Investigation of crude oil and produced water properties on chalk surface wettability alteration

Master Thesis

Frida Franić
Konstantinos Sapounas

Aalborg University
Oil and Gas Technology

AALBORG UNIVERSITY
STUDENT REPORT

Oil and Gas Technology
Aalborg University
http://www.aau.dk

Title:
Investigation of crude oil and produced water properties on chalk surface wettability alteration

Theme:
Scientific Theme

Project Period:
Spring Semester 2018

Project Group:
K10OG4F18

Participant(s):
Frida Franić
Konstantinos Sapounas

Supervisor(s):
Professor Erik Gydesen Søgaard

Copies: 1

Page Numbers: 69

Date of Completion:
07.06.2018

Abstract:

The novelty of this study is the testing of crude oils with different acid number, from the North Sea Danish sector (Halfdan field) and Valhal formation water as aging fluid, at 115°C, applying Modified Flotation Test (MFT) technique in order to investigate the crude oil-brine-rock interactions. Different dilutions of produced water were performed in order to regulate Dan chalk's wettability, by decreasing salinity, and ionic strength. Thus, different combinations of crude oils and brines, comprising different properties and hence displaying different trends, in terms of reactivity towards the chalk surface, were tested. Both crude oil and brine properties were analyzed to obtain better insight of the mechanisms taking place during the wettability alteration.

Contents

Acknowledgment

First of all, we would like to thank professor Erik Gydesen Søgaard who supported us to investigate this subject. The door of professor Søgaard was always open for consultation, word of advise and support in all steps from the beginning to the end.

Further, we would like to thank Linda B. Madsen and Dorte Spangsmark for their help in performing laboratory analysis needed for this project.

Thank you Erica Godinho dos Santos and Nikos Montesantos for your support and advice. Also, thank you for making the time spent in the lab easier when it was hard.

We would like to thank our parents who were of great support from far away, encouraging us till the end.

And finally we would like to thank each other for not giving up when it was hard, for being supportive and being there for one another.

Nomenclature

AN	Acid Number
BN	Base Number
c_i	concentration of ions
COBR	Crude Oil Brine Rock
crude oil M	50:50 mixture of Halfdan and crude oil A
crude oil H	Halfdan crude oil
DW	Deionized Water
10xDPW	10x Diluted Produced Water
20xDPW	20x Diluted Produced Water
100xDPW	100x Diluted Produced Water
10xDTWPW	10x Diluted Produced water with Tap Water
EC	Electrical Conductivity
EOR	Enhanced oil recovery
FW	Formation water
G	vapor phase
g	grams
IC	Ion Chromatography
ICP	Inductive Coupled Plasma spectroscopy
IFT	Interfacial Tension
IOR	Incremental Oil Recovery
KOH	Potassium Hydroxide
L	liquid phase
LSW	Low Salinity Water
m	mass
mD	milliDarcy
MFT	Modified Flotation Test

ml	milliliter
PDI	Potential Determining Ions
PW	Produced Water
S	solid phase
SARA	Saturates Aromatics Resins Asphaltenes
TAN	Total Acid Number
TBN	Total Base Number
TDS	Total Dissolved Salts
TW	Tap Water
V	volume
VFW	Valhal Formation Water
z_i	charge of ions
γ	interfacial tension
γ_{SL}	solid-liquid interfacial energy
γ_{LG}	liquid-gas interfacial energy
γ_{SG}	solid-vapor interfacial energy
θ	contact angle
μ	ionic strength
μm	micrometer
ρ	density

Problem definition

The objective of this thesis is to investigate how different characteristics of crude oil and produced water, affect chalk wettability. The wettability alteration is investigated in the laboratory by applying the Modified Flotation Test (MFT) technique, at constant temperature.

Before conducting the experiments, thorough research was performed on the so far obtained results, from previous studies. Due to the complexity of the COBR system, and the mechanisms behind it, several researches recorded varying results. It is important to mention that the majority of these studies were carried out with focus on sandstone reservoirs. Nevertheless, several hypothesis, based on their results and conclusions, were made for this case, to specify the targets of the investigation.

1. Investigate how different ratios of dilution affect the wettability of chalk.
2. Understand the mechanism behind low salinity water injection and cation exchange that occur between oil/rock and brine/rock interface.
3. Investigate how crude oil properties, more specifically, viscosity, acid number and heavier fractions, such as asphaltenes, affect wettability alteration.
4. Investigate the compatibility of the chosen COBR system. In other words, "Will the water-wetness of chalk increase in order to improve oil recovery?"

Chapter 1

Introduction

Crude oil is a mineral oil that originates from ancient fossilized organic materials, such as zoo-plankton and algae, which geochemical processes converted into oil millions years ago. Over time, the decayed residue was covered by layers of mud and silt, sinking further down into Earth's crust and preserved there between hot and pressured layers, gradually transforming into oil reservoirs, figure 1.1.. It is a mixture of hydrocarbons, and it exists in liquid form in underground pools or reservoirs, in tiny spaces within sedimentary rocks, and near the surface in tar (or oil) sands. Crude oil is organic oil, but it is refereed as mineral oil because its origin is distant and it is obtained in the environs of rocks, underground traps and sands. Together with its refined compounds, petrochemicals, crude oil is widely used everyday.[16]

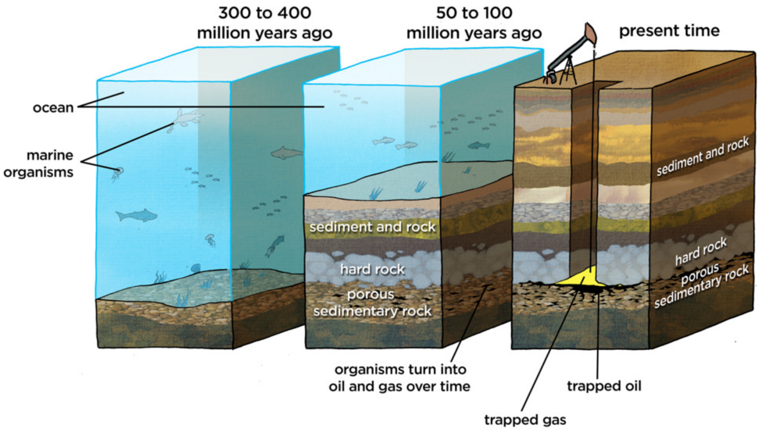


Figure 1.1: Reservoir formation
[21]

The 19th century was an epoch of a great industrialization, not only steel and iron industry, but also the discovery of oil, new fuel source that will form modern world. The petroleum or oil industry includes the processes of exploration, extraction, refining, transporting and marketing of petroleum products on a global scale. The biggest quantity that industry produces are fuel oil and gasoline. Even though petroleum is mostly used as synonym for fuel and gasoline it also reefers to the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, synthetic fragrances, and plastics.

From the discovery of oil, after the Industrial Revolution the oil industry became one of the most powerful industry in the world. Oil and gas companies are among the world's largest corporations and branches in the economy. Crude oil became one of the most present and essential resources in everyday life. Annual global production of oil is measured in billions of metric tons. Over the last decade, the necessity for oil, and its consumption has been raising. Even though Oil and Gas industry faced some tough times in the last six years, it continues to play an important role in terms of energy supply. However, the low oil price translates itself into the need for more efficient, cost-effective and environmental harmless ways of producing hydrocarbons. The most essential thing to focus right now is finding new ways and technologies which will increase the recovery rate. [47]

1.1 Enhanced Oil Recovery

Enhanced oil recovery (EOR) is oil recovery by injection of substances that normally do not occur in the reservoir. EOR covers all model processes and agents of oil recovery. It excludes the water-flooding and is intended to exclude all pressure maintenance processes. Also, it does not restrict to a particular phase of oil recovery.[36]

Oil recovery operations are divided into three stages:

1. *Primary or the initial* production stage, results from the displacement energy naturally existing in a reservoir. These natural energy sources are solution drive gas, water influx, gas cap drive or gravity drainage.
2. *Secondary stage or secondary* operations are implemented usually after primary production has declined. The secondary recovery allude water-flooding, pressure maintenance and gas injection. Nowadays, secondary recovery is synonymous to water-flooding.
3. *Tertiary recovery* takes place after the secondary recovery is done, or becomes uneconomical. It involves miscible gases, chemicals and/or thermal energy to displace additional oil.[28]

It is not always the case that the production operations are conducted in chronological sequence. For example, the reservoirs with very viscous crude oil (heavy oils) may not flow under economic rates under natural energy drives, so primary recovery is insignificant. For this kind of reservoirs water-flooding is not profitable, hence the use of thermal energy might be the only way to recover the significant amount of oil. In this case the tertiary method might be the first and only method used for the recovery. The range of recovered oil from both primary and secondary processes is from 20% to 50% depending on oil and reservoir properties. The goal of EOR is to recover the part of the remaining oil-in-place. It is believed that enhanced oil recovery is able to provide additional 5-30% of the original oil in place, increasing the overall recovery level from the field to 50-70% or even higher. [28, 16]

Unfortunately, there is no single EOR method applicable to all petroleum reservoirs as a general method for enhanced oil recovery. A petroleum reservoir is a porous and permeable medium containing brine, oil and gas which move toward production wells under pressure which may be existing or applied. Several parameters such as shape and size of the pores, rock type and porosity contribute to the formation of the reservoir. Therefore, the criteria for selecting a specific EOR method is complex because of the large number of petrophysical, chemical, geologic and environmental properties that must be considered for each case individually. [19]

The target of EOR processes is the increase of the oil recovery from reservoirs. EOR processes can be divided into four major categories which are further subdivided into various processes as shown in figure 1.2.

- Chemical
- Thermal
- Miscible
- Other

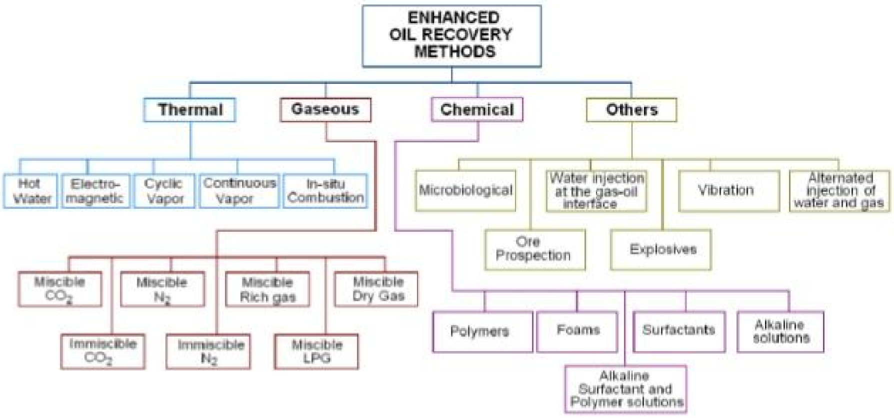


Figure 1.2: EOR categories
[1]

The measure of success is the amount of the incremental oil recovered. Incremental oil is the difference between what was actually recovered and what would have been recovered had the process not been initiated. Figure 1.3 shows incremental recovered oil. From A to B oil rate is declining. At B, an EOR process is initiated and, if successful, the rate should show a deviation from the projected decline at some time after B. If there was no EOR method initiated, the recovery would follow the line from B to C. If the EOR method is initiated, the recovery follows the line connecting B and D.

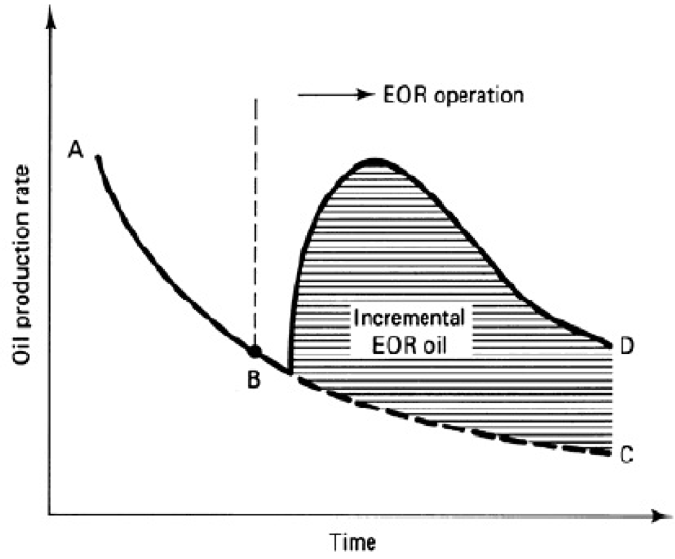


Figure 1.3: Incremental EOR oil
[36]

1.2 Wettability

Wettability is the property of one fluid to spread on, or adhere to, a solid surface in the presence of other immiscible fluids. It refers to the interaction between fluid and solid phases. In a reservoir rock the liquid phase can be water, oil or gas, and the solid phase is the rock mineral assemblage. The understanding of wettability and its formation is crucial for oil recovery optimization. The oil-versus-water wetting preference influences many aspects of reservoir performance, particularly in water flooding and enhanced oil recovery techniques.

Wettability is measured through contact angle of the fluid and the solid phase via Young equation. The thermodynamic explanation of the contact angle lies in the equilibrium between the three phases, the liquid phase (L), the solid phase (S), and the gas or vapor phase (G). The equilibrium contact angle θ_C is determined from these quantities by Young equation:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} - \theta_C = 0 \tag{1.1}$$

where the solid–vapor interfacial energy is γ_{SG}, the solid–liquid interfacial energy is γ_{SL} , and the liquid–vapor interfacial energy (i.e. the surface tension) is γ_{LG}. [4]

Depending on the degree of the contact angle there are several types of wetting surfaces. If the liquid molecules are strongly attracted to the solid molecules then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0°. Typically, if the water contact angle is smaller than 90°, the solid surface is considered hydrophilic and if the water contact angle is larger than 90°, the solid surface is considered hydrophobic. How wettability is related to contact angle is illustrated in figure 1.4. There are possibilities that the angle is bigger than 120° or even 150°. This happens with many polymers and rough surfaces, those surfaces are called super-hydrophobic surfaces. It can be concluded that the contact angle and wettability are inversely proportional, the bigger the contact angle the smaller wettability. Contact angle studies show an increase in water-wetting at higher temperatures.[49, 11, 4]

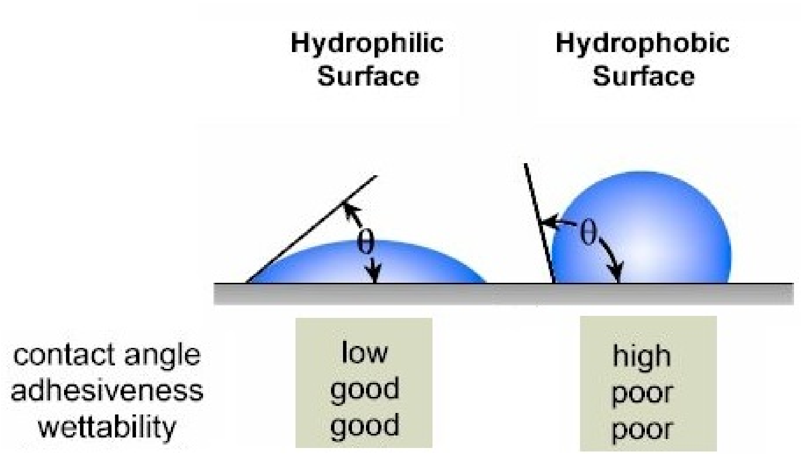


Figure 1.4: Contact angle vs Wettability

1.2.1 Wettability in reservoir

Understanding the wettability is of great importance. It influences the productivity and oil recovery. In reservoir multiphase flow, wettability controls the fluid phase distribution and flow properties.

Wettability in the reservoir depends on the rock type. Reservoir rocks are complex structures, build from layers of various minerals. Each layer of mineral because of its lithology may have different wetting preferences and hence different wettability, making the wetting character of the composite rock difficult to describe. Typically, the reservoirs are made of quartz, carbonate and dolomite. The surface roughness, size, shape and rounding of the rock will affect the wettability.

The complexity and the heterogeneity can affect the recovery. Wetting forces lead to an equilibrium condition between at least three substances: a solid and two fluids. The constituents and conditions for all three substances influence the wetting preference. Thus, we must consider the oil components,the brine chemistry and the mineral surface, as well as the system's temperature and pressure.

The rock in the reservoir can be either water-wet or oil-wet.

- The reservoir is consider to be water-wet when the contact angle θ_C is between 0° and 90° and adhesion tension is negative. When θ is close to 0° the rock is considered 'strongly water-wet'.
- The reservoir is consider to be oil-wet if oil preferentially wets the rock surfaces. The contact angle θ_C is between 90° and 180° and adhesion tension is positive. When θ is close to 180° the rock is considered 'strongly oil-wet'. [27, 69, 13, 25]

Wettability can be classified as:

- *Strongly oil wetting.*
- *Strongly water wetting*
- *Neutral wettability*
- *Fractional wettability* – areas in a reservoir are strongly oil-wet, whereas most of the reservoir is strongly water-wet. It occurs where reservoir rock has variable mineral composition and surface chemistry.
- *Mixed wettability* – smaller pores in a reservoir are water-wet and filled with water, while larger pores are oil-wet and filled with oil. Residual oil saturation is low - occurs where oil with polar organic compounds invades a water-wet rock saturated with brine. [12]

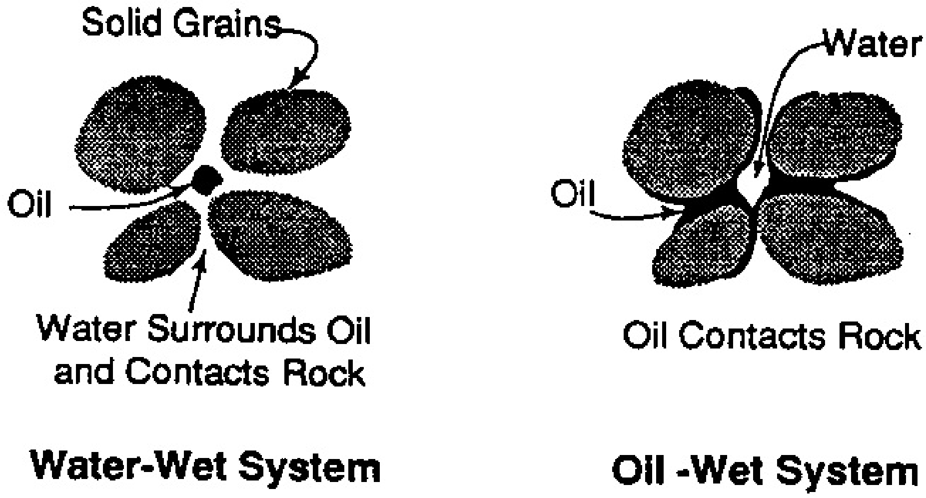


Figure 1.5: Water vs. Oil-wet system
[28]

Figure 1.5. illustrates how the system looks when it is water-wet and when it is oil-wet. In water-wet system oil is trapped in between rock grains and water surrounds oil and contacts rock. In contrary in oil- wet system water is trapped in between rock grains and oil contacts rock. There are several methods developed to determine the wettability of the fluid-rock system. They can be divided into two categories, quantitative and qualitative.

