University of Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

MASTER'S THESIS

Study programme/specialisation: Petroleum Engineering / Reservoir Engineering	Spring semester, 2021 Open

Author: Novia Fazilani

Programme coordinator:

Supervisor(s): Skule Strand and Tina Puntervold

Title of master's thesis:

The Effect of Adsorption of Crude Oil Polar Organic Components on Wettability and EOR Potential by Smart Water on Sandstone Cores

Credits: 30

Keywords: Smart Water EOR Enhance oil recovery Sandstone reservoirs Wettability Adsorption Polar Organic Components	Number of pages: ………62………… + supplemental material/other: ……5…… Stavanger, 15th June 2021 date/year

Acknowledgements

First, I would like to express my sincere gratitude to my supervisors Skule Strand and Tina Puntervold for giving me the opportunity to carry out this thesis. For sharing your professional knowledge and expertise. For supporting me when needed. I am forever grateful to have been part of the Smart Water EOR team.

Then, I would like to thank Alexandr Mamonov, for assisting me and guiding me in the lab. To share your knowledge and experience. And developed my passion to be in the lab. It has been a privilege to work with you.

I would also like to thank all the students and all the people that has been working at the lab. For our great conversations and being there in times of need, making the lab a great place to be. Thank you for making every day fun even when the days were covered with challenges.

And lastly, I would like to thank my family, friends and partner, Thank you for your love, patience and encouragement during this thesis writing.

Abstract

Reservoir wettability is widely acknowledged as one of the most influential parameters in oil recovery processes. The complexity of the underlying crude oil brine rock (CoBR) interactions at the interface boundaries acting within the pores determines the process of establishing and altering wettability. The wettability condition of crude oil is primarily determined by the adsorption or precipitation of the polar organic components (POC). In this study, a series of dynamic adsorption tests were performed to investigate the surface reactivity of acidic and basic POC towards silicate mineral surfaces. The tests were performed by flooding modified crude oil containing low asphaltene content (<1 wt%) with predetermined amounts of acidic and basic POC (~0.2 mg KOH/g) through outcrop and reservoir core samples. Base number (BN) and acid number (AN) of effluent oil samples were compared to the given initial BN and AN of the crude oil to determine adsorption of crude oil components. Because of the presence of negatively charged silica minerals, sandstone minerals showed a preference for organic basic adsorption compared to positively charged acidic components. In addition, oil recovery by spontaneous imbibition test were carried out to determine the effect of POC adsorption on the capillary forces and wettability. The main points to compare were the rate of imbibition and the oil recovery.

Another research point of this study was to investigate if ionic modified Smart water brine can improve capillary forces and mobilize extra oil to recover. Smart Water is made by adjusting the ionic composition of the injected brine. The ionic composition of the injected brine can be modified in such a way that can disrupt the established chemical equilibrium of the reservoir, thus altering the wetting conditions. The adsorbed POC shifts the wettability to a less water-wet condition. By applying Smart Water, desorption of the POC occurs and shifts the wettability to a more water-wet condition. This is the process of wettability alteration and it can be reversible. Parameters such as pH, temperature, pressure, and salinity affect the adsorption/desorption process. Smart Water affects parameters related to fluid flow such as capillary forces as well as the relative permeabilities of oil and water. The increase in capillary forces due to the injection of Smart Water can allows better water imbibition into the smaller pores, resulting in improved sweep efficiency and EOR effect. Both the outcrop and reservoir cores showed improvement in oil recovery in spontaneous imbibition tests (SI) when formation water (FW) was replaced by Smart Water.

The initial wetting condition of the reservoir rock must be of a mixed wettability and not completely water-wet in order to observe wettability alteration by Smart Water EOR. A thorough understanding of the initial wettability is required for the successful implementation of Smart Water EOR. To create a mixed wettability condition, the charged POC in crude oil must adsorb or precipitate on the initially water-wet mineral surfaces that contains active adsorption areas. The results show that before crude oil flooding the core sample was found to be in a water-wet condition. The adsorption of the predominant basic oil components slightly reduced the water-wetness of the core samples.

Nomenclature

μ = Viscosity

ρ = Density

θ_c = Contact angle

E_m = Miscroscopic sweep efficiency

E_{MA} = Macroscopic sweep efficiency

K_{ro} = relative permeability oil

K_{rw} = relative permeability water

P_c = Capillary Pressure

radius = r

S_{wi} = Initial water saturation

AN = Acid number

BET = Brunauer − Emmet − Teller

BN = Base Number

CoBR = Crude oil − Brine − Rock

CEC = Cation exchange capacity

EOR = Enhance oil recovery

FW = Formation Water

LS = Low salinity

SEM = scanning electron miscroscope

USBM = U. S Bureau of Mines

Table of Contents

List of Figures

List of Tables

Chapter 1. Introduction

Enhanced oil recovery (EOR) is becoming an essential production method in meeting the rising energy demand of the global oil production. The decline in production from mature fields as well as new hydrocarbon reservoir discoveries is insufficient to achieve these demands. EOR can improve the recovery factor, extends the life of fields and produce an additional oil production from mature fields.

The definition of wettability in oil reservoir describes the tendency of a fluid to adhere or adsorb to a solid surface in the presence of another immiscible fluid. It can also be defined as a measure of the rock surface's affinity with the oil or water phase. Wettability plays an important role in determining the allocation and flow of reservoir fluids. This affects the relative permeabilities of reservoir fluids and therefore the efficiency of the recovery. As a result, the wettability can determine the amount of oil recovered from a reservoir (Crocker and Marchin, 1988).

The SARA analysis (Fan et al., 2002 and Jewell et al., 1972) groups crude oil components for analytical and chemical applications. Hydrocarbons, i.e. saturates, aromatics, resins, and asphaltenes are the four primary groups. SARA analysis categorises the groups depending on their polarity. Aromatics have aromatic rings that make them slightly polar, while saturates are non-polar. However, resins and asphaltenes are polar because they consist of nitrogen, sulphur, and oxygen (NSO) molecules, commonly known as polar organic components (POC). The amount of nitrogen (N) and oxygen (O) in crude oil rises as the resin and asphaltene concentration rises (Mamonov et al., 2019).

The acidic and basic nature of polar components in crude oils are determined by these elements. When the acidic and basic POC interact with the mineral surfaces in a reservoir, reversible or non-reversible adsorption can occur. In general, sandstone reservoirs are negatively charged in actual reservoir pH range of 5-9 because they are mainly composed of various silicate minerals, therefore the adsorption of the positively charge basic POC is more likely to be more dominant (Buckley, 1998). Previous studies have confirmed that adsorption of basic component was more dominant in sandstone reservoirs (Reed, 1968; Buckley, 1999; Mamonov et al., 2019; Puntervold et al., 2021). The level of adsorption depends on the chemical compositions of the crude oil, ionic composition of the brine and the mineral composition of the rock surfaces. Therefore, the wettability is determined by the amount of crude oil POC adsorbed at the interface between the liquid phases and the mineral rock surfaces. More intense adsorption of POC can result in a less water-wet behaviour.

Previous literature studies show that POC can adsorb onto mineral surfaces and change the wettability of the reservoir (Buckley, 1998; Denekas et al., 1959; Gloton et al., 1992; Hopkins et al., 2016; Mamonov et al., 2019; Puntervold et al., 2021). Therefore, understanding the crude oil adsorption processes is important and can help determine better enhance oil recovery processes.

Crude oil brine rock (CoBR) interactions affect the reservoir fluid flow processes and various surface/interface phenomena, such as interfacial tension (IFT), wettability, capillary forces, reversible crude oil adsorption-desorption processes, or non-reversible asphaltenes precipitation during waterflooding (Kaminsky and Radke, 1997). As a result, CoBR interactions have a big impact on how the reservoir's initial wettability is established (Buckley, 1998; Anderson, 1986).

Waterflooding, or in other words reinjection of produced water through higher permeable zones or fractures to the production well, is applied in oil reservoirs in order to maintain pressure support and improve fluid flow within the porous system (Austad, 2010). If the injecting brine used is FW, then the flooding process will not change the wetting since FW will not disturb the equilibrium state of the existing system. Introducing an ion-modified brine (Smart Water) that differ from FW by ionic composition, can disturb the established chemical equilibrium. It can result in changing the wetting properties and improve oil recovery. This process is called Smart Water flooding and is regarded as an EOR method. A thorough understanding of the initial wettability is required for the successful implementation of Smart Water EOR. The initial wettability is established just when the first crude oil invades a reservoir. The initial wetting condition of the reservoir rock must be of a mixed wettability and not completely water-wet in order to observe wettability alteration by Smart Water. To create a mixed wettability condition, the charged POC in crude oil must adsorb or precipitate on the initially water-wet mineral surfaces that contain active adsorption areas (Puntervold et al., 2021). Due to the complexity of the CoBR interactions, the process of establishing and modifying reservoir wettability are still under discussion in literature. Therefore, it is important to perform detailed analyses of the CoBR interactions with the aim of increasing the efficiency of the oil recovery.

1.1 Thesis Objectives

Sandstones is a heterogenous and complex reservoir rock consisting of a variety of minerals which can react with polar components of crude oil. Polar organic components (POC) of crude oil are usually acidic and basic in nature (Torrijos et al., 2016). The Smart Water EOR potential depends on the quantity and type of adsorbed POC. Therefore, the scope of this work is to study the ability of polar organic acidic and basic components to adsorb on silicate mineral surfaces and alter the wettability in sandstone cores. The adsorption of POC was carried out by flooding a constant total volume of crude oil with known amounts of acidic and basic components through sandstone cores at constant initial water saturation (S_{wi}), and afterwards comparing the effluent AN and BN with the influent value. Lastly, SI tests were performed using FW and LS Smart water as imbibition brines in order to estimate initial wetting and investigate the potential for wettability alteration by ion-modified Smart Water brine.

Thesis objectives can be summarised:

- Study the reactivity of acidic and basic components regarding adsorption onto silicate sandstone outcrop and reservoir mineral surfaces.
- Study how the adsorption of polar components affects rock wettability and capillary forces.
- Study the mineral reactivity towards formation water and smart water.

Chapter 2. Theory

1.1 Minerology of sandstone reservoirs

An important parameter to understand wettability and Smart Water injection is reservoir minerology. The composition of minerals present in the reservoir system will influence the adsorption preferences for POC and thus affect Smart Water EOR effect.

Most of the world's oil and natural gas are formed in sandstones because of their commonly high porosity. The large sand grains which are sedimentary particles can range between 0.0625 and 2mm in diameter, nevertheless most sandstones have a clear-cut upper grain size limit, however can be called conglomeratetic sandstones if it contains a large number of coarser grains (Bjørlykke, 1989). Sandstones are formed of lithified quartz grains, though other mineral grains such as feldspar, mica, and rock fragments, can also be found in small amounts. Silica, calcite, iron compounds, or clay minerals are used to cement the grains together and results in either a tightly packed structure to form compact stone or scattered broadly to form a porous stone. The size of the grains, grain packing, porosity, and composition of the cement all affect the strength and sturdiness of sandstone (Ingham, 2013).

Sandstones can be transported fairly easily at intermediate current velocities (25-60cm/s) by fluvial, ice, gravity or eolian forces because of their small sized grains, but too large to be transported in suspension or to be cohesive. The loosely packed sand grains sediment gradually builds up and buried deeper thus lithification processes occurs called diagenesis (compaction, cementation) and authigenisis (where minerals reforms from existing chemicals e.g., the formation of clay minerals in sedimentary environments due to chemical breakdown of feldspars, or montmorillonite turning into illite) and forming sedimentary rocks. The lithification process can result in creating an impermeable rock, as it lowers the porosity and permeability of the rock itself. This determines the migration or accumulation of hydrocarbons as permeability influences the fluid flow within the porous system. Formation fluids, mineral cements, and clay matrix fill the pore space between framework grains (Sen 2016). Since quartz, feldspar, and clay minerals have different structural characteristics, therefore different surface reactions occur and influences the fluid flow processes in sandstone porous media in different ways.

2.1.1 Quartz

The second most abundant rock-forming mineral is quartz, which is found in sandstone, granites, and metamorphic rocks. It is the simplest form of the silicate minerals, consisting of silicon and oxygen, with the chemical formula SiO_2 and is derived from igneous or metamorphic rocks. Quartz is also a mineral with a high degree of stability. It has a hardness of 7 on the Mohs scale of hardness, making it resistant to chemical degradation at the Earth's surface and ensuring that its grains remain intact over long distances and periods of transport (Nichols, 2009).

The SiO_4 group, which consists of four oxygen atoms surrounding a central silicon atom to form a tetrahedron, is its fundamental building block. Quartz has the formula SiO_2 since each oxygen is a member of two SiO_4 groups. Quartz is classified as a network silicate or tectosilicate because the SiO_4 tetrahedra form a three-dimensional network.

There are two types of quartz: alpha or low, quartz that is stable up to 573 °C and beta or high, quartz that is stable above 573 °C. During the alpha-beta transition, only minor movements of their constituent atoms separate the two. In various geological conditions, quartz crystallizes at a wide range of temperatures. This property makes the reservoir rock's crystal structure and fluid inclusions useful information that helps in determining the temperature and conditions under which it formed.

The cation exchange capacity (CEC) of the silt fraction of quartz varying in size from 2 to 63 μm is 0,6 cmol kg^{-1}, whilst the clay fraction of quartz with a size less than 2 μm has a CEC of 5,3 cmol kg^{-1} (Carroll, 1959). At pH 2, silica particles have no charge, but as the pH rises, the CEC rises as negative charges accumulate on the particle surface (Iler, 1979). Additionally, an increase in quartz content reduces CEC, surface area, and other factors. The reactivity towards the reservoir fluids is low due to their large grain sizes, small surface area, low cation exchange capacity (CEC) and surface charge (Deer et al., 2013).

2.1.2 Feldspars

Feldspar is the most abundant mineral, accounting for about 60% of the earth's crust by weight. Nonetheless, since it is more readily decomposed than quartz, it accounts for just 10-15% of the sandstone's composition. Sandstones with a high feldspar content indicate that chemical weathering has not been thorough. In all parts of the world, they can be found in igneous, metamorphic, and sedimentary rocks. The structures, chemical compositions, and physical properties of feldspar minerals are quite similar. Orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$) are all common feldspars. The general chemical composition of all feldspar minerals is as follows:

$$X(Al,Si)_4O_8$$

K^+, Na^+, Ca^{2+}, Ba^{2+}, Rb^+, Sr^{2+}, and Fe^{2+} are the seven ions that can make up this generalized composition and replaced as X in the equation. Potassium, sodium, and calcium ions are commonly found in feldspars. Feldspars containing barium, rubidium, strontium, and iron are extremely rare.

The feldspar group is represented by two solid solution systems in the following triangular diagram in Figure 2. Between the end members of pure albite ($NaAlSi_3O_8$) and pure anorthite, the plagioclase feldspars form a solid solution series ($CaAl_2Si_2O_8$). Between pure albite and potassium sanidine ($KAlSi_3O_8$), the alkali feldspars form a solid solution series.

The reversible cation exchange activity seems to be applied in feldspars, as Na^+ is being exchanged with H^+ ion. Therefore, feldspars will influence the pH of the formation water as well as the initial wetting conditions, which will be determined by the salinity and composition of the brine to which it is added to (Strand et al., 2014).

The pH of the reservoir can be affected by feldspar minerals by a very fast reaction of exchanging non-framework cations (Na^+, K^+, Ca^{2+}) with H^+ ions from the surrounding aqueous phase (Chou and Wollast, 1985). The intensity of cation exchange reactions varies depending on the chemical stability of the minerals, with the least chemically stable mineral reacting the most with an aqueous solution (Grotzinger and Jordan, 2010). The relative chemical stabilities of common sandstone minerals are shown in Figure 1. Furthermore, as the salinity of the water increases, can result in a less alkaline environment. Due to an increase in the Ca^{2+}, Mg^{2+} and Na^+ ions, the cation exchange reactions can therefore be suppressed.

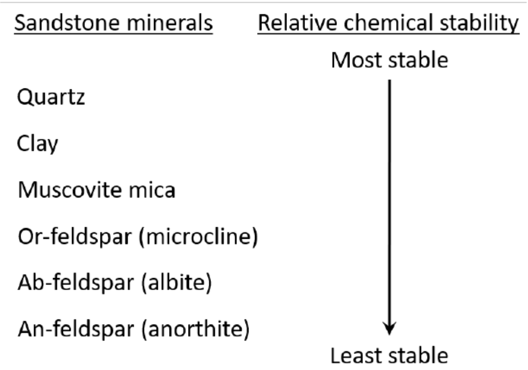

Figure 1 The relative chemical stability of some sandstone minerals (Grotzinger and Jordan, 2010)

2.1.2.1 Surface Chemistry

Ionic exchange between Ca and Na may occur in the outer layer of anorthite when it comes into contact with an aqueous solution of NaCl. In acidic solutions, this will be the case for all feldspars. From the regular K-feldspars to the irregular twisted structure of Ca-feldspars, there is considerable interaction of oxygens and cations in the framework, resulting in large differences in cell dimensions and atomic positions. The cell dimensions are affected by the temperature and pressure of the system. Inorganic ions, organic ions and complexes can come into contact with feldspar surfaces. Organic cations will compete with inorganic cations and interact ionically with a charged aluminiosilicate. The organic cations can be adsorbed to the feldspar surface because it can fit into the feldspar cages. If the hydrogen bonding is weaker than in water, then the hydrophobic saturated organic compounds can be adsorbed on a aluminosilicate surface. A low polarity surface (high Si/Al ratio) has a higher affinity for adsorption of a hydrophobic organic component compared to a high polarity surface. (Smith, 1994).

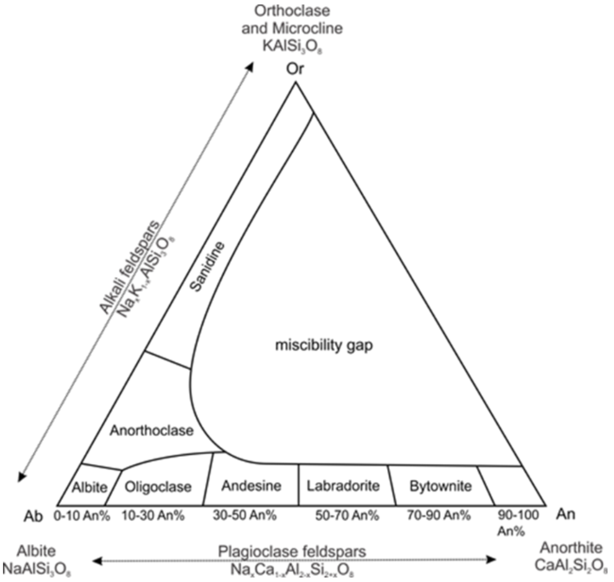

Figure 2 Feldspar ternary diagram (REF. modified from Chemistry of Elements (1998) - p. 357.)

