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Universitetet i Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

Study program/specialization: Petroleum technology/ Reservoir engineering	Spring semester, 2018 Open
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Supervisors: Tine Puntervold and Skule Strand

Title of master's thesis:

Effect of crude oil adsorption and asphaltene precipitation on sandstone wettability

Credits: 30

Keywords: - Crude oil - Wettability - Asphaltene - Sandstone - Wettability alteration	Number of pages: 61 Stavanger, 15 June 2018

Acknowledgments

I would like to thank my supervisors for the opportunity to write this interesting thesis, and all the guidance and help that they offered to write it.

I would like to especially thank Tina Puntervold for her exceptional support, proof-reading and for sticking with me to the end, making this thesis possible.

Helena Gummedal.

Abstract

Wettability is an important property for oil recovery. It affects capillary pressure and controls fluids, location, and flow in the reservoir. By an increase in capillary pressure (due to increased water wetness), previously non-swept pores can be displaced and therefore residual oil saturation will be reduced which increase oil recovery. As such, the alteration of wettability can be used as an EOR method. The injection of Smart Water is one such method that for sandstone rock will be a form for low salinity flooding. For this method to work, the mineralogy of the sandstone is very important as it affects the wettability greatly. The negative rock surface of sandstone, mainly due to clay minerals and their cation exchange capacity, will lead to the adsorption of polar components in slightly acidic environment. Other important parameters that affect wettability are formation water (its composition, pH, and salinity), crude oil, temperature, pressure, COBR interactions, initial water saturation and core restoration.

Crude oil is a complex mixture of many different components, where those components that consist of nitrogen, sulfur or oxygen are associated with polarity. A general division is: oil (saturates and aromatics), resins and asphaltenes. Asphaltenes and resins are the heavier fraction consisting of polar components, where asphaltene is generally accepted to affect wettability the most. They can either be adsorbed onto the rock surface or precipitated from the crude oil. Asphaltene precipitation will change the wetting towards oil-wet conditions, which can be difficult to reverse. However, polar components of acidic and basic nature can also affect wettability by adsorption. Desorption of organic polar components from rock surfaces changes the wetting towards more water-wet conditions (increased by injection of Smart Water; low salinity water).

Asphaltenes have been shown by studies to be responsible for mixed-wet rock. Still, it is not necessary for asphaltenic content for this to occur. Smaller molecules, such as the weak base quinoline, are also capable of altering the wettability by adsorption and making a mixed-wet rock.

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1 Introduction

Global demand for oil and gas remains high. According to the International Energy Agency (IEA) oil is still the most used fuel in the world, where it constituted 31.7 % of the world total primary energy supply (TPES) in 2015. The world's current oil production is still growing, where the majority originates from developed fields. Crude oil is expected to supply 26 % of the world's energy until 2040 (IEA, 2018). Thus, as increasing amounts of oil reservoirs is depleted, there is a need for efficient as well as environmentally friendly EOR methods.

One such EOR method is waterflooding by Smart Water. This method alters the wettability from mixed wettability to more water wet conditions. At more water-wet conditions capillary forces increase the capillary pressure, and water can imbibe into unswept oil-containing smaller pores and increase the microscopic sweep efficiency. This will reduce residual oil saturation, which will then lead to increased oil recovery.

Wettability of the reservoir influences not only the capillary pressure, but also the location of oil and water in the pores and the relative permeabilities of oil and water during waterflooding. Thus, the wettability is important.

Around 60 % of all the petroleum reservoirs is of sandstone (Bjørlykke & Jahren, 2010). For sandstone the most important properties are porosity and permeability. Other important properties are pore geometry and wetting properties, where sandstone reservoirs are known for their wide range of wettability's and their complex mineralogy.

To understand how smart water can improve the wettability in sandstone reservoirs it is important to understand which factors influence the wettability, and especially which components or fractions in the crude oil that are most important. Crude oil is a complex mixture containing saturates, aromates, resins and asphaltenes. Of them, asphaltenes are often in focus, and generally accepted as the fraction responsible for altering the wettability. However, other polar components such as acids and bases will also affect wetting conditions. The question is then: is the wettability of a reservoir caused by adsorption of oil components or precipitation of asphaltenes?

1.1 Objectives

The objective of this literature study is to investigate how the wettability in sandstone rock is affected by crude oil. Asphaltene precipitation or precipitation from the asphaltenic crude oil fraction is believed to reduce the water wetness of the sandstone reservoirs. However, research has also shown that polar organic material, such as crude oil acids and bases, can adsorb to sandstone surfaces and reduce the water wetness.

Therefore, the effect of asphaltene precipitation and crude oil adsorption on sandstone will be discussed, and the question is if high asphaltenic crude oil content is necessary for creating a mixed wettability in sandstone reservoirs.

2 Theory

2.1 Oil recovery methods

Oil recovery methods has traditionally been divided in primary, secondary, and tertiary recovery. The division was based on how the recovery was done chronologically. However, this has not been the case for a while since the last stage is often used whenever in the recovery process. As such, the last stage is more commonly known as enhanced oil recovery (EOR). Figure 1 illustrates the different recovery methods, the usual recovery rate, and what techniques they each consists of.
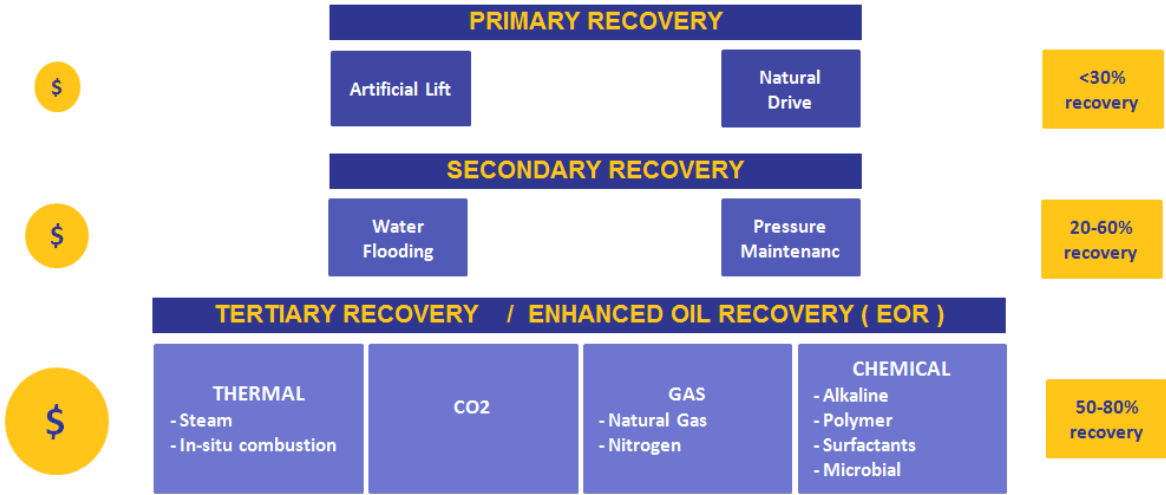
Figure 1: Illustration of the different oil recovery methods ("Enhanced Oil Recovery (EOR) Summary," 2015).

2.1.1 Primary recovery

Primary oil recovery is where natural energy present in the oil reservoir are used as the main source of energy. In other words, the reservoir is produced by merely reducing the pressure in the reservoir. These natural energy sources can come from artificial lift or natural drive, as well as other sources such as gas drive, fluid and rock expansion, and gravity damage (Green & Willhite, 1998).

During the recovery process the reservoir pressure is initially considerably higher than the bottomhole pressure inside the wellbore. This pressure difference drives the hydrocarbons towards the well and up to the surface. The reservoir pressure will however decline because of production and so will the differential pressure. An artificial lift can be used to reduce the bottomhole pressure or increase the differential pressure.

The primary recovery stage reaches its limit when the reservoir pressure is too low for it to be economical viable to continue, or when the production of gas and water in the production stream are too high. The recovery factor for primary recovery is usually lower than 30 %, which means that other methods should be used to further increase the recovery rate.

2.1.2 Secondary recovery

Secondary recovery is where an external fluid such as water or gas are injected into the reservoir to maintain reservoir pressure. Common techniques are waterflooding and gas injection.

The limit of the secondary stage is reached when the injected fluid is produced in considerable amounts from the production and production is no longer economical.

2.1.3 Enhanced oil recovery (EOR)

EOR processes are when there is an injection of a fluid of some kind in the reservoir. This can either be water, gas, polymer, or some other chemical. Traditionally these fluids are injected after a conventional waterflood where the remaining residual oil are targeted. But nowadays EOR processes are often used from day one to improve oil recovery. The earlier the EOR process are thought of, the more money there is to make.

When considering what EOR process one should use, there are several properties that should be considered: oil type, reservoir rock, formation type, oil's distribution, saturation, physical state resulting from past operations and injection rate.

The different EOR processes can be divided into categories depending on their uses:

- Mobility control
- Chemical
- Thermal

- Miscible
- Other methods

Mobility control is a generic term describing any process where there is made an attempt to alter the relative rates at which injected and displacing fluids move through a reservoir (Green & Willhite, 1998). This is done by injecting chemicals such as polymers.

Chemical flooding are processes where special chemical solutions is injected into the reservoir. Surfactant and alkaline flooding are both normal processes.

Thermal recovery is when heat is introduced into the reservoir. Processes such as steam and in-situ combustion are common.

Miscible recovery is when miscible gases, such as carbon dioxide, is used in the injection process.

There also exists *other methods* to increase the oil recovery. One such method is the injection of Smart Water. This is a relatively new EOR method that improves the oil recovery by wettability alteration.

With the use of EOR processes, the recovery rate can reach up to 80% of original oil-in place.

2.1.4 Waterflooding

Waterflooding have been used for over a century with the purpose of pressure support and oil displacement. Because of its success in many and varied reservoirs, it is a very commonly used oil recovery method.

Historical, waterflooding has been a popular method due to several reasons. They are: 1) the general availability for water, 2) that water can be injected with relative ease, 3) the ability with which water spreads through an oil-bearing formation and 4) water's efficiency in displacing oil (Craig, 1971).

Waterflooding has showed itself being very efficient in the Ekofisk field on the Norwegian Continental shelf, where the recovery rate is estimated to be more than 50 %. At first, the expected recovery rate was only 17 %.

Ordinary waterflooding, where there is only injection of formation water, has been looked upon as a secondary recovery method, and not an EOR method. Under this process the reservoir rock will not significantly change its wettability. There have been conducted several studies investigating the possibility of modifying the composition of the injected water (RezaeiDoust, 2011; Strand, 2005; Torrijos, 2017). The purpose is to alter the wettability, and that way increase oil production. One such method is the use of Smart Water.

There are several factors that influence the performance of waterflooding. One important factor is wettability which dictates capillary forces between oil and water and relative permeabilities of oil and water. As such, the use of modified water, like Smart Water, can be used to target oil that have been bypassed in ordinary reservoir waterflooding. In water wet media this oil is believed to remain as small discontinuous blobs that are held in their position in the pore space in the rock by capillary forces (Morrow, 1979). Thus, by altering the wettability (increasing capillary pressure) this oil can be accessed, and oil recovery increased.

The efficiency of waterflooding will depend on the reservoir wettability. It will be more efficient in water-wet reservoirs because more water needs to be injected in oil-wet reservoir to recover the same amount of oil (Anderson, 1987).

2.2 Displacement Forces

The overall displacement is divided in microscopic and macroscopic efficiency. This can be expressed by the equation:

$$E = E_D E_V$$ Equation 1

Where

E		Overall displacement efficiency
E_D		Microscopic sweep efficiency
E_V		Macroscopic sweep efficiency

E_D and E_V are given by fractions. As such, to obtain a high overall displacement efficiency it is best if E_D and E_V are close to one.

Important displacement forces are capillary, gravity and viscous forces which are defined later in this chapter.

2.2.1 Microscopic and macroscopic displacement

Microscopic efficiency details the displacement or mobilization of oil at pore scale, where the goal is to reduce the residual oil saturation. This is an objective that is important for many EOR-methods, and parameters such as wettability, viscosity of the fluids, interfacial tension and others decides the residual oil saturation.

