.44	6.03	-0.08	0.0223
7	8.37	14.49	6.12	0.08	0.0275
8	9.04	15.13	6.09	0.24	0.0236
9	9.01	15.04	6.03	0.39	0.0602
10	8.40	14.47	6.07	0.55	0.0275
11	8.45	14.53	6.08	0.71	0.0563
12	9.00	15.07	6.07	0.86	0.5066
13	8.49	14.49	6.00	1.02	0.9308
14	9.06	15.00	5.94	1.17	1.0080
15	8.98	15.04	6.06	1.33	0.9243
16	9.07	15.04	5.97	1.48	0.9570
17	8.40	14.51	6.11	1.64	0.9648
18	9.17	15.17	6.00	1.80	1.0002
19	8.38	14.45	6.07	1.95	0.9648
20	8.43	14.42	5.99	2.11	0.9531
21	8.51	14.45	5.94	2.26	0.9531
22	8.53	14.58	6.05	2.42	0.9452

23	9.07	15.09	6.02	2.58	0.9478
24	8.47	14.50	6.03	2.73	1.4767
25	9.05	15.17	6.12	2.89	0.9792
26	8.93	14.94	6.01	3.05	1.2790
27	9.10	15.05	5.95	3.20	0.9936
28	8.50	14.57	6.07	3.36	0.9936
29	8.43	14.42	5.99	3.51	0.9923
30	9.01	15.02	6.01	3.67	0.9805
31	8.52	14.58	6.06	3.82	0.9819
32	8.50	14.60	6.10	3.98	0.9897
33	8.44	14.37	5.93	4.14	0.9334
34	8.55	14.68	6.13	4.29	0.9426
35	8.40	14.38	5.98	4.45	0.9963
36	8.45	14.56	6.11	4.61	1.0080
37	8.37	14.27	5.90	4.76	1.0028
38	8.32	14.42	6.10	4.92	1.0002
39	8.99	15.02	6.03	5.07	0.9740
40	8.97	14.99	6.02	5.23	0.9976
41	9.08	15.11	6.03	5.39	1.0146
42	8.40	14.44	6.04	5.54	1.0028

8.7 S1: Chromatographic wettability test

Comment: The red samples are samples which were removed due to having abnormally high values from the IC-test.

Thiocyanide					
Glass number	Before [g]	After [g]	Wt fluid [g]	PV injected*	C/Co
1	8.39	13.25	4.85	0.04	0.0000
2	8.44	13.25	4.80	0.16	0.0000
3	8.42	13.25	4.82	0.28	0.0000
4	9.03	13.85	4.81	0.41	0.0000
5	8.42	13.26	4.83	0.53	0.0000
6	8.44	13.28	4.83	0.66	0.0000
7	9.12	13.96	4.83	0.78	0.0000
8	8.47	13.31	4.83	0.90	0.0900
9	8.44	13.30	4.85	1.03	0.6364
10	9.61	14.45	4.83	1.15	0.9678
11	8.35	13.18	4.82	1.28	0.9985
12	9.07	13.93	4.85	1.40	0.9941
13	9.70	14.52	4.81	1.53	0.9963
14	8.37	13.22	4.84	1.65	1.0315
15	9.00	13.84	4.83	1.78	1.0007
16	9.03	13.90	4.86	1.90	1.0161
17	9.04	13.85	4.80	2.03	1.0007
18	8.49	13.33	4.83	2.15	0.9985
19	9.08	13.91	4.82	2.27	1.0249
20	8.50	13.30	4.79	2.40	0.9920
21	9.09	13.92	4.82	2.52	0.9985
22	8.93	13.74	4.80	2.65	1.0117
23	9.07	13.90	4.82	2.77	0.9920
24	9.13	13.95	4.81	2.89	0.9832
25	8.47	13.30	4.82	3.02	0.9854
26	8.46	13.28	4.81	3.14	0.9963
27	8.47	13.29	4.81	3.27	1.0029
28	9.03	13.87	4.83	3.39	1.0029
29	9.47	14.29	4.81	3.51	1.0139
30	9.01	13.84	4.82	3.64	1.0271
31	8.99	13.81	4.81	3.76	1.0139
32	9.08	13.88	4.79	3.89	0.9963
33	8.86	13.67	4.80	4.01	1.0051
34	8.45	13.28	4.82	4.13	0.9920
35	8.35	13.20	4.84	4.26	1.0029

36	9.55	14.40	4.84	4.38	1.0271
37	8.42	13.26	4.83	4.51	0.9920
38	8.47	13.30	4.82	4.63	0.9941
39	9.02	13.86	4.83	4.76	1.0073
40	9.02	13.88	4.85	4.88	1.0315

Sulfate					
Glass number	Before [g]	After [g]	Wt fluid [g]	PV injected*	C/Co
1	8.39	13.25	4.85	0.04	0.0000
2	8.44	13.25	4.80	0.16	0.0000
3	8.42	13.25	4.82	0.28	0.0000
4	9.03	13.85	4.81	0.41	0.0000
5	8.42	13.26	4.83	0.53	0.0000
6	8.44	13.28	4.83	0.66	0.0000
7	9.12	13.96	4.83	0.78	0.0000
8	8.47	13.31	4.83	0.90	0.0000
9	8.44	13.30	4.85	1.03	0.0320
10	9.61	14.45	4.83	1.15	0.2343
11	8.35	13.18	4.82	1.28	0.6124
12	9.07	13.93	4.85	1.40	0.7641
13	9.70	14.52	4.81	1.53	0.8627
14	8.37	13.22	4.84	1.65	0.9172
15	9.00	13.84	4.83	1.78	0.9665
16	9.03	13.90	4.86	1.90	0.9798
17	9.04	13.85	4.80	2.03	0.9705
18	8.49	13.33	4.83	2.15	0.9519
19	9.08	13.91	4.82	2.27	0.9865
20	8.50	13.30	4.79	2.40	0.9732
21	9.09	13.92	4.82	2.52	0.9825
22	8.93	13.74	4.80	2.65	0.9519
23	9.07	13.90	4.82	2.77	0.9838
24	9.13	13.95	4.81	2.89	0.9811
25	8.47	13.30	4.82	3.02	1.0104

26	8.46	13.28	4.81	3.14	0.9971
27	8.47	13.29	4.81	3.27	1.0118
28	9.03	13.87	4.83	3.39	0.9825
29	9.47	14.29	4.81	3.51	0.9984
30	9.01	13.84	4.82	3.64	1.0011
31	8.99	13.81	4.81	3.76	0.9971
32	9.08	13.88	4.79	3.89	1.0051
33	8.86	13.67	4.80	4.01	0.9945
34	8.45	13.28	4.82	4.13	0.9771
35	8.35	13.20	4.84	4.26	0.9785
36	9.55	14.40	4.84	4.38	1.0024
37	8.42	13.26	4.83	4.51	1.0131
38	8.47	13.30	4.82	4.63	1.0051
39	9.02	13.86	4.83	4.76	0.9984
40	9.02	13.88	4.85	4.88	1.0011