2.1.3 Clay Minerals

Clay minerals, or in other words sheet silicates are primarily composed of oxygen, silicon, aluminium, magnesium, iron and water (H_2O, OH^-). The sheet silicates minerals found in metamorphic and eruptive rocks (e.g., biotite, muscovite and chlorite) partly creates clay minerals in sedimentary basins, but these clastic minerals are usually changed through weathering (breakdown of feldspar and mica) and transport from their original composition in the parent rock (Bjørlykke, 1989). Clay minerals have a number of characteristics that set them apart from other minerals. Clay surfaces are negatively charged in the associated pH range of 5-9 of the formation waters (Strand et al., 2016) in order to maintain chemical equilibrium, therefore attracting positively charged ions and molecules from surrounding fluids. Clay minerals have a high potential for adsorbing ions due to their large specific surface area, which is supported by the fact that they have negatively charged edges due to broken bonds. The relative affinities towards clay surfaces varies with different cations, as the negatively charged surfaces must be charged balanced by the cations through the process of cation exchange. The order of the relative affinities is given by (Velde, 2010):

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} << H^+$$

With proton H^+ having the highest affinity, even at low concentrations can still be reactive towards the clay surfaces.

Sheet silicates have a structure containing of sheets of alternating layers of SiO_4 tetrahedra, which in this layer the silicon or aluminium atoms are surrounded by four oxygen atoms and octahedra which in this layer the bi and trivalent ions can act as cations and is surrounded by six oxygen or hydroxyl ions. With trivalent ions (e.g. Al^{3+}), Only two of the three regions in the octahedral layer are occupied and such minerals are referred to as dioctahedral. Whereas with bivalent ions (Mg^{++}, Fe^{++}), in order to attain a balance charge, all three regions must be filled, and these minerals are called trioctohedral (Bjørlykke, 1989). The common forms of reservoir clays are kaolinite and mica/illite and considered as low-swelling clays.

2.1.3.1 Kaolinite

Kaolinite is a layered silicate mineral is a clay mineral, with the chemical composition $Al_2Si_2O_5(OH)_4$. As shown in Figure 3 the structure consists of one tetrahedral sheet of silica (SiO_4) connected through oxygen atoms to one octahedral sheet of alumina (AlO_6) octahedra (Deer et al., 1992) and is very stable at low temperatures. However, at higher temperatures kaolinite becomes unstable and will convert to illite if K-feldspar or other sources of potassium are available (at 130˚C) or pyrophyllite ($Al_3Si_4O_{10}(OH)_2$) (Bjørlykke, 1989). Because of its 1:1 structure, the ion exchange capacity is smaller for kaolinite than montmorillonite because there is no positions in the structure where ion exchange can occur easily. Since there is no space between the layers for water or larger cations, they are chemically and mineralogically simple compared to other clays. The sheets are bonded by hydrogen bonding.

2.1.3.2 Illite

Illite are clay minerals with a 2:1 stable structure, shown in Figure 3 octahedral alumina layer sandwiched between two tetrahedral silica layers and are bonded together by potassium cations, where its silica tetrahedron (T) – alumina octahedron (O) – silica tetrahedron (T) layers. The poorly hydrated potassium cations that occupies the space between these T-O-T layers causes the minerals to easily cleaves along this plane therefore prevents the occurrence of swelling. The covalent bonds within the tetrahedral and octahedral layers are stronger (Bjørlykke, 1989). The charge imbalance occurs mainly in the silica layers, resulting in a negatively charged surface. Though the cations bind the unit sheets together, however the clay can swell in a low-saline environment (Strand et al., 2016). Illite has a lower cation-exchange potential (CEC) than smectite but a higher CEC than kaolinite, which ranges from 20 to 30 meq/100 g.

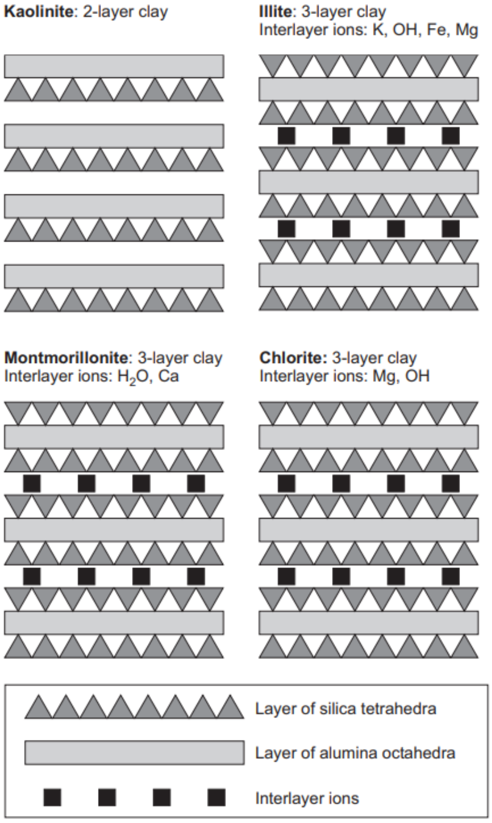

Figure 3. Crystal lattice structure of common clay minerals (Nichols, 2009).

2.1.3.3 Montmorillonite

Montmorillonite has a similar structure to illite with a 2:1 clay structure illustrated in Figure 3. However, most of the potassium cations undergo replacement by water (H_3O^+), other present cations or organic compounds (Bjørlykke, 1989). The montmorillonite has an interlayer space between each triple-sheet layer, unlike other clay nanoparticles. The mineral is made up of isomorphic substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer and Al^{3+} for Mg^{2+} in the octahedral sheet. Because of this arrangement the montmorillonite holds a negative residual charge compensated by cations in the interlayer space (Massaro et al., 2020). The unit sheets are often held together by cations, but Montmorillonite is classified as a swelling clay due to the greater distance between the cations and the negatively charged alumina layer (Strand et al., 2016).

2.2 Hydrocarbon Recovery Mechanisms

2.2.1 Primary Recovery

Natural energy existing in the oil reservoir is used as the primary source of energy in primary oil recovery. In other words, the hydrocarbons in the reservoir are produced by simply lowering the reservoir's pressure. These natural energy sources may include artificial lift and natural drive, as well as gas drive, fluid and rock expansion, and gravity damage (Green and Willhite, 1998).

Natural reservoir energy, such as gas-drive, water-drive, or gravity drainage, displaces hydrocarbons from the reservoir, into the wellbore, and up to the surface in the first stage of hydrocarbon production. The reservoir pressure is initially much higher than the pressure inside the wellbore's bottomhole. Hydrocarbons are drawn toward the well and up to the surface by the high difference in pressure. The differential pressure, on the other hand, decreases as the reservoir pressure decreases due to production. An artificial lift system, such as a rod pump, an electrical submersible pump, or a gas-lift installation, is needed to reduce bottomhole pressure or increase differential pressure to increase hydrocarbon output. Artificial lift production is referred to as primary recovery. When the reservoir pressure is so low that production rates are uneconomical, or when the proportions of gas or water in the production stream are too high, the primary recovery stage reaches its maximum. Only a small percentage of the initial hydrocarbons in place are produced during primary recovery, usually about 10% for oil reservoirs (Schlumberger).

2.2.2 Secondary Recovery

When the location of the injection and production wells are aligned and able to maintain fluid communication between one another, external fluids such as water or gas are injected into the injection wells. This is known as the second stage of hydrocarbon production. Secondary recovery is applied for reservoir pressure maintenance and displacing hydrocarbons with water towards the production well by viscous forces. Gas injection and waterflooding are the most common secondary recovery techniques. To sweep oil from the reservoir, gas is injected into the gas cap and water is injected into the production zone. During the primary recovery stage, a pressure-maintenance program can be started, but it is a type of enhanced recovery. When the injected fluid (water or gas) is produced in large quantities from the production wells, the secondary recovery stage reaches its limit and production becomes uneconomical. In an oil reservoir, the use of primary recovery and secondary recovery in combination produces between 15% to 40% of the original oil in place. While a waterflood will mobilize and displace a certain amount of oil, the majority of it will stay in the reservoir. There may be a number of reasons for this, including: (1) Since water would take the shortest path across a reservoir, a significant portion of the reservoir will be unswept by waterflooding. (2) Water's viscosity would be low in comparison to oil's, resulting in an undesirable mobility ratio. Water will break through before the oil in both cases, producing water and leaving the oil behind (Green and Willhite, 1998).

2.2.3 Tertiary Recovery

The recovery methods that follow waterflooding or pressure maintenance are traditionally referred to as the third stage of hydrocarbon production. Tertiary recovery or enhanced oil recovery methods include changing the internal properties of the reservoir, some of the most common methods are injecting miscible gases, chemicals, modified brines, and/or thermal energy to displace additional oil. The term tertiary recovery is often known as enhanced oil recovery (EOR), but since EOR methods can now be used at any stage of reservoir production, the term is less widely used than in the past. EOR approaches are commonly used when a secondary recovery process is no longer cost-effective, but they may also be used before or instead of a secondary recovery process. There are many criteria to consider when deciding which EOR method to use, amongst them are: density of oil, viscosity, saturation, reservoir thickness and depth, permeability and porosity, temperature, types of fluids and physical condition of the reservoir.

2.2.3.1 Chemical Injection

Chemical injection refers to a wide variety of chemicals used to enable oil flow through various mechanisms. Surface tension reduction, water shut-off, and wettability modification are three main mechanisms that can be considered for chemical injection. Despite the fact that many chemicals are created for EOR, classifications are restricted to Alkaline-Surfactant-Polymer (ASP) and Polymer flooding. The aim of ASP injection is to reduce the interfacial tension between oil and water in order to increase the movement of trapped oil after waterflooding. In situ surfactant is created when alkaline chemicals react with reservoir oil. This chemical increases the efficiency of the ASP by controlling its mobility. Water-soluble polymers are injected into reservoir water sources to control water mobility by viscosity thickening. Polymer injection is commonly used to delay the water breakthrough in the early stages of waterflooding.

2.2.3.2 Thermal injection

Thermal methods refer to processes that increase oil displacement by transferring heat through the reservoir. The two main types of thermal processes are steam drive and fire flooding. Steam drive is a method of transferring heat to reservoir oil by injecting steam into the reservoir from the surface. There are two types of steam injection in this process: cyclic steam injection and continuous steam injection. The huff and puff process, also known as cyclic steam injection, is a method that involves three stages of injection, soaking, and production in a single well. After injecting steam for a set amount of time, the well is closed for a specific amount of time, known as the soak time. The well is required to be closed for a few days at this point to allow heat to pass from the steam to the viscose/heavy oil. The well is then opened for a short period of time, and hot oil is created. This procedure is repeated once more. This method involves a number of mechanisms, including viscosity reduction, oil swelling, and steam stripping. Steam-flooding is the second phase in this classification, in which steam is injected into the injector, then moved into the production well, where oil is produced. Steam condenses to hot water due to heat loss at the steam front. As a result, the oil expands, the viscosity decreases, and the oil displacement improves.

The in-situ combustion in the reservoir provides heat in the fire flooding process. To keep the combustion near the well running, air or a combination of light hydrocarbons and oxygen is continuously injected into the reservoir. Heat is transferred to the oil and gas in the reservoir, as the fire front passes through the production well. The reservoir water evaporates as steam, light hydrocarbon vaporizes, and the viscosity of the oil decreases. Some of the mechanisms that help with oil movement are steam drive, hot water, and light hydrocarbon solvent.

2.2.3.3 Gas Injection

Gas injection is to make the hydrocarbon phases more miscible. Miscible injection of various gases, such as carbon dioxide, nitrogen, flue gas, and natural gas, is used in this technique. By forming a single phase between the injected gas and oil, miscible injection improves oil displacement and reservoir pressure maintenance. The temperature, pressure, and composition of the oil in the reservoir all have an effect on oil displacement during miscible gas injection.

2.2.3.4 Low salinity water flooding

Chemicals used in EOR procedures are a major source of concern in the oil and gas sector because of their negative effects on the environment. The traditional water injection method uses a variety of chemicals to change the reservoir's wettability in order to produce additional oil. Smart Water injection is a relatively recent EOR method that enhances oil recovery by altering wettability with minimal chemical use in both carbonate and sandstone reservoirs. This method modifies inorganic ionic composition within the brine to a more favourable condition to promote wettability alteration. When compared to alternative technologies such as the previous methods mentioned, smart water EOR is both cost-effective and environmentally friendly. Smart water promotes the change in wettability of a surface to make it more water-wet. The oil recovery can be enhanced by the increased in positive capillary forces resulting a better microscopic sweep efficiency in heterogeneous pore systems. EOR potential by Smart Water shows potential and has been proven both by field observations and laboratory research. Reservoir minerology plays an important tole that determines the types of interactions such as adsorption of POC in crude oils. The surface charge of carbonates is positive, whereas the surface charge of sandstones is negative due to the presence of minerals such as clays, quartz, feldspar, and silicate.

2.3 Displacement Forces

During an EOR operation, overall displacement forces are divided into different scales, they are; microscopic and macroscopic scale. The efficiency of displacing fluid, especially in producing residual oil from the pores at the microscopic scale (pore scale) is considered an important aspect of an EOR operation. Such parameters that contribute highly to the efficiency are wettability, viscosity, interfacial tension. In a macroscopic scale, reservoir heterogeneity and gravity forces contribute to the overall efficiency of displacing the fluid in a volumetric scale. In any EOR technique, the amount of hydrocarbon displaced divided by the volume of hydrocarbon at the start of the EOR process is the oil recovery efficiency (overall displacement efficiency, E). It can also be described as the product of the microscopic efficiency (E_D) and the macroscopic efficiency (E_V) presented in **Eq. (1)** below:

$$E = E_D E_V \tag{1}$$

The ability for an injected fluid to displace oil in the pore space at a microscopic scale is critical to any EOR operation, thus the microscopic displacement efficiency, E_D, has substantial influence on the accomplishment of a project. The amount of residual oil (Sor) at the end of the process when the displacing fluid comes into contact with the displaced fluid determines the microscopic efficiency for crude oil. However, In the porous system of the reservoir, the efficiency of each of the fluids varies. since EOR processes are generally associated with the injection of several slugs. Viscous forces are responsible for displacing oil during water flooding, the displacement behaviour between the displacing and displaced fluid does not behave piston-like (where in the pore system water pushes all of the oil to the displacement front) (Buckley and Leverett, 1942). Furthermore, low efficiency and viscosity difference between water and oil forms viscous fingers contributes to early fingering phenomenon and early breakthrough, therefore resulting in poor performance in the waterflooding process. Important parameters that influence microscopic displacements are capillary and viscous forces and viscosity of fluids and their mobility in porous media. In terms of saturation, the microscopic efficiency can also be expressed using Equation below:

$$E_D = \frac{S_{oi} - S_{or}}{S_{oi}} \tag{2}$$

Where during the EOR operation, S_{oi} is initial oil saturation and S_{or} is the residual oil saturation in the pore volume after being swept.

The volume of reservoir contacted by the injected fluid in any displacement phase determines oil recovery. The volumetric displacement (sweep) efficiency, E_V, is a quantitative measurement of this contact. The fraction of the reservoir (pore volume) swept or invaded by displacing fluid is referred to as volumetric efficiency or sweep efficiency. It is also important to predict the volumetric sweep efficiency, in order to distinguish which parts of the reservoir is swept by the invaded fluid (Green and Willhite, 1998). The volumetric sweep efficiency is commonly estimated as the product of areal and vertical sweep efficiencies, expressed as follows:

$$E_V = E_A E_I \tag{3}$$

Where E_A is the areal sweep efficiency and E_I is the vertical sweep efficiency.

In porous media, the primary driving forces in fluid flow are capillary forces. The contribution of interfacial tension and wettability leads to capillary forces, or in other words, the intermolecular forces at the interface results in the liquid to rise within the capillary tube. Capillary pressure is the difference in pressure between two immiscible fluids that are in contact (Green and Willhite, 1998).

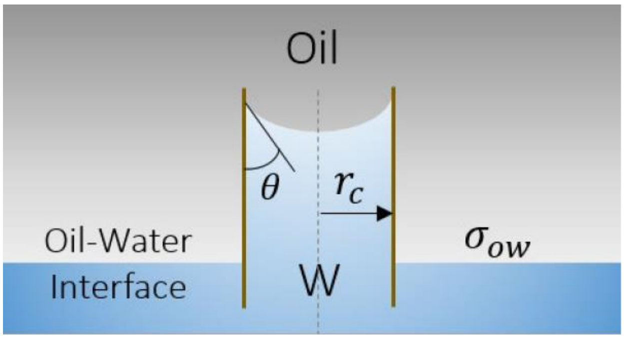

Figure 4 Capillary forces action in an oil-water system (redrawn from (Dake,1978)).

Alternatively stated, the difference in pressure between the non-wetting phase and the wetting phase and can be expressed in the following equation:

$$P_c = P_{nw} - P_w \tag{4}$$

Where P_c is capillary pressure, P_{nw} is non-wetting phase pressure and P_w is wetting phase pressure, and all units are in pascals. An illustration is displayed in Figure 4 when a capillary tube is placed below the interface in a two-phase system, a force balance between the contact angle, IFT and capillary pressure can be written as follows:

$$P_c = \frac{2\sigma cos\theta}{r} \tag{5}$$

$\sigma = \text{Interfacial tension } \left[\frac{\text{N}}{\text{m}}\right]$
$\theta = \text{wetting angle [degree]}$
$\text{r} = \text{radius [m]}$

The reservoir's pore space can be thought of as a network of interconnected capillary tubes of varying diameters, so capillary forces are crucial for oil recovery (Green and Willhite, 1998). However, strong capillary forces during waterflooding can trap oil and result in high residual oil saturation in sandstone reservoirs (Anderson, 1987). On core samples, spontaneous imbibition can be performed to estimate capillary action based on rock wetting condition, whereby the capillary forces drive the imbibition of the wetting fluid into the porous medium (Morrow and Mason, 2001). And the volume that has been spontaneously imbibed will determine the wetting condition of the core.

2.4 Wettability

Understanding the wettability of a formation is critical for maximizing oil recovery. Many aspects of reservoir performance, especially on waterflooding and enhanced oil recovery techniques, are influenced by the oil-versus-water wetting preference. When an oil-wet reservoir is developed as if it were a water-wet reservoir, it results in an irreversible reservoir damage and reduced recovery.

In a reservoir having homogenous characteristics saturated with oil and water within its pores, “strongly water-wet” describes one end of a range in which the pore surfaces prefer contact with water, as the water is strongly bonded to the pore surfaces. Whereas “strongly oil-wet surface prefers contact with oil, as the oil is strongly bonded to the pore surfaces. Another term "intermediate wet" or "neutral wet" refers to a state in which the surfaces does not have a strong preference for one fluid over the other. Wettability is definitive in many oil-field applications; the rock is either water-wet or oil-wet. The complexity of reservoir rock wetting physics is overlooked by this definitive simplification.

Figure 5 shows the wetting state of a heterogenous reservoir that can be categorized as mixed/fractional wet.