The microscopic sweep efficiency, E_d, can be calculated from:

$$E_d = \frac{1 - S_{iw} - S_{or}}{S_{iw}}$$

Equation 2

Where

S_{iw} Initial water saturation

S_{or} Residual oil saturation

Macroscopic displacement efficiency is connected to the effectiveness of the displacing fluid(s) in contacting the reservoir in a volumetric sense (Green & Willhite, 1998). It depends on several properties such as the mobility ratio, well pattern, permeability, injection pattern and communication between layers.

Usually, an improvement in the viscosity is the best method to increase the macroscopic sweep efficiency. This means either the water viscosity is increased (polymer flooding) or oil viscosity is decreased (in-situ combustion and steam drive). In other words, the mobility ratio is decreased.

Mobility of a fluid is defined as its relative permeability divided by viscosity. The mobility ratio is the mobility of the displacing phase (in water/oil case, this will be water) divided by the mobility of the displaced phase (oil). It can be calculated from:

$$M = \frac{k_{rw} * \mu_o}{\mu_w * k_{ro}}$$

Equation 3

Where

k_{rw}	Relative permeability of the water
k_{ro}	Relative permeability of the oil
μ_w	Water viscosity
μ_o	Oil viscosity

A favorable mobility ratio is the case if it is lower than one. Consequences of a high mobility ratio is viscous fingering.

2.2.2 Capillary Forces

Capillary forces are the key factor for fluid flow in porous media. They can act against or in favor of the oil production depending on the type of system.

If the reservoir is fractured, the capillary forces is important for the displacement efficiency of the waterflood. However, if the reservoir is not fractured, which is the case for most sandstone reservoirs, strong capillary forces during waterflood can cause oil trapping and therefore high residual oil saturation.

Capillary pressure is the difference in pressure across a curved surface between two immiscible fluids and is formed due to the tension of the interface (Green and Willhite, 1998). It can be calculated from:

$$P_c = p_o - p_w = \frac{2\sigma_{ow}\cos\theta}{r}$$
Equation 4

Where:

P_c	Capillary pressure
p_o	Pressure of oil-phase at interface
p_w	Pressure of water-phase at interface
σ_{ow}	Interfacial tension between oil and water
θ	Contact angle
r	Pore radius

Capillary pressure across a curved surface can also be expressed by Young – Laplace equation:

$$P_c = \sigma_{ow}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

<div align="right">Equation 5</div>

Where

σ_{ow}	Interfacial tension between oil and water
R_1, R_2	Radii of curvature of interface

The values of R_1, and R_2 are related to the saturation to the wetting-phase fluid within a porous medium (Green & Willhite, 1998). This means that the capillary pressure depends on the saturation of the fluid that wets the system.

2.2.3 Gravity forces

Gravity forces are important for fluid flow, especially when there is a large difference in density between the displacing and displaced fluid. They will dominate when the relative influence of capillary forces is low.

When immiscible fluids occur together, a buoyancy force (given by equation 6) will act on the fluids. The lighter of these fluids will, due to the buoyancy force, segregate.

$$\Delta p = \Delta \rho g H$$

<div align="right">Equation 6</div>

Where

Δp	Pressure difference
$\Delta \rho$	Density difference
g	Gravity acceleration constant, 9.81 m/s^2
H	Height

2.2.4 Viscous forces

Viscous forces in a porous medium are reflected in the magnitude of pressure drop that occurs because of flow through the medium (Green and Willhite 1998). One of the simplest way to calculate it is by thinking of the porous media as a bundle of capillary tubes. The viscous force can then be calculated from Poiseuille's law given by:

$$\Delta P = \frac{8\mu L v_{avg}}{r^2 g_c} \qquad\qquad \text{Equation 7}$$

Where

ΔP	Pressure difference across capillary tube
μ	Viscosity
L	Length of capillary tube
v_{avg}	Average flow velocity in capillary tube
r	Radius of capillary tube
g_c	Conversion factor

2.3 Surface tension and Interfacial tension

In figure 2 a free liquid surface is illustrated, where A, B and C are molecules of the liquid. The molecules are affected by cohesive forces which make similar molecules stick together. This means that molecules far below the surface like A, attract equally in all direction due to the cohesive forces. Forces near or at the surface, like B and C, on the other hand, does not act equally since there are not similar molecules all around them. A net downward force tends to pull the molecules back to the liquid, which makes the surface act like a stretched membrane. This is known as the surface tension, and is defined as a measure of the force acting at a boundary between two phases (Speight, 2006).
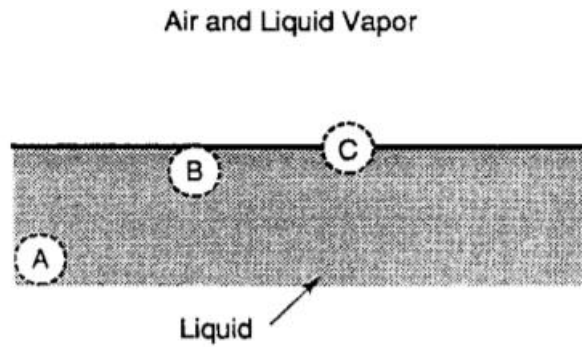
Air and Liquid Vapor

Figure 2: Free liquid surface indicating molecular position (Green & Willhite, 1998).

Surface tension is used in the specific case when we are dealing with the interface between a liquid and its vapor or air. When the surface is between two different liquids, or a liquid and a solid, the term interfacial tension (IFT) is used instead. Mixtures of hydrocarbons such as crude oil will have lower IFT's which depends on the complexity of liquids (Green & Willhite, 1998).

One way to measure the surface tension of a liquid is by using a capillary tube. Another method, simpler and often more practical, is the tensiometer method. This method measures the IFT between oil and water by pulling a platinum/ iridium ring through an interface and measuring the force of the ring at the breaking point. Dividing the force by circumference of the circle yields the surface tension.

In cases where the IFT is extremely low, other methods like spinning-drop and pendant drop must be used as means of measurement.

Low interfacial tensions between oil and water makes the phases more miscible, and it is somewhat easier to displace the oil by viscous forces. The problem is that low IFT also lowers the P_c as seen in equation 4 above. Thus, if the IFT is lowered, capillary forces are also lowered, which can affect the microscopic sweep efficiency by lowering imbibition of water into the smaller pores containing crude oil.

Only small changes in IFT are observed when switching to a Smart Water. On the other hand, large changes in IFT are expected during surfactant injection.

2.4 Wettability

Wettability is defined as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids" (Craig, 1971). The fluid more strongly attracted to the surface, is called the wetting phase.

A way to classify wettability is by dividing it in homogeneous and heterogeneous wetting. Homogeneous wettability is when the reservoir rock has a uniform wetting behavior through the reservoir. Further division of this wettability can be categorized in strongly water-wet, strongly oil-wet, and intermediate-wet (neutral wet). Intermediate wettability assumes that all portions of the rock surface have a slight but equal preference to being wetted by water or oil (Anderson, 1986a).

It was believed that homogeneous wettability was the only wetting property (where most reservoirs was assumed strongly water-wet) for a long time. The realization that rock wettability could be altered by adsorbable crude oil components led to the idea that heterogeneous forms of wettability existed. Heterogeneous wettability is then defined as when the wettability varies in the reservoir as a result of variation of the minerals in the rock. This is far more common than homogeneous wettability. It is divided in fractional and mixed wettability. Fractional wettability (also called heterogenous/spotted/dalmation wettability) is when certain areas of the rock are strongly oil-wet due to adsorption of crude oil and the rest of the rock is strongly water wet (Anderson, 1986a). Mixed wettability was introduced by Salathiel (1973) and is a special kind of fractional wettability in which the oil-wet surfaces form continuous paths through the larger pores. The smaller pores remain water-wet. A small but finite oil permeability will exist down to very low oil saturations, which allows the drainage of oil during a waterflood to continue until very low oil saturations are reached (Anderson, 1986a).

Figure 3 demonstrates what happens at the pore scale when water enters a pore in an oil-wet and water-wet sand. For a strongly oil-wet sand (3a) the oil will occupy the small pores and be in contact with most of the rock surface, while the water will be in the middle of the large pores. During waterflooding, the water will flow through the larger pore channels avoiding the smaller pores, while oil remain on the rock surface. For a strongly water-wet rock (3b) the oil will occupy the center of the larger pores, while the water fills the smallest pores and is in contact with most of the rock surface. During a waterflood, snap-off can occur and will leave behind oil trapped in the form of globules in the middle of the larger pores.
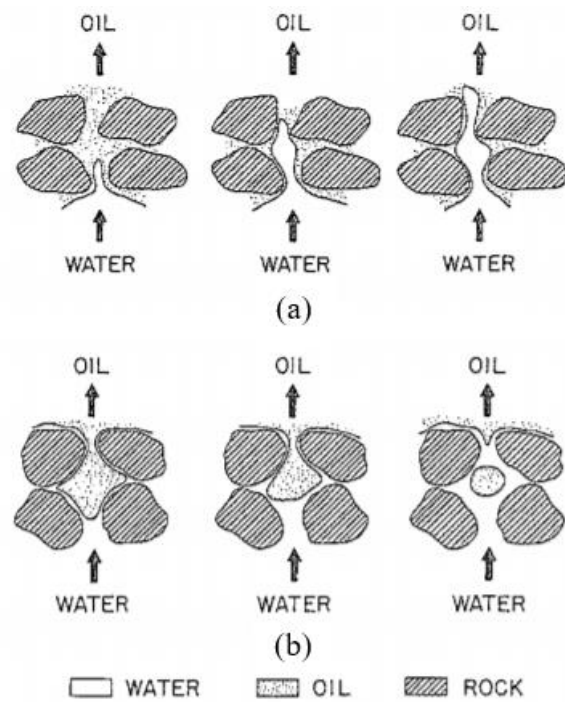
Figure 3: Displacement of oil by water for a) oil-wet sand and b) water-wet sand (Craig, 1971).

Wettability has been recognized as an important factor in remaining oil saturation and in capillary pressure and relative permeability curves. It has also been showed to affect waterflood behavior, dispersion of tracers, simulated tertiary recovery, electrical properties and irreducible water saturation (IWS) (Anderson, 1986a). The initial reservoir wettability is considered an important property since it determines most of these properties.

Wettability is also an important factor for controlling the location, flow, and distribution of fluids in a reservoir. There is evidence that weakly water-wet conditions are the most favorable for oil recovery by waterflooding (Yan et al., 1997). This correspond to the minimum residual oil saturation.

2.4.1 Wettability measurements

Understanding the relationship between wettability, capillary pressure and distribution of oil and water is necessary in the difficult problem of quantifying wettability and its relations

(Anderson, 1986b). Several different methods have been proposed to solve this. These measurements of wettability can be divided in quantitative and qualitative methods. Common quantitative methods are contact angles, imbibition and forced displacement (Amott), and USBM wettability method. Some qualitative methods are imbibition rates (including spontaneous imbibition), microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillary metric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance, and dye adsorption.

Generally, the three quantitative methods are used. The contact angle measures the wettability of a specific surface, while the Amott and USBM methods measure the average wettability of a core. The rest of the methods, being qualitative and having each their own criteria to work, are often imprecise and can lead to uncertainties when comparing experiments in literature (Anderson, 1986b). The two methods contact angle and spontaneous imbibition are described in more detail below.

Contact-angle

The use of contact angle as a wettability measurement is the primary approach to evaluate the wetting state of a rock. This is a popular method and is best suited when pure fluids are used. It is used on smooth surfaces which is necessary for an accurate result. For most rock surfaces though, this is not the case. They are either bulky or porous, and as such the method is often not practical.

In an idealized water-oil-solid system (which is static), demonstrated in figure 4, Young's equation can express the surface energies:

$$\sigma_{ow} \cos \theta = \sigma_{os} - \sigma_{ws} \qquad\qquad \text{Equation 8}$$

Where:

σ_{ow}	Interfacial tension between oil and water
θ	Contact angle
σ_{os}	Interfacial tension between oil and solid
σ_{ws}	Interfacial tension between water and solid

The term $\sigma_{os} - \sigma_{ws}$ is sometimes called the adhesion tension, σ_a. It is positive when the system is water wet, negative when it is oil wet, and near zero when it is neutrally wet.
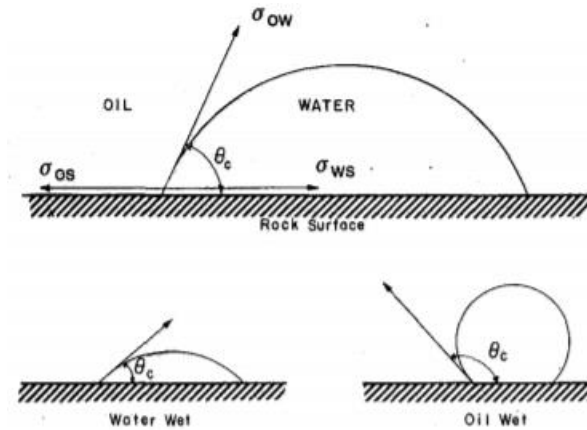

Figure 4: Wettability of oil/water/rock system (Anderson, 1986b).

