Low Salinity Waterflood in Combination with Surfactant/Polymer; Effects of Kinetics and Brine Composition

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Abstract

Improving the oil recovery beyond what is possible by conventional methods is a topic of great interest, and the potential oil recovery for a field can be improved if unconventional methods are implemented. Reducing the salinity of injection water is known to be able to improve the oil recovery. This has been proven in numerous lab studies and some field tests, but the underlying mechanisms are not fully understood. More research is needed to be able to predict when an improvement in recovery can be expected, and how large the improvement would be with low salinity injection.

This master thesis consists of experimental work carried out at Uni CIPR, and is a continuation of earlier research performed at Uni CIPR. The main goal has been to further study the influence on oil recovery by low salinity water, in addition to the effect of combining low salinity injection at reduced capillarity by injection of surfactants.

Dynamic core displacement experiments have been performed for six Berea outcrop rocks with permeability of approximately 400 mD. Four of the six rocks were saturated with a North Sea crude oil and aged to shift the wettability to a less water wet condition. A mixture of crude oil and octane was used for the displacement experiments.

Brine with different salinities has been injected into the cores. Injection of 3000 ppm NaCl and diluted seawater in both secondary and tertiary mode was performed. Two cores were tested to investigate if the mechanisms associated with lowsal could be slower than the timespan of a typical core flooding experiment. Two other cores were injected with water with oscillating salinity to test if a salinity shock could improve the oil recovery.

The six cores were flooded with a surfactant solution in tertiary mode, followed by a polymer injection for mobility control. 3000 ppm NaCl was injected after the polymer solution.

The results did show some response to lowsal for the aged cores, around 3-5 % increased production of original oil in place, but the two cores that had not been aged did not respond to lowsal. Low salinity surfactant flooding did improve the recovery factor from around 60 % to around 75 % of original oil in place. This was not as much as previous studies have shown, and the oil mobilization by surfactant flooding was less than expected from a capillary desaturation curve. Injecting a polymer solution after the surfactant injection, improved the ultimate recovery of oil, and the efficiency of 600 ppm HPAM seemed to be better than using 300 ppm.

Nomenclature:

Abbreviations

BPR	Back pressure regulator
CDC	Capillary desaturation curve
CIPR	Centre for integrated petroleum research
CMC	Critical micelle concentration
COBR	Crude oil, brine and rock
EOR	Enhanced oil recovery
FW	Fractional wet
HPAM	Hydrolyzed Poly-Acrylamide
IFT	Interfacial tension
IOR	Improved oil recovery
LS	Low salinity
MWL	Mixed wet large
MWS	Mixed wet small
NCS	Norwegian continental shelf
OOIP	Oil originally in place
ppm	Parts per million
SCAL	Special core analysis
SSW	Synthetic seawater
SWCTT	Single well chemical tracer test
TDS	Total dissolved solids
WBT	Water breakthrough

Variables

ΔP	Pressure drop	mbar
$\Delta\rho$	Density difference	kg/m^3
μ	Viscosity	Pa·s
μ_I	Viscosity of injection fluid	Pa·s
μ_o	Viscosity of oil	Pa·s
A	Cross sectional area	cm^2
A	Apparatus constant	$g/(s^2cm^3)$
B	Atmospheric air pressure	mmHg
E_D	Microscopic efficiency	Dimensionless
E_r	Recovery factor	Dimensionless
E_{vol}	Volumetric efficiency	Dimensionless
F	Relative humidity of air	[%]
I_{USMB}	USBM wettability index	Dimensionless

K	Absolute permeability	cm
K_{eff}	Effective permeability	m^2
k_r	Relative permeability	Dimensionless
k_{RI}	Relative permeability of injection fluid	Dimensionless
k_{RO}	Relative permeability of oil	Dimensionless
K_{rw} (S_{or})	Relative permeability of water at residual oil saturation	Dimensionless
K_{wp}	Water permeability after polymer flood	m^2
L	Length	cm
M	Mobility ratio	Dimensionless
N	Volume of oil in place	Sm^3
N_c	Capillary number	Dimensionless
N_p	Volume oil produced	Sm^3
P_c	Capillary pressure	Pa
PV	Pore volume	Dimensionless
Q	Flow rate	ml/min
R	Radius	m
r	radius of droplet	m
RRF	Residual resistance factor	Dimensionless
S_g	Gas saturation	Dimensionless
S_o	Oil saturation	Dimensionless
S_{oi}	Initial oil saturation	Dimensionless
S_{or}	Residual oil saturation	Dimensionless
S_{ors}	Residual saturation of oil after surfactant injection	Dimensionless
S_{ors}/S_{orw}	Fraction of residual oil saturation after and before surfactant injection	Dimensionless
S_w	Water saturation	Dimensionless
S_{wi}	Initial water saturation	Dimensionless
T	Time period	s
T	Temperature	Kelvin
u	Darcy velocity	m/s
u	Velocity	m/s
V_b	Bulk volume	ml
V_g	Volume of gas	m^3
V_o	Volume of oil	m^3
V_p	Pore volume	ml
V_w	Volume of water	m^3
y	Length perpendicular to flow direction	m
θ	Contact angle between oil and water	[°]
λ_I	Mobility of injection fluid	$m^2/(Pa \cdot s)$
λ_o	Mobility of oil	$m^2/(Pa \cdot s)$

ρ	Density	g/cm^3
ρ_{air}	Density of air	g/cm^3
σ	Interfacial tension	N/m
τ	Shear stress	Pa
Υ	Interfacial tension	N/m
φ	Porosity	Dimensionless
ω	angular frequency of rotation	s^{-1}

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1 Introduction

The recovery factor for a field on the Norwegian Continental Shelf, NCS, when a field is produced by conventional methods is typically in the range of 40 % to 50 % of original oil in place. This means that approximately half of the oil originally in place is left in the reservoir when a field has ceased production.

The recovery factor is defined as the volume oil produced from a reservoir, N_p, divided by the original volume of oil in place, N:

$$E_R = \frac{N_p}{N} \tag{1}$$

The conventional production strategy on fields on the Norwegian continental shelf, NCS, is to inject sea water and/or dry gas for pressure maintenance and for displacing oil towards the production wells. Ongoing research of enhanced oil recovery is done to improve the oil recovery of a reservoir further than what is possible by conventional methods.

The ion composition in the water has proven from laboratory studies and some field tests to be important. Injection of low salinity water has shown an increase in oil recovery. However, the underlying mechanisms involved are not fully understood and it is still unclear in what combinations of oil, brine and rock an improvement in oil recovery can be expected.

The purpose of this thesis is to perform displacement experiments in order to increase our understanding of low salinity water injection as an enhanced oil recovery method. The hybrid process of combining low salinity water injection at reduced capillarity by the presence of a surfactant will also be investigated.

2 Enhanced oil recovery

Several definitions of enhanced oil recovery, EOR, exist, but a common definition is that it includes unconventional methods that increase the volumetric and/or microscopic efficiency of a production method. Another definition states that EOR is a production method that includes injection of materials that are not originally present in the reservoir. Injection of surfactants and polymers are common examples of EOR. Improved oil recovery, IOR, is a more general term that refers to any economic measure that is intended to increase oil recovery and/or accelerate the production. A typical IOR method is conventional sea water flooding which is very common on the NCS.

The volumetric efficiency is defined as the volume of oil in the reservoir contacted by the injection fluid divided by the original volume of oil:

$$E_{vol} = \frac{\text{Volume of oil contacted}}{\text{Volume of oil originally in place}} \tag{2}$$

This parameter is mostly dependent on the reservoir heterogeneity and mobility ratio of injection fluid and reservoir oil. The mobility ratio is defined as follows:

$$M = \frac{\lambda_I}{\lambda_O} = \frac{\mu_O \cdot k_{RI}}{\mu_I \cdot k_{RO}} \tag{3}$$

A mobility ratio lower or equal to 1 is preferable since that means that the oil is at least as mobile as the injected fluid. This will not be the case for viscous reservoir oils. Adding polymer in the injected water will reduce the mobility ratio and improve the volumetric efficiency by increasing the viscosity of the injection water.

The microscopic efficiency is defined as the volume of oil produced divided by the volume of oil contacted by the injection fluid:

$$E_D = \frac{\text{Volume of oil produced}}{\text{Volume of oil contacted by injection fluid}} \tag{4}$$

The microscopic efficiency is mostly dependent on the capillary number N_c. The capillary number is a dimensionless ratio of viscous to capillary forces in the porous medium. A common way to quantify this ratio is as follows:

$$N_c = \frac{u \cdot \mu}{\gamma} \tag{5}$$

u is the Darcy velocity, μ is the viscosity of the injection fluid and Υ is the interfacial tension between injection fluid and oil. The residual oil in flooded zones is trapped by capillary forces which dominate over the viscous forces in a porous medium. An increase in N_c will therefore lead to a reduction in capillary trapped oil. The most efficient way to increase N_c is by adding surfactants in the injection water. This can reduce the interfacial tension by several orders of magnitude.

Injection of surfactants and polymers are well known to be able to improve the oil recovery. However, the oil companies are still hesitating to implement these methods, mostly due to the uncertainty whether the additional oil recovery make up for the extra cost. More research on these topics will therefore help minimize the uncertainty in evaluating the profit and risks versus reward of using EOR methods.

Some studies in the recent years have shown that combining low salinity water with surfactants can be a very promising EOR method.

3 Basic theory

3.1 Rock properties

A sedimentary rock has several fundamental properties that will be explained in this chapter.

3.1.1 Porosity

Porosity, φ, is defined as the pore volume, V_p, divided by the total bulk volume, V_b, of a porous rock. This is one of the most important rock properties in reservoir engineering. It determines the volume of fluids in a sedimentary rock:

$$\phi = \frac{V_p}{V_b} \tag{6}$$

Effective porosity includes the pore volume that is interconnected, enabling fluids to flow through the pores. Ineffective porosity includes the isolated pore volume that is unable to transport fluids.

3.1.2 Permeability

Permeability is the ease with which fluids can flow through a porous rock. The absolute permeability is a rock property that can be measured if the rock is completely saturated with only one fluid. The permeability, K, of a porous rock can be measured using Darcy's law given as follows:

$$Q = \frac{KA\Delta P}{\mu L} \tag{7}$$

Q = flow rate, [cm^3/s]
A = cross sectional area, [cm^2]
ΔP = pressure drop through the core, [atm]
L = length of core in direction of flow, [cm]
μ = viscosity of fluid, [cP]
K = absolute permeability, [Darcy]

Darcy's law is based on three assumptions:

1. Laminar flow within the rock pores.
2. 100% saturation of one fluid.

3. The fluid does not react with the rock.

A gravity term has to be included in the formula if the direction of flow is non-horizontal. The Klinkenberg effect has to be taken into account if a gas is used for permeability measurements. This is due to gas slippage along the rock surfaces in the pores.

The permeability of a rock is dependent on the direction of flow.

3.1.3 Fluid saturations

A porous rock can typically contain two or three immiscible fluids: water, oil and gas. The saturation of these fluids is defined as follows:

$$S_w = \frac{V_w}{V_p}$$
$$S_o = \frac{V_o}{V_p} \qquad (8, 9, 10)$$
$$S_g = \frac{V_g}{V_p}$$

S_w = water saturation
S_o = oil saturation
S_g = gas saturation

The sum of the saturations is always equal to 1.

3.1.4 Relative and effective permeability

The term effective permeability is used when two or three immiscible phases are present in a porous rock. The presence of other phases greatly affects the ability of a fluid to move. The effective permeability of each phase is therefore very dependent on the saturations. Relative permeability is defined as the ratio of effective permeability to absolute permeability.

Darcy's law can be modified to account for multiple phases by using the effective permeability:

$$Q_i = K_{eff,i} \frac{A\Delta P}{\mu L}$$
$$k_{r,i} = \frac{K_{eff,i}}{K} \qquad (11, 12)$$

i is subscript for an arbitrary phase.

3.1.5 Wettability

A reservoir rock contains multiple phases like water, oil and/or gas. The phase in a porous rock with the strongest attractive forces to the rock surface is denoted as the wetting phase, and will stick to the rock's surface. The other phases will be non-wetting and will typically occupy the center of a pore. The wettability of a rock can be defined as the tendency of one fluid to spread on a solid's surface in the presence of another immiscible fluid[1]. The wettability of a rock is an important parameter that will affect for example relative permeability, capillary pressure and water flood behavior[1].

A solid's wetting preference for two fluids can be estimated by the contact angle between the two fluids, see figure 3-1. The angle is by definition measured through the densest phase, typically water.

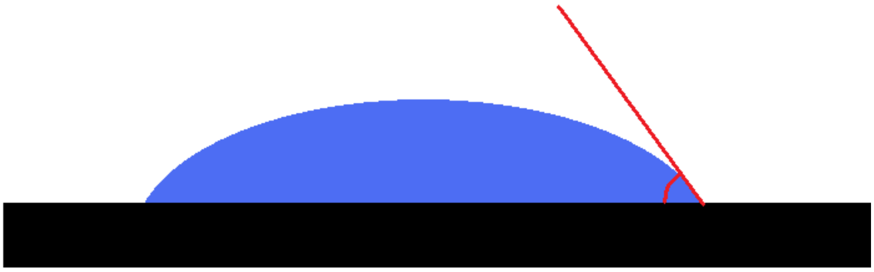

Figure 3-1: An illustration of a water droplet on a solid surface in the presence of air.

The wettability of a reservoir rock can be complex because the wettability can vary among the pores in a rock, and can in some cases be related to pore size. The original wettability of a rock can also be modified. A water wet rock can become oil wet by adsorption of a hydrocarbon molecule with a polar group, or by deposition of organic matter[1]. This leads to scenarios where some pores are water wet and others are oil wet. The wettability can be related to pore size as the three figures below illustrate. The blue area denotes water wet pores, and red denote oil wet pores.

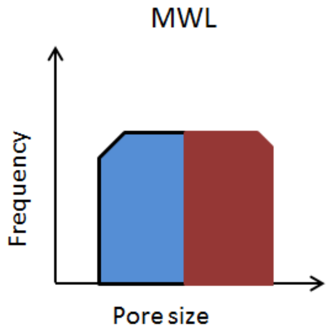

Figure 3-2: Mixed wet large

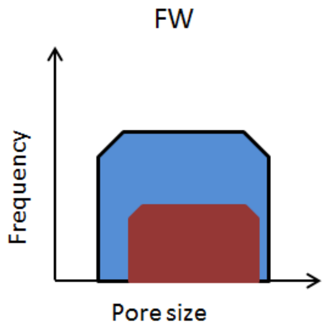

Figure 3-3: Fractional wet

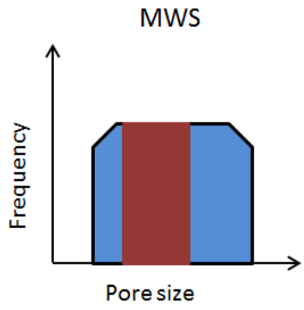

Figure 3-4: Mixed wet small

Two other explanations for oil-wet sites on a porous rock are: The mineralogy of the rock may cause the rock to lack of surface charge and therefore it will show little affinity for a polar water phase. Rupture of the water film that coats the rock surface can also cause oil wet spots. [2]

The wettability of a porous reservoir rock can be measured by various drainage and imbibition experiments. Two common wettability indexes based on these experiments are I_{USMB} and Amott-Harvey. The wettability of a rock can be roughly estimated without calculating any of these indexes. The indication of wettability of rocks in this thesis will be mostly based on the production profile during water injection. No oil production after water breakthrough is generally associated with a water wet rock. If there is two phase production after WBT, indicates that a rock is less water wet. Static parameters like connate water saturation, residual oil saturation, end point permeability for oil-phase at connate water saturation and end point permeability of water at residual oil saturation can also indicate the wettability of a rock.

3.1.6 Capillary pressure

The capillary pressure is defined as the pressure difference between the wetting and non-wetting phase. The pressure difference is a result from the difference in both adhesive and cohesive forces. The Young-Laplace equation gives the relationship between the pressure difference and the curvature of the interface [3]:

$$P_c = \sigma(\frac{1}{R_1} + \frac{1}{R_2}) \tag{13}$$

σ = Interfacial tension
R_1 and R_2 = Principal radii of the interface curvature

The capillary pressure for an oil-water in a capillary pipe is given as:

$$P_c = \frac{2\sigma_{ow}\cos\theta}{r} \tag{14}$$

σ_{ow} = interfacial tension between oil and water
θ = contact angle between oil and water
r = radius of the cylinder pipe

Equation 14 illustrates that the capillary pressure in a porous media is dependent on the wettability, interfacial tension and pore size. The capillary pressure increases with stronger wettability preference, increasing interfacial tension, and with decreasing pore size.

The capillary forces in a porous rock at laboratory scale can cause a deviation of the multi phase flow compared to the flow at reservoir scale. This deviation is caused by what is called capillary end effects. The wetting phase during multi phase flow is held back by capillary forces at the outlet of the rock. This can reduce the production of the non-wetting phase at the outlet. The impact of this effect on lab results is dependent on the length of the core plug, and the ratio of viscous and capillary forces.

3.2 Fluid properties

3.2.1 Viscosity

The viscosity of a fluid is the internal resistance of a fluid to shear [3]. Most fluids obey Newton's law of viscosity that states the following:

$$\tau = \mu \frac{\partial u}{\partial y} \tag{15}$$

τ = shear stress
μ = viscosity of fluid
u = velocity
y = length perpendicular to flow direction

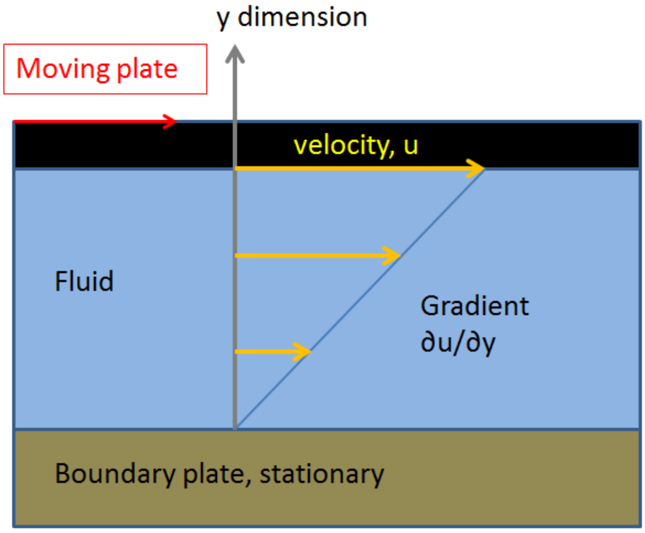

Figure 3-5: Illustration of a moving plate on top of a liquid.

The moving plate exerts a shear stress on the fluid creating a velocity gradient perpendicular to the flow direction. The viscosity is independent of shear rate for Newtonian fluids. The temperature will affect the viscosity of a fluid. This is especially the case for viscous oils. The viscosity of liquids will in general decrease with increasing temperature. The trend is opposite for gases [4].

3.2.2 Interfacial tension

Depending upon the difference in intermolecular forces between two liquids, the liquids can be miscible or immiscible. If the molecules of each liquid are most strongly attracted to the molecules of their own kind, the liquids will be immiscible [3]. The contact area between the two liquids is then minimized. Two liquids are miscible if the molecular attractions between the two molecules are equal or greater in strength, compared to the forces between the molecules of the same kind. Oil and water are not miscible. The polar water molecules are more attracted to each other, compared to the attractions to nonpolar oil molecules.

3.2.3 Density

The density of a fluid is defined as the mass of a unit volume. The density is dependent on pressure and temperature. The general trend is that density will increase with an increase in pressure, and decrease in temperature, and vice versa. Liquid water has a density of approximately 1000 kg/m^3 at atmospheric pressure. The density will slightly increase with increasing salinity. Oil has a density ranging from approximately 700 to 900 kg/m^3, depending on the composition. Gas has roughly a density of 1 kg/m^3 at atmospheric pressure and room temperature. The high compressibility of gases causes the density of gases to be very sensitive to pressure.

4 Surfactants in EOR

A surfactant is a molecule which consists of a long hydrophobic hydrocarbon chain bonded to a hydrophilic head group. The hydrophilic head groups may have charge or it may be built up only of polar uncharged atoms. The head group is usually anionic in EOR purposes. This is due to lower adsorption on the reservoir rocks [5], because most reservoir rocks have a negatively charged surface.

The surfactant molecule usually has limited solubility in both water and oil. The salinity of the water is an important parameter regarding the solubility of a surfactant in the water phase. Co-solvents like alcohols can be used to make the water solubility more favorable [6].

When an anionic surfactant molecule is added to water, it will dissociate into a positively charged ion and an anionic monomer. The monomers will collect into micelles with increasing surfactant concentration. When addition of surfactant molecules in a solution only leads to micelles, the critical micelle concentration, CMC, is reached. The interfacial tension will decrease with increasing surfactant concentration, until the CMC is reached.

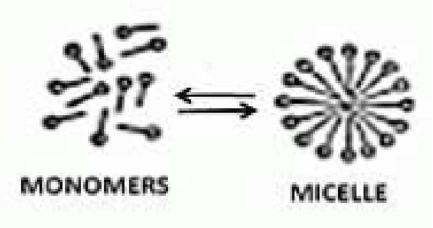

Figure 4-1: A figure of monomers and micelles.

The purpose of surfactant flooding in EOR is to reduce the interfacial tension between oil and water. The surfactant molecule can position itself in the interface between water and oil with the polar head in the water phase and the nonpolar hydrocarbon chain in the oil phase. A surfactant can decrease the interfacial tension by several orders of magnitude. This leads to weaker capillary forces and better microscopic displacement efficiency. This will result in lower residual oil saturation in the flooded areas of a reservoir. The capillary number is related to the residual oil saturation. N_c is in the range of 10^{-7} for conventional water floods. N_c will increase by increasing injection rate, increasing injection fluid viscosity and by reducing interfacial tension between oil and injection fluid. The shape of the CDC curve is affected by parameters like pore size distribution and wettability[7].

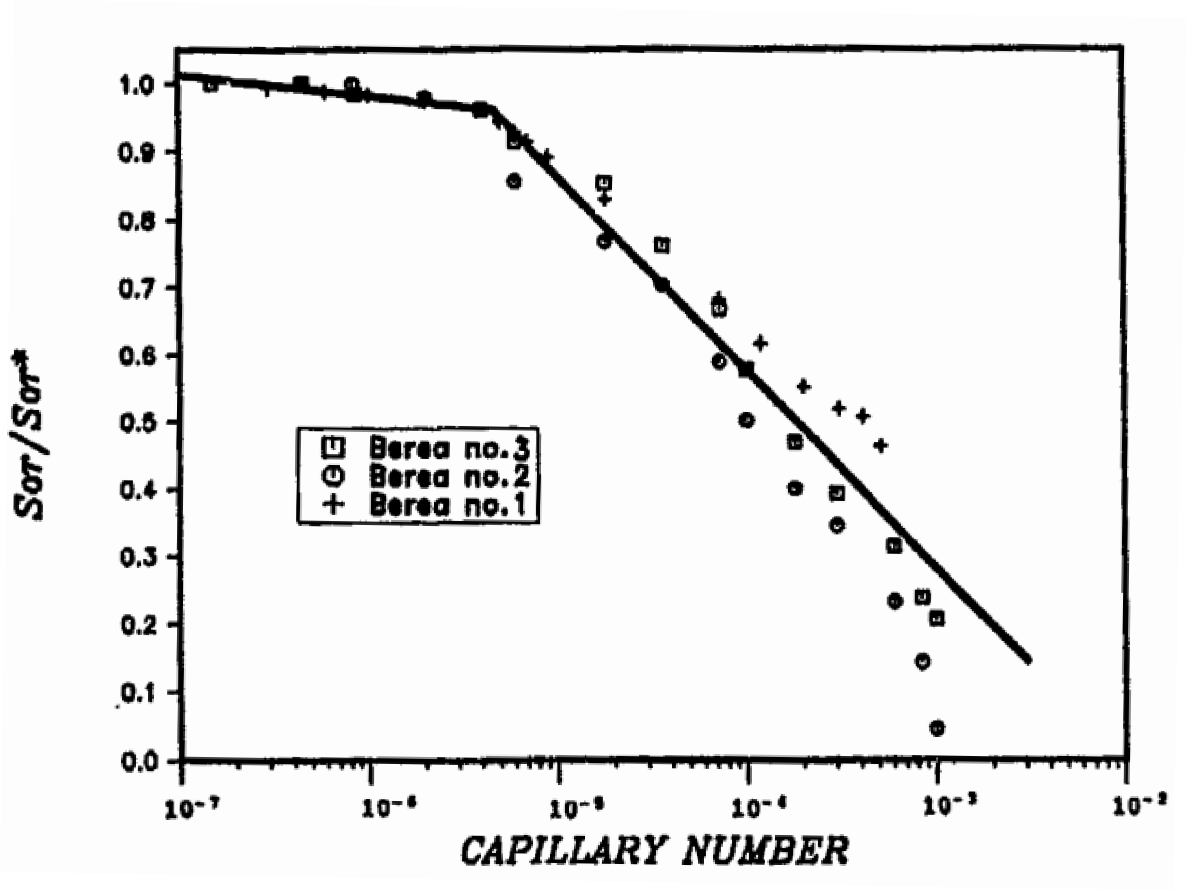

Figure 4-2: CDC curve for three outcrop Berea sandstones. [7]

The phase behavior of a surfactant is dependent on the salinity of the brine [3]. A mixture of water, surfactant and oil, can normally yield three different phases. Type II- has microemulsions in the water phase and type II+ has the microemulsions in the oil phase as the figures below show. A third phase between the oil and brine is present in type III.

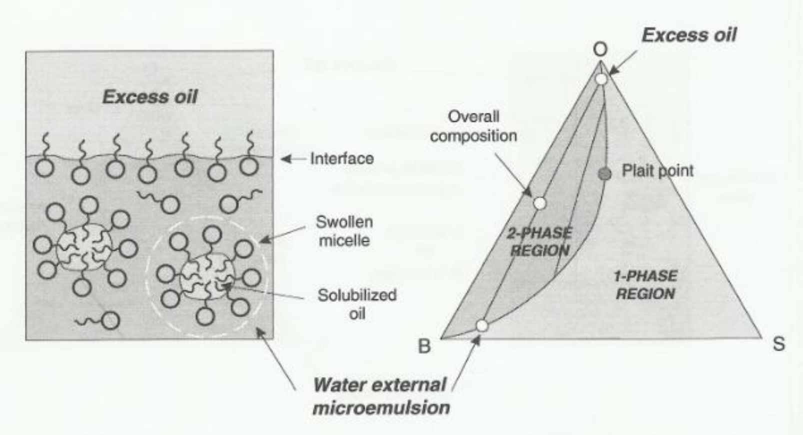

Figure 4-3: Type II- emulsions to the left and ternary diagram to the right. [3]

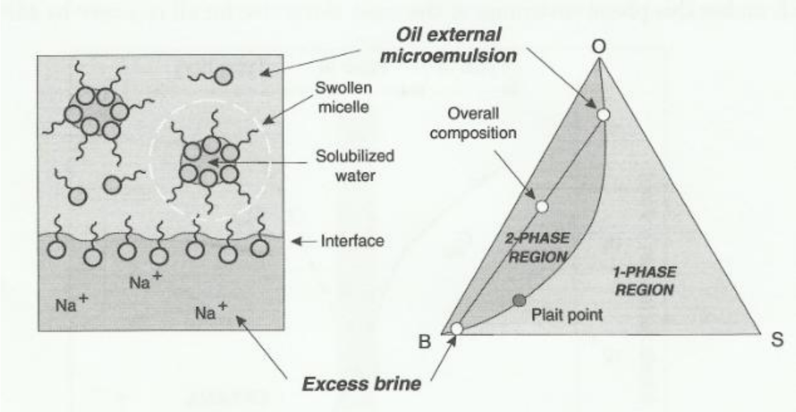

Figure 4-4: Type II+ emulsions to the left and ternary diagram to the right. [3]

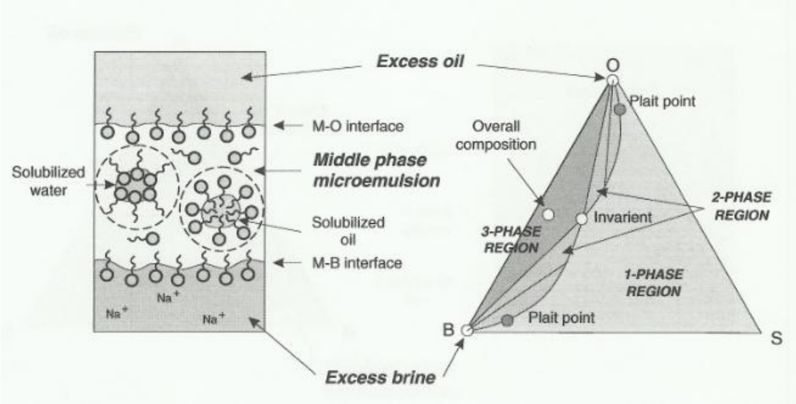

Figure 4-5: Type III emulsions to the left and ternary diagram to the right. [3]

Type II- system is usually present at low salinities. The surfactant has good solubility in the water phase. At high salinities, the surfactant has better solubility in the oil phase, and that will lead to a type II+ system. The type III can occur in between the two types.

