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Dedication

I dedicate this work to my dear parents; Mr. Paul Klewiah and Mrs. Gladys Klewiah. They both received little formal education but have persevered relentlessly to educate all six (6) children, even including myself, their last child. To them, I say Ayekoo!!

Acknowledgement

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Abstract

The wetting state of reservoir rocks, particularly naturally fractured chalk, is fundamental in the efficient application of advanced oil recovery methods by injection of water. In the subsurface crude oil/brine/rock system, a chemical equilibrium between the phases has established a characteristic initial wetting of the system. Experimental studies have revealed the adsorption of polar organic components from crude oil onto the rock surface as the main influence on initial wetting. In the Laboratory, outcrop chalks, are often used as analog materials for chalk reservoir studies. Stevns Klint (SK) chalk, which is a relatively pure outcrop, has been vigorously studied regarding initial wetting but little attention has been given to the adsorption efficiency of polar components onto outcrop chalk of considerable silica impurity.

In this study, experiments have been performed on Aalborg (AA) chalk material, with significant amount of silica (SiO_2) impurity (6-8 At% Si) and possible silicate materials present as clay flakes to quantify the retention of polar acidic and basic components of crude oil onto the chalk surface. In previous experiments, the adsorption has been examined on SK chalk samples (with < 2 At% Si) under the same experimental conditions so the results from this study are analyzed in comparison to the previous knowledge.

Approximately 7PV of Crude oil with known acid number (AN) and base number (BN) was flooded through a core sample (AA#1) at 50°C to measure the changes in AN and BN at the core outlet. The amount of crude oil polar organic components adsorbed was quantified in relation to the area above the curve plot of effluent AN/BN versus PV flooded. Another core (AA#2) was flooded with 5PV of the same crude oil to investigate the impact that crude oil injected volume has on Aalborg chalk wetting. Both oil-saturated samples were aged for 2 weeks at 50°C in the same crude oil and their wetting states evaluated by spontaneous imbibition (SI), forced imbibition (FI) and chromatographic wettability tests (CWT). The studies confirmed that; 1) The adsorption of polar crude oil components is an instantaneous process that occurs as soon as the oil contacts the porous media. 2) Adsorption of acidic components onto Aalborg chalk surface was less profound as compared to SK chalk. 3) The adsorption of basic components was significantly higher compared to SK chalk. 4) Water wetness increased with decreasing the number of pore volumes of crude oil injected.

The high silica content of Aalborg seems to inhibit adsorption of negatively charged acidic components but promotes higher adsorption of basic components and reveals the impact that chalk silica content will have on the initial wetting potential of the different polar components in crude oil. This is a fundamentally essential information for the developments of theoretical and chemical models to explain wettability alteration in chalk reservoirs and highlights the essence of exercising cautions discretion when choosing any outcrop chalk material for parametric laboratory studies to characterize natural reservoir chalk rock behavior.

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Nomenclature

σ	Interfacial Tension
θ	Contact Angle
AA	Aalborg Chalk
AN	Acid Number
BN	Base Number
COBR	Crude Oil/Brine/Rock
CWT	Chromatographic Wettability Method
EOR	Enhanced Oil Recovery
FI	Forced Imbibition
I_{CW}	Wetting Index (CWT)
I_w^*	Wetting index (Amott method)
OOIP	Original Oil In Place
Pc	Capillary pressure
PV	Pore Volumes
RF	Recovery Factor
SI	Spontaneous Imbibition
SK	Stevns Klint Chalk
SW	Seawater
S_{wi}	Initial water saturation
VBOS	Vallhal Formation Water without Sulphate

1 Introduction

1.1 Background

Carbonate reservoirs are known to contain a considerable portion of the global oil reserve and reported also, to have extensive natural fractures (Brownscombe et al., 1952; Mazzullo et al., 1992) and yield low ultimate recovery by conventional waterflooding techniques (Craig, 1971; Al-Lawati et al., 1996; Fidra, 1998) due to their unfavorable mixed- to oil-wet tendencies (Treiber et al., 1972; Chilingar et al., 1983; Salathiel, 1973; Morrow, 1990). Thus, though these fractured reservoirs account for most of the oil produced worldwide, much of the original oil remains trapped in the subsurface and makes them a huge target for Enhanced Oil Recovery (EOR). Brownscombe et al., (1952) revealed spontaneous imbibition (SI) of injected fluids as the chief mechanism to yield high recovery efficiency in carbonate reservoirs. This assertion was confirmed and investigated by several authors (Wade, 1974; Cuiec et al., 1994; Akin et al., 1998; etcetera) and continues to receive attention from the scientific community. Water, however, will only imbibe spontaneously into the rock matrix and expel oil if the initial wettability of the carbonate rock matrixes is altered toward more water-wetness (Hirasaki et al., 2004). Many studies (Donaldson et al., 1969; Morrow 1990; Jadhunandan et al., 1991; Cuiec et al., 1994; Austad et al., 1997; Fidra 1998; Zhou et al., 2000; Morrow et al., 2001; Strand et al., 2006; Bourbiaux, 2009) have been conducted to investigate the effects of carbonate wetting conditions during waterflooding process.

The initial wettability of rocks is a result of the chemical equilibrium between the formation brine, oil and mineral surface (Cuiec, 1984; Cuiec, 1991), established over the geological period that spans the reservoir creation. Initial wetting is important as it governs in-situ fluid distribution, capillary pressure and relative fluid permeabilities; imposing an indirect effect on well rates and limits of economic hydrocarbon production. The brine chemistry has been shown (Israelachvili, 1985; Buckley et al., 1989; Hirasaki, 1991) to influence the wettability by parameters such as ionic composition, ionic concentration and the pH of the solution. It is widely accepted that brine is the first fluid (Buckley, 1996) to occupy the pore space, making the reservoir minerals originally water wet, until oil encroaches the rock-brine system. The idea of wetting alteration by crude oil was indirectly postulated by Burkhardt et al., (1958) and emphasized by Denekes et al., (1959) who investigated the native surface-active materials of crude oil that adsorb on rock mineral surfaces by looking at their chemical type, molecular weight and polarity of crude oil fractions. He concluded that the high molecular weight components had the greatest potential to alter wetting and that the presence of nitrogren- sulfur- or oxygen-containing functional groups [called Asphaltenes, as coined by Boussingault in 1837 (Chrisholm, 1911)] induced polarity of the fractions and enabled the crude to approach the charged mineral surfaces.

In the years that followed, several researchers (Craig, 1971; Cuiec, 1985; Hjelmeland et al., 1986; Morrow et al., 1986; Gonzalez et al., 1986; Gloton et al., 1992; Akhlag et al., 1994; Buckley, 1996) further investigated this assertion and confirmed that crude oils contained components with polar functionality that can exhibit surface-active propensities and may readily attach onto the mineral surfaces to alter the primary wettability when migrating crude oil invades the water-filled pores and accumulates to form the oil reservoirs. The general influence of asphaltenes on wetting, has exclusively been widely studied as summarized by Kaminsky et al., (1998). These surface-active organic components are conveniently grouped as acidic components [represented by the carboxylic group, -COOH and quantified by acid number (Monsterleet et al., 1996; Fan et al., 2006)] and basic components [represented by $-R_3NH^+$ and quantified by base number (Dubey et al., 1993)]. A recent study (Hopkins P. A., 2016) revealed that these polar organic components are intrinsic to the crude oil and not only linked to the heavy end fractions.

The main wetting parameter in carbonates is reported (Andersen 1986a; Skauge et al., 1999; Standnes et al., 2000; Zhang et al., 2005) to be the polar organic acids while the wettability of silica is more affected by the polar organic bases because of differing mineral surface charges. In carbonates, the rock surface is predominantly positively charged at natural reservoir conditions (Zhang et al., 2006), making it possible for negatively charged carboxylic material in oil to approach the rock surface. Silica is also typically negatively charged and positively charged bases could adsorb.

Knowledge of these phenomena and mechanisms has been applied by several researchers (Webb et al., 2005; Austad et al., 2005; Zhang et al., 2006; Strand et al., 2006; Zhang et al., 2007; Fathi et al., 2011; Fernø et al., 2011; etcetera) to study the possibility of reversing the initial wettability of carbonate reservoirs to the original state of preferential water-wetness, in order to maximize the recovery potential of the reservoirs through SI of injected water. Particularly, the concept of Smart Water EOR has received wide attention amongst scientist owing to the huge success of seawater flooding into the Ekofisk chalk field in the North Sea. Since Smart Water is aimed at wettability reversal, it is targeted at COBR systems exhibiting low water-wetting tendencies. In other words, initial wetting of the system considered for smart water application is key since it sets the potential to observe significant EOR effects.

Previously published work (Hopkins et al., 2016; Hopkins et al., 2017; Puntervold et al., 2007b; Mjos et al., 2018) on outcrop chalk wetting using Stevns Klint chalk material have confirmed the assertion of polar organic acids being the principal wetting parameters as compared to the polar bases. In these studies, it was established that the adsorption is immediate, with retention equilibrium reached faster when flooding with crude oil of higher AN whilst the amount of adsorbed species remained the same. The instant adsorption implies that core wettability is not a function of ageing time, and that ageing is not a strictly necessary procedure for core preparations during laboratory experiments. It was established however, that the core wettability was a function of the amount of crude oil exposed to the chalk material. It is further revealed, how that restoration procedures should be done with caution; to acceptably restore reservoir core materials to representative initial wetting conditions during reservoir core characterization studies.

Since studies are frequently performed with outcrop chalk materials as correspondents to reservoir rocks, a comprehensive understanding of initial wetting requires a detailed investigation that also encompasses, the impact of the chalk mineralogical content.

Skovbjerg et al., (2012) used atomic force microscopy (AFM) to show that the grain surfaces in offshore and onshore chalk are heterogeneous and contained nano-sized clay and silica particles. By mass, chalk is dominated by calcite usually with only a minor percentage of silica (SiO_2). The silica in chalk is quartz and opal-CT and minor amounts of silicate minerals are present, mainly in the form of clay. The effects of clay and silica on permeability and capillary entry pressure of chalk reservoirs in the North Sea has been reported by Fabricius et al., (2002). Divergent mechanical and physical characteristics of outcrop chalks based on mineralogical variance has also been documented in a study conducted by Megawati et al., (2015). Andersen et al., (2018) comparatively studied samples from five different outcrop chalks and noted silicates, present in unequal amounts, as the main mineralogical impurity within the chalk types. They further reported this mineralogical variance to have major control over chemo-mechanical interactions during flooding with NaCl and $MgCl_2$ brine.

In terms of chalk wetting behavior, Strand et al., (2007) exposed two different outcrop chalk materials to the same crude oil and reported that the porous media exhibited different wetting characteristics as indicated by their wetting indices. Their observation pointed to the differing surface chemistry of the chalk types. The surface charge of silica and clay is predominantly negative and opposite to chalk, which is positive, at natural reservoir conditions, and it is therefore expected that the wetting condition will be affected by the content of silica and clay. The wetting behavior of chalk in relation to mineralogical heterogeneity is therefore imperative and worthy of investigation, especially as related to their surface reactivity towards the different polar organic components present in crude oil.

1.2 Problem Statement

For many years, scientists have been working to understand crude oil/brine/rock interactions responsible for altering rock wetting state and to implement this learning to develop novel solutions to improve oil production in carbonate reservoirs. Often, in such parametric studies, outcrop chalk material is used as analogs due to its availability and low-cost relative to obtaining reservoir cores. But the wettability of chalk as documented, is influenced by the adsorption of polar oil components onto the mineral surfaces, which is influenced by several factors including the mineralogical composition of the material.

Available outcrop chalk materials are known to vary in mineralogical compositions of silica and clay. Due to the differing surface chemistry of calcite and silica mineral surfaces, it is expected that the degree of adsorption of acidic and basic components in crude oil will be different for the different chalk materials, which will influence the initial wetting conditions. An experimental investigation is therefore necessary to examine this impact and serve as additional knowledge to the already existing literature on chalk wetting by crude oil polar components.

1.3 Objectives

The scope of this thesis is to investigate the adsorption potential of crude oil polar components onto impure outcrop chalk rock by quantifying the amounts of acidic components and basic components that can attach onto the chalk surfaces and its impact on initial wetting. Particularly, the purpose is to determine how silica content can impact the adsorption and to obtain an understanding of the chemistry involved in the mechanism. Further study is conducted to ascertain the extent that the amount of crude oil exposed to chalk matrix can influence the initial wetting. Findings from this study will serve as an additional learning to the Smart Water project at UiS.

This thesis opens with the theory of the research area that presents fundamental concepts required to understand the subject matter. A brief insight is provided into carbonate rock materials and the concept of Smart Water EOR in carbonates, followed by the experimental processes. Finally, the results are discussed in relation to the objectives and previous documented studies.

2 Fundamentals

It is commonly agreed that hydrocarbons are the result of thermal alteration of organic material contained in sediment layers of source rocks and accumulated in porous geological reservoir formations by seals and traps. A useful resource as it is, the main aim is to discover and retrieve it from the natural subterranean environment. This chapter introduces some fundamental concepts of oil recovery with a notion to build a foundation that will introduce most of the terms required to sufficiently understand the subject matter of this thesis. Focus is given to defining enhanced oil recovery and carbonate reservoirs. All concepts in this thesis is presented by the assumption of a two-phase oil-water fluid system.

2.1 Oil recovery

Oil in the reservoir is extracted following several recovery processes that are traditionally divided into three convenient stages based on when they are likely to be implemented in the lifespan of an oil reservoir; primary recovery, secondary recovery and tertiary recovery.

2.1.1 Primary recovery

This refers to the initial stage of production where oil flows spontaneously to the surface owing to the natural energy in the petroleum reservoir. The core mechanisms cause pressure depletion of the reservoir natural pressure, in the form of gas cap drive, solution-gas drive, natural water drive, fluid and rock expansion, gravity drainage or using artificial pumps to drive oil to the surface (Ali et al., 1996; Puntervold, 2008). These forces in the reservoir can either act simultaneously or sequentially; depending on the ability of its composition and properties to displace the oil, but at some point in time, the pressure will diminish. This stage of production recovers only a small fraction of the OOIP (Castor et al., 1981), typically ranging from 10% - 30%.

2.1.2 Secondary recovery

After natural reservoir energy diminishes, secondary recovery mechanism is employed by injection of external fluids, mainly to re-pressurize the reservoir and improve volumetric sweep efficiency. The extra energy is usually provided in the form of gas injection or waterflooding, the latter being the most common. In this stage, depending on properties of the reservoir rock, oil and the injection fluid, usually 30-50 % of OOIP is recovered (Castor et al., 1981) with the remainder trapped in the porous media.

2.1.3 Tertiary recovery

This process uses miscible gases, chemicals and thermal energy to displace additional oil, when secondary recovery becomes uneconomical (Willhite et al., 1998). Additional energy of these kind added to the displacement mechanisms of primary or secondary methods have enormous potential to yield supplemental oil recovery (Lake, 2010).

It is noteworthy, that a virgin reservoir need not be strictly produced according to this chronological sequence. Infact, today, most reservoirs are pressure maintained from day one. Plus, studies have shown that early implementation of optimal EOR techniques has increased advantage as opposed to the traditional recovery process.

Willhite et al., (1998) provide a demonstrative example regarding recovery from a heavy oil reservoir that highlights this assertion. They explain how that if the crude is sufficiently viscous, it may not flow at economic rates under the natural energy drives, so primary production would be negligible. Further on, for such reservoirs, waterflooding would not be feasible; therefore, the use of thermal energy might be the only way to recover a significant amount of oil.

In this case, a method considered to be a tertiary process in the normal chronological depletion sequence presented earlier, would be used as the first, and perhaps final, method of recovery.

2.2 Defining Enhanced Oil Recovery

The benefits of implementing innovative recovery operations earlier in the life cycle of a reservoir has disfavoured use of the "tertiary recovery" term and replaced it with a more complete term, Enhanced Oil Recovery (EOR). EOR is not restricted to a particular production phase or the outlined chronological order in the producing life of a reservoir (Stosur et al., 2003; Hite et al., 2004) and may be defined as the application of techniques for improving displacement efficiency or sweep efficiency, extending the lifetime of a reservoir, and ultimately the improvement of recovery by reducing residual oil saturation (Hopkins, 2016).

However, the action to implement an EOR method might be dictated by such factors as the nature of the reservoir fluid, availability of injectants and economics (Alvarado et al., 2010). Another term, IOR is widely used in the industry to encompass EOR as well as other activities such as reservoir characterization, improved reservoir management, infill drilling, etcetera. According to Taber et al., (1997), EOR simply means that something other than plain water or brine is injected into the oil reservoir, whereas IOR is a term used more broadly to encompass all optimize techniques used to increase the oil production. Available knowledge in the literature (Ali et al., 1996; Taber et al., 1997; Thomas, 2008) portrays that EOR may be split into the broad categories as shown in Figure 2.1 [revised after (Sunil et al., 2010)].

It is not yet established if any single EOR scheme is applicable to all petroleum reservoirs as a general method for enhancement of oil recovery; however, specific processes that are quite distinct from each other have been developed to address reservoirs with special characteristics. On such premise, Smart Water (Austad et al., 2005) injection indisputably deserves an inclusion since seawater is a superb EOR fluid to chalk ((Puntervold et al., 2015; Puntervold, 2008) as it increases capillary forces and improves microscopic sweep efficiency through a wettability alteration process. This concept is discussed later in chapter 5.

It is worth a mention, that the criteria for selecting a particular EOR process are complex because of the large number of petrophysical, chemical, geologic, environmental, and fluid properties that must be considered for each individual case.

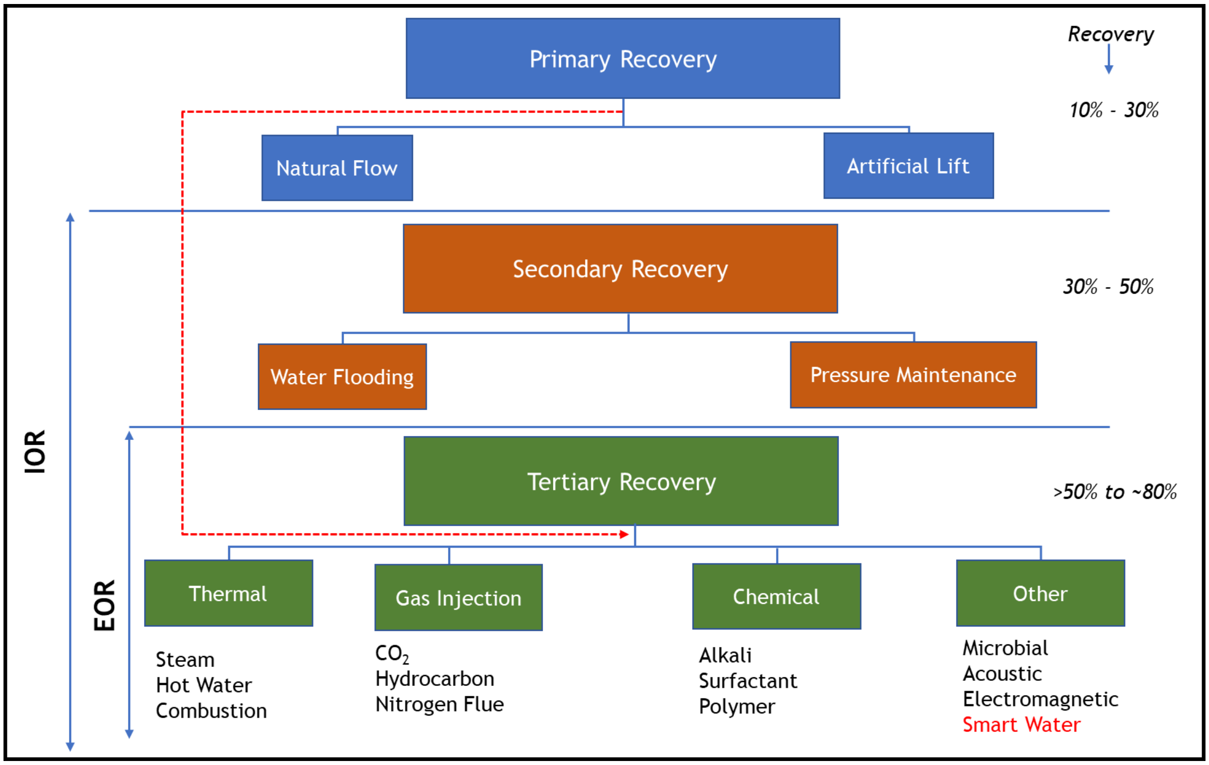

Primary Recovery
Recovery
10% - 30%
Natural Flow
Artificial Lift
Secondary Recovery
30% - 50%
Water Flooding
Pressure Maintenance
IOR
Tertiary Recovery
>50% to ~80%
EOR
Thermal
Gas Injection
Chemical
Other
Steam
Hot Water
Combustion
CO_2
Hydrocarbon
Nitrogen Flue
Alkali
Surfactant
Polymer
Microbial
Acoustic
Electromagnetic
Smart Water

Figure 2.1: *Illustration of the production stages in a reservoir's production life. Smart water is categorized and the essence for implementing EOR methods from day one is emphasized*

2.3 EOR in carbonates

In the 1980's, Roel et al., (1985) documented that about 50% of the world's proven petroleum reserves were contained in carbonate reservoirs. Today, carbonates are estimated to hold more than 60% of the total remaining oil globally and 40% of the world's gas. On average, Sunil et al., (2010) reports the worldwide recovery factor from conventional (primary and secondary) recovery concepts as only about a third of oil originally present in the reservoir. Hence, in most cases between 40 – 60 % of OOIP remains in the reservoir. This is attributed to carbonates being pre-dominantly less water wet and naturally fractured with low matrix permeability. Thus, secondary recovery displacement fluids channel easily through these fractures from the injector to the producer and majority of the oil is left untapped within the matrix. This significant residual oil saturation, ROS (see Figure 2.2), is the main target of EOR in carbonates.

Despite the great potential to improve oil recovery in carbonate reservoirs, EOR application in this area is very limited because of technical and economic challenges. Qing Sun et al., (2003) mentions that most of the field development schemes in carbonate reservoirs are restricted to waterflooding and gas flooding with low ultimate recovery factors

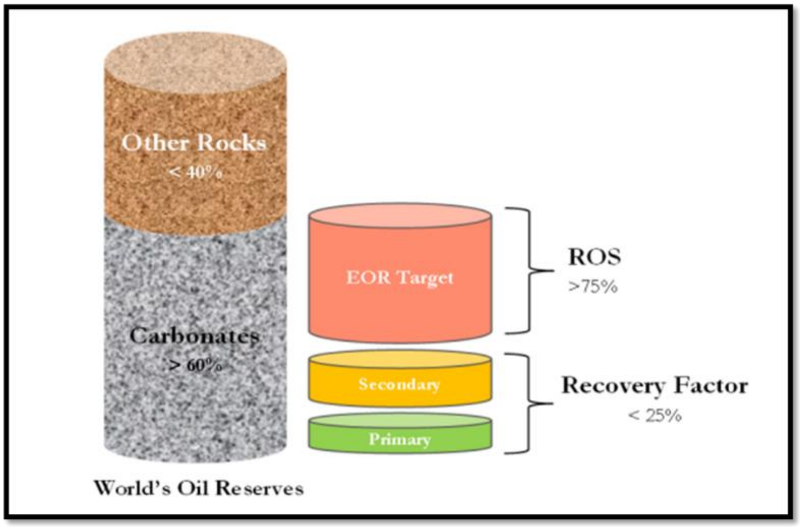

Other Rocks
< 40%
Carbonates
> 60%
World's Oil Reserves
EOR Target
Secondary
Primary
ROS
>75%
Recovery Factor
< 25%

Figure 2.2: *Percent of total oil reserves and recovery factor in carbonates (Suhal, 2016)*

In Figure 2.3, the most commonly implemented EOR methods in carbonates based on the global EOR database compiled by Vladimir et al., (2010) are presented. According to this database, the most frequent method is gas injection, followed by chemically based EOR methods and thermal methods, which represents only 3% of the total applied concepts in carbonates.

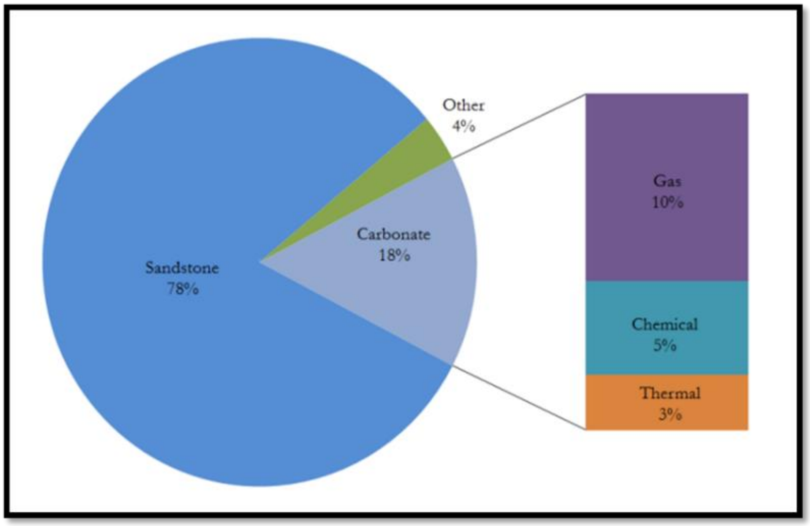


Figure 2.3: *EOR field projects in carbonates (Suhal, 2016)*

Manrique et al., (2004) reports Carbonate EOR activities in the US to be dominated by CO_2 flooding technologies either as continuous or Water Alternating Gas (WAG). This is because of the high availability of low-cost CO_2 in the region. EOR chemical methods in carbonate reservoirs, especially polymer flooding, have been widely tested in the US carbonate reservoirs as well. However, they have resulted in marginal contributions, relatively in terms of total oil recovered.