To calculate the contact angle, equation 8 is used. It is measured on a crystal where quartz or mica is often used as the model surface for sandstone reservoirs. It is not possible to describe wettability of clays with this method. The contact angle can be measured both in a static system (figure 4) or in a dynamic system. In a dynamic system an applied force can bend the contact angle, making it a more realistic method.

There have been performed many kinds of measurements including tilting plate method, sessile drops or bubbles, vertical rod method, tensiometric method, cylinder method, and capillary rise method. Most of these methods are not generally used in the petroleum industry, however, because they are better suited for pure fluids with no adsorption or desorption of surfactants (Anderson, 1986b). The sessile drop (static system) and a modified form of the sessile drop method (dynamic system) are best suited in the petroleum industry, and therefore generally used.

Contact angles in literature are either water-advancing, θ_A, or water-receding, θ_R. The advancing angle is measured by pulling the brink of a drop over the surface, while the receding angle is measured by pushing it back. The difference between them, $\theta_A - \theta_R$, is known as the contact angle hysteresis.

Problems with this type of wettability measurement exist. Hysteresis is one since it is found experimentally that a liquid drop can have many different stable contact angles. On a smooth surface however, the contact angle is fixed. There appears that there are three causes for hysteresis: surface roughness, surface heterogeneity and surface immobility on a macromolecular scale. Another problem is that this method cannot consider the heterogeneity of the rock surface. This means that the method cannot account for when the surface isn't smooth and instead has for example holes in it where the liquid drop should have been measured. And last, no information is achieved about the presence/absence of permanently attached organic coatings on the reservoir rock (Anderson, 1986b).

A general classification of wettability expressed by contact angle is given in Table 1.

Table 1: Wettability for water-oil system expressed by contact angles.

Contact angle (°)	Wettability preference
0-30	Strongly water-wet
30-90	Preferential water-wet
90	Neutral wet
90-150	Preferential oil-wet
150-180	Strongly oil-wet

Spontaneous imbibition

Spontaneous imbibition is a practical method used to characterize the wettability of oil/brine/rock systems (Ma et al., 1999). It is based on the tendency of a rock to imbibe the wetting phase spontaneously.

This method is performed by measuring spontaneous imbibition rate, which depends on the magnitude of the imbibition capillary pressure. As such, this is a suitable method since the driving force for spontaneous imbibition rates is proportional to the imbibition capillary pressure (Morrow, 1990).

For this method, the rock will be immersed in brine and the recovery of oil vs. time is recorded. The results of this method are commonly presented as fractional recovery of oil initially in place vs. either time or log time (Morrow & Mason, 2001).

By measurement of imbibition rates, information on dynamic IFT and wetting circumstance may be provided which can be important in the reservoir but are not reflected by other methods, such as Amott or USBM wettability tests.

The imbibition method is the most widely used (quantitative method) because it is fast, no complicated equipment is required, and gives an idea of the average wettability of the core.

Spontaneous imbibition can also be used to evaluate wettability alteration. When production has reached the plateau by water imbibition, the imbibing brine can be exchanged to e.g. a Smart Water. Then, if a production of oil again is observed, wettability alteration has taken place. The Smart Water is able to imbibe and expel oil due to increased capillary forces and improved microscopic sweep efficiency.

Improved interpretation of spontaneous imbibition behavior for COBR systems is likely to provide an important advance in wettability characterization. This will depend on improved methods of scaling and comparison of results from one system to another (Morrow, 1990).

2.5 Sandstone (mineralogy)

Sandstone is defined as a sedimentary rock with grains between 63 µm to 2 mm. They are part of the clastic sedimentary rocks, and make up 20-25 % of all sedimentary rocks (Boggs Jr & Krumbein, 1996). They consist mainly of silica grains (1/16 to 2 mm) and are therefore often called siliciclastic rocks. These grains make up the framework fraction. Sandstone also consist of various amount of cement or very fine sized (<0.03 mm) material called matrix.

There are a large variety of minerals that can occur in sandstone. The most common minerals are quartz, feldspar, and mica. Other minerals that occur in smaller doses are heavy minerals, around 1 %, such as zircon, tourmaline, apatite, and garnet. It also consists of clay minerals occupying pore spaces created by sand grains where they form coatings.

There have been proposed over fifty different ways of classification for sandstone. Classification is mostly based on framework mineralogy, but the relative abundance of matrix plays role in some classifications (Boggs Jr & Krumbein, 1996).

Sedimentary rocks are formed through several processes such as erosion, weathering, and sedimentation of sediments. Through the sedimentation process, a compression will occur due to higher pressure and temperature in addition to recrystallization that in the end will lead to a

solid rock. Either a layered structure, like slate, or homogeneous structure, like sandstone, will be formed.

2.5.1 Quartz

Quartz is the most common and dominant mineral in sandstones where it on average makes up to 50-60 % of the framework fraction. It is derived from igneous or metamorphic rocks and is the simplest of the silicate minerals consisting of silicon and oxygen, given by the chemical formula SiO_2. Quartz is also a very stable mineral. It is resistant to chemical breakdown at the Earth's surface, and its grains remain intact over long distances and long periods of transport due a hardness of 7 on Mohs' scale of hardness (Nichols, 2009).

The surface of quartz is normally regarded as water-wet with a negative charge at normal reservoir pH (between values of 5-9) (Anderson, 1986a). The charge intensity is dependent on the ion composition in water/ brines.

2.5.2 Clays

Clay minerals refers to diverse groups of minerals that are members of the hydrous aluminous phyllosilicates. They mainly consist of aluminum and silicates, but may also contain other cations, including alkali, alkaline earth, and transition metals. They are constructed by octahedral and tetrahedra layers in a sheet like structure, sharing oxygen ions between Si or Al ions of the adjacent tetrahedra or octahedra (Worden & Morad, 2003).

There exist over 26 different types of clay minerals differentiated by the ratio of silica layer to octahedral layer, where the largest group is the 2:1 layer. The five major clay mineral groups are: kaolinite, illite, chlorite, smectite (montmorillonite) and mixed-layer varieties. Figure 5 illustrates their structure.

Kaolinite is a two-layered clay mineral. It is also a low swelling clay because the charges within the structure are balanced and there are very strong hydrogen bindings between successive layers of basic building units, so no swelling occurs (IDF, 1982). It tends to convert to illite or chlorite at great depth (age).

Montmorillonite is the most common mineral in the smectite clay group. It is three-layered and a swelling (expandable) clay, meaning it can adsorb water within their structure. The charge imbalance is mostly in the aluminum layer which is why it is characterized as a swelling clay.
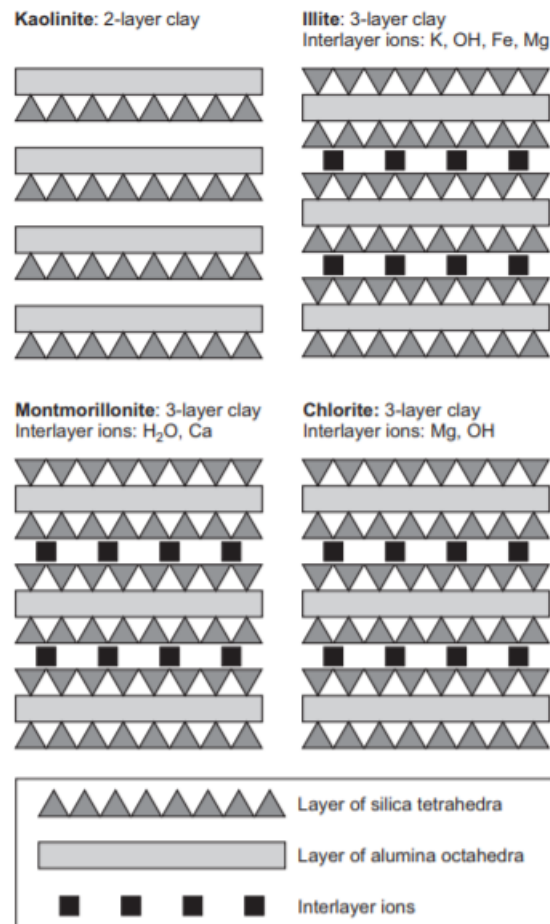

**Figure 5**: Structure of some of the more common clay minerals (Nichols, 2009).

Illite is related to the mica group and is the most common clay mineral in sediments. The charge imbalance is in the silicate sheets, which creates negatively charged surface. Like montmorillonite, illite is also a three-layered clay. It is also a low swelling clay.

Chlorite is a three-layered clay mineral. The bonding between the layers are strong, and similar to kaolinite since they do not adsorb water molecules in the interlayer spaces. Thus, chlorite is also a low swelling clay.

A main characteristic of clay minerals are the permanent negative charges on the clay surface. Clays therefore act as cation exchangers where the clay adsorbs cation to regain its charged balance.

The cation exchange capacity (CEC) is the capacity of a cation exchange for the clay mineral. This capacity will increase with surface area, which will often be dominated by clay minerals due to their large surface area.

It has been shown that different ions have different attractive forces, or affinity, towards the clay minerals. The relative replacing power of cations is expressed as:

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Cu^{2+} < H^+$$
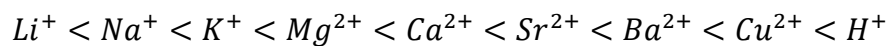
If the concentration of the replacing cation is increased, then the exchanging power of that ion is also increased. This means that it is possible for ions with lower relative replacing power to replace ions of higher relative replacing power if the concentration is high enough. As H^+ has the highest affinity, it also means that it is possible for H^+ to react towards the clay surface even at low concentrations.

Table 2 shows some of the characteristics of the most common clay minerals that are found in sandstone.

Table 2: Properties of the most common clays (IDF, 1982).

Property	Kaolinite	Illite	Montmorillonite	Chlorite
Structure	1:1	2:1	2:1	2:1:1
Particle size [micron]	5-0.5	Large sheets to 0.5	2-0.1	5-0.1
CEC [meq/100g]	3-15	10-40	80-150	10 -40
Surface area BET [m²/g]	15-25	50-110	30-80	140

2.5.3 Feldspar

Feldspar minerals make up about 10-20 percent of the framework grains of average sandstones (Boggs Jr & Krumbein, 1996). The base components are silicon and oxygen, and like quartz, feldspar is also a silicate mineral. Potassium, sodium, and calcium are also present which are the elements that determines how the feldspars are divided. They are divided into two broad groups: alkali feldspars and plagioclase feldspars.

Alkali feldspars are a family where potassium rich feldspar is most common. Because of this, they are often called potassium feldspar or k-feldspar for short. This type of feldspar, such as orthoclase, are most common as grains in sedimentary rocks.

Plagioclase feldspars are a family of minerals that have varying proportions of sodium and calcium. The sodium rich are called albite and the calcium rich anorthite.

Feldspar are chemically less stable than quartz and are more susceptible to chemical destruction during weathering and diagenesis. Of plagioclase and k-feldspar, k-feldspars can resist decomposition better, and the prevalence is therefore higher (Crundwell, 2015) .

Feldspars seems to have reversible cation exchange activity, especially Na^+ can be exchanged with H^+ ions. This means feldspar can influence the pH of formation water and affect initial wetting conditions, which will depend on the salinity and composition of the brine it is exposed to (Strand et al., 2014).

