



University of  
Stavanger

**Faculty of Science and Technology**

## **MASTER'S THESIS**

Study program/ Specialization:  Master in petroleum technology/ Reservoir engineering	Spring semester, 2010  Open
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Title of thesis:  Experimental study of low salinity EOR effects from the Varg field.	
Credits (ECTS): 30	
Key words: - Enhanced oil recovery - LowSal - Waterflooding - Sandstone - Wettability alteration	Pages: 66  + enclosure: 14  Stavanger, 15 <sup>th</sup> of June 2010.

## Acknowledgements

First of all I want to thank my supervisor professor Tor Austad for providing me with a challenging and exciting master thesis. I am grateful for his availability and guidance.

I specially thank PhD. student Alireza Rezaei Doust for all his support and help, especially during the experimental work.

I will also thank associated professor Skule Strand for very good proofreading and for the answers to all of my questions.

I am thankful for the information Arne Onstein and Talisman Energy has provided me with.

I wish to thank my parents for all the encouragement during my studies.

Finally I want to thank Magnus for being very patient and supporting during the work with this thesis.

Elin Melberg

## Abstract

The extra oil recovery obtained when flooding a sandstone reservoir with low saline water is called low salinity (LowSal) effect. The term salinity refers to amount (and type) of salt that makes up the ionic composition of the brine. The injected water must have a different composition and a lower salinity than the initial formation water to promote significant desorption of oil from the rock surface. Several different hypotheses have been proposed as low salinity mechanisms. Fines migration, pH increase and multicomponent ionic exchange (MIE) are among the best known. But none of these hypotheses have so far been generally accepted as the main mechanism. It is assumed that LowSal effect is due to a wettability modification towards more water-wet conditions. Desorption of oil components in a low salinity environment makes the rock more water-wet. There is also a considerable amount of data which shows that oil recovery can be dependent on polar components in the crude oil, divalent cations in the formation water, like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and active clays in the sandstone.

The Varg field in the Norwegian part of the North Sea is at late life production, but low saline waterflooding may increase the lifetime of the field. In this study, two different sandstone reservoir cores from Varg, Varg#5 and Varg#6, were flooded with sea water/low saline water in order to observe LowSal effect. The initial water saturation of the cores was established using a desiccator. The cores were saturated with crude oil, containing  $\text{CO}_2$ , from the Varg reservoir. They were aged for 14 days at reservoir temperature, 130 °C. During the main flooding test, both cores were flooded with high saline Varg formation brine (201 560 ppm) in a secondary stage, sea water (33 390 ppm) in a tertiary stage and finally a 500 ppm NaCl-solution as LowSal fluid. The displacement temperature was 130 °C. The oil recovery by secondary displacement with formation brine was 43% and 27% of the original oil in place (OOIP) for Varg#5 and Varg#6 respectively. No extra oil was recovered by sea water and low saline NaCl-solution. The main reason for no observations of LowSal effect may be the high ageing temperature and increase in relative adsorption of organic material and active cations onto the clay surface.

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# 1. Introduction

Conventional waterflooding is used to displace oil physically from the reservoir and to maintain the reservoir pressure. Although water injection is widely applied, little research has been done on the chemistry of the injected brine and its impact on oil recovery.

Based on laboratory tests from different sandstone reservoirs, Lager et al. have reported that the average increase in oil recovery was about 14% due to LowSal flooding. In some of the cases the recovery was increased by up to 40% compared to a conventional high salinity waterflood (Lager A., 2007). Results from this study are illustrated in appendices A.1.

Although several different low salinity mechanisms have been suggested, it is generally accepted that LowSal effect is due to a wettability modification towards more water-wet conditions (Austad, 2010a). In a low salinity environment, desorption of oil components makes the rock more water-wet. Several studies show that oil recovery can be dependent on polar components in the crude oil, divalent cations in the formation brine and active clays in the sandstone. The chemical mechanism for wettability modification in sandstones and carbonates is different (Austad, 2010a). LowSal effect has therefore not been documented in carbonates.

About 50% of the world's petroleum reservoirs are found in sandstones, and most of these reservoirs contain clay minerals. This, combined with the fact that waterflooding is one of the most used secondary recovery methods, indicate that low salinity water injection has potential and that further research on the method is important. When performing LowSal waterflooding, the injected water is diluted, and no chemicals are necessarily added. This technique is therefore more environmentally friendly compared to many other methods for increased oil recovery.

The Varg field is at late life production, and methods to extend the lifetime for the field are investigated. The purpose of this master thesis is to contribute with experimental studies of the potential for LowSal flooding in Varg. The goal is to observe LowSal effect from two different reservoir cores. The results will also affect the further research on the LowSal mechanism. The salinity of the Varg formation brine is high, around 200 000 ppm, as well as the reservoir temperature of 130 °C. It has been difficult to verify a significant tertiary LowSal effects at reservoir conditions. The Varg reservoir is already flooded with sea water in field. There is a considerable salinity gradient/gradient in active ions between sea water and the initial formation brine. Sea water may therefore act as a LowSal fluid itself in the Varg reservoir. Talisman Energy Norge AS, which operates Varg, and the partners have approved that the name of the field with additional information are mentioned in the thesis.

The thesis starts by introducing general theory, which the rest of the thesis is based upon. Then the theory gets more specific on the LowSal topic and a new hypothesis behind the LowSal effect is proposed. The next chapter, experimental work, contains all the procedures, materials and apparatus used in the experiments. The results are then listed and discussed. Finally, the main results are presented in the conclusion section. Information about the Varg field, large tables and detailed measurement procedures which may be of interest are found in the appendices.

## **2. Theory**

### **2.1 Recovery mechanisms**

Oil recovery has traditionally been divided into three chronologically stages: primary, secondary and tertiary recovery. However, in many situations, oil recovery operations are not conducted in this specific order. The so-called tertiary recovery process might be applied as a secondary process in a chronologically sense. The term tertiary recovery is therefore replaced by the more accepted term “Enhanced Oil Recovery” (EOR). Another commonly used expression is “Improved Oil Recovery” (IOR). This term includes EOR but also a broader range of activities, e.g., reservoir characterization, improved reservoir management and infill drilling (Green, 1998).

#### **2.1.1 Primary recovery**

Primary recovery is the initial production stage resulting from the displacement energy naturally existing in the reservoir. The natural energy sources are solution gas drive, gas-cap drive, natural water drive, fluid and rock expansion and gravity drainage (Green, 1998). The primary recovery classification also includes artificial gas lift and electrical pumps. The recovery factor for this period is usually relatively low, around 5-30% on average of the original oil in place (Bavière, 1991).

#### **2.1.2 Secondary recovery**

Secondary recovery is usually implemented when the primary recovery starts to decline. Since there is not enough energy naturally occurring in the reservoir to produce at an economic rate, energy needs to be supplied from the surface. To produce more oil, the pressure in the reservoir can be maintained by injection of other fluids. Traditional

secondary recovery processes are injection of fluids which already exist in the reservoir, as water and gas. These fluids are injected to ensure pressure support by physical energy and displacement of oil towards the production wells (Robertson, 2007). The most applied secondary recovery process is waterflooding. The recovery factor for a reservoir which has undergone primary production followed by waterflooding may reach 35 to 50% of the original oil in place (Green, 1998).

### **2.1.3 Tertiary recovery/EOR processes**

The target for the tertiary recovery is the residual oil saturation left behind after the secondary recovery process has become uneconomical. An EOR process may involve injection of miscible gases, chemicals and thermal energy into the reservoir to displace additional oil – thereby the classification enhanced oil recovery. In miscible processes the objective is to inject fluids that are directly miscible with the oil or that generate miscibility in the reservoir through composition alteration. Examples are injection of hydrocarbon solvents or carbon dioxide, CO<sub>2</sub>, at miscible conditions. Chemicals applied in an EOR process may be surfactants or alkaline agents, which are injected to use a combination of phase behavior and reduction of interfacial tension (IFT) to displace oil. So-called mobility-control processes are primarily based on maintaining favorable mobility ratios to improve the displacement efficiency. Thickening of water with polymers are one example. Thermal processes rely on the injection of thermal energy or in-situ generation of heat to lower the viscosity of the oil so it flows easier towards the production wells. Steam injection or in-situ combustion from air or oxygen injection are examples (Green, 1998).

Bavières definition of enhanced oil recovery is: “EOR consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents *not* normally present in the reservoir, such as chemicals, solvents oxidizers and heat carriers, in order to induce new mechanisms for displacing oil”. This definition excludes the pressure maintenance by water or gas injection, which uses physical energy alone (Bavière, 1991). But



according to the definition, low salinity water injection is an EOR process since the chemical composition of the injected water is different from the initial formation brine, and because the wetting conditions of the surface is changed in the process.

## **2.2 Displacement forces**

The most important forces determining the flow of oil and water in oil production processes are capillary forces, viscous forces and gravity forces (Morrow, 1979).

### **2.2.1 Capillary forces**

Capillary pressure may be defined as the pressure difference across a curved interface between two immiscible fluids, as shown in figure 2.1, or as the pressure difference between the non-wetting phase and the wetting phase (Ursin, 1997). The capillary pressure can be calculated from the following equation:

$$P_c = P_o - P_w = \frac{2\sigma_{ow} \cdot \cos\theta}{r} \quad (2.1)$$

Where:

$P_c$  = Capillary pressure

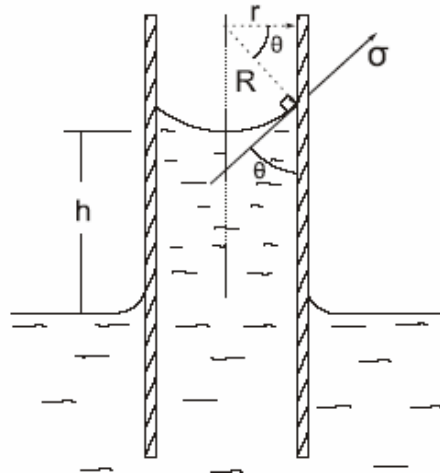
$P_o$  = Oil-phase pressure at a point just above the oil-water interface

$P_w$  = Water-phase pressure just below the interface

$r$  = Radius of the cylindrical pore channel

$\sigma_{ow}$  = Interfacial tension between oil and water

$\theta$  = Contact angle measured through the wetting phase (water)



**Figure 2.1:** Use of a capillary tube to measure capillary pressure (Strand, 2005)

The capillary pressure is thus related to the fluid (IFT), the relative wettability of the rocks (through  $\theta$ ) and the size of the pore/capillary,  $r$ . The capillary pressure may be positive or negative. The sign expresses in which phase the pressure is lower, which will always be in the wetting phase (Green, 1998). Positive values of the capillary pressure therefore indicate that water is the wetting phase and oil is the non-wetting phase.

Strong capillary forces during a waterflooding might trap oil and cause relatively high residual oil saturation (Anderson, 1987b). As seen from equation 2.1, trapping of oil can be reduced by lowering of the IFT or  $\cos \theta$ . The IFT may be reduced by injection of surfactants and the contact angle can be changed by inducing a wettability alteration.

### 2.2.2 Viscous forces

Viscous forces in a porous medium are reflected in the magnitude of the pressure drop that occurs as a result of flow of a fluid through the medium. When fluid is forced through the reservoir or core, viscous forces are used to overcome the capillary barrier in the pores. For typical reservoir-rock conditions, the capillary forces dominate the viscous

forces. The capillary number expresses the ratio of the viscous to capillary forces in flow through a capillary/pore, and is given by the following equation:

$$N_{ca} = \frac{F_v}{F_c} = \frac{v\mu_w}{\sigma_{ow}} \quad (2.2)$$

Where:

$F_v$  = Viscous force

$F_c$  = Capillary force

$v$  = Interstitial pore velocity

$\mu_w$  = Viscosity of the water

$\sigma_{ow}$  = Interfacial tension between oil and water

Waterfloods typically operate at conditions where the capillary number is less than  $10^{-6}$ . At these conditions the residual oil saturation is relatively constant and is not a function of the magnitude of  $N_{ca}$ . But correlations show that if the value of  $N_{ca}$  could be increased to more than about  $10^{-5}$  in a flood, the magnitude of residual oil would decrease (Green, 1998). As seen from equation 2.2,  $N_{ca}$  could be increased by lowering the IFT (adding surfactants), by increasing the interstitial velocity or the injectant viscosity (adding polymers).

### 2.2.3 Gravity forces

Gravity forces are important in reservoirs where there exists a high density difference between the injected and displaced fluid. Gravity forces are also important under low oil-water IFT conditions. The buoyancy forces are always present in mixtures of immiscible fluids, and the lighter phase experiences a pressure pointing upwards, given by the equation:

$$\Delta P_g = \Delta \rho \cdot g \cdot H \quad (2.3)$$

Where:

$\Delta P_g$  = Pressure difference between oil and water due to gravity

$\Delta \rho$  = Density difference between oil and water

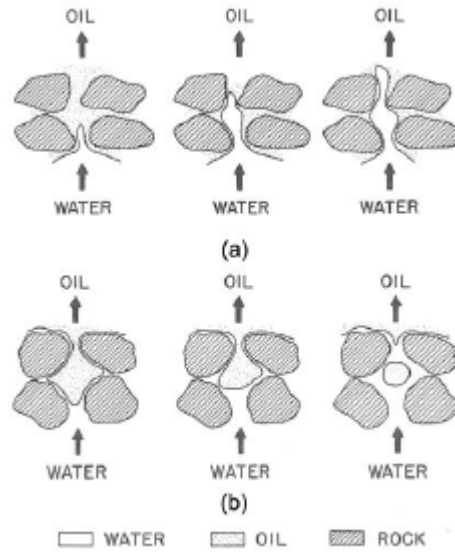
$g$  = Acceleration due to gravity

$H$  = Height of the liquid column

The density difference between the fluid phases, the height of liquid column, the magnitude of capillary forces related to IFT, wettability and permeability are the most important parameters deciding the influence of gravity forces on fluid movement in the reservoir (Strand, 2005).

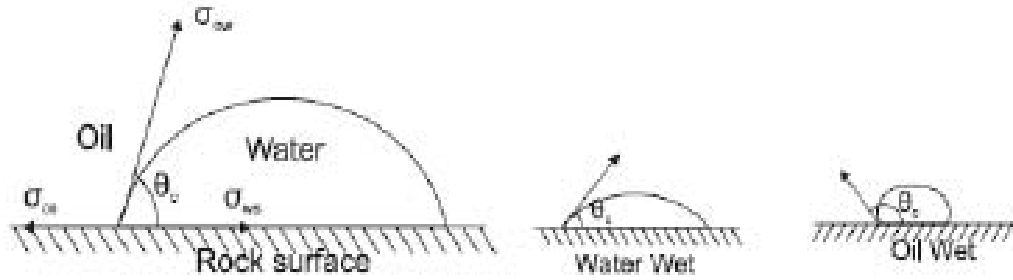
## **2.3 Wettability**

Wettability can be defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of another immiscible fluid. When two immiscible phases are in contact with a solid surface, one phase usually is attached to the solid more strongly than the other. The more strongly attracted phase is called the wetting phase (Green, 1998). The reservoir rock wettability is an important property determining the success of waterflooding, because it has great influence on the location, flow and distribution of the fluids in the reservoir (Punternold, 2008). In a system at equilibrium, the wetting fluid is located on the pore walls and occupies the smallest pores, while the non-wetting fluid is located in the pore bodies (Ahmed, 2000). This phenomenon is illustrated in figure 2.2.



**Figure 2.2:** Displacement of oil by water (Strand, 2005).  
 a) Oil-wet rock, b) Water-wet rock.

The evaluation of reservoir wettability can be made through measurements of IFT and the contact angle  $\theta$ , illustrated in figure 2.3 (Ursin, 1997). This angle can be defined as the tangent to the oil-water surface in the triple-point solid-water-oil, measured through the water phase (wetting phase) (Strand, 2005). In a system containing a reservoir rock, oil and water, as shown in figure 2.3, the rock is typically preferentially water-wet if water occupies the smaller pores and is the spreading fluid ( $\theta < 90^\circ\text{C}$ ). If oil is the spreading fluid ( $\theta > 90^\circ\text{C}$ ), the rock is preferentially oil-wet (Punternold, 2008). The rock is intermediate-/neutral-wet when both fluid phases tend to wet the solid, but one phase is only slightly more attracted to the rock than the other ( $\theta = 90^\circ\text{C}$ ) (Green, 1998). If the formation is strongly water-wet, the oil can be trapped in the middle of the largest pores. The link between contact angle and wettability preference is given in table 2.1.



