University of
Stavanger

Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: Master of science in Petroleum technology Reservoir Engineering	Spring semester, 2012 Open
Writer: Kine Christensen Navrátil	…………………………………………… (Writer's signature)

Faculty supervisor: Tor Austad

External supervisor(s): Tor Austad, Tina Puntervold, Skule Strand

Titel of thesis:

An experimental study of Low Salinity EOR effects on a core from the Yme field

Credits (ECTS): 30

Key words: EOR, wettability, low salinity, water flooding, sandstone, Yme, increased oil recovery, high temperature, Ca^{2+}	Pages: 59 + enclosure: 8 Stavanger, 13.06.2012

Acknowledgements

I would like to thank Prof. Tor Austad, Dr. Skule Stand and Dr. Tina Puntervold for including me in their studies at the University of Stavanger.

I would especially like to thank Hakan Aksulu and Dr.Skule Strand for their excellent supervision, guidance and support during the experimental work in the laboratory, and for answering all my questions.

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

And finally I would like to thank Andrè for being patient and supporting during the work with this thesis.

Kine Christensen Navrátil

Abstract

The best known proposed mechanisms for low salinity effect are fines migration, pH increase, double layer expansion and multicomponent ionic exchange (MIE). Even though many mechanisms have been proposed, none of them have been accepted as the main mechanism behind the low salinity effect. The complex oil/brine/rock interactions are still being debated in the literature. The type of clays present in the sandstone and polar components in the crude oil, are important factors for observing low salinity effect. The temperature and the amount of divalent cations in the formation water, especially Ca^{2+} and Mg^{2+}, are also important factors for observing low salinity effect. It is assumed that the low salinity effect is a result of altering the wettability of the rock to a more water-wet condition. The rock becomes more water-wet when organic material is desorbed from the clay surface. Low initial pH is important in order for adsorption of polar components to the permanent negatively charged clay surface to occur. Desorption of Ca^{2+} ions from the clay surface and desorption of organic material from the clay surface will occur as a result of acid/base reactions. This will promote a pH increase.

In this work the potential of low salinity effect after flooding with seawater and diluted seawater in a Yme core has been evaluated. The oil recovery by formation water was about 65% of the original oil in place (OOIP). No additional oil recovery was observed after flooding with sea water and 50 times diluted sea water. High temperature and a large concentration of Ca^{2+} in the initial formation water, may be the main reasons for why no low salinity effect was observed.

Abbreviations

AN:	Acid number
BN:	Base number
Bopd:	Barrels per day
CEC:	Cation exchange capacity
CFC:	Critical flocculation concentration
COBR:	Crude-oil-brine reactions
d_{50}SW:	50 times diluted seawater
EOR:	Enhanced oil recovery
FW:	Formation water
HS:	High Salinity
IC:	Ion Chromatograph
IFT:	Interfacial tension
LS:	Low Salinity
LowSal:	Low Salinity
MIE:	Multicomponent ion exchange
OOIP:	Original oil in place
Ppm:	Parts per million
PV:	Pore volume
Soi:	Initial oil saturation
SW:	Sea water
Swi:	Initial water saturation
Sw:	Water saturation
TDS:	Total Dissolved Solid
XRD:	X-ray Diffraction Analysis

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1. Introduction

Water flooding has been used for many years to improve oil recovery from reservoirs. In the last decade it has been a growing interest in understanding the low salinity mechanism in sandstone reservoirs which may result in additional oil recovery. Many theories on how low salinity water works have been proposed, but the main mechanism is still debated. Tang and Morrow (1999) and McGuire et al (2005) have proved by experimental work that a decrease in the salinity of the injected brine can improve oil recovery.

If the wettability in the reservoir is altered towards more water-wet conditions, increased oil recovery as a result of low salinity effect can occur. Austad et al (2010) have suggested a new chemical mechanism on the low salinity effect. By substituting Ca^{2+} by H^+ on the permanent negatively charged clay surface when injecting low salinity water instead of high salinity water, it is possible for Ca^{2+} to desorb from the clay surface. By injecting low salinity water, a local pH increase at the clay surface will be created, and organic material will be desorbed from the clay surface. This may result in an increased oil recovery. The Yme reservoir which has been evaluated in this thesis has already been flooded with sea water. By injecting low salinity water into the reservoir, it may be possible to achieve increased oil recovery from the reservoir.

This master’s thesis starts with general theory that will provide background for understanding the results. Earlier proposed mechanisms for low salinity effects will then be presented, along with the new chemical mechanism suggested by Austad et al (2010). The next chapter will be about the materials used in the experiment and the experimental procedure. Results from the experiment will then be presented. Finally, a discussion and a conclusion will be presented.

2. Theory

2.1. Oil recovery

Waterflooding is traditionally considered as a secondary recovery process.

Historically, the water injected in a water flood was only designed to prevent formation damage by avoiding interactions between the injected brine and the brine initially in the reservoir. Lake (1989) defined EOR as “oil recovery by the injection of material not normally present in the reservoir”. By this definition, Low salinity water flooding is an EOR process, since the injected fluid has a different composition than the brine initially in the reservoir.