Quantitative methods are:

1. *Contact angle method* - There are many methods of contact-angle measurement that have been developed. The most common used in O&G industry are sessile drop method and a modified form of the sessile drop method.
2. *Amott method* - It is a macroscopic average wettability of a rock to given fluids. It involves the measurement of the amount of fluids imbibed spontaneously and forcibly by a rock sample. It is employed by industry standard for comparing the wettability of various core plugs.
3. *USBM (U.S. Bureau of Mines) method* - It is also a macroscopic mean wettability of a rock to given fluid. Unlike Amott method it considers the work required to do a forced fluid displacement. USBM is also employed by industry for comparing the wettability of various core plugs.
4. *Electrical Resistivity method*

These methods are considered to be challenging to perform, time consuming and expensive.[13, 27, 29]

Qualitative methods include:

1. *Flotation method*
2. *Relative permeability method*
3. *Recovery curves method*
4. *Imbibition method*
5. *NMR longitudinal relaxation*
6. *Glass slide method*
7. *Dye adsorption method*

As stated before, rocks are build form layers of minerals, and because of its composition complexity, rock surface is charged with ions. When water is introduced into the reservoir, it forms a double layer of water molecules and ions to neutralize any charge on the rock surface. The thickness of the formed water film is inversely proportional to the ionic strength. The water film can be diminished from oil phase.

In COBR (Crude Oil-Brine-Rock) system, electrical charges exist on both oil-brine and mineral-brine interface. In case that the charges on both interfaces (oil-brine and rock brine) are similar, it results in repulsion. Hence the water film will maintain thick and disjoining pressure (combination of structural, electrostatic, and van der Waals forces control the collapse of the water film) will increase. A thick water film prevents active components in the crude oil from adhering to the mineral surface. This goes in favor to water wet conditions. Oppositely, if the charges are dissimilar the electrostatic forces are in attraction making the water film thin. The result in this case is a less water-wet condition. [69, 51, 25]

If the water film can resist the pressure from oil, it will remain stable. However, a high pressure (attractive forces) in the oil phase can reduce the water film thickness sufficiently to allow for the active components in the oil phase to adhere to the mineral surface. Thus, the wetting state in a reservoir should be dependent upon the difference between the oil and water pressure (capillary pressure). [51, 30]

Wettability is also affected by the depth. Higher zones in the reservoir have greater capillary pressure which can counteract the disjoining pressure and destabilize the water film, allowing surface-active components in the oil to interact with

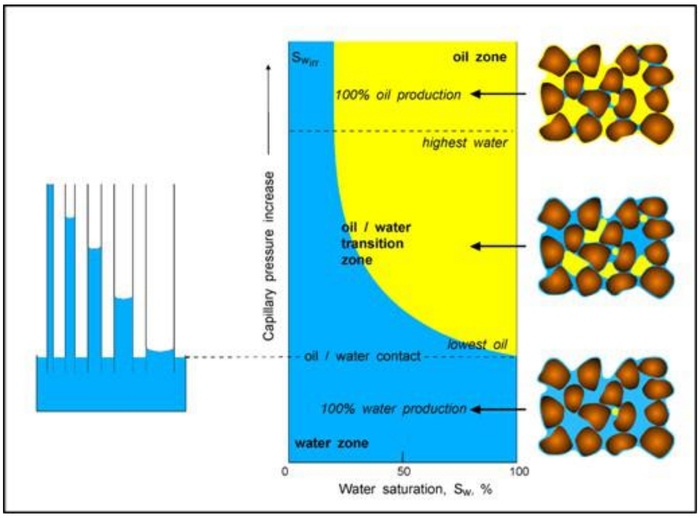


Figure 1.6: Capillary pressure change
[18]

the solid. The closer to the bottom of the transition zone the greater the tendency towards water-wetness. On the contrary, the closer to the top, the greater the tendency towards oil-wetness, figure 1.6.[69]

1.3 Flotation

Unlike measuring contact angle, or using Amott method to measure wettability which are time consuming and expensive techniques, flotation is considered to be a fairly cheap, accurate and quick method. Also, it can be employed to screen possible chemical conditions in the reservoir on their effect on wettability. The results can be obtained in few days instead of months and they are easy to reproduce.[51, 25]

Flotation, as a method in petroleum industry, was introduced 25 years ago, with the experiment conducted by Dubey and Doe, in order to investigate the effect of acid and base numbers of crude oil on wetting characteristics. Nevertheless, it has been routinely used for over a century for separation of suspended mineral particles. Later, this method was used to test the wettability reversal by surfactant solution in carbonates with minor modification. Also, Mwangi et al. used the flotation method to study the effect of rock mineralogy, aqueous chemistry (salinity), surface active compounds and temperature, on wettability. In their experiments the oleic phase was decane. This modified flotation technique (MFT) proved a successful method to investigate the influence of oil and brine chemistry on wettability in sandstone and carbonate reservoirs at different temperatures.[50, 20, 41]

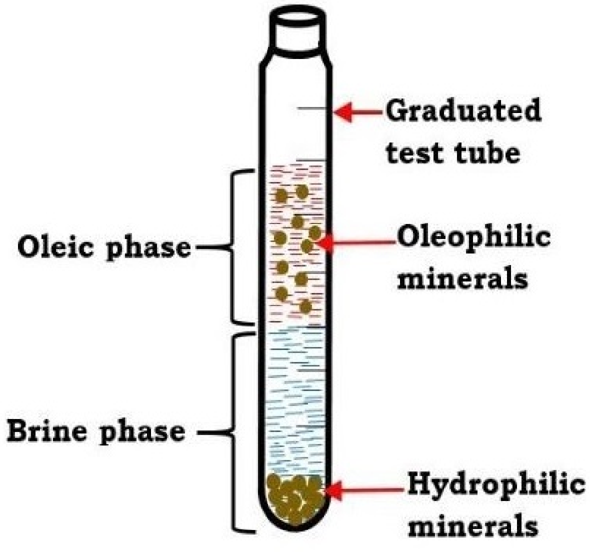


Figure 1.7: Flotation column
[25]

Figure 1.7. illustrates how flotation technique looks when performed in laboratory scale.

The mechanism of the MFT depends on the difference in the surface wettability and the interaction between each mineral in the rock with a particular fluid. The polarity of the solid-brine and oil-brine interfaces, during COBR interactions, also affects the affinity. The method measures wettability quantitatively on a grain scale level, displaying which parts of the rock are oil and which are water-wet.

The advantage of flotation is that the conditions, such as different temperatures, brines, crude oils, and lithotypes, can be changed easily. The execution of flotation is considerably easy. In a glass test tube,water, oil and rock grains are mixed and shaken. Afterwards, the behavior of the rock grains is observed. If the system is strongly oil-wet, the grains will be suspended at the oil/water interface. In the water phase, the oil-wet grains will group and form small oil globules covering rock grains. In opposition, if at the bottom of the bottle, clean rock grains can be spotted, the system is strongly water-wet. Some grains in the oleic phase will cluster coated by thin layer of water.

Chapter 2

Crude oil characteristics

Crude oil is an important fossil fuel that is used daily in many aspects. Crude oil is a naturally occurring, unrefined petroleum product. It is a complex mixture of hydrocarbons, dissolved gases and trace amounts of suspended water, inorganic sediments deposits and other organic materials.

Table 2.1: Crude oil average composition

Component	Percentage (%)
Carbon	84
Hydrogen	14
Sulphur	1-3
Nitrogen	1
Oxygen	1
Minerals and salts	0.1

Since crude oil is a fossil fuel, it belongs to the group of non-renewable resources, thus, it cannot be replaced naturally. It can be refined to produce usable products such as gasoline, diesel and various forms of petrochemicals, which means that it cannot be replaced naturally, at the rate we consume it and is therefore a limited resource.

Generally, crude oil is obtained through drilling. In the reservoirs alongside the crude oil, there are other resources,such as natural gas and saline water. Natural gas is lighter component and therefore it lays above the crude oil. On the other hand, saline water, is denser, and sinks at the bottom. [26, 23]

Extracted crude oil can be refined and processed into a variety of forms, such as gasoline, kerosene, asphalt and etc.

Synonym for crude oil is "black gold". Not all crude oils are of the same type. They can vary in different properties,such as viscosity, color, hydrocarbon composition density and many more. First stage in refining crude oil is distillation process where oil is heated and separated in different components.

There are several ways of crude oil classification. The most known and accepted is based on the API (American Petroleum Institute) gravity. It classifies oil as heavy or light. In literature, there is also classification to medium and extra heavy oil. API gravity is expressed in degrees, (°). Not all oil associations follow the same classification, but generally the rule is the higher the number, the lighter the oil. Table 2.2 shows a rough classification of crude oil. [43]

Table 2.2: API gravity classification

Classification	API gravity
Light	31.1°
Medium	22.3°-31.1°
Heavy	22.3°
Extra heavy	10°

The most valuable oils for refining are the ones with API gravity between 40° and 45°. Above these values, oil contains molecular chains that are shorter and less valuable. Crude oil with API gravity less then 10° are sometimes referred to as bitumen. Bitumen or asphalt is a sticky, black and very viscous liquid. Unlike other heavy oils it is immobile in reservoir. It is derived from oil sands deposits in Alberta, Canada. Sometimes they are diluted with light hydrocarbons to produce diluted bitumen. [3, 43]

Crude oil can also be classified by the amount of the sulfur it contains.

- *Sweet crude oil* contains less then 0.5% of sulfur. It is easier to refine and safer to extract and transport. Some of the reservoirs containing sweet crude are: the Appalachian Basin in Eastern North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, North Africa, Australia, and the Far East including Indonesia.
- *Sour crude oil* has more than 0.5% of sulfur and some of it is present in form of hydrogen sulfide. In sour crude oil, carbon dioxide can be found. Reservoirs

containing sour crude are: the Gulf of Mexico, Mexico, South America, and Canada. [59]

Properties of crude oil that can affect wettability

- Acid and Base number
- Composition

2.1 Acid and Base Number

Acid or total acid number (TAN) is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. Total Base Number (TBN) is a measurement of basicity that is expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of oil sample (mg KOH/g). They are important quality measurements of crude oil as they characterize the polar components in crude oil. These polar components are responsible for adhesion to the rock surface.

ASTM D664 and ASTM D2896 are methods developed to obtain both numbers. In the procedure, the sum of all acid or base compounds present in petrochemical samples can be determined by an acid-base titration using potassium hydroxide (KOH) as titrant. The samples are diluted in a mixture of chloroform and isopropyl alcohol since they are non-aqueous.[14, 50]

As mentioned before, COBR interactions are extremely complicated and there are many aspects that are connected to one another and influence those interactions. The polar components in oil are the one responsible for wetting alteration. The acids have the ability to adsorb onto mineral surface and thereby alter the wetting properties of the rock.

According to Hoeiland et al., wettability alteration based on acid and base number on silica rock was measured and it has been concluded that the higher the acid number, the more water-wet the rock surface. Oppositely, higher base number resulted in more oil-wet behavior. Also, it was observed that increasing the base to acid ratio, the system becomes more oil-wet. [31]

Standnes and Austad reported in their paper that there is a correlation between the acid number and ability to alter wetting preferences of the porous media. They measured spontaneous imbibition of brine. The higher AN led to more oil-wet. Their results are in the line with Buckley but are opposite from the results Hoeiland et al. [54, 10]

There are several reports investigating the effectiveness of temperature on acid and base number and their ability to change the wetting preference. Organic geochemistry teaches us that there is affiliation between acid number of crude and the reservoir temperature, because decarboxylation takes place as the temperature increases. However, the link is inversely proportional. With an increase in temperature the acidic material present in the oil will start to decompose and hence lower the acid number. Zhang et al. investigated in their paper which of the two parameters will dominate the wetting conditions of carbonate. They concluded that the temperature plays the minor role when it comes to chalk wettability. Also, they confirmed that because of the rise in temperature, AN decreased due to the catalytic effect of calcium carbonate ($CaCO_3$) on the decarboxylation process. [68]

2.2 Composition

Crude oil element composition varies due to the geographical position and how petroleum was formed. The composition of the crude is its "fingerprint". What is common to all crude oils, no mater their formation or geographical location, is that they contain two groups of compounds; hydrocarbon and non-hydrocarbons, figure 2.1. [18, 47]

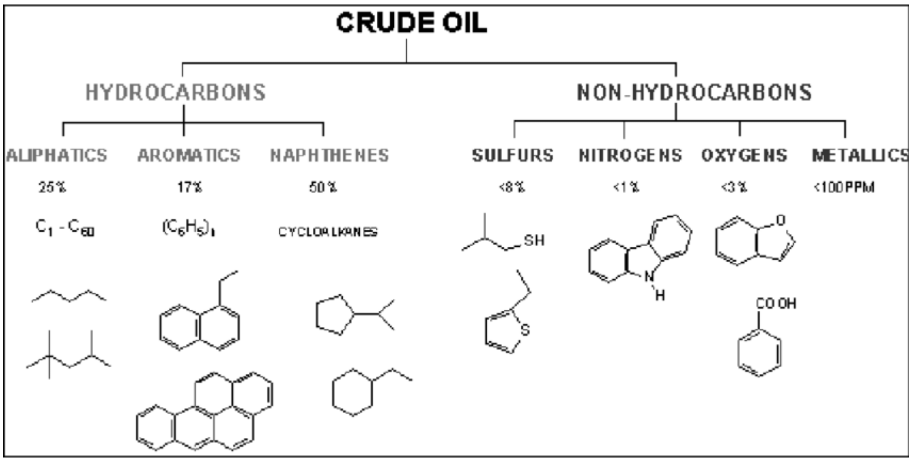


Figure 2.1: Crude oil composition

From the figure above it can be seen that hydrocarbons synthesize nearly 95% of crude oil. When talking about crude oil composition, they are commonly characterized by the superior type of hydrocarbon present; paraffins or alkanes, naphtenes or cycloalkanes and aromatics. Non-hydrocarbons are chemical elements such as sulfurs, oxygens, nitrogens and traces of metals. Sulfurs constitute the highest fraction, being responsible for oil's "sweetness". [23]

The polar compounds in oil are responsible for its inter-facial interactions. For better understanding how polar components affect wettability, oil composition can be classified as SARA separation, figure 2.2.

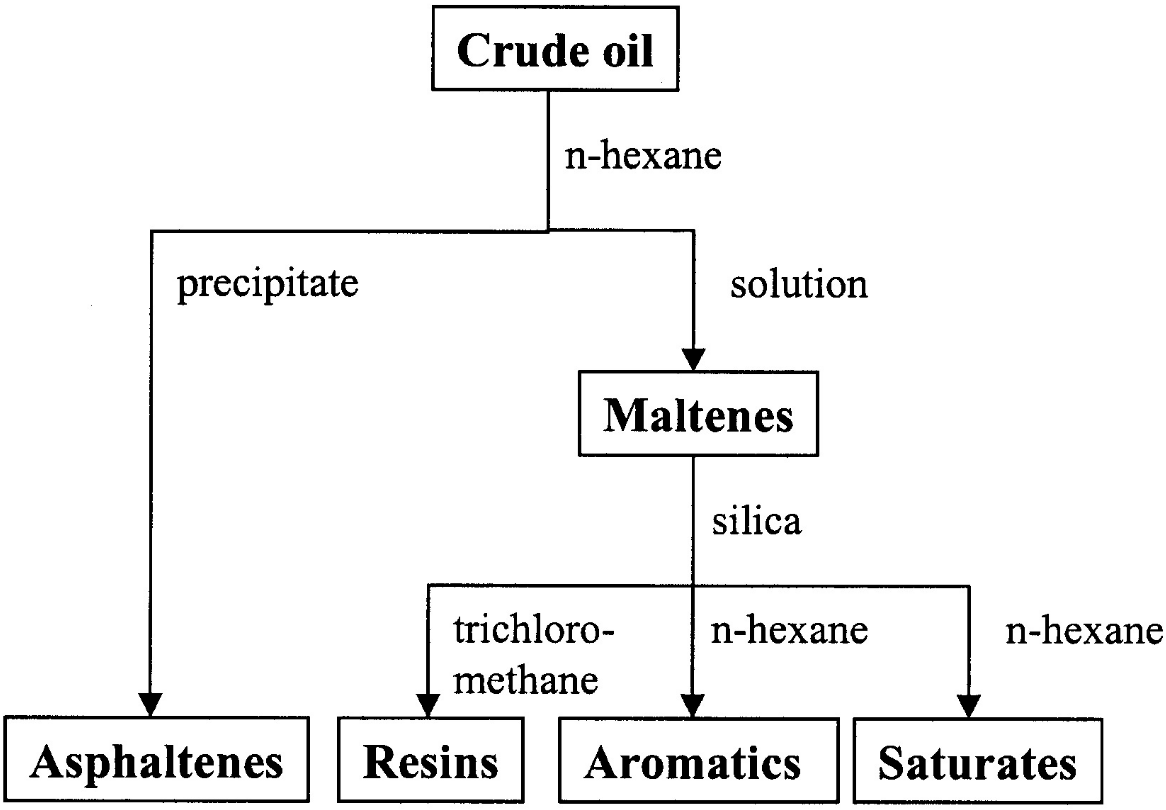


Figure 2.2: SARA separation
[5]

According to SARA scheme, crude oil is divided into four major categories:

- *Saturates* - non-polar components. They can occur as straight-chain, branched or cyclic structures. They are part of light distilled fragments, and can make up to 40-60% of crude oil.
- *Aromatics* - benzene and its derivatives such as toluene, naphthalene and anthracene. Depending on the ring structure, aromatics can be found in lighter fractions (single ring aromatics) and in heavier fractions (complex aromatics). The quality of crude oil depends on the precentage of aromatics (10% - 50%).
- *Resins* - a mixture of organic cmpounds. They are polar compounds that are soluble in different non-polar solvents such as n-heptane, n-hexane and n-pentane.
- *Asphaltenes* - a group polar components with large and complex structure with high molecular weight. Asphaltenes containing large polycyclic aromatic and naphtenic chains. They contain approximately 85% carbon. The highest amount of heteroatom and organometallic constituents is present in asphaltene fractions.

