Optimization of Injection Fluids with Scope of Reservoir Wettability

Master Thesis in Enhanced Oil Recovery

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By signing the author take the full responsibility for the contents of the master thesis.

(Kasper Bundgaard Steffensen)

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Abstract

Determine formation water potential as reinjection water in comparison with LSSW water and plain seawater. The study method is modified flotation technique using synthetic SW as a baseline and oil sample from a representative oilfield in North Sea. The actual effect of reinjection produced water combined with LSSW water in terms of wetability and as a potential enhanced oil recovery method.

Resumé

Formålet med dette projekt at at undersøge formations/ produktionsvands potentiale som injiceringsvæske i olie reservoir, væsken bliver sammenlignet med egenskaber af søvand med lavt sulfat indhold samt almindeligt søvand.

Studiet tager udgangspunkt i prøver taget på et oliefelt i nordsøen.

Projektet undersøger effekten af injiceret produktionsvand i kombination med søvand med lavt sulfat indhold hvordan det påvirker de hydrofile egenskaber i reservoiret og om væskerne kan ses som potentielle kandidater for en EOR metode.

Acronyms

Symbol	Definiton		
ε	Static dielectric constant		
$arepsilon_0$	Relative permittivity		
ζ	Zeta-Potential		
η	Viscosity [cP]		
θ	Contact angle [°]		
κ	Reciprocal Debye-Hückel double layer length [nm]		
κ_B	Boltzmann constant [J/K]		
λ	Electrical conductivity		
$\mu { m m}$	Micrometers		
σ	Interfacial tension		
ψ_r	Reduced potential [nm]		
\sim	approximately		
$ u_e$	Ionization frequency [Hz]		
А	Hamaker constant [J]		
AIMSM	Advanced Ion Management		
AN	Acid number $[mgKOH/g]$		
BHP	Bottom hole Pressure		
BN	Base number $[mgKOH/g]$		
BPR	Back-pressure Regulator		
Brines $(s.l.)$	Various waters tested, including EFW and SW, PW, LSSW and SW *0 SO_4		
BTX	Benzene, Toluene and Xylene		
ca.	Approximately/circa		
CBR	Crude oil - Brine $(s.l.)$ - Rock system		
dP	Voltage differential [V]		
dU	Pressure differential [bar]		
DI water	Deionized water		

DLVO	Derjaguin, Landau, Verwey and Overbeek
EDL	Electrical Double layer
EF	Electrostatic forces
e.g.	for example
EOR	Enhanced Oil Recovery
E&P	Exploration and Production
EFW	Ekofisk Formation Water
FW	Formation Water
GCMS	Gas Chromatrography and Mass Spectrometry
IAP	ion activity product
<i>i.e.</i>	that is/id est (latin)
KOH	potassium hydroxide
LSSW	Low Sulphate Seawater
mD	millidarcy
M_{As}	Mass of Asphaltenes [g]
M_{Co}	Mass of Crude oil [g]
MIE	Multi-component Ion Exchange
MFT	Modified Flotation Technique
OB	Oil-Brine $(s.l.)$
O&G	Oil and Gas
PDAs	Potential Determining Anions
PDIs	Potential Determining Ions
PSFIs	Potential Scale Forming Ions
PW	Produced water
rpm	rotation per minute
SARA	Saturate, Aromatic, Resin, Asphaltene
Secs	Seconds
SND	Sandstone
STDEV	Standard deviation
SW	Synthetic Seawater
SW 2x	Synthetic Seawater diluted 2 times
SW $10x$	Synthetic Seawater diluted 10 times
SW $20x$	Synthetic Seawater diluted 20 times

SW 50x	Synthetic Seawater diluted 50 times
SW 100x	Synthetic Seawater diluted 100 times
$SW * 0SO_4$	Synthetic Seawater, zero sulphate
SwiR	Irreducible water saturation
s.l.	sensu latu/in a broad sense
TDS	Total dissolved solids $[g/l]$
USBM	U.S. Bureau of Mines

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1 Problem Formulation

An oil reservoir will naturally produce from its own pressure up until a certain degree when there is a pressure equalization between the pressure in the reservoir and the differential required in order to make flow to separators, this is called primary recovery, secondary recovery is to utilize injection wells and gas lift. Injection wells are commissioned to increase the reservoir pressure and sweep hydrocarbons to the producer, gas lift is used to lower the hydrostatic to surface.

The purpose of this project is to investigate the properties of the fluids available for injection at a north sea field. The investigation and lab experiments will offset the chemical compositions and determine the key parameters for improving sweeping efficiency and oil recovery.

1.1 Objectives

The first observation of wettability influence was noticed in the Ekofisk North sea field [32] where after a commissioning of a water injection, it was observed, once there was a breakthrough of the waterfront the recovery of oil increased instead of decreasing, as it was expected. When the hypothesis of wettability and ionic modification of the water was investigated it was observed that the ionic composition, reservoir rock composition, pH, temperature and pressure were the main factors affecting the above mentioned phenomenon. Though few other oil characteristics, such as, acid and base number, asphaltene number and zeta potential can give descriptive conditions which can provide an idea regarding the most probable reservoir conditions at current time enabling the construction of a data schematic which can narrow in a proposal of mixtures and treatments for an optimized fluids injection.

Some oil companies have taken in low salinity injection fluids and the complexes around it in and established departments with this specific focus, "Designer Water Flood" by Shell, "Advanced Ion Management (AIMSM)" by ExxonMobil, "Low Salinity Water Flood (LoSal)" by BP and "Smart Water Flooding" by several authors. in recently published articles. Wettability alteration by ionic activity on the rock surface as a possible mechanism behind improved oil recovery by low salinity water flooding has found greater support compared to other possible mechanisms. However, other possible mechanisms such as IFT reduction, electric double layer expansion, and rock dissolution are also found to have contribution in releasing trapped oil in laboratory investigation. [87]

The study take an offset in the current state of the art academic and best practice of studies within wettability. Research is focused on standard practices, probability and efficiency of the findings. Lab works is characterized by the following focus points.

- 1. Examine current state wettability properties of injected fluids present at a field in North Sea.
- 2. Test produced water and Low sulfate seawater ionic composition and chemestry which can affect wettability.
- 3. Test two different types of chalk to investigate the influence of the chalk type.
- 4. Conduct simulation in Phreeqc to investigate saturation curves and determine PDIs.
- 5. Cover coreflooding fundamentals and describe the process for future reference.
- 6. make a proposal of a designed smart brine which can be suggested to a field scale study.

2 Introduction

2.1 Oil and Gas Industry Overview

The last years oil price downturn have forced oil companies to trim and slim the operations and amend the business strategies to fit the new market environment. Essentially, two main focus have been noticed:

- 1. Increased concern on environmental topics, both on sea discharges and air emissions;
- 2. Attempt to recover hydrocarbons with as green foot print as possible.

The previously mentioned factors and a market characterized by a low oil price, lead to a challenging situation to financially justify high cost high risk projects that are frequently required to keep the reservoirs flowing. This is specially relevant when there is an increasing amount of mature fields with depleted zones, highlighting the importance of recovery parameters to maintain the overall flow assurance.

For many years there have been discussions and attempts with Enhanced oil recovery, generally known as tertiary recovery phase. For a brief overview on recovery phases and common EOR methods see Figure 2.1

"It is commonly known that globally average of field recovery from water-flooding currently is about 35% which leaves about 60 - 70% left in reservoir of which each additional % potentially to be recovered is equivalent to significant amounts of hydrocarbons. Due to the potential in matured fields there is an increased focus on suitable EOR methods" [16].





Figure 2.1: Recovery phases and EOR methods.[68]

2.2 Petroleum System: Source Rock, Reservoir Rock, Cap Rock and Traps

Hydrocarbons have matured over millions of years, they are generated from a formation layer composed by various ma types of sediment including live organisms such as algae. As formation layers on to increase the pressure and thereby also the temperature the algae start biodegrade and migrate upwards due to the lesser density than water and formation rock. In practice these layers exist everywhere and do a migration, the hydrocarbon reservoir takes its origin under the perfect conditions of a reservoir rock having sufficient permeability and porosity for the hydrocarbon fluid to displace the saturated water in place. For the oil to be accumulated the condition of a cap is necessary, this can be from a fault or a shale cap or a salt dome.

2.2.1 Source Rock

A source rock is a sediment of organic matter which generates hydrocarbons. Usually algae have settled in a lake or sea basin millions of years ago, and as the layers have build up and becoming more and more compact the fluid migration starts to take place, and a less denser fluid will migrate upwards and displace any mobile fluid with a higher density such as a formation brine positioned in an upper layer.

2.2.2 Hydrocarbon Traps

An hydrocarbon trap is defined by a cap rock usually a shale or clay cap which will create a barrier for the hydrocarbons to migrate further upwards. For the Reservoir to be created the original formation brine which was encapsulated in the formation layer by the time of position of the cap rock the migration of the fluids and ionic composition of same will depends on the interaction between fluid reservoirs, *i.e.*, Ekofisk formation brine has significantly higher ionic composition than Tor brine, due to the concentration of the fluids at the time of lithological positioning.



Figure 2.2: Schematic representation of the most frequent types of hydrocarbon traps, including structural and stratigraphic traps. [23]

2.2.3 North Sea Reservoir Rocks

The danish part of the north sea is mainly composed of chalk as reservoir rock. Chalk sedimentary rock, that can be classified as a variety of the limestone, characteristics of being soft, pure and white.

At microscopic scale, it can be seen there is planktonic algae nannofossils, named coccolithophorids. (Calvert 1974 in [20]). Petrophysical properties are very diverse. Chalk porosity from 30 to 48% and matrix permeability is low in a best case scenario chalk permeability of 5-10mD.[38]

In mineralogical terms chalk is mostly constituted of calcite crystals. Calcite is defined by a rhombohedral lattice system and is the most abundant and thermodynamic stable polymorph of anhydrous $CaCO_3$. Aragonite, which is the second most stable calcium carbonate polymorph is characterized by an orthorombic system. Vaterite, also known as $\mu - CaCO_3$ is the last polymorph, is defined by an hexagonal system, which is less commonly to occur in nature because it is the least thermodynamically stable. "Vaterite can rapidly transform to calcite and aragonite in aqueous solution. Experimental evidence has demonstrated that vaterite can transform to aragonite in 60 minutes at 60C and to calcite in 24 hours at room temperature". [28] A schematic for the mineral structure and relative position of the calcium and carbonate ions at the crystal lattice in all polymorphs can be seen in Figure 2.3.



Figure 2.3: Calcium Carbonate anhydrous polymorphs, showing the ions location at the crystal lattice.Adapted from http://www.chemtube3d.com/solidstate/SS-CaCO3.htm

The importance of the mineral structure is linked to the development of surface charges, which is related to the surface exposed sites of metal groups and carbonate ions. As described by Sohal [59] each ion will develop a coordination number depending on its position inside the crystal lattice. Therefore, the rock surface charge is inducing interaction between exposed sites and the fluids.

Sandstone is another rock type found as reservoir rock in the North sea fields, which is generally characterized by different wetting state when compared to carbonates (see Table 2.1 and [71] for further details). In terms of mineralogical composition, sandstone is mainly constituted by quartz, feldspar, rock fragments and slight clay content depending on its purity. The range for sandstone grains is between 1/8 and 2 mm in diameter. [80]

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

Table 2.1: Relative Wetting Tendencies of Sandstones and Carbonates. [71]

2.2.4 Caprock

The caprock, also commonly called seal is fundamental part of the petroleum system, once it is responsible to prevent the escape of hydrocarbons. It forms a barrier above and around the reservoir rock so that fluids cannot migrate beyond the reservoir. In terms of petrophysical properties, it is considered impermeable. There are rocks frequently recognized as cap rocks, namely, shale and anhydrite.[25]

2.2.5 Reservoir fluid: characteristics

The crude oil consists of two major groups; hydrocarbons and non-hydrocarbons. Alkanes (also called paraffins), cycloalkanes (also called naphthenes or cyclic paraffins) and aromatics.