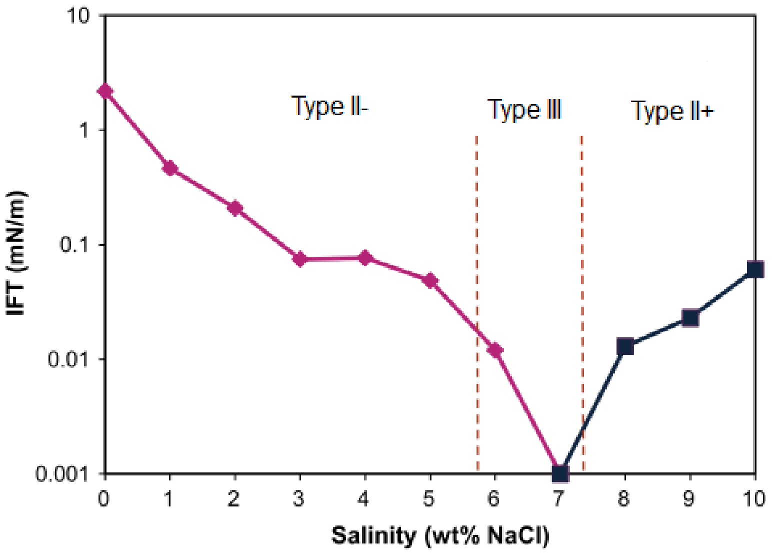

Figure 4-6: Relationship between IFT, micro emulsion system and salinity for a surfactant system. [6]

Many reservoirs that are candidates for surfactant flooding contain water with relatively high salinity. The surfactants salt tolerance need to be sufficient in order for the flooding to be successful.

Retention is a term for the total loss of chemicals in a reservoir. It can result from adsorption, precipitation, ion exchange and phase trapping [8]. In order to assess whether the use of a chemical surfactants are profitable, the amount of the expected retention should be calculated. In general, retention increases with increasing salinity and retention is thus smallest for type II- systems [6]. On this basis, it will not necessarily be the most beneficial economically with type III system, even though this system has the lowest IFTs. Surfactants in combination with low salinity water can therefore be very beneficial because it has the potential to produce low residual oil saturation as well as having low retention. Spildo et al. published a paper where they discussed the best compromise between solubility, phase behavior, interfacial tension and retention. Their conclusion was that type II- would overall be most efficient. [6] A very similar study by Sun et al. concluded that the region in type II- that was close to type III would be the overall best condition for surfactant flooding [9].

The surfactant used in this thesis is a sodium alkyl benzene sulphonate.

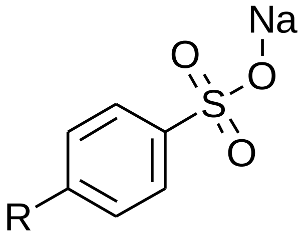

Figure 4-7: Molecular structure of the surfactant. R is a general term for a hydrocarbon chain.

5 Low salinity water injection

5.1 Introduction

Many laboratory studies and some field tests have shown that reducing the salinity of the injected brine can improve the oil recovery. Low salinity water can typically have a salinity of 2000 to 5000 ppm, and synthetic sea water has a salinity of approximately 36000 ppm. The improved recovery of low salinity water has in some cases been present in secondary mode, and in other cases been present in tertiary mode. The combination of the type of crude oil, brine and reservoir rock will greatly influence whether a lowsal effect will take place. The underlying mechanisms are as mentioned not fully understood and that makes it more difficult to predict when an improvement in recovery is to be expected. The increased oil recovery is assumed to be the result of more than one mechanism.

The first research on low salinity flooding started several decades ago, but the topic first got significant attention in recent years. The number of publications was less than three per year until 2006. The number of publications on the topic of lowsal has increased rapidly since 2006.

5.2 Literature study

The first reports of improved oil recovery by low salinity brine dates back to as early as the 1960s, but the topic did not get much attention until the 1990s. Tang and Morrow identified in 1999 that presence of connate water, significant clay fraction and crude oil was necessary, but not a sufficient condition for observing a lowsal effect. Some outcrop rocks that met these requirements did not respond to lowsal [10].

The effect of lowsal flooding has been tested extensively on outcrop rocks, but reservoir rocks have also been tested. Winoto et al. summarized results from 23 outcrop rocks and 18 reservoir rocks and compared the results [11]. There was a clear trend that reservoir rocks responded better to lowsal than outcrop rocks. They did not present any thoughts as to why reservoir rocks responded better.

Winoto et al. also tested injection of high salinity water with high salinity water as initial water, and injection of LS water with LS as initial water. Comparing the results showed that no clear trend was observed. This suggests that a decrease in salinity is necessary. This is supported by the mechanism of double layer expansion which is discussed later.

There are some articles that discuss the lowsal effect on a producing oil field. Robertson posted a paper in 2007 regarding this matter [12]. Three fields in Wyoming with similar reservoir characteristics were compared. The results showed that lower salinity ratio between injected water and connate water corresponded in higher oil recovery. This was a qualitative evidence of improved oil recovery on field scale by lowsal water. Uncertainties in the data include that the salinities of injected water did vary and was only estimated. Polymers were also injected in the three reservoirs to some extent, but the author assumed that the amount of polymers injected were equal.

McGuire et al. published a paper in 2005 where the results from four single well chemical tracer (SWCTT) tests were reported [13]. The residual oil saturation near the wells that were tested was reduced most likely due to lowsal. The incremental recovery increase ranged from 6 % to 12 %.

Batias et al. also reported reduced residual oil saturation in the near wellbore area by SWCTT [14]. The low oil saturation was credited to lowsal effects, although they could not exclude the possibility that it was due to three phase effects from gas.

Not all field tests for lowsal have shown promising results. Tests from core experiments and one SWCTT on the Snorre field were performed by Skrettingland et al. [15]. They compared residual oil saturation after sea water and lowsal flooding. They concluded that the potential for lowsal was low. Their explanation for the low potential was because the wettability of the reservoir already was close to optimal such that sea water was already efficient. They only mention wettability even though there are other possible mechanisms in the literature that could result in increased recovery.

The increased recovery by lowsal can be present in secondary mode, meaning that oil has not been produced by any other means prior to injection. Gamage and Thyne published a paper in 2011 where secondary mode produced more oil compared to tertiary mode [16]. This is not something that should be generalized, as other experiments show better lowsal response in tertiary mode [17]. Zhang and Morrow states in their conclusion in this paper that if lowsal improves recovery, a response is usually observed for both secondary and tertiary mode. Tertiary mode is meant as an injection that starts after another fluid has already been injected, and oil is typically at residual saturation.

The kinetics of lowsal was under investigation in a paper published by Berg et al. in 2013 [18]. They studied contact angles on oil droplets that were attached to clay particles on glass. The oil droplets were put in equilibrium with high salinity water. The water was changed to lowsal and the contact angles were continuously monitored.

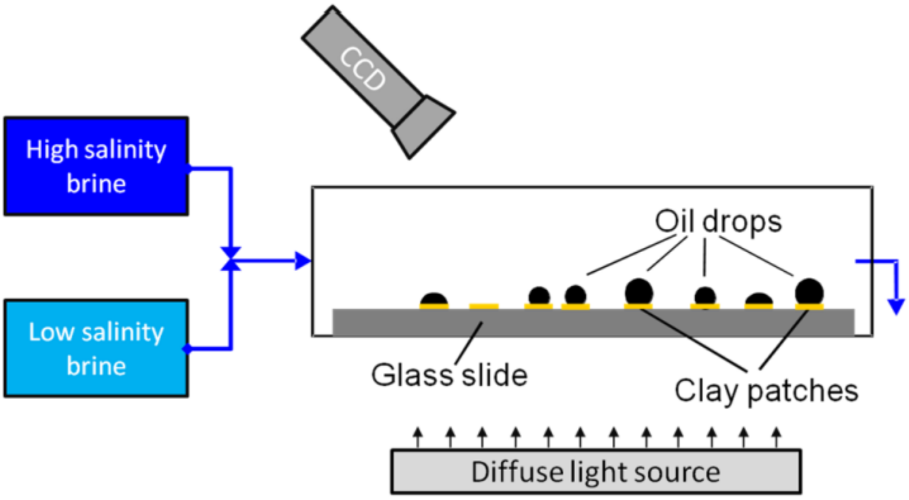

Figure 5-1: Sketch of the experimental setup.

Oil droplets were approximately 100 times larger than their size in a porous media. The water was changed at a very low rate to diminish any viscous force. The forces that determined when and if an oil droplet would detach were buoyancy and adhesion. The experiments showed that lowsal water resulted in more water wet conditions as the contact angles decreased. This resulted in smaller surface area for the oil to adhere to the clay, and eventually the oil would detach at a certain critical contact angle. The conclusion of the paper with regards to kinetics was that the lowsal mechanism of detaching oil required more time than expected by theoretical calculations. They concluded that the time scale for wettability modifications in common SCAL experiments could be long enough to lead to false negative results.

Most of the published research about low salinity flooding has been on sandstone rocks. It was previously believed that low salinity flooding would not give any effect in carbonates, but some positive results on carbonates have been reported in recent years. [19, 20]

5.3 Mechanisms of low salinity water injection

Several mechanisms have been proposed to describe the lowsal effect. These mechanisms include wettability alterations, pH change, multicomponent ionic exchange, expansion of the electrical double layer and fines migration.

Tang and Morrow proposed in 1999 that the lowsal effect could be due to partial stripping of mixed wet fines on the pore wall. These fines were a type of clay. A decrease in salinity leads to expansion of the electrical double layer that promotes partial stripping of fines.[10] Released fines can also possibly improve oil recovery by microscopic diversion if the fines block some pathways for the injected water. A permeability reduction would then be a result of pore blockage. Fines migration is not likely to be the main cause for improved oil recovery based on later studies. There are now many examples in the literature where the lowsal effect is present, but there is no fines migration or permeability reduction. Lager et al. stated in 2006 that fines migration was an effect rather than a cause [21]. These counter examples do not prove that fines migration is not a mechanism that improves recovery, but there are at least other mechanisms that can also improve recovery.

McGuire et al. wrote in 2005 that lowsal flooding appeared to be similar to alkaline flooding and surfactant flooding in terms of affecting the wettability of the rock and interfacial tension[13]. They proposed that the main lowsal mechanism was generation of surfactants from the residual oil at elevated pH. They claimed that the lowsal water had lower interfacial tension with the oil compared to higher salinity water, which could improve microscopic sweep. They also claimed that the oil recovery was improved because the increased pH of the water made the reservoir rock more water wet. Later studies have shown that pH is not an important cause of lowsal effects. Lager et al. reported in 2006 experiments that contradicted the importance of pH [21]. This was demonstrated by results where the lowsal effect was present but the pH was below 7. Experiments where the pH of the effluents was as high as 9, but no lowsal effect was observed is another example. The change in pH associated with lowsal is due to carbonate dissolution and cation exchange. An argument against the pH effect in a reservoir is that the pH in a reservoir is not likely to increase much anyway due to presence of CO_2.

Lager et al. proposed a mechanism in 2006 regarding multi component ionic exchange. [21] This process is that during lowsal injection, cations like Ca^{2+} and Mg^{2+} is adsorbed to the surface of the rock, and desorption of organic-metallic complexes and organic polar components. This also shifts the wettability of the rock towards more water wet which they consider to be more favorable.

Low salinity water can influence the wettability of a rock. This is because changing the salinity affects the thickness of the electrical double layer [22-24]. The thickness increases when the salinity is decreased as the figure below illustrates.

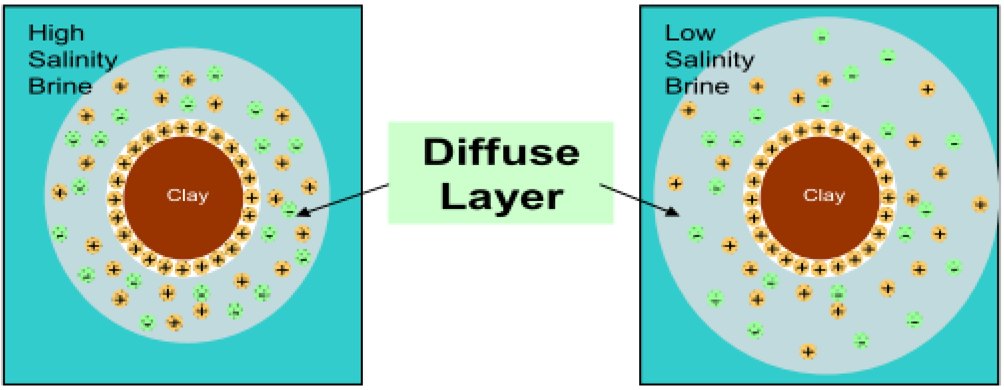

Figure 5-2: Illustration of the electrical double layer around a negatively charged clay particle. [22]

The wettability can also be altered as previously mentioned because lowsal can promote desorption of particles that make the rock surface oil wet and increase the thickness of the water film. If alteration of wettability is beneficial to oil recovery should in theory be determined by the initial wetting state. If the wettability shift is towards more neutral wetting, then one should expect a better microscopic efficiency. The Omar field in Syria is an example where the initial wetting state of the reservoir was strongly oil wet, but injection of low salinity water altered the wettability to be somewhat water wet, resulting in improved recovery[25].

Both crude oil/brine and brine/rock surfaces are negatively charged in the pH range of higher than 6 [26]. These two interfaces should therefore be repelled. This repulsion force is reduced by the presence of multivalent cations in the brine. This equilibrium is disturbed when lowsal is injected, and ions are exchanged until a new equilibrium is reached and the electrical double layer. This could lead to detachment of clay particles leading to fines migration and/or destabilization of oil layers that adhere to pore walls [27].

Disturbing the equilibrated state between oil and high salinity water, with lower salinity water might be important in lowsal mechanisms. Then the reason why reservoir rocks seem to respond better to lowsal might be because these rocks have been equilibrated with high saline water through geologic time, and outcrop rocks have been exposed to freshwater and oxygen and saturating an outcrop rock with seawater for some weeks might not be sufficient to mimic a reservoir rock.

5.4 Low salinity surfactant injection

A combination of using low salinity water with surfactants has several advantages and shown some promising results. [28-30]The two EOR methods can greatly benefit from each other. The challenges for a surfactants phase behavior and stability are reduced in a low salinity environment. Divalent cations can greatly reduce the efficiency of a surfactant flood. Using surfactants can also benefit the lowsal process. The mobilization of additional oil by a lowsal mechanism can later be trapped again in a porous media due to capillarity. This could be prevented by the use of surfactants.

Alagic and Skauge presented in 2010 results from four core floods on Berea cores that had been aged. [28] Two cores were produced by injection of 5000 ppm NaCl, and lowsal surfactant injection afterwards. The surfactant solution had a pH of 11.6. The oil recovery was 92 % and 94 %. The IFT between surfactant solution and oil was $1.24 \cdot 10^{-2}$ mN/m, corresponding to a capillary number of $2.2 \cdot 10^{-4}$. This recovery is much higher than one should expect from CDC for Berea. The extra recovery could be a result of the combined process of lowsal and surfactant. The third core was injected with sea water in secondary mode and lowsal surfactant in tertiary mode. The recovery was much lower with the high salinity environment prior to injection. The fourth core was injected with lowsal in secondary mode and high pH lowsal afterwards. The high pH was injected to test the impact of high pH to recovery and whether the high pH of the surfactant contributed to the high recovery. The lowsal with high pH increased the oil recovery from 61 % to 68 %. Alagic and Skauge concluded that the surfactant alone could not be credited the high recoveries, and that the alkaline effect and lowsal effects also could play an important role.

The effect of surfactant concentration and slug size was evaluated by Alagic et al. [31] Lowsal surfactant was injected in three cores. The first was injected with 1 wt% of surfactant until no more oil was produced. The second core was injected with one pore volume of 1 wt% of surfactant and flushed with NaCl water afterwards until the oil production stopped. The third core had the same procedure as the second, except that the surfactant concentration was 0.3 wt%. The conclusion from the experiments was that the recovery was mostly dependent on surfactant concentration and less on slug size of the surfactant solution.

Alagic et al. published a paper in 2011 about the effect of crude oil aging on low salinity and low salinity surfactant flooding [27]. Four rocks were tested of which two were aged and two were not. The conclusion was that the aged cores had higher oil recovery for both lowsal injections and lowsal surfactant injections.

Spildo et al. tested lowsal and lowsal surfactant on three Berea rocks[30]. Increasing surfactant concentration from 0.2 % to 1 % did not improve recovery in the two experiments, which could perhaps be unexpected from the previous results by Alagic. But their explanation was that the oil recovery was already very high so the potential for the 1 % surfactant was very low. Their conclusion was that lowsal response for the three cores was low. Flooding surfactants in a Winsor type 1 system gave high oil recovery and low retention.

Intermediate wetting gave lower residual oil saturations. Their explanation is that oil layers that stick to a pore wall might be easier to mobilize with lowsal surfactants compared to oil globules that are trapped due to snap off.

Johannessen and Spildo compared the efficiency of surfactant flooding at low salinity and at moderate salinity[29]. The surfactant they used had low IFT in the lowsal region and ultralow IFT at a salinity that was high enough that lowsal effects could not take place. The ultimate recovery for the five rocks that were flooded was very similar. The low salinity surfactant flooding gave the same oil recovery as the surfactant flooding at ultralow IFT even though the capillary number was two orders of magnitude larger in that case. This could be due to the combined effect of low salinity surfactant. The recoveries for the surfactant flooding at moderate salinities corresponded to the CDC for Berea. The recoveries for low salinity surfactant were much higher than the CDC predicts, as also Spildo and Alagic previously have observed. The retention of surfactant during lowsal flooding was much lower compared to at moderate salinity.

6 Polymers in EOR

Polymers are large molecules that are built by a repeating pattern of smaller molecules. These large molecules have higher resistance for flow compared to small molecules. The viscosity of water is therefore increased by adding a polymer. Increasing the viscosity of injection water can be very beneficial, by improving the mobility ratio between the injected liquid and the reservoir oil. Polymer injection can especially be advantageous in heterogeneous reservoirs and in reservoirs with viscous oils. It can also be profitable as assistance in surfactant flooding. A slug of polymer is in that case injected after the surfactant to improve the mobilization and recovery of oil.

There are two types of polymers: synthetic polymers and biopolymers. The most widely used synthetic polymer is partially hydrolyzed polyacrylamide (HPAM). The most common biopolymer is xanthan.

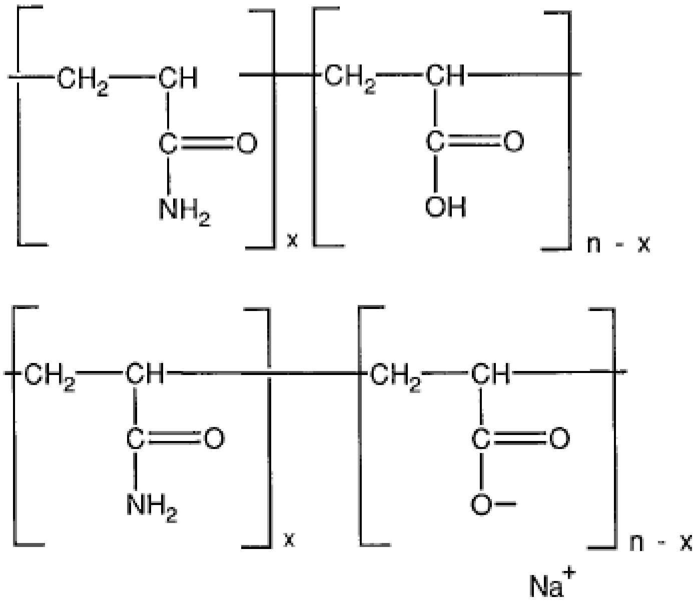

Figure 6-1: The primary chain structure of HPAM. [32].

Polymer solutions are not newtonian liquids. This means that the viscosity of the solution is dependent on shear rate. The viscosity will typically decrease with increasing shear rate at the lowest shear rates, and stabilize somewhat at higher shear rates. The viscosity can also increase again at very high shear rates. It is not straight forward to know the viscosity of the polymer in a porous media, referred to as apparent viscosity. It is difficult to correlate the viscosity measured by a rheometer, with the viscosity in a porous media, as a rotating spindle in a cup is very different from flow in porous media.

The stability of a polymer is important in determining the efficiency and economy of a polymer flood. A polymer is susceptible to several types of degradation. Chemical degradation refers to breakdown of the polymer molecules. This could be due to short term attack by contaminants like oxygen or through longer term attack of the molecule by processes like hydrolysis.[32] Mechanical degradation is breakdown of the molecule due to high mechanical stress usually associated in the region with high flow rates close to the injection well. A synthetic polymer like HPAM is more sensitive to mechanical degradation compared to a biopolymer like xanthan. Biological degradation is degradation of polymer molecules by bacteria. This can especially be a problem for biopolymers if the reservoir temperature is low and if no biocide is injected. [32]

Injectivity can be a challenge when using polymers. The injection rate may have to be decreased as a result of the more viscous injection fluid if the injection pressure is to remain constant. It is important that the injection pressure does not exceed the fracturing pressure, as that would risk major fracturing of the reservoir. A crack in the cap rock could lead to losses of hydrocarbons.

Polymers can reduce the permeability in a reservoir, by molecules being adsorbed or trapped in pores. The residual resistance factor, RRF, is a parameter that quantifies the reduction in permeability after a polymer flood compared to the permeability before the polymer flood. The RRF is defined as follows:

$$RRF = \frac{\lambda_w}{\lambda_{wp}} = \frac{k_w}{k_{wp}} \tag{16}$$

Using polymers at low salinity is beneficial as the viscosity for HPAM is generally higher and retention lower. [32] [33]

7 Experimental apparatus and core material

7.1 Core material

The core material used in this thesis is outcrop Berea sandstone. These sedimentary rocks have been cut in a cylindrical shape with a length of approximately 6.5 cm and a diameter of 3.8 cm. Berea sandstone is considered to be a homogenous rock. Berea sandstone mainly consists of quartz and feldspar, but can contain up to approximately 10 % clay. [34]

7.2 Core lab equipment

Exxon core holders were used in the experimental work.

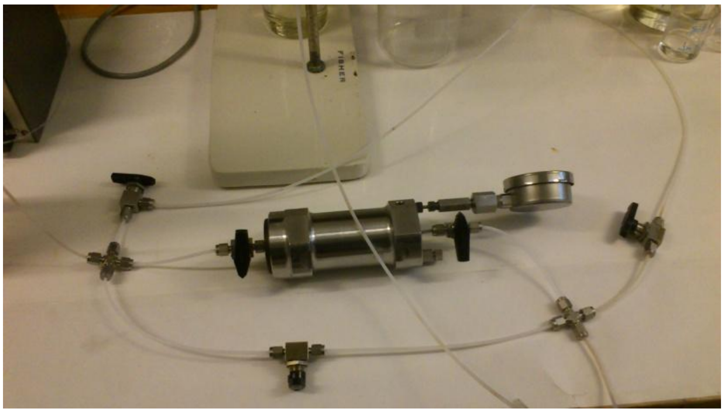

Figure 7-1: Picture of the core holder

Quizix pumps were used for porosity measurements and for pressurizing the surrounding liquid in the core holder, and Pharmacia LKB P-500 pumps have been used in the core flooding experiments.

Cylinders with a movable piston were used to inject fluids into the cores.

The pressure measurements were taken by a pressure transducer from Fuji electric France. The pressure range is from 0 to 5000 mbar.

A fraction collector was used for automatically distributing the effluent in glasses. The instrument switches glasses at predetermined time intervals. The instrument used is a Foxy Jr from Teledyne Isco.

The back pressure regulator used is produced by Grove Valve And Regulator Company and was set to around 6 bars for core flooding experiments.

7.3 Fluid analysis equipment

7.3.1 Density meter

The instrument that was used for density measurements was a DMA 60 density meter produced by Anton Paar. It consists of an oscillating hollow tube that can be filled with a fluid. The instrument has a heating and a cooling device that allows the user to control the temperature of the fluid to be measured. The tube is surrounded by the water that adjusts the temperature, and keeps the temperature stable.

The frequency of the tube's oscillation is a function of the fluids density. The period of the oscillation is measured in a certain time interval.

The instrument must be calibrated by calculating an apparatus constant, A. This is done by measuring the period of two fluids with known density. Distilled water and air have been used for that purpose. The density of distilled water was found in the literature. [35] The density of air can be calculated when the air pressure, humidity and temperature is known by the following equation:

$$\rho_{air} = 0.46464 \cdot \frac{B - 0.08987 \cdot F}{T} \cdot 10^{-3} \tag{17}$$

ρ_{air} = density of air, [g/cm^3]
B = atmospheric air pressure, [mmHg]
T = temperature of fluid, [K]
F = relative humidity of air, [%]

The apparatus constant for a given temperature is then obtained from the following equation:

$$\rho - \rho^* = \frac{1}{A}(T^2 - T^{*2}) \tag{18}$$

ρ = density of fluid [g/cm^3]
A = apparatus constant [g/(s^{2}cm^3]
T = time period [s]

Parameters with asterisk, *, refer to pure solvents.

The density of a fluid is calculated by measuring the period of the tube's oscillation when the apparatus constant is known.

The uncertainty in the density results is dependent on the accuracy in measurement of temperature and period. The uncertainty is roughly estimated to be 0.005 g/cm3 in the results.

7.3.2 Rheometer

A Kinexus Pro+ has been used for viscosity measurements. This is a rotational rheometer with a temperature range of -40 °C to 200 °C. The control mode can be shear stress and shear rate. Different geometries are available for the instrument. The proper geometry to use depends on the viscosity of the liquid of interest, and also whether having the most stable temperature is of importance. The geometries used are double gap, Peltier cylinder and cone-plate.

The temperature of the liquid is controlled by a separate unit that is connected to the rheometer.

The instrument can measure the viscosity of a liquid by rotating the spindle at a given rotational speed yielding a certain shear rate. The corresponding shear stress is found by measuring the torque exerted by the liquid and taking into account the geometry used. The viscosity can be calculated by Newton's law of viscosity when shear rate and shear stress are known.

The uncertainty for the viscosity measurements is 5 %.

7.3.3 Spinning drop

SITE100 from Krüss has been used for interfacial tension measurements. A capillary tube is filled with the heaviest liquid, of the two of interest. A droplet of the lighter phase is injected into the tube. The tube is set to rotate and the heaviest phase is pushed towards the outer diameter of the tube, and the lighter phase is found in the center of the tube. Increasing the angular speed causes the droplet to elongate due to centrifugal forces.

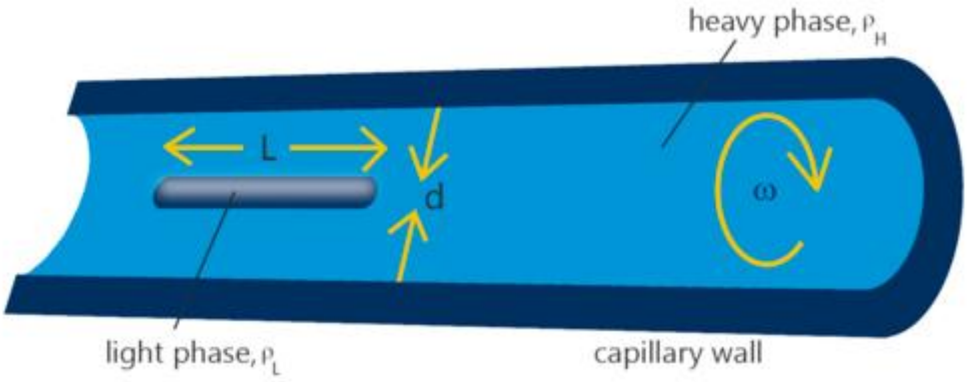

Figure 7-2: Principle of the spinning drop method. [35]

Vonnegut's equation relates the interfacial tension to the radius of the droplet, the density difference and speed of rotation. [36] The interfacial tension is thus obtained by measuring the radius of a droplet of the lightest phase in a spinning capillary tube. The length of the droplet has to be at least 4 times longer than the diameter, in order to neglect the radius parallel to axis of rotation and only take into account the radius perpendicular to axis of rotation. The diameter of the droplet is measured through the instruments magnifying glass.

$$\sigma = \frac{r^3 \cdot \omega^2 \cdot \Delta\rho}{4} \qquad (19)$$

σ = interfacial tension [N/m]
r = radius of droplet [m]
ω = angular frequency of rotation [s^{-1}]
$\Delta\rho$ = density difference for the two liquids [kg/m^3]

The uncertainty in measurements for the spinning drop is dependent on how accurate the diameter of the drop can be measured. This can be measured accurately by the instrument. The biggest uncertainty when measurements in the range of 10^{-2} to 10^{-3} mN/m are made is the reproducibility, which can vary by over 50 % in the mentioned region. However, the measurements are still useful even though the reproducibility is somewhat poor, because the interfacial tension is a parameter that can span several orders of magnitude. The uncertainty in interfacial tension measurements is estimated to be ±0.01 mN/m.

7.3.4 pH

The pH meter used is manufactured by Hach. The resolution of measurements in pH is 0.01.

7.4 Liquids

Brine with the following compositions was used in the experiments.

