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Abstract

The initial wetting condition of the reservoir rock is fundamental in the advanced oil recovery methods by waterflooding, in particular, in Smart Water EOR. The wettability alteration of the rock surface is induced by several parameters include the ionic composition of the injected brine, the polar components of crude oil, the mineralogy of the rock surface, and the temperature. Experimental studies have revealed that the surface active-components in crude oil, such as carboxylic acids, is the main influence on initial wettability. Restoring the initial wetting of the core to representative condition as reservoir is known to be challenging process because the wettability of the rock may have altered during and after the core sampling. Optimal core restoration procedure that reproduces reservoir wettability is essential when core experiments are performed in the laboratory.

This work is related to the effect of initial wetting on oil recovery, core restoration and core cleaning. The oil recovery from imbibition tests were compared to evaluate the correlation between initial wetting and oil recovery. Stevns Klint outcrops chalk material has been used in this experiment, with initial water saturation of 10%. The restored cores were flooded with crude oil (AN=0.5mg KOH/g, BN=0.23mg KOH/g) and spontaneous and forced imbibition test and Chromatographic wettability test were performed on the core at 50 °C to analyze the initial wettability. In previous experiment, the core was flooded with 2.5PV of crude oil after mild cleaning and the restored reservoir cores behaved less water-wet. 1PV of crude oil was injected to minimize the effect of wettability alteration by crude oil, in this study.

It is confirmed from the imbibition tests that the oil recovery increases as the wetting of the core behaves more water-wet. The effect of mild core cleaning on the wettability of restored core have been investigated. The experiment shows that initial wetting of the chalk core can be reproducible with mild core cleaning when the reduced amount of crude oil is introduced to the core after restoration. The result in spontaneous imbibition on second restoration cores gave 1.4% to 2.1% change in oil recovery.

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Symbols and Abbreviations

\emptyset	Porosity, %
θ	Contact Angle
σ	Interfacial Tension, mN/m
A	Area between the SCN^- and SO_4^{2-} curves
A_{Heptane}	Area between the SCN^- and SO_4^{2-} curves using heptane as oil phase – representing a completely water-wet system
AN	Acid Number, mg KOH/g
BN	Base Number, mg KOH/g
CWT	Chromatographic Wettability Test
D	Diameter, cm
EOR	Enhanced Oil Recovery
FI	Forced Imbibition
FW	Formation Water
I_{cw}	Chromatographic Wettability Index
I_w^*	Amott Water Index
k	Permeability, mD
L	Length, cm
OOIP	Original Oil In Place
P_c	Capillary Pressure
PV	Pore Volume
PV/D	Pore Volume per day
SI	Spontaneous Imbibition
SK	Stevens Klint Chalk
SW	Sea Water
SW0T	Sea Water without Tracer and Sulfate
SW1/2T	Sea Water contains Tracer and Sulfate
S_{or}	Residual oil saturation
S_w	Water saturation
S_{wi}	Initial water saturation
T	Temperature, °C
USBM	United States Bureau of Mines
VB0S	Vallhal Formation Water without Sulfate
VF	Viscous Flooding

1 Introduction

Carbonate reservoirs account for about 60% of the world's oil reserves and the economic significance of carbonate reservoirs is enormous (Vissapragada et al., 2000). These carbonate reservoirs are described as among the most complex reservoirs to interpret and characterize due to its heterogeneity and complexity. The main features of carbonate reservoir are extensively fractured, unfavorable wettability and low permeability which lead to a low ultimate recovery by a conventional waterflooding method. Thus, a considerable amount of original oil remains trapped in the reservoir, where the Enhanced Oil Recovery on such reservoirs is regarded as a great promise.

Waterflooding is a cheap oil recovery process compared to other chemical flooding and is by far the most widely applied method for improving the oil recovery. Furthermore, it has been researched that the oil recovery can be improved by adjusting the composition of injected water which is called Smart Water flooding. The aim of the Smart Water flooding is to improve oil recovery by wettability alteration. Initial wetting condition of the carbonate rock is important parameters that governs the capillary forces and affect the oil recovery ultimately. In the years that followed, many researchers (Webb et al., 2005; Austad et al., 2005; Zhang et al., 2006; Strand et al., 2006; Zhang et al., 2007; Fathi et al., 2011; Fernø et al., 2001) further investigated the mechanism of the initial wetting and wettability alteration on carbonate reservoirs. Experimental work on the initial wetting of the carbonate reservoir is necessary to examine this impact on oil recovery and serve as additional knowledge to the already existing literature on wetting of the chalk.

1.1 Oil recovery

Traditionally, the oil recovery process has been divided into three different stages as follows: primary recovery, secondary recovery, and tertiary recovery processes. It refers to chronological stages of oil recovery behind its name.

Primary recovery is the initial stage of oil production, in which naturally existing energy displaced hydrocarbon from the reservoir. The initial pressure in the fluids occupying the pore space in a reservoir is often higher than the hydrostatic pressure; therefore, by opening a well, the pressure at its bottom is reduced, thus driving reservoir fluids towards the well (Baviere, 1991). This naturally existing energy includes the expansion of reservoir fluids, solution gas drive, gas cap drive, water drive and gravity drainage that leads to depletion of pressure in the reservoir.

Without external forces, the primary depletion only produces 10 to 30% of OOIP (Shah, 1981).

Secondary recovery is applied after primary recovery, as the pressure of the reservoir declines. In secondary oil recovery, external fluids such as natural gas or water are injected to re-pressurize the reservoir and displace oil towards the production wells. After the secondary recovery stage, the recovery factor is usually 30-50 percent of the original oil in place (Castor et al., 1981).

After secondary recovery became uneconomical or ineffective, tertiary recovery is applied to displace additional oil by using miscible gases, chemicals or thermal. Since the total oil production by primary and secondary methods is generally less than 50% of the original in place, the potential target for tertiary recovery is greater than the reserves that can be produced by conventional primary and secondary methods (Donaldson et al., 1985).

Oil recovery processes mentioned above which is primary, secondary and tertiary recovery were demonstrated as three successive stages. However, in many cases, those recovery processes are not necessarily conducted in a specific order.

Tertiary recovery process can also be processed in second order depending on a characteristic of tertiary process and economic reasons. For example, if a waterflood before application of the tertiary process would diminish the overall effectiveness, then the waterflooding stage might reasonably be bypassed (Green and Willhite, 1998).

From this case, it is confirmed that recovery processes do not need to be applied in chronological orders. Tertiary recovery process can be conducted at the beginning of the production stage or at the final stage as well as other stages of the processes.

1.2 Definition of Enhanced Oil Recovery

The difficulty of using the name of the chronological order of recovery processes, the term 'Enhanced Oil Recovery (EOR)' had been more widely used in the oil industry. Hence, it is more practical to divide oil recovery processes into primary, secondary and EOR processes rather than using the term tertiary recovery. Baviere, 1991, defines the aim of EOR is to increase ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents, oxidizers, and heat carriers, in order to induce new mechanisms for displacing oil. There is another similar term Improved Oil Recovery (IOR), which encompasses all types of improvements that increase recovery, such as improved flow assurance,

drilling, or reservoir processes. IOR indicates a broader concept of oil recovery which includes EOR. The principles of EOR can be split into two methods; to improve microscopic sweep efficiency (displacement efficiency) and to improve macroscopic sweep efficiency (volumetric sweep efficiency). This will be discussed further in the following section.

1.3 EOR in Carbonates

A considerable portion of the world's oil and gas are trapped in carbonate reservoirs. However, oil recovery from carbonate reservoirs is less than 30% due to the fractured formation, oil-to-mixed wet rock properties, low permeability and formation heterogeneity. The properties of carbonate reservoir will be discussed further in following section 3 Water-based EOR in Carbonates. Carbonate reservoirs also have a complex pore network which can be divided into three types: i) Connected porosity which is porosity between carbonate grains, ii) Vugs which are unconnected pores made as water dissolves the calcite during diagenesis, iii) Fracture porosity resulting from stresses following deposition (Sheng, 2013). With these three types of porosities, carbonate reservoirs have a very complex path for fluids and it also affects the productivity of the well. As previously mentioned in the chapter above, EOR methods improve microscopic sweep efficiency and eventually enhance the fluid flow in reservoir matrix. However, the complexity of the system limits EOR in carbonate reservoirs because of both technical and economic reasons.

The most commonly used recovery methods in carbonate reservoirs are primary recovery, waterflooding and CO₂ flooding with infill drilling. Furthermore, there are several EOR strategies which are being researched to find alternatives that increase the oil recovery economically. CO₂ flooding is the most common EOR process in carbonate reservoirs in the US mostly because of the availability of low-cost CO₂ in that region (Manrique et al., 2006). Chemical flooding is used to reduce the interfacial tension and increase the displacement efficiency. Chemical flooding in carbonate reservoirs has been focused on Surfactant flooding. The main objective of surfactant flooding is the wettability alteration and IFT reduction to reduce the capillary pressure for entrapped oil (Lake, 2010; Seethepalli et al., 2004).

Wettability alteration method can be applied on carbonate reservoirs since carbonate reservoirs are typically less water-wet. When the wettability of the rock alters from oil-wet to water-wet, water imbibes into the reservoir matrix and displaces oil. An emerging EOR method in wettability alteration is to use "Smart Water" with different ionic composition and optimal salinity. This is the main focus

of the present study, where its applicability is well covered in many works of literature (Zhang et al., 2006; Zhang et al., 2007; RezaiDoust et al., 2009; Fathi et al., 2011; Seyed et al., 2012; Adepapo et al., 2014; Puntervold et al., 2015).

2 Objectives

Understanding the initial wetting in carbonate is important in optimizing oil recovery from reservoirs. Especially, the oil recovery during imbibition process is influenced by the initial wetting of the rock surface. Therefore, it is important to restore initial wettability of core in laboratory work that represents the initial wetting conditions of a reservoir.

The scope of this thesis is to investigate the effect of mild core cleaning using kerosene and heptane on the initial wettability of the reservoir cores during core restoration. Particularly, the initial wetting of the core and the oil recovery at the initial wetting will be analyzed and the reproducibility of initial wetting of the core will be evaluated. It is certain that initial wetting affects the oil recovery in spontaneous imbibition by altering capillary forces. Does it also affect the ultimate oil recovery after Forced Imbibition? The initial wetting on viscous flooding and the ultimate oil recovery will be discussed further throughout this study.

Further study is conducted to confirm how the wettability affects the oil recovery and to investigate the heterogeneity of chalk and its effect in oil recovery. There are several parameters govern the initial wetting in carbonate reservoirs which are the polar acidic components, properties of injected brine, ionic composition and salinity, etc. Polar acidic components in oil content which can be expressed as Acid Number (AN) will be briefly discussed.

3 Fundamentals

In this section, some of the fundamental concepts of oil recovery will be introduced that can help to understand the subject matter of this thesis to build a foundation for sufficient understanding. The focus is given to defining displacement forces in oil recovery of the reservoir and also wettability of the system. All concepts in this chapter are presented with the assumption of a two-phase oil-water fluid system.

3.1 *Displacement forces*

The most important forces determining the flow of oil and water in oil production processes are viscous forces, gravity forces and capillary forces (Morrow, 1979). When there is not enough energy to displace oil after primary recovery, secondary or EOR process take place. There are two main mechanisms that drive oil production in these stages; spontaneous imbibition and/or forced imbibition. Spontaneous imbibition is where capillary pressure causes water to invade into water-wet and mixed-wet rock containing oil (Tavassoli et al., 2005). Through spontaneous imbibition, excess oil is drained from the rock. The main forces which dominate spontaneous imbibition are capillary forces and gravity forces. Forced imbibition, which is also called viscous flooding, is where the displacement of the oil from a porous medium or capillary tube under an externally applied pressure difference (Hammond and Unsal, 2009). Viscous force is the main force applied in forced imbibition.

3.1.1 *Gravity forces*

One of the important factors in oil drainage from the reservoir is gravitational segregation caused by the density difference between displacing and displaced fluids (Butler and Jiang, 1996). The density difference may lead to overriding of the injected gas or the under riding of injected water; which in the end, can reduce the vertical sweep efficiency. The pressure difference between oil and water from gravity effect is given by:

$$\Delta P_g = \Delta \rho * g * H \quad (3.1)$$

Where,

- ΔP_g Pressure difference over the oil-water interface due to gravity (Pa)
- $\Delta \rho$ Density difference between oil and water (Kg/m³)

g	Gravitational acceleration constant (m/s ²)
H	Height of the fluid column (m)

In reservoirs, gravity played a significant role in the accumulation of hydrocarbons, however, in the production stage, it can be an obstruction. Gravity leads to segregation of injected water or fluids in the reservoir and to flow through it in fingering, bypassing the hydrocarbon still existed (Hales and Cook, 2011). It needs to be considered how to reduce gravity segregation by optimal injection strategies or mobility control.

3.1.2 Capillary forces

Capillary pressure is defined as the pressure difference across the interface between two immiscible fluids. When there are two immiscible fluids in a capillary tube, one of them is called the wetting fluid which has a better affinity to the tube surface and the other one is the non-wetting fluid. Capillary pressure is given by;

$$P_c = P_{nw} - P_w \quad (3.2)$$

where P_c is the capillary pressure, P_{nw} , P_w is the pressure of non-wetting and wetting phase, respectively. For oil-water two phase system, oil is classically considered as a non-wetting phase and water as a wetting phase. Furthermore, the capillary pressure in the oil-water system can be expressed as:

$$P_c = P_o - P_w = \frac{2\sigma\cos\theta}{r} \quad (3.3)$$

Where,

P_c	Capillary pressure (Pa)
P_o, P_w	Pressure of the oil and water across the interface, respectively (Pa)
σ	Interfacial tension (IFT) (N/m)
θ	Contact angle (°)
r	Radius of the pore (m)

Capillary pressure is one of the most important factors in oil recovery efficiency since the capillary pressure of pore throats determines the fluid distributions in the oil reservoir. The effect of capillary pressure differs from fractured or non-fractured reservoirs. In non-fractured reservoirs, strong capillary forces during waterflooding might trap oil and residual oil saturation will eventually become high which reduces the oil production (Strand, 2005). However, strong capillary pressure in a fractured reservoir controls the rate of water uptake from the fracture

network into the matrix, and results in higher displacement efficiency by spontaneous imbibition (Fernø, 2008).

3.1.3 Viscous forces

Viscous forces in a porous medium relate to the magnitude of the pressure drop from the flow of a fluid through the medium (Green and Willhite, 1998). How the fluid flow through the medium; an oil reservoir, is an important concept to understand in oil recovery. The fluid flow in reservoir rock is connected to the rock permeability. Permeability is a measure of the ability of fluids passing through a porous medium. Darcy's equation defines the fluid flow in permeable media which is assumed to be one-dimensional, homogeneous rock formation with a single fluid phase and constant fluid viscosity:

$$q = \frac{kA \Delta P}{\mu L} \quad (3.4)$$

Where,

q	Flow rate of the fluid (m ³ /s)
k	Permeability (m ²)
A	Cross-section area (m ²)
μ	Fluid viscosity (Pa.s)
ΔP	Differential pressure (Pa)
L	Length of the solid (m)

Capillary force and viscous forces govern phase trapping and mobilization in multiphase fluid systems, which also affect microscopic displacement efficiency (Green and Willhite, 1998). In microscopic pore scale, fluid flows when viscous forces dominate the system over capillary force. This competition between viscous and capillary forces is expressed in the concept of capillary number, N_{ca} :

$$N_{ca} = \frac{F_v}{F_c} = \frac{v\mu_w}{\sigma_{ow}\cos\theta} \quad (3.5)$$

Where,

F_v	Viscous force
F_c	Capillary force
v	Interstitial velocity (m/s)
μ_w	Viscosity of water (Pa.s)
σ_{ow}	Interfacial tension (IFT) between oil and water (N/m)

It is more efficient to displace residual oil in the reservoir with a higher capillary number. Chatzis and Morrow (1984) performed an imbibition test and found that in porous media the critical capillary number to mobilize the residual oil is about 10^{-5} . From the equation above, the capillary number can be increased by increasing the velocity or viscosity of the injected fluid or decreasing the interfacial tension between the displacing and displaced fluids.

