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Smart Water injection into sandstone reservoirs for enhanced oil

recovery – Influence of oil components on sandstone wetting

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Abstract

Both fluid flow and Smart Water EOR process in reservoirs are affected by the reservoir wetting. In order to study the wettability effect of polar organic components present in crude oil, the adsorption of acidic and basic polar components onto mineral surfaces have been investigated. 2 outcrop sandstone cores, B-15 and C-3, were flooded with crude oil and produced effluent oil was sampled and analysed for AN and BN.

Both core B-15 and C-3 had an initial water saturation of 20% and flooded with FW with a salinity of 50 000 ppm and added a small amount $AlCl_3$ to reduce the initial pH conditions in the cores. Thereafter the cores went through a crude oil flooding with AN=0.2 and BN=0.31 and 0.22 respectively. The temperature during both experiments were 50°C.

The experimental observation shows that the adsorption of basic components was instantaneous and the cores became mixed-wet, confirmed through spontaneous experiments with FW as imbibing brine. FW brine pH could be supressed by adding small amounts of Al^{3+} ions to the FW. The acidic components had far less affinity towards the mineral surface at the initial conditions present in the cores. When switching from FW to LS-brine, increased oil production was observed. Confirming a wettability alteration taking place even for mixed-wet neutral sandstone cores.

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1. Introduction

The petroleum industry has been around for a long time, but it is just in modern times that oil has become a key component in politics and society as a whole. The world is craving more oil than ever before, and the oil production have difficulties to keep up with the ever-growing demand. Due to this problem, engineers are challenged to create new ways of enhanced oil recovery (EOR) to exploit the current reservoir with better and more efficient methods ((Kokal & Al-Kaabi, 2010). Also, if better methods are discovered, future reservoirs can reach an even higher recovery rate.
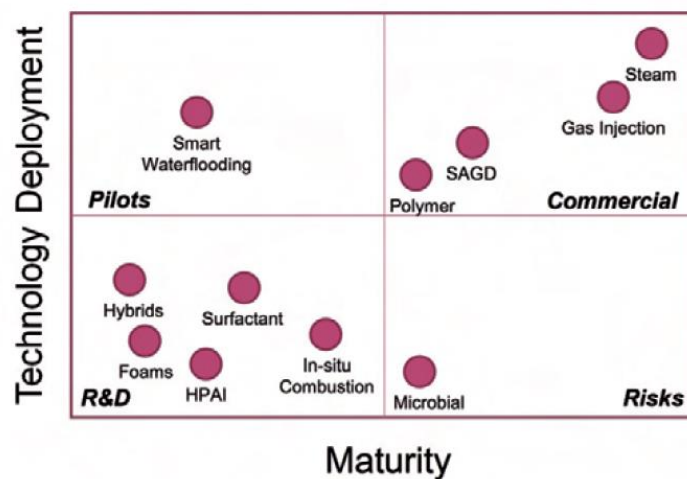
Figure 1.1: IOR/EOR development and maturity (Kokal & Al-Kaabi, 2010).

The most common secondary recovery method that are used is waterflooding. Much of the injected material is linked to the oil price and water is by far the cheapest. Current average recovery factor from hydrocarbon reservoirs worldwide is in the mid 30 per cent, which leaves 2/3 of the existing hydrocarbons underground. There is a growing concern in the petroleum industry that the need to focus on "ultimate" recovery rather than "instant" recovery is beneficial in a long term scenario. Enhancement in the oil recovery technology will further the goal of "ultimate" recovery. One of the technologies that have a huge potential and probably one of the cheapest EOR methods available, is Smart Waterflooding and low salinity waterflooding.

1.1.   Wettability

Wettability is a way to tell how a solid prefers to be in contact with one fluid rather than another. A definition of wettability is "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids" (Craig, 1971). It has been proven that wettability directly affects the displacement of hydrocarbons and the fluid flow towards the producing well.

Wettability is a crucial factor even during the primary recovery. The wettability alters the initial water saturation during and after the hydrocarbons have started to flow, which again will affect the production characteristics of the reservoir. Wettability also affects the amount of oil that can be produced at a certain pore level. In an oil-wet reservoir the oil is most likely connected to a continuous chain of hydrocarbons which increases the chance of oil flowing in the direction of a producing well. While in a water-wet reservoir, the oil is more likely to stay in larger pores and be disconnected from the rest with water filling the smaller pores (Abdallah et al., 2007). Because wettability can be implemented all between micro (pore) and macro (reservoir) level, it can even impact the future economic of projects.

1.2.   Thesis Objective

The objective of this thesis is to take a closer look into the parameters that influences the initial wetting in sandstone i.e. the adsorption of acidic and basic polar organic components in the crude oil onto mineral surfaces in sandstone by flooding crude oil. The pH effects the reactivity of the polar components, and the initial pH established in the core system is controlled by the formation water composition and cation exchange at the mineral surface. The concentration of Ca^{2+} seem to have a severely limiting effect on the adsorption of basic and acidic components. In this work the ionic composition of formation water have been modified by adding Al^{3+} to the formation brine. By lowering the initial pH the adsorption of polar components could be increased.

2. Theory

2.1. Crude oil/brine/rock interactions

All reservoirs consist of three phases; a mineral phase, interstitial brine or FW and crude oil. The initial wetting conditions established in the reservoir are constant interactions between these three phases together with temperature and pressure. All reservoirs are considered to initially be filled with pore water and water-wet. This is because sedimentary rock was formed in aqueous depositional environments. When oil migrates into the reservoir and the water-wet system is in contact with crude oil, the wettability of the system may alter towards a less water-wet conditions. There are some critical key parameters that can affect the wettability. These parameters are considered to be (Austad, 2012; RezaeiDoust, 2011):

- Increase in effluent pH
- Initial pH of formation water (FW)
- Crude oil properties
- Effect of salinity and pH on adsorption

Wettability is a value used for representing the wetting conditions in the reservoir, but must be evaluated as a dynamic condition instead of a fixed value. The wetting of a reservoir is not homogenous, but rather a fractional wetting that change from place to place in the reservoir. The parameters affecting the COBR-system and wettability will be in an equilibrated state and if changed, they can be restored. However, if these parameters are not restored, a new COBR-equilibrium will be established and also a new wettability will be reached. An EOR effect can occur when transitioning from one wetting/equilibrium condition to the next. Smart Water injection through low salinity waterflood is considered to be an EOR method that can significantly alter the wettability and increase the recovery.

2.2. Hydrocarbon recovery mechanisms and applications

The life cycle of a reservoir is conducted by several stages. These stages can be defined as exploration, discovery, delineation, development, production and then abandonment (Dake, 1983). Historically, the oil production has been divided into a more chronologically viewpoint. The different stages are defined as primary recovery, secondary recovery and EOR/tertiary

recovery. However, depending on the type of reservoir present, some of the steps can be altered and bypassed to produce better economic return.

2.2.1.   Primary Recovery

Primary recovery is the first stage in any production process, normally taking advantage of natural occurring displacement forces in the reservoir. Usually these natural displacement forces originate from a gas cap, gas drive, rock expansion, gravity segregation, fluid expansion or water drive. Usually a combination of several of these factors. The process is a consequence of a high differential pressure in the reservoir and the bottom hole pressure. Over time, the production will decrease due to the decreasing pressure in the reservoir. The primary recovery can continue until reservoir pressure declines so much that the economical production rates is failing to meet certain requirements.

2.2.2.   Secondary Recovery

When the decreasing pressure in the reservoir is declining so much that desirable production rates is not met, a secondary recovery process is implemented. The most common techniques are to apply an artificial pressure increase to the reservoir. Waterflooding and gas injection are the most common and frequently methods used in the industry today. These methods are great because they can both maintain the reservoir pressure and displace oil. Water have higher immiscibility properties than gas and much less compressible. Therefore, waterflood is viewed as a better displacement method. From an economical viewpoint water is also much cheaper to acquire.

2.2.3.   Tertiary recovery/EOR

Tertiary recovery is often referred to as EOR (enhanced oil recovery), and is methods that take place when even secondary recovery methods fail to produce enough hydrocarbons. There are a few main categories within the EOR-field where Smart Water is a method that is becoming more and more apparent.

- *Mobility control*, this is a method to maintain a favourable mobility ratio. This is to achieve a macroscopic sweep efficiency that is as high as possible. Some of the ways

to achieve this is to use polymers to thicken water or use foam injection to recuse the mobility of gas injection(Green & Willhite, 1998).

- *Chemical injection* is used to decrease the IFT (interfacial tension) normally through surfactants added to the injection water. This again is to increase the microscopic sweep efficiency. Sometimes mobility control is also a part of chemical injection to take advantage of both macroscopic and microscopic sweep efficiency(Green & Willhite, 1998).

- *Miscible injection* is a process where the goal is to inject a fluid that is miscible with the oil phase and create a composition alteration. This can be done with either CO_2 or hydrocarbon solvents. In this process, phase behaviour is a major function. (Green & Willhite, 1998).

- *Thermal injection* is a method where thermal energy is injected or generate heat by an in-situ process to improve recovery(Green & Willhite, 1998).

- *Smart Water,* is the use of chemically modified water to alter the chemical equilibrium in the reservoir. Through Smart Water the goal is to use a waterflood to make the reservoir preferable more water-wet, and thereafter improve the recovery(Green & Willhite, 1998).

2.3. Displacement Forces

Reservoir are a subject to several different forces which will affect the oil, gas and water equilibrium within the reservoir. Viscous forces, capillary forces and gravity segregation are in most cases the most important forces.

2.3.1. Capillary Forces

There are several definitions about capillary pressure. One of the most common is that the capillary forces in a petroleum system are the result of the combined effect of the surface and interfacial tension of the rock and fluids, the pore size and the geometry and the wetting characteristics of the system(Ahmed, 2000). The capillary pressure is defined as "the pressure difference across a curved interface between two immiscible fluids" (Zolotukhin & Ursin, 2000). It also possible to define the capillary pressure as the pressure difference between the non-wetting

and the wetting phase. In context the capillary pressure would be the pressure in the oil phase minus the pressure in water phase for a water/oil-system. Since the non-wetting phase contains higher pressure, the capillary pressure can be positive or negative depending on which is the wetting phase. The Laplace equation (eq.2.1) provides the capillary across a curved surface in terms of radius of curvature:

$$P_c = P_o - P_w = \sigma_{ow}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$ Eq.: 2.1

Where P_o and P_w is the pressure of oil and water respectively, σ_{ow} is the interfacial tension between oil and water, and R_1, R_2 are the curvature radii of the interfaces between oil and water. If the droplet is small it is possible to assume that the interfacial tension has a greater impact than the gravitational force acting on the droplet (Zolotukhin & Ursin, 2000). When water is injected into the reservoir it often displaces into the fractures rather than displace the oil inside the matrix. To force the water into the matrix and imbibe the water from the fractures, the imbibing force has to exceed the capillary pressure threshold. This capillary pressure threshold is often expressed by the Levrett J-function, which is expressed:

$$P_C = \sigma\sqrt{\frac{\varphi}{k}}J$$ Eq.: 2.2

Here the Pc is the capillary pressure threshold, J is a dimensionless value (often the value 0.25 is chosen), k is permeability and ϕ is porosity. The threshold can also be overcome by gravity forces and viscous forces. The threshold pressure can also be eliminated by altering the rock wettability (Al-Hadhrami & Blunt, 2000).

Another capillary pressure model that is commonly used is the cylindrical tube model, as seen in Figure 2.1. This model is used to idealize the porous media, which in reality is much more complex (Green & Willhite, 1998). The interfacial tension between water and oil can be used to derive a formula to express the capillary pressure of this ideal cylindrical model. Given that the pore throats are filled with oil and water, where water is the wetting fluid, the expression for the capillary pressure is given by:

$$P_C = \frac{2\sigma_{OW}\cos\theta}{r} \qquad \text{Eq.: 2.3}$$

Here P_C is the capillary pressure, r is radius of the pore channels, σ_{OW} is the tension between oil and water, θ is the contact angle.
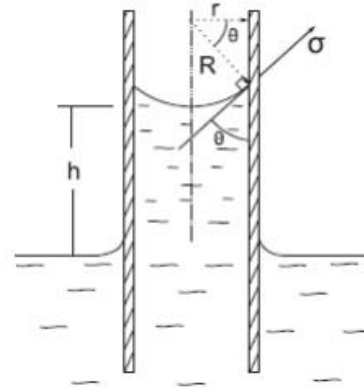
Figure 2.1: The cylindrical tube model

2.3.2.   Gravitational Forces

Gravitational forces exist due to the fact that different fluids and materials have different composition and density. In a process where gas and oil is displaced and there is a low production rate, the gravity forces play a major role. A system with oil, gas and water, the large difference in gas, oil and produced water will make gravitational forces overcome viscous forces and therefore dictate the flow direction in some cases. It is therefore important for the hydrocarbon production. In a reservoir with high permeability, great density difference and low interfacial tension, the gravity segregation will also be greater and more dominant(Chen et al., 2000). In a system where there are two or more immiscible fluids, the lightest fluid will experience a sense of a buoyancy effect as the fluids will segregate, the heavier fluids will "push" the lighter fluids upwards.

$$\Delta P = \Delta\rho \times g \times H \qquad\qquad\qquad \text{Eq.:2.4}$$

Here ΔP is the differential pressure between fluids due to gravity effects, $\Delta\rho$ is the difference in density in the two fluids, g is the gravitational acceleration and H is the height of the liquid column.

2.3.3.   Viscous Forces

Viscous forces in a medium is often reflected on the pressure drop over the fluid as it flows through the medium(Green & Willhite, 1998). When the fluid is flowing, the fluid will experience some resistance from the medium due to frictional interaction. This resistance establishes a force that is opposed to the flow direction. Viscosity is often viewed as a fluids internal resistance to shear(Finnemore & Franzini, 2001). For simplicity the model for viscous forces are often approximated to a medium which is a bundle of several capillary tubes. With that model in mind, it is possible to describe the pressure drop given by Poiseuille's law.

$$\Delta P = -\frac{8\mu L \bar{v}}{r^2 g_c}$$ Eq.: 2.5

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

2.4.   Wettability in porous media

There are a number of various methods to measure wettability in a reservoir. It is possible to divide the methods into two groups; quantitative and qualitative (W. Anderson, 1986b). The most commonly used qualitative method is methods based on imbibition (W. Anderson, 1986). Other examples of qualitative methods are microscope examination, flotation method, relative permeability methods, glass slide method, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, dye adsorption and nuclear magnetic relaxation (W. Anderson, 1986b). This thesis will take a closer look at the contact angle method. However, this method is not real-life applicable, it gives a good theoretical understanding of wettability.

2.4.1.   Contact angle measurements on solid surfaces
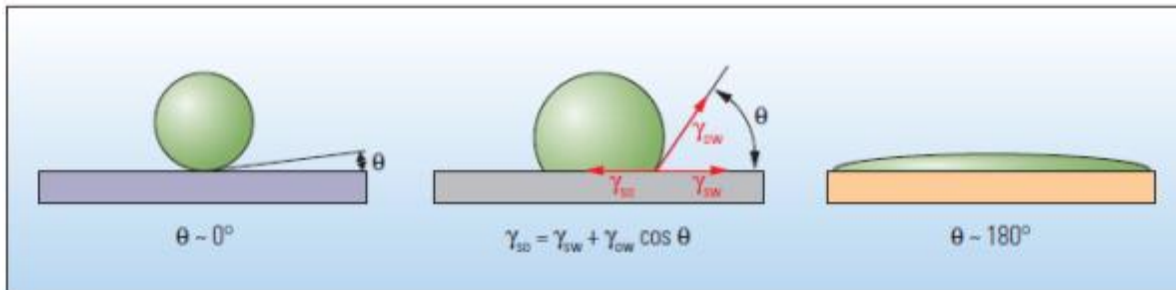
Figure 2.2: Oil droplet ability to contact the surface of the rock as wettability goes from water-wet to oil-wet (left to right)

Contact angle measurements cannot be applied for porous rocks, since the rocks doesn't have a smooth surface, but the method is applicable when using artificial cores. In other words, this method is a theoretical approach to understand wettability. An artificial core is used to remove other obstacles and rather take a closer look on how the fluids themselves alters the wettability. Also pressure, temperature and brine chemistry affects wettability, and by using artificial cores it is possible to see how. There are several different angle measurement methods in existent, but only a few that are used in the petroleum industry today (W. Anderson, 1986b). The contact angle is a measurement to show the equilibrium between the tension of the two liquids towards each other and towards the solid. The angle can be derived by this calculation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW} cos\theta$$

Eq.: 2.6

Here, γ_{SO} and γ_{SW} are the tension between the solid and oil and the solid and water, respectively. The angle θ of one liquids ability to spread out on the pore wall surface in preference to the other liquid is crucial. In this case the two liquids are water and oil. The wettability itself depends on things like the structure of the pore wall and the chemical composition of both fluids. **Table 2.1** shows a simple way to differentiate wettability preferences through different contact angle values (Zolotukhin & Ursin, 2000).

Table 2.1: Wettability Preference expressed by contact angle

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

2.5.   Sandstone Reservoirs

Clastic sandstone reservoirs are always heterogeneous. One core of sandstone can be very different from another core from the same reservoir, even if they are sampled right next to each other. The reason for this property is because of the depositional environment which can vary a lot from place to place, and time to time. This means that sandstones from different depositional eras and locations differs from each other. Due to this property of sandstone it is important to have a good classification system

2.5.1.   Sandstone Mineralogy

Sandstones are sedimentary rocks that has formed due to deposition of clastic materials. The most common places for such depositional environments are beaches, deserts, flood plains and deltas. All these types of depositional environments are high energy sedimentary environments. The particles accumulation is formed due to weathering, fragmentation and erosion of other, older rocks, both igneous, sedimentary and metamorphic rocks. The grains in sandstones have a size ranging from 63 µm to 2 mm. when the particles accumulate and burial increases, the overburden pressure increases as well along with the chemical compaction and cementation processes. This whole process is referred to as diagenesis.

Sandstone reservoir can contain many different types of minerals in addition to the most common mineral which is quartz (SiO_2). Feldspar, mica, heavy minerals, lithic fragments biogenic particles and many other minerals are observed to be within sandstones. Due to the high

concentration of silica, sandstones are often referred to as siliciclastic rocks. Some of the common cements in the sandstone can be silica, calcium carbonate, iron oxide and also clay which can be attached to the sandstone as a type of coating. Normally after diagenesis the rock has a density of about 2,65 g/cm^3.