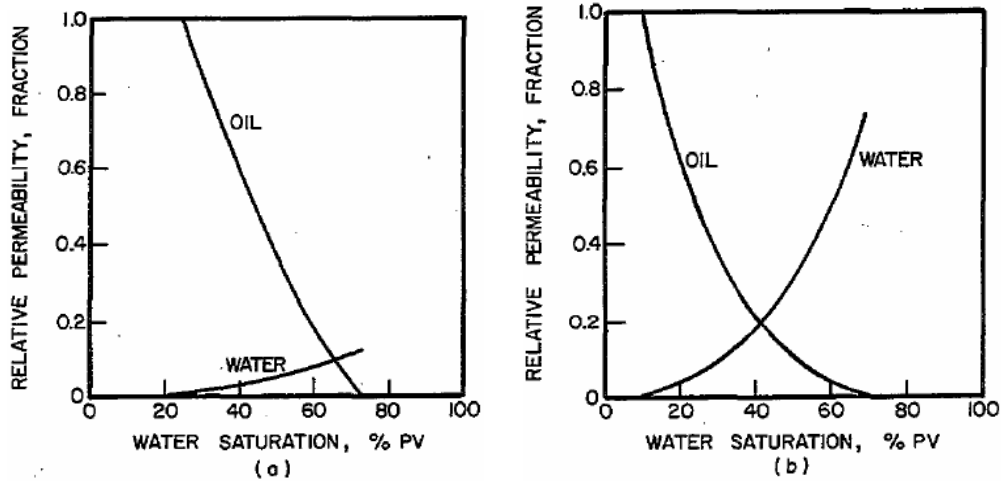
**Figure 2.3:** Measurement of the contact angle  $\theta$ , through the water phase (Strand, 2005).

**Table 2.1:** Wettability preference for a water-oil system (Ursin, 1997).

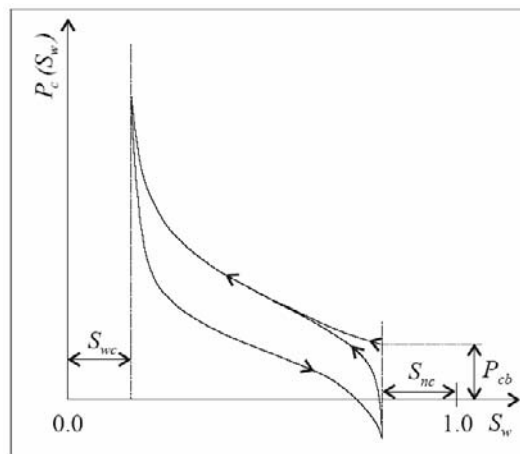
Contact angle values:	Wettability preference:
0-30	Strongly water wet
30-90	Preferentially water wet
90	Neutral wettability
90-150	Preferentially oil wet
150-180	Strongly oil wet

Not all reservoirs have uniform/homogeneously wettability throughout the reservoir, but rather a heterogeneous wettability. Fractional, spotted or dalmatian wettability are terms that are often seen representing heterogeneous wetted reservoirs (Anderson, 1986b). In this type of rock wettability, some areas of the rock are oil-wet, while the rest is water-wet. Mixed wettability is a special type of fractional wettability. Under this wetting conditions small pores and grain contacts are preferentially water-wet and contain no oil, whereas the oil-wet surface form continuous paths through the largest pores and contain all of the oil (Punternold, 2008). Mixed wettability results from a variation or heterogeneity in chemical composition of exposed rock surfaces or cementing-material surfaces in the pores. Because of this mixed chemical exposure, the wettability condition may vary from point to point (Green, 1998). In order to observe a LowSal effect, the increased recovery obtained during low salinity water injection, the reservoir rock must be mixed-wet. In other words, organic material must be adsorbed onto the rock (Punternold, 2010).

The wettability affects the relative permeability, the ability of the porous system to conduct one fluid when one or more fluids are present, and the capillary pressure (Anderson, 1987a; Anderson, 1987c). Relative permeability curves, shown in figure 2.4, and capillary pressure curves, illustrated in figure 2.5, may therefore be used to measure the wettability of a system (Anderson, 1986a).



**Fig 2.4:** Typical water/oil relative permeability curves based on the effective permeability to oil at the reservoir connate water saturation: a) strongly water-wet rock, b) strongly oil-wet rock (Anderson, 1986a).



**Figure 2.5:** Typical capillary pressure curve, capillary pressure vs. water saturation, for a two-phase flow system (Ursin, 1997).

## **2.4 Crude oil/brine/rock interactions**

Originally, all reservoir rocks are thought to be water-wet. Sedimentary rocks were formed by deposition in an aqueous environment. Most sandstones are therefore water-wet by nature. But in contact with crude oil, the wettability of the rock surface may be altered towards more oil-wet (Punternvold, 2008). Reservoir wettability is therefore not fixed as often assumed. It is usually reported as a single value reflecting the initial or final wetting condition. Instead, wettability should be considered as a dynamic condition. The wetting condition is dependent on the crude oil/brine/rock system (COBR) (Maas, 2001). The wetting can be altered when the key parameters affecting it are changed, and it can be restored when the same parameters are restored. If these parameters are not restored, a different wetting state will exist at the new equilibrium condition. The increased oil recovery may take place during the transition from one equilibrium/wetting condition to the next. Wetting parameters which are particularly influenced by brine composition and/or ionic strength are expected to change when the pore fluid is significantly altered, as in the case of low saline waterflooding (Skrettingland, 2010).

It is generally accepted that the LowSal effect is due to a wettability modification towards more water-wet conditions, by desorption of oil components from the rock surface in a low saline environment (Austad, 2010a). The variability of the literature results suggests that the LowSal effect depend on complex crude oil/brine/rock interactions (Cissokho, 2009). When the salinity of the injected water is altered, the thermodynamic equilibrium between the COBR-system is changed. Assessing the potential for any particular oil to alter wetting requires consideration of composition of the crude oil, brine and rock.



Important parameters behind the wettability alteration process in reservoir are listed below (Strandnes, 2001):

- Molecules in the crude oil containing polar functional groups (Strandnes, 2001)
- Mineral composition and surface charge of the rock material (Anderson, 1986b; Buckley, 1989).
- Brine salinity and concentration of divalent and other multivalent ions (Buckley, 1996).
- Capillary pressure and thin film forces, disjoining pressure (Hirasaki, 1991).
- Water solubility of polar oil components (Anderson, 1986b).
- The ability for the oil to stabilize heavy components (Al-Maamari, 2000).
- Temperature, pressure and initial water saturation (Al-Maamari, 2000; Jadhunandan, 1995).

#### **2.4.1 Crude oil**

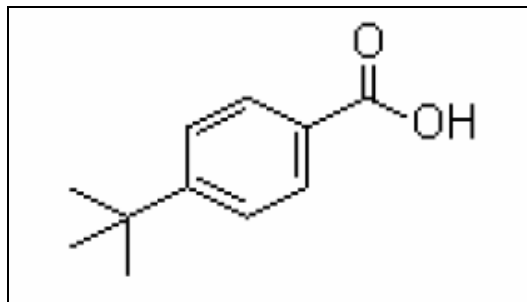
Crude oils are complex mixtures of hydrocarbons and polar organic compounds of nitrogen, sulphur and oxygen (NSO) (Skauge\*\* et al., 1999). Adsorption of these components onto the rock surface may result in a wetting alteration of the COBR system towards less water-wet. Later, in a low salinity process, the oil components may be desorbed from the surface. The NSO- compounds are most common in the heavier fractions of crude oil, such as in the resins and asphaltenes (Anderson, 1986b). Asphaltenes are large complex molecules, somewhat polar, with molecular weights in the range 600-300 000. Resins are smaller molecules, but have in general higher content of the NSO-compounds and are generally more polar than the asphaltenes. In the presence of water, both the solid and the oil interfaces become charged. The polar functional groups belonging to both the mineral and the crude oil phase can behave as acids (giving up a proton and becoming negatively charged) and bases (gaining a proton and thus get a positive charge) (Buckley et al., 1998).

There are different mechanisms by which crude oil components may alter the wetting properties of a rock surface (Buckley et al., 1998; Buckley, 1998):

- Polar interactions that predominate in the absence of a water film between oil and solid.
- Surface precipitation, depending mainly on crude oil solvent properties with respect to asphaltenes.
- Acid/base interactions that control surface charge at oil/water and solid/water interfaces in the presence of water.
- Ion binding or specific interactions between charged sites and higher valency ions.

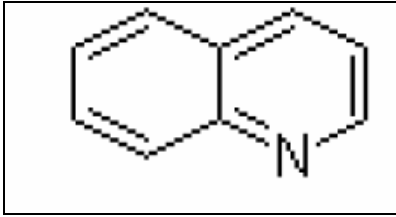
The API gravity, acid number (AN) and base number (BN) (G-AB parameters) of the crude oil can be used to evaluate the potential for a particular crude oil to alter wetting (Buckley et al., 1998). Acid and base numbers have the following definition (Skauge\*\* et al., 1999):

- AN: The amount of base, expressed in mg KOH, necessary for titration of 1 gram sample to a well-defined inflection point. The AN may give an indication of how many carboxylic acids, as shown in figure 2.6, the crude oil contain.



**Figure 2.6:** *The structure of a carboxylic acid.*

- BN: The amount of perchloric acid, expressed in mg KOH, necessary for titration of 1 gram sample to a well-defined inflection point. The BN is a measure of the amount of base in the oil, as the cyclic aromatic nitrogen compounds in figure 2.7.



**Figure 2.7:** *A basic molecule (quinoline) where nitrogen is a part of an aromatic ring structure.*

The adsorption/desorption process of acidic and basic material is mostly depending on the pH, the ion composition of the brine and the type of clay mineral in the sandstone. Both acidic and basic material can adsorb onto clay minerals (Punternold, 2010). The fact that no correlation between the AN and the increase in oil recovery owed to low salinity waterflooding has been observed (Lager A., 2006), may indicate that also basic material also play a role in the process. The adsorption behavior of acidic and basic materials in crude oil appears to have similar properties towards clay minerals regarding variation in pH (Austad, 2010b). Laboratory results from LowSal flooding show similar effects for a crude oil with high AN and low BN, and a crude oil with high BN and low AN. Thus, there appears to be no restrictions to the type of polar components present in the crude oil during low saline flooding, provided that a significant amount is present (Austad, 2010b).

#### **2.4.2 Brine**

Brine chemistry is another important parameter influencing the rock wettability. Initial water saturation is required to see a LowSal effect (Jerauld, 2006). The efficiency is related to this saturation. The presence of divalent cations (ions missing two electrons compared with the neutral atom), as  $Mg^{2+}$  and  $Ca^{2+}$ , and other multivalent cations in the

brine can affect the wettability (Anderson, 1986b) and thereby the LowSal effect. The relative replacing power of cations/positive ions is generally;



Thus, at equal concentrations, calcium will displace sodium more than sodium will displace calcium (IDF, 1982). The proton,  $\text{H}^+$ , has the strongest affinity towards the clay surface. But the concentration of  $\text{H}^+$  is usually much lower than the concentration of cations present in the formation water at typical reservoir conditions with pH values of 4-5. The salinity and pH of the brine strongly affects the surface charge of the rock and fluid interfaces, and thereby the adsorption. Optimal LowSal effects are depending on a balanced initial adsorption of active cations, protons ( $\text{H}^+$ ) and organic material on the clay surface. Thus, for a given crude oil and reservoir rock, both pH and the composition and amount of divalent cations are determined by the properties of the formation water. The initial pH of the formation brine may be between 4-5 due to dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$  (Austad, 2010b).

The term salinity refers to amount and type of salt that makes up the ionic composition of the brine (Tang, 1999). The injected water must have a different composition and a lower salinity than the initial formation water to promote significant desorption of oil from the clay surface. The average salinity of the LowSal fluid is usually in the range of 1000-2000 ppm, but effects have been observed with salinities up to 5000 ppm (Lager A., 2006). It is suggested that the injected brine salinity must be below a salinity concentration threshold to achieve additional recovery by dilute brine displacement (Seccombe, 2008). But recent work indicates that the LowSal effect is not directly linked to the salinity of the LowSal fluid, but rather to the concentration gradient in the most active ions between the initial formation brine and the injected LowSal fluid (Austad, 2010a). In other words it is necessary that the LowSal water has a lower multivalent cation concentration/ionic strength compared to the formation water. The composition of the LowSal fluid therefore appears to be of less importance, as long as the concentration of active ions are low enough to promote a significant desorption from the clay surface.

In recent laboratory tests, it has in fact been observed that tertiary LowSal effects can be obtained without any divalent cations present in the low saline injection fluid (Austad, 2010b).

In general, the LowSal effect may increase as the salinity of the injected water decrease. But a certain salinity is necessary to avoid swelling of clay. And since expanding clays are almost always present in the reservoir, fresh water is not suitable as a LowSal fluid. There is a balance between how low salinity the injected fluid may have and the possibility for decrease in permeability and formation damage.

### **2.4.3 Rock**

The ability of the different polar compounds to alter the rock wettability depends on the mineral composition and surface charge of the rock material. Sandstone which contain active clay minerals is necessary to obtain a low salinity effect (Austad, 2010b). Research has shown that the LowSal effect increases approximately linearly with the clay content of the rock (Lager A., 2007).

#### **2.4.3.1 Sandstone**

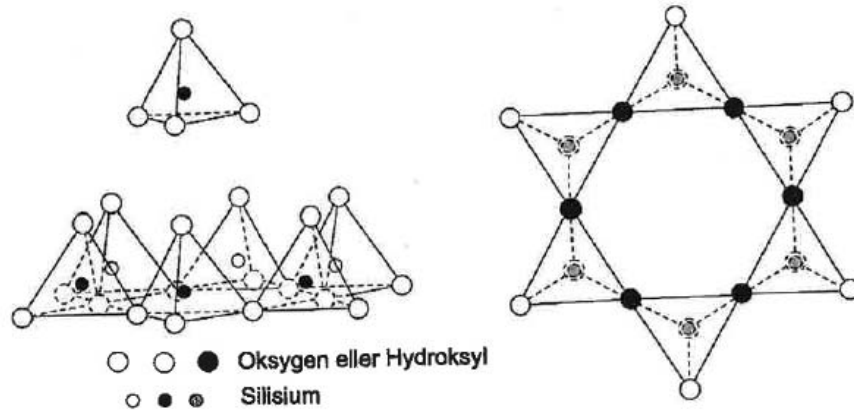
Sandstone is the second most common (siliciclastic) sedimentary rock after shale, constituting about 10-20 % of the sedimentary rocks in the Earth's crust (Britannica, 2010). The rock is economically important as major reservoirs for both petroleum and water, as building materials, as well as valuable sources of metallic ores. Sandstone represents most of the reservoirs in the North Sea. Sedimentary rocks were formed by deposition in an aqueous environment. Most sandstones are therefore water-wet by nature (Punternold, 2008). The chemical composition of sandstone is  $\text{SiO}_2$  and normal density is around  $2.65 \text{ g/cm}^3$  (Ursin, 1997). The principal mineral constituents of sandstone are quartz, feldspar and rock fragments. At the natural pH value of the brine, most of the reservoir minerals (quartz, kaolinite) show a net negative charge (Skjæveland, 1992).

Sandstone consists of a framework composed of sand-sized grains (diameter 0,063-2 mm) and interstitial volume between the grains (pore space/porosity) (Britannica, 2010). This volume may be empty, containing petroleum and/or water or filled with a chemical cement of silica, calcium carbonate, iron-oxide or clay (Ursin, 1997). Sandstone has often high porosity (typically about 7-20%), and may therefore contain large amounts of oil and gas. In general, the porosity is reduced with increasing depth and temperature, due to compaction and cementation. Sandstones are usually non-fractured and have a high permeability. Since sandstone reservoirs are usually unfractured, possible bypassing of oil in the matrix blocks can be avoided. Sandstones are therefore good candidates for waterflooding (Høgenesen, 2005).