According to the North Sea EOR survey (Anwar et al., 2008), five (5) major EOR techniques have been tested in the region with WAG injection highlighted as the most common and successful technology in the region. In 1980, the Joint Chalk Research (JCR) programme was established by the Norwegian Petroleum Directorate (NPD), the Danish Energy Agency and the licensees in the North Sea's chalk fields to undertake study into how recovery from the region's rich carbonate reservoirs can be fully harnessed. It was resolved in 1983 to start a waterflood programme (using seawater) to press more oil out of the field. Three years later, crude output had doubled and estimated recoverable reserves were substantially increased (NPD, 2009). In recent times, the positive effects of seawater injection into the carbonate chalk reservoir has been attributed to a wettability reversal action induced by sulphate in the brine which contributed to the development of strong water wetness of the chalk matrix over the years of flooding. This revelation has turned the attention of many scholars and the industry to the implementation of water-based EOR techniques in carbonates.

The general goal of water-based EOR in carbonates is to imbibe water into the matrix and alongside expel the oil into the fractures, where it is further transported to the producer. This is possible when the injected brine has the potential to alter the unfavourable wetting state of the carbonate material. A brine with such capability is ascribed the term "smart water". The potential of smart water for EOR applicability in carbonates is well covered in the literature (Zhang et al., 2006; Zhang et al., 2007; RezaiDoust et al., 2009; Fathi et al., 2011; Seyed et al., 2012; Adepapo et al., 2014; Puntervold et al., 2015).

2.4 Reservoir displacement Forces

Crude oil has limited intrinsic ability to drive itself from the tortuous pores of the underground rocks in which it is found; instead, it must be forcibly ejected by the accumulation of other fluids. Normally, the methods for oil retrieval from the natural reservoirs will involve an immiscible displacement by water and/or gas of some kind to trigger and facilitate high levels of production. The mechanism of this immiscible expulsion of oil can occur through spontaneous imbibition of water or forced imbibition.

Spontaneous Imbibition: Imbibition is the process of absorbing a wetting phase into the porous rock. Spontaneous imbibition, then, is when the absorption process occurs without any pressure driving the phase into the rock.

Forced Imbibition: This describes an absorption triggered by a pressure drive. A common term used in similitude is viscous flooding, or rather implicatively, forced displacement.

Physically, in an oil reservoir, the most important in-situ driving forces are

a) Viscous forces,
b) Capillary forces
c) Gravity forces.

Viscous driving forces dominate forced imbibition and the latter two are responsible for spontaneous imbibition.

For oil displacement in an ideal EOR process, the overall displacement efficiency (E) is considered a product of macroscopic and microscopic displacement forces (Willhite et al., 1998) and given by;

$$E = E_V * E_D \qquad (2.1)$$

Where E_D and E_V are the microscopic and macroscopic displacement efficiencies respectively.

Macroscopic displacement efficiency: The E_v, also called sweep efficiency, measures how effectively the displacing fluid sweeps out the volume of the reservoir. It shows the effectiveness with which the fluid percolates through the system and contacts the EOR target oil. The most important parameter controlling this term is the mobility of displacing fluid as against that of the displaced oil.

Microscopic displacement efficiency: The E_D measures how effectively the EOR injection fluid mobilizes the oil at those places in the reservoir where it contacts the oil. Basically, it focuses on the effectiveness of an oil recovery process at the pore scale level to reduce the residual oil saturation (S_{or}) to the barest minimum. Interfacial tension, and rock wettability state are the key controlling parameters.

2.4.1 Capillary Forces

When two immiscible fluids coexist in the pores of a reservoir section, a pressure discontinuity arises across the interface separating the two fluids. This pressure difference is termed Capillary Pressure (P_c), and classically defined as the pressure in the non-wetting phase minus pressure in the wetting phase. Mathematically, P_c is expressed as;

$$P_c = P_{NW} - P_W \qquad (2.2)$$

Evidently, the capillary pressure may assume positive or negative values depending on the fluid pressures. For a two phase oil-water system, P_c is defined as;

$$P_c = P_o - P_w = \frac{2\sigma cos\theta}{r} \qquad (2.3)$$

Where: P_o & P_w are the oil and water phase pressures across the interface respectively;
σ = interfacial tension (IFT); θ = contact angle; r = pore channel radius

Drive forces due to capillary are the consequences of the interplay of pore dimension and geometry, pore throat size, wettability and the surface/interfacial tension generated by the fluids and rocks of a given reservoir system. Capillary forces are a decisive influence on oil recovery efficiency and could act against or in favor of the production depending on the formation framework. Displacement in fractured reservoir systems, like carbonates is only supported by positive capillary forces (Cuiec et al., 1994).

The strong capillary forces encourage self-uptake of water through spontaneous imbibition to eject oil. However, in a non-fractured reservoir, strong capillary forces during waterflooding might trap oil and reduce oil production (Strand, 2005). In carbonates, the desired means to induce positive capillary forces is to reduce $\cos\theta$ *(in equation 2.3)* by a wettability reversal to mixed- or water-wet conditions and promoting the imbibition process. The definition of θ is given in section 4.2.1

2.4.2 Gravity Forces

As is expected, immiscible fluids will segregate according to densities by gravity in the porous rock, with the densest fluid (water) at the bottom. The main driving force is determined by the fluid density (Lake, 2010) and plays a significant role in the multiphase fluid system that is usually encountered in the reservoir. Depending on the layer wherein displacement is occurring and differences in fluidic densities, the displacing fluid can segregate; influencing the displacement front and resulting in an ineffective recovery efficiency through overriding or under riding.

The hydrostatic pressure difference between oil and water owing to gravity can be given by;

$$P_d = (\rho_w - \rho_o) * g * H \qquad (2.4)$$

Where: ρ_w & ρ_o = water and oil phase densities respectively; g = gravitational acceleration constant; H = height between the fluid columns.

Chen et al., (2000) highlights that gravity forces can be a major concern when density differences between oil and water are large and can also be important at low oil-water IFT conditions. Implicatively, for stationary laboratory situations when an oil saturated core is submerged in water, segregation by gravity will play a dominant role in the imbibition process since the capillary forces are then reduced (Schechter et al., 1994). It should be recognized, then, that spontaneous imbibition can be driven either by capillary or gravity forces and is a function of interfacial tension (IFT), wettability, density difference and characteristic pore radius.

2.4.3 Viscous Forces

When fluids flow in a porous rock, viscous forces are reflected in the magnitude of pressure drop that occurs as a result of the flow (Willhite et al., 1998; Pinerez, 2017). The concept of fluid flow in reservoir rock is inextricably related to the rock permeability. *Permeability* is a sole property of the porous reservoir rock that determines how fluids are transmitted through it. This rock characterization was first defined mathematically (see equation 2.5) by Henry Darcy in 1856 and it is an important expression when considering fluid flow in porous media.

$$q = \frac{kA}{\mu}\frac{\Delta p}{L} \qquad (2.5)$$

Where: q is the fluid flow rate; k is permeability; A is cross-section area; μ is fluid viscosity; L is length of flow path and Δp is differential pressure.

Usually, by simplification, the flow path in a porous media is considered as a bundle of parallel capillary tubes (Pinerez, 2017). Here, the flow automatically (due to the assumption) becomes laminar and the pressure drop over any length of fluid flow path can be calculated using the Poiseuille's law equation;

$$\Delta P = \frac{8\mu L}{r^2}\frac{v_{avg}}{g_c} \qquad (2.6)$$

Where: ΔP = Pressure difference across capillary tube; μ = viscosity; L = length of tube, v_{avg} = average flow velocity in tube; r = tube radius, g_c = conversion factor.

The prime objective of EOR operations is to mobilize and displace the significant volumes of oil (usually remaining as droplets) left behind after conventional recovery operations. Laboratory studies (Taber, 1969) have indicated that residual oil can be recovered if the pressure differential due to viscous flow is sufficient to overcome capillary forces. The interplay of viscous and capillary forces is captured through the dimensionless group called capillary number, N_{ca}. For a drive mechanism of water displacing oil, N_{ca} is given as;

$$N_{ca} = \frac{F_v}{F_c} = \frac{v\mu_w}{\sigma_{ow}cos\theta} \qquad (2.7)$$

Where Fv = viscous force, Fc = capillary force, v = interstitial velocity, μ_w = water phase viscosity.

From equation 2.7, a high capillary number is a requirement to effectively displace oil. Clearly, this can be achieved by reducing cosθ via wettability alteration and this is the motivation for smart water EOR in carbonates. Morrow (1979) asserts that if the ratio of viscous to capillary forces is raised sufficiently, almost complete recovery of residual oil can be achieved. A review study of the various methods to represent this interplay was reported by Larson (1977).

3 Carbonate rocks

In this chapter, a brief definition of carbonate rocks (limestone, dolomite and chalk) is given with an attempt to provide an understanding into the general classification of carbonates based on mineralogy. The geological and petrophysical heterogeneity of carbonates is faintly highlighted with emphasis given to chalk as a reservoir rock material.

3.1 Classification of carbonate rocks

Carbonates are sedimentary rocks formed either by the deposition and lithification of organic matter sourced from calcareous plant and animal debris, or directly from chemical precipitation of concentrated solutions. Often, they are denoted as biogenic sedimentary rocks (Bissel et al., 1967), to infer their composition of organic material produced by marine living organisms (Figure 3.1). While alive, these organisms extracted Ca^{2+} and CO_3^{2-} ions from the water and used them to form the mineral $CaCO_3$ in the construction of their cellular structures.

Carbonate rocks can be attributed as clastic when formed from fragmented carbonate rocks as opposed to non-clastic if derived from preserved sediments. A bio-clastic rock (Skinner et al., 1991) is a rock type composed of fragmented organic material, that has not been fully homogenized by chemical processes (Puntervold, 2008). Limestone and Dolomite may be classified as clastic or non-clastic, whereas chalk is often classified as bio-clastic. From the Petrology point of view, carbonate rocks have complicated and varied depositional patterns and are subject to extensive post-depositional alteration which can radically alter the original porosity and permeability relationships. Several authors have proposed terms for general classification based on this premise and are extensively discussed by Mazzullo et al., (1992).

Carbonates are abundant and vary in structure, chemical and physical properties depending on the composition of the minerals present. At their basic framework, however, is the fundamental anionic structure of CO_3^{2-} so it is unsurprising to find reports where geologists generally classify carbonate rocks as those containing more than 50% of carbonate minerals. Some common minerals are calcite ($CaCO_3$), Aragonite ($CaCO_3$), Siderite ($FeCO_3$), Magnesite ($MgCO_3$), Dolomite ($CaMg(CO_3)_2$), and Ankerite ($CaFe(CO_3)_2$) (Bjørlykke, 1989). Calcite and Dolomite form the two most abundant and together, make up 90% of all naturally occurring carbonates (Bissel et al., 1967; Bagrintseva, 2015).

In general, Limestone is classified as a sedimentary rock in which the carbonate fraction exceeds the non-carbonate constituents (greater than 50% $CaCO_3$; either as calcite or aragonite). Conversely, the term Dolostone is reserved for those rocks containing more than 50% of the mineral dolomite (Mazzullo et al., 1992). In nature, the two are commonly intimately associated but as relating to their depositional origin and subsequent diagenesis, and chemistry, very different.

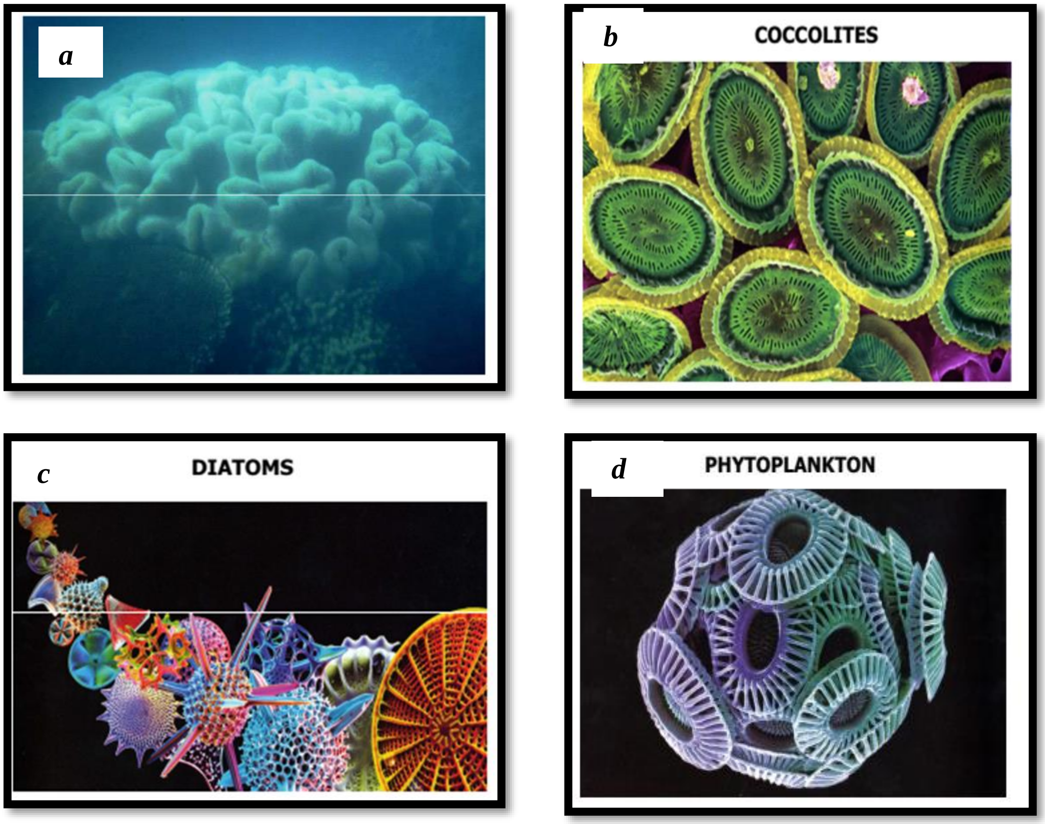


Figure 3.1: *Carbonate material growing in clear water (a), and images of carbonate-source eukaryotes with high degree microscopes.*

Some writers (Pettijohn, 1975; Mollazal 1961; Bissel et al., 1967; Mazzullo et al., 1992) have recognized classification based on the intergradations of these common carbonate-end members as an excellent ground for carbonate rock recognition at the basic level. Pure limestone, (90% calcite), dolomitic limestone (20-50 % dolomite), calcitic dolomite (50-90 % dolomite) were proposed. Originally, only calcite is formed directly and then may undergo a microchemical process of calcium carbonate dissolution and dolomite precipitation. This diagenetic process to yield the dolomite mineral is called dolomitization *(see equation 3.1)*. Dolomite is made up of layers of CO_3^{2-} with alternating layers of Ca^{2+} and Mg^{2+} in between (Puntervold, 2008). The process is reversible and may be triggered in the presence of high calcium waters (Lucia, 1999).

$$2CaCO_3 + Mg^{2+} \rightleftharpoons CaMg(CO_3)_2 + Ca^{2+} \qquad (3.1)$$

Evidence of non-carbonate mineral present in carbonate rocks (Graf, 1960) exist with detrital quartz as the most common impurity (Fabricius et al., 2002). In addition, various forms of authigenic silica, evaporites (gypsum and anhydrite), clay minerals and glauconites are present in various abundances in many limestones and dolomites (Mazzullo et al., 1992).

It is noteworthy to mention that other common classification schemes are used by geologists that may be based on grain size, compositions or texture.

3.2 Geochemistry of Chalk

Chalk is classified as a friable, fine-textured Limestone (Pettijohn, 1975). It is regarded as a pelagic deposit formed from calcareous debris of the unicellular planktonic algae, coccolithophorids. Coccolithophorids *(see figure 3.1d)* have a unique exoskeleton built of internally secreted calcite tablets that are arranged in rings known as coccoliths. These coccoliths are arranged into a hollow coccosphere which encapsulates the soft part of the living algae. On death, the coccospheres falloff and coccoliths are released to form the pelagic deposits that later become chalk (Hardman, 1982). Since the primary constituent of coccolith is calcium carbonate, the resulting chalk is mainly composed of calcite crystals that are held together either by organic material or through mechanical interlocking. This makes chalk a rock of great chemical stability (Hanken et al., 2015).

In addition, chalk may contain coarser calcite grains from planktonic and benthonic foraminifera shell debris of various kinds plus silt-size quartz grains and clay minerals (Jørgensen, 1986). But in general, (Hardman, 1982) emphasizes chalk as a remarkably pure form of calcium carbonate since in many existing forms, these impurities comprise less than 5% of the rock. He notes, in some cases, that early and late stage diagenesis can result in cryptocrystalline silica being concentrated in nodules and tabular layers know as flints. An image of a typical chalk rock is presented in figure 3.2.

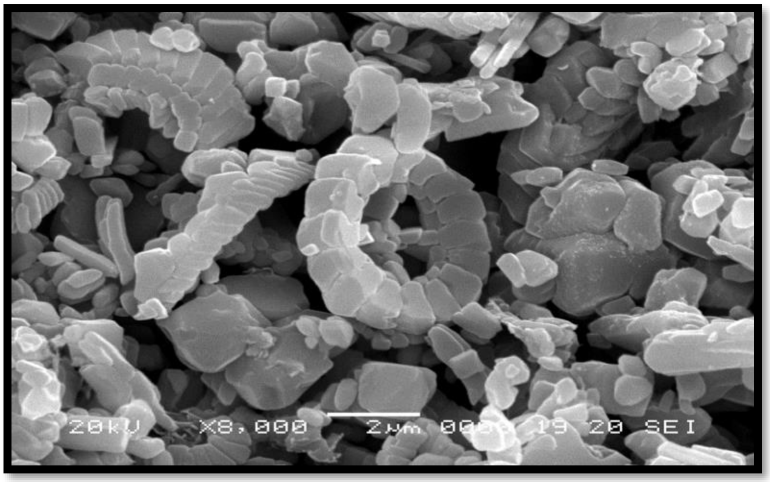


Figure 3.2: *SEM image of chalk showing the coccolithic rings and pore spaces.*

In Chalk, the calcite crystals (Donaldson et al., 2008), composed of complex ions of calcium and carbonate ions are held in a cubic structure with each Ca^{2+} centered between two CO_3^{2-}. These ions are exposed on the rock surface in an alternating cycle. Calcium, in bonding to CO_3^{2-} achieves a stable octet by losing its two outer electrons that results in a doubly charged positive cation, Ca^{2+}. Meanwhile, the oxygens are bonded to the carbons through strong covalent bonds with completed electron octets, leaving a very weak negative electron cloud, compared to the exposed Ca^{2+}. This makes the net surface charge on the rock surface positive and offers the reactive potential to undergo sorption processes when in contact with negatively charged species. Legens et al., (1999) conducted zeta potential measurements of calcite in water and reported a constant value of +32mV as the solution pH is changed from 6.5 to 11. It is informed in their report that even in the presence of 0.1M NaCl, the zeta potential remained linear with respect to increasing pH but was stable at a value equal to about +15mV. It is also reported (Puntervold, 2008) that chalk surface is positively charged if the surrounding brine's pH is < 8. This is also verified by other scholars (Pierre et al., 1990; Zhang et al., 2006; Dawoud et al., 2016; Hassan et al., 2017) who investigated carbonate surface charge versus surrounding brine pH and salinity. It must be noted thus, that carbonates (chalk, dolomite etcetera) predominantly have an overall electrically positive surface, which should favour oil wetting by adsorption of negatively charged polar species in crude oil at favourable conditions.

3.3 Chalk as a reservoir

Chalk forms a fine grained micropore reservoir (i.e. composed of particles which are mainly single crystal laths of calcite produced by the disaggregation of coccoliths) with particles in the size range of 0.5 - 3 microns and pore throat sizes in the optimum case ranging from 0.1 – 1 micron. This makes chalk reservoirs highly porous (black spaces in figure 3.2), with typical values of 35 – 45 % but exhibit low permeabilities, usually in the range 0.1 – 7mD (Hardman, 1982).

Extensive fractures are common to chalk reservoirs and depending on its cautious exploitation, can play a very important role in the oil recovery process as transport routes for oil drained from the matrix blocks during spontaneous imbibition of water.

Chalk reservoir quality is controlled by a variety of factors, predominated by; the purity in terms of $CaCO_3$ content of sediments, the rate of deposition of chalk minerals which in turn determines the degree of early frame-work cement, the tectonic setting of the field area during chalk deposition and the size distribution of the coccoliths being deposited. Hardman (1982) asserts that nearly all reservoir quality variation can be related to these four factors. Ekofisk and Valhall oilfields are examples of chalk reservoirs along the NCS. Besides these Cretaceous to Paleocene deposits in the North Sea, Chalk deposits in the Gulf Coast and in the West interior seaway provinces of North America are important hydrocarbon-producing sites (Mazzullo et al., 1992).

3.4 Outcrop chalk materials

Outcrop chalk materials are used as the primary data sources during laboratory parametric studies. Contrary to real reservoir rock samples, which are deeply buried, outcrop chalk is cheap and readily available (Puntervold, 2008). These outcrops, despite having similar lithology, can contain fewer heterogeneities compared with reservoir material and the decision regarding the choice of outcrop material to be used in geochemical and flooding experiments is crucial. When reservoir chalk characterization is based on testing of outcrop chalks, understanding the diagenetic mechanism and composition of the outcrop material is key. Particularly, silica type and content have been shown to affect the wettability (Strand et al., 2007) and mechanical strength (Megawati et al., 2015; Andersen et al., 2018) of the chalk rock. The geological descriptions of four types of outcrop chalks, Stevns Klint, Aalborg, Liege and Beer Stone are summarized in Table 1

Table 1: *Geological description of some outcrop chalks (Milter et al., 1996; Puntervold, 2008)*

	Stevns Klint	*Aalborg*	*Liege*	*Beer Stone*	*Kansas*
Origin	Singerslev, Denmark	Rørdal, Denmark	Halembaye, Belgium	Beer, England	Niobrara, USA
Geologic age	Maastrichtian	Maastrichtian	Campanian	Turonian	Late Cretaceous
Silica content (wt%)	~ 1	2-7	< 2	-	< 2
Porosity (%)	45-50	44-48	40	24-30	37-40
Permeability (mD)	2-5	3-5	1-2	1-2	1-2
Specific surface area (m^2/g)	~2	~4	~2	~1	< 3

3.4.1 Aalborg chalk material

Aalborg chalk is located in the Rørdal quarry of Denmark. This Rørdal member of the chalk outcrop group is a cyclic-marl unit, about 10m thick, sandwiched between pure white chalks. Aalborg chalk cores were classified by Andersen et al., (2018) as coccolithic mudstones with large numbers of foraminifera shells and even layers of macrofossil debris. Their Coccolithophores are well preserved, but commonly show some overgrowth.

Surlyk et al., (2010) reported the coccolith and brachiopod data of this outcrop chalk member as belonging to the *UC20b-c*^{BP} nannofossil zone of the North Sea scheme for the Upper Cretaceous Boreal province, and the semiglobularis-humboldtii brachiopod zone, both indicative of a lower upper Maastrichtian age. Their interpretation of the Aalborg Isotope data showed that it represents a distinct early late Maastrichtian cooling event.

Typical characteristics of Aalborg chalk is the abundance of well-developed opal-CT ($SiO_2.nH_2O$), formed in blades and lepispheres, present in the non-carbonate phase and occur in the large intra-fossil pores (Megawati et al., 2015). In most outcrop chalks, like Stevns Klint, silica fraction is mostly dominant as quartz. opal-CT, is an abbreviation for a group of silica-stable minerals formed from pelagic phyto-plankton diatoms. Originally, these diatoms are composed of amorphous colloidal silica (opal-A) and are diagenetically lithified upon deposition in water bodies to the more stable opal-CT. At high temperatures, as in the subsurface reservoirs, the opal-CT in turn is altered to a microcrystalline quartz, which is the final and most stable form of silica.

It forms the main source of impurity in the Aalborg outcrop chalk that plays a significant role in porosity and reactivity modification of the outcrop and introduces a non-carbonate chemistry that will most likely impact laboratory results.

Andersen et al., (2018) investigated geochemical properties of Aalborg by flooding cores with $MgCl_2$ and NaCl brine. There was minute dissolution of calcite and Si-bearing minerals, but no new mineral precipitation was observed during NaCl injection. However, silica dissolution and reprecipitation (during $MgCl_2$ injection) as well as a significant concentration of Si^{4+}in the effluent was observed. Their findings suggest that the reactive presence of opal-CT in Aalborg plays a crucial role in the whole geochemical behavior of the outcrop rock.

When Strand et al., (2007) performed SEM analysis on Aalborg chalk, thin clay flakes were reported and suspected to be smectite after EDS (morphological and chemical) analysis showed presence of Aluminium (Al), Magnessium (Mg) and Potassium (K). Skovbjerg et al., (2012) used X-ray Diffraction (XRD) to analyze outcrop chalk residue after acid dissolution and quantified the non-calcite part to be between 1.8 and 4.6 % of which clay minerals contributed between 0.9 to 1.7 %. They also imaged 135 areas on different samples of chalk and reported laths on 75% of these areas. Although no chemical compositional analysis was conducted, they concluded that the observed laths, based on the size and shape, were clay minerals. They characterized the clay to consist of smectite (>85%) and small amounts of illite, kaolinite and mixed layer illite/smectite phases. It is established that due to their thinness, these clay coatings are very hard to observe in SEM and estimates of their size and distribution patterns are nearly impossible to obtain.