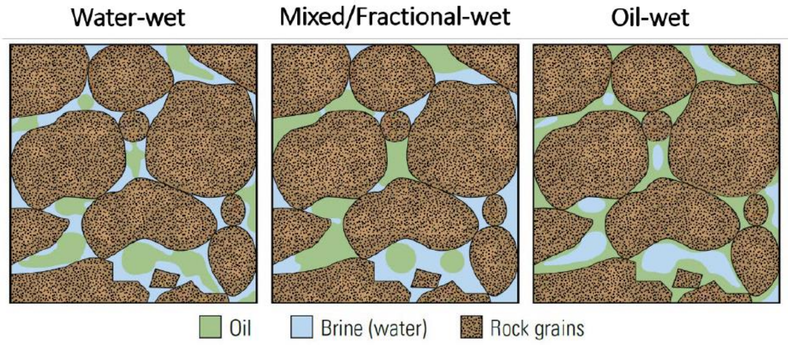

Figure 5 illustration of the wetting scenarios where oil and brine is in contact with the rock surfaces (redrawn from Nolen-Hoeksema (2016)).

A contact angle is created when two immiscible fluids come into contact with a solid surface, indicating the fluids tendency to spread on the surface. The tendency of fluids to adhere to a solid surface is known as wettability, and the fluid that has the most contact surface with the solid is known as wetting fluid. The degree of wettability is measured by the contact angle between two immiscible liquids (Alamooti and Malekabadi, 2018).

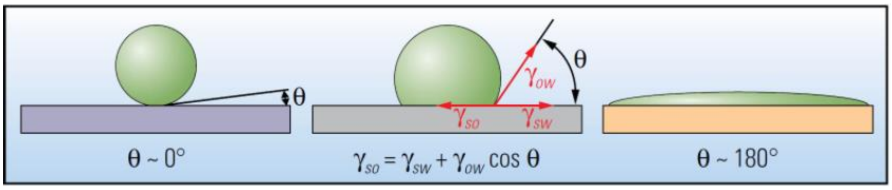

Figure 6 illustration of the wetting scenarios where oil and brine is in contact with the rock surfaces (redrawn from Nolen-Hoeksema (2016)).

For oil-water-solid systems under static equilibrium condition, it can be written:

The Young’s equation shown in Eq.6 can be used to determine the static equilibrium for oil-water-solid systems. It was developed on a thermodynamic basis stated by Gibbs (Berg, 1993).

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos\theta \qquad (6)$$

Where σ_{ws} is the interfacial energy between water and solid, σ_{os} is the interfacial energy between oil and solid, σ_{ow} is the interfacial tension between oil water and θ is the contact angle measured through the denser phase. According to equation above, the right-hand side of the equation is positive for water-wet condition, whereas it’s negative for oil-wet conditions and zero for neutral-wet conditions. And in Figure 7 Illustrates the varying contact angle degree for different wetting conditions:

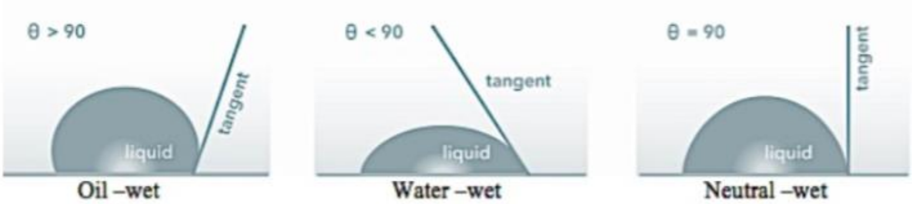

Figure 7 Wettability conditions depending on the contact angle measurement (redrawn from (Abdullah, 2016))

2.4.1 Wettability measurements

Many experimental approaches have been used to obtain reliable results in wettability measurements. They range from fundamental studies on smooth surfaces to complex studies in porous media. Wettability can be determined from both qualitative and quantitative methods. The quantitative method is a more direct approach in determining wettability where reservoir fluid is used on the rock sample. Examples of quantitative methods are: contact angle measurements, Amott test (spontaneous imbibition and forced displacement) (Amott, 1959) and U.S. Bureau of Mines (USBM) method. Examples of qualitative methods are: imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillarimetric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance and dye adsorption (Anderson, 1986). Some of these methods are time consuming and involves in conducting a lot of experiments which can make the results unreliable. It is also difficult to perform these experiments that mimics realistic reservoir conditions. The success of a waterflooding operations depends greatly on a proper estimation of the reservoir wettability. However, due to complex geometry of pores structure, contact angle measurement is not a good representative for the porous media. A brief summary of a few widely used methods for estimating the wettability of a system.

2.4.1.1 Wettability measurements on smooth surfaces

The simplest systems to examine the fundamental concepts of wettability are those that have smooth surfaces. The advantages are quick wettability predictions, good reproducibility, and easy comparisons of different systems.

Contact angle measurements are used to assess the wetting state of a rock surface shown in Figure 8 (Yuan and Lee 2013). Out of all the quantitative methods, it is the most common method used to determine wettability on plain surfaces (Anderson 1986, Morrow 1990).

The degree of wettability in a static equilibrated Oil – Water – Solid system is given as a function of the angle measured through the denser phase, as shown in Figure 8. Table 1 shows a general classification of the wettability as a function of contact angle measure.

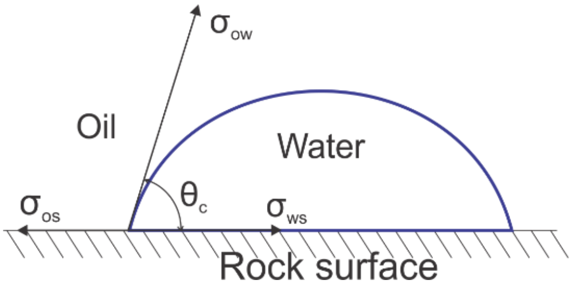

Figure 8 Static contact angle measurements

Table 1 A general classification of the wettability is given as a function of contact angle measurement

Contact angle (°)	Wettability
0 – 30	Strongly water–wet
30 – 90	Water–wet
90	Neutral–wet
90 – 150	Preferentially oil–wet
150 – 180	Strongly oil–wet

The disadvantage with contact angle measurements is that it does not apply for heterogeneity surfaces. This means that it cannot apply when the rock surface is not smooth. Smooth surfaces have fixed contact angle. Before carrying out the experiment, the surface needs to be prepared where this could affect the surface wetting. The contact angle measurements cannot be applied in pore throats with a diameter of a nano or a few micrometres, because the droplet is too large and therefore will not fit into these pore throats.

2.4.1.2 Spontaneous imbibition

Spontaneous imbibition is an ideal way to measure the degree of water-wetness in a porous rock. With an established initial water saturation of FW and saturated with an oil phase, such as crude oil in the core (Anderson, 1986). An illustration of the Amott cell is shown in Figure 9.

A spontaneous experiment is done by placing a core that has establish initial saturation and saturated with oil, in the Amott cell surrounded by the desired brine. If the core shows water-wet behaviour, positive capillary forces will imbibe the FW into the pore channels, mobilizing oil from the core as seen in Figure 9. The parameter that can be measured is the rate of imbibition and ultimate recovery. This is a useful measurement because the driving force of the rate is equivalent to the imbibition capillary pressure (Morrow, 1990). Spontaneous imbibition can be done to estimate initial wetting using FW as the imbibing brine and heptane as the saturated oil. It is important that when conducting wettability measurements, the results should be referenced to that of the initial wettability in order to have a reliable interpretation (Denekas et al. 1959 and Ma et al. 1999).

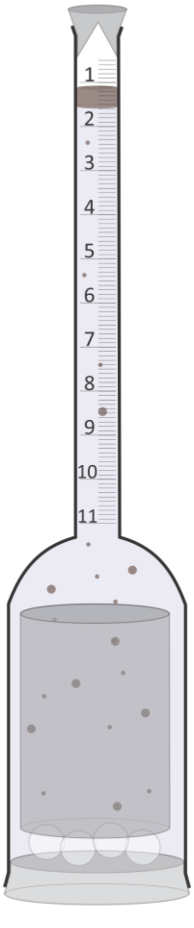

Figure 9 Spontaneous Imbibition Amott cell

2.5 Adsorption processes in polar crude oil components

Intermolecular interactions at phase boundaries often cause adsorption processes in porous media, which can significantly affect wettability and capillary forces. According to IUPAC, the definition of adsorption is a surface phenomenon in which particles or molecules (as of gases, solutes or liquids) bind to the top layer of material with which they are in contact. For reservoir hydrodynamics, the processes of adsorption of polar crude oil components on rock mineral surfaces are crucial (Anderson, 1986).

According to the Saturate, Aromatic, Resin, and Asphaltene (SARA) classification, polar components are often found in the asphaltene and resin fractions of crude oil. Additionally, water is always present in oil reservoirs, its impact on adsorption is a critical feature of asphaltene-rock interactions (Buckley, 1998). The presence of an electrical charge is indicated by the polarity of the molecules, therefore polar crude oil components may interact with one another and be adsorbed onto the charged mineral surfaces.

Previous work had been conducted on adsorption of crude oil components on both carbonate pure chalk outcrop and sandstone silica mineral outcrop rocks (Puntervold et al., 2021). The results of the research showed a correlation between the core minerology and which polar components were adsorbed. The pure chalk outcrop showed preference for acidic polar components, whilst sandstone outcrop showed increase affinity towards the basic polar components. The adsorption of the POC reduced the water-wetness and is confirmed by conducting the oil recovery test by spontaneous imbibition on all cores. Therefore, the mineral compositions of the rock surface affect greatly on the adsorption of POC and determining wettability.

Another previous research where dynamic adsorption was performed by flooding modified crude oil with a low asphaltene content through sandstone outcrop cores (Mamonov et al., 2019). The results showed that the basic components were more reactive towards the silicate rock mineral surfaces. It contained minerals that was so reactive that equilibrium was not reached even after 10 PV of crude oil injected. Oil recovery by spontaneous imbibition was performed to show the affect of crude oil adsorption on the wettability. The results showed that the core sample was in a fractional, slightly water-wet state after crude oil flooding.

Buckley and Liu (1998) described four mechanisms by which polar crude oil components affect wettability. Acid/base interactions, polar interactions, surface precipitation, and ion binding between charged sites and higher valence ions are examples of these processes. Based on their research, they also proposed that the API gravity, acid number, and base number, or G-AB parameters, can be used to assess the potential for wettability change in a given oil.

2.5.1 Acid/base interactions

When water is present in the system, adsorption by acid/base interactions occurs, resulting in charged oil/brine and brine/rock interfaces as a result of acid/base dissociation. Acid/base interactions can be used to modify wettability in two ways. The opposite charge of the rock mineral surfaces causes the water film to breakdown and oil components to adsorb at the oil/brine interface. Since sandstones minerals are negatively charged above the pH of 2, the components that can most readily adsorb are positively charged protonated bases (Anderson, 1986a). Acid and base numbers offer some insight into a particular oil's ability to modify wetting by ionic interactions (Buckley et al, 1998b). Oils with a high acid or base number, but not both, tend to be the most effective in changing wetting via ionic interactions. Acid/base interactions with a sandstone surface can be maximized by a high base number and a low acid number, and studies have shown that as the base to acid number ratio rises, the system becomes more oil-wet (Buckley and Liu, 1998; Hoeiland, 2001).

2.5.2 Polar Interactions

The adsorption of polar components containing NSO-compounds and polar active sites on the rock is perhaps the most common adsorption mechanism in the absence of a water film between the oil and the rock. The binding mechanism itself depends on a number of parameters such as, type of clay, exchangeable cations on the clay mineral surfaces, the nitrogen content in the oil, and the solvent used to dissolve the polar components.

2.5.3 Surface precipitation

Due to the crude oil's inadequate capacity to serve as a solvent for the asphaltene fraction, surface precipitation occurs. API gravity and refractive index are two parameters that can be used to determine how easily an oil can dissolves asphaltenes.

2.5.4 Ion binding

Ion binding is a category of adsorption in which cations, such as Ca^{2+} act as bridges between negatively charged components, allowing components with the same charge as the rock surface to contribute to altering wettability, such as acidic component adsorption on sandstone. In the wettability alteration process, oil with a high acid number and a low base number is dependent on ion binding, and the concentration of divalent ions determines the recovery (Buckley and Liu, 1998).

Chapter 3. Smart Water in Sandstones

3.1 Factors affecting Wettability

Understanding wettability and its relation to EOR is a challenging task, and many resources and efforts have been dedicated to it around the world. The complexity of a crude oil/rock/brine system lies in the various interactions of the three phases. In addition to obtaining an appropriate physical description of the rock, each phase has several components that can affect wetting. Porosity, permeability, and pore size distribution are all included. The chemical composition of brines and oils is critical since they determine the system's wetting conditions as they interact with the rock (Anderson, 1986). The wetting state of the mineral surfaces can vary depending on the process of adsorption or desorption of polar components. The main parameters that influence these processes are mineralogical composition, brine composition, crude oil composition and pH. Additionally, other parameters such as temperature and pressure also contribute to the process of adsorption and desorption of the oil components.

3.1.2 Mineralogical composition

Mineral composition varies greatly between rock types, which has a direct effect on the nature of the rock's surface charge and is thus critical in determining the reservoir's initial wetting state. Sandstone reservoirs are mainly composed of quartz and feldspar minerals, the matrix is made up of these minerals, which are held together by secondary minerals called "cement," which forms after the sandstone matrix is deposited. These secondary minerals for instance anhydrite, dolomite, and non-swelling clay minerals such as kaolinites, chlorites and illites (Hilner et al., 2015). Clays are considered to represent an important part in the success of the smart water flooding process because of their large specific surface area compared to matrix-forming minerals (Zhang and Morrow, 2006). When it comes to wetting, surface area is very important; a larger surface area means more adsorption capacity. Quartz is the most abundant mineral in sandstones, nevertheless its small surface area and low CEC means that it has little impact on chemical CoBR interactions in sandstone reservoirs. Clays are the main wetting mineral in sandstone because of their permanently negatively charge surface at relevant pH conditions, high CEC, and large surface area, which are adsorbed by polar organic components from crude oil. Clays tends to swap cations with other cations of the fluids in the pore space, which makes them act as cation exchangers. The reason is due to the deficiency in their positive charge, and if the clay particles are to remain electrically neutral then they must be balanced by cations from the surrounding formation water (Lake et al., 2014).

3.1.3 Crude Oil

Crude oil is primarily made up of heavier components such as paraffinic, naphthenic, and aromatic hydrocarbons and thought to carry compounds with various functional groups containing oxygen, nitrogen and sulphur atoms (Denekas et al., 1959). The acidic and basic nature of charged polar components in crude oils are determined by these compounds, and can adsorb on mineral surfaces with active adsorption sites. The amount adsorbed depends on the crude oil, brine and mineral compositions, where the wettability is influenced by the adsorption of crude oil components at the interface between the mineral surfaces and liquid compositions. Both acidic and basic polar organic components that has been adsorbed can be quantified by acid number (AN) and base number (BN), and one way to measure the amount is by the acid and base number analysis, where the unit measured in is mg KOH/g. In measuring AN, the amount of KOH needed to neutralize the acidic components in a gram of oil is the unit of measurement in AN analysis. Whilst the unit for BN measurement is the equivalent concentration of basic organic material found in one gram of crude oil. Potentiometric titration is a commonly used technique for estimating these measurements. The American Society for Testing and Materials (ASTM) developed standardized workflows, which have undergone many revisions over time (Torrijos, 2017). In crude oils, the acidic polar components are primarily represented by the carboxylic group, –COOH and the basic polar components is characterized by nitrogen-containing aromatic molecules, R_3N: shown in the following equation:

Acidic material $$\boldsymbol{R-COOH} + H_2O \rightleftharpoons R-COO^- + H_3O^+ \tag{7}$$

Basic Material $$R_3N: + H_2O \rightleftharpoons \boldsymbol{R_3NH^+} + OH^- \tag{8}$$

At the oil-water interface, there is an abundance of these components, which may undergo acid-base reactions and are prone to rapid proton exchange reactions, in other words accept or release protons, H^+. At lower pH values, their presences is favoured. Since both carboxylic acids and protonated bases have a pKa approximately of 5, therefore the pH variation is the same. As a result, both basic and acidic POC will adsorb on negatively charged clay minerals, but protonated polar components such as $\boldsymbol{R-COOH}$ and $\boldsymbol{R_3NH^+}$, have the strongest affinity towards silicate mineral surfaces. Through geological process and temperature, the carboxylic functional group typically decomposes with time, as oppose to basic material where it is more resistant to decomposition (as it is more stable because it is part of the aromatic materials), therefore crude oil samples often have BN values greater than AN (Torrijos, 2017).

3.1.4 Brine Composition

The concentration of divalent and other multivalent ions, salinity and pH are amongst the most important brine properties that can influence the wetting process (Anderson, 1986) where the surface charge of the minerals and the fluid interface is strongly affected, resulting in determining the wettability. Because a charge-balanced surface is needed, the presence of clays and other silicates that can interact with the brine through cation exchange processes is crucial. The wetting state of the system will be determined by the different degrees of affinities produced by CoBR interactions, where electrolytes in the aqueous solution, polar components, and hydrogen ions present in the water will compete for adsorption sites. The pH of the formation brine determines the reactivity of the surface's active organic components towards mineral surfaces, especially in clays, where this impacts greatly in the initial wetting properties of the reservoir (Madsen and Lind, 1998). The salinity of formation brine ranges from 10.000 ppm to 250.000 ppm and contains common ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} thus depending on the concentration of cations, it can react with anions such as Cl^- in the system (Strand et al., 2016).

3.1.5 Temperature

It has been established that as pressure and temperature rise, so does the solubility of polar active components in crude oil (Anderson 1986). When determining wetting conditions in a reservoir, temperature is a critical factor to consider. As the temperature rises, it can accelerate chemical reactions, allowing for a quicker chemical equilibrium establishment. Dehydration of divalent ions and increased adsorption are two effects of temperature on ion-reactivity.

3.1.6 Reservoir heterogeneity

Reservoir heterogeneity is defined as a variation in the reservoir properties as a function of space and location. In an ideal situation where the reservoir is homogenous, measuring reservoir properties at any location would represent the properties for the whole reservoir.

Therefore, reservoir description for a homogenous reservoir is a simple task. However, if the reservoir is heterogenous then the task of reservoir description will not be that simple. Reservoir properties such as permeability, porosity, thickness, saturation, faults and fractures, rock facies and rock characteristics may vary depending on spatial location for a heterogenous reservoir (Ahmed, 2006).