Table 7-1: Ion composition of synthetic water

Synthetic seawater (SSW)	**PPM**
NaCl	24890
CaCl	1394
$MgCl_2$	5209
$NaHCO_3$	192
Na_2SO_4	4056
KCl	668
TDS	36409

Table 7-2: Ion composition of low salinity water.

1/22 SSW	**PPM**
NaCl	1131
CaCl	63
$MgCl_2$	237
$NaHCO_3$	9
Na_2SO_4	184
KCl	30
TDS	1655

Table 7-3: Ion composition of low salinity water.

1/10 SSW	**PPM**
NaCl	2489
CaCl	139
$MgCl_2$	521
$NaHCO_3$	19
Na_2SO_4	406
KCl	67
TDS	3641

Water with 3000 ppm NaCl content was also used as low salinity water.

The oil used during aging was a North Sea crude oil.

The oil used for the dynamic experiments is a mixture of North Sea crude oil and 40 wt% octane. This mixture has a viscosity of 3 cP at room temperature. The octane was added so that water and oil would have roughly equal mobility in the porous media, and this is more representative to the mobility ratio in most reservoirs on NCS. The acid and base number of the oil mixture is respectively 2.84 mg KOH/g and 0.95 mg KOH/g.

Marcol 152 was used to displace water to residual saturations before it was exchanged by another type of oil.

7.5 Experimental procedures

7.5.1 Density measurements

The heating and cooling device connected to the density meter is switched on. The hollow tube is thoroughly cleaned and acetone which evaporates quickly is injected last. Measurements can start when the temperature in the water bath has stabilized to the desired temperature.

The density meter measures the period of oscillation when the tube is filled with air. The instrument measures the period for a certain time interval and the averaged period is shown on the display. An average of five periods is taken when the measurements are stable. The humidity and atmospheric pressure in the room is recorded. The density of air can be found by the equation as described earlier.

Distilled water is injected from a syringe into the tube. The volume of the tube is approximately 1 ml, but a larger volume is injected to flush the tube. The syringe is left in the inlet of the tube, and the outlet is sealed by a rubber plug. An average of 5 readings is taken when the measurements are stable. The density of distilled water can be found in the literature.

The apparatus constant for the current temperature is calculated from equation 18.

The procedure for the following density measurements at the same temperature is done the same way as for distilled water. The tube is cleaned between each sample.

7.5.2 Interfacial tension measurements and phase studies

Two surfactants were evaluated with regards to phase behavior and interfacial tension with oil. 1 wt% of active matter of the two surfactants were added to 3000 ppm NaCl. The two surfactant solutions were observed the following days to look for any precipitation and turbidity.

The surfactants were only going to be used in a low salinity environment with cores pre flushed with 3000 ppm NaCl. A complete phase study with varying salinities and determination of tolerance of divalent cations was therefore not performed.

Filling and calibration

The surfactant solution is injected in the spinning tube and an endpin that seals the tube is inserted on one side. A calibration needle with a diameter of 0.668 mm is placed inside the tube. The distance from the lens to the needle and the amount of light in the tube is adjusted until the interface of the needle is as sharp and clear as possible. The calibration is done when the upper and lower interface of the needle have been recorded by the instrument software.

The needle is removed and more of the surfactant solution is injected in the tube. The tube is tilted with the sealed end at the bottom and spun at 5000 rpm to remove any potential air in the tube. More of the heavy phase is injected, and the tube is spun at 3000 rpm. This can be repeated until the user is confident that there is no air in the tube. The temperature of measurements is set to 23 °C.

Measurements

The difference in density for the two fluids is entered in the software. Approximately 5 µl of the oil phase is injected in the tube with a micro syringe. The endpin is inserted. The tube is set to spin while the tube is tilted to allow oil droplets to reach the middle of the tube, where the lens is located. A suitable oil droplet for measurements should be at least 4 times longer than the diameter. The measurements are continuously made until the interfacial tension is stable. An average interfacial tension is calculated in the time interval of at least 30 minutes after the IFT is stable. This is redone for different rotation speeds.

Measurements are made for pre equilibrated samples and for fresh samples that have not been in contact previously. The oil used is a North Sea crude oil with 40 wt% of added octane.

7.5.3 Rheometry measurements

A Kinexus pro rheometer has been used in this thesis.

The instrument automatically detects the geometry that is mounted. Liquids with viscosity of 5 cP or lower are measured using the double gap. Cone plate is used for more viscous polymer solutions. Measuring the viscosity for marcol152 at different temperatures is done with the Peltier cylinder geometry. The volume needed for a measurement is given by the Kinexus computer program, rSpace. The user determines what sequence to run after zeroing gap is performed and the sample is added. Sequences used are a table of temperatures for a given shear rate and a table of shear rates for a given temperature. Polymer solutions which are not Newtonian are measured at 23 °C for different shear rates. The viscosity of water solutions can be measured at a given shear rate, typically 100 s^{-1}.

7.5.4 Preparation of solutions

Procedure for preparation of HPAM solutions

A mother solution of 5000 ppm in 0.3 weight % NaCl has been prepared in the following way: Approximately 540 g of pre-filtered 0.3 weight % NaCl is added to an 800 ml beaker. A magnetic stirrer is used to create a vortex in the solution. The correct speed is set when the vortex extends about 75% towards the bottom. HPAM is carefully added to the solution until the concentration is 5000 ppm taking into account that the activity of HPAM is 90 %. The polymer powder is added just below the vortex shoulder. The rotation speed is afterwards reduced to the slowest speed where the polymer particles still float in the solution. The beaker is covered with parafilm and the solution is set to stir overnight. The solution is transferred to a Duran flask the next day. The solution is stored in a refrigerator.

Dilution of stock solution

Half of the brine and a magnet are added to a Duran flask. Polymer from the mother solution is added by weight. The rest of the brine is added to match the desired concentration. The lid is put on and parafilm is also used to seal. The solution is stirred at slow speed overnight. The solution is filtered the next day with a 40 µm paper and transferred to a Duran flask. The solution is stored in a refrigerator.

Surfactant solutions

The two surfactants used in this thesis are referred to as DD044/2 and DD044, and are supplied from Huntsman. Both surfactants are of type sodium alkyl benzene sulphonate. They have an active matter of 25.6 % and 24.5 % respectively. The surfactant is added to 3000 ppm NaCl until the concentration of the surfactant is 1 % active matter. The salinity of the water is approximately 2900 ppm NaCl after addition of one of the surfactants.

7.5.5 Core flooding procedures

Six cores have been used for dynamic core displacement experiments: L1, L2, O1, O2, O3 and O4. L1 and L2 have been previously used in other experiments, but have been thoroughly cleaned with toluene and methanol. O1 - O4 have not been used before and are fresh outcrop rock.

Core preparation

The cores are put in a heating cabinet after they were cut to the appropriate size. The cores are dry after a few days. The dry rocks are weighted, and the length and diameter are measured.

Core mounting

Exxon core holders have been used in this thesis. The dead volumes of the inlet and outlet on the core holder are measured with a Quizix pump. The core is put inside a cylindrical piece of rubber that will separate the core from a pressurized liquid on the outside. A metal lattice is placed at both sides of the core. The surrounding liquid is pressurized to approximately 25 bars. The outlets from the core are open when the surrounding liquid is pressurized. The outlets are open to spot any leakages from the surrounding pressure to the core.

Vacuum pump

A vacuum pump is connected to one side of the core and a pressure monitor to the other. The pump will run until the pressure in the core is approximately 1 Torr.

Porosity measurements

A Quizix pump that can deliver a constant pressure is connected to a cylinder which is filled with synthetic seawater. The pressure is set to 5 bars and the cumulative volume of synthetic sea water injected in the core is monitored until no more water is injected. The volume of interconnected pores will be known after subtracting the dead volumes. The effective porosity of the rock is then obtained.

Permeability measurements

The absolute water permeability is measured a few days after the core has been saturated with synthetic sea water.

The permeability is measured by pumping a fluid through the core at different rates. The corresponding pressure drop for the core is measured. A plot of flow rate and pressure drop will yield a linear curve, as can be seen by Darcy's law. The permeability of a rock can be calculated from the slope of the linear curve by Darcy's law.

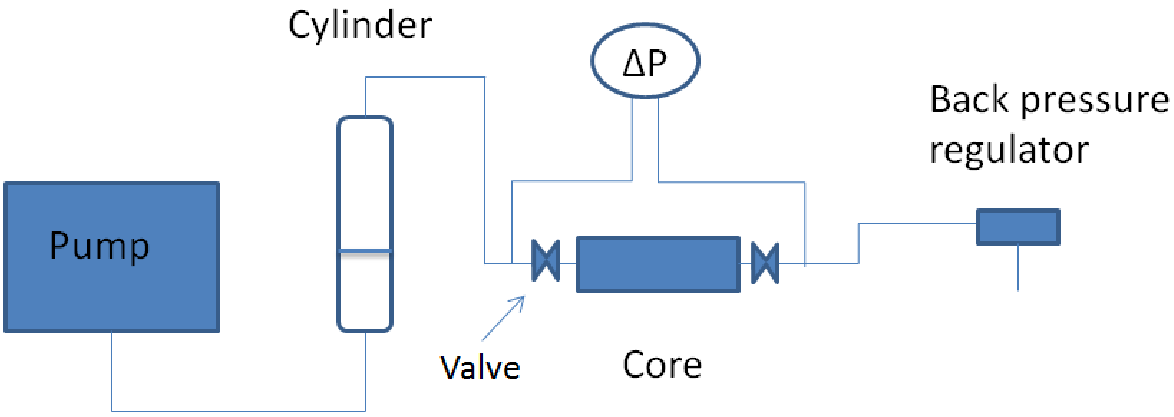

Figure 7-3: Sketch of setup for measuring permeability.

The core is first flooded with 1-2 pore volumes before the pressure drop is monitored. The back pressure regulator is set to approximately 6 bars. Any potential free gas in the core will most likely be solubilized with a fluid pressure of 6 bars. The pressure is measured for 5 rates ranging from 20 to 100 ml/h. The room temperature during the experiment is also measured to get exact values of fluid viscosity. Permeability is measured for both directions of flow.

Injection of marcol 152

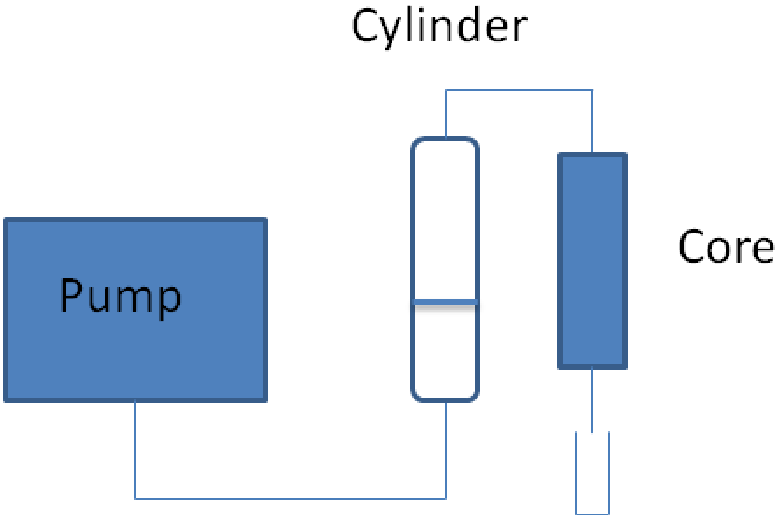

Figure 7-4: Setup for marcol 152 injection.

The core holder is placed vertical and marcol is injected from the top side since the density difference helps stabilize the oil front. Marcol is injected in the core at a rate of 0.1 ml/min until no more water production is observed. The same procedure is then repeated with rate at 0.5 ml/min and finally at 1ml/min. The total water production is measured in a 25 ml measuring cylinder.

Permeability of oil

The procedure for oil permeability at residual water saturation is measured in the same way as for water. A sample of the effluent oil is taken for viscosity measurement. A filter of size 0.5 µm is used for the crude oil.

Aging

The temperature in the cabinet is set to 110°C. The oil in the rocks is exchanged with a North Sea crude oil. The rocks are mounted in a long core holder that can fit several rocks. Marcol 152 is used as surrounding fluid with a pressure of approximately 25 bars and the outlet valve for the surrounding marcol is open and connected to a pressurized canister of gas, so the marcol can expand during heating. The outlet of the core holder is also open and connected to a back pressure regulator set to 8 bars, to prevent the oil from vaporizing. New oil is pumped in to exchange the oil once a week.

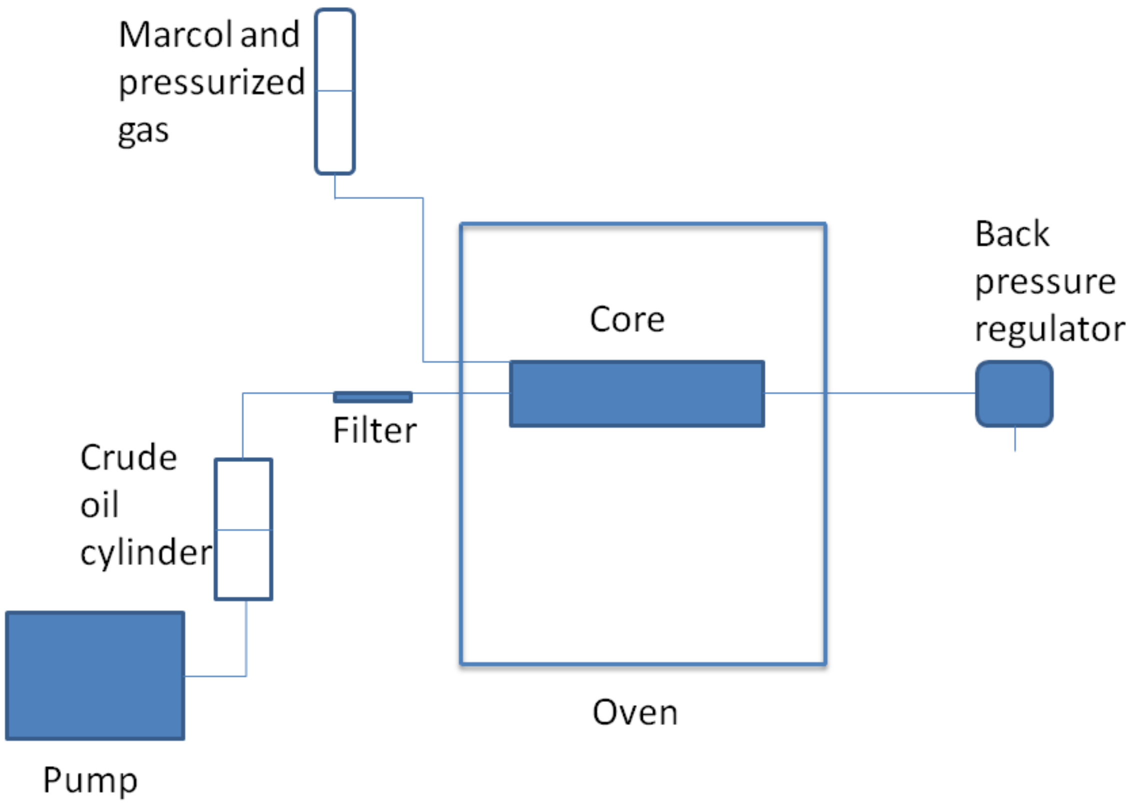

Figure 7-5: Setup for aging of rocks.

Dynamic core displacement experiments

Different types of water based solutions were used in displacement experiments: Low salinity water, synthetic sea water, surfactant solutions and polymer solutions. Two different setups have been used in this thesis, see figures below. The first setup does not have a backpressure regulator, and uses a burette to measure the accumulated oil volume produced. The second setup uses a back pressure regulator and a fraction collector.

Using a back pressure regulator has both advantages and disadvantages. The advantage is that the increased fluid pressure makes it much less likely that light oil components will vaporize from the liquid oil phase. Any gas that may have leaked in to the rock is most likely to be solubilized in the liquid phase and prevent unwanted multi phase flow, which would affect pressure readings.

A disadvantage by using the back pressure regulator is that oil rates versus time becomes more inaccurate. This is especially true when the water cut through the back pressure regulator is relatively high. Small oil droplets that go in to the BPR have a tendency to collect inside and go out as fewer bigger droplets. A small amount of oil will also be trapped inside the BPR and will only come out when a high rate is used to flush the BPR at the end. It will at that point be very difficult to know what time interval to add that oil volume to.

The first setup uses a burette for volume measurements. The volume of oil produced is measured by the burette which is turned upside down. The inlet to the burette is positioned above the outlet, so that oil which floats upwards is trapped, while water can flow out of the burette.

The second setup uses a fraction collector. Using a fraction collector has several advantages. It gives a good overview of oil production and water cut versus time. It opens up opportunities for analysis of the effluent. Measurements like pH and ion composition are possible when using a fraction collector. It is also easier to verify if the pump is delivering the specified rate. The accumulated volume of oil produced is more inaccurate compared to the burette. This is due to the oil is divided into several containers, and more volume readings gives higher uncertainty.

The reading uncertainty in oil volume was reduced by a calibration procedure. That procedure involved adding one droplet at a time of oil into the glass that the fraction collector used. The volume of oil added was determined by weighing the glass and using the known density. Pictures were taken at each step, and these pictures were a reference when the volume of oil after an experiment was to be determined. This procedure was done in an empty glass, but also more importantly on top of a volume of water. The meniscus between water and oil, and oil and air could therefore be more accurately determined.

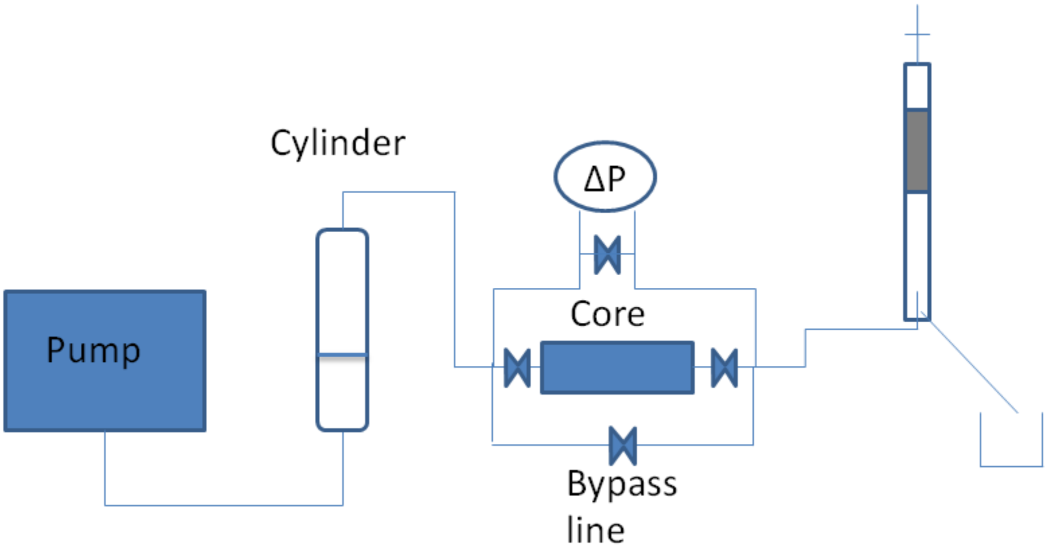

Figure 7-6: Setup for conventional water injection.

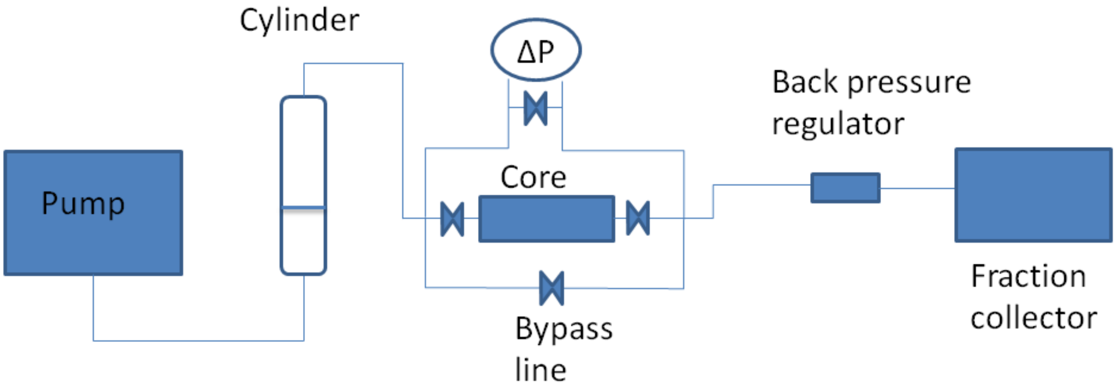

Figure 7-7: Setup for various kinds of injection

General procedure

The pump is set to desired injection rate. The injection fluid is filled in the cylinder and the lines are flushed. The pressure transducer is set to an appropriate range. The pump is set to run at the same injection rate as the experiment for several minutes, to pressurize the lines and improve injection rate and pressure at the beginning of the experiment. This is done with the valve in the bypass line open. The time interval for collection in the fraction collector is set to the desired interval. The experiment starts by closing the bypass line, and opening the inlet and outlet valve on the core holder simultaneously. The fraction collector is set to start at this point. The pressure drop over the core is monitored and recorded by a computer. The back pressure regulator is flushed at high rate through the bypass line to remove trapped oil after the experiment, and also at certain stages during an experiment.

Brine injection

Brine injection starts by injecting SSW or LS at a rate of 0.1 ml/min for approximately 2-3 PV, until no more oil production is observed. The rate is increased to 0.5 ml/min and 2-3 PV are injected. Finally the rate is increased to 1 ml/min and 2-3 PV are injected. Permeability of water at residual oil saturation is measured after the three injection rates. The permeability is measured at each rate by a stepwise decrease in rate.

Shut-in test

Shut-in is tested by water injection of 3000 ppm NaCl in secondary mode, and repeating the experiment approximately 2 weeks after.

Salinity oscillation

Three different fluids are injected: SSW, water with 1/10 of SSW salinity and 3000 ppm NaCl. Approximately 2 PV of each fluid is injected at 0.1 ml/min in this order: SSW, 1/10 SSW, SSW, 1/10SSW, SSW, 3000 ppm NaCl, SSW, 3000 ppm NaCl. Water permeability is measured for each fluid before changing injection fluid. The pH of the effluent is measured.

Surfactant and polymer injection

The rocks have previously been flushed with 3000 ppm NaCl water until no additional oil production is observed. 1 PV of surfactant is injected at a rate of 0.1 ml/min. 1 PV of 300 ppm HPAM is injected at the same rate. 2-3 PV of 3000 ppm NaCl is injected until no more oil production is observed. 1 PV of 600 ppm HPAM is injected. Finally 2-3 PV of 3000 ppm NaCl is injected until no more oil production is observed.

7.6 Uncertainty in core flooding experiments

The uncertainty in experimental procedures and equipment is evaluated in this subchapter.

The pressure transducer has an uncertainty of 0.1% according to the manufacturer. The uncertainty in reality is somewhat higher due to the computers sensitivity to the electric signal from the pressure transducer being the limiting factor.

The uncertainty in the Pharmacia pump according to the manufacturer is the highest of ±1.5 % or 0.5 ml/h. This implies that the uncertainty is ±0.5 ml/h if the flow rate is lower than 33 ml/h, and 1.5 % of the flow rate if it is higher than 33 ml/h. The uncertainty is ±8 % when the rate is set to 6 ml/h. The pump has two cylinders that switch between delivering water. The flow rate drops when this switch occurs. It takes approximately 15 to 30 seconds before the flow rate is back to normal, according to the pressure monitor.

The pore volume of the rocks and the dead volumes are measured with a Quizix pump which has very good precision. The porosity of the rocks is assumed to have an uncertainty of ± 0.1 %.

The parameters contributing to the uncertainty in permeability measurements are uncertainty in flow rate and pressure drop. The viscosity measurements and dimensions of the core are accurate enough to be neglected in this matter, although viscous oils can be somewhat sensitive to the temperature. The viscosity is neglected since effluent samples were taken for oils, and the temperature was recorded during measurements. The significant contribution to the total uncertainty comes from the pumps flow rate, especially at very low flow rates. The accuracy in permeability measurements is estimated to be ±4 %.

Two different setups were used for collecting produced oil as mentioned previously. The reading uncertainty in oil volume produced for the burette is ± 0.05 ml per reading. Two readings need to be taken, the upper interface and lower interface for the oil. The total uncertainty is thus

$$\sqrt{0.05^2 + 0.05^2}\ \mathrm{ml} = 0.07\ \mathrm{ml}$$

This corresponds to an uncertainty in the recovery factor of approximately 1 % since the volume of oil in place is approximately 12 ml for all the rocks. The reading uncertainty in produced oil for the setup with fraction collector is somewhat higher since it involves more readings. The uncertainty in oil recovery is estimated to 2 % for this setup. The uncertainty in the OOIP volume is neglected in this context since the produced oil volume is less precise.

The uncertainty in oil recovery is very dependent on the volume of oil in place. It is therefore clear that smaller rocks will have a much higher uncertainty than a large rock. The uncertainty in residual oil saturations is slightly lower than for the recovery factor. This is because the oil volume is divided by the pore volume which is larger than the OOIP volume. The pore volume is also more precisely measured.

8 Main results and discussion

8.1 Static experiment results

Measurements of density, viscosity and interfacial tension were made to support the dynamic core displacement experiments. Viscosities are needed in permeability calculations and it is also preferable to know the viscosity ratio of oil and the injected liquid since this can influence the experiments. The density of liquids has been used in calibrations of volume readings of produced oil. Interfacial tension measurements were made to compare two different surfactants and to be able to calculate a capillary number for the floods.

8.1.1 Density measurements

The results from the density meter are shown on the figure below.

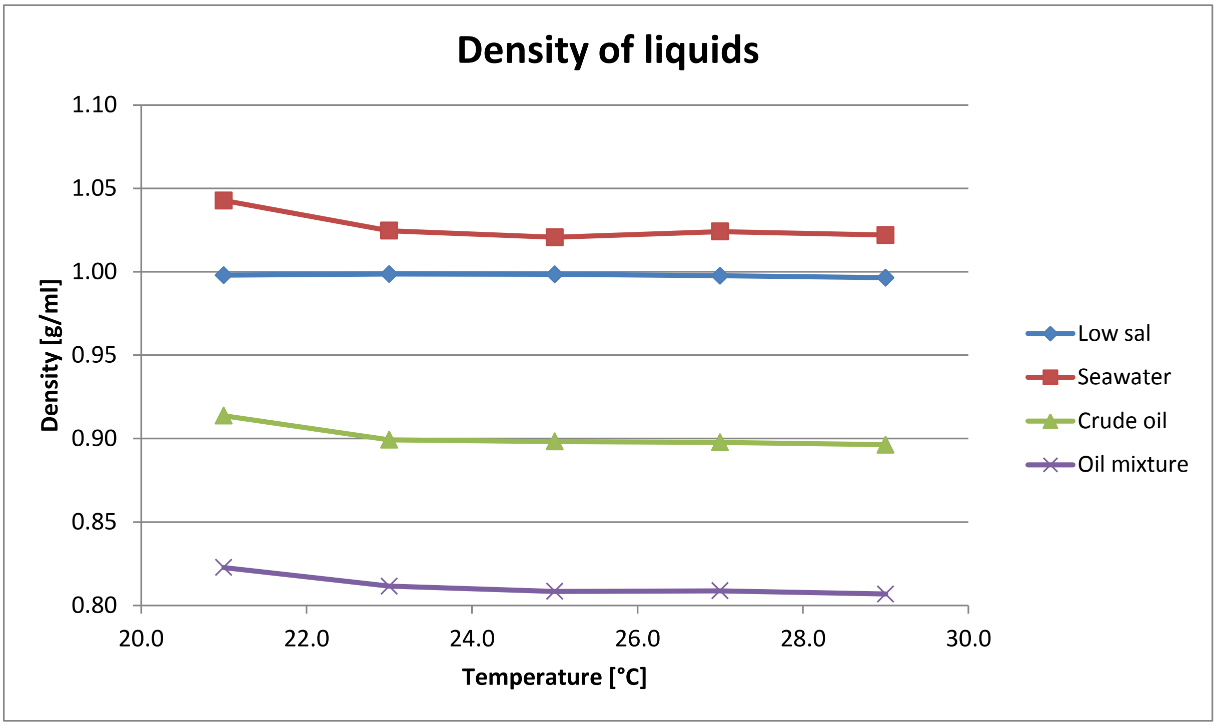

Figure 8-1: Density measurements.

There are some measurements on the graph above that are not following the trend that density decreases with increasing temperature. This is probably due to uncertainty in the measuring instrument or procedure. However, the results are accurate enough for their purpose in this thesis.

8.1.2 Rheology measurements

The results from rheology measurements are plotted on graphs below. All the liquids are Newtonian except for the polymer solutions. The newtonian liquids are plotted versus temperature. This allows for easy calculations of the viscosity at varying room temperatures.