Major fraction of compounds present in crude oil, the hydrocarbons, approximately. 95%. The rest fluid is a proportion of non-hydrocarbons, which are heavy metals, sulfur, nitrogen and oxygen compounds. [30]

"The crude oil heavy ends (mainly asphaltenes and resins) contain the most polar class of compounds found in the crude oil. They contain surface active components which adsorb on reservoir rock and minerals."[39]

For sandstone reservoirs. "Adsorption of asphaltenes and resins on clays can change the wettability from water-wet to oil-wet, and reduce the expansion of swelling clays, the effective surface area and the cation exchange capacity. The adsorption of asphaltenes on the rock surface is strongly influenced by the presence of a water film, which reduces asphaltenes adsorption."[39]

Acid and Base Number

"TAN - the total amount of potassium hydroxide (KOH) in milligrams required to neutralize one one gram of crude oil (ASTM D664);

whereas TBN is defined as the total amount of KOH in milligrams per one gram of crude oil (ASTM D2896).[64, 56] The base number, BN (mg KOH/g) "However, it was observed that the increase in a basic material improved the water wetness of chalk containing oil with a given AN (Puntervold et al., 2007 in [58]).

Asphaltene number

Asphaltenes can be classified as a solubility fraction of the crude oil. Generally, they are classified based on the n-alkane used to precipitate them (commonly, n-pentane, n-hexane or n-heptane). [15]

Several procedures was found to determine the asphaltene number to quantify the asphaltenes fraction for the crude oil, as an example ASTM D3279–97 for n-heptane based precipitation.

2.3 Produced water

Produced water is throughout the E&P cycle, a significant waste stream if seen over a life cycle of a reservoir.

Dealing with such volumes it is of critical importance to determine the correct disposal from environmental and economic point of view. Any operator would prefer the smallest environmental impact and lowest possible cost. Definition of produced water is the water fraction which is separated from the oil in separators at first and further separation via hydrocyclones and in some cases membranes. The produced water can be made up from both the original reservoir brine, and after waterflood break through there is a gradient of injection fluid as well in the composition.



Figure 2.4: Schematic Illustration of wells during a waterflood. Adapted from [57].

Components	Oil Field	Gas field
Suspended oil [mg/l]	30 (15-40)	40 (15-100)
Aliphatics $(< C_5)$ [mg/l]	1 (0-6)	1 (0-6)
Aliphatics $(\geq C_5)$ [mg/l]	5 (0-30)	10 (0-60)
BTX $[mg/l]$	8 (0-20)	25 (0-50)
Naphthalenes $[mg/l]$	1.5(0-4)	1.5(0-4)
Fatty acids $[mg/l]$	300 (30-800)	150 (0-500)
Phenols [mg/l]	5 (1-11)	5 (0-22)
Salinity [%]	3.5 (1-8)	0.5 (0.01-3)
Sulphate $[mg/l]$	500	50
Barium [mg/l]	30	10
Strontium [mg/l]	40	20
Calcium [mg/l]	450	400
Suspended solids [mg/l]	<2(1-20)	$<\!2$ (1-20)

Table 2.2: Comparison of an example of North Sea produced water composition for an oil and gas fields [6].

Table 2.3: Typical chemical additives present at North Sea oil and gas fields produced water [6].

Additives	Oil Field	Gas field
Corrosion Inhibitor	4 (2-10)	4 (2-10)
[mg/l]		
Scale Inhibitor [mg/l]	10 (4-30)	0
Emulsion Breaker [mg/l]	1 (0.1-2)	0
Coagulant $[mg/l]$	2 (0-10)	0
Biocide [mg/l]	0 (0-200)	0
Methanol [mg/l]	0	2000 (1000-15000)
Glycol [mg/l]	0	1000 (500-2000)

2.3.1 Treating Chemicals

Chemical additives are used in various stages of the production mainly to cover the main objective of safety and secondary flow assurance. For safety can be mentioned H_2S scavengers, which will work against the generation of H_2S . If H_2S is present at a high quantities it will compromise piping integrity due to heavy corrosive properties and if released to the air it will cause a health and safety violation.

Flow assurance is an objective that covers the main mission of being installed for producing hydrocarbons, under flow assurance can go piping integrity as components in the flow stream can cause scale and corrosion, and gas hydrates can be formed in a flash if the right components are in place to form gas hydrates. Flow assurance is an objective which can define all risks all together which can influence the stream of continuous flow of hydrocarbons.

2.4 Production and Recovery of Hydrocarbons

Any oil reservoir was water-wet prior migration of oil into the reservoir. Hydrocarbons have over millions of years, they are generated from a formation layer composed by various maturated types of sediment including live organisms such as algae. As formation layers on to increase the pressure and thereby also the temperature the algae start biodegrade and migrate upwards due to the lower density than water and formation rock. In practice these layers exist everywhere and do a migration, the hydrocarbon reservoir takes its origin under the perfect conditions of a reservoir rock having sufficient permeability and porosity for the hydrocarbon fluid to displace the saturated water in place. For the oil to be accumulated the condition of a cap is necessary, this can be from a fault or a shale cap or a salt dome.

The oil accumulates in a so called trap, and develops a reservoir suitable for recovery. The first stage of recovery is called primary recovery where the pressure of the reservoir is big enough to allow the oil to find way to production string and pressure itself to production separators.

When the pressure decrease and production rates fall below satisfactory levels a secondary recovery method can be utilized in terms of a gas lift mechanism.

The gas lift is assisting the hydrocarbons to flow upwards by decreasing the hydrostatic pressure and lifting the hydrocarbons from reservoir to production separators.

When the pressure is decreased in reservoir so the hydrocarbons will not move from reservoir to production string then a third recovery method will have to be introduced which can be water injection. The water injection is made from a nearby drilled well and a fluid is pumped down to pressure up the formation and create a water flooding towards the oil producer. In order for the flooding to work, the injected water will have to push hydrocarbons in front. It is here found that the it is vital to use brine compatible for the formation to make sure the recovery takes place and not plugging the formation by a collapse or escape of fluid.

During the life cycle of a reservoir when stages with gas lift and water injection have recovered the available oil an analyzing phase of appropriate suitable recovery campaigns the following table gives an overview of the selection of known EOR methods.

Main goal of an EOR method is to design a campaign which will have a long term effect, minimize reservoir damage, increase and optimize the oil recovery and at lowest possible cost. If methods can be categorized and evaluated in a risk assessment vs cost/benefit analysis then the most appropriate method will come forward.

The challenge is to fully understand the mechanism and the consequence behind an EOR method, as if a wrong methodology is used it can create reservoir damage or only have a short term effect on recovery. As an example can be mentioned use of plain seawater during early days of using injection wells, the sulfate content in seawater together with oxygen and bacteria created h2s in the reservoir with the consequence of having increased safety precautions on installation, and shorter life time of tubing and surface systems due to corrosion.

Another commonly used method is CO_2 injection, though this method have great environmental benefits as injecting co2 in reservoirs will remove CO_2 from atmosphere and make a reaction.

The EOR method of using smart water requires a vast understanding of surface chemistry, petrochemical properties, geological and ionic chemistry just to name a few. The challenging part of understanding smart water mechanisms is the fact there are no dominating factor which will dictate an enhanced recovery mechanism. It is interrelated between pH, temperature and pressure, ionic composition between injection fluid and formation brine,

in all addition its also related to the surface chemistry for the attachment of the oil to reservoir rock. The general term is to alter the wettability on the reservoir rock in order for the hydrocarbon to repel the surface and start migrating towards the producer for recovery. [12]

2.4.1 Wettability

For a liquid to stay on a surface it need to have an attraction, its commonly known that a water droplet on a surface which is water wet have a low angle, meaning the droplet is rather flat, if an oil droplet is pored on the same surface the droplet will be very round with a high angle to the surface, and effectively repel the surface and act as a rolling ball. This phenomenon can be explained by adhesive and cohesive forces and is determined by the contact angle.



Figure 2.5: Measurement of contact angles for water-oil systems [47].

Techniques to estimate wettability. [10]:

- 1. Direct optical methods;
- 2. Indirect force methods

Amott-Harvey method and the USBM method these methods are, however, industrial standards for core plugs and do not give a reliable result for other types of wettability phenomena [24]. For this study a recent method for screening to estimate wettability is going to be used - Modified Flotation Technique.

2.4.2 Wettability: Development and Modification Mechanisms

In carbonate reservoirs, theam concentration of Ca2+ in the formation water is usually high. Therefore, sulfate is often present as anhydrite, CaSO4(s), and due to a decrease in the solubility of anhydrite at high temperatures, the concentration of sulfate dissolved in the formation water, SO4 2-(aq), is usually low.

- 1. Potential Determining Ions (PDIs) and Multi-component ion exchange (MIE);
- 2. Double layer expansion;
- 3. pH effects;
- 4. fines migration, in case of sandstone reservoirs.

Surface charge

Electrical charge can occur on a surface when in contact with electrolyte solution, Sohal [59] identified three reasons:

- 1. Complexation reactions between surface and dissolved species;
- 2. Lattice imperfections and substitution with in the crystal lattice;
- 3. Dissolution of surface groups.

The calcite surface is characterized by two exposed surface sites Ca+ and CO3-, different versions of adsorption/adhesion of ions, organic molecules and other complexities; these aspects are pH dependent when relating to the surface charge. Essentially, the pH will neutralize surface charge by hydration. Further more, the charge stabilization depend, as well, on the brine composition. When a high saline brine surface is exposed to a significant amount of Ca^{2+} , Mg^{2+} and SO_4^{2-} , these ions compete for surface area and in this specific case pH do not affect surface area. Hence the change in pH does not affect surface charge though it is partly controlled by adsorption for the brine components.



Figure 2.6: Proposed chemical mechanisms for wettability alteration.going from Oilwet state to a more waterwet state. [87]

Double layer Expansion

The Electrical double layer expansion - DLVO theory.

The Ionic strength in a fluid can be defined as a concentration of species in a solution and depends on precent type of ions, hence charge of the ions present as in the electrolyte.

This parameter is considered to be one of the most important The factor affecting charged ions disturbs the pre-established equilibrium in the CBR system and strongly affects the surface charge of the rock [84].

DLVO theory states "the intermolecular surface forces play a significant role within wettability states. There are three different types of surface forces, either attractive or repulsive, governing this equilibrium, namely [17]:

(1) Van der Waals forces, (2) electrostatic forces, (3) structural or solvation forces.

On the basis of the theory of colloidal stability, the total disjoining pressure, which represents the interactive forces between the interface of water-oil and water-rock, derives from the summation of Van der Waals (VDW) and electrostatic forces (EF). The Van der Waals forces are a result of a dipole-dipole interaction and is generally known to be stronger than a London dispersion force. [84, 59]. The formulas to estimate each force are presented in [17].

DLVO theory defines a sum of colloidal particles are larger than electrolyte ions, which confirms the description of the interaction between surface and particle [55]. This statement supports the description of disjoining pressure as a function of surface force per unit area [59]. The total disjoining pressure calculation can be done following the equation 2.4.1 detailed in the next section.

Sohal, 2016 [59] defines that: "A high TDS value or a high concentration of divalent ions compressing the EDL. Then the pattern would create an unstable water film, and allow an oil-wet state of the rock." Furthermore, it also stated that "increase in electrolyte concentration decreases the range of electrostatic repulsion and Van der Waals attractions become more relevant" [59].

Ionic Strength and Surface Forces

Ionic strength is the quantification of the concentration of species in a solution. This parameter is considered to be one of the most important factors that disturbs the preestablished equilibrium in the rock-water-oil system and strongly affects the surface charge of the rock [84] in [17].

The intermolecular surface forces are considered major influencers in what concerns the different states of wettability, as previously mentioned. The total disjoining pressure (Total DP) which defines the interactive forces between the interface of water-oil and water-rock, stems from the combination of Van der Waals (VDW) and electrostatic forces (EF). However, the intervening role of the structural forces (SF) have been found also relevant at a later stage, in order to try to overcome the limitations found in the DLVO theory [84, 59, 17]. The disjoining pressure describes the surface force per unit area [59] and is given by equation 2.4.1 (based in [17]):

$$\prod_{TotalDP} = \prod_{VDW} + \prod_{EF} + \prod_{SF}$$
(2.4.1)

A positive total DP exists when two interfaces show a tendency to separate or disjoin from each other, on the contrary a negative disjoining pressure is representative of the attraction between two interfaces [34]. The disjoing and attractive behaviours will condition the thickness of the EDL and therefore determine the wettability of the rock surface.

Such forces describe the flocculation and stability of lyophobic colloids by the means of Van der Waals and electrostatic forces [34]. Additionally, the total disjoining pressure is the sum of attractive and repulsive forces. [59] With respect to wettability, it is vital to mention following types of forces [15]:

- 1. London dispersion forces (long ranged forces);
- 2. Short-ranged forces;
- 3. Keesom forces originating from Coulombic forces;
- 4. Debye interactions.