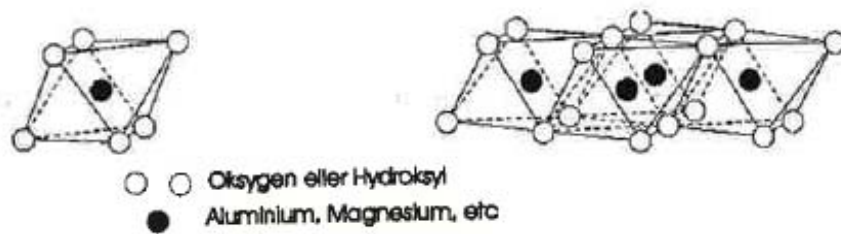
#### **2.4.3.2 Clay**

Most sandstone reservoirs contain some clay minerals in the pore space created by the sand grains. The presence of clay mineral is necessary to obtain LowSal effects. Clay can be described chemically as aluminium silicates. The mineral is composed essentially of silica (Si), alumina (Al) and water. Iron (Fe) and magnesium (Mg) also frequently appears, in addition to smaller quantities of sodium (Na) and potassium (K). Typical properties of clay are fine size, large surface area and chemical reactivity of the surface. (IDF, 1982).

The crystal structure of common sandstone reservoir clays is made up of sheets of tetrahedral silica and octahedral aluminium layers, as illustrated in figure 2.8 and 2.9. Several combinations and chemical modifications of the layers give rise to over 26 different clay minerals with distinct properties (IDF, 1982).



**Figure 2.8:** Structure of a tetrahedral layer (IDF, 1982).



**Figure 2.9:** Structure of an octahedral layer (IDF, 1982).

One of the most important properties of clays is their cation exchange capacity (CEC). Clay minerals are therefore often characterized as cation exchange material. Structural charge imbalance, either in the silica or in the aluminium layer and also at the edge surfaces, cause a *negative* charge on the clay surface (Austad, 2010b).

Because of the small size and ionic character, the clays are extremely reactive to the chemical conditions. Formations with high clay content are often sensitive to water, due to the fact that fresh water increases both the hydration or swelling of clays and the dispersion or deflocculation. Studies have shown that a decrease in the salinity causes a decrease in permeability and formation damage as the clays expand or are mobilized (IDF, 1982). The pH can also affect the expansion of the clays. If the pH value reaches

8.3 or more, the expansion ability to the reactive clays will show a large increase. The adsorption of organic material is also dependent on pH, in addition to the type of clay present (Punternold, 2010). The pH range/windows for optimum adsorption/desorption varies for the different clay types (Austad, 2010b).

Clays usually present in reservoir sandstones are kaolinite, illite/mica, chlorite and smaller contents of montmorillonite. The clays have different properties, as described in table 2.2 and below.

- Kaolinite is known as a non-swelling clay. The charges within the kaolinite structure are well balanced, and the clay has therefore a relative low cation exchange capacity, as shown in table 2.2. The CEC of kaolinite is mainly linked to the edge surface. The clay has a tendency to transform into illite and chlorite at larger depths (Austad, 2010b).
- The difference between illite and mica is only related to the degree of charge imbalance in the silica layers causing a lower negative surface charge on illite compared to mica. The clays may swell in a low saline environment. Both the cation exchange capacity and the surface area are much larger compared to kaolinite.
- Chlorite has a very large surface area, but the cation exchange capacity is in the same range as for illite/mica. Like kaolinite, the edge surfaces will be the active place for cation exchange capacity.
- Montmorillonite has very high cation exchange capacity. But since it is a swelling clay, it is not suitable for LowSal waterflooding.



**Table 2.2:** *Properties of clay minerals (Austad, 2010b).*

Property	Kaolinite	Illite/Mica	Montmorillonite	Chlorite
Layers	1:1	2:1	2:1	2:1:1
Particle size (micron)	5-0.5	large sheets to 0.5	2-0.1	5-0.1
Cation exchange cap. (meq/100g)	3-15	10-40	80-150	10-40
Surface area BET-N <sub>2</sub> (m <sup>2</sup> /g)	15-25	50-110	30-80	140

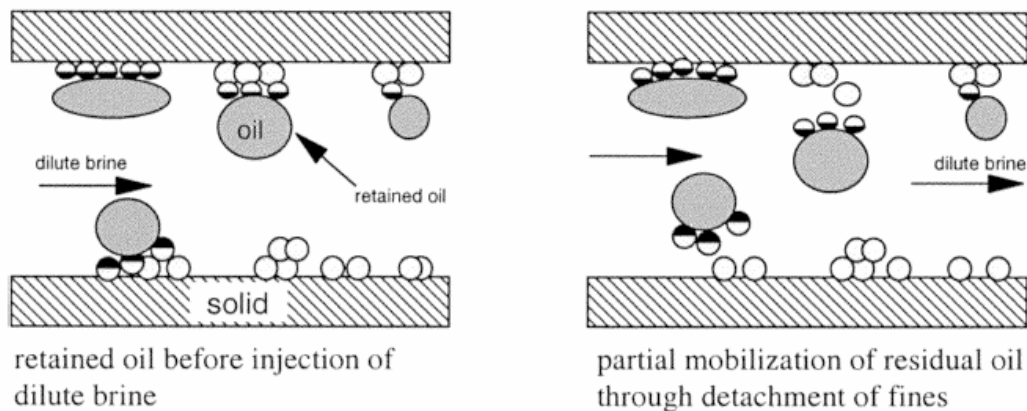
The issue of exactly which type and amount of clay that is necessary to see a low salinity effect is not yet settled. The presence of clays or potentially mobile fines, as one of the proposed mechanisms for low salinity effect, was first suggested by Tang and Morrow in 1999 (a more detailed description of the mechanism is given in chapter 2.5.1). However, they did not specify whether certain clays play a more important role than others (Skrettingland, 2010). Later, Jerauld and Secombe put forward a relationship suggesting that additional oil recovery was directly proportional to the kaolinite content in the rock (Jerauld, 2006; Secombe, 2008). The work done by Pu et al. indicates a positive response for LowSal injection into dolomite samples with very low or no clay content (Pu et al., 2008). Recent work done by Bousseour et al. showed positive results in kaolinite-free sandstone samples after LowSal injection (Bousseour, 2009). Austad et al. have also proposed that kaolinite would be the least favorable clay for LowSal flooding due to its low cation exchange capacity (Austad, 2010b).

## 2.5 Different proposed low salinity mechanisms

Several different hypotheses have been proposed as the mechanism or contribution to the LowSal effect. “Migration of fines” by Tang and Morrow, “pH increase” by McGuire et al., “Multicomponent Ionic Exchange” (MIE) by Lager et al. and “Double layer effects” by Ligthelm et al. are among the best known proposed LowSal mechanisms. None of these mechanisms have so far been generally accepted as the main contributor to the observed LowSal effect. Austad et al. have suggested a new hypothesis; desorption by pH increase. A brief summary of the main history of low salinity is found in appendices A.2.

### 2.5.1 Migration of fines

An attempt to explain the LowSal mechanism was put forward by Tang and Morrow in 1999. In the presence of high salinity brine, clays are undisturbed and retain their oil-wet nature leading to poorer displacement efficiency. But during low salinity water flooding, Tang and Morrow observed that fines (mainly kaolinite clay fragments), were released from the rock (sandstone/clay) surface (Lager A., 2006). They suggested that the mobilization of the fines resulted in exposure of underlying surfaces, which increased the water wetness of the system. In addition, the released clay particles could block pore throats and divert the flow of water into non-swept pores to improve the microscopic sweep efficiency (RezaeiDoust, 2009b). The mobilization of fines with flowing fluid are also associated with a permeability reduction and formation damage resulting from plugging of pores. The migration of fines is illustrated in figure 2.10.



**Figure 2.10:** Detachment of clay particles and mobilization of oil (Tang, 1998).

Although Tang and Morrow have shown that it is possible to have migration of fines during low salinity waterflooding, BP has done numerous LowSal floods showing increase in oil recovery, without any observations of fines migration or significantly permeability reduction (Lager A., 2006). These results question the link between fines migration and oil recovery. The migration of fines may just be an effect of LowSal waterflooding, and not the direct cause of the additional oil recovery observed by LowSal flooding. But migration of fines might still play a positive role in the increased oil recovery process.

### 2.5.2 pH increase

Based on the fact that pH usually increases during low salinity waterflooding, McGuire et al. suggested the LowSal effect could be related to a type of alkaline waterflooding (McGuire, 2005). If the pH level increases to above 9 inside a petroleum reservoir, the flooding process would be equivalent to an alkaline flood. High pH values also enable a reaction of crude oil acid compounds which results in in-situ generation of surfactants (Boussour, 2009). McGuire et al. suggested that a higher pH can increase the oil recovery by generation of surfactants and reduction in interfacial tension. The rise in pH is due to the following chemical reactions (Lager A., 2006):

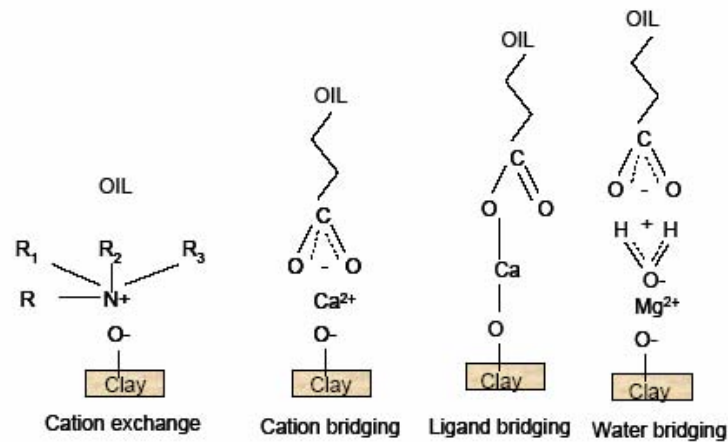
- Cation exchange between clay minerals and invading water. This reaction is relatively fast. The mineral surface will exchange  $H^+$  present in the liquid phase with cations previously adsorbed. Thereby an increase in pH.
- Dissolution of carbonate (calcite and/or dolomite), which results in an excess of  $OH^-$  and increase in pH. The dissolution reaction is slower and dependent on the amount of carbonate material present in the rock;



To generate in-situ surfactants from carboxylic acids, the acid number of the crude oil should be larger than 0.2 mg KOH/g. But low salinity effects have been observed for crude oils with AN less than 0.05 mg KOH/g. Furthermore, the increase in pH of produced water/effluent is in many cases not more than 1 pH unit, which causes the water to become only slightly basic. It is doubtful that the small increase in pH can decrease the IFT enough to promote LowSal effects (RezaeiDoust, 2009b). Equivalent experiments have also shown a reduction in pH during LowSal flooding. High pH is more likely not responsible for the increase in oil recovery by injection of LowSal water, but rather an effect. But as migration of fines, a pH increase might play a positive role when it occurs.

### **2.5.3 MIE**

Lager et al. describe multicomponent ionic exchange as the basis for geochromatography. MIE involves the competition of all the ions in pore fluid for the mineral matrix exchange sites. Natural exchangers, like clay and carbonate minerals, show different selectivity for different cations or anions (Lager A., 2007). Important documentation of the MIE mechanism came from effluent analysis of a low salinity waterflood of cores from a reservoir in Alaska (North Slope). The injected brine and the connate water had similar  $Mg^{2+}$  concentrations (88 ppm). However, the effluent analysis showed a sharp decrease in  $Mg^{2+}$  concentration. This indicates that  $Mg^{2+}$  was strongly adsorbed by the rock matrix. Lager et al. claim that four mechanisms, out of eight proposed mechanisms of organic matter adsorption onto clay mineral given in table 2.3, will be strongly affected by cation exchange occurring during a low salinity brine injection. These mechanisms are cation exchange, ligand bonding, cation bridging and water bridging. Figure 2.11 illustrates these mechanisms.



**Figure 2.11:** Attraction between clay surface and crude oil by divalent cations (Lager A., 2008).

**Table 2.3:** Mechanisms of organic matter adsorption onto clay mineral.

Mechanism:	Organic functional group involved:
Cation exchange	Amino, ring NH, heterocyclic N (aromatic ring)
Protonation	Amino, heterocyclic N, carbonyl, carboxylate
Anion exchange	Carboxylate
Water bridging	Amino, carboxylate, carbonyl, alcoholic OH
Cation bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange	Carboxylate
Hydrogen bonding	Amino, carbonyl, carboxyl, phenolic OH
Van der Waals interaction	Uncharged organic units

Lager et al. assume that the low salinity effect was related to increased water wetness of the clay minerals present in sandstone (RezaeiDoust, 2009b). It was suggested that the  $Mg^{2+}$  and  $Ca^{2+}$  play an important role in the interaction between the clay minerals and surface active components in the crude oil.  $Ca^{2+}$  and  $Mg^{2+}$  may act like a bridge between the negatively charged clay surface and the carboxylic material. The organic material was supposed to be removed by cation exchange between the mineral surface and the invading low salinity brine. Expansion of the electrical double layer due to low salinity flooding enables desorption of polar compounds from the surface (Lager A., 2007).

Computer simulations and laboratory tests performed by Tor Austad et al. have shown that a change in the effluent  $\text{Ca}^{2+}$  concentration is not necessarily caused by a MIE process. It can also be explained by precipitation of  $\text{Mg}(\text{OH})_2$  as a result of a local increase in pH in the injected low saline water. In addition, there are no chemical reasons why the strongly hydrated  $\text{Mg}^{2+}$  ion should have a superior reactivity toward the active sites on the clay surface compared to  $\text{Ca}^{2+}$ . In recent laboratory tests it has also been observed that LowSal effects can be obtained without any divalent cations present in the LowSal fluid (Austad, 2010b).

#### **2.5.4 Double layer effects**

Ligthelm et al. (2009) proposed that the LowSal effect was due to double layer effects. They suggested that a decrease in salinity results in an expansion of the ionic electrical double layer between the clay and the oil interfaces (Ligthelm et al., 2009). Thus, oil is desorbed from the surface and the water wetness increase. This is a pure physical explanation. It was illustrated by supposing a  $\text{Ca}^{2+}$  bridge between the negatively charged clay and oil, similar to the illustrations put forward by Lager et al. in figure 2.11. But, polar oil components may adsorb onto clay minerals without a bridge of divalent cations (Austad, 2010b).

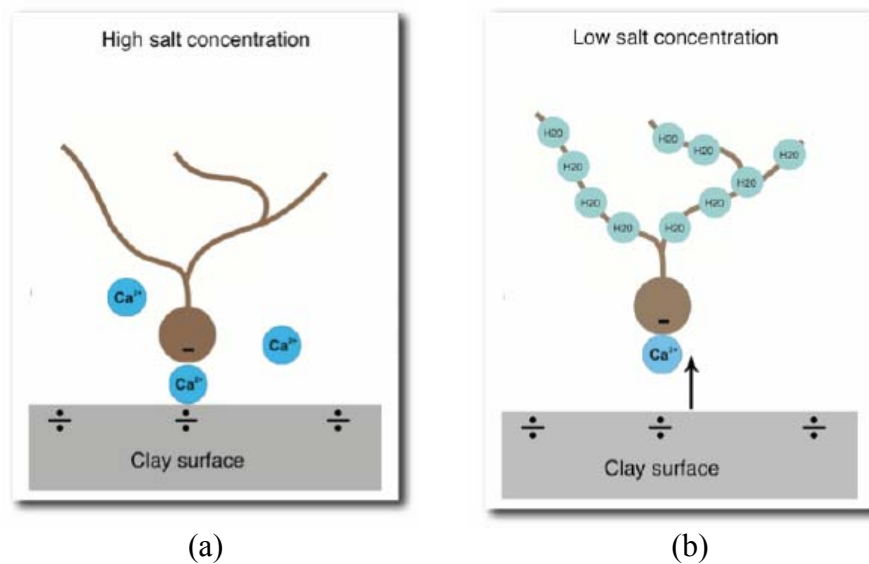
#### **2.5.5 Salting-in effect**

Salting-in effect was the first LowSal working proposal by Austad et al. (2008). The proposal is related to changes in the solubility of polar organic components in the aqueous phase, described as salting in and out effects. In water, the organic material is solvated by the formation of a structure created by hydrogen bonds around the nonpolar part of the organic compounds. The organic components are in that way structure makers. Inorganic ions, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , break up the water structure around the organic molecules and decrease the solubility, and are thereby called structure breakers (RezaeiDoust, 2009b).

**Salting-out effect:** Decrease in the solubility of organic material in water by adding salt to the solution.

**Salting-in effect:** Increase in the solubility of organic material in water by removing salt from the water.

The thermodynamic equilibrium between the crude oil, brine and rock, which has been established during geological time, is disturbed when injecting water with a different salinity than the initial formation water. The solubility of polar organic components in water is affected by ionic composition and salinity, as illustrated in figure 2.12. The terms salting-out and salting-in effects have been used in the chemical literature, and there is a large number of examples where these effects have been observed (Li, 1997; RezaeiDoust, 2009b).