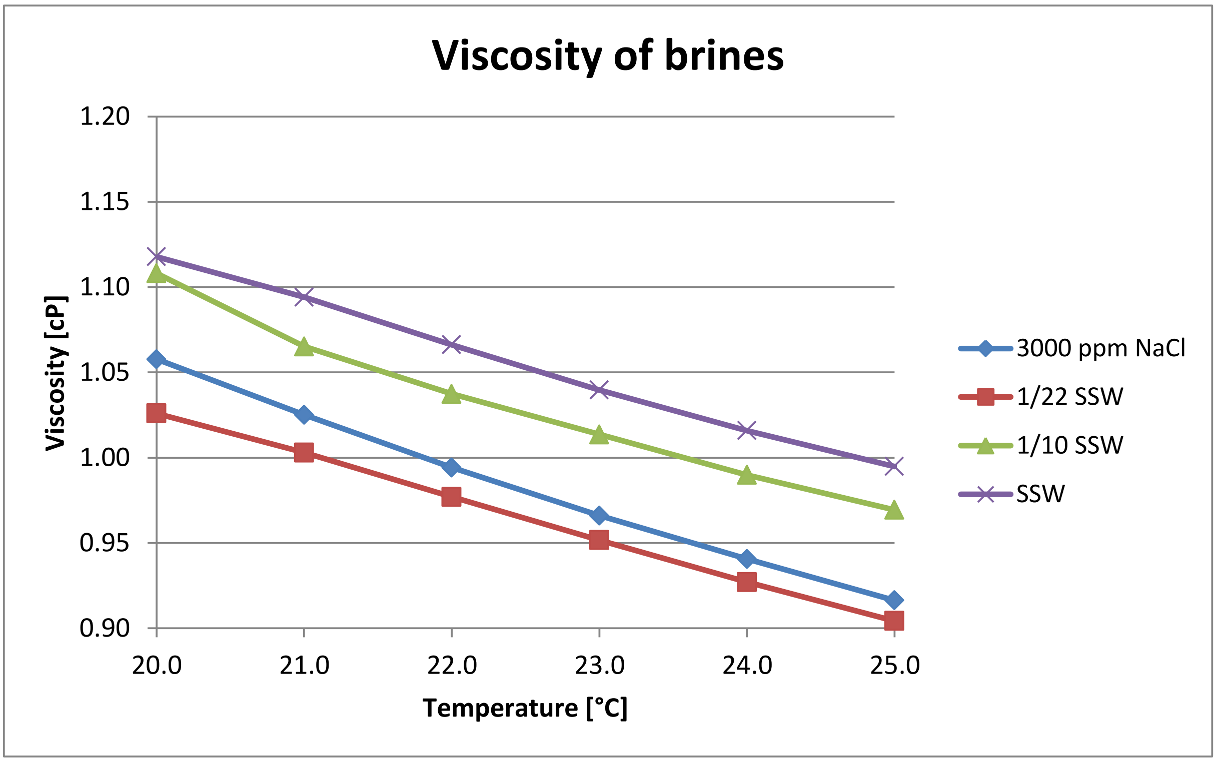

Figure 8-2: Viscosity measurements.

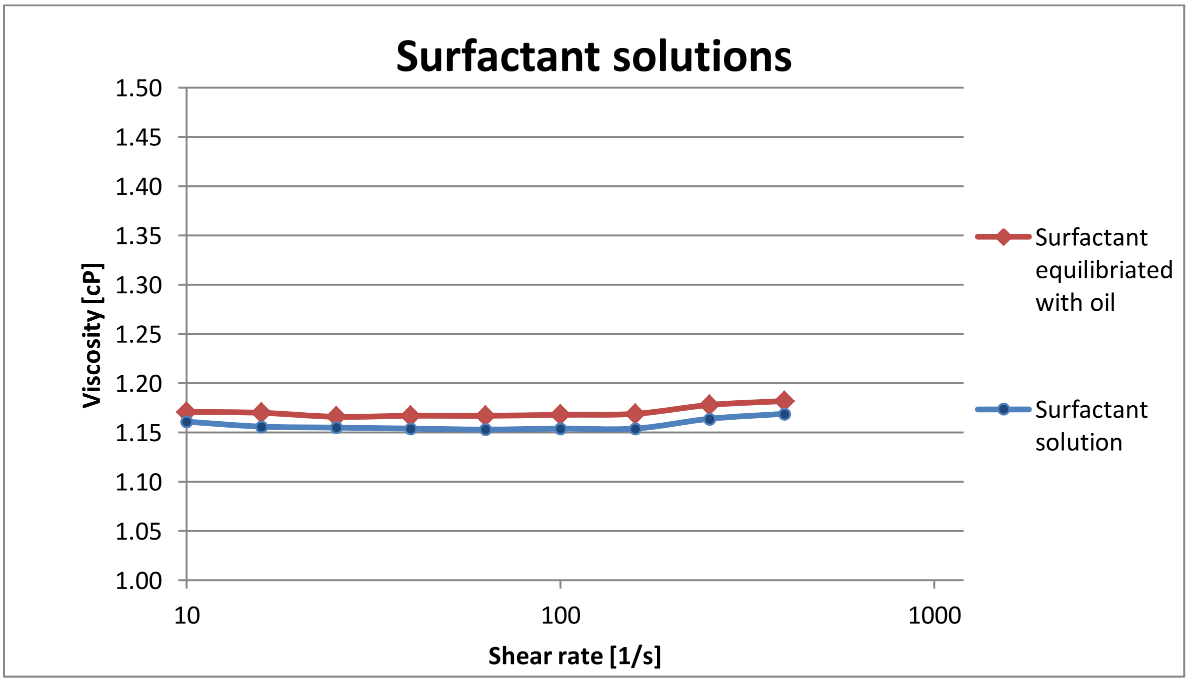

Figure 8-3: Viscosity of the surfactant solution

The surfactant solution is measured at 23° C. The viscosity of the surfactant solution which has been equilibrated with oil has a slightly higher viscosity probably due to the presence of microemulsions.

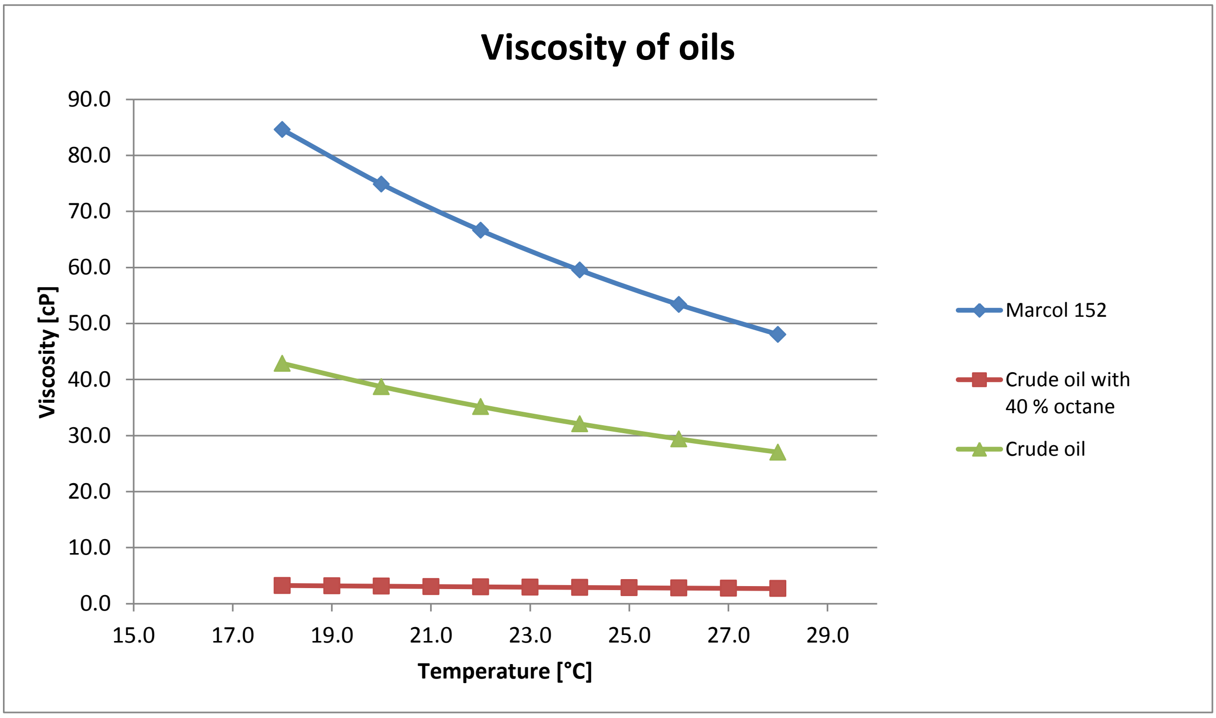

Figure 8-4: Viscosity of oils.

The polymer solutions are measured at 23 °C.

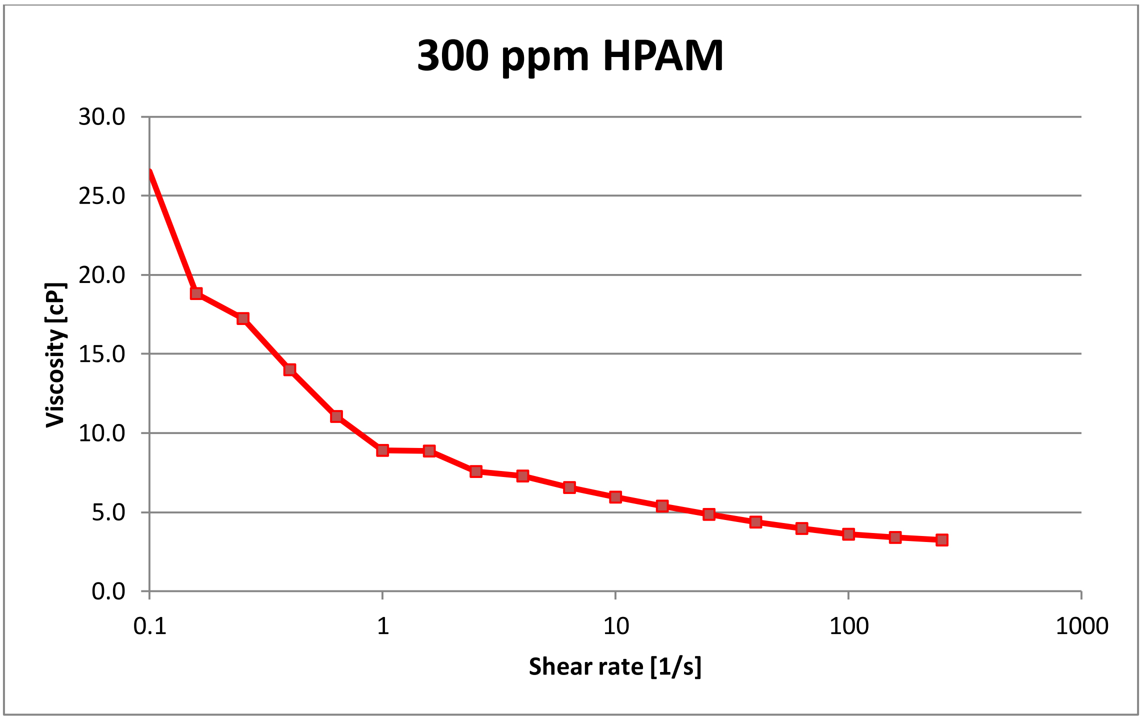

Figure 8-5: Viscosity of 300 ppm HPAM.

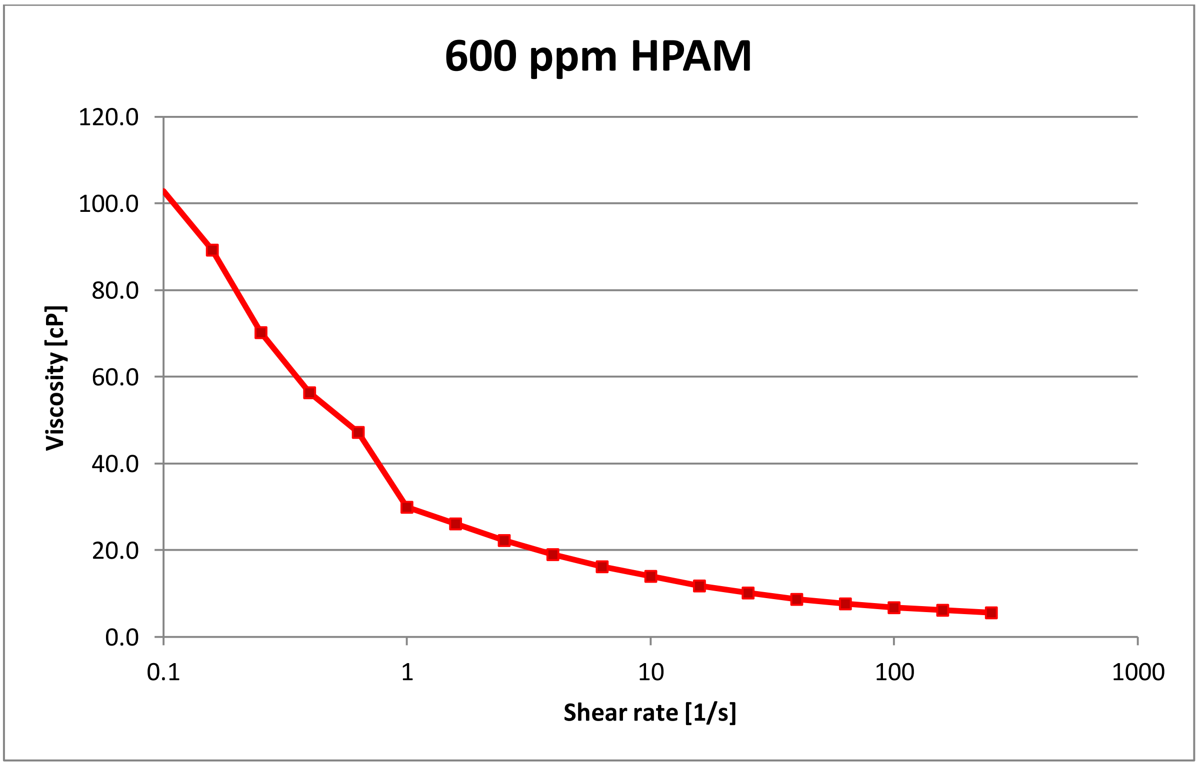

Figure 8-6: Viscosity of 600 ppm HPAM.

The polymer solutions are shear thinning in the region of 0.1 s^{-1} to 250 s^{-1}. The viscosity of 100 ppm HPAM and 1000 ppm HPAM was also tested. 300 and 600 ppm HPAM were used in the flooding experiments because they probably had sufficient viscosity to make sure that the mobility ratio between oil and polymer solution was well below one.

8.1.3 Solubility studies and interfacial tension measurements

Two surfactants were evaluated with regards to solubility and interfacial tension with oil. Both the surfactant solutions had sufficient solubility in 3000 ppm NaCl. No precipitation was observed for the two solutions. DD044 had a light brown color. DD044/2 had a pale white color.

Table 8-1: Results from spinning drop.

	DD044	**DD044/2**
	[mN/m]	[mN/m]
Sample 1	0.03	0.05
Sample 2	0.03	0.04
Sample 3	-	0.05
Fresh sample	0.03	0.02

The average interfacial tension for DD044 was 0.03 mN/m for equilibrated samples, and also 0.03 mN/m for the sample that had not been equilibrated prior to measurements. The interfacial tension for DD044/2 was generally higher. The average IFT was 0.05 mN/m. The IFT for the sample that had not been equilibrated was 0.02 mN/m. DD044 was used in the dynamic core displacement experiments based on generally producing lower IFT with the oil. The reproducibility from the spinning drop method is not excellent, as can be observed from the spinning drop table in the appendix. The percentage deviation between different measurements is quite large. The spinning drop can however still be used to compare different surfactant solutions and give a good estimate of the capillary number during flow in porous media, when viscosity and Darcy velocity is known.

8.2 Dynamic core displacement results

The purpose of these experiments has been to study the impact of injecting brines with different salinities and also to study the combined effect of low salinity water with surfactants. There are numerous results in the literature that have shown an increase in oil recovery with low salinity brine, but also many results where there is no effect. Other observations in the literature include that the pH of the effluent increases during low salinity flooding, and that migrating fines are observed, but there are also many examples where these observations are not present [37].

The kinetics of low salinity mechanisms has also been tested by secondary injection of 3000 ppm and waiting for two weeks when the low salinity brine is in equilibrium with the remaining oil and the rock before repeating the experiment.

Oscillating between injection of sea water and low salinity water has been performed. This was done to test if a salinity shock can help destabilize oil and increase the production.

A surfactant solution was injected at low salinity in tertiary mode. A polymer solution was injected afterwards to increase the viscosity of the injected brine. This reduction in mobility ratio can help produce the oil that the low salinity surfactant has mobilized.

Six cores have been used for dynamic core displacement experiments: L1, L2, O1, O2, O3 and O4. O1 – O4 have been aged according to the procedure described earlier. The water injections for L1 and L2 were performed with the burette setup. A fraction collector was used for the rest of the experiments.

Table 8-2: An overview of the six cores.

Parameter	Unit	O1	O2	O3	O4	L1	L2
Length	cm	6.49	6.28	6.34	6.31	6.29	6.48
Diameter	cm	3.82	3.83	3.83	3.83	3.79	3.80
Porosity	%	22.3	22.5	22.0	21.7	22.0	22.0
Absolute water permeability	mD	294	355	322	315	380	350
Swi	%	23.5	25.2	23.5	22.9	23.5	23.0
Soi	%	76.5	74.8	76.5	77.1	76.5	77.0
Marcol 152 permeabilty before aging	mD	360	405	364	375	357	369
Crude oil permeability before aging	mD	381	410	370	391	-	-
Oil permeability after aging	mD	370	375	362	330	-	-

8.2.1 Core L1

Table 8-3: Injection experiments for L1

PV of SSW injected at rate: 0.1 ml/min	4.00
Oil recovery [% OOIP]	59
WBT [PV]	0.44
S_{or} [%]	31
PV of SSW injected at rate: 0.5 ml/min	3.50
Oil recovery [% OOIP]	59
S_{or} [%]	31
PV of SSW injected at rate: 1 ml/min	2.50
Oil recovery [% OOIP]	59
S_{or} [%]	31
K_{rw} (S_{or})	0.09
Tertiary injection of 1/22 SSW	No additional oil production
Quaternary injection of 3000 ppm NaCl	No additional oil production

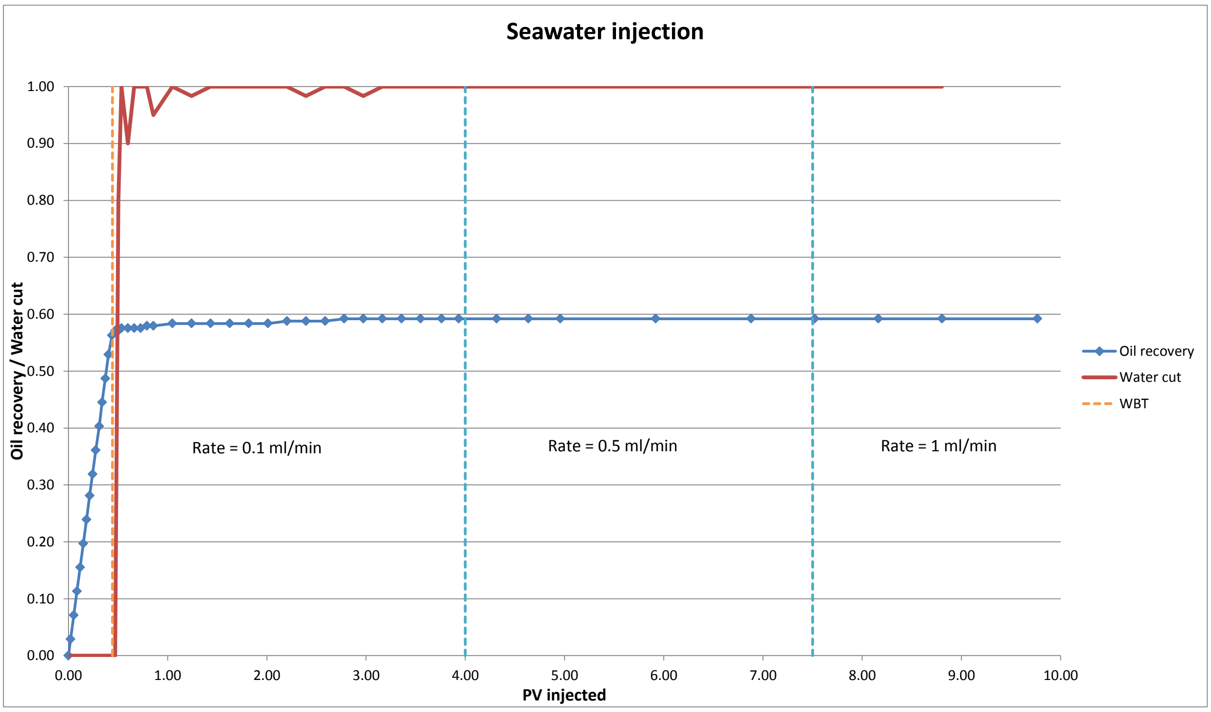

Figure 8-7: Production profile for L1.

Sea water injection resulted in a water break trough, WBT, at 0.44 PV. The oil production after WBT was low. The recovery increased by 3 %, ending up at 59%. Increasing the injection rate to 0.5 ml/min and 1 ml/min did not result in any additional oil production. The relative water permeability at residual oil saturation was 0.09. The low relative permeability of water and the low production of oil after WBT indicate that the wettability is relatively strongly water wet. Two water compositions with low salinity were injected in tertiary mode, first sea water that has been diluted by a factor of 22 (1/22 SSW), and lastly 3000 ppm NaCl. The injection of low salinity water did not result in any extra recovery of oil.

8.2.2 Core L2

Table 8-4: Injection experiments for L2

PV of 1/22 SSW injected at rate: 0.1 ml/min	3.74
Oil recovery [% OOIP]	58
WBT [PV]	0.44
S_{or} [%]	31
PV of 1/22 SSV injected at rate: 0.5 ml/min	2.30
Oil recovery [% OOIP]	58
S_{or} [%]	31
PV of 1/22 SSW injected at rate: 1 ml/min	2.16
Oil recovery [% OOIP]	59
S_{or} [%]	30
K_{rw} (S_{or})	0.11
Tertiary injection of 3000 ppm NaCl	No additional oil production

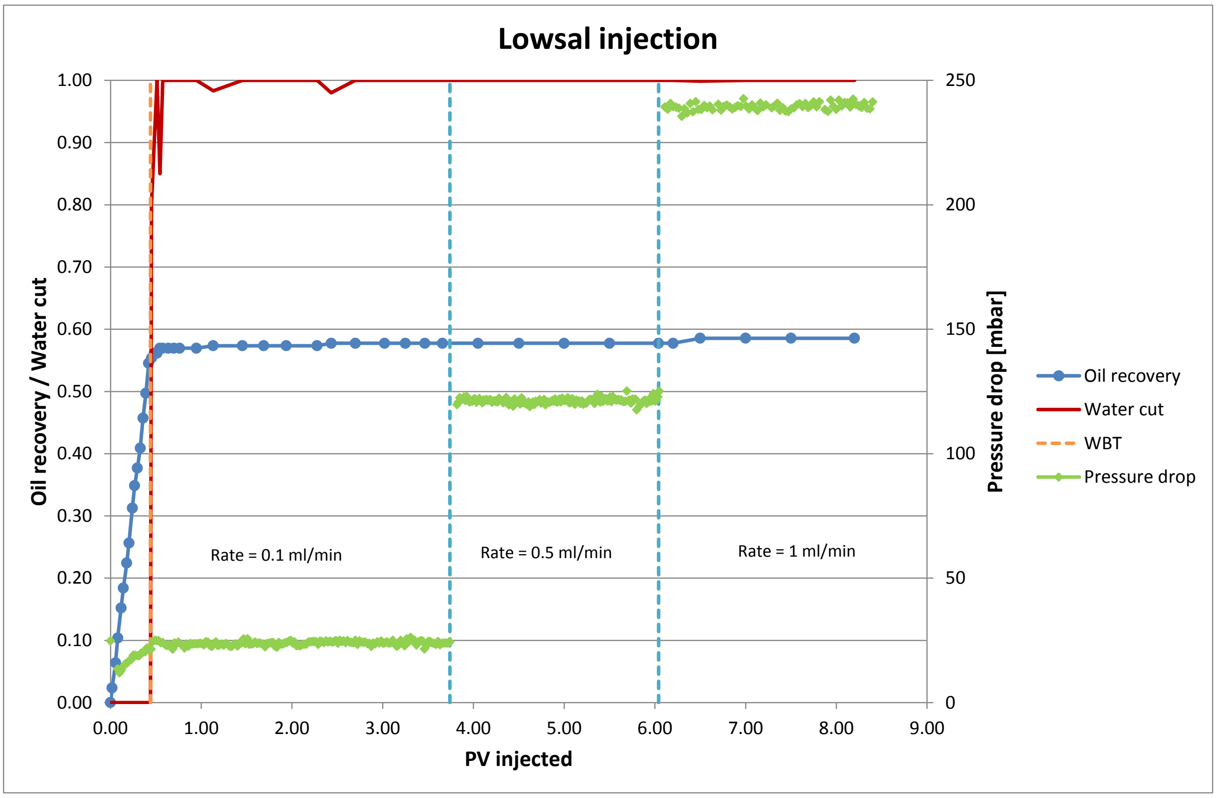

Figure 8-8: Production profile for L2.

1/22 SSW was injected in secondary mode. The WBT occurred at 0.44 PV, the same as for L1. The oil production after WBT was 2% of recovery, giving a total of 58 %. Increasing the rate resulted in a slight increase in production, approximately 1 %. This was produced after the rate was increased to 1 ml/min. The relative water permeability at residual oil saturation was 0.11. 3000 ppm of NaCl was also injected, but no extra oil was recovered.

L1 and L2 yielded very similar results. The ultimate recovery for the two rocks was 59% for both rocks. The WBT was also 0.44 PV for both rocks. The relative permeability of water at S_{or} was similar also; around 0.1. However, L2 responded slightly to bumping up the rate, but L1 did not.

The pressure drop for the tertiary injections of 3000 ppm NaCl was stable for L1 and L2, which indicates no two phase movement in the core and no fines migrations.

8.2.3 Core O1 and O4

A shut in experiment was performed for O1 and O4. This was done to test whether the kinetics of lowsal can be slower than the timespan of an injection experiment as a paper from Berg et al. suggests. [18]

Table 8-5: Injection experiments for O1 and O4.

	O1	**O4**
PV of 3000 ppm NaCl injected at rate: 0.1 ml/min	1.47	2.09
Oil recovery [% OOIP]	65	58
WBT [PV]	0.47	0.46
S_{or} [%]	27	32
PV of 3000 ppm NaCl injected at rate: 0.5 ml/min	1.86	1.92
Oil recovery [% OOIP]	65	61
S_{or} [%]	27	30
PV of 3000 ppm NaCl injected at rate: 1 ml/min	1.85	1.93
Oil recovery [% OOIP]	65	64
S_{or} [%]	27	27
K_{rw} (S_{or})	0.17	0.14
Repeated after approximately two weeks without any oil production		

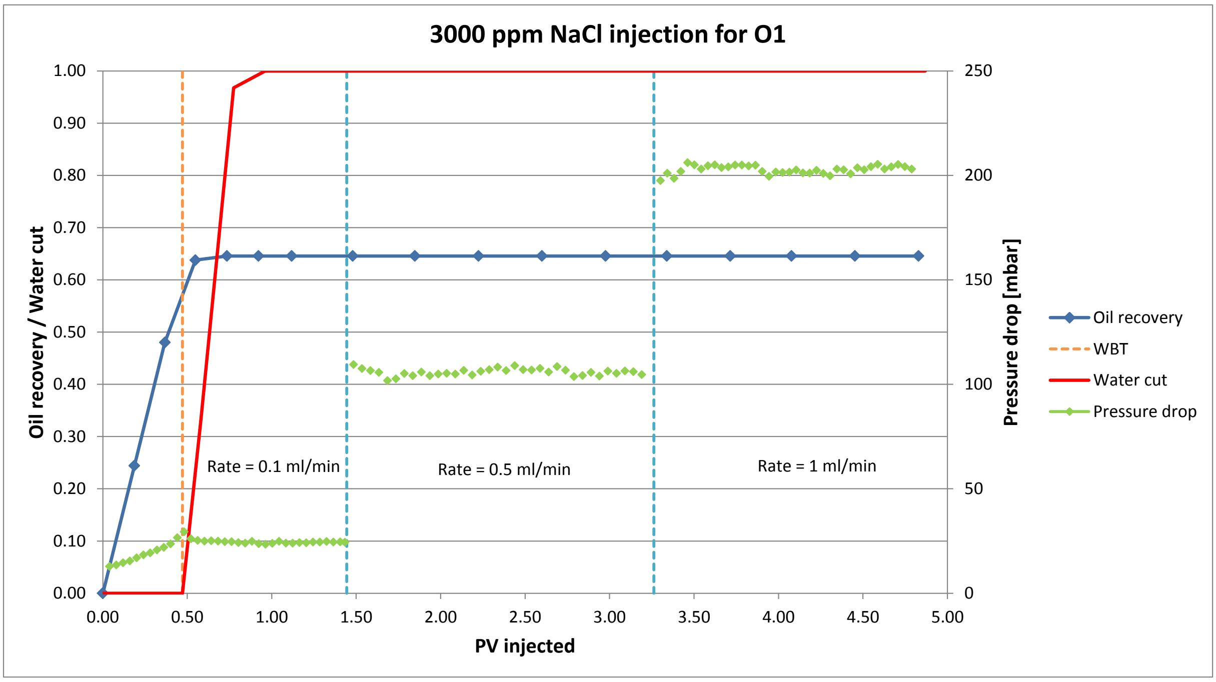

Figure 8-9: Production profile for O1.

