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Abstract

Experimental study of wettability alteration was aimed at three laboratory designated chalk material, collected from the same reservoir block, at different initial water saturations (0%, 10%, and 40%). Crude oil sample with fixed Acid Number (AN=0.35 mgKOH/g) and Base Number (BN=0.20 mgKOH/g) was used to saturate and age the chalk cores at 50°C. Extensive acid and base number measurements of output oil was made during saturation to create a fingerprint of the wettability alteration processes.

It is understood that content and interactions of oil components to rock surfaces affect nature of fluid wetting and has a direct impact on ultimate oil recovery [1]. The observations confirm that initial wetting of Carbonates are mixed-wet at relevant initial water saturation and that wetting condition is strongly related to the acidic oil components.

The following observations were made; 1) Adsorption of the polar oil components take place in two different mechanisms; the adsorption of base groups is related to physical attraction, while acids are adsorbed by chemical covalent bonds. 2) Oil wetting state is related to strength of chemical bonding between the oil and rock surface, this was proved by cleaning the core with oil solvents, to detach loosely bonded oil components, such that only strongly competitive carboxyls can adsorb to the chalk surface during a secondary oil saturation. 3) Presence of water will decrease the rate of adsorption processes and the fractional wetting by water is increased at higher water content. 4) Oil recovery by spontaneous imbibition increased with increasing water wetting.

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Nomenclature

σ	Interfacial Tension [dynescm]
θ	Contact Angle [°]
<i>FI</i>	Forced Imbibition
P_c	Capillary pressure [<i>dynes/cm</i> ²]
<i>SPI</i>	Spontaneous Imbibition
<i>Swi</i>	Initial water saturation
W_I	wetting index (Amott method)
WI_{new}	wetting index (chromatography method)
AN	Acid Number (mgKOH/g Oil)
BN	Base Number (mgKOH/g Oil)
EOR	Enhanced Oil Recovery
MC	Mild cleaned
OOIP	Original Oil In Place [%]
PV	Pore Volumes [<i>cm</i> ³]
RES40	Oil sample used to saturate the core
RF	Recovery Factor
SI	Spontaneous Imbibition
SK	Stevens Klint chalk core
SW	Smart Water
VBOS	Vallhal Formation water

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Objectives

The topic of this study emphasizes optimized oil recovery in carbonate reservoirs by wettability alteration and is a supportive study to the Smart water project.

Understanding initial wetting condition is of primary importance before implementing different EOR-methods such as Smart Water for optimized oil production. Although field related hydrocarbon extraction begins with one or several reservoir performance test, one should understand the initial petrophysical properties of the rock and only then can one claim that a given method is prone to be successful.

The initial wetting condition must be mixed-wet for successful implementation of SW as enhanced oil recovery method, the potential is reduced as continuous wetting by water and oil is increased. Over the past 20 years(+), EOR research team at the University of Stavanger have been working to understand crude-oil/brine/rock interactions responsible for modification to the rock wetting state. Parametric investigation of the wetting condition will be carried out changing rock initial water saturation as part of this ongoing research.

Chapter 1

Introduction

1.1 Oil Recovery from Carbonate Rocks

Recovery mechanism of hydrocarbons is traditionally recognized to take place in three categorical stages. During the initial stage, natural energy present in the reservoir is utilized to displace fluids to producing wells [2]. These energy sources include gas cap drive, solution gas drive, natural water drive, fluid and rock expansion and gravity drainage. Production of fluid takes place simply by opening a valve that allows for communication between the well and reservoir and if necessary decreasing the bottom hole pressure such that a pressure gradient arise. The pressure difference will continuously decrease until there no longer exist energy to sustain spontaneous displacement. The recovery factor at this stage is low, usually less than 15% of the original oil in place (OOIP) [3].

Secondary recovery is exploited to maintain reservoir pressure by injecting viscous fluids throughout the field and is usually implemented before bubble point pressure of the oil is reached. Waterflooding with polymer additives has today become synonymous with this stage in recovery processes. Another commonly used technique is by injecting produced gas into a gas cap or in dipping oil columns, where gravity forces supported by density differences are used to overcome capillary entry pressure. Total recovery for productive reservoirs after this stage is somewhere between 35-50% (OOIP) [4].

Tertiary or enhanced oil recovery (EOR) is the discipline of methods where appropriate agents not typically encountered in the reservoir is injected to aid alteration of reservoir equilibrium in the aim of reducing residual oil saturation to a minimum [5]. The broader terminology used for this production phase is improved oil recovery (IOR) because it includes all modern methods of achieving additional recovery above what can be recovered in primary and secondary methods. For the

record, it should be mentioned despite this general chronological categorization that it is not always necessary to develop oil production according to the stages described, on the contrary, it is more convenient in certain conditions to implement EOR processes as early as possible [4].

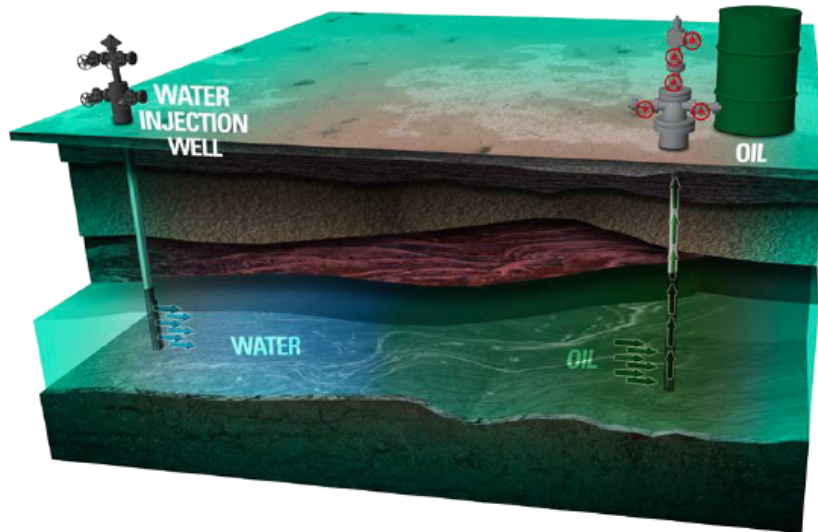


Figure 1.1: Waterflooding from an oil reservoir [6].

Carbonates are porous and permeable rocks that are thought to contain more than half of world's petroleum prospects. According to rough estimations about 70% of oil and 90% of gas reserves in the Middle East are enclosed within carbonate rocks [7]. It's hard to achieve high oil recovery by using conventional waterflooding in carbonate reservoirs, they exhibit highly permeable fractures such that conductivity often reaches 50 times inherent matrix [8], and uneven sweeping of brine is felt. Increasing research on seawater injection as pressure maintenance since the 1960s [9] has brought us to the knowledge that spontaneous imbibition dictates efficient displacement of oil in low permeable and fractured reservoirs into the matrix structure, where most oil is situated. Another great challenge that contribute to increased EOR potential of carbonates is the unfavorable wetting state (discussed in more detail in a later section).

1.2 Classification of Carbonate Rocks

Carbonates are sedimentary rocks composed of the anionic complex; CO_3^{2-} and the cation; Ca^{2+} with one or more of other divalent metallic ions such as Mg^{2+} forming the mineral structure [10]. Calcite ($Ca(CO)_3$) and Dolomite ($CaMg(CO)_2$) are the trivial carbonate minerals that exist. Other groups can be identified primarily from crystal lattice structure, although most families exist in the more stable hexagonal structure [11] with unit size less than 1Å. Chemical bonds between atoms of opposite charge are weak compared to existing covalent bonds within individual carbonate ions. Carbonates are for this reason subjected to brittle fracture during tectonic stress load.

A majority of the grains forming the carbonate matrix are thought to be biological in origin formed at the site of deposition. Good condition for sedimentation includes; warm and shallow seawater with low salinity, good nutrition balance and circulation [12]. The most widely accepted classification of carbonate rock is based on describing the allochems, i.e., individual grains forming the matrix [13]. Alternatively, for hand samples, geologists use the Dunham scheme, this approach describe the inside components (orthochems) that reflect rock texture into consideration. For simplistic approach, type of carbonate rock can be identified as the principal mineral content increases above 50% [14] and from this analogy we can consider ripening of limestone into a third major type of rock, chalk, as calcite content is significantly increased.

From mineralogy point of view carbonates seem to be very homogenous but from porosity/permeability correlations and concerning involved flow mechanism, characterization becomes difficult. Three genetic categories influence the porosity; initial porosity during deposition and sedimentation, secondary porosity due to diagenesis and tertiary porosity caused by fracturing [15], these varieties of porosity contribution give rise to a wide range of permeability value for same total porosity [16].

Chapter 2

Fundamentals of Oil Recovery

2.1 Displacement Forces

A brief introduction to the most significant forces controlling hydrocarbon production is presented in this section.

2.1.1 Capillary Pressure

A pressure difference will arise when two immiscible fluids in rock pores are in contact, this pressure difference is named capillary pressure and is most classically defined as the pressure in the wetting phase minus pressure in the non-wetting phase [17]. The overall effect of pore size, geometry and wetting characteristics of the rock together with surface and interfacial tensions can be expressed in the following equation [5].

$$P_c = \frac{2\sigma_{ow} \cos\theta}{r} \quad (2.1)$$

Where,

P_c = Capillary pressure [*dynes/cm²*]

σ_{ow} = Interfacial tension between oil and water

θ = contact angle measured through the water phase

r = Radius of cylindrical pore channel [cm]

Immiscibility of fluids arise from internal cohesive forces that creates an interface. Capillary action by adhesive forces can yet impact flow of these in narrow spaces, although influence is fundamentally different for fractured and non-fractured core samples [18]. The displacement of oil in fractured reservoir system is only supported by positive capillary forces [19] as opposed to non-fractured reservoirs, where mobilization of oil requires reduction of the interfacial tension.

2.1.2 Gravity Forces

Segregation of fluids by gravity will always take place when immiscible fluids co-exist, and in such circumstances, fluid with the lowest density will experience a net force pointing upwards (case of gas injection). During waterflooding an opposite effect will be seen (gravity under-ride) [4]. The Dietz cell stability equation (Equation 2.2) relates the angle of the oil-water interface to the angle of the layer and can be used to visualize the gravity effects on the displacement front. For static situations, such when a core is submerged in water, segregation by gravity will play an increasing role as capillary forces are reduced [20].

$$G = \frac{g(M-1)\tan\theta}{\tan\theta - \tan\beta} \quad (2.2)$$

Where:

G = Dimensionless gravity parameter

g = gravitational constant

M = Mobility ratio

β = angle of oil-water interface the layer

θ = inclination angle of the layer

2.1.3 Viscous Forces

The active displacement forces in production processes are viscous, gravity and capillary forces. Viscous forces express pressure drop as a result fluid flow and can consist of form drag stemming from pore geometry and fluid interfacial shear [21]. It can be determined using Poiseuille's law if the fluid flow is laminar by approximating the pore space into n-number of tube lines.

$$\Delta P = \frac{8\mu L v_{av} g}{r^2 g_c} \quad (2.3)$$

Where

ΔP = Pressure difference across capillary tube [psi]

μ = Viscosity of the displacing fluid [pas]

L = Length of capillary tube [in]

v_{av} = Average flow velocity in capillary tube [ft/day]

r = Radius of capillary tube [ft]

g_c = Conversion factor

The ratio, viscous to capillary forces is commonly known as capillary number (N_c). Capillary desaturation curves (CDC) can be used to demonstrate the relation between N_c and S_{orw} , and from this plot we see that a capillary number greater than (10^{-5} - 10^{-4}) [22], [23] will be required to mobilize trapped and unconnected oil drops, but at normal flooding rates in the reservoir, N_c can only reach in the range of 10^{-7} . Residual oil fraction trapped after waterflooding in a water-wet reservoir is as postulated due to the dominance of capillary forces over viscous forces, this can happen in two different ways [4];

1. The water imbibes preferentially into the smaller pores while the oil remains in the larger pores (bypassing) and very little oil is produced after breakthrough.
2. The water does not imbibe into the smaller pore throat's with oil in the porebody (snap-off).

2.1.4 Displacement Efficiency

In order to enter and displace oil from the pore space, an entry pressure barrier must be overcome by forces described above. Alternatively, one can apply EOR methods that either reduces or in ideal cases eliminates interfacial tensions between the immiscible fluids with surfactants [24]. Other methods include polymer flooding [25], miscible gas injection [26], and wettability alteration [27]. Choice of recovery method will, however, require the capillary pressure characteristics.

We can now introduce the overall displacement efficiency (E) as a measure of the overall oil recovered by EOR processes on the original oil in place. A large value of this parameter indicates success in the EOR-process through contributions of the vertical sweep efficiency (E_i), areal sweep efficiency (E_a), and the microscopic sweep efficiency (E_d). The product of E_i and E_a has significance on displacement profile and is often referred to as macroscopic displacement efficiency. The most important fluid parameters controlling this term is the mobility of displacing fluid, while (E_d) is related to the rock wetting state.

$$E = E_i E_a E_d \tag{2.4}$$

2.2 Wettability

Wettability is an important parameter in oil recovery processes having a direct impact on fluid location, distribution, and flow within the pore structure. The term wettability refers to the capability of fluids to maintain contact with rock surfaces [28]. The strength of wetting is maneuvered by adhesive forces and offset by cohesive forces [29]. The rock will have a wetting preference for a particular fluid when two immiscible fluids co-exist at a given reservoir condition. This fluid phase will thus be more strongly attracted and is said to be the wetting phase. Wetting phenomena is dominated by outermost rock layer molecules, where a film is generated by adsorption and spreading of fluid components [30].