London dispersion forces are divided as follows:

- 1. Electrostatic forces;
- 2. Dipole moments;
- 3. Dispersion forces.

Deryaguin-Landau-Verwey-Overbeek (DLVO) theory of colloids. Stating, "the permeability reduction occurs if the ionic strength of the injected brine is equal to or less than, the critical flocculation concentration (CFC), which is strongly dependent on the relative concentration of divalent cations such as Ca2+ and Mg 2+" [11, 12].

Lowering the Zeta potential by introducing Divalent cations have been known to stabilize the clay by in the lowering of the repulsive force. Also Bazin and Labrid [13] Indicated that "water sensitivity is related to the cation exchange capacity (CEC) of clay sandstones". Stating "high CEC sandstone will lead to a high potential for permeability reduction". [41]

pH Effects

"Normally, advanced water is characterized by pH greater than 7. The high pH values increase the oil recovery by changing the carbonate surface charge. It has been observed in zeta potential measurements that increasing the pH value of advanced water changes the surface charge of both rock-brine and oil-brine interfaces. Mahani et al.(in [59], have referred that upon low concentration of PDIs in brine (*s.l.*) and so low ionic strength, the H^+ and OH^- ions are the ones controlling the surface charge. [59]

It is pre assumed that the smart water will increase the pH once exposed to reservoir fluid.

2.5 Analytical Techniques: brief theoretical background

This section intend give a basic insight regarding the analytical techniques that have been used during this thesis.

2.5.1 Solid Phase Micro Extraction (SPME)

This technique was used to extract sample.

It is effective and fast sample preparation method, which is based by analytes sorption on the thin fiber layer deposed on quartz spool placed in the hollow needle. It is solvent free method, that is why it can be combined with the gas chromotography, where analytes thermal desorption happens in the chromotograph evaporator.

Features that can influence solid phase micro extraction [51]:

- 1. extraction solvent volume (thickness and with); solvent coating quality (crackings and so on);
- 2. extraction temperature:
- 3. mixing.

All of the above-mentioned parameters have to be constant to achieve in order to achieve repeatability of the results.

2.5.2 Gas Chromatography and Mass Spectrometry (GCMS)

Gas Chromatograpgy (GC) is one of chromatography types where mobile phase is carrier gas, see Figure 2.7. Most often is used inert gas as helium. During GC small hydrodynamic resistance of the column is formed and significantly higher diffusion coefficients for mobile phase. Injected sample is moved by carrier gas to long capillary column, which is constantly thermostatic in high temperature oven.

Mass Spectrometry detector(MS) is used to define compounds composition when the structure of compound is unknown, see Figure 2.8. All compounds that ionize and which ions can exist in the gas phase with this method. Molecules are bombarded by electrons until is composed ion fragrances, which fall in spectrometer mass filter. Ions are filtered according they mass and charge ratio (M/Z). According M/Z ratio in the sample is drawn mass spectre and it is compared with data library identified components.



Figure 2.7: Gas Chromatography schematic

2.5.3 Inductively Coupled Plasma and Mass Spectrometry (ICPMS)

Inductively Coupled Plasma is method used in analytical chemistry for heavy metals to detect inorganic elements. This is achieved by using high temperature inductively coupled plasma and than detecting quantity of separated ions in the mass spectrometer. One of its main advantage is that ICPMS accounts for the isotopic speciation.

This technique was used as a confirmation method for the results obtained using the titration method for the crude oil AN and BN.

2.5.4 Zeta Potential

The Zeta potential also known as the electrokinetic potential for colloidal solutions, can be defined as the potential difference between the mobile dispersion medium and the stationary layer of the dispersion medium attached to the dispersed particle. The most important factor that affects zeta potential is the pH of the medium. Other factors include ionic strength, the concentration of any additives, and temperature.[76] The calcite zeta potential is mainly dependent on the adsorption of ions, such as, Ca^{2+} , Mg^{2+} and CO_3^2 in the Stern layer (the inner part of the EDL). At the high Ca^{2+} and/or Mg^{2+} concentration typical of formation brines, the zeta potential of the calcite surface is positive. Reduction of Ca^{2+} and/or Mg^{2+} concentration, either selectively or by bulk dilution, can invert the polarity, leading to a negative zeta potential. [37]



Figure 2.8: Mass Spectroscopy schematic

Zeta Potential is calculated using the Helmholtz-Smoluchowski equation 2.5.1, which is defined as follows [81]:

$$\zeta = \frac{dU}{dP} \times \frac{\eta}{\varepsilon_0 \times \varepsilon} \times \lambda, \tag{2.5.1}$$

where ζ is the zeta potential, dU is the voltage differential, dP the differential Pressure, η the viscosity, ε the dielectric coefficient of electrolyte, ε_0 the relative permittivity of the solution and λ the electrical conductivity of the solution.

3 Experimental Work

3.1 Experimental Materials and Techniques

The screening method using modified flotation technique are applied in a study with field samples where it is investigated what is the actual influence of wettability in the reservoir using the specific crude oil produced on the field and using the actual fluids injected.

For the study it was taken into account the variables of different types of chalk and a range of compositions of injected brine for the purpose of identifying parameters and behaviours which can alter the wettability.

The benchmark in the project is previous studies made in the department with other known crude oil, synthetic formation brines and known designs of synthetic seawater smart brines. The purpose of comparing is to identify the reality of wettability alteration with current use of fluid and in different mixtures, against results of applying designed brines with controlled ionic modification. the initial state as a screening method is used to clarify wettability at various ionic concentrations and conditions.

To eliminate as many variables as possible the constants will be chalk grain size to be less than 100 microns, this is to ensure the smallest possible surface area to each particle and as the idea behind the flotation technique is to allow water wet particles to settle at bottom and oil wet particles to float. The conclusions from previous studies have identified that the discipline around handling chalk correctly is a vital element for precision and keeping the standard deviation as low as possible for the weight percentage. The chalk is handled carefully to avoid contamination, the chalk was prepared by grinding in a morter and sief throughfind screens and dried thouroughly to ensure no moist present in chalk which can falsify the weighing and thereby the end results.
The flotation study is emphasizing on known temperature and known pH, neglected are pressure (no means of control or measure), porosity and permeability (chalk is fine grind for this elimination).

Table 3.1: Chemical composition of the rock types under investigation. Results provided by XRF analysis.

Component	Dan Chalk	Sandstone
CaO [mass %]	95.3	1.07
$MgO \ [mass \ \%]$	-	0.481
Al_2O_3 [mass %]	0.439	12.3
SiO_2 [mass %]	3.30	79.6
$P_2O_5 \text{ [mass \%]}$	0.346	-
K_2O [mass %]	0.127	4.11
$SrO \ [mass \%]$	0.432	0.155
Fe_2O_3 [mass %]	-	1.42
$SO_3 \text{ [mass \%]}$	0.0591	0.602
Cl [mass $\%$]	0.0125	0.280
Total [mass %]	100.016	100.018

3.1.1 Modified Flotation Technique (MFT) Procedure

The screening technique using the modified flotation technique the technique is to isolate and vary parameters such as presence of $Mg^{2+} Ca^{2+}$, SO_4^{2-} and influence of pH, the study do not intend to alter on pH but it is measured in order to confirm the pH changed. The flotation is proven to give an indication of a wettability state on a given type of chalk exposed to a formation brine and a crude oil.

The water-wet fraction is determined by a weight of the particles which have sunken to the bottom of the test tube, the particles which have an adhesion to water will sink to

$\mathbf{Density} \left[\mathbf{g} / \mathbf{cm}^3 \right]$					
Dan Chalk Sandstone					
0.709760	0.667178				

Table 3.2: Density of the rock types under investigation.

the bottom and the partition of the rock sample which is attracted to oil will float and thereby represent an oil wet fraction of the chalk sample.

The procedure of flotation experiment consists of multiple stages (see Figure 3.1), as follows (adapted from [16]):

- 1. 1 gram of rock (grain size $<100\mu$ m) is aged for a period of 24h in 10 ml of smart brine at temperature of interest (in the present case 90°C). The test tube is shaken in a vortex shaker after addition of smart brine;
- 2. The column of smart water, above the saturated rock powder is decanted and sealed in a tube for pH measurement;
- 3. Smart water-wet grains are then aged with a 5 ml sample of crude oil for 24h at the same temperature of interest;
- 4. After the aging procedure, the decanted smart water is poured into the test tube and gently shaken;
- 5. Mixture of rock, water and oil is allowed to settle for more than 18h;
- The floating grains (oil-wet) are removed and the walls are rinsed with DI water. This step is repeated a couple of times to ensure that the maximum amount of oil-wet grains are removed;
- 7. The test tube containing the water-wet grains is dried at 100°C;
- 8. The dried and cooled test tube is weighed;
- 9. After the previous step, it is important to recognize that the water-wet grains present are partially coated with oil. To remove the coating of oil ca. 3-5ml of pentane is added to the tube, the tube is shaken and the dissolved oil is decanted. This step is repeated until the oil is removed;
- 10. The tube is dried in the oven at a temperature of approximately 38°C;
- 11. The tube is cooled and weighed.

The above described MFT procedure allows modifications in the steps 1 to 4, if one intends to perform aging of the rock sample with formation brine and only at a later stage introduce the smart brine. Details on the this variant of MFT procedure can be found in [16].



Figure 3.1: MFT Laboratory Procedure. The drop shape represent the addition of smart brine (blue) and crude oil (brown). Oven temperature is 90°C. [16]

3.1.2 Brines (s.l.) composition and preparation

In preparation of the lap tests the samples was collected from a field in the North Sea, where at the same time it was taken a produced water sample after hydrocyclone prior injection. Crude oil sample was taken at export line, to achieve lowest possible water content.

In order to compare results with previous studies done by Sohal et al. The current project has as one of the main objectives to investigate the wettability modification of the reservoir rocks upon interaction with brines (s.l.), which differ in composition and origin. The 16 types of brines (s.l.) tested in various combinations are named as shown in Table 3.3.

The preparation of synthetic brines (s.l.) was based on published composition [59, 17] for a reference volume of 1 liter and ambient temperature. Tables 3.4 to 3.6 present the composition of the synthetic brines (s.l.) and following steps were used in order to prepare them:

- 1. Chloride salts are diluted in ca. 400 ml of DI water;
- 2. Sulfate salts are diluted in ca. 200 ml of DI water;
- 3. Carbonate salts are diluted in ca. 200 ml of DI water;

Types of Brines (s.l.)	Origin
LSSW	North Sea
PW	North Sea
EFW	Synthetic
SW	Synthetic
SW2x	Synthetic
SW10x	Synthetic
SW20x	Synthetic
SW50x	Synthetic
SW100x	Synthetic
$SW * SO_4 * 0Ca$	Synthetic
$SW * SO_4 * Ca$	Synthetic
$SW * SO_4 * 2Ca$	Synthetic
$SW * SO_4 * 4Ca$	Synthetic
$SW * SO_4 * 0Mg$	Synthetic
$SW * SO_4 * Mg$	Synthetic
$SW * SO_4 * 2Mg$	Synthetic

Table 3.3: Origin of the brines under investigation.

4. The brines (s.l.) are mixed into a volumetric flask and 200ml are added;

5. The solution is stirred until the salts are fully dissolved.

Synthetic brines were prepared with different concentration of magnesium, calcium and sulfate components, for various mixtures.

It was attempted to determine the ionic and chemical composition of produced water and LSSW, some components was identified with the XRF spectroscopy.

3.1.3 Gas Chromatography and Mass Spectrometry (GCMS)

GCMS was used to clarify organic components present in PW and LSSW North Sea samples. The results were obtained in cooperation with E. dos Santos Godinho [16], and procedure described bellow was followed:

Salt	Concentration (g/l)
NaCl	23.38
Na_2SO_4	3.41
$NaHCO_3$	0.170
KCl	0.750
$MgCl_2 \times 6H_2O$	9.05
$CaCl_2 \times 2H_2O$	1.91
TDS	38.670

Table 3.4: Synthetic seawater recipe.

Table 3.5: Synthetic seawater, zero sulphate recipe.

Salt	Concentration (g/l)
NaCl	23.38
Na_2SO_4	0
$NaHCO_3$	0.170
KCl	0.750
$MgCl_2 \times 6H_2O$	9.05
$CaCl_2 \times 2H_2O$	1.91
TDS	35.26

Table 3.6: Ekofisk formation water recipe.