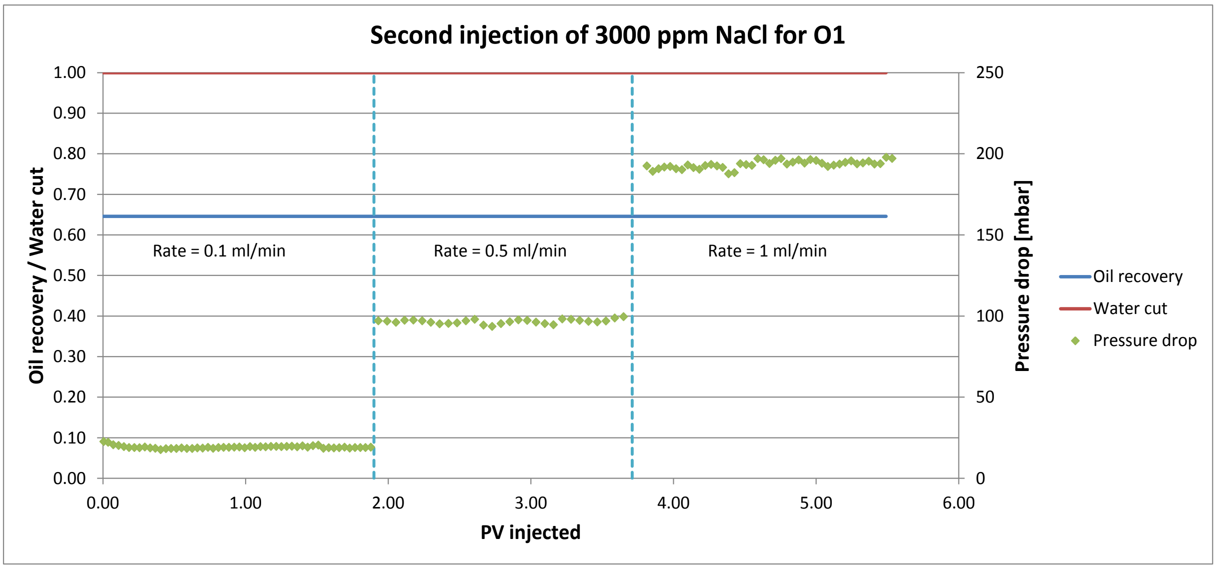

Figure 8-10: Production profile for O1.

3000 ppm NaCl was injected in secondary mode. The WBT occurred at 0.47 PV with a recovery of 64 %. Very little two phase production was observed, 1 % increase in recovery after WBT. Increasing the rate did not result in any additional oil production. The relative water permeability at residual oil saturation was 0.17.

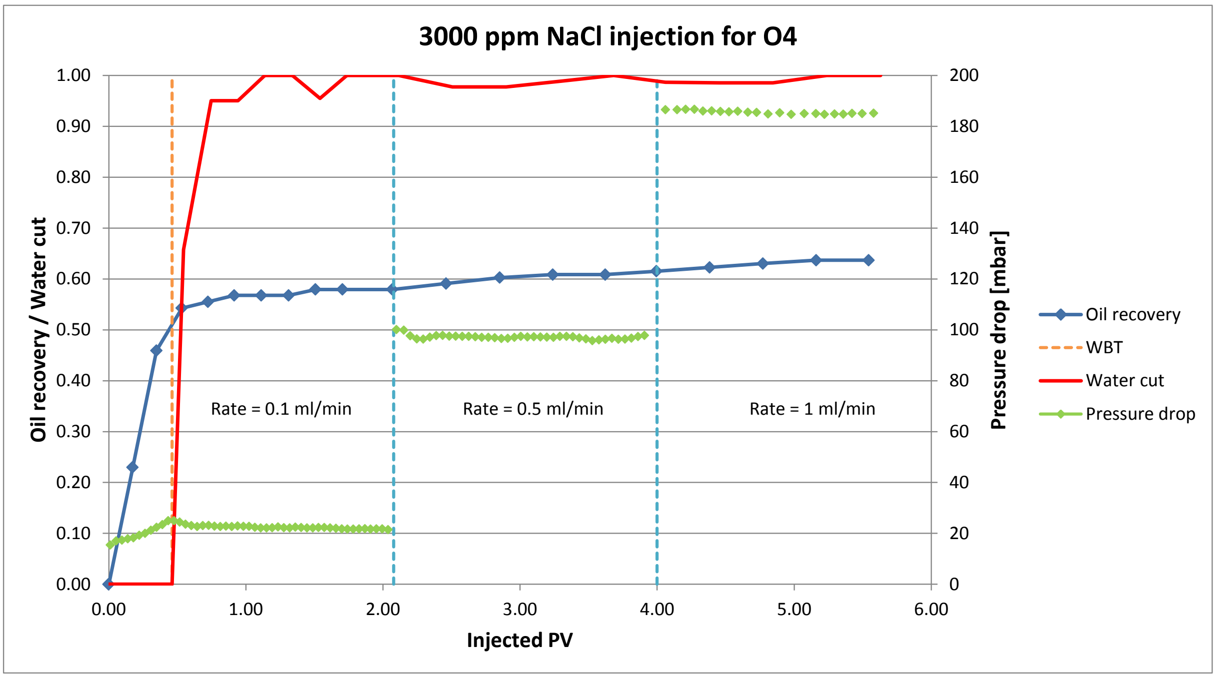

Figure 8-11: Production profile for O4.

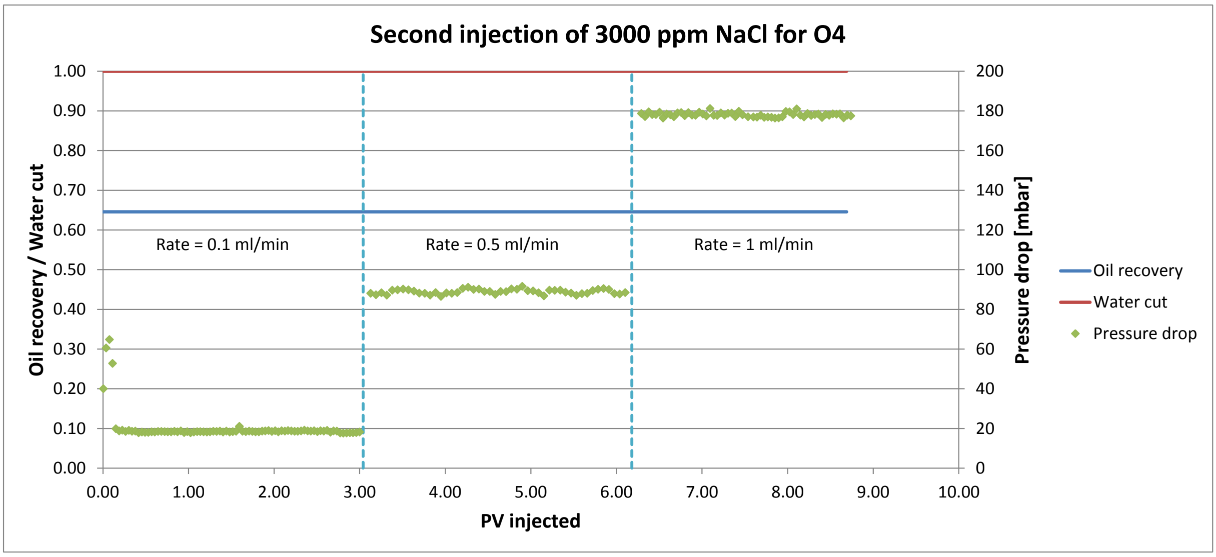

Figure 8-12: Production profile for O4.

The same procedure was used for O1 and O4. WBT for O4 was at 0.46 PV. O4 did have significant two phase production compared to the previous cores. Increasing rate did also increase oil recovery. The oil recovery was 55% at WBT, and increased to 58 % by the end of the low rate. The ultimate recovery was 64 %. The relative water permeability at residual oil saturation was 0.14.

The injection experiment was repeated for O1 and O4 after approximately two weeks, to see if a lowsal effect would occur by exposing the lowsal water in the core for a longer period of time. This effect was not observed within the time frame of this experiment, as no additional oil was produced. The pressures during the second experiment were also stable which means that there was probably not any two phase movement in the cores. Fines migration is also unlikely to have occurred.

8.2.4 Core O2 and O3

Table 8-6: Injection experiments for O2 and O3.

	O2	**O3**
PV of SSW injected at rate: 0.1 ml/min	2.00	2.00
Oil recovery [% OOIP]	58	56
WBT [PV]	0.45	0.51
S_{or} [%]	31	33
K_{rw} (S_{or})	0.20	0.14
PV of 1/10 SSW injected at rate: 0.1 ml/min	2.00	2.00
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.21	0.16
PV of SSW injected at rate: 0.1 ml/min	3.81	4.00
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.21	0.11
PV of 1/10 SSW injected at rate: 0.1 ml/min	2.50	2.39
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.21	0.16
PV SSW injected at rate: 0.1 ml/min	2.50	4.30
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.21	0.11
PV of 3000 ppm NaCl injected at rate: 0.1 ml/min	4.23	2.62
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.20	0.11
PV of SSW injected at rate: 0.1 ml/min	2.00	2.10
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.21	0.11
PV of 3000 ppm NaCl injected at rate: 0.1 ml/min	2.00	3.70
Oil recovery [% OOIP]	63	59
S_{or} [%]	28	32
K_{rw} (S_{or})	0.19	0.16

The equilibrium between brine and oil is disturbed when the injected brine has a different salinity than the present brine. The injected water was oscillated between seawater and low salinity water to test if a change in salinity can lead to extra recovery even if the salinity of the injected water is increased. If switching injection water from lowsal to seawater also could improve the oil recovery, then disturbing the equilibrium between brine and oil might be considered a mechanism in itself.

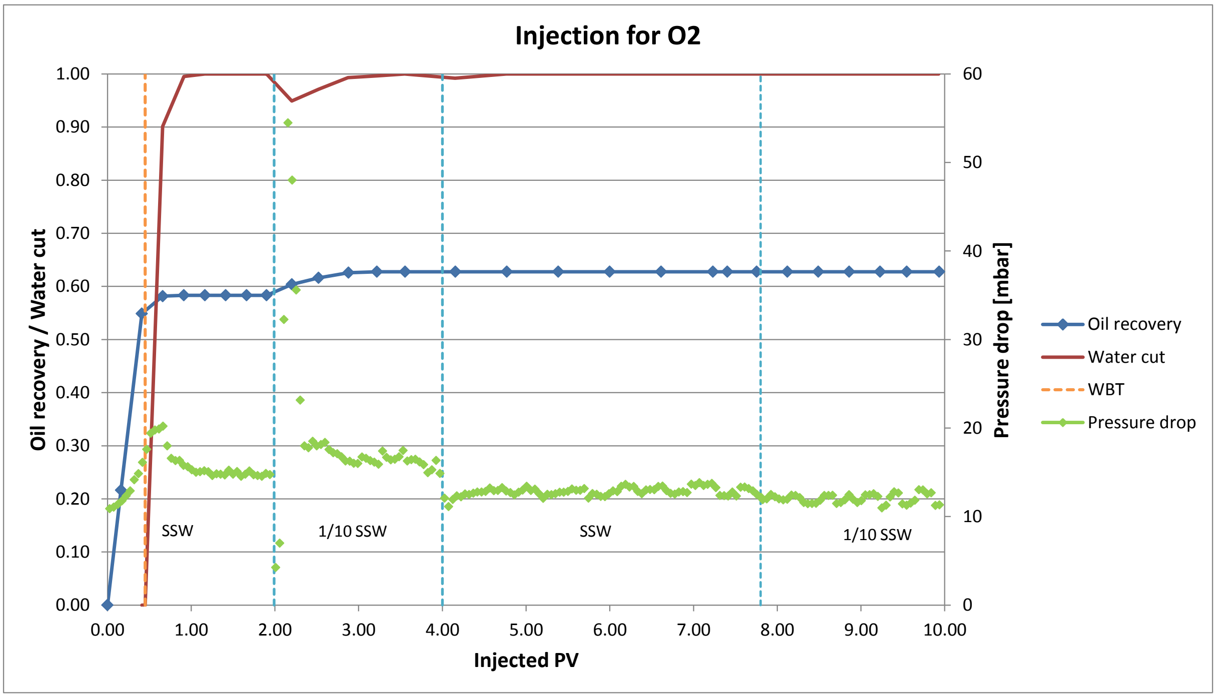

Figure 8-13: Production profile for the first 10 PV of injection.

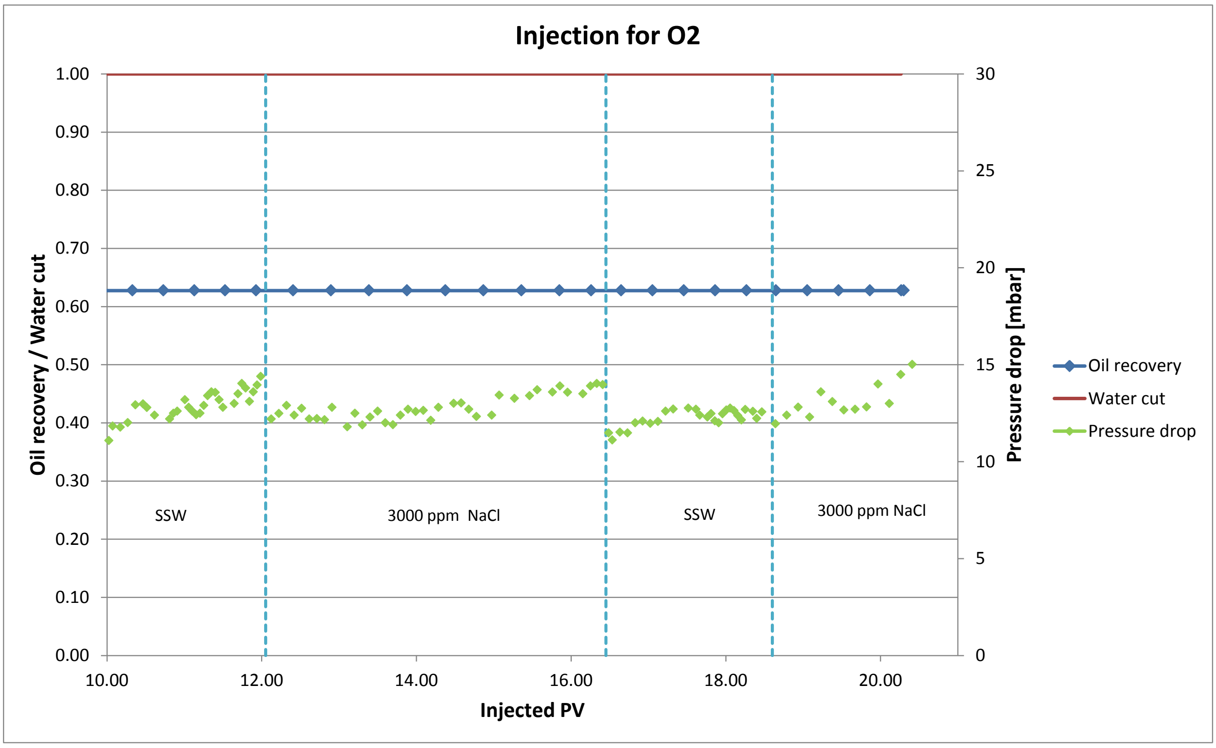

Figure 8-14: Production profile after 10 PV of injection.

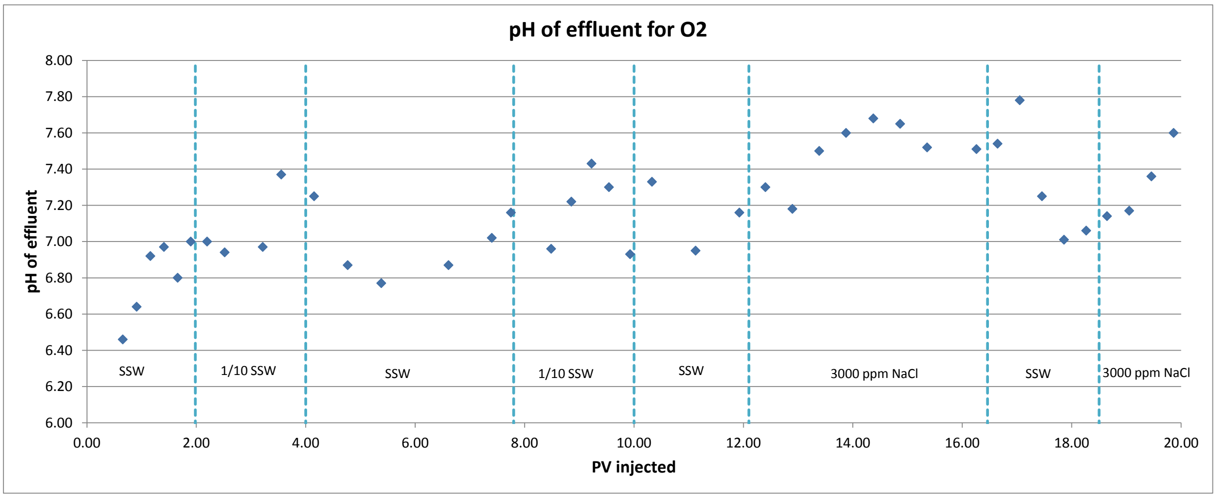

Figure 8-15: Measured pH of effluent for O2.

The entire injection experiment for O2 and O3 is done at 0.1 ml/min. Sea water is injected first. The WBT occurred at 0.51 PV for O2, and had negligible two phase production after WBT. The oil recovery was 58 % after two PV of sea water was injected. The relative water permeability at the present residual oil saturation was 0.20.

Low salinity water with 1/10 of salinity compared to sea water was injected. The pressure drop over the core started out lower than with sea water, but suddenly increased by a factor of five compared to the pressure where the sea water injection ended. This could be a result of a small oil bank mobilized by the lowsal water. It could also be due to interactions between the lowsal water and the rock that could lead to fines migration and pore blockage.

The pressure later decreased back to slightly higher pressure than with sea water. Additional oil production did occur some time after the increase in pressure. The oil recovery increased by 5 % after injecting low salinity water. Relative permeability for water increased to 0.21 after the low salinity flood. The slight increase in permeability for water is expected since the water saturation has increased. This also suggests that the lowsal water did not noticeably damage the rock. No additional oil was produced during the subsequent floods. The pH measurements indicate that sea water has lower pH compared to the lowsal waters, and that 3000 ppm NaCl has the highest pH.

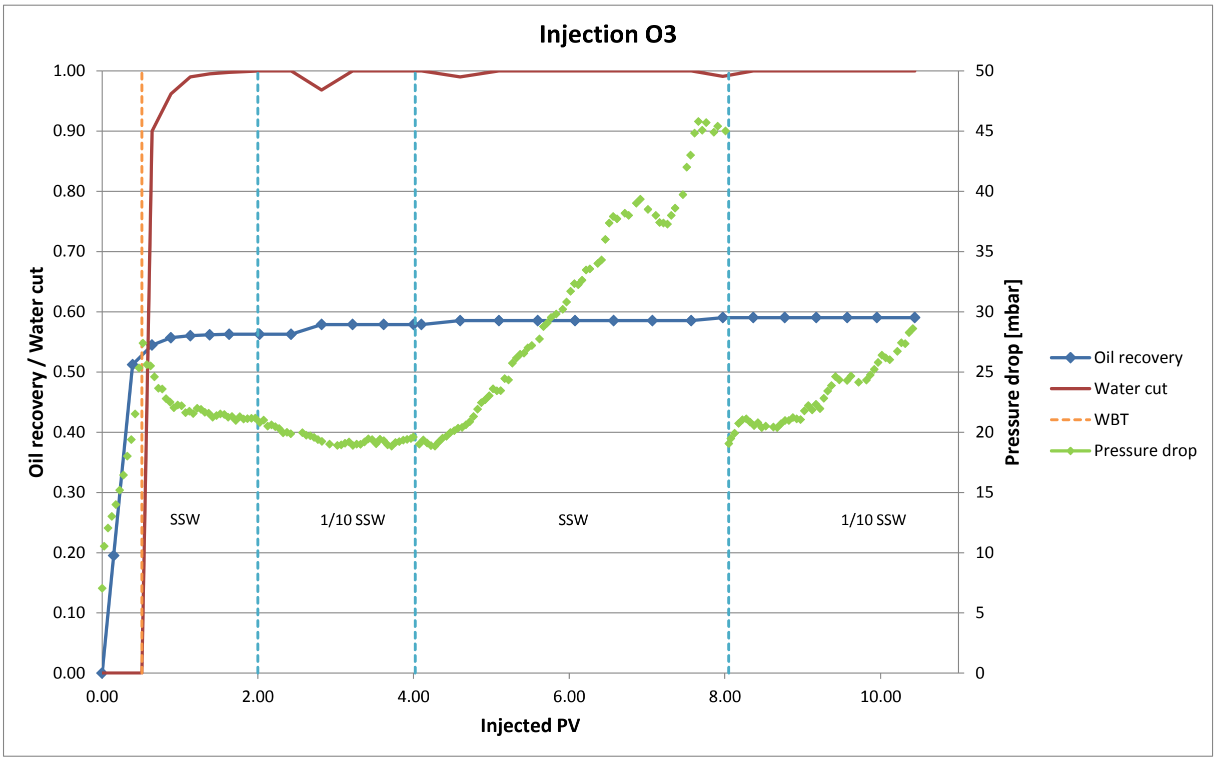

Figure 8-16: Production profile for the first 10 PV of injection.

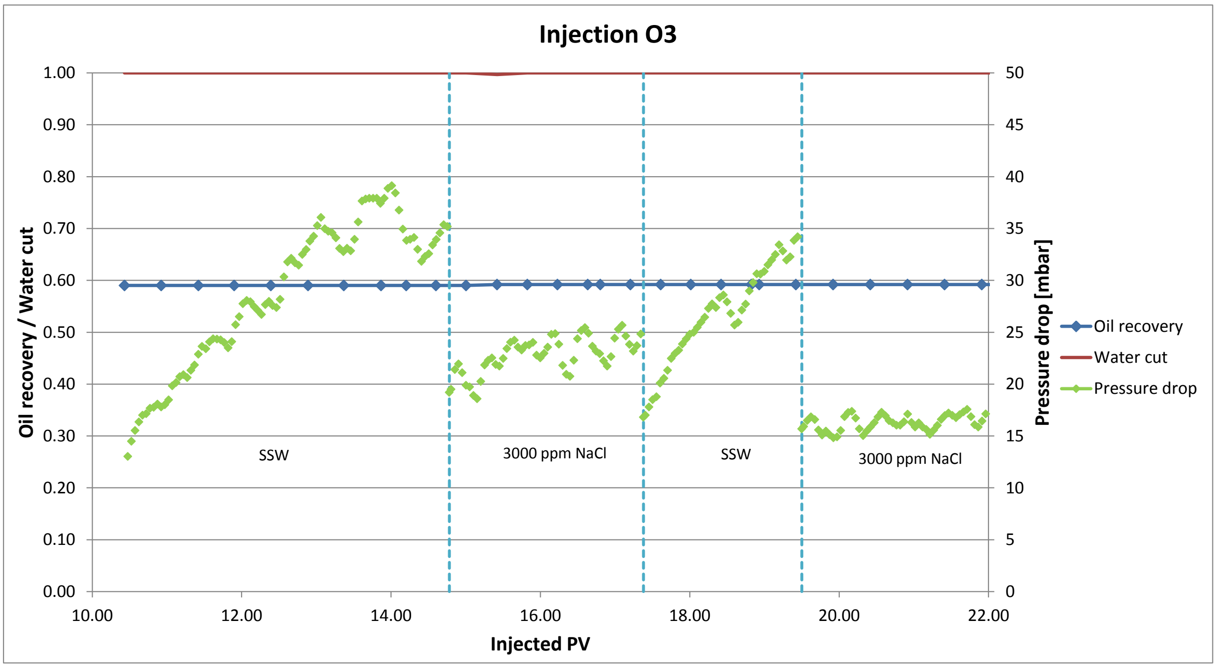

Figure 8-17: Production profile after 10 PV of injection.

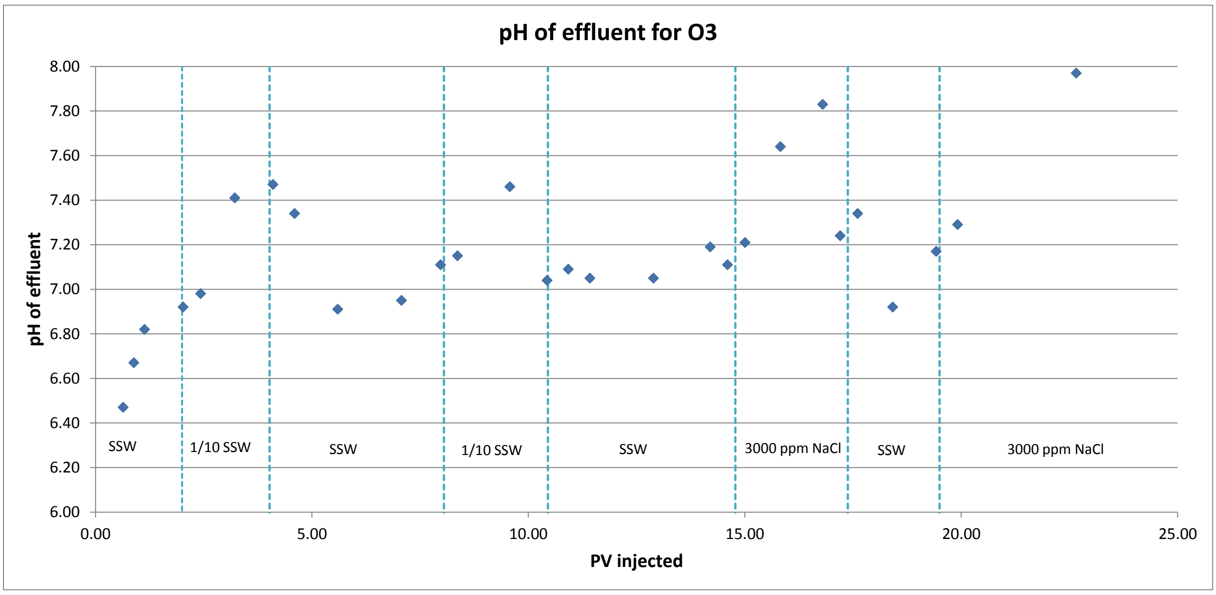

Figure 8-18: pH of effluent for O3.

The sea water had WBT at 0.51 PV with a corresponding recovery of 53 %. The two phase production continued for a while until the recovery reached 56 %. The relative water permeability at the present residual oil saturation was 0.14.

Lowsal water was injected after the sea water. There was no increase in pressure on this core. In fact, the pressure drop is lower than for the sea water injection. Additional oil recovery was still observed. The recovery increased by 3 %, giving an ultimate recovery of 59 % as no more oil was produced in the subsequent floods.

The pressure drop over the core is not stable through the experiment. The pressure significantly increases in some of the floods, and the water permeability after the floods are also not stable. The trend seems to be that the floods where the pressure increases, also have lower permeability for water. The unstable pressures indicate that there might be internal movement of oil or fines in the core. The effluents pH is similar to the trend for O2.

8.2.5 Discussion of low salinity flooding:

Table 8-7: Short summary of the non-aged rocks.

	Uncertainty	**L1**	**L2**
Recovery factor [% OOIP]	± 1 %	59	58
S_{orw} [%]	± 1 %	31	30
K_{rw} (S_{orw})	± 0.01	0.09	0.11

Table 8-8: Short summary of the aged rocks.

	Uncertainty	**O1**	**O2**	**O3**	**O4**
Recovery factor [% OOIP]	± 2 %	65	63	59	64
S_{orw} [%]	± 1 %	27	28	32	27
K_{rw} (S_{orw})	± 0.01	0.17	0.19	0.16	0.14

Low salinity water did not improve the recoveries for L1 and L2. Secondary lowsal resulted in the same recovery as secondary sea water injection and tertiary injection of lowsal did not improve the recoveries either.

Tertiary injection of lowsal increased the oil recovery by 3 % and 5 % for O2 and O3 respectively. The lowsal injection for O1 and O4 was in secondary mode, and it is therefore more difficult to quantify any exact improvement due to lowsal, but the recovery factor for O1 and O4 was not lower than for the other two. It is worth noting that O1 and O4 were injected with higher rates at the end, contrary to O2 and O3, and that did improve the recovery for O4, but not for O1. The increased rate can reduce capillary end effects and result in extra oil production. The capillary number is also increased with higher injection rate, from around $5 \cdot 10^{-8}$ at 0.1 ml/min to $5 \cdot 10^{-7}$ at 1 ml/min, but this increase is not likely to mobilize residual oil based on the capillary desaturation curve.