Heteroatoms present in heavier crude oil fractions are responsible for the polarity of certain species in crude oil. Hence, they are accountable for interactions with brine and/or rock. Sørbø investigating in his thesis how polar components of crude oil affect their physiochemical properties, he found that the asphaltene content was found to be highly correlated to both the zeta potential and IFT measurement. [53] Unfortunately, so far no one can say with certainty whether IFT will increase or decrease wettability.

Chapter 3

Brine characteristics

Brine or produced water can be defined as water with high content of sodium chloride (NaCl). It is water that occurs naturally within the pores of the rock. It is important to highlight that brine is not the water trapped in the pores of a rock during its formation. The original water is called formation water. Formation water is seawater or fresh water that has been trapped for millions of years with oil and natural gas in a geologic reservoir consisting of a porous sedimentary rock formation between layers of impermeable rock within the earth's crust. They can have the same composition but brines are produced in laboratories and they are often referred to as synthetic formation water in literature. In the reservoir, formation water lays between source rock and oil, figure 3.1. [42] [9, 15]

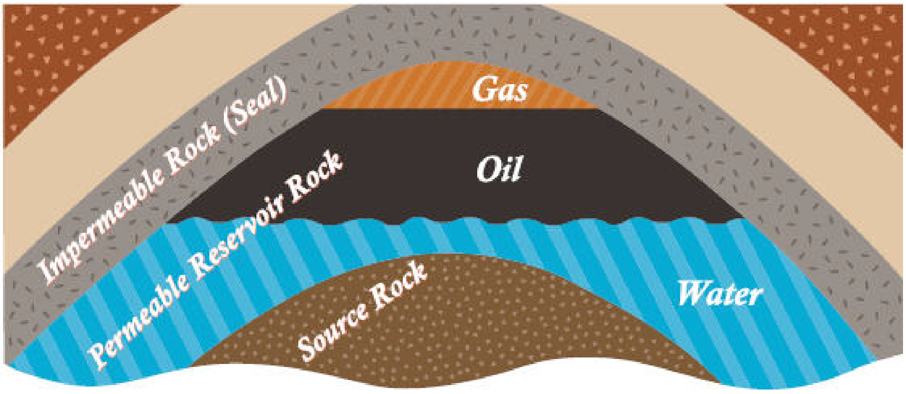


Figure 3.1: Reservoir intersection
[34]

Produced water is mostly used in EOR (water-flooding) as water that is injected to increase oil production. The properties of the produced oil can affect the oil recovery. The nature of produce water is multidisciplinary, hence when it comes to COBR interactions, there are more than one properties involved.

The formation water, is more saline than fresh water. The composition of original formation water may be different than the current seawater. Many oil reservoirs were and are saturated with sea water. During geologic time, pressure and temperature change, the chemical composition of the water also change to maintain the chemical equilibrium.

The composition of the produced water is complex. It is a mixture of several salts and dissolved minerals. Apart from salts and dissolved minerals, produced water also contains organic species. Even though the presence of the organic species was less investigated, their presence may have consequences on water and air pollution. Some of these organic species are: formic, acetic, propionic and butyric acids, napthenic acids, dissolved aromatic compounds like benzene, toluene and xylenes. Dissolved aromatic compounds are important for the measurement of the oil-in-water carryover, which are regulated by law in many areas.

Both physical and chemical properties of the produced water vary in many ways due to their geologic age, depth, and geochemistry of the hydrocarbon-bearing formation. Chemical composition of the oil and gas phases, and added production chemicals in the reservoir, also affect produced water composition. It is wise to highlight that there are no two produced waters alike. [42]

The salinity or salt concentration of the produced water may range from a few parts per thousand to that of a saturated brine (∼300‰■). Salinity is proportional to density, the more concentrated the water the more dense it is.

Produced water and seawater compositions are similar, as mentioned before. Sodium and chloride are the most abundant ions. From the inorganic ions, the most abundant in high-salinity produced water are, sodium, chloride, calcium, magnesium, potassium, sulfate, bromide, bicarbonate, and iodide. Concentration ratios of many of these ions are different in seawater compared to produced water, possibly contributing to the aquatic toxicity of produced water. Also, several metals may be dissolved in or present as micro particulate forms. The type, concentration, and chemical species of metals in produced water vary, depending on the age and the geology of the formations. Metals may come from water-injection into reservoirs. The concentration of metals is higher (1,000-fold or more) than their concentration in clean natural seawater. The most frequently present metals are: [42]

- Barium, Ba
- Iron, Fe
- Manganese, Mn
- Mercury, Hg
- Zinc, Zn

Produced water can be characterized analytically on several ways but the most common are inductively coupled plasma spectroscopy (ICP) and ion chromatography (IC). ICP provides the measurement of metals (cations) in the produced water, and IC provides the amount of anions. [58, 60]

With the production of oil and gas, a large amount of water is produced as well. This water does not have any value, and most companies discharge it (after treatment), or use it again for water flooding. Since this project investigates the effect of wettability in carbonate reservoirs, the further paragraphs will focus on researches being done in that field.

Almost half of the remaining world's reservoir are carbonate reservoirs, specifically chalk and limestone. These reservoirs are characterized to have low primary recovery, meaning that IOR has potential. Application of seawater as an injection liquid proved beneficial in improving the oil recovery from chalk reservoirs in the North Sea. Over the last decade, much research has been done in investigating how brine composition affects wettability, since it was realized that the ions in the brine can alter the wettability in a favorable way to improve oil recovery. The focus has been on the determination of the ions, active in wettability alteration and their proper composition in the injected brines. Many of those researches have demonstrated that water flooding is dependent on the composition of the brine. [67, 44]

Bagci investigated how different compositions of brine can affect oil recovery by using waterflooding as EOR technique. He noted that the highest recovery is obtained when using 2wt% KCl brine compared to NaCl and $CaCl_2$. Further more, Austad and his co-workers investigated oil recovery from chalk using surfactant solutions and modified seawater. They focused on SO_4^{2-} ion, as a potential determining ion (PDI) for improving oil recovery in chalk reservoirs. Sulfate ion must act together with Ca^{2+} and Mg^{2+}. [7] Their research is in line with the one Webb performed, using both sulfate free and sulfate rich brines on North sea carbonate core. It was concluded that the presence of sulfate ion, during the saturation of the core, is responsible for the wettability alteration of carbonate rock. [63]

Many studies have been conducted in order to understand how low salinity water affects wettability. Low salinity water (LSW) is brine with low electrical content which is achieved by lowering the overall salinity and reducing multivalent cations. Reducing the multivalent cations results in reducing oil coated particles, which implies in a change towards water-wetness.

If the injected water's salinity is in between 2000-3000 mg/l, the cations have the ability to destroy the cage structure of the water molecules. Hence, the bivalent cations have grater possibility to affect the dissolution of organic substances present in water, which will lead to an increase in their solubility and result in improving the hydrophilicity of mineral surface. This effect is called salting-in effect and it is in opposition to salting out effect where inorganic cations can destroy the cage structure of water molecules formed around organic molecules. This leads to reducing the solubility of organic substances in water, and rock hydrophilic characteristics. [61, 40]

Mahani et al. found a relation between reduction in electro-kinetic charge and rise in water wettability. Improvements in recovery were obtained in research made by Strand, Hognesen and Austad with brines without NaCl and higher amounts of sulfate. Some scientists investigated the influence of temperature, proving that in order for seawater to be effective, the temperature should be higher than 90°. [38, 55]

It can be concluded that sulfate and divalent cations play an important role in increasing the water-wetness in carbonates. The water molecules are attracted more to the carbonate surface in the presence of sulfate ions. [44]

The pH contribution to alter wettability has not been investigated in depth. So far, a few studies have focused on the effect of pH in COBR interactions. Xie, Sari and their fellow co-workers investigated the pH effect on wettability of oil/brine/carbonate system. They measured contact angles at two different pH (3,8), in the presence of 1 mol Na_2SO_4 and 1 mol $CaCl_2$ solutions. The results they obtained indicated that pH strongly affects the contact angle and is it likely to be one of the factors controlling wettability. In the presence of Na_2SO_4 at low pH (pH=3) oil-brine-carbonate system turned to water-wet. In contrast, high pH (pH=8) led to a strongly oil-wet system. In the presence of $CaCl_2$ for both pH (3 and 8) the system turned out to be water-wet. [64]

Chapter 4

Rock characteristics

Reservoir rock is a porous and permeable rock that contains sufficient hydrocarbon accumulation. Permeability and porosity are important physical properties and they are the result of its lithological, structural and compositional behavior (composition). Reservoir rock is comprised of sedimentary rocks. There are two major types of sedimentary rocks most frequently encountered in petroleum reservoirs:

- Sandstone
- Carbonate

A brief description will be provided on sandstones and a more detailed one on carbonates, since this project focuses on carbonate rock (chalk).

4.1 Sandstone

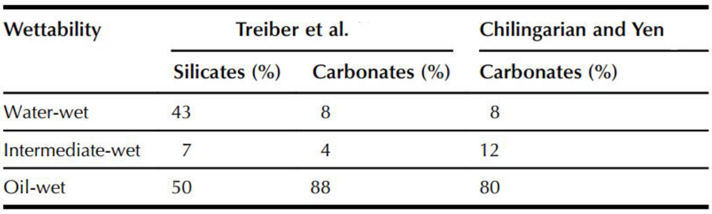
Sandstone reservoirs refers to the specific size of grains. The diameter of the sand grains is between 0.062 and 2 mm. The sandstone texture is interesting as it consists of a framework composed of sand-sized grains and interstitial volume between grains. This volume can be empty, or filled with either a chemical cement of silica or calcium carbonate or a fine-grained matrix. Three components comprise sandstone: quartz, feldspar and clay. 10 to 20% of Earth's sedimentary rock is sandstone. [33, 24]

4.2 Carbonate

Unlike sandstones, which are made of sand grains, carbonates may contain fossils which "range from the very small single cell to the larger shelled animals". The biggest portion of carbonate rock is of course carbonate minerals. Carbonate rocks are categorized into two major types: limestone and dolostone. Dolostone or dolomite rock contains a high percentage of the mineral dolomite, $CaMg(CO_3)_2$ Limestone consists of at least 50% of calcite and aragonite, which are different crystal forms of calcium carbonate ($CaCO_3$).

Environmental deposition is provided by the texture, sedimentary structures, composition, and organic content of carbonates. A significant percentage of oil and gas reserves in the world, especially those in the Middle East, are held in carbonate rocks.

Mineralogy-wise, there is a difference between ancient and modern limestone and dolomite composition. Regarding the ancient composition, apart form calcite and dolomite, minerals such as magnesite ($MgCO_3$), rhodochrosite ($MnCO_3$), and siderite ($FeCO_3$) occurred in limited amounts, in restricted environments. On the other hand, modern carbonate sediments are composed almost entirely of metastable aragonite ($CaCO_3$) and magnesium-rich calcite. [33, 24]
The difference in composition of the rock also contributes to their wettbiliy alternation. Figure 4.1. displays difference in wetability between sandstone and carbonate rock.



Wettability	Treiber et al.		Chilingarian and Yen
	Silicates (%)	Carbonates (%)	Carbonates (%)
Water-wet	43	8	8
Intermediate-wet	7	4	12
Oil-wet	50	88	80

Figure 4.1: Differences between carbonate and sandstone rock
[57]

4.2.1 Chalk

This project aims for the investigation of wettability alteration in chalk, and particularly the North Sea Dan Chalk. The deposition of chalk and its correlative mudstone-dominated succession, in the northern part of the North Sea, took place 35 million years ago. Chalk is one form of limestone reservoir rock, figure 4.2. The grains of chalk are soft, fine-grained, easily pulverized, with white-to-grayish color. Chalk composition involves two groups. The first one is the shells of such minute marine organisms as foraminifera, coccoliths and rhabdoliths. The second group is the mineral calcite. Calcite is an ionic salt called calcium carbonate or

$CaCO_3$. Clay minerals, glauconite, and calcium phosphate also are present in very small amounts. [32, 22]

Figure 4.2: Chalk

The North Sea chalk is a mono-mineralic carbonate rock that consists of 96–99% calcite ($CaCO_3$), non- carbonate biogenic particles (radiolarian, diatoms and sponge spicules). Traces of clay minerals may be present, due to influx of erosional detritus. High porosity (25-30%) characterizes North Sea chalk. The pore throat size is very small and as a result, the range of permeability is fairly low (0.5-2.0 mD). Two characteristics of Danish chalk reservoirs are the significant capillary entry heights and the long transition zones. Due to high capillary entry pressures and wettability characteristics they also display very high HC saturations (up to 97%).[2]

4.3 Wettability alteration

The surface of the rock is composed of different minerals, meaning that the rock surface is filled with ions that can take part in COBR interactions and affect wettability. Carbonate surfaces develop electrical charge when they are in contact with electrolyte solution for three reasons:

1. Complexional reactions between the surface and dissolved species.
2. Lattice imperfections as well as substitution within the crystal lattice.
3. Dissolution of surface groups.

The calcite surface, leading mineral of chalk, has rectangular cell shape with two calcium (Ca^{2+}) and two carbonate ions (CO_3^{2-}). For all types of carbonate minerals, carbonate units are the basic block, and divalent ions such as Ca^{2+} , Mg^{2+} , Mn^{2+}, Fe^{2+} are coordinated around it. It is important to mention that the charge of the surface is dependent of the position of the ions in the lattice, corner, edge or face. If the polar surfaces are unstable, they will adsorb ions to neutralize the charge. Figure 4.3. presents the lattice of calcite, vaterite and aragonite.[47, 52]

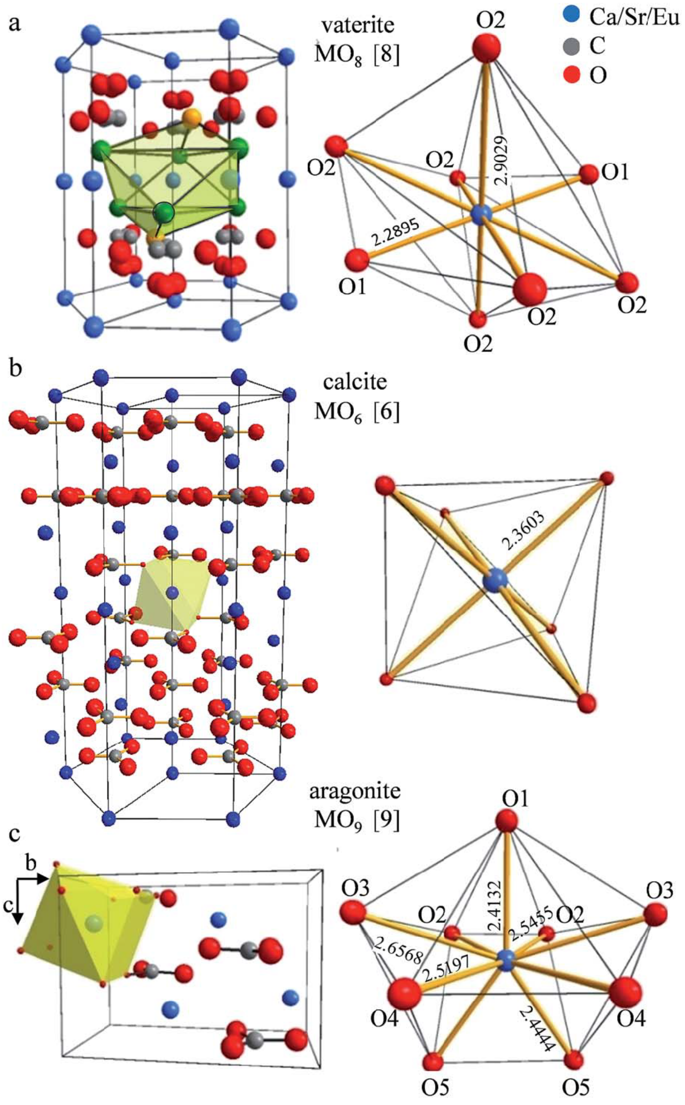


Figure 4.3: Lattice formations of vaterite (a), calcite (b) and aragonite (c) [8]

In interactions with water (brine), the surface charge of calcite is controlled by calcium and carbonate ions. Water dissociates into hydroxyl (OH^-) and hydrogen (H^+) ions. Therefore, when in contact, they produce CaOH and CO_3H. The surface charge can be effected by the divalent metal cations (Me(II)= Ca^{2+}, Mg^{2+}, Mn^{2+}, etc.) present in bulk solution. The salinity of the brine affects the stabilization of surface charge and hence, the wettability. In a highly saline brine, the surface sites are crowded with PDIs and these ions compete for the surface sites. In interactions with oil, the wettability depends on the the hydrocarbon compounds that contain oxygen (organic acids) and nitrogen (bases), because these compounds of crude oil show an affinity to adhere to rock surface.[52]

When it comes to the chemical groups on the rock surface, as explained earlier, carbonate and sandstone reservoirs have obvious differences. The bonding mechanism between chemical groups in carbonate rocks and polar components in oil also differ from the ones between oil and sandstone rocks. The surface hydrophilicity of carbonate rock is enhanced in the presence of divalent ions such as SO_4^{2-}, Ca^{2+} and Mg^{2+} thus improving the recovery of these reservoirs.[45].

The mechanism of wettability alteration in carbonate rock is illustrated in figure 4.4.