Salt	Concentration (g/l)
NaCl	67.3
$NaHCO_3$	0.332
KCl	0.549
$MgCl_2 \times 6H_2O$	4.45
$CaCl_2 \times 2H_2O$	14.69
$BaCl_2 \times 2H_2O$	0.45
$SrCl_2 \times 6H_2O$	2.270
Na_2SO_4	0.0
TDS	90.041

Ions	Concentration (ppm)
Na ⁺	19200
Cl ⁻	34900
K^+	310
Ca^{2+}	2320
Mg^{2+}	445
Ba^{2+}	285
Sr^{2+}	235
SO_{4}^{2-}	12

Table 3.7: North Sea Produced Water Ionic Composition.

- 1. A sample (ca.20ml) was taken and inserted into a sealed tube (the lid should allow perforation) and heated up to 50°C for 30 minutes;
- 2. Meanwhile, the GCMS was set to the operating temperature of 40°C.
- 3. A blank sample was run to check if the GC column was clean;
- 4. The SPME was inserted through the lid and the fiber exposed to the vapors for 10 minutes;
- 5. SPME was inserted into the injection port and the GCMS run for 20minutes;
- 6. The spectra were obtained and analyzed.

From the analysis of the GCMS spectra the following organic components were identified:

- PW: showed abundant organic components given aromatics hydrocarbons, in a smaller extent alcohol groups (e.g. Isooctyl alcohol), limonene and phenols.
- LSSW: showed the presence of long chain alkanes, such as hexadecane and some alcohol groups (once again Isooctyl alcohol) and aldehydes (e.g. hexanal and Butanal,4hydroxy-3-methyl) as the most abundant organic compound.

3.1.4 Crude Oil Density and Acid and Base Number

Crude oil density was determined by using Anton paar DMA35 portable density meter, whereas AN, BN were determined using Metrohm autotitrator tiamo 2.4 following the

AN (mgKOH/g)	BN (mgKOH/g)	Density @ 25°C
		(g/cm^3)
0.2	0.2	0.834

Table 3.8: Properties of Crude Oil from a North Sea reservoir)

Metrohm OIL PAC methods 1/2 and 4/5 for estimation of the BN and AN, respectively.



Figure 3.2: Titration Results for Acid Number, where U is the potential (mV), V is the added volume of titrant and EP stands for equivalence point.



Figure 3.3: Titration Results for Acid Number, where U is the potential (mV), V is the added volume of titrant and EP stands for equivalence point.

3.1.5 Crude Oil Asphaltene Number

Research to determine the asphaltene number did not give a specific standard for a test procedure, a methodology of using pentane as a method to separate heavy components from light and it is anticipated the settlement is asphaltene components therefore the weight percentage of settling out is concluded to be asphaltene and thereby the fraction of weight percent is given as the asphaltene number. See below the detailed procedure applied [16]:

- 1. Shake the crude oil container and measure one part of crude oil (8ml);
- 2. Weigh an empty centrifugation tube (W1), tare, and pour the measured crude oil into it and weigh the mass of crude oil (M_{co}) ;
- 3. Measure four parts of pentane (4x8ml = 32ml) and add it into the centrifugation tube;
- 4. Shake the mixture in a vortex shaker for 10secs;
- 5. Centrifuge the mixture for 2hours at 5000rpm;
- 6. Remove the liquid fraction (mixture of pentane + light hydrocarbons) using a pipete;
- 7. Place the tube without the lid inside the fume hood and allow the remaining pentane to evaporate (ca. 10 minutes);
- 8. Weigh the tube + solid fraction (asphaltenes)(W2);
- 9. Calculate the asphatenes mass using the equation 3.1.1;
- 10. Calculate the average mass of asphaltenes;
- 11. Calculate the percentage of asphaltenes using the equation 3.1.2.

The asphaltenes mass for each sample can be roughly estimated using the following equation:

Asphaltenes mass (g) =
$$W1(g) - W2(g)$$
 (3.1.1)

The asphaltenes percentage can be roughly estimated using the following equation:

$$\% \text{ Asphaltenes} = \frac{Average M_{As} * 100}{M_{Co}}$$
(3.1.2)

3.2 Ionic concentration and composition of the brines (*s.l.*)

The composition of ions and the related strength and activity have proven to have a significant effect on the wetting state. It is one of the main hypothesis of understanding wettability that the control of ions and understanding the influence in the reservoir state will increase the sweeping effect.

the elements in ionic bonds is a reaction between positive charged cations and negatively charged anions. When dissolved in a fluid the ions are allowed to dissociate and can conduct electrical current also called electrolysis.

The saturation point is calculated from Total dissolved solids and is the sum of salt present in aqueous phase, see sequence for calculation procedure below.

- 1. Knowing the molecular weight of particular salt and the amount of mass added to the solution, one can calculate the molarity;
- 2. According to the general dissociation theory, the amount of moles of each dissociated cation and anion is calculated;
- 3. The total amount of each cation and anion is summed;
- 4. TDS is equal to the sum of total amount of salts added to the aqueous phase.

Ionic strength is used to express the ionic composition of the solution. The equation 3.2.1 used to determine the ionic strength:

$$\mu = \frac{1}{2} \sum_{i} c_i z_i^2, \tag{3.2.1}$$

where μ is the ionic strength in (mol/l) c_i is the concentration of the ion (mol/l) and z_i is the charge of the ion. The calculated molar concentrations, ionic strengths, TDS and densities are shown in Table 3.9. The ionic composition and strength for brines (*s.l.*) containing different chemicals is constant and independent of the type of added chemical, as these are organic compounds and do not contribute to the ionic strength.

Brines (s.l.)	Na (mmol/l)	Cl (mmol/l)	K (mmol/l)	Mg (mmol/l)	Ca (mmol/l)	Ba (mmol/l)	Sr (mmol/l)	SO₄ (mmol/I)	HCO₃ (mmol/l)	TDS (g/L)	Ionic strength (mol/I)	Density (g/cm ³)
SW	450.11	525.14	10.06	44.51	12.99	0.00	0.00	24.01	2.02	38.67	0.66	1.02
SW 2x	225.05	262.57	5.03	22.26	6.50	0.00	0.00	12.00	1.01	19.34	0.33	1.01
SW 10x	45.01	52.51	1.01	4.45	1.30	0.00	0.00	2.40	0.20	3.87	0.07	1.00
SW 20x	22.51	26.26	0.50	2.23	0.65	0.00	0.00	1.20	0.10	1.93	0.03	1.00
SW 50x	9.00	10.50	0.20	0.89	0.26	0.00	0.00	0.48	0.04	0.77	0.01	1.00
SW 100x	4.50	5.25	0.10	0.45	0.13	0.00	0.00	0.24	0.02	0.39	0.01	1.00
EFW	1155.56	1423.31	7.36	21.89	99.92	1.84	8.51	0.00	3.95	90.04	1.56	1.06
PW	835.15	984.49	7.93	18.31	57.89	2.08	2.68	0.12	0.00	65.20	1.08	1.04
75%PW+25%LSSW	726.88	869.65	8.46	24.86	46.66	1.56	2.01	0.11	0.51	57.72	0.95	1.03
50%PW+50%LSSW	618.62	754.81	8.99	31.41	35.44	1.04	1.34	0.10	1.01	50.23	0.83	1.03
25%PW+75%LSSW	510.36	639.98	9.53	37.96	24.22	0.52	0.67	0.08	1.52	42.75	0.71	1.02
LSSW	402.09	525.14	10.06	44.51	12.99	0.00	0.00	0.07	2.02	35.26	0.58	1.02
50%PW+50%SW	642.63	754.81	8.99	31.41	35.44	1.04	1.34	12.07	1.01	51.94	0.87	1.03
50%LSSW+50%SW	426.10	525.14	10.06	44.51	12.99	0.00	0.00	12.04	2.02	36.97	0.62	1.02
SW*0SO 4	402.09	525.14	10.06	44.51	12.99	0.00	0.00	0.00	2.02	35.26	0.58	1.02
SW*0SO4*0Ca	402.09	499.16	10.06	44.51	0.00	0.00	0.00	0.00	2.02	33.35	0.55	1.02
SW*0SO4*Ca	402.09	525.14	10.06	44.51	12.99	0.00	0.00	0.00	2.02	35.26	0.58	1.02
SW*0SO4*2Ca	402.09	551.13	10.06	44.51	25.98	0.00	0.00	0.00	2.02	37.17	0.62	1.02
SW*0SO4*4Ca	402.09	603.09	10.06	44.51	51.97	0.00	0.00	0.00	2.02	40.99	0.70	1.02
SW*0SO4*0Mg	402.09	436.11	10.06	0.00	12.99	0.00	0.00	0.00	2.02	26.21	0.45	1.02
SW*0SO4*Mg	402.09	525.14	10.06	44.51	12.99	0.00	0.00	0.00	2.02	35.26	0.58	1.02
SW*0SO4*2Ma	402.09	614.17	10.06	89.03	12,99	0.00	0.00	0.00	2.02	44.31	0.72	1.02

Table 3.9: Ionic Composition (mmol/l), ionic strength (mol/l), TDS (g/l) and density for brines (s.l.).

3.3 Brines (s.l.) density and pH

pH for brines (s.l.) used pH/Conductometer Metrohm 914. pH meter calibrated with buffer pH=4 and pH=7 at 23°C. Calibration curve checked prior measurements.

Anton Paar DMA 35 portable density meter (accuracy $0.001 \ g/cm^3$, reproducibility $0.0005 \ g/cm^3$). The pH and density measurements for the brines (*s.l.*) are presented in Table 3.10.

Le Chatelier's principle or equilibrium law, "when any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, the system readjusts itself to counteract (partially) the effect of the applied change and a new equilibrium is established". If temperature is changed the equilibrium state is changed as well. The consequence of

This behaviour can be denoted by analyzing the table 3.10.

Note that in pure water and temperature of $25^{\circ}C$, $K_w = [OH^-] = [H3O^+] = 10^{-14}$.

The proton exchange during autoionization of water can be written as the following bal-

Brine (s.l.)	Brine (s.l.) Density (23ºC)		Avg. pH decanted brine (90°C)		
SW	1.022	7.55	7.80		
SW 2x	1.013	7.84	7.82		
SW 10x	1.001	7.35	8.12		
SW 20x	0.999	6.91	8.26		
SW 50x	1.000	6.72	8.37		
SW 100x	0.998	6.81	8.54		
EFW	1.056	7.22	1.20		
LSSW	1.018	7.53	7.64		
PW	1.041	6.70	6.82		
75%PW+25%LSSW	1.034	6.83	7.17		
50%PW+50%LSSW	1.032	7.83	7.10		
25%PW+75%LSSW	1.024	7.88	7.42		
50%PW+50%SW	1.031	7.69	7.02		
50%LSSW+50%SW	1.020	8.09	7.52		
SW*0SO4*0Ca	1.018	7.48	7.87		
SW*0SO4*Ca	1.019	7.36	7.59		
SW*0SO4*2Ca	1.021	7.80	7.33		
SW*0SO4*4Ca	1.022	7.49	7.27		
SW*0SO4*0Mg	1.016	7.47	7.66		
SW*0SO4*Mg	1.019	7.39	7.65		
SW*0SO4*2Mg	1.022	7.10	7.60		

Table 3.10: Density and pH measurements for the brines (s.l.) at 23°C and 90°C (after interaction with reservoir rock sample).

anced equation [3]:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
(3.3.1)

3.4 Reservoir rock water and oil-wet fractions

The data needed to calculate water and oil wet fraction was collected during the experiment by high precision weight (+- 0,0005g tolerance) and calculated using teh following equations.

Water-Wet
$$\% = \frac{\text{weight of water-wet particles } (g) \times 100}{\text{initial weight of rock particles } (g)}$$
 (3.4.1)

Oil-Wet $\% = \frac{\text{weight of oil-wet particles } (g) \times 100}{\text{initial weight of rock particles } (g)}$ (3.4.2)

4.1 General Principles

The modified flotation technique was chosen based on the leanings from Sohal [59].

Objective to use the screening method is to compare and evaluate the wetting properties with controlled variation of the parameters, such as the quantity and type of ions $(Ca^{2+} \text{ and } Mg^{2+} \text{ and sulphate})$ present in a range of concentrations which will enable the investigation of the impact on water wettability as a function of weight percent.

A total of 10 sets of experiments were carried out. Evaluation of the reservoir rock between two different chalks was briefly covered to correlate influence between chalk composition and water wettability. Aditionally, a set of tests was run on sandstone to investigate effect linked to the presence of clays. During laboratory experiments two different temperatures were considered: 90 degrees celcius and 115 degrees celcius. Between the two temperatures it was varied the formation brine as well, where for the run of 90 degrees the chalk was exclusively matured in the smart brine used. Which might create a unknown parameter variation as the chalk did not mature in the exact same way. Whether this is of significance to the end result can be discussed, but in fact, such is not a homogeneous base achieved for the preparation.