If the salinity in the formation water is low, equation 9 can illustrate what can happen.

$$NaAlSi_3O_8 + H_2O \rightarrow Na^+ + HAlSi_3O_8 + OH^- \qquad \text{Equation 9}$$
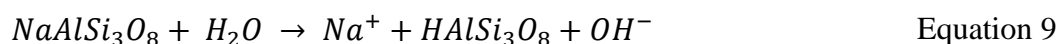
The Na^+ ion is exchanged with the H^+ ion, and it causes the formation water to become more basic. This will lead to a more water-wet initial wetting, because the crude oil components will be in their least reactive state toward the negatively charged sandstone surface; negatively charged carboxylated and neutrally charged nitrogen-bases. If the formation water instead has high salinity the reservoir will be less water-wet (due to lower initial pH – eq. 9 is moved to the left). But when the low salinity Smart Water is injected, the equation is moved towards right, pH increases, and the wettability is altered toward more water-wet; increasing oil recovery. The stability of feldspars is temperature dependent. However, in the pH range from 5 to 9 (normal

reservoir pH) the variation of dissolution rates is not very high. This is the case in a wide range of temperatures that can go from 3 °C to 300 °C (Gruber et al., 2016).

Chemical weathering of feldspar result in the formation of clay minerals such as kaolinite.

2.6 Wettability Alteration by smart water in sandstones

Adsorption of polar compounds and/or deposition of organic matter from the crude oil onto sandstone reservoir rock can change its wettability. This is one way to alter the wettability of the reservoir toward less water-wet.

The term Smart Water is used as a characterization of the injection brines that can change wetting properties of the rock toward more water-wet and increase oil recovery. This is another way to alter the reservoir wettability. For sandstone reservoirs this will be a form for low salinity injection.

In sandstone, experimental work (Tang & Morrow, 1999; Tang & Morrow, 1997) has confirmed that low salinity flooding can enhance the oil recovery. Tang and Morrow (1997) showed that oil recovery was increased by use of spontaneous imbibition.

The popularity of this technology is mainly because of its efficiency in displacing crude oil, low investment, easy operation, ease of injection, and environmental protection, all of which bring economic benefits compared to other chemical EOR methods (Doryani et al., 2018).

Even though it is generally accepted that wettability alteration is what causes the low salinity effects, several mechanisms for the low salinity effect have been proposed. Some of them are:

- Migration of fines (Tang & Morrow, 1999).
- Multi-ion exchange (MIE) (Lager et al., 2008).
- Extension of electrical double layer (Ligthelm et al., 2009).
- Desorption by local pH increase (Austad et al., 2010) – Smart Water injection.

The last mechanism, Smart Water injection, will be described in further detail.

Before the injection of Smart Water should be considered in sandstone reservoirs, there are some conditions that needs to be fulfilled which are based on experimental facts (Tang & Morrow, 1999):

- *Porous medium*: clay must be present.
- *Crude oil*: polar components (acids/ or bases) must be present.
- *Formation water*: must contain active ions toward the clay (Ca^{2+} and H^+ are the most important ones).

By injection of Smart Water, the capillary pressure will increase. This means that the water imbibition of the smaller pores, where oil is trapped, gets better, thus improving the sweep efficiency. This is illustrated in figure 6.
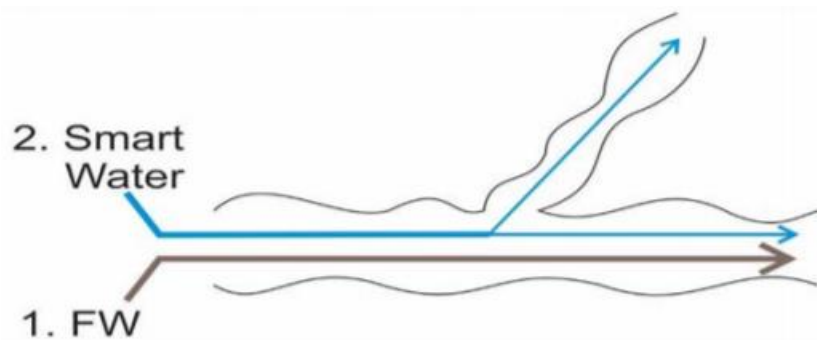

Figure 6: Illustration of how injection of smart water leads to increased sweep efficiency.

The use of Smart Water is a relatively new EOR-method that uses wettability alteration by modifying the ion composition of the injected water. This is both an effective and environmentally friendly method, where no expensive chemicals are added (like surfactants and polymers).

There are several ways for the wettability alteration in Smart Water mechanism to happen. For the most part, it is said to be due to the adsorption of crude oil components onto the rock surface. This means that the crude oil composition is important for the wettability alteration.

This mechanism will depend strongly on the mineralogy of formation and can prove difficult in sandstone due to the complexity of its mineralogy. Other important factors for Smart Water injection is the reversibility of the adsorption process and pH dependence.

Water-wetness can be increased in a sandstone reservoir if:

- The concentration of Ca^{2+} in formation water is increased.
- Increased pH in brine.
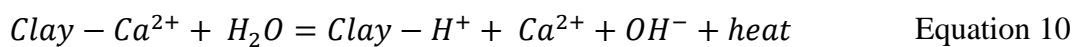- Reservoir temperature is increased.

The established initial wetting properties of an oil reservoir are related to the present COBR-system. In most cases it will not be optimum for oil recovery, and this can be improved with Smart Water injection. The initial wetting is therefore strongly linked to smart water EOR potential. Sandstone reservoirs are known to cover many ranges of values for wettability, from strongly water-wet to strongly oil-wet. This means that initial wetting should be considered thoroughly.

The actual Smart Water mechanism will depend on the initial wetting as well as the initial pH. Most often, the initial pH will lie between 5-6 due to the sour gases that crude oil contains.
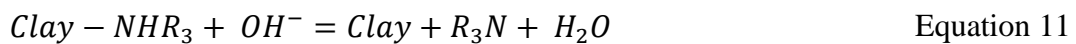
So, when low salinity water is injected into the reservoir, containing much lower ion concentration, the existing chemical equilibrium associated with the formation water will be disturbed. To reestablish equilibrium, desorption of cations (Ca^{2+}) from the surface occur. Due to the lower content of ions in the injected water, there is an absence of active cations to balance out the negative charges on the clay surface. H^+ ions from the water close to the rock surface will then be adsorbed onto the clay (Ca^{2+} substituted with H^+, but also Na^+). This leads to a local increase of pH close to the clay surface. The adsorbed molecules undergo ordinary acid-base proton transfer reactions. This is illustrated in figure 7.

This can also be demonstrated chemically by the reactions listed below:

Desorption of cations by LS water (slow):

$$Clay - Ca^{2+} + H_2O = Clay - H^+ + Ca^{2+} + OH^- + heat \qquad \text{Equation 10}$$

Wettability alteration (fast): Basic material

$$Clay - NHR_3 + OH^- = Clay + R_3N + H_2O \qquad \text{Equation 11}$$

Acidic material (fast)

$$Clay - RCOOH + OH^- = Clay + RCOO^- + H_2O \qquad \text{Equation 12}$$

The best condition when using Smart Water is when the wettability is neutral to slight water-wet. This is because it is necessary to be able to alter the wettability to more water-wet. If the rock is already completely water-wet, there is little potential for EOR effects by Smart Water or low salinity water, any method that relies on altering the wettability to something more water-wet.
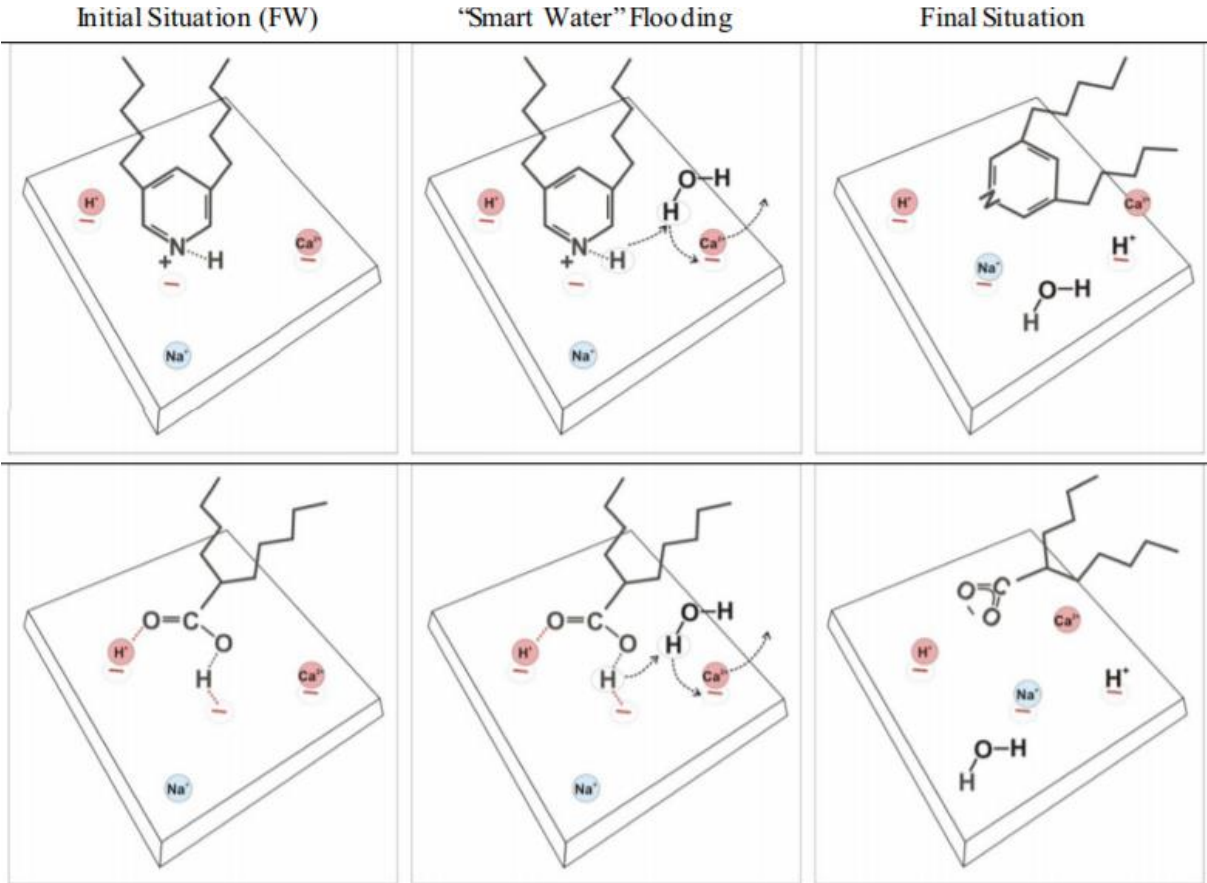

Figure 7: Acidic and basic material adsorbed onto negatively charged clay is removed in alkaline environment caused by desorption of Ca^{2+} from clay surface (Strand et al., 2016).

By use of Smart Water, or low salinity (LS) flooding, there have been observed a decent increase in oil recovery compared to high salinity (HS) flooding. This is demonstrated in figure 8. It should be noted that it isn't the decrease in salinity that makes the clay more water-wet, but rather the increase in pH that follows.
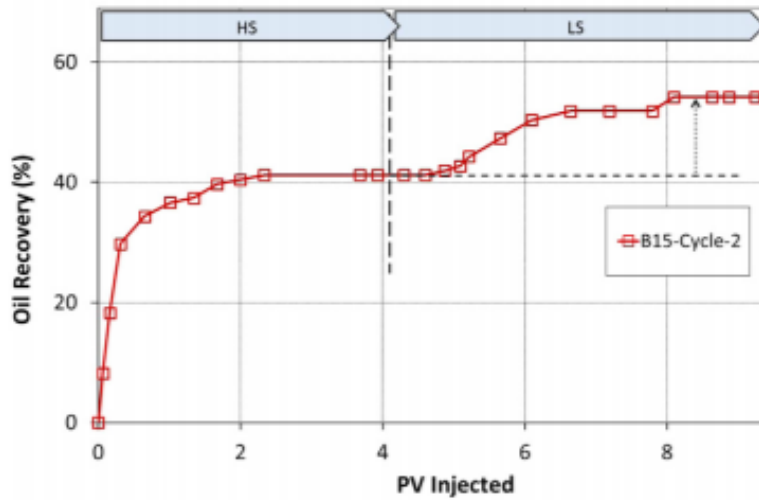
Figure 8: Difference in oil recovery between HS (100 000 ppm) and LS (750 ppm) flooding (Austad et al., 2010).

