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MASTER'S THESIS

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Dedication

I dedicate this thesis to my dear Birgit Margareta Johnsson and Valter Johnsson who have always been on access way to me that I found them with me whenever I needed.

It is their support and endorsement that motivates me to set higher target.

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Abstract

During the last few years studies of the low salinity water flooding effect, in general, have demonstrated an additional oil recovery associated with flooding oil reservoirs with low salinity water. Numerous theories have been suggested as explanation for the mechanism of the incremental oil recovery; however they are debatable.

Those theories are based on researches performed using wide variations of porous media and types of oils and experimental conditions. This is perhaps the reason that it is still debatable. Furthermore almost certainly, low salinity water flooding is an effect of various mechanisms acting together.

To perform the first laboratory experiments, initially the four cores from Obourg out crop chalk from Belgium were established for initial water saturation (Swi) using synthetic sea water (SSW) by flooding of n-Decane + stearic acid, 0.005 mole/l, aged for two weeks at 50 ºC and then flooded for oil production at 70 ºC.

The experimental scheme that was followed here is by flooding chalk cores first with seawater (SSW), followed by low salinity water (LSW) or single ion water such as SO_4^{2-} or Mg^{2+}. To address the change of the surface of the flooded cores, the cores were re-saturated with modified oil (n-C10) with stearic acid (SA), representing a one of the natural surfactant in the oil, and aged for 2weeks before running the imbibition experiments. The imbibing fluids were SSW followed by LSW or SO_4^{2-} or Mg^{2+}.

The used chalk cores are Stevns Klint outcrop chalk (SK) from Denmark. These type of cores showed to be persistent to chemical reaction with the modified oil (n-C10 and SA). This enabled us to carry out the planned work.

An additional oil recovery of about 1 % from secondary flooding (after SSW) of SK cores with LSW and Mg^{2+} was obtained. The imbibition experiments with LSW and Mg^{2+} after the re-saturation, aging and use of SSW as first imbibing fluid, showed estimated recovery of 1.3% (≈1%) and 1.6%, for LSW and Mg^{2+}, respectively. In the case secondary flooding with SO_4^{2-} , no additional recovery was observed, however in the imbibition experiments as a second imbibing fluid (after SSW), an additional recovery of approximately 1% was obtained.

It is observed in the flooding experiments with low salinity water, that the pressure drop across the core was reduced by about 2 bar (from 3.2 to 1.2). It was also noted in both flooding and imbibition presence of fines and a third phase, which is suspected to be an emulsion phase. This may suggest wettability change with fine migration and effective sweep/contacted oils during flooding and imbibition.

Objectivities

The main objective of the thesis work is to investigate possible mechanism with low salinity flooding as a secondary oil recovery method and imbibition from the flooded cores after oil re-saturation and aging. This is to address the effect of flooding with different water compositions on the surface, hence imbibition.

In order to check the influence of the composition on the oil recovery, two fluids were used, first synthetic seawater (SSW) as a base flooding and imbibing fluid. Second flooding and imbibing fluids were low salinity water (LSW), sodium sulphate ($SO_4{}^{2-}$) and magnesium chloride (Mg^{2+}). The two ions were selected based on that these ions are active ions in seawater that shown in literature to enhance oil recovery. The concentrations of these ions are same as that in the seawater.

List of Symbols

D	*Core diameter (cm)*
K	*Absolute permeability , mD*
Lc	*Length of the core (m)*
Pc	*Capillary pressure (Pa)*
PV	*Pore volume, ml*
Soi	*Initial oil saturation*
Sro	*Residual oil saturation*
Sw	*Water saturation*
Swi	*Initial water saturation*
V	*Darcy velocity (apparent velocity) (qw/A) (m/s)*
Φ	*Porosity fraction or %*
A	*Area [cm2]*
Cm	*Centimeter*
Cr	*Rock compressibility*
K eff	*Effective permeability, [md]*
Krg	*Relative permeability of gas, dimensionless*
Kro	*Relative permeability of oil, dimensionless*
Krw	*Relative permeability of water, dimensionless*
mD	*Mili Darcy*
P	*Pressure [bar]*
Q	*Flow rate [cm3/sec] or [ml/min]*
T	*Temperature, [˚C]*
V	*Volume, [cm3]*
ΔP	*Pressure drop [bar] or [atm]*
µ	*Interfacial tension, mN/m*

Nomenclature

AN	*Acid number, mg KOH/g*
C/Co	*Relative concentration of effluent ions*
COBR	*Crude/oil/brine/rock*
DI	*Deionized water*
EOR	*Enhanced oil recovery*
FW	*Formation brine*
IFT	*Interfacial tension, mN/m*
IOR	*Improved Oil Recovery*
IS	*Ionic strength, mole/l*
OOIP	*Original Oil in Place*
STOOIP	*Stock Tank Original Oil In Place*
SCAL	*Special Core Analysis Laboratory*
AN	*Acid Number*
BN	*Base Number*
CEC	*Cation Exchange Capacity*
SSW	*Sea Water*
SK	*Stevns Klint*
SSW	*synthetic sea water*
Swi	*initial water saturation*
Timb	*imbibition temperature*
TDS	*total dissolved solid*
LSW	*Low salinity brine water*
DW	*Distilled water*
IR	*Injection rate, ml/min*
SA	*Stearic Acid*

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1. Introduction

1.1. Carbonate Reservoirs for Oil recovery

Being the sources of approximately 50 % of all existing reserves of oil, carbonate reservoirs amount for the time being 20 % of all reservoirs round the world. (Nadeau P. 2013). The origin of the majority of carbonate reservoir rocks is a marine one. The precipitation from either the water or induced by nautical organisms to making their shells or skeletons is the reason of carbonates formation in different environments. Whereas the coastal dunes typically constitute a component of the beach or the marine environment on the shores are included as well.

Carbonate rocks belong to the type of sedimentary rocks which are made mainly of carbonate minerals, CaCO3. They are composed of particles which are ended of less than a half of carbonate minerals that are embed in cement. The accumulation of calcareous organisms known as bioclasts causes the formation of the majority of carbonate rocks. Thus, the territories which are favourable to different kinds of biological activity are abundant in carbonate rocks. For instance, it can be a warm and shallow sea characteristic of no or minor silica clastic input.

Chalk is mainly deposited in the epicratonic basins with middle or inner ramp areas, sub tidal shelves or certain shallow seas which flooded the territories especially in the west of North America, north-west of Europe and the Middle East during in the Middle - Late Cretaceous periods. According to Wayene, 2008, the deposits of chalk were found in basinal zones, although the majority of them are deposited in shallow seas.

Fig1*.The Needles, situated off the Isle of Wight, are part of the extensive Southern England Chalk formation.*

Chalk and limestone belong to the group of wide-spread carbonate rocks. Being a type of calcium carbonate in its pure form, chalk comprises cocoliths or calcitic microfossils along with different forms of foraminifera. Its creation resembles the one of limestone.

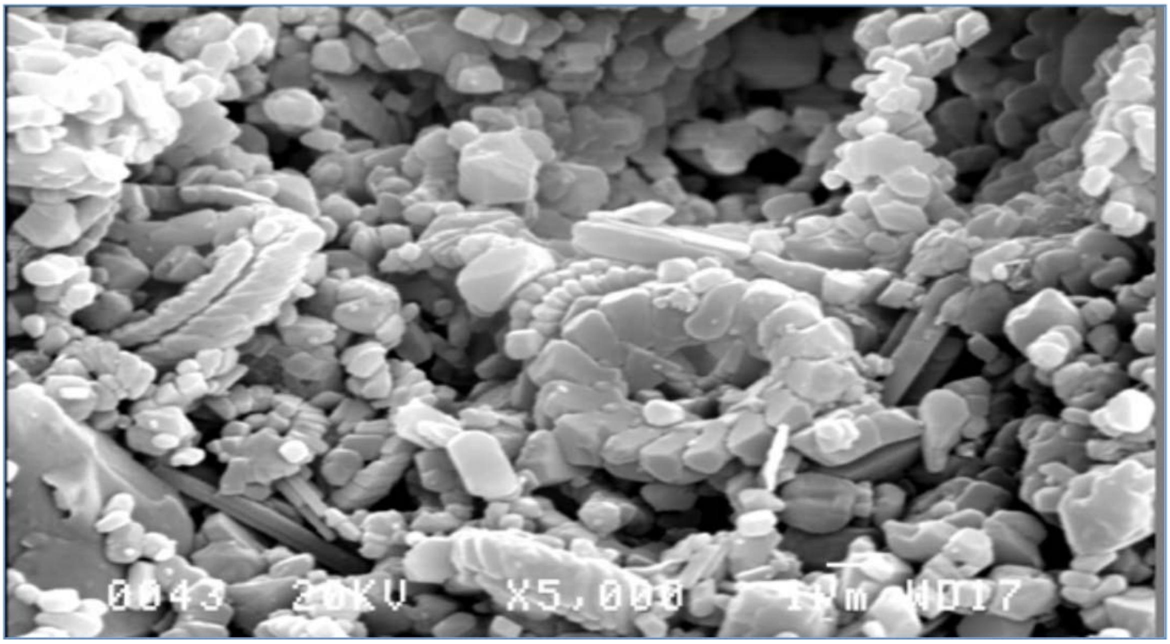


Figure 2. *SEM picture of chalk showing the coccolithic rings, ring fragments and pore space*

In general the percentage of oil recovery from reservoirs of carbonate reservoirs is to approximately 30 per cent. The matrix medium of low permeability and fractures of high permeability are the main characteristics of the carbonate reservoirs. Spontaneous water imbibition exerts influence on the ensuing oil recovery from the rock matrix under the conditions of aquifer drive or water injection. However, the prevailing majority of all carbonate reservoirs (approximately 90 %) are inert to oil-wet. Such neutral attitude means that the chances of spontaneous water imbibition are very low or zero. Water-wet rock predetermines positive capillary pressure, while oil-wet rocks result in negative capillary pressure.

Spontaneous water imbibition is also prevented providing that the reservoirs are completely or partially oil-wet. In that case, oil pressure in the matrix blocks is suppressed with the water pressure. Therefore, increase in oil recovery from carbonate rocks can be implemented via the change of wettability. The oil-wet type is supposed to be replaced with the water-wet one so that it resulted in the raise of capillary pressure (Tabary et al., 2009).

2. Background Theory

2.1 Recovery methods

There are definite phases of the reservoir production period which are defined with the amount of energy or pressure inside the reservoir. From the historical point of view those phases marked the chronological stages of the production. In general, there is a conventional subdivision of operations related to oil recovery into **a primary, a secondary and a tertiary stage.** The initial stage or **primary** recovery is caused by the natural substitution of reservoir energy. The decrease in the primary recovery initiates the **secondary** stage of recovery, which is implemented usually via water injection to support reservoir pressure. Another type of a secondary stage of recovery is gas injection.

The final phase is **the tertiary** recovery of the production process. The secondary stage proved to be operating later uneconomical, thus tertiary recovery has succeeded it. The processes of tertiary recovery comprise chemical flooding involving surfactant, polymer or other substances, thermal methods, miscible gas flooding, or the before mentioned methods combined. The focus of the third phase is the recovery enhancement from the areas which have already been swept.

According to Green and Willhite (1998), the term “tertiary oil recovery” has been substituted with the concept of “enhanced oil recovery” or EOR owing to the chronologic commotion. Certain economic and technical factors resulted in exclusion of numerous reservoir operations from the specified order.

Enhanced oil recovery or EOR is defined by Norwegian Petroleum Directorate as the advanced method of diminishing the saturation of residual oil in a reservoir (NPD, 2012). EOR is also defined as a process that involves injecting into the reservoir some kinds of fluids (Green & Willhite, 1998). This process provides extra or artificial energy that is required for displacing oil to a production well as well as interacting with the rock or reservoir oil systems. It is aimed at creating the most favourable conditions for the recovery of oil. According Zolotuchin and Ursin, 2000, EOR is targeted at oil that is complicated in production and oil that remains after the first two phases of oil recovery. There are two major domains of displacement in the process of enhanced oil recovery. They are microscopic displacement that is related to the pore scale mobilization of oil and macroscopic displacement related to the sweep efficiency.

The wettability alteration via modifications of seawater is a new method of enhanced oil recovery for chalk or a potential method for any kinds of carbonates. Enhanced oil recovery can be done under the condition of high temperatures and improved level of water-wetness of chalk with the help of sea water spontaneous imbibition (Strand et al., 2006a; Zhang and Austad, 2006; Zhang et al., 2006). In 1991, sea water was acknowledged by Sulak to be an appropriate EOR fluid. Injecting sea water into the mixed-wet and highly fractured Ekofisk chalk field served as an evidence of its high efficiency in oil recovery. The capability of sea water to make alterations in the wettability of chalk is proven. The chalk is transformed from the oil-wet type into the water-wet one through the intermediate stage, thus facilitating the water imbibition into the rock matrix. Oil recovery is also influenced by the rock compaction caused by the injection of sea water. Having studied the low-permeable, high fractured and high porosity North Sea chalk reservoirs (Puntervold, 2008) concluded that seawater injection is a key factor of oil recovery.

The primary objectives of enhanced oil recovery are the following:

1. Maintaining the required level of pressure in the reservoir along with the secondary oil recovery;

2. Reduction in the saturation of residual oil and enhancement of displacement efficiency. The latter demonstrates the oil mobilization at the pore scale. The efficiency of microscopic displacement is in direct correlation with certain chemical and physical interactions between the oil and displacing fluid including expansion of oil volume, reduction of oil viscosity, decrease in the interfacial tension between the fluids and the process of fluids miscibility;

3. Improvement of mobility ratios between the displaced and displacing fluids over the course of the whole process which results in the improvement of the sweep efficiency (Green & Willhite, 1998). It is a vertical and horizontal degree or measure to which the displaced fluid is moved by the flood in the reservoir before it reaches the producing well.

2.2 Petrochemistry and Petrophysic Parameters

2.2.1 Porosity

Porosity, designated by the symbol ϕ, is a correlation (percentage) of void to V_b, i.e. V_b is the rock bulk volume. It is a key parameter of forming, evaluating and calculating of the reserves. Calculation of porosity is done on the basis of such materials as acoustic logs, density and neutron logs. Generally, the relation between the core analysis porosities and three above mentioned conventional porosity logs is done in order to obtain the reservoir porosity. It is established on the basis of the principles of volume physical model.

2.2.2 Water saturation

Water saturation, designated by S_w, is expressed in per cent, correlation of volume to volume, or saturation units. It is a certain water fraction that can be found in a certain pore space. Saturation as such is a relative amount of gas, water or oil in the rock pores, typically presented as a volume percentage, designated by V. Total water saturation is defined as the saturation type with the total porosity of the pore space. Effective water saturation is defined as the saturation type with the effective porosity of the pore space. Saturation without any specific qualification typically implies the effective water saturation type.

2.2.3 Permeability

Torsater and Abtahi, 2003) defined the porous medium permeability as the medium's capacity to transmit fluids. The high level of permeability provides for the smooth flow of fluids through the medium. The low level of permeability provides for the obstacles in fluid flow through the medium. Permeability depends on such parameters as fractures and size and shape of pore throats. A generally accepted permeability unit is Darcy, denoted as D or m^2 according to the unit system SI.

There are certain common situations encountered in the relations between permeability and porosity in the case of carbonate rock.

- Large pores of high volume are characteristic of vuggy rocks. The isolation of the vuggs in a microporous matrix predetermines low permeability (K <10 mD).
- The pore network is dominated with micro porous type. The rock of highly porous type predetermines negligible or extremely low level of permeability (K<1 mD).
- Well-connected and homogeneous character of pore network, especially cemented partially with oolitic grainstone creates other conditions. Moderate porosity of the rock type equal to 15 - 20 % predetermines high level of permeability (K>100 mD).
- Well-connected fracture network and the lowest level of porosity equal to 2 - 5 % predetermine good permeability.

Darcy law (eq.1) is the equation that makes it possible to calculate the medium permeability in milli Darcy units. **Q** denotes the fluid flow rate in the porous medium measured in cm^3/s. $\mathbf{P_2}$ and $\mathbf{P_1}$ are measured in atmosphere, being the applied pressures in the outlet and inlet of the core. A is the area or cross-sector of the fluid measured in cm^2. **L** is the core length measured in cm. The fluid dynamic viscosity is measured in centipoises (cP) and denoted as **μ**.

$$K = \frac{QL\mu}{A(P1 - P2)} \quad \text{Eq,1}$$

2.2.4 Wettability

Anderson (1986) defines wettability as the property of the fluid to tend to spreading over the rock or solid surface provided that other immiscible fluids are available. The non-wetting phase relates to the different immiscible fluid, while the wetting phase provides for the fluid spreading or adhering to the solid surface. According to Cuiec, (1984) the characteristics of the fluid and the nature of the rock are the factors that influence the wetting process of formation. Under the conditions of a solid surface contacting two of the immiscible phases, the attraction of one of the fluids is typically stronger than of the other one. The wetting phase is the phase that is attracted more strongly.

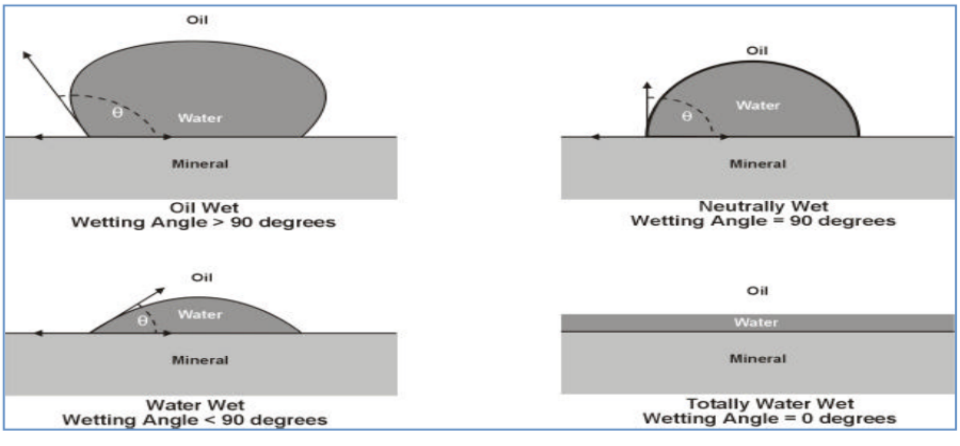


Figure 3. *Different wetting angles for various wetting properties. Formation Evaluation MSc Course Notes*

Figure 3 shows a range of different wetting conditions where **ϴ** - contact angle between interface of the water/oil/solid interface; the measurement is done through water Providing that water predominately makes the surface of the rock wet, the rock of the reservoir is considered to be water wet. The following condition are obligatory for making the rock water wet: 0° ≤ ϴ ≤ 90°

Providing that ϴ is next to 0°, the rock is defined as "strongly water wet".

Providing that oil predominately makes the surface of the rock wet, the rock of the reservoir is considered to be oil wet. The following condition are obligatory for making the rock oil wet: 90 ≤ ϴ ≤ 180°

Providing that ϴ is next to 180°, the rock is defined as "strongly oil wet".

Mixed and / or intermediate wettability is characteristic of rock. There is certain interdependence between the wettability and chemical or physical composition of rock. The oil phase composition is another factor that influences the wettability. The tendency of both phases to adsorption to the surface of the rock results in the intermediate wettability. However, the attraction of one phase to the surface always prevails over the attraction of the other. Heterogeneity or variation in chemical composition of the cementing-material surface of the pores, as well as the exposed surface of the rock, results in the mixed wettability. The mixed chemical exposure causes variability in the wettability conditions from point to point. A part of the solid surface is occasionally wetted by the water while the remaining part is wetted with oil (Dake, 1994; Green et al, 1998).

Figure 4 shows the wetting in pores model, water-wet case (left), mixe-wet case (center) and oil-wet case

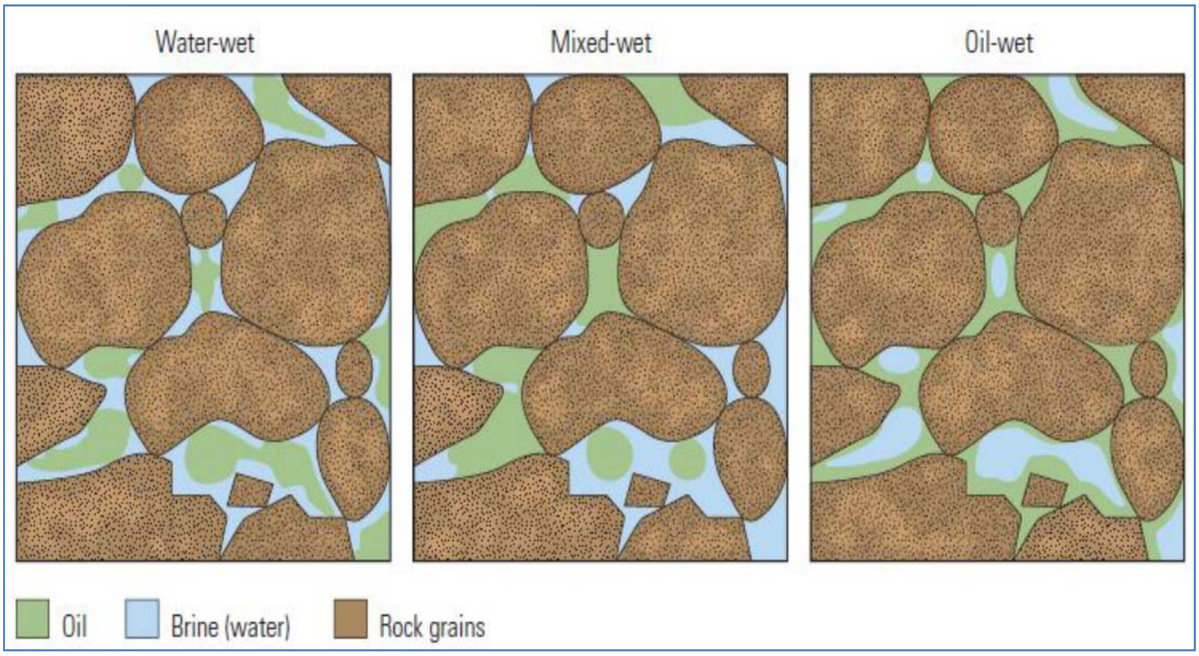


Fig.4. *The wetting in pores model, by Wael, A, et. al., (2007).*

2.2.5 Relative permeability

A strong function ascribed to the saturation phase is defined as relative permeability (S), demonstrated in the figure. The function between the saturation and relative permeability is a rock-fluid property and a function between wettability and rock properties, in particular the distribution of the pore size. Saturation of the petroleum reservoir rocks is typically done with more than two fluids, like gas, water or oil. Introduction of effective permeability occurs in case of availability of two or more fluids. According to Torsater and Abtahi, (2003) effective permeability is the capacity of transmitting fluids under the condition of saturation equal to less than 100 % peculiar to a porous medium. Phase relative permeability is the correlation between the phase effective permeability and absolute permeability.

The following equations express the relative permeability (denoted as K_r) of the gas, oil and water, where the relative permeability of the gas is K_g, the relative permeability of the oil is K_o, relative permeability of the water is K_w, measured in mD.

$K_{rg} = K_g / K_a,$ $K_{rw} = K_w / K_a,$ $K_{ro} = K_o / K_a,$

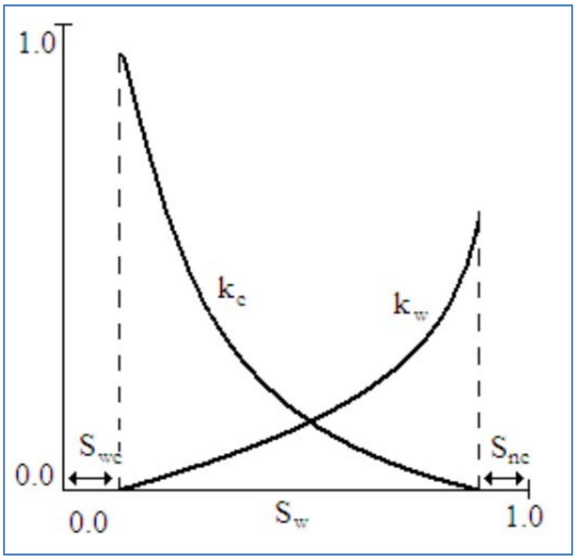


Figure 5. *Typical characteristics of relative permeability for a flow of two phases.*

2.2.6 Carbonate wettability

One of the most important parameters of the processes related to oil recovery is wettability, which exerts significant influence on the location, distribution and flow of water and oil throughout the production process in the reservoir (Hjelmeland & Torsaeter, 1980; Anderson, 1986; Anderson, 1987; Morrow, 1990). The middle of the pores of the water-wet uniform systems is occupied with the small droplets of resided oil while the narrowest pores are taken by water. The oil-wet reservoir is the place for the reverse distribution of fluid. The implemented evaluation aimed at determining the wetting state for various types of reservoirs proved that the majority of carbonate reservoirs are oil-wet neutral, approximately 65% of carbonate rocks are oil-wet, while about 12% are intermediately wet (Chilingar &Yen, 1983; Cuiec, 1994). Hognesen et al. 2005 claimed that according to the research data, from 80 to 90 % of the carbonate reservoirs around the globe are predominately oil-wet. According to

Treiber et al., 1972 who studied the fifty crude oils to measure their equilibrated water advancing contact angles, 84 % of all tested carbonate reservoir crude oil-water systems were oil-wet, 8 % were intermediate, and the other 8 % were water-wet.

2.2.7 Determining wettability through the contact angle method

The researchers proposed a lot of various methods meant for doing the measurement of wettability of fluid/rock systems including quantitative methods like contact angles, USBM method of wettability, forced displacement and imbibition (Amott). Anderson (1986) noted that wettability of a certain surface can be measured with the contact angle method while the average core wettability is measured with the USBM and Amott methods.

Artificial cores and pure fluids predetermine application of the contact angle method for measuring the wettability, as well as examining the influence of pressure, brine chemistry and temperature on wettability. The most widely used contact-angle measurement methods among a large variety of them are the method of a modified form of the sessile drop and the method of the sessile drop. They are applied in the petroleum industry. The method of the sessile drop uses one polished flat mineral crystal. The method of a modified form of the sessile drop uses two polished flat mineral crystals which are located on adjustable posts in parallel to each other, as seen in Figure 6.

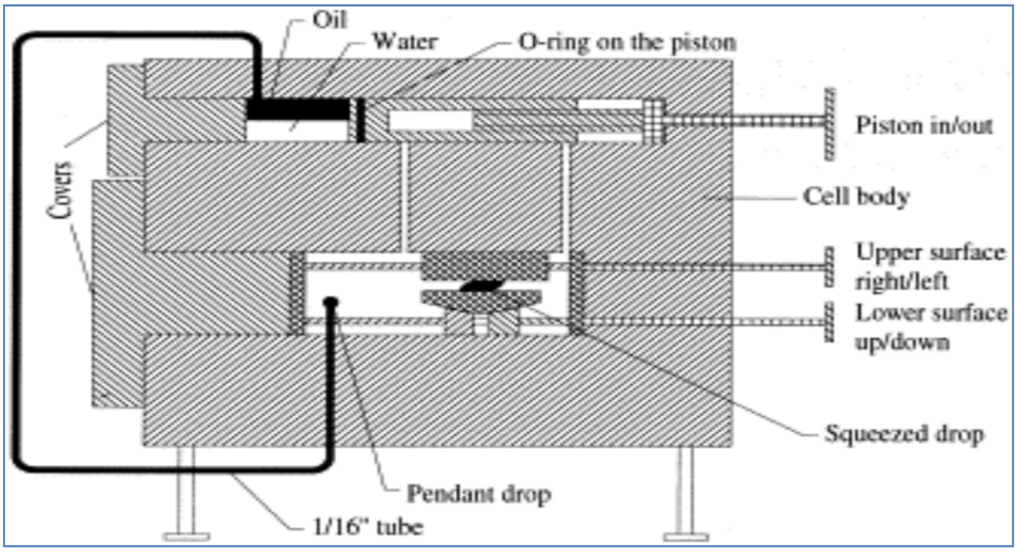


Fig.6. *A cross-section of the contact angle cell (Hansen, Hamouda, & Denoyel, 2000)*

2.3 Factors that affect the rock wettability alteration

Spontaneous water imbibition is caused by altering the wetting state for water-wet from oil-wet. In such cases, there is a turn of the capillary forces from the barrier negative to positive ones. There are thermal and chemical methods of wettability alteration.