For the 115 degrees sets all chalk samples were matured with synthetic ekofisk formation brine.For this test it was given an homogeneous base for the start, though, it can be argued whether the original formation brine in place is representative of the actual current "as it is" state condition.

For the understanding of the objective of a current state it is vital to follow and document the historical timeline of a given reservoir. First oil and production in primary recovery phase is of course to compare with an untouched virgin reservoir, though as soon as the secondary recovery methods are being used there will occur some alterations in the formation brine composition with the waterflood interaction of the injected fluid. Therefore, it is crucial to have a current state understanding of an ionic composition of the well fluid. The reason is to understand the saturation point at different stages through out the reservoir and ensure the testing design is as close as possible to the actual state.

	Reservoir Rock					
Brines (s.l.)	Dan Chalk (T= 90°C)	Dan Chalk (T= 115°C)	Sandstone (T= 115°C)			
SW	×	28 3 3	-			
SW 2x	× .	2242	-			
SW 10x	×	323				
SW 20x	×	128	25			
SW 50x	~	1.5%	2			
SW 100x	~	10.52	1			
LSSW	×	1970	-			
PW	×	3 9 3				
75%PW+25%LSSW	×	(14)	-			
50%PW+50%LSSW	×		√			
25%PW+75%LSSW	×	323				
50%PW+50%SW	×	122	~			
50PW%+50%LSSW	~	1.5%	2			
50%SW+50%LSSW	~	10.52				
EFW+LSSW		~				
EFW+PW	0.00	~				
EFW+75%PW+25%LSSW		1				
EFW+50%PW+50%LSSW	-	~	~			
EFW+25%PW+75%LSSW	100	×	-			
EFW+50%PW+50%SW	-	1	~			
SW*0SO4*0Ca	~	1976	2			
SW*0SO4*Ca	~	1070	5 53			
SW*0SO4*2Ca	×	1000	-			
SW*0SO4*4Ca	×	() * ()	÷			
SW*0SO4*0Mg	×	(14)				
SW*0SO4*Mg	×	1.4	-			
SW*0SO4*2Mg	V	528				

Table 4.1: Laboratory experiments used in current study, in which different brines (s.l.), temperatures and reservoir rock samples were investigated.

The mixtures of brines and the reservoir rock exposure is summarized in Table 4.1. For this study, a temperature of 90C was selected in order to favour a less than boiling point, though when heating up the closed test tube pressure will be created which might induce an increase in boiling point; this is not accounted for in any evaluation of the study. The saturation of the chalk was done with the mixture of brine prepared, so one homogeneous fluid was mixed with chalk and exposed for hydrocarbons to determine wettability at 90 C.

In comparison to the lab studies made by Godinho 2017 [16] for mixtures with Ekofisk formation brine and at a temperature of 115C. This study takes in favour original formation brine in place, allowing the chalk to be matured in formation brine, and mixed with hydrocarbons, for hereafter to be exposed to the injected brine of a variation of mixtures to see the effect of wettability.

As an addition the most promising mixtures of fluids were mixed and applied in sandstone in order to see the wettability properties and give an opportunity to elaborate on the variations between two different reservoir rock types.



4.2 Synthetic Seawater and diluted SW as Smart Water

Figure 4.1: Dan Chalk wettability alteration upon interaction with non-diluted synthetic SW and 2x, 10x, 20x, 50x and 100x diluted SW at $90^{\circ}C$.Error bars represent the standard deviation (in percent) of the data.

Testing synthetic seawater and diluted SW (Figure 4.1) as smart water shows in the study that the highest achieved wettability was achieved with a Synthetic seawater diluted 10 times with distilled water, resulting in a wettability of approx 57,5% with a standard deviation around 1 shows a result with high confidence level. The test set for SW diluted 20 times its seen the wettability properties dropped to about 50% for this test run the standard deviation was above 3 which indicates the variation and confidence is slightly lower, though the trend is clear and confirms results from studies from Sohal 2016, who mention a decrease in water-wet fraction at 20x dilution.



Figure 4.2: Dan Chalk Water-wet fraction and Variation of Ca, Mg and SO_4 ions for nondiluted synthetic SW and 2x, 10x, 20x, 50x and 100x diluted SW at $90^{\circ}C$.

As it is known from the research the presence of Mg^{2+} and Ca^{2+} and SO_4^{2-} will alter the water wettability. Current study investigated the water-wetness fraction as a function of the concentration of Mg^{2+} , Ca^{2+} and SO_4^{2-} each of them as isolated variation (see Figure 4.2). From the analysis of the graph can be seen that Ca^{2+} achieves the wettability of 57% with the lowest concentration of around 1 mmol/l, the presence of SO_4^{2-} in the smart brine alter the water wettability to 57%.

If taking the data of a pH and keeping it up against the TDS concentration and plotting



Figure 4.3: Dan Chalk wettability dependency on TDS (g/l) and pH of Ox, 2x, 10x, 20x, 50x and 100x diluted SW at $90^{\circ}C$.

the determined average water wettability in % the curves plotted as a function of TDS and pH following the yellow line with the pH increasing as the dilution of the synthetic SW takes place, the pH is expected to increase as the presence of ions will decrease and therefore less carboxylic groups to react. from the point of SW x0 dilution to SW x2 dilution there are no signs of increase in pH nor in the change of TDS in the fluid, but a significant decrease in the average waterwetness state. Following the green curve for TDS (4.3) it is as expected with a dilution that the concentration of TDS will decrease, on the plot its decreasing 39 g/l down to 19 g/l which with the dilution gives an expected decrease of of concentration of 50% and follows the trend of water-wettability as its taken out of the same context as the pH. When diluting the brine x10 it is observed that the pH increases from 7,82 to 8,13 this can be explained by the change in the ionic charge equilibrium which interacts on the surface on the chalk surface. When the test fluid is diluted 20x and above it is observed the waterwetness is further decreased and indicates further increase of pH, little decrease in the concentration of TDS which indicates there at this stage is from 10x dilution to 20x dilution is the most significant decrease of waterwetness but pH increasing from 8,12 to 8,27 and concentration of TDS only decreases from 4,2g/l to 4 g/l this can

be explained by

4.3 Wettability alteration by Ca and Mg ions

Isolating the variation of Ca^{2+} and Mg^{2+} the graphs, see Figures 4.4 and 4.5, for increasing calcium shows a decreasing trend of wettability when increasing Ca^{2+} concentration from 0 to $2x Ca^{2+}$ concentration (compared to original synthetic SW recipe) for the 4x calcium concentration the wettability property is at the highest of a 59% As concluded in Zhang et al.[87] to improve water wettability and thereby oil recovery, sulfate has to be present to act with Ca^{2+} and/ or Mg^{2+} . The activity and waterwetness is stated in the conclusion of Zhang et al.[87] to increase as temperature increases, so the flat trend in the water wettability could be an expression of lack of sulphate.



Figure 4.4: Dan Chalk wettability variation upon interaction with non-diluted synthetic SW zero sulfate, which has and Ca at various ratios. Aging temperature is $90^{\circ}C$. Error bars represent the standard deviation (in percent) of the data.



Figure 4.5: Dan Chalk wettability variation upon interaction with non-diluted synthetic SW zero sulfate, which has and Mg at various ratios. Aging temperature is $90^{\circ}C$. Error bars represent the standard deviation (in percent) of the data.

4.4 Produced Water and Low Sulfate Seawater altering wettability

One of the main objectives in this study is to determine what produced water does to the wettability in the reservoir and determine if the produced water can be seen as an asset and worth handling as a part of a EOR objective.

When looking at Figure 4.7 it is clearly seen that the test tubes with low sulphate seawater will only allow a low degree of water wetness, which support the widely understood mechanism of a no presence of sulphate will lower the wettability as the SO_4^{2-} works as a catalyst for the Ca2+ and Mg2+ interaction between the surface of the chalk and the carboxylic groups attached to the chalk surface.

The test run to see wettability using the Dan chalk (see Figure 4.6) as a reservoir rock and produced water Low salinity seawater and synthetic seawater, its seen on the graph that with low salinity seawater it gives a poor wettability could be due to missing catalyst as sulphate to free hydrophilic groups from chalk surface. Produced water can be observed as giving the highest possible water wettability, in the produced water there is measured from



Figure 4.6: Dan Chalk Wettability for various ratios of PW, LSSW and SW, after Ekofisk Formation Water aging (T=90°C). Error bars represent the standard deviation of the data in percent.

sample point provider a very low content of oil (less than 10 ppm) though the aromatic compounds and chemical components that can influence the wettability.

For the unknown chalk investigated in Godinho 2017, see Figure 4.7, investigation of the chalk showed a big variation in wettability where the correlation between the test runs is significant, though the standard deviation is low, emphasizing on trust worthy results. The range from the lowest wettability with 50% PW/50% SW where wettability is about 68% against 50% LSSW / 50% SW. Difference in the two sets is components in PW such as SO_4^{2-} and from the ionic composition from measurements it is seen that there is a presence of 0,1249 mmol/l. As in the compositions there are only Cl- and SO_4^{2-} are the only anions in the test fluid and between the two tests the Cl- is present in both, so unless there are a chemical reaction which will alter the wettability then it must be concluded that a very small presence of SO_4^{2-} will catalyze the wettability on the chalk. If comparing the results between 75% PW / 25% SSW and 50% PW / 50% LSSW it is seen that with the reduction of PW concentration VS LSSW concentration it is improving wettability from 59% to 68%if the same objective is taken of SO_4^{2-} taken as catalyst it can be argued that a presence of 0,0625 mmol/l SO_4^{2-} is optimal catalyst conditions, this is given for the concentrations of 57,88 mmol/l Ca^{2+} and 18,3 mmol/l Mq^{2+} present in the PW composition (Table 3.9) which is then diluted back with 50% SSW. which for this test run gives optimal conditions. When compared to the mix of 25% PW and / 75% SSW then if the SO_4^{2-} is seen as the



Figure 4.7: Unknown Chalk Wettability for various ratios of PW, LSSW and SW at an aging temperature of =90°C. Error bars represent the standard deviation of the data in percent.

catalyst can be concluded that a 3ppm presence of SO_4^{2-} is too low as a concentration.

The variation of the chalk changes the wettability

The test run with Ekofisk formation brine and at a temperature of 115C (Figure 4.8) shows the highest wettability at 60% WT% . The test tubes were weighted out with 1 g of chalk and saturated with Ekofisk brine which will make a 20% of the total fluid sample. For the designed brine providing the lowest water-wetness its seen to be 51% with the mixture of Ekofisk Formation water 20% and 80% of LSSW. The highest achieved water-wet percentage for this condition was Ekofisk formation brine mixed with smart brine constituted by 75%pw / 25% LSSW; it has to be mentioned that this run has increased standard deviation, which makes the variation of the results slightly bigger than in other runs. Though, it can be argued that the origin of Ekofisk brine with 99,92 mmol/l Ca^{2+} and 21,88mmol/l Mg^{2+} and 0,0 mmol/l SO_4^{2-} mixed with PW which has 0,1249mmol/l SO_4^{2-} which was seen on figure 4.6

The table 4.9 indicates how the ionic strength varies depending on the different mixes between PW and LSSW, and how the ionic strength via the MFT methodology varies to an alteration. the mixture of 50% PW + 50% LSSW shows the highest alteration of wettability, in this specific case it could be the combination of the presence of SO4 2acting as a catalyst. The graph can indicate that a low ionic strength in the fluid can



Figure 4.8: Dan Chalk Wettability for various ratios of PW, LSSW and SW, after Ekofisk Formation Water aging (T=115°C).Error bars represent the standard deviation of the data in percent (adapted from [16]).

result in a low water wet WT% though this cannot be an conclusion on its own as its known from previous studies that a dilution of synthetic seawater with 10x and 20x will improve the general water wetness of chalk. In this specific case it can be argued to be a balanced ionic composition which is seen in 4.10 the optimum range for wettability is for a concentration of magnesium being between 20mmol/l to 32-35 mmol/l for calcium the range is a bit longer and a more stable trend to altering water wet wettability on chalk with a range from below 20 mmol/l up til around 40 mmol/l. where the concentration of sulphate is seen to have a an influence on wettability from 0,35mmol/l up to as high as 0,7mmol/l. It has to be emphasized that these results is achieved at 90C and at pressure conditions achieved inside the tube, which is for these studies neglected. The results are highly temperature related and depended.