3.2 Displacement Efficiency

For oil displacement in an ideal EOR process, the overall displacement efficiency (E) is described as a product of macroscopic and microscopic forces (Green and Willhite, 1998; Lake, 2010):

$$E = E_D E_V \quad (3.6)$$

Where, E_D =microscopic displacement efficiency, and E_V =macroscopic displacement efficiency.

The microscopic displacement efficiency is related to how fluid is mobilized or displaced at the pore scale. It is influenced by the interfacial and surface tension, capillary pressure, relative permeability, and wettability. E_D can be expressed as the residual oil saturation, S_{or} , at the contact with the displacing fluid. The macroscopic displacement efficiency is also called sweep efficiency, represents how effective the displacement of the reservoir in volumetric wise. The sweep efficiency is determined by heterogeneities, the mobility ratio between the displacing fluids and displaced fluids, the pattern of injection and production wells, and the type of rock matrix where the oil exists.

Each EOR methods is either to increase the microscopic displacement efficiency in pore scale or to increase the sweep efficiency by increasing the area swept by the injected fluids (Figure 1).

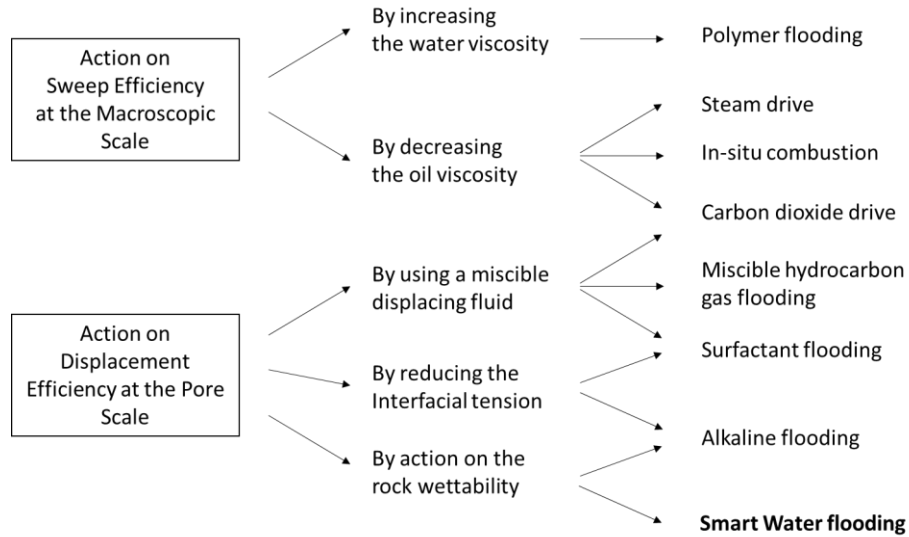


Figure 1 EOR methods acting on the sweep efficiency or displacement efficiency. Redrawn after Baviere, (1999).

3.3 Wettability

Wettability is described as the tendency when one fluid has spread on or adhere to a solid surface in the presence of other immiscible fluids (Craig, 1971). In reservoir rock, the wettability is an important property concerning multiphase flow in porous media. It dictates the physical parameters of the rock such as capillary pressure, relative permeability and fluid distributions. In this chapter, the wettability will be defined and different wettability classification which is observed in reservoir rocks will be demonstrated, and then the methods for wettability measurement will be presented.

3.3.1 Wettability Classification

A general classification of the wetting state of a reservoir is divided into water-wet, oil-wet, mixed-wet, and fractional wettability (Donaldson et al., 2008). In water-wet system, at irreducible water saturation, water is spreading as a wetting phase, be present in the smallest pores and contacts most of the rock surface. The non-wetting phase, oil will be located in the center of larger pores while surrounded by a water film. A rock in water-wet condition, water will spontaneously imbibe to displace oil until a state of static equilibrium is reached between the capillary and surface energy forces (Donaldson et al., 2008). Similarly, in an oil-wet system, the oil will occupy the smallest pores and cover the rock surface, while the water is in

the middle of the larger pores. When this rock in oil-wet condition is flooded with water, the oil will not be displaced efficiently since the oil remains on the rock surface and the water does not penetrate into the smallest pores. The water will mostly flow through the larger pore channels of the rock (Figure 2). A very small oil permeability exists at significantly low saturation due to the uninterrupted oil-wet area in the larger pores of the system (Torrijos, 2017). This explains how the oil recovery by waterflooding processed until reaching low oil saturation (Donaldson et al., 1969; Anderson 1986b).

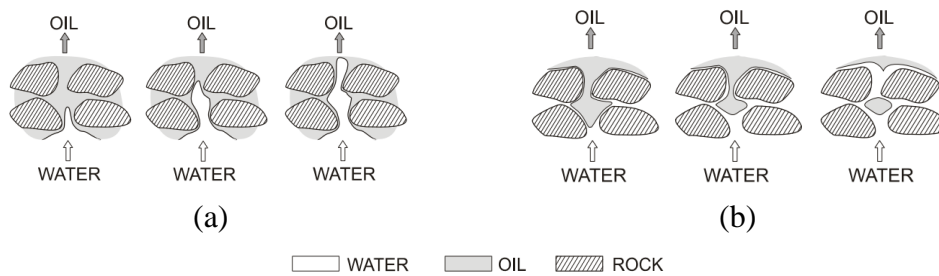


Figure 2 Displacement of oil by water in (a) oil-wet sand, and (b) water-wet sand. (Strand, 2005; Forrest, 1980)

The wettability of rocks could be divided into two main categories; homogeneous and heterogeneous wetting (Anderson, 1986b). Homogeneous wettability refers when the reservoir rock has a uniform wetting throughout the reservoir which could range from strongly water-wet to strongly oil-wet conditions. When the rock does not show a strong preference in wetting, then the rock maintains neutral or intermediate wettability (Anderson, 1986b). Mixed-wet and fractionally-wet are categorized as heterogeneous wettability. The surface of the rock with mixed-wet has oil-wet surface exists in larger pores, while the smallest pores of the rock are water-wet. In some cases, water-wet and oil-wet area are coexisting that the different parts of the rock may have different wetting preferences. It is called fractional wettability where oil-wet or water-wet pores are not related to the pore sizes (Salathiel, 1973; Skauge et al., 1999).

The wettability influences the oil migration from the source rocks to the reservoir rock, and also the efficiency of the oil recovery in waterflooding. Thus, it is important to understand different wettability states in a reservoir to plan a better recovery strategy for the reservoir.

3.3.2 Wettability measurement

A wide variety of methods in wettability measurement have been discussed both in qualitative and quantitative ways. In this section, wettability measurements which are universally used will be described briefly including contact angle, Amott water index, United States Bureau of Mining (USBM) and Chromatographic wettability test.

Contact angle measurements

When measuring the surface wetting condition, the measurement of contact angles is usually involved as the primary data, which indicates the degree of wetting at the intersection of solid and fluids (Yuan and Lee, 2013). For a rock/brine/oil system, Young's equation demonstrates the contact angle in equilibrium with the interfacial/surface tensions between the solid and fluids:

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos\theta \quad (3.7)$$

Where,

- σ_{os} Interfacial tension between oil and solid
- σ_{ws} Interfacial tension between water and solid
- σ_{ow} Interfacial tension between oil and water
- θ Contact angle of the water/oil/solid interface

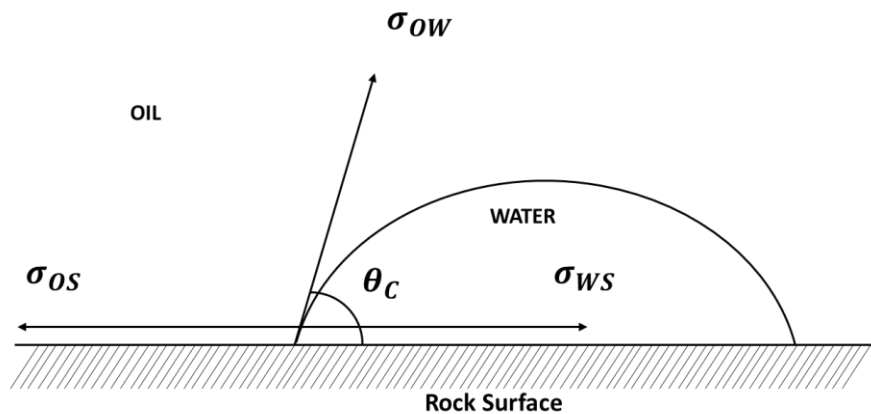


Figure 3 Schematic measurement of contact angle at the water/oil/rock system. Redrawn after Anderson (1986).

The contact angle indicates the wettability of the rock surface. If the rock is preferentially more water wet, a droplet of water is spreading, and the contact angle

is less than 90°. The rock is considered as preferentially oil-wet when the contact angle is greater than 90° and contact between the water droplet and rock surface is minimized. When the contact angle is 90° or close to this value, the surface is known as intermediate or neutral wettability, and both oil and water do not have a strong affinity to the surface (Dullien, 1992).

Especially for pure fluids and artificial cores, the contact angle measurement is the best wettability measurement method, since neither surfactants nor other compounds change the wettability (Anderson, 1986). However, because of adsorption or desorption of minerals in crude oil which could alter the wettability, there are some difficulties in using contact angle method in reservoir cores.

Amott wettability index

The Amott wettability test is used to measure the average wettability of a core which involves spontaneous imbibition (SI) and forced displacement. The principle of Amott method is that the wetting fluid spontaneously imbibes into the core and displace the nonwetting phase (Anderson, 1986). The core is first prepared by centrifuging under brine to achieve residual oil saturation, and the test is conducted by following four steps (Anderson, 1986; Morrow, 1990).

- 1) The core, at residual oil saturation, is immersed in oil and the volume of water displaced during the spontaneous imbibition is measured.
- 2) The core is centrifuged in oil to reach irreducible water saturation, and the total amount of water displaced, including the volume from step 1 is measured.
- 3) Immerse the core, at irreducible water saturation, in brine and record the volume of oil displaced by the spontaneous imbibition.
- 4) The core is then centrifuged in water to achieve residual oil saturation. The total volume of oil produced between both step 3 and step 4 is measured.

The Amott index to water and oil is then defined as follows, respectively:

$$I_w^* = V_{osp}/V_{ot} \quad (3.8)$$

$$I_o^* = V_{wsp}/V_{wt} \quad (3.9)$$

Where,

- I_w^* Amott index to water (displacement-by-water ratio)
- I_o^* Amott index to oil (displacement-by-oil ratio)

V_{osp}	Volume of oil displaced by SI
V_{ot}	Total volume of oil displaced by SI and Forced displacement
V_{wsp}	Volume of water displaced by SI
V_{wt}	Total volume of water displaced by SI and Forced displacement

In strong water-wet cores, most of the oil is displaced by spontaneous imbibition, thus, I_w^* is close to 1, while I_o^* approaches 0. Similarly, in strong oil-wet cores, I_o^* is close to 1 and I_w^* will be 0.

The modified Amott index, which is the Amott-Harvey index, I_{AH} , is more commonly used by researchers. It is defined as the difference between the displacement-by-water ratio and the displacement-by-oil ratio (Morrow, 1990):

$$I_{AH} = I_w - I_o \quad (3.10)$$

This index I_{AH} has a value varies from -1 (strongly oil-wet) to +1 (strongly water-wet). The system is considered as water-wet when $+0.3 < I_{AH} < 1$, intermediate-wet when $-0.3 < I_{AH} < +0.3$, and oil-wet when $-1 < I_{AH} < -0.3$ (Cuiec, 1984).

United States Bureau of Mining (USBM)

Another quantitative method to measure the wettability of the core is the USBM method introduced by Donaldson et al. (1969). This method is relatively fast, and one of its advantages over the Amott method is its sensitivity when it is close to neutral wettability. A minor disadvantage is that the sample for the USBM wettability index should be in plug sized to place it in a centrifuge (Anderson, 1986).

The wettability using USBM is determined by comparing the work required to displace wetting or non-wetting phase with each other. The forced drainage and forced imbibition capillary pressures are measured by centrifuging and plotted versus water saturation (Anderson, 1986), and the work necessary is proportional to the area under those capillary pressure curves. If the core is strongly water-wet, most of the water would be displaced by spontaneous imbibition and the area under the forced drainage curve becomes larger than the area under the forced imbibition curve as shown in Figure 4.

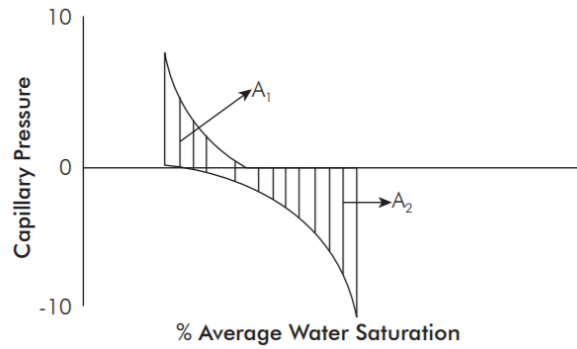
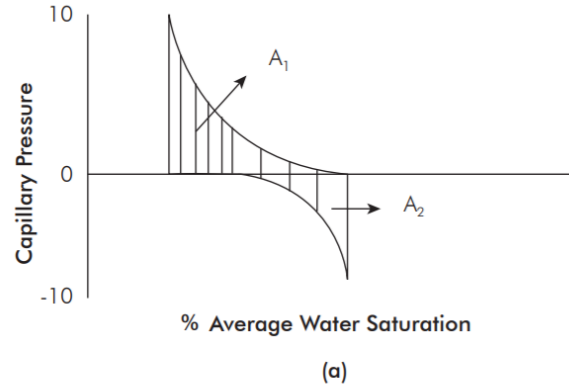


Figure 4 USBM Method to determine wettability.
a) Water wet, b) Oil wet (León-Pabón et al., 2014).

The wettability index (WI_{USBM}) is defined by a logarithmic ratio of the areas under the two capillary pressure curves:

$$WI_{USBM} = \log \frac{A_1}{A_2} \quad (3.11)$$

where A_1 is the area under the forced drainage curve and A_2 is the area under the forced imbibition curve. The USBM wettability index WI_{USBM} has a positive value when the sample is relatively water-wet and if WI_{USBM} has negative value, the sample is relatively oil-wet. As the absolute value of the index is larger, the greater the wetting preference is.