There are a number of factors related to the porous media and two immiscible fluids that have an impact on wettability. They include pore size, pore geometry, pore structure, brine composition, temperature, salinity, rock mineral composition, oil composition and pH. The effect of those factors on wettability is different; therefore, it is complicated to study those parameters of wettability separately. A provisional list of interactions that affect the wettability attainment comprises surface precipitation, polar interactions, ion binding, and base/acid interactions (Buckley et al., 1998).

2.3.1 Fluid – mineral interactions

It has been proven by researchers that organic matter as a component of crude oil comprises asphaltenes and resins. They are abundant in polar compounds of basic and acidic nature (Anderson, 1986; Buckley & Liu et al., 1998). According to Buckley at al., there are two reasons for the importance of wetting alteration for the crude oil composition. They are:

- oil is an environment of solvent nature;
- polar components demonstrate surface activity.

Researchers have identified the following wetting alteration mechanisms implemented by crude oil:

1. Base/acid interaction that takes place between the interfaces of opposite charge;
2. Polar interactions that take place without water between the solid and oil;
3. Specific or ion binding interactions that take place between the charge sites and multivalent ions;
4. Surface precipitation that is under the influence of oil as a solvent required for heavy fractions.

2.3.2 Mineral composition

As a result of observation during the experiment, the researchers concluded that the type of rock influences the peculiarities of changes to the rock wettability caused by polar compounds. Treiber et al. in 1972 and Chilingar and Yen in 1983 proved that sandstones are more water-wet than carbonate rock. According to Pierre et at., (1990) the carbonate surface can adsorb acidic groups with negative charge and has positive charge under basic conditions. It is complicated to alter silicate based minerals and increase their oil-wetness. Protonation of basic functional groups occurs at lower values of pH, such as $pH<2$; thus, they get positive charge at the interface of water or oil leading to the attraction to silicate surface with unlike charge (Zheng, 2001).

Another way of altering the quartz wettability is supplementing water solution with multivalent ions. For instance, dissociation of sodium laurate into laurate ions with negative charge is done when it is added to the aqueous phase. Laurate ions carry like charges and are not able of adsorbing onto the quartz surface, but adsorption of those ions onto the surface can be promoted if Mg^{2+} or Ca^{2+} is added (Zheng, 2001). According to Tissot and Welte,1984 such basic amino acids as C6 H14 N2O2 (Lysine), that can be found in various geological environments, tend to adsorption on silicate minerals and are water-soluble. Resins and asphaltenes, being the crude oil heavy ends, contain surface active components as well. Thus, they can alter wettability, adsorbing on clay and quartz minerals (Kokal et al., 1994).

Series of researches carried out by Hamouda and his colleagues with oil, water, and calcite demonstrated that there are the following factors that affect the wettability of calcite mineral surfaces: ions composition, temperature, pH, oil composition, fatty acids chemical structure, and characteristics of rock surface (Rezaei Gomari et al., 2006; Karoussi and Hamouda, 2007; Hamouda and Karoussi, 2008; Chukwudeme and Hamouda, 2009).

Numerous researchers concluded that there is considerable effect of $SO_4{}^{2-}$ ions and Mg^{2+} on the final wetting state of reservoir rocks that are water-flooded (Petrovich and Hamouda, 1998; Rezaei Gomari et al., 2006; Karoussi and Hamouda, 2007; Hamouda and Karoussi, 2008; Chukwudeme and Hamouda, 2009). The experiments of Petrovich and Hamouda, 1998 showed a decrease in the concentration of magnesium ions and an increase in the concentration of calcium ions in the produced water if E Ekofisk field samples in the chalk reservoirs are injected with seawater. The researchers hypothesized the exchange processes or adsorption on a field scale between Ca^{2+} in calcite and Mg^{2+} in seawater. Provided that $SO_4{}^{2-}$ ions are available, the change of modified calcite surface wettability occurs owing to potential decrease in the present active sites on the surfaces of calcite nature. Besides, one of the possible reasons can be a displacement process of different carboxylate ions of the tested fatty acids after pre-adsorption (Rezaei Gomari et al., 2006). Exchange processes and /or adsorption take place if Mg^{2+} and $SO_4{}^{2-}$ ions are available, then such change is correspondent to alteration of calcite particles' ζ potential (Rezaei Gomari et al., 2006).

The results of preliminary imbibition test demonstrated the increase in concentration of sulphates in the imbibing fluid and their effect on the improvement by of oil recovery on chalk and oil-wet carbonates due to altering the wettability (Zhang & Austad, 2005). Among the ionic species appropriate for brine analyses there is Carbonate ($HCO_3{}^-$), Magnesium (Mg^{2+}), Potassium (K^+), Iodide (I^-), Sodium (Na^+), Chloride (Cl^-), Calcium (Ca^{2+}) and $SO_4{}^{2-}$. One more determining ion potentially capable of improved oil recovery (IOR) in chalk reservoirs is $SO_4{}^{2-}$ or the Anion Sulphate, which is supposed to act with cations Ca2+ and Mg^{2+}, since individual anion $SO_4{}^{2-}$ cannot affect spontaneous imbibition (Zhang, et. al., 2007; Tina, et. al., 2009).

2.3.3 Temperature

There are the two following effects of the increase in temperature which revolve themselves to making the core more wet with water (Anderson,1986):

- increase of temperature results in the decrease in the contact angle and IFT, if they are measured in the water;
- increase of temperature results in the corresponding increase in the solubility of compounds that are able to alter wettability in oil.

The preceding experiments and researches showed that the temperature in the reservoir tends to conform either to the local or regional geothermal gradient. Its normal value is approximately 1.6 ˚F/100 ft. It results from the considerable thermal capacity peculiar to the rock matrix. It typically comprises presumably 80 % of the volume of the bulk reservoir. Furthermore, in most instances a considerable area within the reservoir envisaged for heat transfer conditions is isothermal.

According to the results of the experiments, increase in temperature (T) causes increase in oil recovery (OR) and imbibition rate. It can be explained with the considerable adsorption of

Calcium (Ca2+) and Sulphate (SO4, 2) on the chalk surface (Idowu et. al., 2011). Besides, the increase of oil recovery within the reservoir depends on low salinity of water, temperature, and the potential of determined ions.

Other researches carried on the basis of chalk rocks in reservoirs under the conditions of high temperature were aimed at observing the effect of temperature on the results of oil recovery. They demonstrated that the effect of the temperature of the injected fluid is not the only factor that influences the ultimate oil recovered and the rate of oil recovery. One more factor is the difference between the reservoir temperature and the temperature of injected fluid (Hamouda & Karoussi., 2008; Yousef et. al., 2011). If the temperature is above the critical one, its effect is adverse. The relative permeability, denoted as Kr, tends more to oil-wet type of behaviour. If the temperature is above 80 ˚C (130 ˚C during the test), there is a shift of relative permeability intersection towards lower water. Therefore, there is less oil recovery.

2.3.4. Pressure

According to Anderson,(1986), the importance of the pressure factor is less significant than that of the temperature; therefore, there is no direct correlation between wettability and pressure .

2.3.5 Crude oil components

Asphaltenes and resins were acknowledged as major crude oil fractions that affect the wettability in the rock of porous type (Buckley et al., 1996; Xie et al., 2000; Buckley, 2001). They are abundant in such polar elements as sulphur, nitrogen, and oxygen as NSO compounds. The experiments demonstrated that wettability change is less affected by a certain group of polar components from the resin and asphaltene fractions, which are mostly if basic and acidic nature (Cuiec, 1984; Anderson, 1986; Crocker & Marchin, 1988). According to Buckley, 2011 and his colleagues, there are four mechanisms for altering the wetting by crude oil, which are linked to the acid number, brine composition, content of asphaltenes in the oil and base number.

1. Binding of ions. Multivalent ions including divalent ones in the brine tend to binding to the brine/oil interface and the mineral surface creating bridges.
2. Base / acid interactions between the sites with opposite electrical charge.
3. Precipitation of the surface. If the oil acts as a bad solvent for heavy fractions, it results in asphaltene precipitation.
4. Polar binding. In case there is no water in the porous environment, the process of adsorption most probably happens between the polar atoms of molecules (NSO compounds) and the polar surface sites.

According to Buckley and Liu,(1998) there is a dependency between the ability of crude oil to change the wettability, the rock material (carbonate or sandstone rock) and oil G-AB profile, including the acid number, the base number and the API gravity.

2.3.6 Multivalent cations

Researchers have proved that promotion of oil wettability, as well as enhancement of adsorption on the mineral surfaces even if the concentrations are low, can be done with multivalent ions through reduction in solubility of surfactants as part of the crude (Anderson., 1986; Bavière., 1991). Suijkerbuijk and Hofman et al. (2012) concluded that the extent of changing the wettability towards greater oil-wetness is dependent on the kinds of cations available throughout the process of water formation at the COBR system aging.

2.3.7 Clays

Clays are the silicates of hydrous aluminium type, the molecular lattice of which can contain iron, sodium, potassium, and magnesium in increasing prevalence. Minerals of clay make up 40 % of minerals available in sedimentary rock sediments. Clay has the following properties:

- clay is chemically reactive;
- pore grain surfaces are the typical location of clay;
- the surface area of clay is mostly large and specific.

There is the direct effect of clay on the enhanced oil recovery (EOR) processes, as clay influences the permeability of the medium (K) or changes the ionic state of resident fluids. Lake documented that one of the most outstanding features of clay is its capacity of exchanging cations with fluids under the conditions of the pore space.

2.3.8 Brine concentration

An emerging technology of EOR resulted from the injecting the brine of perfectly selected composition of ions into the carbonate reservoir. It is aimed at the improvement of microscopic sweep efficiency and decrease in the saturation of remaining oil (So). Injection of low salinity brine into the reservoir causes the improvement of oil recovery up to 15 %. However, the researchers have not settled the exact mechanism of LSB (low salinity brine) in reservoirs yet.

It was found out by an experimental approach that the rock wettability (W) is modified and water-wet type of behaviour is increased under the reduced or ambient conditions while applying dead fluids and adding sulphate at the concentration of the sea-water (Webb et al., 2005). The ability of low salinity water to change the Kr (relative permeability) is considered by Idowu (2011) to be one of its most important effects. Such a change results in the improvement of reservoir wettability and its change to a state of greater water-wetness. One more conclusion drawn on the basis of experiments is that the role of potential determining ions in changing the wettability in carbonates is essential. Moreover, the adsorption of Sulphate ($SO_4{}^{2-}$) charged material of carboxylic nature is facilitated by the adsorption of anion Sulphate ($SO_4{}^{2-}$) onto chalk surface. It is done through altering the surface chalk if SO4 2- is available resulting in the increase in cation Ca^{2+} concentration which is close to the chalk surface. That change serves as a facilitator in the reaction with the carboxylic group.

According to Zahid et al., (2010) the performance of water flooding depends on the composition of the brine solution injected. There was another research carried out on chalk in order to make conclusions regarding IOR on chalk with the help of surfactant solutions and subsequent usage of modified sea water. The results of the research demonstrated that the reason for enhancement of oil recovery is the change of wettability towards the conditions of more intensive water wetting (WW). The laboratory work of Bagci et al. was aimed at observing the dependence of oil recovery on brine composition in the process of water flooding with the use of KCl (Potassium Chloride), NaCl (Sodium Chloride), and CaCl2 (Calcium Chloride) brines.

The salinity mechanisms are typically connected to oil composition, the availability of clay minerals along with the availability of formation water if the concentration of such divalent cations as Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) is high. The range of salinity level of water at low salinity level can be from 1,000 to 5,000 ppm (part per million) (Yousef et. al., 2011).

The conclusion drawn out of the experiment was the following: increasing the content of sulphate ion in the effluent brine is the confirmation of the anhydrite dissolution for three types of rock, i.e. calcite, dolomite and eolean sandstone (Pu et. al., 2010).

According to Zhang et al., (2007) both field tests and laboratory experiments demonstrated that injecting brine of different salinity levels into reservoir cores caused different effects on oil recovery. Significant increase in the oil recovery was noted at injecting low versus high salinity brine under the conditions of secondary recovery. The increase in oil recovery is closely connected to the increase in pressure drop for both tertiary and secondary modes across the core. Considerable reduction of residual oil saturation (Sor) and immense enhancement of oil recovery can be obtained if the total dissolved solid (TDS) of the injected water is lowered and the quality of its ionic composition is taken into account.

2.4 Wettability Alteration Mechanism

2.4.1 Chemical reactions typical of chalk

If a piece of chalk gets into reaction with a drop of dilute hydrochloric acid, there are carbon Dioxide bubbles (CO2) as the calcite reacts with the acid. It is a typical fizzle reaction of limestone. Upon the application of heat, decomposition of the calcium carbonate as a component of chalk to calcium oxide or lime takes place. It is an easy way to identify limestone; hence, geologists typically get a bottle of dilute hydrochloric acid to go into the field.

2.4.2 Acid number

Zhang and Austad in 2005 and Austad in 2008 carried independent studies to conclude that the most essential wettability parameter for chalk is the acid number of the crude oil. Moreover, there is a decrease in AN (the acid number) of the crude oil if there is an increase in the reservoir temperature. The process is caused by decarboxylation under the conditions of high temperatures. Thus, the oil-wetness of carbonate reservoirs is higher as the reservoir temperature gets lower. The opposite process takes place when it goes about sandstone. One of the experiments provided for using model Ekofisk formation water as initial water available in the cores and experimental carried seawater as the base imbibing fluid. The subsequent observations were made under the conditions of various temperatures in the range from 40 – 20 ˚C and the acid numbers of the cores aged in crude oils were in the range from 0.17 to 2.07 mg KOH/g oil:

- spontaneous imbibition is possible if the water-wet chalk surface fraction exceeds 0.6;
- oil recovery and the new wetting index are in good relationship;
- dissolution of the cationic surfactant, the type [R-N(CH3)3]+, is significant in the imbibing fluid IOR, in particular if the conditions are close to neutral wetting;
- a wettability modifying effect of sulphate available in the imbibing fluid becomes apparent under the conditions of low water-wetness.

Alteration of calcite surface to oil-wet condition is done with the help of fatty acids if water film is available (Rezaei Gomari & Hamouda, 2006). Changing of wettability depends on water composition, pH and the structure of fatty acids. Contact angle measurements indicated that the absorption from oil phase Q (n-C10) of stearic acid (long chain fatty acid) in the calcite/water/oil system onto the calcite surface is strong.

Although wetting properties of chalk are considered to be an essential factor, the acid content in the crude oil that is specified with the acid number is of greatest importance (Hognesen et. al., 2005). Therefore, carbonate reservoir under the conditions of high temperature typically contains crude oils the acid number of which is lower and consequently, the behaviour is closer to water-wet.

2.4.3 Multiple-Component Ionic Exchange (MIE)

Multiple-component ionic exchange (MIE) takes place between the clay mineral surfaces, absorbed components of crude oil, and cations found in the in-situ brine. Understanding of low salinity in the context of multiple-component ionic exchange provides for the consistency between the MIS mechanism, chemistry of associated water and enhanced oil production. Multiple-component ionic exchange between the injected brine and clay material influences the oil recovery improvement caused by injecting water of low salinity (Lager et. al., 2003).

Tang and Morrow presented certain examples of injecting brine of low ionic strength into both field and outcrop samples in order to improve oil recovery (1997, 2002). The researchers specified the conditions required for improvements in oil recovery, in particular initial water saturation (S_{wi}), the type of rock and oil, composition of the injected water and formation. It should be noted that the list is not exhausted. Moreover, the researchers demonstrated that the implemented displacement tests and laboratory tests aimed at determining the relative permeability (Kr) applied synthetic formation water (injected and formation water), not solely formation water.

2.4.4 Migrations of fines

According to the research outputs, there is migration of the released fines with the fluid flowing. Afterwards, such fines are captured at pore constrictions and pore throats and consequently they cause the formation damage. Lager et al. (2006) carried out experiments that proved that clay is undisturbed retaining their oil-wet characteristics if HSB (high salinity brine) is available; thus, the displacement efficiency deteriorates. Clay particles in contact with water of low salinity separate from the pore surface. Various phenomena contribute to the improvement of oil recovery, including availability of fines migration, pH increase or alkalinity, MIE at the period of flooding with water of low salinity (Ashraf, Hadia, & Torsæter, 2010).

2.5 Spontaneous imbibition

According to Brownscombe and Dyes (1952) capillary or spontaneous imbibition is an essential mechanism of recovery in reservoirs of water-wet fractured nature (1952). It can also be defined as the process of spontaneous uptake of fluid into the solid of porous type, when the initial fluid is expelled from the porous medium and subsequently substituted with imbibing fluid. Capillary forces make the water flow in the medium of porous nature, causing water imbibition.

Imbibition is able to affect the real sweep and hinder or advance movement of water; thus, its importance in the water drive reservoir cannot be overestimated. The absorption process without any pressure that drives the phase in the rock is referred to as spontaneous imbibition. The same rock can imbibe oil and water. The oil imbibes under the condition of low in-situ oil saturation (S_o) and displaces excessive water from the rock grains surface. The water imbibes under the condition of low in-situ water saturation and displaces excessive oil. Evaluation of the rock wettability implies determining the phase which imbibes at the larger scale. Imbibition tests are meant to get the comparison between the potentials of oil and water into the rock.

The importance of imbibition is great in various types of recovery processes, namely steam injection through the condensed water imbibition, alternate injecting of gas and water, or water flooding at heterogeneous reservoirs (Tabary et. al., 2009). The characteristics of capillary pressure of imbibition (P_c) control the oil drainage from the surfaces of oil-wet pores and interactions of fracture matrix, thus being the key to evaluating the recovery properties of fractured carbonates. Therefore, it is possible to identify any type of modifications in wettability towards the system of greater water-wetness in the capillary pressure data of imbibition (Webb et. al., 2005).

Other researchers consider spontaneous water imbibition into the carbonate matrix blocks as the primary mechanism for the improvement of oil recovery implemented with the process of water flooding (Zhang & Austad, 2005). The rate of oil recovery is significantly influenced with the imbibition tests that change the concentration of sulphates for carbonates. If the reserves are kept in matrix blocks of extremely low permeability in the fractured reservoirs, brine spontaneous imbibition into the reservoir rock resulting in oil recovery grows in importance. Tabary et al.2009 documented that there is the dependence of consequent oil recovery from the rock matrix under the influence of aquifer drive and water injection on the comparatively slow process of spontaneous water imbibition.

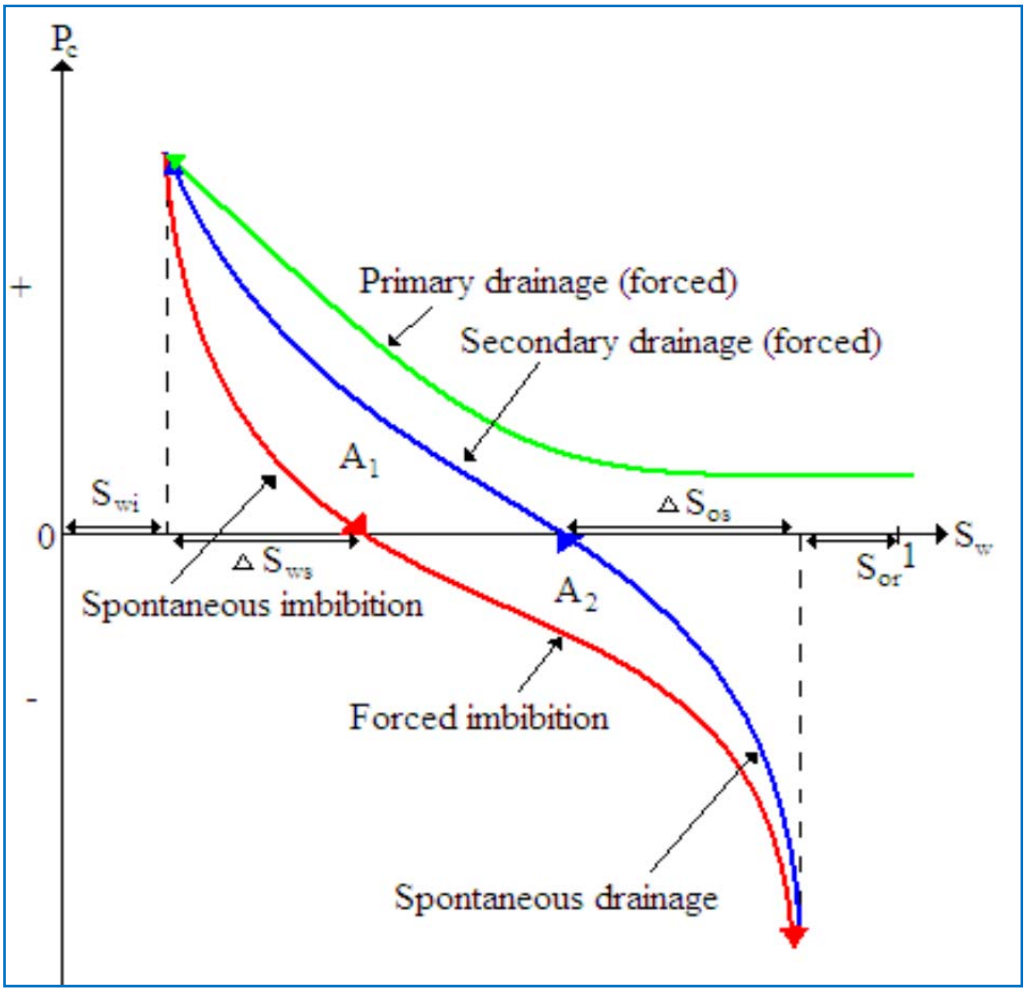


***Figure.** 7. Water saturation vs. capillary pressure, forced and spontaneous imbibition and drainage capillary pressure curves.*

2.6 Forces of Displacement

2.6.1 Capillary pressure and transition zone

A homogeneous formation shows a transition zone from high water saturation (Sw) seen at the bottom on blue curves to the high oil saturation (So) at the top (Wael et. al., 2007). It is seen in Figure 7. The origin of the saturation transition is in the capillary pressure denoted as P_c. It is the difference between the pressure of water and oil at the interface which can be presented in the equations :

$P_c = P_{nw} - P_w$, eq.2

P_w is the wetting phase pressure; P_{nw} is the non-wetting phase pressure

$P_c = g*h*\rho$ eq.3

g is the acceleration of gravity; ρ is the difference in the density of phases; h is the capillary rise height.

3. $$Pc = \frac{2\gamma\cos\theta}{r} \qquad \text{eq.4}$$

r is the capillary inner radius; ɣ is the interfacial tension; θ is the contact angle.

The forces in the capillary tube going from the surface of water wetting (WW) result in the left-side rise of water and oil displacement. However, the oil pushes water down which is seen on the right side providing that the inner surface of the tube is oil-wetting (OW). The capillary radius is inversely proportional to the capillary pressure as well as the wetting forces. The weight of fluid that is being displaced from the interface of the bulk fluid along with the wetting forces balance determine the capillary rise, denoted as h. In a porous formation the capillary pressure between oil and water equals to zero and there is a definition of a FWL or free water level.

Porous rocks are characterized with the distribution between the pore throat size and pores. It is similar to the capillary tubes distribution, being relevant at any height located above the FWL. Thus, a part of the size distribution capable of sustaining water at the certain height will be saturated with water.

If the height is greater, higher capillary pressure denoted as Pc is provided by the oil buoyancy in the water. It forces the water out of small-size voids. The contact of water or oil in the water-wet formation seen on the left side occurs above the FWL. It signifies that forcing the oil into the large-size pores requires pressure. The contact in the oil-wet formation seen on the right side occurs below the FWL. It indicates that forcing the water phase into the large-size pores requires pressure. The contact of oil and water (OWC) shows the division of the zones. One that predominantly contains oil is separated from the other one with water mostly. (Wael et. al., 2007).

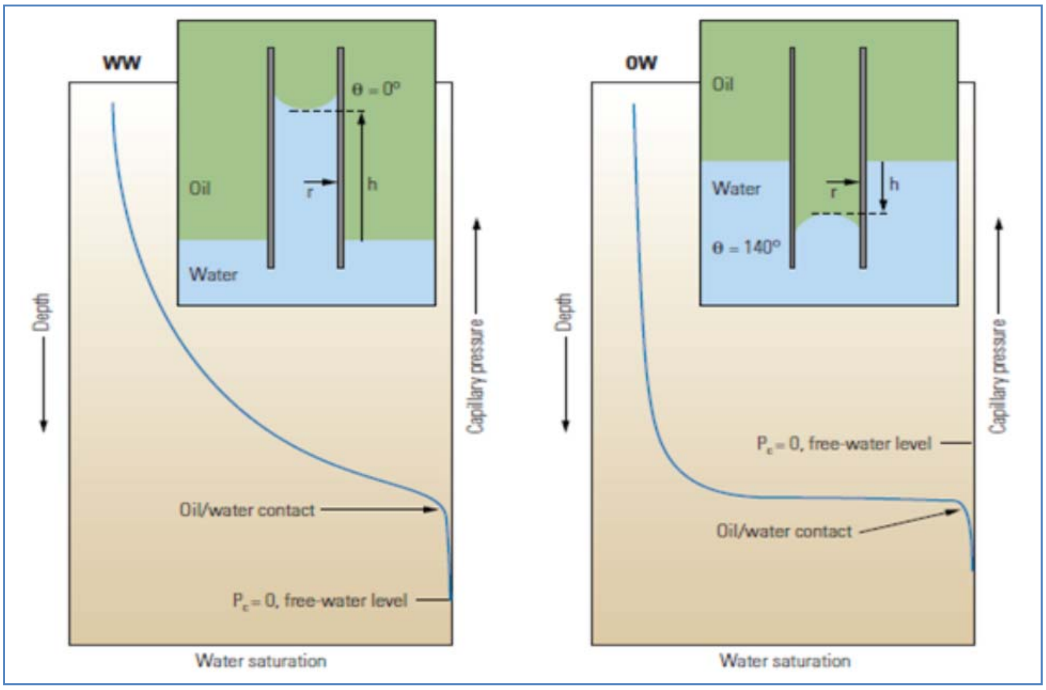


Figure.8. *Formation of the transition zone under oil-wet (OW) and water-wet (WW) conditions (Wael et. al., 2007).*

$$P_c \equiv p_o - p_w = \sigma_{ow}\left(\frac{1}{r1} + \frac{1}{r2}\right) \qquad \text{eq.5}$$

Namba and Hiraoka presented a definition of the capillary pressure force (P_c) as the difference between oil phase pressure (p_o) and the water phase pressure (p_w). It is demonstrated in the above mentioned Laplace equation, where p_w is the water phase pressure; p_o is the oil phase pressure; σ_{ow} is the interfacial tension between water and oil; r1 and r2 are the curvature radii of the interface. The conventional definition of the capillary pressure is the following: $P_c \equiv p_o - p_w$. The result can be either negative or positive. It depends on the phase of the wetting phase. Positive capillary pressure predetermines oil as a non-wetting phase and water as a wetting phase.

Rocks of low permeability typically get higher absolute capillary pressure in comparison with rocks of high permeability (Tabary et. al., 2009). Positive capillary pressure predetermines water-wet rocks, while negative capillary pressure provides for oil-wet rocks. Determination of values for the curvature radii is not possible in the porous media with high complexity of pore geometry. Therefore, determining the capillary pressure can be implemented only by an experiment.

The factors that affect capillary pressure in a medium of porous nature include the wetting condition, saturation history, saturation, pore geometry and pore size, and interfacial tension of immiscible fluids. Capillary pressure determines the distribution of saturation and either facilitates or disrupts the fluid displacement in the porous environment.

Taking into consideration the process of core flooding, the water saturation at the out-flow end is denoted as $P_c(S_{we}) = 0$, while the boundary condition is typically determined as Pc = 0. Sufficiently low S_{we} in the the case of oil-wetness of the core may distort the average saturation of water in the core at the flooding end. Other reasons may include the short core and low flow rate, since the capillary forces are to be overcome with high viscous forces at the remaining part of the core. It is known as capillary end effect. The coordination and interplay of all involved forces determines the flooding process outcomes. Therefore, the relative magnitude of the involved forces is of great importance for the recovery caused with the core flood. The ratio of the viscous forces to the capillary forces is known as the capillary number (Nc).

According to the researches carried out by numerous authors, reducing of the residual saturation subsequent to the water flood can be done through the increase in the capillary number to the value that exceeds the critical one. The non-wetting phase is, therefore, displaced. It is possible to increase the capillary number by different methods, for example by interfacial tension reduction, increase in the speed of the displacing fluid, increase in the viscosity of the displacing fluid, or changing the wettability (Green & Willhite, 1998). It should be noted that increase in the speed is a complicated task in the field, while the mobility control and altering the interfacial tension are doable in the field.