2.5.2. Plagioclase

Plagioclase feldspar is a rock-forming poly-silicate mineral consisting of mostly a mixture between albite and anorthite end-members ("Plagioclase," 2005). Plagioclase largely consist of the same chemical structure, with varying concentrations of sodium, $NaAlSi_3O_8$, to calcium, $CaAl_2Si_2O_8$. These minerals can substitute each other in any proportion and therefore there exists several form with various mixtures of these molecules (Ford, 1912). The formation of plagioclase is pH dependant and different mixes may occur depending on the environment these chemical equations will occur (with albite as reference):

$$HAlSi_3O_8 + Na^+ \leftrightarrow NaAlSi_3O_8 + H^+ \qquad \text{Eq.: 2.7}$$

$$NaAlSi_3O_8 + H_2O \leftrightarrow HAlSi_3O_8 + Na^+ + OH^- \qquad \text{Eq.: 2.8}$$
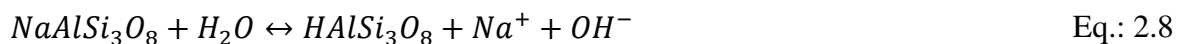
The presence of plagioclase in the reservoir will affect the EOR-effect occurring. It will also dictate the initial pH as well as the FW in the reservoir, which both have an impact on the initial wetting conditions in the reservoir (Austad, 2012). Table 2.1 show the different plagioclase forms depending mineral composition:

Table 2.2: Different plagioclase variation depending on sodium and calcium content

Mineral Class	% of albite (Ab) and anorthite (An)	Amount of calcium and sodium
Albite	0-10% An, 90-100% Ab	$Na_{100\%}Ca_{0\%}$
Oligoclase	10-30% An, 70-90% Ab	$Na_{90\%}Ca_{10\%}$
Andesine	30-50% An, 50-70% Ab	$Na_{70\%}Ca_{30\%}$
Labradorite	50-70% An, 30-50% Ab	$Na_{30\%}Ca_{70\%}$
Bytownite	70-90% An, 10-30% Ab	$Na_{10\%}Ca_{90\%}$
Anorthite	100-90% An, 0-10% Ab	$Na_{0\%}Ca_{100\%}$

2.5.3. Clay

Clay is very important in sandstone and can be described in many ways, but chemically it is best described as aluminium silicates. First of all, clay is the finest sedimentary particles classified and have a particle size typically less than 4 microns. They are basically composed of silica, alumina and water with frequently large amounts of iron and magnesium. Sometimes also small amounts of sodium and potassium. Clay is in simpler words a hugely important component in sandstone. Thus, it is important to fully understand its significance to be able to maximize the recovery from reservoirs.

The crystal structure of clays that are found in sandstones are made from two different basic units. The first one is a tetrahedral silica layer and the second unit is octahedral aluminium layer. The layers are linked to each other into planar layers by sharing oxygen ions between either the silica ions or the alumina ions in the adjacent layer, whether that layer is a tetrahedral or octahedral. The Si^{4+} and Al^{3+} ions occupy space on the surface of each layer but other cations are required, such as iron, potassium, calcium and magnesium and ensure charge balance. The structure of clays is determined by how the different tetrahedral and octahedral layers are joined together to form the different units of clay.
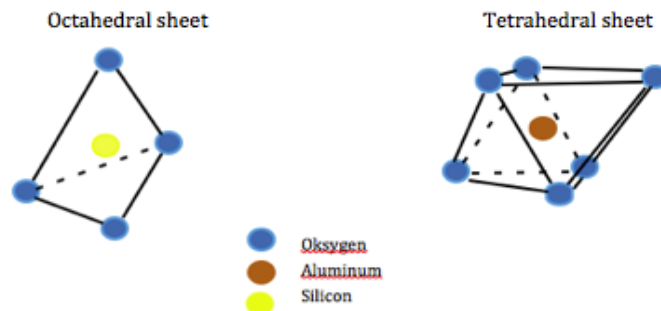
Figure 2.3: The difference in a octahedral and tetrahedral layer (IDF, 1982)

Different sequences of clay units can be defined as different structures with special chemical composition and attributes, the most common types in sandstones are kaolinite, illite, chlorite and montmorillonite and each is compacted with the same crystal structures, just in different order.
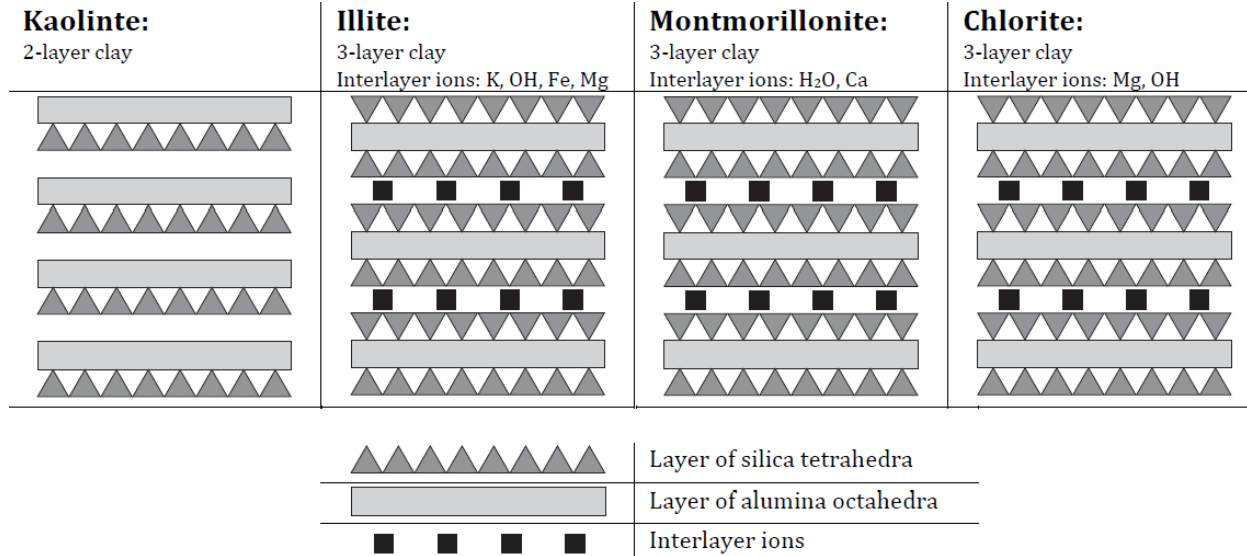
Figure 2.4: Different clay formations (Nichols, 2009)

Kaolinite is comprised of one tetrahedral and one octahedral layer in a 1:1 ratio. These layers have no interlayer cations but rather connected by O-H-O bonds. Kaolinite is composed of $Al_2Si_2O_5(OH)_4$ (Worden & Morad, 2003). Kaolinite has a very distinctive trait on a macro scale, in the way it is layered like many sheets of paper stacked together, which does not weather from chemical exposure(RezaeiDoust, 2011). Rather on a micro scale, kaolinite can block pores if moved by flowing liquid.

Illite is different to kaolinite in that way that it contains interlayered cations. This cation is potassium and illite is layered in a 2:1 structure with two tetrahedral layers and one octahedral layer. O-K-O bonds connects two opposing tetrahedral layers(RezaeiDoust, 2011). In the tetrahedral layers there will be some substitution of Al^{3+} for Si^{4+} and in the octahedral layer Al^{3+} will substitute divalent cations. Therefore, potassium is therefore needed for charge balance. Swelling behaviour in the illite is avoided to a certain extend due to the strong O-K-O bonding.

Chlorite 2:1:1 structure, where there are a 2:1 with tetrahedral-octahedral-tetrahedral layered. This 2:1 layer is negatively charged with a interlayered octahedral layer which in turn is positively charged and contains cations and hydroxyl ions (Worden & Morad, 2003).

Montmorillonite, which is part of the smectite family, and is structured the same order as illite in a 2:1 fashion with one octahedral layer in between two tetrahedral layers. Montmorillonite has the ability to absorb water and swell, but the water content can vary. The volume of montmorillonite is hugely dependent on the volume of water that has been absorbed. The cation content of montmorillonite can vary a lot, but montmorillonite is chemically hydrated sodium calcium aluminium magnesium silicate hydroxide(RezaeiDoust, 2011). Usually montmorillonite can contain other cations as substitutes such as potassium and iron.

One thing that illite, chlorite and montmorillonite has on commons is that they are a product of weathered volcanic rock.

2.6.   Cation Exchange Capacity (CEC)

The unique property of clay minerals is that they have a permanent negative charge on the surfaces, which is what separates clay minerals from other silicate minerals. These negative charges come from substitution of metal ions within the structure, usually a cation of a low valence for another cation with higher valence (e.g. substitution of Al^{3+} for Si^{4+}). If the structure was orientated in a way where the octahedral and tetrahedral layers combined themselves in perfect unit-structure clay, there would be a neutral charge balance on the clay surface. In reality these unbalanced negatively charges located at the edges of unit cells. From the broken bonds at the edges there will be disconnected of hydroxyl groups, which in turn makes it possible for the attraction of positively charged ions that occur in the surrounding fluid, and consequently obtain neutrality. The amount of exchanged cations at a given pH, normally at pH 7, is described as the cation exchange capacity (CEC). More specifically, the CEC is a measure of a certain clay's ability to attract cations from a solution and hold on to them. This does not mean that the clay holds on to the cations permanently, but the cations may be exchanged as stated from the definition the CEC. This again depends on a large number of factors and conditions. Some of these factors can be; number of exchange sites, concentrations of ions in the present fluid, and the nature of the ions and clay minerals at different temperatures and pressures. These conditions make this a very complex process and might be difficult to fully comprehend. Nonetheless, there has been proven that different ions have affinity to the surface at room temperature. This means

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that some ions have stronger "replacing power" than other ions and is dependent on the type of boning occurring. The relative replacing dominance of cations at room temperature and at equal concentrations is as follows(IDF, 1982):

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} << H^+$$

2.7.   Initial Wetting and Conditions

Due to migration accumulation of oil within the reservoir, the wettability of a certain rock doesn't have to be consistent over time. Usually the sandstone reservoir is regarded as water-wet in its initial state. When crude oil is migrating into the sandstone reservoir and displaces partly the present formation water, a new equilibrium are established between the water, oil, mineral surfaces and temperature (Abdallah et al., 2007). It is also important to be aware that there will be several factor that influence the wetting properties of all three substances in the reservoir. Conditions like oil components, brine chemistry and surface area of the solid must be considered. Furthermore, reservoir temperature, pH, pressure and saturation history also must be considered (W. Anderson, 1986b):

- Temperature

Temperature will naturally effect the reactivity of all chemical components in the reservoir. Any change in temperature has two effects, where both are wettability-altering making the system more water-wet at increasing temperature (W. G. Anderson, 1986a). The first effect is that an increase in temperature will increase the solubility of the wettability-altering components within the crude oil. Secondly, the IFT (interfacial tension) and the contact angle measured will decrease if the temperature is risen. Furthermore, the amount basic components and acid components are reservoir temperature dependant. It seems like the concentration of acidic components decrease as the temperature increases due to the effect of decarboxylation (Austad et al., 2010). Therefore, at temperatures above 100ºC there is relative greater amounts of basic components in the crude oil than acidic components (Austad et al., 2010).

- Mineral surface

Sandstone reservoirs are very special since they generally consist of many different minerals. Minerals that contain silica tends to have a negative charge, which naturally have great affinity towards components of opposite charge. Clay minerals usually have a much greater CEC and adsorbs more easily. H^+ have the highest affinity towards the surface of the rock, but in a typical pH range for a sandstone reservoir between 6-8 the concentration of hydrogen ions is low. Basic and acidic polar components in the crude oil tends to adsorb towards the surface in competition with cations (Austad, 2012) as illustrated in Figure 2.5. The silica minerals are negatively charged in the pH range typical for sandstone reservoirs.
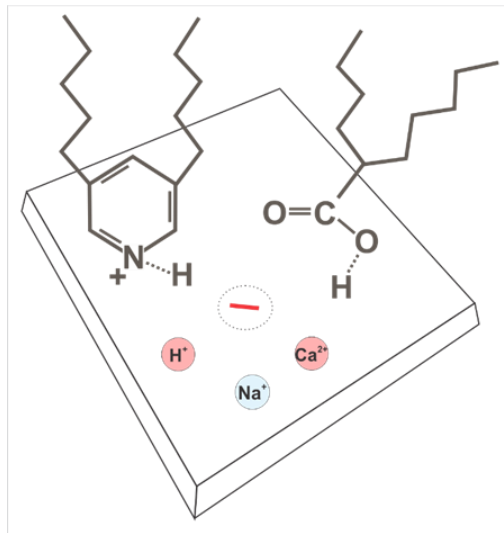
Figure 2.5: Illustration of polar organic components present in the crude oil adhering to the negatively charged clay surface

- Effects of reservoir pH

The adsorption and desorption potential of polar organic components is highly sensitive to pH. The amount that can adsorption and desorption can vary a lot within the pH range 5<pH<8 (Burgos et al., 2002; Madsen & Lind, 1998; RezaeiDoust, 2011). Acidic and basic components have different affinities towards curtain types of clay and are discussed in more detail later in the thesis.

- Brine chemistry

At a curtain pH, the adsorption of polar organic components increases as the salinity decreases due to the competition between the different species present. These species can be protonated basic components (R_3NH^+) and acidic components (R-COOH), cations like calcium ions and protons. They will all have affinity towards the negatively charged clay surface. Thus, the brine chemistry of the brines and CEC of mineral surfaces will dictate the reservoir pH (W. G. Anderson, 1986a). If there is a lot of acidic gases present in the reservoir fluids, some of these components can be dissolved in the liquid phase and decrease the pH, according to equation 2.9 and 2.10. Dissolved gas usually gives a pH in a range of 5-6.5.

$$H_2S \leftrightarrow H^+ + HS^-$$
$$HS^- \leftrightarrow H^+ + S^{2-}$$

Eq.: 2.9

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

Eq.: 2.10
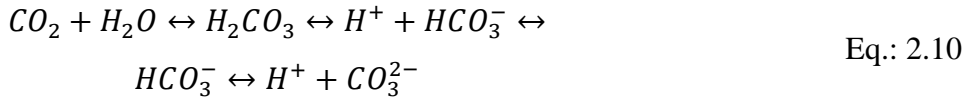
Furthermore, in this thesis the brines that are being used during lab experiments have a pH<7. To get to a satisfactory pH $AlCl_3$ is being used. There is a couple of reason for $AlCl_3$ being used; aluminium ions are already present in the formation, so hopefully a small addition of Al^{3+} ions would not compete to much with other anions present in the system. However, the most important factor for using this is due to Al^{3+} has the ability to hydrolyse 3 times. For each added mole of Al^{3+} there is the potential for 3 moles OH$^-$ from water to react and further the decrease of pH. These reaction is given by the chemical equations 2.11 – 2.13:

$$AlCl_3 + H_2O \leftrightarrow AlOH^{2+} + H^+ + 3Cl^-$$ Eq.: 2.11
$$AlOH^{2+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+$$ Eq.: 2.12
$$Al(OH)_2^+ + H_2O \leftrightarrow Al(OH)_3 + H^+$$ Eq.: 2.13

- Components in crude oil

The key properties to wetting alteration in an already water-wet system are the components present in crude oil, because all the wettability-altering components are in the oil phase. The

crude oil contains organic components with nitrogen, oxygen and/or sulphur. The crude oil components that have the largest impact on the wetting of the mineral surface is the resins and asphaltene (Buckley et al., 1998). These components could have a hydrophobic hydrocarbon-tail in one end and a polar organic end in the other. The charged polar end could adhere to charged sites on the rock surface. These components acts as anchor molecules making the reservoir less water-wet (W. G. Anderson, 1986a). Additionally, the reactivity of polar organic components towards negatively charged mineral surfaces is pH dependant.

Often the acidic component in crude oil is represented by a carboxylic group, R-COOH. These molecules are often part of the heavier end fraction of the crude oil, like the asphaltene and resin fraction. Basic material on the other hand, contain nitrogen as part of an aromatic ring, R_3N or protonated as R_3NH^+ (Strand et al., 2016). Generally, the carboxylic group will decompose over geological time and exposed to high temperature, while basic material is more resistant. That is why crude oil often contain higher BN values than AN values (Piñerez Torrijos et al., 2017).

AN and BN is one of the parameters that can be used to evaluate the potential for a particular crude oil to alter wettability (Buckley et al., 1998). AN and BN is defined as amount of titration solvent needed titrate 1 gram of oil sample to a well-defined inflection point. As an example, benzoic acid is used as acid component and quionline is used as basic components. At a high pH the molecules have released a proton, while at low pH the H^+ is integrated in their structure, as illustrated in Figure 2.6.

Figure 2.6: Micro species of benzoic acid (a) and quinoline (c) at low pH (left), micro species of benzoic acid (b) and quinoline (d) at high pH (right) (Piñerez Torrijos et al., 2017)

3. EOR with Smart Water in Sandstones

Usually sandstone reservoirs are put through water injection as a secondary oil recovery option. This is done through pressure maintenance and sweep efficiency to maximize the hydrocarbon recovery. Water injection is considered a reliable and effective option by using an injection brine that is compatible with the already present formation water in the reservoir. Injection of a Smart Water can be done in both secondary and tertiary oil recovery. Laboratory experiments have proven to provide a EOR effect, which is explained as a wettability alteration of the rock surface from mixed-wet to more water-wet conditions. This wettability alteration at the rock surface will increase the capillary forces which in turn, increases the microscopic sweep efficiency and overall production of oil (Austad et al., 2010).

3.1. Mechanisms of wettability alteration

There is no secret that the wettability and the mechanisms of wettability alteration in a reservoir is a highly complex process. The complexity of the crude oil composition, the variety of surface minerals and the ion composition of the brines present makes a very intertwined system(Buckley et al., 1998). It has been shown that polar components in the crude oil can adsorb to minerals surfaces by several mechanisms(Buckley et al., 1998). They all are controlled by ion composition in the brine and the properties of the crude oil. This system is also referred to as COBR-system (crude oil-brine-rock-system). Most research groups are in agreement on that the observed Smart Water EOR-effect is a wettability alteration towards more water-wet conditions. However, there does not yet exist an agreed explanation for the mechanism for the enhanced oil recovery in sandstones. Both chemical and physical explanations have been proposed(Austad et al., 2010).