Chromatographic wettability test

Chromatographic wettability test is recently introduced by Strand et al. (2004) to determine the water-wet fraction of carbonate rock surface. This new method is based on the chromatographic separation between thiocyanate (SCN^-), a non-

adsorbing tracer, and sulfate (SO_4^{2-}), the potential determining ion, at the water-wet areas on the carbonate surface (Strand et al., 2006). The schematic illustration of the chromatographic separation between SO_4^{2-} and SCN^- is shown in Figure 5.

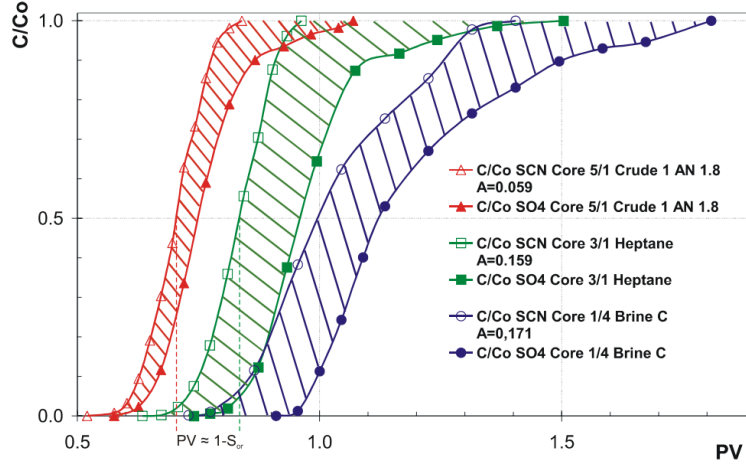


Figure 5 Schematic illustration of the chromatographic separation between SO_4^{2-} and SCN^- (Strand et al., 2006)

SO_4^{2-} can adsorb onto the water-wet sites of the carbonate surface and there will be a delay of sulfate concentration in the effluent. However, SCN^- does not adsorb onto the rock surface and passes through the surface without any retardations. Ionic concentrations of the effluent are measured by Ion Chromatography (IC) and concentration curves of SO_4^{2-} and SCN^- are obtained. The area between these effluent curves of two ions is proportional to the water-wet sites of chalk core. A chromatography wettability index (I_{cw}) is calculated using A_{wet} , the area between the tracer and sulfate curves, and $A_{heptane}$, the areas of separation between the same ions in a completely water-wet system which uses heptane as reference oil:

$$I_{cw} = \frac{A_{wet}}{A_{heptane}} \quad (3.12)$$

The chromatography wettability index (I_{cw}) has a range between 0 and 1, where 0 indicates a completely oil-wet surface, and 1 represents a completely water-wet surface. It is very useful close to a neutral wetting condition which has I_{cw} value near 0.5, however, the limitation is that this method is only applicable to carbonate core material (Strand et al., 2006). Also, since $A_{heptane}$ refers to a completely water-wet condition, there is a difficulty in application this index in reservoir condition.

3.4 Acid number and Base number

Acid number (AN) and Base number (BN) are the main parameters regarding alteration of wettability in specific crude oil (Buckley et al., 1998). A carbonate surface reacts with acidic and basic groups which are the content of crude oil. The acidic components are negatively charged and expressed by carboxyl (COO^-) and the positively charged basic components are given by R_3NH^+ . The carboxylic groups form strong bonds to the positively charged carbonate surface (Zhang et al., 2006), and the amount of carboxylic material can be quantified as an AN (mg KOH/g). The water wetness area in carbonate decreases by increasing AN. This wettability alteration will be discussed in section 3.4. AN and BN of crude oil is measured by potentiometric titration with the unit of mg KOH/g. Spontaneous Imbibition tests on chalk cores with various AN content oil shows the impact of AN on wettability alteration (Figure 6).

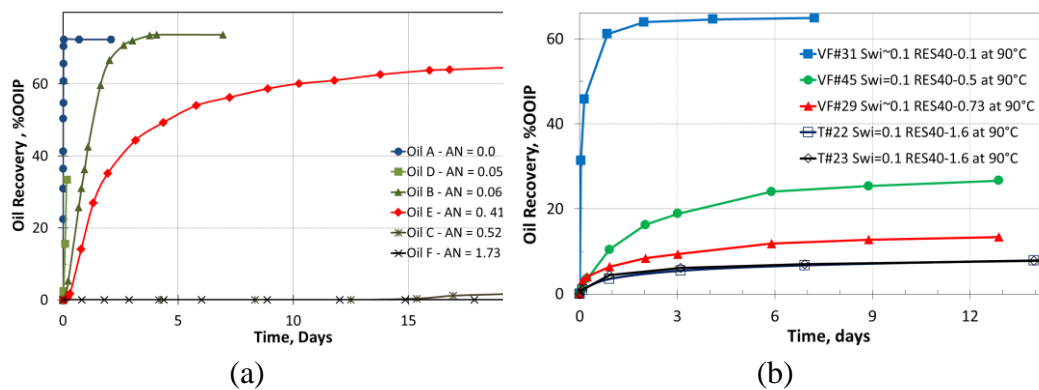


Figure 6 Effect of oil AN on oil recovery from spontaneous imbibition test on chalk cores saturated with (a) different crude oils and (b) different model oils (Standnes and Austad, 2000; Puntervold, 2008).

It is observed that imbibition rate and oil recovery reduce as the AN increases showing that higher AN modifies the mineral surface towards more oil wet (Standnes and Austad, 2000). This also indicates that, in a laboratory, as more crude oil is exposed to the core, more acidic component is introduced to the core and the wettability of the core will become less water-wet.

The effect of basic materials on the wetting conditions in carbonates has not been studied in detail, however, the study by Puntervold et al. (2007) suggests that the natural bases in crude oil may delay or partially prevent the carboxylic material from adsorbing onto the positively charged chalk surface by forming acid-base complexes with the carboxylates. It will be more focused on AN than BN in the following experiment with chalk cores.

4 Water-based EOR in Carbonates

Traditionally, the formation water which has the same composition as the water present in the reservoir is injected in the secondary recovery. Waterflooding improves the oil recovery with maintaining reservoir pressure and improving sweep efficiency of the reservoir. Smart water EOR is regarded as a tertiary recovery involves injecting modified water which has a different ionic composition from the formation water. Smart water can be applied to both in Sandstone and Carbonate rocks with wettability alteration, however, the mechanisms of alteration in each rock are very different. It is fundamental to understand initial wetting and wettability alteration process in oil recovery with waterflooding. Carbonate rock is the focus of this study and the main mechanisms in oil recovery in carbonates will be introduced in the following chapter.

4.1 *Carbonate reservoirs*

Schlumberger Market Analysis (2007) reported that more than 60% of the world's oil and 40% of the world's gas reserves are trapped in carbonate reservoirs. Carbonate reservoirs are porous and permeable rock formations which are divided into limestone, chalk, and dolomite. Usually, carbonate reservoirs are in oil-wet/neutral-wet condition and also known as naturally fractured reservoirs.

The fractures exist in carbonate reservoirs are very complex which are in different sizes and lengths ranging from microscopic fissures to kilometer sized features. Consequently, it is hard to predict the movement of oil, gas or other injected fluids in the fractures. Fractures in carbonate reservoirs create complex flow networks, and it is important to understand its physical properties which vary in every fracture. For instance, in low porosity and low permeability carbonate rocks, the flow of the fluid in the reservoir may be completely dependent on the fracture network, while the matrix only plays a source role when natural gas flows in tight sand formations (Manrique et al., 2006).

The ultimate oil recovery of carbonate reservoirs is less than 30% because of these factors; oil-wet/mix-wet rock formation, low permeability, fractures formation, and heterogeneous rock properties. Thus, the EOR potential in these carbonate reservoirs is very high and in a great challenge.

4.2 Wettability alteration by crude oil

Originally, the reservoir rocks are assumed to be strongly water-wet, and the deposition of organic material and the adsorption of polar compounds in crude oil could alter the wettability of the system (Anderson, 1986). The carbonate rock surface is generally positively charged and in slightly basic pH ($\text{pH} < 9.5$) conditions (Zhang, 2006; Pierre et al., 1990; Austad et al., 2005) and thus, it is sensitive to negatively charged surface-active materials. If the oil-water interface is negatively charged due to the content of carboxylic material in crude oil, then the water film becomes unstable, and oil will have a contact to the carbonate surface (Zhang, 2006). The wettability of the carbonate surface is then altered by adsorption of the carboxylic group onto the rock surface.

4.3 Wettability alteration in Carbonates by Smart Water

“Smart Water” is the adjusted/optimized injected fluid in ion composition that modifies the initial wetting condition with equilibrium in the rock, brine and crude oil system (Austad, 2012). The principle of smart water EOR method is to alter the wettability of the system that improves oil recovery by affecting capillary pressure and relative permeability of water and oil. This technique is environmentally friendly, does not have injection problems, and also costs less since no additional expensive chemicals are required. Smart water should be injected from the beginning of the water flooding process to be smartest, from an economical point of view (Austad, 2012).

The wettability alteration process is governed by the interaction between determining ions Ca^{2+} , SO_4^{2-} and the carbonate surface. The mechanism of Smart Water in carbonates has been researched in many works of literature (Strand et al., 2006; Zhang et al., 2007; Strand et al., 2008; Fathi et al. 2010; Austad, 2013) and a schematic representation is shown in Figure 7.

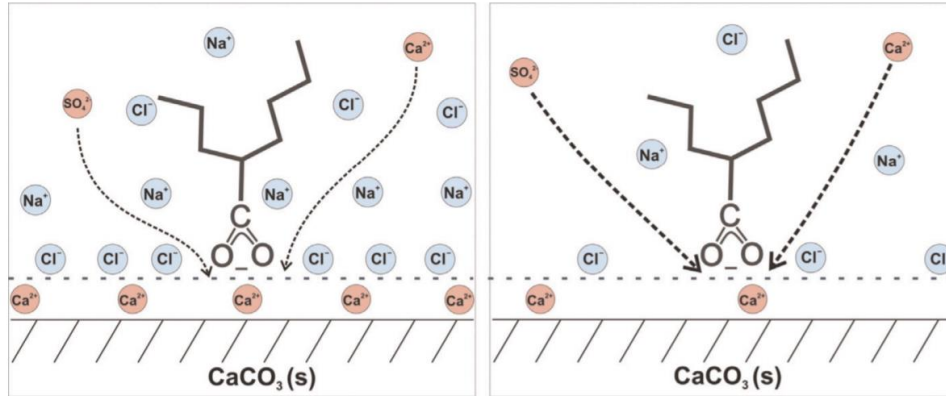


Figure 7 Schematic mechanism of wettability alteration at carbonate surfaces (Punternold, 2015).

In the initial state of rock, brine, and oil system, the oil-water interface is negatively charged from dissociation of carboxylic material from crude oil (Zhang et al., 2006). On the other hand, the interface between rock and water is positively charged due to the high concentration of the Ca^{2+} ion in the initial brine. The carboxylic groups in crude oil which are negatively charged then are adsorbed strongly onto the chalk surface, thus, the water wetness decreases drastically. When seawater (SW), where the concentration of SO_4^{2-} is about twice the concentration of Ca^{2+} , is injected, SO_4^{2-} adsorbs onto the chalk surface. The adsorption of sulfate onto the water-wet sites of the chalk surface decreases the surface charge, which will increase the adsorption of Ca^{2+} and release negatively charged carboxylic materials (Zhang et al., 2006; Zhang and Austad, 2006).

4.4 Initial wetting condition of Carbonate

Initial wetting condition of the rock is an essential property to achieve a successive oil recovery from carbonate reservoir. For naturally fractured carbonate reservoirs, especially, capillary forces are the main driving force to displace oil into the fracture networks, thus, initial wetting condition should be considered. The initial wetting is established by the chemical interaction between brine, oil, and rock over millions of years.

It is generally believed that most carbonate reservoirs to be oil-wet or have neutral wettability. The wettability of 50 oil producing reservoirs is evaluated by contact angle measurement in a laboratory by Treiber et al. (1972). Of the carbonate reservoir, it is shown that 84 percent of carbonate reservoirs are oil-wet, 8 percent are intermediate (neutral), and 8 percent are water-wet. Of all the reservoir that is

tested, carbonates constitute 45 percent of the reservoir systems, while they constitute 58 percent of those found to be oil-wet (Treiber et al., 1972). Similarly, Cuiec (1984) examined and reported the wettability of 15 carbonate reservoir cores from three different continents; Europe, North Africa and the Middle East. The result shows that 50 percent of the tested cores are oil-wet, 42 percent are intermediate, and only 8 percent are water-wet.

It is demonstrated that the majority of carbonates are preferentially oil-wet through these experiments on the carbonate cores from across the world. Therefore, wettability alteration on carbonate reservoirs is one of the driving mechanisms to displace the residual oil by altering the wetting preference from oil-wet to water-wet.

Besides these determining ions Ca^{2+} and SO_4^{2-} , the effect of Mg^{2+} ions on smart water mechanism also has been studied. Zhang et al. (2007) showed that Mg^{2+} in seawater substitutes Ca^{2+} at the chalk surface at high temperature. At low temperature, Ca^{2+} has a stronger affinity than Mg^{2+} in adsorption onto the chalk surface, however, Mg^{2+} substitutes Ca^{2+} at high temperature. Adsorption of SO_4^{2-} on the surface increases as the temperature increases that the efficiency of wettability alteration increases. The experiment result of the spontaneous imbibition tests at high temperature is presented in Figure 8.

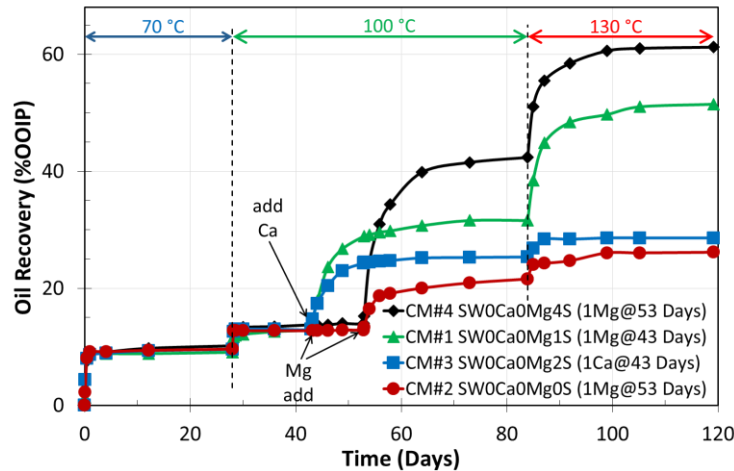


Figure 8 SI tests at different temperature with modified brine in different ion composition. Mg^{2+} or Ca^{2+} was added later on with a concentration of seawater concentration (Zhang et al., 2007).

These interactions between determining ions Ca^{2+} , Mg^{2+} and SO_4^{2-} release the carboxylic materials from the chalk surface which result in a positive effect on capillary forces and improving spontaneous imbibition of water into the matrix.

4.5 Effect of wetting on oil recovery during core flooding and forced imbibition

The generally accepted knowledge in the oil industry is that the ultimate oil recovery is influenced by the reservoir wettability, and that the optimal oil recovery or the lowest residual oil saturation (S_{or}) are observed at slightly water-wet conditions, in line with the work published by Jadhunandan and Morrow (1995).