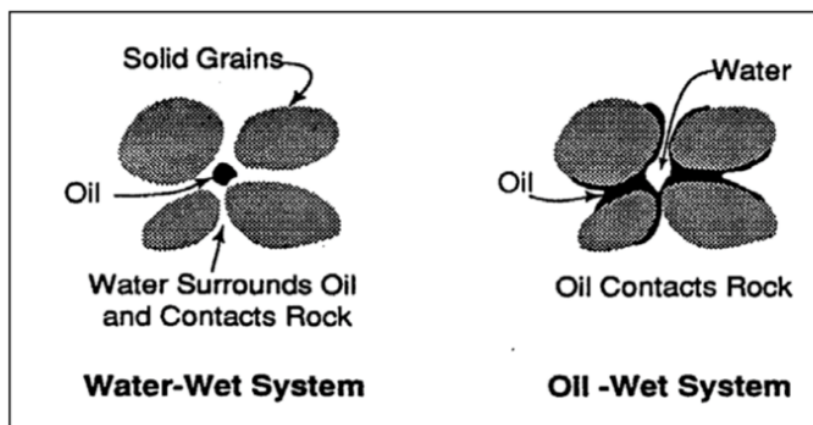


Figure 2.1: Homogeneous wetting system (Water vs oil) [4].

2.2.1 Wettability Measurement Techniques

There exist wide variety wettability assessment methods, each assigned to pinpoint certain reservoir characteristics. This section will introduce some of the classical methods and a more modern version of quantifying the wetting condition. Others methods include qualitative assessment of wettability through the study of imbibition rates and relative permeability curves e.g.

2.2.1.1 Contact Angle Method

One of the most recognized wettability measuring method is by means of contact angle test. It is one of the best methods when pure fluids and representative rock cores are used but has the weakness of not accounting for heterogeneity and roughness of the rock surface such that hysteresis might develop between the advancing and residing water angles [31].

Figure 2.2 shows an idealized example of contact angle method, where two small droplets of liquids, oil and water are placed on a smooth solid surface. This figure illustrates that water tends to spread while oil retains more like a spherical shape. This spreading behavior can be expressed quantitatively by measuring the angle of contact at the liquid-solid surface.

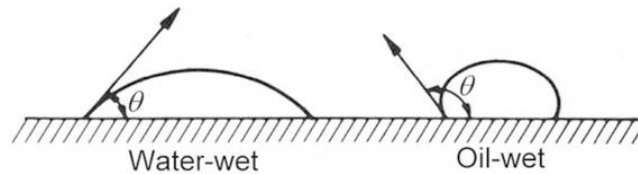


Figure 2.2: Wettability in a simple water/rock and oil/rock system [29].

Theoretically, 100% water-wetting would be established by 0° contact angle, while completely oil wetting is evident for contact angle greater than 115° . For real reservoirs one seldom experience uniform wetting, rather fractional wetting of both oil and water can be expected to co-exist in different parts of the porous media. Contact angle for mixed wet reservoirs lies somewhere between $(75-115)^\circ$ [32].

2.2.1.2 Chromatographic Wettability test

Chromatographic test, developed by Strand et.al [33], determines amount of water-wet carbonate surface by chromatographic separation between sulphate (SO_4^{2-}) and thiocyanate (SCN^-) ions. The experiment is run at residual oil saturation and 25°C but can also be initiated from 100% saturated core. Thiocyanate is a tracer that has no affinity for the surface and not expected to engage in chemical interaction within the core and for this reason designated to keep track of the fluid front. Any deviation in effluent concentration between SCN^- and SO_4^{2-} on Figure 2.3 indicates area of separation (A_{wett}) and is directly proportional to water-wet surface because sulphate ions in theory only adsorb to water-molecules.

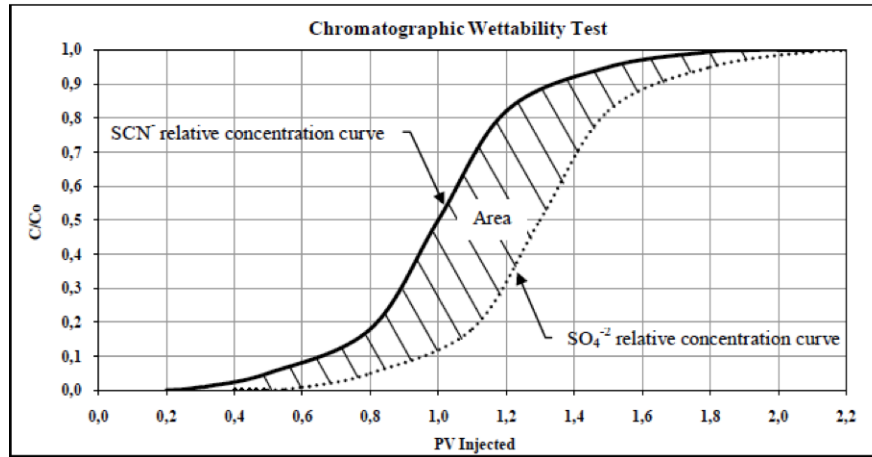


Figure 2.3: Schematic illustration of the chromatographic separation between Sulphate and thiocyanate

The area of separation, A_{wett} , is calculated using trapezoidal method;

$$Area = \sum \frac{(AN_1 + AN_2)(PV_2 - PV_1)^{SCN}}{2} - \sum \frac{(AN_1 + AN_2)(PV_2 - PV_1)^{SO_4}}{2} \quad (2.5)$$

Flooding a core aged and saturated with heptane gives a reference area ($A_{heptane}$) of 100% water-wet surface, from which a wetting index ranging from 0 to 1 can be evaluated.

$$WI_{new} = \frac{A_{wett}}{A_{heptane}} \quad (2.6)$$

2.2.1.3 Amott Method

Amott test [34] is based on saturation changes related to capillary pressure during spontaneous imbibition (SPI) and forced imbibition (FI). The principle method can be described in four steps, where maximum amount of oil and water produced are recorded;

- 1 amount of oil spontaneous imbibed by water or brine (V_{wsp})
- 2 amount of oil forcibly imbibed by the water (V_{wt})
- 3 amount of water spontaneously imbibed by oil (V_{sp})
- 4 amount of water forcibly imbibed by oil (V_{ot})

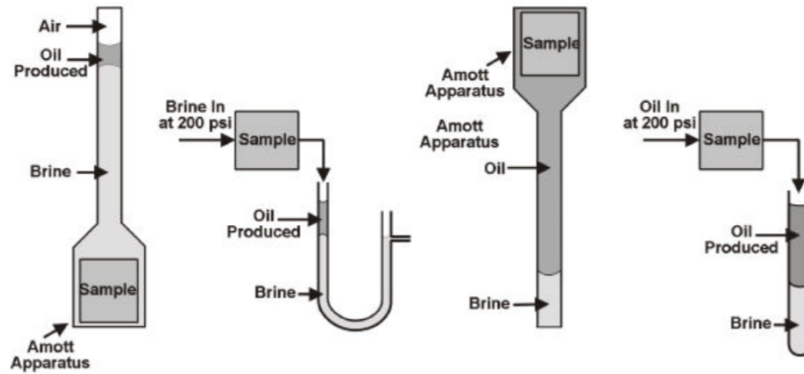


Figure 2.4: Mechanisms of Amott wettability test [35].

Duration and amount recovered spontaneously will vary depending on the rock/fluid properties at the given condition, for more consistent correlation between several cores one should perform for same period of time, and similarly for the forced imbibition rate of viscous flooding should be at a fixed value. The Amott wetting index is often given in the extended version where modification is made to the procedure of core preparation, which consist of centrifuging to accelerate the recovery processes (gravity forces are prevented) first with brine then in crude oil such that irreducible saturation's are established. Amott-Harvey index (I_{AH}) used to reduce the effects of relative permeability, viscosity and initial wetting thus become the difference between displacement by water ratio and displacement by oil ratio;

$$I_{AH} = \frac{V_{wsp}}{V_{wt}} - \frac{V_{osp}}{V_{ot}} \quad (2.7)$$

I_{AH} range from (-1) for strongly oil wet system to (+1) at the other extreme end when the core is strongly water wet.

2.2.1.4 USBM Method

Additional method with similar measuring principle to the Amott method is the United States Bureau of Mines (USBM). USBM test compares the work done by one fluid to displace the other by measuring area in the two regions of capillary pressure curves produced during the forced drainage and imbibition processes, this method is time efficient and more sensitive close to the neutral wetting [36]. The wetting index I_{USB} defined as the logarithmic ratio between the measured areas range from negative infinity (oil wet) to positive infinity (water wet).

2.2.2 Initial Wetting in Carbonates

Carbonate reservoirs were initially filled with water as deposition and sedimentation take place in an aqueous phase, hydrocarbons later migrated into the reservoir pores and a chemical equilibrium established over geological time with respect to the following important parameters;

- Initial water saturation and thin film forces
- Brine salinity and content of divalent ions
- Rock mineral and surface charge [37]
- Polar oil components, solubility and stability [38]
- Temperature/pressure [39]
- Capillary pressure (Hirasaki,1991) [40]

Information collected from more than 50 oil producing carbonate reservoirs around the world [41] and another study made on 161 different carbonate reservoir rocks (limestone, chalk, and dolomite) [42] demonstrated that majority of carbonate rocks become oil-wet over time by destabilization of coating water and attachment of oil components to the surface. This tendency is generated by a complex and non static crude-oil/brine/rock (COBR) interactions [43].

2.2.2.1 Water

Initial water is important in the reservoir affecting the overall fluid-rock equilibrium. Determination of the corresponding saturation (s_{wi}) and its distribution is highly complex although variety of methods are available. Accurate estimation will be important as small variation will make a big difference on the prediction of oil in place and fluid mobilities.

Important notice from Equation 2.8 on volume hydrocarbon encountered within the pores media is through the relations between porosity and initial water saturation.

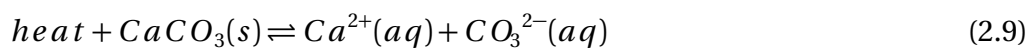
$$S_{oi} = 1 - s_{wi} - s_{gi} \quad (2.8)$$

Where; S_{oi} = initial oil saturation, s_{wi} = initial water saturation and s_{gi} = initial gas saturation. Water can exist throughout the reservoir as either formation water, injection water and as a stimulation chemical mixture. Composition of reservoir water will largely depend on rock mineral it has been in contact with at the given conditions. Most brines usually consist of large quantity Sodium Chloride (NaCl),

and electrolytes; Magnesium (Mg), Calcium (Ca), sulphate (SO₄), Bicarbonate (HCO₃), Iodide (I) and Bromide (Br) [44]. The composition will give water properties such as pH and salinity, which again will have significant effect on wettability and oil recovery [45, 46]. Water molecules are known by their dipolar characteristics that allows them to easily bond to other polar components by hydrogen bonding's. The relative small size will also allow these molecules to surround other molecules, and it will require high energy to break these bonds [47]. Thickness and stability of the water enclosing the rock are explained to be a function of attractive electrostatic Van der Waal forces between the charged surface and surrounding inter-ionic phase, known as the disjoining pressure [48, 49, 50].

2.2.2.2 Rock

Rock type will be a major wetting parameter as chemical interactions will vary with surface charge and area exposed to the crude oil and brine. Calcite surface charge is pH and salinity dependent [31], at standard conditions calcite is poorly soluble in pure water, but at higher pressures and temperature the equilibrium of its solution will move towards the right forming $HC O_3^-$ (bicarbonate) which is much more soluble in water. Similar to water, this substance will also act as an amphoteric substance, and due to differences in subsequent equilibrium constants a net pH increase will be observed in the aqueous solution. Surface charge of calcite is reported to remain positive for pH values lower than about 9.5[51, 52].



Distribution of fluid phase and also the ions contained in the electrolyte solution will be a function of the charged surface [50]. All chemical systems wants to stay in lowest possible energy state (Gibbs free energy), there will therefore be equally high concentration of counter ions (negatively charged) close to the surface making up the so called Stern layer [53] where the ions are immobile and strongly bound. The outer part is known as the electrical double layer, ions present in this region will be more mobile and less firmly associated because charge density generated around the rock surface decreases with distance from the solid surface.

2.2.2.3 Crude Oil

Crude oil is a complex mixture of hydrocarbon and non-hydrocarbon substances that can be characterized according to chemical structure. The most important components include Paraffins, Naphthenes, and Aromatics. The main crude oil components affecting wettability are asphaltenes and resins [49, 54], which both are from the heavy end fraction of the crude oil and contain acidic and basic components. Asphaltenes are large ring structured substances while resins are smaller but contain more polar compounds, like Nitrogen, sulfur and Oxygen (NSO). They are both found as aggregates and differentiation between them is on bases of solubility in different solvents [55]. Asphaltenes are soluble in resins but will precipitate in n-heptane and toluene i.e. increased aggregate size [56]. The acidic components are negatively charged, represented by carboxyls ($COOH^-$) and quantified by acid number (AN) while the base component, represented by (R_3NH^+) are positive and quantified by base number (BN) [55].

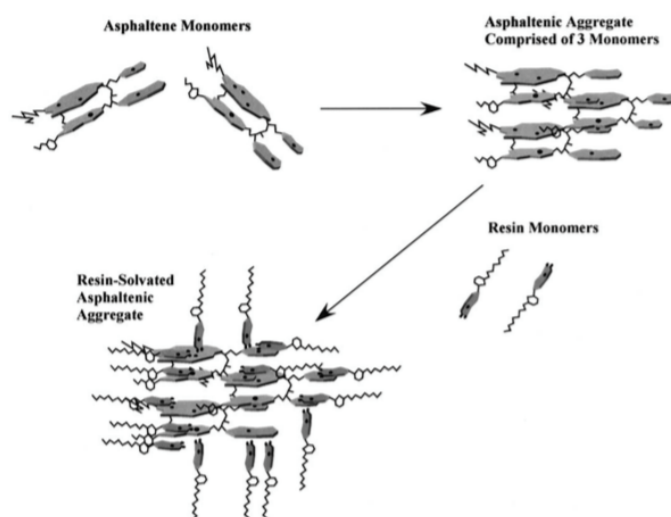


Figure 2.5: Illustration of archipelago model of asphaltene monomers, asphaltenic aggregate in absence of resins, and asphaltenic aggregate in presence of resins [56].