3.2 Low salinity EOR mechanism

A large number of laboratory tests conducted by Morrow and co-workers (Tang and Morrow, 1999a; Tang and Morrow, 1999b; Zhang and Morrow, 2006; Zhang et al., 2007b), as well as BP researchers (Lager et al., 2007; Webb et al., 2005a; Webb et al., 2005b), have shown that a tertiary low salinity waterflood, with salinity in the range of 1000-2000 ppm, will result in increased oil recovery. Low-salinity water may therefore be used as a smart EOR fluid in a sandstone oil reservoir. While it is now widely agreed that the LS EOR effect is primarily caused by changes in the rock's wetting properties, the mechanism for these wettability changes is still debated. Numerous attempts are still being developed to come to a mutual understanding. Several mechanisms have been proposed, some of which are mentioned below:

- Migration of fines (Tang and Morrow, 1999).
- Alkaline flooding as a result of pH rise (McGuire et al., 2005).
- Multi-component ion exchange at the clay mineral surfaces (Lager et al., 2007).
- Due to fines migration, the flow has been redirected microscopically (Skauge, 2008)
- Expansion of the ionic double-layer at the mineral surfaces (Ligthelm et al., 2009).

Previous research of a detailed chemical evaluation of water based EOR by wettability alteration was conducted (Strand et al., 2016). The chemical mechanisms are based on carrying out experiments of static adsorptions and dynamic studies at different temperatures and mineral properties of the core. The conclusion presented was that wettability alteration with Smart Water are mostly affected by the process of ion exchange at the surfaces, as well as the pH change when the salinity and the ionic compositions of the injected brine was modified.

Another previous research also confirms that to observe low salinity EOR effects in sandstones, a balanced initial adsorption of POC and divalent ions onto the clay mineral surfaces is important (Austad, 2010). For different types of clay minerals, both the adsorption level and the pH gradient for adsorption/desorption of organic materials reacts differently. An understanding of the chemical mechanism based on the brine compositions, oil properties and types of clay mineral present will determine the Smart Water EOR potential.

During LS/Smart Water injection, the chemical processes of wettability alteration can be divided into two main phases:

3.2.1 Establishing initial wettability:

The term "initial wettability" defines the wetting condition of rock surfaces when the porous medium is saturated with formation brine, crude oil and gases prior to waterflooding, and all phases have established chemical equilibrium. Microscopic-scale interactions at the crude oil-water interface will express the chemical equilibrium between crude oil and FW brine. At the oil-water interface, there may be a higher concentration of polar crude oil components, which can induce acid-base proton transfer reactions, i.e., accept or release protons, H^+ (Austad et al., 2010). Clays play an important role in clastic formations because of their large surface area and the presence of permanent localized negative charges. The point of zero charge for silicate minerals is about pH 2-3, implying that silicates would be negatively charged above pH 2-3 (Kosmulski, 2011), though the actual reservoir pH is usually in the range of 5-9 (Strand et al., 2016). Clays have the highest affinity for crude oil components due to these characteristics, thus they are the primary wetting mineral in a clastic formation. Due to dissolved acidic gases like CO_2 and H_2S, the pH of formation water is about 5 at reservoir conditions. At this pH, clay minerals act as cation exchangers, allowing protonated acidic and basic crude oil components, as well as cations from formation water (FW), to be adsorbed. The nitrogen-containing aromatic molecules, R_3N: with reactive pairs of electrons, of the pyridine form, can be described as the basic material in crude oils. The carboxylic group, –COOH, is the most common representation of acidic content (Strand et al., 2016).

Basic Components Alkaline pH Acidic pH

$$R_3N: + H_20 \leftrightarrow \boldsymbol{R_3NH^+} + OH^- \tag{9}$$

Acidic Components Alkaline pH Acidic pH

$$\boldsymbol{R - COOH} + H_2O \leftrightarrow RCOO^- + H_3O^+ \tag{10}$$

Adsorption of polar components on clay minerals is a pH-dependent process, interface reaction is shown in equations… In the acidic region of pH less than 7, basic material, R_3NH^+, can be adsorbed onto the clay surface via electrostatic interaction, whilst protonated acidic material can interact and be adsorbed by hydrogen bonding (Madsen and Ida, 1998, Burgos et al., 2002). Additionally, Ca^{2+} and other divalent cations are effective adsorbing cations. Calcium plays an important role in initial wetting since a high Ca^{2+} concentration can displace some H^+ from the clay surface at water-wet sites, resulting in a pH decrease that can increase the adsorption of polar components, reducing the water wetness (RezaeiDoust et al. 2011). Since the hydration number decreases as the temperature rises, temperature may also increase the reactivity of divalent ions like Ca^{2+} or Mg^{2+} (Zavitsas, 2005). This effect will result in increased Ca^{2+} adsorption on the clay surface. As a result, at a given reservoir temperature the overall interaction of active surface species distributed on the clay surface will be determined by the pH conditions, thus will dictate the species' relative affinity for the clay minerals. The degree of oil wetting will be determined by the affinity of polar components in particular temperature, pH, and brine composition/salinity conditions; these are the components that will effectively initiate oil wetting on the surface. Adsorption of positively charged protonated organic species and inorganic cations from pore fluids onto negatively charged silicate surfaces can thus be used to express the chemical equilibrium between rock minerals and formation fluids. The organic components of crude oil serve as trigger molecules for wetting rock surfaces in this process, and thus the initial rock wettability state is determined by the amount of adsorbed polar molecules. The illustration in Figure 10 shows a diagram displaying various components adsorbed on clay mineral surfaces.

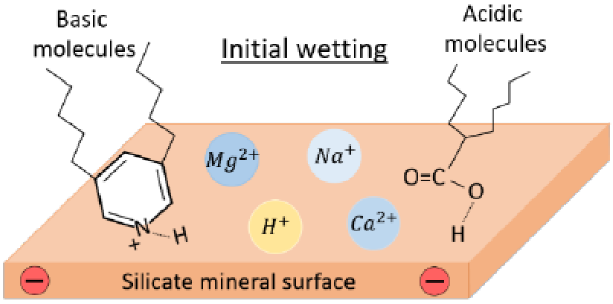

Figure 10. Different components adsorbed on the mineral surfaces (Mamonov 2019, (redrawn after Strand et al., (2016)).

3.2.2 Wettability alteration by Smart Water Injection

The chemical equilibrium associated with the FW–rock interactions is disrupted when the LS brine with much lower ion concentrations is injected into the reservoir, resulting in desorption of cations, especially Ca^{2+}, resulting in a local pH increase near the clay-brine interface. The desorption of polar organic components from the clay surface is illustrated in Figure. From the absence of active cations in the LS brine, Protons H^+, from the brine near the surface are adsorbed on to the clay surfaces replacing $Ca^{2+,}$ this creates an increase in pH close to the clay surfaces which is caused by a decrease in H^+ in the FW, in order to balance the negative charges on the surfaces and maintain equilibrium, the process is described in equation 11 using Ca2+ as an example:

Slow reaction: $$clay - ca^{2+} + H_2O \leftrightarrow clay - H^+ + Ca^{2+} + OH^- + heat \tag{11}$$

Adsorbed organic molecules undergo ordinary acid-base proton transfer reactions, resulting in a local increase in pH near the clay surface. The organic material is desorbed from the clay surface by a fast reaction between OH- and the adsorbed acidic and protonated basic material shown in equation 12 and equation 13 below:

Fast reaction: $$clay - R_3NH^+ + OH^- \leftrightarrow clay + R_3N\colon + H_2O \tag{12}$$

Fast reaction: $$clay - RCOOH + OH^- \leftrightarrow clay + RCOO^- + H_2O \tag{13}$$

As the surface becomes more water-wet, an increase in recovery may be seen. The chemical equations 11-13 may be used to represent the chemical wettability alteration mechanism. Changes in pH have a significant impact on the adsorption of basic and acidic materials onto clay minerals. As a result, the key process in increasing the pH of the water that is localized close to the clay surface is the desorption of the initially adsorbed cations onto the clay surfaces. To remove or desorbed some of the adsorbed organic material on the clay surface, a pH increase is needed. An illustration of the mechanism is presented in Figure 11 for adsorbed basic and acidic material.

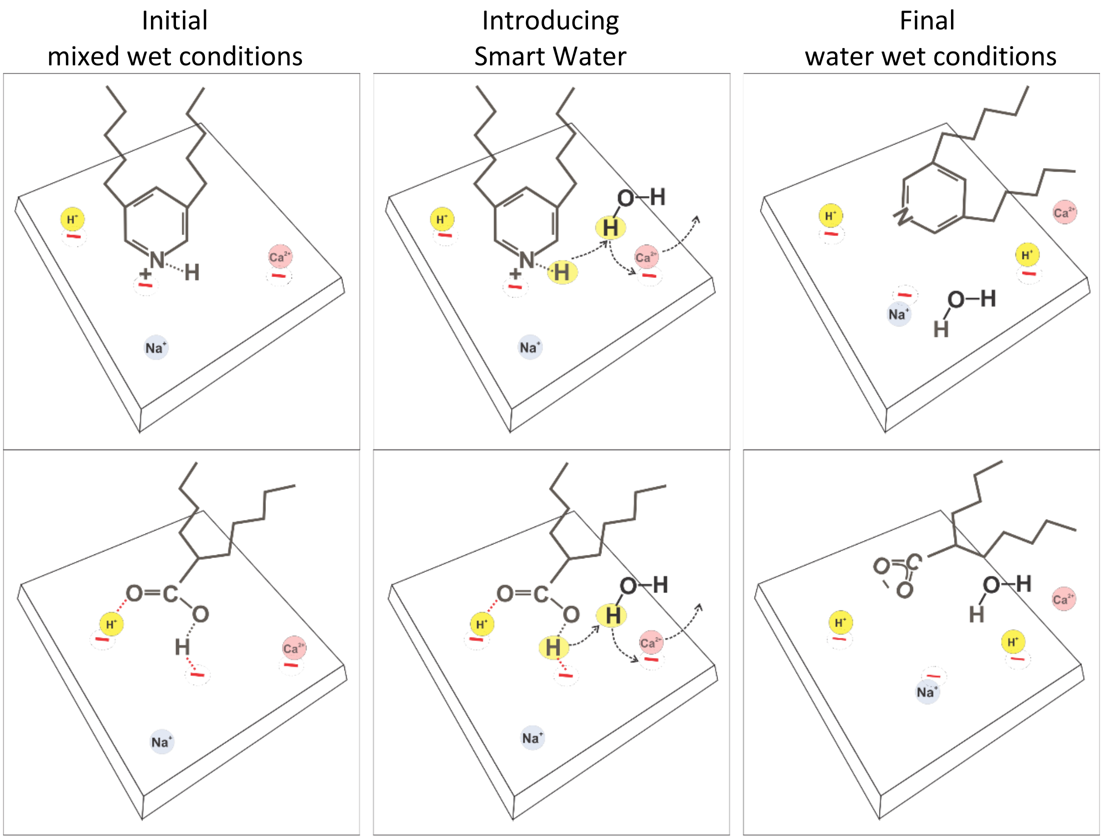

Figure 11 Illustration of LS Smart Water EOR mechanism in sandstone reservoir from initial situation to final situation (Austad et al., 2010).

3.2.3 Parameters that impact low salinity EOR effect

The conditions for observing low salinity effects are largely based on Tang and Morrow's comprehensive experimental work (Tang and Morrow, 1999a), but some observations from BP researchers are also included (Lager et al., 2007; Lager et al., 2008a).

- Porous medium
  - Clay minerals must be present in sandstones
- Oil
  - Polar organic components must be present (acids and bases)
- Formation water
  - Divalent Cations must be present in the formation water, i.e Ca^{2+}, Mg^{2+}
  - Initial water saturation, Swi, impacts efficiency
- LS injection fluid
  - The range for salinity should be approximately 1000-2000 ppm, but salinity at 5000 ppm has also showed effects.

- Produced water
  - The pH of the LS effluent samples increases 1-3 pH units after switching from formation water flooding.
  -

Each sandstone mineral has its own reactivity to formation fluids and therefore must be considered separately. Furthermore, the role of specific minerals in Smart Water EOR processes can be influenced by reservoir conditions. The parameters that could affect the LS EOR by influencing the initial wetting conditions and the wettability alteration process are temperature, ion composition and salinity of brine, and minerology.

Chapter 4. Experimental Procedures

A systematic diagram in Figure 12 shows the experimental procedures conducted on the cores and is explained in details below. Starting from establishing S_{wi} and ending in SI test to observe the oil recovery.

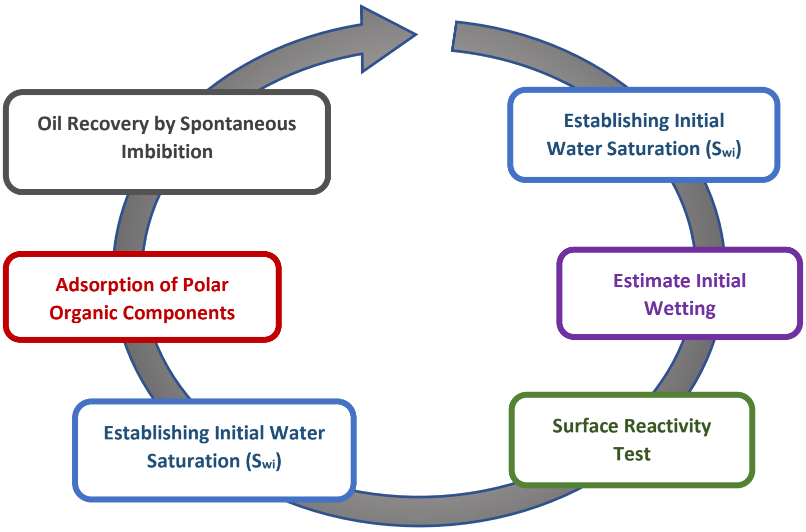

Figure 12 Diagram flow of the experimental steps

4.1 Experiment materials

4.1.1 Rock Materials

Three sandstone cores were used in experimental studies, outcrop cores Leopard-1 (LP1), Leopard-2 (LP2) and reservoir core Varg 9S2 (VG1). X-ray diffraction (XRD) analysis of the core samples were carried out to determine the mineral compositions, specifically the clay contents. Table 2 shows the core mineral composition of the different core samples, and Table 3 displays the physical properties obtained on the core samples:

Table 2. Mineral composition of the different cores

Core	**Mineral Composition (wt%)**							
	Quartz	**K-Feldspars**	**Plagioclase**	**Kaolinite**	**Illite + Mica**	**Calcite / Dolomite**	**Other**	**Sum**
Leopard	67.6	5.6	8.7	1.1	9.5	0.6	6.9	100
Varg 9S2	62.3	4.5	8.4	1.1	15.4	-	8.3	100

Table 3. Physical properties obtained for the different cores

Core	**Weight (g)**	**Diameter (cm)**	**Length (cm)**	**PV (ml)**	**Porosity (%)**	**Permeability [mD]**	**BET (m^2/g)**
LP1	147.47	3.81	6.27	14.02	19.62	220	2.45
LP2	143.75	3.72	6.14	13.97	20.94	1372	
VG1	166.16	3.8	7.73	18.67	21.30	11	3.01

4.1.2 Crude oils

Adsorption tests were conducted in order to compare the adsorption affinity for POC using a modified crude oil that is made by mixing of 3 different crude oils with known acid number (AN) and base number (BN). By calculating different mixing ratios 73.8 wt% of Res40, 9.4 wt% of Varg oil and 16.7 wt% of Res40-0. The crude oils resulting oil had AN = BN = 0.2 mg KOH/g. This value is sufficient to detect adsorption as well as to reduce analytical uncertainties. The oil mixture-1 was used in crude oil flooding with the Leopard-1 and Varg core, whilst the modified total crude oil was used on the Leopard-2 core. The crude oil mixture did not show asphaltene precipitation when left for storage.

Table 4. The physical and chemical properties of the different crude oils used

Crude Oil	Density at 20°C (g/cm^3)	AN	BN	Absolute Error
		Mg KOH/g		
OM1	0.81	0.23	0.23	±0.02
OM2	0.80	0.20	0.20	

4.1.3 Brines

The synthetic brines used in the experiments were FW brine and low salinity (LS) brine. The brines were prepared, and filtered through a 0.22 um millipore filter. Both FW and LS brines were used to perform the surface reactivity test and as the imbibing brines for the spontaneous imbibition (SI) oil recovery tests. Ionic composition and properties of the brines are listed in Table 5:

Table 5. The compositions and properties of different brines used

Brine	Ion composition (mM)			Salinity, ppm	Bulk pH
	Na^+	Ca^{2+}	Cl^-		
FW (50.000 ppm 20 Ca)	817.6	20	857.6	50 000	6.30
LS (1000 ppm)	17.1	0	17.1	1000	6.88

4.2 Methods

Core cleaning

Reservoir core sample VG1 was cleaned with toluene and methanol prior to surface reactivity test and adsorption test. Cleaning was performed to obtain more water-wet state. Outcrop cores LP1 and LP2 were used in experimental studies without additional cleaning.

Surface reactivity test

Both sandstone outcrop and reservoir cores were used in surface reactivity test to determine ion-exchange interactions between rock minerals and injected brines. The core was placed in a temperature-controlled Hassler core holder with conditions such as temperature of 60°C, confining pressure of 20 bar, backpressure of 10 bar and injection rate of 0.1 ml/min. After flooding with both FW and LS brines at a 4 PV per day, pH values of effluent samples were collected and analysed at room temperature. The test was performed by 100% saturating core with FW and flooding with FW until stable effluent pH. When effluent pH values of FW were stable, the injection brine was switch to LS Smart Water. After reaching pH plateau with LS, injection brine was switched to 5 times diluted FW (FW 5xD) with 3 different injection rates (0.5, 1 and 2 ml/min) to determine absolute permeability.

Initial water saturation

The desiccator technique was used to establish the initial water saturation of close to 20% (Springer et al., 2003). For that the core was saturated 100% with FW 5xD and then water was evaporated until reaching desired weight of core with S_{wi} ~ 20%.

Initial Wetting

To estimate the initial wetting, the cores with S_{wi} ~ 20% were saturated with heptane (C_7H_{16}) and placed in an Amott imbibition cell and spontaneously imbibed with FW prior to crude oil adsorption test. The tests were performed at 60°C and continued until no heptane production was observed.

Crude oil saturation

After re-establishing initial water saturation of approximately 20%, the cores were inserted into a temperature-controlled Hassler core holder, under the stable conditions of temperature reaching 60°C, confining pressure of 20 bar and backpressure of 10 bar. When the system has reached 10 bars, the core was flooded with a volume of 10 PV predetermined crude oil mixture with known AN and BN values at a rate of 0.1 ml/min in order to develop oil saturation. The autosampler (fraction collector) collected the effluent oil samples produced after crude oil flooding in an airtight sample glasses, where it can undergo further testing. The schematic illustration of the experimental setup is shown in Figure 13.

Adsorption of POC

The effluent oil samples are then analysed on BN values for every odd sample and AN value for every even sample by potentiometric titration using a Mettler Toledo T50 auto-titrator. The methods used were developed by Fan and Buckley (Fan and Buckley, 2007) and are modified versions of the standard methods ASTM D664 for AN titration and ASTM D2896 for BN titration. The reproducibility of both AN and BN measurements was ± 0.01 mg KOH/g. The AN and BN of the produced crude oil were then plotted as a function of PV crude oil injected. The difference between each AN or BN bulk and effluent AN or BN values is the amount of POC adsorbed. The higher the difference or the bigger the gap therefore the more the mineral surfaces are reactive towards the POC which suggests better adsorption.