2.6.2 Gravity forces

Domination of gravity forces is possible under the conditions of decrease in the relative effect of capillary forces. According to Willhite, gravity forces result from the difference in density of the phases (1986). The following equation is applicable to the description of gravity forces:

$$\Delta P_g = \Delta\rho * g \sin\alpha, \qquad \text{eq.6}$$

where α is the dip angle of the formation; ρ is the difference in density of two phases; ΔP_g is the gradient of pressure caused by gravity.

The equation demonstrates that large formation dip and larger difference in density of the phases correspond to more severe gravity forces. The buoyancy forces magnitude is determined by the height of the fluid column and the difference in densities of two fluids. Mixtures of immiscible fluids are their permanent locations; however, the capillary forces magnitude determines their relative effect on the fluid flow in the conditions of the porous medium. The capillary forces magnitude is dependent on wettability and IFT.

2.6.3 Viscous forces

Green and Willhite, (1998) relate the viscous force to the pressure drop which is caused by the fluid flow in the medium of porous nature. The definition of viscous forces in the single-phase porous media can be given on the basis of Darcy’s law that includes the concepts of velocity, porous medium permeability, and the pressure gradient under the effect of the viscous forces. mentioned that determining mobilization on the two-phase settings as well as phase trapping is frequently done by the combination of the viscous forces and capillary forces.

2.7 Parameters that affect imbibition

Spontaneous imbibition is under the influence of certain fluid properties including viscosity, IFT and density, as well as other parameters such as wetting state, permeability, heterogeneity, and fluid saturations (Mattax & Kyte, 1962; Cuiec et al., 1993; Cuiec et al., 1994; Schecter et al., 1994). The most important of the above mentioned parameters are briefly discussed below

2.7.1Wetting State

A curved interface between the water and oil occurs if water and oil are simultaneously on the same surface. It is possible to determine the contact angle between the oil and water towards the solid at the triple point at which water, oil, and solid get in contact. The measurement of a contact angle is done through the phase of water. It is typically within the range of 0 ^{0} and 180 $^{0.}$ The wetting state is defined as preferentially oil-wet if the contact angle is in the range between 105-120 ^{0} and 180 ^{0}. It is defined as predominantly water-wet if the contact angle is in the range between 0 ^{0} and 60-75 ^{0}. It is defined as neutrally wet or intermediate if it is between those two mentioned ranges (Anderson, 1987). Cut-off values for the contact angles may differ among different researchers (Morrow, 1976; Chilingar & Yen, 1983).

According to the conclusions drawn by Zhou et al.,(2000) on the basis of the experimental work carried out on Berea sandstones, the sensitivity of imbibition rate to wettability is high. Increase in water-wetness results in the enhancement of the imbibition rate. The imbibition tests performed on the outcrop chalk demonstrated the decrease both in the imbibition rate and ultimate recovery related to the increase in the ageing time. The factor the increased ageing time accords with the greater oil-wetness.

2.7.2 Permeability

The role of imbibition in the reservoirs of low permeability has been defined by the researchers as the one of an essential recovery mechanism. The experiments demonstrated that the oil recovery for chalk with low permeability is efficient and fast if implemented by water imbibition as the chalk is strongly water-wet (Cuiec et al., 1994). The increase in the core permeability results in the increased imbibition rate (Al-Lawathi & Saleh, 1996). According to the observations of Allan and Sun, the increased permeability for diatomite, chalk and siliceous shale leads to a moderately increased ultimate recovery (2003). The gravity dominated imbibition which adheres to Darcy's law leads to the increased permeability and consequently, the higher rate of flow.

2.7.3 Fluid Density

The correlation of oil density with the factor of recovery in the fractured reservoirs has been reported to be moderate positive (Allan & Sun, 2003). One of the significant recovery factors is gravity (Iffly et al., 1972); Austad & Milter, 1997).

2.7.4 Viscosity

The viscosity of non-wetting and wetting phases affects critically the imbibition extent and rate (Ma et al., 1997; Zhou et al., 2002). Experiments based on the water-wet sandstone demonstrated that there is inverse proportion between spontaneous imbibition and geometrical meaning of water and oil viscosity (Zhang et al., 1995). Theoretically, it was verified in 2002 by Zhou et al.

2.7.5 Heterogeneity

Numerical prediction of the curve of actual recovery of oil was considered to be impossible owing to heterogeneities of small scale in the core permeability (Hamon & Vidal, 1986). As far back as 1984, Torsaeter studied the potential effects of micro heterogeneties concerning the pore structure, roughness of the surface in core plugs (Ekofisk field), and permeability. The properties of fluid (Speight, 1999) and rock (Torsaeter, 1984; Hamon, 2000) in actual reservoirs may be different depending on the peculiarities of location.

2.7.6 Interfacial tension (IFT)

IFT or interfacial tension can be defined is work required in order to increase the area of the surface by one unit. According to Mork, (2001) it is also force per unit of distance that is parallel to the interface which is placed perpendicularly to any line of the interface. IFT between immiscible fluids is the energy free of surface between such immiscible liquids as water and oil.

Reduction of the oil-water interfacial tension while carrying out imbibition tests on chalk requires the use of surfactants (Austad & Milter, 1997). Availability of surfactant solutions in comparison with pure brine enhances the significant decrease in the imbibition rate. The rock-fluid and fluid-fluid interactions govern the mechanics of reservoir fluid that involves the flow the water, gas and oil in the porous medium. Both of the components of fluid-fluid interactions, i.e. miscibility aspects and phase behaviour, are dependent on the IFT under the operating thermodynamic conditions of temperature, pressure and composition. The water-oil IFT provides for the interconnection between adhesion and wettability.

Rock wettability is the determinant factor for relative permeability and capillary pressure. They are also dependent on the location and type of distribution of gas, water and oil phases that is determined by the coefficient of spreading. This coefficient varies with the IFT of the gas/oil/water interfaces. Thus, it can be concluded that the majority of parameters governing the trapping mechanisms and flow behaviour depend on the interfacial tension at the interfaces between gas, water and oil phases. So, the peculiarities of water, gas and oil IFT in the reservoir conditions are to be studied and observed.

2.7.7 Boundary conditions

The rate of oil recovery is dependent on the boundary conditions of matrix blocks. However, there is no dependency of ultimate recovery for water-wet rocks on the boundary conditions (Hamon and Vidal, 1986).

2.7.8 Thermodynamic conditions

Rao (1999) summarized the effect of the temperature rise in the literature review. Such rise has an influence on the majority of parameters of fluid low in the porous medium. The increase in temperature results in the increased water-wetness of carbonate rock.

2.7.9 Initial water saturation, S_{wi}

Having done numerous experiments related to Berea sandstones, Zhou et al., 2000 have reached the conclusion that a 15 – 25 % decrease in the saturation of initial water leads to the reduction of water-wetness (2000). The wetting state has a strong effect on the rate of imbibition, which is also affected by the saturation of initial water. Jadhunandan and Morrow (1991) reported the contradictory results of observations . Altering the wettability can be a determining process for the imbibition rate, although saturation of initial water in chalk that is in the process of wettability alteration has insignificant effect on the process of imbibition (Standnes & Austad, 2000).

2.7.10 Chemical Composition

According to Anderson, (1986) certain components of crude oil such as resins and asphaltenes may enhance the alteration of the initially water-wet rock to a more oil-wet state. If chalk is clean, it is originally water-wet. However, of the pores are invaded by oil, there is rupture of water film and the active surface crude oil components deposit on the rock (Standnes & Austad, 2000). Madsen et al. refers such surface active components to the compounds of polar organic nature such as carboxylic acids (1996). According to Iffly et al., 1972 a critical parameter for the process of spontaneous imbibition is the chemical composition of the imbibition fluid.

3. Water Flooding

The access to the total reservoir oil capacity provided by the primary recovery is minor. The techniques of secondary recovery are intended at the increase in the productivity to at least a third. The tertiary recovery ensures the enhanced oil recovery and enables the extraction of up to 50 % of the original oil content of the reservoir. The amount depends on the peculiarities of the EOR process and the reservoir itself. The increase in production can be obtained if the pressure maintenance or the pressure from the water drive declines. It can be done through the water flooding techniques which imply injecting the water through injection wells in order to ensure pushing the crude oil in the direction of the producing wells.

Water-pumping into the productive layer is done through the bore holes at the pressure of injection. The volume is the same or exceeding the volume of extracted oil. The level of the formation energy is optimum in the deposit. The prolonged original lifetime of the oil well ensures the considerable reduction in the number of drilling operations and subsequent reduction in the oil cost. Improvement of oil recovery or IOR in the oil reservoirs can be done through the water flooding technique which is widely used. However, it is always largely designed not taking into consideration composition of the injected brine. The only exception is the necessity to avoid the formation damage. Altering the composition of the injected brine is capable of recovery improvement. Jerauld et. al., 2006 claims that water flood recovery can be optimized through the variability in the composition of the brine. Webb et al. in their turn demonstrate on the basis of their research that the water flooding recovery is affected with the composition of the injected brine within the clastic reservoirs.

3.1 Advantages of the Water Flooding Process

The most efficient method of oil recovery in the reservoir is water flooding. The major preconditions that influence the efficiency of water flooding process are the following:

- availability of water, its low price;
- the ability of water to serve as an effective injectant so that the oil of light gravity could be displaced with the oil of the medium gravity;
- oil-bearing formations are easily injected with water;
- the economics of water flooding is more favourable in comparison with other methods of EOR since it requires fewer operating costs and lower capital investment.

The considerably lower requirement for capital ensures higher profitability of the water flooding method. There are certain cases which stipulate for considering the composition of injected water and result both in the increased recovery of oil and prospective rise of the economic profitability of the water flood method.

Numerous laboratory studies on the core flood have demonstrated the effect of water flooding on the increase in oil recovery with the usage of low salinity water as opposed to produced water of high salinity or seawater (Webb et al., 2004). The improvement of the oil recovery is accounted for the removal of clay constituents under control and / or effective changes in wettability.

3.2 Water Flooding of Low Salinity

3.2.1 The proposed chemical mechanism for low salinity

In accordance with the results of research carried out by Alotaibi Nasr-El-Din in 2009, there is the following classification of saline water related to the levels of salinity concentration applied by the US Geological Survey:

1. water of slight salinity – 1,000 – 3,000 ppm of salt;
2. water of moderate salinity – 3,000 – 10,000 ppm of salt;
3. water of high salinity – 10,000 – 35,000 ppm of salt.

The salinity of sea water is approximately 35,000 ppm of salt, but this rate can vary depending on the place. The combination of pressure, temperature and reservoir pH establish the chemical equilibrium. It is done between the inorganic cations Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) of the formation brine and the absorbed oil polar components. At the initial stage, the adsorption of both basic organic materials and acid onto the clay is done together with inorganic cations, (Calcium Ca^{2+}) in particular. Sulphurous acid (H_2S) and the dissolved Carbon Dioxide (CO_2) result in the initial pH of the formation water in the reservoir equal to 5-6. Rezaei Doust et. al. claims, that such environment with low pH facilitates the absorption onto the clay surface of both basic and acidic components (2010). The experiment stipulated injecting water of low salinity (LSW) into the reservoir where the ion concentration of the initial formation brine, in particular Calcium (Ca^{2+}), exceeds that of the reservoir. A net desorption of cations in the reservoir results from the disturbance of the equilibrium related to the rock and brine interaction. Thus, compensation for the lost hydroxyl (H^+), proton, and cation from the water near to the clay surface takes place through adsorption onto negative parts of clay. It is in the form of substitution of Ca^{2+} for Hydroxyl (H^+). The process entails a local pH increase close to the clay surface which in its turn is the cause of reactions. Figure 9 shows the peculiarities of the chemical mechanism. The upper line is the basic material desorption. The lower line is the acidic material desorption. The range of the initial pH under the conditions within the reservoir is 4-5.

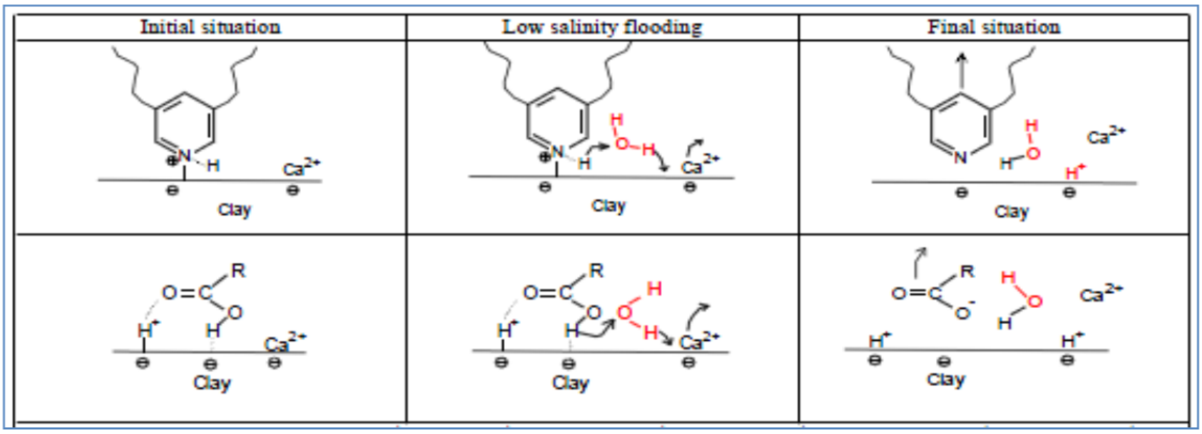


Figure.9. *Suggested chemical mechanism for low salinity*

The above mentioned mechanism is based on the interaction with the minerals of clay poor of carbonates (Lager et al., 2008). The potential of flooding with low salinity water for carbonates has not been studied thoroughly. Spontaneous imbibition tests along with the flooding tests with brine solutions of low salinity carried out by Fathi et al., 2011used Stevens Klint outcrop chalk core plugs at the temperature of 110 – 120 °C. Diluting the sea water to low level of salinity has the negative effect and entails significant decrease in oil recovery at spontaneous imbibition. No extra oil was produced through tertiary diluted seawater flooding. It was concluded that a reason for reduction in oil recovery is caused by the active ions concentration (Mg^{2+}, Ca^{2+} and SO_4^{2-})

Saudi Aramco reported contrary results, observing the OOIP increase in oil recovery by 16-18 % through water flooding of low salinity in the samples of composite rock from carbonate reservoirs in Saudi Arabia (Ali et al., 2011). The conditions of the carried out experiments provided for reservoir temperature of 100 °C and usage of live oil. Using twice diluted sea water resulted in the additional oil recovery that amounted to – 8.5 % beyond secondary recovery. Ten times diluted sea water resulted in 10 %, while twenty times diluted sea water ensured 1 %. One hundred times diluted sea water resulted in zero oil recovery. Ali et al.,(2011) reported wettability alteration as a major mechanism of oil recovery increment. Such wettability alteration is determined by contact angle measurement and NMR T2 distribution.

Austad and his colleagues carried out a number of laboratory experiments and researches with injected water of high salinity. They considered recovery to be a function of temperature and brine composition (Austad et al , 2005; Zhang, Tweheyo, & Austad, 2007; Strand, Puntervold, & Austad, 2008). The potential determining ions capable of doing improvement in oil recovery are Mg^{2+}, SO_4^{2-}, and Ca^{2+}. It goes about the conditions of high temperatures exceeding 90 °C in chalk reservoirs. It has been concluded that the ions are supposed to act together. Taken separately, each of them loses its effect on spontaneous imbibition. Those results of the experiments afforded the ground for the assumption that wettability alteration is the major reason for the oil recovery improvement.

Notwithstanding the generally accepted view that oil recovery in chalk reservoirs can be increased through flooding with water of high salinity (Webb et al, 2005; Karoussi, Hamouda, 2007), profound understanding of the mechanisms that ensure that increase has not been obtained yet. The majority of the researches were carried out using outcrop chalk core plugs for spontaneous imbibition. Few researches stipulated using reservoir chalk core plugs for forced injections. Moreover, the evidence of altering wettability has been indirect in the reports, totally based on the increased spontaneous imbibition. Furthermore, those researches typically disregarded brine and crude oil interactions, although they could be beneficial for the increase in recovery as well. Nevertheless, there are limited experimental data on the flooding of low salinity water in carbonates; that is why additional research and mechanistic study are required.

3.2.2 pH Increase

Low salinity action can result from certain saponification actions under the conditions of the increased pH and low salinity (McGuire et al., 2005). The increased pH at the conditions of low salinity can be attributed to a combination of dissolution and ion exchange. The experiments demonstrated the following simulation results. Dissolution of kaolinite resulted in the reduction of pH. Dissolution of calcite resulted in the increase in pH.

CaCO3 ↔ Ca2+ + CO32-

CO32- + H2O HCO3- + OH-

It is anticipated that the in-situ generated alkaline will act in order to improve the oil recovery. The mechanism in question has certain drawbacks. One of them is the absence of correlation between the acid number of the oil phase with the recovery that is supposed to be a typical alkaline flood (Lager et al., 2006). The experiments demonstrated the low salinity effect but did not show high pH. According to the lab results, the availability of CO2 in reservoirs can serve as a buffer preventing the high pH attainment.

3.2.3 Mineral dissolution

Certain researchers put forth the idea that the mechanism of low salinity flood can be represented by the dissolution of anhydrite minerals and / or carbonate minerals which serve as cement for particles of mixed wetness or are oil-wet (Lebedeva et al., 2009; Pub et al., 2008, 2010). A few cores that demonstrated low salinity effect without significant clay content served as a ground for such assumption. The researchers used AFM and CT imaging technique on cores and identified certain anhydrite and dolomite particles in the high salinity water flood. Flooding done with low salinity brine caused no particles of such kind. The mechanism of low salinity flood bears likeness with changing wettability through mineral dissolution in carbonate rocks (Hiorth et al., 2010). Tang and Morrow (1999) identified the main drawback of the mechanism as insufficient explanation of the requirement to the oil related to ageing in connate water (1999). Another disadvantage is insufficient explanation of the role initial divalent ions play in the connate brine. The mechanism cannot provide clarifications regarding the salinity threshold observed in the carried out experiments.

3.2.4 Local pH increase

Austad et al. (2010) were the first to propose the local pH increase chemical mechanism, in which desorption of the acidic and basic oil components from the rock surface is caused by the local pH increase. The theory provides for the initial occupation of clay surface by oil components and divalent ions (in particular Ca^{2+}). Salinity difference at the low salinity water invasion leads to the displacement of Ca^{2+} ion, subsequent occupancy with H+ and local increase in pH. The oil components desorption is the result of the increase in pH. However, the suggested mechanism cannot provide any explanation of the nature of local pH increase that occurs in the reservoir subject to the presence of CO_2 and serving as a buffer. Other disadvantages are calcite dissolution and complicated measuring the level of local pH increase experimentally. Desorption of Ca^{2+} ion from the rock can be prevented with the calcite dissolution that generally gets stronger under the conditions of lower salinity. Thus, pH increase can be prevented as well.

3.2.5 Double layer expansion

Lighthelm et al. suggested the mechanism of double layer effects in 2009. The attraction of highly reactive clay particles with negative charge to multivalent metal cations (Mg^{2+}, Ca^{2+}) which ensure the connection of negatively charged oil with the clay particles occurs owing to the imperfect crystal lattice. Those conditions predetermine the creation of the electric double layer. The electrical potential is defined as zeta potential at that plane. The inner layer of positive charge is formed from the adsorbed multivalent metal cations. The outer layer is formed from the oil with negative charge. The screening potential of cations is affected by the ion concentration of the water. If the water salinity goes down, the electric repulsion between the oil and clay particle increases and the screening potential of the cation is reduced. Desorption of the oil particles from the clay surface occurs when the binding forces are exceeded by repulsive forces. Ligthelm, Gronsveld et al. (2009) claim that this mechanism is able to alter the wettability and increase its water-wetness. However, every water flooding of low salinity would be efficient provided that the suggested mechanism were the exclusive cause of ultimate recovery of oil.

3.2.6 Exchange of multi-component ions

Lager et al. (2006) advanced the idea of the major role of divalent ions in the oil adsorption on the rock surface and subsequently established the concept of multicomponent ion exchange mechanism. Expansion of the double layer after the injection of low salinity water facilitates the invasion of ions and displacement of the oil droplets and divalent ions. The researchers carried out numerous experiments to prove the fact that ageing of the rock deprived of divalent cations causes the removal of low salinity effect. Furthermore, they indicated the prevalence of the formation water concentration and the injected low salinity over the concentration of effluent low salinity divalent ions, using Mg^{2+} during their experiments. They suggested the idea of the availability of certain stripped divalent ions in the oil phase. According to Austad et al., (2010) precipitation of Mg^{2+} may take place inside the core. Lager et al. (2011) supported the idea of MIE mechanism and presented the results of the experiments based on the BP's inter-well low salinity injection. Those results revealed the prevailing number of divalent ions (Fe^{2+}) in the effluent as opposed to high salinity brine or injected low salinity brine. According to their assumption, the ion originated from the displacement of Fe^{2+} ion that acted as a link between the clay surface and oil.

4. Wettability Alteration Summary

There is a direct interrelation between the water film stability between oil and rock and the initial wetting condition meant for carbonate rock. The stability of water film is predetermined with the sign and value of zeta potential which is termed as electrical potential of the water-rock and oil-water interfaces. The charge of oil-water interface is typically negative. It is ensured with the carboxylic acid content of the crude oil. The charge of water-rock surface is typically positive owing to Ca^{2+} high content in the formation brine and $pH<9.5$.

Those conditions result in the instability of the water film. Thus, the absorption of the carboxylic group onto the carbonate surface is strong through the water displacement. Therefore, AN (acid number) of the crude oil is the factor of crucial importance for the carbonates wetting state. The increase in the acid number leads to the decrease in the water-wetness. The experiments also showed that the rise of reservoir temperature results in the increase in water-wetting condition in the carbonate reservoir.

5. Material and Methods

5.1. The Cores

The chalk cores that used in this study are from Obourg (Mons Basin, Belgium) and Stevns Klint (SK, Denmark) outcrop chalks. SK chalk of Maastrichtian age is 99 % pure biogenic chalk is very porous (45-50 %) and of low matrix permeability (1-2 mD) and has a rather reactive surface area of around 2 m2/g (Frykman, 2001; Røgen and Fabricius, 2002). Proceeding to any experimental studies, it is significant to decide on the type of outcrop material to be used, because they may behave differently even with having similar lithology (Milter and Øxnevad, 1996; Strand et al., 2007). Especially content and silica type has been shown to distress the wettability and the mechanical strength of the rock. (DaSilva et al., 1985; Strand et al., 2007). Ekofisk reservoirs chalk in the North Sea is believed to be more or less similar to these chalk types. The geological descriptions of two types of outcrop chalks, SK and Obourg are summarized in Table 1.

Table 1. *Carbonate content and calculated mineral content for the chalk outcrops (Hjuler and Fabricius, 2009).*

Chalk type	Carbonate content (wt.%)	Calculated mineral content (normalized)			
		Silica (wt.%)	Smectite (wt.%)	Mica (wt.%)	Kaolinite (wt.%)
Obourg	94.3	35	50	10	5
SK	99.8	25	60	15	-

5.2 Brines

Synthetic Sea Water (SSW) was used as primary brine to establish SWI, in the flooding and in the imbibition experiments on the cores. The compositions of SSW and the other fluids LSW-1, LSW-2 and LSW-3 used in this study are given in table 2.

Table 2. *Compositions of brines*

Salt	SSW		LSW-1		LSW-2		LSW-3	
	g/l	mole/l	g/l	mole/l	g/l	mole/l	g/l	mole/l
NaCl	23.38	0.400	0.9352	0.016	-	-	-	-
Na2SO4	3.41	0.024	0.1364	0.00096	-	-	3.41	0.024
NaHCO3	0.17	0.002	0.0068	0.00008	-	-	-	-
KCl	0.75	0.010	0.03	0.0004	-	-	-	-
MgCl26H2O	9.05	0.045	0.362	0.0018	9.05	0.045	-	-
CaCl22H2O	1.91	0.013	0.0764	0.00052	-	-	-	-

LSW-1 is a modification of synthetic sea water (SSW). This brine is dissolved SSW in distil water (DW) in rate of 1:25. The brine LSW-2 is DW with only the magnesium ions, Mg^{2+}, in the same concentration as in SSW. LSW-3 is DW with only the sulphate active ions, SO_4^{2-} in the similar concentration as in SSW as well. In the spontaneous imbibition experiments were used similar brines.

5.3 Oil

For the experiments n-Decane with dissolved Stearic Acid (SA) was used as oil phase, table 3. The oil was prepared by adding 1.42 g (0.005 mole/l) SA to 1 liter of n-Decane and mixed using a magnetic stirrer for at least 6 hours in advance to be sure that the two components were mixed properly. The n-decane was supplied by Merck Manufacture of purity equal to 95%.

Table.3 *Type of oil used for the experiments.*

Oil	Stearic Acid (mol/l)	Density, g/cm^3	Viscosity at 23°C, cP
N- Decane	0.005	0.737	0.879

5.4 Methods

5.4.1 Preparation of cores for flooding.

1. The cores were dried at 110 °C to constant weight
2. Measure length, diameter and weight of dry cores
3. Saturation by SSW under vacuum, weighting of wet cores
4. Pore volume and porosity calculation
5. Establishment of initial water saturation
6. Aging of cores

An only SSW -saturated core (SK_R) is used for calculation of Absolute permeability.

5.4.2 Calculation of porosity and pore volume

The dry weight and the dimensions were measured of each core. After the saturation the cores were weighted again to establish saturated weight. Pore volume (PV) was then calculated:

$PV = (W_w - \ )/\rho_{SSw}$ Eq.7

W_d = Dry weight

W_w = Saturated weight

ρ_{SSW} = Density of SSW

Porosity calculate as : $\phi = PV/V_b$, where V_b is bulk volume. Eq.8

Flooding and establishment of initial water saturation were performed using Hassler core flooding equipment, fig 11.

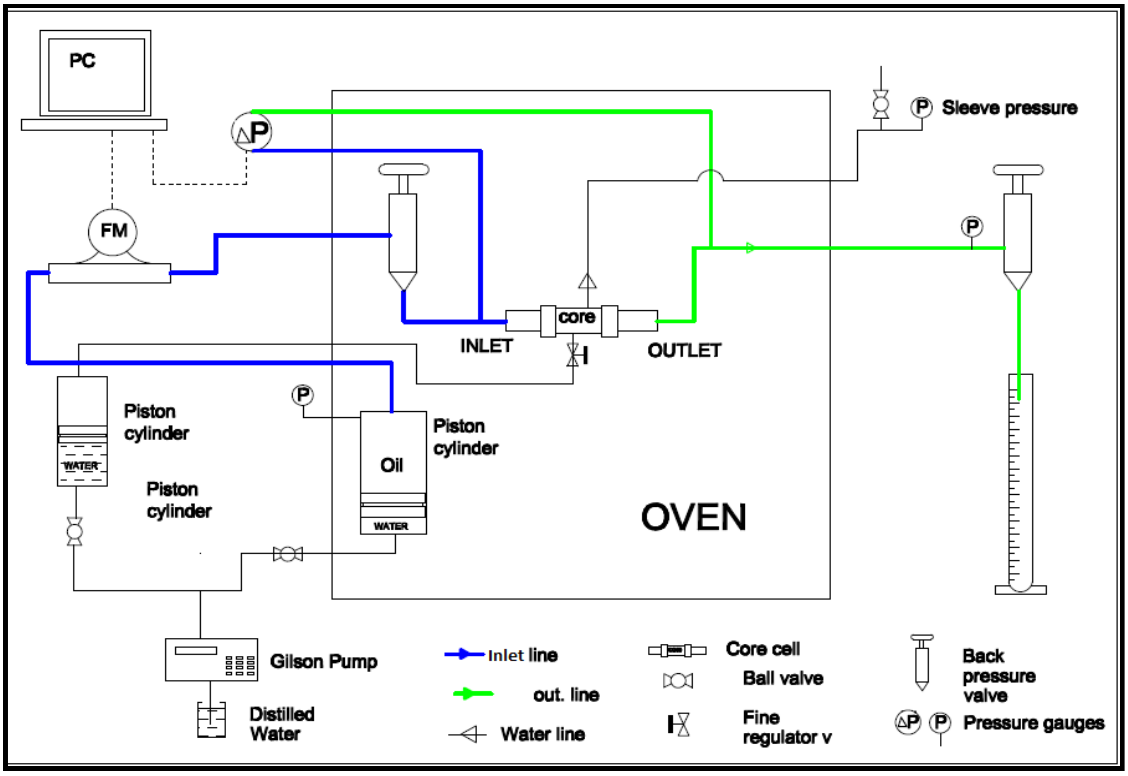


Figure 10. *Schematic of the setup used for flooding experiments.* **(***Edwin A. Chukwudeme and Aly A. Hamouda. 2009***)**

5.4.3. Establishment of Initial Water Saturation

The dried cores were saturated with Synthetic sea water (SSW) under vacuum. The SSW was filtrated with a 2 µm filter paper before being used to avoid congestion of the pore space. The initial water saturation (S_{wi}) was established using Hassler core flooding equipment by injection of oil. Creation of initial water saturation for 100% SSW saturated core was carried out at 50°C.