2.7 Crude oil

Crude oil is a mixture of many different components where both the chemical structure and molecular weight varies. The elemental composition of crude oil from heavier asphaltenic to lighter crude oils will also vary over narrow limits which is illustrated in table 3. The composition varies upon its source but can be classified in three major fractions: oil, asphaltene and resins. Oils are mixtures of saturated hydrocarbons (alkanes and cycloalkanes) and aromatics of moderate molecular weight. The structure of these hydrocarbons is illustrated in figure 9 and 10. Asphaltenes refer to the heavy fraction of the crude oil mixture. Resins can be defined as the fraction of the deasphalted oil which is strongly adsorbed in surface-active materials (da Silva et al., 2013).

Table 3: Elemental composition of crude oil (Speight, 2006).

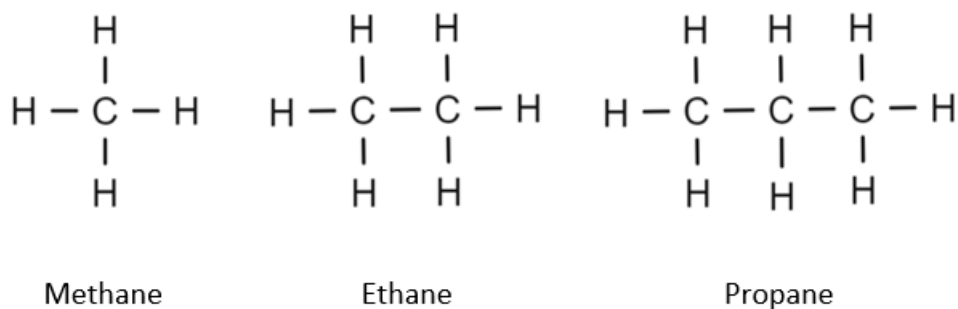| Element	% by weight
Carbon, C	83.0 – 87.0
Hydrogen, H	10.0 – 14.0
Nitrogen, N	0.1 – 2.0
Sulfur, S	0.05 – 6.0
Oxygen, O	0.05 – 1.5

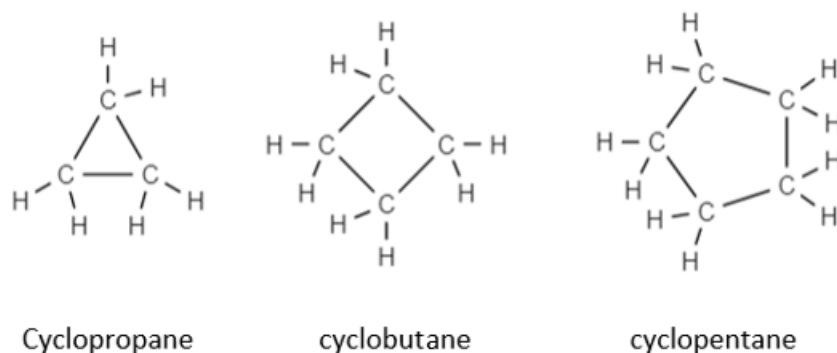**Figure 9**: Chemical structures of different types of alkanes.

Figure 10: Chemical structures of different types of cycloalkanes.

Since the structures vary, the different components of the crude oil boil at different temperatures and can be separated into a variety of generic fractions by distillation. Most of the more aromatic species and the heteroatoms occur in the higher boiling fractions.

Crude oil also contains inorganic gases such as CO_2, H_2S and N_2. The two first gases are acidic gases which causes the formation water's pH to decrease; lowering the initial pH of the reservoir.

Small amounts (<1000 ppm) of metals can be found in crude oil. They are present as oil-soluble compounds and are almost certain to have been present in plant and animal source materials. Normal metal constituents include nickel (Ni), iron (Fe) and vanadium (V).

Crude oil consists of several polar components. They exist in asphaltenes and resins, and the polarity is associated with the inclusion of the elements nitrogen, sulfur, and oxygen.

There exist several ways for quantifications of polar components. For the most part potentiometric titration is used where either TAN (for acidic components) or TBN (for basic components) are used.

Since the crude oil composition is important, there have been proposed several ways to describe it. One such method is SARA which divide the crude oil into its saturated, aromatic, resin and asphaltene fraction. This method analyzes the polarity of the different groups. The saturates are non-polar, either linear /branched hydrocarbons or cyclic saturated hydrocarbons, while the aromatics consists of one or more aromatic rings which are slightly more polarizable. The last fractions, asphaltenes and resins, have polar substitutes. Since results from this method is highly dependent on methodology, results of different methods may not be comparable and should be done with caution (Fan et al., 2002).

The density and specific gravity of crude oil are two properties that are used for preliminary determination of the character and quality of crude oil. Even though the chemical composition of crude oil can influence specific gravity, the quantitative correlation will be difficult to determine. Still, generally increased amounts of aromatic compounds will result in increased density, while an increase in saturated compounds results in a decrease in density (Speight, 2006).

The stability of crude oil can be described simply by a system where asphaltenes, aromatics (including resins), and saturates are in a delicately balanced harmony. Various factors, such as oxidation, can affect the system in an unfavorable way, leading to instability or incompatibility as a result of changing the polarity, and bonding arrangements, of the species in crude oil (Andersen & Speight, 2001).

2.7.1 Polar components

Crude oil consists of several different polar components. They occur in organic components that belong to the NSO–components (nitrogen, sulfur, and oxygen) and in asphaltenes and resins as huge molecules with low chemical reactivity.

The organic components are for the most part either bases or acids. Most oxygen compounds found in crude oil are weakly acidic such as carboxylic acids, cresylic acids, phenol and naphthenic. Nitrogen compounds are on the other hand mostly bases such as quinoline and pyridine.

Carboxylic acids can at acidic pH be represented by RCOOH (illustrated in figure 11) and the nitrogen – containing bases by R_3NH^+ (non-protonated quinoline illustrated in figure 12).
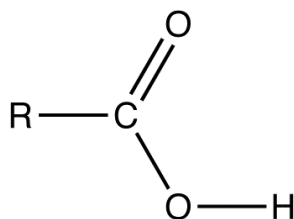

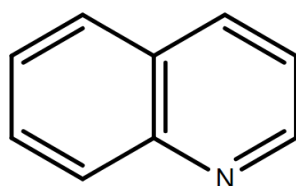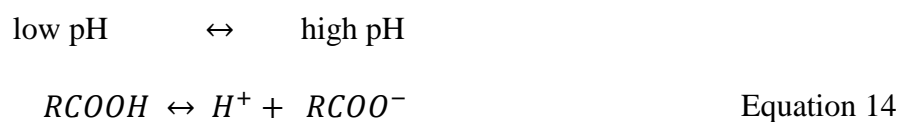**Figure 11**: Chemical structure of carboxylic acids.

Figure 12: Chemical structure of quinoline.

For the acids and bases, pH will decide the charge they will have. The two reactions below can express this.

low pH　　　　↔　　　high pH

$$R_3NH^+ \leftrightarrow H^+ + R_3N \qquad\qquad \text{Equation 13}$$

Where a neutrally charged base, R_3N:, is present in excess at alkaline pH.

low pH　　　　↔　　　high pH

$$RCOOH \leftrightarrow H^+ + RCOO^- \qquad\qquad \text{Equation 14}$$

If the pH is low, both equations 13 and 14 will be moved to the left. If the pH is high, both equations 13 and 14 will be moved to the right. Components that are acidic and basic in nature are important for wettability alteration. Acidic behavior includes proton donation, making the compound negatively charged, while basic behavior means accepting a proton and becoming positively charged.

The resin fraction is a collection of those constituents that are soluble in n-pentane or n-heptane, whichever hydrocarbon is used for the separation of asphaltene constituents, but insoluble in liquid propane (Speight, 2006). Like asphaltenes, resins are also said to be responsible for wettability alteration.

Compared to asphaltenes, resins have lower molecular weight that usually don't vary. Still, they generally consist of more polar components. The data available on the resin structure (there has not been done as much research as with asphaltenes) indicate that their molecules are smaller than asphaltenes. It has also been theorized that asphaltenes and resins are small fragments of kerogen, and therefore have some kind relationship to it.

The constituents of the resin fraction have an important role in crude oil. They are responsible for the stability of the system and maintain the asphaltenes and other constituents as a single phase. (Andersen & Speight, 2001).

Polar components are also found in crude oil that have lower asphaltic content. They have then lower molecular weight and higher chemical reactivity. They are also partly soluble in water and the solubility depends on pH.

Asphaltenes, being in most cases the group responsible for most of the polar components, will be described in greater detail next.

2.7.2 Asphaltenes

Asphaltenes is a complex fraction (0-50 %) of crude oil, which appears as a dark brown to black friable solid. The amount of asphaltene depends on several factors such as the source of the crude, burial depth, API gravity of the crude, and the sulfur content (Speight, 2006). Most often though, it amounts to the heaviest part of the crude oil. However, the amount of asphaltenes can vary from negligible amounts in volatile oils to tens of weight percent in bitumen and heavy crude oils. It is defined as a solubility class rather than chemical (classic definition based on its solubility in a specific solvent), i.e. being soluble in aromatic solvents such as toluene whereas insoluble in light normal alkanes like n-pentane or n-heptane (Speight, 2006). As such, there exist a wide range of chemical formulas. There is no definite melting point either.

The main features of their behavior include their readiness to precipitate, tendency to aggregate, instability, surface activity, and low reactivity (Ramirez-Corredores, 2017).

There is limited information of the structure of asphaltene due to the complexity of its molecules and are therefore difficult determination. Still, asphaltene can be said to generally consists of aromatic nuclei that contains alkyl and alicyclic (naphthenic) systems, and hetero elements (nitrogen, oxygen, and sulfur) that are scattered in different locations (Speight, 1991). A general structure can be seen in figure 13. It is believed that hetero elements coexisting with metals in asphaltene makes these molecules the most charged component in crude oil (Al-Safran, 2018).
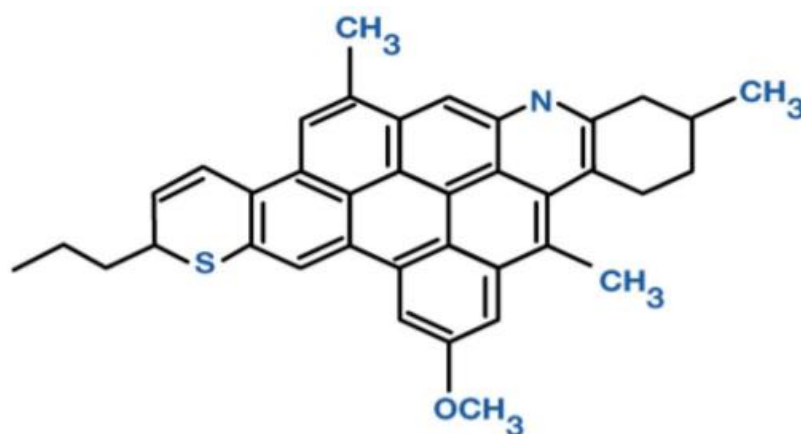

Figure 13: General structure model of asphaltene (Al-Qasim & Bubshait, 2017).

Determination of accurate molecular weight of asphaltene is also a challenge. The low solubility of asphaltene used in solvents in molecular weight measurement, and the presence of adsorbed resin in asphaltene are the two main challenges to determine asphaltene molecular weight (Speight, 2006). The reported molecular weight of asphaltene varies within 1000–2,000,000, which depends on the method of determination as well as measurement conditions. Therefore, a careful precipitation of the asphaltene to extract all resin and the right choice of the measurement method are key factors for reliable molecular weight determination (Speight, 1991).

A comparison of elemental composition of asphaltene from many sources shows that the hydrogen to carbon ratio (H/C) varies over 1.15 ± 0.5 %wt. This unvaried H/C ratio is the main reasoning behind the general belief that unaltered asphaltene constituents from crude oil have a definite composition. On the other hand, notable variations are seen for the hetero-elements oxygen and sulfur. Oxygen content are seen to vary from 0.3 to 4.9 %wt., and sulfur from 0.3 to 10.3 %wt. Nitrogen content though, varies somewhat less, from 0.6 to 3.3 %wt. at extremes.

From this comparison, the change in composition of asphaltene appears to be due to variation of hetero-elements content and not hydrocarbons molecules (Speight, 2006).

Due to their high effect on crude oil, the determination of the properties and composition of asphaltenes are important. Properties such as phase behavior, viscosity and interface are also strongly influenced by asphaltene components (Solaimany-Nazar & Zonnouri, 2011). The stability of crude oil, and therefore asphaltenes, is important. Asphaltene stability depends on properties of itself and properties of the rest of the fractions of crude oil. Inhibitors can stabilize the asphaltenes. They act like resins, who also are said to be able to stabilize asphaltenes.