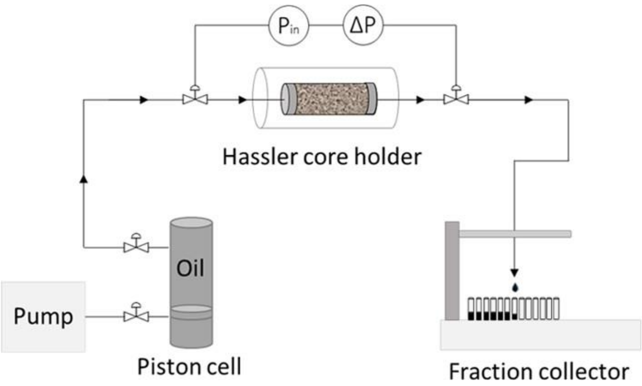

Figure 13 Illustration of the setup used for core flooding (Puntervold et al., 2021)

Oil recovery tests by spontaneous imbibition (SI).

After crude oil adsorption tests, the cores were placed in an Amott cell for SI oil recovery at 60^{o}C. The amount of recovered oil was recorded and plotted as a function of time. The SI method provides the effect of the capillary and gravity forces therefore, the total amount of the capillary-driven oil produced can be observed. Once the oil recovery reached a plateau and no more oil is produced, the imbibing brine was switch to LS in order to promote wettability alteration to a more water-wet state in favour of improving in the oil recovery and observing the potential of an ion-modified LS smart water effect.

Chapter 5. Experimental Results

One of the many methods of oil recovery is waterflooding, other than its purpose of giving pressure support, it also can improve the fluid flow through the porous media. This method can increase the displacement efficiency depending on the chemical and physical interactions of the brine, crude oil and mineralogy phases. Each phase is complex because it contains variation in species, therefore in reality when these phases interact with one another in reservoir conditions, it furthers the complexity and uncertainties.

Laboratory analysis can cover these aspects such as surface reactivity tests where it demonstrates the chemical interactions between the surfaces of the pores within the rocks and the ionic composition of the brine. A series of experiments were conducted such as estimate initial wetting using non polar component oil, adsorption of polar organic components and its effect on wettability by measuring and comparing acids and bases. Then finally observe the smart water EOR effect in sandstone cores.

5.1 Outcrop Leopard-1

The properties of the outcrop LP1 are shown in Table 3. The interaction between the brine and mineral surfaces determines the initial pH at reservoir condition prior to crude oil exposure. Interactions such as cation exchange between clays and other silicates with the brine is an important process in order to maintain a charge balance on the rock surface.

Surface reactivity test was performed to determine pH measurements during FW and LS flooding. The pH of the influent and effluent samples were taken for each brine as a function of PV injected and then plotted shown on Figure 14.

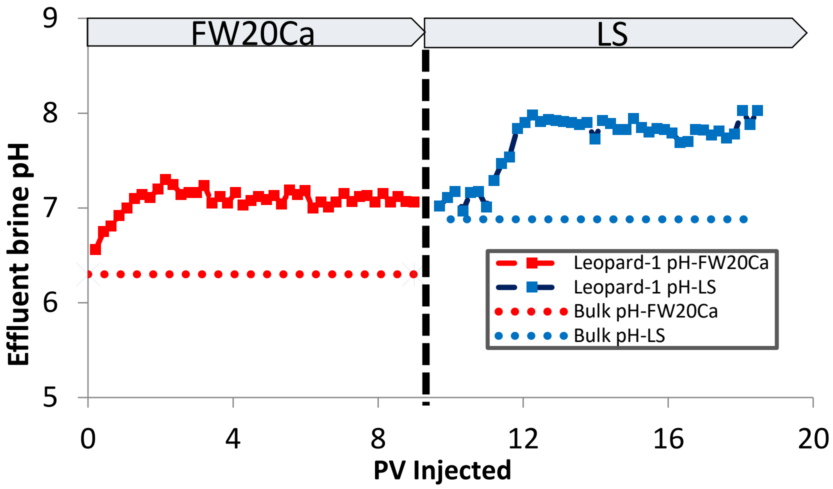

Figure 14. pH screening test on LP1 with flooding sequence 4 PV/ day of FW then switch to LS with temperature 60°C

The pH measurement with FW flooding of the first effluent sample at 0.21 PV is 6.56, it gradually increases reaching a peak pH value of 7.30, furthermore it becomes consistent at an average pH value of 7.06 within 9 PV injected. Switching to LS flooding, the effluent sample at 9.70 PV has a pH value of 7.02, after which shows a steep increase reaching a pH value of 7.98 at 12 PV and decreasing slightly where it finally somewhat increases again reaching pH value of 8.03 at almost 19 PV.

Determining absolute permeability was performed by flooding diluted 5 times formation water at 3 different injection rates, which are 0.5 ml/min, 1 ml/min and 2 ml/min as shown in Figure 15.

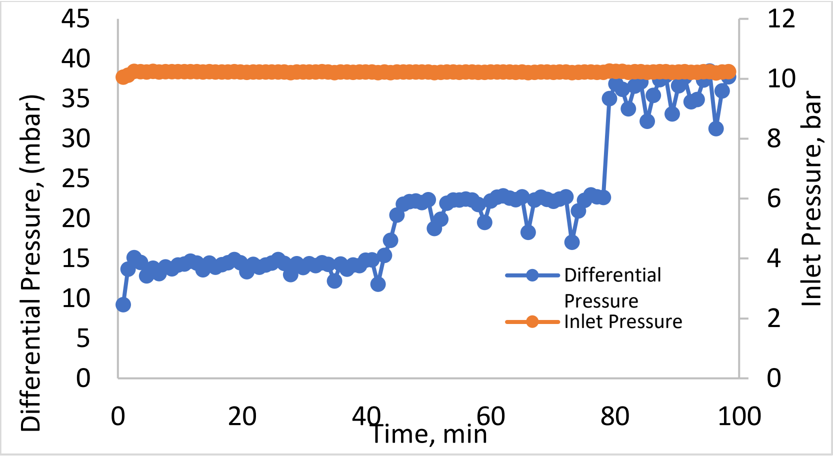

Figure *15* Permeability test on LP1 at 60°C with three different injection rates of 0.5, 1 and 2 ml/min

Table 6. Different properties obtained to determine permeability for LP1

Salinity (ppm)	**Temperature (Degrees °C)**	**Density (gr/cm^3)**	**Viscosity (cP)**	**Injection Rate (ml/min)**	**Differential Pressure (mBar)**	**Absolute Permeability (mD)**	**Average permeability (mD)**
10.000	60	0.9902	0.478	0.5	14.8	150	205
				1.0	22.4	211	
				2.0	37.0	256	

After the pH was measured and permeability calculated, the core underwent further testing to estimate the initial wetting condition prior to crude oil flooding. This is done by a similar SI test with the core established S_{wi} ~20%, saturated with heptane and FW as the imbibing fluid. The results in Figure 16 shows that there is an instant high imbibition rate reaching to 29% in heptane recovery at the first 15 minutes and then reaching a plateau of 36% in the next 2 days. The steep slope at the beginning indicates the capillary region which confirms strong positive capillary forces, and the high recovery itself showing water-wet behaviour.

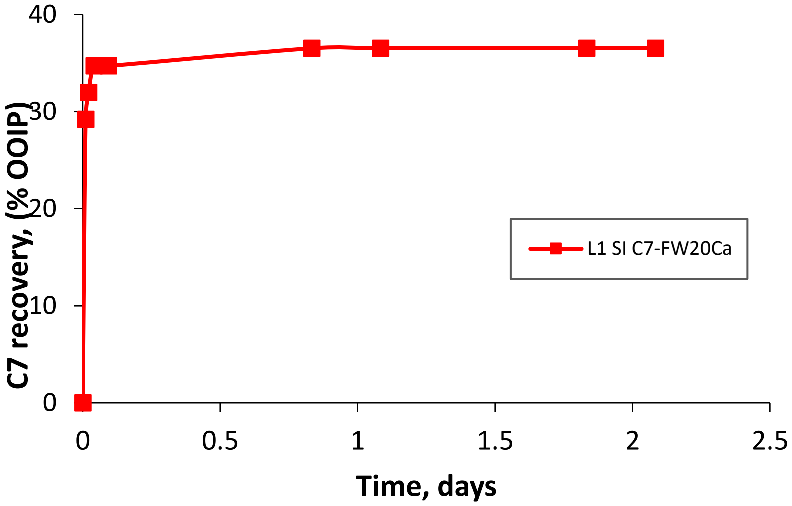

Figure 16. Heptane recovery by SI test on LP1 with Swi= 22% with FW, at 60°C to estimate initial wetting

The next procedure in the experiment was to carry out crude oil flooding. The core with established S_{wi} of 21% with FW was flooded 10 PV of predetermined crude oil in order to create oil saturation. The initial core wettability can be influenced by increasing the amount of crude oil injected, which can result in a less water-wet condition (Mamonov et al., 2019). Therefore, no more than 10 PV of crude oil should be flooded through the core. Flooding process was left for one night and the produced oil was collected in the auto-sampler to test

POC adsorption. The effluent samples were then analysed and the results are illustrated in Figure 17. The adsorption level is determined by the difference between the effluent oil BN and the bulk oil BN. The overall results show very low adsorption as there is slight decrease in BN values of the effluent oil BN compared to bulk oil. The most adsorption present was at ~4.9 PV where BN is 0.21 mg KOH/g, just 0.04 mg KOH/g decrease from the bulk BN of 0.25 mg KOH/g. This also led to very low adsorption. Adsorption equilibrium was achieved from the beginning, suggesting that hardly any retention of the basic POC with the pore surface mineral occurred. Furthermore, similar results are observed between the effluent oil AN compared to the bulk oil AN, where the highest decrease is at ~3PV with AN of 0.17 mg KOH/g, just 0.07 mg KOH/g difference from the bulk AN 0.24 mg KOH/g. There is a slight decrease at the beginning, but then reached equilibrium at ~9 PV injected. Both BN and AN exhibit similar results where slight adsorption occurred.

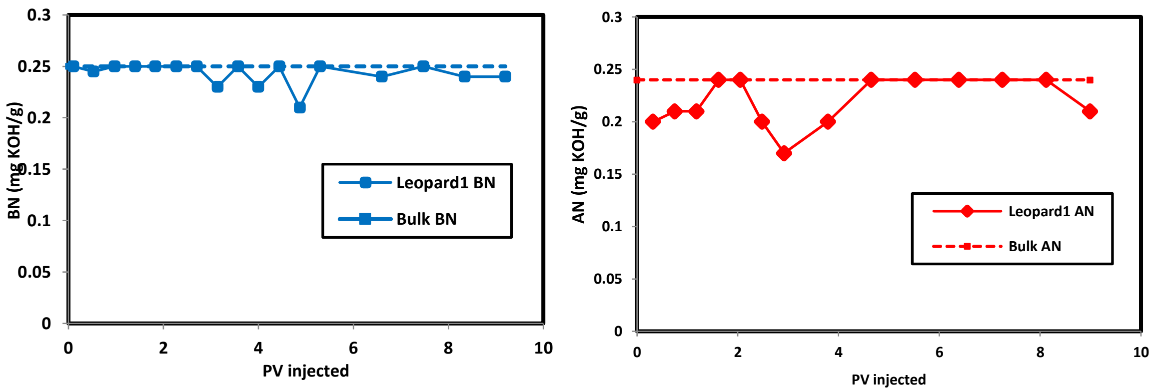

Figure 17. Adsorption test results on LP1, flooded at 60°C with OM1 with BN = 0.25 and AN = 0.24 mg KOH/g. Measure (left) base number (BN) and (left) acid number (AN) in effluent crude oil samples during the crude oil flooding. A total of 10PV flooded

After the core has been saturated by crude oil flooding, SI test was carried out with FW as the imbibing brine. SI was performed to test how the adsorption of the basic and acidic components affects the capillary forces and core wettability. Using the FW brine as an imbibition fluid is unlikely to alter wettability. Therefore, the oil produced during SI test with FW is an indicator of the degree of water wetness and the trendline should be similar to the results when estimating initial wetting with heptane recovery. On core samples, spontaneous imbibition is performed to estimate capillary action based on rock wetting condition, whereby the capillary forces drive the imbibition of the wetting fluid into the porous medium (Morrow and Mason, 2001). And the volume of oil produced that has been spontaneously imbibed will determine the wetting condition of the core. Figure 18 shows there is a sharp increase in the capillary-driven oil recovery in the first 24 hours at 23 % oil recovery, and continues to slowly rise until reaching a stable production of 34% oil recovery after 13 days. Furthermore, the imbibition rate is lower for that of the oil-FW compared to the C7-FW, suggesting that adsorption of the polar organic components did affect the capillary forces. Once there is no more production with FW, then the imbibing brine is switched to LS. The results displayed additional oil production reaching an ultimate recovery of 45% with a total of 27 days of imbibition.

When injecting smart water brine into the formation, the chemical equilibrium gets disrupted and results in a chemical imbalance. This may lead to a sequence of ion exchange reactions, resulting a rise in pH towards a more alkaline environment. The alkaline environment can trigger the formation of non-protonated components in the crude oil. The negatively charged sandstone minerals have a lower affinity towards the non-protonated components in the crude oil. When the initially adsorbed polar organic components undergo desorption, this may cause an alteration in wetting towards a more water-wet condition. This process can result in an increase in the capillary-driven oil production and improve in the ultimate recovery. The results obtained support the significance of capillary forces in oil recovery.

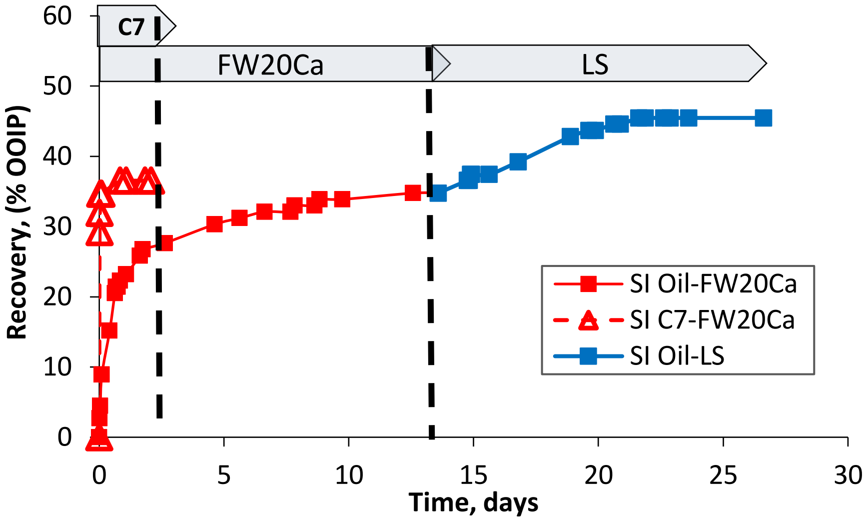

Figure 18. Oil Recovery Test by SI with different brines on LP1 core with S_{wi} = 21% at 60°C

5.2 Outcrop Leopard-2

The properties of the outcrop LP2 are shown in Table 3. The core underwent testing to estimate the initial wetting condition prior to crude oil flooding. This is done by a similar SI test with the core established S_{wi} ~20%, saturated with heptane and FW as the imbibing fluid.

The results in Figure 19 shows that there is a steep increase in heptane recovery of 43% at the first hour of imbibition and then reaching a plateau of 46% heptane recovery in the next 3 days. A high recovery of 46% indicates water-wet behaviour.

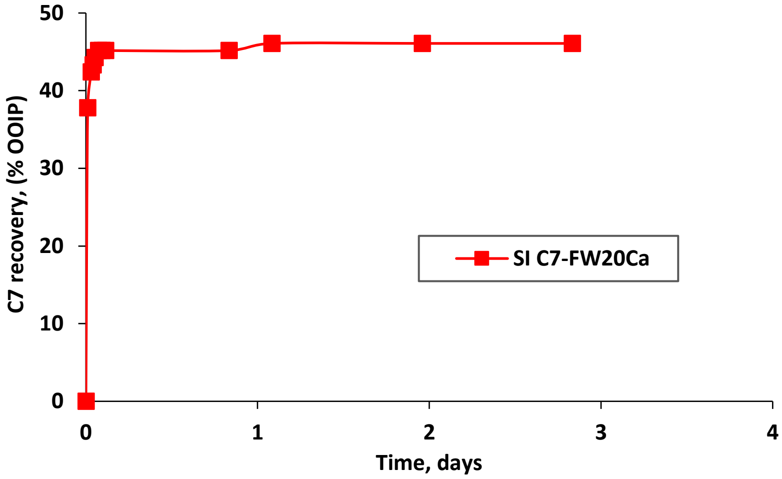

Figure 19. Heptane recovery by SI test on LP2 with Swi= 24% at 60°C to estimate initial wetting

Determining absolute permeability was performed by flooding diluted 5 times formation water at 4 different injection rates, which are 0.5 ml/min, 1 ml/min, 2 ml/min and 2.5 ml/min as shown in Figure 20.

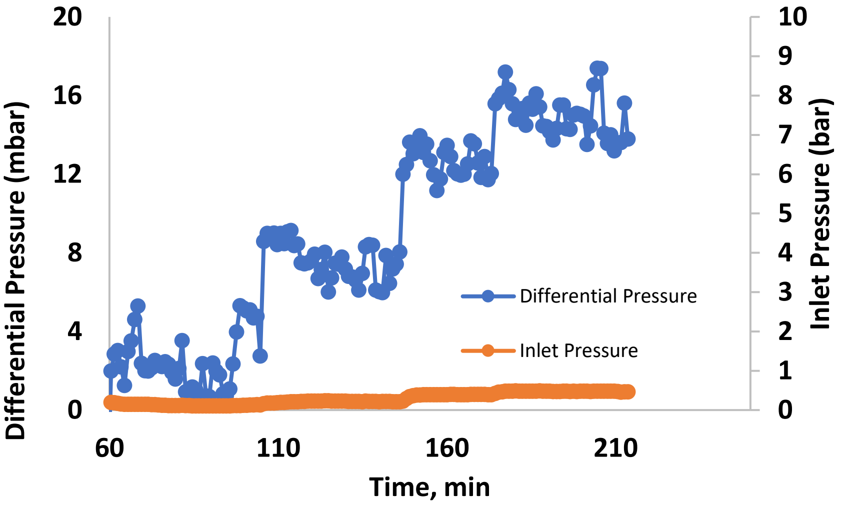

Figure 20 Permeability test at 20°C for LP2 with four different injection rates of 0.5, 1, 2 and 2.5 ml/min

Modified total oil of 10 PV was flooded through the core in order to create oil saturation after establishing S_{wi} ~ 20.94%. Adsorption test was carried out on the collected samples and the results are shown in Figure 21.