The maximum oil recovery is found at the slightly water-wet condition which is close to the neutral wettability (Figure 9(b)).

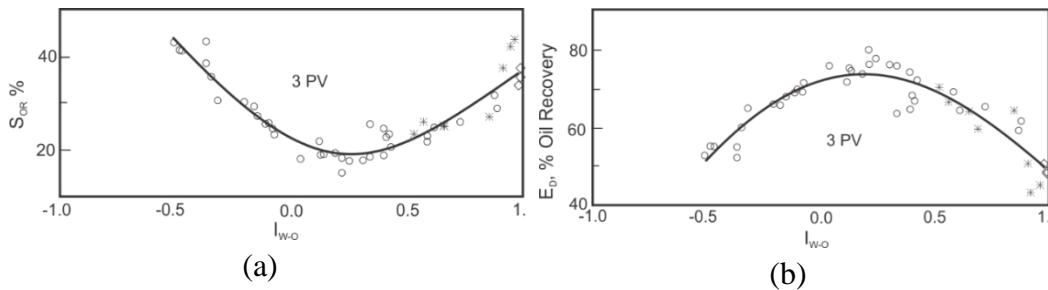


Figure 9 Oil recovery experiments on restored Berea sandstone gave at slightly water-wet conditions (Amott Harvey Index, I_{w-o}) and (a) lowest S_{or} and (b) highest oil recoveries (Jadhunandan and Morrow, 1995).

However, the experiment by Puntervold (2008) indicates the different influence of initial wetting on oil recovery (Figure 10)

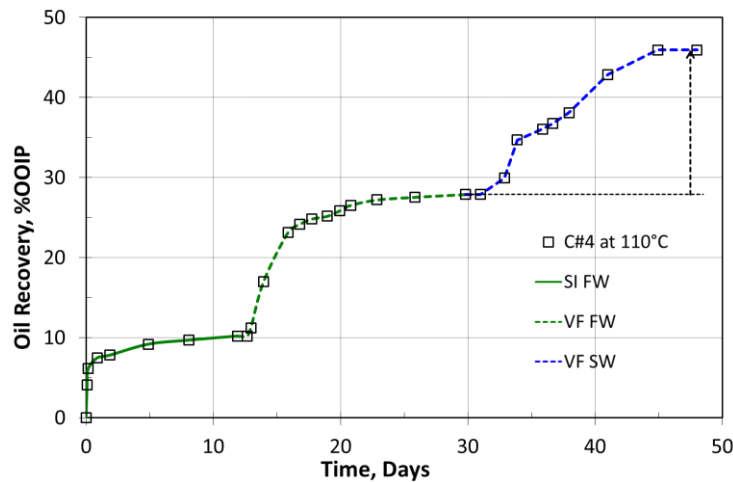


Figure 10 Oil recovery from the core C#4 at 110 °C by spontaneous and forced imbibition. The SW is injected from 30 days after flooded with FW. $S_{wi}=0.1$ and $AN=1.9\text{mg KOH/g}$ (Puntervold, 2008).

First, the spontaneous imbibition test with FW was performed and then forced imbibition with FW and then SW were conducted on the core. From forced imbibition test, SW acted as a smart water generating wettability alteration toward more water-wet conditions. It gave an improvement in oil recovery which is not linked to the research by Jadhunandan and Morrow (1995). In this study, the experiment to confirm the effect of wetting on oil recovery during forced imbibition was investigated and it will be further stated in the result of experiment and discussion.

4.6 Mild core cleaning and core restoration

The core samples are commonly cleaned to a completely water-wet state prior to core restoration (Shariatapanahi et al., 2012). During the cleaning procedure, the solvent can alter the initial wettability of the core in a significant way. Several restoration methods exist and are used in industry. Many procedures include an organic solvent such as toluene and methanol to remove surface-active components completely. In this experiment, mild core cleaning is used as a restoration method. The aim of mild cleaning is to preserve the surface-active components which influence the initial wettability of the reservoir instead of removing them (Hopkins, 2017). In previous studies, mild core cleaning method is investigated and compared to the methods using other solvents (Figure 11) (Hopkins et al., 2015; Hopkins et al., 2016).

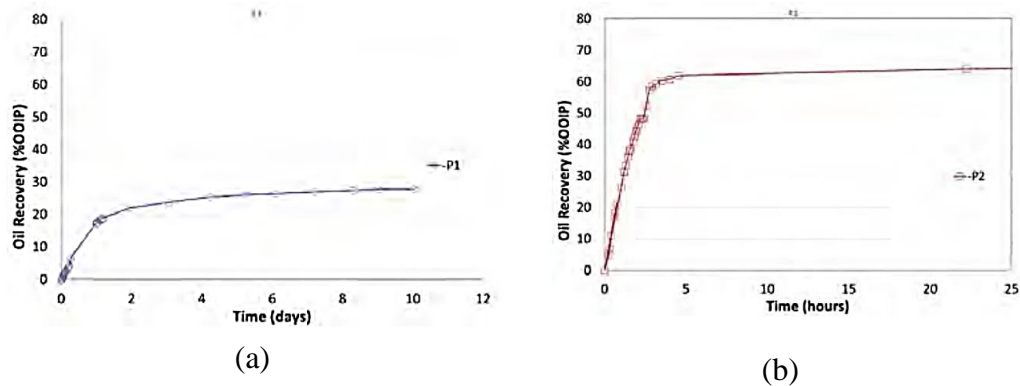


Figure 11 Spontaneous imbibition on (a) kerosene/heptane cleaned core P1 and on a (b) toluene/methanol cleaned core P2. Both cores were 100% saturated with heptane and imbibed with DI water (Hopkins et al., 2016)

5

After core cleaning on 100% heptane-saturated cores, SI shows that both solvent systems removed the polar components and the capillary forces had increased

(Hopkins et al., 2016). It is also observed that the toluene-methanol removed more polar components from the pore surface than the mild cleaning using kerosene-heptane (Figure 11). This makes toluene-methanol solvent system more efficient in cleaning by improving capillary forces while removing polar components from the porous rock surface. On the other hand, on a second core restoration, the core cleaned with kerosene-heptane resulted in less water wetness than the toluene-methanol cleaned core (Hopkins et al., 2016). The initial wetting of the reservoir in core restoration is governed by the desorption of the polar components from the pore surface. Thus, the alteration of initial wetting of the system during core cleaning can be minimized by limiting the kerosene-heptane injection. The reproducibility of chalk cores using mild core cleaning will be further discussed.

5 Material and Methods

The materials and methods used in the experimental work of this thesis are described in this section.

5.1 Materials

5.1.1 Chalk materials

A total of five outcrop chalk cores were used in this study as porous media, which were from Stevns Klint, SK, nearby Copenhagen, Denmark. The cores have high porosity and low permeability in the range of 1-3mD and 46-49%, respectively. The cores were prepared in same dimensions of which lengths were 7cm, and diameters were 3.8cm. The pore volume (PV) was determined by the weight difference between dry and saturated core ($M_{sat} - M_{dry}$) divided by water density (ρ_{brine}), and the porosity (ϕ) was calculated by pore volume divided by bulk volume and presented in percentage as the following equation:

$$\phi = \frac{PV}{V_{bulk}} = \frac{M_{sat} - M_{dry} / \rho_{brine}}{V_{bulk}} \quad (5.1)$$

Core Name	SKS2	SKS4	SKS5	SKS7	K1
Length (cm)	6.92	7.00	6.93	6.93	7.04
Diameter (cm)	3.82	3.80	3.80	3.80	3.80
Porosity (%)	47.6	46.9	48.9	48.9	47.7
Permeability (mD)	0.76	1.56	3.77	1.07	2.27
Pore Volume (ml)	37.73	37.29	38.51	38.48	37.98

Table 1 Core sample data

5.1.2 Crude Oils

A crude oil RES40 with an acid number AN of 2.23 mg KOH/g and a base number BN of 0.89 mg KOH/g is used to obtain RES40-0. 100g of silica gel is added into 500ml of RES40 and stirred on a magnetic stirrer at room temperature for 8 days. The treated crude oil RES40-0 has an AN of 0.01 and a BN of 0.04. The oil RES40-0.5 with AN of 0.5 and BN of 0.23 is used in this study which is prepared by mixing RES40 and RES40-0 in a certain volume ratio of 22% and 78%, respectively. All

the crude oils were centrifuged and filtered through a 5µm Millipore filter prior to introduction into the core materials.

Oil	AN (mgKOH/g)	BN (mgKOH/g)	Density ρ (g/cm ³)	Viscosity μ (cPs)	
				T=25 °C	T=50 °C
RES40-0.5	0.5	0.23	0.81	2.4	1.6

Table 2 Oil properties

5.1.3 Brines

The three brines used in this study VB0S, SW0T, and SW1/2T were prepared in the laboratory with distilled water (DI water) by dissolving specific salts. All the brines were then filtered through a 0.22 µm Millipore filters. The formation water, VB0S used for the chalk studies is based on the Valhall formation located in the North Sea. SW0T and SW1/2T were used for chromatography wettability test, where SW0T does not contain sulfate (SO₄²⁻) and thiocyanate (SCN⁻). SW1/2T contains thiocyanate (SCN⁻) as a tracer and sulfate.

	VB0S	SW	SW0T	SW1/2T	
Ions	<i>mmole/l</i>	<i>mmole/l</i>	<i>mmole/l</i>	<i>mmole/l</i>	
Na ⁺	997.0	450.1	460.0	427.0	
Li ⁺	0.0	0.0	0.0	12.0	
K ⁺	5.0	10.0	10.0	22.0	
Ca ²⁺	29.0	13.1	13.0	13.0	
Mg ²⁺	8.0	44.5	45.0	45.0	
SO ₄ ²⁻	0.0	24.0	0.0	12.0	
SCN ⁻	0.0	0.0	0.0	12.0	
HCO ₃ ²⁻	9.0	2.0	2.0	2.0	
Cl ⁻	1066.0	525.1	583.0	583.0	
Density (gr/ml)	1.041	1.023	1.022	1.022	
Viscosity (cPs)	T=25 °C	1.03	1.03	1.02	1.03
	T=50 °C	0.65	0.72	0.61	0.62
TDS (g/l)	62.83	33.39	33.38	33.38	
pH (bottle)	7.06	7.71	8.01	7.76	

Table 3 Formation and chromatographic brine composition and properties

5.1.4 Additional chemicals

n-Heptane: which is free from surface-active components from the core surface, was used as both a cleaning solvent and as reference oil for completely water-wet core

Kerosene: used for core cleaning of chalk core

Barium Chloride: used to confirm the removal of sulfate during the core cleaning by adding to a sample effluent to observe precipitation of BaSO₄.

5.2 Methods

All core materials need to be prepared in the same procedure in every experiment for the reproducible results and comparative analysis. The main experimental and analytical methods used in the experimental work are briefly described as follows.

5.2.1 Core restoration

The cores were firstly cleaned with DI water to remove dissolvable salts, especially SO₄²⁻ which may affect the wettability. The cores were flooded with 5PV of DI water at the rate of 0.1ml/min. At the end of the flooding, effluent was tested by a batch test using Ba²⁺ to confirm removal of sulfate in the cores. BaSO₄ would precipitate if the sulfate have existed in the effluent. Then, the cores were dried in the oven at 90°C to a constant weight.

5.2.2 Establishing initial water saturation

The initial water saturation of the dried core was established with ten times diluted VBOS brine. The diluted brine (VBOS 10D) was introduced to the core under vacuum, and the core was fully saturated with the initial fluid. The porosity can be calculated from the difference of the weight between dried and saturated core. The core was placed into a desiccator which contains silica gel, to evaporate water until the core reached a target weight of 10% water saturation.

5.2.3 Crude oil saturation and aging

The core with the initial saturation was flooded with 5PV of crude oil with AN 0.5 mg KOH/g in total. First, the core was flooded with 1PV of crude oil in both directions and then to establish uniform wettability, 2PV of oil was injected in each direction at the constant rate of 0.165ml/min. After oil saturation, the core was wrapped with Teflon tape to avoid unrepresentative adsorption of polar components onto the chalk surfaces and introduced in the aging cell. The core was aged for 14 days at 50 °C.

5.2.4 Spontaneous imbibition test

The aged core after 14 days was introduced in a glass Amott cell to perform spontaneous imbibition test (Figure 12). The core was immersed in the formation water VB0S in Amott cell at the specified temperature, 50 °C. The oil produced during this process was collected in the burette, and the volume was measured. The volume of oil produced is plotted versus a function of time.

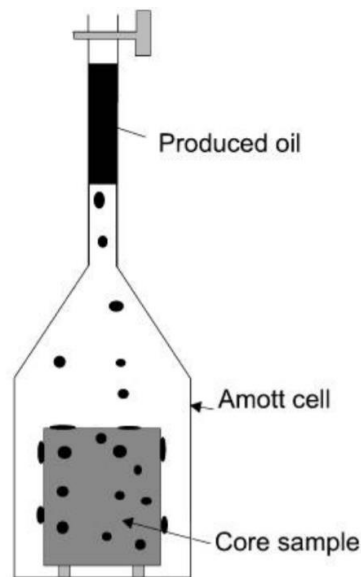


Figure 12 Schematic illustration of spontaneous imbibition in Amott cell (Standnes et al., 2002).

5.2.5 Forced imbibition test

Forced imbibition, also known as viscous flooding is followed by spontaneous imbibition. The core was mounted in a Hassler core holder, and formation water (VB0S) is flooded through the core, forcing the displacement of oil. The forced

imbibition experiment was under an overburden and back pressure of 20 and 7 bars, respectively. Volume oil produced was collected in a burette, and the total oil recovery is recorded as a percentage of original oil in place (%OOIP). Both spontaneous imbibition and forced imbibition experiments are similar that the water is displacing oil in the core. However, in forced imbibition, the formation water is injected through the core and force the displacement of oil, while the core is spontaneously imbibed with water in spontaneous imbibition experiment.

5.2.6 Chromatographic wettability test

The chromatographic wettability test is based on the chromatographic separation of the non-adsorbing tracer thiocyanate (SCN^-) and sulfate (SO_4^{2-}) at the water-wet sites in a core. The principles of the test were explained in section 2.2.1. At room temperature, the chalk core is flooded with SW0T, which is a brine without tracer and sulfate, until it reaches the S_{or} . Then it is flooded with SW1/2T with tracer and sulfate at a constant rate of 0.2 ml/min. The effluent samples during SW1/2T flooding are collected in a fraction collector and the concentration of thiocyanate and sulfate is analyzed with ion chromatography test. The relative ion concentration is plotted against the PV injected. The area between the two effluent curves is calculated using the trapezoid method.

5.2.7 Mild core cleaning

Mild cleaning procedure is applied in this experiment for core restoration to preserve the adsorbed polar components on the surface rather than to remove it. On each core, 10PV of kerosene is flooded to displace oil and water, and 5PV of heptane is used to displace kerosene. Extra 5PV of DI water is flooded after the flooding of kerosene and heptane to remove initial water. The effluent at each flooding stages is collected and the cleaning is confirmed when the effluent becomes transparent (Figure 13).