3.2. Conditions for Low Salinity Smart Water EOR-Effects

Experiments have been performed to identify the criteria and conditions for LS injection to have the most beneficial effects. First attempt to explain the low salinity production mechanism was done by Tang and Murrow(1996) and further research done by BP (Lager et al., 2008) have identified that low salinity water with a concentration of 1000-2000 ppm during a tertiary flooding results in enhanced recovery. The list of conditions below shows the recognized points which provides a low salinity effect:

- Porous medium: The sandstone reservoir must contain clay minerals
- Oil: The oil in the reservoir must contain polar components (acid and/or basic)
- Formation Water: The formation present in the reservoir must contain free divalent cations, i.e. calcium ions or magnesium ions
- Low salinity injection fluid: The fluid usually must contain a concentration between 1000-2000 ppm, however, LS injection with higher concentrations have been observed to provide an EOR-effect, which indicates that not only the salinity but also the ionic composition is important.
- Produced water: The pH of the effluent normally increases 1-3 units for a non-buffered system, when changing from a high salinity brine to a low salinity brine. It is unclear if an increase in pH is necessary to observe a EOR-effect from the LS injection. In some cases, migration of fines has been detected, but is not necessarily required for an EOR-effect.
- Permeability: The differential pressure has been observed to both increase and decrease over the length of the core when switching from HS to LS, which can be an alteration in permeability.
- Temperature: As of today, there is not observed any temperature limitations for low salinity effects. However, most of the studies performed have been executed at temperatures below 100ºC.

3.3. Low Salinity Mechanisms

Because of the highly complex system due to mineralogical properties, the study of "Smart Water"- effect in sandstone is more complicated relative to wettability alteration studies performed on carbonates. It is likely that several steps have undergone for the low salinity effect to take place and it's not unlikely some mechanisms can happen simultaneously. It is generally

accepted that wettability alteration is necessary for observing the low salinity effect. In addition, some physical mechanisms have also been proposed. Some of the most relevant mechanism proposed are:

- Migration of fines
- Multi-ion exchange (MIE)
- Electrical double layer

3.3.1. Migration of Fines

The theory of fines migration was first proposed by Tang and Morrow (1999). From their researched they concluded that due to the negatively charged nature of sandstone, low salinity brine injection into the formation could weaken it. This would promote desorption of clay and silt, which would migrate in the higher permeable pores in the formation. If oil were attached to the loose fines it could be produced and a wettability alteration would take place. Thus, some of the fines would migrate into smaller pores and get cramped, blocking the pore. In turn, this would improve the sweep efficiency. Later research have shown that low salinity effect have been observed without the fines migration, and experiments confirming fines migration without observing LS EOR question the relationship between migration of fines and low salinity effects(Dang et al., 2013).
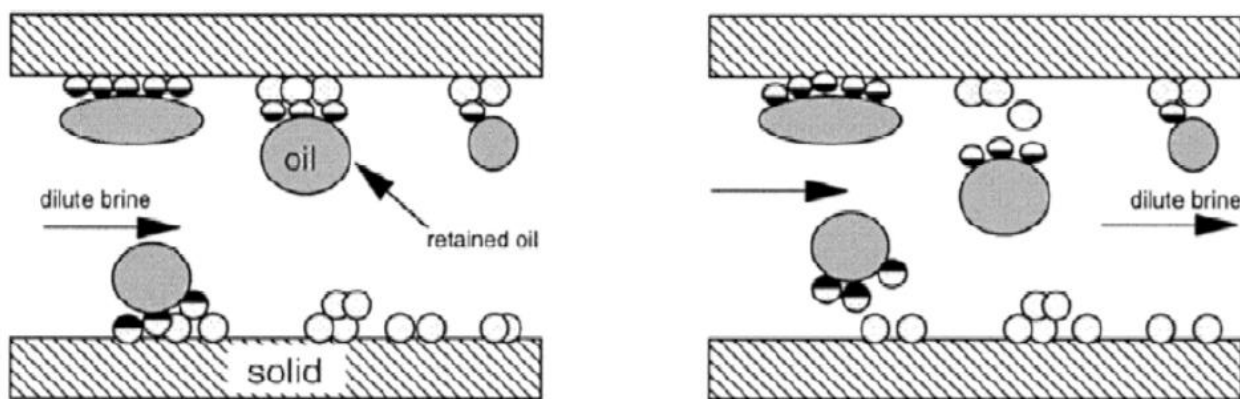
Figure 3.1: Illustration on the left shows the oil before the LS injection and the illustration on the right shows the oil which desorbs from the fines during LS injection

3.3.2. Multi-component Ionic Exchange (MIE)

Lager et al. (2008a) proposed that the multi-component ionic exchange (MIE) was the reason for the observed low salinity effect and called MIE as the basis of geochromatography. MIE involves the ionic competition between all ions in the fluid for the mineral exchange sites. Lager found that there was a severe decrease in the concentration of Mg^{2+} ions in the effluent from core floods. From these results, he stated that there were four mechanisms that contribute to the reservoir wettability (Dang et al., 2013) :

- cation exchange
- cation bridging
- ligand bonding
- water bridging

Also, it was assumed that anion exchange, hydrogen bonding, protonation and Van der Waals interaction could contribute to the overall ionic exchange. Lager also stated that Ca^{2+}-ions and Mg^{2+}-ions could act as a bridge between the negatively charged clay surface and the negatively charged carboxylate (R-COOH$^-$). As seen in the far right illustration in Figure 3.2, the organic material could be released from the surface when cation exchange takes place. However, Lager did not take into account the possibility of precipitation of $Mg(OH)_2$, which could also explain the decrease in magnesium ions in the effluent. Also, there is no reason for Mg^{2+} to adhere more strongly to the clay surface than the Ca^{2+} (Melberg, 2010).
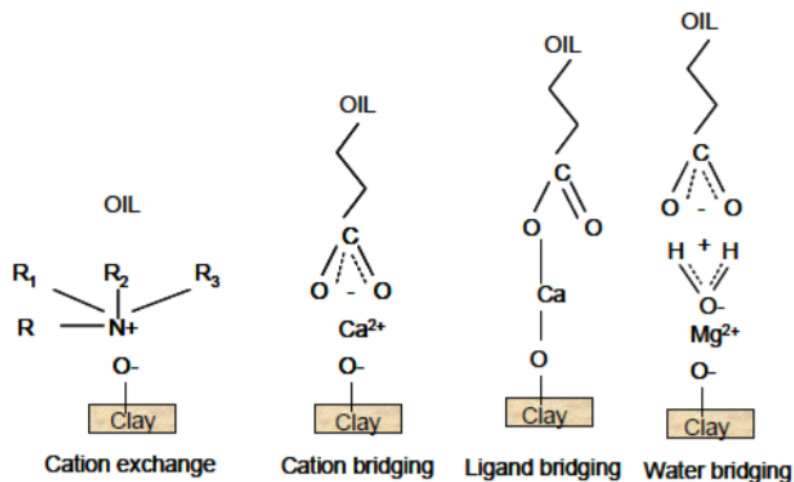
Figure 3.2: A representation of the different adhesion mechanisms occurring between crude oil and the clay surface (Lager et al., 2008a)

3.3.3.   Double Layer Effect

Lighthelm et al. (2009) stated that as the salinity decreases the electrical double layer will expand termed the double layer effect. The results states that an injection of a lower saline water than the formation water will disturb the chemical equilibrium in the COBR-system. The cation reduction will also reduce the ionic strength of the electrolyte content. Lighthelm stated that this will yield an increase in the absolute zeta potential and further the expansion of the diffuse double layers that surrounds the clay and oil particles (Ligthelm et al., 2009), but this has not been proven. This means that the attractive forces will decline relative to the repulsive forces, leading to a desorption of organic material. Later research shows that the presence of divalent cations is not necessary for oil components to adsorb onto clay (Austad, 2012).

3.3.4.   Salting-in Effect

The salting-in effect corresponds to when salt is being used to alter the solubility of organic compound in the aqueous phase. When using low salinity water as injection fluid the salting-in effect applies, further the desorption of organic material from the clay surface. The salting-in effect was first proposed by RazaeiDoust et al. (2009) as a wetting hypothesis for the LS effect. The hypothesis was incomplete because it could not explain the local pH increase, the mineral composition needed or the change in concentration of ions (Dang et al., 2013).

RazaeiDoust et al. (2011) continued to investigate the salting-in effect and studied the acidic and basic form of quinoline and its affinity towards kaolinite as a function of pH and salinity. Interestingly enough, the result showed that a change in pH rather than a change in salinity concentration dictated the adsorption of organic material onto the clay surface(RezaeiDoust, 2011). The salting-in effect was therefore disregarded as a low salinity mechanism. Figure 3.3 shows the results from the study.
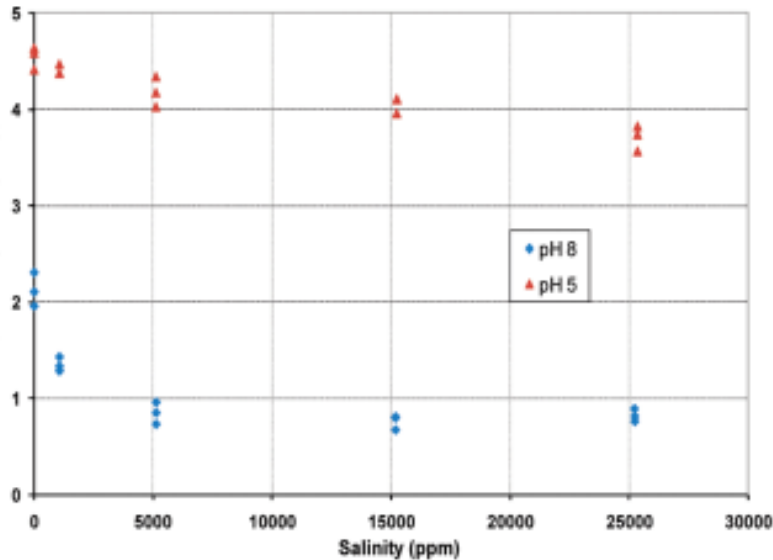
Figure 3.3: Adsorption of quinoline onto kaolinite as function of salinity at pH 5 and pH 8 (RezaeiDoust, 2011)

The adsorption of quinoline towards kaolinite was highest in a LS brine, and was reduced with increasing salinity at constant pH=5. This confirms that a LS brine should result in a less water wet system. When the pH was increased to 8, the adsorption dramatically decreased both for LS brines and brines with increased salinities.

3.3.5.   Desorption due to acidic and basic reactions

The desorption of polar organic components is clearly pH dependant and Austad et al. (2010) proposed that the main mechanism for the pH increase could be due to the desorption and adsorption of cations onto mineral surfaces. Clay could in a way act as cation exchanger due to its permanent negatively charged site on the surface. Initially in the reservoir, there will be a chemical equilibrium and the clay minerals will have adsorbed acidic and/or basic organic components in addition to inorganic cations (i.e. Ca^{2+}, Mg^{2+}) present in the FW. When introducing an injection brine with low cation concentration, Ca^{2+} could dissolve from the clay surface. Protons from water molecules could compensate the negative charge on the clay surface. In other word, a local pH increase will occur due to their higher affinity towards to the clay

surface. The water wetness of the system increases as OH⁻ will interact with the basic or acidic material. The proposed mechanisms are illustrated in Figure 3.4 and in equation (3.1 – 3.3).

$$Clay - RCOOH + H_2O \leftrightarrow Clay + RCOO^- + H_2O \qquad \text{(3.1)}$$

$$Clay - R_3N + H_2O \leftrightarrow Clay + R_3NH^+ + OH^- \qquad \text{(3.2)}$$

$$Clay - Ca^{2+} + H^+ \leftrightarrow ClayH^+ + Ca^{2+} \qquad \text{(3.3)}$$
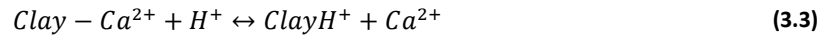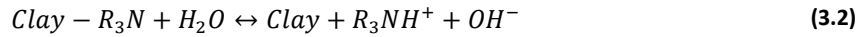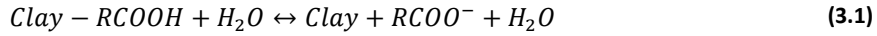
The polarity and the reactivity of the polar components towards the negatively charged mineral surface is pH dependant. The acidic material that are present in crude oil is often represented by a carboxylic type, R-COOH. Most of the basic components contain nitrogen as a part of aromatic molecules, R₃N, with a reactive par of electrons (Strand et al., 2016). The NSO components increases with increasing molecule weight of the crude oil and are represented in the heavy end fraction. But also crude oils with high API could have considerate amount of both acidic and basic components. After the low salinity water interact with the polar components there will also be a desorption of Ca^{2+} as Figure 3.4 illustrates.
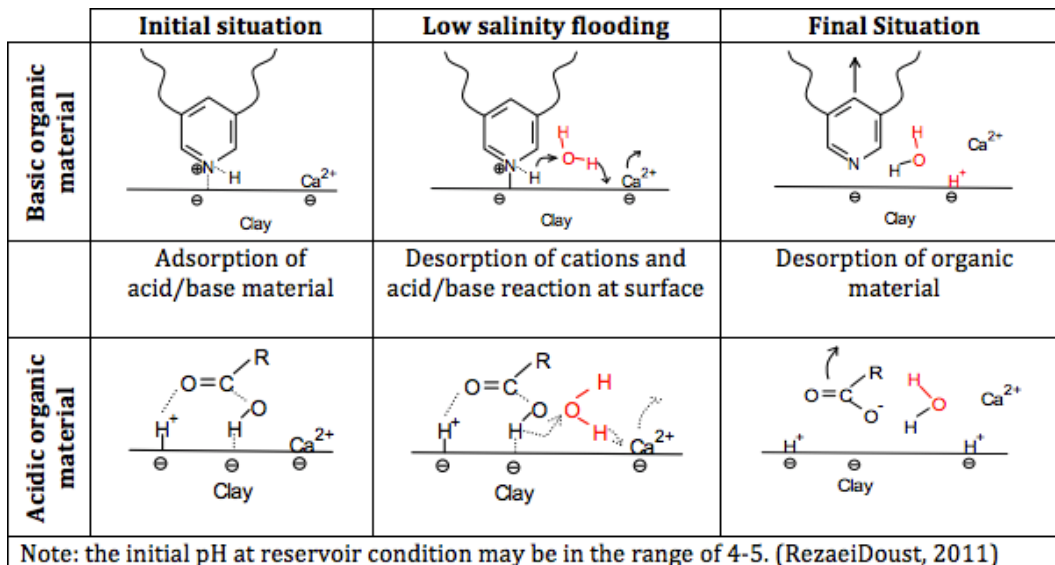
Figure 3.4: Illustration of the proposed low salinity mechanism due to pH increase

Adsorption of basic material

There have been several studies performed investigating the effect pH dictates on the adsorption and desorption of organic material. Burgos et al. (2002) studied quinoline as a basic material and its ability to adsorb onto kaolinite and montmorillonite clay in $CaCl_2$-solutions. Quinoline is a basic polar component that are present in crude oils. Figure 3.5 illustrates the results from the experiments and clearly shows that the adsorption of quinoline is a pH dependent process.
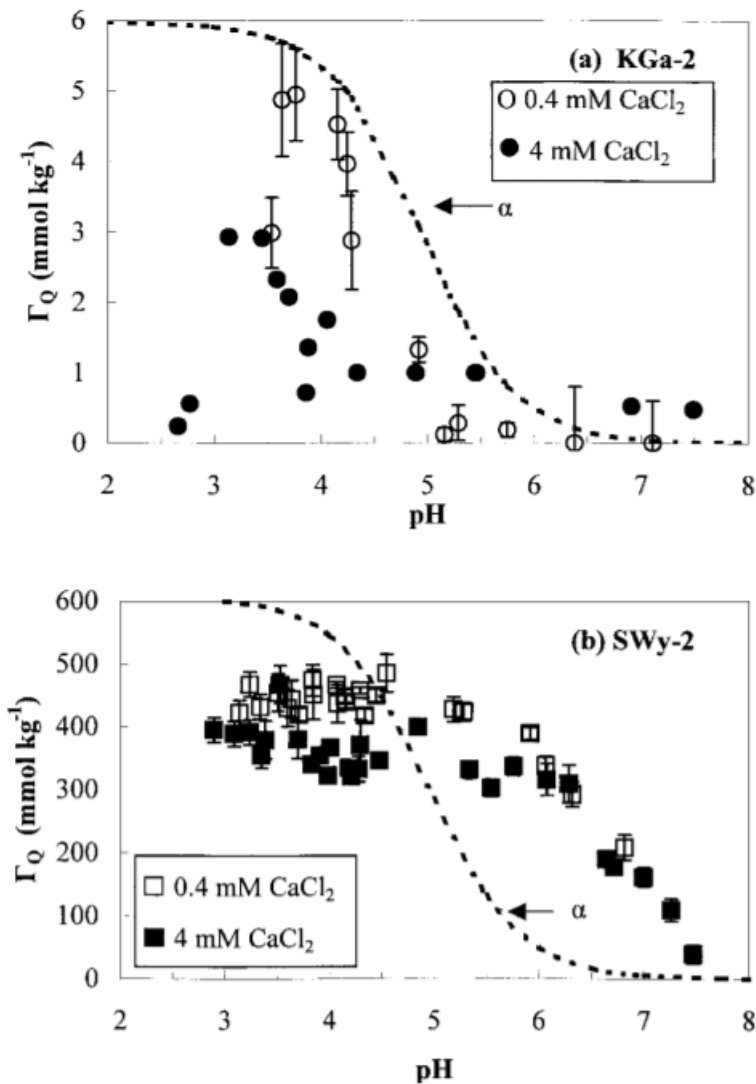
Figure 3.5: (a): Quinoline adsorption onto kaolinite. **(b):** Quinoline adsorption onto montmorillonite (Burgos et al., 2002). The stippled line is the fraction of protonated Quinoline.