The extra recovery from tertiary lowsal injection can in some cases be a result of reducing the capillary end effects. This is because injection of lowsal can result in an increase in pressure. The extra recovery could in that case come from the increase in pressure and not due to lowsal mechanisms. This can not be the case for O3 since the pressure during lowsal injection is actually lower than with sea water. One could argue that the increase in pressure for O2 during lowsal could be the cause for the extra oil recovery, but that does not have to be the case since O3 did produce extra oil without the pressure increase.

The wettability of O1, O2, O3 and O4 seems to be less water wet compared to L1, L2. This is most likely because L1 and L2 have not been aged. L1 and L2 have lower end point permeability for water, which indicates stronger water wetness. The uncertainty in relative permeability for water is estimated to be ±0.01 for the rocks, so the non-aged cores clearly have lower relative water permeability. The higher end point permeability for the other rocks could either be a result of a wettability shift during aging, but also because O1, O2 and O4 have higher water saturation at their end point. O3 has lower water saturation at the end point than L1 and L2, but O3 still has much higher water permeability.

The two phase production after water break trough was low for all the cores. The increased recovery factor ranged from 1 % to 3 %. A core will generally have more two phase production if the core is less water wet. There does not seem to be a trend between two phase production and end point permeability for water. The water break trough for L1 and L2 is earlier than for the aged cores. The opposite could generally be expected since less water wetness will generally result in earlier WBT.

The oil recovery for the aged cores is roughly 6 % higher than L1 and L2, except for O3. The aging seems to have had impact on the recovery and this is mostly because the non-aged cores did not respond to lowsal. The higher recovery for aged cores could also have been influenced by the shift in wettability, because shifting a strongly water wet core towards more neutral wettability will have a tendency to give higher recoveries [38].

Mahani et al. showed that detachment of oil droplets in a model system was slower than expected, and that their results could impact SCAL experiments as previously mentioned [18]. Their results in a model system are not necessarily transferable to the situation in a porous medium. The forces involved are not similar in magnitude. The model system had a force balance between buoyancy and adhesion and negligible viscous forces. This is different from the forces involved in a porous media where viscous forces will also affect detachment of oil, and the buoyancy will be less dominating.

The best way to try to reproduce the results from Mahani et al. in a porous medium would be to use the same oil and a rock that contains the same type of clay, which was Na-Montmorillonite, in dynamic core flooding experiments.

Oscillating between sea water and low salinity water will affect the water film that coats the rock surface for water wet rocks and disturbs the equilibrium. The thickness of the electrical double layer is increased when the salinity and especially divalent ions are reduced [22-24]. This is because the positively charged ions like Ca^{2+} and Mg^{2+} can screen the repulsions between the rock surface and oil which usually are negatively charged. Repulsion forces between the rock surface and an oil droplet will therefore be more significant at lower salinities, and the water film thickness increases. Oscillating the salinity did not increase the oil production, except for in the tertiary injection of low salinity water. Disturbing the equilibrium between brine and oil did therefore not result in any extra oil production in these experiments, except for maybe in the tertiary lowsal injection where it could have contributed to the extra recovery. It is possible that the unstable pressure is due to mobilized oil resulting in two phase flow due the salinity oscillation, but at least no extra oil was produced so the oil was later re-trapped if this was the case.

8.2.6 Low salinity surfactant flooding with polymer

The procedure has been very similar for the six cores. The procedure and results are summarized in table 8-9. The salinity of the brine in the cores before surfactant injection is 3000 ppm NaCl.

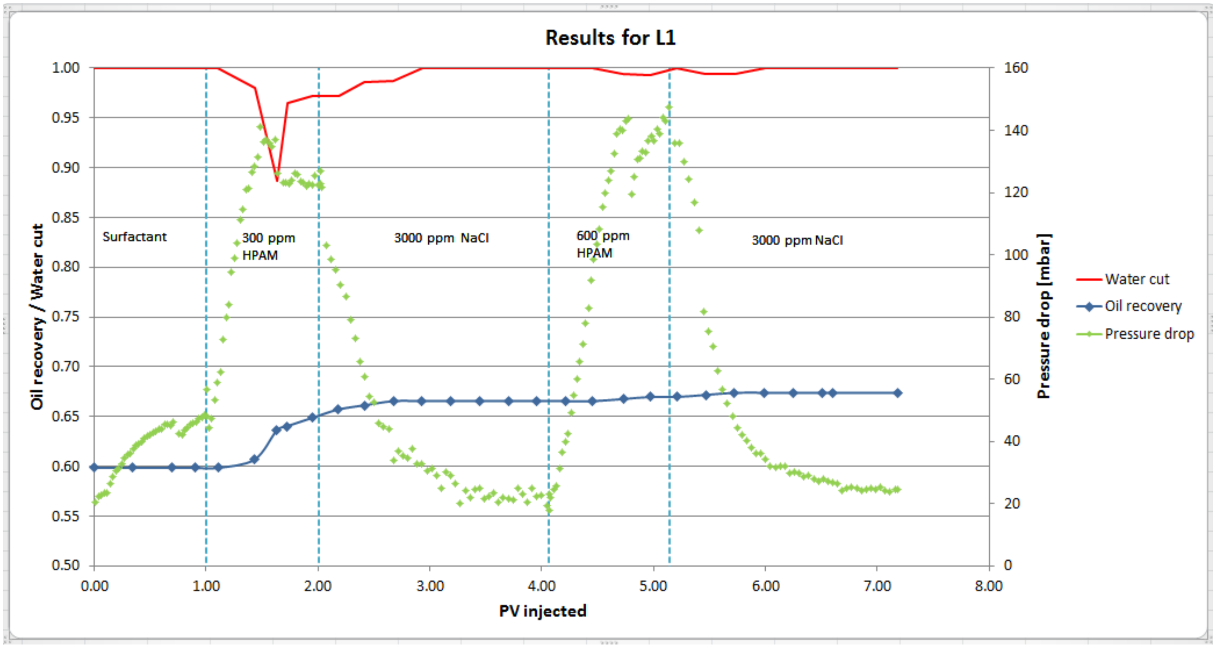

Figure 8-19: Production profile for L1.

Injection of surfactant resulted in pressure build up due to two phase flow. 1 PV was injected and 1 PV of 300 PPM HPAM was injected afterwards. The oil production started after half of the polymer was injected. 3000 ppm NaCl was injected after the polymer until no more oil production was observed. Injection of 600 HPAM improved the oil recovery by almost 1 %, giving an ultimate recovery of 67 %.

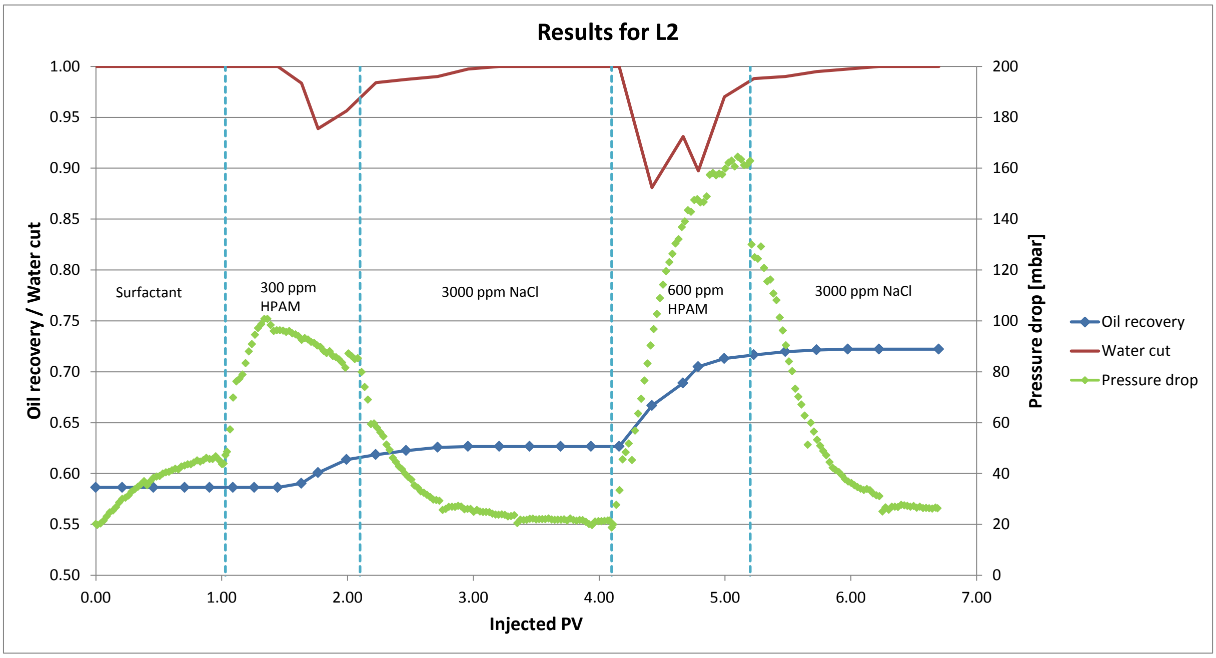

Figure 8-20: Production profile for L2

The production profile for L2 is similar to L1, except the efficiency of the second HPAM injection. The oil production increases by 10 % due to the second injection, resulting in a total oil recovery of 72 %.

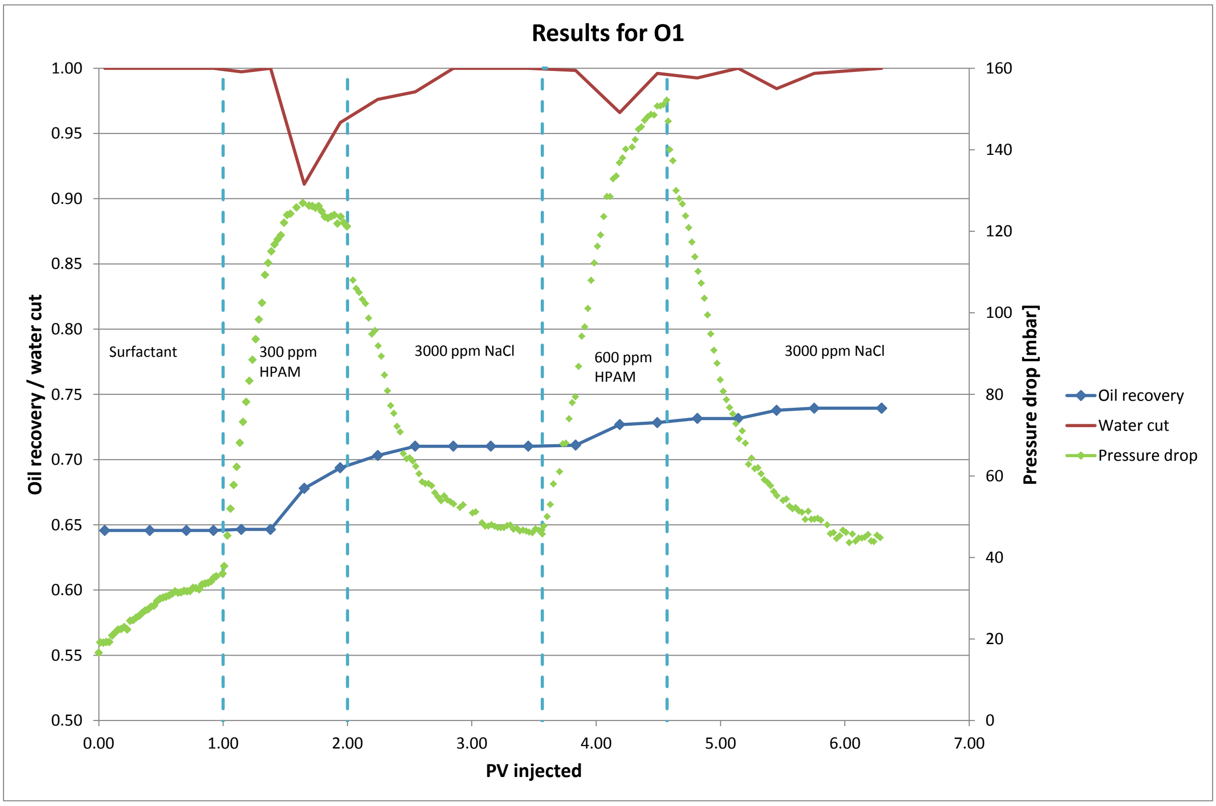

Figure 8-21: Production profile for O1.

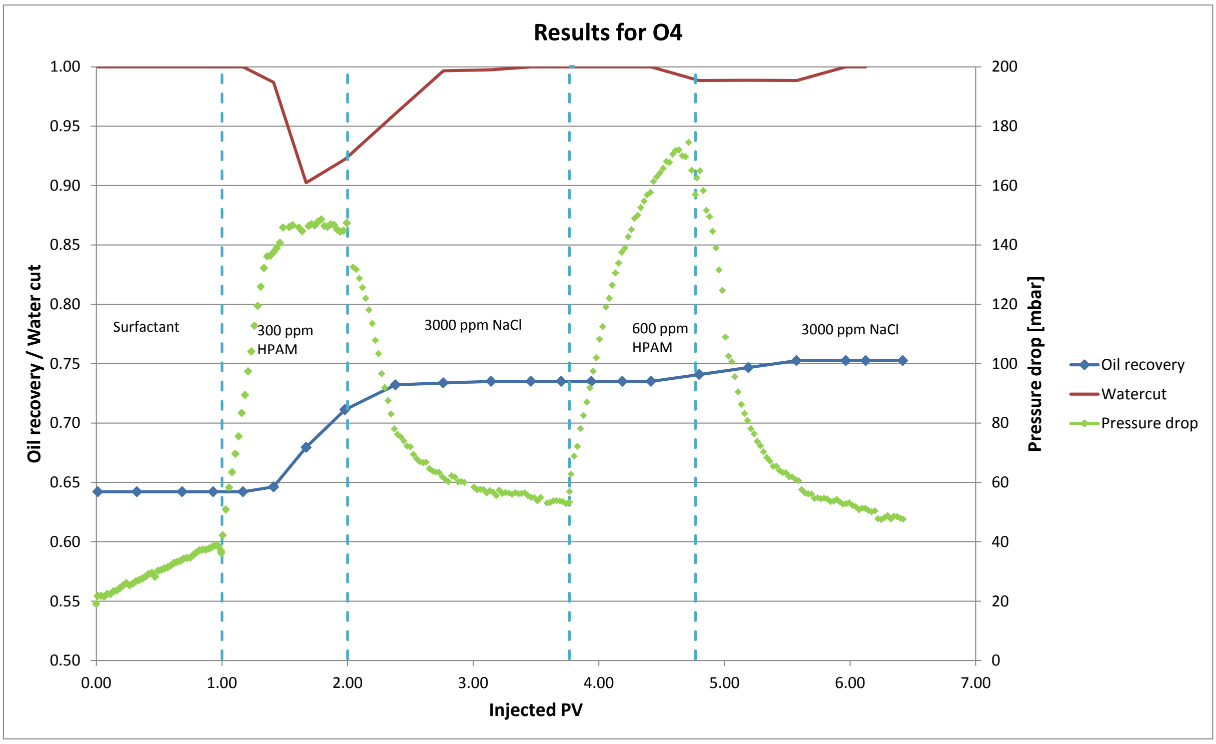

Figure 8-22: Production profile for O4.

The results for O1 and O4 are similar. Most of the oil production came during injection of 300 ppm HPAM and the water flood afterwards. But injecting 600 ppm HPAM did improve the recovery by a few percent.

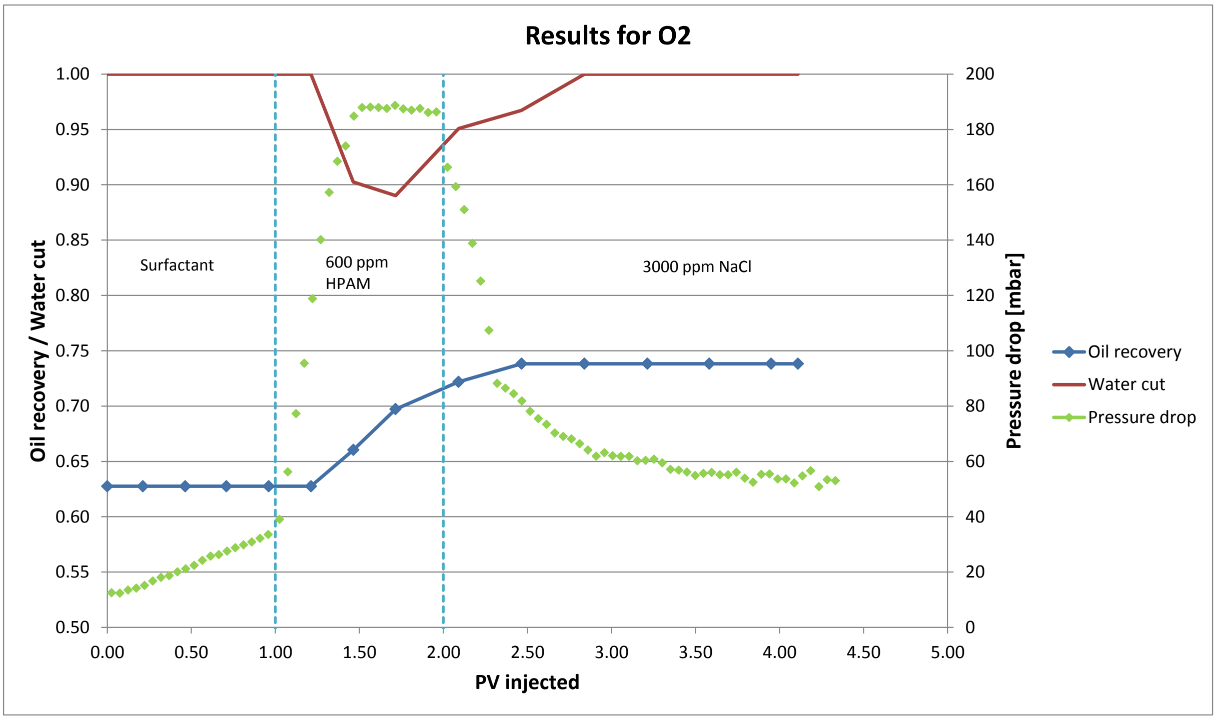

Figure 8-23: Production profile for O2.

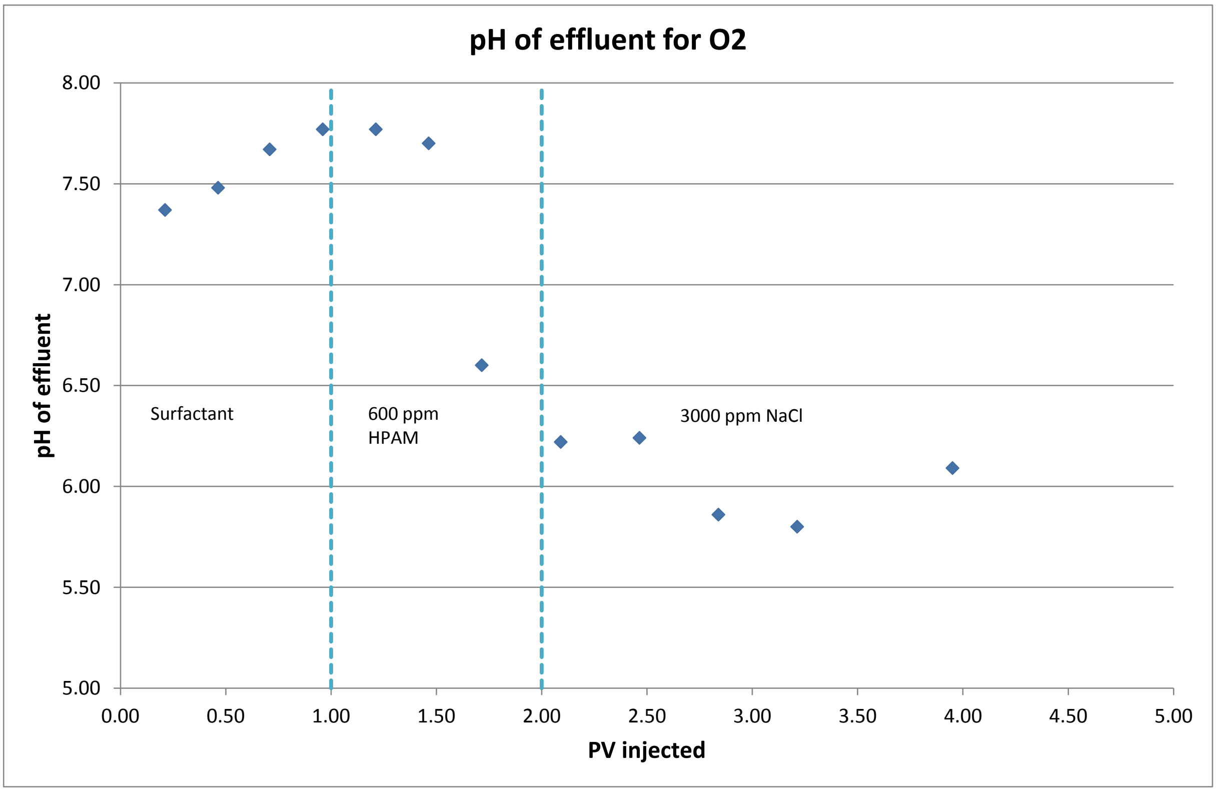

Figure 8-24: pH of effluent for O2.

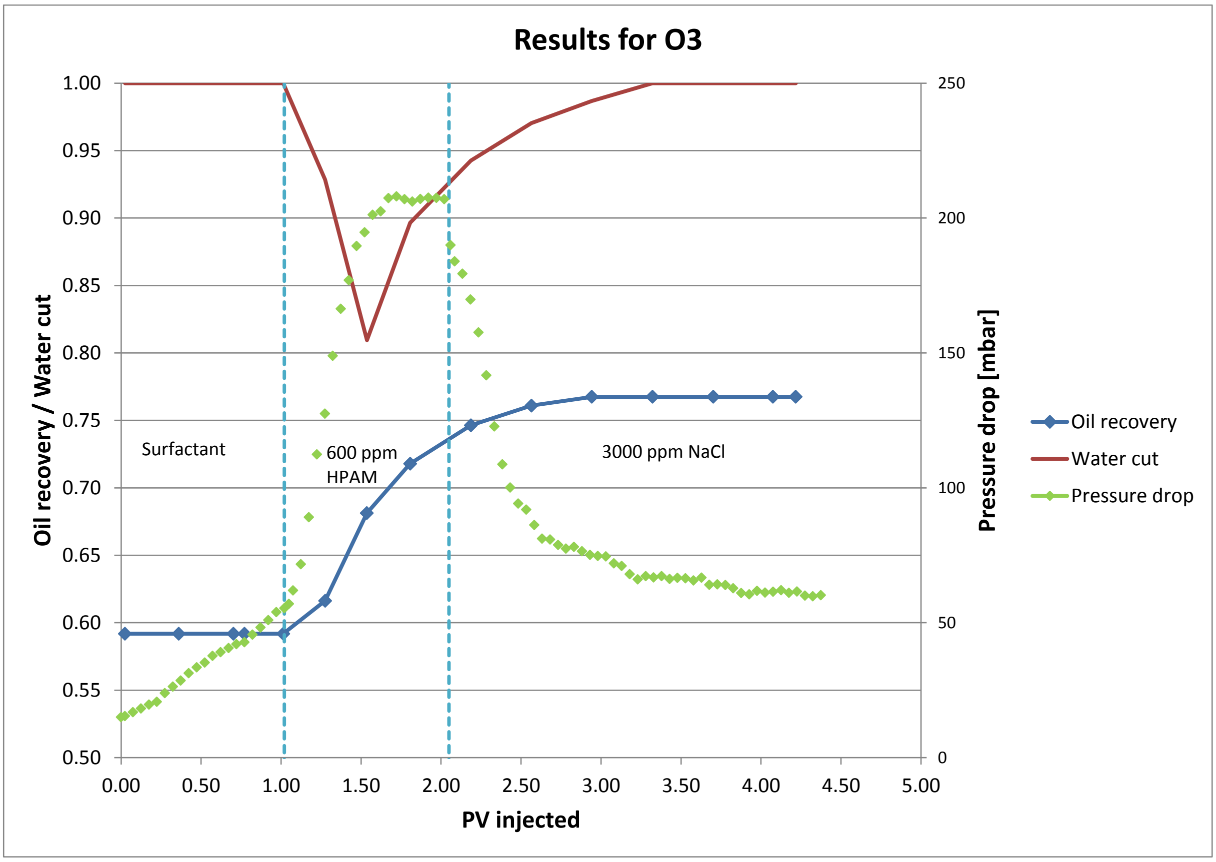

Figure 8-25: Production profile for O3.

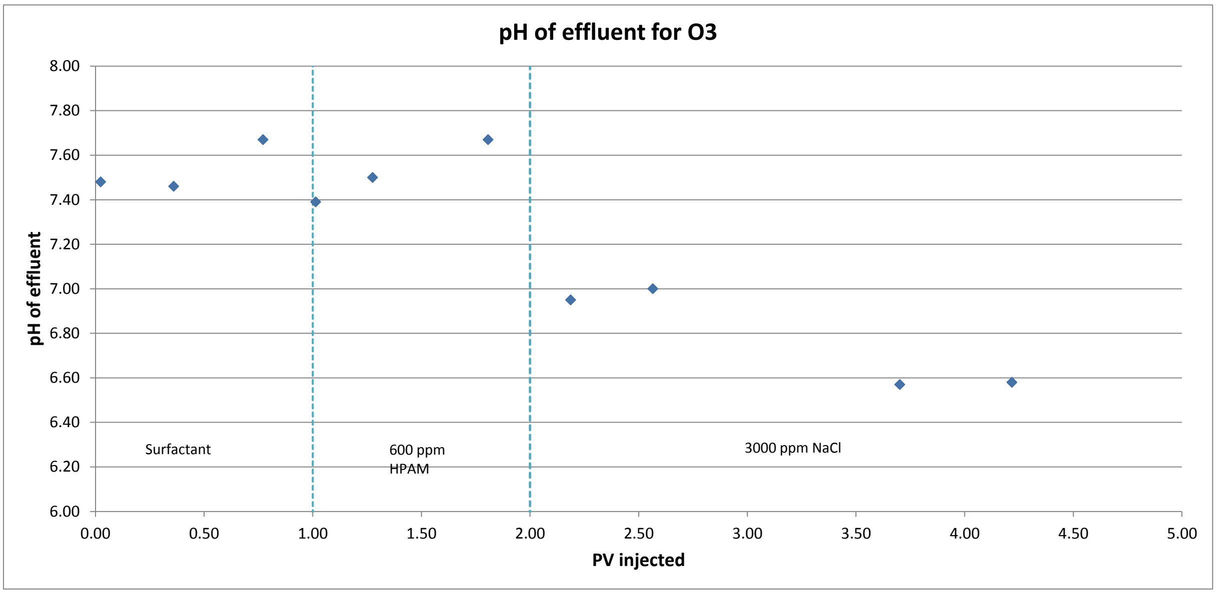

Figure 8-26: pH of effluent for O3.

The pressure builds up during the surfactant flood and the oil production starts after approximately 1.5 PV after the start of injection for O2 and O3, similar to the previous cores. The pH of the effluent for the two cores generally decreases after the polymer is started to be produced because of the lower pH of the polymer solution. The ultimate recovery factor for O2 and O3 is 74 % and 77 % respectively.

8.2.7 Discussion of low salinity flooding with surfactants and polymer

Table 8-9: Injection experiments for the six cores.

	L1	**L2**	**O1**	**O2**	**O3**	**O4**
PV injected of surfactant at rate: 0.1 ml/min	1.00	1.00	1.00	1.00	1.00	1.00
Oil recovery after waterflooding [% OOIP]	59	58	65	63	59	64
Additional oil recovery [% OOIP]	0	0	0	0	0	0
Recovery factor of residual oil [%]	0	0	0	0	0	0
S_{ors} [%]	31	32	27	28	32	27
PV injected of 300 ppm HPAM at rate: 0.1 ml/min	1.00	1.00	1.00	-	-	1.00
Additional oil recovery [% OOIP]	6	3	5			7
Recovery factor of residual oil [%]	14	7	14			19
S_{ors} [%]	27	30	23			22
PV injected of 3000 ppm NaCl at rate: 0.1 ml/min	2.00	1.99	2.00	-	-	1.80
Additional oil recovery after waterflood [% OOIP]	8	4	6			9
Recovery factor of residual oil [%]	18	10	18			26
S_{ors} [%]	26	29	22			20
PV injected of 600 ppm HPAM at rate: 0.1 ml/min	1.00	1.00	1.00	1.00	1.00	1.00
Additional oil recovery after waterflood [% OOIP]	8	13	8	9	15	9
Recovery factor of residual oil [%]	19	30	23	25	38	26
S_{ors} [%]	25	23	21	21	19	20
PV injected of 3000 ppm NaCl at rate: 0.1 ml/min	2.02	1.50	1.74	2.31	2.30	1.73
Additional oil recovery after waterflood [% OOIP]	8	14	9	11	18	11
Recovery factor of residual oil [%]	20	32	26	30	43	31
S_{ors} [%]	25	22	20	20	18	19
K_{rw} (S_{or}) (Before surfactant flood started)	0.09	0.11	0.17	0.19	0.16	0.14
K_{rw} (S_{ors}) (After the last injection)	0.08	0.12	0.07	0.05	0.05	0.07

Table 8-10: Ultimate oil recovery for the six cores.