2.2.2.4 Adsorption of Oil Components

The different modes of establishing oil-wet condition has been described by Buckley [55];

- (i) adsorption from the oil phase
- (ii) adsorption through the wetting phase (water)
- (iii) adsorption from the oil/water interface
- (iv) surface precipitation

The adsorption processes is considered irreversible, fast and independent of temperature when water is not present [39, 49]. Total adsorption and change in wettability are taught to depend on both acid number[57] and the chalk material that should have a certain capacity limited to available adsorption sites. The capacity will somewhat also relate to effective grain size, shape and mass and expressed in terms of surface area [58]. The relationship can be expressed by different adsorption isotherms as function of adsorbent concentration/pressure at constant temperature [38, 59]. Most of the negatively charged oil components will for this reason attach to the rock surface in the initial stage but as available sites for adsorption decreases, only acidic components with the highest affinity will be able to compete.

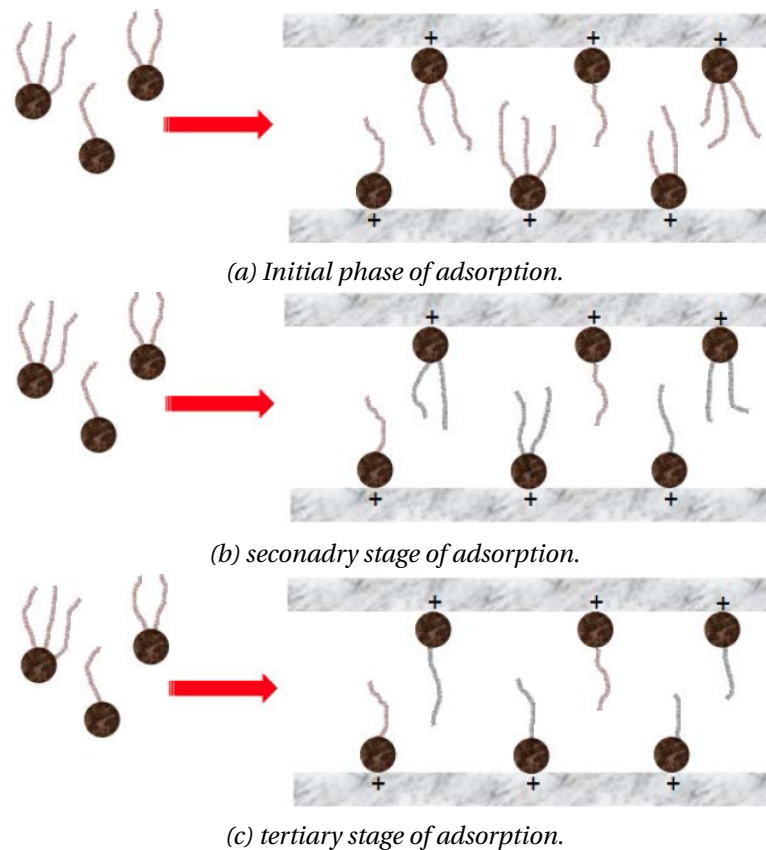


Figure 2.6: Suggested mechanism in adsorption of different carboxylic group during oil saturation

The effect of increasing cationic valences and decreasing initial water saturation was also investigated by Yan et.al [60]. The result showed increased oil-wetting and demonstrate that water will prevent access towards the surface while ions bound in the stern double layer might aid accessibility by creating bridges to the surface. Another important consideration is the ratio between resin and asphaltenes, which both are found capable of organizing and forming a rigid film at the oil/water interface [56, 61], the solubility in water is small, but acid/base

reactions can enable destabilisation of the stern layer and influence the adsorption process [8, 62]. The adsorption processes will be a function of pH, ionic strength, concentration of the monomers and also surface charge of the mineral. Equation 2.10 can be used to represent the acid base reaction of carboxylic group in water. The equilibrium has pKa at ca 5pH.

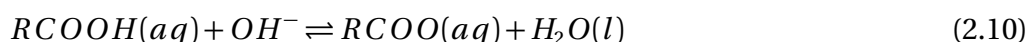


Figure 2.7 shows the change in effluent oil acid and base number during oil flooding of an outcrop chalk material. Walrond (Msc 2015) reported that adsorption of acids was more pronounced than base components.

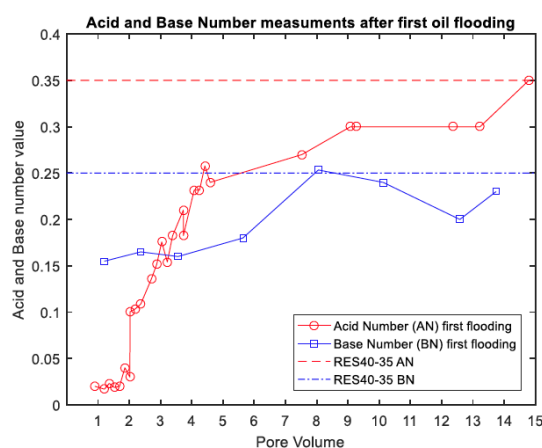


Figure 2.7: Acid and Base number change during oil flooding (Walrond Msc 2015).

Figure 2.8 illustrate that acid number will have a direct impact on wetting condition and subsequent oil recovery by spontaneous imbibition.

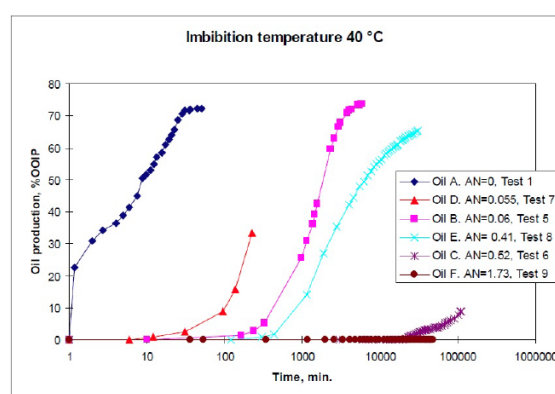


Figure 2.8: Effect of acid number on spontaneous imbibition [57].

Chapter 3

Water-Based EOR in Carbonate Reservoirs

Enhanced oil recovery methods in carbonate systems are primarily related to improving spontaneous uptake of water into the matrix, where most of the oil is trapped, this is especially true when the wetting condition is of oil-wet nature [63, 64]. In fractured reservoirs, we desire water-wet systems such that capillary forces, which is the main drive mechanism for spontaneous imbibition is increased [65]. Slightly water-wet rocks give accelerated recovery and can be observed as a straight-line modification of relative permeability curves because injected water is allowed to invade into the matrix network and displace oil into a bank. The problem with oil-wet system during waterflooding is early breakthrough time and high water production [4]. Normally we produce water/oil in a ratio from 7/1 or 8/1. We want to produce as much oil as possible but how fast we recover is even more important when taking rig cost into consideration.

3.1 Smart Water mechanism in Carbonates

Re-pressurization projects in Ekofisk field with sea water injection initiated the research on Smart Water at the University of Stavanger, with the purpose of explaining the mechanism causing recovery factor to increase far above expectations. "It was very astonishing to me that you could have such a high recovery at Ekofisk" said Tor Austad, team leader of UIS smart water project, thinking that seawater must have some kind of special effect [66]. Smart water in carbonates focuses mainly on the negatively charged oil components attached to positive carbonate sites [67], there are however documentations suggesting that positively charged components also have some play in this.

Smart water is the concept later developed for the injection of any modified reservoir brine regarding salinity and ionic composition [68]. There exist two

possibilities; injection of low salinity brine, relevant for sandstones and the injection of high salinity brine ca. 33 000ppm [69], relevant in carbonates [70]. The last mentioned is considered more challenging due to considerations that must be made to compatibility problems like; precipitation, well damage, dissolution and compaction of the rock minerals.

Smart Water injection falls under the category of water-based EOR as it arguably changes rock properties such as wettability and provides adjustments to relative permeability curve and capillary pressure in the optimization of fluid flow within the porous media. It has the main purpose of increasing the microscopic sweep efficiency, the parameter which is responsible for more than 50% of the oil left behind [4]. Recovery factor can be increased 10% or higher compared to un-optimized water injection [71].

3.1.1 Wettability Alteration By Seawater

Studies of wettability modification by seawater injection was explained by presence symbiotic interactions between the potential determining ions; Ca^{2+} , Mg^{2+} and SO_4^{2-} in the presence of pH controlling ions such as CO_3^{2-} and the adsorbed carboxylic material ($-COO^-$) [33, 72]. Figure 3.1 illustrate the proposed mechanical processes of wettability change towards a water-wet state. In the initial stage negatively charged carboxylic material is adsorbed on positively charged chalk surface, and the carbonate reservoir system is in equilibrium with formation water containing an excess of Ca^{2+} .

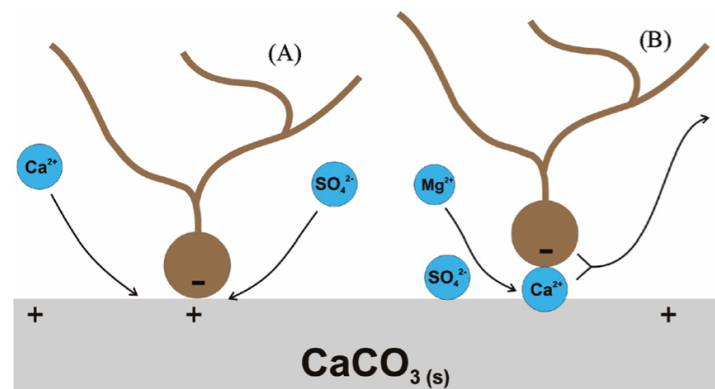


Figure 3.1: Wettability alteration by Seawater.

When seawater is injected into the reservoir the equilibrium is disturbed by sulphate adsorption (A), in response, surface charge density is reduced and Ca^{2+} from the aqueous phase can approach the surface and create ion-bonding to the carboxylic group. At high-temperature conditions, in the range 90-100°C activity of Mg^{2+} ions are increased and the main step of wettability alteration is initiated by a substitution reaction with bridging calcium ions (B).

Chapter 4

Experimental Work

4.1 Materials and Methods

4.1.1 Core Material

The porous media is an outcrop from Stevns Klint near Copenhagen (Denmark), dated ' age and quite similar to North Sea chalk. Low permeability, in the range (1-2)mD [73], very good porosity and with specific surface area $2m^2/g$ [74]. Experiments for this study are carried out on three representative chalk cores cut from the same reservoir block.

Table 4.1: collected core data.

Chalk: Stevns Klint	unit	SK-0	SK-10	SK-40	SK-10-MC
Dry weight	[gr]	93.01	94.6	93.01	93.63
length	[cm]	6.018	5.962	6.018	5.962
Diameter	[cm]	3.898	3.8	3.898	3.8
Bulk volume	[ml]	71.817	67.616	67.543	67.616
Density (diluted VBOS)	[gr/ml]	1.04	(1.003)	(1.0168)	(1.003)
Saturation weight (VBOS)	[gr]	—	126.75	126.81	123.83
Pore volume	[ml]	36.6	32.1	32.7	30.1
Porosity	[%]	51	47	48	45
Initial water saturation	[%]	0	10	40	10

$$\phi = \frac{W_{Dry} - W_{sat}}{\rho_f} \quad (4.1)$$

Porosity is calculated using weight difference between brine saturated core after cleaning with DI-water (W_{sat}) and dry weight (W_{dry}) according to Equation 4.1. The high porosity value indicates that source of the chalk material has undergone a low degree of combined compaction/cementation or merely the resultant of a high degree micro-pores between the material constituents.

4.1.1.1 Core Preparation

Preparation method for all cores includes drilling, cutting and milling to same dimensions. To restore natural properties of the chalk material, most importantly the removal of sulphate impurities a suggestion of flooding 250ml DI-water at ambient temperature and 0.2ml/min is made a standard cleaning procedure [75]. Batch test, which is a simple precipitation test, is used as an indicator for core free for sulphate contamination. Chemical equation where Barium sulphate ($BaSO_4$) is precipitated by adding Barium Chloride salt to collected effluent is presented by Equation 4.2.



4.1.2 Brines

The brine solutions were prepared by dissolving appropriate amount of salts in distilled water. Carbonate, chlorite and sulphate salts are all first dissolved separately to avoid precipitation during mixing. When all salts are added to one solution, it is left to stir for one day to ensure full dissolution and filtrated using VWR vacuum gas pump with a $0.22 \mu m$ filter. The different types of salts and specific ionic compositions are to be found in Table 4.2.

VBOS, Synthetic Valhall formation water, i.e. not 100% identical, but fits well considering salinity variations. This brine is used as native water and as imbibing fluid during spontaneous imbibition for all cores.

SWOT, Seawater depleted in sulphate and thiocyanate $[SO_4^{2-}] = [SCN^-] = 0$. SO_4^{2-} is considered surface active, potential determining ion, SCN^- is not and hence functions as a tracer in the chromatographic wettability test.