Arrangements: The core was first wrapped up with Teflon tape and then a plastic tube sleeve was heated up to make it stick to to the core covered by Teflon and then top part of sleeve cut. After this the core was placed inside of a Hassler coreholder. Tellus 52 V was used as the liquid for creation of coffining pressure and was filled into the Hassler core holder formerly closing it. Confining pressure outside of the core hold onto at around 20 bar that is larger than the inlet pressure.

The tests were run with an injection rate at 5 PV/day from the start with gradually increasing this rate as the oil-breakthrough taking place to continually produce water. Outlet valve kept completely open from the start. This method was used because the only objective with these tests was to establish S_{wi}. The formula for S_{wi} calculation is next:

$$S_{wi} = \frac{PV - V_{SSW}}{PV}$$

where V_{SSW} is volume of water produced. eq.9

The cores properties and experimental data are shown in table 4.

Table.4 *The cores properties*

Cores Properties	SK_B	SK_C	SK_D	SK_E	#1	#2	#3	#4
Diameter, D (cm)	3.73	3.73	3.73	3.73	3.78	3.72	3.73	3.78
Length, L (cm)	5.81	5.78	5.95	5.80	5.73	5.68	5.78	5.69
Bulk volume, cm^3	63.45	63.12	64.98	63.34	64.30	62.06	63.15	63.85
Pore volume, PV,cm^3	29.91	30.02	31.24	30.40	28.36	27.18	27.92	28.03
ϕ, %	47.1	47.5	48.0	47.9	44.1	43.7	44.2	43.8
Weight Dry, Wd, g	89.04	88.60	90.33	87.90	95.45	91.71	93.67	95.18
Weight Wet, Ww, g	119.85	119.53	122.51	119.22	124.67	119.71	122.43	124.06
Volume of SSW, ml	29.91	30.02	31.24	30.40	28.36	27.18	27.92	28.03
Weight with oil, W o, g	112.49	112.14	114.88	111.75	117.41	113.11	115.64	117.46
Water from core, ml	23.2	23.0	24.3	23.7	21	20.5	20.8	20.8
PH swi	7.25	7.27	7.28	7.25	7.30	7.38	7.23	7.28
Initial water saturation, %	22.5	23.5	22.2	22.1	25.9	24.6	25.5	26.2

5.4.4 Aging of cores

After establishment of initial water saturation by displacement with n-Decane oil, the core was completed for aging. The aging method makes the wettability into a core to more oil-wet state. The cores were taken out from the holder, immersed inside a steel aging container filled with n-Decane. The steel container was completely closed and held in an oven at temperature of 50 ˚C for 14 days. During the aging process an amount of surface - active components from the oil will adsorb onto the remotest surface of the core. After that all cores were prepared for flooding.

5.5 Flooding procedure

During the experiments of establishing of initial water saturation and flooding procedures for me and other students it was trouble with leakage inside the core holder. Leakage occurred due to weakness of tighten of plastic sleeve resulted confining pressure could not retain stable. This short plastic tube keeps the core isolated inside cylinder from oil -TELUS 52 that used for create overburden pressure around the core. Objective for creation of confining pressure is to simulate reservoir conditions and do not allowed the injection fluid take easiest way between the plastic sleeve and self-core.

On some cores detected yellow tones that become aware afterwards flooding as well as during aging. It is believed that this outcome of leakage due to confining pressure with consequence several cores became useless and time and materials were lost.

Due to those unexpected test disturbed occurrences I modified the core setting and merged this with other type of Hasler core holder, see fig 11, section 4

First the core was wrapped in Teflon tape to avoid adsorption of unrepresentative organic material on the chalk surface, placed between inlet and outlet distributor by heating up in the plastic sleeve and then inserted it in a rubber sleeve, fig11, sections1, 2 and 3.

Since this the problem was solved, no leakage occurred and confining pressure held stable.

On the outlet of the Hassler cell a back pressure valve system was attached, fig11. With this valve the outlet flow could be controlled. Flooding procedures were performed by at a rate of 4 pore volumes per day at 70 °C using a backpressure of 10 bar. At the end of each production test the injection rate was increased up to 16 pore volume per day.

As a driving force for flooding of the core, a Gilson 307 HPCL piston pump was used.

Fig.11 . *Modified Hasler core holder.*

Because this chalk is rather weak, the confining pressure in the Hassler cell should not go above double of inlet pressure or not more than 35 bar. After oil production, each core were flooded again with n-decane +stearic acid (SA) for establish the same initial water saturation as before production flooding. Then they were aged second times at 50° C during 2 weeks to perform the imbibition tests.

5.6 Ionic composition analysis

ICS-3000 ions-exchange chromatograph produced by Dionex Corporation, USA was used to analyze the ionic concentrations of ions in flooded fluids. Before the solvent may possibly be analyzed by the ion chromatograph the effluent have to be diluted.
The effluent samples were diluted 1:200 for SSW, LSW-2, LSW-3 and 1:50 for LSW-1 by deionized water (DI) foregoing to the analysis and the ions concentrations were deliberated based on an external standard. Ion exchange chromatography is a process that agrees to the separation of ions and polar molecules based on the charge properties of the molecules.
It was made to measure concentrations of both anions and cations at the same time. The ion chromatograph is shown in figure 12.

After dilution of samples they have to be filtrated. The filtration was simply achieved with a syringe filter. The samples have to be sifted to prevent particles to move in the columns inside the ion chromatograph since these were very sensitive to particles. Particles may easily block the tubing and cause an over pressure.

Fig. 12. *Dionex IC-3000 ion chromatography system*

5.7 pH measurements

For the measure of the hydronium ion concentration of the effluent samples were used Seven Easy Mettler Toledo pH-meter, fig 13. In order to be sure to get as accurate measurements as possible, the pH-meter was calibrated for 4, 7 and 10 pH units before using.

Fig. 13. *Toledo pH meter.*

5.8 Interfaces tension measurement (IFT)

The interfaces tension measurements were performed using Kruss SITE 04 ascending drop tensiometer. The IFT measurements between the oil and the brines were performed at 23°C , 50°C and 70 °C. The value reported in table 5 is the average of the IFT quantities.

Fig 14. *Kruss SITE 04 tensiometer*

5.9 Spontaneous Imbibition

At elevated temperatures (23°C, 50°C and 70 °C) spontaneous imbibition tests were performed in standard Amott glass cells. After aging the core was put inside the cell and surrounded with imbibition brine. The volume of oil expelled from the core in the graded burette was recorded versus time. An imbibition cell is shown in figure _and SK cores were the cores that used in the spontaneous imbibition experiments. Synthetic seawater was as first imbibition brine as well.

Fig 15*.Standard Amott cell*

5.9.1 Preparations for imbibition test

In the bottom part of the cell four plastic balls were put with purpose to get access of imbibing fluid to whole surface of the core. Then valves were placed on the bottom and top parts of the cell. After that high vacuum silicone grease was anointed on the foot part there two parts connects to prevent leakage from that assembly. Then two parts were fitted together and moved slightly revolved to avoid glass-glass contact. Springs were used to keep two parts tightly connected. The imbibing fluid was then filled from the valve at the foot part till it reached up to 9-10 ml mark of the burette.

The pressure builds up in the glass cell due to extension at elevated temperature and the imbibing liquid will force whole system and leakage can occur. The leakage does not have a serious impact on the system, i.e. the liquid level will not fall to the point where the oil touches the core. The pressure increase inside of the Amott cell is releasing as soon one open the valve at the top part

The test was then performed at the elevated temperature stages. As the oil production steadied at 70°C a brine sample was taken to measure the pH of the imbibing liguid.
A new sample was taken for pH-measurements later when the experiment got hold of its final recovery with the second imbibing brine.

6. Main results and observations

Obourg (Mons Basin, Belgium) outcrop chalk cores.

6.1 Flooding experiment - 1 (Test-1) was carried out at 70°C using core #1. Synthetic Sea Water (SSW) was injected with the rate of 0.08 ml/min that corresponds to 4 pore volume per day. When the oil recovery stopped the injection rate (IR) was increased up to 16 PV/day to be sure that there is not more mobile oil in the core. Injection of the SSW at two different injection rates led to the final recovery of the 39.5 % of the OOIP. The increasing in pH is slightly from 7.15 to 7.66 pH units, fig.16

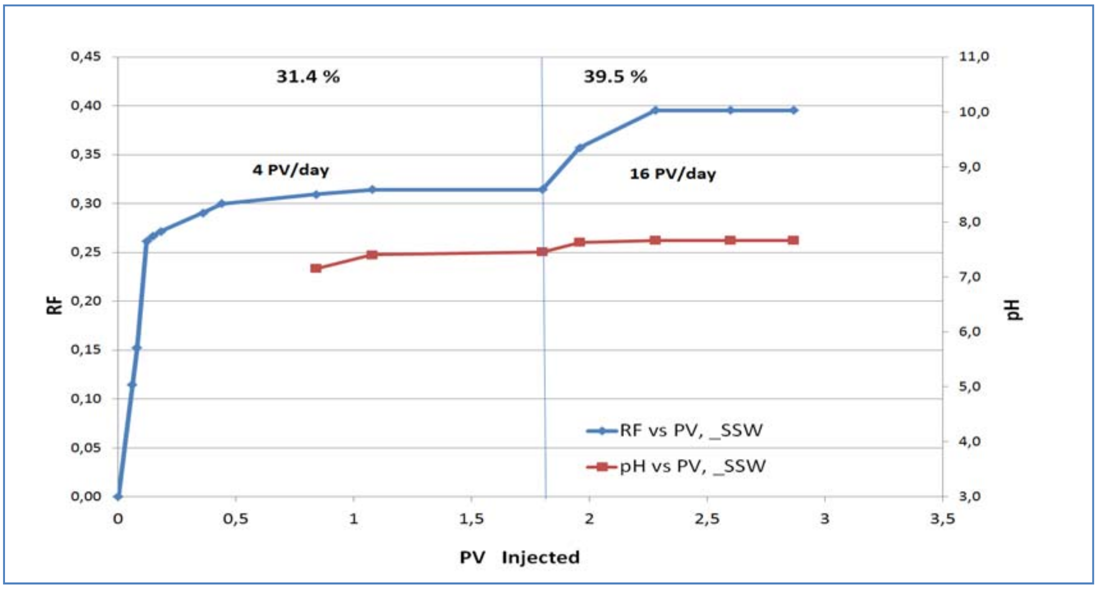


Fig 16 . *Oil recovery and pH as function of PV injected for core #1 at 70°C.*

The pressure drop variation in this test is shown in fig.17 Average pressure drop across the core # 1 is around 3.5 bars before increasing of IR. Jump induced by increment of IR consequence of rising of pressure drop up to 6 bars.

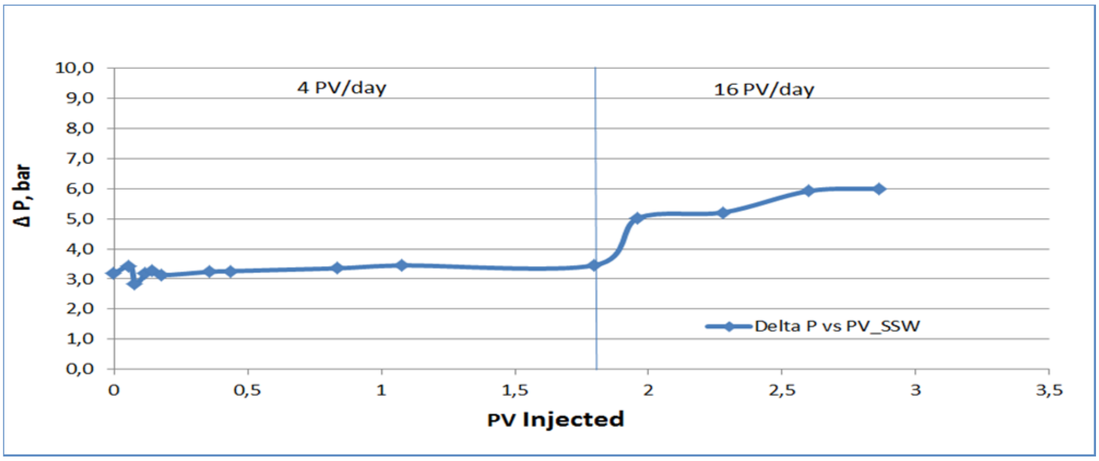


Fig. 17. *Pressure drop variation as function of pore volume injected at different rate for core #1 at 70 °C*

6.2 Flooding experiment - 2 (Test - 2) with the chalk core #2 was performed by injecting SSW first with IR of 4 PV/day and increasing to 16 PV/day in the end of the flooding experiment, similar to previous test. Injection rate of 0.073 ml/min (4 PV/day) calculated based on pore volume of core 2. As shown in fig_ 45.2% of OOIP was reached after increasing of IR to 16PV/day. After flooding SSW injection was continuous by low salinity water (LSW-1) in the same sequence as SSW. Continuity flooding by LSW-1either increasing of IR did not products additional oil. Increasing of pH is noteworthy from 7.32 to 8.07.fig.18

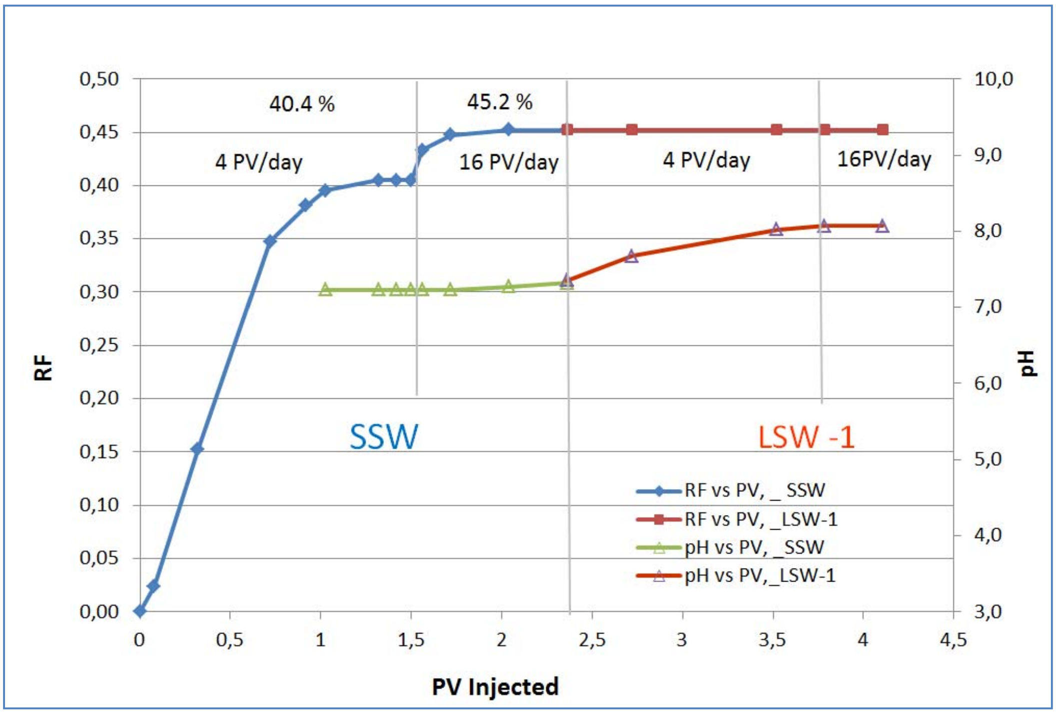


Fig 18_. *Oil recovery and pH as a function of injected pore volume for core #2 at 70°C.*

The average pressure drop variation through core - 2 for first injection of SSW continuously with LSW-1 is shown in fig.19. During injection of SSW by rate of 4 PV/day average delta P was around 2.6 bar. Jump in the pressure drop curve induced by increasing the IR at the end of the flooding procedure with purpose to take out any mobile oil alike previous test. Differences in the delta P on 2.6 bar at IR at 4PV/day and around 4 bar at 16 PV/day in compares with around 3.2 bar respectively 6 bar at the same IR from previously test can be explained by properties of cores namely core 1 could have higher grade of cementation as result on lower permeability.

A decreasing in pressure drop we can observe in this test with continuously flooding by LSW-1. It means that reducing in salinity of injection brine resulted in decreasing of delta P.

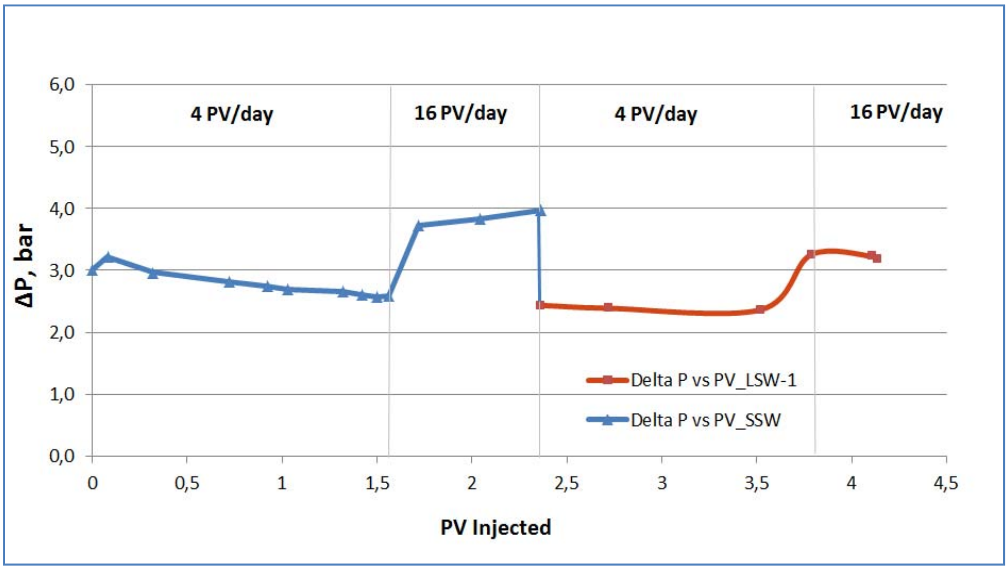


Fig19. *Pressure drop variation as function of pore volume injected at different rate for core #2 at 70 °C*

6.3 Flooding experiment - 3 (Test - 3) was carried out with core #3 at 70°C with the equal flooding and injection rate order as was applied for the test 2. Flooding by SSW resulted in final oil recovery of 57% of OOIP. In the second step LSW-2 was injected but not additional oil was produced. pH was increased up to 9 units that is significant in compares with LSW-1. This effect of pH increment should associate with active SO_4^{2-} ions. (fig.20)

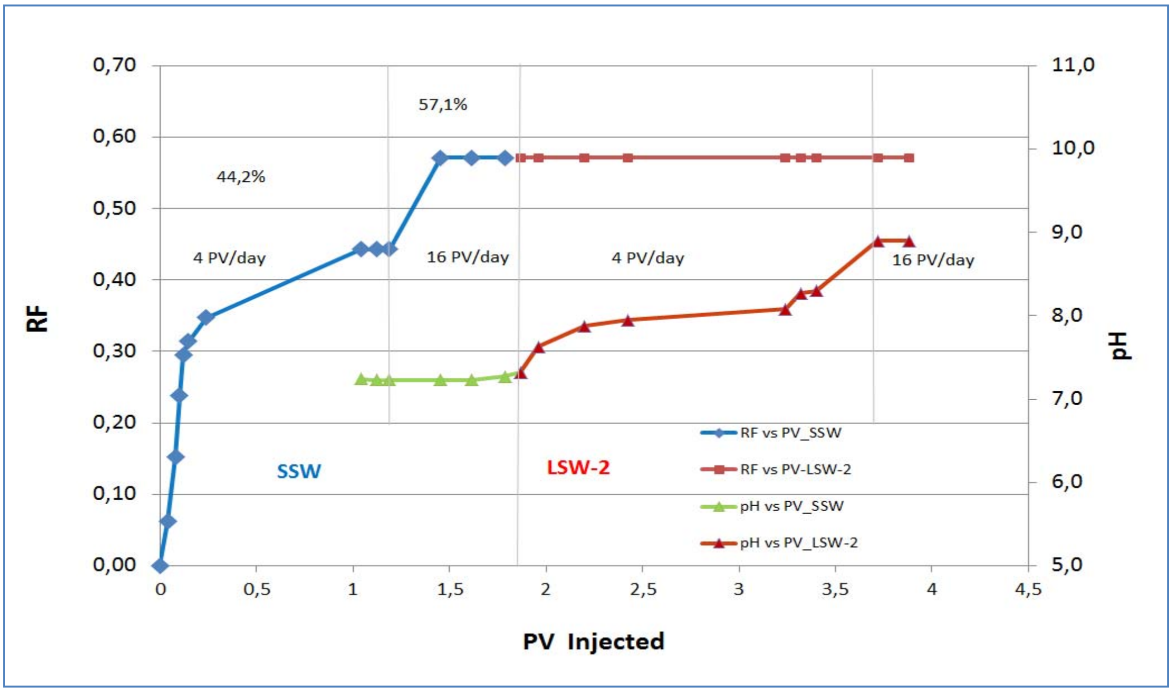


Fig 20. *Oil recovery and pH as a function of injected pore volume for core #3 at 70°C.*

Average pressure drop variation reflects in fig.21. Average delta P is around 2.5 bar at standard injection rate of 4 PV/day and increases up to 3.8 bar at16PV/day of IR for SSW. This consists with previous test for core-2. But noteworthy decreasing of delta P to 1 bar at the start of flooding by LSW-2 with slowly increasing up to 2 bar and then decreasing to 1.3 bar at IR of 4 PV/day and increment of pressure drop up to 2.3 bar at higher injection rate. This slowly growing of average pressure drop at standard IR of 4PV/day can be explained by the migration of fines (Z. Yongsheng et al, SPE, 2007)

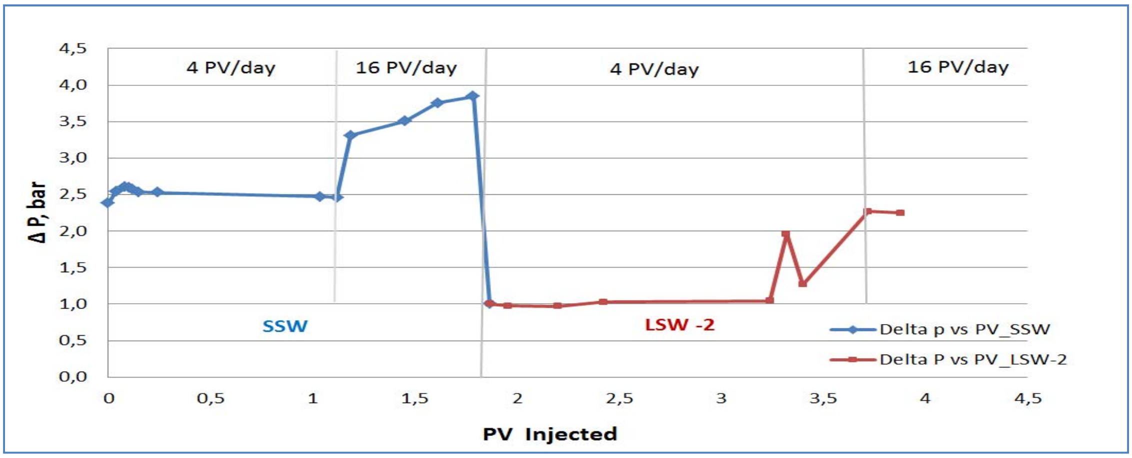


Fig 21.Pressure drop variation as function of pore volume injected of different brines and rates for core #3 at 70 °C

6.4 Flooding experiment – 4 (test-4) was performed using core #4 at similar conditions as previous two tests. Injection of SSW first led to final oil recovery equivalent 47.6 % of OOIP. In the next step LSW -3 was continuously injected. Not additional oil recovery had obtained. Measurement of pH shows slightly increasing from about 7 to 7.5 units, fig.22.

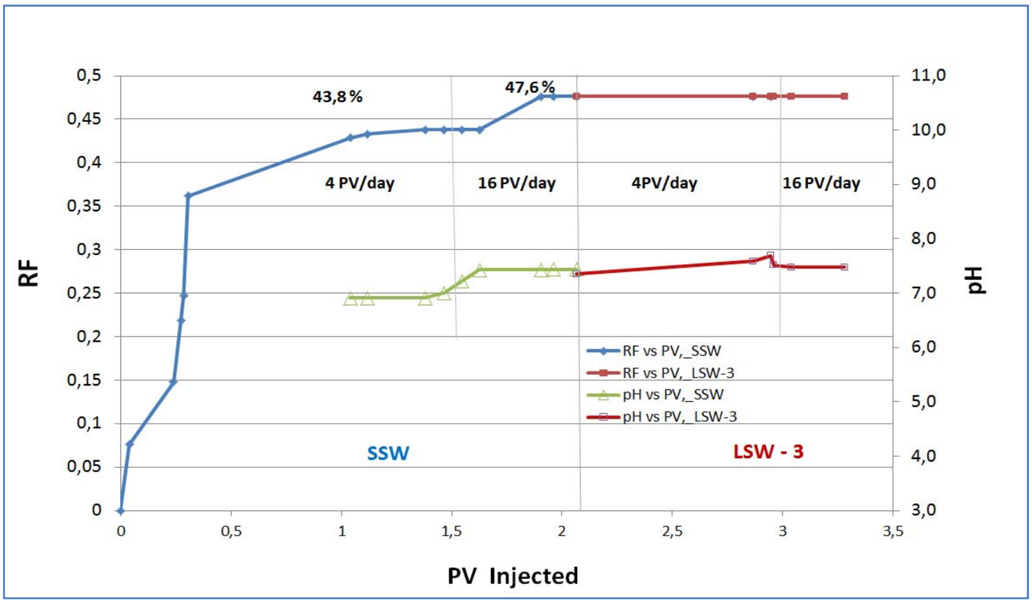


***Fig 22**. Oil recovery and pH as a function of injected pore volume for core #4 at 70°C.*

Fig. 23 illustrates the pressure drop curve for this test. Average delta P for SSW injection is around 2.6 bar at standard IR and around 4.2 bar at higher IR that is similar to previous two tests. LSW – 3 flooding shows decreasing of average pressure drop below 1 bar at ordinary IR of 4 PV/day and slowly increasing up to 1.7 bar at upper IR.

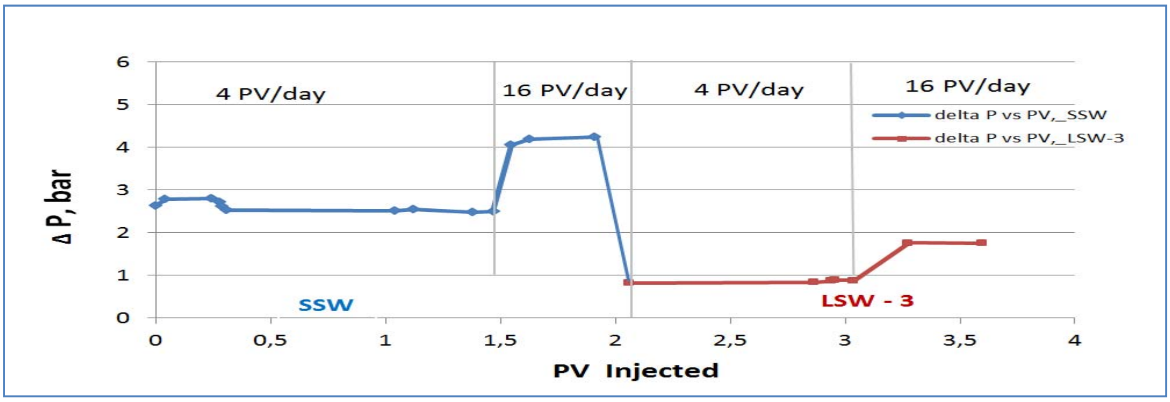


Fig 23. *Pressure drop variation as function of pore volume injected of different brines and rates for core #4 at 70 °C*

Stevns Klint, Denmark outcrop chalk cores.