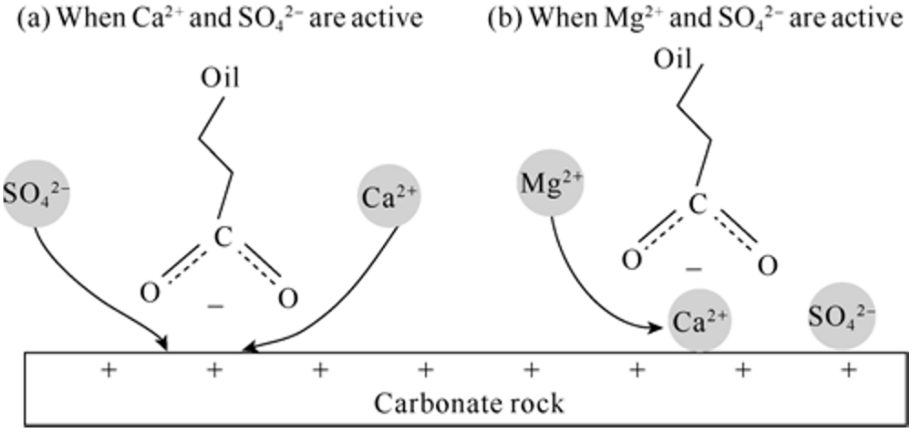


Figure 4.4: Mechanism of wettability alteration in carbonate rock [40]

In figure 4.4.a, when SO_4^{2-} and Ca^{2+} ions are involved in wettability alteration, SO_4^{2-} ions will be adsorbed onto the surface of the rock because of the charge difference, which will lead to neutralization of the rock charge. The repulsive force between Ca^{2+} ions and carbonate surface will weaken, allowing more Ca^{2+} ions to be adsorbed onto the rock surface. Ca^{2+} will react with the carboxylic acid present at the surface and replace it. Figure 4.4.b, illustrates the mechanism when Mg^{2+}

and SO_4^{2-} ions are involved and it is similar to the previous described.

It can be said that SO_4^{2-} acts as a catalyst and benefits the enrichment of Ca^{2+} ions on the rock surface. The equations that describe both mechanisms are presented in figure 4.5.[40]

$$RCOO^{-}—Ca—CaCO_3 + Ca^{2+} + SO_4^{2-} = RCOO—Ca^{+} + Ca—CaCO_3 + SO_4^{2-}$$

$$RCOO^{-}—Ca—CaCO_{3(s)} + Mg^{2+} + SO_4^{2-} = RCOO—Ca^{+} + Mg—CaCO_{3(s)} + SO_4^{2-}$$

Figure 4.5: Equations for wettability alteration mechanism using divalent ions [40]

Various researches investigated how the salinity of brine affects the wetness of the rock. Alshakhs and Kovascek investigated the impact of injection water composition in oil recovery from carbonate rocks. They perceive that increasing divalent ion concentration (with slight change to the total salinity), shows strong impact on oil recovery. Furthermore, they noticed an increase in incremental recovery when the injection switched from seawater brine to $MgSO_4$ brine, and the wettability of surface shifted towards water-wetness. [6]

Sulfates and cation surfactants can affect wettability, making carbonate rocks more water-wet. Wettability alteration in carbonate rocks can be achieved using brines that contain SO_4^{2-} with Ca^{2+} and/or Mg^{2+} in a higher than 90°C temperature environment. The ions have the potential to change the rock surface charge by releasing adsorbed carboxylic material onto the rock surface.[66]

Moreover, numerous researches investigated the effect of low salinity water injection in both carbonate and sandstone rocks. There are several conclusions that they reached:

- Low salinity water can cause wettability alteration in both rock types, but for sandstones the concentration needs to be < 5000 ppm.
- Due to strong organic bounding, salting-in effect does not comply with carbonates, on the other hand, due to the presence of clay in sandstone, salting-in is very effective.
- Reducing non-active salts concentration (Na^{+} and Cl^{-}), leads to more water-wet rock surface, since they prevent the access of active potential ions to adsorb onto the surface.

- Regarding sandstone rock, the presence of divalent cations in water should be less then 500 ppm and in combination its low ionic strength, results in higher percentages of water-wetness.
- Regarding carbonate rock, it is advisable to use low to moderate salinity diluted seawater (2-10 times dilution/ 28000-6000 ppm), modified seawater with low values of monovalent ions and high amount of divalent ions.
- LSW injection is considered to be complicated for sandstone because of various contributing parameters, including fine migration, pH increase, multi-ion exchange and salting-in effects. [45, 35, 39, 56, 65]

Chapter 5

Experimental work

In this study, 17 sets of experiments were conducted, with 5 samples/set, to ensure reproducibility. In all 17 sets, Valhal FW was used to age the Dan Chalk and the (oven) temperature was 115°C. Four sets of experiments were conducted using crude oil H and PW. In three out of four sets PW was diluted, with deionized water, with three different dilution factors, 10, 20, 100. The same number of sets, with the same combinations of smart water, were conducted using crude oil M, and another batch of four experiments, using crude oil A. Three sets were performed using a 10 times diluted PW, with tap water (TW), and the three different crude oils, H, M and A. One set, using Valhal FW, both for aging the chalk and as smart water, with crude oil H was conducted. Finally, one set with crude oil H and PW was prepared and left to settle for 48 hours in the oven. A virtual representation of the work performed in this project, can be seen in table 5.1.

Table 5.1: Overview of Experiments

Brine	Crude Oil H	Crude Oil M	Crude Oil A
PW	✓	✓	✓
10*DPW	✓	✓	✓
20*DPW	✓	✓	✓
100*DPW	✓	✓	✓
10*DTWPW	✓	✓	✓
VFW	✓		
PW 48H	✓		

5.1 Materials

In order to perform the experiments, the use of the following materials was required. In the current project only one lithotype was employed, Dan chalk, as the research needed to apply for the North Sea oil reservoirs and more specifically for the Danish sector. The Dan chalk chemical composition can be seen in table 5.2.[47]

Table 5.2: Dan Chalk composition

Component	Mass (%)
CaO	95.3
Al_2O_3	0.439
SiO_2	3.3
P_2O_5	0.346
K_2O	0.127
SrO	0.432
SO_3	0.0591
Cl	0.0125

Three different samples, in terms of properties, of crude oil were investigated. Two of the samples (crude oil H, crude oil A) were crude oil produced from different wells, while the third one was a 50:50 mixture of the first two (crude oil M). The dilution of the two different crude oils was performed in order to investigate a third "novel" one with alternate properties, for reasons that will be discussed in a later section. All samples came from North Sea Danish sector oil reservoirs, albeit from different wells. Since crude oil properties play a significant role in wettability alteration, which in turn has a semantic impact on oil recovery, various analysis was performed.

Aside from the crude oil variations in the wettability alteration investigation, various types of brine were tested, in order to realize its effect in wettability. Thus, a preparation procedure was required in order to compose the Valhal brine, and dilute the PW which originates from North Sea.

5.2 Methods

In this section, the procedure, that has been followed for the conduct of the MFT experiment, is described, as well as all the analysis performed,in order to obtain the properties of the crude oils and the brines investigated in this study.

5.2.1 Flotation Experiment

As it has already been mentioned, in this study, various combinations of crude oil and brines have been employed, performing the modified flotation technique. The MFT has been documented an effective quantitative method in order to quick investigate the effect of oil and brine chemical composition on wettability on both carbonate and sandstone lithotypes at varying temperatures. The modified flotation technique involves the following steps:

1. 1 g of rock is aged for ca. 24 hours in 10 ml of formation water FW, in this case Valhal brine, at 115°C.
2. 6-8 ml of the FW are decanted into a test tube in which a pH measurement takes place.
3. Water wet grains are aged with 5 ml of crude oil at the same temperature for another 24 hours.
4. 6-8 ml of modified water, respectively, are added back to the tube and the mixture is shaken gently using the vortex shaker.
5. The COBR mixture settles for another 24 hours at the same temperature.
6. The tube walls are rinsed with deionized water and the oil wet (floating) grains are removed.
7. The tube with the water wet grains, including the oil coated ones, is dried at the above temperature.
8. Pentane is added in order to remove the oil coating from the water wet grains and the dissolved oil is decanted.
9. The tube containing only water wet grains is dried.
10. The sample is weighed.

After the implementation of the MFT, the relative fractions of water wet rock particles were calculated, applying the following equation 5.1:

$$\text{Water Wet } \% = \frac{\text{mass of water wet particles (g) * 100}}{\text{initial mass of rock particles (g)}}\% \tag{5.1}$$

It has to be mentioned that all the experiment sets (aging process) were conducted under the same (oven) temperature, namely 115°C. Moreover, the rock sample was subject to a preparation procedure. The sample was initially dried and then sifted through a sieve to a fraction of less than 100 μm.

5.2.2 Brine Composition and Analysis

The only synthetic brine used in this research was Valhal FW, which was compounded by dissolving grade salts in deionized water. The composition of Valhal brine and the total dissolved solids (TDS) are shown in table 5.3. [48]

Table 5.3: Valhal Composition

Salt Formula	Concentration (g/l)
NaCl	57.6
$NaSO_4$	0.1
$NaHCO_3$	0.75
KCl	0.35
$MgCl_2$*$6H_2O$	1.6
$CaCl_2$*$2H_2O$	4.3
TDS	64.7

The density and the pH of all brines, tested in this study, was measured using DMA 35 Anton Paar portable density meter and pH Meter/Conductometer Metrohm 914, respectively, at room temperature, ca. 23-25°C. The obtained data can be seen in table 5.4.

Table 5.4: Brine Properties

Type of Brine	pH	Density (g/cm^3)
VFW	7.3	1.0392
PW	7.25	1.0329
10*DPW	8.02	1.0003
20*DPW	8.15	0.9991
100*DPW	8.54	0.9977
10*DTWPW	7.87	1.0008

Furthermore, the oil in water percentage was measured, for the PW, by conducting GC/FID (Gas Chromatography with Flame-Ionization Detector) analysis using Perkin Elmer Clarus 680 apparatus. The samples were prepared in the following steps:

1. 30 grams of produced water and 10 grams of n-hexane were measured and poured into separation funnel.
2. The liquids were shaken vigorously for 2 minutes.
3. The funnel was placed in vertical position allowing the mixture to settle and separate (ca. 5 minutes).
4. When the clear interface is formed, the sample is extracted from the organic phase (upper phase) with a syringe.
5. The organic sample is weighed. The weight of the organic sample is dependent on the residence time and in the range of 1–3 g.
6. The rest of the organic phase is decanted from the aqueous phase and weighed.

GC-FID is calibrated with the proper standards and the calibration curve is obtained. For this particular experiment, the obtained calibration curve is for the concentration range 200-1200ppm. The process of calibration is repeated until the calibration shows an R^2 value below 0.985 so that the samples can be analyzed. It is important to analyze three replicates. The values obtained from the chromatogram are analyzed and the average value from the response area (μV*sec.) is calculated. From the calibration curve, the concentration of oil in PW is determined and the obtained value is 67.25 ppm. Figure 5.1 below, shows the calibration curve.

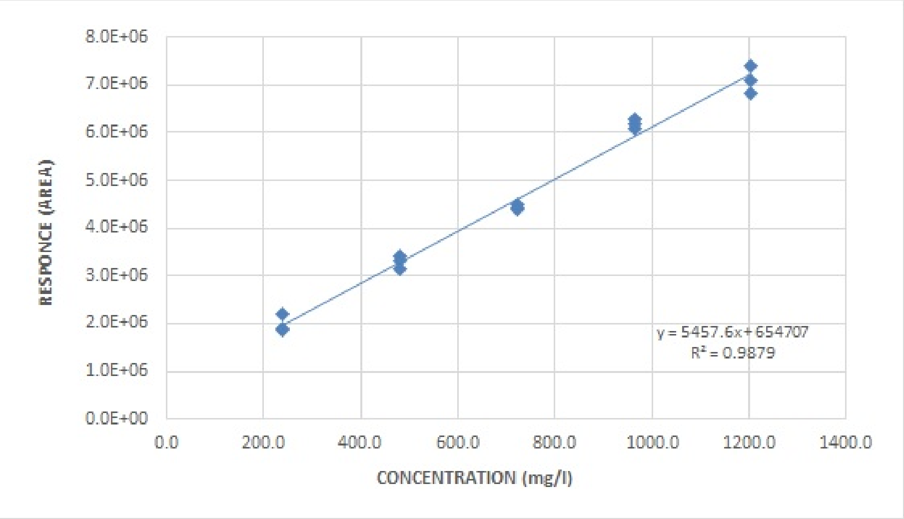


Figure 5.1: Calibration curve

Additionally, Inductively Coupled Plasma (ICP) and Ion Chromatography (IC) analysis was run, using Perkin Elmer Optima 8000 ICP-OES and Metrohm IC, respectively, in order to detect the metals and measure the ionic composition and concentration of the brines. By measuring the ionic composition, the ionic strength was calculated, so that a comparison can be made between the brines. The estimation of the ionic strength was determined using the following equation 5.1:

$$\mu = \frac{1}{2}\sum_{i} c_i z_i^2 \tag{5.2}$$

where μ is the ionic strength (mol/l), c_i is the concentration of each ion (mol/l) and z_i is the charge of each ion. It has to be mentioned that, in this study, no particular PDIs and their effect on wettability alteration were investigated. The ionic composition, concentration and strength, in mmol/l, of each brine are presented in table 5.5.

Table 5.5: Ionic Composition, Concentration and Strength of All Used Brines

Ion	VFW (mmol/l)	PW (mmol/l)	10*DPW (mmol/l)	20*DPW (mmol/l)	100*DPW (mmol/l)	10*DTWPW (mmol/l)
Ba^{2+}	0.00691	0.00436	0.00044	0.00022	0.00004	0.00083
K^{+}	7.73179	11.9775	1.19775	0.59888	0.11978	1.34276
Mg^{2+}	10.7797	12.8081	1.28081	0.64040	0.12808	1.45895
Na^{+}	883.437	629.411	62.9411	31.4705	6.29411	63.0716
Zn^{2+}	0	0	0	0	0	0.01659
Sr^{2+}	0.13124	1.27824	0.12782	0.06391	0.01278	0.13238
Ca^{2+}	24.2041	18.7310	1.87310	0.93655	0.18731	2.90683
F^{-}	0	0	0	0	0	0.17054
Cl^{-}	807.256	675.367	67.5367	33.7684	6.75367	83.9421
Br^{-}	0	1.43797	0.14380	0.07190	0.01438	0.35717
SO_4^{2-}	6.13870	8.16467	0.81647	0.40823	0.08165	0.79833
Ionic Strength (mmol/l)	931.7	741.1	74.11	37.05	7.411	85.07

Finally, it has to be noted that the total dissolved solids (TDS) value of the supplied PW, was not provided. Thus, its estimation for both the PW and the diluted PW was attempted by measuring the electrical conductivity (EC) with a 912 Metrohm conductometer at 25°C. EC and TDS are two parameters that are used as indicators of salinity levels. These two parameters are correlated. The correlation of these parameters can be estimated by the following equation 5.2:

$$TDS\left(\frac{g}{l}\right) = k * EC\left(\frac{mS}{cm}\right) \tag{5.3}$$

where k is ratio of TDS/EC. [46] The EC, TDS and k values of PW and its dilutions, are shown in table 5.7.

Table 5.6: Brine EC & TDS

Type of Brine	EC (mS/cm)	k	TDS (g/l)
PW	71.8	0.75	53.85
10*DPW	7.796	0.5	3.898
20*DPW	4.694	0.5	2.347
100*DPW	1.518	0.5	0.759
10*DTWPW	8.594	0.55	4.727

5.2.3 Crude Oil Analysis

The density of the crude oils was determined by measuring the mass and the volume of the sample. Thus, the density is calculated applying the formula 5.4 below:

$$\rho = \frac{m}{V}\left(\frac{g}{ml}\right) \tag{5.4}$$

where ρ is the density in g/ml, m is the mass in g and V is the volume in ml.

The viscosity of the three different crude oils was also measured, at 23°C, using Brookfield DV-III + Programmable Rheometer equipped with an SC4-18 spindle.

As it has already been mentioned in the "Crude Oil Characteristics" section, the TAN of the crude oil is quite significant with respect to the wettability alteration. As a result, the TAN of all crude oils, tested in this project, was measured using Metrohm Autotitrator Tiamo 2.4, applying the ASTM D664 method. According to this method, ca. 5 gr of crude oil are diluted in 50 ml of the following solvent: 500 ml toluene + 495 ml isopropanol + 5ml deionized water. The titrant is Tetrabutylammonium Hydroxide (TBAOH/TBAH) 0.1 M in isopropanol. The detection limit is 0.2 mg KOH/g of crude oil. An example of a titration result for TAN, is shown below in figure 5.1, where U is the potential in mV, V is the added volume of the titrant in ml and EP represents equivalent point.

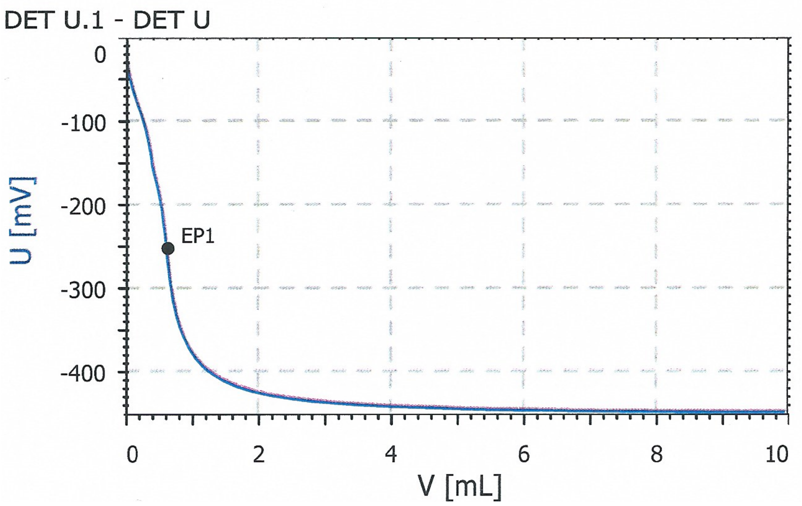


Figure 5.2: Example of TAN Titration

Since different crude oils, in terms of properties, are investigated, the asphaltenes content, being a parameter that could potentially affect the wettability of the COBR system, was also measured. According to the widely-recognized standard procedure ASTM D2007-80, the analysis was performed as follows:

1. 10 ml of crude oil was mixed with 400 ml of n-heptane (asphaltene precipitant) in a glass flask.
2. The mixture was left to equilibrate for two days in the fume hood at ambient conditions while being shaken a couple of times during this aging period.
3. A weighing vessel and the filter paper (mixed cellulose ester membrane filter with a diameter of 47mm and pore size 0.2μm) were weighed and the filter was installed into the funnel filter assembly (VWR chemical-porcelain).
4. A vacuum pump was connected to the side arm of the filtration flask and the oil/precipitant mixture was poured into the funnel cup in doses, while after each dose the cup was being sealed with aluminum foil to reduce evaporation during filtration.
5. When the filtration was done, the vacuum pump was turned off, the filter paper was carefully pealed off and placed in the weighing vessel.
6. The weighing vessel with the filter paper was left to dry in the fume hood for several days.
7. The vessel and the filter with the dried asphaltenes was weighed.