4 Introduction to Wettability

4.1 Wettability classification

Wettability describes the preferential tendency of a fluid to spread on or adhere to the surface of a solid material in the presence of other immiscible fluids (Donaldson et al., 2008). It plays a direct role in determining the relative permeabilities and distribution of reservoir fluids, and ultimately the success or failure of an EOR operation by drive fluids. In the reservoir, wettability of the crude oil/brine/rock (COBR) system and its effect on oil recovery is an extremely challenging problem and many studies (Donaldson et al., 1969; Andersen, 1987; Morrow, 1990; Cuiec, 1991; Drummond et al., 2004; Donaldson et al., 2008) have been dedicated to understanding its complexity. In the reservoir, several COBR interactions have established an equilibrium that has defined a specific wetting condition prevailing in the subterranean rock, which are suitably categorized into four general forms (Donaldson et al., 2008);

a) water-wet
b) oil-wet
c) fractional wettability
d) mixed-wettability

A COBR system is considered water-wet or oil wet when more than 50% of its surface is wet by water or oil respectively. In water-wet conditions, if the water saturation is reduced to its irreducible saturation (S_{wi}), water remains as a continuous phase in the small pores throughout the rock structure and the oil is reserved to larger pores with high enough saturation to exist as a continuous phase. A rock under such wetting state will spontaneously imbibe water (the wetting phase) to expel the oil (which is non-wetting) until a state of static equilibrium is reached between the capillary and surface energy forces (Donaldson et al., 2008). As the water saturation increases, the oil phase experiences a snap-off effect, becoming discontinuous and existing as globules in the center of the larger pores (Hopkins, 2016). A reverse of the above-mentioned fluid distribution through the pore network is true for an oil-wet system as illustrated in figure 4.1. The terms water-wet and oil-wet are included in the frequently used term *homogeneous wettability*.

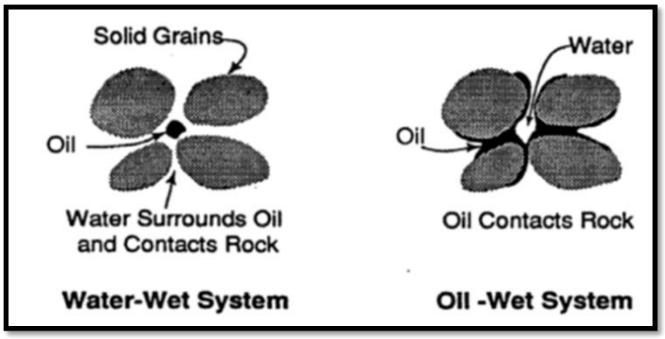


Figure 4.1: *Illustration of homogeneous wettability (Willhite et al., 1998)*

Fractional wetting typifies heterogeneous wetting of the pore surfaces where the preferential wetting is randomly distributed throughout the rock. Mixed wetting, introduced by Salathiel (1973), also characterizes a condition where the small pores in the pore network are water-wet and saturated with water, but the larger pores are oil-wet and filled with oil that connects to form a continuous path throughout the rock matrix. Both terms are included in the often-used general term *neutral-wettability*. Under such wetting state of distinctive oil-wet and water-wet zones, water and oil may be spontaneously imbibed respectively at high oil and water saturations (Andersen 1987; Cuiec, 1991; Agbalaka et al., 2008).

The wetting phase that will result in optimal recovery of oil has been the subject of intense debate, as pointed out by Agbalaka et al., (2008) in a review of wettability effect on oil recovery. The reason for this divergence in observed report is attributable to a number of modifying factors which include; constraint of/difficulty in wetting state reproducibility, the lack of unified standard or procedure for coring, core handling and core storage and the wetting state characterization method adopted. In this regard, many published reports have proposed ways of maintaining and restoring in-situ core wetting state to ensure that reservoir rock wettability is accurately measured and used in laboratory and/or field-wide determination of recovery efficiency. A study by Puntervold et al., (2007), for example, suggested a new method to prepare outcrop chalk cores for wettability and oil recovery studies at low S_{wi} and is employed during core preparations for experiments conducted in this thesis work.

4.2 Wettability measurement techniques

A wide variety of methods have been proposed for wettability assessment of surfaces. This section introduces the quantitative measurements; contact angle, Amott water index, United States Bureau of Mining (USBM) and a more modern technique; Chromatographic wettability test. Using imbibition as a qualitative method is also briefly described. The terms imbibition and drainage will be frequently used in this section. Drainage defines the process that leads to increased saturation of the non-wetting fluid and imbibition refers to increase in the saturation of the wetting fluid. By considering water to be wetting, Imbibition, the increase of water saturation, may proceed by either spontaneous imbibition or forced imbibition (see also section 2.4). Similarly, the increase in oil saturation may proceed by spontaneous drainage or forced drainage.

4.2.1 Contact angle measurements

The surface energies of typical COBR system as shown in figure 4.2, are related by Young's equation:

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow} cos\theta \qquad (4.1)$$

Where σ_{os} is the interfacial energy between the oil and solid, σ_{ws} is the interfacial energy between the water and solid, σ_{ow} is the interfacial energy [interfacial tension (IFT)] between the oil and water and θ is the contact angle of the water/oil/solid contact line (Andersen , 1986).

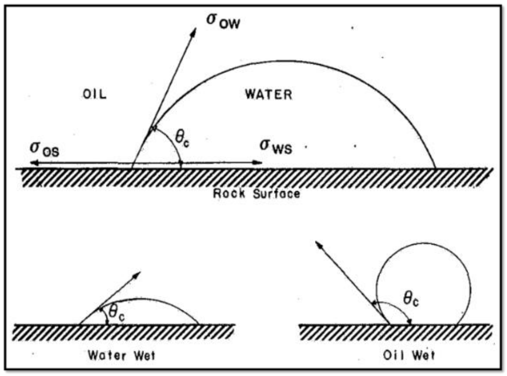


***Figure 4.2:** Wettability of the COBR system (Andersen , 1986)*

As shown above, when the contact angle is less than 90° the surface is preferentially water-wet, and when it is greater than 90° it is regarded as oil-wet. By convention, the contact angle is measured through the water phase. For almost all pure fluids and clean surfaces, the IFTs have values such that $\theta = 0^{\circ}$. In the reservoir however, due to compositional differences in the 3 phases, the IFTs are changed unequally and results in different values of θ. A universal classification of the wettability as a function of θ is described in table 2. Preferably, this method of wettability characterization is used when pure fluids and clean surfaces are under study.

Many modifications of this method (including the tilting plate method, sessile drops or bubbles, vertical rod method, cylinder method, capillary rise method, etc.) have been proposed but because of the surface-active agents in crude, a significant length of time is needed for a contact angle measured with reservoir core and fluids to reach equilibrium and thus, has seen less usage in the petroleum industry. It is noteworthy however, that it is the most universal measure of surface wetting conditions.

***Table 2:** Approximate relationship between contact angle and wettability*

Contact Angle, (º)	***Wettability***
0-30	Strongly water-wet
30-90	Water-wet
90	Neutral wet
90-150	Preferentially oil-wet
150-180	Strongly oil-wet

4.2.2 Spontaneous imbibition

Wettability description by imbibition gives a quick but rough idea of the wettability state without requiring any complicated equipment and has become the most commonly used qualitative wettability measurement (Andersen , 1986). In an imbibition test, a core at S_{wi} is first submerged in brine underneath a graduated cylinder, and the rate and amount of oil displaced by brine imbibition are measured. The wettability characterization is then aided by referring to reference samples that are close to perfect wetting conditions (Morrow, 1990; Hopkins, 2016).

The core is strongly water-wet if large volumes of brine are rapidly imbibed, while lower rates and smaller volumes imply a weakly water-wet core. If no water is imbibed, the core is either oil-wet or neutrally wet. The set-up can be inverted to characterize oil wetness by driving the core to residual oil saturation (Sor) and repeating the process. It is notable, that some cores will imbibe both oil and water spontaneously and are either classified as fractional or mixed wet.

4.2.3 Amott wettability index

The Amott method (Amott, 1959) combines imbibition and forced displacement tests to measure the average wettability of a core. The principle is based on the premise that the wetting fluid will generally imbibe spontaneously into the core, displacing the non-wetting fluid. The procedure is elaborated in four steps below Morrow (1990);

1) The core, at S_{or} filled with brine, is immersed in oil, and the brine volume displaced by the oil during SI is recorded as V_{wsp}
2) The core is then taken through a forced displacement procedure (using oil) until irreducible water saturation (S_{wir}) is achieved. The total amount of water displaced between both steps 1 and 2 is recorded as V_{wt}
3) Then the core, at S_{wir} , is immersed in brine, where oil volume displaced by water during SI is recorded as V_{osp}.
4) Step 2 is repeated using brine as displacing fluid until residual oil saturation is achieved. The total oil produced from steps 3 and 4 is recorded as V_{ot}.

The capillary pressure during the different imbibition stages is measured. Figure 4.3 shows the relationships of saturation changes to capillary pressure vs saturation curves. The Amott wettability indices to water (displacement-by-water ratio, I_w) and oil (displacement-by-oil ratio, I_o) are then expressed by:

$$I_w^* = V_{osp}/V_{ot} \qquad (4.2)$$

$$I_o^* = V_{wsp}/V_{wt} \qquad (4.3)$$

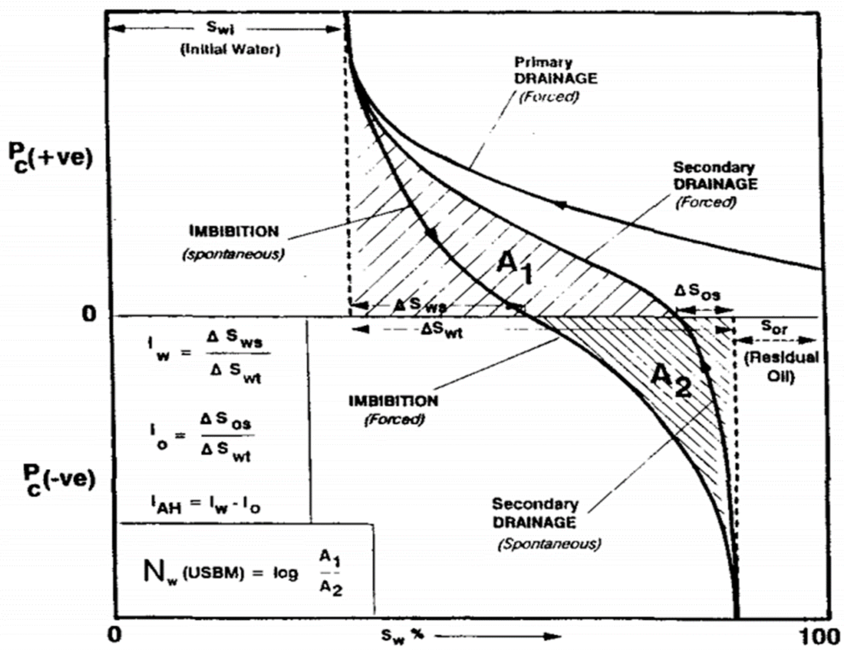
For any sample, the I_w approaches 1 as the water wetness increases. A strongly water-wet core would have $I_w^* = 1$ and $I_o^* = 0$. The Amott-method is the approach implemented in this thesis study to evaluate core wetting.

A modification of the Amott test, called the Amott Harvey relative displacement index (I_{AH}) is a more common representation used to characterize the wettability by a single number (Morrow et al., 1986).

$$I_{AH} = I_w^* - I_o^* \qquad (4.4)$$

This combines the two Amott indices into a single wettability index that varies from +1 for complete water wetness to -1 for complete oil wetness. Cuiec (1991) reported that the system is water-wet when $+0.3 \leq I_{AH} \leq 1$, intermediate wet when $-0.3 \leq I_{AH} \leq 0.3$ and oil wet when $-1 \leq I_{AH}$

≤ -0.3. The main drawback with the Amott wettability test and its modifications are their insensitivity near neutral wettability (Morrow, 1990; Strand et al., 2006b; Ghedan et al., 2014).



S_{wi}
(Initial Water)
Primary DRAINAGE (Forced)
P_c(+ve)
Secondary DRAINAGE (Forced)
IMBIBITION (spontaneous)
A_1
ΔS_{os}
0
ΔS_{ws}
ΔS_{wt}
S_{or}
(Residual Oil)
$I_w = \frac{\Delta S_{ws}}{\Delta S_{wt}}$
$I_o = \frac{\Delta S_{os}}{\Delta S_{wt}}$
A_2
IMBIBITION (Forced)
P_c(-ve)
$I_{AH} = I_w - I_o$
Secondary DRAINAGE (Spontaneous)
N_w (USBM) = log $\frac{A_1}{A_2}$
0
S_w %
100

Figure 4.3: *Relationship of wettability measurement by Amott and USBM testes to Pc curves for a mixed wettability system (Morrow, 1990)*

4.2.4 United States Bureau of Mines (USBM)

In the USBM method (Donaldson et al., 1969), both drainage and imbibition capillary pressures are measured usually by centrifuging. This testing procedure also measures the average wettability of the core with a major advantage over the Amott test due to its improved sensitivity near neutral wettability (Morrow, 1990). The test compares the work done by one fluid to displace the other by measuring the area in the two regions of capillary pressure curves produced during the forced drainage and imbibition processes (see figure 4.3).

The USBM wettability number is then defined by;

$$WI_{USBM}\ or\ N_W = log\frac{A_1}{A_2} \tag{4.5}$$

Where A_1 is the area under the secondary water-drainage curve (resulting from oil displacing water) and A_2 is the area under the imbibition curve falling below the zero P_c axis (resulting from water displacing oil). Clearly, WI_{USBM} values should theoretically range from -∞ to +∞ but Strand et al (2006) pointed out that values between -2 and +2 occur most commonly. The procedure is rapid and simple and its adaptation to relative permeability measurements makes it a choice method for wettability characterization of cores. A minor disadvantage reported by Andersen (1986) is that the WI_{USBM} can only be measured on plug-size samples because a necessary step in the procedure is to spin the cores in a centrifuge.

4.2.5 Chromatographic wettability test

This wettability test method was developed by Strand et al. (2006b) to characterize the wetting state of carbonates by the chromatographic separation of two water soluble components; SCN$^-$ and SO$_4^{2-}$. The sulphate (SO$_4^{2-}$) is a potential determining ion towards chalk whilst thiocyanate (SCN$^-$) acts as a tracer; thus, during core flooding using water spiked with equal amounts of these components, SO$_4^{2-}$ is adsorbed onto the sites contacted by water (i.e the water-wet areas of the core) and its transport through the media is delayed accordingly as against SCN$^-$ which is non-adsorbing and experiences no retardation. This combined property is used to quantify the water-wet surface area of the core material during flooding at room temperature.

In the procedure, an oil saturated core is driven to S$_{or}$ with a brine striped of SO$_4^{2-}$ and SCN$^-$ before flooded with the test brine containing equal amounts of the soluble components. The effluent is sampled and analyzed for ionic compositions of SO$_4^{2-}$ and SCN$^-$. A plot (see figure 4.4) is generated using the relative ion concentration against the pore volume (PV) injected and the area between the effluent curves is computed using the trapezoidal rule.

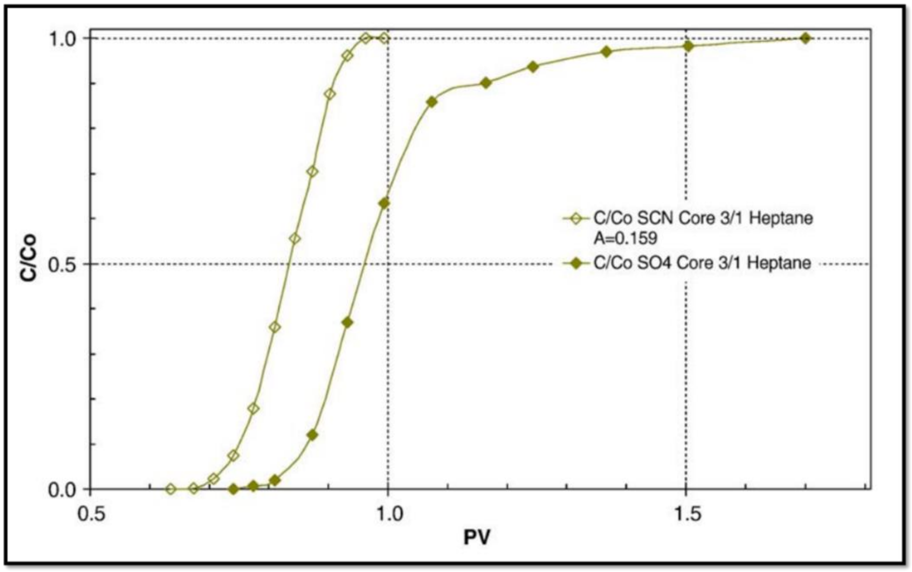


Figure 4.4: *Chromatographic separation of SCN– and SO42- for a preferentially water-wet system using heptane as oil phase (Strand, Standnes, & Austad, New wettability test for chalk based on chromatographic separation of thiocyante and sulphate, 2006b)*

This area is directly proportional to the water-wet surface area inside the core. The wetting index, I$_{CW}$, representing the fraction of water-wet area within the core matrix is calculated by the equation;

$$I_{CW} = \frac{A_{wett}}{A_{heptane}} \qquad (4.6)$$

Where A$_{heptane}$ and A$_{wett}$ corresponds to the areas between the effluent curves for a completely water-wet system (using Heptane as the oil phase) and the actual crude oil system, respectively. Clearly, I$_{CW}$ will range between 0 and 1; denoting completely oil-wet and completely water-wet conditions, respectively. This characterization method is excellent to be used close to neutral conditions, which will give a wetting index of 0.5 (Strand et al., 2006b).

Moreover, the test is fast and can be conducted at residual saturations without performing any long-term imbibition tests. The only drawback is its limitation to carbonate core material and cores without anhydrite present within the core mineralogy (Hopkins, 2016).

4.3 Crude Oil/Brine/Rock Interactions

Originally, before oil encroached the reservoirs, the rock surfaces were water-wet, but crude oil modified the wetting behavior of the initially established equilibrium through several mechanisms of different relative importance depending on the reservoir mineral and the associated brine that yielded the secondary wettability equilibrium states observed in the subsurface formations when discovered (Buckley, 1998). A mechanistic study of the crude oil/brine/rock (COBR) system was investigated by Buckley et al., (1998) and they postulated what later became the core emphasis for the mechanisms by which these components adsorbed onto rock mineral surfaces. Experiments performed by Drummond et al., (2004) to study the crude-oil-surface water interactions and its relationship to reservoir wettability, established that depending on the nature of the oil and brine, different species in a crude oil will adsorb on the mineral surface and at the oil-water interface, thereby determining the wetting behavior of a reservoir rock. Of particular significance is the Zeta potential of the crude oil/brine (OB) interface and of the rock/brine (RB) interface that develops as a result of the complex COBR interactions (Hirasaki, 1991; Buckley, 1996; Strand, 2005).

When carbonate mineral is in contact with brine, ionic interactions (Chapman, 1913) between the charged components at the mineral surface and those in the brine yields an electrical double layer (EDL) made of a static inner part (stern layer) and a dynamically formed diffuse cloud of ions (forming the outer layer) near the rock surface. The electrical potential across the plane separating these two layers is the zeta-potential (Verwey et al., 1939). It provides indication of the surface charge that exists at the carbonate rock surface and captures the effects of pH, salinity, temperature and mineralogy since it is affected by all these factors. The interactions between the EDL and an oil-brine interface containing the polar organic molecules contributes significantly to the overall wettability of the rock (Buckley et al., 1989).

An opposite charge between the OB and RB interfaces results in an electrostatic attraction that yields negative disjoining pressure (total pressure between two interfaces at very small separation distance) and the oil can approach and adhere to the mineral surface. On the other hand, positive disjoining pressure causes repulsion of the interfaces and the original water film remains stable, minimizing the ability of oil to adsorb onto the surface. This phenomenon is well covered in the literature (Derjaguin et al., 1987; Buckley et al., 1989; Hirasaki, 1991; Legens et al., 1999) and a rather simple illustrative outline is presented in figure 4.5.

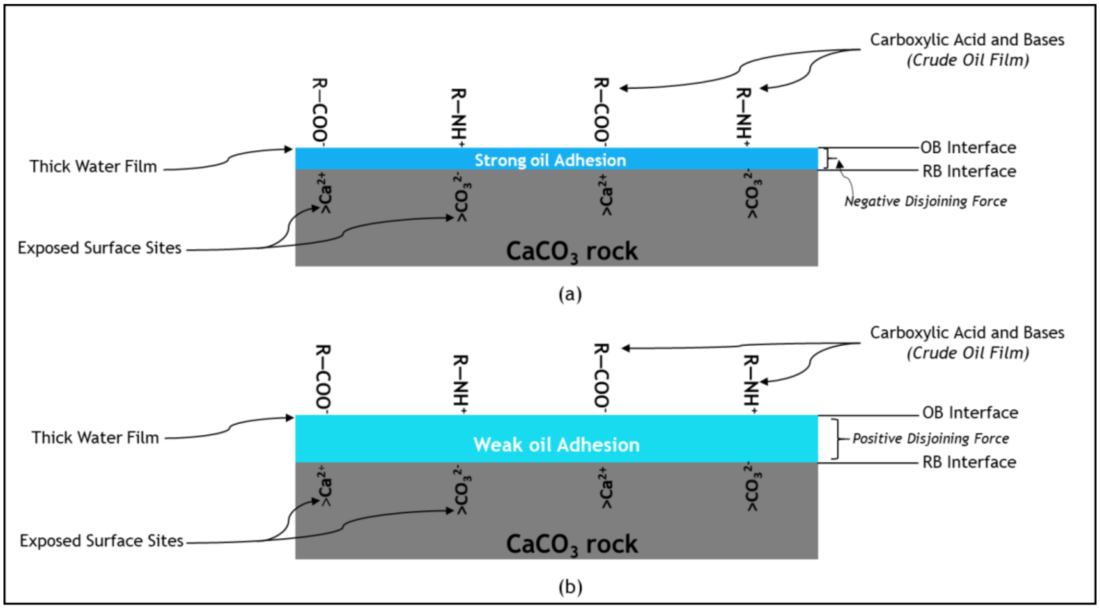

Carboxylic Acid and Bases
(Crude Oil Film)
R—COO-
R—NH+
R—COO-
R—NH+
Thick Water Film
Strong oil Adhesion
OB Interface
RB Interface
Negative Disjoining Force
>Ca2+
>CO3 2-
>Ca2+
>CO3 2-
Exposed Surface Sites
CaCO3 rock
(a)
Carboxylic Acid and Bases
(Crude Oil Film)
R—COO-
R—NH+
R—COO-
R—NH+
Thick Water Film
Weak oil Adhesion
OB Interface
Positive Disjoining Force
RB Interface
>Ca2+
>CO3 2-
>Ca2+
>CO3 2-
Exposed Surface Sites
CaCO3 rock
(b)

Figure 4.5: *Illustration of oil adherence onto carbonate mineral surface in relation to the surface forces and interfacial interactions of Oil/Brine and Rock/Brine interfaces*

4.4 Carbonate wetting

It is generally acknowledged that carbonate rocks exhibit neutral to oil-wet tendencies. (Treiber et al., 1972) investigated 50 hydrocarbon reservoirs and indicated that 64% of carbonate rocks were intermediate wet, 28% were oil wet, and 8% were water wet. In fact, out of 25 carbonate hydrocarbon systems tested in the West Texas-New Mexico province, their study reported 90% of the carbonate reservoirs to be oil-wet. In another extensive research work, (Chilingar et al., 1983) evaluated the wettability for 161 carbonate rocks (involving limestone, dolomitic limestone, calcitic dolomite and dolomite rock samples) and concluded that 15% of them were strongly oil-wet, 65% were oil-wet, 12% had intermediate wettability, and 8% were water-wet. Contrary to the preceding findings, a study by (Mansour, 1974) on 120 carbonate reservoir samples from Iranian oilfields reported only 4 to have intermediate wettability, with all the others being water wet. This is hardly a random selection and makes his findings somewhat biased and barely qualifies for a general evaluation of carbonate wetting. In an effort to establish coherence in the early assertions made, (Cuiec, 1984) examined the wetting state of 15 carbonate reservoir cores selected from three continents (Europe-6, North Africa-3 and Middle East-6). He reported 50% of the cores to have clearcut oil wettability, 42% of the cores in the intermediate zone and only 1 core exhibited strong water wettability. These results on carbonate rock cores from across the world depicts that most carbonates are preferentially oil-wet.

The degree to which a carbonate rock is either water wet or oil wet is affected by several complex and ever changing COBR interactions and applying EOR techniques requires the consideration of the current wetting conditions sustained in the reservoir at the time of implementation.

But, the initial wettability conditions of a rock, in a reservoir, at equilibrium, is elusive to ascertain; since the subsurface COBR equilibrium is virtually always altered when the sample rock is drilled, cored, and transported to the laboratory. Certain reports (Puntervold et al., 2007; Hopkins, 2016) have further documented that changes may occur during handling and experimental preparations in the laboratory, which further complicates reservoir core material restoration in the laboratory to representative states that will mimic the initial wetting conditions of the reservoir.

In this section, some of the main factors that can impact initial wettability of carbonates is presented. The essence of circumspective methods for core restoration during laboratory studies is highlighted.