6.5 Flooding experiment - 5 (Test-5) was carried out at 70°C using core **SK_B**. Synthetic Sea Water was injected only in this test with the standard injection rate of 4 pore volume per day. When the oil recovery stopped the injection rate (IR) was increased up to 16 PV/day to be sure that there is not more movable oil in the core. Continuous injection of the SSW at two different injection rates was result in the concluding recovery of 67 % of the OOIP. The increasing in pH is slightly from 6.74 to 7.41 pH units and the slowly decreasing up to 7.26 during higher IR, see fig 24

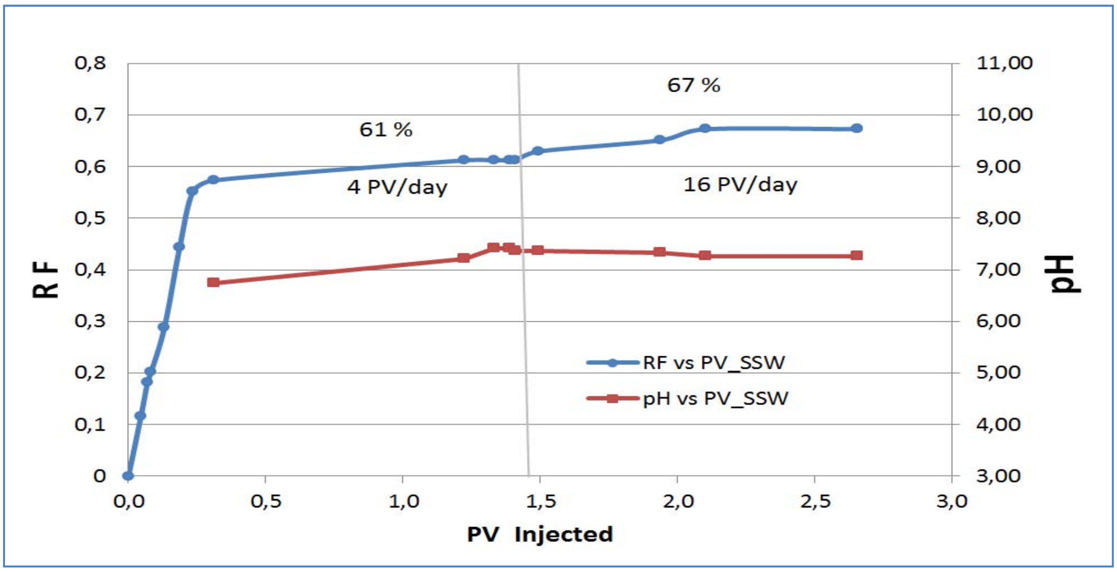


Fig 24. *Oil recovery and pH as functions of PV injected for core SK_B at 70°C.*

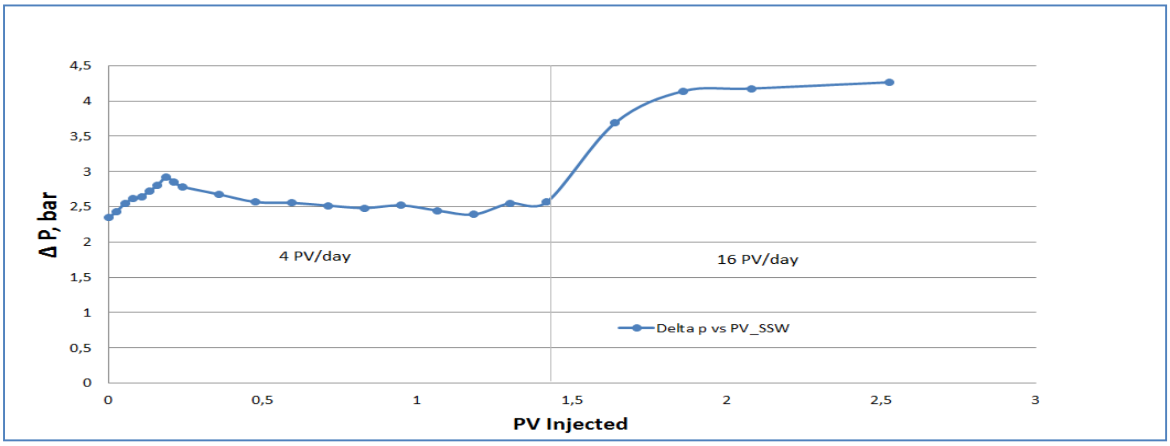


Fig 25. *Pressure drop variation as function of pore volume injected of different rates for core SK_B at 70 °C*

6.6 Flooding experiment - 6 (Test-6) was carried out at 70°C using core **SK_C.**

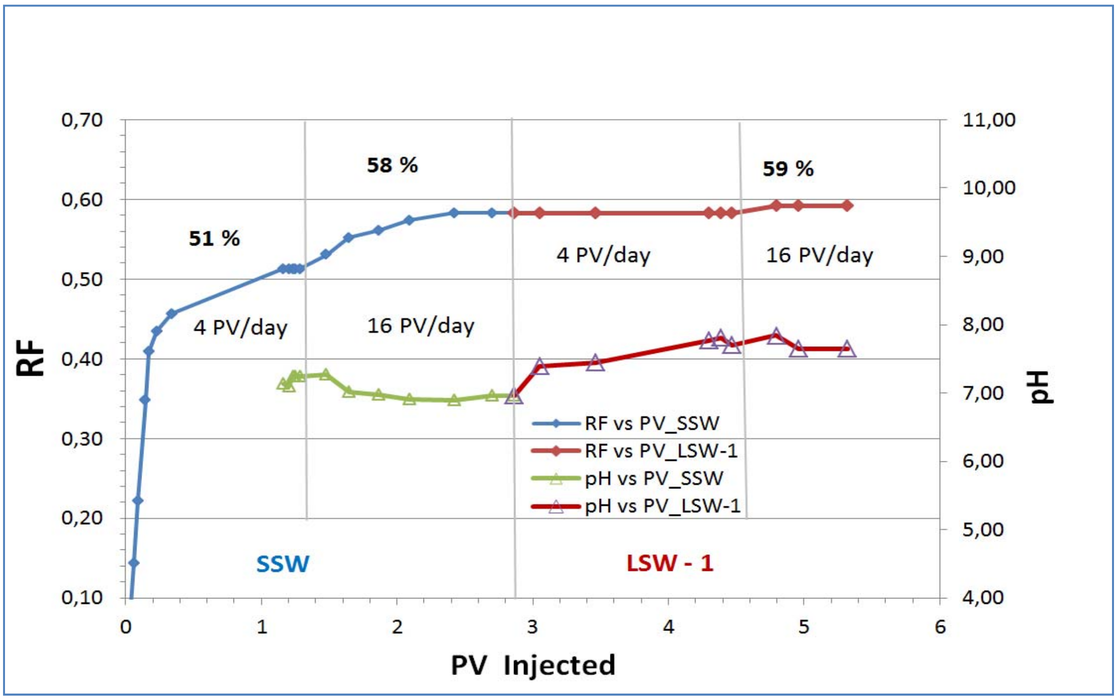


Fig 26. *Oil recovery and pH as functions of injected pore volume for core SK_C at 70°C.*

SSW was first injected with IR of 4 PV/day which 0.083 ml/min. As shown in fig.26 58% of OOIP was reached after increasing of IR to 16PV/day. After flooding SSW injection was continuous by low salinity water (LSW-1) in the same sequence as SSW. Continuity flooding by LSW-1 resulted in additional oil of about 1%.

Declining in pressure drop, fig.27 we can observe in this test with continuously flooding by LSW-1. It means that reducing in salinity of injection brine resulted in decreasing of delta P.

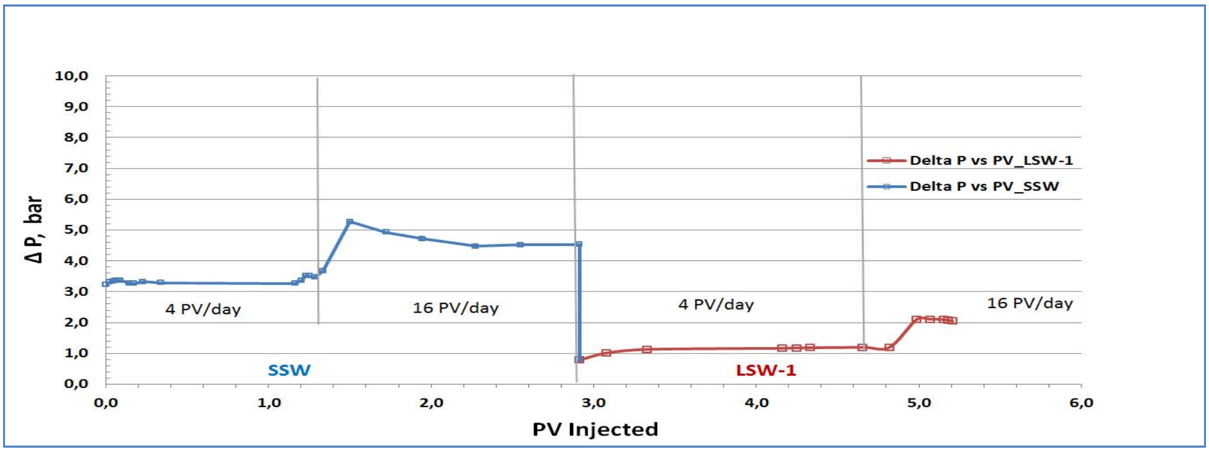


Fig 27. *Pressure drop variation as function of pore volume injected of different brines and rates for core SK_C at 70 °C*

6.7 Flooding experiment - 7 (Test-7) performed at 70°C using core **SK_D,** fig. 28, at similar conditions as previous two tests. Injection of SSW first led to final oil recovery equivalent 61 % of OOIP. In the next step LSW -2 was continuously injected with result of additional oil recovery with about 1%. Pressure drop curves behaved similar, fig.28. Value of delta P is approximately the same around 2.7 bar in both case as SSW as well as LSW-2 before increasing of injection rate (IR).

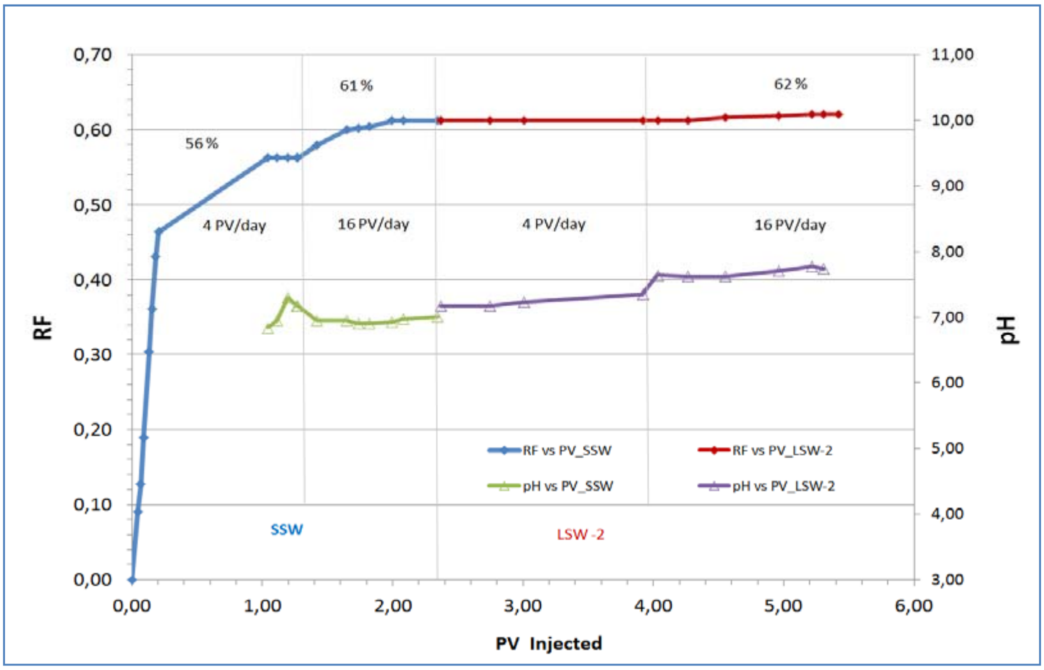


Fig 28. *Oil recovery and pH as functions of injected pore volume for core SK_D at 70°C.*

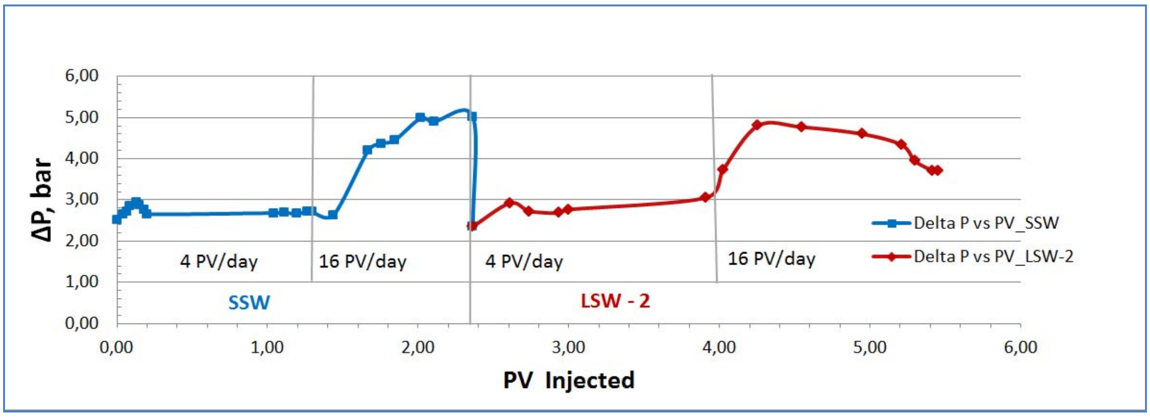


Fig 29. *Pressure drop variation as function of pore volume injected of different brines and rates for core SK_D at 70 °C*

Magnitude of pressure drop after increasing of IR that is about 5 bar with SSW injection and decreasing from 4.8 to 3.7 bar in LSW-2 case.(fig.29)

6.8 Flooding experiment - 8 (Test-8) was carried out at 70°C using core **SK_E.**

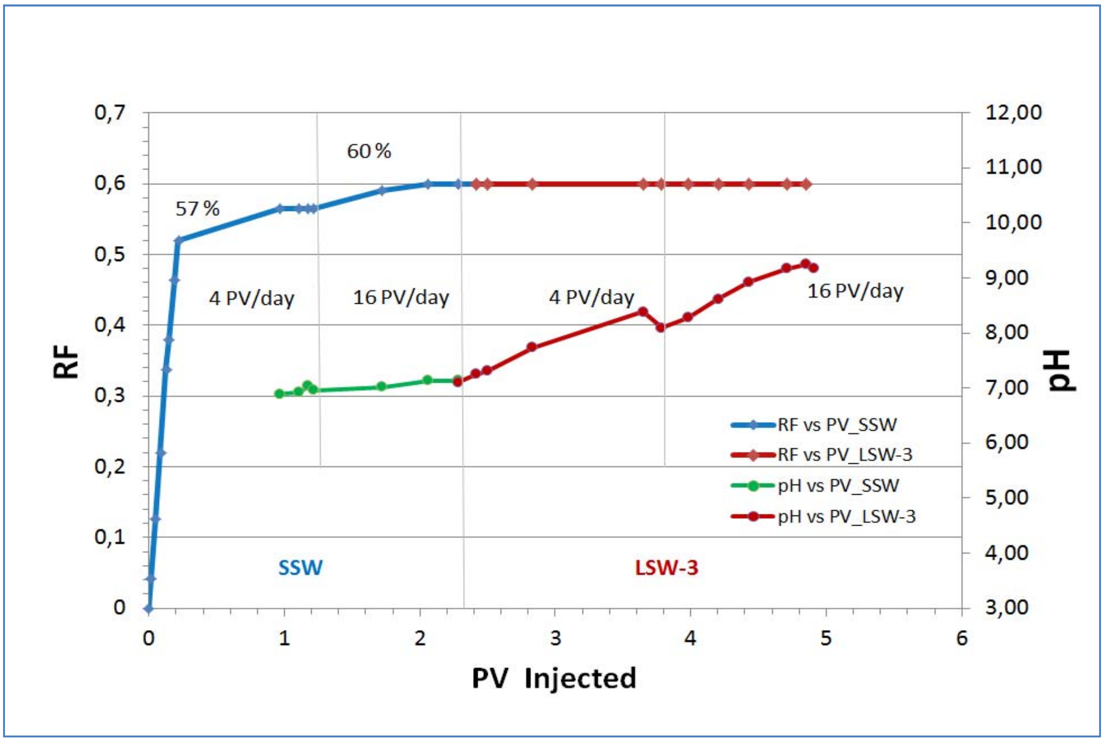


Fig 30. *Oil recovery and pH as functions of injected pore volume for core SK_E at 70°C.*

Injection of SSW first led to final oil recovery equivalent 60 % of OOIP. In the next step LSW -3 was continuously injected. Not additional oil recovery had obtained. Measurement of pH shows increasing from about 7 up to 9.2 units, fig 30.

Fig. 31 illustrates the pressure drop curve for this experiment. Average delta P for SSW injection is around 3 bar at standard IR and around 5.5 bar at higher IR that is similar to previous two tests. LSW – 3 flooding shows decreasing of average pressure drop below 2 bar at ordinary IR of 4 PV/day and increasing up to 4 bar at upper IR.

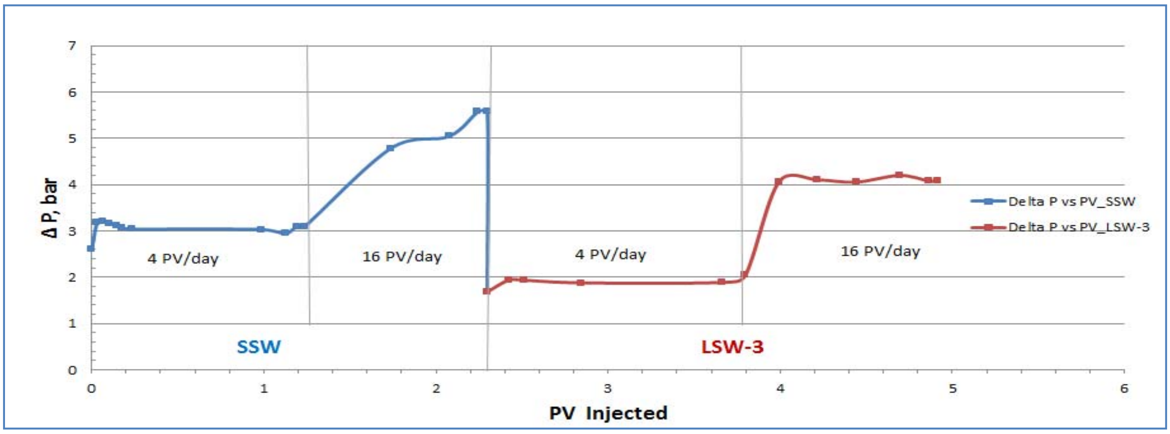


Fig 31. *Pressure drop variation as function of pore volume injected of different brines and rates for core SK_E at 70 °C*

6.9 Ions chromatography analysis result

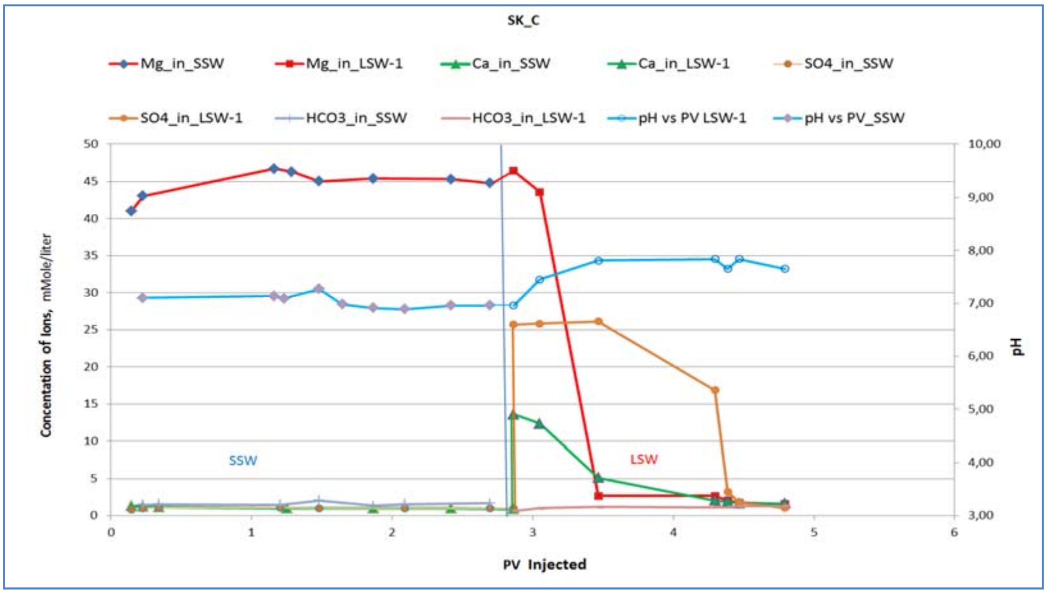


Fig 32. Molecular concentration of potential determining ions for core SK_C

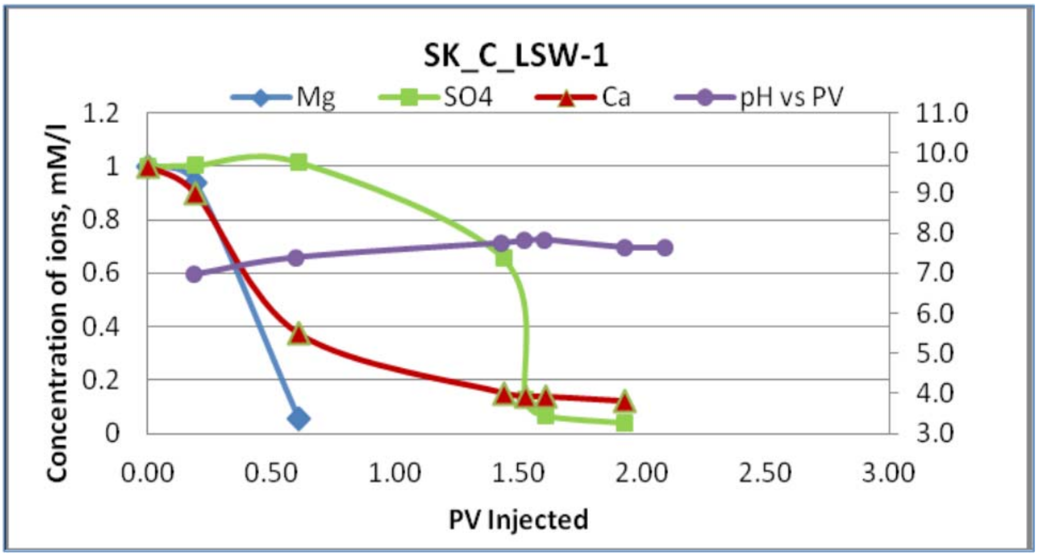


Fig 33 *.Normalized ions concentration curves for core SK_C*

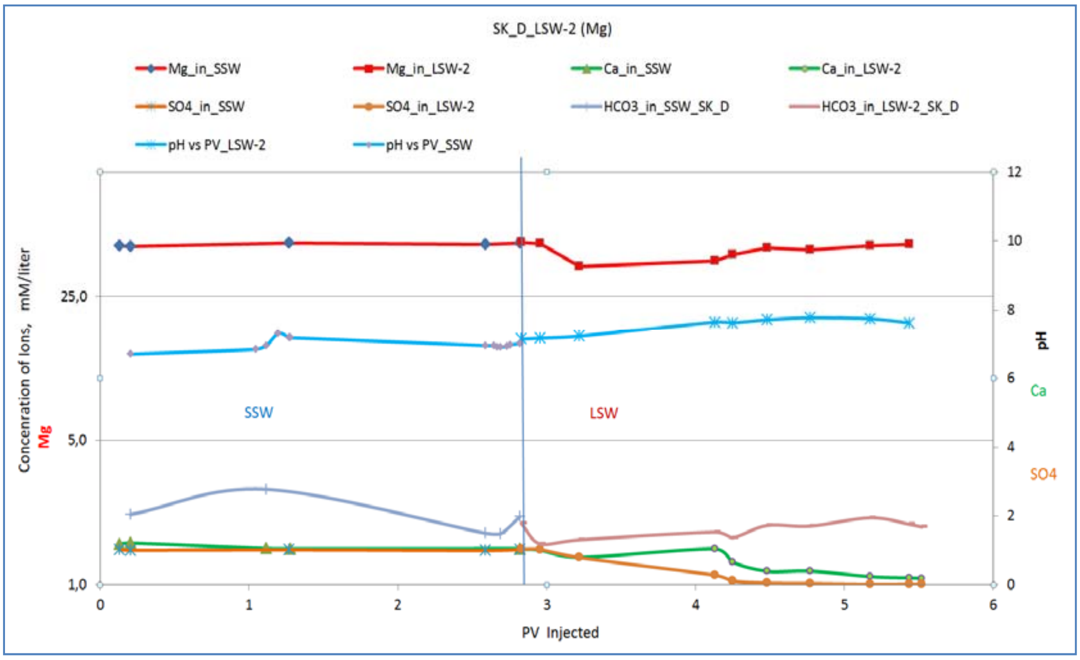


Fig 34. *Effluent ions concentrations during LSW-2 brine injection in SK_D core.* Mg^{2+} *in the logarifmic scale*

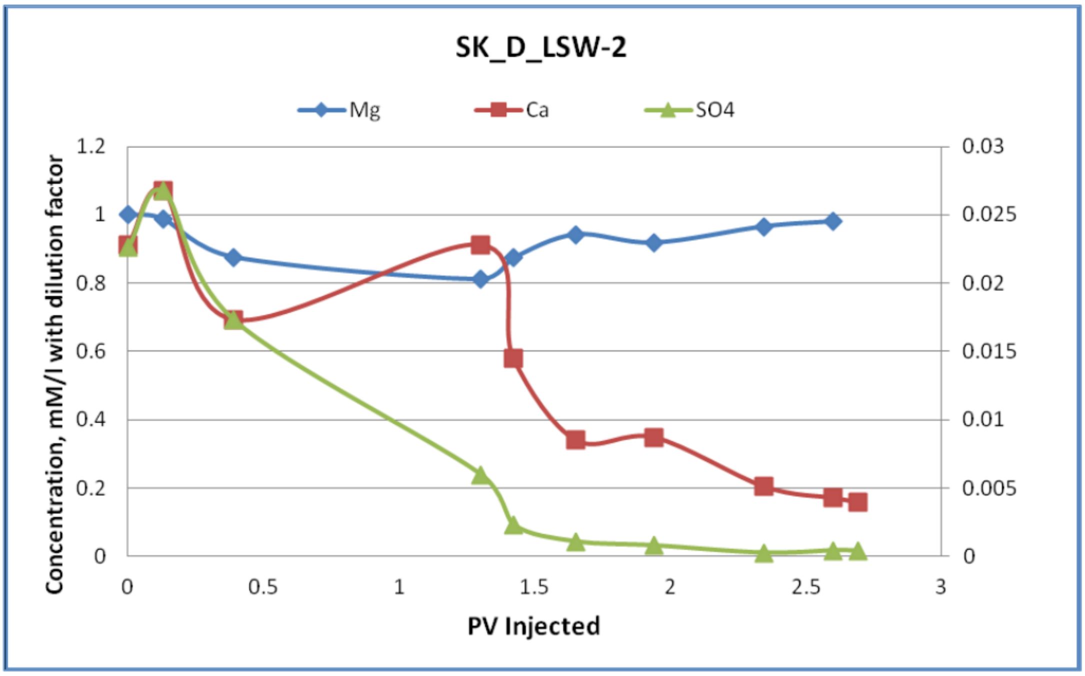


Fig 35.*Normalized effluent* ions concentrations for SK_D core.