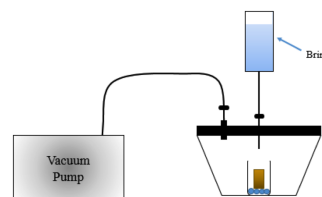
SW1/2T, This brine has equal amounts, 12mM, of SO_4^{2-} and SCN^- and is used in the secondary seawater flooding after residual oil saturation (S_{orw}) is reached with SWOT.

Table 4.2: properties and composition of brines used.

Brine Ionic Content	VBOS [mole/l]	SWOT [mole/l]	SW1/2T [mole/l]
HCO_3^-	0.009	0.002	0.002
Cl^-	1.066	0.583	0.583
SO_4^{2-}	—	—	0.012
SCN^-	—	—	0.012
Mg^{2+}	0.008	0.045	0.045
Ca^{2+}	0.029	0.013	0.013
Na^+	0.997	0.460	0.427
Li^+	—	—	0.012
K^+	0.005	0.010	0.022
TDS	62.83	33.39	33.39
Ionic strength	1.112	0.643	0.645
Density [20C, g/ml]	1.042	1.024	1.024

4.1.3 Initial Water Saturation by Desiccator method

Initial water saturation was established placing dry and cleaned core inside vacuum pump container, this equipment creates a vacuum inside the chamber and allows diluted Valhall brine (VBOS) to imbibe and fully saturate the core. Dilution with distilled water at calculated proportions was made to preserve composition of formation water after vapourisation processes in the desiccator method. The target saturations are 0%, 10% and 40% in the three respective cores; SK-0, SK-10 and SK-40. Uniform distribution of initial water was ensured placing the core plug in a closed container and letting it to equilibrate for three days time before saturating with oil.

**Figure 4.1:** Vacuum pump by Frida Layti (BSc 2015).

4.1.4 Crude Oil

Acid Number (AN) and Base Number (BN) of oil is very important parameter with regards to surface reactivity and oil recovery [76], for this experiment we are using fixed values to have an oil composition that allows comparison of results with previous studies. Base oil is Heidrun Crude Oil (sample nr.14, well 6507/7–8,

dated 22/7–87, and delivered by ConocoPhillips) with heptane and silica gel additives. Dilution of crude oil with heptane is made to reduce oil viscosity and hence required pressure to displace the oil. Accordingly, we prevent risk of fracturing the core sample. This does not necessarily give poor representation since gas naturally present at reservoir conditions also contribute to reduce the oil viscosity. It is more important to keep control of the displacement velocity.

Normally, reservoir fluids flow at ca. 1ft/day = 0.02cm/min [77].

Synthesization is made diluting base oil with heptane at volume ratio 60:40, followed by mixing procedure with silica gel til desired AN is reached. Quantity of silica gel required is observed to be sensitive to method used, one recommendation is to add about 35wt% (with respect to crude oil), this gives an oil sample with 0AN when gradually added over 3 days. Caution should however be taken to oil consumption since silica gel eliminates acidic components of the oil by precipitation. In the final step, oil with 0AN is mixed by weight percent with an untreated oil/heptane blend to give RES40(AN = 0.33mgKOH/g, BN = 0.20mgKOH/g, and density=0.8078g/ml). From correlation with Emeka (MSc 2011), viscosity should be ca. 2.45.

Removal of precipitates was done by centrifuging at ca. 45 mph for about one hour, and no further precipitation was observed during storage. Filtering was performed through a 3 μ m Millipore filter as part of flow capacity improvement.

4.1.5 Experimental Setup for Core Flooding

All viscous flooding procedure is performed in similar manner. The low permeable chalk material was placed in a protective rubber sleeve and mounted to Hassler core holder inside a heating cabinet. The core can easily crack, for this reason a rather low confining pressure of 15-20 bar was applied, this should be sufficient to keep the core fixed in place and preventing fluid to flow around the core plug. Backpressure is set at 6 bars to prevent boiling of fluid inside the heating chamber. Flooding processes are done at 50°C, higher temperatures, give risk of fracturing the core [78]. Flow rate was controlled using a Gilson High Performance Liquid Chromatography (HPLC) pump, with an accuracy of about ± 1 % . The pump is connected to a desktop computer that controls fluid sampling. The computer will automatically stop when exceeding the limit set for the various parameters and thus ensure that we can perform the experiment in a security safe manner.

4.1.6 Oil Flooding and Aging

Initial oil saturation in all cores was established flooding 15PV oil in one and same direction at 50°C and a constant rate of 0.1 ml/min. All flow-lines were cleaned after each flooding using heptane and DI-water, followed by drying with Nitrogen

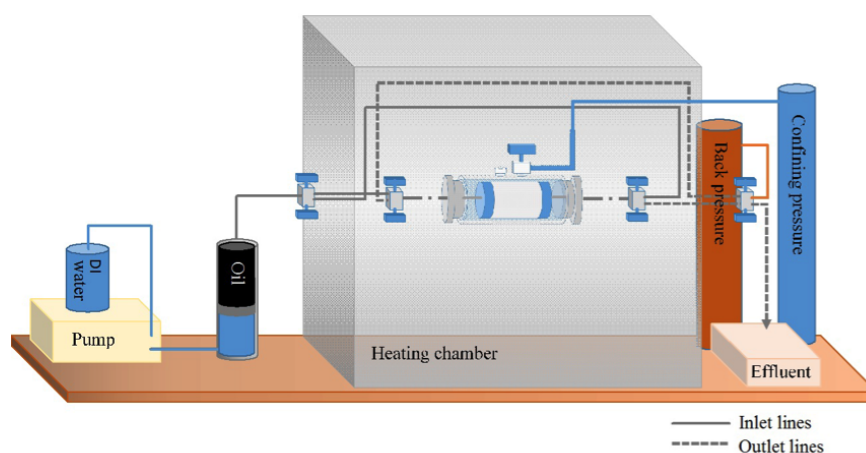


Figure 4.2: Oil saturation and flooding setup by Ingrid Omland (BSc 2015).

gas. Volume oil injected/produced is controlled by calculating weight change in sealed vials before and after effluent sampling divided by the oil density. Output oil is then put for Acid Number and Base Number measurements.

Aging is made using Teflon tape as a protective shield around the core samples saturated with oil and isolated inside aging cell at 50°C for two weeks. Aging is considered a necessary step for generating a homogeneous wetting state that best mimic real reservoir conditions [79]. The aging cell is airtight and filled with oil used for saturation.

4.1.7 Mild Cleaning

Additional investigation to observe impact of core restoration is made on core (SK-10%) by cleaning the core with kerosene, n-heptane and DI-water. The core is restored back to initial water saturation of 10% using same formation water and put for a secondary oil saturation and subsequent acid and base number measurements.

4.1.8 Wettability Measurements

Wettability measurement in this thesis is by means of chromatographic wettability test and an incomplete Amott-test.

4.1.8.1 Amott Method

In the first step a core saturated with oil is immersed in formation water inside Amott-apparatus and placed in a heating chamber monitored at 50°C, see illustration Figure 4.3a. Amount of oil produced by spontaneous imbibition (SPI)

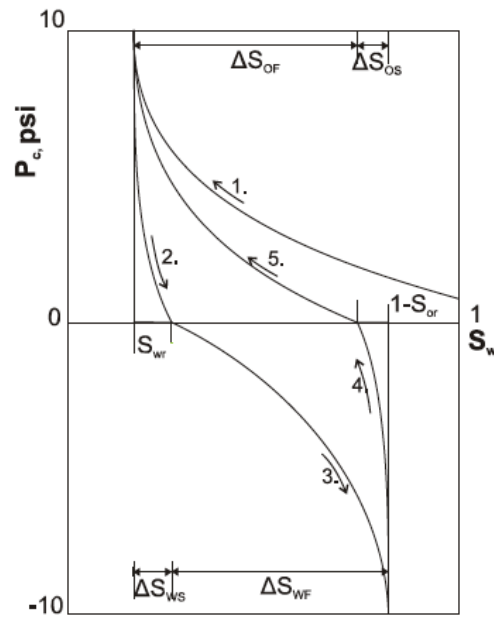
is recorded directly from the funnel-shaped lucite tubes regularly over a period of one week. During drainage of oil a simultaneous imbibition processes of surrounding fluid take place with a counter-current flow.

In the second step, forced displacement of oil is performed by injecting same brine with an externally applied pressure until residual oil saturation (S_{orw}) is reached. Amott [34] has also reported that extracting or drying the core during testing should be avoided due to possible impact on measured wettability. The ratio of spontaneous imbibition to forced imbibition is then used as final average measure of wettability in the porous media. Completely oil-wet system should have Amott index close to 0 and its Amott index for water in the range of 1.

$$I_w = \frac{\text{Spontaneous imbibition}}{\text{Forced imbibition}} \quad (4.3)$$



(a) two in front) Spontaneous imbibition of SK-10 and SK-0; and aging of SK-40 (back).



(b) Capillary pressure curve.

Figure 4.3: Combined cycles of spontaneous and forced imbibition gives the entire Capillary pressure envelope

Forced imbibition with formation water (VB0S) was started once spontaneous imbibition ceased off at same temperature with the injection rate 1PV/day. The flow rate was increased when recovery plateau is reached, first to 4PV/day then 8PV/day. Produced fluid was collected in a burette, from which the oil level could be recorded directly.

4.1.8.2 Chromatographic Wettability test

Chromatography wettability test is usually performed after the forced imbibition processes by simply monitoring the temperature to 25°C and producing remaining oil inside the core by SWOT brine at 0.2ml/min until a new residual saturation is reached. Before proceeding to the main step one must ensure no trace of sulphate inside the core with the Batch test. Flooding processes at S_{orw} is continued by injecting the brine containing equal amount in SCN^- and SO_4^{2-} (SW1/2T) while maintain same injection rate, (3-4)PV is normally sufficient. The area of separation between tracer and sulphate is then evaluated, from Ion chromatography analysis on effluent fluid, and compared to 100% water-wet core as an indication of core wetting state.

4.1.9 Chemical and Physical Analysis

4.1.9.1 Determination of Acid Number and Base Number

Polar components of interest in our wettability study is mainly acids of type carboxyls (-COOH) but measurement on base groups (RNH^{3+}) is also made. Measurements are done with Mettler Toledo DL55 auto-titrator with an internal standard developed by Fan and Buckley [80]. The instrument uses a blank test as a reference during potentiometric titration of oil samples, where measurement of electronic potential is converted to equivalent Acid and Base number. Total number of acidic groups per molecule determines the acid number (AN) because it indicates quantity of KOH required to neutralize the oil sample on a mole-bases. Each measurement requires respective titration solvent and spiking solution. Refer to Table A.2 and Table A.1 for chemical description.

Application of Mettler Toledo weight instrument with an accuracy down to 4th decimal appeared to be essential for the test repeatability. Previous method only relied on persistent use of the pipettes, accuracy will not be sufficient as both titration solvent and spiking solution are volatile. Instrument reading is especially sensitive to the last mentioned. Procedure used to resolve this challenge is as follows; Add 1ml spiking solution and put on easily retrievable cap-lock (make note of measured weight for consistency), finally add 50ml titration solvent and the oil sample (collected with a syringe ca. 1.2ml)

Calibration and blank measurements are made regularly to compensate for changes in electrode properties with time exposed to air and with slightly changing oil composition. Determination of acid number measurements is seen to be reproducible within the uncertainty ± 0.02 . Calculation method for Acid Number is shown below, similar calculation also exists for Base Number. Starting

point is standardization where true concentration of titrant is evaluated and stored on the computer.

$$C_{KOH}[mol/L] = 1000 * \frac{M_{KHP}[g]}{204.23 V_{st}[ml]} \quad (4.4)$$

Where, M_{KHP} is mas (grams) of KHP, and V_{st} is volume titrant used to neutralize 50ml of the standard solution. The constant 204.23 is molar mass (grams/mole) of KHP, while 1000 is a conversion factor from milligrams to grams. The acid number (AN) is then calculated as follows;

$$AN[mgKOH/g] = \frac{[V_t - V_b] C_{KOH} 56.1}{W_{oil}} \quad (4.5)$$

V_t and V_b is the amount (ml) of the titrant required to neutralize the crude oil and blank sample respectively, and W_{oil} is weight of oil, which is in an input parameter. The number 56.1 is molar mass of KOH.

4.1.9.2 Ion Chromatography

Ion-exchange chromatography is a process of ion separation and identification from a diluted sample based on their interaction with a resin. A liquid known as eluent runs through a pressurized column, where ions absorbed to a strong anion/cation exchange stationary phases (columns) can be separated. The computer uses retention time, travel time through the columns, as fingerprints of the components and maps out plot of retention time vs conductivity, where area under respective peaks corresponds to their relative concentrations. The tracer (SCN) has a retention time of 13.60 min, while sulphate is detected after only 3.91 min.

All our samples were diluted 500X, using a Gilson Gx-271 Liquid Handler, to stay in the linear region of the calibration curve, and reference samples used are; SWOT, SW1/2T, and DI-water.

Chapter 5

Results & Discussion

With the objective of understanding initial wetting conditions in carbonate reservoir representative chalk cores, collected from the same quarry, were drilled and dimensioned; (length \approx 6cm, diameter \approx 3.8cm). Cleaning procedure was made before establishing initial water saturation(s) with Vallhal formation water (VBOS).

5.1 Reference Core

Figure 5.1 and Figure 5.2 are collected reference cores that is 100% water-wet. Core REF1 is collected from Walrond (MSc 2015), his preparation method of the Stevns Klint core (SK-REF1) is similar to descriptions made in this work. Area of separation from core SK-REF1 will be relevant in determination of core wetting state.