Figure 4.9: Dan Chalk Wettability and its connection with brines (s.l.)ionic strength at 90°C.



Figure 4.10: Dan chalk wettability variation at 90°C upon different concentration of Calcium, Magnesium and Sulfate ions (adapted from[16]).



Figure 4.11: Dan Chalk wettability dependency on TDS (g/l) and pH for PW and LSSW in various mixing ratios at $90^{\circ}C$.

Figure 4.11 shows the concentration of Total Dissolved Solids, compared to the pH, indicating that the highest possible water wetting is achieved with TDS around 50 g/l and a pH around 7,2 which supports the general understanding that TDS is not of highest relevance, but the presence of correct amount of Ca^{2+} and Mg^{2+} plus a little amount of SO_4^{2-} .

4.4.1 Proposed solution: Chalk and Sandstone reservoirs

Figure 4.12 shows the results obtained while used the best designed brine if chalk reservoirs are considered. From this one can get a first idea on the wettability effect caused if sandstone layers are subjected to waterflood using the same advanced brine. The waterwetness depicted for current case, is approximately 85-90%. Such values are considered overestimated, due to lack aging time, as sandstone, mainly constituted by quartz grains is significantly less chemically reactive if compared to carbonate rocks. This means that most probably, in order to achieve comparable results higher aging time would be required.



Figure 4.12: Impact on Sandstone Wettability upon interaction with optimal solution for chalk and influence of Ekofisk Formation Water aging (T=115°C). Orange bars represent the standard deviation of the data in percent.

4.5 Flotation Wettability Index (FWI)

The newly developed wetting index [59] can be defined by the equation 4.5.1.

$$FWI = \frac{(\text{mass of water-wet fraction}) - (\text{mass of oil-wet fraction})}{\text{total mass}},$$
 (4.5.1)

The wetting index is a scale used to express the degree of wettability detained by the rock samples under investigation at a specific temperature. FWI ranges from -1 (completely oil-wet) to 1 (total water-wet), where 0 is considered neutral wet. Figure 4.13, shows the FWI gathered if EFW is not used during chalk saturation procedure. For 90°C, it can be seen that maximum water-wetness (c.a. 0,5) is achieved for the smart brines containing either 50%PW+50%SW or 50%PW+50%LSSW.

For the plotting of wetting index with samples using Ekofisk formation brine (see Figure 4.14) to saturate and mature the chalk sample under conditions of 115°C using the same mixtures as for the maturing with exclusively smart brine its seen that the wetting index is more consistent around 0,2 - 0,25 which could indicate the presence of original formation brine in place with high ionic content which will prevent the increase in water wetness and could introduce precipitating ions in the micro reservoir environment. Further considerations are provided in chapter 5.



Figure 4.13: Flotation Wettability Index at T=90°C for Dan Chalk aged exclusively with PW, LSSW and SW at different ratios and mixtures.



Figure 4.14: Flotation Wettability Index at T=115°C for Dan Chalk aged with Ekofisk Formation water and waterflooded with PW, LSSW and SW at different ratios and mixtures.



Figure 4.15: Flotation Wettabilty Index at T=90°C for Dan Chalk with $SW * 0SO_4$ containing Ca ion at various concentrations.

Figure 4.15 illustrates the FWI results for synthetic SW with zero sulphate, but increased concentrations of Ca ion up to 4x. Maximum water-wet percentage is achieved for smart brines incorporating 4x calcium. These results are compatible to the trend observed in Figure 4.4.

The wetting index graph shown for Dan Chalk with SW varying Magnesium (Figure 4.16) at different concentrations shows a consistent water wetness ranging from 56% up to 58%, if zero magnesium present to a magnesium concentration equivalent to the one present in SW up to the double amount of magnesium do not give any additional affect towards the wettability, from studies done by Godinho 2017 it showed that magnesium will take a more active part for conditions which is above 100°C this corresponds with findings in literature.

The MFT tests on sandstone showed results in the very high end of the wettability index scale. The test runs were made with both mature sandstone in Ekofisk formation brine and sandstone aged exclusively in smart brine, at a test temperature of 115°C the range from 0,7 up to 0,85 indicates a high affinity towards the water wet side. Which could be explained by the quartz a like surface which is neutrally charged and give indication of the presence of ions, i.e. higher ionic strength improves the water wettability and thereby



Figure 4.16: Flotation Wettabilty Index at T=90°C for Dan Chalk with $SW * 0SO_4$ containing Ca ion at various concentrations.



Figure 4.17: Flotation Wettabilty Index at T=115°C for Sandstone either initially aged with EFW and subsequently waterflooded with mixtures of PW, LSSW and SW or exclusively aged with mixtures of PW, LSSW and SW (adapted from [16]).

the sweeping effect. It could be argued that in a sandstone reservoir that the injection fluid should contain a higher degree of ionic composition in order to sweep formation as the poorest recovery was with 50% PW + 50% LSSW.

4.6 Crude Oil: TAN, TBN and Asphaltene Number

Acid and Base Number are two of the fundamental crude oil properties, which as previously referred provide an estimation on the quantity of polar components present in each sample. In order to obtain these values the procedure described on chapter 3 was followed. The plots obtained by the Oil PAC methodology are presented in Figures 4.18 and 4.19. As can be seen the results have revealed a considerably low value both for AN and BN (0.2 mgKOH (see Table 3.8). From this, it can be said that if present the polar components /heteroatoms represent a very low concentrations. Having a neutral oil its a uncommon situation, that brought to attention the importance of the crude oil sampling point, meaning that for wettabilty studies it is essential to know if the have been exposed to treating chemicals exposure in order to account for its presence while performing the calculations.

Another possible justification for the registered results could be the inadequacy of the applied standard method as described in [18], "ASTM Standard D664-81 23 does not titrate weak bases but only stronger bases, such as primary amines (pKa= 10,6), which are not present in crude oils." However, such hypothesis seems to be less probable once the crude oil element analysis was carried out in order to confirm the presence or absence of heteroatoms. The results are presented in Table 4.2. From the analysis of Table 4.2, it can be verified that only trace amounts of N, S and C were found in crude oil. From this, it seems that the crude oil acidity has been neutralized.



Figure 4.18: Acid Number titration, where U is the potential (mV), V is the added volume of titrant and EP stands for equivalence point.[16]



Figure 4.19: Base Number titration Results, where U is the potential (mV), V is the added volume of titrant and EP stands for equivalence point.[16]

Run D	Details					
Run	Weight	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
CRUDE3	3.653	86.8	14.02	0.69	0.96	-
CRUDE2	4.505	86.29	12.2	0.53	0.8	2 1
CRUDE1	5.455	86.03	10.13	0.64	0.75	

Table 4.2: Crude oil Element Analysis for N, S, C and O. Results provided by ICP-MS.[16]

Regarding the asphaltene number estimation, which calculation procedure is provided in section 3.1.5, it can be seen from Table 4.3 that an average value of 13% was obtain after 3 runs. As mentioned by Godinho, 2017 [16] such value seems to be overestimated, this high percentages are frequently associated with waxy crude oils [9]. It is of understanding that one possible justification for the present overestimation is the insufficient addition of organic solvent. For future experiments and further investigations this value should be re-evaluated following the standard procedure ASTM D2007-80.

Table 4.3: Crude oil asphaltenes content, where M_{Co} is the initial mass of crude oil and M_{AS} the weighed mass of asphaltenes.[16]

M _{Co} (g)	M _{As} (g)	Avg. M _{AS} (g)	Asphaltenes (%)
6.6720	0.7758	0.8907	13.3498
	1.1803		
	0.7160		

5 Simulation

This chapter will present the results gathered while simulating the rock-brine (s.l.) interactions upon different compositions for the injection fluid. This simulation intend to provide the first insights to the reservoir modeling and to serve as a basis for future works. For this purpose, an open-source software, PHREEQC version 3.3, developed by USGS was used. USGS describes PHREEQC as "a general purpose geochemical model for reactions in water and between water and rocks and sediments. Reactions include aqueous equilibria, mineral dissolution and precipitation, ion exchange, surface complexation, solid solutions, gas-water equilibrium, and kinetic biogeochemical reactions".

Essentially, the following simulations were carried out:

- 1. Evaluation of the calcite, anhydrite, dolomite and barite saturation indexes and pH variation for different "brines" (s.l.), at a constant concentration of EFW;
- 2. Evaluation of the influence linked to the presence of EFW in terms of pH and calcite, anhydrite, dolomite and barite saturation indexes.

Simulations are based on defining various brine compositions and bringing them to a thermodynamic equilibrium with a certain amount of cation-exchange cites (CEC), which is initially defined by cation-exchange capacity. [22] In current modeling $CaCO_3$ is the variable in excess, resembling the reservoir rock, followed by interaction is formation water, which is brought to an equilibrium with the potential oilfield scale minerals under investigation. The following step was to establish the equilibrium between smart brine and atmospheric CO_2 (it was assumed that a reasonable value for atmospheric CO2 partialpressure would be -3.5[74]). At last, the formation brine and smart brines were put into contact with $CaCO_3$ in an incremental reaction, in which the designed brine will sequentially react with the reservoir rock, here resemble by the $CaCO_3$. Following this analogy, one can get an rough understanding on the possible scale minerals precipitation or dissolution, as the brines (*s.l.*) move along the reservoir (with excess of $CaCO_3$ availability).
5.1 Saturation Index

One advantage of the mass action formalism is that we can express the degree of solution saturation relative to the saturated condition as an index. In order to calculate the degree of saturation, PHREEQC calculates the ion activity product (IAP) of the actual solution (the numerator of the dissolution reaction expression) and uses that quantity and the solubility constant (Ksp) to compute the SI, following the equation 5.1.1.[74]

Saturation Index (SI) =
$$\frac{IAP}{Ksp}$$
 (5.1.1)

In PHREEQC the SI is reported in units of log SI. There will be three possible chemical conditions, which will determine if the system will favor mineral's crystallization or dissolution. The previous chemical states are as follows (based on [74]:

- 1. SI = 0 is saturated, meaning the system is in equilibrium, there will be no observation of minerals precipitation or dilution;
- 2. SI >0 is super-saturated. One can possible verify the existence of mineral precipitation;
- 3. SI<0 is under-saturated, meaning there occur dilution of the mineral, whose saturation index shows a value bellow zero.

Current simulation work takes into account the atmospheric interaction of brines (s.l.) with CO_2 , a weak acid, which has its activity translated in terms of partial pressure. Addition of CO2 gas, introduces acidity into the system and slightly lowers the pH value. [74]

5.1.1 Brines (s.l.) influence on SI

All simulations presented in current section take into consideration the presence of Ekofisk FW at 5% concentration. This percentage is constant through all the graphical results, that will be analyzed. The experimental temperature is 90°C.

The sequence of the Figures from 5.1 to 5.4 illustrate the variation of the potential scale forming mineral' saturation indexes upon interaction with smart brine. For this specific

sequence the smart brine there is a relative increase of LSSW in comparison to PW. Therefore, PW shows a decrease in concentration from Figure 5.1 to 5.4. If smart brine with 95% PW is used, one can verify that anhydrite would be dissolving independently of the pH variation at specified simulation conditions. The depicted saturation index is approximately -2 for a pH range of 7.6 to 8.6. Barite shows a constant saturation ratio of approximately 0.7 for a pH variation ranging from 7.55 to 8.67. In what concerns calcite and dolomite, these two minerals exhibit an increasing precipitation tendency as the pH becomes more basic. Such tendency is even more accentuated for dolomite, which reach a SI value close to 5 for a maximum pH of \sim 8.65.

Figure 5.2 presents the exact same behaviour described above in Figure 5.1. Here, one has registered a slight increase in all SI.

The analysis of Figure 5.3 provided the same trends previously verified, however, one can clearly see, that the relative increased quantities of LSSW led to a differentiation in terms of achieved saturation indexes at low pH values. This behaviour can be identified by comparing the all SI at low pH conditions from Figures 5.4 and 5.1.

At last, Figure 5.5 depicts the minerals SI indexes variation upon interaction with smart brine composed by 50%PW and 50% SW. From this graph various indications can be taken:

- 1. Anhydrite is on verge of being in equilibrium, exhibiting and SI close to zero. The higher the pH the closer the SI will be to zero;
- 2. For a pH 7.8 barite show a slight higher SI if compared to dolomite. However with an increased in pH, this observation gets reversed;
- 3. At high pH (\sim 8.65), calcite presents a slight bigger SI relative to barite;
- 4. At high pH, dolomite shows the largest SI, achieving values over SI=5.