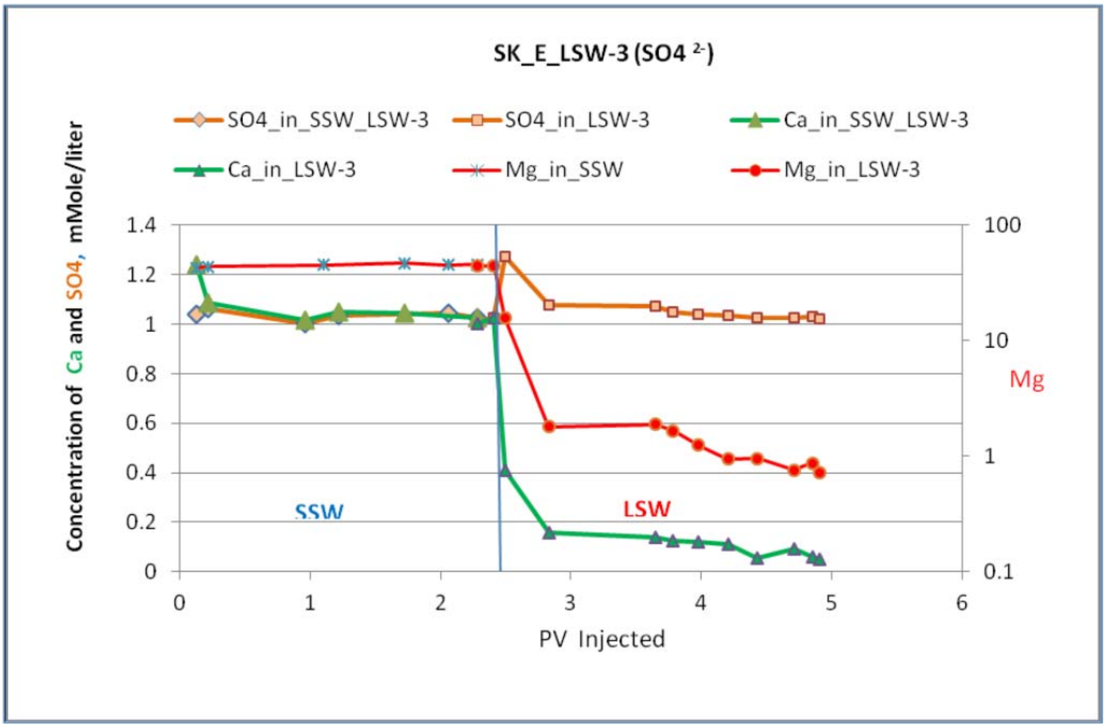


Fig 36. Effluent ions concentrations during LSW-3 brine injection in SK_E core

6.10 IFT measurement tests result

IFT measurements were performed between n – Decane + SA and brines at different temperature including flooding temperature and atmospheric pressure. Refers to Saudi Aramco finding of concentration of SSW of 10 times I did additional measurement IFT for 10 times diluted SSW that is LSW_10.

Average IFT values are summarized in Table 5. Deviations in measurement are between 0.05 up to 0.15

Table 5, *IFT measurements data*

	SSW	LSW-1	LSW-2	LSW-3	LSW_10	Temperature, °C
IFT, mN/m	28.75	36.11	37.84	37.88	29.54	23
	18.68	29.11	31.93	31.85	23.74	50
	12.72	32.04	36.11	32.58	21.25	70

From fig. 37 we can see that IFT decreases at 50° C for all type of brines but then slightly increase for LSW-1, remains for LSW-3 and increasing for LSW-2 which is only Magnesium ions contented distil water. But ten times diluted sea water which I called LSW_10 showed decreasing for IFT close to SSW.(this LSW_10 is ten times diluted SSW which was prepared later of this thesis work)

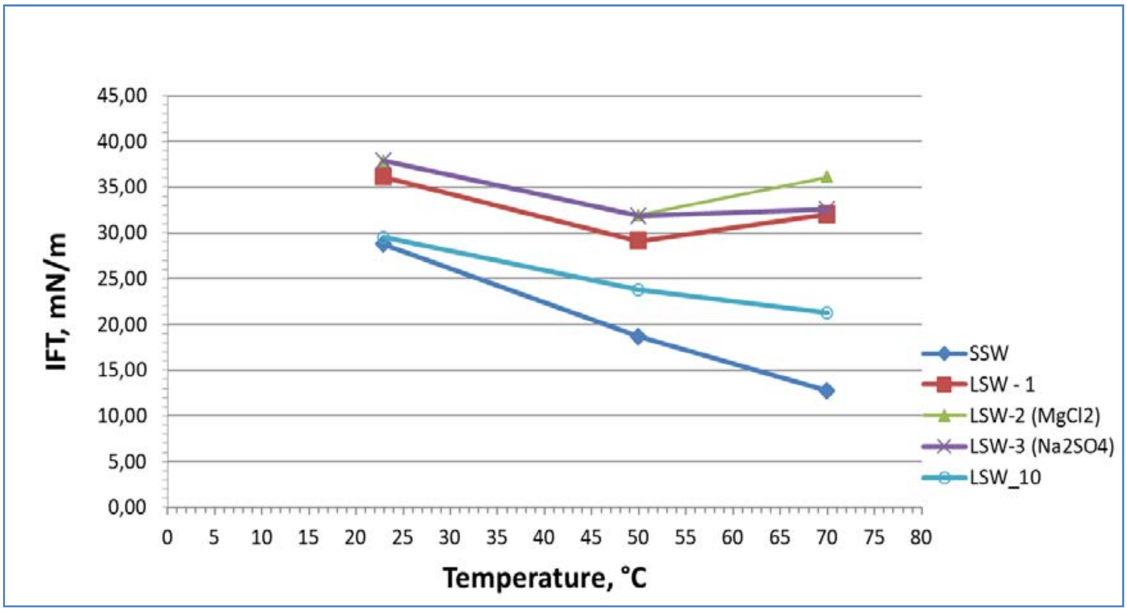


Fig 37*. IFT measurements of n-decane + SA with different types of brines.*

6.11 Relative permeability simulation result by Sendra

SENDRA or Sendra simulator is a two-phase 1D black-oil simulation model. Sendra is used for analyzing single SCAL experiments as well as several SCAL experiments at once. This program has automated history identical routine for history matching SCAL tests. The needed input data to start simulation are the core plug data such as dimensions of core, porosity, absolute permeability, fluid viscosities, injection rates, initial water saturation (S_{wi}), pressure drop across the core and production history as well as end point relative permeability and saturations. Corey correlations (Corey, 1954) for the relative permeability and the Skjæveland correlation (Skjæveland et al., 2000) for the capillary pressure were chosen for perform simulation to generate best K_{ro} and K_{rw} curves. Result of relative permeability for Stevns Klint cores displayed in the graphs below.

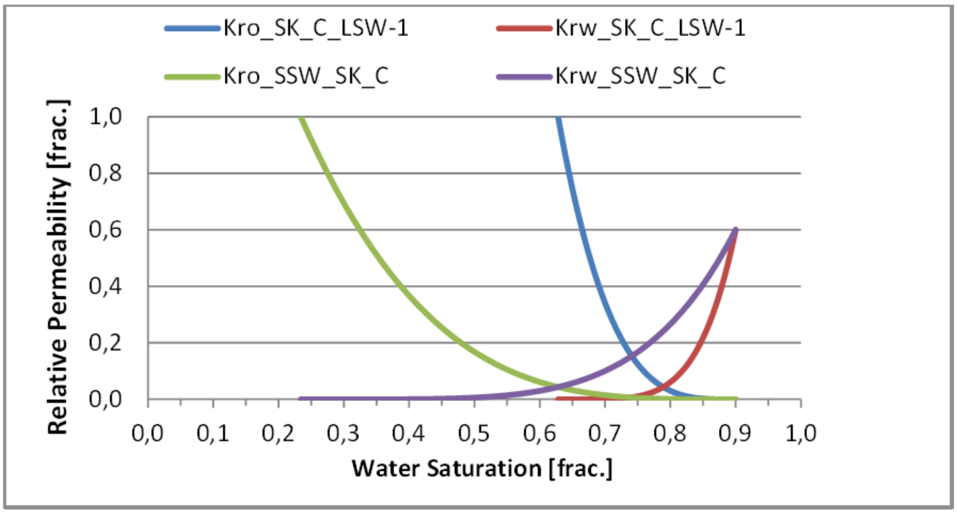


Fig 38. *K_{ro} and K_{rw} for SK_C core during SSW and continuous LSW-1 injection*

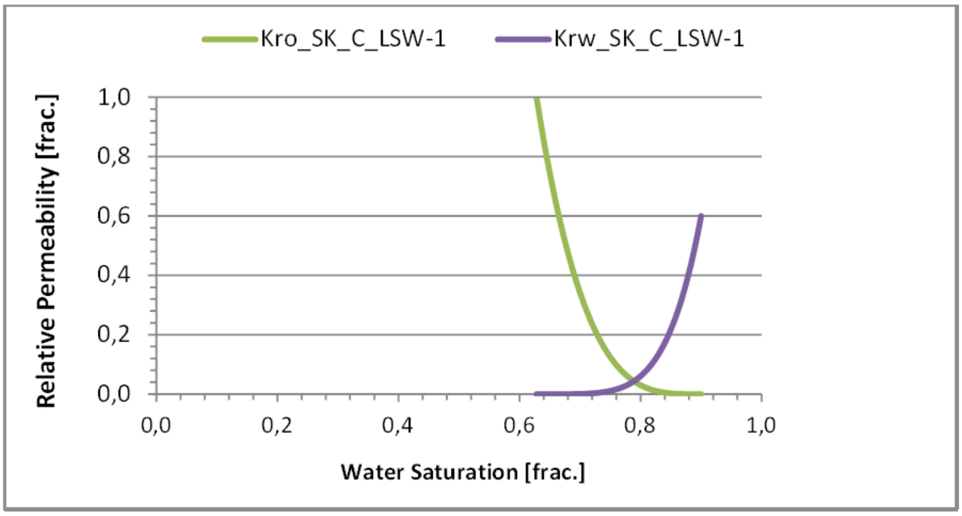


Fig 39. *K_{ro} and K_{rw} for SK_C core during LSW-1 injection*

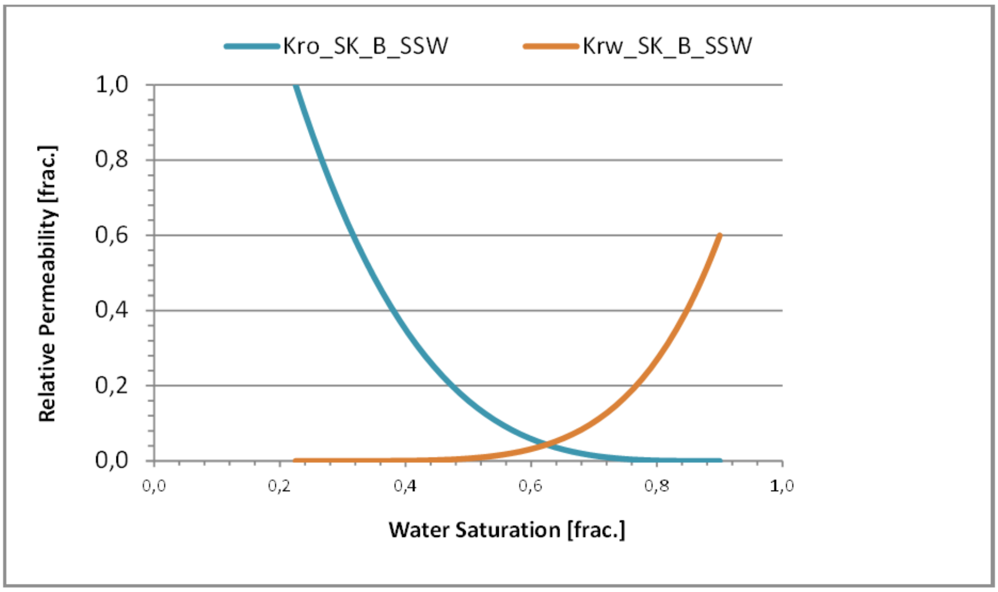


Fig 40. *K_{ro} and K_{rw} for SK_B core during SSW injection*

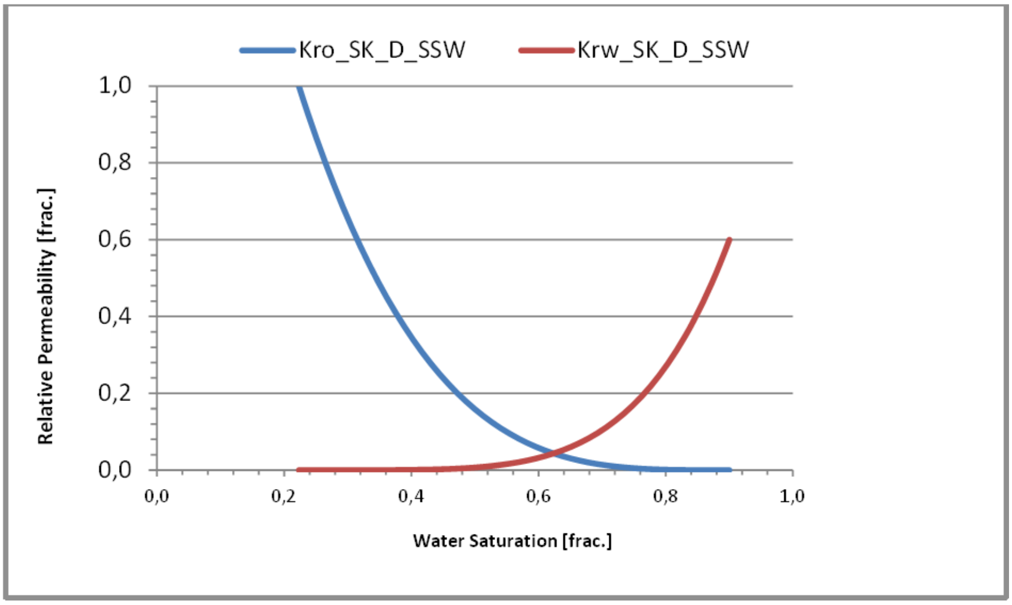


Fig 41. *K_{ro} and K_{rw} for SK_D core during SSW injection*

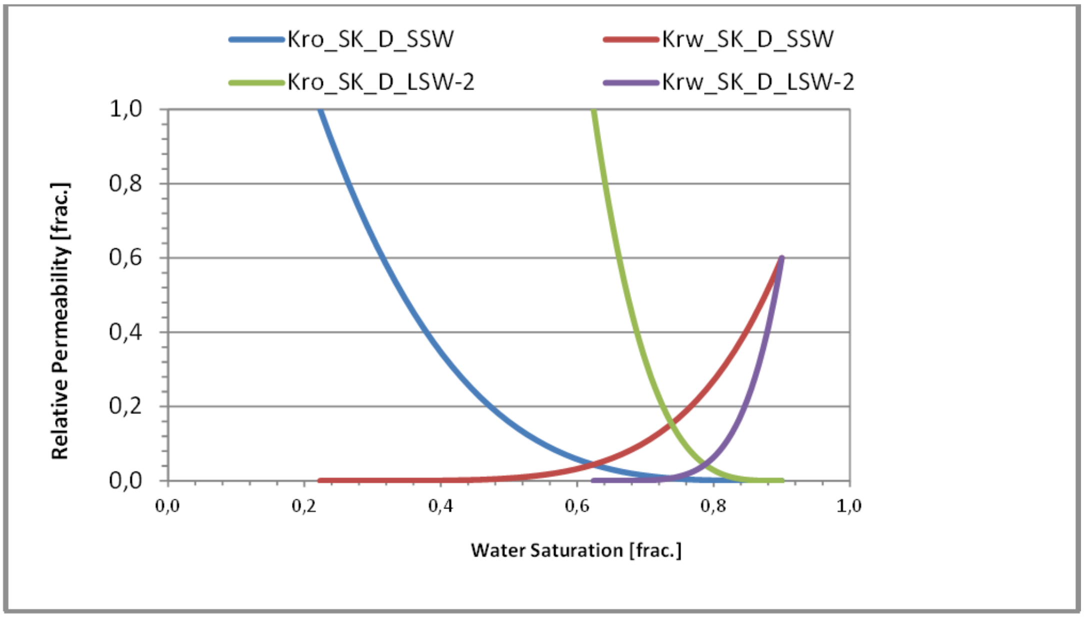


Fig42. *K_{ro} and K_{rw} for SK_D core during SSW and continuous LSW-1 injection*

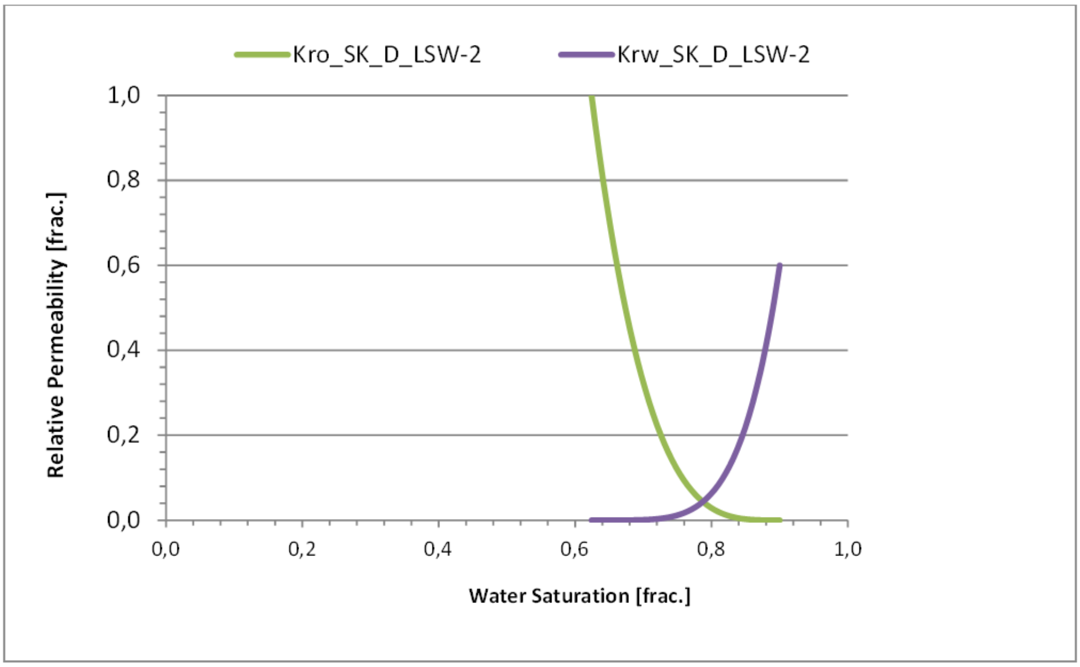


Fig 43. *K_{ro} and K_{rw} for SK_D core during LSW-2 injection*

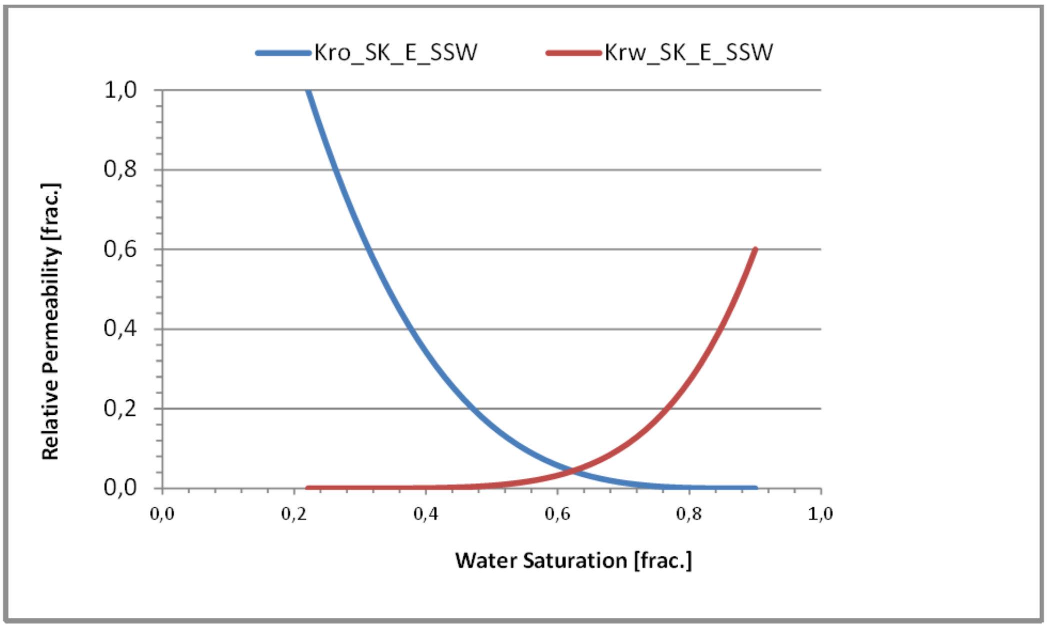


Fig 44. *K_{ro} and K_{rw} for SK_E core during SSW injection*

6.12 Imbibition result

Spontaneous imbibition experiments were carried out in the standard Amott cells. The first part of the test was performed with SSW as the primary imbibing fluid for all four SK cores.

Imbibition tests with Obourg cores could not be performed unfortunately due to this type of chalk is very weak and become attenuated on border sides (fig.45), nearly unconsolidated after second time of aging.

Fig 45. *Obourg cores after second aging*

The tests using SK cores started at room temperature and then performed at 50°C and 70° C. Since oil recovery stabilize changing of imbibing fluid done. All four SK cores did not give oil recovery at room temperature but provided imbibition at 50°C and 70° C.

The results of imbibition tests are shown below, fig.46. The recovery factor (RF) is plotted as a function of the time, where RF is deliberated from the volume of oil produced divided by the amount of oil in each of the SK cores.

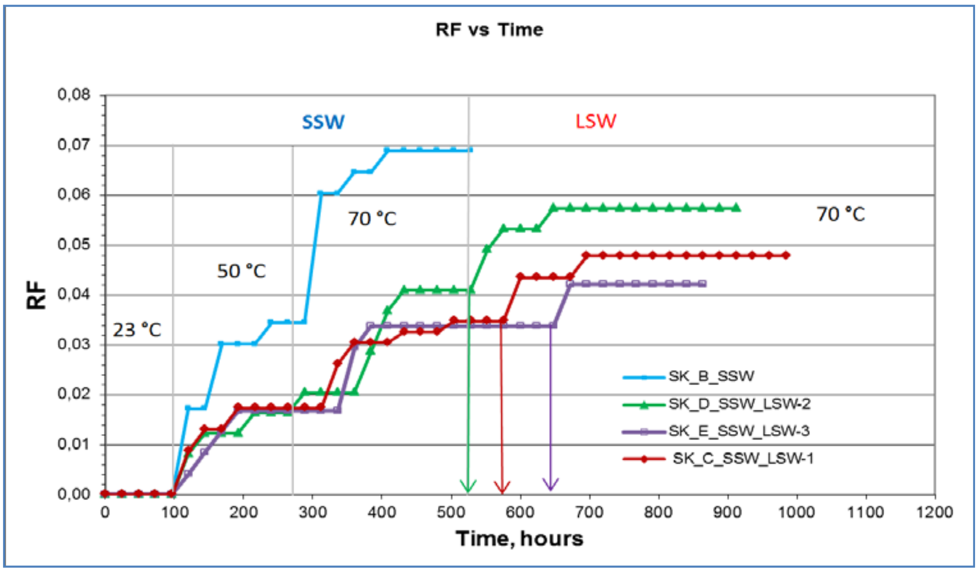


Figure 46. *Spontaneous imbibition experiments for all four SK chalk cores at different temperature phases. Arrows show at what time second imbibing liquid was filled for each of the cores.*

The imbibition test performed by SSW for all cores as initial imbibing fluid seems to follow more or less the same trend for 50°C and 70° C. Highest recovery, 6.9 % gave SK_B. The curves for three other SK cores shifted on the right due to the core SK_B was first ready for imbibition and did not test with second imbibing liquid. Arrows in the graph display that time when second imbibition test started depending on second aging time after flooding.

Normalized recovery factor versus time chart (fig.47) display that all four cores reach 50 % of total recovery at 50° C. Core SK_E produce oil fastest of all other cores at 50°C. But at 70°C trend of oil producing from SK_D and SK_E cores is similar as well as alike for SK_B and SK_C cores.

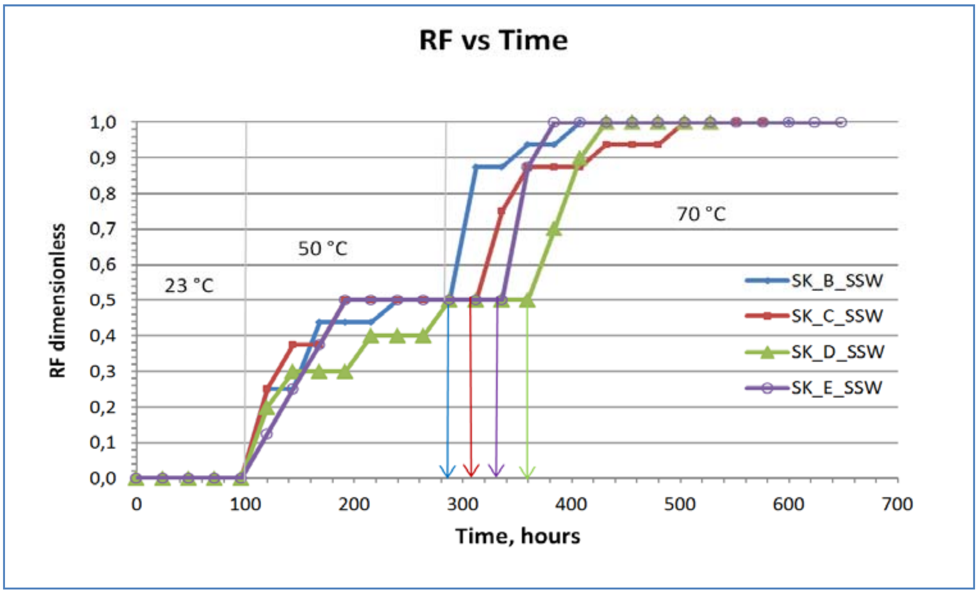


Figure 47. *Normalized imbibition result with SSW as first imbibing fluid for all four SK cores*

From fig. 16 we can see result of second imbibing fluid for three SK cores. The imbibition test was performed at 70°C. Maximum additional recovery around 1.7 % reaches core SK_D imbibed by LSW-2 that is only Mg^{2+} ions contained distil water; (table 1).The core imbibed by LSW-1 which is diluted SSW in the ratio of 1:25 by distil water provided extra 1.3 %.oil recovery.

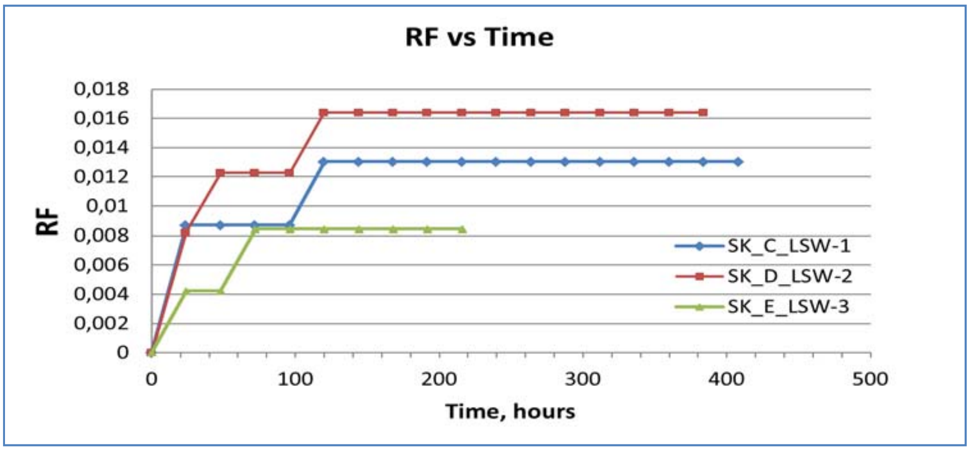


Figure 48. *Results from spontaneous imbibition tests carried out at 70°C with the different brines as second imbibing fluid for three SK cores.*

If we normalize the result of final recovery for all three SK cores with second imbibing fluid, fig. 49, we can see that fastest to achieve final oil recovery was core SK_E

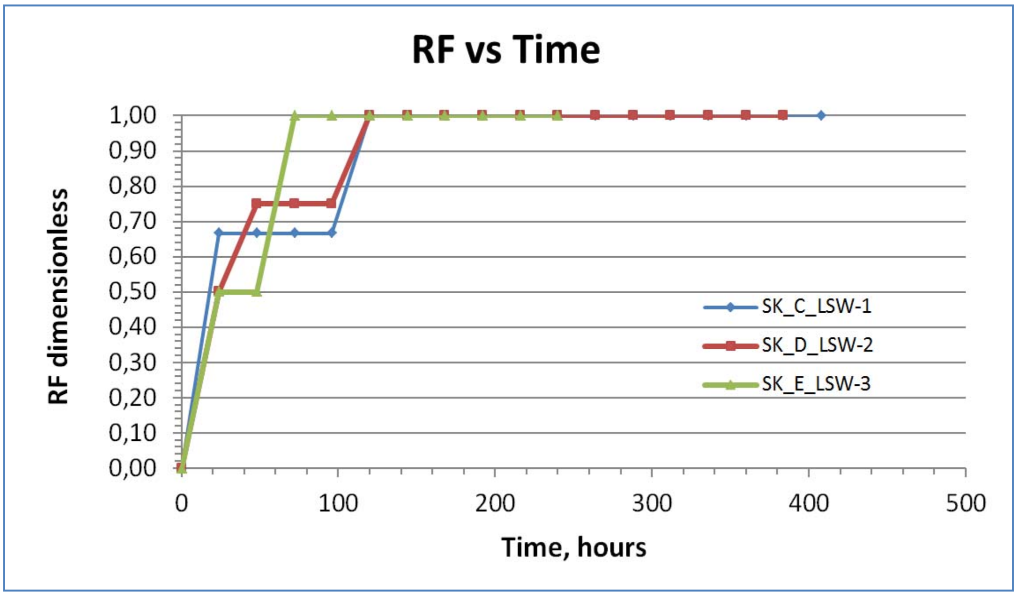


Figure 49. *Normalized results from spontaneous imbibition tests carried out at 70°C with the different brines as second imbibing fluid for three SK cores.*

7. Discussion

The different suggested mechanisms behind low salinity water flooding effect on oil recovery found from prior laboratory researching and literatures are briefly described below.