Asphaltenes can affect wettability alteration either by precipitation or adsorption on the rock surface. Asphaltene precipitation is assumed reversible in most cases and are known to cause many problems. Adsorption on the other hand, reacts differently and may be controlled and reversed. Still, it is important that the adsorbed asphaltene doesn't cover the entire rock surface so that the injected formation water still can reach the rock surface.

A good part of the asphaltenes are aromatics (around 50 %) which is one of the points that differentiate them from resins (resins amount is lower). Asphaltene constituents in crude oil is also said to depend to a degree on the source of the crude oil.

Asphaltene has also a wide range of densities which is related to the size of the molecules. It is also generally understood that asphaltene content increase with decrease in API gravity (Speight, 2006), which is illustrated in figure 14.
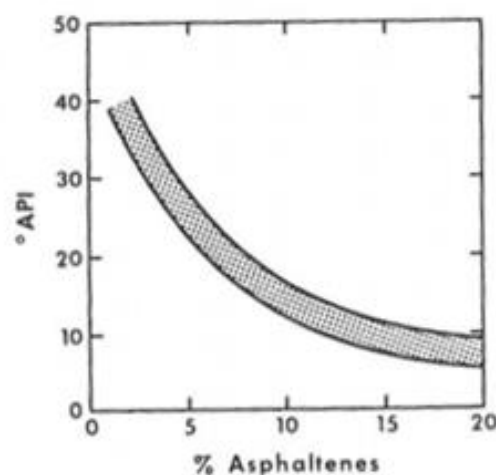

Figure 14: Relationship of the asphaltene content of a crude oil to API gravity (Speight, 1991).

3 What affects wettability in sandstone reservoirs

Wettability occurs due to interactions between oil, rock, formation water composition or water saturation, temperature and more; where the factors influencing wettability are mostly bound to the mineralogy of the rock, brine composition and crude oil. Wetting properties are also linked to the distribution of fluids in the porous network. The way each of the factors change can considerably affect the wettability. The most important factors that affect wettability will be discussed in further detail below.

3.1 Mineralogy

Sandstone consist of many and varied types of minerals and its mineralogy is considered complex as well as important for wettability. This is because it determines the adsorption of polar components of crude oil onto the rock surface.

The surface of sandstone is generally negatively charged at normal reservoir pH conditions. As such, monovalent and divalent cations will interact with the rock surface and the fluids in reservoir. This will disturb the charges stability.

The negative charged surface is mostly because of clay minerals. Due to their fine size, large surface area and chemical reactivity of the surface, clay minerals are most strongly adsorbed by polar components from the crude oil. Adsorption of basic and acidic material onto the clay is sensitive to the pH, and it can change drastic when below 5. Clays are normally not uniformly distributed in an oil reservoir either, and therefore, certain areas can be less water-wet than others.

The type of clay mineral and their amount will also affect wettability considerably. Formations with high clay content are often sensitive to water and tend to undergo hydration and dispersion when in contact with water. Studies have shown that a decrease in the salinity of brines below the critical salt concentration (CSC) causes expansion or mobilization of clays (IDF, 1982).

Another mineral, plagioclase, of sandstone may also affect the wettability. Depending on the formation water's salinity, plagioclase can change the pH and the wettability will then change accordingly (when the salinity is low, the pH increase, and the reservoir will be more water-wet).

Anhydrite, CaSO4 (s), may be present in high temperature reservoirs with high formation salinity. In a flooding with low salinity Smart Water, anhydrite can dissolve and increase the concentration of Ca^{2+} (Strand et al., 2016). This can affect the ion exchange at the clay minerals and prevent the low salinity EOR effects.

Significant variation in wettability may be related to variation in pore-surface roughness and mineralogic composition (Crocker & Marchin, 1988).

3.2 Formation water

The composition of formation water is of great importance for wettability and can vary greatly. The most dominating factors are chemical composition, salinity, and the pH. The effect of each of these factors will constantly depend on the interactions created in crude oil-rock-brine system.

There is a large variety in chemical composition in the formation water. The most common ions are alkali and alkali earth metals: Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, which can react to the anion in the system which depend on the relative concentration of cations. The most common anions are Cl^-.

The pH of formation water can be affected in several ways. For example, the presence of feldspar (plagioclase) can make the formation water more basic in cases where the salinity is low. Acidic condition can also be observed in cases where acidic gases such as CO_2 and H_2S exist. pH of formation water has also a great impact on initial wetting properties because it dictates the reactivity of surface active organic components toward mineral surfaces, especially clay (Burgos et al., 2002).

The salinity in the formation water can vary considerably. It can be as low as 10 000 ppm and reach peaks as high as 300 000. The higher salinity, the more ions there are that can react to other components that exist in the formation water.

Salinity and pH will also be important in determining wettability because they strongly affect surface charge on rock surface and fluid interfaces which again will affect the adsorption of polar components.

3.3 Crude oil

Crude oil is one of the most complex mixtures of organic compounds. As such, its composition is hard to determine. Still, it greatly influences the wettability and therefore important to establish. The crude oil composition is also known to vary considerably.

Crude oil contains, as mentioned earlier, sour gases. These gases will lower the initial pH, and therefore affect the initial wetting situation.

There are two distinct ways crude oil can be said to alter the wettability (Buckley et al., 1998):

- Polar components present in the crude oil.
- The oil itself is the solvent environment that influences the partitioning of the surface-active components between bulk oil and oil/water or oil/water/solid interfaces.
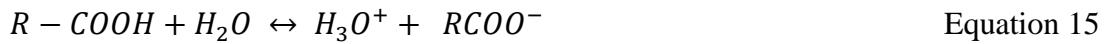
Crude oil contains several polar components. These are in asphaltenes and resins, and as acids and basic organic components. They affect the wettability by adsorption on the negatively charged clay surface.

Both acidic and basic organic components can be quantified by acid number (AN) and base number (BN). The unit of measurement is mg KOH/g. For AN = X, this means that X mg KOH is needed to neutralize the acidic components present in 1 g of oil, and for the BN = X the equivalent amount of basic material is needed instead (Strand et al., 2016). BN will typically be much higher than AN.

API gravity is a way to measure the solvent quality of the crude oil. This is often a useful measure for asphaltene precipitation. Together with AN and BN, it can be used to characterize the crude oil.

Acidic material is represented by -COOH which is mostly part of large molecules of the heavy fraction, and most of the basic material contains nitrogen as part of aromatic molecules, R_3N:.

Due to excess concentration at oil-water interface, the acidic and basic components will undergo fast proton reactions as pH changes, which is describe by the two equations below:

$$R - COOH + H_2O \leftrightarrow H_3O^+ + RCOO^- \qquad\qquad \text{Equation 15}$$

$$R_3N: + H_2O \leftrightarrow OH^- + R_3NH^+ \qquad\qquad \text{Equation 16}$$

Which will both adsorb onto negatively charged clay minerals at low pH, and that can desorb from the surface at high pH.

Asphaltenes will according to several researches have the greatest effect on wettability of the crude oil fraction (Buckley et al., 1996). They can either be adsorbed on the rock surface or precipitated from crude oil.

3.4 Temperature and Pressure

Properties such as temperature and pressure will also influence the wettability. They will both effect the solubility of polar active components in crude oil when they increase, where the solubility will be increasing too.

The temperature will also depend on pH, which can influence the initial wetting properties. When the temperature increase, the rate of chemical reactions increase, which means the chemical equilibrium is established faster at higher temperatures (Strand et al., 2016). It also has a high influence on reactivity and partition of individual components between the different phases and interfaces. These factors mean that chemical reactions can be temperature dependent, like chemical reactions involving Ca^{2+} and Mg^{2+}, which often depend on temperature. Adsorption of Ca^{2+} onto clay surface is also observed to increase as temperature increase.

Pressure is also shown to affect wettability in other ways. Morrow et al. (1998) showed that COBR interactions where sensitive to pressure, where the change in wettability with removal of light ends or addition of alkanes suggested that reservoir wettability would change with reservoir pressure. If asphaltene precipitation occur during production as the reservoir pressure is depleted, this will also influence the wettability (Al-Maamari & Buckley, 2003).

3.5 Crude oil/brine/rock interactions

Buckley and Liu (1998) identified four different mechanisms/adsorption types in which crude oil components can alter the wettability. They are polar interactions, surface precipitation, acid/base interactions, and ion binding between charged sites and higher valency ions. Figure 15 demonstrate these interactions.
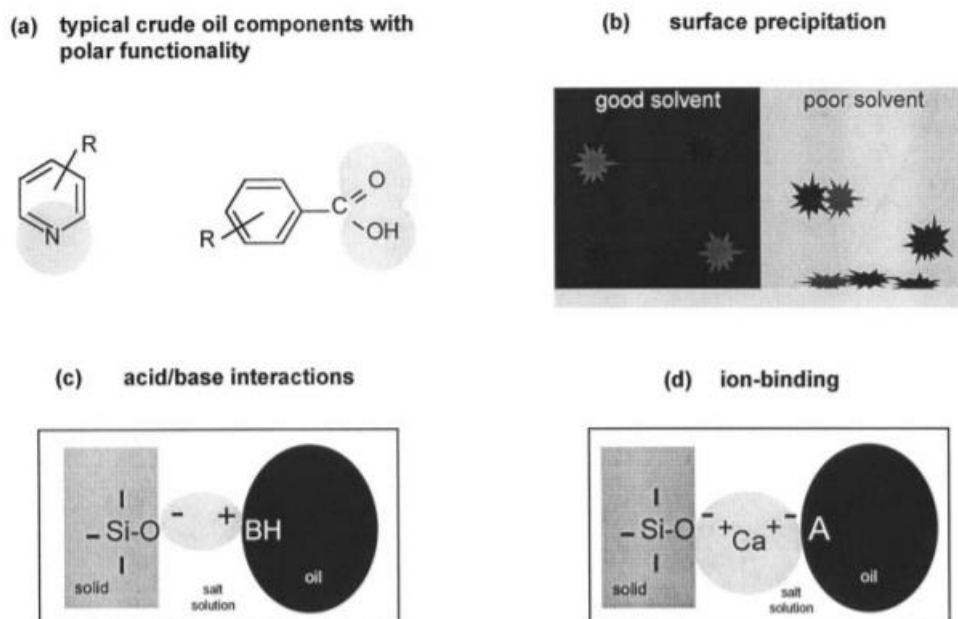

Figure 15: The mechanisms of interactions between crude oil components and solid surfaces (Buckley et al., 1998).

It is likely that more than one mechanism contributes to the crude/brine/rock interactions at the same time. Still, it is possible to see differences in wetting alteration that can identify the different interactions by comparing acids and bases and varying solvent quality.

These interactions can also be divided in three categories when the adsorption is onto high-energy surfaces, which are illustrated in table 4, where the polar interactions can be acid/ base interactions. Adsorption from crude oils onto high-energy surfaces often results in surfaces that exhibit contact angle hysteresis (Xie et al., 2002).

Table 4: Mechanisms of interaction by which crude oil components can adsorb on silicate surfaces (Liu & Buckley, 1999).

Interaction category:	Occur between:	Resulting wettability:
polar	oil and dry surfaces	low to intermediate contact angles
ionic	oil and surfaces prewetted with aqueous solutions	depends on stability of water film and specific interactions
surface precipitation	colloidal asphaltenes and surfaces	oil-wet

3.5.1 Polar interactions

There have been observed adsorption of asphaltenes directly on mineral surface where the interactions that alter the surface wetting occur between polar functional groups and polar sites. Monolayer adsorption is another type, where the thickness of monolayer depends on the solvent from which it is adsorbed. Acid and bases adsorption processes is a complex polar interaction.

Polar interactions will predominate in the absence of a water film between oil and solid. The strongest interactions will then be between polar heteroatoms (N, S, O) and polar surface sites.

Two of the of functional groups that are likely involved in polar interactions are illustrated in figure 15a.

3.5.2 Surface precipitation

Surface precipitation occurs when oil is a poor solvent for its asphaltenes. If this is the case, there is a tendency for wetting alteration to be enhanced. Some indicators of poor solvent quality are low refractive index or high API gravity (low density) (Buckley et al., 1998).