4.4.1 Influence of crude oil composition and properties

Crude oil is a complex mixture of hydrocarbons and polar organic compounds of nitrogen, sulphur and oxygen (NSO) and may include metal-containing compounds such as nickel, iron, vanadium and copper. All crude oils contain surface-active components, as documented in the literature (Buckley, 1996; Andersen, 1986a; Drummond et al., 2004; Denekes et al., 1959; Puntervold et al., 2007b; Shariatpanahi et al., 2016) and this makes them reactive to charged surfaces by adsorbing with the polar end onto the rock surface, and positioning the hydrocarbon end outwards to make the surface oil-wet (Puntervold, 2008).

It is originally believed, as previously mentioned, that reservoirs were water-wet and contact with crude oil that encroached due to migration altered the wetting states to less water-wetness. In fact, it seems only in unique cases where an original mineral is intrinsically oil-wet or where the reservoir is itself a source-rock, that the postulation of initial water-wetness is rendered inapplicable. But since both special cases are highly unlikely, especially for carbonate reservoirs, the alteration of wettability by surface-active components in crude oil is undisputable.

Thus, though they differ greatly with respect to the kinds, concentrations, and states of aggregation of surface-active materials present, crude oil polar components is recognized as the most important wetting parameter in reservoirs. The polar compounds of acidic and basic nature are primarily found to be especially important regarding adsorption onto mineral surfaces to initiate wettability alteration (Andersen, 1986a; Cuiec, 1984). The acidic material is usually represented by the carboxylic group ($RCOO^-$) and the basic material (those compounds which contain nitrogen), with high polarity, is represented as R_3NH^+.

The mechanisms by which these polar components can adsorb was first proposed by Buckley (Buckley, 1996), who identified four main associations:

a) Polar interactions that predominate in the absence of a water film between the rock and the crude oil.
b) Surface precipitation, dependent mainly on crude oil solvent properties with respect to the asphaltenes and other heavy components.

c) Acid/base interactions that occur where charges at oil-brine and rock-brine interfaces changes the pH of the system.
d) Ion binding or specific interactions between charged sites and higher valency ions that binds oil components to the brine and rock.

Affinities of the acidic or basic components towards actual reservoir minerals varies depending on the chemical composition of the crude oil, the rock and the initial brine, thus, both mineralogy and brine chemistry are key factors when considering the potential of any crude oil to alter the wettability of a surface. In carbonates the wettability is more affected by the organic acids while the wettability of silica is more affected by the organic bases due to the effect of mineral surface charges (Puntervold, 2008). In Chalk, (Thomas et al., 1993) reported the carboxylic group as adsorbing very strongly onto the positively charged calcite surface through chemisorption and only removable by a solvent that provided both good solubility for the adsorbate and an ionic species to replace it at the mineral surface.

A figurative summary of pure chalk wetting at the often-alkaline environment observed in reservoirs is illustrated in figure 4.6.

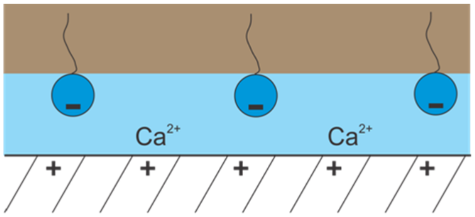
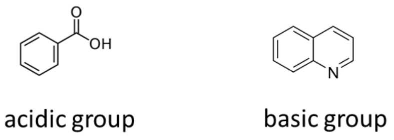
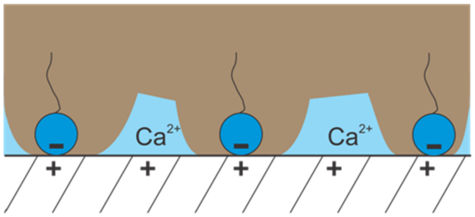
a) Chalk (Calcite) dissociation in a closed environment $CaCO_3 + 2H_2O \rightleftharpoons Ca^{2+} + H_2CO_3 + 2OH^-$ **Alkaline conditions** will favour equilibrium shift to right and **more divalent cations** $[Ca^{2+}]$ **are released**	
b) Crude Oil disposition in alkaline conditions: ➢ Acidic components deprotonated to release negatively charged R-COO- ➢ Basic components deprotonated and exist as uncharged R_3NH	
a)+b) The phases will begin to interact ➢ Negatively charged R-COO- will attach unto the + charged chalk surface and serve as anchor for the oil phase to adsorb ➢ Neutral R_3NH will not interact with the surface	

Figure 4.6: *Illustration of initial wetting of carbonate chalk rock in alkaline conditions. pH of the system influences the dissociation of polar organic components and dictates their ability to adhere onto charged surfaces.*

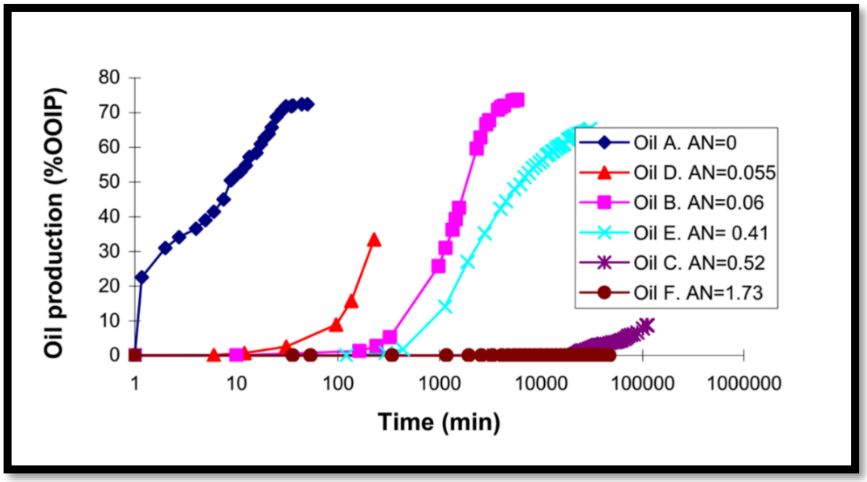


Figure 4.7: *The influence of AN, on oil recovery from chalk by spontaneous imbibition (Standnes et al., 2000). Increasing AN gives less water-wetness*

The acid number (AN) and base number (BN) may be measured (Fan et al., 2006) to quantify the relative amounts of each group contained in a crude oil. Several authors (Standnes et al., 2000; Zhang et al., 2005; Puntervold et al., 2007b; Ravari et al., 2011; Mjos et al., 2018) have shown that the acidic component has the greatest impact on chalk wettability alteration; where increasing the AN is shown to lower the water-wetness of chalk. This is illustrated in figure 4.7.

In natural crude oils, the BN is known to be much higher than the AN, but, in a study (Puntervold et al., 2007b) to examine the impact of natural bases on chalk wettability, it was revealed that the direct adsorption of basic components onto pure chalk surfaces was limited and that the relative impact of BN on wettability modification was related to the molecular size of the basic components. More directly, it was postulated in the study that bases in natural crude have the tendency to complex with acidic components and hinder the carboxylic groups from adsorbing onto surfaces to alter wettability (see Figure 4.8). Thus, by such indirect mechanisms, BN may play a critical role in wettability reversal of carbonated minerals.

Due to the high impact of crude oils on altering the wetting state of chalk mineral surfaces, the amount of crude oil a chalk core is exposed to during experimental investigations will be crucial and must always be considered during wettability characterization of cores.

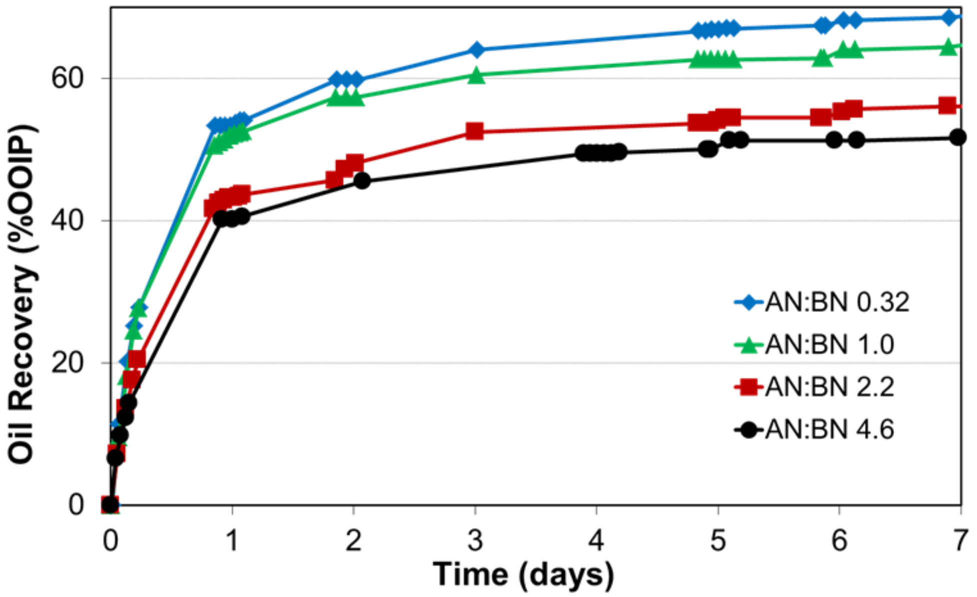


Figure 4.8: *Influence of BN on chalk wetting. Investigation at constant AN=0.5 shows increased water wetness with increasing BN (Puntervold, 2008)*

4.4.2 Influence of rock mineralogy

The preferential wetting of a carbonate mineral surface is dictated by which of the fluid phases; crude oil or the aqueous brine has the highest affinity for the minerals defining the chemistry of the rock surface. Salathiel (1973) illustrated the effect of mineralogy on wetting that introduced the development of the term mixed-wettability into the petroleum literature. Carbonate reservoirs have varied mineralogical makeup and the retention of oil components is influenced by the composition of the rock material as chemical interactions will vary with surface charge and area exposed to the crude oil and brine.

In a study aimed at investigating carbonate rock wettability changes, Abdulrazag et al., (2003) examined the effect of four different carbonate rock types by modifying the mineralogical compositions of Calcium, Iron, Magnesium, Potassium, Aluminium and Copper. All rock types showed oil-wet tendencies with differing degree of propensities that suggested carbonate rock mineralogy to influence wetting conditions. As pointed out in section 4.3, it is well documented, that adsorption and desorption of oil and brine species from mineral surfaces is controlled by rock surface charge. Carbonate rock surfaces are positively charged at basic conditions (Andersen, 1986a) due to relatively high composition of positive divalent ions (such as Ca^{2+} and Mg^{2+}) therefore making it possible for negatively charged organic acids in crude oil to adsorb onto the carbonate surfaces (Hopkins, 2016). The ability of the crude oil or brine to clinch onto the chalk surface and influence the wetting thus will depend on the mineral surface chemistry, which is defined by the chemical composition of the rock.

Strand et al., (2007) studied the impact of silica and clay content on the wettability of chalk and reported that their presence caused a more-water wet condition compared to chalk specimen containing lower silica content. They explained that the negatively charged silica stabilizes the water film coating the chalk surface and inhibited the overlaying oil from contacting the surface. It has been reported (Shariatpanahi et al., 2016) that the presence of Mg^{2+} in formation water appeared to make a carbonate surface more water-wet and it is therefore rational to suggest that this effect could be exhibited in dolomitic carbonates, due to their high concentrations of Mg^{2+}. Furthermore, SO_4^{2-} has been reported as a potential determining ion towards chalk surfaces that increases the water-wetness (Strand et al., 2006b; Puntervold et al., 2007; Shariatpanahi et al., 2016). Thus, the presence of anhydrite ($CaSO_4$) in a carbonate rock (as is the case in most U.A.E carbonate reservoirs) may induce tertiary low-salinity EOR effects in carbonates due to dissolution of the $CaSO_4$ mineral. It is therefore imperative that in understanding the impact of wettability on EOR processes and how to optimize the knowledge of wettability reversal potential of injected brines, much more attention should be geared towards the chemistry of the prevailing factors.

4.4.3 Core Restoration

During laboratory characterization of reservoir rocks, it is a common routine to clean the samples by flooding with solvents. However, the effectiveness of the core cleaning procedure will influence the amount of originally adsorbed surface-active components that would remain on a core. The desorption of originally adsorbed polar components will influence the initial wetting of the core (Grist et al., 1975; Shariatapanahi et al., 2012; Hopkins, 2016) and may result in wetting states that are unrepresentative of the rock minerals in the subsurface reservoir.

The appropriate solvents and cleaning mechanisms therefore must be implemented during core restoration procedure to minimize experimental errors. Puntervold et al., (2007) pointed out that outcrop core investigations for wettability studies ought to be cleaned in a manner that strips the material of originally present PDIs that may adsorb onto the mineral surface and contribute potential errors to the analysis procedure. (Hopkins et al., 2015) recommended mild cleaning of reservoir core material using kerosene followed by heptane as ideal in preserving a large amount of the initially adsorbed polar components. Results from petrophysical analysis of reservoir rocks contribute a huge part in the entire assessment of a reservoir field and it is therefore imperative that core restoration procedures be conducted with extreme caution to yield reliable results.

4.4.4 Influence of Initial brine composition and water saturation

Connate water is always present in oil reservoirs (Buckley, 1996), and is usually different to the additional brine introduced during production either as natural aquifer drive or as injected water during water floods. In a chalk rock formation, this connate water contains excess Ca^{2+} ions, which yields a positive carbonate surface. Moderate concentrations of Mg^{2+} and negligible concentrations of SO_4^{2-} may also be present depending on the mineralogy of the reservoir rock matrix and the minerals this water has been in contact with, prior to its arrival in the host reservoir rock. The ionic compositions of the initial brine will instigate properties such as pH and salinity, which will have imminent impact on the surface charge of chalk and the preferable state (protonated or deprotonated) of existence for the polar components (see figure 4.6) and their corresponding wettability alteration tendencies.

Minor concentrations of sulphate in the formation water of outcrop chalks has been reported (Puntervold et al., 2007) to have significant impact on initial core wettability by making the chalk seem preferentially more water-wet (Hopkins, 2016).

Hirasaki (1991) observed that variations in wettability are often related to the presence or absence of water films between the reservoir and the reservoir rock surface. He argues that wetting in COBR systems will be determined by the thickness of the water film coating the mineral surfaces. Such crude adsorption processes are considered irreversible, fast and independent of temperature in the absence of water (Buckley J. , 1996). This assertion introduces the effect of water saturation on initial wetting of carbonate mineral surfaces (as depicted in Figure 4.5). (Yan et al., 1997) reported increased oil-wetness at lower S_{wi}. In an experiment (Puntervold et al., 2007), increasing S_{wi} improved water-wetness and resulted in increased oil recovery via spontaneous imbibition. The improved water-wetness was attributed to increased water saturation that minimized available sites for crude oil adsorption onto surfaces. Similar results have been reported by (Mjos et al., 2018) who measured AN/BN of crude oil effluent flooded through different chalk cores at varied the S_{wi} and observed a reduced adsorption of polar components with increasing S_{wi}.

Maintenance of water-wetness, thus, in a reservoir correlates with the amount and stability of water films at pore walls. If stable thick water films coat the surface and separate the oil from the chalk surface, the system will be water-wet (Agbalaka et al., 2008). Conversely, if the water films are unstable, they desorb, and the crude oil can have easy access to the solid surface in the region of contact and consequent adsorption of polar compounds can drastically, and often permanently, render the contacted surface area more oil-wet (Morrow N. R., 1990). It must be noted that the changes of brine salinity and/or the type of salt can disturb the balance of forces causing rupture of a water film separating oil from contact with the chalk surface. This should be taken into account when choosing and preparing synthetic brines for laboratory experiments.

4.4.5 Effect of Ageing

The wettability equilibrium conditions of a carbonate reservoir have been established by a physical and chemical interaction between the crude oil, brine and rock, that has been preserved in the subsurface formation over many years. Within the scientific community, ageing a core to establish and restore uniform COBR system during laboratory core preparation procedures, is still debated. In some reports (Puntervold et al., 2007b), increasing ageing time changed wettability from strongly water-wet to near neutral-wet by spontaneous imbibition tests using chalk. This is supported by another literature (Graue et al., 2003) where ageing of chalk cores resulted in reduced water-wetness. An experimental study by Hopkins et al., (2016) using chalk cores have reported immediate adsorption of polar crude components upon exposure to oil. A similar observation has been reported by (Mjos et al., 2018). It seems then, that though a certain finite amount of ageing time may be required for representative wettability changes to take place after a rock has been first saturated with water and then with oil, the adsorption process is profoundly instant and characterizing core wettability as a function of ageing time is irrelevant.

4.4.6 Temperature and pressure effects

A report on crude oil adsorption by Wang et al., (1995) showed temperature and pressure to exert influence on the solubility of surface-active components in the crude oil. The relationship was observed to be linear. It is also documented (Puntervold et al., 2007b) that crude AN decrease at elevated temperatures. In carbonate reservoirs, $CaCO_3$ plays a catalytic role at elevated temperatures, that causes decarboxylation of oil carboxylic group, which decomposes this key surface-active component and lowers the AN (Shimoyama et al., 1972; Zhang et al., 2005). This is consistent with Rao's observation that high temperature carbonate reservoirs exhibited preferentially water-wet tendencies (Rao, 1996). It is therefore a general observation for carbonate reservoirs that the water-wetness increases as the reservoir temperature increases. However, wettability tests (Puntervold et al., 2007b) by ageing chalk cores in crude oils of different AN at different temperatures confirmed that the AN played the principal role concerning chalk wetting. Thus, though the temperature/pressure effect is important in initial wetting, it may be minimal in cases where the crude oil content is heavily spiked with acidic components. The temperature and AN as wetting parameters for carbonates are therefore independent variables.

4.5 Implication of carbonate wetting on waterflooding

Waterflooding is a secondary oil recovery process in which water is injected into a reservoir to remove additional volumes of residual oil after primary recovery. The success or failure of this technique is strongly connected to the wettability of the subsurface system and the fact that it affects oil recovery efficiency is widely acknowledged. One of the influential works on the importance of wettability on waterflooding performance was by Buckley and Leverett in 1941 (Buckley et al., 1942). Carbonates are usually highly fractured and coupled with the unfavourable wetting conditions, these intrinsic characteristics will have consequences on water flood EOR operations. In a fractured reservoir, the matrix blocks that contain most of the oil are bounded by a fracture network with permeability that is several orders of magnitude higher than that of the matrix. This leads to injected fluids channeling readily through the fracture system (see figure 4.9) from injector to producing wells and limiting their entry into the matrix structure, where most of the oil is contained. This causes early water-breakthrough and an uneconomical water/oil producing ratio.

Under such rock framework, capillary forces will dominate the flow mechanism (Morrow, 1979; Morrow et al., 2001) and spontaneous imbibition of the injection fluid into the blocks, accompanied by displacement of oil from the blocks, constitutes the principal drive mechanism to obtain high recovery. For a water-wet matrix system, water will imbibe until the capillary pressure becomes zero

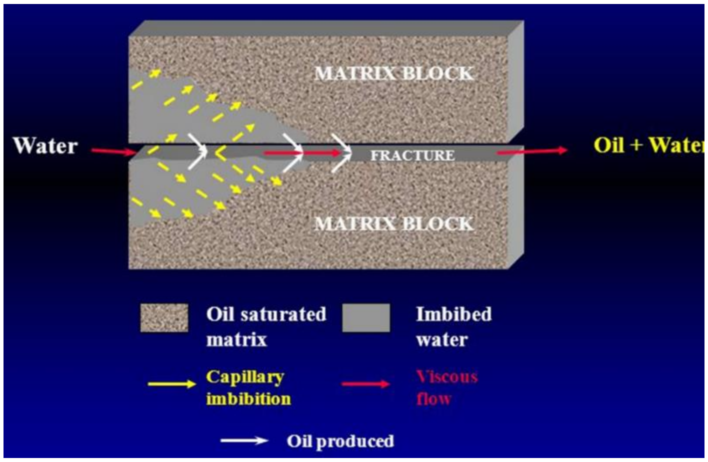

MATRIX BLOCK
Water
FRACTURE
Oil + Water
MATRIX BLOCK
Oil saturated matrix
Imbibed water
Capillary imbibition
Viscous flow
Oil produced

Figure 4.9: *Schematic representation of the displacement process in fractured medium*

A combination of pressure exerted by gravity and induced by the injection can further displace oil even after imbibition has stopped (Donaldson et al., 2008). As described in section 4.4, carbonates are mostly neutral to oil-wet and consequently, spontaneous uptake of water is limited due to a negative capillary pressure and therefore, the injected water will sweep a much smaller volume of the reservoir resulting in a low degree of oil production.

Thus, to achieve high recoveries from carbonate rocks, the capillary pressure should be increased through a wettability reversal of the rock surface towards a less oil-wet state, in that way promoting spontaneous imbibition of water to expel the oil (Puntervold, 2008). Smart water EOR application is a proven method that can accomplish this desired wetting state.

5 Smart Water EOR in Carbonates

Smart water is brine with modified ionic composition that has potential for wettability reversal to more water-wet conditions when introduced into the COBR system. The desired wetting conditions to yield positive capillary pressure that stimulate SI of water for improved oil recovery in carbonates can be achieved through Smart Water EOR application. This chapter briefly discusses this phenomenon in carbonates, with emphasis on chalk reservoir.

5.1 EOR by seawater injection

Seawater has been injected into the naturally fractured Ekofisk chalk reservoir in the North Sea with great success (Sytte et al., 1988; Austad et al., 2005). This is due to its ability to induce wettability modifications of the rock towards more water-wet conditions by interactions between its active ions; Mg^{2+}, Ca^{2+}, and SO_4^{2-} (referred to as potential determining ions, PDIs) and the calcite surface. Several studies have confirmed this intrinsic ability of seawater on chalk (Austad et al., 2005; Zhang and Austad, 2005a; Høgnesen et al., 2005; Zhang and Austad, 2006; Strand et al., 2006) limestone (Strand et al., 2008; Austad et al., 2012) and dolomites (Shariatpanahi et al., 2016; Puntervold et al., 2016). It was observed in these studies that temperature and the PDIs from the injected seawater were the key factors influencing the observed phenomenon. Zhang et al., (2006) reported the water-wetness of chalk material to be increasing with rising temperature and concentration of sulphate in the seawater. Seawater, through this characteristic, is regarded as a smart water (Figure 5.1).

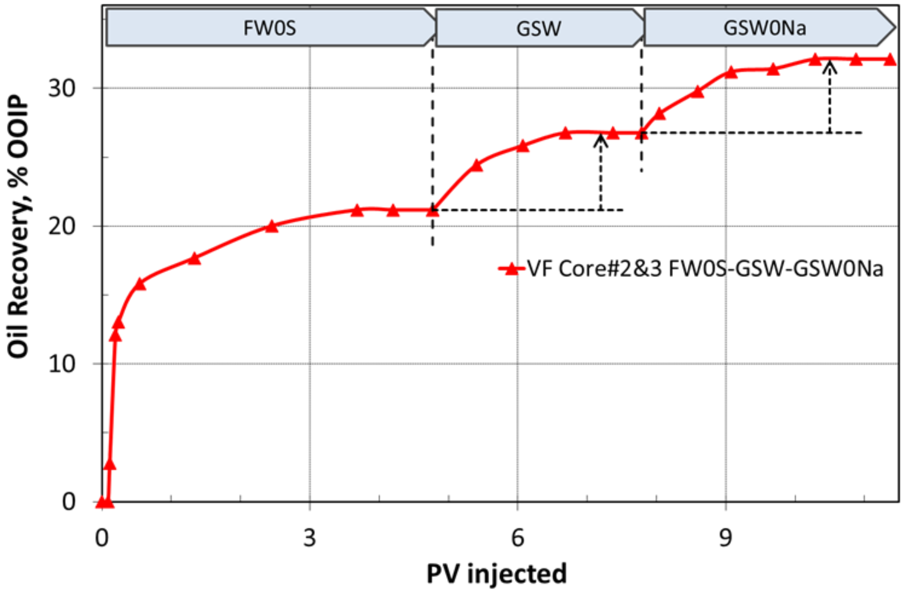


Figure 5.1: *Illustration of the potential of ordinary seawater as an EOR fluid (Shariatpanahi et al., 2010)*

Knowledge of the chemistry governing the wettability alteration mechanism (see section 5.2) has been applied in laboratory examinations to even make seawater "smarter" by optimizing its ionic composition. Fathi et al., (2011) observed the concentration of non-active ions to be important in the process. Their report (Figure 5.2) shows removing NaCl from synthetic seawater to have improved oil recovery by about 8% of OOIP compared to ordinary seawater. Spiking the NaCl depleted seawater with SO_4^{2-} improved the recovery even more by adding an extra 2% OOIP.