Alteration of wettability of the porous medium to more water - wet condition was stated as a main reason for enhanced oil recovery. It is proposed that when wettability changes from less to more water-wet state , oil is released from rock surfaces and recovery is increased (Austad et al., 2005 , Fernø et al., 2011 and Fjelde and Aasen, 2009).However approval for altering in wettability is often unintended such as from changes in relative permeability curves or contact angle measurement.

According Strand et al., (2009) the wettability alteration in carbonates can take place to more water wet condition at sea water (SSW) salinity. Injection of diluted sea water to low salinity state, 2000 ppm will decrease oil recovery depending of temperature due to decreasing of active ions such as Mg^{2+}, Ca^{2+} and SO_4^{2-}

A research trend performed by Austad et al.,2005; Strand et al., 2006; Zhang et al 2007; Austad et al., 2010 toward the chalk reservoirs states that seawater injection quite than all other types of water will improve oil recovery. This outcome is attributed to the reactivity of main seawater ions Mg^{2+}, Ca^{2+} and SO_4^{2-}. They have the ability to alter rock surface charges, release the adsorbed carboxylic oil components from rock surface, alter rock wettability and eventually increase oil recovery.

Lager et al., 2008 suggested a multi ion exchange (MIE) as a mechanism of for LSW.

McGuire et al., put forward that mechanism of action for LSW looks as if that alkaline flooding: in-situ forming of surfactant, alter wettability and reduction in IFT.

Hamouda and Rezaei Gomari (2006) reported increasing of oil recovery up to 8% for core altered with 0.001 Mole Stearic Acid in n - decane and imbibed by distilled water (DW) at elevated temperature from 70 ºC to 90ºC.

Karoussi and Hamouda (2007), with DLVO (Derjaguin, Landau, Verway, Overbeek) theory and experimental records concluded that fine migration could be one of the mechanisms that alter the wettability of the rock at raised temperature. Migrations of fines and redistribution of adsorbed molecules may well be explanation of higher oil recovery in magnesium case. They conclude that ionic interaction, fine migration and redistribution of adsorbed molecules on the surface are potential mechanisms that could increase oil recovery.

Contact angle measurements on calcite surface modified with oil performed by Tweheyo et al. and Gomari et al.2006 at different temperatures of different compositions of brines shows that Mg^{2+}, Ca^{2+} and SO_4^{2-} become more effective as temperature increases. .

Zhang et Al., 2007 reported that sulphate ions did not make contribution to variation of the IFT. IFT measurements had done between oil and brines (with different concentrations of

SO_4^{2-}) at room temperature. The impact of temperature on the IFT is not fully investigated, but in the most cases, the IFT between water/oil falls at elevated temperature.

Creation of a an emulsion phase with the Middle East crude oil at high temperature, pressure, and sulphate concentration stated by Zahid, A, et al,.(2011)

Saudi Aramco reported noteworthy increased oil recovery with various diluted versions of seawater, A.Y. Ali et al., (2011). The writers of this work pointed out that a mechanism for enhanced oil recovery was perhaps the other than from the reported in the before published works.

Austad et al. 2009 also stated low salinity effect (LSE) from core material sampled from the aqueous zone of a limestone reservoir. They saw 2-5 % increment in oil recovery by flooding the cores with diluted seawater. The chemical mechanisms for LSE were reported to be similar to the wettability modification taking place by high salinity water flooding in carbonates.

Most of above published research work were performed with testing crude oil/brine/rock or brine/rock interplays. The attraction of ions for the chalk surface which increases with temperature and then this contribute to improve oil recovery was that main conclusion of this general works.

SK_C core flooding with LSW-1 subsequent to synthetic sea water injection resulted in additional oil recovery at the end of the test when injection rate (IR) was increased to 16 PV/day after time of 4.6 PV have been flooded. A decrease of the pressure drop across the core, from about 3.2 to about 1.2 bar when switched from flooding with SSW to LSW.

In this work another type of outcrop chalk was used, Obourg chalk, core #2 flooded by LSW did not show a significant difference in pressure drop, where it was recorded a change from 2.6 to. 2.36 bar, fig.19 In this case no additional oil recovery was observed from this core. This outcrop core contains silicate, as shown in table 2.

From fig.27 with the pressure drop curves we can see a large increase when injection rate was increased at the end of the flooding with SSW. When the same core was flooded with low salinity water, the pressure drop fell across the chalk core. This is consistent with the results by, Ali A. et al., 2010, (Saudi Aramco). They reported general trend in the pressure drop curves as follow; ''As the salinity of sea water decreases the pressure drop across composite core also decreases, because the oil left in the composite cores at the end of regular seawater injection is residual oil and the pressure drop at this moment also reflects the capillary forces. Therefore constant reduction of pressure drop with injection of different diluted versions of sea water is another evidence of brine/oil/rock alterations. This is also consistent with contact angle measurements'' (Ali A. et al., 2010,)

I observed a formation of a third phase which could be emulsion in presence of some fines during LSW-1 water flooding and imbibition as well performed by LSW-1 as second imbibing fluid as shown in fig 50.

Fig. 50 *Formed emulsion with presence of some fines during imbibition test with SK_C core*

Samples were collected during the flooding experiments for ion tracking with ion chromatograph. Fig. 32 and 33 show a steady decrease in Mg $^{2+}$ ion concentration which reflects the SSW dilution with LSW as shown in Fig.33 (dimenssionlession concentration). Ca $^{2+}$ concentration (Fig.33) shows similar concentration decline curve as that with Mg $^{2+}$, however it starts to deviate from the steady declining rate of Mg $^{2+}$ after about 0.3 PV, which delays reaching of the steady state calcium concentration of the LSW. This may be explained based on dissolution of the precipitated calcium salt or the produced fines, causing a near equilibrium state with sulphate that reduces the declining rate of the calcium ion concentration until it reaches the steady state concentration (Ca $^{2+}$ in LSW).

In the case of sulphate ions concentration stable concentration as that in seawater until 0.5 PV of the core was flooded, where the declining rate of both Ca $^{2+}$ and SO_4^{2-} are almost equal before a large drop in the SO_4^{2-} ion concentration occurred at about 1.5PV, after which almost a steady state has been reached. It is known that SO_4^{2-} ions adsorbs on calcite surface, which then is released keeping seawater concentration, after which (at 0.5 PV) showed a steady decline curve (dissolution/precipitation took place) having almost same decline rate observed in the case of the calcium ions. This perhaps supports the above hypothesis of dissolution/precipitation that took place in the case of calcium. It is also supported by the pH, whereas the increase of the pH from 7.0 to about 7.3 both Mg^{2+} and Ca^{2+} have same declining rate (Fig.33), however the deviation coincided with further increase of the pH and declining of SO_4^{2-} concentration with same trend. As the pH continued to increase to about 8.0, SO_4^{2-} concentration had sharp drop and Ca^{2+} ions concentration finally reached to steady state concentration of the injected LSW.
IFT measurement LSW-1 with modified oil shows 32 mN/m at 70 °C which consistent with the results obtained by Ali A. et al., 2011 (Saudi Aramco) for LSW with 20 times diluted sea water. With this diluted ratio of injected low salinity water they reported additional oil recovery by about 1%which is similar what is obtained in this work.

Relative permeability curves generated by Sendra , Fig 38, shows that water saturation reached 60% before core SK_C when flooded with LSW-1. With low salinity injection relative permeability curves shifted in the right with water saturation near 80 % in the end of the flooding as shown in Fig 39.

Imbibition of the same core aged second times show additional result of oil recovery by LSW after SSW with 1.3 %. pH of about 8.12 was measured at the end of the tests.

Core SK_D that was flooded with LSW-2 which is the distilled water with only Mg^{2+} with concentration to SSW, showed similar result in tertiary oil recovery as in the LSW-1case but highest in imbibition as second imbibing fluid. Tertiary oil recovery is about one per cent at injection rate of 16 PV/day and 1.7 per cent increment in the imbibition test.

Pressure drop curves behaved similar, fig.29. Value of delta P is approximately the same around 2.7 bar in both case as SSW as well as LSW-2 before increasing of injection rate (IR). Magnitude of pressure drop after increasing of IR that is about 5 bar with SSW injection and decreasing from 4.8 to 3.7 bar in LSW-2 case.

No emulsion was formed in this case, but some special in ions concentration profile, fig 35. First when Mg^{2+} water stared inject Ca^{2+} and SO_4^{2-} ions concentrations increase during 0,2 PV but then start decreasing. SO4 2- continue reduce but Ca^{2+} went up during of injection of about 1,5 PV. That means that precipitation from rock surface still to produce them. During this time Mg^{2+} ions slightly declined and then these two curves interact. That means that possible replacing between Ca^{2+} and Mg^{2+} occurred.

While delayed with decreasing in Ca^{2+} happened under 2 PV injected sulphate still strong decreased but Mg 2+ continue increase cause this is water with only Mg^{2+} content. From around injected of 2 PV injections rate was increased with result in Ca^{2+} cations production ceased. pH in this case was growing slightly before increasing of IR 4 times.

Imbibition result was highest in compares with other result. With this type water as second imbibing liquid additional oil recovery showed 1.7% increment and pH became 7.8 pH units. IFT measurement showed quite high value of 36.11 mN/m at 70° C.

State of relative permeability curves was approximately similar to case with LSW-1, fig 41.

No result was achieved with flooding of core SK_E which was injected by LSW-3 neither some special in ions concentration behaviour.
Pressure drop curves performance more or less similar to case of LSW-1 injection. Pressure drop in case with SSW injection about 3 bar vs. about 2 bar with sulphate anions continuously injection and around 5 bar with SSW vs. 4 bar with LSW-3 at higher of 16 PV/day.

IFT measurement showed 32.58 mN/m that is very close to LSW-1 case.

Relative permeability curves show similarity to other cores, fig. 44. The core SK_E had lowest initial water saturation namely 22.1 per cent.

In imbibition SK_E core resulted in with about one per cent additional oil recovery. Noticeable that the pH was highest in compares of all previously test to be exact 8.77 pH units.

8. Conclusions

It may be concluded in this work that flooding of Stevens Klint outcrop chalk cores with LSW gave additional 1% oil recovery. For LSW as a secondary imbibing fluid an additional oil recovery of about 1.3% was obtained. This is compared to no additional recovery by flooding #2, #3 and #4 Cores. Those cores have silicate content which may have then affected the performance of the LSW.

In the case of chalk cores it is shown that Mg^{2+} ions gave additional increase of oil recovery during both flooding and imbibition (secondary imbibing fluid after SSW).
This work may suggest the mechanisms of incremental increase of the oil recovery by LSW are due to combined effects of lowering the IFT, fine migration and possible formation of emulsion. Certainly emulsion depends on the type of surfactants that are present in the oil and reduction of IFT may enhance the formation of emulsion.

9. References

1. Ahmed, T., 2010. *Reservoir Engineering Handbook, 4th Edition*. Oxford: Gulf Professional Publishing.

2. A.Y. Ali, A.-S. Salah Hamad, A.-K. Abdulaziz, A.-J. Mohammed Saleh, *Laboratory Investigation of the Impact of Injection-Water Salinity and Ionic Content on Oil Recovery from Carbonate Reservoirs*, SPE Reservoir Evaluation & Engineering (2011).

3. Al-Lawati, S. and Saleh, S., 1996. *Oil Recovery in Fractured Oil Reservoirs by Low IFT Imbibition Process*. Denver: Society of Petroleum Engineers.

4. Anderson, W.G., 1986a. *Wettability Literature Survey: Part 1. Rock/Oil/Brine Interactions and the Effects of Core Handling on wettability*. Journal of Petroleum Technology, October: 1125-1144.

5. Anderson, W.G., 1986b. *Wettability Literature Survey – Part 2: Wettability measurement.* Journal of Petroleum Technology, November: 1246-1262.

6. Ashraf, A.; Hadia, N.J., and Torsæter, O., 2010. “*Laboratory Investigation of Low Salinity Water flooding as Secondary Recovery Process: Effect of Wettability*”. SPE 129012 Paper was Prepared for Presentation at the SPE Oil and Gas India Conference and Exhibition held in Mumbai, India, January 20 - 22.

7. Austad, T., Rezaeidoust, A., & Puntervold, T. (2010). *Chemical mech- anism of low salinity water flooding in sandstone reservoirs. In 17th Symposium on Improved Oil Recovery* SPE 129767. Tulsa, Oklahoma, USA.

8. Austad, T., Strand, S., Hognesen, E., & Zhang, P. (2005). *Seawater as IOR fluid in fractured chalk. In SPE International Symposium on Oil field Chemistry* SPE 93000. Houston, Texas, USA.

9. Austad, T., 2012. *Water Based EOR in Carbonates and Sandstones: New Chemical Understanding of the EOR-Potential Using “Smart Water”.* Muscat: University of Stavanger.

10. Austad, T., 2008. *Seawater in Chalk: An EOR and Compaction Fluid*. San Francisco: American Rock Mechanics Association.

11. Austad, T. and Milter, J., 1997. *Spontaneous Imbibition of Water Into Low Permeable Chalk at Different Wettabilities Using Surfactants*. Houston: Society of Petroleum Engineers.

12. Austad, T., RezaeiDoust, A., & Puntervold, T., 2010. *Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs*. Tulsa: Society of Petroleum Engineers.

13. Boussour, S., Cissokho, M., Cordier, P., Bertin, H. & Hamon, G., 2009. *Oil Recovery by Low Salinity Brine Injection: Laboratory Results on Outcrop and Reservoir Cores.* New Orleans: Society of Petroleum Engineers.

14. Brownscobe ER, Dyes AB. *A Water-imbibition Displacement-A Possibility for the Spraberry~*'Drilling and Production Practice, of API. 1952; 383-390.

15. Buckley, J. S., Liu, Y. and Monsterleet, S., 1998. *Mechanisms of Wetting Alteration by Crude Oils.* SPE Journal, March: 54-61.

16. Baviére, M., 1991. *Basic concepts in enhanced oil recovery processes. Critical reports on applied chemistry*. Published for the Society of Chemical Industry by Blackwell., Oxford, XIV: 412. In: RezaeiDoust, A., 201140.

17. Babadagli, T., Al-Bermani, A. and Boukadi, F., 1999. *Analysis of Capillary Imbibition Recovery Considering the Simultaneous Effects of Gravity, Low IFT, and Boundary Conditions*. Kuala Lumpur: Society of Petroleum Engineers.

18. Baviére, *M., 1991. Basic concepts in enhanced oil recovery processes. Critical reports on applied chemistry. Published for the Society of Chemical Industry by Blackwell., Oxford, XIV: 412. In: RezaeiDoust, A., 201140.*

19. Cuiec, L., Bourbiaux, B. and Kalaydijian, F., 1994. *Oil Recovery by Imbibition in Low-Permeability Chalk.* SPE formation Evaluation, 9: 200-208.

20. Gomari, K. A. R., Hamouda, A. A. and Denoyel, R., 2006. *Influence of sulfate ions on the interaction between fatty acids and calcite surface.* Colloids and Surfaces A: Physicochem. Eng. Aspects, 287: 29–35.

21. Fjelde, I., Asen, S., & Omekeh, A. (2012). *Low salinity water flooding experiments and interpretation by simulations*. In SPE Improved Oil Recovery Symposium SPE 154144. Tulsa, Oklahoma, USA.

22. Gomari, K. A. R., Karoussi, O. and Hamouda A. A., 2006a. *Mechanistic Study of Interaction Between Water and Carbonate Rocks for Enhancing Oil Recovery*. Vienna: Society of Petroleum Engineers.

23. Graue, A., Viksund, B. G., Baldwin, B. A., 1999. *Reproducible Wettability Alteration of Low-Permeable Outcrop Chalk.* SPE Reservoir Evaluation & Engineering 2(2): 134-140.

24. Green D. W. and Willhite, G. P., 1998. *Enhanced oil recovery*. SPE textbook series.Richardson: Society of Petroleum Engineers.

25. Hamouda, A. A., Rezaei Gomari, K. A., 2005. *Effect of fatty acids, water composition and pH on the wettability alteration of calcite surface*. Tulsa: Society of Petroleum Engineers.

26. Hamon,G and Vidal,J.1986.*Scaling-Up the Capillary Imbibition Process from laboratory experiments on homogeneous and heterogeneous samples*. Paper SPE 15852 presented at the SPE European Petroleum Conference, London, 20-22 October

27. Fjelde, I., Asen, S., & Omekeh, A. (2012). *Low salinity water flooding experiments and interpretation by simulations. In SPE Improved Oil Recovery Symposium,* SPE 154144. Tulsa, Oklahoma, USA.

28. Hamouda, A. A., Rezaei Gomari, K. A., 2005. *Effect of fatty acids, water composition and pH on the wettability alteration of calcite surface*. Tulsa: Society of Petroleum Engineers.

29. Hansen G, A.A. Hamouda A.A. , Denoyel R.,2000. *The effect of pressure on contact angles and wettability in the mica:water:n-decane system and the calcite_stearic acid:water:n-decane system.* Colloids and Surfaces A: Physicochemical and Engineering Aspects 172 (2000) 7–16

30. Hjuler, M. L. and Fabricius, I. L., 2009. *Engineering properties of chalk related to diagenetic variations of Upper Cretaceous onshore and offshore chalk in the North Sea area*. Journal of Petroleum Science and Engineering: 68: 151-170.

31. Hiorth, A.; Cathles, L.M., and Madland, M.V., 2010. “The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability”. Trans. Porous Media. DOI: 10.1007/s11242-010-9543-3.

32. Idowu, J.; Somerville, J.; Adebari, D., and Meshioye, O., 2011. “*Effect of Salinity Changes of the Injected Water on Water Flooding Performance in Carbonate Reservoirs”.* SPE150816 Paper was Prepared for Presentation at the International Conference and Exhibition held in Abuja, Nigeria, July 30 - August 03.

33. Iffly, R., Rousselet, D.C., Vermeulen, J.L., 1972. *Fundamental study of imbibition in fissured oil fields.* SPE Annual Fall Meet, San Antonio, TX, Oct. 8 –11. SPE Paper 4102.

34. Høgnesen, E. J., 2005. *EOR in fractured oil-wet chalk: Spontaneous imbibition of water by wettability alteration*. Ph.D. Thesis. University of Stavanger.

35. Karoussi, O. and Hamouda, A. A., 2007. *Imbibition of Sulfate and Magnesium Ions into Carbonate Rocks at Elevated Temperatures and Their Influence on Wettability Alteration and Oil Recovery*. Energy & Fuels: 21: 2138-2146.

36. Lager, A., Webb, K. J., and Black, C. J. J., 2007. *Impact of brine chemistry on oil recovery.* Paper A24 presented at the 14th European Symposium on Improved Oil Recovery, Cairo, Egypt, 2007. In: Håmsø, 2011[28].

37. Lager, A., Webb, K. J., Collins, I. R and Richmond, D. M., 2008. *LoSal Enhanced Oil Recovery: Evidence of Enhanced Oil Recovery at the Reservoir Scale*. Oklahoma: Society of Petroleum Engineers.

38. A. Lager, K.J. Webb, I.R. Collins, D.M. Richmond, LoSal Enhanced Oil Recovery: *Evidence of Enhanced Oil Recovery at the Reservoir Scale,* SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, 2008.

39. Lager, A., Webb, K., Black, C., Singleton, M., & Sorbie, K. (2006). *Low salinity oil recovery: An experimental investigation.* In International Symposium of the Society of Core Analyst. Trondhiem, Norway.

40. Lager, A., Webb, K., Collins, I., & Richmond, D. (2008*). LoSaltm en- hanced oil recovery : Evidence of enhanced oil recovery at the reservoir scale*. In SPE/DOE Symposium on Improved Oil Recovery SPE 113976. Tulsa, Oklahoma, USA.

41. Lager, A., Webb, K., & Seccombe, J. (2011*). Low salinity waterood, Endicott, Alaska: Geochemical study & _eld evidence of multicompo- nent ion exchange.* In European Symposium on Improved Oil Recovery. Cambridge, UK.

42. Lebedeva, E., Senden, T., Knackstedt, M., & Morrow, N. (2009). *Improved oil recovery from tensleep sandstone.* In European symposium of improved oil recovery. Paris, France.

43. Ligthelm, D., Gronsveld, J., Hofman, J. P., Brussee, N. J., Marcelis, F., & van der Linde, H. (2009). *Novel waterooding strategy by manipula- tion of injection brine composition*. In SPE EUROPEC/EAGE Annual Conference and Exhibition SPE 119835. Amsterdam, Netherlands.

44. Masalmeh, S. K., Jing, X., van Vark, W., Christiansen, S., van derWeerd, H., & van Dorp, J. (2003). *Impact of SCAL on carbonate reservoirs: How capillary forces can affect field performance predictions*. In Inter- national Symposium of the Society of Core Analysts. Pau, France.

45. McGuire, P., Chatham, J., Paskvan, F., Sommer, D., & Carini, F. (2005). *Low salinity oil recovery: An exciting new EOR oppurtuin- ity for alaska's north slope*. In SPE Western Regional Meeting SPE 93903. Irvine, CA, USA.

46. Morrow, N., & Buckley, J. (2011). *Improved oil recovery by low-salinity waterooding.* Journal of Petroleum Technology, 63 , 106-112.

47. Milter, J., 1996. *Improved Oil Recovery in Chalk. Spontaneous imbibition affected by Wettability, Rock Framework and Interfacial Tension. Ph.D. Thesis. Department of Chemistry, University of Bergen.*

48. Morrow, N.R., 1990. *Wettability and its effect on oil recovery.* Journal of Petroleum Technology, December: 1476-1484.

49. Morrow, N. R. and Mason, G., 2001. *Recovery of oil by spontaneous imbibition.* Colloid & Interface Science, 6(4): 321-337.

50. Morrow, N. R., Zhou, X. and Ma, S., 1996. *Interrelationship of Wettability, Initial Water Saturation, Aging Time, and Oil Recovery by Spontaneous Imbibition and Waterflooding.* Tusla: Society of Petroleum Engineers.

51. Nadeau, P. 2013.*Geological overview of Reservoir Quality in Global Sandstone Resevoirs*.UIS,Department of Petroleum Engineering, MPE110.

52. Petrovich, R. and Hamouda, A. A., 1998. *Dolomitization of Ekofisk Oil Field Reservoir Chalk by Injected Seawater, Water Rock Interaction.* Arehart& Hulston (eds.), Balkema, Rotterdam (1998) 345. In: Gomari et al., 200621.

53. Puntervold, T., 2008. *Waterflooding of carbonate reservoirs: EOR by wettability alteration.* Ph.D. Thesis. University of Stavanger.

54. RezaeiDoust, A., 2011. *Low Salinity Water Flooding in Sandstone Reservoirs: A Chemical Wettability Alteration Mechanism.* Ph.D. Thesis. University of Stavanger.

55. RezaeiDoust, A., Puntervold, T. and Strand, S., 2009. *Smart Water as Wettability Modifier in Carbonate and Sandstone: A Discussion of Similarities/Differences in the Chemical Mechanisms*. Energy Fuels, 23: 4479–4485

56. Romanuka, J., Hofman, J. P., Ligtheilm, D. J., Suijkerbuijk, B. M. J. M., Marcelis, A. H. M., Oedai, S., Brussee, N. J., van der Linde, H. A., Aksulu, H. and Austad, T., 2012. *Low Salinity EOR in Carbonates*. Tulsa: Society of Petroleum Engineers.

57. Sandersen, S.B; Stenby, E. H.; Solms, N.V. and Shapiro, A. A. *Advanced Waterflooding in Chalk Reservoirs: Understanding of Underlying Mechanisms* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 389 (2011) 281–290

58. SENDRA (2009). *User guide, sendra windows version 2011.03*. www.sendra.no. Downloaded 22 June 2012.

59. Schechter, D.S., Zhou, D., Orr, F.M., 1994. *Low IFT drainage and imbibition*. J. Pet. Sci. Eng. 11, 283-300.

60. Standnes, D. C., & Austad, T. (2003). *Wettability alteration in car- bonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet con- ditions.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 216 , 243 - 259.

61. Strand, S., Hagnesen, E. J., & Austad, T. (2006). *Wettability alteration of carbonates- effects of potential determining ions (Ca^{2+} and SO_4^{2-}) and temperature*. Colloids and Surfaces A: Physicochemical and Engi- neering Aspects, 275 , 1 - 10.

62. Suijkerbuijk, B., Hofman, J. P., Ligthelm, D., a, J. R., Brussee, N., van der Linde, H., & Marcelis, A. (2012). *Fundamental investigation into wettability and low salinity*

flooding by parameter isolation. In SPE Symposium on Improved Oil Recovery SPE 154204. Tulsa, Oklahoma, USA.

63. Sulak, R.M., 1991. *Ekofisk field: The first 20 years*. Journal of Petroleum Technology, October: 1265-1271

64. Tang, G., & Morrow, N. (1997). *Salinity, temperature, oil composition, and oil recovery by water ooding. SPE Reservoir Engineering,* 12, 269-276.

65. Tabary, R.; Fornari, A.; Bazin, B.; Bourbiaux, B., and Dalmazzone, C., 2009. "*Improved Oil Recovery With Chemicals in Fractured Carbonate Formations*". Doc ID. 121668-MS. Conference Paper SPE International Symposium on Oilfield Chemistry. Woodlands, Taxas, April 20 - 22.

66. Tang, G., & Morrow, N. (1999a). *Oil recovery by water ooding and imbibition - invading brine cation valency and salinity*. In International Symposium of the Society of Core Analysts. Golden, CO.

67. Tang, G. Q., & Morrow, N. R. (1999b). *Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery.* Journal of Petroleum Science and Engineering, 24, 99 - 111.

68. Treiber, L. E., Archer, Duane L, Owens, W.W. Amoco Production Co. Tulsa Okla. 1972. A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs. Paper SPEJ 3526 p.531-540 was presented at SPE 46th Annual Fall Meeting, held in New Orleans, Oct 3-6, 1972

69. Wael, A.; Buckley, J.S.; Carnegie, A.; Edwards, J.; Fordham, E.; Graue, A.; Habashy, T.;Seleznev, N.; Signer, C.; Hussain, H.; Montaron, B., and Ziauddin, M., 2007. "Fundamentals of Wettability". Oilfield Review, Summer, pp. 44 - 61.

70. Wayne M Ahr, Geology of Carbonate Reservoirs The Identification, Description and Characterization of Hydrocarbon Reservoirs in Carbonate Rocks

71. Willhite, G. (1986). Waterooding. Spe Textbook Series. Society of Petroleum Engineers.

72. Yousef, A. A., Al-Saleh, S., Al-Kaabi, A., & Al-Ja , M. (2011). Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs. SPE Reservoir Eval- uation & Engineering, 15, 578-593.