**Figure 2.12:** System containing crude oil components,  $Ca^{2+}$ -iones in the water and clay.  
a) Salting-out effect, b) Salting-in effect.

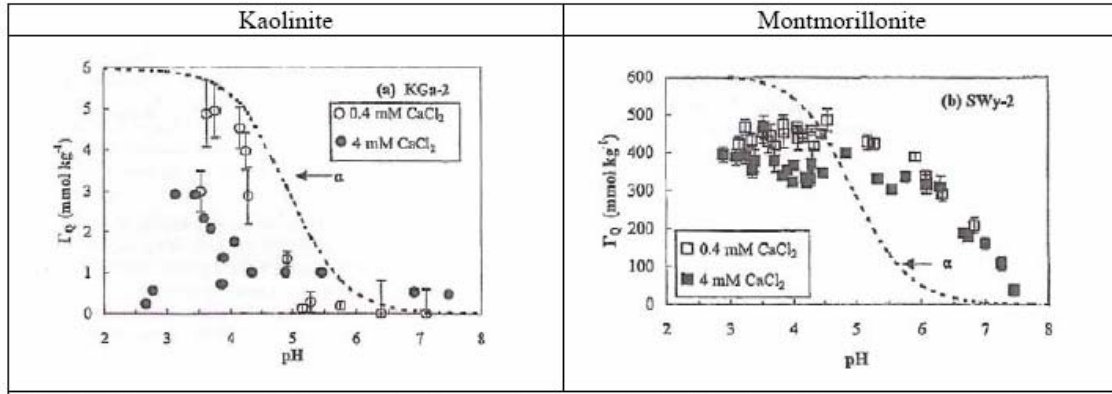
Recent studies indicate that adsorption of the base quinoline onto kaolinite clay in the presence of brine seem to increase with a decrease in salinity (Punternold, 2010). These observations are in direct contradiction to the salting-in mechanism and to the fact that oil components are released in a low salinity waterflood.

### **2.5.6 Desorption by pH increase**

Desorption of acids and bases by pH increase is the latest proposed LowSal mechanism by Austad et al. Desorption of initially adsorbed cations onto the clay is the key process in increasing the pH of the water at the clay surface. This pH increase cause desorption of organic material from the surface by an acid-base interaction. In order to observe tertiary LowSal effects in sandstone, there must be an initial balanced adsorption of organic material and active cations onto the negatively charged clays present in sandstone. In other words, enough organic material must be present to make the clay oil-wet, and enough cations must be present to create an increase in the pH at the water-clay interface when cations are desorbed from the clay surface. The adsorption process is completely reversible by pH adjustment and the reactions are very fast because of rapid acid/base reactions. The strong dependence of pH regarding adsorption/desorption was confirmed by static adsorption studies of a model base onto kaolinite (Punternold, 2010).

One of the main statements in this new hypothesis is that a *local increase in pH* at the clay surface, promoted by desorption of cations, is necessary to release oil components from the rock and thus see LowSal effect. The adsorption of the organic material onto the clay surface is very sensitive to changes in pH. Both acidic and basic crude oil material are released from the surface as the pH is increased from 5-6 to about 8-9 (Austad, 2010b). Adsorption of the base quinoline onto kaolinite and montmorillonite versus different pH values is shown in figure 2.13. The adsorption decreases as the pH increases. In lab experiments, increase in pH is usually verified, but due to buffering effects in field situations (due to CO<sub>2</sub> and H<sub>2</sub>S), an increase in pH is seldom observed (Punternold, 2010).



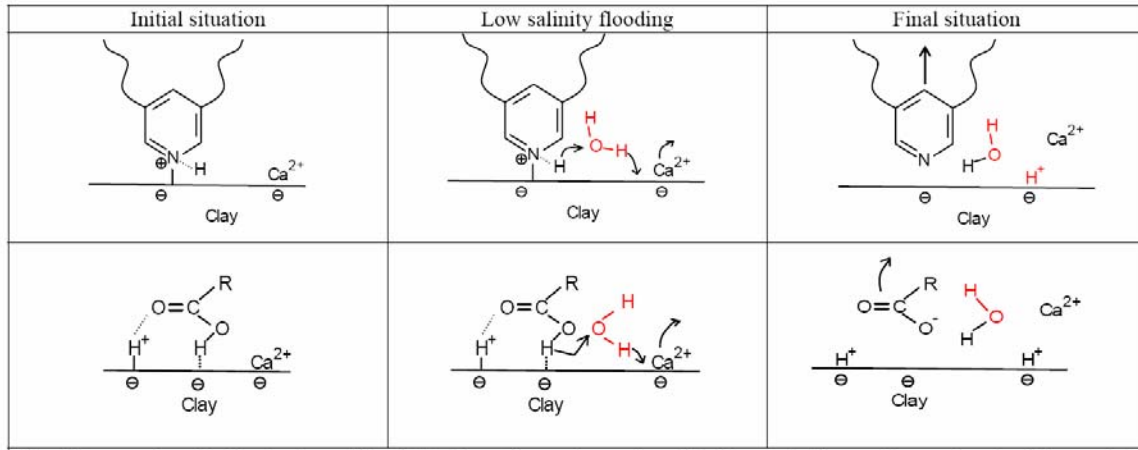
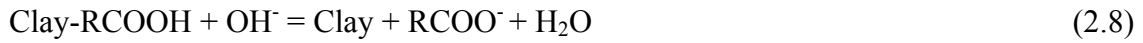


**Figure 2.13:** Adsorption of quinoline onto kaolinite and montmorillonite (Burgos, 2002).

The suggested mechanism is schematically illustrated in figure 2.14 for adsorbed basic and acidic material. The clay acts as a cation exchanger with relatively large surface area. Initially, both acidic and basic organic materials are adsorbed onto the negatively charged clay surface together with inorganic cations, especially  $\text{Ca}^{2+}$ , from the formation water. A chemical equilibrium is then established at actual reservoir conditions regarding pH, temperature, pressure etc. It is important to remember that the initial pH of the formation water may be even below 5 due to dissolved  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The crude oil should therefore be saturated with  $\text{CO}_2$  at lab. When the low saline water is injected into the reservoir with an ion concentration much lower than the initial formation brine, the equilibrium associated with the brine-rock interaction is disturbed, and a net desorption of cations, especially of  $\text{Ca}^{2+}$ , occurs. To compensate for the loss of cations, protons ( $\text{H}^+$ ) from the water close to the clay surface, adsorb onto the clay. Substitution of  $\text{Ca}^{2+}$  by  $\text{H}^+$  is taking place. This creates a local increase in pH close to the clay surface as illustrated by the following equation, using  $\text{Ca}^{2+}$  as an example:



A fast reaction between  $\text{OH}^-$  and the adsorbed acidic and basic material will cause desorption of organic material from the clay surface. Thus, the water wetness of the rock is improved. The reactions can be described by ordinary acid-base proton transfer reactions, as shown by the following equations:



**Figure 2.14:** Proposed mechanism for LowSal EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5 (Austad, 2010b).

### 3. Experimental work

#### 3.1 Experimental materials

##### 3.1.1 Oil

Reservoir crude oil from the Varg field was used in the experiments. The oil was centrifuged for one hour and filtered through a 5.0  $\mu\text{m}$  filter paper (with a vacuum pump) to remove any possible particles and water. Table 3.1 includes some of the properties of the Varg oil at room temperature (20°C). The viscosity measurements of the oil were conducted at 30 °C to reduce problems with asphaltenes. The centrifuge and filtration process are shown in appendices A.5.1 and A.5.2.

**Table 3.1:** *Properties of Varg oil.*

AN (20°C) [mg KOH/g]	BN (20°C) [mg KOH/g]	Density (20°C) [g/cm <sup>3</sup> ]	Viscosity (30°C) [cp]
0.11	0.82	0.835	6.3

The Varg oil was saturated with carbon dioxide (CO<sub>2</sub>) at 6 bars in a recombination cell. The accumulated CO<sub>2</sub> in the top of the recombination cell was bled off before the cell was connected to the flooding setup. In laboratory core floods, the pH of the initial formation water seems to have influence on the obtainable initial wetting condition of the core. CO<sub>2</sub> is an acidic gas, and was added to the crude oil to lower the pH of the formation water during ageing. In reservoirs, the pH of formation water is low due to dissolved acidic gases like CO<sub>2</sub> and H<sub>2</sub>S. A low initial pH increases the adsorption of organic material onto the clay and creates a less water-wet condition inside the core.

### 3.1.2 Brines

The brines used in the flooding experiments were synthetic Varg formation water (Varg FW), synthetic sea water (SW) and a 500 ppm sodium chloride (NaCl) solution as LowSal water. The brines were prepared by dissolving reagent grade salts in distilled water to the compositions given in table 3.3. All the salts is produced by "Merck". The solutions were stirred with a magnetic bar, as shown in figure A.5 All brines were filtrated through a 0.22  $\mu\text{m}$  filter paper to remove possible particles, and vacuumed to remove dissolved gas prior to each test. Table 3.2 includes some of the properties of the brines at 20°C. The density and viscosity of diluted Varg FW (five times) were used in the calculations of pore volume, porosity and permeability.

**Table 3.2:** *Brine properties*

Brine	Density [g/cm <sup>3</sup> ]	Salinity [ppm]	Viscosity [cp]
Varg FW	1.1406	201 560	-
Diluted Varg FW (5 times)	1.0283	40312	1.3
SW	1.0230	33 390	-
NaCl-solution	0.9984	500	-
Distilled water	0.9982	0	-

**Table 3.3:** *Molar (mol/l) compositions of brines.*

Iones	Varg FW	SW	NaCl-Solution
Cl <sup>-</sup>	3.526	0.525	0.00856
Mg <sup>2+</sup>	0.144	0.045	-
Ca <sup>2+</sup>	0.536	0.013	-
Na <sup>+</sup>	2.086	0.450	0.00856
K <sup>+</sup>	0.051	0.010	-
Ba <sup>2+</sup>	0.007	-	-
Si <sup>2+</sup>	0.008	-	-
HCO <sub>3</sub> <sup>-</sup>	-	0.002	-
SO <sub>4</sub> <sup>2-</sup>	-	0.024	-
TDS [g/l]	201.56	33.39	0.5

The complete table is found in appendices A.4.

### 3.1.3 Cores

Two preserved sandstone reservoir cores from the Varg field, Varg#5 and Varg#6, were selected for the experiments. Varg is a sandstone oil reservoir located in the southern part of the Norwegian North Sea, with Talisman Energy Norge AS as operator. Sea water is already injected into the reservoir. More details about Varg are found in appendices A.3. The cores were taken from well 15/12-A-5-T2 at a depth of 3506.83 m for Varg#5 and 3506.87 m for Varg#6. This was a low permeable part of the reservoir, which had not been flooded before. The cores were selected based on the clay content, listed in table 3.4. The content of clays was measured with X-ray diffraction analysis (XRD) and provided by Talisman Energy. It is assumed that the clay content for the cores is in the area between the given depths. The cores contain most illite/mica, some kaolinite and a smaller content of chlorite. The complete XRD-analysis is found in appendices A.4. The cores had a smooth surface and the edges were cut until the cores got a cylindrical shape, as shown in figure 3.1. The dimensions and other core properties are given in table 3.5.



**Figure 3.1:** Varg core.

**Table 3.4:** Clay content of Varg cores.

Depth [m]	Illite/mica [%]	Kaolinite [%]	Chlorite [%]
3506.50	11.5	4.1	2.5
3506.90	9.1	2.7	2.1

**Table 3.5: Core properties.**

Core	L [cm]	D [cm]	V <sub>b</sub> [cm <sup>3</sup> ]	W <sub>s</sub> [g]	W <sub>d</sub> [g]	W <sub>f</sub> [g]	PV [cm <sup>3</sup> ]	Φ [%]	k [mD]	Sw <sub>i</sub> [%]
Varg#5	5.18	3.79	58.44	127.66	111.39	115	15.82	0.27	14.33	20
Varg#6	4.92	3.78	55.21	121.19	105.78	109.2	14.990	0.27	20.91	20

Where:

L = Length of core

D = Diameter of core

V<sub>b</sub> = Bulk volume of core

W<sub>s</sub> = Weight of core 100 % saturated with diluted Varg FW

W<sub>d</sub> = Weight of dry core

W<sub>f</sub> = Final weight of core after desiccator

PV = Pore volume of core

Φ = Porosity of core

k = Permeability

Sw<sub>i</sub> = Initial water saturation

## **3.2 Experimental procedures**

### **3.2.1 Core cleaning**

The purpose of the cleaning process is to achieve a state as close as possible to water-wet. The core was mounted in a Hassler core holder, which was a part of the cleaning setup. Nitrogen (N<sub>2</sub>) was used as confining/overburden pressure. The system was degassed and checked for leakages. Series of approximately 3 PV of water saturated toluene and methanol were injected in both directions at ambient temperature. The injection rate was 0.2 ml/min. The purpose of injecting toluene was to displace oil and organic material

inside the core, while methanol removes brine (water and salt) from the core. Toluene is blank and the core is therefore regarded cleaned when there is no oil in the effluent toluene. When the effluent toluene was clear, methanol was injected to displace all the toxic toluene after the core was put in a heating chamber for drying. Finally, a 10 000 ppm NaCl-solution was injected to remove the rest of the salt inside the core (and formation water to prevent swelling of clays). The core was put inside a heating chamber at 90 °C for at least 24 hours. The weight of the core was measured at different times to check when it was dry. The dry weight was used to calculate the pore volume and porosity of the core.

### **3.2.2 Measurement of acid and base numbers**

The acid and base numbers of the Varg crude oil were measured using the automatic titrator Mettler Toledo DL55, shown in figure A.7. The method were an improved procedure developed by Fan and Buckley (Fan, 2007). A detailed description of the procedure is found in appendices A.5.3.

### **3.2.3 Measurement of viscosity**

Viscosity measurements of the oil and brine were performed using the universal dynamic spectrometer, Physica UDS 200 from Paar Physica, shown in figure 3.2. The instrument accuracy was tested with dionised water. 2.2 ml fluid was placed on the metal plate. The apparatus was set in measuring position, with the plates close to each other. More liquid was filled around the plates if not filled completely. The shear rates were set between 100-600 1/s. At each shear rate value, shear stress was measured. Then a curve of shear stress versus shear rate was made. The slope of the area which shear rate and shear stress had a linear correlation, the viscosity was found. The viscosity measurements of the diluted FW were conducted at 20 °C and 30 °C for the Varg oil to avoid problems with asphaltenes. The measurements were repeated to obtain necessary accuracy. The viscosity of diluted Varg FW (five times) was used to calculate the permeability.



**Figure 3.2:** *Measurement of viscosity by a spectrometer.*

### **3.2.4 Measurement of density**

Density measurements of the oil and brine were performed using a densitometer, DMA 4500 from Anton Paar, shown in figure 3.3. The measurements were performed at 20 °C. Before the oil and brine samples were injected, the tube was cleaned with white spirit and acetone. White spirit removes oil, while acetone adsorbs water and dissolves white spirit. It was important that no gas bubbles entered the first tube during the injection of fluid. The measurements were repeated to ensure accuracy. The density of diluted Varg FW (five times) was used to calculate the pore volume and porosity. The salinity of the effluent brine during waterflooding was found from the density of the brine.



**Figure 3.3:** *Measurement of density by a densitometer.*



### 3.2.5 Calculation of effluent salinity

To be able to determine the salinity of the effluent brine, known densities of Varg FW and distilled water were used. By using a linear fit, the salinity of any mixture between these two brines could be determined from the following equation:

$$TDS_e = TDS_{FW} - \frac{(\rho_{FW} - \rho_e)}{(\rho_{FW} - \rho_{DW})} \cdot TDS_{FW} \quad (3.1)$$

Where:

$TDS_e$  = Total dissolved solid of effluent brine [ppm]

$TDS_{FW}$  = Total dissolved solid of formation water [ppm]

$\rho_{FW}$  = Density of Varg FW [ $g/cm^3$ ]

$\rho_e$  = Density of effluent brine [ $g/cm^3$ ]

$\rho_{DW}$  = Density of distilled water [ $g/cm^3$ ]

### 3.2.6 Water saturation

The clean and dry core was put into a bottle connected to the setup shown in figure 3.4. When vacuum was achieved, the core was saturated with diluted (five times) and degassed Varg FW. The saturated weight was used to calculate the pore volume and porosity of the core. It was assumed that the core was 100% saturated with the diluted Varg FW.