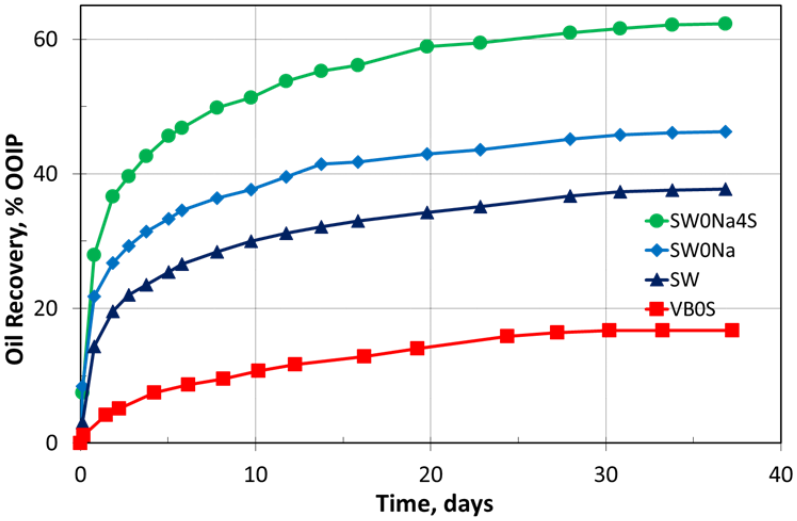
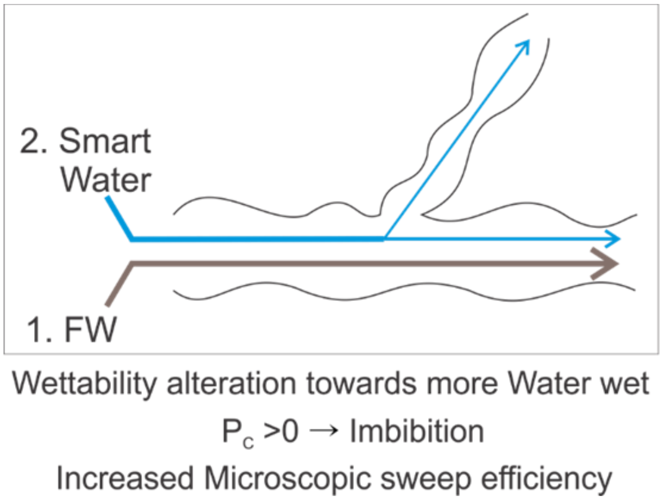


Figure 5.2: *Oil recovery from carbonate material demonstrating the benefit of optimizing seawater ionic compositions (Fathi et al., 2011)*

The wettability alteration induced by smart water will stimulate positive capillary forces within the porous media. This means that injected EOR fluid will spontaneously imbibe into the rock matrix (Figure 5.3) and access the pore spaces that otherwise could not be reached by dull water. This yields an increased microscopic sweep efficiency that eventually optimizes the recovery factor.



2. Smart Water
1. FW
Wettability alteration towards more Water wet
P_c >0 → Imbibition
Increased Microscopic sweep efficiency

Figure 5.3: *Mechanistic illustration of smart water migration through a porous medium*

In a study, the possibility of incremental oil by applying low salinity water in limestone was reported by Yousef et al., (2010). It was later confirmed by Austad et al., (2012) that dissolution of originally present anhydrite CaSO4(s) in the limestone material contributed SO_4^{2-} into the aqueous system that influenced the wetting alteration process. It was established by their report that in-situ generation of SO_4^{2-} from dissolvable anhydrite was a condition for observing low-salinity EOR effect in carbonates. The profound influence of SO_4^{2-} has been reported as well by Adepapo et al., (2014). Though increasing temperature and SO_4^{2-} content is desirable, the reviewed literature points to the fact that spiking seawater with SO_4^{2-} at too high temperatures may have detrimental impact due to possible precipitation of anhydrite.

A recent investigation by Yousef et al., (2014) has confirmed the technical possibility to produce these optimized seawater compositions by combining nano-filtration and reversed osmosis. Their findings give a positive note to the applicability of modified seawater injection at the field-level. From an economical point of view, Puntervold, et al., (2015) highlights the importance of injecitng optimized fluid from the start of the waterflood on oil reservoirs.

The industry is well abreast with waterflooding and since smart water is environmentally friendly and cheap, it is lucrative for field implementation.

5.2 Smart water mechanism

The mechanism for the increased water-wetness in chalk was chemically interpreted by Zhang, et al., (2007) and a symbolic representation is shown in figure 5.4. In the initial equilibrium state, the negatively charged carboxylic component is adsorbed unto the positively charged chalk surface with surrounding formation water (FW) containing excess Ca^{2+}.

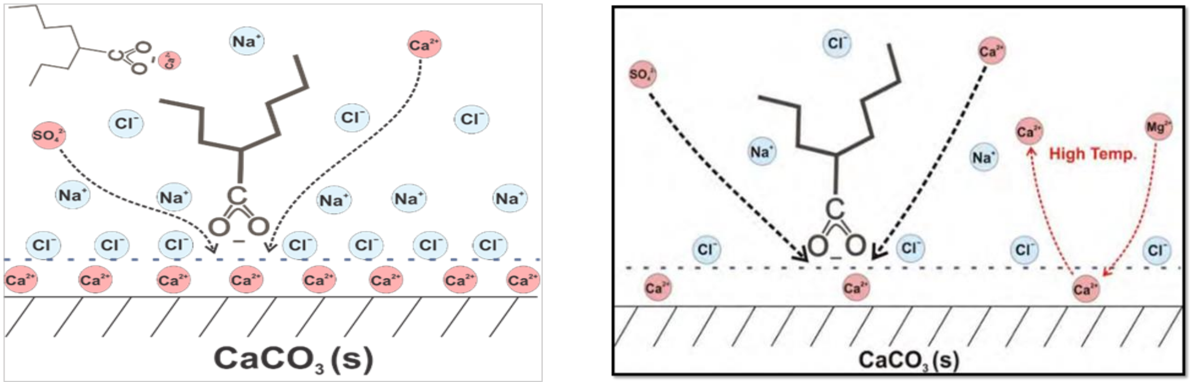


Figure 5.4: *Proposed mechanism for the wettability alteration induced by seawater at ordinary temperature (left) and at high temperature (right) (Zhang, et al., 2007)*

When seawater (SW) is injected, SO_4^{2-} attaches unto the chalk surface, which reduces the positive charge density on the chalk surface. The surface repulsion for excess positively charged Ca^{2+} ions in FW is reduced and thus, Ca^{2+} can approach the surface and release some of the attached carboxylic material by ion-binding.

This disruption of the chalk/oil/brine system's original chemical equilibrium will re-establish a modified equilibrium with less oil components adhered unto the chalk surface. SW is known to contain good amount of solvated Mg^{2+} ions which become dehydrated as temperature increases in the range 90-100°C. Mg^{2+} has high reactivity and will join the already ensued geochemical interaction (Korsnes, et al., 2007) by adsorbing unto the chalk surface and improve the wetting alteration process. An illustration of the high temperature mechanism is presented in figure 5.4. It has been experimentally demonstrated (Zhang et al., 2007) that the wettability reversal mechanism is a collective interaction that requires all the PDIs to be effective. The inability of sulphate ions alone to yield the desired wettability reversal is shown in Figure 5.5.

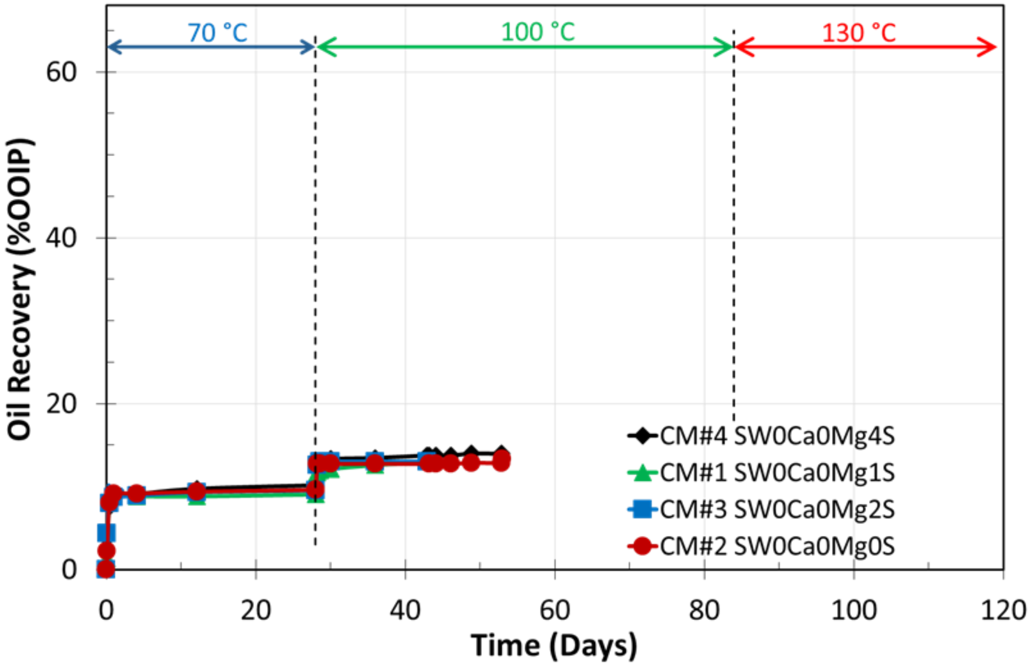


Figure 5.5: *Illustration of the symbiotic interaction between the PDIs in relation to the wetting alteration potential of brine (Zhang, et al., 2007). Spiking the brine with* SO_4^{2-} *in the absence of* Mg^{2+} *and* Ca^{2+} *ions has no effect on ultimate recovery.*

These symbiotic interactions between Mg^{2+}, Ca^{2+}, and SO_4^{2-}, which are all components of SW, by removing some of the carboxylic material from the chalk surface will increase the capillary forces of the chalk material to promote spontaneous imbibition of water into the matrix blocks as desired.

6 Materials, Fluids and Methods

This section outlines the materials and methods used in the experimental process.

6.1 Materials and Fluids

6.1.1 Chalk sample

The research study has been performed on Aalborg (AA) outcrop chalk material acquired from the Rørdal quarry in Aalborg, Denmark. The general geological characteristics of AA was presented in table 1 under section 3.4. The AA core samples used in this study were highly porous and of low matrix permeability, with a specific surface area measured to be about 3.9 m^2/g. Though relatively impure with a calcite content of around 95%, data from Surlyk et al., (2010) indicates that this lower upper Maastrichtian chalk belongs to a nannofossil zone of the North Sea scheme for the Upper Cretaceous Boreal province. Thus, the parametric studies on these cores can be considered representative of some carbonate reservoirs in the North Sea. The core properties are presented in table 3.

BET analysis: Brunauer-Emmett-Teller (BET) specific surface area was performed by analyzing carefully sized pieces of the core material.

Table 3: *core sample data.*

	AA#1	AA#2	AA#3
Length, cm	6.548	6.548	6.429
Diameter, cm	3.790	3.794	3.791
Bulk volume, ml	73.87	73.46	72.57
Pore volume, ml	35.50	35.09	34.09
Porosity, %	48	47	47
Permeability, mD	3.658	4.029	3.08
BET, m^2/g	~4		

6.1.2 Crude Oils

A single model crude oil, Oil A, with AN~0.35 mgKOH/g and BN~0.35 mgKOH/g was used throughout the experiment. Oil A was prepared by a calculated volume ratio of Oil X and Oil Y; both prepared by diluting Heidrun Oil with n-Heptane in a ratio 60:40, then centrifuged and filtered through a 5µm Millipore filter. Oil X with AN~1.92 mgKOH/g and BN~0.84 mgKOH/g is similitude to the heptane-diluted Heidrun (H-dilute) and Oil Y was prepared by treating H-dilute with silica gel and placed on a magnetic stirrer for 3 days. The silica gel removes most of the surface-active components in the oil, bringing the AN and BN close to 0 mgKOH/g. Summarized descriptions of the oils used are given in Table 4.

Measuring oil density and viscosity: The density of the oils was measured at room temperature (~23°C) using the Anton Paar DMA 4500 density meter and viscosities was measured using the Anton Paar MCR 302 modular compact rheometer at ambient temperature

Measuring oil acid and base numbers: A Mettler Toledo DL55 auto-titrator was used to measure AN and BN by potentiometric titrations. The methods used are modified versions of the standard methods ASTM D664 for AN titrations and ASTM D2896 for BN titration developed by Fan et al., (2006). The AN/BN measurement involved four solutions perculiar to each measurement as presented in Appendix A1 & A2; an electrolyte, titration solution, standard solution and a spiking solution (SS) . 50ml of titration solution is initially spiked with 1ml of SS before a precision auto-pipette is used to deliver 1ml of the crude sample to form the mixture. The prepared mixture is mounted on the auto-titrator device and run till an equivalent point is reached and the respective value recorded. A blank test (mixture without oil sample) is run betwween actual test samples to enhance the device's operation. Prior to the usage of each electrode, a standard measurement is run to balance the measuring parameters.

Table 4: *Oil properties*

	Density (g/cm^3)	**AN (mgKOH/g)**	**BN (mgKOH/g)**	**Viscosity (cP)**
Oil X	0.81	1.92	0.84	2.39
Oil Y	0.81	0.00	0.10	2.13
Oil A	0.81	0.35	0.35	2.28

6.1.3 Brines

All brines that have been used were synthetically made by dissolving a specific quantity of salts in De-Ionized (DI) water, stirred thoroughly using the magnetic stirrer and filtered to 0.22µm. Carbonate, Sulphate and Chloride salts are diluted and stirred separately before mixing to avoid complications of precipitation. The model formation water (FW) used was based on the Valhall formation brine located in the North Sea, but, depleted of SO_4^{2-} and designated as VB0S (Table 5). It was used as the native brine to establish initial water saturation and as imbibing fluid for spontaneous and forced imbibition experiments of all cores.

Chromatographic Wettability Tests (CWT) were performed using SW0T and SW1/2T brines. SWOT is Sea Water (SW) depleted of sulphate [SO_4^{2-}] whilst SW1/2T represents Sea Water with equal amounts of sulphate and the tracer thiocyanate [SCN^-]. SW was used as standard in the ionic analysis of effluent brine during the CWT tests. Brine compositions are summarized in Table 5.

Measuring pH: The brine pH was measured using the pH meter seven easy™ from Mettler Toledo. The electrode semi micro-pH was used. The repeatability of the measurement was +/- 0.01 pH units at room temperature.

Table 5: *Formation and Chromatographic brine composition and properties*

	VB0S	SW	SW0T	SW1/2T
Ions	*mM*	*mM*	*mM*	*mM*
Na^+	997.0	450.1	460.0	427.0
Li^+	0.0	0.0	0.0	12.0
K^+	5.0	10.0	10.0	22.0
Ca^{2+}	29.0	13.1	13.0	13.0
Mg^{2+}	8.0	44.5	45.0	45.0
SO_4^{2-}	0.0	24.0	0.0	12.0
SCN^-	0.0	0.0	0.0	12.0
HCO_3^{2-}	9.0	2.0	2.0	2.0
Cl^-	1066.0	525.1	583.0	583.0
Density (gr/ml)	1.041	1.023	1.022	1.022
TDS	62.83	33.39	33.38	33.38
Ionic strength	1.112	0.657	0.643	0.645

6.1.4 Additional chemicals and Solutions

n-Heptane: Completely free from surface-active components, this chemical was used as the oil phase in cores representing a completely water-wet condition. It was also used in the preparation of model oils and for thorough pre-cleaning of the experimental set-up.

Barium Chloride: This chemical was used to confirm the removal of sulphate during the core cleaning procedure by adding to a sampled effluent to observe precipitation of $BaSO_4$.

6.2 Aalborg chalk core preparation and procedures

As outcrop cores have been uplifted from their original underground formations, parametric studies involving their use must be conducted in a manner to mimic the subsurface reservoir. Also, to draw comparative analysis from different tests, it is important that all core plugs are prepared in the same way every time, giving reproducible results (Puntervold, 2008). This section outlines the methods used to prepare the core samples and the experimental setup procedures.

6.2.1 Aalborg core characterization

Core physical and chemical analysis: Scanning Electron Microscopy (SEM) analysis was performed on the chalk material to study the grain size distribution, particle shape and nature, including elemental composition identification. The SEM sample was prepared by placing a sliced piece of the chalk on the carbon adhesive disc mounted on an aluminium stub.

A thin platinum layer was applied to avoid charging of the samples. Surface detail of the chalk was conducted using a Zeiss Supra 35VP field emission microscope equipped with an Energy Dispersive Spectrometer (EDS) using accelerating voltages down to 0.2kV to optimize the process.

Porosity and Pore Volume estimation: Porosity was calculated (see equation 6.1) from the difference between the dry and wet weight after saturating the dried core plugs with 10 times diluted formation water (d_{10}VBOS). The cores were evacuated by vacuum prior to being saturated with brine and then weighed to obtain the saturated mass. Figure 6.1 illustrates this saturation set-up.

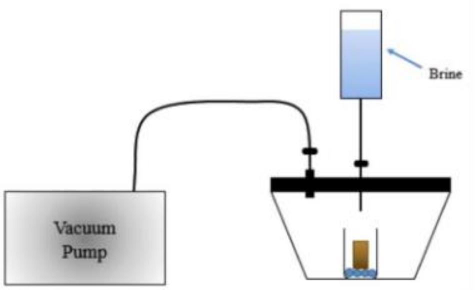


Figure 6.1: *Vacuum setup for brine saturation of cores, by Frida Layti (BSc 2015)*

Pore Volume (PV) was approximated as the total volume of brine required to fully saturate each core plug.

$$\emptyset = \frac{PV}{V_{bulk}} = \frac{(M_{sat} - M_{dry})/\rho_{brine}}{V_{bulk}} \qquad (6.1)$$

Permeability estimation: The core cleaning set-up is conducted in a manner that enabled recordings of stable pressure drops across the core at determined time intervals during the flooding. The permeability (k) of each core plug is then approximated by deploying the Darcy law equation together with known core and injecting fluid data. The values reported in table 3 agrees with reported values in other scientific literature and confirms the usually low permeability of carbonate minerals

6.2.2 Aalborg core restoration

Preparation of all cores was done according to the standard procedure outlined by Puntervold et al., (2007). All cores were mounted in a Hassler core holder (figure 6.2) and pre-flushed at a rate of 0.1ml/min with approximately 5PVs of deionized water (DI) at ambient temperature, to restore natural properties of the chalk material by removing easily dissolvable salts; specific focus is given to sulphate-bound salts since connate SO_4^{2-} may influence wetting properties. A batch test on the effluent using Ba^{2+} is conducted to ensure cores were free of sulphate contamination. SO_4^{2-} in the effluent reacts with Ba^{2+} to form a visible $BaSO_4$ precipitate as shown below;

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightleftharpoons BaSO_4(s)$$

The cores were then dried to constant weight in an oven heated to 90ºC. The cleaning setup is presented in figure 6.3

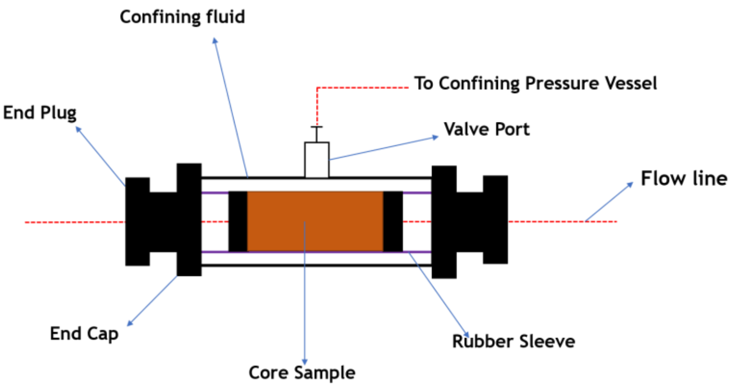

Confining fluid
To Confining Pressure Vessel
End Plug
Valve Port
Flow line
End Cap
Rubber Sleeve
Core Sample

Figure 6.2: Hassler Core Holder used for all core flooding experiments

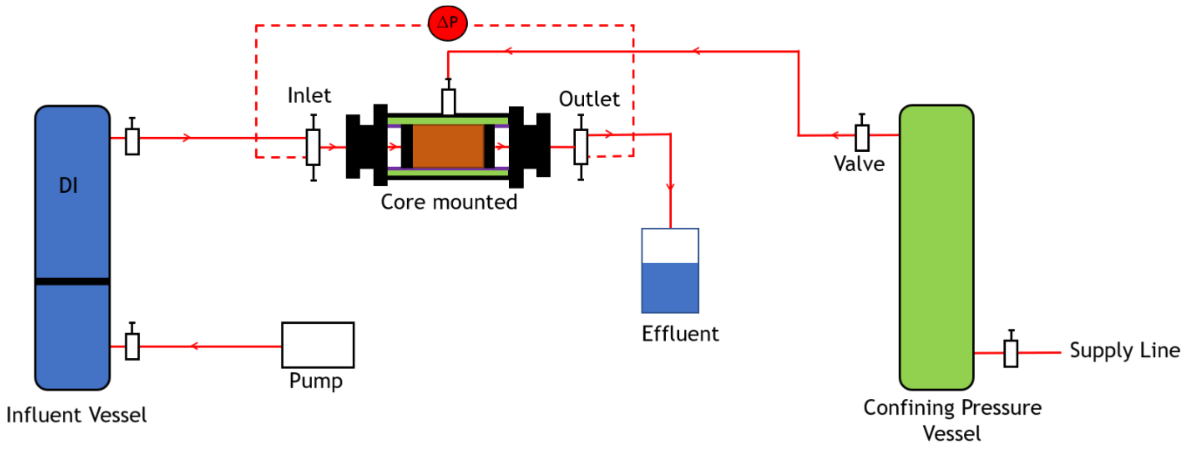

ΔP
Inlet
Outlet
DI
Valve
Core mounted
Effluent
Pump
Supply Line
Influent Vessel
Confining Pressure Vessel

Figure 6.3: Core cleaning experimental set-up

6.2.3 Establishing initial water saturation

Initial water saturation (S_{wi}) for all cores was established to 10%. First, the dried cores were 100% saturated d_{10}VBOS and drained down to the target S_{wi} using a desiccator containing Silica gel. This chemical is hygroscopic and facilitates gradual vaporization of the imbibed water to obtain a uniform target initial water saturation throughout the core. The procedure is described by Springer et al., (2003). The cores were then equilibrated in a sealed container for 4 days.

6.2.4 Crude oil saturation and flooding

All studies involving flooding with oil was conducted by mounting the equilibrated cores in a Hassler core holder with an overburden and back pressure of 20 and 7 bars, respectively. The study investigating crude oil relative adsorption amount was performed on AA#1 by flooding ~7PV of Oil A at 50ºC through the core from one end, with effluent oil samples collected from the other end and analyzed for AN and BN by titration. In another study, a different core *(AA#2)* was simply saturated by flooding 2.5PV of Oil A in each direction to reach a target saturation level of 5PV. Wetting characteristics of AA#1 and AA#2 infers the impact that oil volume flooded through a core sample will have on initial wetting.

The experimental procedures flooded oil at 0.1ml/min. Figure 6.4 illustrates the experimental setup for AA#1 during oil flooding in one direction. The flooding setup was altered as required to undertake other test studies.

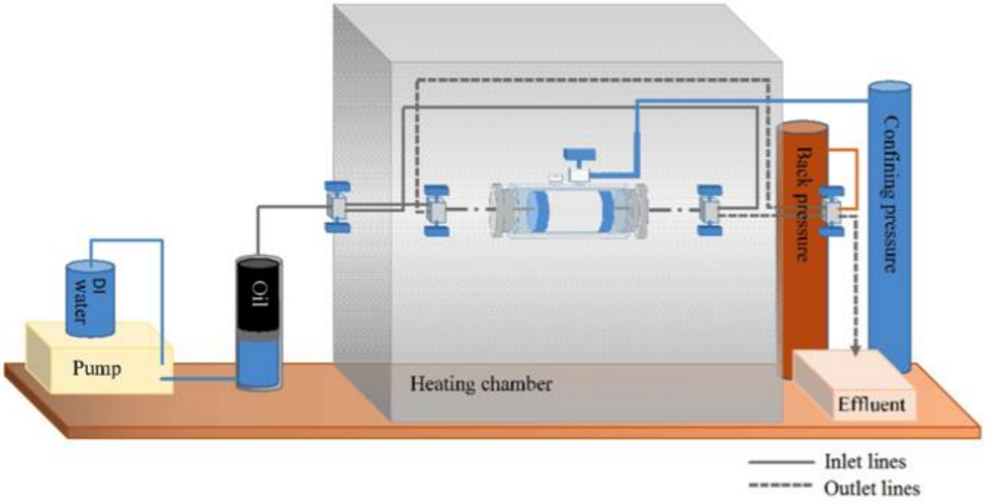


Figure 6.4: *Oil saturation and fluid flooding setup Ingrid (BSc 2015)*

6.2.5 Ageing of chalk cores

Following oil saturation and flooding, the core plugs were aged in a stainless-steel ageing cell for 2 weeks at 50ºC. The cores were wrapped with Teflon tape to avoid unrepresentative adsorption of polar components onto the chalk surfaces. Ageing is regarded an essential step for establishing a homogeneous wetting state that best mimic the reservoir conditions Rao et al., (1996). The cell is airtight and filled with Oil A to cover up the entire length of the core plug.

6.2.6 Oil recovery by spontaneous imbibition (SI)

Spontaneous imbibition was performed at 50ºC in sealed steel containers with a piston cell providing 10 bars pressure support to prevent oil from boiling (figure 6.5). FW (VB0S) was used as the imbibing fluid and thus no chemical wettability alteration was expected to occur. All produced oil was collected in a burette and the oil recovery as percentage of original oil in place, %OOIP, was reported versus time.

In other to test capillary forces, a spontaneous imbibition test using AA#3 (as a reference core) 100% saturated with heptane (as reference oil) was performed. Heptane is free of polar components and will not affect the wetting properties of the chalk since no adsorption will occur. DI water is used as the imbibing fluid, with the experiment conducted at room temperature in a glass Amott cell (figure 6.6).

Results from this study is used as a reference to represent a strongly water-wet condition. The procedure is rapid, due to the strong-wetting condition and so at the early stage of the test, oil volume was recorded every 1min and steadily increased the recording intervals to 24 hours.