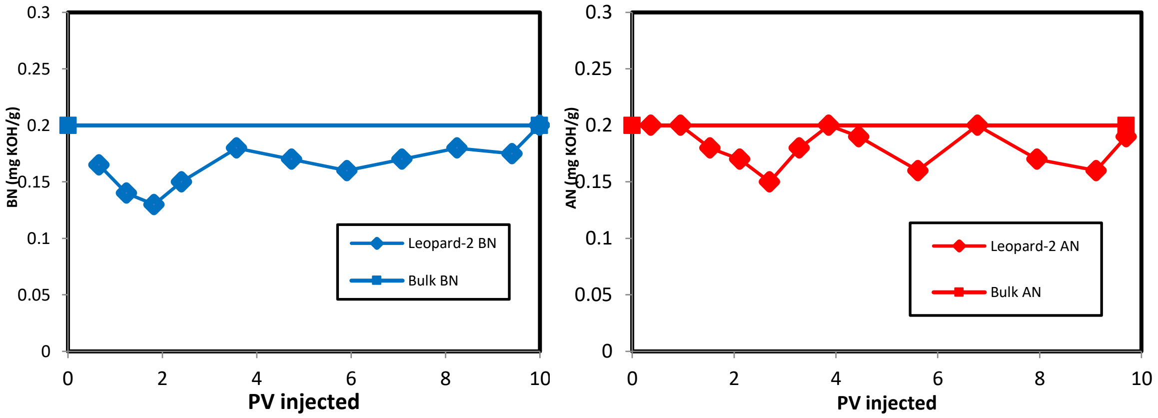

Figure 21 Adsorption test results on LP2 core flooded at 60ºC with OM2 with BN = 0.20 and AN = 0.20 mg KOH/g. Measure (left) base number (BN) and (left) acid number (AN) in effluent crude oil samples during the crude oil flooding. A total of 10PV flooded

The overall results show adsorption in both acid components and base components. Adsorption occurred instantly for the basic components and continues until equilibrium is achieved at ~10 PV injected, suggesting there is retention of the basic POC with the pore surface mineral. However, inconsistent results are shown between the effluent oil AN and bulk oil AN, where equilibrium is reached at different PV injected points. Both BN and AN show unlike results where AN displayed inconsistent adsorption whilst BN displayed consistent adsorption.

Spontaneous imbibition test is carried out with FW as the imbibing brine to test how the adsorption of the predominant basic components affects the capillary forces after the core has been exposed to oil. Figure 22 demonstrate that the oil-FW trend displays a sharp increase in the capillary-driven oil recovery in the first 24 hours at 42 % oil recovery, and continues to increase until reaching a stable production of 47% oil recovery after 12 days.

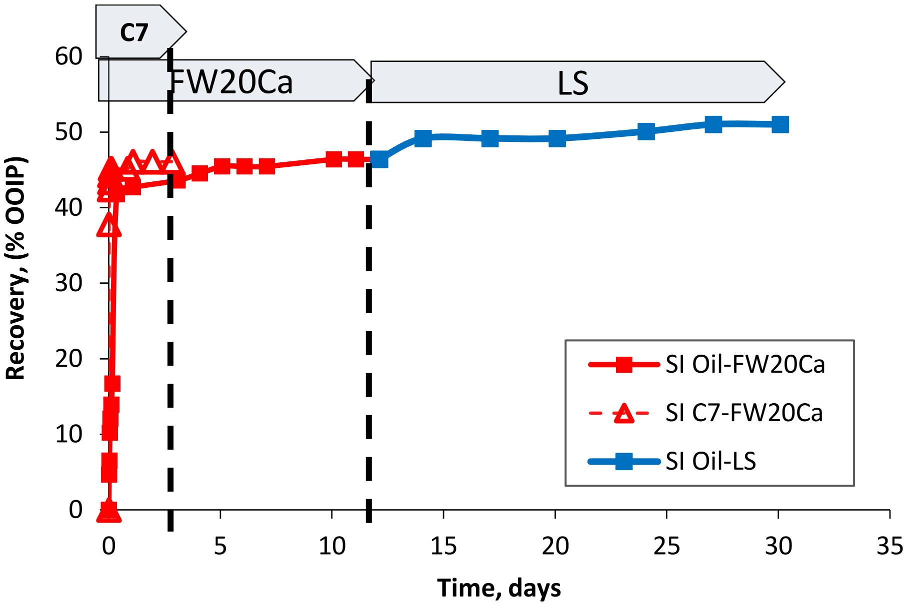

Figure 22 Oil Recovery Test by SI with FW and LS brines on LP2 core with Swi = 20% at 60ºC

Similar ultimate recovery percentage is observed between the C7-FW and oil-FW, though the imbibition rate is slightly lower for that of the oil-FW compared to the C7-FW. This suggests that adsorption of the predominant basic components may not affect the capillary forces. Once there is no more production with FW, the imbibing brine was switched to LS. The smart water effect is able to mobilise an additional 5% oil even though production is already high with the formation water, reaching an ultimate recovery plateau of 51% with a total of 30 days of imbibition.

5.3 Reservoir Varg Core

The properties of the reservoir core VG1 are shown in Table 3. The pH measurement shown in Figure 23 with FW flooding of the first effluent sample at 0.30 PV was 7.71, with increase amount of PV injected the pH shows fluctuations. Though the most basic pH was 8.44 at 2.45 PV injected. The average pH with FW flooding can be estimated around pH of 8.0.

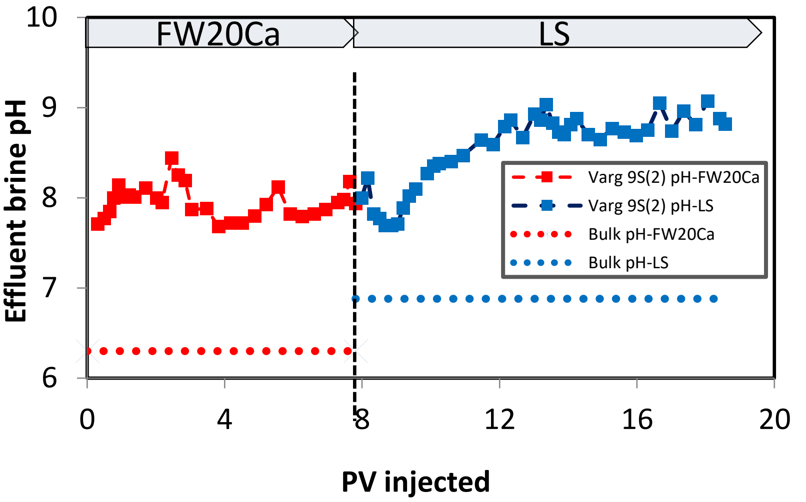

Figure 23. pH screening test on VG1 core with flooding sequence 4 PV/ day of FW then switch to LS with temperature 60°C

Switching to LS flooding, the effluent sample at ~9 PV has a pH value of 8.0, after which shows a fall in the trend reaching a minimum pH value of 7.69 at ~8.8 PV. From here, the trend gradually increases then fluctuates where the maximum pH Value was 9 at almost 18 PV.

Determining absolute permeability was done by flooding diluted 5 times formation water at 3 different injection rates, which are 0.11 ml/min, 0.19 ml/min and 0.39 ml/min shown in Figure 24.

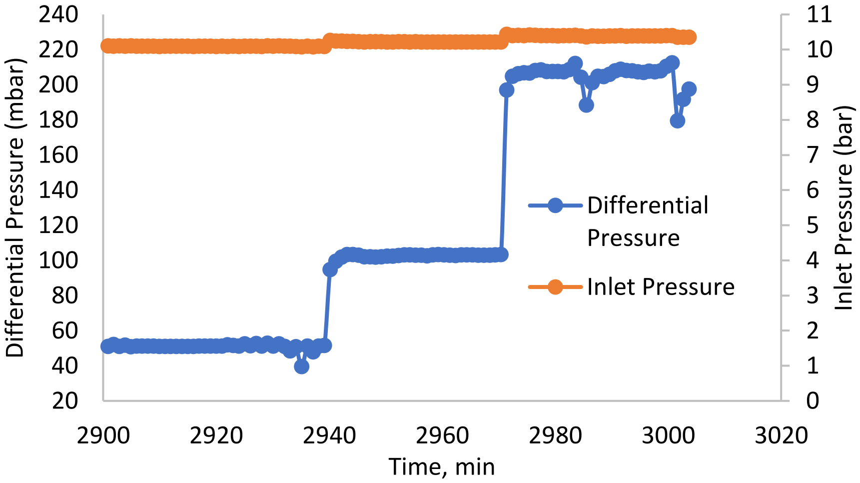

Figure *24* Permeability test at 60°C for VG1 core with three different injection rates of 0.1, 0.2 and 0.4 ml/min

Table 7. Different properties obtained to determine permeability for VG1

Salinity (ppm)	**Temperature (degrees °C)**	**Density (gr/cm^3)**	**Viscosity (cP)**	**Injection Rate (ml/min)**	**Differential Pressure (mBar)**	**Absolute Permeability (mD)**	**Average permeability (mD)**
10.000	60	0.9902	0.478	0.11	50	12.1	11
				0.19	102	10.2	
				0.39	207	10.4	

The core underwent further testing to estimate the initial wetting condition prior to crude oil flooding. The results in Figure 25 shows that there is an instant high imbibition rate reaching to 49% in heptane recovery at the first hour and then reaching a plateau of 55% in the next 12 days. The steep production at the beginning indicates the capillary region which confirms strong positive capillary forces, and the high recovery itself showing water-wet behaviour.

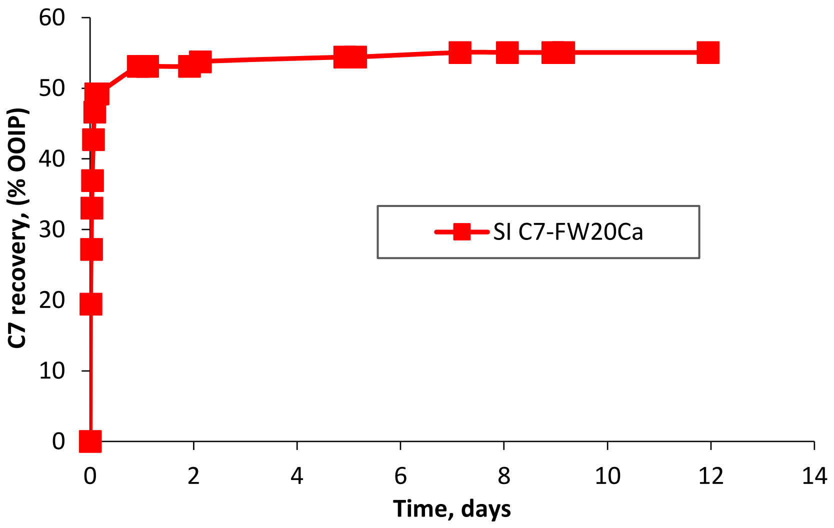

Figure 25 Heptane recovery by SI test on VG1 with Swi= 20% at 60°C to estimate initial wetting

Initial saturation was established at S_{wi} of ~19% with FW. Predetermined crude oil of 10 PV was flooded through the core in order to create oil saturation. Adsorption test was carried out on the collected samples and the results are shown in Figure 26.

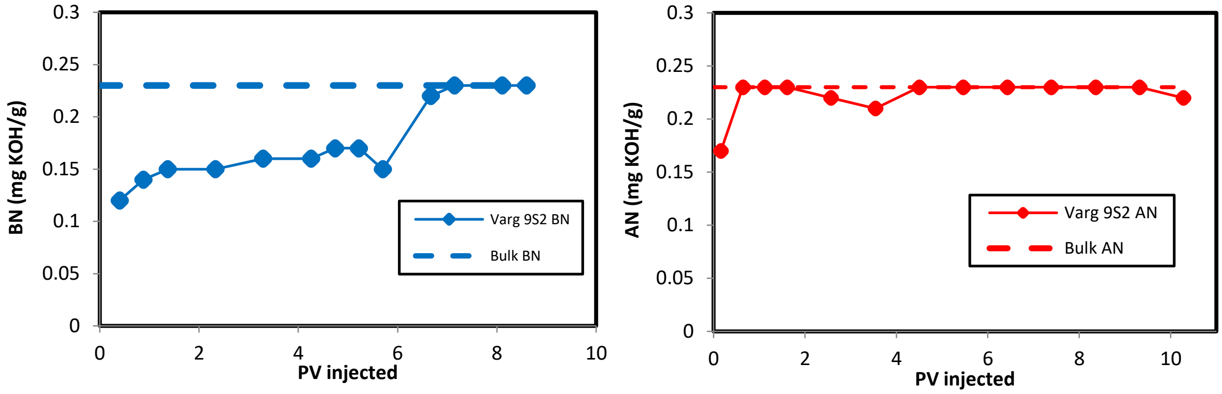

Figure 26 Adsorption test results on VG1 core, flooded with OM1 with BN = 0.23 and AN = 0.23 mg KOH/g. Measure (left) base number (BN) and (left) acid number (AN) in effluent crude oil samples during the crude oil flooding. A total of 10PV flooded

The overall results show low adsorption as there is slight decrease in AN value between the effluent oil AN value and bulk oil AN. The most adsorption present was at the beginning at 0.16 PV where AN is 0.17 mg KOH/g, just 0.06 mg KOH/g decrease from the Bulk AN of 0.23 mg KOH/g. And this too concluded very low adsorption. Adsorption equilibrium was achieved at different PV injected amounts of PV injected. The results show that hardly any retention of the acidic POC with the pore surface mineral occurred. However, contrary results are shown between the effluent oil BN and bulk oil BN, where there is an instant decrease is in the beginning at ~1PV with BN of 0.12 mg KOH/g, 0.11 mg KOH/g difference from the bulk BN of 0.23 mg KOH/g. The trend displayed a large decrease at first and then continuous adsorption of the basic components onto the mineral surfaces throughout the flooding until reaching an equilibrium at to 8.6 PV injected. Both BN and AN exhibit unalike results where AN displayed low adsorption whilst BN shows adsorption. Therefore, the basic components seem to be the predominant component as it appears to show strong affinity to the mineral surfaces. This will affect the cores wettability and determine the capillary forces within the pores.

After the core has been saturated by crude oil flooding, spontaneous imbibition test is carried out with FW as the imbibing brine to test how the adsorption of the predominant basic components affected the capillary forces after crude oil has been flooded. In Figure 27 the oil-FW trend displays a sharp increase in the capillary-driven oil recovery in the first 24 hours at

30 % OOIP recovery, and continues to slowly rise until reaching a stable production of 47% oil recovery after 21 days. There is a difference of 8% OOIP recovery between the C7-FW and oil-FW, which indicates there are still oil left in the core. Additionally, the imbibition rate is lower for that of the oil-FW compared to the C7-FW, suggesting that adsorption of the predominant basic components did affect the capillary forces. Once there is no more production with FW, then the process is switched to LS as the imbibing brine. The smart water effect is able to mobilise an additional 10% oil even though production is already high with the formation water, reaching an ultimate recovery plateau of 58% with a total of 50 days of imbibition.

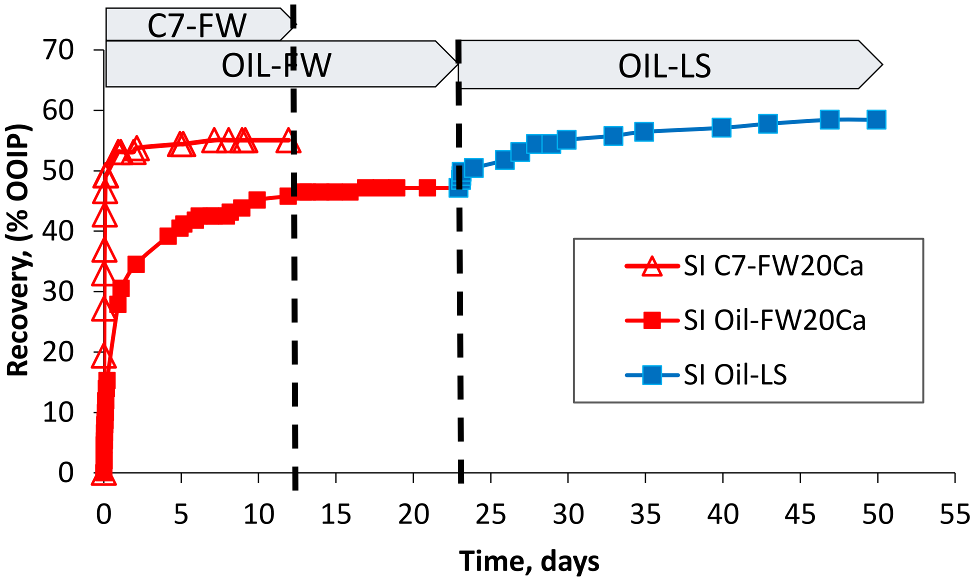

Figure 27 Oil Recovery Test by SI with different brines on VG1 core with Swi = 19% at 60ºC

A summary of the ultimate recovery for all three cores for both oil and heptane are shown in Table 8 where the highest oil production observed was for the VG1 core for both FW and LS brines.

Table 8. Summarised result of the recovery from all cores

Cores	**Crude Oil Used**	**Ultimate Oil Recovery (%)**		**Heptane Recovery with FW (%)**
		Imbibing Brine		
		FW	**LS**	
LP1	OM1	34.7	45.4	36.5
LP2	OM2	46.3	51.0	46.0
VG1	OM1	47.1	58.4	55.0

Chapter 6. Discussions

The chemical interactions between all phases of the CoBR system: crude oil, brine, rock determine the initial wettability of the rock. These interactions such as ion exchanges between the brine and mineral surfaces influences the initial pH of the reservoir before introducing the crude oil. The pH of the reservoir can affect the process of adsorption of POC from the crude oil and therefore establish and alter wettability. The polar crude oil components and the ions from the brine phase would always react and compete in order to balance the surface charge of the silicate minerals to establish initial wettability. This process can be influenced by the pH of the system. As stated in the theory, the main parameters that influence these processes are mineralogical composition, brine composition, crude oil composition and pH. Therefore, these parameters are going to be discussed further in this chapter along with supporting experimental results.

6.1 Influence on minerology

Sandstone is mostly made up of varying quantities of silica-containing minerals such as quartz, clays, and feldspars etc. The pH of sandstones is slightly acidic and are generally negatively charged above pH 2-3 (Kosmulski, 2011). Depending on the structure, each sandstone mineral has different reactivity levels with the reservoir fluids. Referring to Table 2, even though quartz minerals are the most abundant in composition, the reactivity towards the reservoir fluids is low due to their large grain sizes, small surface area, low cation exchange capacity (CEC) and surface charge. The most important minerals for a Smart water EOR processes are the clay and feldspar. Previous studies have reported that feldspar minerals have CEC, which might affect the initial pH of the reservoir as well as the pH development during LS Smart Water injection (Strand et al., 2014; Piñerez T. et al., 2016; Mamonov et al., 2020). The increase in pH promotes the desorption of POC and can result in a wettability alteration to a more water-wet state. Clay minerals have the highest affinity towards the crude oil polar components, where the reactivity at the phases observed can be higher than other rock minerals. The negatively charged sites on clay surfaces attract positively charged ions from the surrounding aqueous phase in order to achieve a balanced charge. The leopard cores contain low clay content which can be the reason why it shows low adsorption during the adsorption test. VG1 has high clay content which results in a higher adsorption capacity.