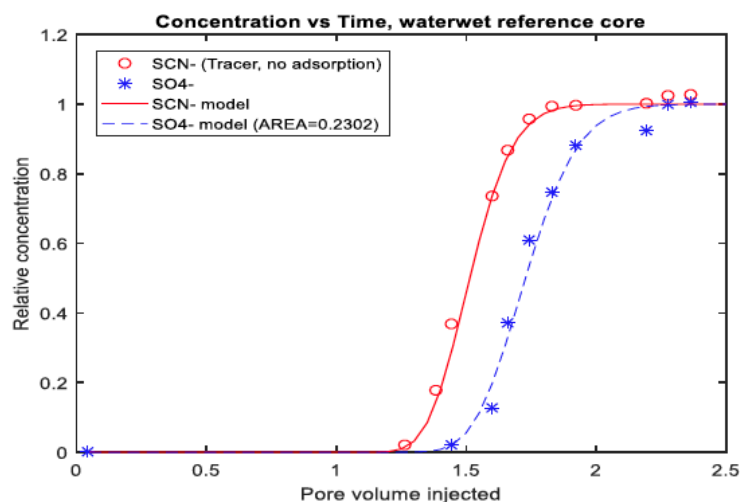


Figure 5.1: Chromatographic wettability analysis for core REF1 at 25°C, Walrond (MSc 2015).

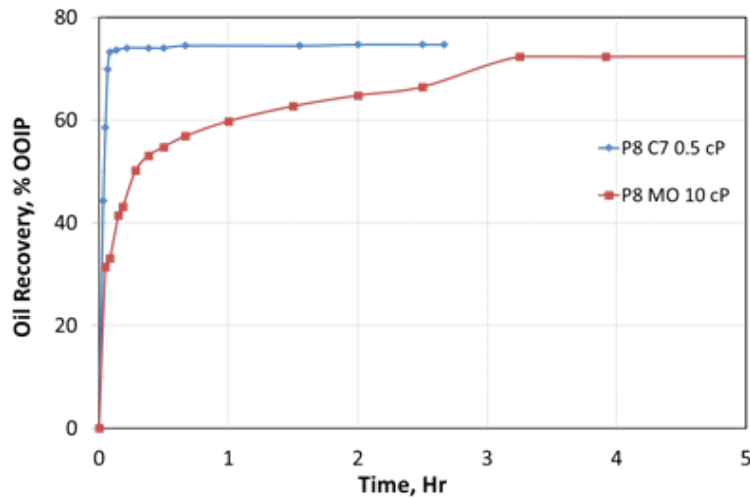


Figure 5.2: Spontaneous imbibition at 50°C, and $S_{wi}=10\%$, using two different mineral oil Jaarvik (MSc 2015)

Optimum imbibition can be observed using an oil sample with zero AN or in other terms, completely water-wet core. Resultant recovery of about 70% was observed within 20 minutes time by SPI processes alone. The oil phase is n-heptane that is free from heavy end oil fraction and adjusted at two different viscosity's. Core SK-REF2 is only representative for a core with 10% initial water saturation.

5.2 Adsorption of polar oil components onto water wet chalk surface

Three chalk cores (SK-0% ,SK-10% and SK-40%) at different initial water saturation of 0%, 10% and 40% respectively where subjected to oil flooding and corresponding effluents were investigated for adsorption of polar components. Oil sample (RES-40) with Acid Number = 0.33mgKOH/g and Base Number=0.20 mgKOH/g was flood 15PV at a rate 0.1 ml/min under thermal condition of 50°C. All flooding procedure in this work is carried out in one and same direction through the core.

5.2.1 Effect of initial water saturation

We are looking to investigate effect of initial water saturation on wettability modification during oil saturation for cores that are initially 100% water-wet. Results from Acid and Base Number measurements are plotted as a function of injected pore volume.

5.2.2 SK-0%

Figure 5.3 show adsorption studies on a core with 0% initial water saturation.

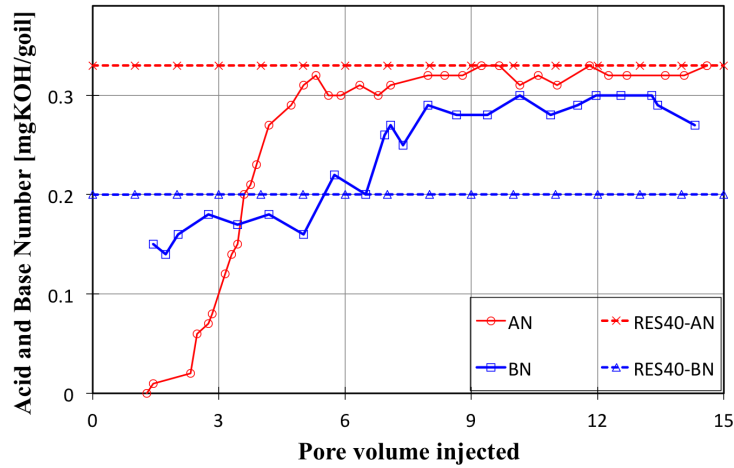


Figure 5.3: Acid and base number measurements of [SK-0%].

Acid Number starts off at zero and increases progressively towards the originally injected value where a plateau is established. All retention of acidic components according to our present understanding is related to adsorption. Cumulative adsorption to the chalk surface is quantified in terms of total area ($PV \cdot mgKOH/g$), represented as space between the initial acid number of the injected oil (RES-40-AN) and respective output AN curves. The area is determined using the trapezoidal method; $Area_{SK-0\%} = 1.20 (PV \cdot mgKOH/g)$.

Base Number is initially at a lower value but more or less stable in the first 5PV injected, the next three pore volumes is dictated by an increasing trend such that stabilisation take place above injected BN value.

5.2.3 SK-10%

AN/BN measurements on core with 10% initial water saturation.

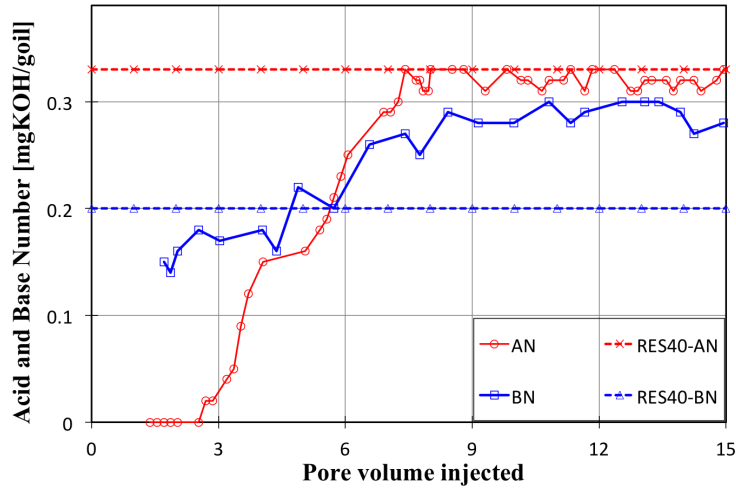


Figure 5.4: Acid and base number measurements of [SK-10%].

Again, Acid Number increase start off at zero but the retention time at this value is longer. Adsorption equilibrium is also reached at a later stage (8PV) such that total area become larger; Area SK-10%=1.61(PV*mgKOH/g).

Adsorption of Base Number is so insignificant that adsorption area is not calculated, in fact, it would have become negative as indicated by the integral of base number curve from (0-15)PV with respect to RES40-BN line. The increasing trend of BN is similar to the behaviour when water is absent (SK0%), starting close to 5PV injected and showing decreasing trend at the end of the oil flooding. It is also noted that BN increase is not triggered by establishment of AN adsorption equilibrium.

5.2.4 SK-40%

Adsorption onto 40% initial water saturated Stevns Klint core.

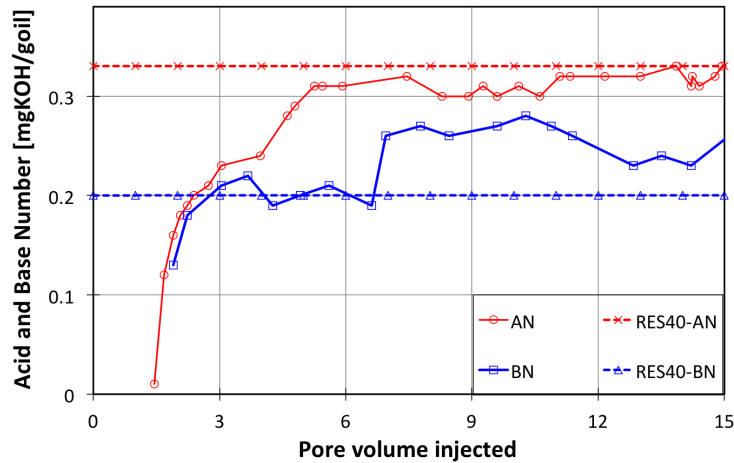


Figure 5.5: Acid and base number measurements of [SK-40%].

There was a concern that water at this saturation might be mobile and it proved to be so as traces of water was seen in the first oil samples collected. Although an attempt was made to carefully extract and remove it, human error and possibility exist for water to be present in the oil sample used for acid/base number measurements. Rapid Acid Number increase is observed during the first 2PV injected, from AN value slightly above zero, this give rise to the question weather produced water might cause this abnormal behaviour. In order to verify this an experiment was carried out mixing oil and water at different proportions according to descriptions in Section 5.2.6. Furthermore, we see that adsorption equilibrium is not clearly reached until about 11PV injected. Despite the delay in adsorption equilibrium total adsorption area is lower than at previous two initial water saturations; Area SK-40=0.97(PV*mgKOH/g).

Corresponding Base Number is also lifted in early data, and the disturbance seem to seas off after ca. 6PV injected. BN increase will after this point follow same behaviour as in previous two cores but with a more evident decreasing trend at the end.

5.2.5 SK-10%MC

Figure 5.6 show the secondary oil saturation on restored SK-10% after mildly cleaning the core with solvents. The study seeks to clean a core in such way that some of the originally adsorbed carboxylic group are still bound to the pore surface. The idea is to modify initial wetting and see contribution made on adsorption during secondary oil flooding.

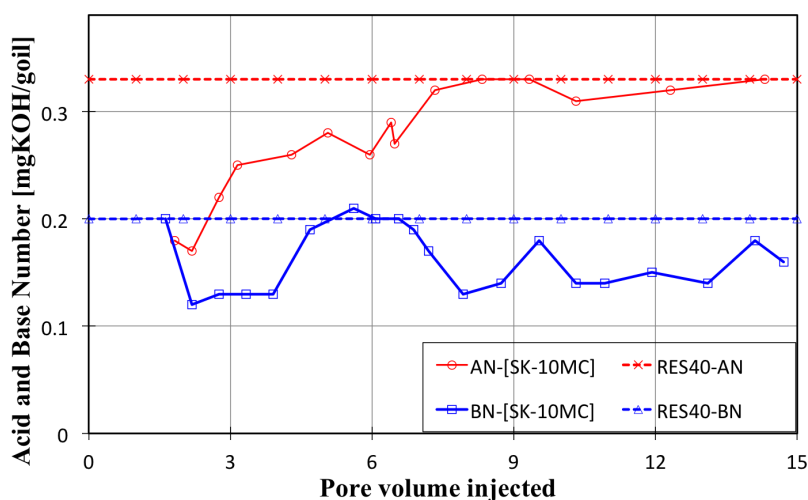


Figure 5.6: Acid and base number measurements of [SK-10% MC].

Adsorption of acids on restored core appear to be smaller. The AN starts at much higher value in the first data samples collected, but the adsorption equilibrium is reached after about same pore volume injected. Total adsorption has been reduced from 1.61 (pre-cleaning state) to 0.81 i.e. about half of the adsorption sites are lost or pre-occupied.

It is also evident that reactivity of base number is significantly changed. Mild cleaning appears to somehow modify affinity between chalk surface and the positively charged basic groups such that a co-adsorption take place.

5.2.6 Effect of water and chalk on AN/BN measurements

To better understand the impact of water on AN/BN measurements a simple test was carried out mixing oil and water at different ratios on autorotating equipment. In a secondary test, cleaned chalk of Stevns Klint type was crushed into powder and added to equivalent oil/water mixtures to see changes in adsorption behaviour, if any. The only changing variable is water volume; oil volume is 5ml, and chalk weight is 0.5g. Measurement of AN and BN is made once equilibrium is established by carefully collecting the gravity segregated oil portion.

Table 5.1: Effect of water and chalk on BN(mgKOH/g) measurements

Water content	BN, zero chalk	BN, 0.5g chalk
[1.5ml]	0.26	0.23
[1.0ml]	0.32	0.35
[0.5ml]	0.37	0.31

Table 5.2: Effect of Water and Chalk on AN(mgKOH/g) measurements

Water content	AN, zero chalk	AN, 0.5g chalk
[1.5ml]	0.86	0.36
[1.0ml]	0.82	0.33
[0.5ml]	0.88	0.56

The expectation was to measure acid number, AN = 0.33 and BN=0.20 when no chalk is present in the mixture, this would ensure precision to sample extraction in mixtures where traces of water exist. The presence of water in collected oil sample will cause uncertainty to the collected oil weight, which is an input parameter, but also to the concentration of acids and bases in the RES-40 oil sample.

Presence of water is seen to cause a change in both AN and BN, more so for the acid number; $(0.88/0.33)=2.66$, $0.37/0.20= 1.85$. The secondary test confirmed adsorption of acids to chalk and that bases don't.

5.3 Effect of Swi on adsorption of acid components

Figure 5.7 show comparison of Acid Number measurements at the three initial water saturations; 0%, 10% and 40%.