3.5.3 Acid/base interactions

Acid/ base interactions controls charge at oil/water and solid/water interfaces, which becomes charged in the presence of oil and water. Since polar functional groups belong to both the

mineral and crude oil phases, they can behave as acids (giving up a proton and becoming negatively charged) and bases (gaining a proton and a positive charge) (Cuiec, 1975). There are two major ways that surface charge impacts interactions between crude oil, brine, and solid surfaces.

1. *Net charge affects water film stability*. Surface charge and thus water film stability is influenced by pH, most significantly under conditions where the brine phase salinity is low and composed of monovalent ions.
2. *Ionized acidic and/ or basic sites influence adsorption*. Collapse of water film leads to the possibility where crude oil components at the oil/brine interface adsorb on the solid surface.

There is considerable diversity between crude oils in the extent to which they alter wetting by acid/ base interactions.

3.5.4 Ion binding

Ion binding is an alternative mechanism for wetting alteration where ions of the same sign as the solid surface can contribute. Cations, such as Ca^{2+}, can mask the purely acid/ base interaction. There are several of these interactions that are possible:

oil–Ca–oil   mineral–Ca–mineral   oil–Ca–mineral.
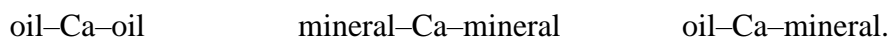
The first two interactions can limit the wettability alteration while the last one promotes it. This means that pH is not a major determining factor in adhesion experiments, as well as adhesion not being a good indicator for interactions with longer exposure time. Oil with a high acid number and a low base number is dependent on ion binding in the wettability alteration process and recovery is sensitive to the concentration of divalent ions (Buckley et al., 1998).

3.6 Initial water saturation

When water films are present in the reservoir, they can protect the rock surface from interaction from polar components from the crude oil (Anderson, 1986a). The degree of this protection depends on both the amount of water (the thickness of the water film) and the concentration of the intruding components. In experiments the initial water saturation is shown to be sensitive

to wettability, where an increase in initial water saturation will lead to more water-wet conditions (Jadhunandan & Morrow, 1995; Zhou et al., 2000).

3.7 Core restoration

Another important factor that affect the wettability is core restoration, or how the core is handled in the lab. Depending on which methods are used, the wettability can be affected considerably; promoting uncertainties and changes to the wettability. A basic problem is knowing whether the nature and distribution of surface properties and fluid phases as they occur in the reservoir are maintained in the core (Anderson, 1986a).

The wettability of a core must be the same as of that in an undisturbed reservoir rock for an accurate prediction of the behavior of the reservoir with core analysis. A serious problem occurs because many aspects of core handling can drastically affect wettability and therefore rendering the core completely different (Anderson, 1986a).

Cores in three different states of preservation are used in core analysis: native state, cleaned, and restored state. The best results for multiphase-type flow analyses are obtained with native-state cores, where alterations to the wettability of the undisturbed reservoir rock are minimized (Anderson, 1986a). On the other hand, cleaned cores are better suited when wettability is not important or cases of strongly water-wet reservoirs.

The process behind core handling can in most cases be summed up to three different stages: core cleaning, core saturation and aging of the core.

In most cases the core will be cleaned to water-wet condition. This is the most difficult stage, since the solvent chosen can significantly change the rock wetting (Shariatpanahi et al., 2012). This makes it not only difficult, but near impossible to clean the core 100 %. There will always be something left, like oil components that weren't possible to remove. While the core is wetted, there will also occur reactions between the rock minerals and the formation water that may also influence the wettability.

The wettability of the core can be controlled in three ways: 1) Organochlorosilanes, which is used for sandstone (treatment of a clean, dry core with various chemicals), 2) Artificial Cores and 3) Surface-Active Agents. The first method is used for a uniform wetted core, where

inconsistency in wetting condition with time was discovered (Jadhunandan & Morrow, 1995). The two other methods are better suited when the wettability is more varied.

The wettability alteration depends on the crude oil/brine/rock (COBR) systems (Jadhunandan & Morrow, 1995). Through the preparation and use of the core, there will be several factors that affect it, like the aging time and aging temperature:

- *Aging time*: wettability will depend on how long the core is aged (which in some cases can take significant time), where an increase in aging time can decrease the imbibition, resulting in a reduction of the water-wetness (Morrow et al., 1998; Zhou et al., 2000).

- *Aging temperature (T_A)*: measurements of rate and extent of spontaneous imbibition showed that aging temperature, had a dominant effect on wetting behavior (Morrow, 1990). Change in wettability toward less water-wet conditions were obtained with an increase in T_A and a decrease in the water content established before aging (Jadhunandan & Morrow, 1995).

4 Influence of crude oil on wettability

The polar components in crude oil is of great importance for the alteration of wettability. Which of these components are important, or has the greatest effect on the alteration, can be difficult to identify. However, asphaltenes is considered to be of great importance, either if it is precipitated or adsorbed on the rock surface. Polar components, like acids and bases, can also affect the wettability by adsorption on the rock surface.

4.1 Wettability by asphaltene precipitation

Precipitation can be defined as an insoluble solid formed by a reaction in a solution (Brown, 2009). Asphaltene precipitation can then be defined as the separation of the asphaltene molecules from the oil phase, and the forming of a new phase. N-pentane or n-heptane is often used to achieve this in experiments as asphaltene are insoluble in them.

Asphaltene precipitation can cause a lot of problems which can be prevented by keeping the asphaltene stable. Other ways to prevent asphaltene precipitation has also been proposed, including varied models, methods, and simulations with the goal of reducing asphaltene precipitation.

There are several factors that can influence asphaltene precipitation. The main factors are change in pressure, temperature, and crude oil composition. The ratio of polar/non-polar components as well as the ratio of light/heavy molecules are significant factors which should also be taken into consideration when evaluating asphaltene precipitation and deposition (Ali Mansoori, 1997).

Pressure: High density molecules precipitate at onset pressure and those of lower density at lower pressures. Onset pressure is the pressure at which the oil fraction reaches a threshold limit that initiates the asphaltene flocculation (when precipitated asphaltene particles aggregate and form bigger particles) or precipitation. Maximum asphaltene precipitation is expected at bubble point pressure (as can be seen from figure 16).
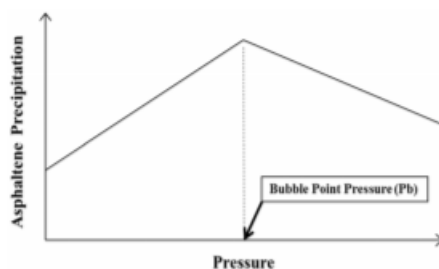
Figure 16: Amount of asphaltene precipitation as a function of pressure depletion (Al-Qasim & Bubshait, 2017).

Temperature: There appear to be no clear trend of temperature effects on asphaltene precipitation in literature due to variations in crude oil composition. There have been suggested several theories, some of which contradict each other. It has been suggested that the higher the temperature is, the higher the solubility of resins are and the less soluble asphaltenes are in the crude oil (Takhar et al., 1995).

Crude oil composition: is very complex, and variations can lead to precipitation of asphaltenes. Introducing n-alkanes into the system will have an effect since it upsets resin concentration equilibrium which promotes asphaltene flocculation and deposition (Takhar et al., 1995).

Asphaltene is one of the most important factors in crude oil stability, and the stability of asphaltene is important to avoid precipitation. A proper understanding of the condition of asphaltene instability in different oil reservoirs can result in avoiding precipitation and deposition problems. To assure the stability, a stabilizer (an amphiphile) can be injected into the reservoir to control asphaltene precipitation. They will act like resins peptizing (or coating) asphaltenes and keeping them in the solution. Its effectiveness is controlled mostly by its chemical and structural characteristics, but also depends on its solvent or dispersion medium (Al-Qasim & AlDawsari, 2017).

Resins are also known to stabilize the asphaltenes. It depends on the resins molecular self-interaction intensity and there have been seen a correlation between the resin adsorption behavior and asphaltene stability/instability phenomena in crude oil (Pereira et al., 2007).

Under normal conditions asphaltenes are held in suspension in crude oil by resins since resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions, which will prevent asphaltene from precipitating. Changes in the crude oil composition or pressure and

temperature can alter their association with the resins. The resins will then be unable to prevent the asphaltene species from aggregation into unstable clusters and asphaltene precipitate from the crude oil (Andersen & Speight, 2001).

Several methods can be used to measure where asphaltene precipitation starts. Rogel et al. (2001) used a titration method where n-heptane was added to crude oil. According to the results, the stability behavior of the asphaltenes was influenced strongly by their structural characteristics. However, it was also found that stabilization by means of a commercial inhibitor was affected by the composition of the crude oil (Rogel et al., 2001). Other methods include the use of either refractive index or API gravity.

Asphaltene precipitation is most often reversible, which is well-agreed upon in literature (Porte et al., 2003). Note however that redissolution may sometimes be very slow, and among the heavy organic depositions, asphaltene precipitation is considered an irreversible process (Ali Mansoori, 1997).

Asphaltene precipitation occur mainly due to two factors. Either high asphaltene content or high difference between reservoir pressure and oil bubble-point pressure, which can be the case even if asphaltene content is low (Al-Safran, 2018).

Wettability alteration can occur due to asphaltene precipitation, where they are thought to coat the pore surface (Buckley, 1995). The amount of water is a factor that will affect the role asphaltene precipitation will have on wettability. When there is absence of water, the mineral surfaces are expected to change to oil-wet conditions. On the other hand, when water is present, the situation will be more complicated. Depending on if the water film is stable or unstable (established in different ranges of pH and ionic composition), the effect will be different. If it is stable, the water films can maintain water-wet conditions, even in systems dominated by surface precipitation. If the water film is unstable, wettability alteration makes a "jump" close to onset of precipitation (relationship between the volumes of precipitant and solvent present in mixtures that show the first evidence of precipitation has been reported) to fairly oil-wet conditions (Al-Maamari & Buckley, 2003). This is illustrated in figure 17. Surface precipitation will then be the primary interaction that takes place.

Asphaltenes that has been flocculated could only be poorly adsorbed, which in some cases could be removed in the rising step was also concluded by Al-Maamari and Buckley (2003).
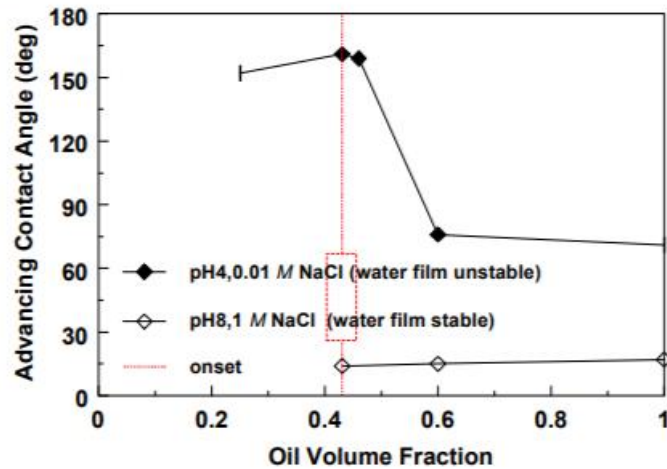
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Figure 17: Mica samples, where high-pH brine has stable water films and remain water-wet and low pH brine have unstable water films which breaks, allowing wettability alteration that are strongest near onset of precipitation (Al-Maamari & Buckley, 2000).

There has also been observed that there can be an effect on wetting even before asphaltene precipitation is detected in the crude oil. Surfaces will namely become increasingly oil-wet as the oil approaches the point of precipitation. (Buckley et al., 1998).

Complex functions of pressure, temperature, and crude oil composition will decide if and where either wetting alteration or bulk precipitation happen (Al-Maamari & Buckley, 2003). Asphaltene precipitation has also been found to increase with salinity (Doryani et al., 2018), as well as make the surface rougher (Sayyad Amin et al., 2010). Amount of asphaltene precipitation will be influenced by the lighter cosolubilizing components in the crude oil which can also be concluded from a detailed discussion on the influence of solvent type on asphaltene precipitation for a western Canadian bitumen by Speight (1991). These factors can affect how asphaltene precipitation affect wettability.