6.2 Initial Wetting observations

SI results to determine the initial wettability in Figure 16, Figure 19 and Figure 25, show that all three cores display more water-wet behaviour. The steep oil production slope at the beginning of the test indicates the capillary region which confirms strong positive capillary forces, and the high recovery itself suggests water-wet behaviour. However, during waterflooding, the strong capillary forces can trap oil, as the imbibition fluid didn’t sweep through the smaller pore channels, resulting in a lower sweep efficiency and a high residual oil saturation in sandstone reservoirs. For this reason, the method of heptane recovery by SI test is just an estimation of the initial wetting behaviour. Heptane is a non-polar oil which results in no chemical interactions with mineral phase, hence the ultimate recovery with modified crude oil can exhibit different results.

The heptane recovery between the leopard cores exhibits different ultimate recovery results. This could be because of the heterogeneity throughout the leopard rock, since all procedures carried out were the same.

6.3 Effect of pH

Comparing the surface reactivity test results from the LP1 and VG1 core on Figure 14 and Figure 23, there are two points for comparison, (1) the pH between the effluent brines and the bulk, and (2) the increasing pH trend from flooding FW to LS. The values between the effluent samples and bulk shows a difference for both FW and LS suggesting that the minerals are reactive and that ion exchange reactions took place. Having FW and LS with an average effluent pH values of 8 and 9 respectively for VG1 and 7 and 8 respectively for LP1, there is a one-unit pH increase, which implies that the minerals are reactive and interactions have occurred between the brine and the mineral surface. An increase in pH from FW to LS indicates that there is a potential desorption environment for polar components and wettability alteration potential. This can result in mobilizing extra oil in the capillary channels and leads to improving in the sweep efficiency and increase in ultimate recovery. The initial pH from both cores showed slightly acidic level of pH around 7. The negatively charged surfaces of silicate minerals are more likely to attract positively charged basic POC from crude oil at this pH level.

6.4 Adsorption of POC and its effect on wettability

A number of experiments were carried out to investigate the adsorption capacity of the acidic and basic POC on three sandstone cores and its effect on wettability and capillary forces in order to alter the wettability.

To determine the adsorption of the acidic and basic components with the silicate mineral surfaces, three of the cores underwent crude oil flooding, LP1 and VG1 was flooded with OM1 whilst LP2 with OM2, that was previously been prepared by Ove Kvandal (Kvandal, 2016). To measure the acidic and basic components adsorption capacity on certain minerals, the difference between the influent and effluent AN and BN values were obtained and plotted. The LP1 silicate minerals show low affinity with the crude oil polar components where adsorption of both basic and acidic components is low. LP2 showed higher adsorption of both basic and acidic POC compared to LP1, based on these results it is expected that the capillary forces are much stronger in LP2. Nevertheless, VG1 displays the highest adsorption on the basic components compared to the leopard cores. The adsorption of basic and acidic polar components is important to induce the oil-wetness of the clay in sandstone cores, because to achieve any smart water effect, mixed wet to slightly water wet initial conditions are needed. Because of the slightly acidic initial pH condition observed in the surface reactivity tests, it is thought according to **Eq. (9)**, the adsorption increases as the relative amount of the more reactive species (R_3NH^+) in the crude oil increases. The positively charged nitrogen-containing bases electrostatically adsorbed to the rock surface in order to balance the negative charges of the silicate surface.

Testing was carried out on LP2 with the same procedures but with different crude oil compared to LP1 and VG1. The purpose was to test whether a different oil OM2 with similar AN and BN values compared to OM1 would give different results. Even though both of the crude oil has similar AN and BN values, it may contain different polar components, resulting in different reactivity capacity where it can affect the adsorption level of the POC. Based on the results, different oils applied on the leopard cores with similar mineral composition can affect the adsorption capacities.

Previous research had been conducted on adsorption of POC with OM2 crude oil on core B15 where it contains 10wt% of clay, 30wt% of feldspar and high amount of quartz minerals, the adsorption test results is shown in Figure 28 (Mamonov et al., 2019).

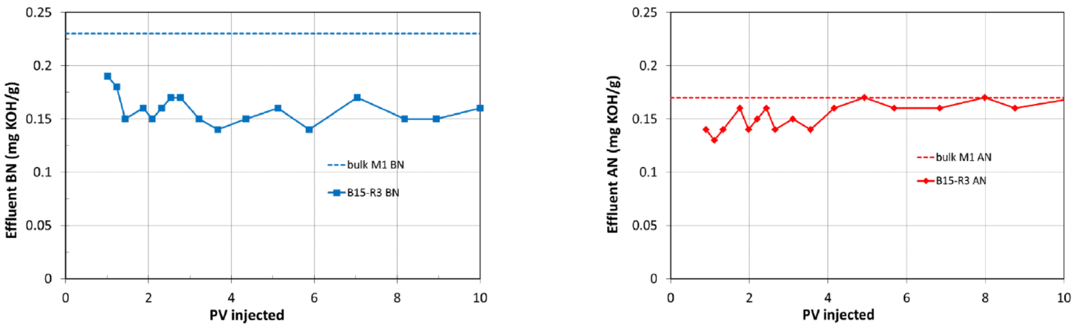

Figure 28 Core B15-R3 with Swi of 21 % with FW was flooded at 50 °C with crude oil M1 with BN= 0.23 and AN = 0.17 mg KOH/g. Measured (left) base number (BN) and (right) acid number (AN) in effluent crude oil samples during the crude oil flooding, a total of 10 PV flooded (Mamonov et al., 2019).

The same crude oil was used on LP2 and same procedures were carried out. The results of the adsorption test for both cores showed similar trend lines for the basic components, where there was continues adsorption throughout the PV injected. However, the LP2 reached equilibrium at 10 PV injected, whilst B15 never reached equilibrium. Additionally, adsorption capacity was much higher in B15 compared to LP2 suggesting B15 contained more reactive minerals towards the basic POC. It is also important to note that the adsorption of polar components occurred instantly when the core with S_{wi} was exposed to crude oil. The adsorption test for the acidic components also showed similar trendlines for both cores. Equilibrium was reached for several times as the PV injected increase, this could be due to experimental accuracies and uncertainties in the analyses and procedures.

To analyse how the adsorption of the polar components affected the capillary forces, SI oil recovery tests with FW as the imbibing fluid is conducted. A comparison of the SI oil recovery tests with FW as the imbibing fluid was conducted before and after the core was exposed to crude oil in order to predict the wettability. The main points to compare were the rate of imbibition and the oil recovery. According to the SI results for LP1, the recovery of heptane compared to oil-FW (recovery of oil with FW as the imbibing brine) is only 2% difference posing similar ultimate recoveries, whereas VG1 displayed 8% difference. The bigger difference in recovery for VG1 is due to the higher adsorption of the predominant basic components that influences the capillary action which drives the imbibition of the wetting fluid. Since LP1 showed lower adsorption for both polar components therefore the difference in recoveries is low. LP2 showed higher adsorption for both basic and acidic POC compared to LP1 and is expected that this would affect the capillary forces more. However, LP2 SI test displayed results of a high oil recovery of 46% where there was fast imbibition rate and only reduce the water-wetness slightly. This suggests adsorption only slightly affected the capillary actions. It is hard to conclude which polar components has higher adsorption. But there could be an uncertainty as to why with more adsorption, the cores wettability only slightly reduces its water-wetness. Therefore, LP2 core needs to be further tested and will be further discussed below. The fact that the imbibition rate for the oil-FW in all cores is much lower than its respective heptane recovery indicates there is some level of adsorption occurred.

6.5 Smart Water EOR effect

When smart water (LS brine) is applied, the results shows that there is an increase in recovery for all cores as LP1, VG1 and LP2 shows that there is an increase in 11%, 8% and 5% OOIP% respectively. As mentioned in the theory, when injecting smart water brine into the formation, then the chemical equilibrium gets disrupted and results in a chemical imbalance. This may lead to a sequence of ion exchange reactions, consequently resulting in a change in pH towards a more alkaline environment. As the FW is replaced by the smart water, an increase in pH was observed in the surface reactivity tests for LP1 and VG1. This is also a strong indicator of a potential smart water effect. When the local pH near the mineral surfaces increases, it creates the conditions for polar components to desorb. When the initially adsorbed polar organic components undergo desorption, this may cause an alteration in wetting leading to increase in water-wet behaviour. This results in an increase in the capillary-driven oil production and is able to mobilize some extra oil. The results support the significance of capillary forces in oil recovery.

6.6 Reservoir heterogeneity and pore size distribution

LP2 core underwent the same procedures as LP1 and VG1, however pH screening process was not conducted for this core. OM2 was flooded through the core instead of the OM1. From the adsorption test, it is observed that there is adsorption of the polar organic components. However, the oil recovery SI test shows that the adsorption only affects the capillary forces slightly, as the heptane recovery and oil-FW recovery is quite similar. This could be due to the heterogeneity of the core. Heterogenous reservoir properties such as permeability, porosity, thickness, saturation, faults and fractures, rock facies and rock characteristics may vary depending on spatial location. After conducting the permeability test, the results shows that the LP2 core has quite a high permeability of 1372 mD compared to LP1 of 220 mD, almost 7 times larger. Even though both LP1 and LP2 are from the same rock, the different physical properties present between the two cores could pose different observations and thus unable to conclude a valid comparison. The pressure difference across the interface between two immiscible fluids caused by capillary forces is known as capillary pressure (P_c). The capillary pressure can be influenced by the permeability of the reservoir rock, specifically on the pore sizes, size distribution and fluid properties. As the permeability is high, the pore sizes are also bigger, and according to **Eq. (5)** the resulting capillary pressure decreases which explains the weak capillary forces and high imbibition rate observed for LP2 core.

Previous research involved where an outcrop sandstone mineral undergo mercury injection capillary pressure (MICP) test to determine the pore size distribution shown in Figure 29 (Piñerez Torrijos et al., 2020). The observations were that the pores range from ~0.01 to 100 μm with most of them located in the macro pore region close to of 10 μm. The outcrop itself contains 10%wt of clay minerals and a high content of feldspar and quartz.

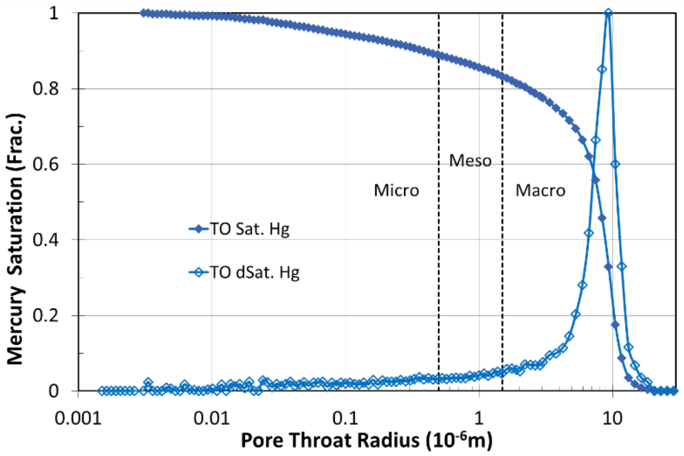

Figure *29* Mercury injection (MICP) for pore throat radius distribution of porous outcrop T sandstone rock. ((TO) samples (Piñerez Torrijos et al., 2020).

Chapter 7. Conclusions

Because of the complexity of the underlying CoBR interactions, the process of establishing and altering wettability are still being discussed and researched. The main interacting parameters are polar components in the crude oil, ionic composition of the brine and the charged surfaces of the rock minerals. The charged polar components of the crude oil can be adsorbed on to the mineral surfaces containing active adsorption areas. How much is adsorbed and which components are more reactive depends on the chemical compositions of the CoBR components, which leads to the establishing the wettability of the reservoir. The objective of this study was to investigate the reactivity of acidic and basic components regarding adsorption and wetting tendencies onto silicate sandstone mineral surfaces. Additionally, the reactivity of the minerals towards formation water and smart water in terms of pH and how the adsorption of polar components potentially affected the capillary forces of the core samples. The main conclusions in this study are:

- A comparative analysis of the adsorption of acidic and basic POC confirmed that the adsorption of basic components was more noticeable in the core samples, therefore indicating the significance of the basic components in terms of its ability to influence the wetting of the mineral surfaces.
- The most important minerals for a Smart water EOR processes are the clay and feldspar. The leopard cores contain low clay content which can be the reason why it shows low adsorption during the adsorption test. VG1 has higher clay content which results in a higher adsorption capacity.
- A comparative analysis of the adsorption of acidic and basic POC between the leopard cores results in different adsorption capacities, where LP1 showed less adsorption compared to LP2. However, there is stronger capillary effect shown in LP1 compared to LP2. LP2 showed inconsistent results and needs to be repeated or apply further testing.
- Reservoir heterogeneity such as permeability of the reservoir rock, specifically on the pore sizes, distribution and fluid properties, can influence the capillary forces. As seen in the leopard rock, one outcrop can vary in heterogeneity than the other. Showing different results in terms of adsorption, capillary forces and OOIP% recovery.
- Both cores showed initial pH conditions that are slightly acidic, which is favourable for POC to adsorb onto clay surfaces to promote less water-wet initial conditions.

- The pH screening shows almost a one pH unit increase when flooding FW then switching to Smart Water, signifying reactivity occurred between the rock surfaces and the ions in the brine. The basic condition promotes a desorption environment which can alter the wettability, indicating a potential Smart Water EOR effect.
- When Smart Water (LS brine) is applied, the results shows that there is an increase in recovery for all cores as LP1, VG1 and LP2 shows an increase in 11%, 8% and 5% OOIP% respectively compared to FW.
- For further testing, MICP test should be performed on the leopard cores in order to retrieve the pore size distributions and confirmed that inconsistent results could be due to reservoir heterogeneity.

References

Abdullah, N. 2016, Reservoir wetting in sandstone reservoirs, adsorption of polar basic oil components onto quartz and feldspar minerals. Master's thesis, University of Stavanger.

Ahmed, T. H., 2006, Reservoir engineering handbook, 3rd ed ed. (revised): Burlington, MA, Elsevier/Gulf Professional, 1360 p.

Alamooti, A. M., and F. K. Malekabadi, 2018, An Introduction to Enhanced Oil Recovery, *in* Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs: Elsevier, p. 1–40, doi:10.1016/B978-0-12-813027-8.00001-1.

Amott, E., 1959, Observations relating to the wettability of porous rock, Trans. AIME 219, pp. 156–162.

Anderson, W. G., 1987, Wettability Literature Survey-Part 6: The Effects of Wettability on Waterflooding: Journal of Petroleum Technology, v. 39, no. 12, p. 1605–1622, doi:10.2118/16471-PA.

Anderson, W. G., 1986, Wettability Literature Survey- Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability: Journal of Petroleum Technology, v. 38, no. 10, p. 1125–1144, doi:10.2118/13932-PA.

ASTM, I., ASTM2896−88, 1988, Standard test method for base number of petroleum products by potentiometric perchloric acid titration. American Society for Testing Materials: Philadelphia.

ASTM, I., ASTM664−89, 1989, Standard test method for acid number of petroleum products by potentiometric titration. American Society for Testing Materials: Philadelphia.

Austad, T., A. RezaeiDoust, and T. Puntervold, 2010, Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs: doi:10.2118/129767-MS.

Austad, T., 2013, Water-Based EOR in Carbonates and Sandstones, *in* Enhanced Oil Recovery Field Case Studies: Elsevier, p. 301–335, doi:10.1016/B978-0-12-386545-8.00013-0.

Bjorlykke, Knut., 1989, Sedimentology and Petroleum Geology: Springer Berlin Heidelberg.

Buckley, S. E., and M. C. Leverett, 1942, Mechanism of Fluid Displacement in Sands: Transactions of the AIME, v. 146, no. 01, p. 107–116, doi:10.2118/942107-G.

Buckley, J. S., Y. Liu, and S. Monsterleet, 1998, Mechanisms of Wetting Alteration by Crude Oils: SPE Journal, v. 3, no. 01, p. 54–61, doi:10.2118/37230-PA.

Buckley J.S., Liu Y. and Monsterleet S, 1998b, Mechanisms of wetting alteration by crude oils. SPEJ, March 1998, 54-61.

Burgos, W. D., N. Pisutpaisal, M. C. Mazzarese, and J. Chorover, 2002, Adsorption of Quinoline to Kaolinite and Montmorillonite: Environmental Engineering Science, v. 19, no. 2, p. 59–68, doi:10.1089/10928750252953697.

Carroll, D., 1959, Ion Exchange in Clay and Other Minerals: GSA Bulletin, v. 70, no. 6, p. 749–779, doi:10.1130/0016-7606(1959)70[749:IEICAO]2.0.CO;2.

Chou, L., and R. Wollast, 1985, Steady-state kinetics and dissolution mechanisms of albite: American Journal of Science, v. 285, no. 10, p. 963–993, doi:10.2475/ajs.285.10.963.

Crocker, M. E., and L. M. Marchin, 1988, Wettability and Adsorption Characteristics of Crude-Oil Asphaltene and Polar Fractions: Journal of Petroleum Technology, v. 40, no. 04, p. 470–474, doi:10.2118/14885-PA.

Deer, W. A., R. A. Howie, J. Zussman, and J. Zussman, 1992, An Introduction to the Rock-forming Minerals: Longman Scientific & Technical.

Deer, W. A., FRS, R. A. Howie, and J. Zussman, 2013, An Introduction to the Rock-Forming Minerals: Mineralogical Society of Great Britain and Ireland, doi:10.1180/DHZ.

Denekas, M. O., C. C. Mattax, and G. T. Davis, 1959, Effects of Crude Oil Components on Rock Wettability: Transactions of the AIME, v. 216, no. 01, p. 330–333, doi:10.2118/1276-G.

Fan, T., J. Wang, and J. S. Buckley, 2002, Evaluating Crude Oils by SARA Analysis: doi:10.2118/75228-MS.

Green, D. W., and G. P. Willhite, 1998, Enhanced Oil Recovery: Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, SPE textbook series.

Grotzinger, J.; Jordan, T., *Understanding earth*. 6th ed.; W.H.Freeman & Co Ltd.: New York, 2010.

Hetland, B. 2018. Smart Water injection into sandstone reservoir for EOR – Optimal mineral sample preparation and influence of feldspar minerals. Master's thesis, University of Stavanger.