**Figure 3.4:** *Saturation of core under vacuum.*

### **3.2.7 Determination of pore volume and porosity**

The pore volume of the core was calculated from equation 3.2. The calculation is based upon the weight difference between dry and wet core 100% saturated with diluted Varg FW (five times) with known density. The porosity was then determined from equation 3.3.

$$PV = \frac{W_s - W_d}{\rho_{DFW}} \quad (3.2)$$

Where:

PV = Pore volume core [cm<sup>3</sup>]

W<sub>s</sub> = Weight of core 100 % saturated with diluted Varg FW [g]

W<sub>d</sub> = Weight of dry core [g]

ρ<sub>DFW</sub> = Density of diluted Varg FW [g/cm<sup>3</sup>]

$$\phi = \frac{PV}{V_b} \cdot 100 \quad (3.3)$$

Where:

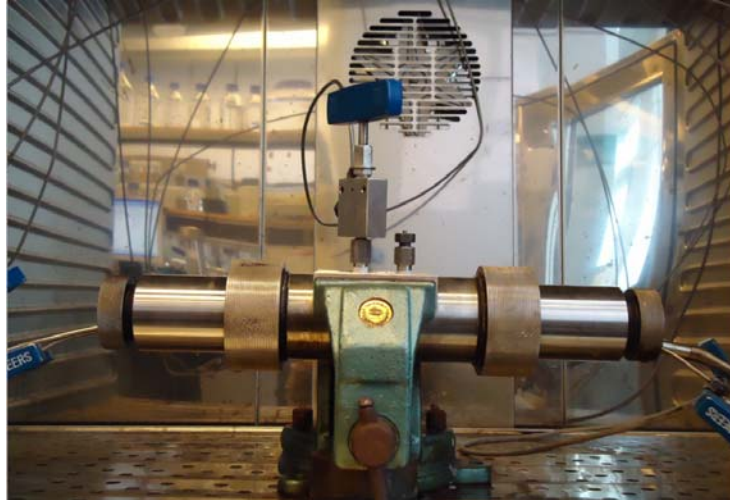
$\Phi$  = Porosity of core [%]

PV = Pore volume of core [cm<sup>3</sup>]

V<sub>b</sub> = Bulk volume of core [cm<sup>3</sup>]

### 3.2.8 Brine permeability measurements

The core was mounted in a rubber sleeve inside a Hassler core holder, shown in figure 3.5, and flooded with degassed and diluted Varg FW in one direction. The flooding rate was 0.2 ml/min. A confining/overburden pressure (water and N<sub>2</sub>) of 20 bars and a back pressure/working pressure (N<sub>2</sub>) of 10 bars were used in the setup. The confining pressure must be higher than the back pressure to ensure good sealing between the core and the rubber sleeve inside the core holder. The flooding was conducted at room temperature until establishment of a stabilized density at the outlet and also a constant pressure drop across the core (steady state conditions). In a given time interval, the weight of the effluent water was measured and the rate was determined/controlled. The permeability of the core to brine was then calculated from Darcy's law (equation 3.4). Since the experiments only involve single phase, the brine permeability is equal to the absolute permeability.



**Figure 3.5:** Hassler core holder.

Darcy's law is given by the following equation:

$$Q = \frac{-kA\Delta P}{\mu_{DFW}L} \quad (3.4)$$

Where:

Q = Volumetric flow rate

k = Permeability

A = Cross section area of core

$\Delta P$  = Pressure difference across the core

$\mu_{DFW}$  = Viscosity of diluted Varg FW

L = Length of core

### **3.2.9 Establishment of initial water saturation**

It was decided to lower the initial water saturation of the core to 20 % (assuming this value is below the irreducible water saturation such that water will not move during flooding). The core was therefore saturated with five times diluted Varg FW to get the same salinity as the original formation water when put into desiccator, shown in figure

3.6. Silica gel was put into the desiccator to adsorb water from the core (only distilled water evaporates in the desiccator, because the salt stays behind in the core). The weight of the core was taken at different times to find out when the final weight was reached. The core was left inside the desiccator for approximately three days. After the core had reached the desired final weight, it was kept in an enclosed container for at least three days to obtain a uniform water saturation distribution throughout the core. The final weight of the core, corresponding to an initial water saturation of 20%, was calculated by the formula:

$$W_f = W_d + (0.20 \cdot PV \cdot \rho_{FW}) \quad (3.5)$$

Where:

$W_f$  = Final weight of core after desiccator [g]

$W_d$  = Weight of dry core [g]

$PV$  = Pore volume of the core [ $\text{cm}^3$ ]

$\rho_{FW}$  = Density of Varg FW [ $\text{g}/\text{cm}^3$ ]



**Figure 3.6:** Lowering of initial water saturation by a desiccator.

### **3.2.10 Oil saturation**

A dummy core was mounted in a rubber sleeve inside the Hassler core holder, shown in figure 3.5, which already was put into a heating chamber. The system was pressurized to ensure no pressure drop during the main waterflooding tests. Then the Varg core was mounted in the core holder. The temperature of the oven was set to 50 °C for Varg#5 and for Varg#6 it was set to 130 °C, equal to the Varg reservoir temperature. The system was vacuumed for 10 minutes and the tubes were filled with oil. Both cores were saturated and flooded with 2 PV of crude oil (containing CO<sub>2</sub>) in each direction at a rate of 0.1 ml/min. The back pressure was 10 bars (high enough to prevent boiling of the fluid at elevated temperature and larger than 6 bar saturation pressure to avoid release of CO<sub>2</sub> from oil).

### **3.2.11 Ageing of core**

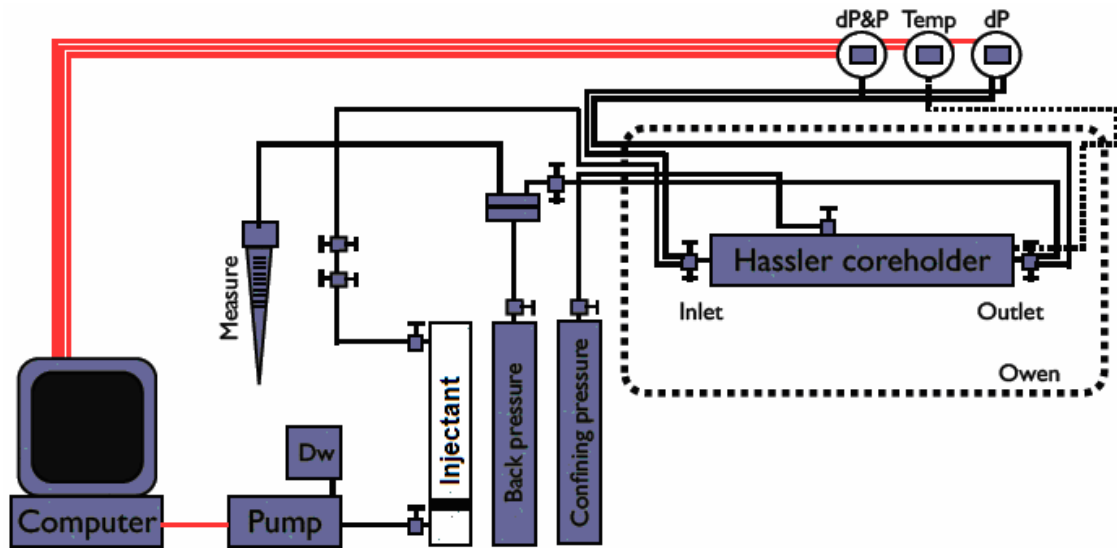
The core was aged in Varg crude oil inside the Hassler core holder in the heating chamber for 14 days. The ageing temperature was equal to the Varg reservoir temperature, 130 °C, and the back pressure was 10 bars. The idea is that the wettability of the core is changed to less water-wet conditions during ageing in crude oil. In other words, the oil components could be adsorbed onto the clay/sandstone surface. Thus, during water injection, it may be possible to see a wettability alteration towards a more water-wet surface.

### **3.2.12 Waterflooding – main test**

The waterflooding represents the main test in the experimental work. Each core was flooded first with Varg formation water in a secondary stage. When the oil production reached the plateau (salinity approximately constant), the core was flooded with sea water in a tertiary stage. Finally a 500 ppm NaCl-solution was injected as LowSal fluid. The flooding rate was 2 PV per day and the displacement temperature was equal to the Varg reservoir temperature, 130 °C. The back pressure was 10 bars and the confining

pressure was 20 bars. The oil production was recorded as well as the pH and density (salinity) of the effluent brine. The main test data are found in appendices A.6.

The flooding setup, shown in figure 3.7, consists of a Gilson 307 pump, an oven, a Hassler core holder, piston cells, a measuring burette and a computer. The pump is connected to a computer program (Lab view) which determines the injection rate, minimum back pressure and maximum injection pressure. The program logs inlet pressure, pressure drop across the core and temperature.



**Figure 3.7:** Apparatus for waterflooding test. The injectant cylinder contains first oil saturated with CO<sub>2</sub>, then FW, SW and LowSal water.

Results are presented as plots of oil recovery versus injected pore volumes of brine. The recovery factor was calculated from the following equation:

$$R = \frac{V_{prod}}{OOIP} \cdot 100 \quad (3.6)$$

Where:

R = Oil recovery factor [%]

V<sub>prod</sub> = Volume of oil produced [ml]

OOIP = Original oil in place [ml]

## 4. Results

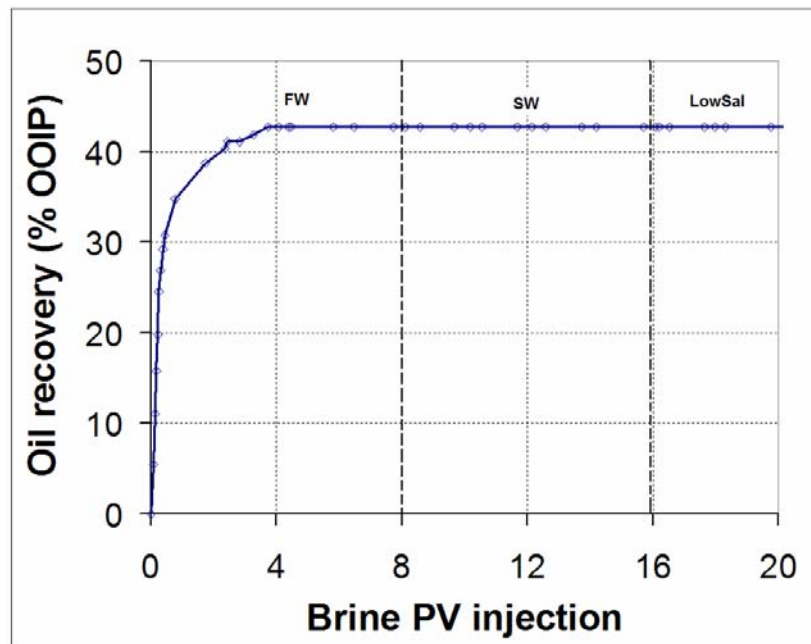
### 4.1 Results from Varg core #5

#### 4.1.1 Oil recovery

The test conditions for Varg#5 is given in table 4.1. Varg#5 was flooded with formation brine, sea water and 500 ppm NaCl-solution. Figure 4.1 shows the oil recovery versus PV of brine injected. There was a piston like displacement of oil until 25% recovery. Then both oil and water were produced. After injection of 4 PV formation brine, the oil recovery reached the plateau at 43% of OOIP. The injection of sea water and NaCl-solution did not give any LowSal effect. The data corresponding to figure 4.1 is found in appendices A.6.1.

**Table 4.1:** Test conditions for Varg core #5.

Core	Sw <sub>i</sub>	T <sub>ageing</sub> [°C]	T <sub>flooding</sub> [°C]	Test sequence
Varg#5	20	130	130	FW-SW-LowSal



**Figure 4.1:** Oil recovery vs. PV brine injected.



### 4.1.2 Salinity and pH

Figure 4.2 illustrates the salinity and pH of the effluent brine versus number of PV brine injected into Varg core #5. The salinity decreases corresponding to the type of brine injected. A small increase in pH, about 1 pH unit, was observed when switching from formation brine to the sea water. The same increase was also seen when replacing sea water with the NaCl-solution. The data corresponding to figure 4.2 is found in appendices A.6.1.

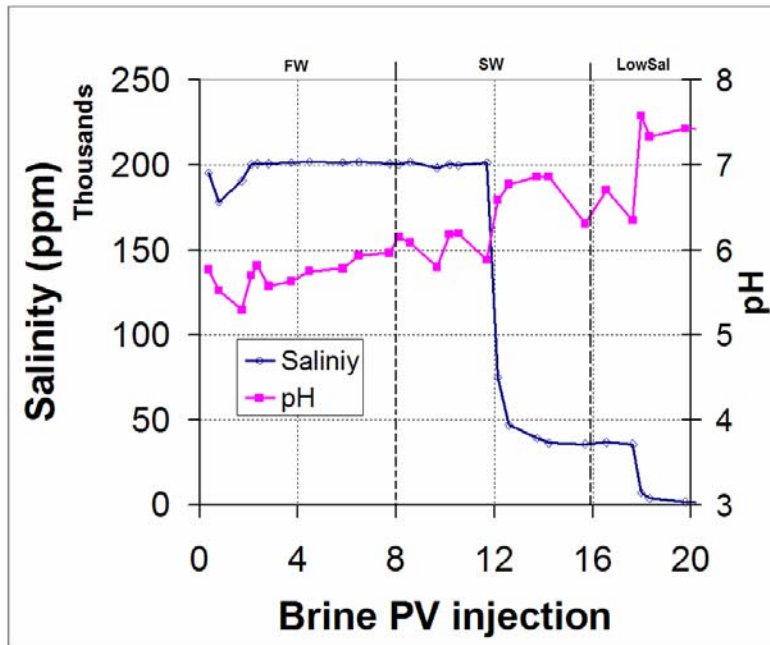
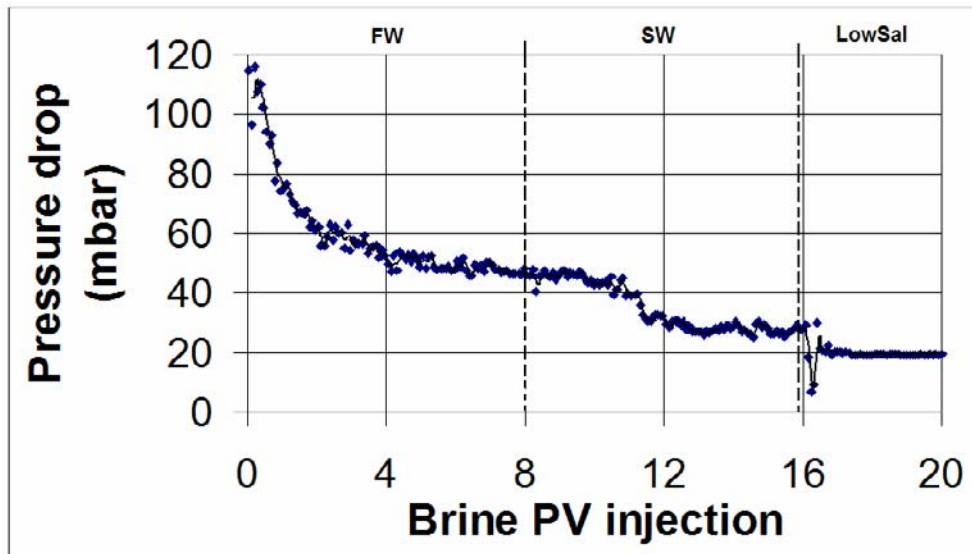


Figure 4.2: Salinity and pH vs. PV brine injected.

### 4.1.3 Pressure data

Figure 4.3 shows the pressure drop across Varg core #5 versus PV of brine injected. The curve shows a normal decrease in pressure drop during production, i.e. the pressure drop decrease as the water saturation increase. No rapid changes or fluctuations in pressure drop were observed.