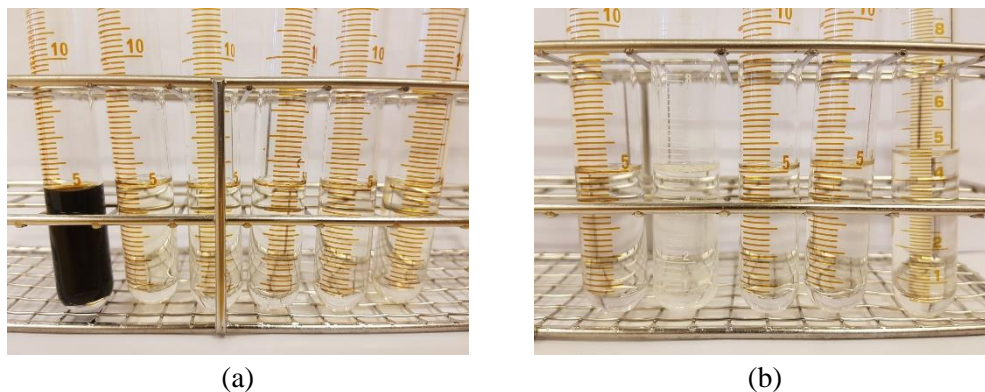


Figure 13 Effluent samples collected from (a) kerosene flooding and (b) heptane flooding of SKS4 during the mild cleaning.

The effluent samples from SKS4 was collected at every 1~2PV of kerosene or heptane was injected (from left to right) (Figure 13). It is observed that the effluents were becoming clearer as the core was cleaned and transparent after all the solvents were flooded.

5.2.8 AN and BN determination

The acidic and basic polar components of crude oil were measured in mg KOH/g. TA Mettler Toledo DL55 auto-titrator was used to determine AN and BN by potentiometric titrations using an internal standard. The modified version of the standard methods developed by Fan and Buckley (2006) was used, which is ASTM2896 for BN titration and ASTM D664 for AN titration. The spiking agents were used to increase the precision of the measurements, which are stearic acid and quinoline, respectively for AN and BN measurement (Fan and Buckley, 2006). Both spiking solutions would increase the inflection points compared to the previous ASTM method.

6 Main results

This research study was conducted to investigate the initial wettability and its alteration of Stevns Klint outcrop chalk cores. How the initial wetting of this chalk material is reproducible through the mild cleaning is examined. In this section, the main results will be presented from the experimental work.

6.1 Initial wetting of a completely water-wet chalk core

The initial water wetness of the outcrop chalk cores is evaluated with the reference core K1. The chalk core with initial water saturation, $S_{wi}=0.1$ is saturated with heptane. The spontaneous imbibition experiment with formation water (VB0S) confirms that the core behaved as a very strong water-wet (Figure 14).

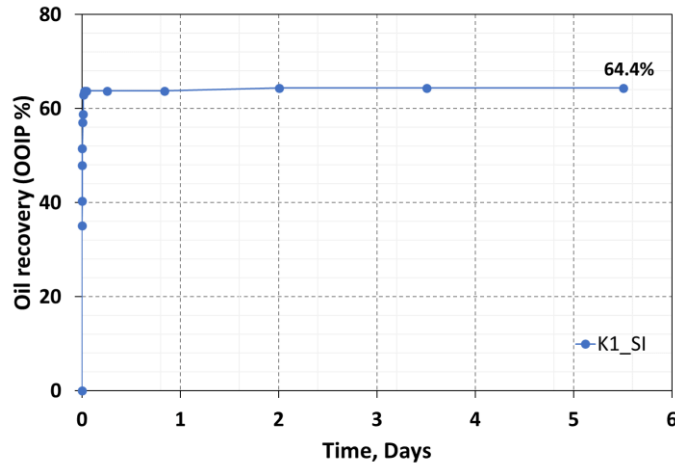


Figure 14 Spontaneous imbibition tests conducted on a completely water-wet chalk core K1 (reference). $S_{wi}=0.1$, and 0.9 saturated with heptane. The core was spontaneously imbibed with DI water at room temperature.

The oil recovery of 63.2% was observed within 30 minutes due to strong capillary forces. Final recovery of 64.4% reached a plateau in 2 days, and no more production is observed for an extra 3 more days. The chromatographic wettability test using SW0T and SW1/2T is performed on the reference core of the same block of Stevns Klint reservoir by Kapstad (2018).

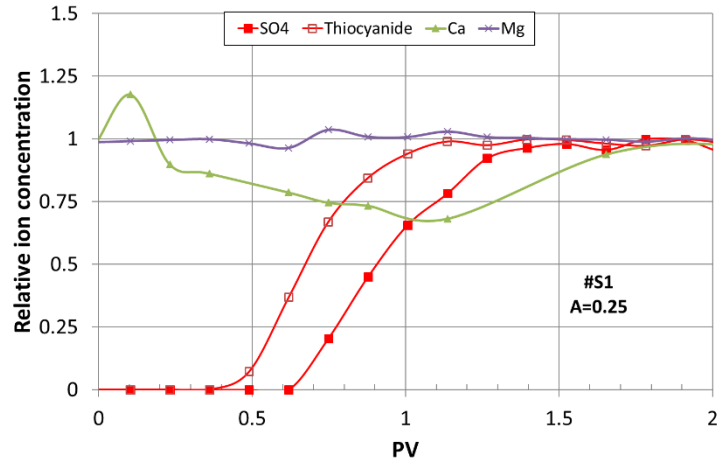


Figure 15 Chromatographic wettability test conducted on reference chalk core S1 from the same block (Kapstad, 2018). The separation area between the two curves was calculated to $A=0.25$.

The area of separation between the tracer (SCN^-) and sulfate (SO_4^{2-}) curves indicates the fraction of the water wet surface area. The reference core S1 is assumed to be the completely water wet core where the Amott water index (I_w^*) is set to be 1 with the assumption of 100% recovery in forced imbibition. A water-wet surface area A_w from chromatographic wettability test is calculated as 0.2493 (Figure 15).

6.2 Initial wetting of restored outcrop chalk core, SKS4

The chalk core sample, SKS4 with initial water saturation of 10% and exposed to crude oil to evaluate initial wetting, oil recovery, pressure drops in forced imbibition and chromatographic wettability index. The results will be delivered in this section.

6.2.1 Oil recovery at initial water saturation

The Stevns Klint core, SKS4, was aged for 14 days after being flooded with $\sim 5\text{PV}$ of the crude oil, RES40-0.5 ($\text{AN}=0.5 \text{ mg KOH/g oil}$).

To evaluate the core wettability and effect of wetting on oil recovery in viscous flooding SI, VF and CWT were conducted for the recovery test (Figure 16). Formation Water (VB0S) is used as an imbibing brine and therefore, no wettability

alteration is expected to take place. Spontaneous imbibition experiments were performed at 50 °C with imbibing of VBOS.

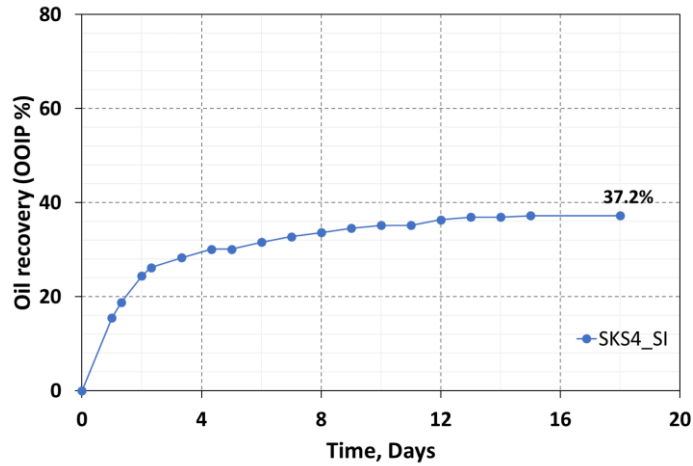


Figure 16 Spontaneous Imbibition tests conducted on chalk core sample SKS4 with FW, VBOS as the imbibing brine. $S_{wi}=0.1$, the core was aged and saturated with RES40-0.5, AN of 0.5mg KOH/g.

The oil recovery from the spontaneous imbibition was 37.2% OOIP and this result will be compared to the oil recovery of other cores and also the water-wetness of the core. The spontaneous imbibition was followed for 18 days, and the rate is slow as the plateau is reached after 15days.

6.2.2 Oil recovery in Forced Imbibition test

FI is performed when there is no extra oil production observed at two different injection rates; 1 and 4PV/D. Viscous forces by injection of FW improved oil recovery significantly.

During the Forced Imbibition test, the pressures are measured at the inlet, where the FW is injected and outlet, where the injected brine and oil which passed through the core is produced. The pressure differences (dP) between the inlet and outlet of the system was also recorded and the results are shown in Figure 17.

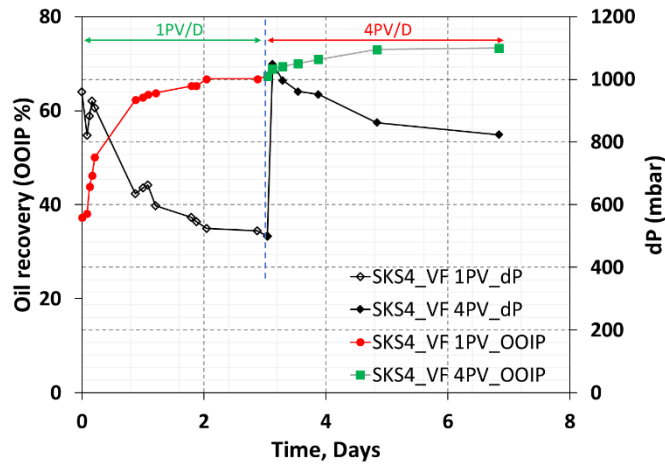


Figure 17 Oil recovery and Pressure drops during the Forced Imbibition tests on chalk core sample SKS4. The FW was injected in two different injection rates which are 1PV/D and 4PV/D.

The recovery for SKS4 showed a recovery of 30.1% OOIP by imbibing FW at a rate of 1PV/D and an increase of 10.0% OOIP at a rate of 4PV/D. The ultimate oil recoveries are 67.3% and 73.3% OOIP, respectively, at the different injection rates.

The pressure difference at the beginning of the injection of FW was 960.2mbar and it is decreased to 499.9mbar at the end of the flow with the injection rate of 1PV/D. When the injection rate was increased to 4PV/D, the pressure difference had a higher value of 1049.0mbar and was decreased to 823.6mbar as the oil recovery reached the plateau. The more oil is produced, the larger pressure drops observed are declined. However, the observed pressure drop was lower than expected where the injection rate became 4 times higher while pressure drop only increased from about 500mbar to 1000mbar.

During the Forced Imbibition test, the effluent samples of the brine after core flooding was collected and pH of the effluent was measured. The observed pH of the effluent was 7.11 in average which became more alkaline after flooding compared to the pH test on the brine VB0S (pH=7.06) from the bottle.

The oil recovery from spontaneous and forced imbibition is shown in Figure 18.

The Amott water index (I_w^*) for the cores is computed as;

$$I_w^* = \frac{SI_{core}}{SI_{ww}}$$

where, SI_{core} is the oil recovery from the spontaneous imbibition of each core and SI_{ww} is the oil recovery in spontaneous imbibition of the completely water-wet core. In this experiment, $SI_{ww}=0.644$ from chapter 6.1 (Figure 14).

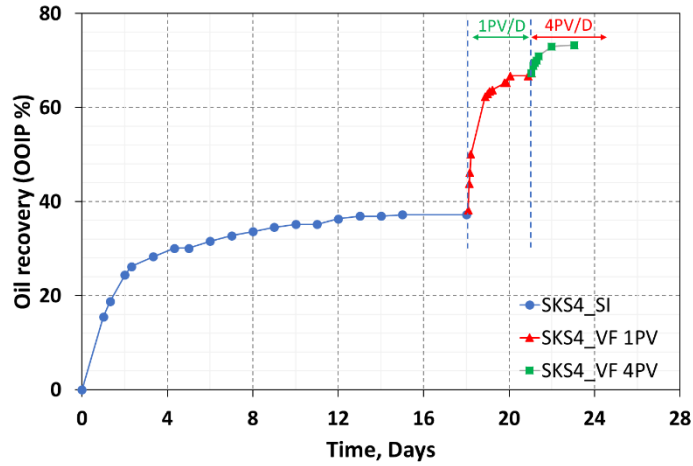


Figure 18 Spontaneous and forced imbibition tests conducted on SKS4 with an ultimate recovery of 73.3% OOIP and $I_w^*=0.58$.

The Amott water index for SKS4 (I_w^*) is calculated to be 0.58 and depicts the core tends to have preferentially water-wet. The wetting of the core will be further analyzed by quantifying the fraction of water-wet surface available in the core by chromatographic wettability test, which will be presented in the next chapter.

6.2.3 Chromatographic wettability test

Following the FI, the core was flooded with SW0T to S_{or} and then flooded with SW1/2T which contains the tracer SCN^- . The effluent was collected and analyzed by Ion Chromatographic to plot the concentration of SO_4^{2-} and SCN^- (Figure 19).

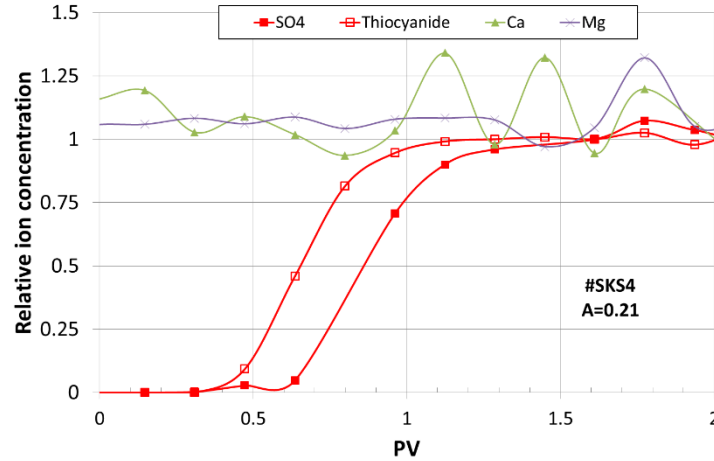


Figure 19 Chromatographic wettability test performed on SKS4 at room temperature. The core was flooded at 0.1ml/min and the effluent samples were collected to analyze the concentration of SO_4^{2-} and SCN^- . $A_{cw}=0.21$.

The area of separation which demonstrates the water-wet area of SKS4 was 0.21 as compared to 0.25 in the completely water-wet core. The chromatography wettability index (I_{cw}) for SKS4, is then evaluated as;

$$I_{CW,SKS4} = \frac{0.21}{0.25} = 0.86$$

which corresponds to preferentially water-wet condition (Strand et al., 2006). The chromatography wettability index has a range between 0 to 1, where 0 indicates a completely oil-wet and 1 as a completely water-wet. The chalk core sample SKS4 was confirmed preferentially water-wet, supporting the spontaneous imbibition results in Figure 16.

6.2.4 Initial wetting after restoration of the core

After chromatography wettability test, the core was mildly cleaned with kerosene and heptane. First, the core was flooded with ~10PV of kerosene to displace the crude oil, ~5PV of heptane to remove kerosene and ~5PV of DI water. The restored core SKS4 with initial water saturation was then saturated with 1PV of crude oil and aged for 14 days at the same condition as the first oil recovery test. The spontaneous imbibition test was conducted, and the result is shown in Figure 20.