Hilner, E., M. P. Andersson, T. Hassenkam, J. Matthiesen, P. A. Salino, and S. L. S. Stipp, 2015, The effect of ionic strength on oil adhesion in sandstone – the search for the low salinity mechanism: Scientific Reports, v. 5, no. 1, p. 9933, doi:10.1038/srep09933.

Hoeiland, S., Barth, T., Blokhus, A. M. and Skauge, A., 2001. The effect of crude oil acid fractions on wettability as studied by interfacial tension and contact angles. Petroleum Science and Engineering, 30: 91-103

Iler, R. K., 1979, The chemistry of silica: solubility, polymerization, colloid and surface properties, and biochemistry, Wiley.

Ingham, J. P., 2013, 2 - Building stone, *in* J. P. Ingham, ed., Geomaterials Under the Microscope: Boston, Academic Press, p. 21–50, doi:10.1016/B978-0-12-407230-5.50010-8.

Jewell, D. M., J. H. Weber, J. W. Bunger, Henry. Plancher, and D. R. Latham, 1972, Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates: Analytical Chemistry, v. 44, no. 8, p. 1391–1395, doi:10.1021/ac60316a003.

Kaminsky, R., & Radke, C. J. (1997). Asphaltenes, Water Films, and Wettability Reversal. doi:10.2118/39087-PA

Kosmulski, M., 2011, The pH-dependent surface charging and points of zero charge: V. Update: Journal of Colloid and Interface Science, v. 353, no. 1, p. 1–15, doi:10.1016/j.jcis.2010.08.023.

Lager, A., K. J. Webb, and C. J. J. Black, 2007, Impact of Brine Chemistry on Oil Recovery: cp-24-00020, European Association of Geoscientists & Engineers,.

Lake, R. T. J. etc L. W., R. Johns, B. Rossen, and L. Lake, 2014, Fundamentals of Enhanced Oil Recovery.

Ligthelm, D. J., J. Gronsveld, J. Hofman, N. Brussee, F. Marcelis, and H. van der Linde, 2009, Novel Waterflooding Strategy By Manipulation Of Injection Brine Composition.: doi:10.2118/119835-MS.

Ma, S. M., X. Zhang, N. R. Morrow, and X. Zhou, 1999, Characterization of Wettability From Spontaneous Imbibition Measurements: Journal of Canadian Petroleum Technology, v. 38, no. 13, doi:10.2118/99-13-49.

MacKenzie, W. S. and A. E. Adams., 1994, A color atlas of rocks and minerals in thin section, Halsted Press.

Madsen, L., and L. Ida, 1998, Adsorption of Carboxylic Acids on Reservoir Minerals From Organic and Aqueous Phase: SPE Reservoir Evaluation & Engineering, v. 1, no. 01, p. 47–51, doi:10.2118/37292-PA.

Mamonov, A., 2019, EOR by Smart Water Flooding in Sandstone Reservoirs – Effect of Mineralogy on Rock Wetting and Wettability Alteration, PhD thesis, University of Stavanger.

Mamonov, A., T. Puntervold, S. Strand, B. Hetland, Y. Andersen, A. Wealth, and P. H. Nadeau, 2020, Contribution of Feldspar Minerals to pH during Smart Water EOR Processes in Sandstones: Energy & Fuels, v. 34, no. 1, p. 55–64, doi:10.1021/acs.energyfuels.9b01064.

Massaro, M., G. Cavallaro, G. Lazzara, and S. Riela, 2020, 13 - Covalently modified nanoclays: synthesis, properties and applications, *in* G. Cavallaro, R. Fakhrullin, and P. Pasbakhsh, eds., Clay Nanoparticles: Elsevier, p. 305–333, doi:10.1016/B978-0-12-816783-0.00013-X.

McGuire, P. L., J. R. Chatham, F. K. Paskvan, D. M. Sommer, and F. H. Carini, 2005, Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska’s North Slope: doi:10.2118/93903-MS.

Morrow, N. R., 1990, Wettability and Its Effect on Oil Recovery: Vol. 42, p 1476-1484.

Morrow, N. R., and G. Mason, 2001, Recovery of oil by spontaneous imbibition: Current Opinion in Colloid & Interface Science, v. 6, no. 4, p. 321–337, doi:10.1016/S1359-0294(01)00100-5.

Nichols, G., 2009, Sedimentology and stratigraphy, 2nd ed ed. (revised): Chichester, UK ; Hoboken, NJ, Wiley-Blackwell, 419 p.

Piñerez T., I. D., T. Austad, S. Strand, T. Puntervold, S. Wrobel, and G. Hamon, 2016, Linking Low Salinity EOR Effects in Sandstone to pH, Mineral Properties and Water Composition: doi:10.2118/179625-MS.

Piñerez Torrijos, I. D., A. Mamonov, S. Strand, and T. Puntervold, 2020, The role of polar organic components in dynamic crude oil adsorption on sandstones and carbonates: CT&F - Ciencia, Tecnología y Futuro, v. 10, no. 2, p. 5–16, doi:10.29047/01225383.251.

Puntervold, T., A. Mamonov, I. D. Piñerez Torrijos, and S. Strand, 2021, Adsorption of Crude Oil Components onto Carbonate and Sandstone Outcrop Rocks and Its Effect on Wettability: Energy & Fuels, v. 35, no. 7, p. 5738–5747, doi:10.1021/acs.energyfuels.0c03003.

Sen, G. 2016. Petrology Principles and Practice. Berlin: Springer-Verlag Gmb, H.

Skauge, A., 2008. Microscopic diversion – A new EOR technique. The 29th IEA Workshop & Symposium, Beijing, China. Nov3–5.

Smith, J. V., 1994. Surface chemistry in feldspars. In Parsons, I., editor, Feldspars and their reactions, pages 541-580. Springer-Science+Business Media, B.V. https://doi.org/10.1007/978- 94-011-1106-5.

Strand, S., T. Austad, T. Puntervold, H. Aksulu, B. Haaland, and A. RezaeiDoust, 2014, Impact of Plagioclase on the Low Salinity EOR-Effect in Sandstone: Energy & Fuels, v. 28, no. 4, p. 2378–2383, doi:10.1021/ef4024383.

Strand, S., T. Puntervold, and T. Austad, 2016, Water based EOR from clastic oil reservoirs by wettability alteration_ A review of chemical aspects: Journal of Petroleum Science and Engineering, p. 13.

Springer, N., U. Korsbech, and H. K. Aage, n.d., 2003: Resistivity index Measurement Without the Porous Plate: a Desaturation Technique Based on Evaporation Produces Uniform Water Saturation Profiles and More Reliable Results for Tight North Sea Chalk: p. 12.

Tang, G.-Q., and N. R. Morrow, 1999a, Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery: Journal of Petroleum Science and Engineering, v. 24, no. 2, p. 99–111, doi:10.1016/S0920-4105(99)00034-0.

Tang, G., and N. R. Morrow, n.d., 1999b: Oil Recovery by Waterflooding and Imbibition - invading Brine Cation Valency and Salinity: p. 12.

Torrijos, I. D. P., T. Puntervold, S. Strand, T. Austad, H. I. Abdullah, and K. Olsen, 2016, Experimental Study of the Response Time of the Low-Salinity Enhanced Oil Recovery Effect during Secondary and Tertiary Low-Salinity Waterflooding: Energy & Fuels, v. 30, no. 6, p. 4733–4739, doi:10.1021/acs.energyfuels.6b00641

Torrijos, I. D. P., 2017., Enhanced oil recovery from Sandstones and Carbonates with “Smart Water”:, Phd Thesis, University of Stavanger.

Velde, B. 2010. *Origin and mineralogy of clays: clays and the environment*. Berlin; New York: Springer.

Yuan, Y. and Lee, T.R., 2013, Contact Angle and Wetting Properties. In: Bracco, G. and Holst, B., Eds., Surface Science Techniques Springer Series, Surface Sciences, Volume 51, Springer Berlin Heidelberg, Berlin and Heidelberg, 3-34. http://dx.doi.org/10.1007/978-3-642-34243-1

Zavitsas, A. A., 2005, Aqueous Solutions of Calcium Ions: Hydration Numbers and the Effect of Temperature: The Journal of Physical Chemistry B, v. 109, no. 43, p. 20636–20640, doi:10.1021/jp053909i.

Zhang, Y., and N. R. Morrow, 2006, Comparison of Secondary and Tertiary Recovery With Change in Injection Brine Composition for Crude-Oil/Sandstone Combinations: doi:10.2118/99757-MS.

Appendix

A.1 Adsorption test result of LP1

Oil (ANBN=0.2) Flooding for Leopard-1					
PV Injected	**Effluent AN**	**Bulk AN**	**PV injected**	**Effluent BN**	**Bulk BN**
0		0.24	0		0.25
0.32	0.2		0.10	0.25	
0.75	0.21		0.53	0.245	
1.18	0.21		0.97	0.25	
1.62	0.24		1.40	0.25	
2.05	0.24		1.83	0.25	
2.48	0.2		2.27	0.25	
2.92	0.17		2.70	0.25	
3.79	0.2		3.14	0.23	
4.65	0.24		3.57	0.25	
5.52	0.24		4.00	0.23	
6.39	0.24		4.44	0.25	
7.25	0.24		4.87	0.21	
8.12	0.24		5.30	0.25	
8.99	0.21	0.24	6.60	0.24	
			7.47	0.25	
			8.34	0.24	
			9.20	0.24	0.25

A.2 Oil recovery by SI test on LP1 for FW and LS brine

		SI test				
Date	Time	Poroduction Time	Poroduction Time, h	Oil recovered, ml	Oil recovery, (% OOIP)	Time, Days
02/03/2021	20:00	0	0	0	0	0.00
	20:30	30 min	0.50	0.3	2.67	0.02
	21:00	1 h	1.00	0.5	4.46	0.04
	22:30	2 h 30 min	2.50	1	8.92	0.10
03/03/2021	6:00	10 h	10.00	1.7	15.16	0.42
	11:00	15 h	15.00	2.3	20.51	0.63
	12:00	16 h	16.00	2.4	21.40	0.67
	14:00	18 h	18.00	2.4	21.40	0.75
	16:00	20 h	20	2.5	22.29	0.83
	22:00	26 h	26	2.6	23.18	1.08
04/03/2021	11:00	39 h	39	2.9	25.86	1.63
	14:00	42 h	42	3	26.75	1.75
05/03/2021	11:00	63 h	63	3.1	27.64	2.63
07/03/2021	11:00	111 h	111	3.4	30.31	4.63
08/03/2021	11:00	135 h	135	3.5	31.21	5.63
09/03/2021	11:00	159 h	159	3.6	32.10	6.625
10/03/2021	12:00	184 h	184	3.6	32.10	7.67
	16:00	188 h	188	3.7	32.99	7.83
11/03/2021	11:00	207 hr	207	3.7	32.99	8.63
	16:00	212 hr	212	3.8	33.88	8.83
12/03/2021	14:00	234 hr	234	3.8	33.88	9.75
15/03/2021	10:00	302 hr	302	3.9	34.77	12.58
16/03/2021	10:00	326 hr	326	3.9	34.77	13.58
Switch to Lo-Sal						
16/03/2021	10:00	326 hr	326	3.9	34.77	13.58
17/03/2021	14:00	354 hr	354	0.2	36.56	14.75
	14:30	354 hr 30 min	354.5	0.2	36.56	14.77
	15:00	355 hr	355	0.2	36.56	14.79
	16:00	356 hr	356	0.2	36.56	14.83
	17:00	357 hr	357	0.3	37.45	14.88
	18:00	358 hr	358	0.3	37.45	14.92
18/03/2021	11:00	375 hr	375	0.3	37.45	15.63
19/03/2021	15:00	403 hr	403	0.5	39.23	16.79
21/03/2021	17:00	453 hr	453	0.9	42.80	18.88
22/03/2021	11:00	471 hr	471	1	43.69	19.63
	17:00	477 hr	477	1	43.69	19.88
23/03/2021	11:00	495 hr	495	1.1	44.58	20.63
	17:00	501 hr	501	1.1	44.58	20.88
24/03/2021	11:00	519 hr	519	1.2	45.47	21.63
	17:00	525 hr	525	1.2	45.47	21.88
25/03/2021	11:00	543 hr	543	1.2	45.47	22.63
	17:00	549 hr	549	1.2	45.47	22.88
26/03/2021	11:00	567 hr	567	1.2	45.47	23.63
29/03/2021	11:00	639 hr	639	1.2	45.47	26.63

A.3 Adsorption test result for LP2

Oil (ANBN=0.2) Flooding for Leopard-1					
PV Injected	**Effluent AN**	**Bulk AN**	**PV injected**	**Effluent BN**	**Bulk BN**
0		0.2	0		0.2
0.36	0.2		0.66	0.165	
0.95	0.2		1.24	0.14	
1.53	0.18		1.82	0.13	
2.11	0.17		2.41	0.15	
2.70	0.15		3.57	0.18	
3.28	0.18		4.74	0.17	
3.86	0.2		5.91	0.16	
4.45	0.19		7.07	0.17	
5.61	0.16		8.24	0.18	
6.78	0.2		9.41	0.175	
7.95	0.17		9.99	0.2	0.2
9.11	0.16				
9.70	0.19	0.2			

A.4 Oil recovery by SI on LP2 for FW and LS brine

		SI test				
Date	Time	Production Time	Poroduction Time, h	Oil recovered, ml	Oil recovery, (% OOIP)	Time, Days
09/04/2021	13:15	0	0	0	0	0.00
	13:45	30 min	0.50	0.5	4.64	0.02
	14:00	45 min	0.75	0.7	6.49	0.03
	14:30	1 hr 15 min	1.25	1.1	10.20	0.05
	15:00	1 hr 45 min	1.75	1.3	12.06	0.07
	16:00	2 hr 45 min	2.75	1.5	13.92	0.11
	17:00	3 hr 45 min	3.75	1.8	16.70	0.16
	22:00	8 hr 45 min	8.75	4.5	41.75	0.36
10/04/2021	11:15	26 hr	26.00	4.6	42.67	1.08
12/04/2021	11:15	74 hr	74.00	4.7	43.60	3.08
13/04/2021	11:15	98 hr	98	4.8	44.53	4.08
14/04/2021	11:15	122 hr	122	4.9	45.46	5.08
15/04/2021	11:15	146 hr	146	4.9	45.46	6.08
16/04/2021	11:15	170 hr	170	4.9	45.46	7.08
19/04/2021	11:15	242 hr	242	5.0	46.39	10.08
20/04/2021	11:15	266 hr	266	5.0	46.39	11.08
21/04/2021	11:15	290 hr	290	5.0	46.39	12.08
Switch to Lo-Sal						
21/04/2021	11:15	290 hr	290	5.0	46.39	12.08
21/04/2021	12:15	291 hr	291	0	46.39	12.13
23/04/2021	11:15	338 hr	338	0.3	49.17	14.08
26/04/2021	11:15	410 hr	410	0.3	49.17	17.08
29/04/2021	11:15	482 hr	482	0.3	49.17	20.08
03/05/2021	11:15	578 hr	578	0.4	50.10	24.08
06/05/2021	11:15	650 hr	650	0.5	51.02	27.08
09/05/2021	11:15	722 hr	722	0.5	51.02	30.08

A.5 Adsorption test results on VG1

Oil (ANBN=0.2) Flooding for Leopard-1					
PV Injected	**Effluent AN**	**Bulk AN**	**PV injected**	**Effluent BN**	**Bulk BN**
0		0.23	0		0.23
0.16	0.17		0.40	0.12	
0.64	0.23		0.88	0.14	
1.12	0.23		1.37	0.15	
1.61	0.23		2.33	0.15	
2.57	0.22		3.29	0.16	
3.54	0.21		4.26	0.16	
4.50	0.23		4.74	0.17	
5.46	0.23		5.22	0.17	
6.43	0.23		5.70	0.15	
7.39	0.23		6.67	0.22	
8.36	0.23		7.15	0.23	
9.32	0.23		8.11	0.23	
10.28	0.22	0.23	8.60	0.23	0.23

A.6 Oil recovery test by SI on VG1 for FW and LS brine

		SI test				
Date	Time	Poroduction Time	Poroduction Time, h	Oil recovered, ml	Oil recovery, (% OOIP)	Time, Days
02/03/2021	20:00	0	0	0	0	0.00
	20:30	30 min	0.50	0.3	2.67	0.02
	21:00	1 h	1.00	0.5	4.46	0.04
	22:30	2 h 30 min	2.50	1	8.92	0.10
03/03/2021	6:00	10 h	10.00	1.7	15.16	0.42
	11:00	15 h	15.00	2.3	20.51	0.63
	12:00	16 h	16.00	2.4	21.40	0.67
	14:00	18 h	18.00	2.4	21.40	0.75
	16:00	20 h	20	2.5	22.29	0.83
	22:00	26 h	26	2.6	23.18	1.08
04/03/2021	11:00	39 h	39	2.9	25.86	1.63
	14:00	42 h	42	3	26.75	1.75
05/03/2021	11:00	63 h	63	3.1	27.64	2.63
07/03/2021	11:00	111 h	111	3.4	30.31	4.63
08/03/2021	11:00	135 h	135	3.5	31.21	5.63
09/03/2021	11:00	159 h	159	3.6	32.10	6.625
10/03/2021	12:00	184 h	184	3.6	32.10	7.67
	16:00	188 h	188	3.7	32.99	7.83
11/03/2021	11:00	207 hr	207	3.7	32.99	8.63
	16:00	212 hr	212	3.8	33.88	8.83
12/03/2021	14:00	234 hr	234	3.8	33.88	9.75
15/03/2021	10:00	302 hr	302	3.9	34.77	12.58
16/03/2021	10:00	326 hr	326	3.9	34.77	13.58
Switch to Lo-Sal						
16/03/2021	10:00	326 hr	326	3.9	34.77	13.58
17/03/2021	14:00	354 hr	354	0.2	36.56	14.75
	14:30	354 hr 30 min	354.5	0.2	36.56	14.77
	15:00	355 hr	355	0.2	36.56	14.79
	16:00	356 hr	356	0.2	36.56	14.83
	17:00	357 hr	357	0.3	37.45	14.88
	18:00	358 hr	358	0.3	37.45	14.92
18/03/2021	11:00	375 hr	375	0.3	37.45	15.63
19/03/2021	15:00	403 hr	403	0.5	39.23	16.79
21/03/2021	17:00	453 hr	453	0.9	42.80	18.88
22/03/2021	11:00	471 hr	471	1	43.69	19.63
	17:00	477 hr	477	1	43.69	19.88
23/03/2021	11:00	495 hr	495	1.1	44.58	20.63
	17:00	501 hr	501	1.1	44.58	20.88
24/03/2021	11:00	519 hr	519	1.2	45.47	21.63
	17:00	525 hr	525	1.2	45.47	21.88
25/03/2021	11:00	543 hr	543	1.2	45.47	22.63
	17:00	549 hr	549	1.2	45.47	22.88
26/03/2021	11:00	567 hr	567	1.2	45.47	23.63
29/03/2021	11:00	639 hr	639	1.2	45.47	26.63