**Figure 4.3:** *Pressure drop across Varg core #5 vs. PV brine injected.*

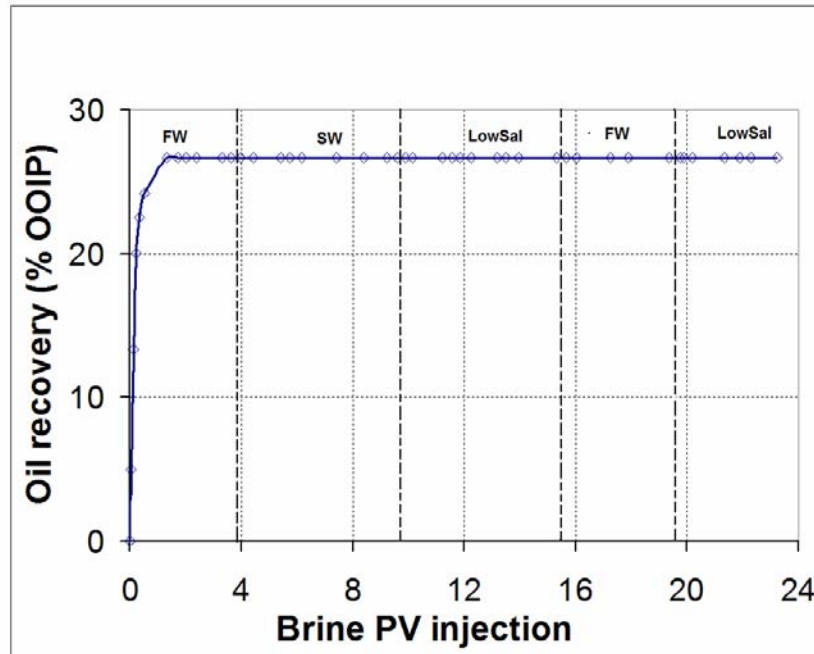
## 4.2 Results from Varg core #6

### 4.2.1 Oil recovery

The test conditions for Varg#6 is given in table 4.2. The displacement was piston like until 20% oil recovery, as seen from figure 4.4. When 1.3 PV formation brine was injected, the oil recovery reached the plateau at 27% of OOIP. After injection of formation brine, the core was flooded with sea water and 500 ppm NaCl-solution. Since no LowSal effects were observed, the core was flooded with high saline formation brine again followed directly by low saline water. The purpose with this was to get a rapid decrease in salinity and thereby increase the recovery. But this was an unsuccessful attempt. In other words, no LowSal effects were observed for Varg#6. The data corresponding to figure 4.4 is found in appendices A.6.2.

**Table 4.2:** Test conditions for Varg core #5.

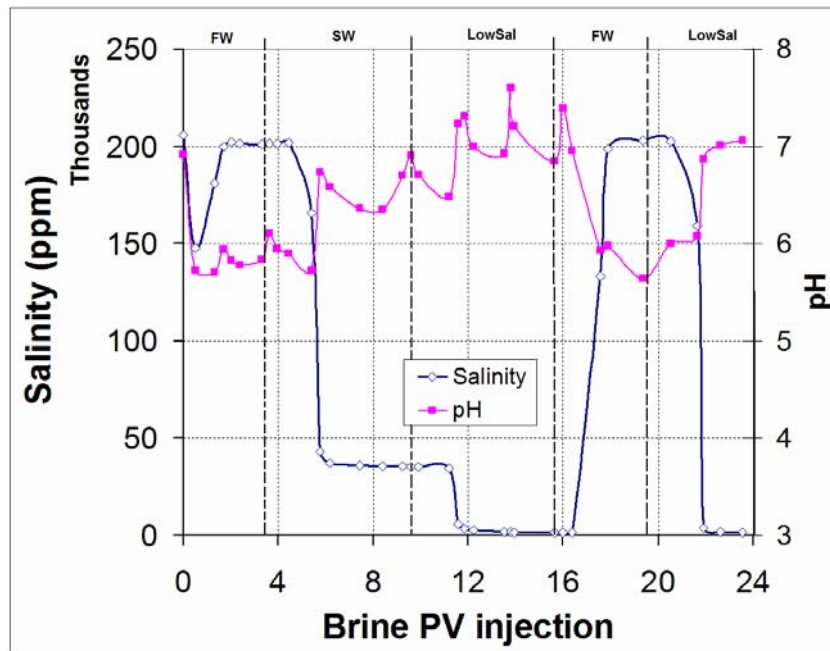
Core	Sw <sub>i</sub>	T <sub>ageing</sub> [°C]	T <sub>flooding</sub> [°C]	Test sequence
Varg#5	20	130	130	FW-SW-LowSal-FW-LowSal



**Figure 4.4:** Oil recovery vs. PV brine injected.

### 4.2.2 Salinity and pH

As seen from figure 4.5, the salinity of the effluent brine varies corresponding to the type of brine injected into Varg core #6. A small increase in pH, about 1 pH unit, was seen when switching from formation brine to sea water and the NaCl-solution. An increase in pH, about 1.5 pH units, was also observed when changing directly to LowSal water after injection of formation brine at the end of the flood. The data corresponding to figure 4.5 is found in appendices A.6.2.



**Figure 4.5:** *Salinity and pH vs. PV brine injected.*

### 4.2.3 Pressure data

The pressure drop across Varg core #6 decreases during injection and corresponding to the salinity of the injected brine, shown in figure 4.6. The increase in pressure drop across the core after injection of around 15 PV brine, was due to injection of formation brine with higher viscosity. The curve shows no rapid changes or fluctuations in pressure drop.

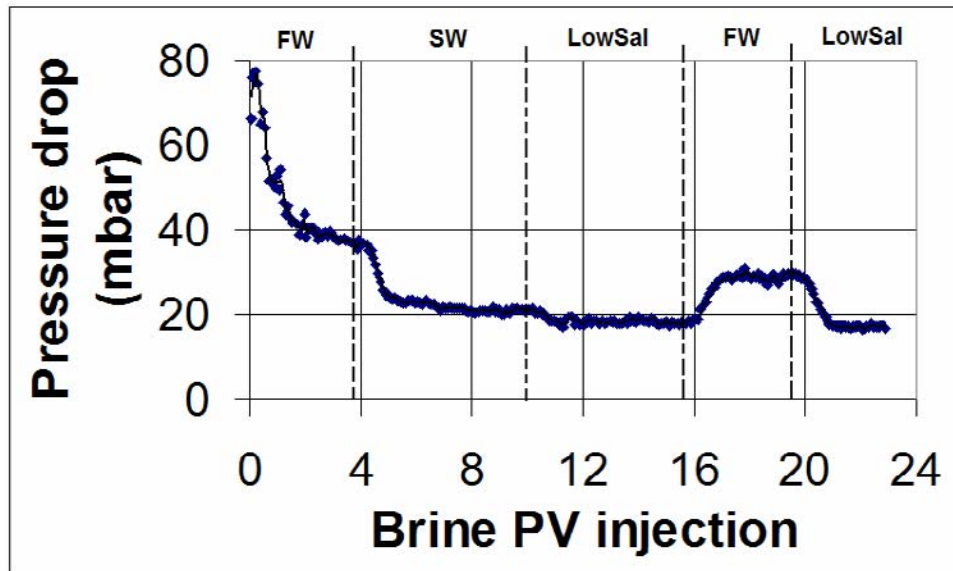
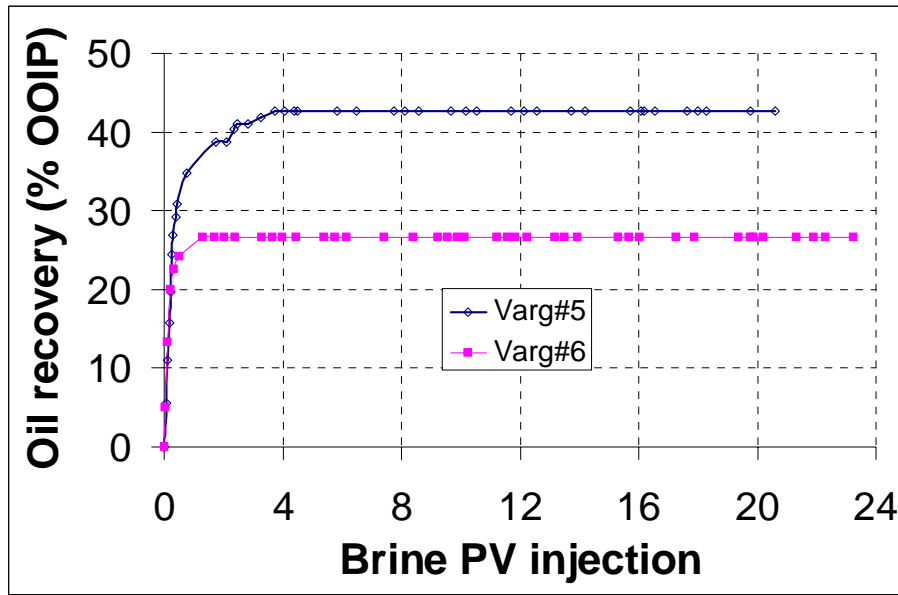


Figure 4.6: Pressure drop across Varg core #6 vs. PV brine injected.

## 5. Discussion

The clay content in the Varg cores was relatively high, about 15 wt% (~ 10 wt% illite/mica, 3 wt% kaolinite, 2 wt% chlorite). The Varg formation brine also contains a significant amount of divalent cations, 0.54 mol/l  $\text{Ca}^{2+}$  and 0.14 mol/l  $\text{Mg}^{2+}$ . The amount of acidic material in the Varg crude oil is limited, as indicated by the acid number 0.11 mg KOH/g. However, the base number is moderate, 0.82 mg KOH/g. There should therefore be enough basic material present in the oil to adsorb onto the clay surface. Previous low salinity floods showed that there appeared to be no restrictions to the type of polar components present in the crude oil, acids or bases, provided that a significant amount is present (Austad, 2010b). Thus, with a reasonable high base number of the oil, concentration of  $\text{Ca}^{2+}$  in the formation brine and content of clays in the sandstone, the criteria for observing low salinity effect from Varg should be in place.

The oil recovery from Varg core #5 was 16% higher than the recovery from Varg core #6, illustrated in figure 5.1. This indicates differences in the initial properties of the cores after ageing. The core preparation was similar for both cores, except for the temperature when saturating and flooding the cores with crude oil (containing  $\text{CO}_2$ ). The temperature was 50 °C for Varg#5 and 130 °C for Varg#6. This difference in temperature may have influenced the initial wetting of the cores, even though the cores were aged at the same temperature, 130 °C, for 14 days.



**Figure 5.1:** Oil recovery vs. PV brine injected for Varg#5 and Varg#6.

The shape of the recovery curves, shown in figure 5.1, indicate that Varg#6 had a more piston like displacement and behaved more water-wet compared to Varg#5. In a more water-wet system, less organic components are adsorbed onto the clay surface. It may therefore be hard to observe any large oil recoveries after flooding.

As seen from figure 4.3 and 4.6, no increase in pressure drop across the core was observed when changing to an injection brine with lower salinity. Rapid changes or fluctuations in pressure drop could have indicated remobilization of oil inside the core, migration of fines and diverted flow.

Both core floods showed a pH increase in the effluent brine when switching from formation brine to sea water and the LowSal NaCl-solution. The increase was about 1 pH unit, illustrated in figure 4.2 and 4.5. This could be explained by desorption of active cations from the clay surface. To compensate for the loss of cations, protons ( $H^+$ ) from the water close to the clay surface adsorb onto the clay, resulting in a local increase in

pH. Although there was a pH increase during the LowSal flooding, no increased oil recovery was observed.

The increase in pH when changing to sea water and NaCl-solution was small. This can be explained by buffering effects from carbon dioxide. CO<sub>2</sub> is an acidic gas, and was added to the crude oil to lower the pH of the formation water during ageing. In reservoirs, the pH of formation water is low due to dissolved acidic gases like CO<sub>2</sub> and H<sub>2</sub>S. A low initial pH increases the adsorption of organic material onto the clay and creates a less water-wet condition inside the core. Although the observed pH increase in the effluent brine was small, the local increase in pH close to the clay surface may be larger and cause desorption of organic material from the rock (Austad, 2010b). Still, no LowSal effects were seen from the core flooding.

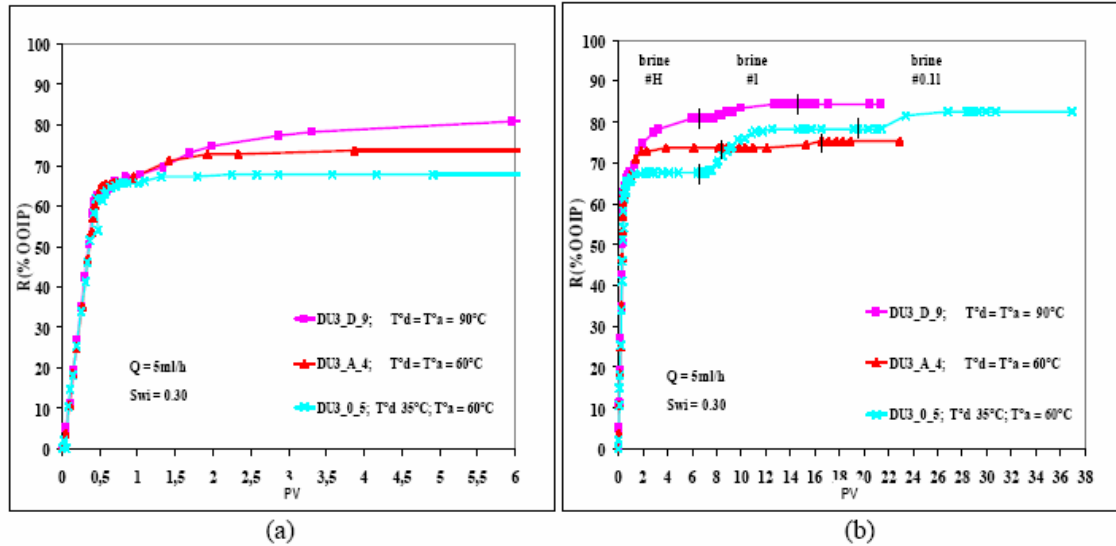
There is a considerable gradient in the active ions, especially in Ca<sup>2+</sup>, between the initial Varg formation brine (0.536 mol/l Ca<sup>2+</sup>) and sea water (0.013 mol/l Ca<sup>2+</sup>). Sea water may therefore act as a LowSal fluid itself. But the flooding experiments did not show any increased oil recovery when changing from high saline formation brine to sea water with lower salinity. It can therefore be questioned whether it is possible to recover more oil in the low salinity process after first flooding with sea water. When sea water is injected before the LowSal NaCl-solution, the salinity gradient/gradient in active ions (Ca<sup>2+</sup>) is reduced. The increase in pH is not that rapid as it could be if LowSal brine was injected directly after formation water, illustrated in figure 4.5.

Most of the reported studies on low salinity waterflooding are performed at lower temperatures, less than 90 °C. The effect of temperature on enhanced oil recovery by LowSal flooding has been of low interest. The reason may be that the relative affinity of organic material and active cations onto clay minerals is quite similar at temperatures below 90 °C. The Varg cores were aged and flooded at reservoir temperature, 130 °C. High flooding temperatures may decrease the viscosity of oil and thus improve the mobility ratio. On the other hand, the high reservoir temperature and temperature effects



can be the main reason for no observations of LowSal effect. The kinetics of the desorption process of cations is different for different cations and changes with temperatures. At temperatures close to 100 °C and above, the relative reactivity of cations may change significantly, both regarding adsorption and desorption due to solubility affects. Divalent cations have strong affinity towards the clay surface, especially  $\text{Ca}^{2+}$ . And the reactivity of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  increases drastically with increasing temperatures due to dehydration. At 130 °C, the  $\text{Ca}^{2+}$  ions may be so strongly bonded to the clay surface, that the adsorption of organic material from the crude oil are prevented. The wetting condition of the core is therefore not favorable for low saline flooding. If the divalent cations are strongly adsorbed to the clay surface, the rate of desorption of  $\text{Ca}^{2+}$  from the surface as the front of the LowSal water passes through the porous medium is low. Desorption of active ions are important for creating a rapid increase in pH and thereby desorb oil components from the surface.

Low saline waterfloods on outcrop cores confirm that the benefits may vary against the flooding temperature (Boussour, 2009). The study performed by Boussour and Cissokho states that temperature controls the initial wettability state, which in turn affects the low salinity process. The response of additional oil recovery in a tertiary mode (injection of LowSal water after formation brine) is more positive at lower temperatures. Figure 5.2 shows experimental results regarding different aging and displacement temperatures (Cissokho, 2009). No significant additional oil recovery by low saline water injection was observed for high temperature floods with LowSal brine #1 (1 g/l with 95%w NaCl and 5%w  $\text{CaCl}_2$ ) or LowSal brine #0.11 (with salt concentration of 0.1 times the concentration of brine #1). However, with the same oil/brine/rock system, low salinity water injection at a temperature of 35 °C exhibited a gain of oil production of +11% of OOIP with brine #1 and +4.2% of OOIP with brine #0.11 (Cissokho, 2009). It should be mentioned that the maximum ageing and displacement temperature in this experiment were 90 °C, and not as high as the Varg reservoir temperature.