Figure 5.1: Calcite, Barite, Anhydrite and Dolomite saturation indexes upon interaction with produced water as smart brine.



Figure 5.2: Calcite, Barite, Anhydrite and Dolomite saturation indexes upon interaction with PW and LSSW as smart brine in a ratio of 0.75:0.25.



Figure 5.3: Calcite, Barite, Anhydrite and Dolomite saturation indexes upon interaction with PW and LSSW as smart brine in a ratio of 0.5:0.5.



Figure 5.4: Calcite, Barite, Anhydrite and Dolomite saturation indexes upon interaction with LSSW as smart brine.



Figure 5.5: Calcite, Barite, Anhydrite and Dolomite saturation indexes upon interaction with PW and SW as smart brine in a ratio of 0.5:0.5.

5.1.2 Ekofisk Formation Water influence on SI

In this section, one intend to simulate the effect in saturation indexes of inorganic scale minerals linked to the increasing amounts of formation brine. For this case study, ekofisk formation water was used. Chemical composition of EFW can be seen in Table 3.6, chapter 3. The simulations were carried out for a group of selected minerals that are recognized to be potential scale minerals, *i.e.*, calcite, barite, dolomite and anhydrite at a constant temperature of 90°C.

Calcite

Calcite scale formation main driver is the loss of CO_2 from the water to the hydrocarbon phase(s) as pressure falls. This removes carbonic acid from the water phase, which had kept the basic calcite dissolved. Another possibility for decreased solubility of calcite is the temperature decrease (at constant CO_2 partial pressure).[65]. In current simulation model, the temperature and pressure variations through the reservoir and along production tubing were not considered, however these should be investigated in current work.

From the analysis of the Figures 5.6 to 5.9, it is clearly seen that the higher the EFW present the higher the saturation index achieved for the same pH value, meaning increased probability of calcite precipitation. As an example, if one looks into the plot depicted in Figure 5.6 for a pH=8.6, it can be verified that if the designed brine contains 1% EFW a value of approximately 2.4 of calcite SI is obtained. However, if for the same pH, one consider the trending line provided for 20% EFW, a value of ~ 2.75 SI is achieved. Furthermore, it can also be seen that for all performed simulations that there is a positive correlation between the increase in pH and the increase in calcite SI, meaning that, basic fluid will detain a higher probability to precipitate calcite, as would be expected.

The comparison between Figures 5.6, 5.7, 5.8 and 5.9, facilitate the understanding of the effects in terms of calcite precipitation probability due to interaction of the reservoir rock with various brines (*s.l.*). If a reference pH value is taken for the analysis, as for suggestion pH=8.4, one can verify that:

1. If smart brine is exclusively constituted by PW, for higher incorporated percentage of EFW (20%) a calcite saturation index of approximately 2.3 is registered. On the





Figure 5.6: Calcite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using produced water as the smart brine.

other hand, in presence of smaller quantities of EFW (1%) a value around 2.05 of calcite SI is observed;

- 2. If a combination of 50%PW and 50%LSSW is used as smart brine and EFW is present in a concentration of 20% a calcite saturation index of 2.25 is achieved. For smaller values of EFW, c.a, 1%, the calcite SI registered values of 2;
- 3. For a LSSW smart brine, one could verify that the presence of bigger EFW concentrations would lead to a value of 2.4 calcite SI, while concentrations of 1% would provide a calcite saturation index of 2.15;
- 4. The use of 50%PW and 50%SW as smart brine will provide similar results to the ones described in point 1. However, contrarily to the observed in Figure 5.6, in this case (Figure 5.9), even with concentrations of only 1% EFW the calcite SI will not reach values below 1.



Figure 5.7: Calcite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and low sulphate seawater as smart brine.



Figure 5.8: Calcite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using low sulphate seawater as smart brine.



Figure 5.9: Calcite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and synthetic seawater as smart brine.

Barite

The presence of barite scale is frequently associated to the chemical interaction of incompatible waters, as for example the mixture of formation water, characterized by high-barium content (as described in Table 3.6) and seawater, which has a high-sulfate content.[65] Similarly, to the described for calcite in subsection 5.1.2, the barite saturation index will be evaluated considering the presence of increasing quantities of EFW in association with various designed brines.

The analysis of the Figure 5.10 shows that the smaller the concentration of PW the lower the achieved saturation indexes for barite. This is equal as saying that the higher the concentration of EFW the smaller the barite saturation index, once the we are working with relative concentrations. This tendency seems to be counterintuitive, as formation brines are enriched in barium ion. However, from this one can verify that Ba concentration is even more relevant in produced water, surpassing the possible effect caused by high concentration in EFW. Additionally, it can be seen that barite SI is constant through the range of pH (7.4 to 8.2) after which it shows a slight decrease. The maximum saturation index value is 0.75 and it was reached for the advanced brine characterized by the highest concentration of PW (99%).

The graphical interpretation of the Figure 5.11 has revealed the same tendencies descried for Figure 5.10, although the maximum value reached for the barite saturation index was 0.75. In both cases there is possibility for $BaSO_4$ precipitation as the present SI values are bigger than zero.

From Figure 5.12 one can verify all designed brines are put into contact with the chalk reservoir rock, there will be dissolution of barite, as the achieved values of SI are bellow zero. At this case, in which PW is not present, once the smart water is exclusively constituted by LSSW, it can be seen that the increase in EFW concentration originated higher SI values. The maximum barite SI for this chemical conditions was registered at a value of -0.3.

If a designed brine constituted by 50%PW+50%SW and variable concentration of EFW is considered, one can observe similar behaviour as for the conditions depicted in Figures 5.10 and 5.11. However, it should be mentioned that the saturation indexes are significantly higher. Maximum SI is 2.46 (for a advanced brine composed by 1% EFW and 99% of PW and SW in a 0.5:0.5 ratio).



Figure 5.10: Barite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using produced water as the smart brine.



Figure 5.11: Barite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and low sulphate seawater as smart brine.



Figure 5.12: Barite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using low sulphate seawater as smart brine.



Figure 5.13: Barite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and synthetic seawater as smart brine.

Anhydrite

The interaction of formation water with high calcium and high sulfate contents can lead to the deposition of anhydrite or gypsum (hydrated mineral form of calcium sulphate) due to chemical incompatibility as mentioned for barite. It is known that "Calcium sulfate scale solubility, unlike that of barite scale, actually increases with decreasing temperature (until about 40C). This can decrease the likelihood of scale after the initial mixing deposition. The reversal in solubility falloff below 40C accounts for the gypsum scaling observed in surface equipment. This inverse temperature effect can result in the generation of anhydrite scale when injecting seawater. Anhydrite solubility falls as pressure falls"[65]

In current subsection, the variation of anhydrite SI and pH will be analyzed for various brines (s.l.) in which EFW concentration is variable. From the Figures 5.14, 5.15, 5.16 and 5.17 the following tendencies were noticed:

- Figure 5.14 shows that larger concentrations of EFW will lead to higher dissolution of anhydrite, as there is decrease in the saturation index. The maximum value registered for the saturation index is -1.99;
- 2. From Figure 5.15, it seems that brines (s.l.) containing concentrations in the range 1% to 10% show approximately the same behaviour and the same probability in terms of chemical dissolution, specially for pH>8.3. For EFW at 20% and high pH, this condition represents the minimum SI achieved, however, for smaller pH values the minimum value is associated to the 1% EFW concentration;
- 3. When PW is not present (Figure 5.16) it can be verified that the increase in EFW is translated into increased SI. The maximum anhydrite saturation index for such conditions is reached at -2.55;
- 4. Figure 5.17 is characterized by the same trends described in the point 2. The maximum SI is achieved at -0.155.
- 5. For all simulated cases, the increase in pH has shown a positive correlation with the increase on anhydrite saturation index.





Figure 5.14: Anhydrite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using produced water as the smart brine.



Figure 5.15: Anhydrite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and low sulphate seawater as smart brine.



Figure 5.16: Anhydrite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using low sulphate seawater as smart brine.



Figure 5.17: Anhydrite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and synthetic seawater as smart brine.

Dolomite

Dolomite scale can basically occur for the conditions described for calcite, however it occurs when there is presence of high magnesium content.

From the analysis of the the Figures 5.18, 5.19, 5.20 and 5.21, it can be seen that although different brines (*s.l.*) have been simulated the same trends were obtained are can be described as follows: the increment in EFW percentage led to a higher dolomite saturation index; the pH increase is followed by a rise in the SI; The dolomite maximum saturation index (approximately 5.4) was reached for the designed brine containing exclusively LSSW.



Figure 5.18: Dolomite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using produced water as the smart brine.



Figure 5.19: Dolomite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and low sulphate seawater as smart brine.



Figure 5.20: Dolomite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using low sulphate seawater as smart brine.



Figure 5.21: Dolomite Saturation index and pH variation for increased concentration of Ekofisk Formation Water using a ratio of 0.5:0.5 of produced water and synthetic seawater as smart brine.

6 Coreflooding

6.1 What is it?

Coreflooding can be described as a laboratory test in which a fluid or mixture of fluids is injected into a rock sample, with the purpose of quantifying the permeability, the relative permeability, the saturation change, the formation damage caused by the fluid injection, or interactions between the fluid and the rock. The core material often comes from an oil reservoir, but some tests use outcrop rocks. The fluid in place at the start of the test is typically either a simulated formation brine, oil (either crude oil or refined oil), or a combination of brine and oil. Injected fluids may include crude oil, simulated reservoir brine, refined fluids, drilling mud filtrate, acids, foam or other chemicals used in the oil field. Depending on the purpose of the test, conditions may be either ambient temperature and low confining pressure or high temperature and pressure of a subject reservoir. Pressures and flow rates at both ends of the core are measured, and the core can also be investigated using other measurements techniques such as nuclear magnetic resonance (NMR) during the test. This method is typically used to determine or to confirm the optimum development option for an oil reservoir and often helps evaluate the effect of injecting fluids specially designed to improve or enhance oil recovery.[12]

Core flooding experiments are to be used to complement the results presented on chapter 4, in which modified flotation technique was used. One intend to refine the selection of the optimal solution found using MFT and to improve the understanding of the chemical and physical processes at reservoir pressure and temperature conditions.

6.2 Experimental Setup

The laboratory setup for coreflooding experiments can vary according to the purpose to which is being used for. A common procedure is described as follows (adapted from [8, 48]):

- 1. Rock core sample is cleaned by Soxhlet extraction using toluene and methanol;
- 2. Rock core sample is dried at a temperature of 130 °C for 24h and weighed;
- 3. The core plug is saturated under vacuum for 3 days with FW, in order to establish the ionic equilibrium with the brine and ensure full brine saturation;
- 4. The wet weight of the core plug is measured, and the pore volume is computed from the difference in weight before and after saturation;
- 5. The saturated core is flooded with reservoir oil until water production ceased which indicated the establishment of the irreducible water saturation (SwiR). This step is applied if the experiment intend to investigate the oil recovery;
- 6. The oil permeability at irreducible water saturation is also measured, and the core plugs are aged in the reservoir oil at a pressure and temperature of interest for at least 6 weeks, aiming to restore rock wettability;
- 7. For the waterflood tests, the core sample is placed inside a rubber sleeve to a central position, mounted in the core-holder and connected at both ends with two end plugs (one to the inlet and another to the outlet flow-line, respectively);
- 8. Reservoir oil and brines (s.l.) are supplied from the piston accumulators operated by high-pressure displacement pumps;
- 9. An overburden pressure is applied on the core by injecting hydraulic oil into the annulus between the rubber sleeve and inner surface of the core-holder;
- 10. Pore pressure is maintained by a back-pressure regulator (BPR) and measured by the differential pressure transducers;
- 11. The waterflood test begins with with a base brine (s.l.), for example SW, at constant injection rate. Once the oil production cease, the injection of ionically controlled waterflood starts at an adequate pressure and temperature;
- 12. The produced fluid is collected to quantify the oil recovery, and ionic analysis is conducted for the effluent brine (s.l.);

- 13. Collected brine (s.l.) samples at specific brine injected pore volumes are to be analyzed by ion chromatography;
- 14. Ionic analysis comparison is done by normalizing the effluent brine concentration against the injected brine concentration at specific brine injected pore volume.

The pH and densities for all injected and effluent brines (s.l.) should be registered and the initial TDS and final TDS for injected and effluent brine, respectively, should be estimated.