The asphaltenes weight was determined by subtracting the weight of the vessel and the filter paper from the total weight. Thus, the asphaltene content was calculated applying the following equation 5.5: [62]

$$\text{Asphaltene Content}\left(\frac{\text{g}}{100\text{ml}}\right) = \frac{\text{weight of dried asphaltenes (g)} * 100}{\text{crude oil volume (ml)}}\% \tag{5.5}$$

All crude oil properties measured for the needs of this research are presented in table 5.7.

Table 5.7: Crude Oil properties

Crude Oil Type	Density @ 23°C (g/cm^3)	AN (mgKOH/g)	Viscocity @ 23°C (cP)	Asphaltene Content (%)
Crude oil H	0.8589	0.795	16.23	0.1743
Crude oil A	0.8488	0.564	11.97	0.1661
Crude oil M	0.8491	0.758	13.80	0.1264

Lastly, the water content, in all three different crude oils tested, was measured using a Metrohm 870 KF Titrino plus apparatus and the results, obtained by the Karl Fischer titration, were too low (∼0.1%) not to be considered negligible. Detailed calculation of crude oil properties are presented in appendix A.

Chapter 6

Results and discussion

During the last years, a lot of research has been conducted in order to realize the interactions that occur in a COBR system, and how they affect wettability. This project intended to investigate how different combinations of oil and produced water, from the same field, affect the wettability of carbonate reservoirs, and more specifically, chalk.

As mentioned in an earlier chapter, the method employed to scrutinize wettability, is modified flotation technique. Throughout this project, 18 sets in total were carried out at the same temperature (115°). Figure 6.1 and 6.2 illustrate an overview of all the sets of the experiment.

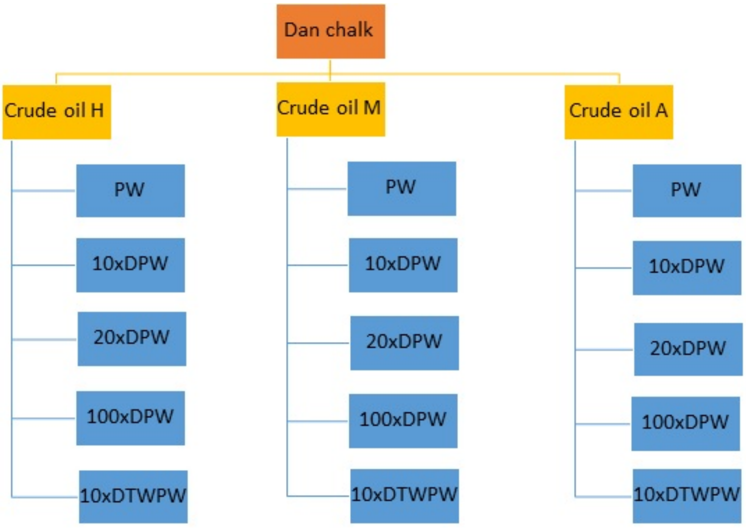


Figure 6.1: Common sets for the three crude oil samples

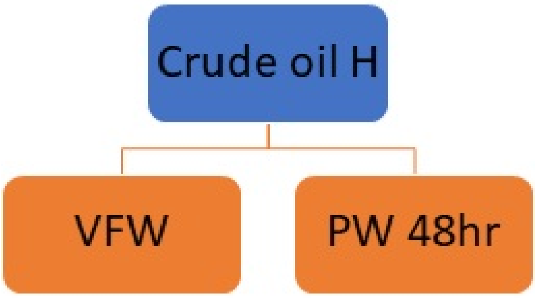


Figure 6.2: Additional sets for crude oil H

6.1 Effect of different brines on crude oil H

In this chapter, the effect of different brines on crude oil H is discussed. First of all, it has to be mentioned that since both PW and crude oil H originate from the same Halfdan field, the applicability of the lab work, to the field is also under investigation. Thus, the obtained results could potentially prove beneficial for the industry. Another significant fact is that no thorough investigation of any particular PDIs was attempted. The modification of the brines (PW and VFW) was limited. The alteration in ionic concentration and hence in ionic strength and salinity, was achieved by diluting the brine (PW).

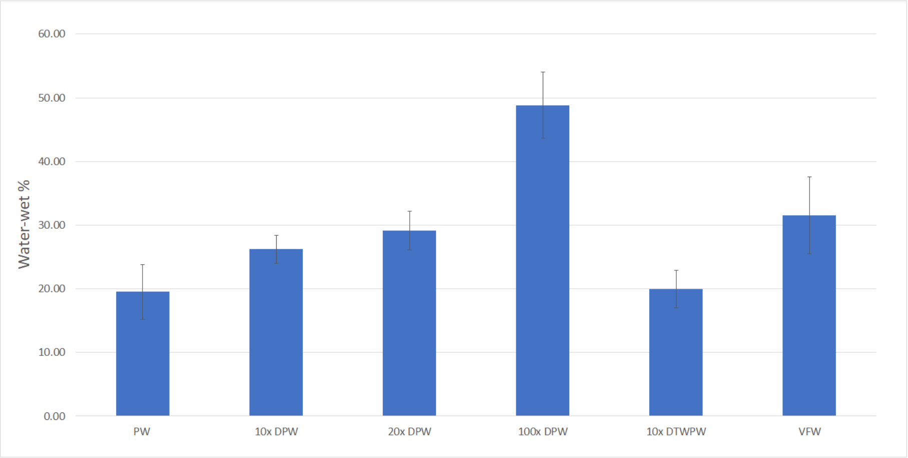


Figure 6.3: Average water-wet % of crude oil H and different brines

From the figure 6.3 above, one can notice that by using PW for brine flooding, the water-wetness of the chalk is not providing remarkable results. This led to an early assumption that the components of the COBR system, in combination with the conditions (temperature), are not perfectly compatible. The water-wetness of the chalk increased reasonably when the PW was diluted 10 and 20 times with deionized water (DW). However, a quite significant increment in the rock's water-wet % was observed when the PW was diluted 100 times with DW. The water-wet % climbed from ∼20% to ∼50%. It has to be noted that this water-wet % (48.82%), was the highest obtained throughout all the sets conducted in this study. Since diluting the PW with deionized water in offshore operations, can be costly, 10 times dilution of PW was attempted, this time with TW. The result obtained was 19.98%. Compared to the value obtained by using non-diluted PW (19.53%), no changes were observed. Moreover, it is even lower, compared to the result obtained by using 10xDPW (26.21%). The only difference between these two brines is the Ca^{2+} concentration. In the case of 10xDTWPW, the TW increases the Ca^{2+} concentration in the brine, since it contains ca. 50mg/l of this ion. This comes in opposition with the current literature that suggests that higher Ca^{2+} concentration results in higher % of water-wetness in carbonates. [40] The last brine that was tested was VFW, which was also the water used to saturate (age) the chalk. The 31.54% that was obtained, was far from the highest (48.82%), yet satisfying enough, considering its high salinity. All in all, the results for crude oil H are in line with the literature that suggests that, by decreasing the ionic strength and thus the salinity of the brine (here achieved by dilution), the rock becomes more water-wet. [40, 17]

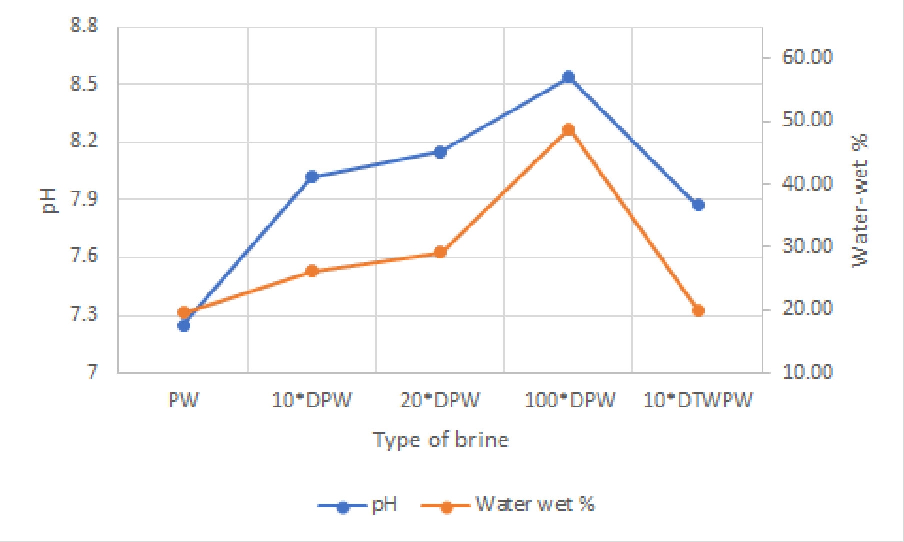


Figure 6.4: pH vs water-wetness for crude oil H

Figure 6.4, illustrates the influence of pH of the PW and its dilutions on water-wetness. It is remarkable how consistently correlated these properties are. By increasing the pH of the brine, the water-wetness also increases. The highest water-wet % is obtained by using the brine with the highest pH, 8.54. It is documented that the zeta potentials of the two interfaces become even more negative, due to the increase of the pH. That strengthens the electrostatic repulsive force between rock/brine interface and crude oil/brine interface, which results in the stability of the water film and hence the rock surface becomes more hydrophilic. [40, 44, 64] Moreover, as it can be seen in figure 6.5, lowering the ionic concentrations and thus the ionic strength, results in improvements in chalk's water-wetness. Even though there are inconsistencies in the literature with respect to the optimal ionic concentration of the brine, LSW has proved to improve oil recovery in most cases. It has also been proposed that diluted brine with low quantities of PDIs is able to improve water-wetness in carbonates at high temperature. [37]

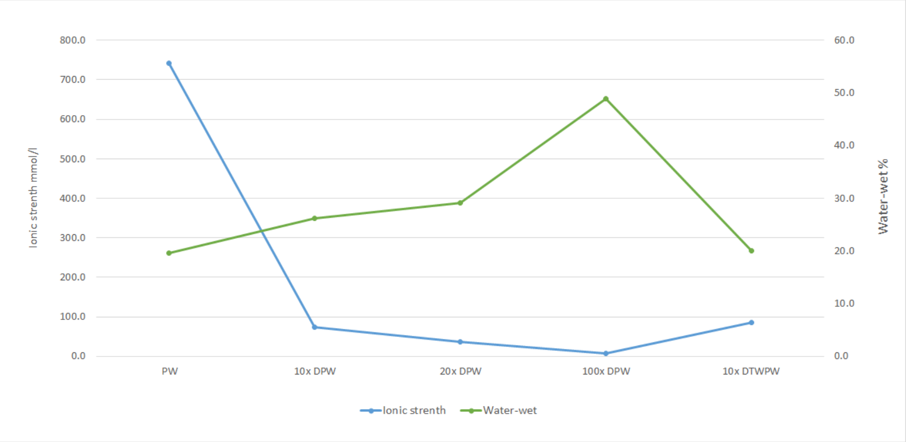


Figure 6.5: Ionic strenth vs water-wet % for crude oil H

However, it was observed that the COBR system formed emulsions. The water phase decreased since the oleic phase had expanded and had occupied most of the space in the glass test tube. A number of water wet grains were trapped in between the oil-wet grains and formed water-wet grain layer. These trapped water-wet grains were oil coated, making it clear that excessive oil coating occurred. This asymmetrical stratification of water-wet-grain layers, in the oleic phase, is illustrated in figure 6.6.

It is assumed that crude oil's H viscosity led to the formation of these emulsions. Crude oil's acidic components are heavy fractions that are regarded as surface-active agents and thus, form strong pairs with carbonates. [44]

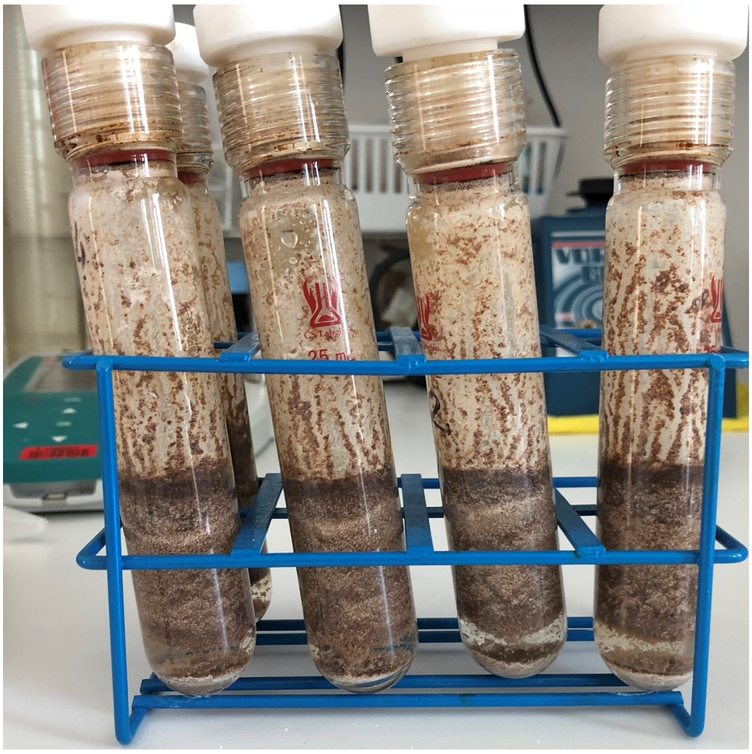


Figure 6.6: Example of emulsification phenomena in the test tubes

Due to the emulsification phenomena, one set with the same components (crude oil H and PW) and temperature was carried out. The only difference was that the settling time of the mixture in the oven, was increased from 24 hours to 48 hours. This aimed for a better separation between the water and the oleic phase, since more time was given to the water-wet grains to settle at the bottom of the test tube. A 6% increase in water-wetness, from 19.53% to 25.71%, was achieved, as it can be seen in figure 6.7.

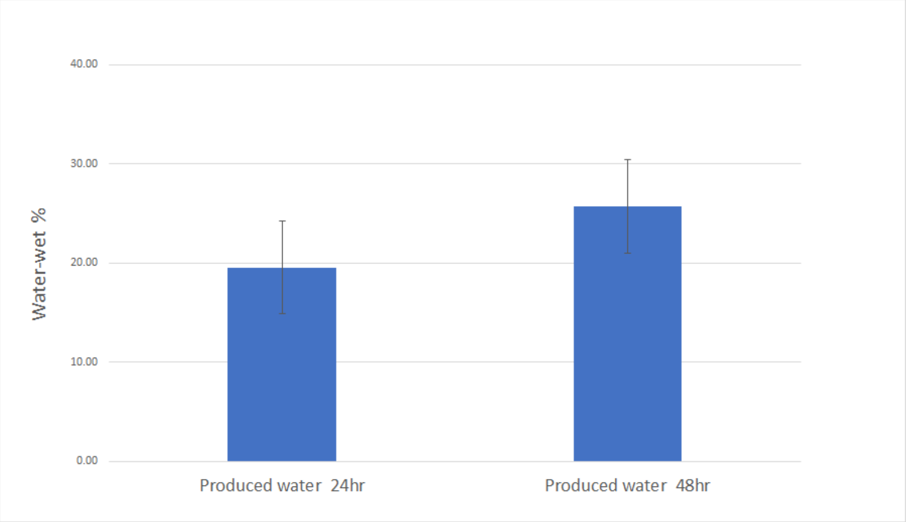


Figure 6.7: Water-wetness alteration with settling time for crude oil H

6.2 Comparison of crude oil H, M and A

Due to the observation of emulsification phenomena in the COBR system and since crude oil's H density and viscosity are 0.86 g/cm^3 and 16.23 cP respectively, it was decided less viscous crude oils to be tested. In order to see how viscosity affects water-wetness of chalk, additional sets of experiments, with less dense and viscous oil samples, were carried out. Figure 6.8 confirms what was expected. Less viscous oils will minimize emulsification, since they contain less heavy fractions which act as surface-active agents. The water-wet grains stratification is still present but in much lesser extent compared to crude oil H, figure 6.6.

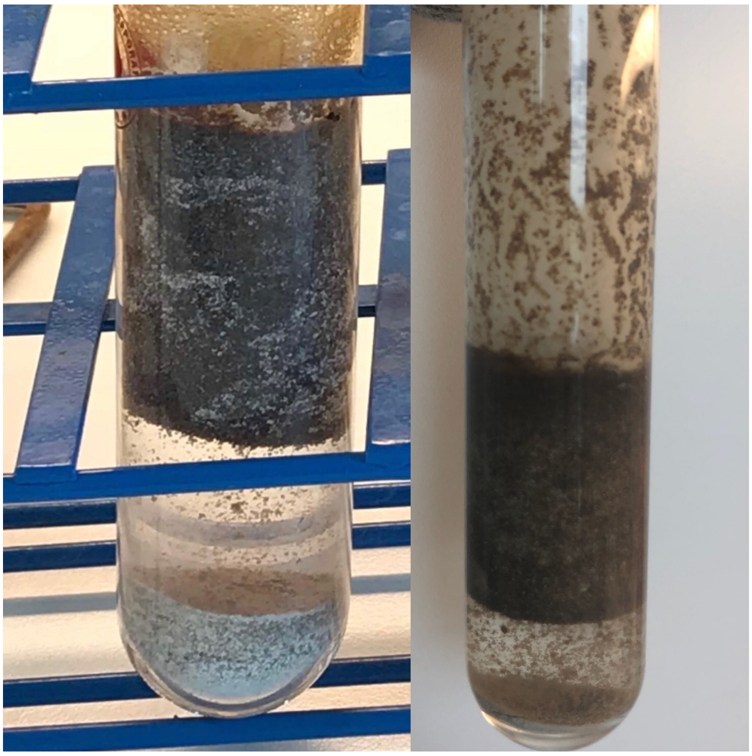


Figure 6.8: The water-wet grains stratification in crude oil M (left) and crude oil A (right)

The results obtained, also display that the less viscous the oil, the greater the hydrophilicity of the rock. From the figure 6.9, one can observe that the water-wetness of the rock improved when less viscous crude oils were used, climbing from 19.53% to 32.79% and finally to 37.42% for crude oil H, M and A respectively.