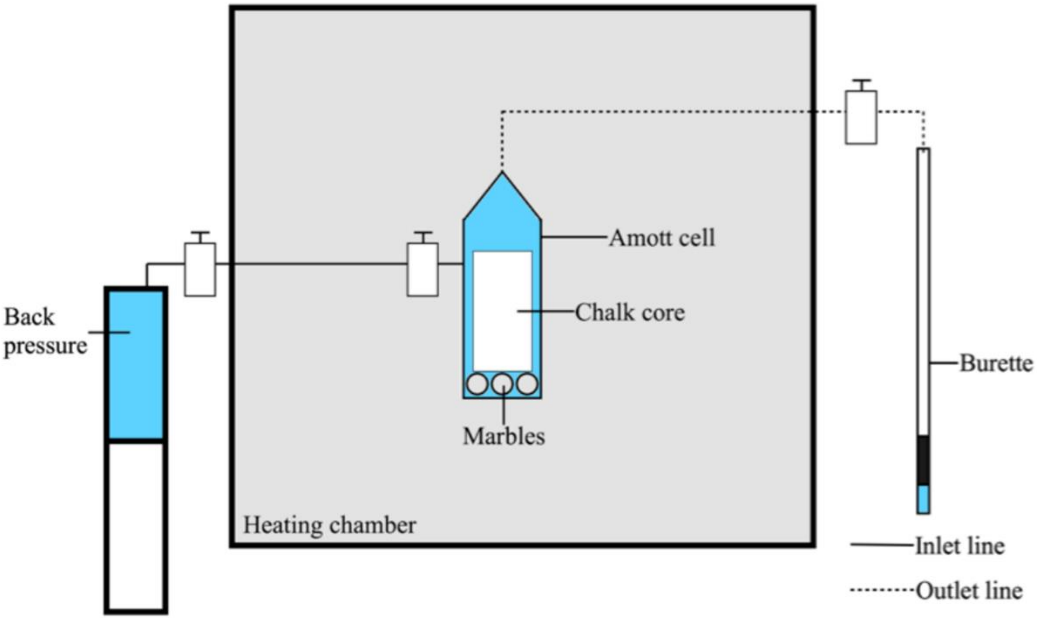

Back
pressure
Amott cell
Chalk core
Marbles
Heating chamber
Burette
Inlet line
Outlet line

Figure 6.5: *Schematic of spontaneous imbibition in steel cells at high temperature Kristoffer (BSc 2018)*

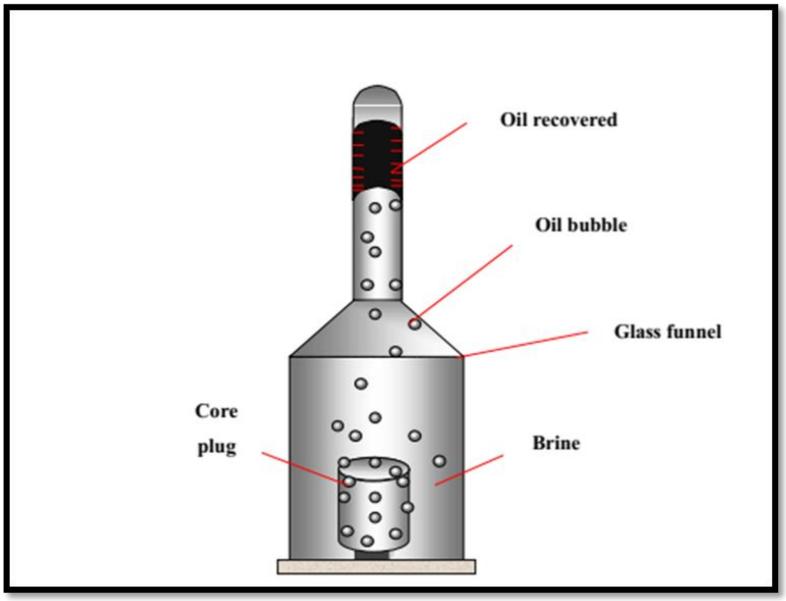

Oil recovered
Oil bubble
Glass funnel
Core
plug
Brine

Figure 6.6: *Schematic for spontaneous imbibition conducted at room temperature*

6.2.7 Oil recovery by forced imbibition (FI)

Forced imbibition, also known as viscous flooding/displacement, was conducted in a Hassler core holder following the spontaneous imbibition experiment. Both procedures are similar, in that they involve water displacing oil from the core; except with forced imbibition, the FW is injected through the core, forcing the displacement of oil as opposed to allowing the spontaneous uptake of FW by the core in the SI procedure.

A setup like figure 6.4 was used, with FW (VB0S) as the injecting brine and produced oil collected in a standard burette. The experiment was conducted with an overburden and back pressure of 20 and 7 bars, respectively. The total oil recovery, as %OOIP was recorded.

Oil recoveries from SI and FI were performed for cores AA#1 and AA#2 and the data used to evaluate the wetting conditions by the Amott method (see section 4.2.3).

6.2.8 Chromatographic Wettability Test (CWT)

The chromatographic wettability test was developed by Strand et al., (2006). The test determines the water-wet fraction of the chalk surface based on the chromatographic separation between the adsorbing SO_4^{2-} and the tracer, SCN^-. Principles of the test were outlined in section 4.2.5

Initially, the cores were flooded at constant rate of 1PV/day with seawater devoid of the ions, SW0T, to ensure the core is at residual oil saturation (S_{or}). Next, SW1/2T, which contains equal concentrations of the ions was flooded under same conditions. Effluent was collected and analyzed to plot the ionic concentrations of SO_4^{2-} and SCN^- relative to their initial amounts in the injection brine against the PV injected. The area between the effluent curves for SCN^- and SO_4^{2-} is proportional to the water-wet surface area in the core. Tests were conducted for all core samples, with the output for AA#3 used as reference to characterize the wetting state of AA#1 and AA#2.

The test was conducted at ambient temperature with effluent samples analyzed for their relative concentrations of SO_4^{2-} and SCN^- using a Dionex ICS-3000 Ion Chromatograph. DI, SW, SW0T & SW1/2T were used as external standards in the analysis. The selected set of samples were analyzed for SO_4^{2-} and SCN^- and the concentrations thereof were computed based on values obtained for the external standard.

‘

7 Results and Discussion

This research study was conducted to investigate retention of polar acidic and basic oil components onto Aalborg outcrop chalk mineral surface. How the surface chemistry and mineralogical composition of this chalk material influences initial wetting through the preferential adsorption of the polar organic components is examined. Then, the observed behavior is compared to previously observed responses in a relatively purer chalk, Stevn Klint. This section presents results of the study and discussions with respect to the research goal.

7.1 Geological and Mineralogical property of Chalk

7.1.1 Aalborg Chalk

The general overview of Aalborg (AA) chalk as reported in the reviewed literature was presented in section 3.4.1. SEM images of the unflooded Aalborg chalk sample used in this study is depicted in figure 7.1.

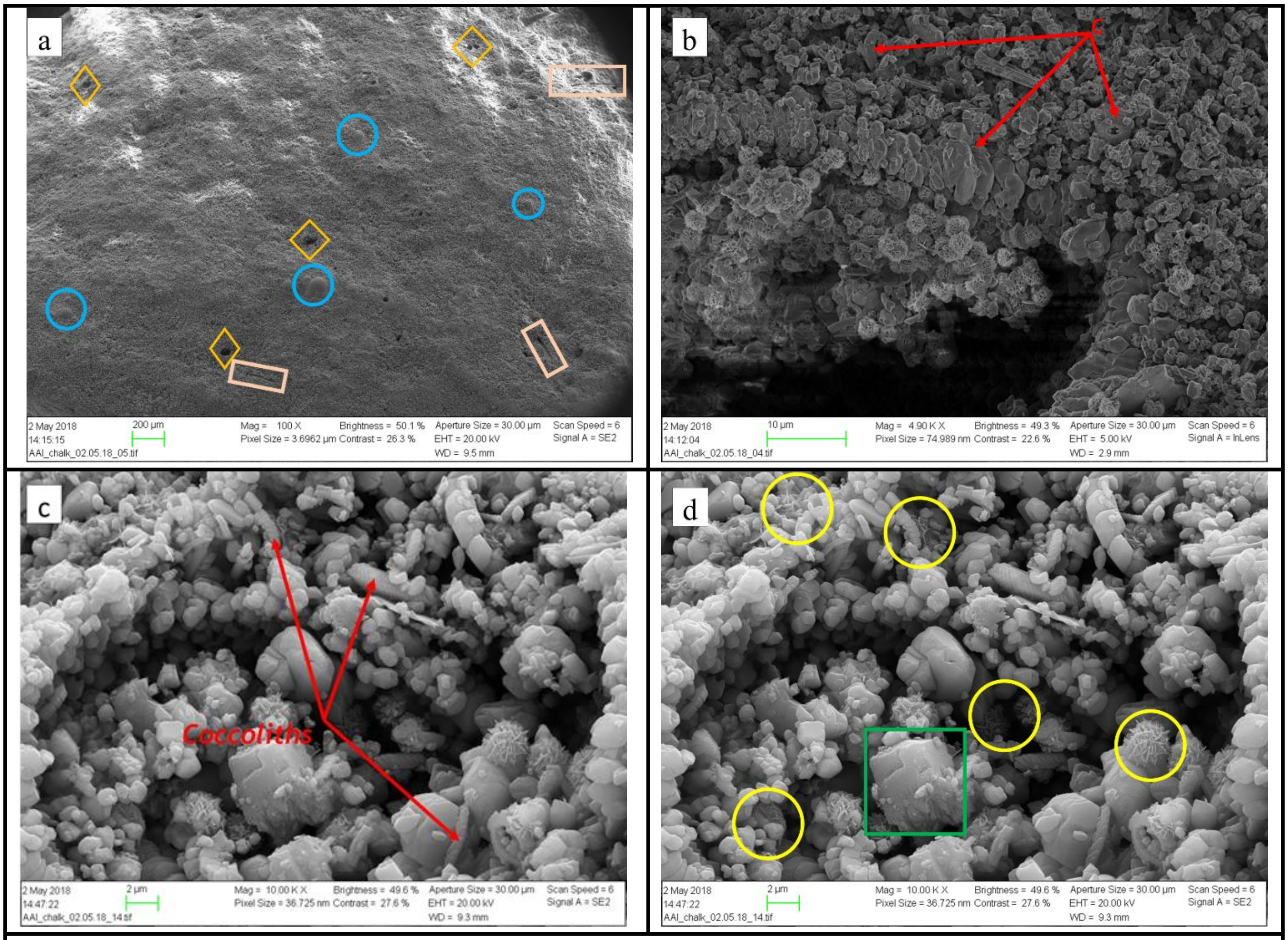

a
2 May 2018
14:15:15
AAl_chalk_02.05.18_05.tif
200 µm
Mag = 100 X
Pixel Size = 3.6962 µm
Brightness = 50.1 %
Contrast = 26.3 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.5 mm
Scan Speed = 6
Signal A = SE2
b
c
2 May 2018
14:12:04
AAl_chalk_02.05.18_04.tif
10 µm
Mag = 4.90 K X
Pixel Size = 74.989 nm
Brightness = 49.3 %
Contrast = 22.6 %
Aperture Size = 30.00 µm
EHT = 5.00 kV
WD = 2.9 mm
Scan Speed = 6
Signal A = InLens
c
Coccoliths
2 May 2018
14:47:22
AAl_chalk_02.05.18_14.tif
2 µm
Mag = 10.00 K X
Pixel Size = 36.725 nm
Brightness = 49.6 %
Contrast = 27.6 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.3 mm
Scan Speed = 6
Signal A = SE2
d
2 May 2018
14:47:22
AAl_chalk_02.05.18_14.tif
2 µm
Mag = 10.00 K X
Pixel Size = 36.725 nm
Brightness = 49.6 %
Contrast = 27.6 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.3 mm
Scan Speed = 6
Signal A = SE2

Figure 7.1: *SEM secondary electron image of unflooded Aalborg chalk core at magnification capacity of 100 (a); 5K (b) and 10K (c&d).*

The outcrop can be classified as a mildly preserved coccolithic wackestone with numerously dispersed silica-rich opal-CT lepispheres.

The observed coccoliths (Fig. 7.1c, red arrows) are mildly conserved and in most cases the calcite tablets are dispersed. A well preserved coccolithophore with appreciable accumulations of opal-CT lepispheres within the porous opening can be sited in 7.1b. The opal-CT lepispheres are well developed and occur within the intra-fossil pores (Fig. 7.1d, yellow circles). It is appreciated how porosity is mostly preserved in chalk cores (seen as dark spaces between the grains). A very close look on the surface scan reveals thin elongated pores (Fig. 7.1a, brown rectangular shapes) of what used to be sites of diatoms that have undergone complete dissolution. Diatoms are unicellular, with cell walls made of silica. My hypothesis is that dissolution of these phytoplanktons served as the source of silica that formed opal-CT. Bumps of foraminifera can also be spotted (Fig. 7.1c, blue circles). These are much larger eukaryotes, and their shell-like feature is visible over the surface. Existence of foraminifer shell fragments have been reported by Andersen et al., (2018). Their dissolution most likely yielded the rounded pores (Fig. 7.1c, orange diamond shapes). Mg bearing minerals were also observed (Fig. 7.1d, green square). Their distinctive square like shape is obvious and their existence in the mineralogy is confirmed in the EDS analysis presented in table 6.

It was hard to observe clay phases on the Aalborg sample used in this study but a single image (Figure 7.2) could probably be interpreted as a clay flake. Existence of silicate minerals as clay in chalk is common and has previously been reported by (Fabricius et al., 2002; Strand et al., 2007; Skovbjerg et al., 2012; Megawati et al., 2015; Andersen et al., 2018). If they exist in the samples used, clearly, they are minute and I doubt that these clay coatings may cover a significant percentage of the chalk material.

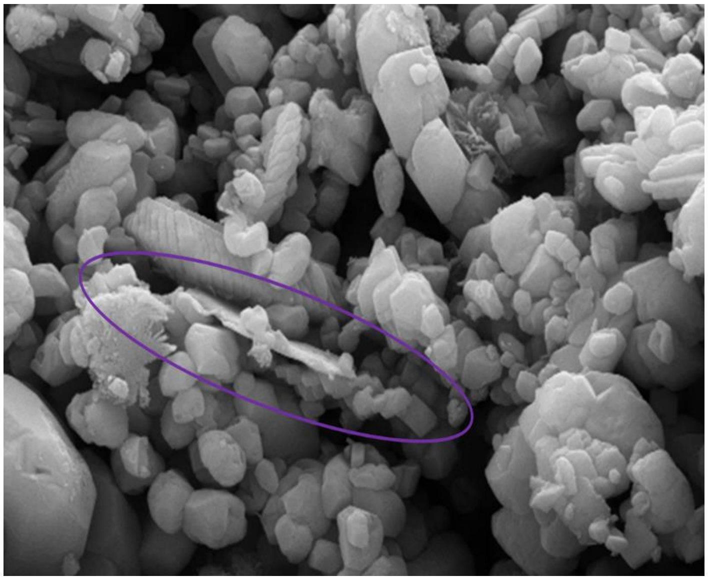


Figure 7.2: *Capture of a possible clay flake protruding underneath a coccolith in the Aalborg core at a magnification capacity of 10, 000*

7.1.2 Aalborg versus Stevns Klint

Chalk cores from Stevns Klint (SK) are reported to consist of extremely pure coccolithic mudstones with trace compositions of Si-bearing minerals. Coccolithophores of SK are well-preserved with complete calcite grains forming the coccoliths. The physical outlook of AA and SK at two different magnification scales are illustrated in figure 7.3.

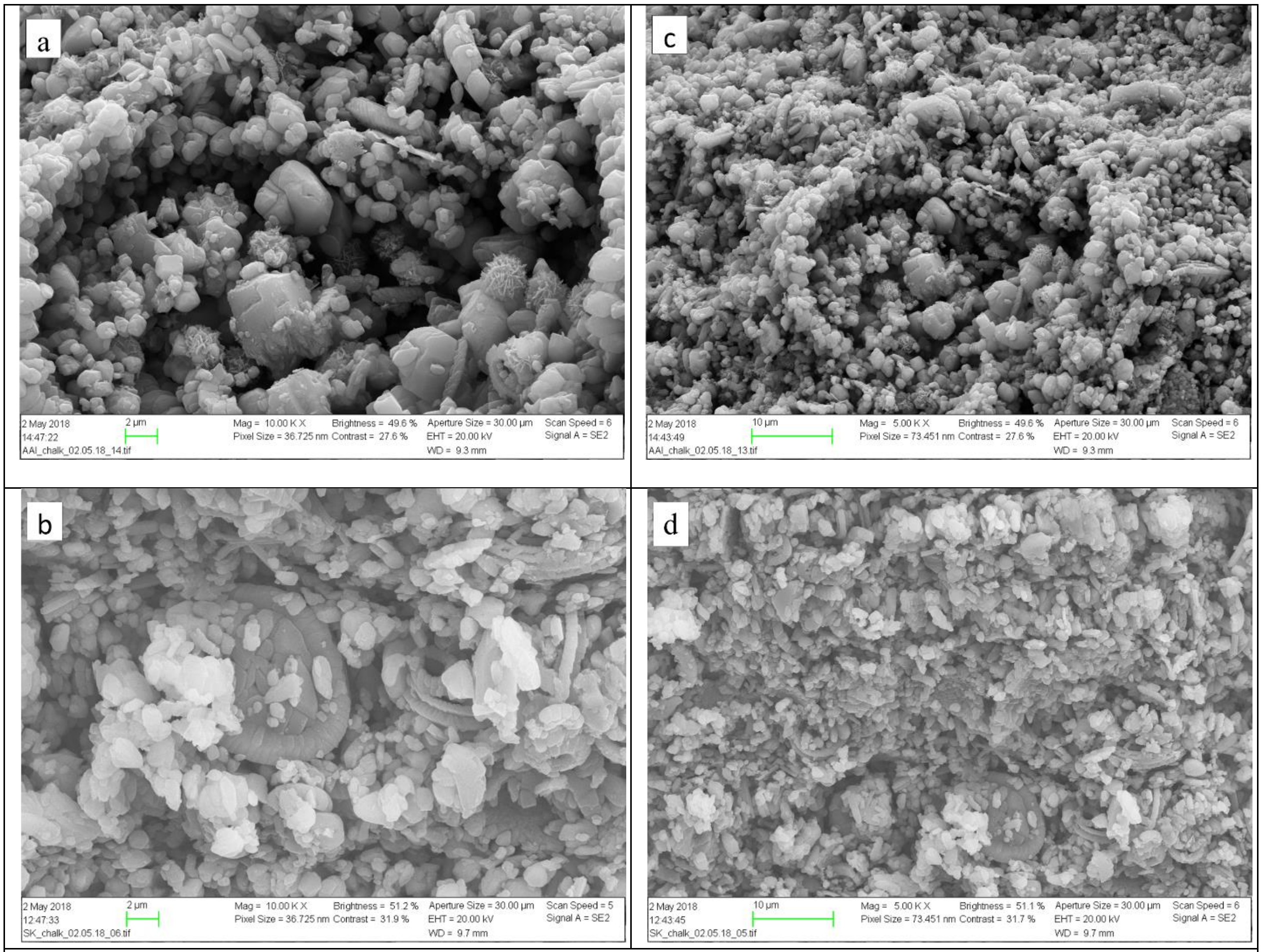

a
2 May 2018
14:47:22
AAl_chalk_02.05.18_14.tif
2 µm
Mag = 10.00 K X
Pixel Size = 36.725 nm
Brightness = 49.6 %
Contrast = 27.6 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.3 mm
Scan Speed = 6
Signal A = SE2
c
2 May 2018
14:43:49
AAl_chalk_02.05.18_13.tif
10 µm
Mag = 5.00 K X
Pixel Size = 73.451 nm
Brightness = 49.6 %
Contrast = 27.6 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.3 mm
Scan Speed = 6
Signal A = SE2
b
2 May 2018
12:47:33
SK_chalk_02.05.18_06.tif
2 µm
Mag = 10.00 K X
Pixel Size = 36.725 nm
Brightness = 51.2 %
Contrast = 31.9 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.7 mm
Scan Speed = 5
Signal A = SE2
d
2 May 2018
12:43:45
SK_chalk_02.05.18_05.tif
10 µm
Mag = 5.00 K X
Pixel Size = 73.451 nm
Brightness = 51.1 %
Contrast = 31.7 %
Aperture Size = 30.00 µm
EHT = 20.00 kV
WD = 9.7 mm
Scan Speed = 6
Signal A = SE2

Figure 7.3: *SEM of Aalborg (a &c) compared to Stevns Klint (b & d) at a magnification capacity of 5K (c&d) and 10K (a&d)*

Clearly, in the Aalborg chalk, calcite is not the only mineral present but has some authigenic crystals that decorate the pore throats and possibly the mineral surfaces. It is therefore noteworthy to mention that the distinctive characteristics of these Si-compounds (silica and clay) to overlay on surfaces and differing chemical behaviour may have enormous impact on the overall adsorption performance of the AA chalk as compared to SK chalk.

7.1.3 Mineralogical property of Aalborg

Energy Dispersive Spectrometry (EDS) analysis was conducted on the Aalborg core to examine elemental composition of the samples used in this study. The reported values (table 6) are the average of eight EDS analyses. Chalk-particle Ca obviously dominates the AA mineral content with Calcium At% of 89.86. The Silica content is relatively high, at 7.54 At% Si. Altogether, Al, Mg and S content contributes < 2.6 At%. From the SEM analysis in section 7.1, most Si appears to be concentrated as SiO_2 in the observable opal-CT lepispheres. Attention should be given to the low clay content (1.14 At% Al) as compared to silica. For comparison, EDS report on SK by Strand et al., (2007) is included alongside in table 6. The chalk from Stevns Klint obviously differ from Aalborg as it is composed of almost pure calcite ($CaCO_3$) minerals. It is worthy of mention that opal-CT is absent in reservoir formations due to its conversion to quartz, which is a much more stable form of silica. Details of this phase transition has been discussed earlier in section 3.4.1

Table 6: *EDS analysis on Aalborg, plus SK for comparison*

	Aalborg		***Stevns Klint***	
	Atomic %	Weight %	*Atomic %*	*Weight %*
MgK	1.34	0.84	*1.13*	*0.69*
AlK	1.14	0.79	*0.68*	*0.47*
SiK	7.54	5.47	*2.03*	*1.44*
SK	0.1	0.18	*0.00*	*0.00*
CaK	89.86	92.81	*96.18*	*97.42*

7.2 Adsorption of Polar components on Aalborg chalk surface

Polar acidic and basic components in the crude oil can adsorb onto the specific minerals present in chalk, making the rock less water-wet. The adsorption experiment was performed on Aalborg core sample labelled AA#1. The aim is to examine the impact of varying mineralogy on the retention potential of polar oil components and thus, all experimental conditions (core preparation and cleaning, S_{wi}, temperature, etcetera) and fluids (brine and crude-oil) used in previously performed tests with SK chalk were imitated herein to provide an unbiased foundation for comparing results. Crude oil is flooded through AA#1 and eluted oil AN & BN is measured for collected samples to observe the adsorption process.

Adsorption of the polar components on Aalborg is initially presented, followed by a discussion of the physico-chemical adsorption observed in SK chalk.

7.2.1 Initial adsorption of carboxylic material onto Aalborg

The adsorption curve for acidic components onto initially water-wet Aalborg chalk core AA#1 is shown in figure 7.4

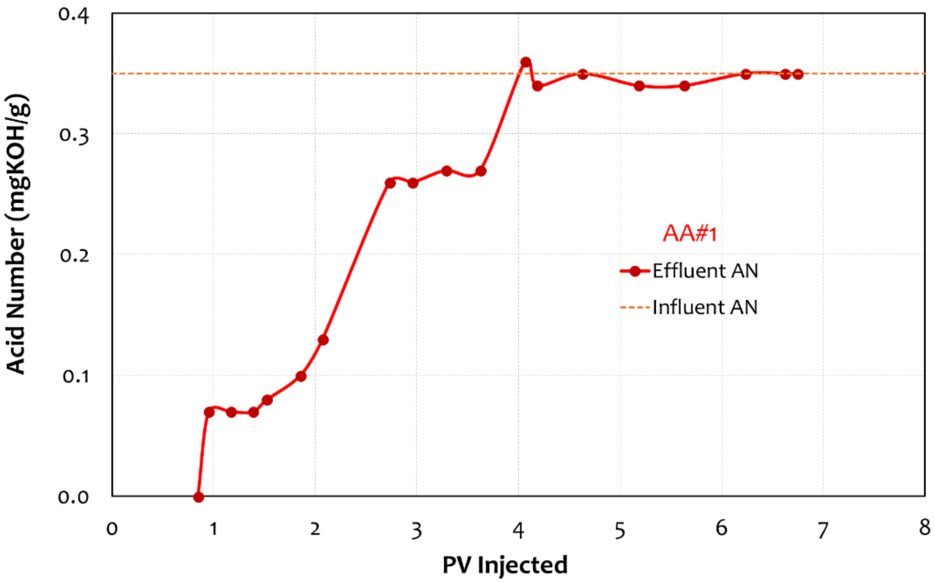


Figure 7.4: *Adsorption of carboxylic material onto AA#1 chalk surface;* S_{wi} */ T =0.1/50°C. Core was flooded with crude oil of AN=0.35 mgKOH/g at a flow rate of 0.1ml/min. Total adsorbed species is 0.83*

AN in the first eluted oil sample is completely drained of acidic components and confirms instant adsorption of carboxylic material onto the water-wet chalk surface. This is in line with reports by Hopkins et al., (2016) and Mjos et al., (2018). The eluted fractions that follow are also depleted in acidic components with a steady rise in AN as the injected crude oil volume increases. Dynamic equilibrium is established after flooding 4 PV of oil, where effluent AN reaches the original AN of the injected oil. This occurs when available sites on the chalk surface is occupied as retention progresses. The fact that equilibrium is attained confirms the retention process to be principally controlled by an adsorption mechanism, as opposed to crude oil component precipitation.