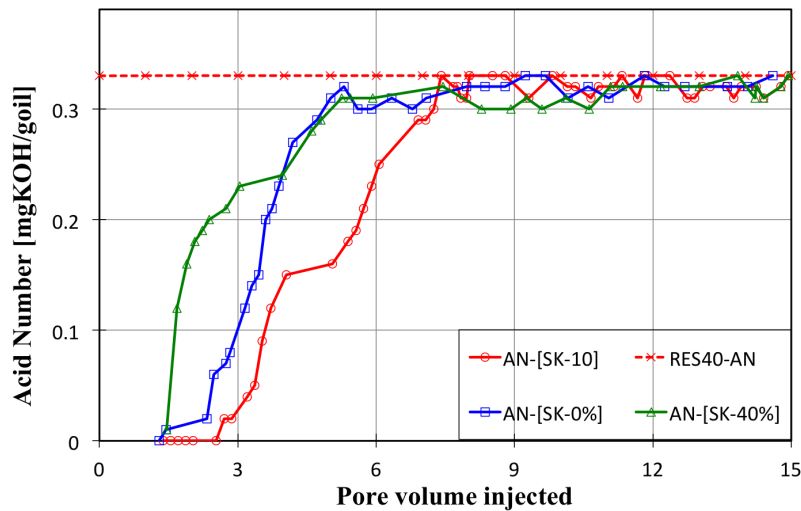


Figure 5.7: Effect of initial water on Acid Number.

The increase of AN for SK-0% and SK-10% starts after ca. (2-3)PV and effluent color in early data are seen to change from light to natural dark, i.e. free from heavy end fraction of the crude oil. The core saturated with 40% water behave somewhat different in early time and explanation for the deviation was verified by the results presented in Table 5.2.

The rate of adsorption is relatively high to start with, and this makes sense as there are more surface exposed to the first oil droplets entering the core. With time, as more oil diffuses through the core there will be less available sites and subsequent rate of adsorption reduced.

Although we are plotting against PV injected, we can't expect the entire void fraction to be contacted after 1PV injected due to poor displacement front. Presence of natural fractures and artificial channels induced by fluid flow will also contribute preventing plug flow of the complex fluid system. Frida Layti (Bcs 2014) performed a two directional flooding test and observed a sudden jump in acid number upon change in flooding direction. Her observations could demonstrate the effect of adjustments made to the displacement front were a smaller time within the core is experienced by the injected fluid. Nevertheless, adsorption equilibrium of the three cores is established at different times and it appears that water is responsible for the delay, similar to the observation made by cuiec [81].

Presence of water will in view of the observations cause a charged interface where more interactions between dissolved solids and oleic phase take place, and as water saturation increases (larger diffuse double layer) longer time will be required to establish a stable equilibrium. Ions present in the brine can interact with the surface, create a water-film and make it difficult for oil components to come through [39]. A similar contribution could also come from dissolved bicarbonate such that increased repulsive forces towards the negatively charged carboxyls is experienced.

5.4 Effect of Swi on adsorption of base components

Following figure compares Base Number measurements on the three chalk cores SK-0%, SK-10% and SK-40% to see the effect of initial water saturation.

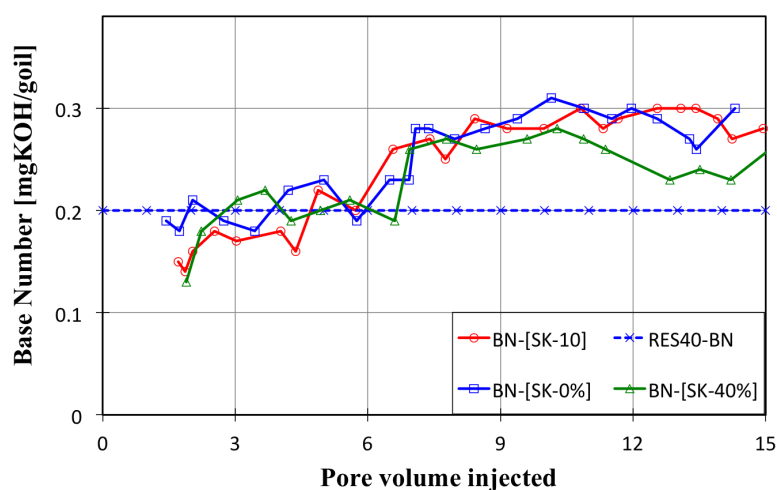


Figure 5.8: Effect of initial water on base Number.

In scope of the overall Base Number measurements we see smaller variation and less scattering from one core to the other. Similarly from chalk/water/oil mixture test we see negligible base number variation. Average change was 0.02 mgKOH/g, which is within the range of uncertainty. Adsorption to chalk surface is for this reason not believed to take place chemically by strong covalent bonds, but rather a physical adsorption if any, depending on ions close to the surface. The observations are thus in line with current theory, the basic oil components will not have competitive adsorption affinity as long as the chalk surface remains positive.

For some reason, we see a sudden increase of BN (higher than injected value) after about 6PV followed by a decreasing trend as AN come to equilibrium with the rock surface. It cannot be the effect of produced water. This would be encountered at early time, same behavior was also seen for cores with immobile initial water. There must be some kind of a chemical reaction taking place between the rock and oil components. Explanation can be given with support from the theory part and with observations by Puntervold [82], she described existence equilibrated acid-base complexes within an oil sample, under such conditions, it appears here as if complexing ability of acids are weakened as more adhesion take place to the chalk surface. Alternative possibility is the dissolution of chalk material, which in aqueous solution is slightly alkaline, and where the decreasing trend of BN after about 12PV could be a result of le chatelier's principle.

5.4.1 Effect of Core Restoration

Figure 5.9 illustrate a change in surface reactivity of oil components towards the chalk in response to core restoration by mildly cleaning core SK-10% and performing a secondary oil flooding. The base number is seen to be fully reversible considering the most important period of interaction while AN is completely different, this adds another characteristic dimension to chemical vs physical adsorption [83].

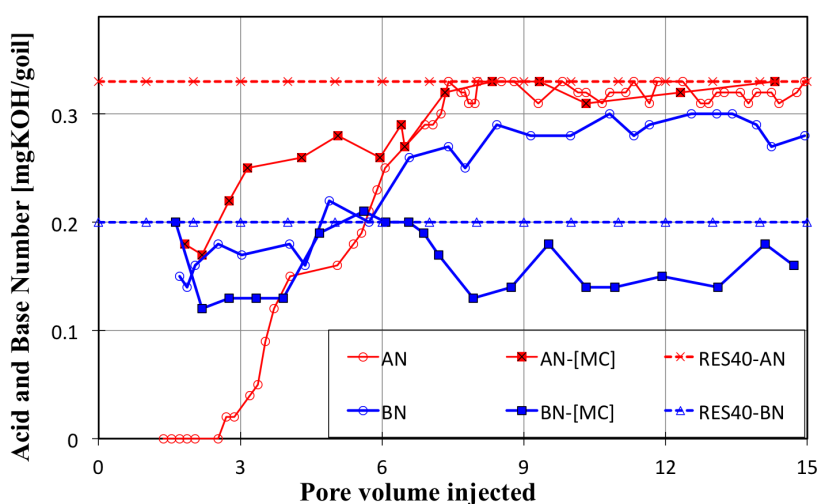


Figure 5.9: Effect of core restoration [SK-10%].

The explanation for observing smaller total adsorption of acids on the mildly cleaned core is due to modifications made to the initial wetting by insufficient removal of originally adsorbed carboxyls. This gives reason to believe that only

weakly bonded acid components are removed while smaller components which are strongly bonded still remain at the surface and will continue adsorbing in the secondary flooding due to higher affinity for the available sites. Refer to the theory regarding adsorption of different oil components Section 2.2.2.4.

Higher adsorption of the base material is seen in the secondary flooding with mild cleaning similar to observation by Walrond (MSc 2015). To resolve this problem, we must go back to the analogy of preserved carboxyls. In this case, rock surface charge will be low and lower zeta potential will reduce repulsive forces such that base components are more strongly bonded within the diffuse double layer.

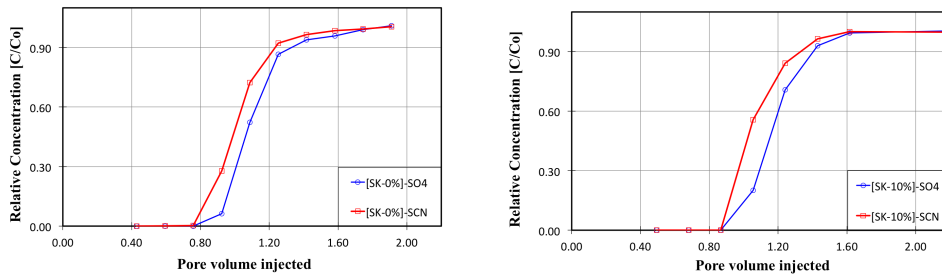
There are some published papers claiming that chalk from Denmark contain clay coating [84]. Dr.Strand performed EDS analyses on Stevns Klint chalk material [73], resulting calcite purity was 96.18%, whereby the impurities come from Silica, Sodium and Magnesium, which in fact are main ions found in clays. The possibility thus exists for rapid adsorption of small portion base material to the negatively charged clay surfaces in early data.

5.5 Wettability alteration

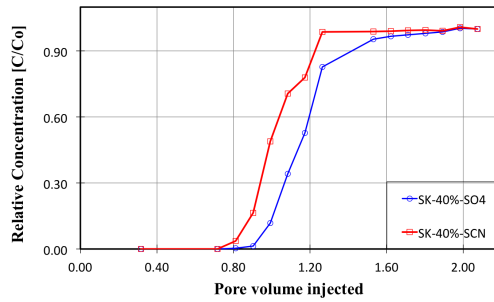
This section will investigate wettability alteration resulting from the adsorption of oil components by chromatographic separation method. Wettability determination by Amott method was skipped due to uncertainties in collected data from forced imbibition test. Results from the spontaneous imbibition will however still be relevant for discussion.

5.5.1 Chromatographic Wettability test

Once residual oil saturation is established in the forced imbibition, seawater brine (SWOT) with zero sulphate and tracer content is injected in the same direction as part of the first run in the chromatographic wettability analysis. After a dynamic equilibrium is reached at 0.1ml/min, subsequent flooding with main brine (SW1/2T) is made at a constant rate, this is the only test conducted at ambient temperature. Effluent concentration relative to brine concentration of ions (C/C_0) is plotted with respect PV-injected.



(a) Chromatographic separation of SK-0% . (b) Chromatographic separation of SK-10% .



(c) Chromatographic separation of SK-40% .

Figure 5.10: Chromatographic wettability analysis at 25°C.

The S-shaped trend is a footprint of the chromatographic separation method. Increasing concentration of both $[SCN^-]$ and $[SO_4^{2-}]$ with time is observed. Tracer ions are in unbound state within the core, retention is neither caused by sorption, precipitation nor complexation. The tracer is assumed to be described by diffusion, dispersion and advection only, no chemical interaction is expected for (SCN^-) at low temperature [85]. The potential ions are seen to be shifted relative each other on all three charts, with sulphate on the right-hand side.

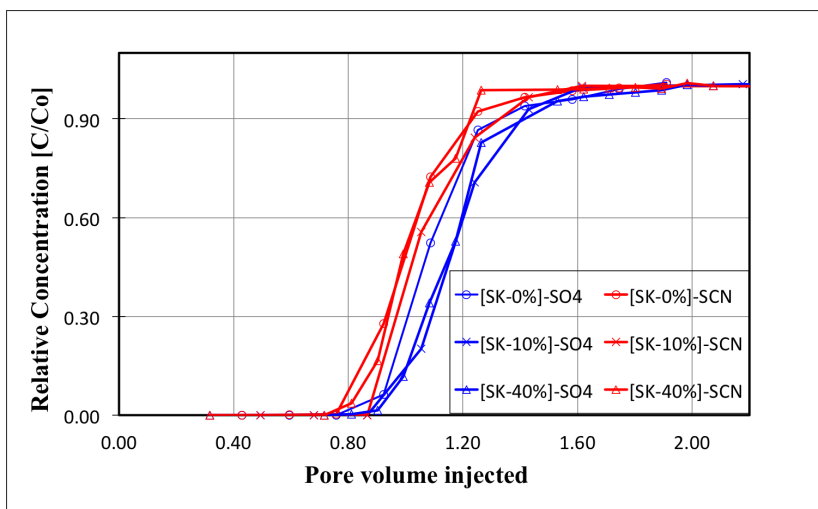


Figure 5.11: Effluent profiles of cores (SK-0% ,SK-10% and SK-40%) (comparison).

The test is designated to prevent precipitation of sulphate by using relatively low concentration and monitoring temperature such that activity increase through decomplexation is not experienced. Retention of sulphate is entirely related to adsorption at water-wet fraction, we can for this reason relate the area of separation to water wetting state (given reference core is representative)

The area of separation (A_{wet}) is clearly different and seem to increase with increasing water saturation. Calculated values using trapezoidal method are as follows from low to high water saturation; 0.09, 0.12 and 0.14. Reference core (100% water-wet) has area $A_{ref} = 0.2302$. Wetting index by chromatography method can thus be calculated from following relation $W I_{new} = A_{wet}/A_{ref}$; SK-0%=0.382 (more oil wet), SK-10%=0.521 (neutral wet), SK-40%=0.593 (more water wet).

5.5.2 Effect of adsorption on wetting condition

Previous adsorption studies conducted on SK-cores were performed at 10% initial water saturation and it was believed that resulting wetting condition reflected the total adsorption area of acids. Table 5.3 give an overview of the collected results at 10% S_{wi} . SK1= Walrond (MSc 2015), SK2=Omland (BSc 2015) and SK3=Layti (BSc 2015). The oil samples were prepared such that final acid number was close to 0.33. Respective results after mild cleaning and core restoration is indicated in parenthesis. PhD student Paul Hopkins has the credit for continuing my work on the mildly cleaned core (SK-10%MC).