The adsorption of quinoline decreases as the pH is increasing, whereas the largest adsorption seems to be observed at approximately pH 4. Relatively, the decrease was more significant when adsorbing onto kaolinite than montmorillonite. For the kaolinite experiment, when passing a pH value of 5, the adsorption was less than 1 mmol/kg. However, for the montmorillonite experiment, the adsorption was over 100 mmol/kg when passing a pH of 7. In any case, there seem to be decreasing adsorption of basic components with increasing pH for both high and low concentrations of Ca^{2+}. Highest adsorption observed for the LS brine with a concentration of 1000 ppm rather than 25000 ppm.

RezaeiDoust et al. (2011) also experimented with quinoline, but studied the adsorption onto kaolinite only. They showed that the quinoline adsorption was a completely reversible process, with regards to pH. It is very interesting to observe that as the experiment progressed the adsorption decreased when pH increased from 5-8, but also decreased adsorption from pH 5 to 2.5. The lower adsorption at low pH can be explained by the fact that the concentration of H^+ will be very high. H^+ is the cation with the highest affinity towards the negative clay charge and will compete with the other active species present in the brine (Helmy et al., 1983).
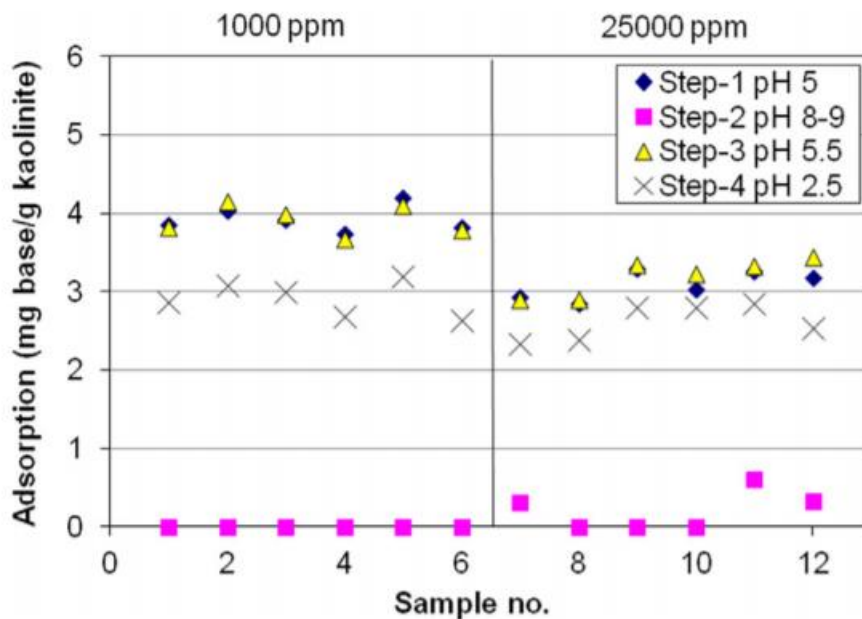
Figure 3.6: Reversible adsorption of Quinoline onto Kaolinite regarding pH at ambient temperature. Sample 1-6 contains salinity of 1000 ppm.
Sample 7-12 contains salinity of 25000 ppm

Further studies with quinoline was performed by Aksulu et al (2012) and the ability quinoline has to adsorb onto illite. As observed in previous experiments (Burgos et al., 2002; RezaeiDoust, 2011) the adsorption was highest for the low salinity brine. Furthermore, the adsorption peaked when the pH was close to the pK_a value for quinoline (≈ 4.9). The active specie is the protonated form of quinoline, $(R_3N\text{-}H)^+$ (Aksulu et al., 2012). So when the system experiences alkaline conditions (8>pH) the adsorption drastically drops due to the lower concentration of positively charged species (Aksulu et al., 2012). Figure 3.7 illustrates quinoline adsorb onto illite using both HS and LS brines at different pH values.
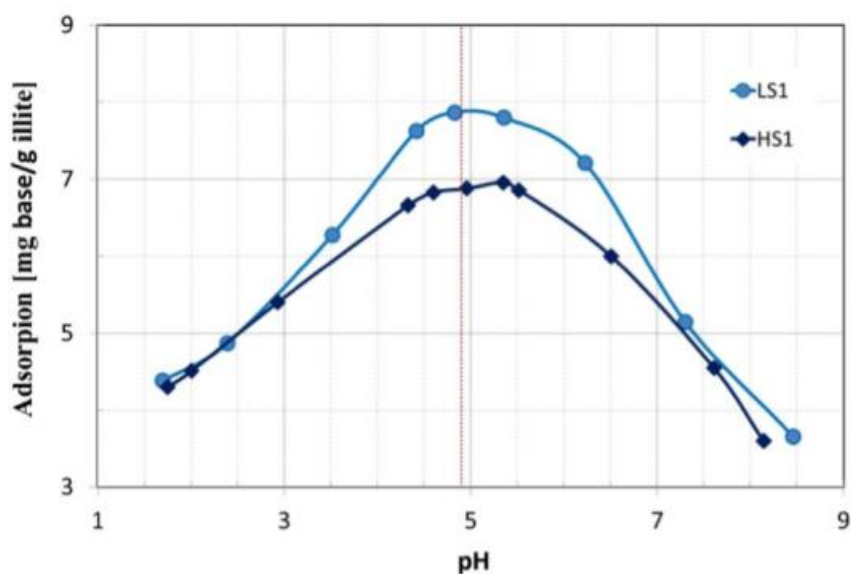
Figure 3.7: Adsorption of quinoline onto Illite using both HS-brine (25000 ppm) and LS-brine (1000) ppm as a function of pH at ambient temperature (Aksulu et al., 2012)
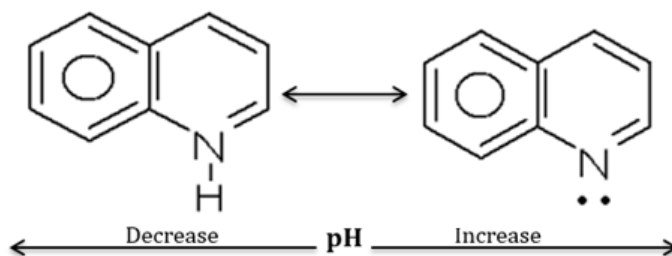
Figure 3.8: Illustration of quinoline. Left is protonated form, right is neutral form

Adsorption of acidic material

As there seem to exist a general trend for the adsorption of basic components, surely a trend can be found for acidic components as well. Madsen and Lind (1998) performed experiments to study exactly that. They used benzoic acid in an NaCl solution and observed its ability to adsorb onto kaolinite. The result from their test shows that acidic adsorption is also highly pH dependant and the result can be seen in Table 3.1 below:

Table 3.1: Adsorption of Benzoic acid in NaCl-brine onto Kaolinite at 32ºC, as a function of pH (Madsen & Lind, 1998)	
pH$_{initial}$	**G$_{max}$ at 32°C mmole/m^2**
5.3	3.7
6.0	1.2
8.1	0.1

Benzoic acid has a pK$_a$ value of 4.2. When the pH value equals the pK$_a$ value, the concentration of benzoic acid on the protonated form and the deprotonated form will be equal. The neutral protonated carboxylic material could adhere towards the clay surface through hydrogen bonds.
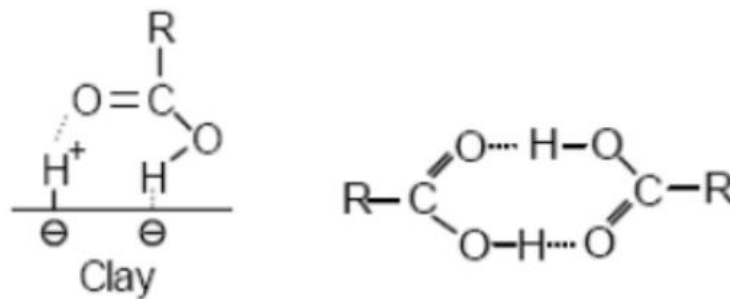
Figure 3.9: Adsorption of carboxylic group onto clay by H-bonding (Austad et al., 2010)

4. Materials and Methods

4.1.   Safety Measures

All of the experiments were executed with precaution and by following the proper HSE-regulation. Several risk assessments were performed to ensure that the people working in the lab had the knowledge and knowhow to handle every situation, if something bad should occur or go wrong. The specified security equipment, googles, lab coat, gloves, and mask were used during experiments when required.

4.2.   Outcrop sandstone cores

The two outcrop sandstone cores used in these experiments were both delivered by Total. B-15 were also used in previous experiments which makes it a good basis for comparison of results. Both cores are from the same quarry and cut to same dimensions and have a clay content of approximately 10-11 wt%. They have a low porosity and a high permeability and are therefore representative for other sandstone materials. All of the core data can be seen in Table 4.1:

Table 4.1: Core data for both cores

Outcrop core	B-15	C-3
Dry weight, gr	163,14	165,80
Length, mm	70,35	70,44
Diameter, mm	37,95	37,90
Bulk Volume, cm^3	1470	1521
Sat. Weight, g	178,78	181,75
Pore Volume, ml	15,64	15,95
Porosity,	9,58%	9,62%
Permeability, mD	8,89	-

Table 4.2: Key mineral composition of the cores

Core	Albite	Quartz	Calcite	Chlorite C	Illite	Clays & micas	Tot
	(Mass %)	(Mass %)	(Mass %)	(Mass %)	(Mass %)	(Mass%)	(Mass%)
B15	31,9	56,7	0,3	1,9	8,4	10,3	99,2
C3	30,6	56,6	0,3	2,2	9,4	11,6	99,1

4.3. Crude Oil

The crude oil used in these experiments was a mixture of 3 different oils, Total oil (T-Oil) with BN=1.9, Heidrun oil (HDN) with AN=1.8 and BN=0.5 and a Res40-0 oil depleted in acid and bases. The resulting oil should have both a AN and BN close to 0.2. The crude oil used was largely based on Res40-0 with smaller amounts of T-Oil and HDN. The resulting density of the crude oil was measured to be 0.8g/cc. More information about the crude oil recipe can be found in appendix A1.

Table: 4.3: AN and BN for the different crude oil used to make the final oil mix used in in further experiments

	AN (mgKOH/g oil)	BN (mgKOH/g oil)
Res40-0	0.00	0.00
HDN	2.80	1.14
T-Oil	1.85	0.36
M1-Oil	0.20	0.31
M2-Oil	0.20	0.22

4.4. Brines

The different brines that were used in the project were made in the laboratory with de-ionized, DI, water. To avoid precipitation of salts when preparing the brines. All the chlorides, sulphates and carbonates were mixed respectively with roughly 400ml (chloride) and 200ml (sulphates and carbonates) of DI water. After that all solutions were blended and diluted with DI water, until

1.00 litres were reached. The mineral solution was filtered with a 0.22μm Millipore filter. Density and viscosity was measured by using the Anton Parr DMA 4500 Density Meter at 20°C.

- **FWCa20:** Synthetic formation water with a salinity of 50 000 ppm and a concentration of 20mmol Ca^{2+}.

- **FWCa20Al0.4:** Synthetic formation water with a salinity of 50 000 ppm and a concentration of 20mmol Ca^{2+} and 0.4mmol Al^{3+}.

- **d5FWCa20Al0.4:** Synthetic formation water made from FWCa$_{20}$Al$_{0.4}$, then diluted 5 times with DI-water.

- **Total LS1:** Synthetic formation water with low salinity. Whereas the salinity concentration was 1000 ppm

Table 4.4: Composition of brines

Salt	FWCa20 mM	FWCa20Al0.4 mM	d5FWCa20Al0.4 mM	Total LS1 mM
NaCl	817.6	817.6	163.6	17.1
CaCl$_2$ x 6H$_2$O	20.0	20.0	4.0	0.0
AlCl$_3$	0.0	0.4	0.08	0.0
Cl$^-$	857.6	858.8	174	0.0
Ca^{2+}	20.0	20.0	4.0	0.0
Na$^+$	817.6	817.6	163.6	17.1
Al^{3+}	0.0	0.4	0.08	0.0

4.4.1.   Chemicals

Silica gel used for crude oil treatment has the grade 60, with the particle size of 0.035-0.070 mm and was supplied by Fluka Chemica. Heptane used in the experiments has a purity of 98% and was supplied by Merck. All other chemical used for brines and chemical reagents were PA-graded and delivered by either Riedel de Haën or Merck.

4.5.   Core cleaning

4.5.1.   Cleaning and drying

Cores with residual oil was mildly cleaned. Kerosene was used to displace the crude oil and heptane was used to displace the kerosene. At the end of the mild cleaning the cores flooded ~15PV with a 1000 ppm NaCl solution to displace initial brines. The NaCl solution was used to avoid any clay swelling. The core cleaning was performed at 20ºC at a rate of 0.1 ml/min. Thereafter the cores were placed in an oven at 80ºC until constant weight was achieved.

4.5.2.   Brine flooding and effluent pH

The reactivity of polar organic components towards negatively charged surfaces are effected by the initial pH. Interactions between ions in FW and the mineral pore surface are important when the initial reservoir pH is established.

The effect of FW brine composition on effluent pH was tested. FW brines with different salinities and ion composition was flooded through the core at 50ºC. The pH in fresh effluent samples was measured to evaluate brine and brine-rock interactions effect.

4.5.3.   Initial water saturation

The dried core was saturated with $d_5FWCa_{20}Al_{0.4}$ – brine. The initial water saturation was established by using the desiccator technique and water was evaporated in the desiccator with silica gel as the adsorbent. When the core was brought down to saturation of 20% the concentration of the brine will increase. This will cause the salt concentration of the brine to increase, and the water to evaporation was stopped when the core had water saturation of 20%. The core was taken out and placed in a sealed container for at least 3 days. To equilibrate for an even ion distribution.

4.5.4.   Crude Oil Saturation and Flooding

The core with $S_{wi}=20\%$ was mounted in the core holder at 50ºC with a confining pressure of 20 bar and back pressure of 10 bar. The core was flooded with the crude oil mixture at a rate of 0.1ml/min. Effluent crude oil samples were collected and the AN and BN were analysed. A schematic illustration of the setup is shown in Figure 4.1. More information about the crude oil saturation and flooding procedure can be found in appendix A2.
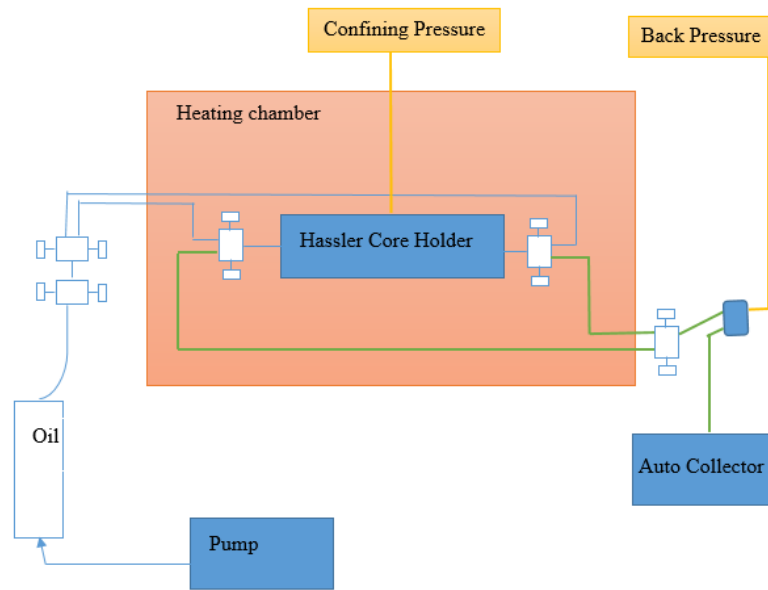
Figure 4.1: Schematic overview of the setup during oil flooding and brine flooding

4.5.5.   AN and BN measurements

The amount of polar organic components in crude oil could be quantified through AN and BN analysis. The method and procedure used during AN and BN measurements is a modified version of the method developed by Fan and Buckley (Fan & Buckley, 2006), which again, is based on the experimental method proposed by Dubey and Doe on BN measurements (Dubey & Doe, 1993) and Zheng and Powers for the AN measurements (Zheng & Powers, 2003). The methods used for AN and BN experiments are using an oil sample with known mass, 50 ml of titration solvent and 1 ml of spiking solution. This is then tested against a blank sample without any oil.

The AN measurements used a titration solvent made by diluting 6 ml DI water with 2-propanl until 500 ml was reached, then adding 500 ml of toluene. The spiking solution was made by diluting 0.5 g stearic acid with the AN titration solvent until 100 ml was reached. The spiking solution was stirring for ~24 hours to ensure that the stearic acid had dissolved.

The BN measurements used Methyl-iso-butyl-ketone (MIBK) as titration solvent, which was came premade in 1 litre bottles. The BN spiking solution was made by diluting 0.5g of quinoline with n-decane until 100 ml was reached and stirred for ~24 hours with a magnetic stirrer. More information about the AN and BN measurements can be found in appendix A3.

Additionally, the total adsorption from the crude oil flooding can be calculated by applying equation 4.1:

$$Total\ Adsorption = AN_{initial} \times PV_{injected} - \int_{test\ start}^{test\ end} AN\ d(PV_{inj}) \qquad \text{Eq.: 4.1}$$

The formula can be equally used for BN calculation by changing the AN values in equation 4.1 with BN values.

4.5.6.   Spontaneous imbibition

Spontaneous imbibition test was performed on the cores after the oil flooding. The spontaneous imbibition was performed at 50ºC with a standard Amott Glass Cells. Initially the cores were placed in the SI setup using FW as the imbibing fluid, because no chemical induced wettability alteration is expected to take place. After a oil recovery plateau was reached, the SI brine was changed to LS brine to evaluate if this brine could induce a wettability alteration towards more water-wet conditions and increase the oil recovery. The amount of oil produced was recorded. A schematic set-up of the spontaneous imbibition test is shown in Figure 4.2.
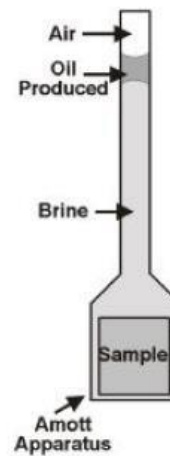
Figure 4.2: Spontaneous imbibition test in Amott Glass

5. Results

The main goal of this experimental work was to be able to evaluate the influence of both acidic and basic components towards the sandstone surface at specific pH. The observed Smart Water EOR is a wettability alteration process. Smart Water EOR potential is dependent on initial wetting. The cores were 100% saturated with FW and dried using the desiccator technique until S_{wi}=20%.