The total adsorption of acidic components ($\mathrm{AN_{ads}}$) is computed (equation 7.1) as the integrated area between the adsorption curve and the equilibrium value. This area is a quantitative measure of the amount of acidic functional groups retained and is determined for AA#1 as 0.83.

$$\mathrm{AN}_{ads} = (\mathrm{AN}_i)(PV_n) - \sum_{x=2}^{n} \frac{(\mathrm{AN}_x+\mathrm{AN}_{x+1})}{2} * (\mathrm{PV}_{x+1} - \mathrm{PV}_x) \qquad (7.1)$$

7.2.2 Initial adsorption of basic components onto Aalborg

The BN of effluent oil was quantified to evaluate adsorption of basic components. The adsorption curve is depicted in figure 7.5

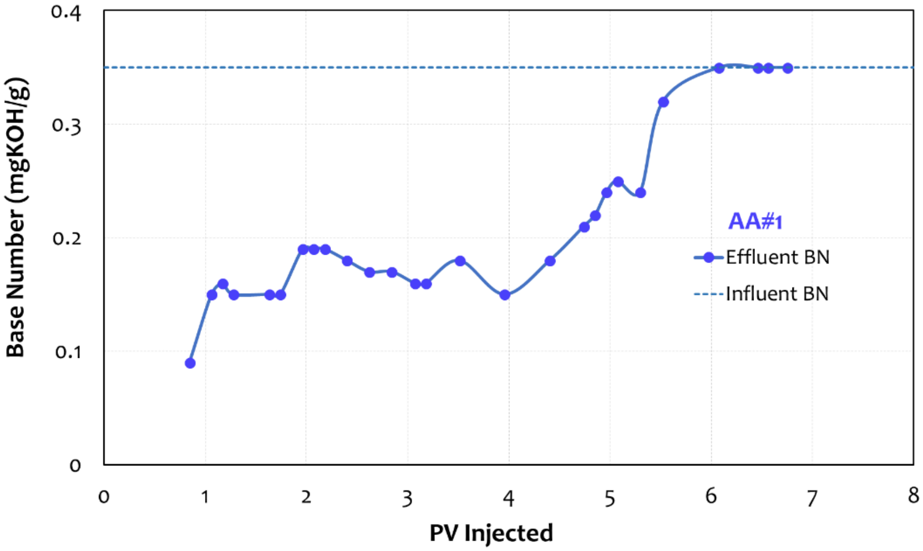


Figure 7.5: *Adsorption of basic material onto AA#1 chalk surface;* S_{wi} */ T =0.1/50°C. Core was flooded with crude oil of BN=0.35 mgKOH/g at a flow rate of 0.1ml/min. Total adsorbed species is 1.02*

Notable depletion in basic components of the effluent crude oil fractions is observed as represented in the effluent BN plot. The initial adsorption doesn't seem pronounced as observed for the polar acidic components but increment of BN is less rapid than for the AN adsorption. It can be deduced that there seems to be available sites in the Aalborg core that favours retention of some polar basic components. Also, the polar interactions appear to be slower and reflects as a less steep rise in the measured BN as well as an extended equilibrium realization that occurs after flooding 6 PV of oil. In chalk, Puntervold et al., (2007b) observed, as earlier reported by Skauge et al., (1999) that organic bases formed complexes with the carboxylic acids and more-or-less mimicked the adsorption pattern of the polar acids. The observed retention for the polar basic components in AA appears to be independent of AN adsorption and this suggests a direct adsorption of some basic polar components in the crude oil unto the mineral surfaces in Aalborg.

The total adsorption of basic components is determined as BN_{ads} = 1.02

7.2.3 Aalborg versus Stevns Klint

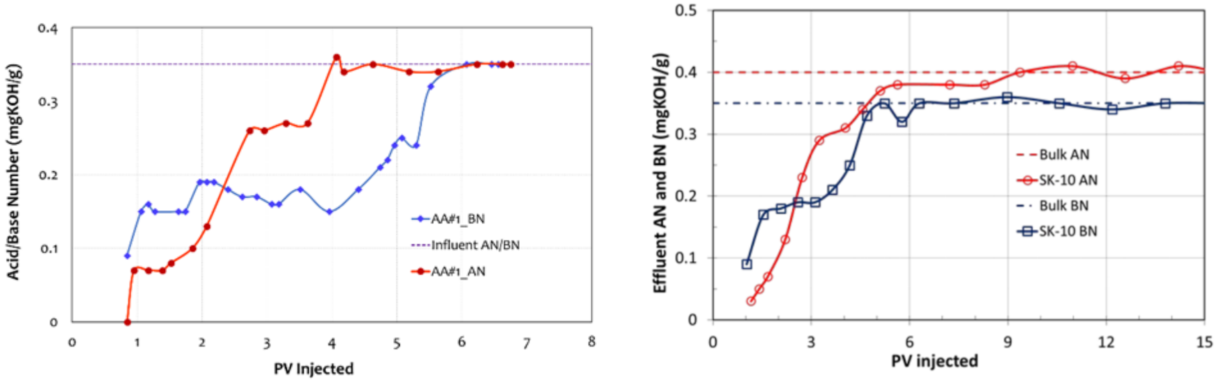
As demonstrated in section 7.1, Aalborg and Stevns Klint have differing geological and mineralogical content and that is expected to influence the surface reactivity towards the adsorption propensities of polar acidic and basic components. The results obtained for Aalborg chalk in this reasearch work is discussed in comparison to a recent study conducted by Mjos et al., (2018), where adsorption onto SK chalk with S_{wi} = 0.1 has been examined with crude oil of AN/BN = 0.40/0.35 mg of KOH/g. They noted reproducibility of observed responses to other similar past studies (Hopkins et al., 2016; Hopkins et al., 2017). The reproducibitlity confirms the adsorption interaction to be controlled by the prevailing chemistry of the system and therefore, a comparison to Aalborg, an outcrop chalk of different geo-chemical characteristics is justified.

Figure 7.6 illustrates the observed adsorption for AA#1 and SK-10 (Mjos et al., 2018). Properties of these cores are presented in Table 7

***Table 7:** core sample / adsorption data.*

	AA#1	***SK-10***
Length, cm	6.55	*6.40*
Diameter, cm	3.79	*3.75*
Bulk volume, ml	73.87	*70.60*
Pore volume, ml	35.50	*31.69*
Porosity, %	48	*45*
Permeability, mD	3.66	*1.27*
BET, m^2/g	4	*2.2*
Adsorption Amounts		
AN_{ads}	0.83	*1.33*
BN_{ads}	1.02	*0.93*
BN_{ads}/AN_{ads}	**1.22**	***0.70***

The two cores have similar physical characteristics with SK-10 having a lower permeability as typified by chalk formations. Porosity of chalk is well known to be high and this can be appreciated for both AA and SK chalk.


Aalborg Adsorption

Stevns Klint Adsorption

***Figure 7.6:** BN/AN adsorptioncomparison for AA#1 (AN_{ads} =0.83 & BN_{ads} =1.02) and SK-10 (AN_{ads} =1.33 & BN_{ads} =0.93) outcrop chalks*

The adsorption trend for the cores have noticeable differences:

a) BN equilibrium in each core is reached after flooding approximately the same PV of oil but adsorption of basic components is more profound in AA#1 than for SK-10

b) AN adsorption is more profound in SK-10 than for AA#1 and requires more volume of oil to be flooded before equilibrium is reached.

c) Effluent AN for SK-10 is steeper than AA#1, which shows a fast-paced adsorption process and one would expect equilibrium to be attained earlier. The observed trend can be attributed to the higher availability of positively charged calcite sites in SK chalk for the adsorption of negatively charged carboxylic acids.

A suitable scale for comparing the adsorption potential is by employing the relation

$$A_f = \frac{BN_{ads}}{AN_{ads}}$$

Where A_f is introduced as an adsorption factor. The computed value for AA#1 would then become **1.22** as compared to **0.70** for SK-10. By using such an expression for A_f it becomes clear that AN adsorption is lower in AA#1 than for SK-10 whereas BN adsorption is higher for AA#1 and lower for SK-10.

In pure chalk, like SK-10, the BN adsorption has been reported (Puntervold et al., 2007b) to be minimal and in some cases only retained by co-adsorbing with the carboxylic groups. This manner of behaviour can almost be inferred from the plot for SK-10, as the BN appears to mimic the AN curve from the start to the point of plateau. A recent experiment investigating BN adsorption at AN = 0 has been conducted by Anna (MSc 2018) and the reported observation confirms the impact of basic components on initial wetting of pure chalk to be extremely low. However, a look at the Aalborg adsorption portrays the adsorption of AN to be limited, and a distinctive BN adsorption that appears profound. Seeing as adsorption is a chemical process, the chemistry introduced by silica in Aalborg clearly is responsible for the different adsorption efficiencies of crude oil polar components and this is further discussed in section 7.2.4

7.2.4 Mechanism of crude oil adsorption in Aalborg and Stevns Klint

The oil-wetting properties of the chalk-brine-oil system is attributed to adsorption, which in literal terms is an electrostatic reaction between the oil-brine interface and the rock surface. The dissociation of acidic and basic components in crude oil is demonstrated in Figure 7.7.

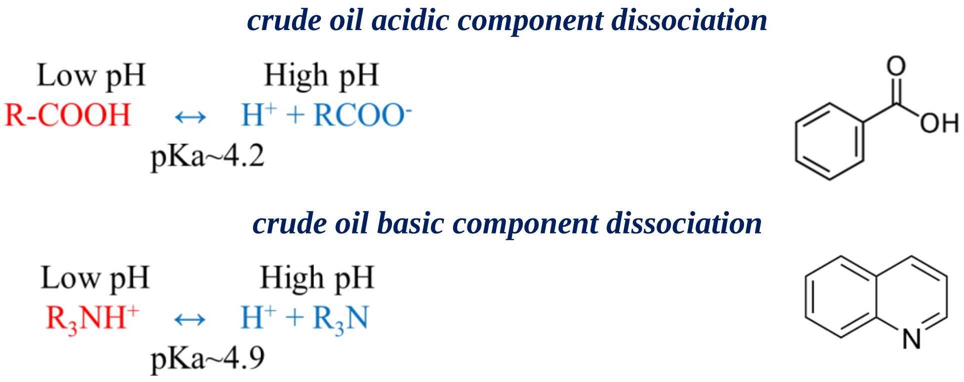


Figure 7.7: *Dissociation of polar organic species in crude oil and*

The pH for Aalborg core AA#1 during flooding with FW to establish S_{wi} ranged between 7.2 to 7.55 which depicts an alkaline environment. Alkaline conditions is common in chalk reservoirs. In pure chalk, like SK, the chalk surface is positively charged below a pH of 9.5 (Pierre et al., 1990) and the crude oil polarity will be predominantly negative due to the acidic components deprotonating to yield $RCOO^-$. The polar acids will therefore approach the positively charged calcite surfaces and adsorb. The basic components will exist in the neutral state R_3N and will not interact directly with the calcite surface. This explains why AN adsorption is dominant in SK relative to BN adsorption. Even under conditions where some of the polar basic component are polarized as R_3NH^+, its interaction with the positively charged calcite surface will be inhibited due to repulsion and thus, a resort to complexing with the carboxylates as proposed by Puntervold et al., (2007b) is laudable.

In Aalborg, calcite and silicate-mineral co-exist. Silica mineral surfaces are negative when the pH is greater than 2 (Donaldson et al., 2008). It must be pointed out that crude oil is a complex mixture and that R_3NH^+ is a generalized representation and thus, any positively charged basic component will readily interact with the silica surfaces. This accounts for the differing BN adsorption trend observed for AA#1 and SK-10. The presence of negatively charged silica minerals on the chalk surface will furthermore reduce the overall positive charge density in AA#2 which will limit the ionic interaction between the negatively charged carboxylate group and the Aalborg mineral surface. This phenomenon accounts for the reduced AN adsorption observed in AA#2 as compared to SK-10. It is unclear the contribution of silica to the specific surface area of AA#2 as measured by the BET analysis. However, it can be argued that the adsorption amounts of AN and BN observed implies that silica is contributing a large part to the measured surface area. Skovbjerg et al., (2012) reported that the impurities in chalk have high potential of decorating the chalk surfaces even though they may be present in minute quantities.

As previously mentioned, the adsorption of acidic components onto calcite surfaces is deemed to be chemically strong and inhibition to this interaction as introduced by silica mineralogy in AA#2 will limit the overall wetting alteration potential of crude oil polar components. It was imperative then, that the wetting conditions of the core be analyzed.

7.3 Wettability determination

Crude-oil wetting behaviour corelates well with acid and base numbers as reported in the reviewed literature. The Amott test is employed to characterize the wettability through spontaneous imbibition and forced imbibition tests at 50°C. Chromatographic wettability test (CWT) is also conducted to determine the water-wet fraction of the cores. CWT is conducted at room temperature.

7.3.1 Initial wetting of completely water-wet chalk

Wetting tests were performed on AA#3, designated as a completely water-wet core to use as reference. S_{wi} was established at 0.1 and the core was not aged prior to recovery tests. The heptane-saturated core behaved very water-wet, confirmed by the SI experiment (figure 7.8).

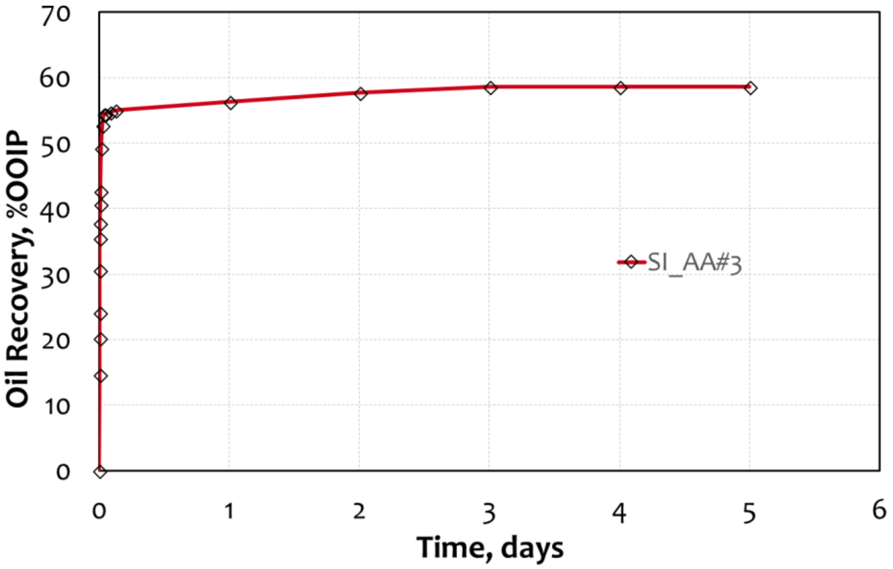


Figure 7.8: *SI experiment on completely water-wet Aalborg Chalk, AA#3 (reference). Core was spontaneously imbibed at room temperature with DI water*

Due to strong capillary forces, more than half of the original heptane is recovered within 30 minutes, with a final recovery plateau of ~59% reached within 3 days. The SI test is monitored for 2 more days with no extra production observed. Forced imbibition on AA#3 is assumed to be able to yield 100% recovery and thus, the Amott water index is set as $I_w^* = 1$ for the completely water-wet core. The CWT test is further performed on the same core (Figure 7.9) to obtain the water-surface area for completely water-wet Aalborg chalk.

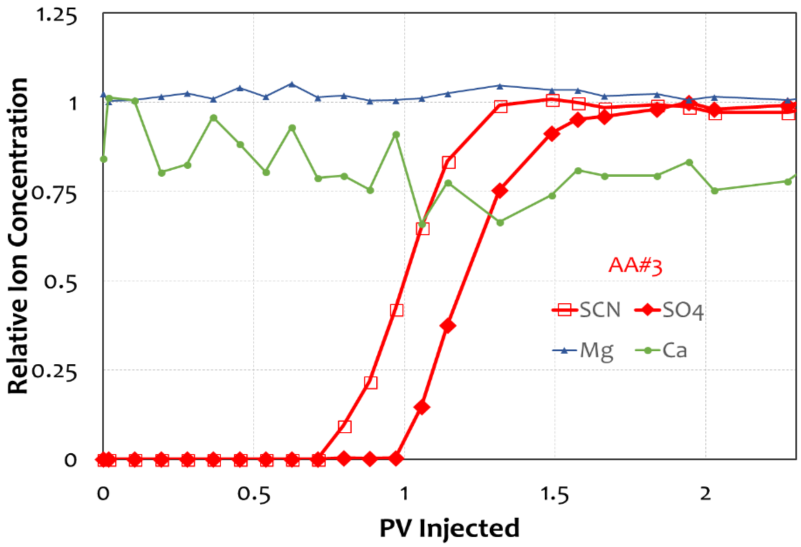


Figure 7.9: *Chromatographic wettability test for Aalborg reference core (AA#3) at room temperature.*

The area of separation between the SCN^- and SO_4^{2-} curves is a quantitative measure of the Aalborg surface fraction that can be wetted by water. The area calculated for the completely water-wet Aalborg chalk was $A_{ww} = 0.2273$

7.3.2 Initial wetting of Aalborg Core

The Aalborg core, AA#1, which was previously exposed to ~7PV of the model crude oil during the adsorption test was aged for 2 weeks and tested for recovery by SI, FI and CWT. Imbibition tests (Figure 7.10) are performed using Formation Water (VB0S) and therefore, no wettability reversal is expected to occur.

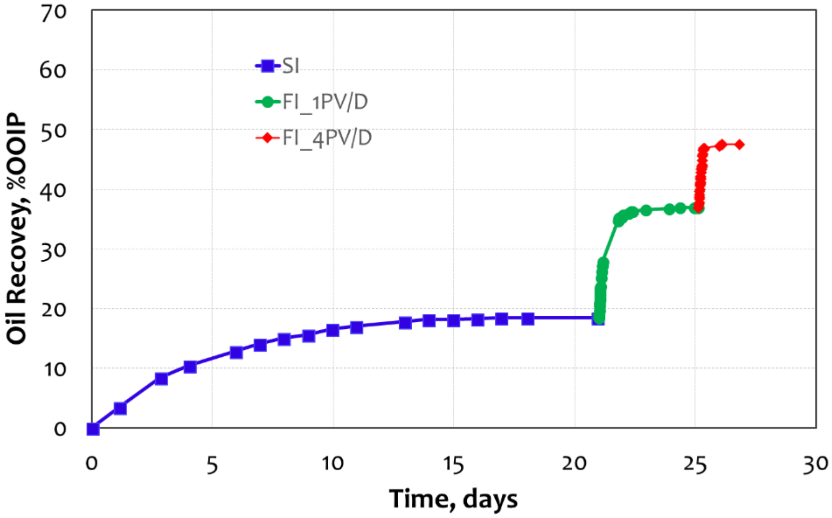


Figure 7.10: *Spontaneous and Forced Imbibition tests conducted on AA#1with an ultimate recovery of 47.6% OOIP and* $I_w^* = 0.39$

The core behaved less water-wet as revealed in the low SI recovery of 18.5% OOIP. The spontaneous imbibition rate is slow, as plateau is reached after 17 days. This depicts reduced capillary forces due to oil adsorption that has altered the mineral's ability to automatically soak the surrounding FW. No extra oil is produced after an extension period of 3 days. Following that, the FI is conducted at two different rates; 1 and 4 PV/D. The result shows an increase in oil recovery as viscous forces is increased by the injection of FW. The oil recovery reaches 36.9% and 47.6% OOIP respectively at the injected rates. The extra oil yielded by flooding at 4PV/D is only 22% of the total recovered oil and demonstrates the fact that recovery in the chalk system is controlled by capillary forces and increasing the viscous forces by flooding at higher rate would yield no extra recovery since the wetting alteration by crude oil adsorption is imminent and capillary trapped oil will be retained in the core.

The Amott water index for AA#1 is computed to be 0.39 and depicts the core to have become predominantly oil-wet. The wetting conditions of the core was further analysed by quantifying the fraction of water-wet surface available in the core. This was conducted by performing a chromatographic wettability test on the same core, which is shown in figure (7.11).

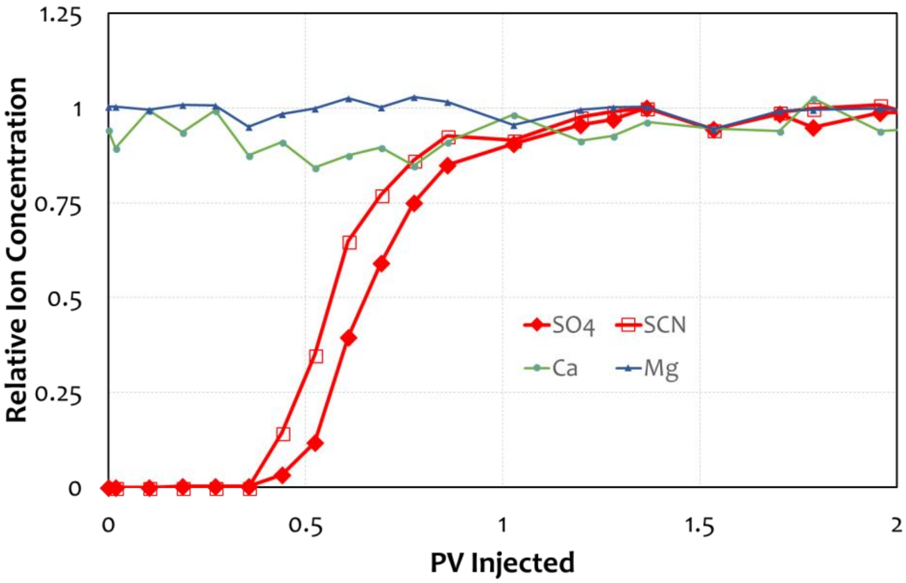


Figure 7.11: *Chromatographic wettability test on Aalborg core AA#1 saturated with ~7PV Oil*

Water-wet area for AA#1 was determined to be 0.0905 as compared to 0.2273 in the completely water-wet state. The Wetting Index for AA#1, is then computed as;

$$I_{CW,AA\#1} = \frac{0.0905}{0.2273} = 0.398$$

According to the established work by Strand et al., (2006b), this corresponds to a preferentially oil-wet condition. WI for AA#2 is comparable to the reported values in the study by Strand et al., (2007) for Aalborg chalk with $S_{wi} = 0$ (reported WI = 0.36) and SK chalk with $S_{wi} = 0$ (reported WI = 0.37). Mjos et al., (2018) also reported SK chalk with $S_{wi} = 0$ to have a WI = 0.35.

It appears that CWT for the AA#2 in comparison to SK depicts the surface adsorption mechanism to be proceeding as though the initial water saturation of 10% PV was negligible to serve as a viable barrier between the crude oil and the Aalborg surfaces, such that they readily adsorbed. The role played by S_{wi} in the chalk-brine-oil interaction was previously presented in section 4.3. It is worthy of note also, that the active brines used in the CWT test are not potential determining ions towards silica and this will influence the test results based on the contribution of silica to the total surface area of the ineral surface.

It is however clear, that the adsorption of crude oil polar components has altered the initial wetting and the subsequent low recovery by FW shows how that AN and BN adsorption correlates well with recovery as asserted by Dubey et al., (1993).

Another interesting phenomenon is the evolution of Ca^{2+} ions as shown in Figure 7.11. There is little co-adsorption of Ca^{2+} with SO_4^{2-} . It can be inferred from this observation that smart water EOR effect on Aalborg chalk will be less.

7.3.3 Effect of crude oil quantity on initial wetting of Aalborg chalk

It is commonly agreed that initial wetting of chalk is influenced by the amount of crude oil flooded through the core. This concession is tested on the Aalborg outcrop chalk to demonstrate its reproducibility regarding this general observation.

An Aalborg core sample, labelled AA#2 is prepared in same manner as AA#1 but exposed to 5 PV of crude oil in a systematic procedure as described in section 6.2.4. SI, FI and CWT experimental tests are conducted on the core to characterize its wetting conditions. A comparative illustration of recovery by SI for all cores is depicted in figure 7.12

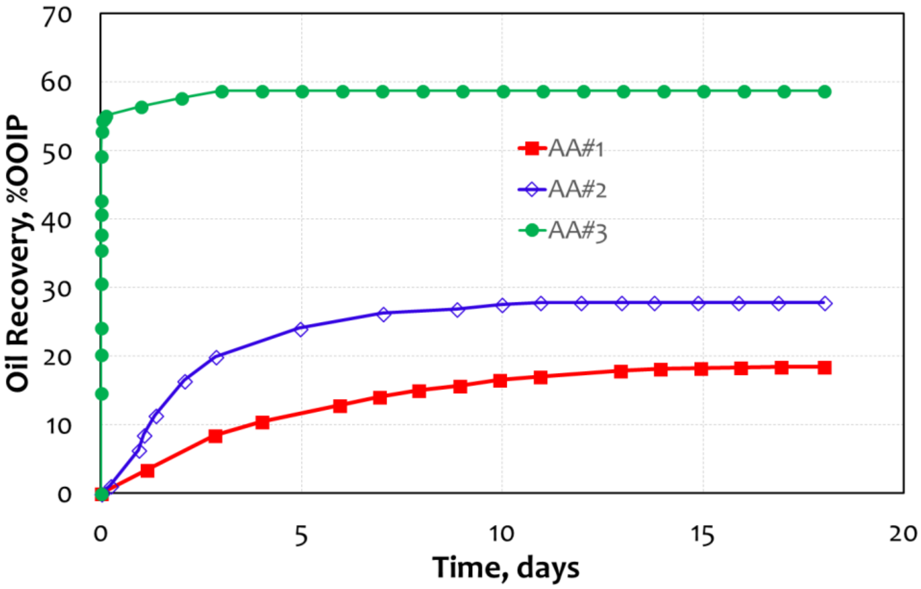


Figure 7.12: *Recovery by spontaneous imbibition tests on 3 Aalborg cores at different wetting conditions. Oil recovery decreases as the water-wetness decreases.*

Oil production by SI in AA#2 is profound due to greater capillary forces that yield an ultimate production of 27.9% OOIP. Production is higher and faster than observed for AA#1 as plateau is reached after only 10 days as compared to 17 days for AA#1. The result agrees well with the initial assertion and corresponds to reports in other documented research (Puntervold et al., 2007b; Hopkins et al., 2016; Hopkins et al., 2017). This trend is attributed to to increased adsorption of polar oil components as more oil is flooded through the core. Certainty of the chemistry defining this phenomenon is undisputable; as more crude is flooded through a core, relatively unaccessed mineral surfaces within the core matrix become reacheable by the oil and consequent adsorption of polar components occur which further makes the surfaces less water-wet and diminishes capillary forces responsible for uptake of imbibing water during SI tests.