Table 5.3: Comparison at 10% initial water saturation

test	total acid adsorption	A_{wett}	$W I_{new}$	wettability
SK-10%	1.61 (0.81)	0.12 (0.08)	0.521 (0.347)	neutral wet (Oil wet)
SK1	1.60 (0.80)	0.12 (0.09)	0.52 (0.41)	neutral wet (more oil wet)
SK2	1.31	0.13	0.520	neutral wet
SK3	1.22	0.15	0.579	neutral wet

It should be noted that reference value used for determining the wetting indexes are different; Layti and Omland are using $A_{wett} = 0.255$, while Walrond is using the reference core SK-REF1 with $A_{wett} = 0.2302$. Normalizing all results with respect to SK-REF1 would give a higher $W I_{new}$ for SK2 and SK3 such that a systematic increase in water wetting is observed with reduced adsorption area of acids.

5.5.3 Effect of wetting condition on spontaneous imbibition

Spontaneous imbibition was performed at 50° prior to chromatographic wettability analysis. The imbibing brine is of same composition as the initial water within the core, chemical interactions by smart effect is thus not anticipated. Discussion will be made assuming core wetting state established through the two weeks of aging at 50°C is unchanged by the imbibition process. Results are presented in terms of original oil in place (OOIP%).

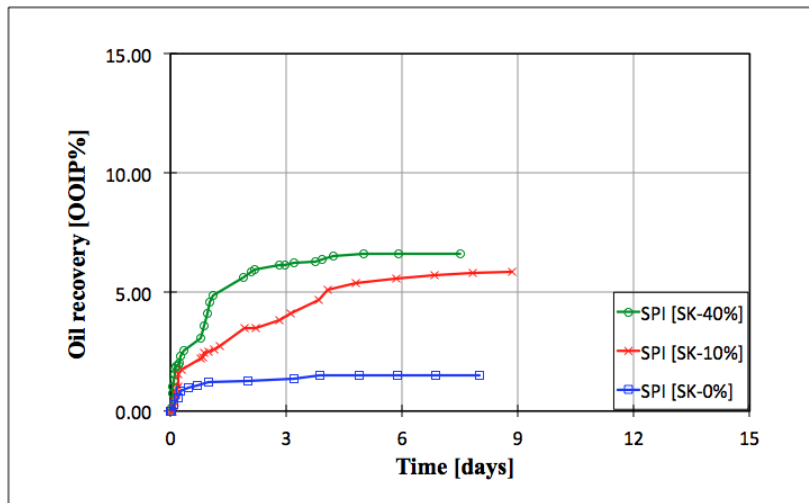


Figure 5.12: Spontaneous imbibition on three chak cores at 50°C.

5.5.3.1 SK-0%

We observe lowest spontaneous imbibition in core SK-0% due to insufficient driving capillary forces. Total recovery was found to be 1.50% OOIP. The recovery value is not entirely related to capillary forces as thermal expansion of fluids will be an important contributor to the oil recovery. [86] reported that thermal expansion can account for about two thirds of the recovery in early stage and that later stage incremental recovery is partially influenced by vaporization and viscosity reduction. Expansion of the fluid with temperature increases its volume and thereby the production pressure gradient. General rule of thumb for the expansion is about $10^{-3}/^{\circ}\text{C}$. We can thus expect up to 3% incremental recovery when temperature is increased from (20-50)°C. Expansion of the rock and corresponding reduction in flow path is negligible since it takes large amount of energy to effectively heat and expand the rock.

5.5.3.2 SK-10%

The recovery value of SK-10% ($\mu=2.45$) is relatively poor and reside longer compared to the reference core (SK-REF2). Recovery plateau on Figure 5.12 was established at 5.82%. This gives demonstrations to effects of Acid Number, which is not favourably low, according to theory, a core saturated with higher AN tend to behave more oil-wet. We could question the significance of viscosity/density differences but looking at results from the reference core we see that change in viscosity from (0.5-10)cP only delayed the recovery for some hours.

5.5.3.3 SK-40%

Highest oil recovery by SPI was encountered in the core with 40% S_{wi} (6.62%). As described in the theory part, wetting condition affects fluid distribution but also capillary forces which either assist or prevent surrounding brine entering the pores. Recovery by SPI is compliant with the theory of accelerated recovery with increasing water-wetness and on the order of total recovery.

5.5.4 Summary

Table 5.4 is a summary of the experimental results. None of the cores showed trend of accelerated recovery with time by spontaneous imbibition (SPI). Wetting condition is hence most likely to be homogeneous due to sufficient aging time (no wettability gradient as described by Austand and Standnes [57]).

Chromatographic wettability test also reflected recovery by SPI very well and proved that fractional wetting by water did not change after the oil recovery processes, A_{wett} increased with initial water in place.

Table 5.4: Summary of the experimental results

Core	SPI[%OOIP]	$[W I_{new}]$	Total adsorption	Wettability
SK-0%	1.50	0.382	1.20	more oil wet
SK-10%	5.82	0.521	1.61	neutral wet
SK-40%	6.62	0.593	0.97	more water-wet
SK-10% MC	4.16	0.347	0.81	oil wet

In view of the adsorption study at different initial water saturation there seem to be a relation between rate of adsorption and water content. Reduced total area indicates high rate of adsorption due to strongly reactive acidic components for

available sites (except in mild cleaning where competition and exchange take place). Area of SK-40% is lower than expect for two main reasons, i) affinity of low reactive oil components is reduced by a larger water-film ii) disturbance of acid number measurements by produced water in early sample data. However, at a given initial water saturation we see that it is probable to get a more oil wetting state with increased total adsorption of acids as discussed in Section 5.5.2.

Simonsen (BSc 2014) performed adsorption studies using two different oil samples and found that total adsorption area was slightly reduced with increasing acid number. AN=0.35 had total are =1.94 and AN=0.69 had total area = 1.83, this finding show difference in rate of adsorption (reactivity increase at higher acid number). It would have been interesting to see corresponding result on the wetting index.

Conclusions

1. Adsorption of oil polar components take place in two different mechanisms, acidic components adsorb chemically while positively charged base components are adsorbed due to attractive Van Der Waal forces.
2. Chalk-crude oil adsorption equilibria appear to establish rather slow, and increased delay can be expected with increasing initial water saturation.
3. Initial water saturation has a profound effect on the wetting condition, reduced water saturation is seen to give a more oil-wet condition due to a higher amount of available sites for adsorption within the core.
4. Further oil saturation after core restoration appeared to give a more oil wetting and there are two probable reasons for why this is;
 - (i) Insufficient adsorption during the first oil saturation such that adsorption isotherm was not reached. This can happen due to existence of inaccessible pore volume caused by rapid adsorption and pore blocking, which then was regained by cleaning solvents. The new total area will thus add to the previous adsorption and give a higher total area within the mild cleaned core.
 - (ii) The second explanation and most likely reason is replacement of low affinity acidic groups by smaller and more reactive acid components at the chalk surface.
5. Wettability test has proven to reproduce initial wetting condition of carbonate rocks and implementation of Smart Water will be possible at relevant initial water saturation.

For future work, one should consider starting with chromatographic wettability determination on a completely cleaned core, such that individual core has reference value, A_{ref} , related to its petrophysical properties and not to a standard core that might be from a different reservoir block.

Appendix A

Chemical And Physical Analysis

A.1 Titration chemicals

A.1.1 Acid Number solutions

Table A.1: Chemicals for AN measurements

Solution	Chemicals	Chemical Formula	Description
Titrant	Potassium Hydroxide 2-propanol	KOH>85% $CH_3CHOHCH_3$	2.8g KOH dilute to 1000 ml with 2-propanol
Spiking Solution	Stearic acid Acid titration solvent	$CH_3(CH_2)_{16}COOH$	0.5g Stearic acid dilute to 100 ml with acid titration solvent
Standard Solution	Potassium Hydrogen Phthalate (KHP) DI-water	$HOOC C_6H_4 COOK$	0.2g KHP diluted to 500 ml with DI-Water
Titration Solvent	DI-water 2-propanol (HPLC) Toluene (HPLC)	$CH_3CHOHCH_3$ $C_6H_5CH_3$	6 ml DI-Water with 494 ml 2-propanol and with 500 ml Toulene
Electrode Electrolyte	Potassium chloride DI-water	KCl	Mettler DG-114 3M KCl in Di-water

A.1.2 Base Number solutions

Table A.2: Chemicals for BN measurements

Solution	Chemicals	Chemical Formula	Description
Titrant	Perchloric acid Acetic anhydride Acetic acid	$HClO_4$ (70%) $(CH_3CO)_2O$ $CH_3CHOHCH_3$	5ml $HClO_4$, 15ml $(CH_3CO)_2O$ diluted to 1000 ml with Acetic acid
Spiking Solution	Quinoline Decane	C_9H_7N $CH_3(CH_2)_8CH_3$	0.5g Quinoline dilute to 100 ml with Decane
Standard Solution	Potassium Hydrogen Phthalate (KHP) Acetic acid	$HOOC C_6H_4 COOK$ CH_3COOH	0.2 g KHP dilute to 250 ml with Acetic Acid
Titration Solvent	Methyl Isobutyl Ketone (MIBK)	$CH_3CHCH_2COHCH_3$	provided in the lab
Electrode Electrolyte	sodium perchlorate 2-propanol	$NaClO_4$ $CH_3CHOHCH_3$	Mettler DG-113 saturated sodium per- chlorate in 2-propanol

A.2 Automatic titrator

Mettler Toledo DL55, programmed volumetric titrator used in measurement of oil sample Acid and Base Number according to descriptions by Fan and Buckley (2007). The electrodes measuring solution potential (mV) are calibrated to pH=4,7 and 10 prior to use.



Figure A.1: Illustration of the Mettler Toledo DL55

A.3 Sentrifuge

The Centrifuge utilizes centrifugal force, when rotating at great speed, to separate microscopic particles from a liquid substance and such that particles are settled according to gravity.



Figure A.2: Illustration of the centrifuge

A.4 Filtration pump

Filtration is the processes of removing undissolved salts and large particle impurities from the brine, this will ensure a homogeneous mixture with the intended fluid composition and density. Presence of consolidated particles in the brine may cause pore blocking of tight porous media during flooding.

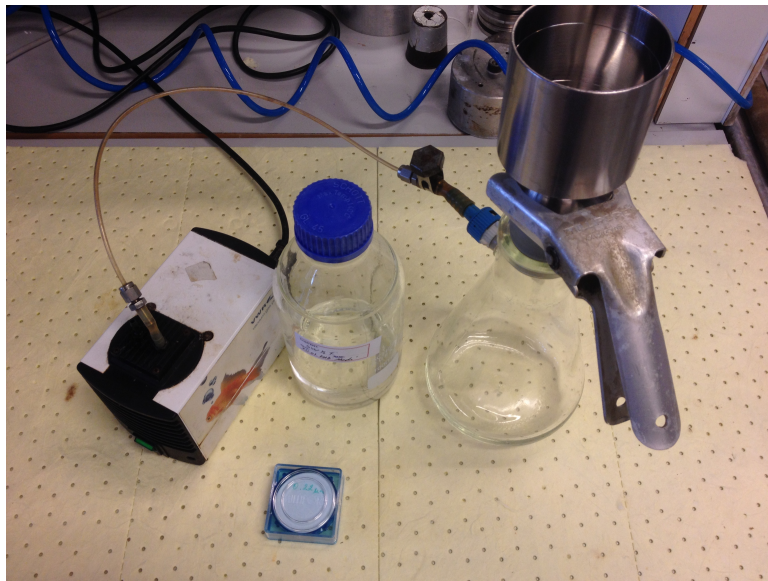


Figure A.3: Illustration of filtration setup

A.5 Vacuum pump

Vacuum pump was used to saturate the cores with formation water as part of the first step in establishing initial water saturation. Completely clean and dry core plugs were evacuated inside the vacuum container to remove any gas/liquid molecules inside the sealed volume such that a stable vacuum is established.

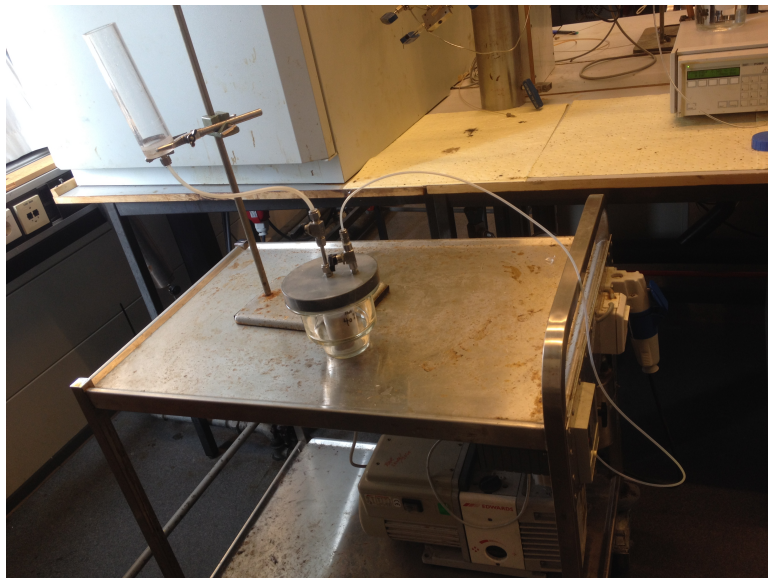


Figure A.4: Illustration of Vacuum pump

A.6 Desiccator

Establishing initial water saturation with desiccator method is very simple, 100% saturated core is placed inside the desiccator with silica-gel. The silica will function as a drying agent because of its high affinity for moisture. Rate of mass change as water is vaporized will depend on amount of silica added and also, how often the silica is changed, because it can be reused by heating it in 90°C over the night.