5.1.   Core Material

Two outcrop sandstone cores sampled from the same quarry, but are from two different blocks. Mineral composition analyses are confirmed to be very similar as seen in Figure 4.2. The cores contain 56% quartz, 31% albite feldspar, 10% clay mostly in the or of illite. The main difference is that core B-15 have previously been used in core experiments, while C-3 is a virgin core and never seen crude oil. Therefore, it was very interesting to see of these two cores behaved similarly.

5.2.   Core B-15

5.2.1.   FW composition and initial pH

FW-rock interaction will affect the initial pH established in a core. The polarity and reactivity of acidic and basic organic component in the crude oil toward rock surfaces are pH dependant. The concentration of positively charged protonated bases increases with decreasing pH.

To evaluate the effect of FW composition on initial pH. Core B-15 was used in brine flooding experiments. By adding different concentrations of Al^{3+}-ions to the FW20Ca-brine a lower pH would be reached. The core was tested with 3 different brines with aluminium concentration of 0.1 mM, 0.2 mM and 0.4. The core mM was flooded with 4-5 PV of the brine. Thereafter, the core was flooded with 4-5 PV of a 5 times diluted version of the same brine. Effluent samples were collected and the corresponding pH value are presented in Figure 5.1.
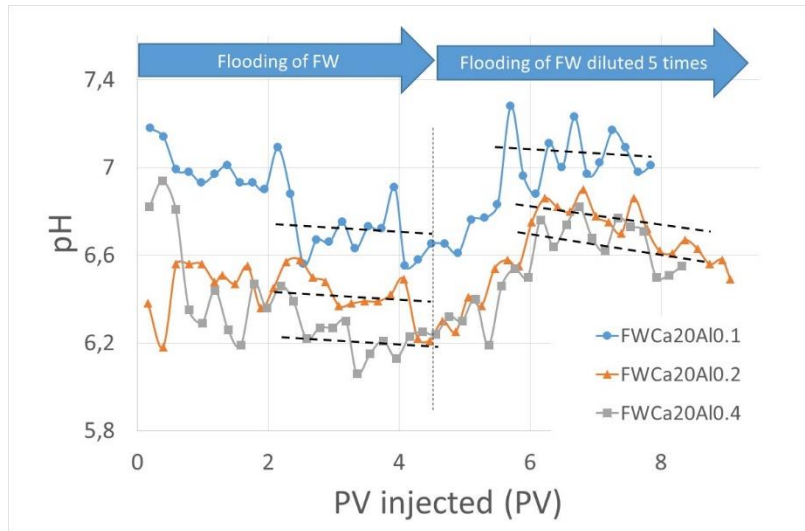
Figure 5.1: Core B-15 was 100% saturated and flooded with FW with different concentration of $AlCl_3$ at 50°C at a rate of 0.1 ml/min

During the $FWCa_{20}Al_{0.1}$ flooding, the effluent reached a pH close to 6.7. Then the 5 times diluted brine was introduced, and an increase in pH to 7.1 was observed. The $FWCa_{20}Al_{0.2}$ reached a pH of 6.4, while the 5 times diluted brine gave a pH of 6.7. The third brine $FWCa_{20}Al_{0.4}$ reached a pH around 6.2. When the diluted brine was introduced to the system, the pH increased to 6.5. Between each brine flooding the core was flushed with 1 PV of the next brine.

The dynamic pH established during brine flooding confirmed that the pH decreases with increasing aluminium concentration in the FW. During the diluted brine flooding, a smaller increase of 0.3 pH units was observed. 5 times diluted FW is used during establishing a $S_{wi}=0.2$ by the desiccator technique and the results confirms that this procedure could not have a dynamic effect on the initial core pH. A complete set of data point can be found in appendix A.4.

5.2.2.   Adsorption of polar organic components

Core B-15 with $S_{wi}=20\%$ using $FWCa_{20}Al_{0.4}$ as FW was flooded at a rate of 0.1 ml/min with M1-Oil (AN=0.2 and BN=0.31). The core was totally flooded 32 PV and effluent samples were collected and the corresponding AN and BN analysed. The experiment results for the AN are plotted in Figure 5.2.
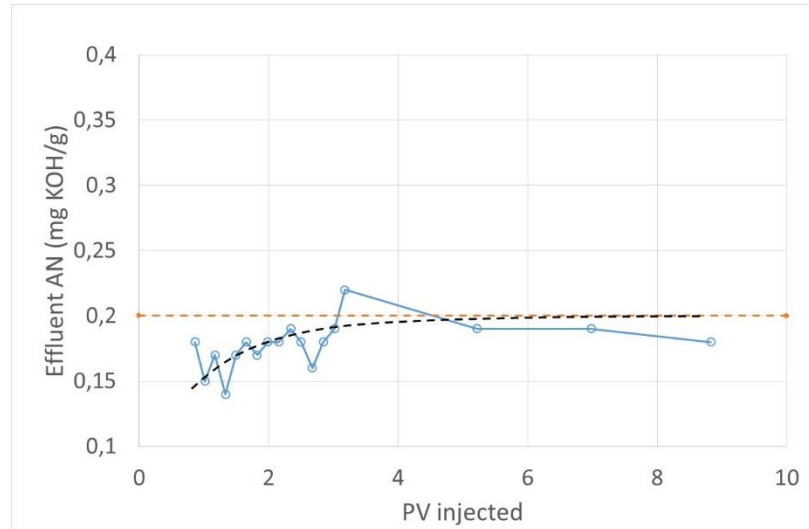
Figure 5.2: Core B-15 with $S_{wi}=0.2$, flooded with M1-Oil at 50°C with a rate of 0.1 ml/min. The AN in effluent samples is plotted as a function of PV injected.

In the first effluent samples we observed a reduced AN. After 4 PV, the AN stabilized close to the initial value, as seen in the general trend (Dotted black line). The lowest value was reduced as much as 0.06 units down to an AN of 0.16. The average AN for the first three PV is approximately 0.17 mg KOH/g, representing 15% reduction in AN, confirming a significant reduction in acidic polar components due to adsorption. Furthermore, the overall lowest value of 0.14, which corresponds to a 30% lower value than the AN of the injected oil.

The results from BN analysis are presented in Figure 5.3:
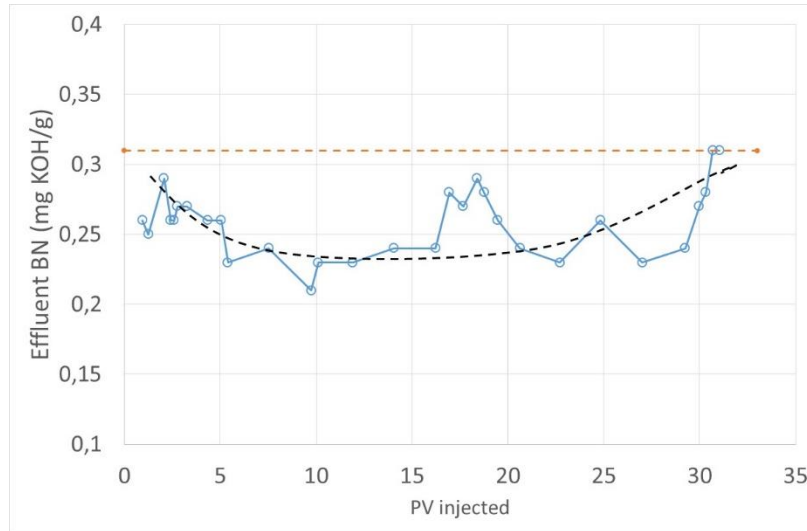
Figure 5.3: Core B-15 with S_{wi}=0.2, flooded with M1-Oil at 50°C with a rate of 0.1 ml/min. The BN in effluent samples is plotted as a function of PV injected

As seen in Figure 5.3 we observe a clear adsorption of basic components. The BN reach the initial value after 31 PV of M1-Oil injected, which is equal to the total number of PV injected. There is some fluctuation in the BN of the effluent, but a general trend can be observed. The average values measured was a BN of 0.25, which is 0.06 units lower than the injected BN. This corresponds to an average reduction of 20%, which is quite significant. The absolute lowest BN value measured was 0.21, which is a reduction of 33% below the injected BN.

The experimental results confirm that the basic components adsorb immediately towards the mineral rock surface. Total adsorption can also be calculated by subtraction the AN and BN value measure in each sample glass from the initial value and add them together. This value is evaluated in greater detail in the next chapter of this thesis.

5.2.3.   Spontaneous Imbibition Test

After core B-15 was oil flooded with 32 PV of M1-Oil, the core was spontaneous imbibed in an Amott Cell to evaluate the initial core wettability and to evaluate if a LS brine could induce a wettability alteration and improve the oil recovery. The first imbibing brine used was the FW, which means $FWCa_{20}Al_{0.4}$. When the FW is used no chemical induced wettability alteration is expected. The SI test was performed at 50°C which is the same temperature as for the oil flooding. The results from the SI test is presented in Figure 5.4.
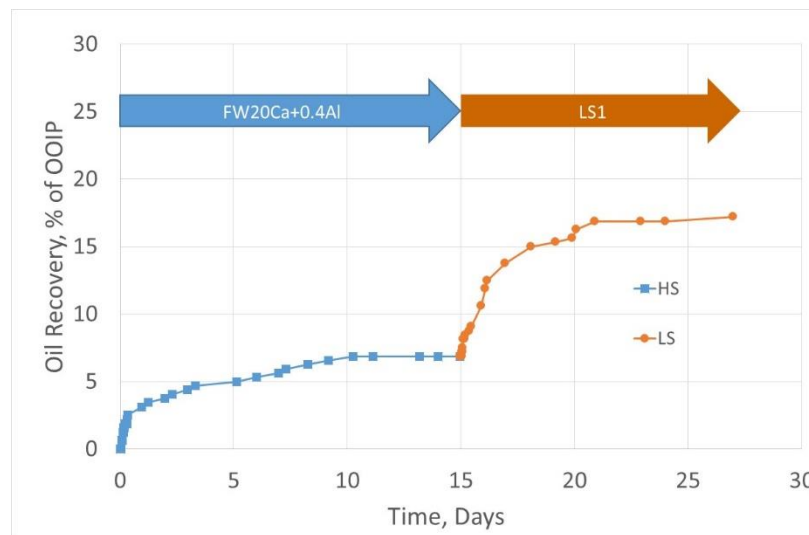
Figure 5.4: Spontaneous imbibition test on Core B-15 at 50°C. The core had S_{wi}=0.2 with $FWCa_{20}Al_{0.4}$ and flooded 32 PV with M1-Oil, was SI with FW followed by a SI with a 1000 ppm NaCl brine as LS

A gradually increase in oil recovery was observed during FW imbibition with a recovery plateau of 7% OOIP after 11 days. After 15 days the imbibing fluid was changed to LS. A rapid oil recovery was observed and a new oil recovery plateau of 17% of OOIP was reached after 21 days. The results confirm that the core behaved slightly water-wet after it have been exposed to 32 PV M1-Oil. The results also confirm that the LS brine was able to change the core wettability and improve oil recovery 10% OOIP.

5.3. Core C-3

5.3.1. FW composition and initial pH

FW composition was performed on Core B-15 and the effect of different $AlCl_3$ was evaluated. A second adsorption experiments was performed on Core C-3 to double check the results from the previous core to see if they behaved equally. Core C-3 is a fresh core that had previous never been introduced to oil and restored. The experiment was designed equal to the experiment for core B-15. The core was first flooded with $d_5FWCa_{20}Al_{0.4}$ during the establishing of 20% S_{wi}. The effluent pH during $d_5FWCa_{20}Al_{0.4}$ flooding are presented in Figure 5.5.
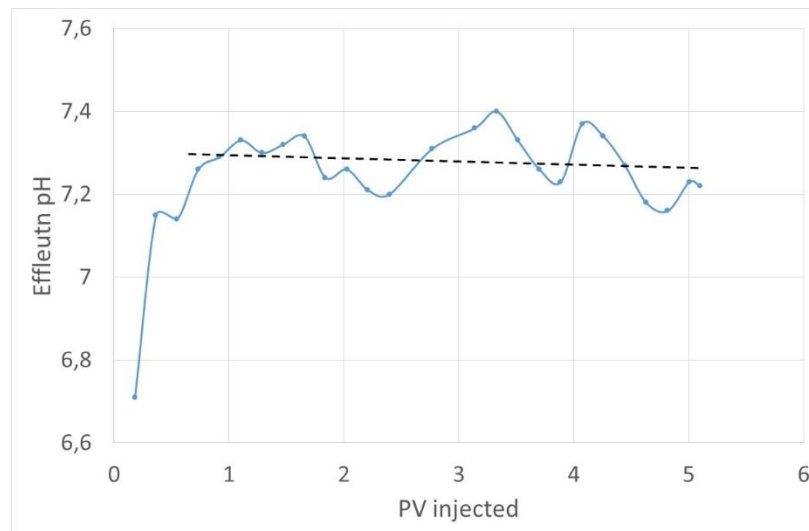
Figure 5.5: Core C-3 was 100% saturated and flooded with $d_5FWCa_{20}Al_{0.4}$ at 50°C at a rate of 0.1 ml/min

The effect of pH decrease using aluminium was confirmed with B-15 and therefore the same diluted brine was used ($d_5FWCa_{20}Al_{0.4}$). The pH values are stabilizing at a pH of 7.3 after 5 PV injected. The $d_5FWCa_{20}Al_{0.4}$ were used to establish a $S_{wi}=0.2$ by the desiccator technique. A complete set of data point can be found in appendix A10.

5.3.2. Adsorption of polar organic components

Core C-3 with S_{wi}=20% using FWCa$_{20}$Al$_{0.4}$ aw FW was flooded at a rate of 0.1 ml/min with M2-Oil (AN=0.2 and BN=0.22). The core was totally flooded 45 PV and effluent samples were collected and the corresponding AN and BN analysed. The experimental results for the AN are plotted in Figure 5.6.
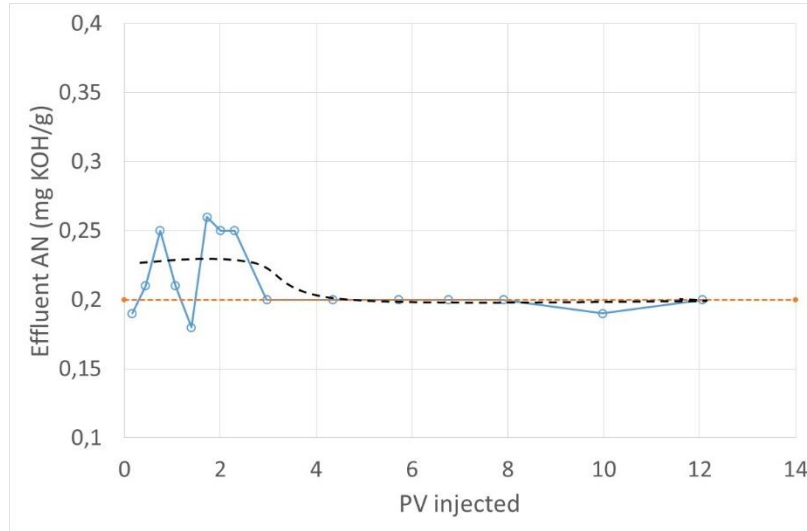
Figure 5.6: Core C-3 with S_{wi}=0.2, flooded with M2-Oil at 50°C with a rate of 0.1 ml/min. The AN in effluent samples is plotted as a function of PV injected

In the first effluent samples we observed an increase in the AN. After 3 PV, the AN stabilized at initial value, as seen in the general trend (dotted black line). These results could be explained by presence of humic acids that are desorbed from the outcrop core when more reactive components are introduced during crude oil flooding. Thereafter, the values seem to be back to initial values and if any adsorption is taking place it is not detected by the machine or negligible. A complete set of data point can be found in appendix A8.

The results from BN analysis are presented in Figure 5.7:
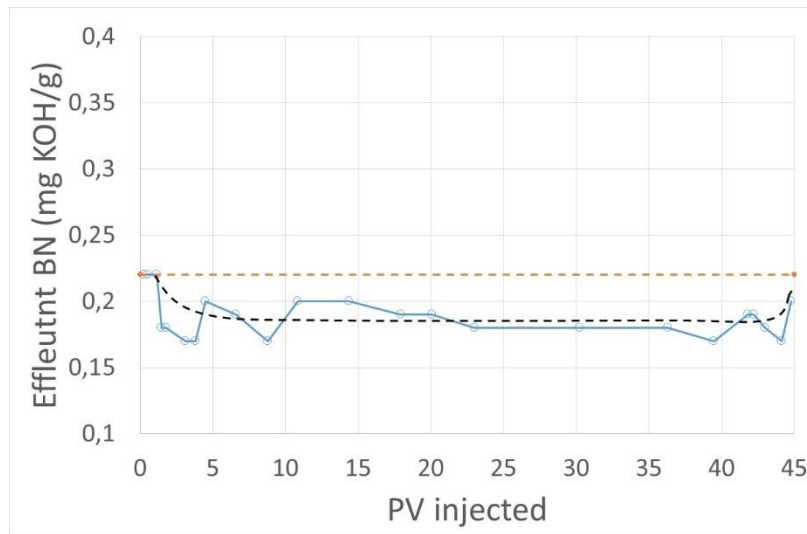
Figure 5.7: Core C-3 with S_{wi}=0.2, flooded with M2-Oil at 50°C with a rate of 0.1 ml/min. The BN in effluent samples is plotted as a function of PV injected

In the first effluent samples, no adsorption is observed, but after 2 PV injected the effluent samples have reduced BN, which stabilises close to 0.18 during the whole flooding of 45 PV M2-Oil. AN adsorption of 0.04 units represents 18% reduction in basic content which is significant. A general trend can be clearly observed. The lowest BN value that was measured was 0.17, which is approximately 23% lower than the BN of the oil flooded through the core.

The result seems to vary consistently throughout the experiment. Even if there are some samples of the effluent that seems to come back to the initial value, there is not consistent enough at the end to assume that the core has fully adsorbed basic components to all surfaces of the rock. A complete set of data point can be found in appendix A7.