	Uncertainty	**L1**	**L2**	**O1**	**O2**	**O3**	**O4**
Ultimate oil recovery [% OOIP]	± 2 %	67	72	74	74	77	75

The oil recovery for the four aged cores was similar after all the experiments were done. The results indicate that the oil recovery is slightly improved when the cores have been aged. This is in agreement with previous results. [27]

The oil production for all the cores started later than expected. It took around half of a pore volume of injected polymer before the oil production started. The efficiency of the surfactant has therefore not been optimal. The delay in production could be because of retention of the surfactant. The retention of a surfactant should in general not be a big problem at low salinity and without any divalent cations in the brine, but this can not be said for certain without doing retention tests in similar Berea outcrop rocks.

Injecting only 600 ppm HPAM seems to have the same efficiency as injecting both 300 and 600 ppm HPAM. The recovery factor increased for all the four cores when the second polymer solution with higher concentration was injected. One could therefore question whether a higher concentration than 600 ppm would have given even higher oil recovery. The production profiles indicate that the polymer flood was necessary to reach a recovery of around 75 % because the oil production stopped after injection of two pore volumes of lowsal water, and the recovery would probably not have increased more if the 600 ppm polymer was not used.

Table 8-11: Short summary of previous low salinity surfactant flooding results at similar conditions. **[26-28]**

	Alagic and Skauge (2010)	**Spildo et al. (2012)**	**Johannesen and Spildo (2013)**
Oil	Crude oil with 14 cP viscosity	Crude oil + xylene with 3 cP viscosity	Crude oil + xylene with 3 cP viscosity
Surfactant	1 wt % Internal olefin sulphonate	0.2 or 1 % Isotridecyl alcohol 13PO sulphate	3.33 wt % Internal olefin sulphonate
Rock	Aged Berea	Aged Berea	Aged Berea
Brine	5000 ppm NaCl	3000 ppm NaCl	0.07 x SSW
Cosolvent	1 wt % Isoamyl alcohol	None	3 wt % secondary butanol
PV injected of surfactant	Approximately 10 PV	16 PV and 8 PV	9 PV, 8 PV and 4 PV
Recovery of oil [% OOIP]	92 % and 94 %	90 % and 68 %	84 %, 86 % and 90 %

The previous results have used different surfactants and two of the papers also used cosolvents to improve the phase behavior. The rock material, brine and oil are generally similar to material used in this thesis. The procedure is somewhat different in this thesis. The previous results have been with continuous injection of surfactant solution until no more oil production was observed, and no polymers were injected. The results can still be compared qualitatively, especially regarding capillary numbers as these are in the same order of magnitude since the IFTs are similar.

The previously mentioned results regarding low salinity surfactant flooding have produced more oil than estimated from CDC estimations and the oil recoveries are generally very high, which is one of the reasons why the combined effect of lowsal and surfactants seems to be very beneficial.

The capillary number for the surfactant flood in this thesis is estimated to be $3 \cdot 10^{-4}$. This was calculated by equation 5. Inputs were $1.47 \cdot 10^{-6}$ m/s, 0.006 Pa·s and $3 \cdot 10^{-5}$ N/m. The viscosity was estimated by pressure data during injection of 600 ppm HPAM. The ratio of residual oil saturation after and before surfactant flooding should be around 0.4 at the estimated capillary number for the CDC curve on Berea outcrop, see figure 4-2.

Table 8-12: Ratio of residual oil saturation before and after SP flood.

Rock	L1	L2	O1	O2	O3	O4
S_{ors}/S_{orw}	0.81	0.69	0.74	0.71	0.56	0.70

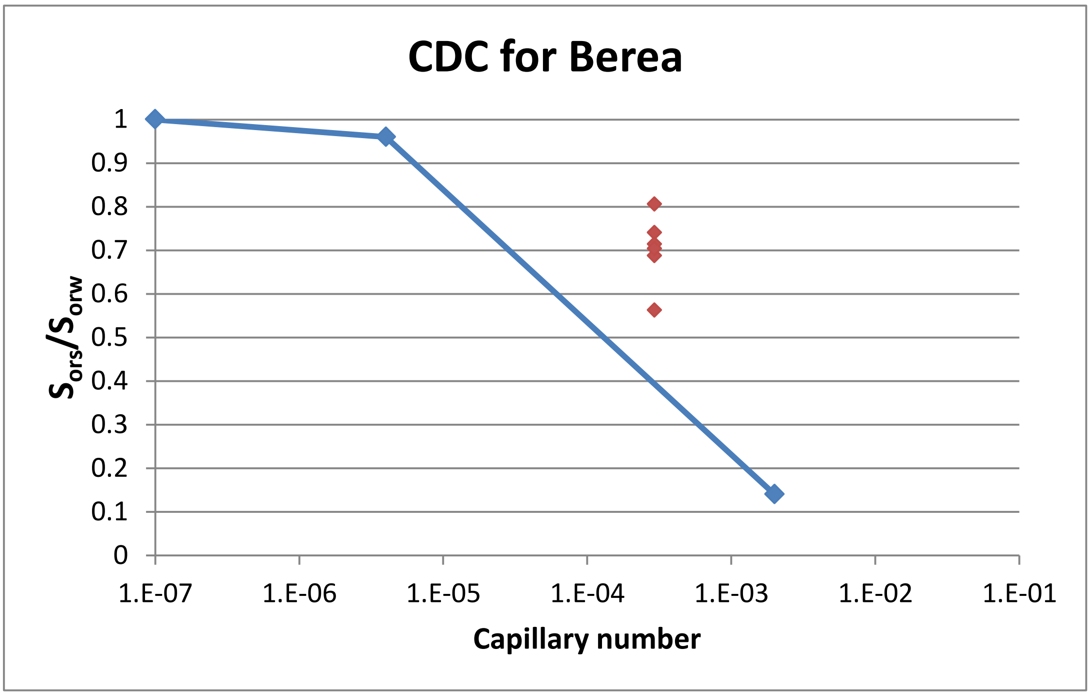

Figure 8-27: The CDC curve redrawn from figure 4-2 and the ratio for the six cores.

The efficiency of the low salinity surfactant flood was lower than expected from a capillary desaturation curve, and also much lower ultimate oil recovery than the previous results. This could be because of the surfactants performance in the rock, but more tests on the surfactant must be made to be able to make any conclusions about that. The physical volume of oil that is in the rock before the surfactant injection will influence the ratio in this context. The volume of oil before surfactant injection was around 5 ml for the cores, and this is smaller than the oil volume in the previous studies where larger rocks were used.

There seems to be no difference between the aged cores and the others in the ratio in table 8-12 although L1 and L2 might have benefited in this context due to higher oil saturation at the start of the surfactant flood. O3 which started with the same residual oil saturation as L1 and L2 might have had a better ratio due to this. This is because more oil available before the surfactant flood means that there is a bigger potential in recovering the residual oil. The residual oil saturation is also related to Swi. The residual oil saturation will in general increase with decreasing Swi. The connate water saturation in the six rocks in this thesis and the previous studies, however, is very similar.

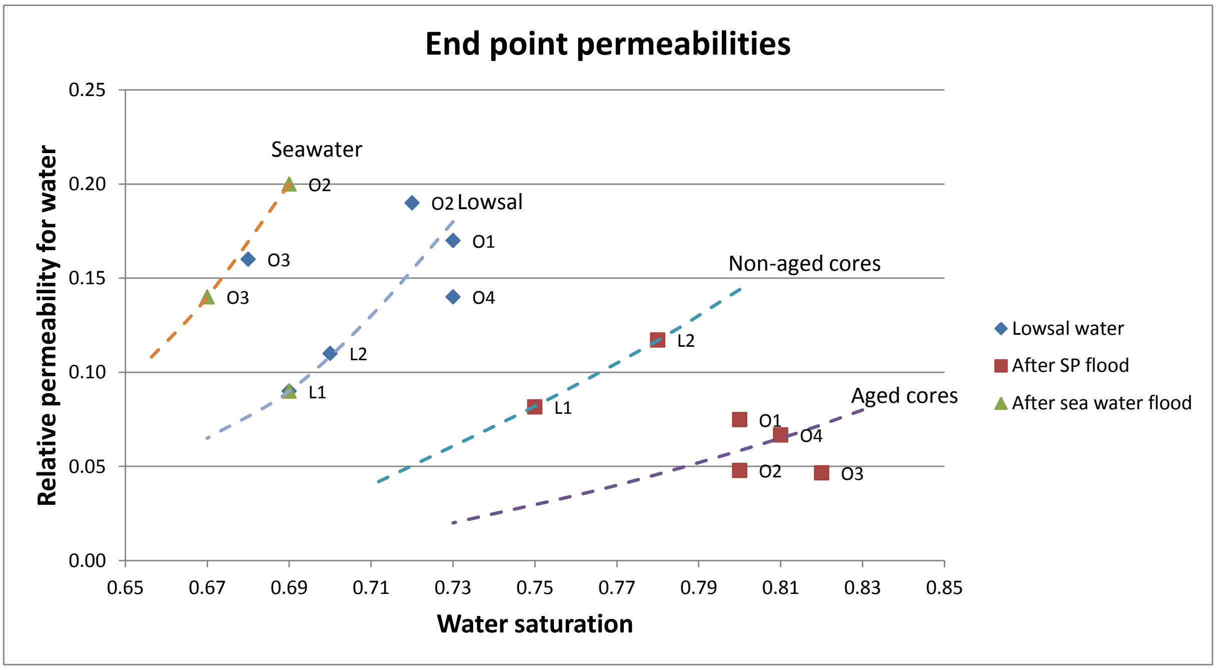

Figure 8-28: Relative permeabilities for water at residual oil saturations.

Four general trends are highlighted in figure 8-28. Lowsal has lower water permeability than seawater. Lowsal has not reduced the permeability for O3, but a small reduction for O2 seems to be the case, compared to seawater permeability. The non-aged cores have decreased water permeability after the surfactant and polymer flood, but the decrease is clearer for the aged rocks.

The water permeability is influenced by several factors. Low salinity water can promote stronger water wetness and this can lead to a reduction in water permeability. Lowsal can also mobilize fines that block pore throats and this could also decrease water permeability.

It is apparent from the end point permeabilities that the polymer injection has contributed to a reduction in permeability even though the water saturation has increased. This is due to adsorption of polymer molecules or because of trapping in small pores. The residual resistance factor is approximately 2.5 to 3 for the aged cores and around 2 for L1 and L2. The reason why the aged cores have a larger reduction in water permeability could be because the lowsal surfactant has destabilized oil layers, but not all of this oil has been produced, and this redistribution of oil could hinder the water flow. This is because oil that is in the middle of a pore will be a larger obstacle than if the oil is adhered to the pore wall.

9 Conclusion

Whether low salinity flooding improves oil recovery is already known to be dependent on the COBR combination. Low salinity flooding did not improve recoveries for the two cores that had not been aged. However, the four cores that had been aged showed some positive response to lowsal. This is easier to conclude for O2 and O3 where the lowsal flooding was in tertiary mode. The recovery increased by 3-5 % of original oil in place. O1 and O4 were flooded with lowsal in secondary mode, but a lowsal effect is very possible to be present since the recovery factors were not lower than for O2 and O3.

It was not possible to detect any lowsal mechanism that reacted slower than the timespan of an experiment for O1 and O4, but more experiments with more similar conditions to the model system are necessary to make any conclusions on the kinetics of low salinity mechanisms.

Oscillating the salinity did not improve the oil recovery, except for the increase in the tertiary injection of lowsal. Unstable pressures were observed during the core flood for O3, but whether this was due to two phase flow from mobilized oil or movement of fines is difficult to conclude.

The combination of low salinity and surfactant flooding did not produce as high oil recovery as the previously mentioned studies have shown. Oil recovery was approximately 75 % in these experiments, but some cores in previous studies have produced over 90 % at very similar capillary numbers. The lower recovery in these experiments could be due to the performance of the surfactant being lower than in the previous studies. One similar trend to previous results was that aged cores seemed to give higher oil recovery.

Injecting polymer solutions after the surfactant improved the efficiency of the flooding. Increasing the concentration of the polymer also increased the oil production. The polymer reduced the permeability of the rock, but the permeability of the rocks was high enough to not observe any problems in these experiments.

10 Further work

It is already well known that decreasing the salinity of injected water may improve the recovery, but the underlying mechanisms are still unclear. Answering these questions will require much more research on the topic.

More experiments with similar conditions to the model system for the kinetics experiments are necessary to make any conclusions on the kinetics of low salinity mechanisms. More experiments with oscillating salinity are also needed to understand how this can affect oil mobilization and oil recovery.

The combination of low salinity surfactant has given very high recoveries in previous studies, and the efficiency of this process should be tested further. The impact of polymer injection on oil recovery should be tested. The results from these experiments suggest that polymer injection was necessary to reach a recovery factor of 75 %. The optimal concentration for the polymer solution should be tested. Low salinity injection with only polymer and no surfactant is also a topic of interest.

Retention measurements for the surfactant used should be done in Berea rocks to investigate if retention has impacted the results in this thesis.

The efficiency of injecting surfactant and polymer simultaneously should also be tested to investigate if it is more efficient than injecting the polymer solution after the surfactant.

11 References

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Appendix

A.1 Density measurements

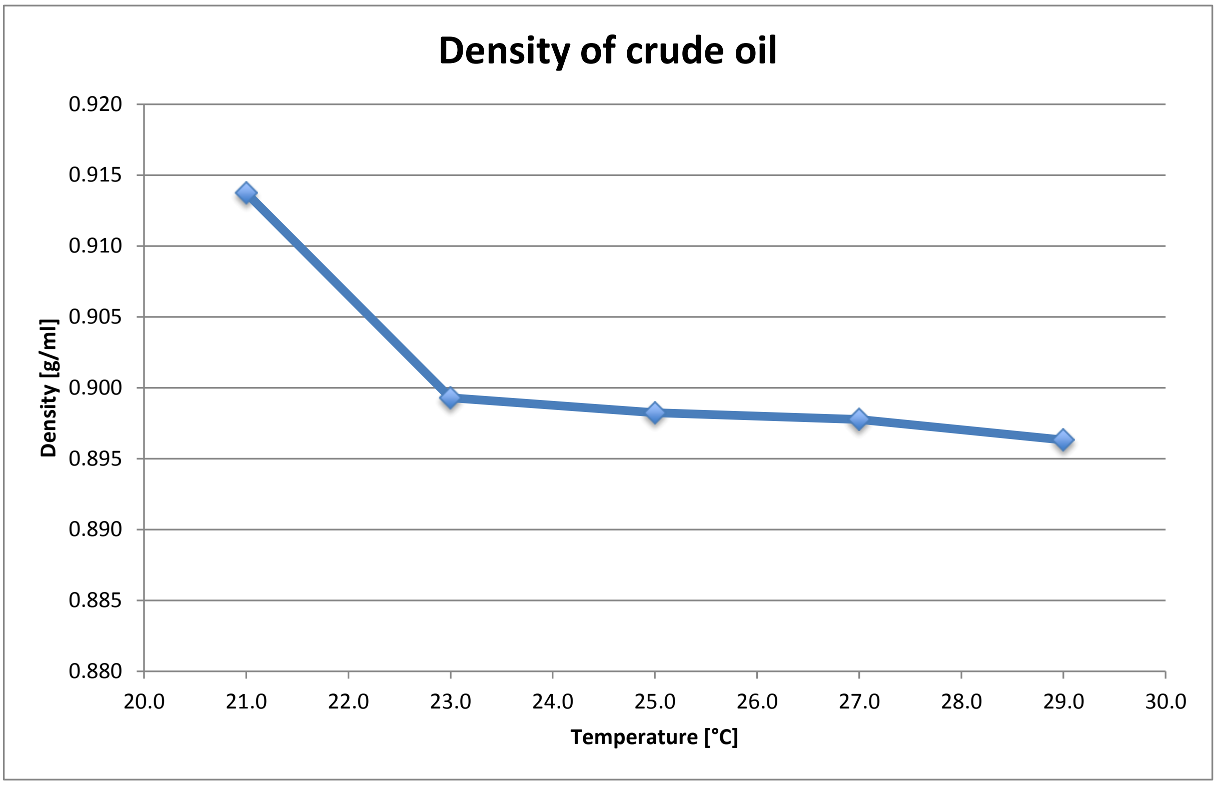

Figure A.1-1: Density of crude oil.

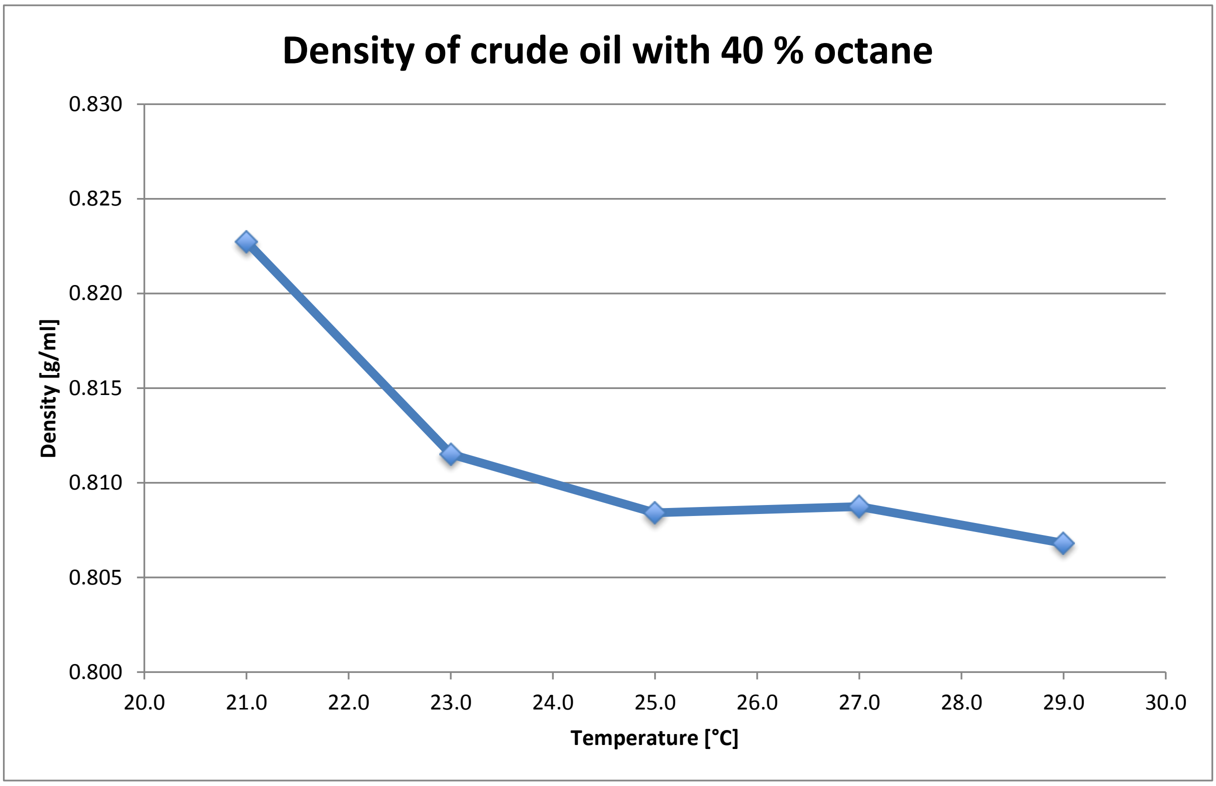

Figure A.1-2: Density of crude oil with 40 % octane.

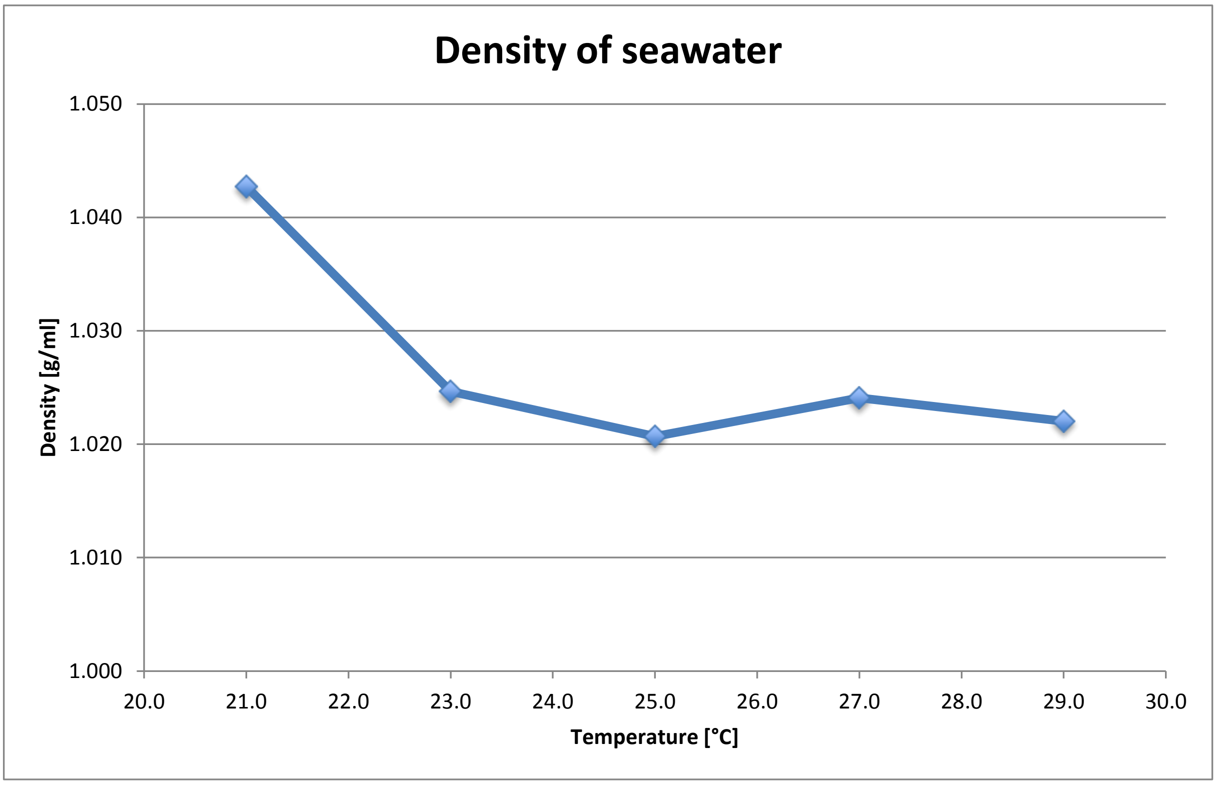

Figure A.1-3: Density of seawater.

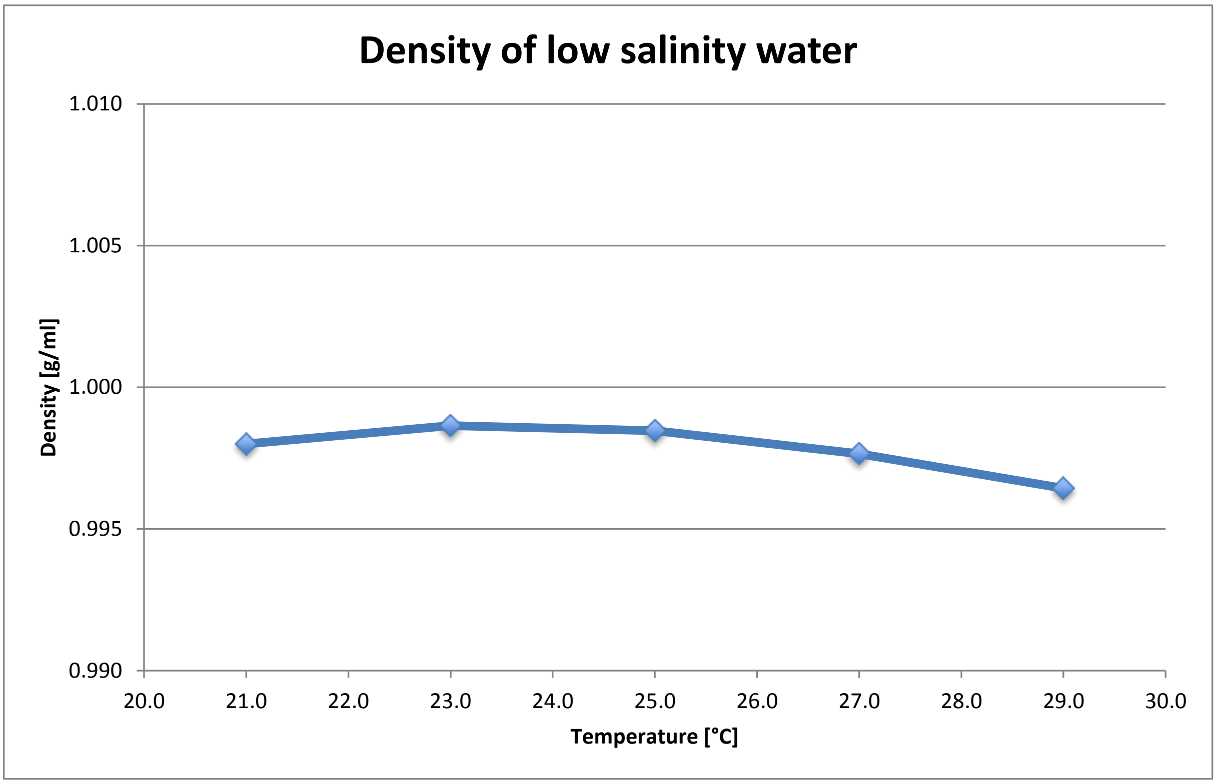

Figure A.1-4: Density of 1/22 synthetic sea water.

A.2 Viscosity measurements

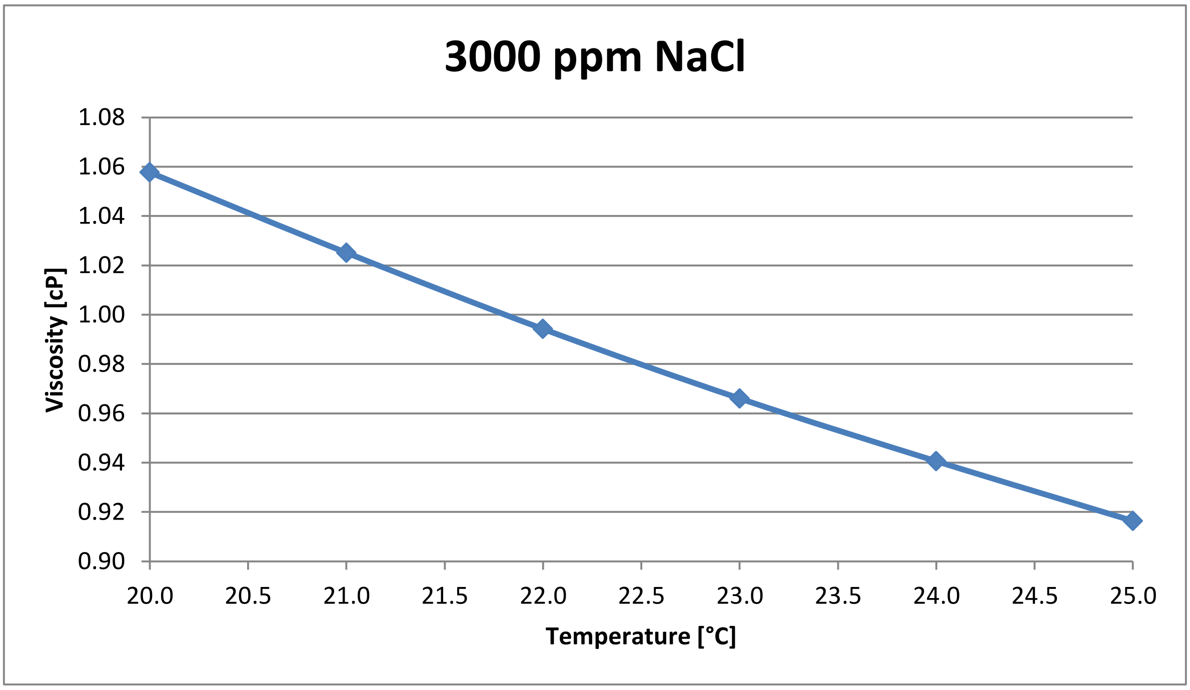

Figure A.2-1: Viscosity of 3000 ppm NaCl.