Figure A.5: Illustration of the desiccator

A.7 Density Instrument

Density of fluids is measured using Anton Paar DMA 4500 density meter. Density is important for accurate knowledge of flow behaviour and porosity determination.



Figure A.6: Illustration of Anton Paar DMA 4500

A.8 Hassler core holder

During experiments of core flooding, the chalk core was placed inside central position of a rubber sleeve and mounted inside the Hassler core holder. Figure A.8 show the reason for performing core cleaning, there are lots of impurities within the core.

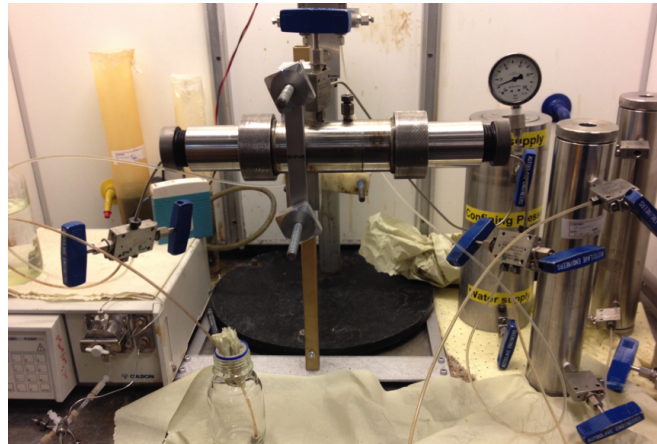


Figure A.7: Hassler Core holder, illustrated during core cleaning with simple flooding system

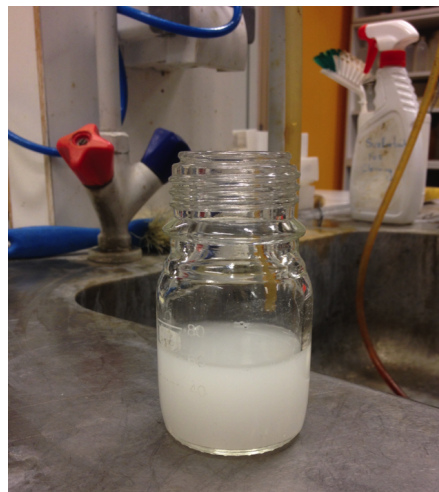


Figure A.8: Illustration of impurities within uncleaned core samples

Appendix B

Experimental data

B.1 Spontaneous imbibition data

Table B.1: Spontaneous imbibition SK-0%

Date	Time (min)	Time (hrs)	Time (days)	Oil prod (ml)	Recovery (%OOIP)
15.Mar	16:00	0	0	0	0
15.Mar	16:30	0.5	0.02	0	0
15.Mar	17:30	2	0.08	0.1	0.27
15.Mar	18:30	4.5	0.19	0.2	0.55
15.Mar	19:30	6	0.25	0.3	0.82
15.Mar	21:00	11	0.46	0.35	0.96
15.Mar	22:00	17	0.71	0.4	1.09
16.Mar	10:00	24	1	0.45	1.23
16.Mar	16:00	48	2	0.455	1.24
16.Mar	20:30	76.5	3.19	0.5	1.37
17.Mar	13:00	93	3.88	0.5	1.5
18.Mar	10:00	117	4.88	0.5	1.5
19.Mar	10:00	141	5.88	0.55	1.5
20.Mar	10:00	165	6.88	0.55	1.5
21.Mar	13:00	192	8	0.55	1.5

Table B.2: *Spontaneous imbibition SK-10%*

Date	Time (min)	Time (hrs)	Time (days)	Oil prod (ml)	Recovery (%OOIP)
11-Mar-16	14:00	0	0	0	0
11-Mar-16	15:30	1.5	0.06	0	0
11-Mar-16	16:20	2.33	0.1	0.05	0.17
11-Mar-16	17:00	3	0.13	0.1	0.35
11-Mar-16	17:30	3.5	0.15	0.2	0.69
11-Mar-16	18:00	4	0.17	0.28	0.95
11-Mar-16	18:30	4.5	0.19	0.3	1.04
11-Mar-16	19:00	5	0.21	0.45	1.56
11-Mar-16	21:00	7	0.29	0.5	1.73
12-Mar-16	09:00	19	0.79	0.63	2.18
12-Mar-16	10:00	20	0.83	0.65	2.25
12-Mar-16	11:00	21	0.88	0.7	2.43
12-Mar-16	13:30	23.5	0.9	8	0.72
12-Mar-16	17:00	27	1.13	0.75	2.6
12-Mar-16	21:00	31	1.29	0.78	2.7
13-Mar-16	12:00	46	1.92	1	3.47
13-Mar-16	19:00	53	2.21	1	3.47
14-Mar-16	10:00	68	2.83	1.1	3.81
14-Mar-16	17:00	75	3.13	1.18	4.09
15-Mar-16	10:00	92	3.83	1.35	4.68
16-Mar-16	16:00	98	4.08	1.47	5.1
17-Mar-16	09:00	115	4.79	1.55	5.37
18-Mar-16	10:00	140	5.83	1.6	5.55
19-Mar-16	10:00	164	6.83	1.65	5.72
20-Mar-16	10:00	188	7.83	1.67	5.79
21-Mar-16	10:00	212	8.83	1.68	5.82

Table B.3: Spontaneous imbibition SK-40%

Date	Time (min)	Time (hrs)	Time (days)	Oil prod (ml)	Recovery (%OOIP)
28-Mar-16	14:00	0	0	0	0
28-Mar-16	14:30	0.5	0.02	0.025	0.13
28-Mar-16	15:00	1	0.04	0.15	0.76
28-Mar-16	15:30	1.5	0.06	0.2	1.02
28-Mar-16	16:00	2	0.08	0.25	1.27
28-Mar-16	16:30	2.5	0.1	0.3	1.53
28-Mar-16	17:00	3	0.13	0.35	1.78
28-Mar-16	17:30	3.5	0.15	0.37	1.88
28-Mar-16	18:30	4.5	0.19	0.38	1.94
28-Mar-16	19:30	5.5	0.23	0.4	2.04
28-Mar-16	20:00	6	0.25	0.45	2.29
28-Mar-16	22:00	8	0.33	0.5	2.55
29-Mar-16	08:30	18.5	0.77	0.6	3.06
29-Mar-16	11:00	21	0.88	0.7	3.56
29-Mar-16	13:00	23	0.96	0.8	4.07
29-Mar-16	14:30	24.5	1.02	0.9	4.58
29-Mar-16	16:30	26.5	1.1	0.95	4.84
30-Mar-16	10:00	44	1.83	1	5.09
30-Mar-16	11:00	45	1.88	1.1	5.6
30-Mar-16	16:00	50	2.08	1.15	5.86
30-Mar-16	18:00	52	2.17	1.17	5.96
31-Mar-16	10:00	68	2.83	1.2	6.11
31-Mar-16	13:00	71	2.96	1.2	6.11
31-Mar-16	18:30	76.5	3.19	1.22	6.21
01-Apr-16	08:00	90	3.75	1.23	6.26
01-Apr-16	12:00	94	3.92	1.25	6.37
01-Apr-16	19:30	101.5	4.23	1.28	6.52
02-Apr-16	14:00	120	5	1.3	6.62

B.2 Chromatography data

Table B.4: Ion chromatography SK-0%

Sample#	C/C0 [SO4]	C/C0 [SCN]	PV corrected	Area (trapezoidal)
2	0	0.001	0.59	-
3	0	0.003	0.76	-
4	0.0111	0.278	0.92	0.035578282
5	0.0936	0.724	1.09	0.032908045
6	0.1548	0.922	1.25	0.009178169
7	0.1678	0.965	1.42	0.004355415
8	0.1715	0.985	1.58	0.004246761
9	0.1769	0.994	1.75	0.000741347
10	0.1805	1.005	1.91	0.000854863
				sum=0.09 (WI=0.382)

Table B.5: Ion chromatography SK-10%

Sample#	PV corrected	C/C0 [SO4]	C/C0 [SCN]	Area (trapezoidal)
5	0.87	0	0	-
6	1.05	0.201	0.557	0.07
7	1.24	0.707	0.842	0.03
8	1.43	0.93	0.965	0.01
9	1.62	0.994	1	0
10	2.18	1.005	0.998	0.01
11	2.36	1	0.963	0.01
				sum=0.121 (WI=0.521)

Table B.6: Ion chromatography SK-40%

Sample#	C/C0 [SO4]	C/C0 [SCN]	PV corrected	Area (trapezoidal)
3	0.0005	0.0357	0.81	0
4	0.0023	0.1648	0.9	0.01
5	0.0194	0.4900	0.99	0.03
6	0.0565	0.7067	1.08	0.03
7	0.0874	0.7794	1.17	0.02
8	0.1372	0.9869	1.26	0.01
9	0.1579	0.9892	1.53	0.01
10	0.1602	0.9903	1.62	0
11	0.1613	0.9938	1.71	0
12	0.1624	0.9950	1.8	0
13	0.1634	0.9915	1.89	0
14	0.1663	1.0088	1.98	0
15	0.1657	0.9996	2.07	0
				sum=0.137 (WI=0.593)

B.3 Acid Number and Base Number

Table B.7: Acid Number and Base Number data SK-0%

PV (AN)	AN	PV (BN)	BN
1.29	0	1.44	0.19
1.44	0.01	1.74	0.18
2.33	0.02	2.03	0.21
2.47	0.06	2.74	0.19
2.74	0.07	3.45	0.18
2.83	0.08	4.19	0.22
3.15	0.12	5.01	0.23
3.3	0.14	5.75	0.19
3.45	0.15	6.49	0.23
3.6	0.2	6.93	0.23
3.75	0.21	7.08	0.28
3.9	0.23	7.38	0.28
4.19	0.27	7.96	0.27
4.71	0.29	8.65	0.28
5.01	0.31	9.38	0.29
5.31	0.32	10.15	0.31
5.6	0.3	10.89	0.3
5.9	0.3	11.52	0.29
6.34	0.31	11.96	0.3
6.79	0.3	12.55	0.29
7.08	0.31	13.28	0.27
7.96	0.32	13.43	0.26
8.36	0.32	14.31	0.3
8.79	0.32		
9.23	0.33		
9.67	0.33		
10.15	0.31		
10.59	0.32		
11.04	0.31		
11.81	0.33		
12.26	0.32		
12.7	0.32		
13.61	0.32		
14.06	0.32		
14.6	0.33		

Table B.8: Acid Number and Base Number data SK-10%

PV (AN)	AN	PV (BN)	BN
1.38	0	1.71	0.15
1.54	0	1.71	0.15
1.71	0	1.87	0.14
1.87	0	2.04	0.16
2.04	0	2.53	0.18
2.53	0	3.03	0.17
2.7	0.02	4.04	0.18
2.87	0.02	4.37	0.16
3.2	0.04	4.88	0.22
3.37	0.05	5.73	0.2
3.53	0.09	6.57	0.26
3.71	0.12	7.41	0.27
4.05	0.15	7.76	0.25
5.05	0.16	8.42	0.29
5.39	0.18	9.14	0.28
5.56	0.19	9.98	0.28
5.73	0.21	10.82	0.3
5.9	0.23	11.33	0.28
6.07	0.25	11.66	0.29
6.91	0.29	12.54	0.3
7.08	0.29	13.08	0.3
7.24	0.3	13.42	0.3
7.41	0.33	13.92	0.29
7.67	0.32	14.24	0.27
7.76	0.32	14.94	0.28
7.83	0.31		
7.96	0.31		
8.02	0.33		
8.53	0.33		
8.8	0.33		
9.31	0.31		
9.81	0.33		
10.15	0.32		
10.32	0.32		

Table B.9: Acid Number and Base Number data SK-40%

PV (AN)	AN	PV (BN)	BN
1.45	0.01	1.9	0.13
1.68	0.12	2.23	0.18
1.9	0.16	3.05	0.21
2.07	0.18	3.68	0.22
2.23	0.19	4.26	0.19
2.38	0.2	4.92	0.2
2.74	0.21	5.6	0.21
3.05	0.23	6.61	0.19
3.97	0.24	6.95	0.26
4.61	0.28	7.77	0.27
4.8	0.29	8.45	0.26
5.25	0.31	9.6	0.27
5.44	0.31	10.28	0.28
5.92	0.31	10.88	0.27
6.78	0.33	11.38	0.26
7.45	0.32	12.84	0.23
8.28	0.3	13.51	0.24
8.92	0.3	14.22	0.23
9.26	0.31	15.41	0.27
9.6	0.3		
10.11	0.31		
10.61	0.3		
11.08	0.32		
11.34	0.32		
12.16	0.32		
13.01	0.32		
13.85	0.33		
14.22	0.31		
14.24	0.32		
14.4	0.31		
14.78	0.32		
14.94	0.33		
15.56	0.32		

Table B.10: Acid Number and Base Number data SK-10% MC

PV (AN)	AN	PV (BN)	BN
1.82	0.18	1.63	0.2
2.19	0.17	2.19	0.12
2.76	0.22	2.76	0.13
3.15	0.25	3.33	0.13
4.3	0.26	3.91	0.13
5.06	0.28	4.68	0.19
5.95	0.26	5.61	0.21
6.4	0.29	6.08	0.2
6.48	0.27	6.56	0.2
7.33	0.32	6.88	0.19
8.33	0.33	7.2	0.17
9.33	0.33	7.93	0.13
10.32	0.31	8.73	0.14
12.32	0.32	9.53	0.18
14.31	0.33	10.32	0.14
	10.92	0.14	
	11.92	0.15	
	13.11	0.14	
	14.11	0.18	
	14.71	0.16	

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