In this core restored for the first time, the adsorption of basic components continues throughout the experiment and equilibrium is not reached after 45 PV crude oil injected. The adsorption results confirm the results from the B-15 core. The basic oil components have a much higher affinity towards the mineral surface and could be the polar organic components that dictates the reservoir wettability in sandstone reservoirs.

5.3.3.   Spontaneous Imbibition Test

After the oil flooding process was finished on core C-3, a SI test was performed to evaluate the core wettability. The test was performed at 50°C using FW continued by LS imbibing brines. When the oil recovery had plateaued, the initial brine was replaced with the low salinity brine Total LS1, with a salinity of 1000 ppm. The Amott Cell was placed in an oven set to 50°C during the whole experiment. The SI with FW gave an ultimate oil recovery of 2.5% OOIP. Corresponding values of oil recovery can be seen in Figure 5.8:
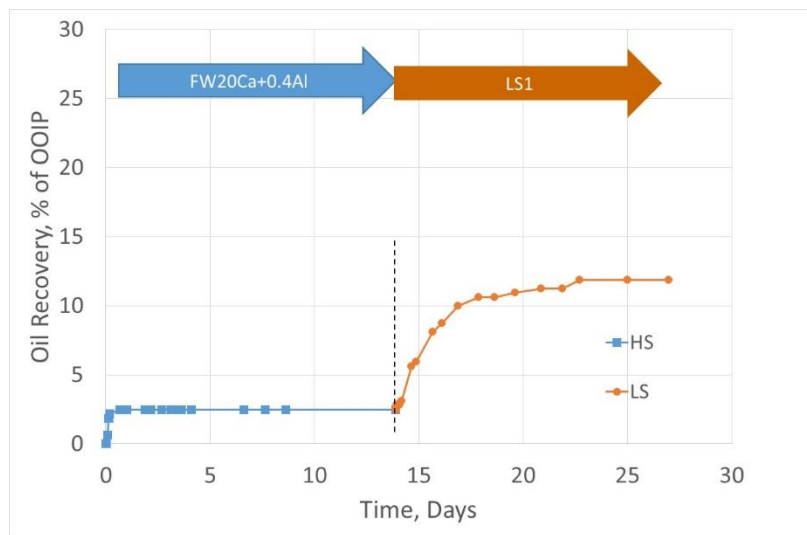
Figure 5.8: Spontaneous imbibition test on Core C-3 at 50°C. The core had S_{wi}=0.2 with FWCa$_{20}$Al$_{0.4}$ and flooded 45 PV with M2-Oil, was SI with FW followed by a SI with a 1000 ppm NaCl brine as LS

This oil was produced within the first hours and could be linked to thermal expansion, confirming mixed-wet conditions which could be linked to the adsorption of basic organic components. After 14 days the imbibing fluid was changed to the LS brine, with a NaCl concentration of 1000 ppm. A gradually increase in the oil recovery was observed, and after 23 days a recovery plateau of 12% OOIP was reached. The results confirm that the LS brine is able to change the core wettability and behave as a Smart Water even in porous systems with very low water-wetness.

6. Discussion

The following section will discuss and compare the acquired result from B-15 and C-3. The experiments will also be compared to previous experiments done by BSc student Ove Kvandal (Kvandal, 2016) and PhD student Ivan Torrijos (Piñerez Torrijos et al., 2017). The two outcrop cores used in these experiments are very well described and have shown Smart Water EOR effects in previous experiments published by the Smart Water Group at the University of Stavanger. Both cores had high concentrations of albite feldspars and illite clays. The initial chemical condition is of very high importance as it dictates both the initial wetting and the potential of observing EOR-effect with a brine, which is controlled by a wettability alteration towards more water-wet conditions.

6.1. Initial pH Conditions

It is considered that the outcrop sandstone used in these experiments initially have been exposed to rainwater. If the albite plagioclase ($NaAlSi_3O_8$) has been exposed to rainwater some of the Na^+ could be substituted with H^+, and the albite present in outcrop could also be on form $HAlSi_3O_8$. When flooding with a high salinity brine with high Na^+ concentration, equation 6.1 is shifted towards the right creating a more acidic environment, due to an increase of H^+ a lower initial pH will occur. Increased concentration of protonated polar organic components; especially positively charged basic components which could interact with negatively mineral surfaces. A reduced initial water-wetness will also increase the LS EOR potential.

$$HAlSi_3O_8 + Na^+ \leftrightarrow NaAlSi_3O_8 + H^+ \qquad \text{Eq.: 6.1}$$

When introducing a LS brine to the albite system a reduced Na^+ concentration, will promote that equation 6.2 is shifted to the right. An increased pH will promote less protonated positively charged organic polar components. This will make the system more water-wet and an EOR-effect is observed.

$$NaAlSi_3O_8 + H_2O \leftrightarrow HAlSi_3O_8 + Na^+ + OH^- \qquad \text{Eq.: 6.2}$$
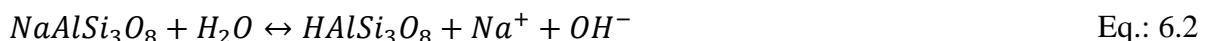
Furthermore, the clay minerals also contribute with permanent negative charge and CEC together with large surfaces. The negative charge must be balanced. FW with high concentration of Ca^{2+} ions will shift this chemical equilibrium towards the left as equation 6.3 states. When a LS brine is injected the calcium ions will desorb and protons will adsorb due to their higher affinity towards the clay surface.

$$Clay - Ca^{2+} + H_2O \leftrightarrow Clay - H^+ + Ca^{2+} + OH^- \qquad\qquad \text{Eq.: 6.3}$$
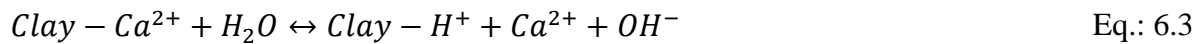
This will create a local pH increase close to the clay surface, which also could contribute in promoting a wettability alteration towards more water-wet conditions.

6.2.   Adsorption of Polar Organic Components

The crude oil used in the experiments performed on B-15 and C-3 have an AN and BN that is relatively low. But, the cores have been flooded with 30-45 PV making the amount of polar components exposed to the core quite high. The initial pH established in a core is also dependant on the polar organic components present in the introduced crude oil. According to the observed results from brine flooding, initial conditions with a lower pH, adsorption of polar organic components in core B-15 and C-3 are expected.

Basic polar adsorption
The first core was flooded with several types of FW brines with different concentrations of $AlCl_3$ to be able to reach an acceptable pH in the system close to 6. This will affect the plagioclase present, since at pH below 7 the plagioclase is considered to be protonated because of the higher H^+ concentration. This means that it will be on the form $HAlSi_3O_8$. Hence, the mineral surface is considered to be oil-wet. Since the FW in the final flooding had a pH of 4.80, it is possible to assume that there were a sizable amount of protons that adhered towards the surface, moving the chemical equilibrium in eq. 6.1 to the left.
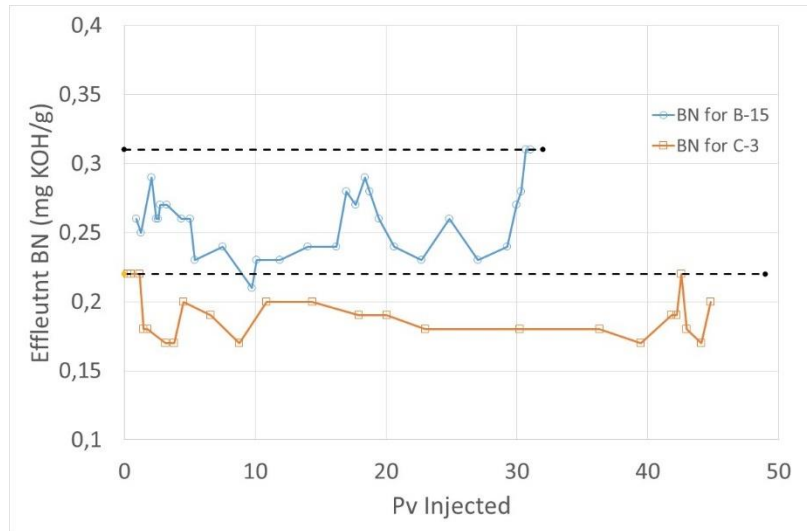
Figure 6.1: Comparison of BN for both Core B-15 and Core C-3

B-15 was subsequently flooded with M1-Oil with AN=0.20 and BN=0.31 and assumable a marginal lower initial pH than C-3. A lower pH should promote the adsorption of organic polar components. When comparing Figure 6.1 to 6.2 there is a clear trend. As seen in figure 6.2, Kvandal was not able to restore the BN to initial values, meaning the basic polar components still had affinity towards the mineral surface. Through the experiments performed in this thesis we were able to have samples that reached initial values. Unfortunately, the experiment stopped and it was not possible to see if the BN stabilized at initial values. C-3 on the other hand, were flooded with even more PV to see if that was the case. The same BN observations have also been observed in previous experiments (Kvandal, 2016).

Figure 6.2: BN result for B-15. Both experiments performed by Ove Kvandal **a)** Oil flooding performed Spring 2016. **b)** Oil flooding performed Atumn 2016

The end result from the BN test for B-15 concur with Kvandal's results along with the theory. However, there may be several basic components in the oil and they might have different affinities towards the negatively charged surface. If that is the case, it would not be strange that the crude oil is varying due to the different affinities of basic polar components. C-3 was initially a fresh core that had never been introduced to crude oil. C-3 was subsequently flooded with the same FW as B-15. There are a little less variety in the BN result compared to core B-15, but the same trend as for B-15 can still be observed. The experimental results confirm that basic crude oil components are active towards rock surfaces and could create mixed-wet conditions in sandstone cores.

Acidic polar adsorption

When it comes to the AN results, it seems to be nearly negligible relative to the BN results. It is possible to compare the results from Figure 6.3.
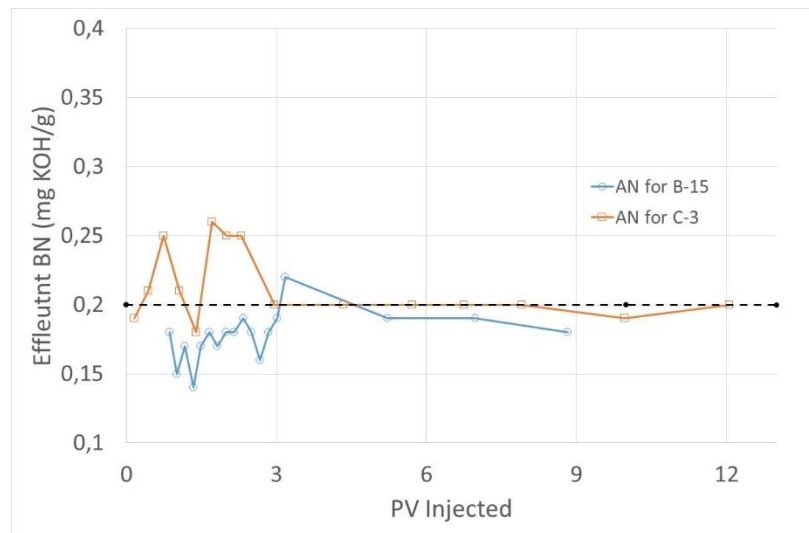
Figure 6.3: Comparison of AN for both Core B-15 and Core C-3

The acidic polar components in the crude oils seem to be back at initial values after about 3 PV, which is relatively quick. Due to the negatively charged nature of sandstone it is not strange that there is little to no affinity of acidic polar components towards the surface. There has been proven that adsorption of acidic components towards kaolinite also are pH dependant (Madsen & Lind, 1998). The pH in core systems might not be low enough for the acidic components to adsorb. The

pK_a value for benzoic acid (pK_a=4.2), which is often used as a model oil component is almost one pH unit lower than for the basic component quinoline (pK_a=4.9).

When comparing Figure 6.3 to Figure 6.4 there seems to be the same trends and the AN is restored to initial values after a few PV. The experimenatl results are equal to the results obtained from Kvandal (2016). The results also confirms a very low adsorption.
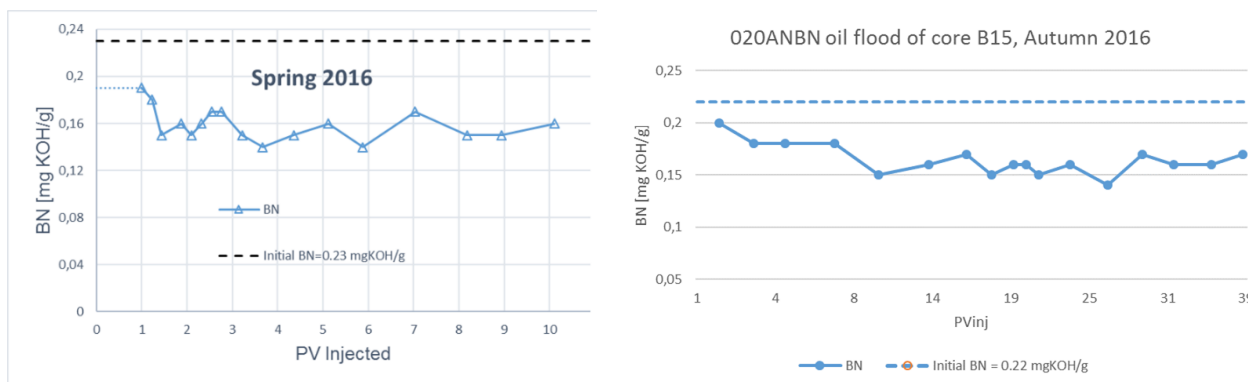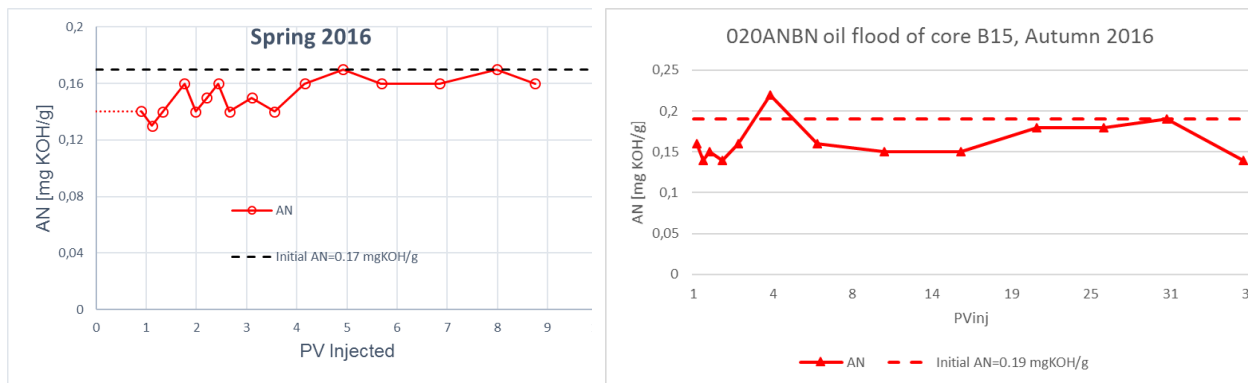

Figure 6.4: AN result for B-15. Both experiments performed by Ove Kvandal **a)** Oil flooding performed Spring 2016. **b)** Oil flooding performed Atumn 2016

Furthermore, it is very interesting to see that the adsorption of both basic and acidic components in the beginning of each oil flooding is instantaneous. This means that the cores don't have to be aged or matured to make sure that the polar components adsorb onto the surface.

6.3.   Total Adsorption of Polar components

Figure 6.3 shows the total adsorption of polar components in core B-15 and C-3. In Kvandal's experiment, B-15 was flooded 40 PV of crude oil, which is 10 more than the experiments in this thesis, and the core had an initial pH at approximately 7. The total adsorption of polar components is approximately the same (1.9 mgKOH/g), as seen in Figure 6.5. The only difference in these two experiments are the initial pH established with FW, which was somewhat higher in the work by Kvandal. This results confirms that the basic crude oil components are far more active and adsorbs more easily to the rock surface.
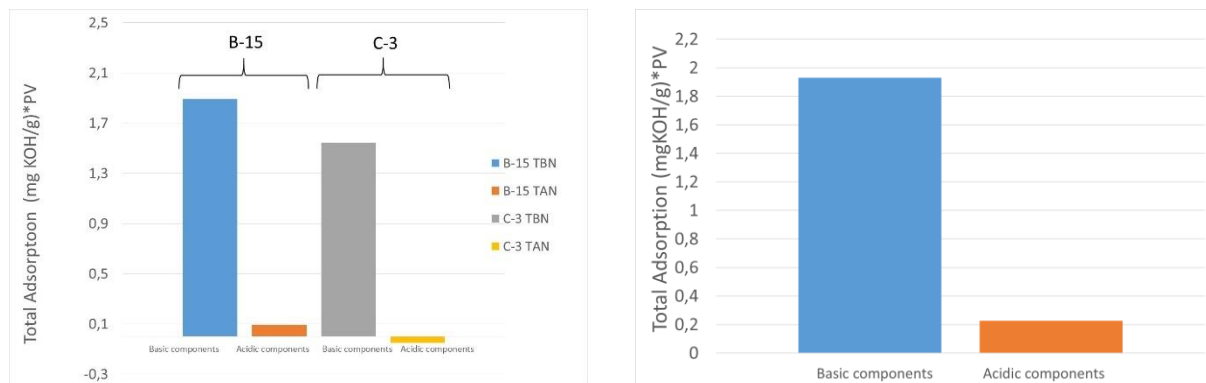
Figure 6.5: a) Total adsorption in B-15 and C-3 throughout the oil flooding.
b) Total adsorption of B-15 from Ove Kvadal's experiments

The adsorption observed in C-3 are in line with the observations for core B-15. This can be explained by the slightly higher pH observed during FW flooding in C-3, and that an adsorption equilibrium was not achieved after 45 PV injected. The adsorption of acidic components was negative. This is most likely because the core was not cleaned initially before the core restoration/oil flooding. Humic acids may be desorbed when reactive basic components are introduced during the oil flooding.