73. Zahid, A.; Shapiro, A. A.; Stenby, E. H. and Yan, W. *Managing Injected Water Composition to Improve Oil Recovery: A Case Study of North Sea Chalk Reservoirs* Submitted to Energy & Fuels (2011)

74. Zhang, P., Tweheyo, M. T., & Austad, T. (2007). Wettability alter- ation and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions(Ca2+, Mg2+ and SO2□ 4). Colloids and Surfaces A: Physicochemical and Engineering As- pects, 301 , 199 - 208.

75. Zhang, P, M.T. Tweheyo, T. Austad, *Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate,* Energy & fuels 20 (2006) 2056-2062.

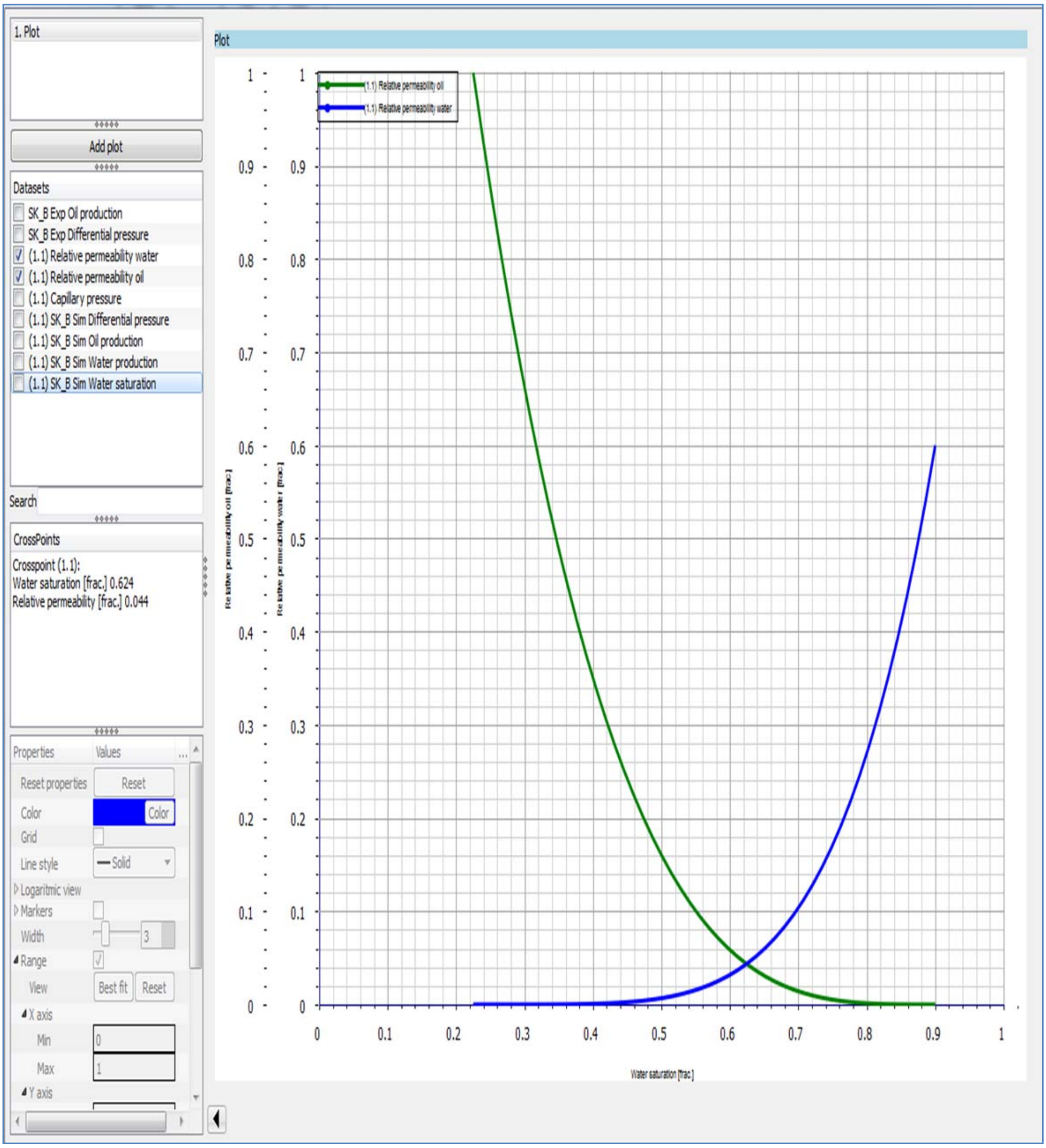
76. Zheng, J., 2001. *Mechanisms that Affect the Wettability of Quartz Exposed to Coal Derived NAPL.* Ph.D Thesis, Clarkson University, New York, USA.

77. Zolotukhin, A., & Ursin, J. (2000). *Introduction to Petroleum Reservoir Engineering*. Høyskoleforlaget, Norwegian Academic Press.

78. Zhou, Monson, Teng, Schulz, and Zakian (2000*). Pif1p helicase, a catalytic inhibitor of telomerase in yeast.* Science 289: 771-774

Appendix

Graphs on the relative permeability generated by Sendra simulation



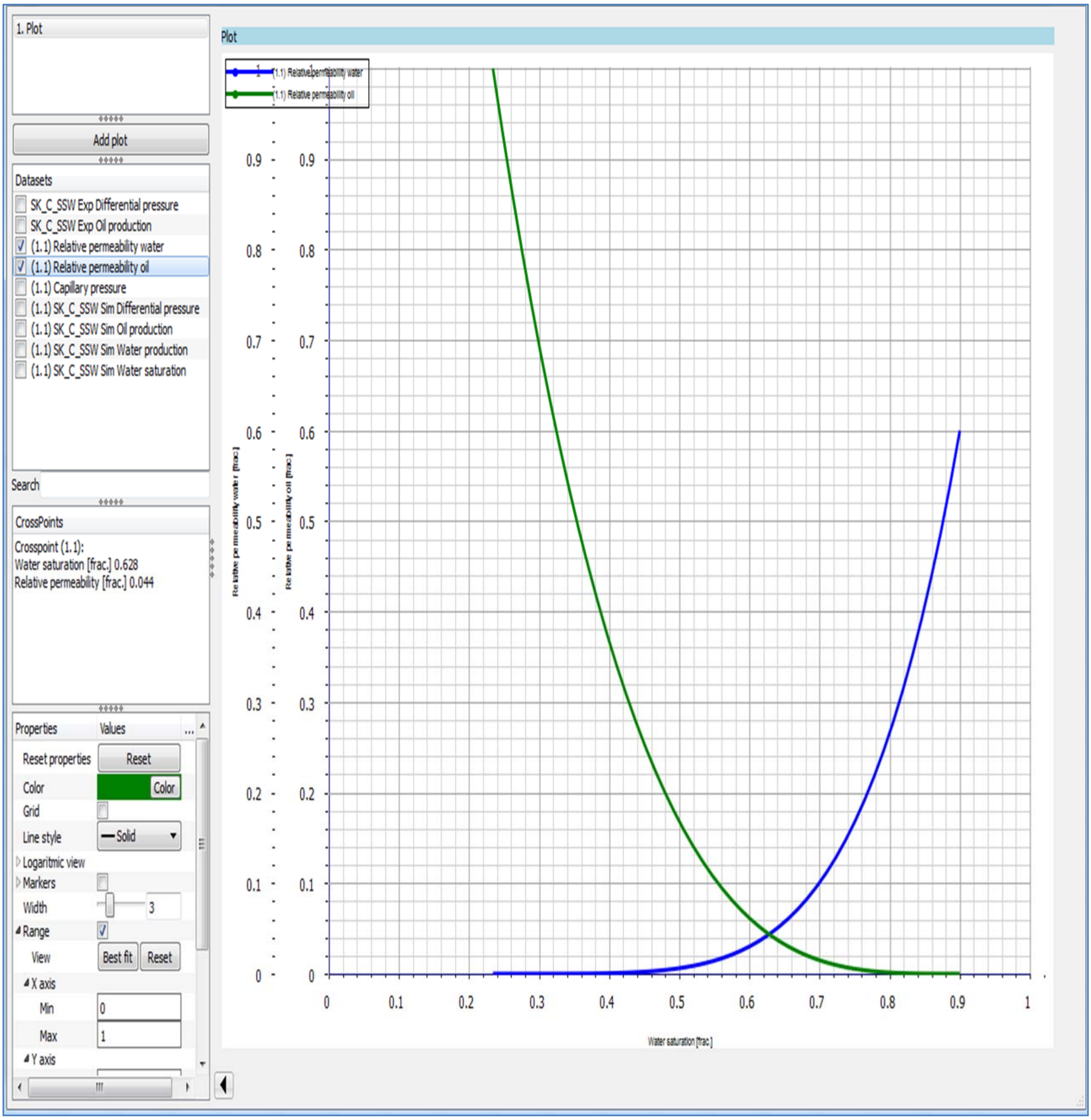
Datasets

- ☐ SK_B Exp Oil production
- ☐ SK_B Exp Differential pressure
- ☑ (1.1) Relative permeability water
- ☑ (1.1) Relative permeability oil
- ☐ (1.1) Capillary pressure
- ☐ (1.1) SK_B Sim Differential pressure
- ☐ (1.1) SK_B Sim Oil production
- ☐ (1.1) SK_B Sim Water production
- ☐ (1.1) SK_B Sim Water saturation

CrossPoints

Crosspoint (1.1):
Water saturation [frac.] 0.624
Relative permeability [frac.] 0.044

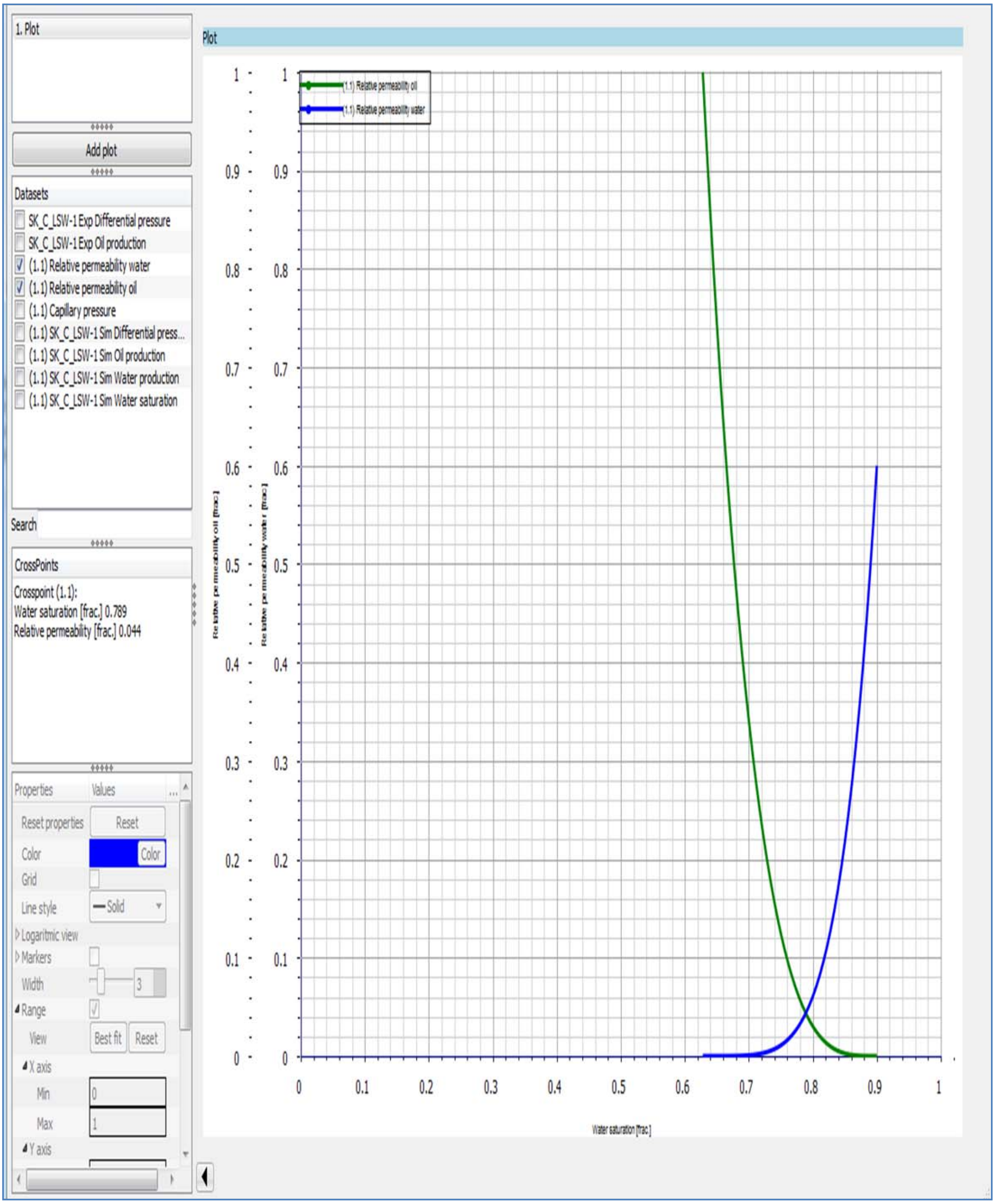
Properties	Values
Reset properties	Reset
Color	Color
Grid	☐
Line style	Solid
Logaritmic view	
Markers	☐
Width	3
Range	☑
View	Best fit / Reset
X axis	
Min	0
Max	1
Y axis	



☐ SK_C_SSW Exp Differential pressure
☐ SK_C_SSW Exp Oil production
☑ (1.1) Relative permeability water
☑ (1.1) Relative permeability oil
☐ (1.1) Capillary pressure
☐ (1.1) SK_C_SSW Sim Differential pressure
☐ (1.1) SK_C_SSW Sim Oil production
☐ (1.1) SK_C_SSW Sim Water production
☐ (1.1) SK_C_SSW Sim Water saturation

Crosspoint (1.1):
Water saturation [frac.] 0.628
Relative permeability [frac.] 0.044

Properties	Values
Reset properties	Reset
Color	🟩 Color
Grid	☐
Line style	Solid
Logaritmic view	
Markers	☐
Width	3
Range	☑
View	Best fit Reset
X axis	
Min	0
Max	1
Y axis	



Datasets

☐ SK_C_LSW-1 Exp Differential pressure
☐ SK_C_LSW-1 Exp Oil production
☑ (1.1) Relative permeability water
☑ (1.1) Relative permeability oil
☐ (1.1) Capillary pressure
☐ (1.1) SK_C_LSW-1 Sim Differential press...
☐ (1.1) SK_C_LSW-1 Sim Oil production
☐ (1.1) SK_C_LSW-1 Sim Water production
☐ (1.1) SK_C_LSW-1 Sim Water saturation

CrossPoints

Crosspoint (1.1):
Water saturation [frac.] 0.789
Relative permeability [frac.] 0.044

Reset properties: Reset
Color: Color
Grid: ☐
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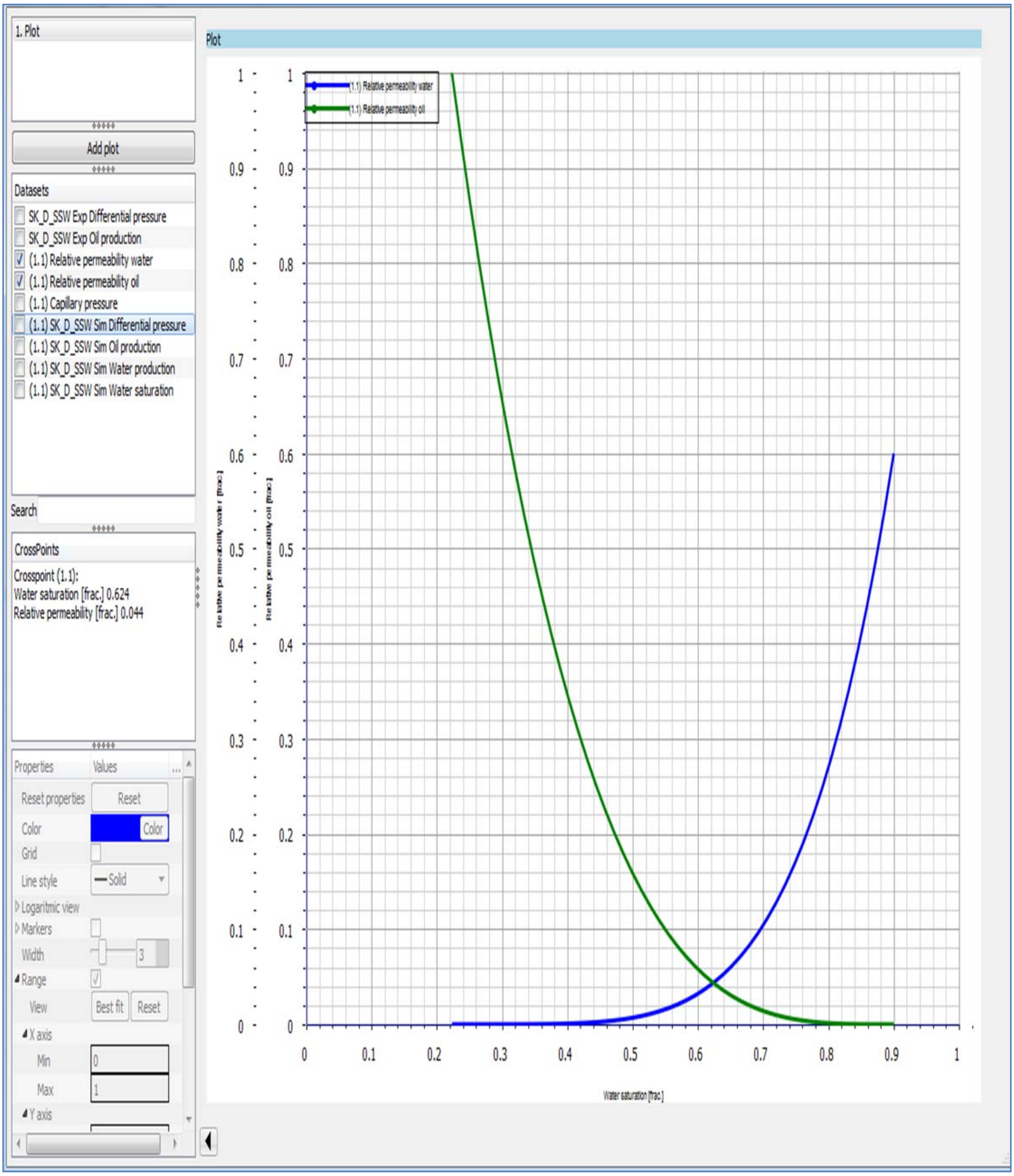

☐ SK_D_SSW Exp Differential pressure
☐ SK_D_SSW Exp Oil production
☑ (1.1) Relative permeability water
☑ (1.1) Relative permeability oil
☐ (1.1) Capillary pressure
☐ (1.1) SK_D_SSW Sim Differential pressure
☐ (1.1) SK_D_SSW Sim Oil production
☐ (1.1) SK_D_SSW Sim Water production
☐ (1.1) SK_D_SSW Sim Water saturation

Crosspoint (1.1):
Water saturation [frac.] 0.624
Relative permeability [frac.] 0.044

Properties	Values
Reset properties	Reset
Color	Color
Grid	☐
Line style	Solid
Logaritmic view	
Markers	☐
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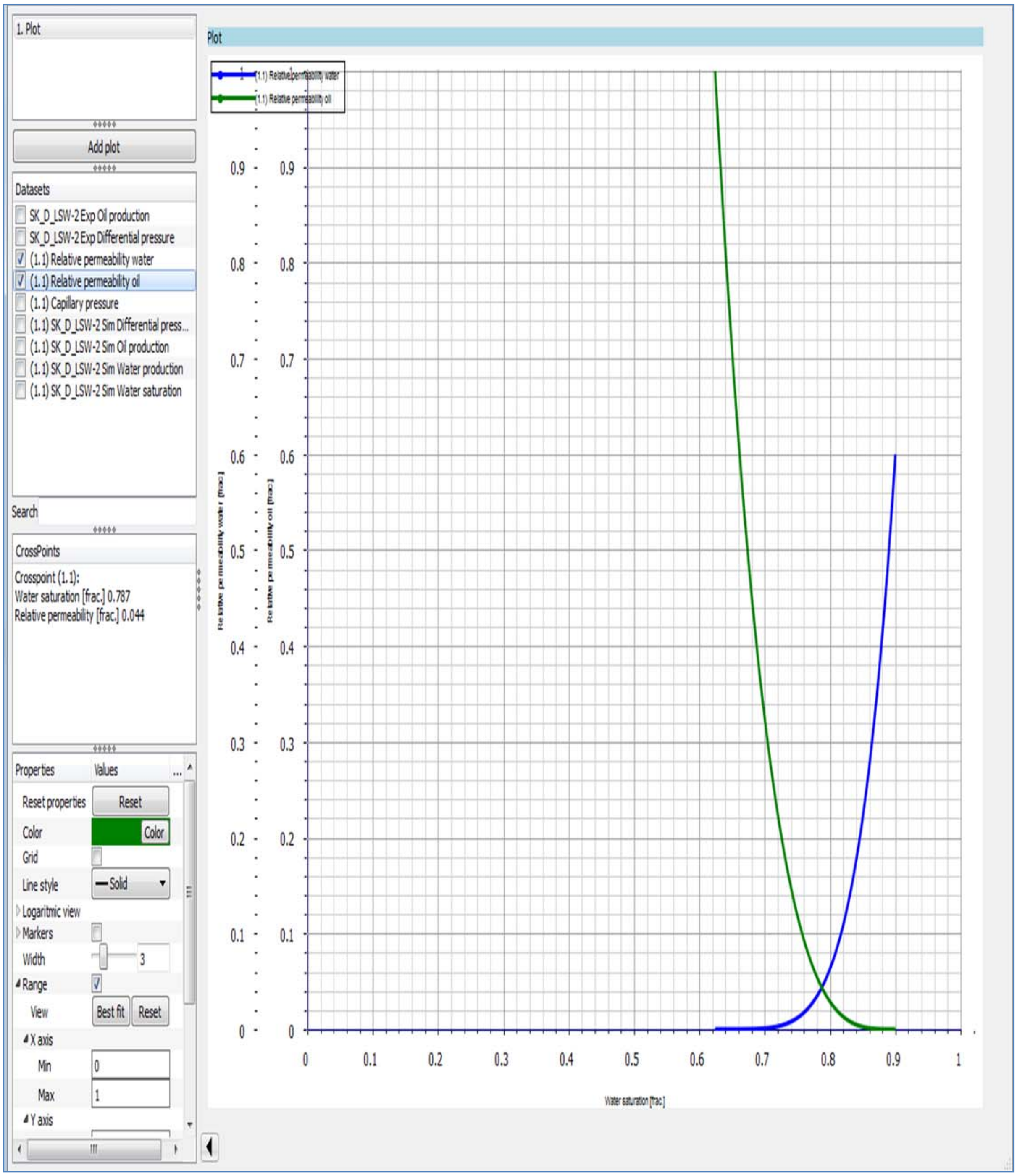
Range	☑
View	Best fit Reset
X axis	
Min	0
Max	1
Y axis	



Datasets

☐ SK_D_LSW-2 Exp Oil production
☐ SK_D_LSW-2 Exp Differential pressure
☑ (1.1) Relative permeability water
☑ (1.1) Relative permeability oil
☐ (1.1) Capillary pressure
☐ (1.1) SK_D_LSW-2 Sim Differential press...
☐ (1.1) SK_D_LSW-2 Sim Oil production
☐ (1.1) SK_D_LSW-2 Sim Water production
☐ (1.1) SK_D_LSW-2 Sim Water saturation

CrossPoints

Crosspoint (1.1):
Water saturation [frac] 0.787
Relative permeability [frac] 0.044

Properties	Values
Reset properties	Reset
Color	🟩 Color
Grid	☐
Line style	— Solid
Logaritmic view	
Markers	☐
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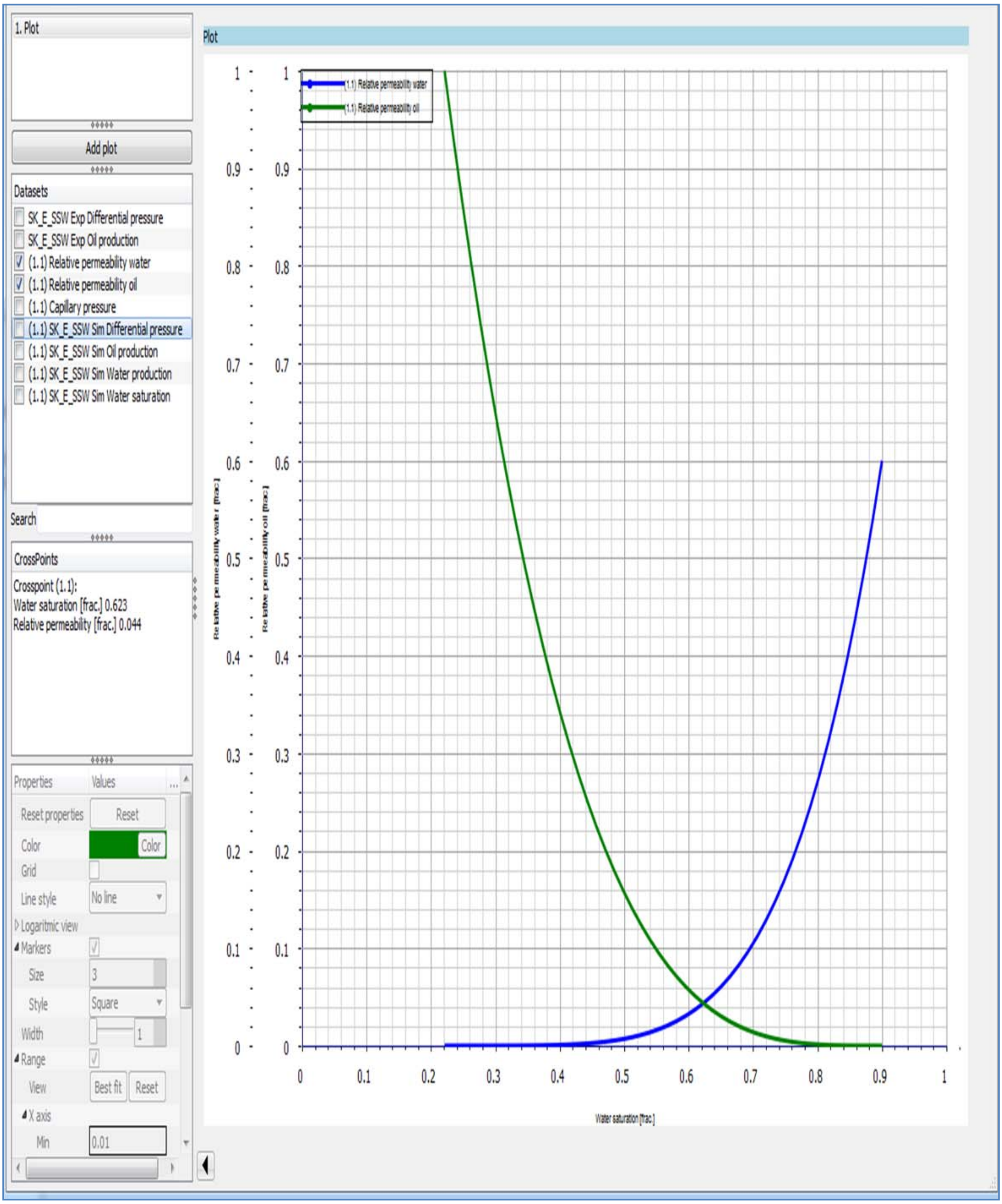
View	Best fit Reset
X axis	
Min	0
Max	1
Y axis	



Datasets

☐ SK_E_SSW Exp Differential pressure
☐ SK_E_SSW Exp Oil production
☑ (1.1) Relative permeability water
☑ (1.1) Relative permeability oil
☐ (1.1) Capillary pressure
☐ (1.1) SK_E_SSW Sim Differential pressure
☐ (1.1) SK_E_SSW Sim Oil production
☐ (1.1) SK_E_SSW Sim Water production
☐ (1.1) SK_E_SSW Sim Water saturation

CrossPoints

Crosspoint (1.1):
Water saturation [frac.] 0.623
Relative permeability [frac.] 0.044

Properties	Values
Reset properties	Reset
Color	🟩 Color
Grid	☐
Line style	No line
▷ Logaritmic view	
◢ Markers	☑
Size	3
Style	Square
Width	1
◢ Range	☑
View	Best fit Reset
◢ X axis	
Min	0.01