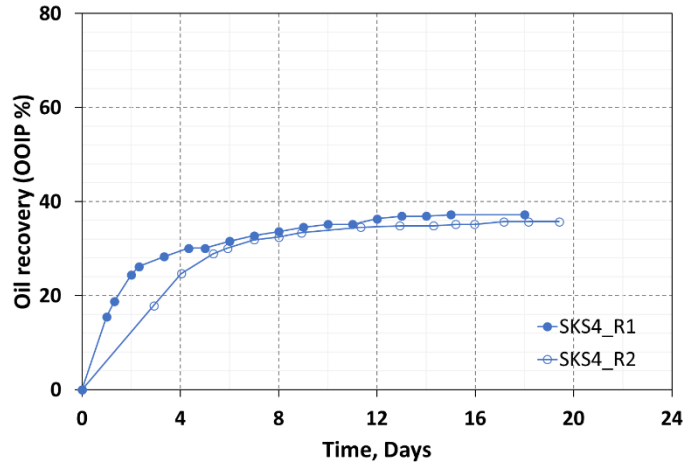


Figure 20 Spontaneous Imbibition tests conducted on chalk core sample SKS4 on first and second restorations. In the second restoration, the core was flooded with 1PV of crude oil.

In spontaneous imbibition test, the total volume of oil produced was reduced from 12.5ml to 12.0ml after restoration. The recovery for SKS4 core reached 35.8% OOIP in the second restoration while it was 37.2% on the first restoration which shows 1.4 percentage point decrease in oil recovery. Taking into account the uncertainty in the data, no significant difference in the oil recovery after core restoration could be detected.

6.3 Initial wetting of restored outcrop chalk core, SKS2

The second chalk core sample, SKS2 is from the same block of Stevns Klint as SKS4. The corresponding procedures from SKS4 were applied on SKS2 to confirm the initial wetting of outcrop chalk. The core was initially saturated with 10% of formation water, and the results of the experiments will be presented in the following section.

6.3.1 Oil recovery at initial water saturation

The second core, SKS2 was first flooded ~4PV in total with RES40-0.5 and aged for 14 days in 50 °C. The core was prepared using brine VB0S, which is Formation Water. The oil recovery test with spontaneous imbibition was performed using formation water as an imbibing fluid (Figure 21).

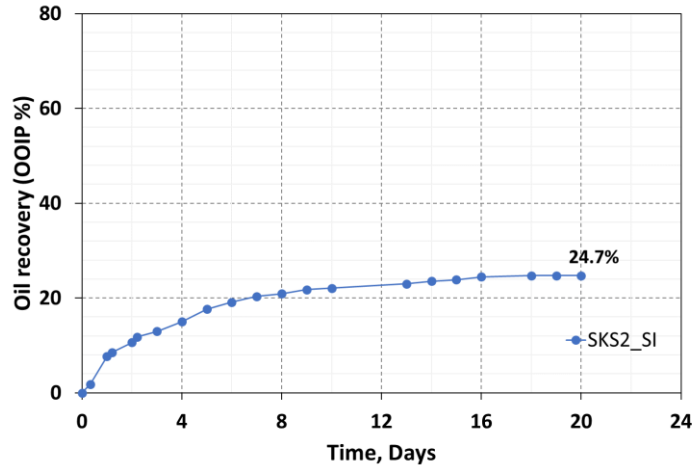


Figure 21 Spontaneous imbibition tests conducted on SKS2 with VB0S as the imbibing brine. $S_{wi}=0.1$, the core was aged and saturated with 5PV of RES40-0.5, AN of 0.5mg KOH/g. The oil recovery at the spontaneous imbibition is 24.7%.

The oil recovery in SI has a lower value of 24.7% OOIP than the oil recovery in SKS4, which implies SKS2 behaved less water-wet. Also, the recovery in SI was slower than in SKS4 as the plateau was reached after 18 days.

6.3.2 Oil recovery in Forced Imbibition test

Following that no extra oil is produced, the FI is conducted with the rates of 1 and 4PV/D. The total recoveries at two different injection rates were 52.7% and 60.4% OOIP, respectively. The oil recovery in both SI and FI in SKS2 have lower values than in SKS4, which indicates that SKS4 has a better water wettability. This heterogeneity of the chalk cores will be discussed in the following chapter.

The pressure differences (dP) during the forced imbibition test were measured (Figure 22) and presented with the volume of oil produced in % OOIP.

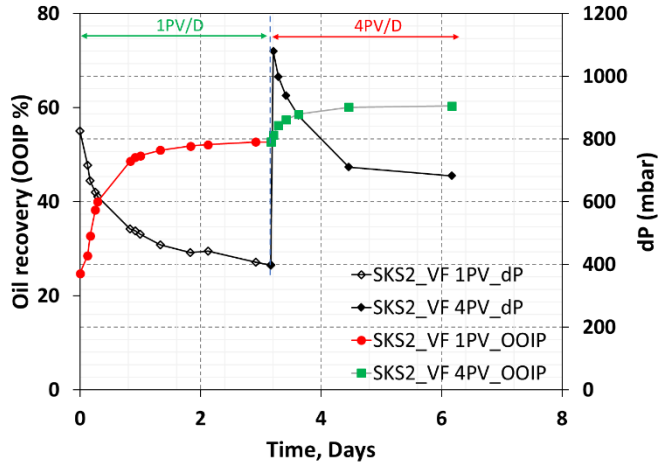


Figure 22 Oil recovery and Pressure drops during the Forced Imbibition tests on chalk core sample SKS2 at two different injection rate of 1PV/D and 4PV/D.

The pressure drops observed was initially 825.8mbar and declined to 398.5mbar at S_{or} when the injection rate was 1PV/D. Then, the dP got a value of 1080.3mbar as the injection rate was increased to 4PV/D. At the end of FI test, it declined to 683.2mbar which is lower than in FI with SKS4. It is mentioned that the pressure drops increase as more oil is produced, and this is confirmed since dP has a higher value in SKS4 with higher oil recovery than in SKS2 with lower oil recovery.

The oil recovery after SI and FI is plotted in Figure 23 with the ultimate recovery of 60.4% OOIP.

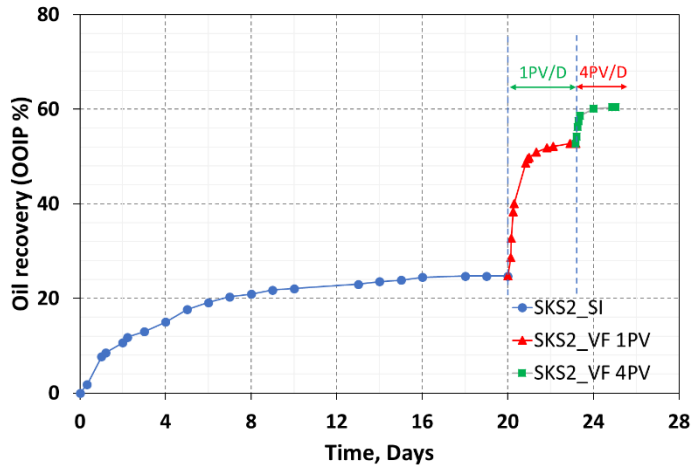


Figure 23 Spontaneous and Forced Imbibition tests conducted on SKS2 with an ultimate recovery of 60.4% OOIP and $I_w^*=0.38$.

The Amott water index in SKS2 is computed as $I_{w,SKS2}^* = 0.38$ which is lower than in SKS4 ($I_{w,SKS4}^* = 0.58$). This comparison of Amott water index confirms that SKS4 is more water-wet than SKS2 which was also observed in spontaneous imbibition test. The wettability of these two cores will be studied further with chromatographic wettability test in the following section.

6.3.3 Chromatographic wettability test

Chromatographic wettability test is conducted on SKS2 in the same procedure of SKS4 by flooding SW0T and SW1/2T and collecting effluent samples. The concentration of sulfate and thiocyanate as a result of Ion Chromatography is plotted in Figure 24.

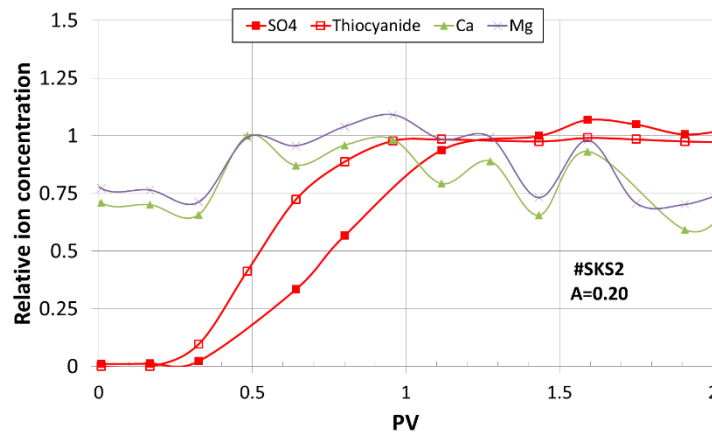


Figure 24 Chromatographic wettability test performed on SKS2 at room temperature. The core was flooded at 0.1ml/min and the effluent samples were collected to analyze the concentration of SO_4^{2-} and SCN^- . The area between two concentration curves is calculated as $A=0.20$.

The area between the two concentration curves of sulfate and thiocyanate of SKS2 was 0.20 as compared to 0.21 in SKS4. The water-wet area calculated for SKS2 is:

$$I_{CW,SKS2} = \frac{0.20}{0.25} = 0.82$$

The chromatography wettability index of SKS2, $I_{CW,SKS2}$ has a smaller value than in SKS4 which was 0.86 and it is confirmed that SKS4 is more water-wet than SKS2, supporting the comparison in total oil recovery in SI and FI test and Amott water index I_w^* .

6.3.4 Initial wetting after restoration of the core

The core was restored using ~10PV of kerosene, ~5PV of heptane to remove the residual oil and ~5PV of DI water to remove heptane and salts. The aged core after flooded with 1PV of RES40-0.5 (AN=0.5mg KOH/g) was performed through the SI test. The oil recovery results are presented in Figure 25.

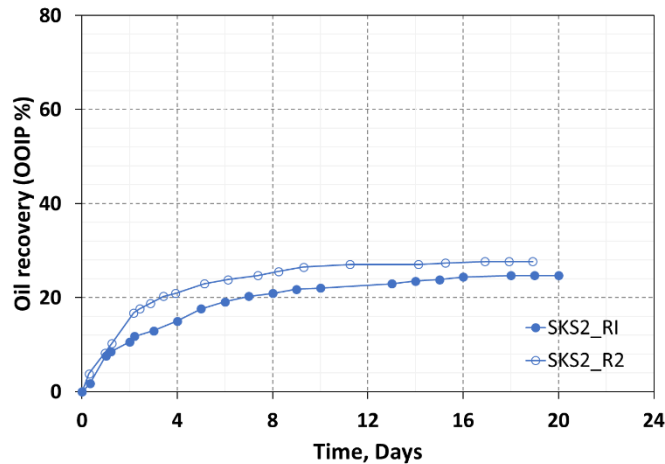


Figure 25 Oil recovery by spontaneous imbibition of VB0S into the chalk core SKS2 at first and second restorations. The core was flooded with 1PV of crude oil at second restoration.

The total volume oil produced is increased from 8.4ml to 9.4ml which shows a slightly higher recovery in restoration. In consideration of the oil recovery, it was 26.8% OOIP from SI for SKS restored core. Compared to the first SI test, which was 24.7% OOIP, it is increased by 2.1 percentage point (pp). The reproducibility of the core will be studied further in the discussion.

6.4 Initial wetting of restored outcrop chalk core, SKS5/SKS7

The initial wetting of the previous two cores SKS2 and SKS4 tested by spontaneous and forced imbibition test showed a significant difference in the total oil recovery. SKS5 and SKS7 were used as reference cores to verify which core experiences between SKS2 and SKS4 can be representative to Stevns Klint chalk initial wetting.

6.4.1 Oil recovery at initial water saturation

The same procedure to SKS2 and SKS4 is repeated on SKS5 and SKS7. Initially, both cores were saturated with formation water, VB0S for 10% and 5PV of crude oil was flooded through the core. The oil recovery results of both cores were plotted in Figure 26 versus time in days.

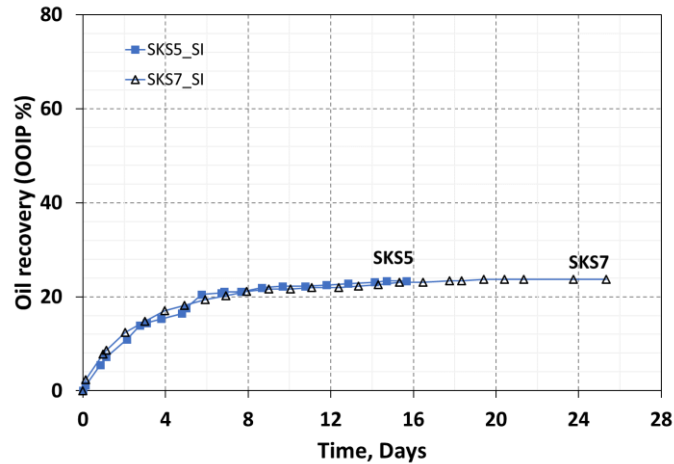


Figure 26 Spontaneous Imbibition test on SKS5 and SKS7. The initial saturation for both cores was 10% saturated with FW(VB0S) and exposed to 5PV with RES40-0.5 (AN=0.5mg KOH/g).

The total oil recovery of spontaneous imbibition test on SKS5 is 23.4% OOIP and 23.7% OOIP on SKS7. This result duplicates the oil recovery of core sample SKS2 which had a value of 24.7% OOIP.

6.4.2 Oil recovery in Forced Imbibition test

Forced Imbibition test was conducted on SKS5 (Figure 27) after spontaneous imbibition.

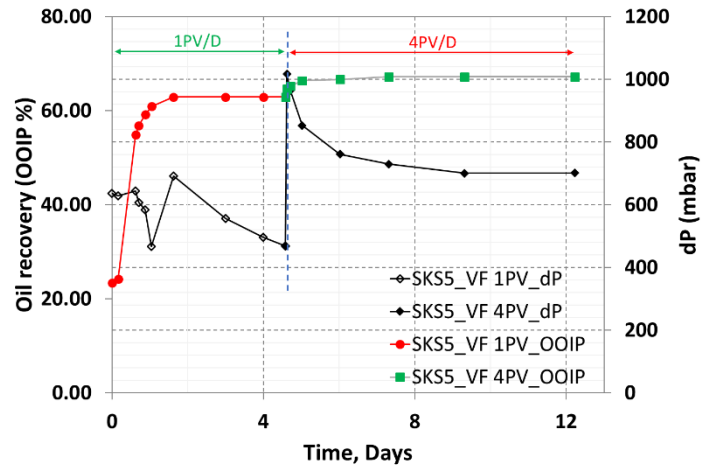


Figure 27 Forced Imbibition conducted on SKS5 at two different rates of 1PV/D and 4PV/D. The ultimate oil recovery 67.2% OOIP.

After Forced Imbibition test, the final oil recovery reaches 62.9% and 67.2% OOIP respectively at the injected rates. Although the oil recovery in SI was similar to that of SKS2, FI shows a different aspect from either SKS2 or SKS4 in total oil recovery.