6.4.   Wettability Alteration

Both core B-15 and C-3 were SI after the crude oil flooding. When imbibing with FW there is very low recovery from the cores. This confirms that both cores are very low in water-wetness. Due to the fact that the cores are flooded with high numbers of PV with crude oil, the results are in line with the expectation. Additionally, the cores were not aged. The core wetting condition is not dependant on an aging process. When a LS brine was introduced, increased oil recovery was observed confirming that the Smart Water EOR effect could also be at initially mixed-wet conditions.
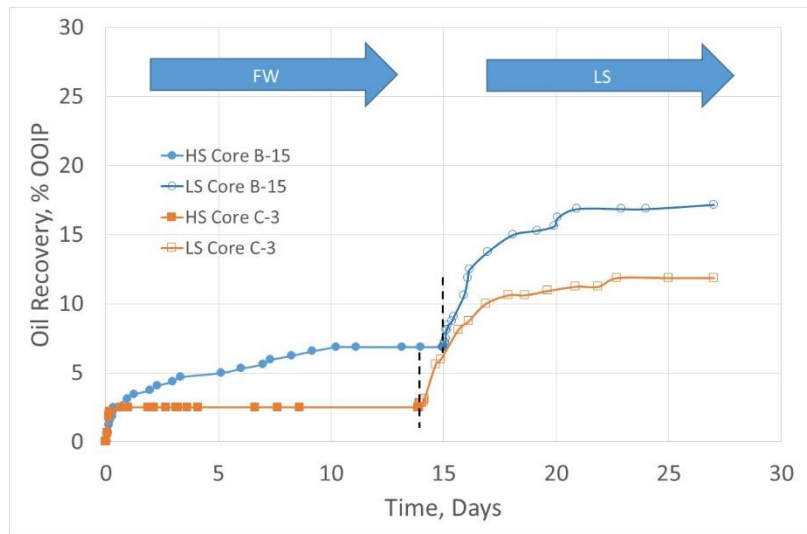
Figure 6.6: Spontaneous imbibition test on core B-15 and C-3 at 50°C. The cores had S_{wi}=0.2 with $FWCa_{20}Al_{0.4}$ and flooded 32 and 45 PV respectively, with crude oil. SI with FW followed by a SI with a 1000 ppm NaCl brine as LS

The plagioclase is assumed to be in a protonated state before the LS brine is applied and from equation 6.2 the chemical equilibrium is shifted towards the right. The lack of cations in the water will continue the desorption of organic polar components from the surface of the porous medium, leading to wettability alteration and increased overall oil recovery.
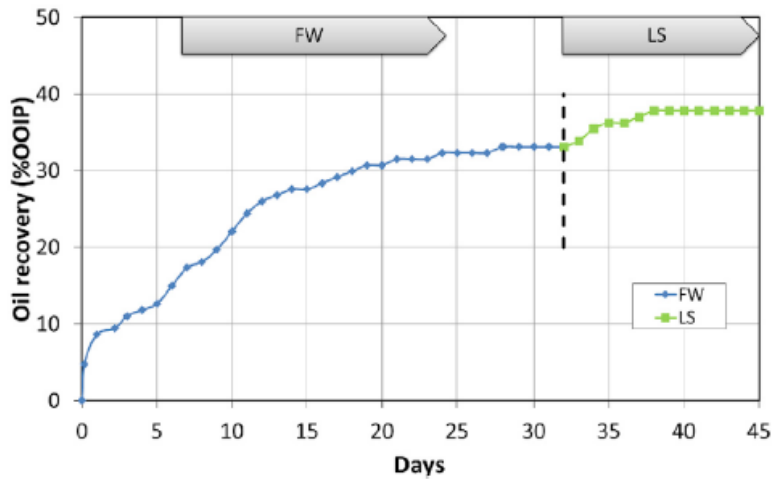
Figure 6.7: Spontaneous Imbibition of C-2 with FW and LS (Piñerez Torrijos et al., 2017)

Ivan Torrijos (2017) used the same outcrop sandstone core in experiments and performed a spontaneous imbibition test on core C-2. The core had an initial water saturation of 20%, but he used the T-Oil instead with high BN. During the core restoration, the core was exposed to only 5 PV T-Oil. SI test were performed at 60°C with FW as the imbibing brine. His experiment showed a more water-wet initial conditions as expected after being exposed to only 5 PV with T-Oil. 33 % OOIP was produced, confirming quite water-wet conditions compared to the results from core B-15 and C-3. Introducing LS brine to core C-2, an increased oil recovery of 5% OOIP was observed in the next 6 days, confirming also Smart Water EOR effects in the core system that behaves quite water-wet.

7. Uncertainties

There will always be some degree of uncertainties during lab experiments.

Potentiometric titrations, here using a Mettler Toledo DL55 Autotitrator for measuring AN and BN, is extremely sensitive and need to have trained personnel to improve repeatability. This means that the electrode must be properly calibrated with three pH buffers (pH 4, 7 and 10). Even if the machine is calibrated correctly, it is experienced that the repeatability is less than 0.02 units due to uncertainties in adding crude oil sample, spiking solution and titrant solvent. The electrode is contaminated by crude oil and needs to be cleaned and recalibrated after frequent use.

The pH in brine solutions was measured by using a Mettler Toledo Seven Compact pH-meter with an uncertainty of 0.04. The electrode was cleaned between each test. The machine was also frequently calibrated with three pH buffers (pH 4, 7 and 10) to ensure that the electrode responded correctly.

Uncertainties are also linked to the core flooding setups. The SS piston cells, inlet and outlet steel tubing are cleaned between each experiment. All SS components exposed to high salinity brines might contain rust that could be a source of error.

8. Conclusion

The experimental work performed in this thesis work was performed to improve the understanding of initial wetting and the EOR-effect observed during Smart Water flooding in sandstone reservoirs. The Smart Water EOR-effect is a wettability alteration towards more water-wet conditions, inducing increased positive capillary forces and improved microscopic sweep efficiency.

It is highly important to understand the parameters effecting the initial reservoir wettability, when the Smart Water EOR potential for a reservoir should be predicted. In this work the influence of acidic and basic polar organic components on adsorption towards mineral surfaces have been evaluated, and how they affect initial wetting and Smart Water EOR potential.

The experimental observation shows that:

- Variations in the adsorption of basic components even when the adsorption is instantaneous. Most likely due to different affinities to the negatively charged surface of different basic components.
- pH<7 will give higher total adsorption of basic components
- More exposure to crude oil will give more mixed-wet conditions in the core
- When switching from FW to LS-brine the capillary forces is increased and a wettability alteration is taking place.
- FW brine pH could be supressed by adding small amounts of Al^{3+} ions to the FW
- At initial pH with FW in the range of 7, crude oil with polar components was introduced and the initial condition established favoured adsorption of polar components toward the mineral surface.
- At the established initial conditions, the basic components in the crude oil was strongly retained.
- The acidic components had far less affinity towards the mineral surface.
- The outcrop sandstone core became mixed-wet after extensive crude oil flooding.
- LS EOR effect was observed also for mixed-wet neutral sandstone cores.

9. Future Work

This thesis has tried to highlight the importance of initial wetting in sandstone. The results confirm the mechanism suggested by Austad et al. (2010) highlighting the polar components in the crude oil as the main wetting parameter. To improve the understanding further, more experiments and testing is required:

- The effect of initial pH of adsorption of polar component need to be further investigated. Work performed by (Burgos et al., 2002; RezaeiDoust, 2011) suggests that the adsorption will be even higher at lower pH-values.

- In this work we have crude oil with BN from 0.20-0.30. The effect of increased BN in the crude oil should be evaluated. Then an adsorption equilibrium should be easier to achieve.

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Appendix: A1 - Crude oil recipe

The Res40-0 was made by blending 60% Heidrun crude oil and 40% n-heptane. A magnet stirrer was put in the mixture so that the stirring would go continuously. Thereafter, 10 wt% of silica gel was put in every third day until a total of 30-35 wt% was put in. This would correspond to 80g every third day until 240-280g per litre crude oil had been added. The meaning this procedure is to remove all polar compounds and decrease the acid number down to 0. After that, the oil mixture was placed in a centrifuge for 1 hour and the remaining liquid was filtered, first with a filter of 8 µm and again with a filter of 5µm and 3µm.

The goal was to get oil with an acid number and base number close to 0.20. When the treated oil was done filtering, it was mixed with relative small amounts of both Heidrun oil and oil retrieved from Total. The untreated oil had originally a very high acid number and the Total oil had a very high base number. To get the right AN and BN a Mettler Toledo DL55 auto-titrator was used. In the end an oil mixture with AN=0.20 and BN=0.31 was reached. The acid number values and base number values were reliable, and they were the values noted and used for further experiments.

A2 – Crude oil Saturation and Flooding Procedure

Prior to the oil flooding, the lines were prepared so that no free salt or other contaminants were present. Then, the inlet line was filled to the distributor ends with the oil with a AN=of 0.20 and BN=0.31. the back-pressure was 10 bar, which was within the parameters constraints of 6-15 bar. The confining pressure was 20 bar, which was within the parameter of 15-25 bar. When everything was connected the oven was set to 50°C. The by-pass on the system was closed and flooding started when the core had reached correct temperature. The rate was set to be 0.1 ml/min, which would go on until adsorption of polar components in the core had stopped and AN and BN values of the effluent would be back at initial values. Since this was unknown the experiment continued until 40 PVs had been flooded, which was similar to previous experiments.

A3 – AN and BN measurements

Previously, a method using 20 g of crude oil to measure AN was used as the standard procedure (ASTM Standard Test Method D664-01). By using the modified procedure rather an oil sample of 0.5 to 1.5 g crude oil was necessary. To increase the precision of the measurements a known amount of quinoline was used as the spiking agent for the BN measurements and stearic acid was used as spiking agent for the AN measurement (Fan & Buckley, 2006). Both of these spiking solution would increase the inflection points compared to the previous ASTM method.

The acid number and base number of the different oil samples were determined by potentiometric titration using a Mettler Toledo DL55 autotitrator. Experimental materials used for AN measurements were as follows:

- Titrant: 2.8 g KOH diluted to 1000 ml with 2-propanol.
- Titration solvent: 6 ml DI water and 494 ml 2-propanol and 500 ml toluene.
- Spiking Solution: 0.5 g stearic acid diluted to 100 ml with acid titration solvent.
- Standard solution: 0.2 g KHP diluted to 500 ml with DI water.

Experimental materials used for BN measurements were as follows:

- Titrant: 5 ml 70% $HClO_4$ and 15 ml Acetic anhydride diluted to 1000 ml with acetic Acid.
- Titration solvent: Methyl Isobutyl Ketone (MIBK).
- Spiking Solution: 0.5 g quinoline diluted to 100 ml with Decane.
- Standard solution: 0.2 g KHP diluted to 150 ml with acetic acid.

Before the measuring begun, the electrode used in the autotitrator was calibrated with pH buffers of pH 4, pH 7 and pH 10. The autotitrator used two electrodes, one for the AN determination and one for the BN determination. The titrant was standardized by using the standard solution respectively to determine the amount of titrant added to each oil sample. These calibrations were carried out in the beginning of each day with measurements. After a certain number of measurements, the electrode could be worn out. The solution to this problem was to place the electrode in a 0.1 M HCl for couple of hours to refresh it. When the electrode was not used they were placed in a container with ~0.5 M KCl solution.

The procedure used a blank (reference solution) with known AN or BN, which all of the oil samples were compared against. The blank was made with 50 ml titration solvent and 1 ml spiking solution. A molecular weight was used to ensure that each sample was as equal as possible and to neglect uncertainty. The actual oil samples were made with 50 ml titration solvent, 1 ml spiking solution and approximately 1.0 g crude oil. The stirrer and electrode was cleaned with DI water between each oil sample. The acidic number was calculated by using this formula:

$$AN = \frac{(V_{eq} - V_b) \times N \times MW}{W} \qquad \text{Eq.: A3.1}$$

Where, V_{eq} is the amount of titrant consumed by the crude oil sample at the equivalent point (ml), V_b is the amount of titrant consumed by the blank at the equivalent point (ml), N is the molecular concentration of the KOH titrant (mol/l), MW is the molecular weight of KOH (56.1 g/mol), and W is the amount of oil used in the oil sample (g).

A4 – Initial pH preparation

		FWCa20Al0.1				
		Weight of glasses				
	Glass number	Before	After	Fluid wt	PV injected	pH
	1	9,01	12,13	3,12	0,2048992	7,18
	2	8,85	11,87	3,02	0,4032311	7,14
PV	3	8,98	11,95	2,97	0,5982794	6,99
15,227	4	8,45	11,44	2,99	0,7946411	6,98
	5	8,99	11,96	2,97	0,9896894	6,93
	6	8,44	11,41	2,97	1,1847376	6,97
	7	8,36	11,31	2,95	1,3784725	7,01
	8	9,14	12,13	2,99	1,5748342	6,93
	9	8,9	11,89	2,99	1,7711959	6,93
	10	9,08	11,87	2,79	1,9544231	6,9
	11	8,88	11,84	2,96	2,1488146	7,09
	12	8,97	11,94	2,97	2,3438629	6,88
	13	8,36	11,36	3	2,5408813	6,56
	14	8,46	11,46	3	2,7378998	6,67
	15	8,94	11,94	3	2,9349182	6,66
	16	8,37	11,43	3,06	3,1358771	6,75
	17	9,13	12,13	3	3,3328955	6,63
	18	9,11	12,14	3,03	3,5318842	6,73
	19	9,26	12,33	3,07	3,7334997	6,72
	20	8,96	12,03	3,07	3,9351153	6,91
	21	9,02	11,48	2,46	4,0966704	6,55
	22	9,03	12,12	3,09	4,2995994	6,58
	23	8,46	11,54	3,08	4,5018717	6,65
	24	8,98	12,05	3,07	4,7034872	6,65
	25	8,34	11,39	3,05	4,9037893	6,61
	26	9,07	12,15	3,08	5,1060616	6,76
	27	8,4	11,47	3,07	5,3076772	6,77
	28	9,02	12,06	3,04	5,5073225	6,83
	29	8,98	12,02	3,04	5,7069679	7,28
	30	9,46	12,47	3,01	5,9046431	6,96
	31	8,49	11,45	2,96	6,0990346	6,88
	32	8,4	11,41	3,01	6,2967098	7,11
	33	9,1	12,05	2,95	6,4904446	7
	34	8,4	11,36	2,96	6,6848361	7,23
	35	9,05	12	2,95	6,878571	6,97
	36	9,54	12,5	2,96	7,0729625	7,02
	37	9,47	12,42	2,95	7,2666973	7,17
	38	9,05	12,01	2,96	7,4610889	7,09
	39	8,48	11,44	2,96	7,6554804	6,98

	40	8,93	11,92	2,99	7,8518421	7,01

FWCa20Al0.2					
Weight of glasses					
Glass number	Before	After	Fluid wt	PV injected	pH
1	8,41	10,91	2,5	0,164182	6,38
2	8,46	11,96	3,5	0,3940369	6,18
3	8,99	12,04	3,05	0,594339	6,56
4	9,09	12,05	2,96	0,7887305	6,56
5	8,95	11,96	3,01	0,9864057	6,56
6	8,47	11,46	2,99	1,1827675	6,48
7	9	10,74	1,74	1,2970382	6,51
9	9,5	12,45	2,95	1,490773	6,47
10	9,06	12,09	3,03	1,6897616	6,55
11	8,87	11,84	2,97	1,8848099	6,36
12	9,1	12,08	2,98	2,0805149	6,45
13	9,06	12,03	2,97	2,2755631	6,57
14	9,15	12,37	3,22	2,4870296	6,58
15	8,49	11,45	2,96	2,6814212	6,5
16	8,44	11,38	2,94	2,8744992	6,48
17	8,47	11,62	3,15	3,0813686	6,37
18	9,04	11,95	2,91	3,2724765	6,38
19	8,48	11,52	3,04	3,4721219	6,39
20	8,44	11,6	3,16	3,679648	6,39
21	9,08	12,03	2,95	3,8733828	6,42
22	8,37	11,46	3,09	4,0763118	6,49
23	9,02	12,17	3,15	4,2831812	6,22
24	9,04	11,84	2,8	4,4670651	6,21
25	8,44	11,46	3,02	4,665397	6,3
26	8,3	11,32	3,02	4,8637289	6,25
27	8,41	11,43	3,02	5,0620608	6,41
28	8,41	11,44	3,03	5,2610495	6,37
29	8,95	12	3,05	5,4613515	6,54
30	9,09	12,13	3,04	5,6609969	6,58
31	8,54	11,13	2,59	5,8310895	6,55
32	8,48	11,48	3	6,028108	6,75
33	8,34	11,35	3,01	6,2257831	6,86
34	9,12	12,1	2,98	6,4214881	6,82
35	9,61	12,57	2,96	6,6158797	6,8
36	9,06	12,04	2,98	6,8115847	6,9
37	8,4	11,36	2,96	7,0059762	6,78
38	8,4	11,4	3	7,2029947	6,75
39	9,01	11,97	2,96	7,3973862	6,7

40	9,11	12,06	2,95	7,591121	6,86
41	9,06	12,03	2,97	7,7861693	6,72
42	9,07	12,05	2,98	7,9818743	6,62
43	9,12	12,07	2,95	8,1756091	6,61
44	8,99	11,97	2,98	8,3713141	6,67
45	8,37	11,24	2,87	8,5597951	6,63
46	8,48	11,35	2,87	8,7482761	6,56
47	8,41	11,24	2,83	8,9341302	6,58
48	9,07	11,04	1,97	9,0635056	6,49

FWCa20Al0.2					
Weight of glasses					
Glass number	Before	After	Fluid wt	PV injected	pH
1	8,41	10,91	2,5	0,164182	6,38
2	8,46	11,96	3,5	0,3940369	6,18
3	8,99	12,04	3,05	0,594339	6,56
4	9,09	12,05	2,96	0,7887305	6,56
5	8,95	11,96	3,01	0,9864057	6,56
6	8,47	11,46	2,99	1,1827675	6,48
7	9	10,74	1,74	1,2970382	6,51
9	9,5	12,45	2,95	1,490773	6,47
10	9,06	12,09	3,03	1,6897616	6,55
11	8,87	11,84	2,97	1,8848099	6,36
12	9,1	12,08	2,98	2,0805149	6,45
13	9,06	12,03	2,97	2,2755631	6,57
14	9,15	12,37	3,22	2,4870296	6,58
15	8,49	11,45	2,96	2,6814212	6,5
16	8,44	11,38	2,94	2,8744992	6,48
17	8,47	11,62	3,15	3,0813686	6,37
18	9,04	11,95	2,91	3,2724765	6,38
19	8,48	11,52	3,04	3,4721219	6,39
20	8,44	11,6	3,16	3,679648	6,39
21	9,08	12,03	2,95	3,8733828	6,42
22	8,37	11,46	3,09	4,0763118	6,49
23	9,02	12,17	3,15	4,2831812	6,22
24	9,04	11,84	2,8	4,4670651	6,21
25	8,44	11,46	3,02	4,665397	6,3
26	8,3	11,32	3,02	4,8637289	6,25
27	8,41	11,43	3,02	5,0620608	6,41
28	8,41	11,44	3,03	5,2610495	6,37
29	8,95	12	3,05	5,4613515	6,54
30	9,09	12,13	3,04	5,6609969	6,58