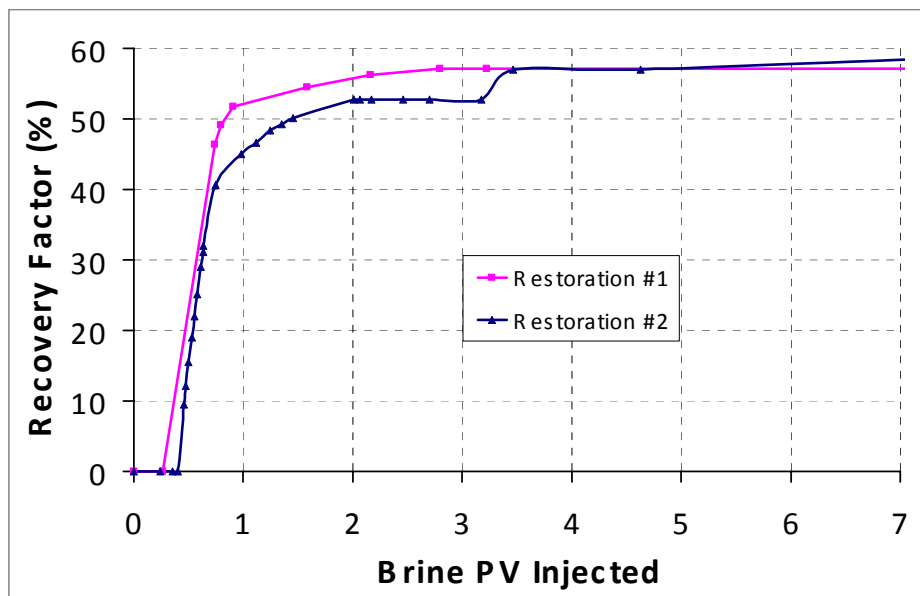
**Figure 5.2:** Evolution on oil recovery during tertiary experiments on selected core samples at different displacement temperatures (Cissokho, 2009).

PhD student Alireza Rezaei Doust at the University of Stavanger has done similar LowSal waterfloods on Varg cores as in the experimental work in this master thesis, but with different ageing temperatures (RezaeiDoust, 2009a). The cores were saturated with synthetic Varg formation brine and crude oil from the Varg field, without CO<sub>2</sub>. Varg core #2 had a clay content of 10.3 wt% illite/mica, 3.4 wt% kaolinite and 2.3 wt% chlorite. This is almost the same as for Varg#5 and Varg#6. Several different restorations were performed. The test conditions for two of the restorations are shown in table 5.1. Test 1 and 2 was performed under tertiary conditions, i.e. flooding with high saline formation brine in secondary mode and diluted sea water as LowSal fluid in tertiary mode. For restoration 1, the ageing temperature was 60 °C and the displacement temperature was similar to the Varg reservoir temperature, about 130 °C. This restoration did not show any LowSal effect, as illustrated in figure 5.3. The ageing temperature for restoration 2 was 90 °C and the flooding temperature was 130 °C. The tertiary LowSal effect for this restoration was 6% of OOIP, shown in figure 5.3, despite the high displacement temperature. In all the other restorations increased oil recovery was observed under tertiary conditions. An increase in pH was also observed when switching from the high saline brine to low salinity brine. This indicates desorption of divalent cations. The

observed LowSal effect when the core was aged at 90 °C and not 60 °C, may confirm what Tang also has shown, that an increase in ageing temperature can alter the wettability from water-wet towards more oil-wet conditions (Tang, 1998). With an ageing temperature of 60 °C, the core appears to be more water-wet based on the shape of the production curve.

**Table 5.1:** Test conditions for Varg core #2 (RezaeiDoust, 2009a).

Test Name	$S_{wi}$ %	$T_{aging}$ °C	$T_{flooding}$ °C	Test Sequence	Max. oil recovery (% OOIP)	Low Sal effect (% OOIP)
Restoration # 1	42.2	60	130	HS-LS	57	0
Restoration # 2	40.1	90	130	HS-LS	53	6



**Figure 5.3:** Oil recovery from Varg core #2 at restoration 1 and 2 (RezaeiDoust, 2009a).

The ageing temperature and the displacement temperature for Varg#5 and Varg#6 were equal to the Varg reservoir temperature, about 130 °C, and the floods did not result in any LowSal effect. When the ageing temperature for Varg core #2 was 90 ° and the flooding temperature was 130 °C, the floods gave a LowSal effect by up to 6% of OOIP. The main

difference in the test conditions of Varg core #2 and Varg#5/Varg#6, is that the ageing temperature for Varg core #2 was lower than the reservoir temperature. Based on these results, the oil recovery by low saline waterflooding seems to be dependent on the ageing temperature. When the ageing temperature is increased from 90 °C to 130 °C, less organic compounds may be adsorbed onto the clay surface due to increased reactivity of  $\text{Ca}^{2+}$  ions, and the core stays water-wet. This seems to be in contrast to the results from Tang, that an increase in ageing temperature promotes a initial wetting towards less water-wet conditions (Tang, 1998). But Tang performed these tests (spontaneous imbibition) with ageing temperatures of 75 °C and below. And as already described, the reactivity of divalent cations can change drastically at higher temperatures.

## 6. Conclusions

Two cores from the Varg field were tested for low salinity effects by flooding the cores successively with formation brine, sea water and a 500 ppm NaCl-solution. CO<sub>2</sub> was added to the crude oil to lower the pH of the formation water during ageing. The core ageing and flooding were performed at reservoir temperature, 130 °C. The main conclusions from the work are:

- The oil recovery by secondary displacement with formation brine was 43% and 27% of OOIP for Varg core #5 and core #6 respectively.
- No extra oil was recovered by sea water and low saline NaCl-solution.
- An increase in pH, about 1 pH unit, when switching to sea water and NaCl-solution was observed.
- Previous studies where the ageing temperature was 90° and the displacement temperature was 130 °C have shown LowSal effects. This may indicate that the ageing temperature is crucial in the low salinity flooding process.
- The relative adsorption of organic material and active cations, Ca<sup>2+</sup> and Mg<sup>2+</sup>, onto clay at temperatures higher than 100 °C appears to be important in the understanding of the LowSal mechanism. Further study on this topic is therefore needed.

## 7. Nomenclature

LowSal: Low Salinity

OOIP: Original Oil in Place

IFT: Interfacial tension

COBR: Crude Oil Brine Rock

NSO: Nitrogen, sulphur, oxygen

AN: Acid number

BN: Base number

G-AB: Gravity, acidity, basicity

CEC: Cation Exchange Capacity

FW: Formation Water

SW: Sea Water

TDS: Total Dissolved Solid

XRD: X-ray Diffraction Analysis

TVD: True Vertical Depth

WAG: Water Alternating Gas

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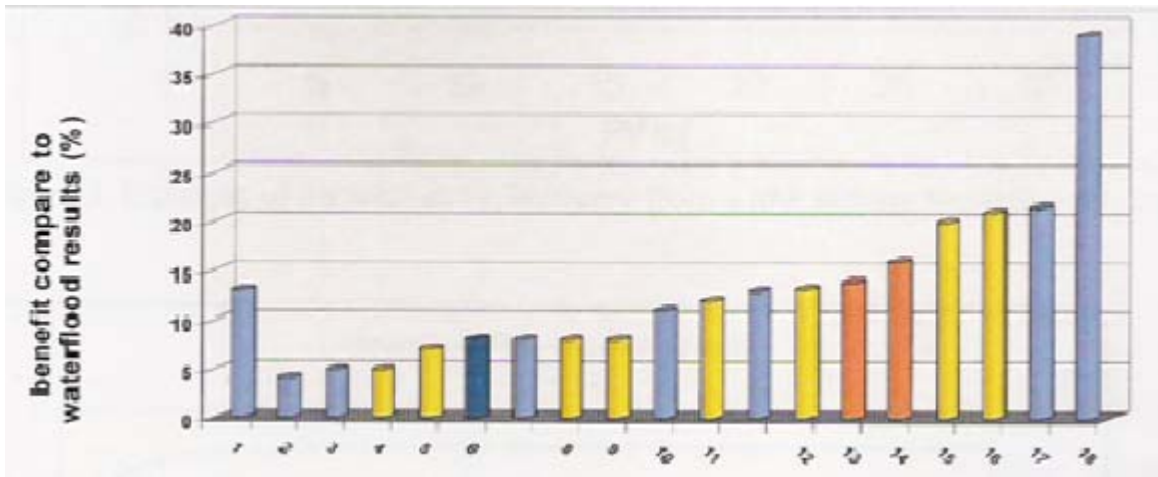


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# Appendices

## A.1 Summary of low salinity recovery for selected fields



**Figure A.1:** Summary of low salinity recovery for various fields. The average benefit represent 14 % increase in oil recovery (Lager A., 2007).

## ***A.2 History of low salinity***

The following is a brief summary of the main history of LowSal, mainly based upon the text from (Zhang, 2007).

**1942:** The question of the effect of the injection brine salinity on oil recovery was raised. Initial studies with Kansas crude oil and cores showed no significant difference in recoveries for brine versus fresh water. Documented results for recovery of Bradford crude oil and sandstones with a range of permeabilities showed overall recoveries to be less for fresh water than for a brine of 40% higher viscosity. The difference was explained by swelling of clays (Smith, 1942).

**1959:** Observation of increased recovery of heavy oil through injection of fresh water. The effect of clay swelling and emulsification were suggested as possible causes (Martin, 1959).

**1967:** From laboratory tests on recovery of mineral oil it was concluded that swelling clays and/or dispersion accompanied by increased pressure drop resulted in additional oil production by injection of fresh water or 1000 ppm NaCl (Bernard, 1967).

**1999:** “Migration of Fines” by Tang and Morrow.

**2005:** “pH increase” by McGuire et al.

**2006:** “Multicomponent Ionic Exchange” by Lager et al.

**2008:** “Salting in effect” by Austad et al. This was only a working proposal.

**2009:** “Double layer effects” by Ligthelm et al.

**2010:** “Desorption by pH increase” by Austad et al.

### **A.3 The Varg field**

The Varg field is a sandstone oil reservoir located in the southern part of the Norwegian North Sea. Varg was discovered in 1984 and the production started in 1998. The field is located at a water depth of 84 meters and the crest of the field structure at 2700 meters true vertical depth (TVDSS). The reservoir depth map for Varg is shown in figure A.3. The average porosity ranges from 15-27% with average permeability around 100 mD, sometimes reaching 1000 mD. The reservoir fluid can broadly be characterized as black oil of approximately 35°API, with solution gas-oil ratio in the range 110-140 Sm<sup>3</sup>/Sm<sup>3</sup> and a viscosity of approximately 0.5 cp. The salinity of the Varg brine is approximately 200 000 ppm. The reservoir temperature is about 130 °C and the initial reservoir pressure is taken to be 347 bara at 2940 mTVDSS.

Dependent on the reservoir segment, various recovery mechanisms come in to play at Varg:

- Depletion drive
- Waterflood
- Gas injection
- Water alternating gas (WAG) injection

The expected cumulative production is 82 millions barrels (13 millions Sm<sup>3</sup>), which represents an oil recovery of 30 %. The remaining recourses per September 2006 were estimated to 23 millions barrels of oil (3.6 millions Sm<sup>3</sup>).

Today Talisman Energy Norge AS operates Varg. The field was developed using a normally unmanned wellhead platform (Varg A), tied back to a production vessel named Petrojarl Varg (or Varg B), shown in figure A.2 (Talisman, 2007).



**Figure A.2:** *Varg A to left and Petrojarl Varg to right.*

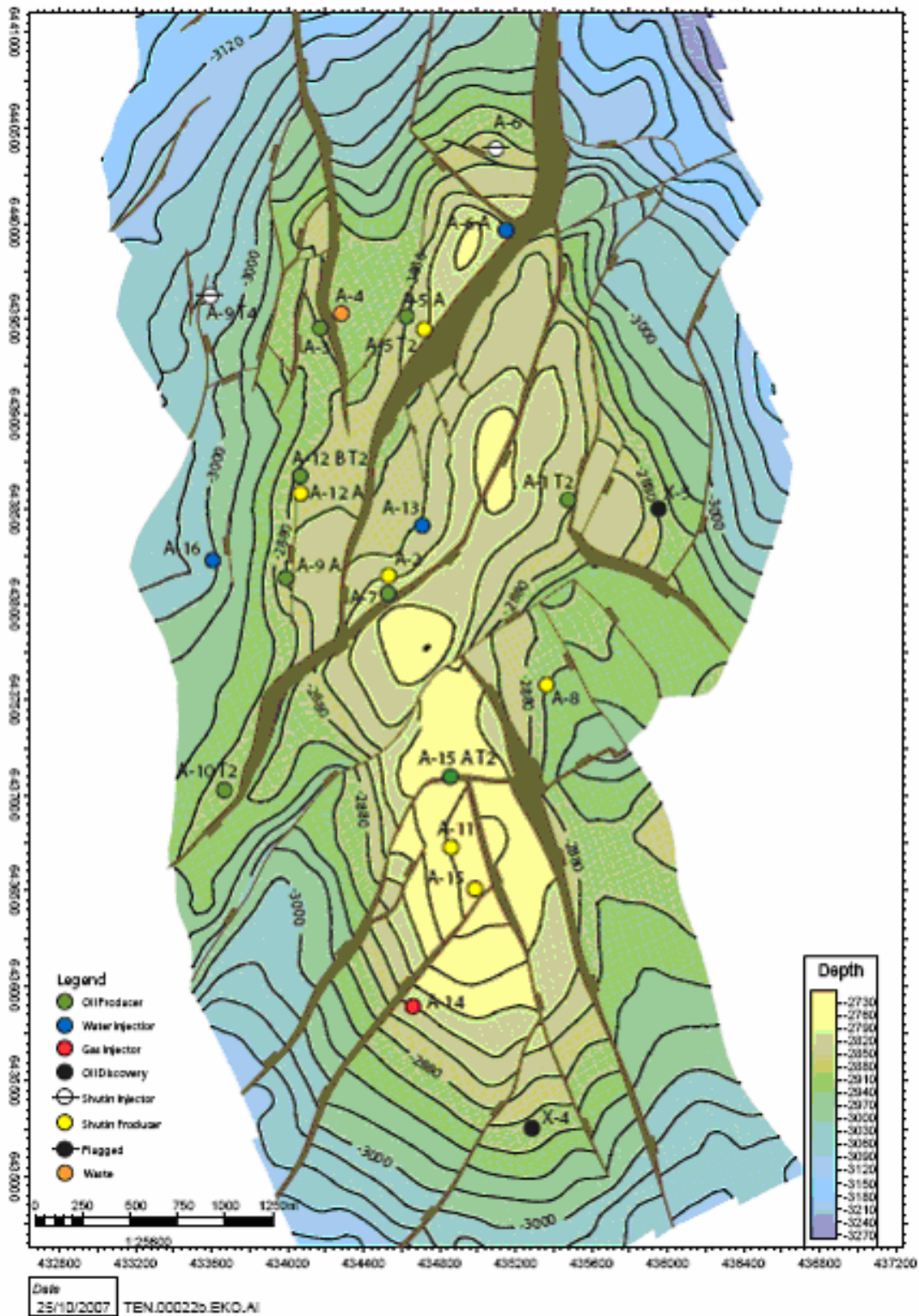


Figure A.3: Varg field top reservoir depth map [m].