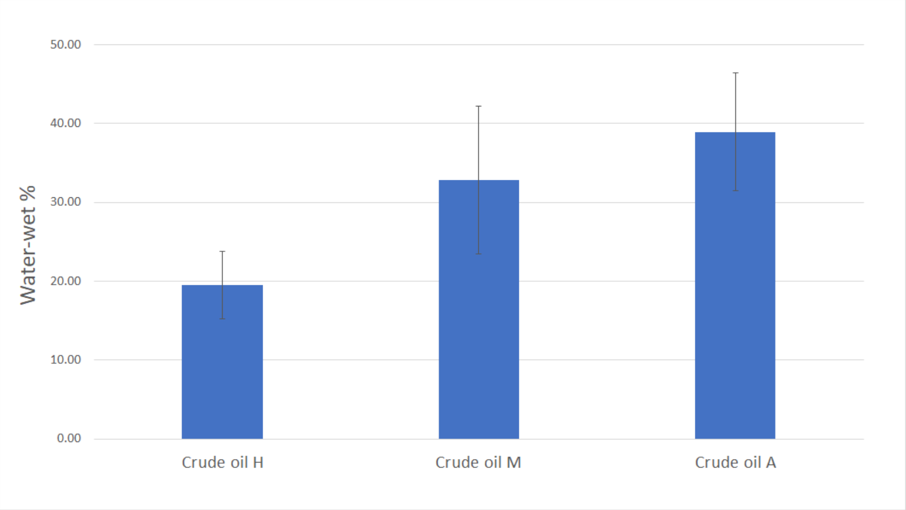


Figure 6.9: Comparison of three different oils and PW

This is strongly connected to the AN of the crude, since the heavier fractions are acidic, polar components which determine oil's AN. Knowing from Standnes and Austad research [54], that lower AN resulted in higher water-wetness, the obtained result was expected. In this case, crude oil A (table 5.7) was the least viscous, hence it had the lowest AN and it provided the highest water-wetness from all three oils. Figure 6.10, below shows the dependence of water-wetness on AN.

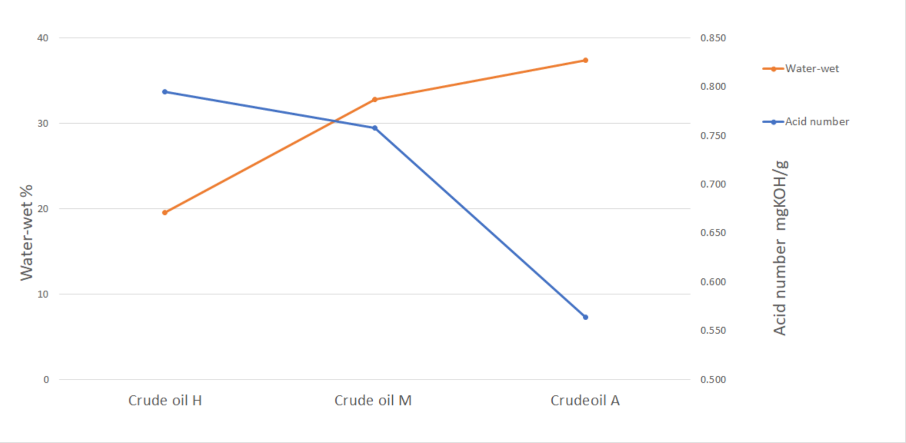


Figure 6.10: AN vs water-wet %

Over and above, figure 6.11 presents a comparison of all three oils and all five brine variations. From the obtained results, it is observed the only crude oil H shows consistency in wettability alteration. The increase in dilution factor resulted in higher water-wetness. On the other hand, crude oils M and A, showed no consistency at all, since the water-wet % is fluctuating. Taking the high standard deviation into consideration, the results can not be 100% reliable. The highest water-wet % (46.89%) for crude oil M, was obtained by using 10xDPW, which is close to 45.86% obtained by using 100xDPW. In crude oil A case, the highest water-wetness (41.36%) was achieved by using 20xDPW, although all brines yielded around 40%. Nevertheless, it is noticeable that the same water-wet % (∼39%) was attained for crude oil M and A by using 10xDTWPW, which is almost twice as much as the ∼19% obtained for crude oil H.

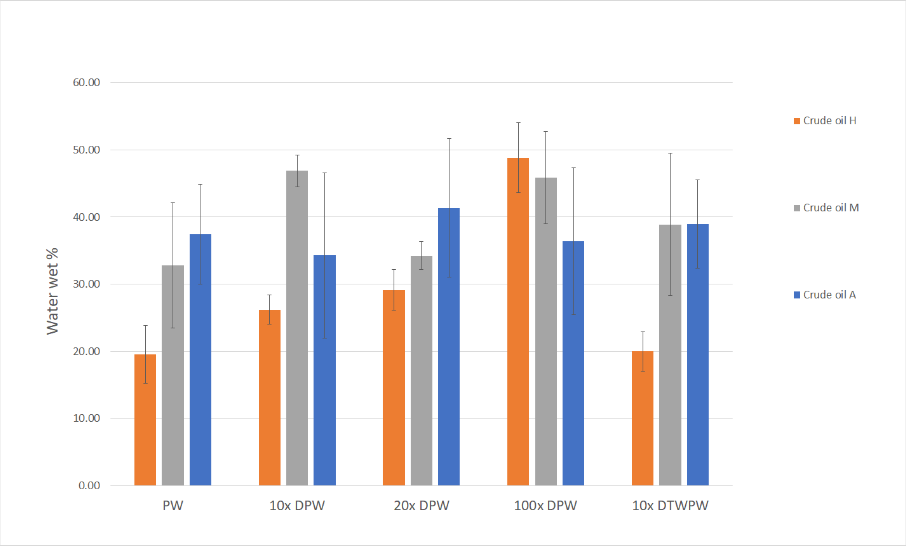


Figure 6.11: Comparison of all crude oil and brine combinations

As mentioned before, a COBR system is pretty complex and numerous factors are involved when it comes to wettability alteration. The salinity of PW is decreased when it is diluted since the ionic concentration and thus the ionic strength are decreased. With lower salinity, the cation exchange between rock and brine occurs. The simple cations adsorb to the rock, which leads to the dislocation of inter-facial active components and organometallic complexes in crude oil and hence change the wettability preference of the rock to more water-wet.[40]

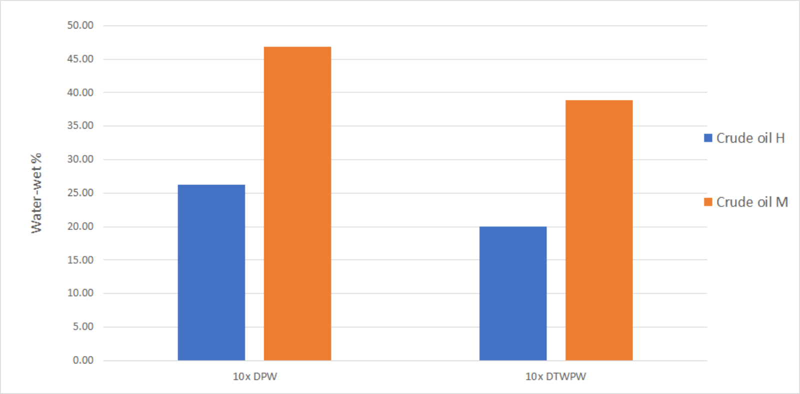


Figure 6.12: Comparison of crude oil H and M with 10xD brine

Both crude oil H and crude oil M showed interesting results for water-wetness when produced water was diluted 10 times. In both cases, higher water-wetness was attained when PW was diluted with DW compared to TW, figure 6.12. As it has been mentioned in the previous section, the obtained results are in contrary to the research performed by Standen, Hognesen and Zhang and others, who concluded that higher concentration of divalent ions (mostly Ca^{2+} in this case) will affect wettability alteration, turning carbonate rock more water-wet [68, 54].

Also noteworthy, is that both crude oil H and crude oil M showed the same trend and moreover the difference between the two cases (10xDPW, 10xDTWPW) is the same, $\sim$6%.

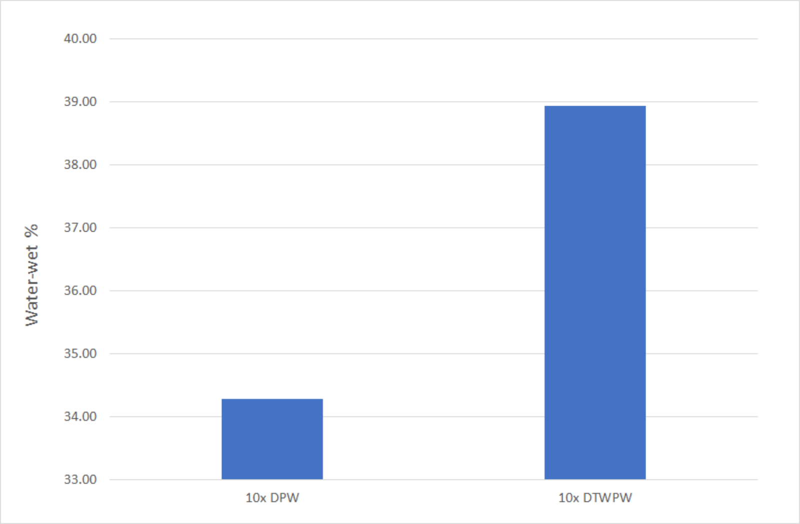


Figure 6.13: Water-wetness increment with increase of divalent ions for crude oil A

In contrast, crude oil A showed results that are in line with the results obtained in the above mentioned researches. Figure 6.13, shows the increment in water-wetness caused by the increase of the concentrations of divalent ions (Ca^{2+} and Mg^{2+}). Ca^{2+} concentration in 10xDPW is 1.83 mmol/l, while in 10xDTWPW it is 2.90 mmol/l. Respectively, the concentration of Mg^{2+} ion increased from 1.28mmol/l to 1.46mmol/l.

6.3 Asphalthenes and water in oil content

Besides measuring the crude oil properties that are presented in the table 5.7, water in oil content for every oil sample, was also estimated in two ways. The first method applied, included centrifugation of the oil samples for 1 hour at 3800rpm. The amount of water after centrifugation was barely visible (transparent liquid at the very bottom of the tube), figure 6.14. The second method, as mentioned in the "experimental work" chapter, was the implementation of the Karl Fischer titration method. The second method confirmed the first one, as the amount of water in oil samples was approximately 0.1% and it is considered negligible.

Figure 6.14: Water content in oil after centrifugation

Regarding the measurement of the asphaltene content, the applied method is also described in the "experimental work" chapter. The amount of precipitated asphaltenes was fairly low, thus it was considered negligible. Figure 6.15 shows the filter paper with asphaltenes.

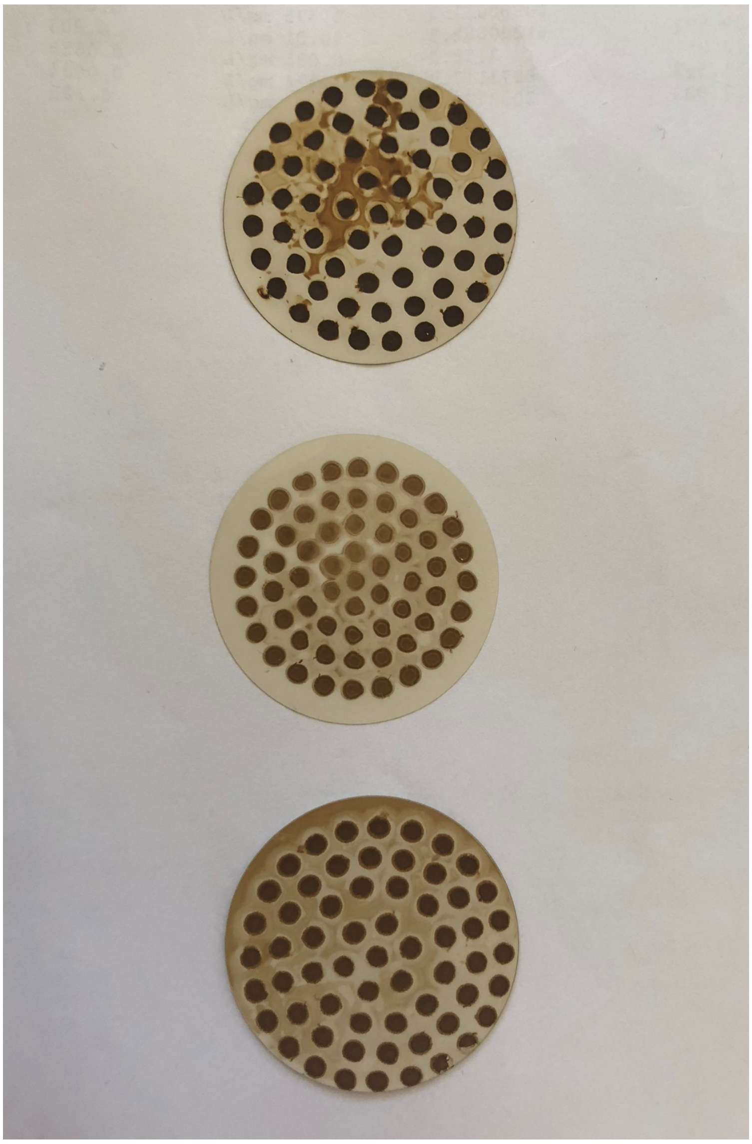


Figure 6.15: Asphaltene precipitates, from top to bottom; crude oil A, crude oil H, crude oil M

Chapter 7

Conclusion

The rock wettability inside a COBR system,is fundamentally the performance of the interactions between crude oil, brine and rock. The differently electric charged ions of the rock surface, react with the organic compounds in crude oil via various forces and bonds. The accession of brine alters the equilibria between them, hence resulting in the wettability alteration of the rock surface. The processes of controlling the wettability involve multicomponent ionic exchange, interface potential alteration, pH variations etc. By modifying the ionic composition of the brine, by either increasing or decreasing the concentration of particular ions, the wettability of the rock can efficiently be regulated in order to increase the oil recovery. This latter, is the ulterior objective of any project-study conducted within this field, including this very one.

In the current project different combinations of crude oils and brines (from the same field in the North Sea Danish sector) in terms of properties, were tested in order to investigate the wettability alteration of chalk (Dan chalk), at the same temperature (115°). The method applied to implement this investigation was the MFT, since it is considerably easy and provides quick results compared to other techniques, i.e. imbibition, core flooding etc. It was concluded that, although several parameters are introduced in such a system, there is a correlation between them. Thus valid assumptions can be made and can be crosschecked with the already existing literature. Parameters such as pH, salinity, ionic strength, ionic charge in brine, acid number, viscosity and asphaltene content in crude oil play a significant role in the wetting conditions of the Dan chalk. Some of the results obtained were in line with previous researches, whereas some other were in opposition.

First of all, it can be deduced that the system: crude oil H, PW and Valhal FW is not perfectly compatible. The 20% of water-wetness can not be considered remarkable, compared to other systems using different FW. Nevertheless, for field operations, injecting produced water for brine flooding, without further treatment, could be beneficial cost-wise.

Furthermore, just by diluting the PW either with DW or with TW, the water-wetness of the chalk can increase up to $\sim$50%. That suggests that by decreasing the ionic strength and the salinity of the brine to low or moderate levels, the oil recovery can improve. However, diluting PW with TW, instead of DW, which is more economic does not increase significantly the water-wet % of the rock, no matter the crude oil under investigation.

Nonetheless, crude oil's AN (in particular crude oil H) is proved to be an important factor regarding the wettability alteration of the chalk's surface. It was shown that the higher the AN of a crude oil sample, the lower the water-wet %. This is already suggested in previous research, since low AN translates into less acidic, polar components that act as surface-active agents between oil and the rock, turning the surface to more oil-wet.

Regarding the asphaltene content in crude oil, which are heavy fractions, although the measurements showed that there is a small amount contained, the same trend as with the AN was observed. The higher the asphaltene precipitates in the crude oil, the lower the water-wetness of the rock.

All in all, it can be inferred that even though the investigation of wettability alteration in carbonates is lacking research, compared to the research conducted for sandstones, the results of this project and the next to come, (will) provide the scientific community with valuable results.

7.1 Improvements

It can be said that water flooding is still a "hot topic" for researchers. Therefore, it is used widely in order to improve oil recovery and extract what is left of the original oil in place inside the reservoirs. Considering the work done in this project and the obtained results, there is room for improvements.

First of all, more detailed analysis of the crude oil needs to be done. In other words, elemental analysis should be conducted, in order to determine the heteroatoms, i.e. sulfur, nitrogen and oxygen in oil. Secondly, GC-MS analysis (Gas Chromatography-Mass Spectroscopy) for organic substances in oil, could be performed, as this will give better insight in polar components of oil.

Regarding the PW, it would be useful to investigate wettability alterations using further dilutions (20 and 100 times) with TW, which will provide brines with higher Ca^{2+} concentration, compared to 20xDPW and 100xDPW. Also, using modified brines, varying SO_4^{2-}, Ca^{2+} and Mg^{2+} concentration. It should also be attempted to use different dilution factors, i.e. between 2 and 100 times, aiming for the optimum wetting conditions for this particular COBR system.

These experiments were carried out at 115°, changing temperature of the system will also have impact on overall results. Finally, considering the high standard deviation in some of the results of this study, repetitions of some sets should be performed.

Bibliography

[1] Gurgel A et al. "A Review on Chemical Flooding Methods Applied in Enhanced Oil Recovery". In: *Brazilian Journal of Petroleum and Gas* 2.2 (July 2008), pp. 83–95.

[2] Tala Maria Aabø. "Background study of the Kraka, Dan, and Halfdan Fields." In: ().

[3] Herbert Abraham. *Asphalts and allied substances: their occurrence, modes of production, uses in the arts and methods of testing*. D. van Nostrand, 1918.

[4] NK Adam. "Use of the term 'Young's Equation'for contact angles". In: *Nature* 180.4590 (1957), p. 809.