At the beginning of the Forced Imbibition on SKS5 showed discontinuity on pressure drops. This forced imbibition test was not conducted on the same conditions to other cores due to plugging of injection lines during core flooding. The pressure drops became stable as the test continued and is declined as the oil is produced until the injection rate is increased to 4PV/D. It declined from 636.7mbar to 468.0mbar and 1016.4mbar to 701.4mbar at the different injection rates, respectively.

The ultimate oil recovery from spontaneous and forced imbibition in SKS5 and SKS7 is presented in Figure 28.

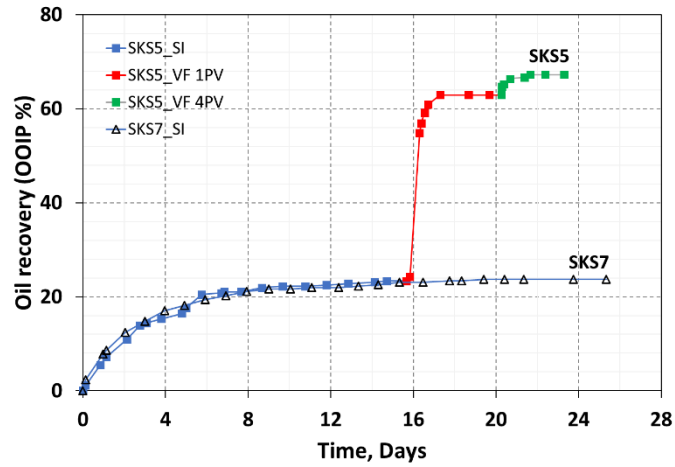


Figure 28 Spontaneous and forced imbibition tests of FW at 50 °C on SKS5 and SKS7. Both cores were saturated with 10% FW and exposed to 5PV with RES40-0.5. For SKS7, only SI test was performed and both SI and FI tests on SKS5.

The Amott water wet index of the core SKS5 and SKS7 is 0.36 and 0.37, respectively, which is corresponding to that value of SKS2.

7 Discussions

In this section, the main results from the experimental work with the outcrop chalk cores will be discussed and compared.

7.1 Core restoration and Mild core cleaning

In reservoir rocks, the interaction between the crude oil, brine and rock establishes the initial wettability over geological time. The capillary pressure, relative permeability and fluid distribution which determine the oil recovery in carbonate reservoirs are dictated by the initial wetting of the rock surface. The smart water EOR on carbonate reservoirs is to alter the wettability towards more water-wet conditions. Therefore, it is important to mimic the reservoir wetting condition for core materials to evaluate and understand the mechanisms of oil recovery by smart water injection.

7.1.1 Reservoir wetting and the effect on oil recovery

The oil recovery result from SI and FI on the chalk core SKS6 from unpublished work by Torrijos and Aslanidis (2018) is referred to compare the relevance of initial wettability and oil recovery (Figure 29). Spontaneous and forced imbibition test show that ultimate recovery is higher when the system is in more water-wet condition.

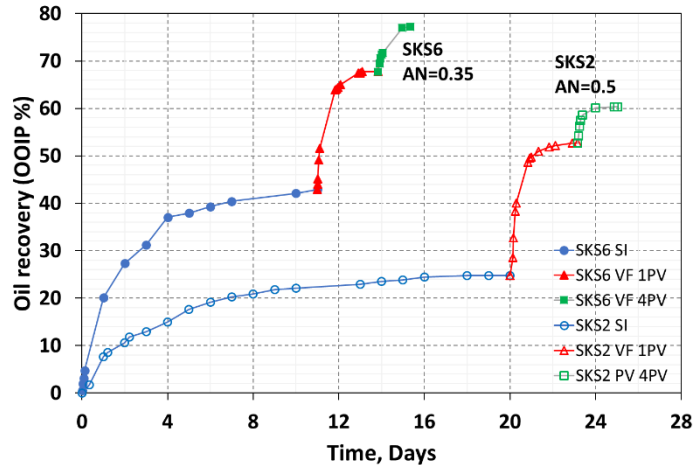


Figure 29 Spontaneous and forced imbibition tests conducted on chalk cores SKS2 and SKS6 (Unpublished work by Torrijos and Aslanidis, 2018). Both cores were saturated with 10% FW. SKS6 was aged and saturated with 5PV of crude oil with AN of 0.35mg KOH/g and SKS2 with RES40-0.5 with AN of 0.5mg KOH/g.

SKS6 is the core from the same outcrop chalk as SKS2 and was flooded with the crude oil with AN=0.35 mg KOH/g. The wettability of the core becomes more water-wet with lower AN as stated above in chapter 2.4 which demonstrates that SKS6 tends to be more water-wet than SKS2. Figure 29 identifies that the oil recovery is higher in SKS6 with the value of 42.9% OOIP in spontaneous imbibition test in comparison to 24.7% OOIP in SKS2. Initial wetting affects the oil recovery by the capillary forces in the porous media. Given that the capillary forces are the main driving force in displacing oil in spontaneous imbibition, the initial wetting affects the oil recovery as confirmed in the figure above with comparison of the oil recovery of the cores SKS2 and SKS6.

However, extra oil recoveries in Forced Imbibition in SKS2 and SKS6 do not show a significant difference. On the other hand, in Forced Imbibition, viscous forces take part in oil recovery other than capillary forces and this could explain why oil recovery in Forced Imbibition is not as affected by the initial wetting condition as that in spontaneous imbibition. Thus, the effect of initial wetting of the chalk core on oil recovery could be more comparable in spontaneous imbibition rather than forced imbibition. However, The ultimate recovery after Forced Imbibition test was also higher in SKS6 as 77.23% OOIP than 60.37% OOIP in SKS2. Thus, initial wetting of the chalk core could indicate the ultimate oil recovery after both spontaneous and forced imbibition.

7.1.2 Core cleaning and initial wettability in chalk

Experimental studies have tested wettability alteration using Smart Water on carbonate rocks. The importance of potential determining ions in Smart Water, which are Ca^{2+} , Mg^{2+} , and SO_4^{2-} , is confirmed in chalk reservoir (Zhang et al., 2007). Oil recovery in carbonate reservoirs is improved by increase in sulphate concentration (Zhang et al., 2007; Shariatpanahi et al., 2011), increase in temperature (Strand et al., 2008; Fathi et al., 2011), and increase in the concentration of the potential determining ions (Strand et al., 2006; Zhang et al., 2007). The composition of crude oil is the most important factors that influence the initial wettability (Anderson, 1986a). The carbonate rock surface is generally positively charged, and the negatively charged carboxylates which are the acidic components in crude oil is known to be the main wetting parameter (Standnes and Austad, 2000; Zhang and Austad, 2005).

The wettability of the rock surface can be altered towards a more mixed-wet condition when the carboxylates adsorb to the rock surface. In a laboratory, it is essential to preserve initial wettability of the system that the core samples can be investigated as a representative core of the reservoir. Two outcrop chalk cores were used in this experiment to investigate the effect of core cleaning on initial wettability and the results were shown in 5.2.4 and 5.3.4, respectively (Figure 30).

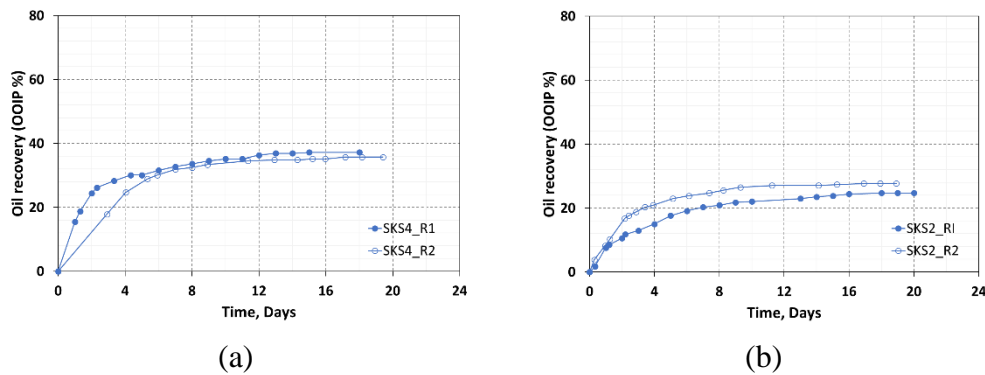


Figure 30 The oil recovery from SI on the first and second restoration of the outcrop chalk core (a) SKS4 and (b) SKS2. The core had $S_{wi}=0.1$ FW and was saturated and aged in RES40-0.5 (AN=0.5mg KOH/g).

The results of spontaneous imbibition tests indicate the capillary forces and the wettability of the cores. The core SKS4 is confirmed to be more water-wet than SKS2 from the results of the oil recovery from the spontaneous imbibition and chromatographic wettability tests. After confirming the initial wetting conditions, both cores were mildly cleaned by ~10PV kerosene and ~5PV heptane.

After this second restoration, the core was saturated with 1PV of crude oil RES40-0.5 inside the desiccator. When the more oil is flooded through the core, the core becomes more oil-wet which will decrease the oil recovery in spontaneous imbibition. Thus, instead of flooding 5PV of crude oil as the first restoration, 1PV of crude oil is flooded to fill up the pore spaces where the polar components were removed from the mild core cleaning. SI tests were then performed on both cores to analyze the alteration of the wetting properties. After mild core cleaning, the oil recovery (%OOIP) in spontaneous imbibition in core SKS4 had decreased 1.4 percentage point and increased 2.1 percentage point in core SKS2.

The polar components adsorbed onto the rock surface are determining the wettability of the cores. Low aromatic kerosene and heptane used in the mild core cleaning could preserve a large amount of the adsorbed polar organic material on the rock surface (Hopkins et al., 2016). The oil recoveries from the spontaneous imbibition tests performed on outcrop chalk core after the second restoration show a minor difference (1.4% to 2.1%) compare to the first restoration results. Therefore, it is demonstrated that the initial wetting conditions can be reproducible with the mild core cleaning method.

Wettability alteration by crude oil flooding and its effect on core restoration

The experiment of restoration using mild cleaning was performed on the outcrop chalk core from the same block of Stevns Klint by Kapstad (2018). The chalk core S2 was mildly cleaned and exposed to 2.5PV of crude oil (AN=0.35mg KOH/g). The difference in oil recovery from the first and second restoration was about 20% OOIP (Figure 31).

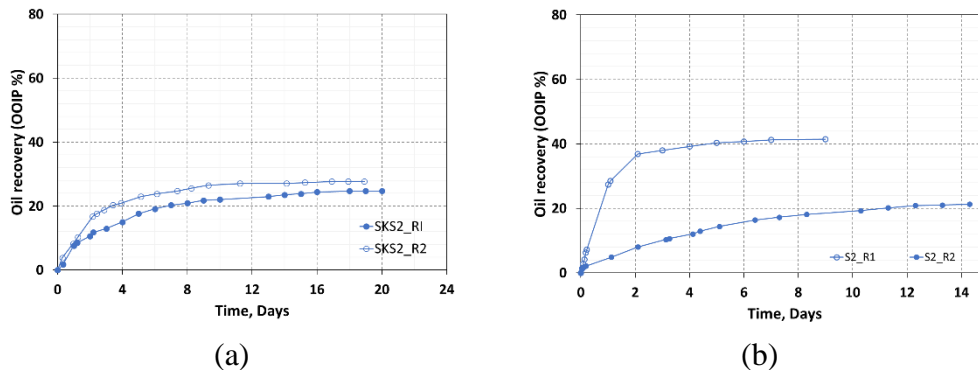


Figure 31 The oil recovery from spontaneous Imbibition on first and second restoration of the outcrop chalk core (a) SKS2 (AN=0.5mg KOH/g and 1PV crude oil saturated) and (b) S2 (AN=0.35mg KOH/g and 2.5PV crude oil injected). The core had $S_{wi}=0.1$ FW and were saturated and aged in crude oil.

The spontaneous imbibition test on first and second restoration gives 20% OOIP difference in oil recovery. It is observed that the core after the second restoration behaved less water-wet than at the first restoration and the reproducibility of the core was relatively low than in SKS2 and SKS4. The decrease in oil recovery can be explained with the effect of crude oil flooding on wettability alteration. It can be demonstrated by the adsorption of the acidic polar component during core flooding (Figure 32).

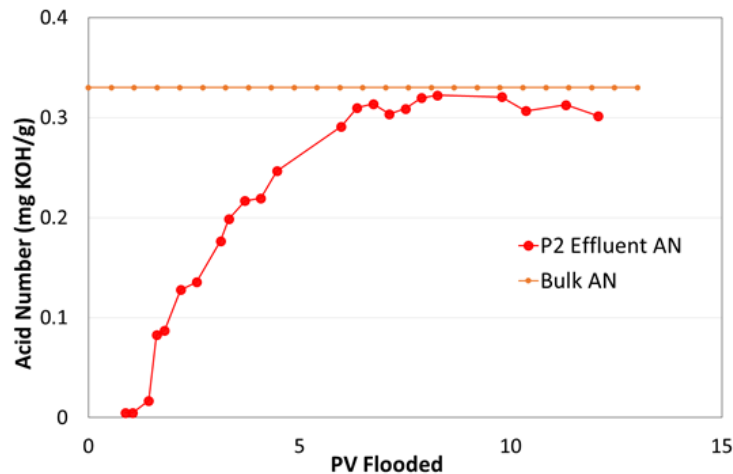


Figure 32 The adsorption of polar components plotted by PV flooded by crude oil. AN=0.34mg KOH/g, at 50 °C (Hopkins, 2016).

The AN of effluent sample collected during the core flooding is measured and plotted versus PV crude oil flooded (Figure 32) (Hopkins, 2016). Acidic polar components adsorb onto the positively charged mineral surface. It is shown that the AN from the effluent becomes stable after 8-9 of crude oil flooded. Even though the wettability-dictation components are mostly preserved by mild core cleaning, it was observed that the core behaved less water-wet when the core was flooded with 2.5PV crude oil. In the comparison of S2 to SKS2 and SKS4, the result of experiments indicates that the reproducibility of the core after mild cleaning will be more efficient with minimizing the amount of crude oil to be flooded.

7.2 Heterogeneity of Chalk cores

Heterogeneity is defined as the complex and variable nature of the reservoir. The depositional environment of carbonate varies the degrees of connectivity and

produces complex and irregular pore networks. These heterogeneities of carbonate are poorly understood, and it can occur at all scales of observations and measurement from the pore-scale to the basin-scale (Fitch et al., 2016). Fractures and stylolite are two main factors that increase the heterogeneity of carbonates.

The cores used in this experiment is all from the same outcrop, Stevns Klint, SK, nearby Copenhagen, Denmark, and were prepared from the same block of the reservoir. However, the oil recovery test in spontaneous imbibition and forced imbibition showed a considerably different result (Figure 33).