Thus, SI recovery trend for the cores would be AA#3 > AA#2 > AA#1 which is in decreasing order of the cores' water-wetness. Since oil production in the chalk rock material is hugely influenced by positive capillary forces, oil recovery by forced imbition (figure 7.13) will produce a similar trend.

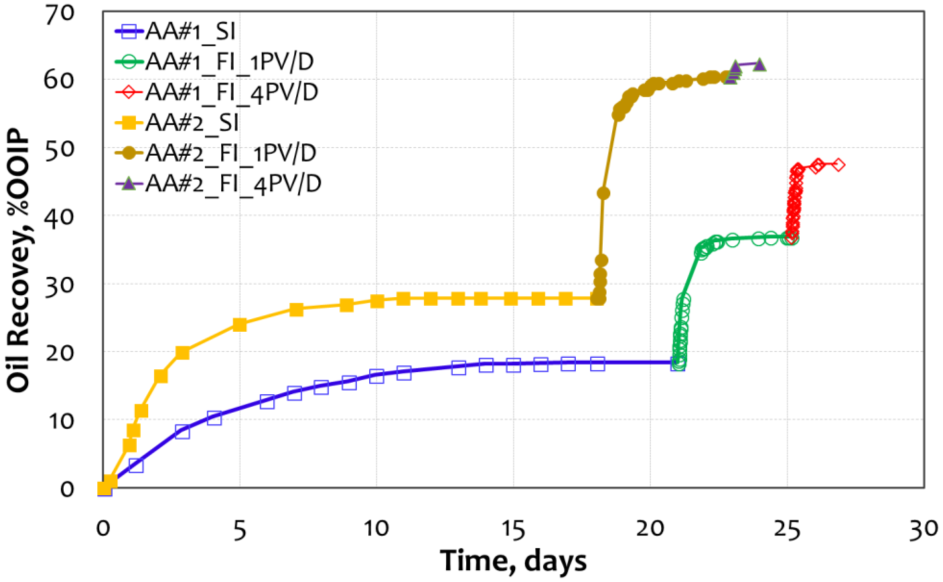


Figure 7.13: *Recovey by Spontaneous Imbibition and Forced Imbibiton of FW in AA#1 (I_w^*= 0.39) and AA#2 (I_w^*= 0.45)*

Ultimate oil recovery in AA#2 by forced imbibition is 62.37% OOIP and the Amott water index, $I_{w,\ AA\#2}$, is computed to be 0.45 which indicates wetting close to neutral conditions. The core was exposed to 5 PV of crude oil as compared to AA#1 (exposed to ~7 PV of oil and $I_{w,\ AA\#1}$ = 0.39) and thus a wetting condition as determined above is justified.

Wettability characterization by the CWT procedure (Figure 7.14) produced the water-wet area of AA#2 to be 0.0916 and compared to the area at completely water-wet conditions (0.2273), the water-wet fraction of the core is computed as:

$$I_{CW,AA\#2} = \frac{0.0916}{0.2273} = 0.4$$

The wetting index depicts a prefernatial oil-wet to mixed-wet surface. Reproducibility of the wetting conditions by the CWT as portrayed by the Amott Index is a rather remarkeable observation with the Aalborg cores examined in this research work.

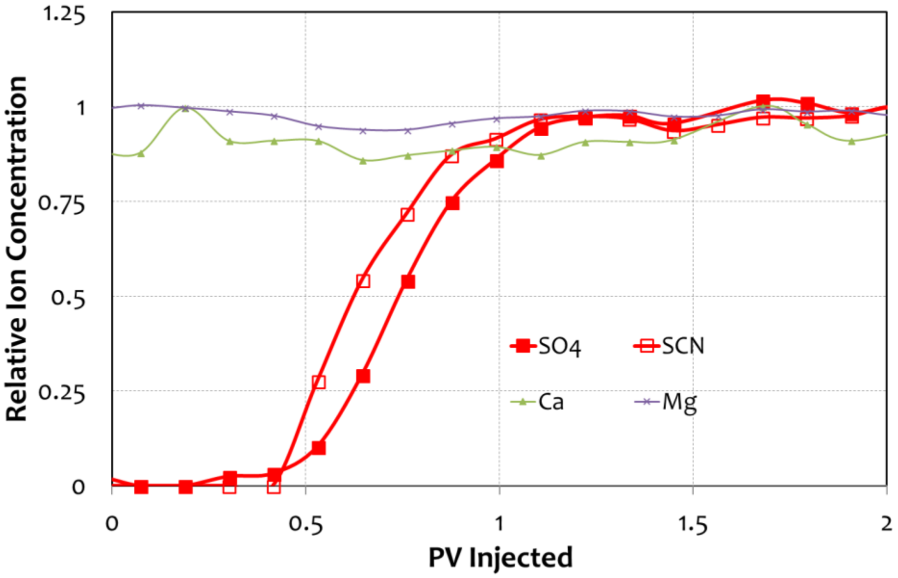


Figure 7.14: *Chromatographic wettability test on Aalborg core AA#2 saturated with 5PV Oil*

In some cases, when the pore openings are predominantly oil-wet as compared to the inner rock matrix, recovery by SI may be low and points to neutral conditions meanwhile, analysis of the water-wet surface area by CWT will reveal the right wetting conditions to be more water wet. The good agreement between these two methods on the wetting conditions of the cores used in this experiment portrays a uniform setting within the core materials.

Table 8 presents a summarry of the results obtained from the experimental studies conducted

Table 8: *Summary of results from wettability tests for the Aalborg core samples*

	Oil Phase	**Oil Recovery, %OOIP**		***Wetting Conditions***	
		SI	FI	*Amott* I_w^*	A_w
AA#1	~7PV Oil A	18.47	36.93	*0.39*	*0.0905*
AA#2	5PV Oil A	27.86	62.37	*0.45*	*0.0916*
AA#3	Heptane	~59	~100	*1*	*0.2273*

8 Conclusions

The experiments conducted in this research work proved effective in demonstrating the effect of chalk silica (SiO_2) content on initial wetting. The results obtained from the experiments and subsequent analysis demonstrated that:

- Polar organic components in crude oil adsorb instantly and affect initial wetting. Wettability then, is not corelated to the ageing time.
- Equilibrium adsorption for polar acidic components is achieved after 4PV and shows a low AN adsorption onto chalk of high silica content.
- Equilibrium adsorption for polar basic components is achieved after 6PV and shows a profound BN adsorption onto chalk of high silica content.
- BN_{ads}/AN_{ads} ratio for Aalborg chalk is higher than for Stevns Klint chalk and reveals silicates to be contributing a large fraction of available mineral surface.
- Core exposed to 5PV of crude oil behaved more water-wet compared to core exposed to 7PV of oil. This confirms that increased adsorption to the pore surface will lead to less water-wetness of the porous media.

I recommend the following as potential research areas for further studies regarding the subject matter:

- Evaluation of wettability alteration by smart water injection into Aalborg chalk could give better insight to the significance of BN_{ads}
- Adsorption evaluation conducted by using crude oil of AN = 0 and varied BN could give a better understanding to the role played by the polar basic components

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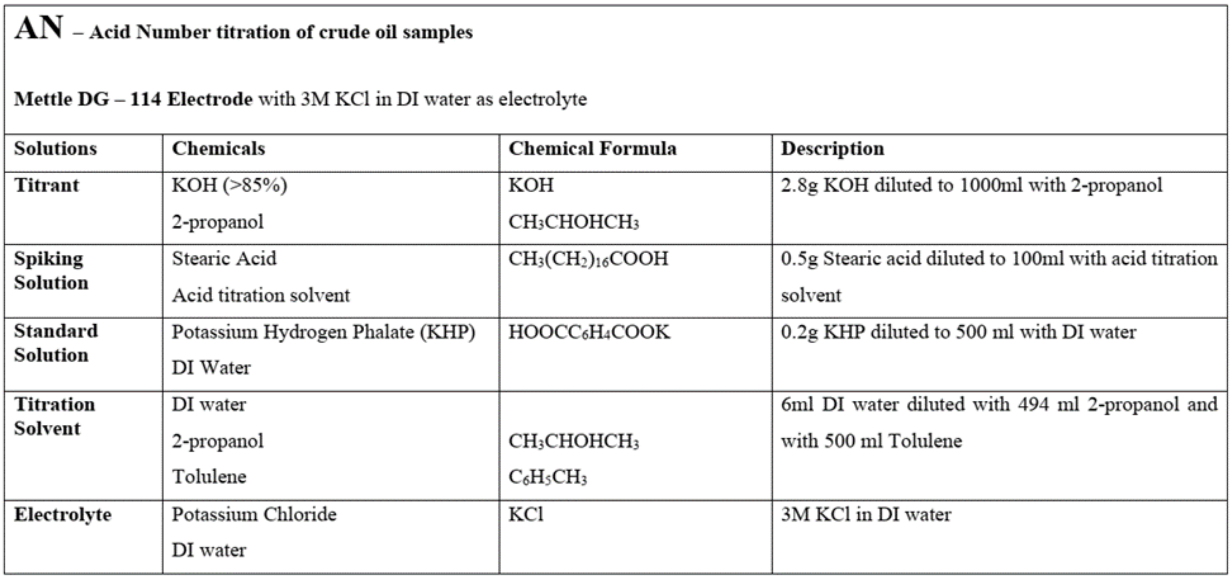
10 Appendix

A1 - Acid Number Measurement Solutions

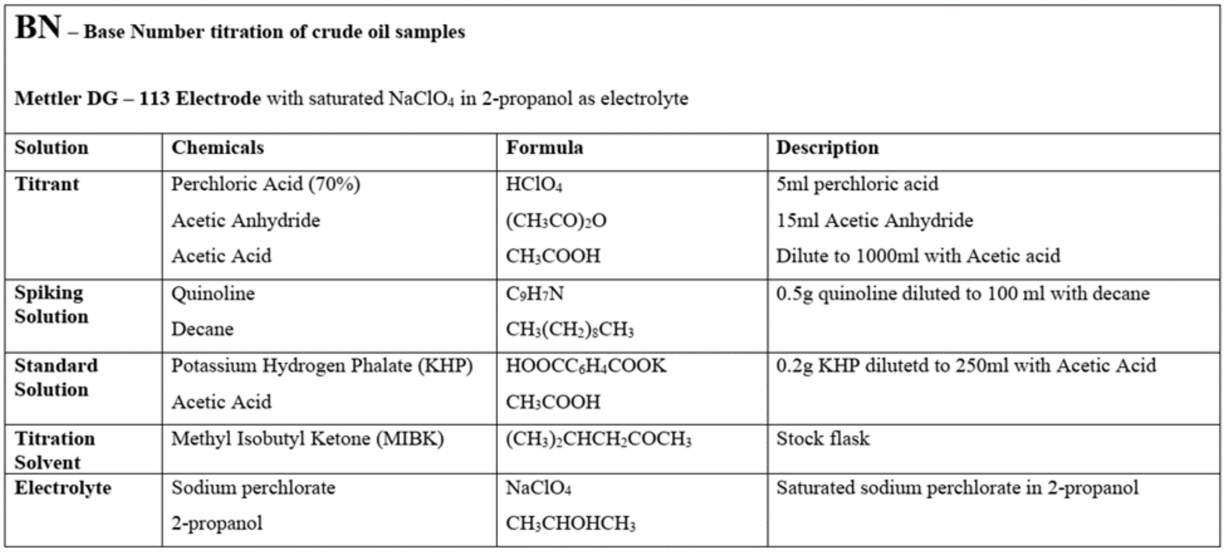


AN – **Acid Number titration of crude oil samples**

Mettle DG – 114 Electrode with 3M KCl in DI water as electrolyte

Solutions	**Chemicals**	**Chemical Formula**	**Description**
Titrant	KOH (>85%) 2-propanol	KOH $CH_3CHOHCH_3$	2.8g KOH diluted to 1000ml with 2-propanol
Spiking Solution	Stearic Acid Acid titration solvent	$CH_3(CH_2)_{16}COOH$	0.5g Stearic acid diluted to 100ml with acid titration solvent
Standard Solution	Potassium Hydrogen Phalate (KHP) DI Water	$HOOCC_6H_4COOK$	0.2g KHP diluted to 500 ml with DI water
Titration Solvent	DI water 2-propanol Tolulene	 $CH_3CHOHCH_3$ $C_6H_5CH_3$	6ml DI water diluted with 494 ml 2-propanol and with 500 ml Tolulene
Electrolyte	Potassium Chloride DI water	KCl	3M KCl in DI water

A2 - Base Number Measurement Solutions



BN – **Base Number titration of crude oil samples**

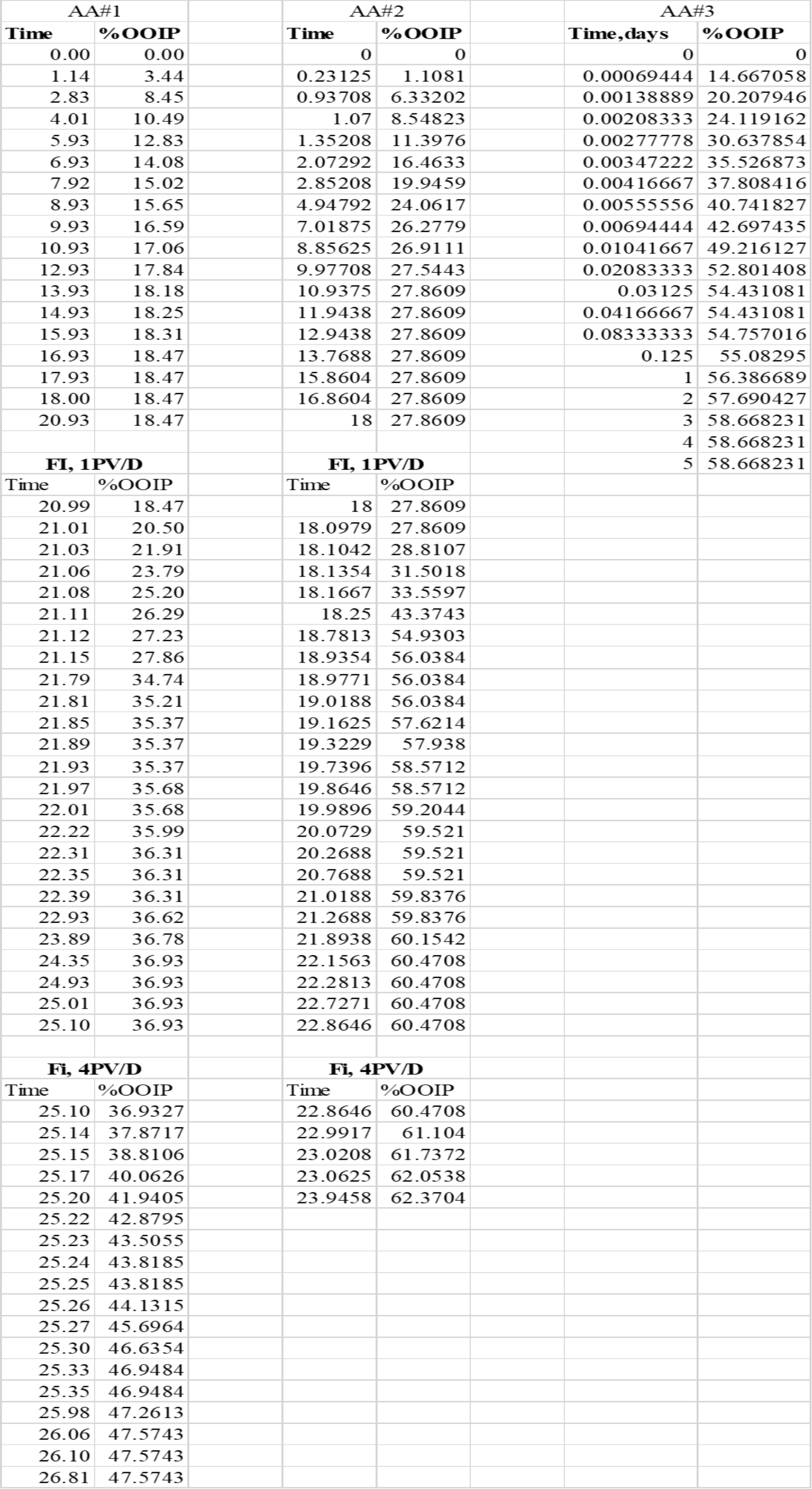
Mettler DG – 113 Electrode with saturated $NaClO_4$ in 2-propanol as electrolyte

Solution	**Chemicals**	**Formula**	**Description**
Titrant	Perchloric Acid (70%) Acetic Anhydride Acetic Acid	$HClO_4$ $(CH_3CO)_2O$ CH_3COOH	5ml perchloric acid 15ml Acetic Anhydride Dilute to 1000ml with Acetic acid
Spiking Solution	Quinoline Decane	C_9H_7N $CH_3(CH_2)_8CH_3$	0.5g quinoline diluted to 100 ml with decane
Standard Solution	Potassium Hydrogen Phalate (KHP) Acetic Acid	$HOOCC_6H_4COOK$ CH_3COOH	0.2g KHP dilutetd to 250ml with Acetic Acid
Titration Solvent	Methyl Isobutyl Ketone (MIBK)	$(CH_3)_2CHCH_2COCH_3$	Stock flask
Electrolyte	Sodium perchlorate 2-propanol	$NaClO_4$ $CH_3CHOHCH_3$	Saturated sodium perchlorate in 2-propanol

A3 – AN/BN of analyzed effluent samples on AA#1

AN Data		**BN Data**	
PV Injected	AN	PV Injected	BN
0.84	0.00	0.84	0.09
0.95	0.07	1.06	0.15
1.17	0.07	1.17	0.16
1.38	0.07	1.27	0.15
1.52	0.08	1.63	0.15
1.85	0.10	1.74	0.15
2.07	0.13	1.96	0.19
2.73	0.26	2.07	0.19
2.95	0.26	2.18	0.19
3.29	0.27	2.40	0.18
3.62	0.27	2.62	0.17
4.07	0.36	2.84	0.17
4.18	0.34	3.07	0.16
4.63	0.35	3.18	0.16
5.18	0.34	3.51	0.18
5.63	0.34	3.96	0.15
6.23	0.35	4.40	0.18
6.62	0.35	4.74	0.21
6.75	0.35	4.85	0.22
		4.96	0.24
		5.07	0.25
		5.29	0.24
		5.52	0.32
		6.07	0.35
		6.45	0.35
		6.56	0.35
		6.75	0.35

A4 – Wettability test by Oil Recovery data



AA#1		AA#2		AA#3	
Time	**%OOIP**	**Time**	**%OOIP**	**Time,days**	**%OOIP**
0.00	0.00	0	0	0	0
1.14	3.44	0.23125	1.1081	0.00069444	14.667058
2.83	8.45	0.93708	6.33202	0.00138889	20.207946
4.01	10.49	1.07	8.54823	0.00208333	24.119162
5.93	12.83	1.35208	11.3976	0.00277778	30.637854
6.93	14.08	2.07292	16.4633	0.00347222	35.526873
7.92	15.02	2.85208	19.9459	0.00416667	37.808416
8.93	15.65	4.94792	24.0617	0.00555556	40.741827
9.93	16.59	7.01875	26.2779	0.00694444	42.697435
10.93	17.06	8.85625	26.9111	0.01041667	49.216127
12.93	17.84	9.97708	27.5443	0.02083333	52.801408
13.93	18.18	10.9375	27.8609	0.03125	54.431081
14.93	18.25	11.9438	27.8609	0.04166667	54.431081
15.93	18.31	12.9438	27.8609	0.08333333	54.757016
16.93	18.47	13.7688	27.8609	0.125	55.08295
17.93	18.47	15.8604	27.8609	1	56.386689
18.00	18.47	16.8604	27.8609	2	57.690427
20.93	18.47	18	27.8609	3	58.668231
				4	58.668231
FI, 1PV/D		**FI, 1PV/D**		5	58.668231
Time	%OOIP	Time	%OOIP		
20.99	18.47	18	27.8609		
21.01	20.50	18.0979	27.8609		
21.03	21.91	18.1042	28.8107		
21.06	23.79	18.1354	31.5018		
21.08	25.20	18.1667	33.5597		
21.11	26.29	18.25	43.3743		
21.12	27.23	18.7813	54.9303		
21.15	27.86	18.9354	56.0384		
21.79	34.74	18.9771	56.0384		
21.81	35.21	19.0188	56.0384		
21.85	35.37	19.1625	57.6214		
21.89	35.37	19.3229	57.938		
21.93	35.37	19.7396	58.5712		
21.97	35.68	19.8646	58.5712		
22.01	35.68	19.9896	59.2044		
22.22	35.99	20.0729	59.521		
22.31	36.31	20.2688	59.521		
22.35	36.31	20.7688	59.521		
22.39	36.31	21.0188	59.8376		
22.93	36.62	21.2688	59.8376		
23.89	36.78	21.8938	60.1542		
24.35	36.93	22.1563	60.4708		
24.93	36.93	22.2813	60.4708		
25.01	36.93	22.7271	60.4708		
25.10	36.93	22.8646	60.4708		
Fi, 4PV/D		**Fi, 4PV/D**			
Time	%OOIP	Time	%OOIP		
25.10	36.9327	22.8646	60.4708		
25.14	37.8717	22.9917	61.104		
25.15	38.8106	23.0208	61.7372		
25.17	40.0626	23.0625	62.0538		
25.20	41.9405	23.9458	62.3704		
25.22	42.8795				
25.23	43.5055				
25.24	43.8185				
25.25	43.8185				
25.26	44.1315				
25.27	45.6964				
25.30	46.6354				
25.33	46.9484				
25.35	46.9484				
25.98	47.2613				
26.06	47.5743				
26.10	47.5743				
26.81	47.5743				

A5 – Chromatography data for AA#1

Thiocyanate				Sufate		
PV	C/C0	Area under curve		PV	C/C0	Area under curve
0.3556	0			0.3556	0	
0.4398	0.1444	0.006079393		0.4398	0.0335766	0.001413646
0.52359	0.34914	0.020676796		0.52359	0.1182482	0.006360753
0.60725	0.64871	0.041736292		0.60725	0.3956204	0.021493292
0.69104	0.77155	0.059502221		0.69104	0.5912409	0.041344893
0.77496	0.86207	0.068553666		0.77496	0.750365	0.056299482
0.85917	0.92672	0.07531188		0.85917	0.849635	0.067363301
1.02744	0.91595	0.155033647		1.02744	0.9051095	0.147635815
1.19585	0.97629	0.159334531		1.19585	0.9547445	0.156607381
1.28005	0.99138	0.082843068		1.28005	0.9693431	0.081008057
1.36426	1	0.083841177		1.36426	1	0.082913406
	Sum	**0.75291267**			**Sum**	**0.662440024**
			Area between curves = 0.09047			

A6 - Chromatography data for AA#2

Thiocyanade				Sulfate		
PV	C/C0	Area under curve		PV	C/C0	Area under curve
0.42	0.0000			0.42	0.0329	
0.53	0.2765	0.015879175		0.53	0.1038	0.0060
0.65	0.5431	0.047190955		0.65	0.2930	0.0228
0.76	0.7176	0.072413543		0.76	0.5427	0.0480
0.87	0.8725	0.091107339		0.87	0.7490	0.0740
0.99	0.9157	0.102453629		0.99	0.8607	0.0922
1.10	0.9667	0.107845925		1.10	0.9461	0.1035
1.22	0.9745	0.110940139		1.22	0.9724	0.1096
	SUM	**0.547830705**				**0.4562**
		Area between curves = 0.0916				

A7 - Chromatography data for AA#3

Thiocyanate				**Sufate**		
PV	C/C0	Area under curve		PV	C/C0	Area under curve
0.7110223	0			0.71102	0	
0.7975608	0.09402	0.00406805		0.79756	0.00297	0.000128395
0.8838123	0.21795	0.013453757		0.88381	0.00148	0.000191954
0.9697768	0.42094	0.027460869		0.96978	0.00297	0.000191316
1.0558848	0.64957	0.046089844		1.05588	0.14688	0.00645171
1.1422798	0.83547	0.064150132		1.14228	0.37537	0.022560118
1.3146392	0.99145	0.157443734		1.31464	0.75371	0.097303818
1.4880033	1.00855	0.173364049		1.488	0.91395	0.14455578
1.5749723	1	0.087340714		1.57497	0.95252	0.081162512
1.6619414	0.98504	0.086318642		1.66194	0.95994	0.083162542
1.83631	0.99359	0.172505729		1.83631	0.98071	0.169194498
1.942175	0.98718	0.104847067		1.94218	1	0.104844046
	Sum	**0.937042585**			**Sum**	**0.709746689**
		Area between curves = 0.2273				