## A.4 Compositions

**Table A.1:** *Composition of synthetic Varg formation water.*

Salt	m [g/l]	m [mole/l] (molar)
	237.49	
NaCl	121.90	2.086
KCl	3.8	0.051
MgCl <sub>2</sub>	13.7	
CaCl <sub>2</sub> (dry)	59.5	
BaCl <sub>2</sub>	1.45	
SrCl <sub>2</sub>	1.21	
MgCl <sub>2</sub> · 6H <sub>2</sub> O	29.25	0.144
CaCl <sub>2</sub> · 2H <sub>2</sub> O	78.81	0.536
BaCl <sub>2</sub> · 2H <sub>2</sub> O	1.70	0.007
SrCl <sub>2</sub> · 6H <sub>2</sub> O	2.03	0.010
Density	(1.006)	
Weight %	20.27	
TDS [g/l]	201.56	201.56
Ionic Strength	4.221	4.221
Ions	m [g/l]	m [mole/l]
Cl <sup>-</sup>	125.01	3.526
Mg <sup>2+</sup>	3.50	0.144
Ca <sup>2+</sup>	21.49	0.536
Na <sup>+</sup>	47.95	2.086
K <sup>+</sup>	1.99	0.051
Ba <sup>2+</sup>	0.96	0.007
Sr <sup>2+</sup>	0.67	0.008
	201.56	201.56



**Table A.2:** *Composition of synthetic sea water.*

Salt	m[g/l]	m [mole/l] (molar)
SSW	38.67	
NaCl	23.38	0.400
Na <sub>2</sub> SO <sub>4</sub>	3.41	0.024
NaHCO <sub>3</sub>	0.17	0.002
KCl	0.75	0.010
MgCl <sub>2</sub>	4.24	
CaCl <sub>2</sub> (dry)	1.44	
MgCl <sub>2</sub> · 6H <sub>2</sub> O	9.05	0.045
CaCl <sub>2</sub> · 2H <sub>2</sub> O	1.91	0.013
Density	1.024	
Weight %	3.42	
TDS [g/l]	33.39	33.39
Ionic Strength		0.657
Ca <sup>2+</sup> /SO <sub>4</sub> <sup>-</sup>		0.540
Ions	m [g/l]	m [mole/l]
HCO <sub>3</sub> <sup>-</sup>	0.12	0.002
Cl <sup>-</sup>	18.62	0.525
SO <sub>4</sub> <sup>2-</sup>	2.31	0.0240
Mg <sup>2+</sup>	1.08	0.045
Ca <sup>2+</sup>	0.52	0.013
Na <sup>+</sup>	10.35	0.450
K <sup>+</sup>	0.39	0.010
	33.39	

**Table A.3:** X-ray Diffraction Analysis for well 15/12-A-5-T2. The clay content/mineral composition for Varg core #5 and #6 is assumed to be between the given depths.

Depth [m]	Illite+Mica	Kaolinite	Chlorite	Quartz	K Feldspar	Plagioclase	Calcite	Dolomite	Barite	Pyrite	Total
3506.50	11.5	4.1	2.5	63.7	5.7	7.2	0.0	2.4	0.7	2.2	100
3506.90	9.1	2.7	2.1	66.4	5.2	9.4	TR	2.8	0.5	1.8	100

## ***A.5 Measurement procedures***

### **A.5.1 Centrifuging**

The crude oil was centrifuged for one hour to remove possible particles and water. To avoid unstable movements, the oil samples were put on each side of the centrifuge IEC Model K, shown in figure A.4.



**Figure A.4:** *Centrifuge.*

### **A.5.2 Filtration**

Before the brines were filtrated, they were stirred with a magnetic bar, as shown in figure A5. Figure A.6 shows the setup for filtration of the oil and brines used in the experiments. The brines were filtrated through a 0.22  $\mu\text{m}$  filter paper and the oil through a 5  $\mu\text{m}$  paper to remove possible particles. A VWR vacuum gas pump, showed to left in figure A.6, was used to accelerate the filtration process.



**Figure A5:** *The brines were stirred with a magnetic bar.*



**Figure A.6:** *Filtration setup.*

### A.5.3 Procedure for measurement of acid and base numbers

The acid and base numbers of the oil are determined by the automatic titrator, Mettler Toledo DL55, shown in figure A.7. The procedure for measurements of AN and BN is the same, but different types of solvents are used, described in table A.4.

- Calibrate the pH probes with standard buffer solution with pH 4, 7 and 10.
- Standardize the titrant with 50 ml standard solution.
- Make a sample of 1 ml spiking solution and 50 ml titration solvent (called the blank solution). The spiking solution is added to improve the accuracy of the measurements of oils that have low AN. The total acid/base content of the sample is measured using the titrant.
- Make a new sample of 1 ml spiking solution and 50 ml titration solvent (blank), and add 1 ml oil to it. The total acid/base content of the new sample is also measured using the titrant.
- The difference in the total acid/base content between the blank and the sample containing oil is related to the amount of oil added.



**Figure A.7:** *Measurement of AN and BN by a titrator.*

**Table A.4:** *Materials for measurements of AN and BN.*

	AN	BN
Titrant	0.05 M tetrabutyl ammonium hydroxide in ethanol or methanol	5 ml 70% HClO <sub>4</sub> , 15 ml (CH <sub>3</sub> CO) <sub>2</sub> O diluted to 1000 ml with glacial HAc
Spiking solution	~0.5 g stearic acid diluted to 100 ml with acid titration solvent or decane	~0.5 g quinoline diluted to 100 ml with n-decane
Standard solution	~0.2 g potassium hydrogen phthalate (KHP) diluted to 500 ml with dionised water	~0.2 g KHP diluted to 250 ml with glacial acetic acid (HAc)
Titration solvent	6 ml dionised water and 494 ml HPLC grade 2-propanol and 500 ml HPLC grade toluene	Methyl isobutyl ketone (MIBK)

## A.6 Main test data

### A.6.1 Varg core #5

Table A.5: Flooding test data for Varg#5.

Sample	Date	Time min	Brine Injected ml	PV injected	Amount oil ml	Recovery %OOIP	Density gr/cm3	TDS [ppm]	pH	Total injected ml	Water ml	WCT %	Description
	10.02.2010	09:28	0,00	0,00	0	0,00				0,00	0,00		Start of test (FW)
	10.02.2010	12:00	3,34	0,21	0	0,00				3,34	3,34	100,00	
	10.02.2010	12:55	4,55	0,29	0,7	5,53				1,21	0,51	42,08	
	10.02.2010	13:30	5,32	0,34	1,4	11,06				0,77	0,07	8,98	
	10.02.2010	14:00	5,98	0,38	2	15,80				0,66	0,06	8,98	
	10.02.2010	14:30	6,64	0,42	2,5	19,75				0,66	0,16	24,15	
	10.02.2010	15:00	7,29	0,46	3,1	24,49				0,66	0,06	8,98	
	10.02.2010	15:40	8,17	0,52	3,4	26,86				0,88	0,58	65,87	
1	10.02.2010	16:35	9,38	0,59	3,7	29,24	1,13546	195681	5,77	1,21	0,91	75,18	
	10.02.2010	17:17	10,30	0,65	3,9	30,82				0,92	0,72	78,33	
2	10.02.2010	21:10	15,42	0,98	4,4	34,77	1,12335	178412	5,52	5,12	4,62	90,23	
3	11.02.2010	08:45	30,70	1,94	4,9	38,72	1,13203	190790	5,3	15,27	14,77	96,73	
4	11.02.2010	13:10	36,52	2,31	4,9	38,72	1,13874	200358	5,7	5,82	5,82	100,00	
5	11.02.2010	16:10	40,47	2,56	5,1	40,30	1,13912	200900	5,82	3,96	3,76	94,94	
	11.02.2010	17:25	42,12	2,66	5,2	41,09				1,65	1,55	93,93	
6	11.02.2010	21:45	47,83	3,02	5,2	41,09	1,13907	200829	5,57	5,71	5,71	100,00	
	12.02.2010	03:02	54,80	3,46	5,3	41,88				6,97	6,87	98,56	
7	12.02.2010	08:45	62,34	3,94	5,4	42,67	1,13929	201143	5,63	7,54	7,44	98,67	
	12.02.2010	12:30	67,28	4,25	5,4	42,67				4,94	4,94	100,00	
	12.02.2010	16:30	72,55	4,59	5,4	42,67				5,27	5,27	100,00	
8	12.02.2010	17:45	74,20	4,69	5,4	42,67	1,13966	201670	5,75	1,65	1,65	100,00	
9	13.02.2010	11:10	95,40	6,03	5,4	42,67	1,13940	201299	5,78	21,20	21,20	100,00	
10	13.02.2010	18:56	105,64	6,68	5,4	42,67	1,13974	201784	5,94	10,24	10,24	100,00	
11	14.02.2010	10:10	125,73	7,95	5,4	42,67	1,13919	201000	5,97	20,08	20,08	100,00	
12	14.02.2010	14:45	131,77	8,33	5,4	42,67	1,13890	200586	6,15	6,04	6,04	100,00	Change to SW
13	14.02.2010	20:20	139,13	8,79	5,4	42,67	1,13995	202084	6,08	7,36	7,36	100,00	
14	15.02.2010	09:20	156,27	9,88	5,4	42,67	1,13735	198376	5,8	17,14	17,14	100,00	
15	15.02.2010	15:20	164,18	10,38	5,4	42,67	1,13882	200472	6,18	7,91	7,91	100,00	
16	15.02.2010	19:50	170,11	10,75	5,4	42,67	1,13833	199774	6,19	5,93	5,93	100,00	
17	16.02.2010	09:30	188,13	11,89	5,4	42,67	1,13951	201456	5,89	18,02	18,02	100,00	
18	16.02.2010	14:50	195,16	12,34	5,4	42,67	1,05090	75100	6,59	7,03	7,03	100,00	
19	16.02.2010	20:15	202,30	12,79	5,4	42,67	1,03127	47107	6,77	7,14	7,14	100,00	
20	17.02.2010	10:00	220,43	13,93	5,4	42,67	1,02581	39322	6,86	18,13	18,13	100,00	
21	17.02.2010	15:40	227,90	14,41	5,4	42,67	1,02357	36127	6,86	7,47	7,47	100,00	
22	18.02.2010	09:47	251,78	15,92	5,4	42,67	1,02321	35614	6,31	23,88	23,88	100,00	
	18.02.2010	14:22	257,82	16,30	5,4	42,67				6,04	6,04	100,00	Change to LowSal
	18.02.2010	15:40	259,54	16,41	5,4	42,67				1,71	1,71	100,00	
23	18.02.2010	19:40	264,81	16,74	5,4	42,67	1,02416	36969	6,7	5,27	5,27	100,00	
24	19.02.2010	08:55	282,28	17,84	5,4	42,67	1,02347	35985	6,35	17,47	17,47	100,00	
25	19.02.2010	13:05	287,77	18,19	5,4	42,67	1,00327	7180	7,58	5,49	5,49	100,00	
26	19.02.2010	16:50	292,71	18,50	5,4	42,67	1,00101	3957	7,33	4,94	4,94	100,00	
27	20.02.2010	10:30	316,00	19,98	5,4	42,67	0,99964	2004	7,43	23,29	23,29	100,00	
28	20.02.2010	20:30	329,19	20,81	5,4	42,67	0,99918	1348	7,42	13,18	13,18	100,00	

## A.6.2 Varg core #6

Table A.6: Flooding test data for Varg#6.

Sample	Date	Time min	Brine Injected ml	PV injected	Amount oil ml	Recovery %OOIP	Density gr/cm3	TDS [ppm]	pH	Total injected ml	Water ml	WCT %	Description
	07.04.2010	12:40	0	0	0	0,00				0	0		Start of FW injection
1	07.04.2010	16:33	4,85	0,32	0	0,00	1,1427	205597	6,92	4,85	4,85	100,00	
	07.04.2010	17:05	5,52	0,37	0,6	5,00				0,67	0,07	9,94	
	07.04.2010	18:00	6,66	0,44	1,6	13,34				1,15	0,15	12,67	
	07.04.2010	19:12	8,16	0,54	2,4	20,01				1,50	0,70	46,63	
	07.04.2010	20:40	9,99	0,67	2,7	22,52				1,83	1,53	83,63	
2	07.04.2010	22:40	12,49	0,83	2,9	24,18	1,10209	147802	5,73	2,50	2,30	91,99	
3	08.04.2010	08:20	24,57	1,64	3,2	26,68	1,12547	181076	5,7	12,08	11,78	97,52	
4	08.04.2010	13:00	30,40	2,03	3,2	26,68	1,13875	199975	5,94	5,83	5,83	100,00	
5	08.04.2010	16:50	35,18	2,35	3,2	26,68	1,1403	202181	5,83	4,79	4,79	100,00	
6	08.04.2010	21:10	40,60	2,71	3,2	26,68	1,13974	201384	5,78	5,41	5,41	100,00	
7	09.04.2010	08:10	54,34	3,62	3,2	26,68	1,13961	201199	5,84	13,74	13,74	100,00	
8	09.04.2010	12:20	59,54	3,97	3,2	26,68	1,13968	201299	6,1	5,20	5,20	100,00	
9	09.04.2010	16:10	64,33	4,29	3,2	26,68	1,13974	201384	5,95	4,79	4,79	100,00	Change to SW
10	09.04.2010	21:50	71,41	4,76	3,2	26,68	1,14001	201769	5,9	7,08	7,08	100,00	
11	10.04.2010	09:25	85,88	5,73	3,2	26,68	1,11466	165691	5,73	14,47	14,47	100,00	
12	10.04.2010	13:30	90,98	6,07	3,2	26,68	1,02858	43186	6,74	5,10	5,10	100,00	
13	10.04.2010	18:30	97,22	6,49	3,2	26,68	1,02446	37322	6,58	6,25	6,25	100,00	
14	11.04.2010	09:45	116,27	7,76	3,2	26,68	1,0235	35956	6,36	19,05	19,05	100,00	
15	11.04.2010	21:25	130,85	8,73	3,2	26,68	1,02327	35629	6,35	14,57	14,57	100,00	
16	12.04.2010	08:35	143,13	9,55	3,2	26,68	1,02317	35486	6,7	12,28	12,28	100,00	
17	12.04.2010	12:46	148,36	9,90	3,2	26,68	1,02315	35458	6,91	5,23	5,23	100,00	
18	12.04.2010	16:40	153,23	10,22	3,2	26,68	1,02298	35216	6,71	4,87	4,87	100,00	Change to LowSal
	12.04.2010	19:40	156,98	10,47	3,2	26,68				3,75	3,75	100,00	
19	13.04.2010	08:20	172,80	11,53	3,2	26,68	1,02248	34505	6,48	15,82	15,82	100,00	
20	13.04.2010	12:55	178,52	11,91	3,2	26,68	1,00234	5842	7,23	5,73	5,73	100,00	
21	13.04.2010	16:05	182,48	12,17	3,2	26,68	1,00076	3593	7,31	3,96	3,96	100,00	
22	13.04.2010	20:45	188,31	12,56	3,2	26,68	1,00015	2725	7	5,83	5,83	100,00	
23	14.04.2010	08:00	202,36	13,50	3,2	26,68	0,99966	2028	6,93	14,05	14,05	100,00	
24	14.04.2010	11:45	207,04	13,81	3,2	26,68	0,99971	2099	7,6	4,68	4,68	100,00	
25	14.04.2010	17:10	213,81	14,26	3,2	26,68	0,99939	1644	7,21	6,77	6,77	100,00	
26	15.04.2010	09:40	234,42	15,64	3,2	26,68	0,99931	1530	6,85	20,61	20,61	100,00	
27	15.04.2010	13:55	239,73	15,99	3,2	26,68	0,99924	1430	7,39	5,31	5,31	100,00	Change to FW
28	15.04.2010	18:20	245,25	16,36	3,2	26,68	0,99922	1402	6,96	5,52	5,52	100,00	
29	16.04.2010	08:58	263,53	17,58	3,2	26,68	1,09196	133386	5,93	18,28	18,28	100,00	
30	16.04.2010	16:30	272,94	18,21	3,2	26,68	1,1379	198766	5,98	9,41	9,41	100,00	
31	17.04.2010	10:10	295,01	19,68	3,2	26,68	1,14073	202793	5,64	22,07	22,07	100,00	
	17.04.2010	15:10	301,25	20,10	3,2	26,68				6,25	6,25	100,00	Change to LowSal
32	17.04.2010	16:20	302,71	20,19	3,2	26,68			5,90	1,46	1,46	100,00	
33	17.04.2010	20:08	307,45	20,51	3,2	26,68	1,14062	202637	6,00	4,75	4,75	100,00	
34	18.04.2010	09:50	324,57	21,65	3,2	26,68	1,10996	159003	6,08	17,11	17,11	100,00	
35	18.04.2010	16:42	333,15	22,22	3,2	26,68	1,00112	4106	6,87	8,58	8,58	100,00	
36	18.04.2010	21:25	339,04	22,62	3,2	26,68	0,99951	1815	7,01	5,89	5,89	100,00	
37	19.04.2010	08:38	353,05	23,55	3,2	26,68	0,99934	1573	7,06	14,01	14,01	100,00	
38	19.04.2010	14:45	360,69	24,06	3,2	26,68	0,99913	1274	7	7,64	7,64	100,00	Temp down