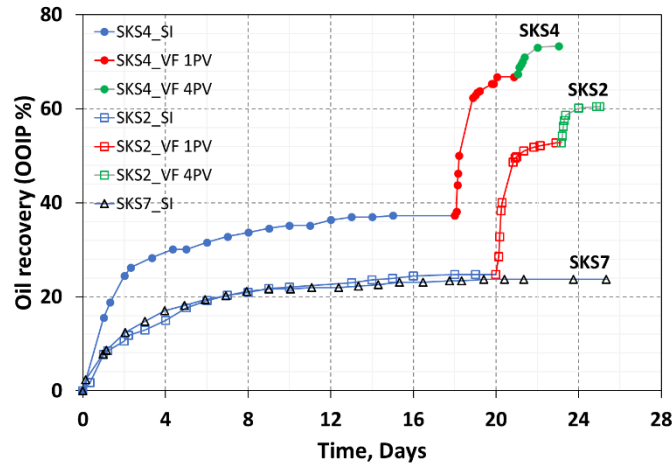


Figure 33 Spontaneous and forced imbibition tests conducted on chalk cores SKS2, SKS4 and SKS7 with FW as the imbibing brine. $S_{wi}=0.1$ for all cores and the cores were aged and saturated with 5PV of RES40-0.5 (AN=0.5mg KOH/g).

The first and second cores conducted in the oil recovery tests were SKS4 and SKS2, respectively. The volume oil produced during SI in SKS4 was nearly 1.5 times larger than that of SKS2, although the PV of these two cores were almost identical (37.29ml from SKS4, 37.73ml from SKS2). Thus, the other two cores, SKS5 and SKS7 were used to verify the representative core sample between SKS2 and SKS4. Consequently, SKS5 and SKS7 showed less than 1% difference in volume oil recovery in spontaneous imbibition with SKS2.

Different behavior of SKS4 in imbibition test to other cores can be interpreted as i) errors in preparation and ii) varied properties of the cores. This variation of the property in chalk core which is heterogeneity of chalk. Microfracture in chalk cores can be one of the features that lead to heterogeneity (Figure 34).



Figure 34 Chalk core photographs of microfractures.

Physical properties of rock can be influenced by microfractures for example; strength, elastic wave velocity, and permeability (Anders et al., 2014). When microfractures exist in the core especially horizontally, the fluid will flow through the microfractures and will increase the permeability of the cores. As the heterogeneity of the system becomes larger, there is a possibility that oil goes through less to the matrix but more to the fractures. Heterogeneity of chalk core may influence in initial wetting of the sample cores. In the previous chapter, it is confirmed that restoration using the mild core cleaning method is practicable on both SKS2 and SKS4 core though these two cores showed incompatible oil recovery in imbibition test. Thus, it can be considered that SKS4 had a different oil recovery in spontaneous imbibition test due to its heterogeneity in addition to possible errors in preparation.

7.3 Pressure drops in core

Because of a variety of drilling and completion practices, it is observed that the area near the wellbore is either more permeable or less permeable than the reservoir. Thus, the oil recovery experiments performed on cores in the laboratory can be representative rather in the main part of the reservoir. In this experiment, the pressure drops in Forced Imbibition test were recorded and will be discussed that if these pressure drops would have a realistic pressure drops to represent expected conditions observed in the main part of the reservoir. The pressure drops dictate viscous flow regimes and will also influence the contribution of the capillary forces.

7.3.1 Pressure drops in reservoir during brine injection

When the brine is injected through the injection wells, injection wells are mostly exposed to the injection rate which is governed by the maximum injection pressures controlled by the leak off pressures of cap rock/formations. As the crude oil in the reservoir is displaced by the injected brine and produced through the reservoir to the production well, pressure drops in the overall reservoir area take place.

In a radial five-spot well pattern, significant pressure drops are observed close to the injection well and significant drawdown pressures close to production wells in simulation (Figure 35).

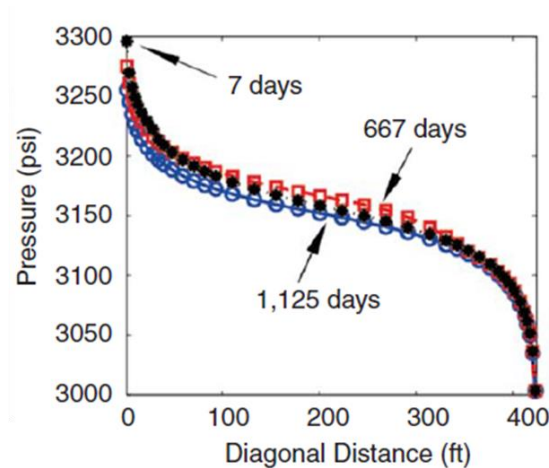


Figure 35 Modelled pressure profiles along the five-spot pattern in formation water injection (Qiao et al., 2015)

It is shown in the figure where the injection well located in diagonal distance 0 and production well at 400ft using geochemical simulation (Qiao et al., 2015). Lower average pressure drops will then be expected in the main part of the reservoir due to typically radial well configurations.

7.3.2 Pressure drops in core flooding experiment

Laboratory oil recovery experiments performed on the cores should mimic the flow conditions in the main part of the reservoir, and the pressure drops need to be close to reservoir conditions. In the low permeable Ekofisk chalk reservoir, the average well distance between the injectors and producers are typically 350 meters. Excluding the wellbore effects, 300 meters could be a rough estimation of main

reservoir distance. Core experiments with a pressure drop of 1mbar/cm will then give a pressure drop at reservoir scale;

$$1\text{mbar/cm} = 10\text{bar}/100\text{m} = 30\text{bar}/300\text{m}$$

where the value is most likely significantly higher than expected at the real reservoir conditions.

In this project, the oil recovery core flooding experiments are performed with two different injection rates of 1PV/D and 4PV/D on core with lengths of 7cm. The minimum pressure drops in every core samples are in a range between 400mbar to 500mbar. In the core SKS2 at the injection rate of 1PV/D, pressure drops observed were initially close to ~800mbar and declined to ~400mbar at S_{or} , giving pressure drops of minimum 60mbar/cm (400mbar/7cm) (Figure 36).

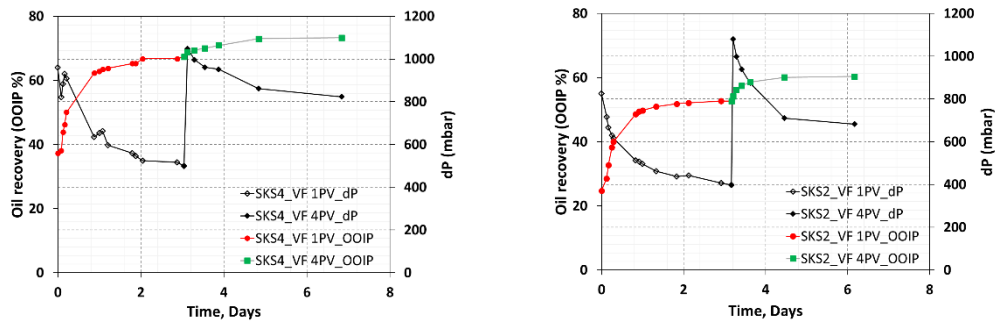


Figure 36 Pressure drops and oil recovery in Forced Imbibition tests on the outcrop chalk core (a) SKS4 and (b) SKS2. The FW, VB0S was injected at 50 °C with injection rates of 1PV/D and 4PV/D.

As mentioned above, when pressure drops of 1mbar/cm give a 30bar/300m of pressure drops in reservoir scale, this can be converted to Ekofisk conditions with minimum pressure drops of 60mbar/cm between injectors and producers which gives:

$$30 * 60 = 1800\text{Bar}/300\text{m}$$

With initial pressure of 7000psi (500bar) at Ekofisk, the pressure drops from the core experiments even at the injection rates of 1PV/D are unrealistic high.

7.3.3 Effect of injection rates on Capillary pressure

Fluid flow in porous media is controlled by three main forces, which are capillary forces, viscous forces and gravity forces as previously mentioned. On restored core systems, the presence of capillary forces is easily observed by performing

spontaneous imbibition tests and are controlled by the wettability. If the pore radius is increased in the same condition, permeability will also increase, and the capillary forces will be reduced as observed in eq 7.1.:

$$P_c = \frac{2\sigma\cos\theta}{r} \quad (7.1)$$

In situ generated capillary forces are dependent on wettability and permeability, and at slightly water-wet conditions and/or higher permeabilities the capillary forces could be relatively small but still need to be accounted for. Weak capillary forces are easily suppressed by increasing viscous forces and pressure drops in the laboratory core experiments, as done to eliminate capillary end effects. Thus, the pressure drops from the core experiments designed with unrealistic high injection rates will not be able to be compared well to the realistic pressure drops in the reservoir condition.

8 Conclusion remarks and future work

The importance of the initial wetting in chalk has been highlighted throughout this work to improve the understanding of initial wetting and the restoration of it in chalk reservoir. Initial wetting of the chalk influences the oil recovery in spontaneous imbibition and restoration of initial wettability of the core is essential in the laboratory experiment.

8.1 Conclusion

The experiments conducted in this research work proved the effect of the mild core cleaning in the restoration of initial wetting on chalk cores. The results obtained from the experiments and subsequent analysis demonstrated that:

- From the SI test after first and second restoration, the initial wettability of the chalk core can be reproducible with the mild core cleaning using kerosene and heptane preserving polar component on mineral surfaces and the limited amount of crude oil
- The chalk cores from the same outcrop could have different initial wettability due to the heterogeneity of carbonate.
- Initial wetting of the chalk affects the oil recovery in spontaneous imbibition and also the ultimate recovery of spontaneous and forced imbibition.
- Spontaneous imbibition results on chalk core with different initial wetting condition confirmed that oil recovery in SI is increased as the water-wetness of the core increases.
- Heterogeneity of the chalk core does not affect the result of the restoration and the heterogeneous core is reproducible with the mild core cleaning.
- The pressure drops in the laboratory experiments are not applicable in reservoir condition since increasing viscous forces and pressure drops in the laboratory experiment can easily suppress the weak capillary forces.

8.2 Recommendations for future studies

This work has shown that the importance of initial wetting in carbonate and its restoration. To improve the understanding further, the following work could extend the research already obtained in this study:

- The effect of Acid number on alteration of initial wetting is briefly introduced; however, the effect of different AN and BN in the oil on initial wetting requires further investigation.
- Evaluation of initial wetting connected to wettability alteration by Smart Water could give a better understanding of the mechanism of wetting on the porous rock surface.
- The mild core cleaning effect on various conditions could be investigated. With the chalk cores that have different initial wetting, crude oil with different AN or BN will confirm the reproducibility of the cores in laboratory work.

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10 Appendix

A1-Oil recovery from the chalk cores

Oil recovery	SI (%OOIP)	FI, 1PV/D (%OOIP)		FI, 4PV/D (%OOIP)	
			Increase		Increase
SKS4	37.24	67.34	30.1	73.3	5.96
SKS2	24.74	52.71	27.97	60.37	7.66
SKS5	23.37	62.9	39.53	67.23	4.33
SKS7	23.68	-	-	-	-

A2-Wettability test by Oil Recovery data

SKS4		SKS2		SKS5		SKS7	
Time	%OOIP	Time	%OOIP	Time	%OOIP	Time	%OOIP
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0	15.5	0.3	1.8	0.1	1.2	0.1	2.3
1.3	18.8	1.0	7.7	0.8	5.5	1.0	7.8
2.0	24.4	1.2	8.5	1.1	7.2	1.1	8.7
2.3	26.2	2.0	10.6	2.1	11.0	2.0	12.4
3.3	28.3	2.2	11.8	2.8	13.8	3.0	14.7
4.3	30.1	3.0	13.0	3.1	14.4	4.0	17.0
5.0	30.1	4.0	15.0	3.8	15.3	4.9	18.2
6.0	31.6	5.0	17.7	4.8	16.4	5.9	19.3
7.0	32.8	6.0	19.1	5.0	17.6	6.9	20.2
8.0	33.7	7.0	20.3	5.8	20.5	7.9	21.1
9.0	34.6	8.0	20.9	6.7	20.8	9.0	21.7
10.0	35.2	9.0	21.8	6.8	21.1	10.0	21.7
11.0	35.2	10.0	22.1	7.7	21.1	11.1	21.9
12.0	36.4	13.0	23.0	8.7	21.9	12.4	21.9
13.0	36.9	14.0	23.6	9.7	22.2	13.3	22.2
14.0	36.9	15.0	23.9	10.8	22.2	14.3	22.5
15.0	37.2	16.0	24.4	11.8	22.5	15.3	23.1
18.0	37.2	18.0	24.7	12.8	22.8	16.5	23.1
		19.0	24.7	14.1	23.1	17.8	23.4
		20.0	24.7	14.7	23.4	18.3	23.4
				15.7	23.4	19.4	23.7
FI, 1PV/D		FI, 1PV/D		FI, 1PV/D		20.4	23.7
18.1	38.1	20.1	28.6	15.8	24.2	21.3	23.7
18.1	43.8	20.2	32.7	16.3	54.8	23.8	23.7
18.2	46.2	20.3	38.3	16.4	56.8	25.3	23.7
18.2	50.1	20.3	40.1	16.5	59.1		
18.9	62.3	20.8	48.6	16.7	60.9		
19.0	62.9	20.9	49.5	17.3	62.9		
19.1	63.5	21.0	49.8	18.7	62.9		
19.2	63.8	21.3	50.9	19.7	62.9		
19.8	65.3	21.8	51.8	20.3	62.9		
19.9	65.3	22.1	52.1				
20.0	66.7	22.9	52.7				
20.9	66.7	23.2	52.7				
21.0	67.3						
FI, 4PV/D		FI, 4PV/D		FI, 4PV/D			
21.1	68.8	23.2	54.2	20.3	64.6		
21.2	69.4	23.3	56.2	20.4	65.2		
21.3	70.0	23.3	57.4	20.7	66.4		
21.4	70.9	23.4	58.6	21.4	66.7		
22.0	73.0	24.0	60.1	21.7	67.2		
23.0	73.3	24.9	60.4	22.4	67.2		
		25.0	60.4				

A3-Chromatography data for SKS4

Thiocyanade		
PV	C/C0	Area under curve
0.31	0.0000	0
0.47	0.0927	0.0076
0.64	0.4591	0.045068165
0.80	0.8147	0.103703236
0.96	0.9461	0.143477432
1.12	0.9914	0.157229756
1.29	1.0000	0.161868558
1.45	1.0086	0.163135639
1.61	1.0000	0.162866882
	SUM	0.944913511

Sulfate		
PV	C/C0	Area under curve
0.31	0.0033	0.0000
0.47	0.0283	0.0023
0.64	0.0483	0.0063
0.96	0.7072	0.1231
1.12	0.9002	0.1304
1.29	0.9601	0.1512
1.61	1.0000	0.3181
	SUM	0.7314
Area between curves = 0.2135		

A4-Chromatography data for SKS2

Thiocyanade		
PV	C/C0	Area under curve
0.17	0.0000	0
0.33	0.0970	0.0077
0.48	0.4138	0.040426144
0.64	0.7241	0.09013855
0.80	0.8879	0.127589688
0.96	0.9784	0.146977034
1.12	0.9849	0.154874047
1.43	0.9763	0.310964203
	SUM	0.878632692

Sulfate		
PV	C/C0	Area under curve
0.17	0.0133	0.0000
0.33	0.0232	0.0018
0.64	0.3350	0.0567
0.80	0.5672	0.0714
1.12	0.9386	0.2374
1.43	1.0000	0.3074
	SUM	0.6747
Area between curves = 0.2039		