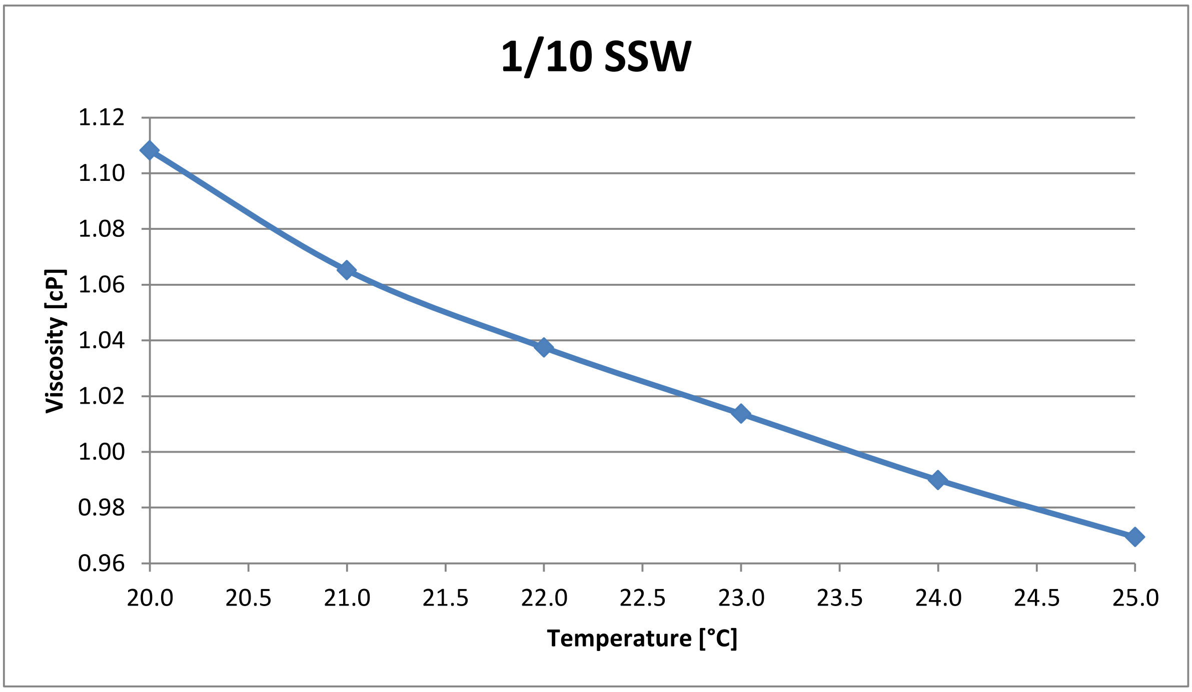

Figure A.2-2: Viscosity of 1/10 synthetic seawater.

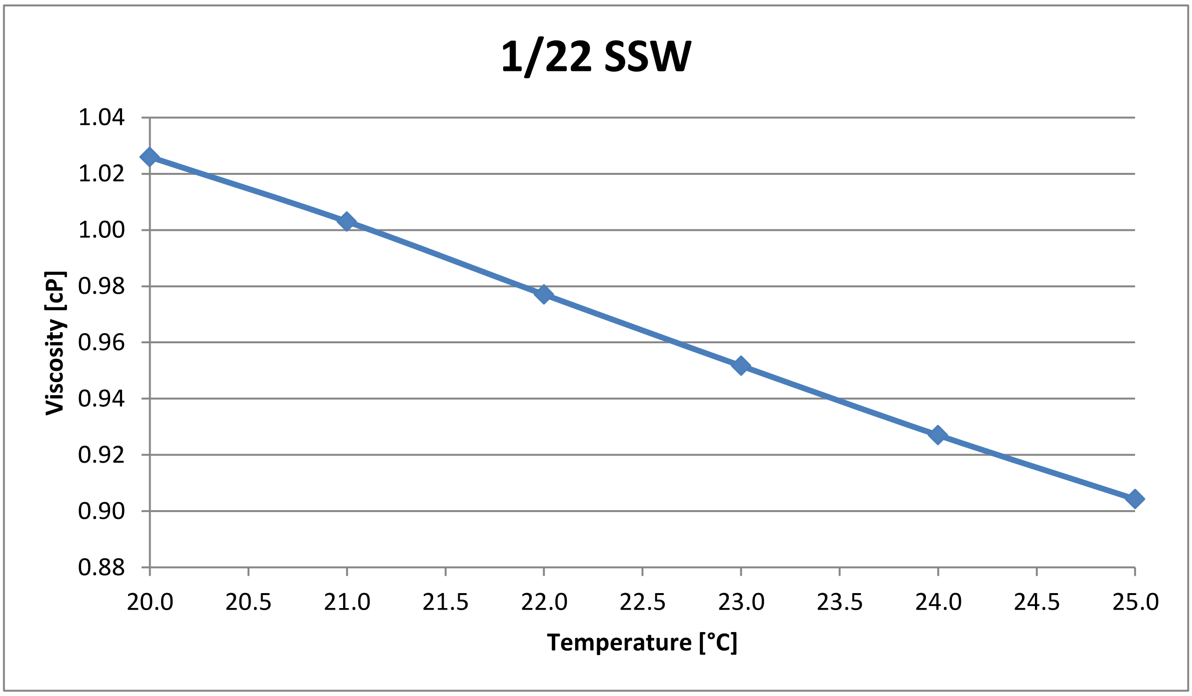

Figure A.2-3: Viscosity of 1/22 synthetic seawater.

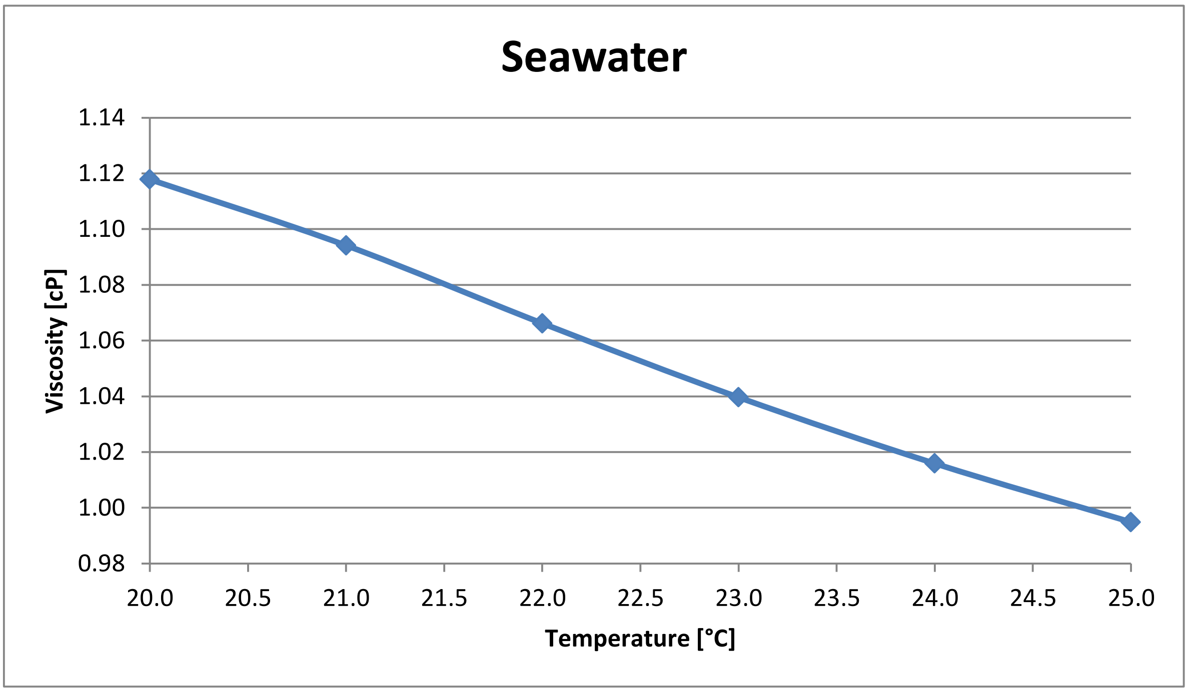

Figure A.2-4: Viscosity of seawater.

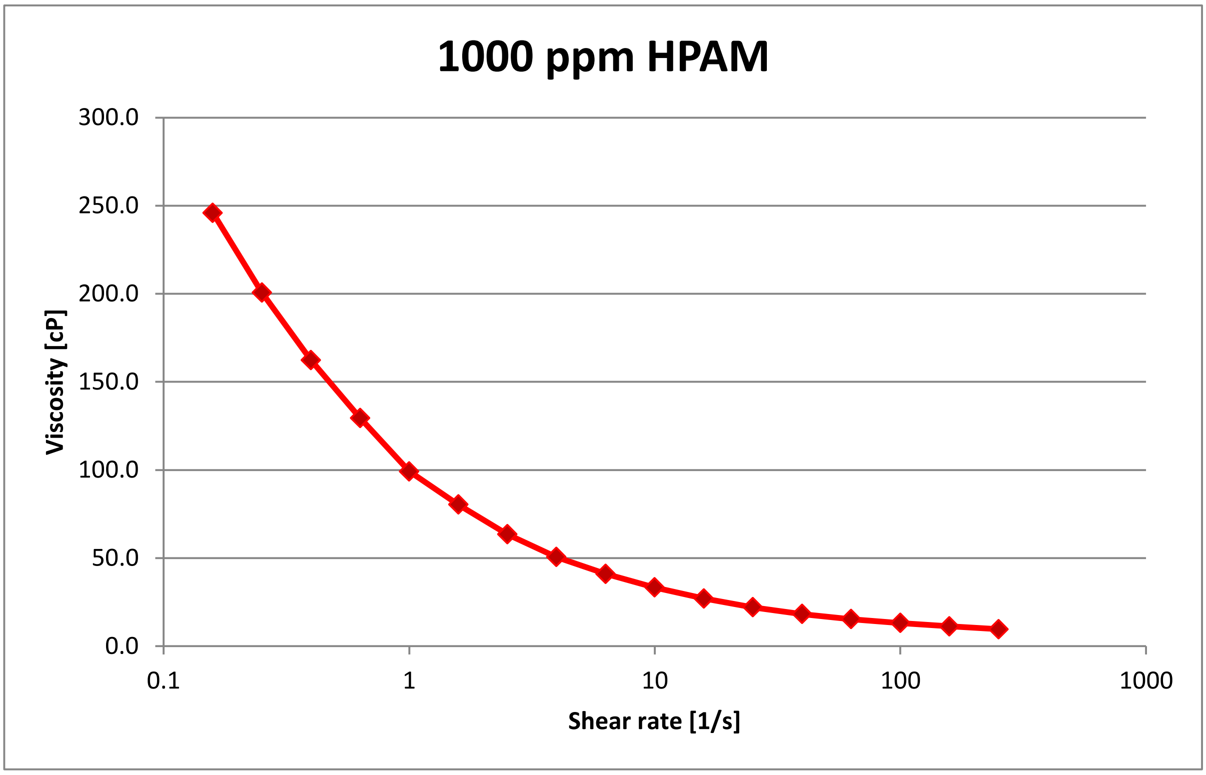

Figure A.2-5: Viscosity of 1000 ppm HPAM.

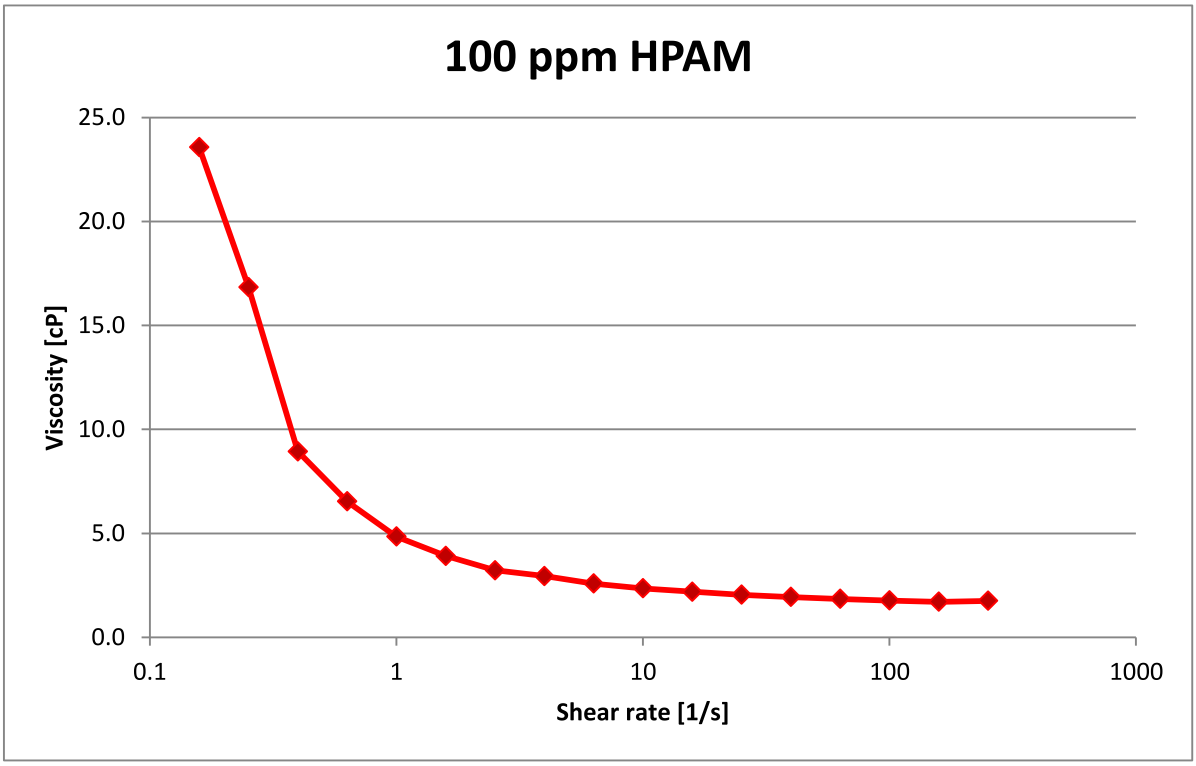

Figure A.2-6: Viscosity of 100 ppm HPAM.

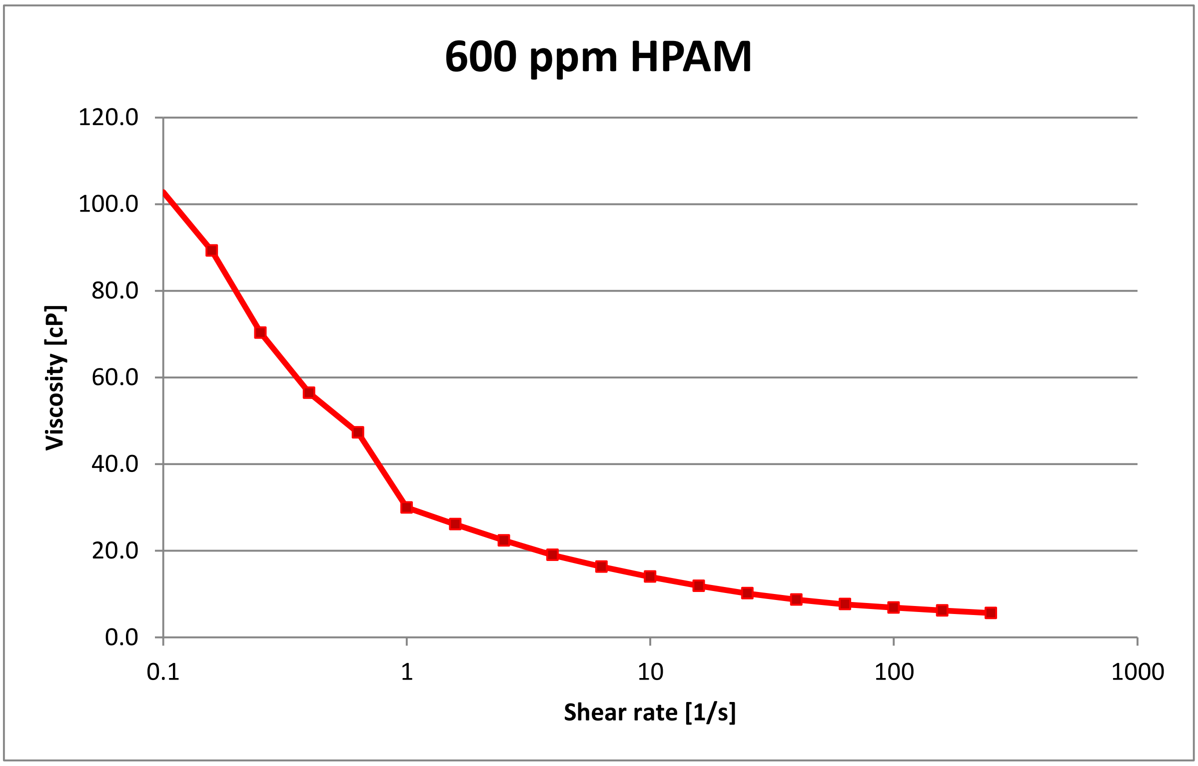

Figure A.2-7: Viscosity of 600 ppm HPAM.

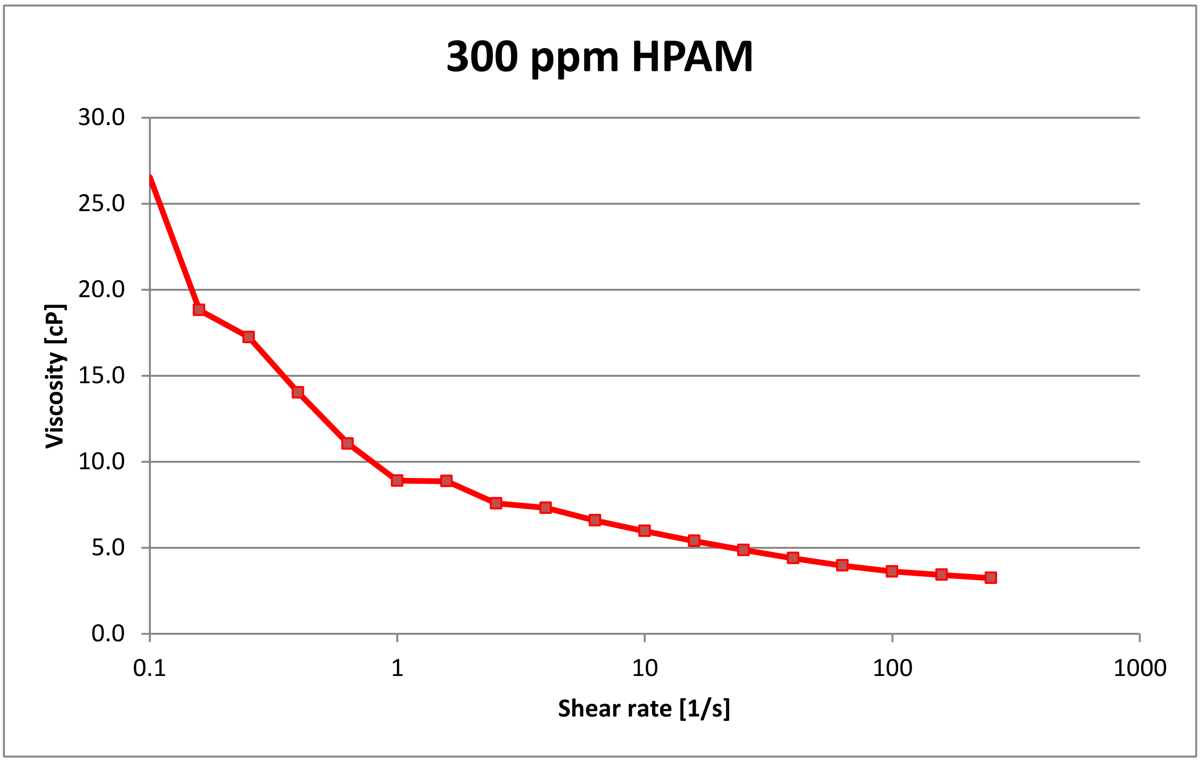

Figure A.2-8: Viscosity of 300 ppm HPAM.

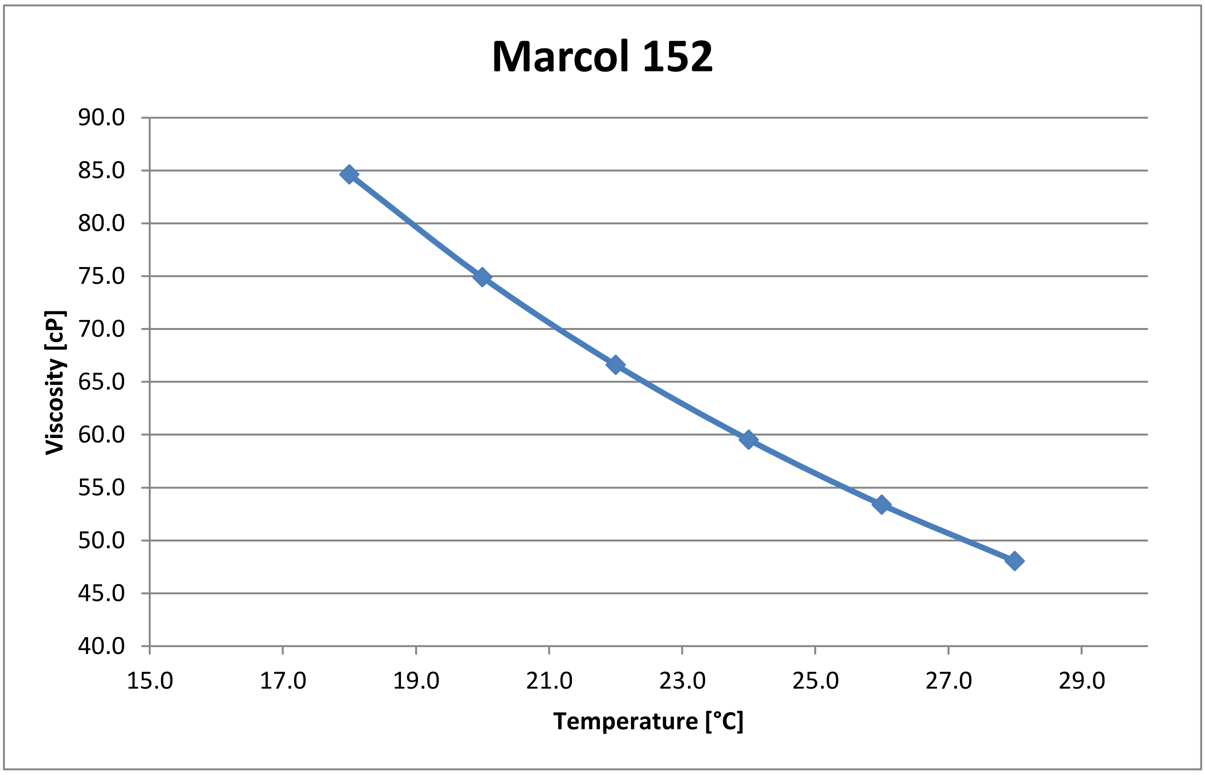

Figure A.2-9: Viscosity of marcol 152.

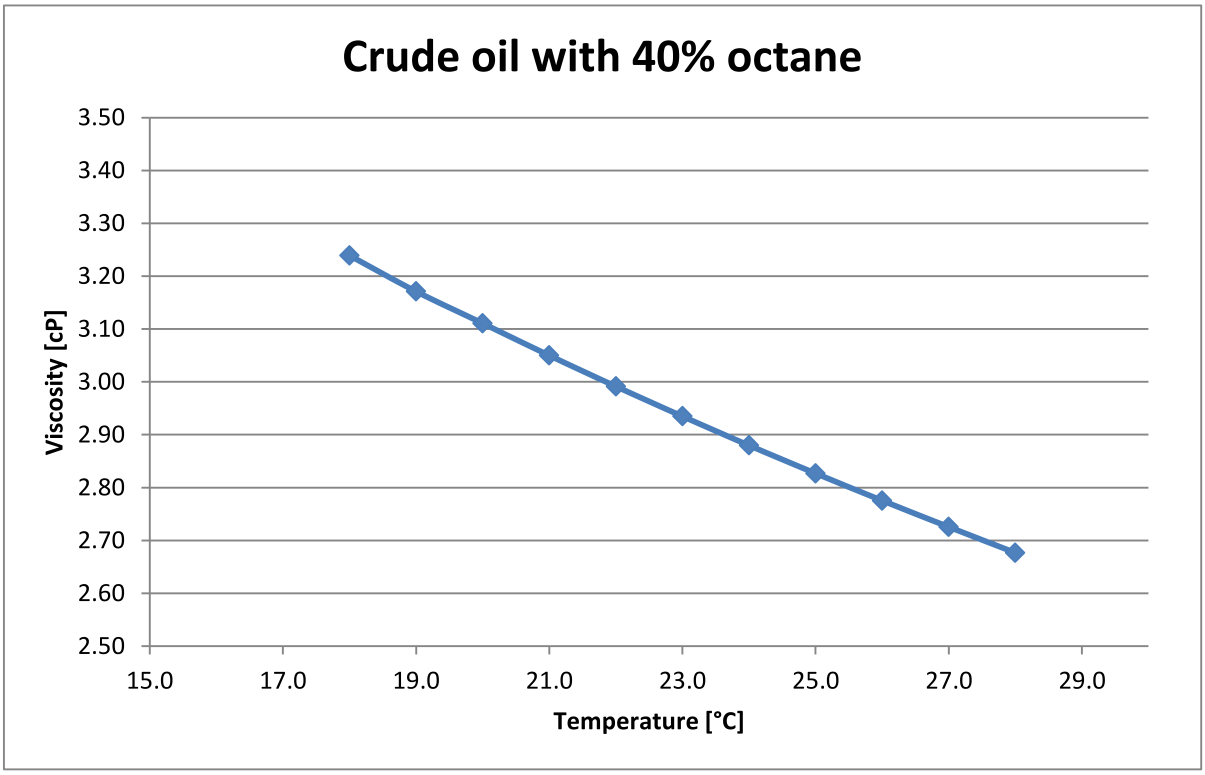

Figure A.2-10: Viscosity of crude oil mixture.

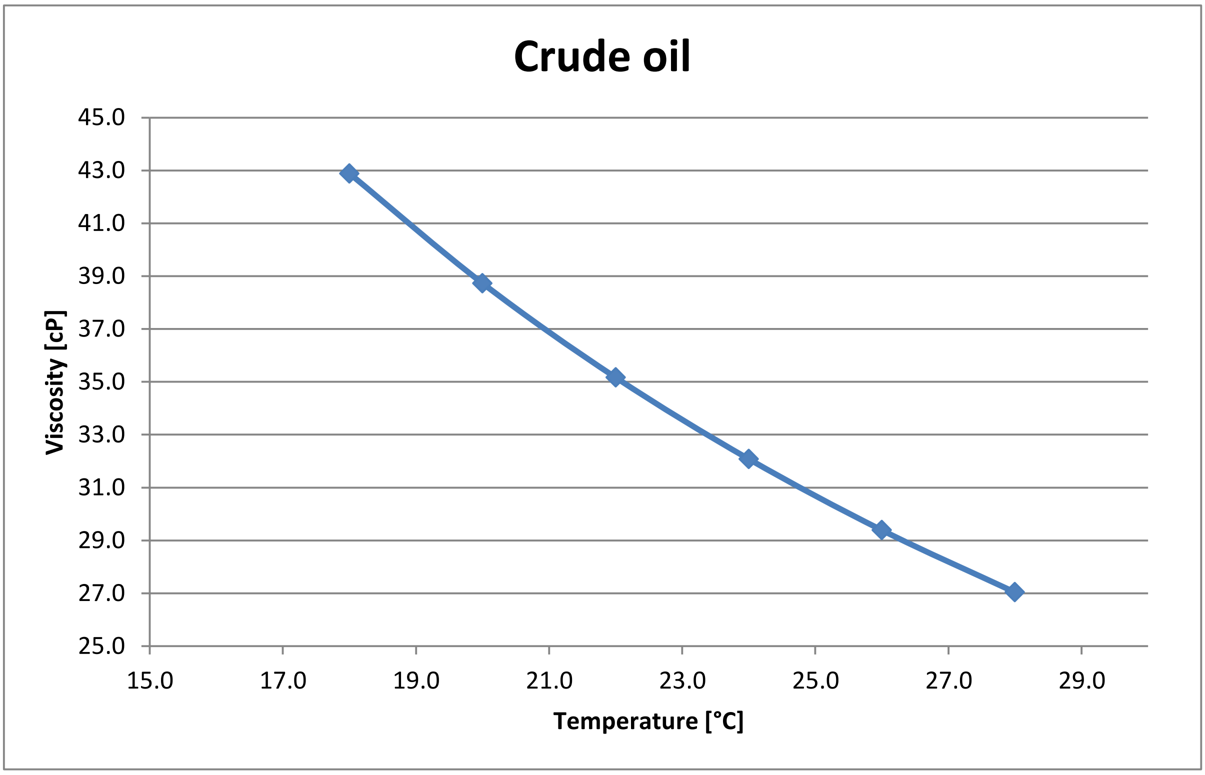

Figure A.2-11: Viscosity of crude oil.

A.3 Spinning drop measurements

Table A.3-1: Spinning drop results.

	DD044		DD044/2	
	IFT [mN/m]	Angular frequency [rpm]	**IFT [mN/m]**	Angular frequency [rpm]
Sample 1	0.03	2400	0.06	2400
	0.03	3400	0.04	3400
	0.06	3900	0.04	3900
	0.01	5600	0.06	5600
Sample 2	0.05	2400	0.04	2400
	0.02	3400	0.04	3400
	0.02	3900	0.04	3900
Sample 3	-		0.05	2400
	-		0.05	3400
	-		0.05	3900
	-		0.06	5600
Fresh sample	0.03	4000	0.02	3400