[5] Sjblom J. et al. "Our current understanding of water-in-crude oil emulsions.: Recent characterization techniques and high pressure performance". In: *Advances in Colloid and Interface Science* 100 (2003), pp. 399–473.

[6] Mohammed J Alshakhs, Anthony R Kovscek, et al. "An experimental study of the impact of injection water composition on oil recovery from carbonate rocks". In: *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers. 2015.

[7] T Austad et al. "Seawater as IOR fluid in fractured chalk". In: *SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers. 2005.

[8] Veronica Blanco-Gutierrez et al. "Eu (iii)/Eu (ii)-doped (Ca 0.7 Sr 0.3) CO 3 phosphors with vaterite/calcite/aragonite forms as shock/temperature detectors". In: *Journal of Materials Chemistry C* 2.46 (2014), pp. 9969–9977.

[9] Brine. *The Editors of Encyclopaedia Britannica*. https://www.britannica.com/science/brine. Access Date: June 01,2018. Mar. 2018.

[10] Jill S Buckley. "Mechanisms and consequences of wettability alteration by crude oils". PhD thesis. Heriot-Watt University, 1996.

[11] Reme Hart Instrument Co. *Information on contact angle*. 1999. URL: `http://www.ramehart.com/contactangle.htm` (visited on 05/24/2018).

[12] E. R. (Ross) Crain. *Wettability of a porous rocks*. https://www.spec2000.net/09-wettability.htm. Accessed 24.05.2018. Jan. 2015.

[13] Silvio Alejandro Criollo. “Water and surfactant flooding at different wettability conditions”. MA thesis. University of Stavanger, Norway, 2011.

[14] ASTM D2896. “Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration”. In: *Annual Book of Standards* (2007).

[15] E. Dwyann Dalrymple. *Produced oilfield water*. 2018. URL: http://petrowiki.org/Produced_oilfield_water.

[16] James E Darnell, Harvey Lodish, David Baltimore, et al. *Molecular cell biology*. Vol. 2. Scientific American Books New York, 1990.

[17] Maryam H Derkani et al. “Low Salinity Waterflooding in Carbonate Reservoirs: Review of Interfacial Mechanisms”. In: *Colloids and Interfaces* 2.2 (2018), p. 20.

[18] Narendra Kumar Dewangan. *Reservoir rock & fluid*. https://www.slideshare.net/narendrakum rock-fluid-46167260. Mar. 2015.

[19] Erle C Donaldson, George V Chilingarian, and Teh Fu Yen. *Enhanced oil recovery, II: Processes and operations*. Elsevier, 1989.

[20] ST Dubey, PH Doe, et al. “Base number and wetting properties of crude oils”. In: *SPE Reservoir Engineering* 8.03 (1993), pp. 195–200.

[21] Siyavula Education. *Natural gas formation*. 2014. URL: "https://www.flickr.com/photos/121935927@N06/".

[22] The Editors of Encyclopaedia Britannica. *Chalk*. https://www.britannica.com/science/chalk. Access Date:May 31, 2018. Encyclopædia Britannica, inc., Oct. 2013.

[23] The Editors of Encyclopaedia Britannica. *Crude oil*. 2017. URL: https://www.britannica.com/science/crude-oil.

[24] The Editors of Encyclopaedia Britannica. *Sandstone*. 2018. URL: https://www.britannica.com/science/sandstone.

[25] S Erzuah, I Fjelde, and AV Omekeh. “Wettability Characterization Using the Flotation Technique Coupled with Geochemical Simulation”. In: *IOR 2017-19th European Symposium on Improved Oil Recovery*. 2017.

[26] Sarah Friedl. *Crude Oil: Properties & Uses*. https://study.com/academy/lesson/crude-oil-roperties-uses. An optional note. May 2018.

[27] PWJ Glover. *Formulation Evaluation MSc Course Notes—Wettability*. 2001.

[28] Don W Green, G Paul Willhite, et al. *Enhanced oil recovery*. Vol. 6. Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers Richardson, TX, 1998.

[29] Preben Emil Haugen. “Characterization of Wettability Alteration by Flotation”. MA thesis. University of Stavanger, Norway, 2016.

[30] A Hiorth, LM Cathles, and MV Madland. "The impact of pore water chemistry on carbonate surface charge and oil wettability". In: *Transport in porous media* 85.1 (2010), pp. 1–21.

[31] S Hoeiland et al. "The effect of crude oil acid fractions on wettability as studied by interfacial tension and contact angles". In: *Journal of Petroleum Science and Engineering* 30.2 (2001), pp. 91–103.

[32] Thomas Henry Huxley and Loren C Eiseley. *On a piece of chalk*. Scribner, 1967.

[33] Donatien Ishimwe. *Reservoir rock properties*. 2014. URL: `http://connect.spe.org/blogs/donatien-ishimwe/2014/09/29/reservoir-rock-properties`.

[34] Owais Khattak. *Classification of types of Oil and Gas accumulations and Traps*. http://geologylearn.blogspot.com/2015/06/classification-of-types-of-oil-and-gas. Accessed 01.06.2018. Jan. 2016.

[35] A Lager, KJ Webb, and CJJ Black. "Impact of brine chemistry on oil recovery". In: *IOR 2007-14th European Symposium on Improved Oil Recovery*. 2007.

[36] Larry W Lake et al. "Enhanced oil recovery". In: (1989).

[37] Hassan Mahani et al. "Insights into the impact of temperature on the wettability alteration by low salinity in carbonate rocks". In: *Energy & Fuels* 31.8 (2017), pp. 7839–7853.

[38] Hassan Mahani et al. "Kinetics of low-salinity-flooding effect". In: *SPE Journal* 20.01 (2015), pp. 8–20.

[39] PL McGuire et al. "Low salinity oil recovery: An exciting new EOR opportunity for Alaska's North Slope". In: *SPE Western Regional Meeting*. Society of Petroleum Engineers. 2005.

[40] LIN Meiqin, HUA Zhao, and LI Mingyuan. "Surface wettability control of reservoir rocks by brine". In: *Petroleum Exploration and Development* 45.1 (2018), pp. 145–153.

[41] Paulina Mwangi, Geoffrey Thyne, and Dandina Rao. "Extensive experimental wettability study in sandstone and carbonate-oil-brine systems: Part 1–screening tool development". In: *International Symposium of the Society of Core Analysts held in Napa Valley, California, USA*. 2013, pp. 16–19.

[42] Jerry Neff, Kenneth Lee, and Elisabeth M DeBlois. "Produced water: overview of composition, fates, and effects". In: *Produced water*. Springer, 2011, pp. 3–54.

[43] Sharleen Overland, Steven Schamel, and Ravil Ibatulin. "Bitumen and Heavy Oil Committee". In: ().

[44] Can Polat and Mahmut Parlaktuna. "A study on the effect of the chemical composition of brine to improve oil recovery from carbonates". In: *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 39.23 (2017), pp. 2151–2156.

[45] A RezaeiDoust et al. "Smart water as wettability modifier in carbonate and sandstone: A discussion of similarities/differences in the chemical mechanisms". In: *Energy & fuels* 23.9 (2009), pp. 4479–4485.

[46] Anna F Rusydi. "Correlation between conductivity and total dissolved solid in various type of water: A review". In: *IOP Conference Series: Earth and Environmental Science*. Vol. 118. 1. IOP Publishing. 2018, p. 012019.

[47] Erica dos Santos Godinho. "Effectiveness of Produced Water in Advanced Waterflooding: estimation of the wettability alteration by modified flotation technique". unpublished 9th Semester Report. 2017.

[48] Erica dos Santos Godinho and Konstantin Jefimov. *Wettability alteration in chalk using flotation technique*. unpublished 8th semester report in Oil and Gas Production. Aalborg University, 2017.

[49] M Adeel Sohal, Geoffrey Thyne, and Erik G Søgaard. "Effect of the temperature on wettability and optimum wetting conditions for maximum oil recovery in a carbonate reservoir system". In: *Energy & Fuels* 31.4 (2017), pp. 3557–3566.

[50] M Adeel Sohal, Geoffrey Thyne, and Erik G Søgaard. "Novel application of the flotation technique to measure the wettability changes by ionically modified water for improved oil recovery in carbonates". In: *Energy & Fuels* 30.8 (2016), pp. 6306–6320.

[51] M Adeel Sohal, Geoffrey Thyne, and Erik G Søgaard. "Review of recovery mechanisms of ionically modified waterflood in carbonate reservoirs". In: *Energy & Fuels* 30.3 (2016), pp. 1904–1914.

[52] Muhammad Adeel Nassar Sohal. "Wettability Modification in Chalk". In: ().

[53] Inger Gine Sørbø. "Polar Components in Crude Oils and Their Correlation to Physiochemical Properties." MA thesis. The University of Bergen, 2016.

[54] Dag C Standnes and Tor Austad. "Wettability alteration in chalk: 1. Preparation of core material and oil properties". In: *Journal of Petroleum Science and Engineering* 28.3 (2000), pp. 111–121.

[55] Skule Strand et al. ""Smart water" for oil recovery from fractured limestone: a preliminary study". In: *Energy & fuels* 22.5 (2008), pp. 3126–3133.

[56] GQ Tang, Norman R Morrow, et al. "Salinity, temperature, oil composition, and oil recovery by waterflooding". In: *SPE Reservoir Engineering* 12.04 (1997), pp. 269–276.

[57] Djebbar Tiab and Erle C Donaldson. *Petrophysics: theory and practice of measuring reservoir rock and fluid transport properties*. Gulf professional publishing, 2015.

[58] Tatjana Tomić and Nada Uzorinac Nasipak. "Application of ion chromatography in oilfield water analysis". In: *The holistic approach to environment* 2.1 (2012), pp. 41–48.

[59] Petroleum Co Uk. *Sweet vs. Sour Crude Oil*. 2018. URL: `http://www.petroleum.co.uk/sweet-vs-sour`.

[60] Toril I Røe Utvik. "Chemical characterisation of produced water from four offshore oil production platforms in the North Sea". In: *Chemosphere* 39.15 (1999), pp. 2593–2606.

[61] Paul Vledder et al. "Low salinity water flooding: proof of wettability alteration on a field wide scale". In: *SPE Improved Oil Recovery Symposium*. Society of Petroleum Engineers. 2010.

[62] Jianxin Wang, Jill Buckley, and New Mexico Tech PRRC. "Standard Procedure for Separating Asphaltenes from Crude Oils". In: *Petroleum Recovery Research Center* (2002).

[63] Kevin John Webb, Clifford James J Black, Gunnar Tjetland, et al. "A laboratory study investigating methods for improving oil recovery in carbonates". In: *International Petroleum Technology Conference*. International Petroleum Technology Conference. 2005.

[64] Quan Xie et al. "pH effect on wettability of oil/brine/carbonate system: Implications for low salinity water flooding". In: *Journal of Petroleum Science and Engineering* (2018).

[65] Ali Yousef, Subhash Ayirala, et al. "Optimization study of a novel water-ionic technology for smart-waterflooding application in carbonate reservoirs". In: *Oil and Gas Facilities* 3.05 (2014), pp. 72–82.

[66] Ali A Yousef et al. "Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs". In: *SPE Reservoir Evaluation & Engineering* 14.05 (2011), pp. 578–593.

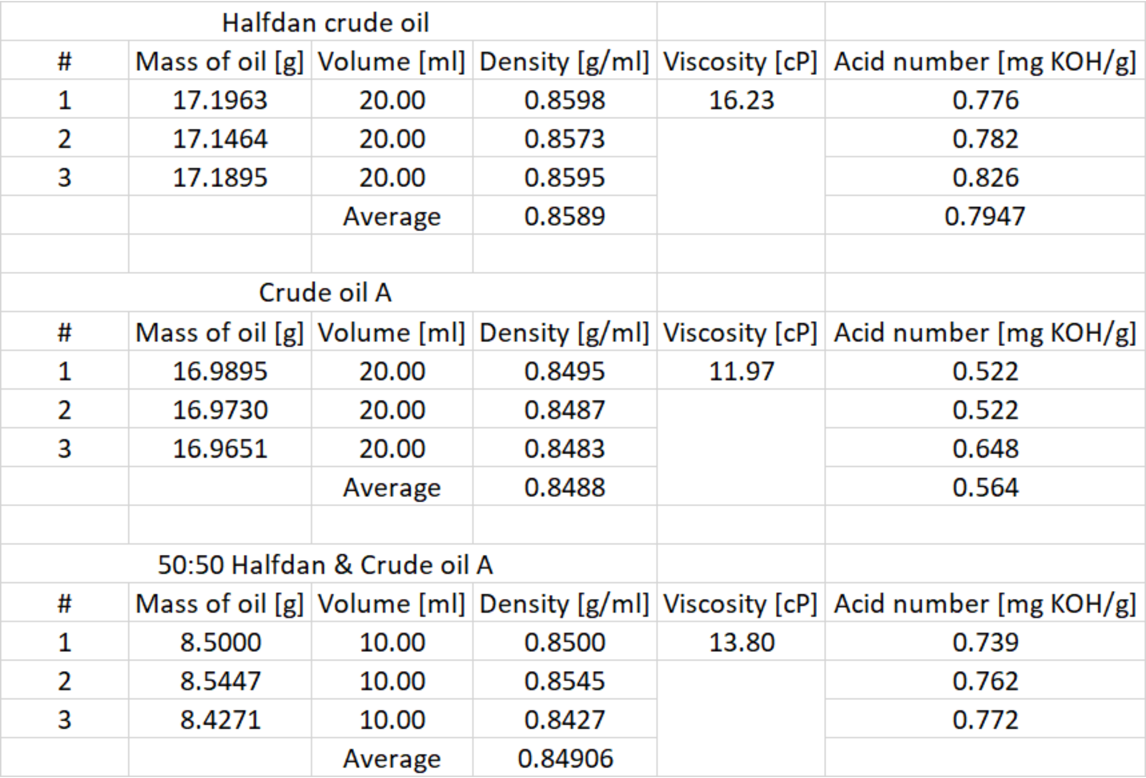
[67] Adeel Zahid, Erling Halfdan Stenby, Alexander A Shapiro, et al. "Improved oil recovery in chalk: wettability alteration or something else?" In: *SPE Europec/EAGE annual conference and exhibition*. Society of Petroleum Engineers. 2010.

[68] P Zhang, Tor Austad, et al. "The relative effects of acid number and temperature on chalk wettability". In: *SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers. 2005.

[69] Murtaza ZIAUDDIN et al. “Fundamentals of Wettability”. In: *Schlumberger Oilfield Review* (2007).

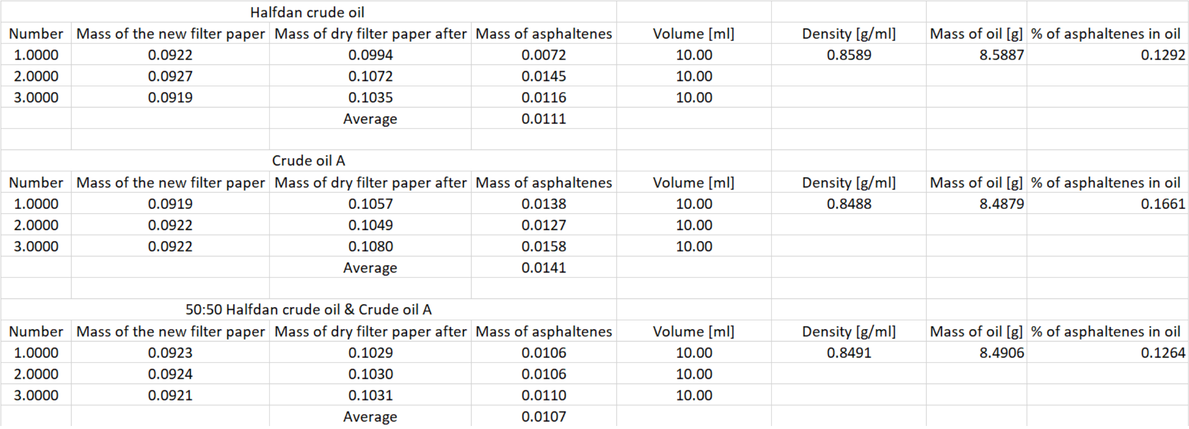
Appendix A

Appendix



Halfdan crude oil					
#	Mass of oil [g]	Volume [ml]	Density [g/ml]	Viscosity [cP]	Acid number [mg KOH/g]
1	17.1963	20.00	0.8598	16.23	0.776
2	17.1464	20.00	0.8573		0.782
3	17.1895	20.00	0.8595		0.826
		Average	0.8589		0.7947
Crude oil A					
#	Mass of oil [g]	Volume [ml]	Density [g/ml]	Viscosity [cP]	Acid number [mg KOH/g]
1	16.9895	20.00	0.8495	11.97	0.522
2	16.9730	20.00	0.8487		0.522
3	16.9651	20.00	0.8483		0.648
		Average	0.8488		0.564
50:50 Halfdan & Crude oil A					
#	Mass of oil [g]	Volume [ml]	Density [g/ml]	Viscosity [cP]	Acid number [mg KOH/g]
1	8.5000	10.00	0.8500	13.80	0.739
2	8.5447	10.00	0.8545		0.762
3	8.4271	10.00	0.8427		0.772
		Average	0.84906		

Figure A.1: Density of oil calculations



Halfdan crude oil

Number	Mass of the new filter paper	Mass of dry filter paper after	Mass of asphaltenes	Volume [ml]	Density [g/ml]	Mass of oil [g]	% of asphaltenes in oil
1.0000	0.0922	0.0994	0.0072	10.00	0.8589	8.5887	0.1292
2.0000	0.0927	0.1072	0.0145	10.00			
3.0000	0.0919	0.1035	0.0116	10.00			
		Average	0.0111				