31	8,54	11,13	2,59	5,8310895	6,55
32	8,48	11,48	3	6,028108	6,75
33	8,34	11,35	3,01	6,2257831	6,86
34	9,12	12,1	2,98	6,4214881	6,82
35	9,61	12,57	2,96	6,6158797	6,8
36	9,06	12,04	2,98	6,8115847	6,9
37	8,4	11,36	2,96	7,0059762	6,78
38	8,4	11,4	3	7,2029947	6,75
39	9,01	11,97	2,96	7,3973862	6,7
40	9,11	12,06	2,95	7,591121	6,86
41	9,06	12,03	2,97	7,7861693	6,72
42	9,07	12,05	2,98	7,9818743	6,62
43	9,12	12,07	2,95	8,1756091	6,61
44	8,99	11,97	2,98	8,3713141	6,67
45	8,37	11,24	2,87	8,5597951	6,63
46	8,48	11,35	2,87	8,7482761	6,56
47	8,41	11,24	2,83	8,9341302	6,58
48	9,07	11,04	1,97	9,0635056	6,49

FWCa20Al0.4					
Weight of glasses					
Glass number	Before	After	Fluid wt	PV injected	pH
1	9,1	11,96	2,86	0,187824	6,82
2	8,32	11,42	3,1	0,39141	6,94
3	8,39	11,4	3,01	0,589085	6,81
4	9,01	12,13	3,12	0,793984	6,35
5	8,95	11,97	3,02	0,992316	6,29
6	8,37	11,39	3,02	1,190648	6,44
7	8,29	11,34	3,05	1,39095	6,26
8	8,46	11,45	2,99	1,587312	6,19
9	8,38	11,41	3,03	1,786301	6,47
10	8,39	11,38	2,99	1,982662	6,36
11	8,82	12,01	3,19	2,192159	6,46
12	8,4	11,43	3,03	2,391147	6,39
13	8,99	12,01	3,02	2,589479	6,22
14	8,39	11,46	3,07	2,791095	6,27
15	8,33	11,35	3,02	2,989427	6,27
16	8,44	11,52	3,08	3,191699	6,3
17	8,85	11,4	2,55	3,359165	6,06
18	8,44	11,49	3,05	3,559467	6,15

19	9,14	12,2	3,06	3,760426	6,21
20	9,09	12,17	3,08	3,962698	6,13
21	8,97	12,06	3,09	4,165627	6,23
22	8,4	11,36	2,96	4,360018	6,25
23	9,35	12,43	3,08	4,562291	6,24
24	9,08	12,18	3,1	4,765876	6,32
25	8,89	11,96	3,07	4,967492	6,3
26	9,15	12,22	3,07	5,169108	6,4
27	9,02	12,07	3,05	5,36941	6,19
28	8,54	11,61	3,07	5,571025	6,46
29	8,87	11,92	3,05	5,771327	6,54
30	8,32	11,33	3,01	5,969002	6,5
31	8,94	11,94	3	6,166021	6,76
32	8,4	11,41	3,01	6,363696	6,64
33	9,04	12,05	3,01	6,561371	6,74
34	9,07	12,07	3	6,75839	6,82
35	9,05	12	2,95	6,952125	6,68
36	8,98	11,96	2,98	7,14783	6,62
37	8,99	11,96	2,97	7,342878	6,77
38	9	11,98	2,98	7,538583	6,73
39	9,05	12,04	2,99	7,734945	6,71
40	9,04	12,03	2,99	7,931306	6,5
41	9,08	12,07	2,99	8,127668	6,51
42	8,48	11,46	2,98	8,323373	6,55
43	8,94	9,62	0,68	8,36803	
44	9,03			8,36803	

A5 – BN values for B15

Glass number	Weight Before, g	Weight After, g	Liquid, ml	Total Liquid volume, ml	PV	BN
2	8,88	9,78	1,119	2,051	0,935	0,26
6	8,5	9,45	1,181	6,861	1,251	0,25
16	8,45	9,49	1,293	19,390	2,073	0,29
20	8,89	9,84	1,181	24,622	2,417	0,26
22	8,38	9,4	1,268	27,133	2,582	0,26
24	8,85	9,88	1,280	29,818	2,758	0,27
30	8,45	9,43	1,218	37,449	3,259	0,27
36	9,09	11,3	2,747	53,955	4,343	0,26
40	9,01	11,2	2,722	64,731	5,051	0,26
42	9,04	11,18	2,660	70,001	5,397	0,23
54	8,45	10,7	2,797	102,442	7,528	0,24
66	8,51	10,81	2,859	136,237	9,747	0,21
68	8,42	10,68	2,809	141,755	10,109	0,23
78	8,43	10,69	2,809	169,212	11,913	0,23
90	9,07	11,13	2,560	201,615	14,041	0,24
102	9,59	11,78	2,722	234,850	16,223	0,24
106	8,43	10,71	2,834	245,900	16,949	0,28
110	8,39	10,63	2,784	256,838	17,667	0,27
114	8,94	11,26	2,884	267,887	18,393	0,29
116	8,98	11,22	2,784	273,431	18,757	0,28
120	9,08	11,32	2,784	284,306	19,471	0,26
126	8,49	11,69	3,977	302,155	20,643	0,24
138	8,38	10,72	2,908	333,812	22,722	0,23
150	8,99	11,32	2,896	365,879	24,828	0,26
162	8,41	10,66	2,797	399,177	27,015	0,23
174	8,44	10,72	2,834	433,084	29,242	0,24
178	8,38	10,63	2,797	444,246	29,975	0,27
180	8,43	10,64	2,747	449,652	30,330	0,28
182	9,09	11,42	2,896	455,196	30,694	0,31
184	8,5	10,54	2,536	460,354	31,033	0,31

A6 – AN values for B15

Glass number	Weight Before, g	Weight After, g	Liquid, ml	Total Liquid volume, ml	PV	AN
1	8,36	9,11	0,932	0,932	0,861	0,18
3	8,36	9,34	1,218	3,269	1,015	0,15
5	8,49	9,42	1,156	5,680	1,173	0,17
7	9,01	10,07	1,317	8,178	1,337	0,14
9	8,44	9,46	1,268	10,552	1,493	0,17
11	8,42	9,46	1,293	13,013	1,655	0,18
13	8,44	9,49	1,305	15,599	1,824	0,17
15	8,31	9,37	1,317	18,097	1,988	0,18
17	9,1	10,11	1,255	20,645	2,156	0,18
19	8,96	10,09	1,405	23,442	2,339	0,19
21	9,62	10,62	1,243	25,865	2,499	0,18
23	9,07	10,2	1,405	28,538	2,674	0,16
25	8,33	9,4	1,330	31,148	2,846	0,18
27	8,37	9,43	1,317	33,745	3,016	0,19
29	8,5	9,44	1,168	36,231	3,179	0,22
41	8,39	10,49	2,610	67,342	5,223	0,19
51	8,93	11,12	2,722	94,089	6,979	0,19
61	8,36	10,64	2,834	122,291	8,831	0,18

A7 – BN values for C3

Glass number	Weight Before, g	Weight After, g	Liquid, ml	Total Liquid volume, ml	PV	BN
3	8,89	9,83	1,175	3,7125	0,232759	0,22
7	8,39	9,37	1,225	8,275	0,518809	0,22
15	8,96	9,97	1,2625	18,275	1,145768	0,22
19	8,34	9,41	1,3375	23,5625	1,477273	0,18
23	8,51	9,47	1,2	28,6125	1,793887	0,18
35	9,12	11,35	2,7875	50,15	3,144201	0,17
39	9,13	11,34	2,7625	60,85	3,815047	0,17
43	8,43	10,53	2,625	71,9375	4,510188	0,2
55	9,59	11,77	2,725	104,975	6,581505	0,19
67	9,04	11,26	2,775	140,0625	8,781348	0,17
79	9,08	11,21	2,6625	173,1125	10,85345	0,2
99	8,43	10,66	2,7875	229,55	14,39185	0,2
119	9,12	11,5	2,975	286,175	17,94201	0,19
131	9,06	11,38	2,9	320,3125	20,08229	0,19
147	8,38	10,75	2,9625	366,9125	23,00392	0,18
187	8,36	10,67	2,8875	482,4	30,24451	0,18
219	8,88	11,29	3,0125	579,5375	36,33464	0,18
235	8,37	10,87	3,125	629,8	39,48589	0,17
247	8,4	10,89	3,1125	666,975	41,81661	0,19
249	8,34	10,81	3,0875	673,1	42,20063	0,19
253	8,35	10,8	3,0625	685,45	42,97492	0,18
259	8,91	11,3	2,9875	703,85	44,12853	0,17
263	8,47	9,6	1,4125	714,5	44,79624	0,2

A8 – AN values for C3

Glass number	Weight Before, g	Weight After, g	Liquid, ml	Total Liquid volume, ml	PV	AN
2	8,43	9,5	1,3375	2,5375	0,159091	0,19
6	9,03	9,96	1,1625	7,05	0,442006	0,21
10	9,59	10,55	1,2	11,8875	0,745298	0,25
14	9,14	10,18	1,3	17,0125	1,066614	0,21
18	8,37	9,51	1,425	22,225	1,393417	0,18
22	9,1	9,99	1,1125	27,4125	1,718652	0,26
26	9,64	10,58	1,175	32,05	2,009404	0,25
30	8,41	9,31	1,125	36,65	2,297806	0,25
34	8,46	10,64	2,725	47,3625	2,969436	0,2
42	8,51	10,82	2,8875	69,3125	4,345611	0,2
50	8,44	10,73	2,8625	91,1875	5,717085	0,2
56	8,39	10,6	2,7625	107,7375	6,754702	0,2
62	9,05	11,34	2,8625	126,1625	7,909875	0,2
74	9,02	11,29	2,8375	159,05	9,971787	0,19
86	8,43	10,62	2,7375	192,4125	12,06348	0,2

A9 – Values for SI test for B-15

Imbibition	Date	Time	Time Passed	Volume	% OOIP	Vekt av kjerne tørr	163,14	g
HS	tirsdag 4. april 2017	12:00	0	0	0	Vekt av kjerne med olje	176,01	g
HS		12:30	0,02083333	0	0			
HS		13:00	0,04166667	0	0	Gram olje i kjerne	12,87	g
HS		13:30	0,0625	0,1	0,624709			
HS		14:00	0,08333333	0,1	0,624709	OOIP	16,00746	ml
HS		14:30	0,10416667	0,1	0,624709			
HS		15:00	0,125	0,2	1,249417			
HS		15:30	0,14583333	0,2	1,249417			
HS		16:00	0,16666667	0,25	1,561772			
HS		16:30	0,1875	0,25	1,561772			
HS		17:00	0,20833333	0,3	1,874126			
HS		17:30	0,22916667	0,3	1,874126			
HS		18:00	0,25	0,3	1,874126			
HS		18:30	0,27083333	0,3	1,874126			
HS		19:00	0,29166667	0,3	1,874126			
HS		21:00	0,3125	0,35	2,18648			
HS		22:30	0,33333333	0,4	2,498834			
HS	05.apr	11:00	0,95833333	0,5	3,123543			
HS		17:00	1,25	0,55	3,435897			
HS	06.apr	11:00	1,95833333	0,6	3,748252			
HS		19:00	2,29166667	0,65	4,060606			
HS	07.apr	11:30	2,97916667	0,7	4,37296			
HS		19:30	3,3125	0,75	4,685315			
HS	09.apr	15:00	5,125	0,8	4,997669			
HS	10.apr	12:30	6,02083333	0,85	5,310023			
HS	11.apr	11:30	6,97916667	0,9	5,622378			
HS		19:30	7,3125	0,95	5,934732			
HS	12.apr	18:00	8,25	1	6,247086			
HS	13.apr	16:00	9,16666667	1,05	6,559441			
HS	14.apr	17:00	10,25	1,1	6,871795			
HS	15.apr	15:00	11,125	1,1	6,871795			
HS	17.apr	16:00	13,1666667	1,1	6,871795			
HS	18.apr	12:00	14	1,1	6,871795			
HS	19.apr	11:00	14,9583333	1,1	6,871795			
LS		11:15	14,96875	0	6,871795			
LS		12:00	15	0	6,871795			
LS		13:15	15,0520833	0	6,871795			
LS		13:30	15,0625	0,05	7,184149			

LS		14:00	15,0833333	0,05	7,184149			
LS		14:15	15,09375	0,1	7,496503			
LS		14:45	15,1145833	0,2	8,121212			
LS		15:45	15,15625	0,2	8,121212			
LS		17:00	15,2083333	0,25	8,433566			
LS		21:00	15,375	0,3	8,745921			
LS		23:00	15,4583333	0,35	9,058275			
LS	20.apr	10:00	15,9166667	0,6	10,62005			
LS		14:00	16,0833333	0,8	11,86946			
		16:00	16,1666667	0,9	12,49417			
	21.apr	11:00	16,9583333	1,1	13,74359			
	22.apr	14:00	18,0833333	1,3	14,99301			
	23.apr	16:00	19,1666667	1,35	15,30536			
	24.apr	10:00	19,9166667	1,4	15,61772			
		16:00	20,0833333	1,5	16,24242			
	25.apr	10:00	20,9166667	1,6	16,86713			
	27.apr	10:00	22,9166667	1,6	16,86713			
	28.apr	14:00	24	1,6	16,86713			
	01.mai	14:00	27	1,65	17,17949			

A10 – Values for SI test for C-3

Imbibition	Date	Time	Time Passed	Volume	% OOIP		Vekt av kjerne tørr	163,14	g
HS	12.mai	18:00	0	0	0		Vekt av kjerne med olje	176,01	g
HS		18:45	0,03125	0	0				
HS		19:45	0,072917	0,1	0,624709		Gram olje i kjerne	12,87	g
HS		21:00	0,125	0,3	1,874126				
HS		21:30	0,145833	0,3	1,874126		OOIP	16,01	ml
HS		22:00	0,166667	0,35	2,18648				
HS		22:30	0,1875	0,35	2,18648				
HS	13.mai	12:00	0,666667	0,4	2,498834				
HS		14:00	0,75	0,4	2,498834				
HS		18:00	1	0,4	2,498834				
HS	14.mai	15:00	1,875	0,4	2,498834				
HS		17:00	1,958333	0,4	2,498834				
HS		20:00	2,083333	0,4	2,498834				
HS		21:30	2,145833	0,4	2,498834				
HS	15.mai	12:00	2,666667	0,4	2,498834				
HS		21:00	3,125	0,4	2,498834				
HS		23:00	3,208333	0,4	2,498834				
HS	16.mai	11:00	3,625	0,4	2,498834				
HS		20:30	4,104167	0,4	2,498834				
HS	19.mai	11:00	6,625	0,4	2,498834				
HS	20.mai	11:00	7,625	0,4	2,498834				
HS	21.mai	11:00	8,625	0,4	2,498834				
HS	26.mai	15:00	13,875	0,4	2,498834				
LS		15:10	13,88194	0	2,498834				
LS		15:30	13,89583	0	2,498834				
LS		15:45	13,90625	0	2,498834				
LS		16:15	13,92708	0	2,498834				
LS		16:30	13,9375	0,05	2,811189				
LS		16:45	13,94792	0,05	2,811189				
LS		17:00	13,95833	0,05	2,811189				
LS		18:00	14	0,05	2,811189				
LS		19:00	14,04167	0,05	2,811189				
LS		20:00	14,08333	0,05	2,811189				
LS		21:00	14,125	0,075	2,967366				
LS		22:00	14,16667	0,1	3,123543				
LS	27.mai	12:00	14,66667	0,5	5,622378				
LS		15:00	14,875	0,55	5,934732				
LS	28.mai	12:00	15,66667	0,9	8,121212				

LS		21:00	16,125	1	8,745921			
LS	29.mai	15:00	16,875	1,2	9,995338			
LS	30.mai	15:00	17,875	1,3	10,62005			
LS	31.mai	11:00	18,625	1,3	10,62005			
LS	01.jun	11:00	19,625	1,35	10,9324			
LS	02.jun	15:00	20,875	1,4	11,24476			
LS	03.jun	15:00	21,875	1,4	11,24476			
LS	04.jun	13:00	22,70833	1,5	11,86946			

A11 - Values for the TAN and TBN

		B-15		C-3	
		TBN	TAN	TBN	TAN
		0,080553	0,02532	0,062931	0,056583
		0,222154	0,025337	0,137931	0,069757
		0,094503	0,025431	0,066301	0,073903
		0,04287	0,024165	0,056991	0,063726
		0,046723	0,028284	0,236305	0,071552
		0,13532	0,029712	0,114044	0,074142
		0,287259	0,028712	0,128601	0,0721
		0,184002	0,03012	0,403907	0,151117
		0,084793	0,033977	0,395972	0,275235
		0,500655	0,029447	0,383339	0,274295
		0,499369	0,029834	0,70768	0,207524
		0,079733	0,029141	0,692281	0,231034
		0,414719	0,031561	0,406654	0,402073
		0,500079	0,033467	0,540502	0,40788
		0,523845	0,418837	1,303307	
		0,188671	0,333753	1,096223	
		0,197536	0,342638	0,551469	
		0,203184		0,41953	
		0,103755		0,072962	
		0,192842		0,079365	
		0,293038		0,077429	
		0,48857		0,201881	
		0,51596		0,123527	
		0,535758			
		0,52329			
		0,186916			
		0,097645			
		0,107396			
		0,105012			
	Sum	7,436148	1,499736	8,25913	2,430921
	Tot Squ	9,330396	1,593998	9,803966	2,380878
	TBN	1,894248	0,094262	1,544835	-0,05004