6.2.1 Notes on experimental procedure

The execution of experimental works and laboratory procedures and setup should be carefully planned as it is crucial to represent the reservoir conditions as close as possible. Also, it is vital to preserve original conditions in samples, which can change during coring procedures and core handling. The wetting state of the reservoir rock is directly connected "to the reservoir parameters such as initial and residual fluid saturation, relative permeabilities, capillary pressures" [4], therefore original wetting properties of the reservoir sample can be altered if inadequate procedures are used and the core preservation methods are not applied [4]. As an example, it is particularly important the type of mud used while drilling the core sample, "as cores that have been drilled with oil based mud are generally contaminated and native wetting state of the cores are altered because of the surfactant components in this type of mud"[4].

As previously described, the first step in coreflooding procedure is the core cleaning, in which the so-called extraction/distillation methods (Soxhlet method) or the flow-through technique (which uses a Hassler type core holder) are implement. Both methods require injection of cleaning solvents, which if not correctly selected can cause irreversible changes in the core, leading to inaccurate results in subsequent experiments. "In an oil reservoir, the initial wettability is established by a chemical equilibrium between oil, brine and rock over millions of years of interaction the crude oil acid number, measure of the content of surface-active components is regarded as one of the most important parameters dictating the initial wetting of a carbonate rock." [35] Consequently, it is of extreme importance to preserve the original wetting state, rather than trying to restore it. Hopkins et al. [35] have been suggesting the use of a "mild cleaning step" instead of the normal cleaning with toluene and methanol. This new approach consists in the use of kerosene and heptane to remove the residual oil. After this, the core is flooded with DI water to remove heptane and easily dissolvable salts, whereas the water and heptane are afterwards removed by evaporation in a standard heating chamber (at 90C), until constant weight [77, 35].



Figure 6.1: Schematic experimental setup of coreflooding equipment.[8]

6.3 Brief insight on previous studies

Yousef et al.[86] have demonstrated by several laboratory coreflooding studies that substantial tertiary oil recovery beyond conventional waterflooding can be achieved by altering the salinity and ionic content of field injected water. All experimental procedures and parameters were designed considering the current reservoir conditions and injection practices, namely, reservoir pressure, temperature, formation water salinity. For this case, in which the core sample is constituted by a composite carbonate core, it was found that 10-fold diluted seawater was the one able to recover the maximum crude oil at a tertiary stage, reaching a 9 to 10% additional oil recovery.

6.4 Importance for Future Work

Current has been demonstrating potential for the usage of produced water in tertiary recovery, if its ionic composition is regulated. From this stems the requirement for a confirmation of the gathered results at reservoir conditions, which can be done using coreflooding experimental studies and chemical modeling. Moreover, it is of great interest to better understand precipitation and dissolution mechanisms governing the potential scale forming ions (PSFIs), throughout the process starting at the injection fluid, passing through the reservoir until production wells. Additionally, ionically modified water can also be tested for the purpose of preventing or treating the scaling problems, connected to the precipitation of scale minerals such as $BaSO_4$, $CaSO_4$, $CaCO_3$, etc. Moreover, it is thought that controlled precipitation of such mineral can benefit the hydrocarbons recovery and the sweeping efficiency, if such phenomenon occurs at the reservoir level and forces the injected fluid to flow through unswept areas, this way sealing off the pathways where there is no oil left to recover. Moreover, the combined study of ionic control of scale and environmentally compatible scale dissolver chemicals, such as, BASOL 2000 hp [44], GYPSOL [46] and CAL-ACID [45] would be of interest in order to evaluate if there would be increased performance considering increased oil recovery and the non-development of scaling. These studies if proved successful, might be able to provide a cost-efficient solution to avoid well intervention campaigns.

7 Conclusions

The primary objective of current work was to investigate the rock wetting state considering the reservoir fluids. Various laboratory experiments were carried out, for the set of samples from the same field in the North sea containing a oil sample, produced water sample and injection water sample. The wettablilty alteration study was performed based on the modified flotation technique. In following sections the major conclusions will be presented:

Two types of chalk was used to verify the significance and importance of having the specific chalk type from the field where screening takes place.

- The MFT methodology requires practice and experience to master to get reliable and consistent results, small variations through out the testing period can cost days of work. However, after acquired experience both consistence and reliability can be achieved as demonstrated by calculation of the data standard deviation;
- It is crucial to understand the current state in terms of ionic composition in order to adequately evaluate the potential for altering reservoir wettability and possibly improve the oil recovery;
- Synthetic Seawater highest wettability alteration was achieved with 2x and 10 x dilution. An average water-wetness of 57 wt% was registered;
- Experiments with Ca^{2+} ion in various concentration and SW with exclusion of sulphate ion showed a decreasing trend up until 4x Calcium. The water-wet fraction reached a value of 59%;
- The test run on Seawater with zero sulphate revealed the same trend as for Ca^{2+} ; the wettability variation is very small and around 59%;
- Test run for injection of pure fluids have shown that in presence pf 100% LSSW the reservoir rock will have the poorest wettability alteration leading to water-wet

fractions of about 38%, whereas produced water has the highest water-wet percentage with 62%. Seawater is right below with 60% water wet.

- Lack of sulphate in injection fluid renders the system more oil wet;
- Chemicals present in Produced water have improved water-wet conditions on chalk rock under test conditions;
- Best mix for water-wet percentage is 50% PW+50% SW with 69%, followed by 50% PW+50 % LSSW resulting in 67% water-wet;
- Experiments with Chalk saturated with Ekofisk formation brine give for best designed brine composition 75% PW +25% LSSW achieving a water-wetness of 60% at 115C which is lower than the values presented for chalk exclusively saturated with smart brine;
- Ionic strength above 0,75 mol/l have a stable and positive influence on the water-wet state. Ionic strength can be as high as 1.1 mol/l;
- Sulphate ionic concentration up to 0,7mmol/l have a positive effect on the waterwetness;
- Magnesium cation was confirmed to play a more active role for fluids in which temperature is close to 100C;
- TDS value plays a less significant role in water-wet state; It is the presence of Ca^{2+} , Mg^{2+} and SO_4^{2-} that is main driver for the verified increased water-wetness, though the temperature and pH also play a significant role;
- Sandstone water-wet state can be as high as 93% with a mix between 50% PW and 50% SW. In this case the poorest water-wet was achieved for 50% PW and 50% LSSW.
- Wetting index provides a good overview and an easy understanding of the wettabilty altering potential linked to the various brines(*s.l.*);
- From simulation it was observed that relative increase in LSSW quantities led to higher precipitation of barite, calcite and dolomite and less dissolution of anhydrite;
- At a constant EFW concentration of 5% : If smart brine with 95% PW or 95% (75%PW+25%LSSW) are used, anhydrite would be dissolving independently of the pH variation; Barite shows a constant saturation ratio of approximately 0.7 for a

pH variation ranging from 7.55 to 8.67; Calcite and dolomite exhibit an increasing precipitation tendency as the pH becomes more basic;

- For a advanced brine constituted by 5%EFW + 95% (50%PW+50%SW) the following was noticed:
 - 1. Anhydrite is on verge of being in equilibrium, exhibiting and SI close to zero. The higher the pH the closer the SI will be to zero;
 - 2. For a pH 7.8 barite show a slight higher SI if compared to dolomite. However with an increased in pH, this observation gets reversed;
 - 3. At high pH (\sim 8.65), calcite presents a slight bigger SI relative to barite;
 - 4. At high pH, dolomite shows the largest SI, achieving values over SI=5.
- When advanced brines containing PW and PW and SW in 0.5:0.5 ratio it is clearly seen that the higher the EFW percentage present the higher the saturation index achieved for calcite at the same pH value;
- From Figure 5.10 it was seen that the smaller the concentration of PW the lower the achieved saturation indexes for barite;
- If PW is incorporate in smart brine the Ba concentration is even more relevant than the possible effect caused by high concentration in EFW.
- Barite SI is constant through the range of pH (7.4 to 8.2) after which it shows a slight decrease;
- When PW is not present in smart brines it can be verified that the increase in EFW is translated into increased anhydrite SI and vice versa;
- For all simulated cases, the increase in pH has shown a positive correlation with the increase on anhydrite saturation index.
- Increments in EFW percentage led to a higher dolomite saturation index;
- pH increase is followed by a rise in the dolomite SI;

Besides the outcomes with direct provenience from laboratory testing or simulations, it is also of importance to refer the following points:

- Sampling point for crude oil: Acid and base number results have categorized the crude oil sample as neutral; the crude oil sample point was close to the export line which was initially thought to be a good sample point in order to have a fluid as clean as possible and mix up with produced water. However, after further consideration this was observed not to be the case. It is relevant to double check the results in this study with a sample taken at a wellhead to confirm the actual influence on wettability based on a taken live oil sample;
- samples of produced water should also be taken as close to the point of lab works as possible since it is well known that the fluid will degrade over time;
- Injection water from Low salinity treatment plant should be taken as close to injection point as possible;
- Any chemicals added into the stream prior injection into reservoir should be informed, so they can be taken into account in disturbance of the water-wet properties. This will be particularly relevant for a coreflooding study;
- Produced water can be seen as an asset to improve sweeping efficiency and justify further study in order to optimize its usage.

7.1 Recommendations for Future Work

During the process of the this project it was identified the need for controlling ions and the prediction of precipitations in order avoid the design a waterflood fluid which would lead to uncontrolled minerals precipitation in the formation causing unintentional plugging. It came forward that there was a potential to approach the waterflood as a closed circulation system where the water takes the main part and as much of the circulating water should stay inside the closed system. Ionic control and additives should be taken into consideration for precipitation and scale control.

The risk of sulfate based scale formation, like barium sulfate is to be carefully analyzed. Seawater contains around 2800 mg/l of sulfate. Reservoirs can have high concentration of barium and strontium. If nothing is done to prevent the mixing of these two fluids, scale deposits can occur at the production wells once the breakthrough has happened, with the decrease of production and subsequently decreasing security of flow assurance.

The solution of taking out the sulfate from seawater prior injection is possible. There are various examples of field application of such desulfation process, normally based on membrane technology, as for example the Girassol, Dalia and Pazflor FPSO (offshore Angola) [49].

In the Danish North Sea the South Arne field is an excellent example of a field implementation of a sulfate removal technology, in which the scaling problem has been minimized but not eliminated[16].

Conclusion of this study reveals that there is a maximum value of sulfate concentration, that has to be investigated each specific case study (specific reservoir), up to which it will lead to an elevated water-wetness and potentially increased oil recovery.

Furthermore, sulfate concentration knowledge is required in order to predict the probability of scale formation avoid the total removal of sulfate, which is not beneficial.

It is recommended from this study to take a next step and address the issue of ionic control and design of injection fluid based on a specific well case where it is known to have downhole scale precipitation and where it is possible to sample and to some extent control the injection fluids composition, as a minimum for an initial state, which is fundamental to enable the design and optimization of the injection fluid that will reduce, avoid or reverse the mineral precipitation of $BaSO_4$, $CaSO_4$ and $SrSO_4$ upon interaction with the formation water and in the production well.

The study of the potential scale mineral's kinetics will be crucial to understand the physical properties and forces between the ions and the interaction with reservoir rock and surrounding fluids.[16]

A significant improvement to the study would be to get a hold on a core plug from the field under investigation, which is known to have low permeability maybe due to presence of $BaSO_4$, $CaSO_4$ and $SrSO_4$.

Additional reservoir simulation for reservoir conditions would be of major interest to further narrow in the knowledge and refine the decision making based on the data collected.

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A Appendix

A.1 Laboratory Template

Fractions of oil and water-wet were registered using the following template, which was kindly provided by Res. Ass. Dr. Adeel Sohal:

Test Tube 1		
Parameters	Amount	Unit
Empty Test Tube Weight		g
Sample Name		
Sample Mass		0.0
Brine Used		- 10 - 1
Grain Size		μm
Brine Volume		ml
Oil Volume		ml
Test Temperature		°C
pH of Decanted Brine		
Start Brine Aging		
End Brine Aging		
Total Brine Aging Time		hrs
Start Oil Aging		
End Oil Aging		
Total Oil Aging Time		hrs
Start Oil/Brine/Grain Aging		
End Oil/Brine/Grain Aging		
Total Mixture Aging Time		hrs
Test Tube Weight with dry grains		g
Weight of Oil-wet grains		g
Weight of Water-wet grains		g
Amount of oil-wet grains		%
Amount of water-wet grains		%

Table A.1: Calculation template for mass fractions [59]