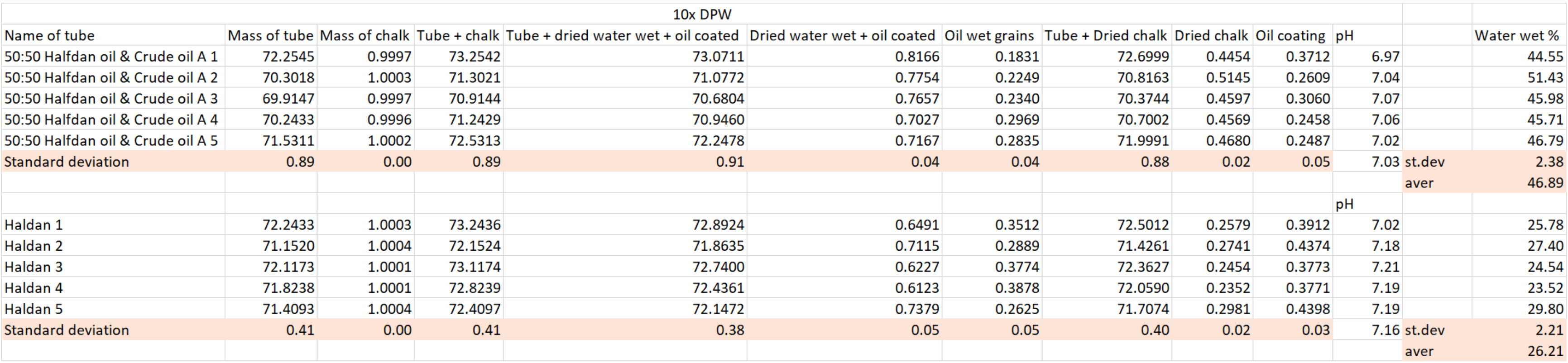
Crude oil A

Number	Mass of the new filter paper	Mass of dry filter paper after	Mass of asphaltenes	Volume [ml]	Density [g/ml]	Mass of oil [g]	% of asphaltenes in oil
1.0000	0.0919	0.1057	0.0138	10.00	0.8488	8.4879	0.1661
2.0000	0.0922	0.1049	0.0127	10.00			
3.0000	0.0922	0.1080	0.0158	10.00			
		Average	0.0141				

50:50 Halfdan crude oil & Crude oil A

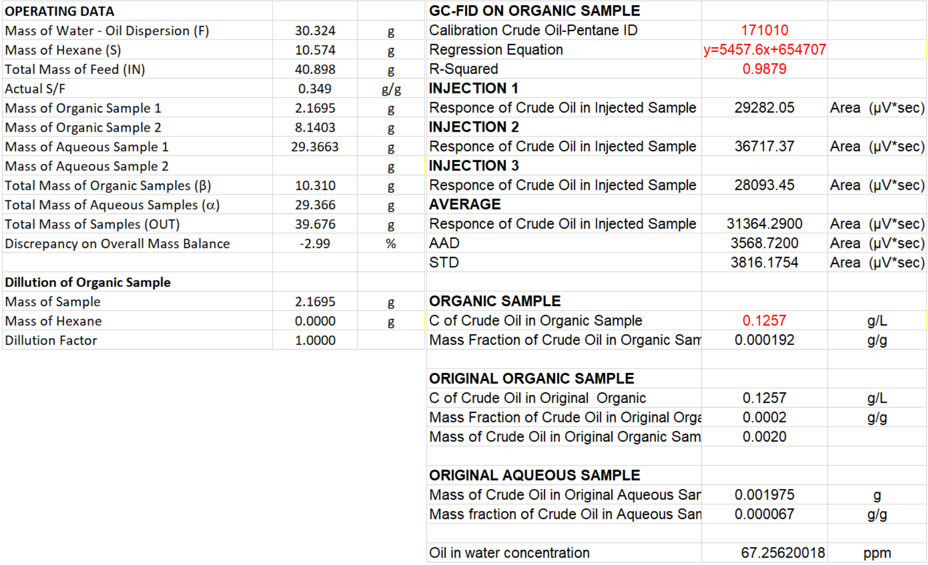
Number	Mass of the new filter paper	Mass of dry filter paper after	Mass of asphaltenes	Volume [ml]	Density [g/ml]	Mass of oil [g]	% of asphaltenes in oil
1.0000	0.0923	0.1029	0.0106	10.00	0.8491	8.4906	0.1264
2.0000	0.0924	0.1030	0.0106	10.00			
3.0000	0.0921	0.1031	0.0110	10.00			
		Average	0.0107				

Figure A.2: Asphaltenes calculation



				10x DPW								
Name of tube	Mass of tube	Mass of chalk	Tube + chalk	Tube + dried water wet + oil coated	Dried water wet + oil coated	Oil wet grains	Tube + Dried chalk	Dried chalk	Oil coating	pH		Water wet %
50:50 Halfdan oil & Crude oil A 1	72.2545	0.9997	73.2542	73.0711	0.8166	0.1831	72.6999	0.4454	0.3712	6.97		44.55
50:50 Halfdan oil & Crude oil A 2	70.3018	1.0003	71.3021	71.0772	0.7754	0.2249	70.8163	0.5145	0.2609	7.04		51.43
50:50 Halfdan oil & Crude oil A 3	69.9147	0.9997	70.9144	70.6804	0.7657	0.2340	70.3744	0.4597	0.3060	7.07		45.98
50:50 Halfdan oil & Crude oil A 4	70.2433	0.9996	71.2429	70.9460	0.7027	0.2969	70.7002	0.4569	0.2458	7.06		45.71
50:50 Halfdan oil & Crude oil A 5	71.5311	1.0002	72.5313	72.2478	0.7167	0.2835	71.9991	0.4680	0.2487	7.02		46.79
Standard deviation	0.89	0.00	0.89	0.91	0.04	0.04	0.88	0.02	0.05	7.03	st.dev	2.38
											aver	46.89
										pH		
Haldan 1	72.2433	1.0003	73.2436	72.8924	0.6491	0.3512	72.5012	0.2579	0.3912	7.02		25.78
Haldan 2	71.1520	1.0004	72.1524	71.8635	0.7115	0.2889	71.4261	0.2741	0.4374	7.18		27.40
Haldan 3	72.1173	1.0001	73.1174	72.7400	0.6227	0.3774	72.3627	0.2454	0.3773	7.21		24.54
Haldan 4	71.8238	1.0001	72.8239	72.4361	0.6123	0.3878	72.0590	0.2352	0.3771	7.19		23.52
Haldan 5	71.4093	1.0004	72.4097	72.1472	0.7379	0.2625	71.7074	0.2981	0.4398	7.19		29.80
Standard deviation	0.41	0.00	0.41	0.38	0.05	0.05	0.40	0.02	0.03	7.16	st.dev	2.21
											aver	26.21

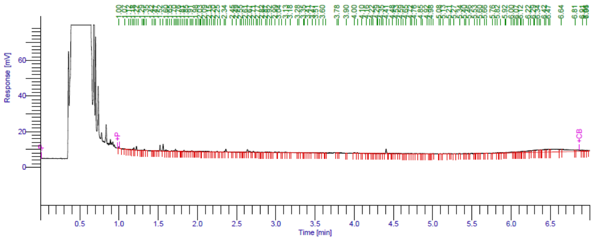
Figure A.3: Example of water-wet calculations



OPERATING DATA		
Mass of Water - Oil Dispersion (F)	30.324	g
Mass of Hexane (S)	10.574	g
Total Mass of Feed (IN)	40.898	g
Actual S/F	0.349	g/g
Mass of Organic Sample 1	2.1695	g
Mass of Organic Sample 2	8.1403	g
Mass of Aqueous Sample 1	29.3663	g
Mass of Aqueous Sample 2		g
Total Mass of Organic Samples (β)	10.310	g
Total Mass of Aqueous Samples (α)	29.366	g
Total Mass of Samples (OUT)	39.676	g
Discrepancy on Overall Mass Balance	-2.99	%
Dillution of Organic Sample		
Mass of Sample	2.1695	g
Mass of Hexane	0.0000	g
Dillution Factor	1.0000	

GC-FID ON ORGANIC SAMPLE		
Calibration Crude Oil-Pentane ID	171010	
Regression Equation	y=5457.6x+654707	
R-Squared	0.9879	
INJECTION 1		
Responce of Crude Oil in Injected Sample	29282.05	Area (μV*sec)
INJECTION 2		
Responce of Crude Oil in Injected Sample	36717.37	Area (μV*sec)
INJECTION 3		
Responce of Crude Oil in Injected Sample	28093.45	Area (μV*sec)
AVERAGE		
Responce of Crude Oil in Injected Sample	31364.2900	Area (μV*sec)
AAD	3568.7200	Area (μV*sec)
STD	3816.1754	Area (μV*sec)
ORGANIC SAMPLE		
C of Crude Oil in Organic Sample	0.1257	g/L
Mass Fraction of Crude Oil in Organic Sam	0.000192	g/g
ORIGINAL ORGANIC SAMPLE		
C of Crude Oil in Original Organic	0.1257	g/L
Mass Fraction of Crude Oil in Original Orga	0.0002	g/g
Mass of Crude Oil in Original Organic Sam	0.0020	
ORIGINAL AQUEOUS SAMPLE		
Mass of Crude Oil in Original Aqueous Sar	0.001975	g
Mass fraction of Crude Oil in Aqueous San	0.000067	g/g
Oil in water concentration	67.25620018	ppm

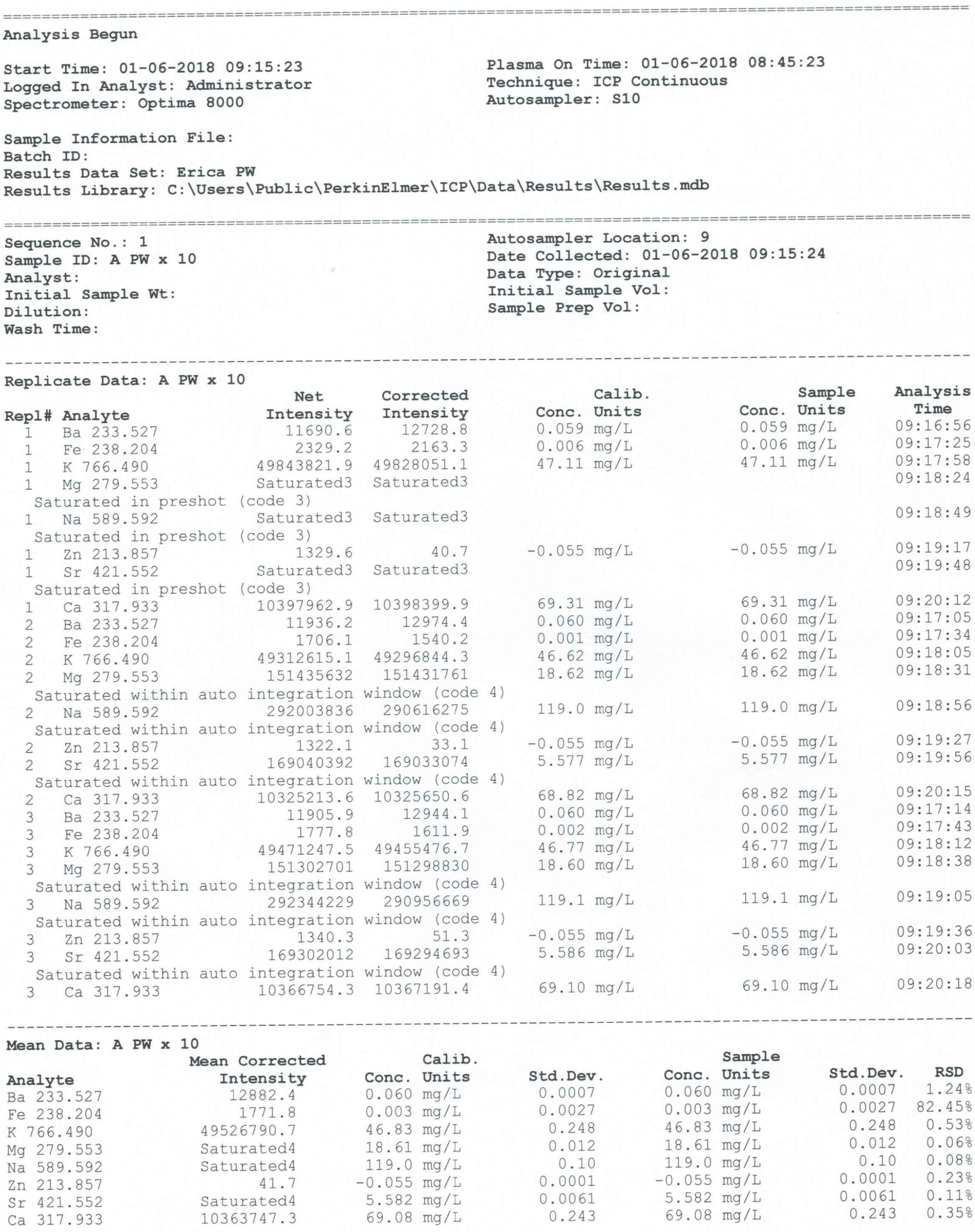
Figure A.4: Calculations performed to obtain oil in water



Kemilaboratoriet crude

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Adjusted Amount
16		1.523	2063.39	3324.08	0.0021
17		1.562	2484.41	3898.68	0.0025
57		2.638	1510.50	1557.15	0.0015
99		4.405	2021.60	2607.22	0.0020
146		6.220	2542.34	943.01	0.0025
148		6.286	2481.46	1159.99	0.0025
150		6.336	3024.35	1332.76	0.0030
151		6.355	1636.98	1357.77	0.0016
153		6.424	3625.01	1486.82	0.0036
154		6.440	1990.96	1497.98	0.0020
155		6.474	3073.91	1598.56	0.0031
157		6.638	2827.14	1349.32	0.0028
			29282.05	22113.34	0.0293

Figure A.5: Response from GCFID



```
======================================================================================
Analysis Begun

Start Time: 01-06-2018 09:15:23                    Plasma On Time: 01-06-2018 08:45:23
Logged In Analyst: Administrator                   Technique: ICP Continuous
Spectrometer: Optima 8000                          Autosampler: S10

Sample Information File:
Batch ID:
Results Data Set: Erica PW
Results Library: C:\Users\Public\PerkinElmer\ICP\Data\Results\Results.mdb

======================================================================================
Sequence No.: 1                                    Autosampler Location: 9
Sample ID: A PW x 10                               Date Collected: 01-06-2018 09:15:24
Analyst:                                           Data Type: Original
Initial Sample Wt:                                 Initial Sample Vol:
Dilution:                                          Sample Prep Vol:
Wash Time:

--------------------------------------------------------------------------------------
Replicate Data: A PW x 10
                             Net   Corrected          Calib.                Sample  Analysis
Repl# Analyte          Intensity   Intensity      Conc. Units          Conc. Units      Time
  1   Ba 233.527         11690.6     12728.8      0.059 mg/L           0.059 mg/L   09:16:56
  1   Fe 238.204          2329.2      2163.3      0.006 mg/L           0.006 mg/L   09:17:25
  1   K 766.490       49843821.9  49828051.1      47.11 mg/L           47.11 mg/L   09:17:58
  1   Mg 279.553     Saturated3  Saturated3                                         09:18:24
   Saturated in preshot (code 3)
  1   Na 589.592     Saturated3  Saturated3                                         09:18:49
   Saturated in preshot (code 3)
  1   Zn 213.857          1329.6        40.7     -0.055 mg/L          -0.055 mg/L   09:19:17
  1   Sr 421.552     Saturated3  Saturated3                                         09:19:48
   Saturated in preshot (code 3)
  1   Ca 317.933      10397962.9  10398399.9      69.31 mg/L           69.31 mg/L   09:20:12
  2   Ba 233.527         11936.2     12974.4      0.060 mg/L           0.060 mg/L   09:17:05
  2   Fe 238.204          1706.1      1540.2      0.001 mg/L           0.001 mg/L   09:17:34
  2   K 766.490       49312615.1  49296844.3      46.62 mg/L           46.62 mg/L   09:18:05
  2   Mg 279.553       151435632   151431761      18.62 mg/L           18.62 mg/L   09:18:31
   Saturated within auto integration window (code 4)
  2   Na 589.592       292003836   290616275      119.0 mg/L           119.0 mg/L   09:18:56
   Saturated within auto integration window (code 4)
  2   Zn 213.857          1322.1        33.1     -0.055 mg/L          -0.055 mg/L   09:19:27
  2   Sr 421.552       169040392   169033074      5.577 mg/L           5.577 mg/L   09:19:56
   Saturated within auto integration window (code 4)
  2   Ca 317.933      10325213.6  10325650.6      68.82 mg/L           68.82 mg/L   09:20:15
  3   Ba 233.527         11905.9     12944.1      0.060 mg/L           0.060 mg/L   09:17:14
  3   Fe 238.204          1777.8      1611.9      0.002 mg/L           0.002 mg/L   09:17:43
  3   K 766.490       49471247.5  49455476.7      46.77 mg/L           46.77 mg/L   09:18:12
  3   Mg 279.553       151302701   151298830      18.60 mg/L           18.60 mg/L   09:18:38
   Saturated within auto integration window (code 4)
  3   Na 589.592       292344229   290956669      119.1 mg/L           119.1 mg/L   09:19:05
   Saturated within auto integration window (code 4)
  3   Zn 213.857          1340.3        51.3     -0.055 mg/L          -0.055 mg/L   09:19:36
  3   Sr 421.552       169302012   169294693      5.586 mg/L           5.586 mg/L   09:20:03
   Saturated within auto integration window (code 4)
  3   Ca 317.933      10366754.3  10367191.4      69.10 mg/L           69.10 mg/L   09:20:18

--------------------------------------------------------------------------------------
Mean Data: A PW x 10
                Mean Corrected        Calib.                      Sample
Analyte              Intensity    Conc. Units    Std.Dev.    Conc. Units    Std.Dev.    RSD
Ba 233.527             12882.4    0.060 mg/L       0.0007    0.060 mg/L       0.0007   1.24%
Fe 238.204              1771.8    0.003 mg/L       0.0027    0.003 mg/L       0.0027  82.45%
K 766.490           49526790.7    46.83 mg/L        0.248    46.83 mg/L        0.248   0.53%
Mg 279.553         Saturated4     18.61 mg/L        0.012    18.61 mg/L        0.012   0.06%
Na 589.592         Saturated4     119.0 mg/L         0.10    119.0 mg/L         0.10   0.08%
Zn 213.857                41.7   -0.055 mg/L       0.0001   -0.055 mg/L       0.0001   0.23%
Sr 421.552         Saturated4     5.582 mg/L       0.0061    5.582 mg/L       0.0061   0.11%
Ca 317.933          10363747.3    69.08 mg/L        0.243    69.08 mg/L        0.243   0.35%
```

Figure A.6: ICP report for 10x DPW