4.2 Wettability by adsorption of polar organic components

It is probable that the organic compounds in crude oils that are most likely to be adsorbed on reservoir rock are components which contain elements such as nitrogen, sulphur and oxygen atoms in addition to carbon and hydrogen. These can appear as part of the heavy fraction of crude oil, asphaltenes and resins, or as smaller molecules of basic and acidic nature. Adsorption of crude oil components can also be seen as fairly restricted since the adsorbing species exist almost exclusively at the oil/ brine surface, not in either the oil or water phase (Buckley et al., 1998).

The adsorption of asphaltene has been investigated a good deal. It is shown to be reduced in the presence of connate water, and that it is affected by salinity (Doryani et al., 2018). Asphaltene adsorption is also influenced their tendency to aggregate, where the extent varies with solvent quality. As the asphaltenes approach phase separation, their tendency to partition to either oil/water or oil/solid interfaces can be expected to increase (Buckley, 2001).

Comparing adsorption with or without water has shown that the water film reduce or protects against asphaltene adsorption since it prevents contact of asphaltene with the rock (Anderson, 1986a; Kaminsky & Radke, 1997). The more water there are, the less asphaltene will be adsorbed. If the water film is thick and stable, the surface will remain water-wet where nonadhesion is observed, and low contact angles are measured (Yu & Buckley, 1997). Contact angle experiments have shown the that acid–base interactions between the crude oil–water and silicate–water interfaces has a deciding factor for the stabilization of water films, and if oil adhesion occur (Lebedeva & Fogden, 2011).

Alteration of wettability by adsorption from crude oil was investigated for 10 crude oils by Xie et al. (2002). Unstable wetting was observed for 6 of the 10 crude oils. Oil with large base numbers (BN) and low acid number (AN) interacted the most with negatively charged quartz, where stable wetting was related to adsorption of positively charge oil species. For high AN, unstable wetting conditions was observed, and for high BN stable wetting conditions was observed. With advancing angles that were 40–70° higher than the corresponding receding angles, the wetting condition can have significant meaning for oil recovery processes (Xie et al., 2002).

Skauge et al. (1999) investigated the correlation between AN and BN, crude oil composition and wettability for twelve North Sea crude oils. It was discovered that acid/base interactions, can affect the crude oil/brine/solid interactions in two significant ways: The net charge will affect the stability of a water film, and ionized acidic or basic sites will influence the adsorption behavior. These discoveries can better explain the role that acidic and basic polar components has on the wettability. The role of the base quinoline and carboxylic acids has been investigated in greater detail and is discussed next.

Burgos et al. (2002) investigated the adsorption of quinoline onto the clay minerals kaolinite and montmorillonite. Quinoline is a weak base (pK_a= 4.92) that will protonate to cationic form under acidic conditions. There are two sorption (electrostatic interactions) mechanism that have been observed in these circumstances. At low pH values, it was observed that quinolinium cation (OH^+) was sorbed primarily via ion exchange. When the pH values were high, neutral quinolinium species sorbed less, but strongly, via hydrophobic interactions.

The adsorption of quinoline onto kaolinite and montmorillonite as a function of pH in $CaCl_2$ is illustrated in figure 18. From this, the adsorption is always higher at low concentration of Ca^{2+}; at any given pH. The adsorption will also decrease as the pH increases for both high and low concentration of Ca^{2+}. At their respective pH max adsorption, the sorption capacity is 100 times greater with montmorillonite compared to kaolinite on a mass basis (Burgos et al., 2002).

Pyridinic-type functional group, which is also a weak base, is also believed to be a polar component involved in polar interaction between crude oil and mineral surfaces (Buckley et al., 1998).

Adsorption of carboxylic acids (benzoic acid) onto the clay mineral kaolinite has been investigated by Madsen and Lind (1998). As with basic material, the adsorption process was sensitive to pH, and decrease in pH lead to increased adsorption. This is illustrated in table 5, where the adsorption of benzoic acid onto kaolinite increases significantly when the pH decreases from 8.1 to 5.3.

From these two studies, it appears that the adsorption behavior for both basic and acidic material in crude oil have similar adsorption properties toward clay minerals regarding pH variations.
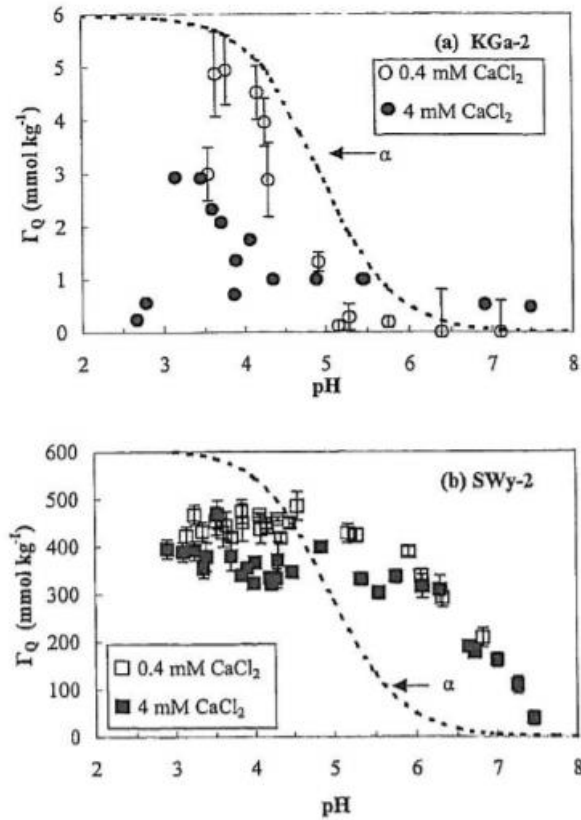
Figure 18: Quinoline adsorption onto (a) kaolinite and (b) montmorillonite as function of pH in 0.4 and 4 mM CaCl$_2$ solutions. The dotted line is the fraction of protonated quinoline (Burgos et al., 2002).

Table 5: Adsorption of benzoic acid onto kaolinite using 0.1 NaCl solution (Madsen & Lind, 1998).

$pH_{initial}$	Γ_{max}, μmole/m^2
5.3	3.7
6.0	1.2
8.1	0.1

The effect of organic acids on wettability has also been investigated by Mwangi et al. (2018) in a very new study. Both long-chained and short-chained (acetic acid) organic acids was investigated, where long-chained acid increased oil wetting by dilution while acetic acid increased the water-wetting. These trends showed some temperature sensitivity with greater wettability shift at higher temperatures.

4.3 Is asphaltenic content a requirement for mixed-wet rock?

Most studies and research conclude that asphaltenes are important for wettability alteration to occur. This can either be in the form as precipitation or as adsorption onto the rock surface from crude oil. However, is asphaltenes really a requirement for a mixed-wet rock?

The effect of asphaltene on wettability has been seen in several cases and can often contribute as both ionic interactions (adsorption) and surface precipitation (asphaltene precipitation) on the mineral surface. Here, ionic interactions will dominate in oil mixtures in which asphaltenes are in stable dispersion. Near the onset of asphaltene flocculation, a sharp transition to surface precipitation can occur, which produces more oil-wet conditions (Al-Maamari & Buckley, 2003).

Several other conducted experiments has also confirmed the affect asphaltenic content has on wettability. Buckley (1995) observed that adsorption of asphaltene from toluene solution onto the surfaces of evacuated sandstone made cores weakly water-wet. Sharma and Wunderlich (1987) also reported that asphaltene precipitation in a dry, oil-filled Berea sandstone core flooded with n-pentane resulted in mixed-wet core.

Buckley (1995) conducted experiments on several crude oils. She showed that crude oil could alter wettability both with or without asphaltene precipitation. The wettability alteration happened mostly after contact with the crude oil where components adsorbed from the oil phase made the cores less water-wet, even oil wet. It was also confirmed that wetting alteration occurred primarily during crude oil/brine/solid contact and that subsequent precipitation had at most a secondary effect on wetting and displacement mechanisms (Buckley, 1995). As such, asphaltene precipitation doesn't appear to be necessary for alteration of wettability. However, asphaltene adsorption onto rock surfaces is still a factor.

González and Moreira (1991) compared dry surfaces exposed to solutions of asphaltenes and resins and found that the asphaltene-treated surfaces experienced greater change in wetting. However, comparisons of glass surfaces treated either with crude oils or with their asphaltenes in toluene solution (brine effects were considered) showed that significantly more oil-wet conditions could be produced by the whole oil than by the asphaltene fraction alone (Buckley

et al., 1997). Thus, asphaltene doesn't seem to contribute as much to wettability as assumed, and other components in crude oil can also affect the wettability considerably.

There seems to be a correlation between wettability and pH changes. This has been confirmed by Buckley and Morrow (1990) where adhesion test was performed on several crude oils. For the majority of the crude oils, pH was the dominant variable in deciding the extent of adhesive behavior. If pH changes, charges of the polar components can change and give rise to wettability alteration. This was again confirmed during a later experiments, where the adhesion and adsorption tests suggested that more water-wet conditions should be expected in siliceous porous media saturated with solutions of higher pH (pH=8) and less water-wet for those saturated with lower pH solutions (pH=4) (Buckley et al., 1996).

RezaeiDoust et al. (2011) also added to this where the adsorption of quinoline onto kaolinite as a function of salinity and pH was investigated. It was shown that regarding pH changes, between 5 and 8, that adsorption was completely reversible at both high and low salinity. This is seen in figure 19. This shows that the reversibility in the adsorption/desorption of organic material onto clay minerals is mostly related to proton exchange reactions, i.e. pH changes.
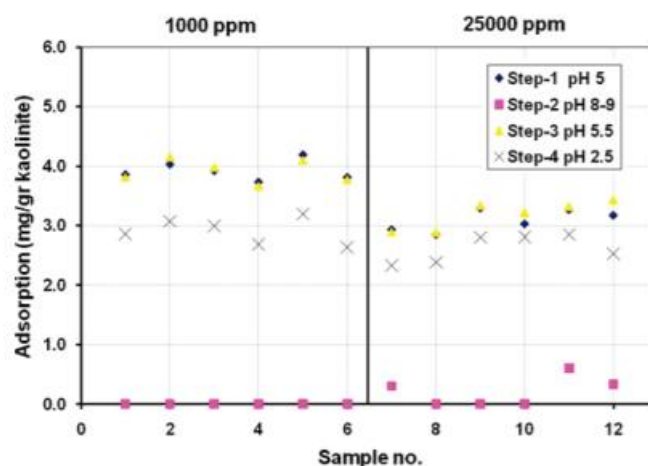

Figure 19: Adsorption reversibility by pH variation in systems containing quinoline, kaolinite and brine at room temperature (RezaeiDoust et al., 2011).

The question is then if asphaltenes are necessary for obtaining mixed-wet rock. The answer is no, since small molecules (that are not asphaltene since they are too small, but it is possible that they are part of it) have shown to affect adsorption depending on pH, as shown in figure 19.

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The need for asphaltenic content for a mixed-wet rock does then not seem to be a requirement. As mentioned earlier, the wettability seems to be strongly related to pH changes, causing charge shifts of the polar organic acids and bases. A shift in charge will affect the molecule's affinity to a charged solid surface such as a clay mineral surface.

5 Conclusions

Through this literature study, the effect of crude oil adsorption and asphaltene precipitation on sandstone wettability has been assessed. Crude oil has a complex composition that consist among others of polar components. These are heavy molecules such as resins and asphaltenes, and smaller molecules such as organic components of acidic and basic nature.

The crude oil can therefore alter the wettability as:

- *Asphaltene precipitation*: which makes the rock more oil wet and are strongest on onset of precipitation where surface precipitation interactions are dominating.
- *Adsorption of polar crude components onto the rock surface*: where organic components such as acids and bases adsorb to make the rock mixed wet, but that can desorb and make the rock more water-wet again; especially with addition of low salinity flooding (Smart Water).

There are several factors that will affect to which degree this will happen (or at all), where the mineralogy of the sandstone is very important (clay should be present for Smart Water mechanism). Other factors include formation water (its composition, pH, and salinity), crude oil, temperature, pressure, initial water saturation, COBR interactions and core restoration.

Asphaltene precipitation may not have as much of a prominent effect as the adsorption of the polar basic and acidic components; as it has been seen that the asphaltene precipitation's effect on wettability in some cases is secondary to the effect adsorption has.

And to answer the question if asphaltenic content is needed for a mixed rock; the answer is no. This is the case since it is observed that small molecules, that cannot be asphaltene, can change the wetting by adsorption onto the rock surface. The use of quinoline demonstrated this matter.

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