Changing the chemical composition of the injected fluid in waterflooding may therefore traditionally be considered as a secondary recovery method, but also as a tertiary recovery method. Improved oil recovery by low salinity water flooding has been shown for both secondary and tertiary recovery process (Agbalaka et al., 2008; Austad et al., 2010)

2.1.1. Primary recovery

When displacing oil from the reservoir to the production wells in primary recovery, the driving source is the natural energy in the reservoir. Reservoir energy may be natural water drive, gas drive, gas cap drive, fluid and rock expansion and gravity drainage. (Green and Willhite, 1998) After a while of producing from the reservoir, the pressure will drop. The amount of water and gas in the produced fluid will at some point become so large that it is not economic to continue producing. The recovery factor after primary recovery is normally 5-30 % of OOIP (oil originally in place) (Ahmed and McKinney, 2005)

2.1.2. Secondary recovery

When the natural energy in the field is no longer able to produce oil at an economic rate, a secondary recovery process can be applied. In a secondary recovery process, water or gas is injected into the reservoir to improve the reservoir energy, so that more oil can be displaced (Green and Willhite, 1998). More oil can be displaced, by injecting other fluids into the reservoir so that the pressure in the reservoir is maintained (Robertson, 2007)

2.1.3. Tertiary recovery

In tertiary recovery process (EOR process), the chemical and/or physical properties of the injected fluid is altered, so that the sweep efficiency of the injected fluid is enhanced. More oil will then be displaced after a primary or secondary recovery process. When injecting liquids or gases, the energy in the reservoir is enhanced and favorable displacement are created. The sweep efficiency may be improved by altering the interfacial tension (IFT), altering the wettability, altering the fluid viscosities or by injecting gas that displaces oil through a favorable phase behavior. There are four categories which almost all tertiary oil recovery methods are described by: mobility- control processes, miscible processes, chemical processes and thermal processes. In some cases the primary and/or secondary stages are replaced by only tertiary recovery, to get the best possible amount of oil recovery. It is also possible to only omit one of the primary or secondary stages, if this will reduce the total efficiency. The more wide term “enhanced oil recovery” is therefore more appropriate to use for the tertiary recovery stage (Green and Willhite, 1998).

2.1.4. Low salinity water injection

Low salinity water flooding can be used after a primary recovery process or after a secondary process. For secondary flooding with Low salinity water, the core is first flooded with high saline water, such as formation water. After the flooding with FW is ended, the core is restored. Low salinity water is then flooded after the restoration is complete (Austad et al., 2010). The oil recovery can reach up to 70 % of OOIP in good sandstone reservoirs. In poor sandstone reservoir where the permeability contrast between the layers are large (heterogeneous reservoir rocks), the oil recovery can be as low as 30 % (Bavière, 1999; Castor et al., 1981).

For tertiary flooding with Low salinity water, the core is first flooded with high saline water until the plateau for oil production is reached. The core is then flooded by dilute water in the salinity range of normally 1000-2000 ppm (Austad et al., 2010).

Loahardjo et al. (2008) showed increased oil recovery from restored cores in a study on secondary oil recovery from cyclic waterflooding of mixed-wet sandstone. The same formation water was used in both the first and second flood. Reliable low salinity effect should therefore only be verified under tertiary flooding conditions, since observed low salinity effects by secondary flooding conditions does not need to be linked to the decrease in salinity of the injected fluid (Austad et al., 2010)

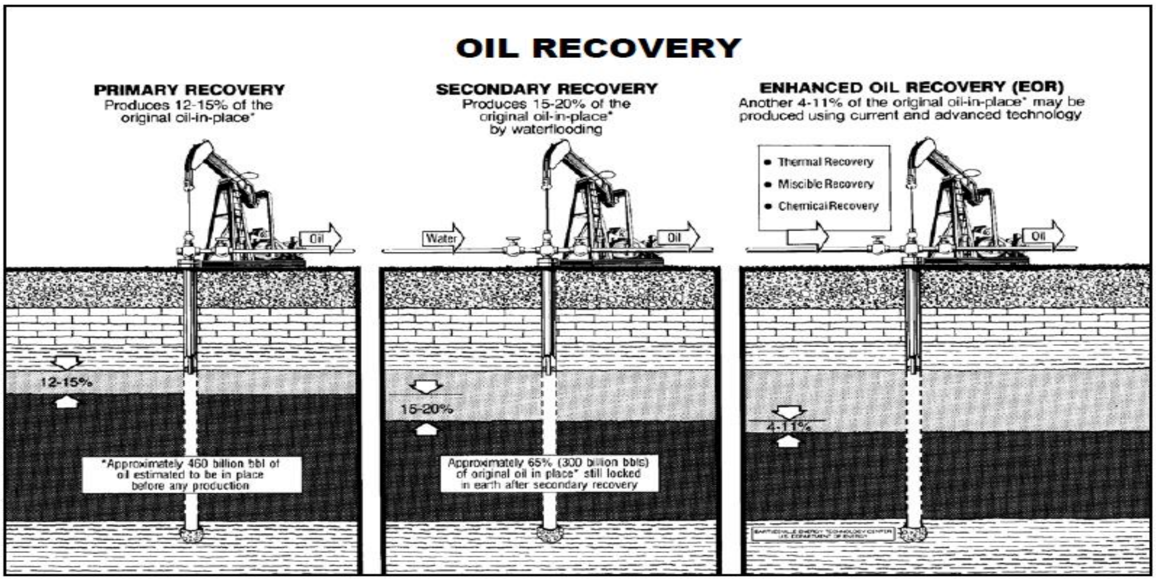


Figure 2.1: Oil recovery processes (http://www.temcoinstruments.com/products_detail.asp?ProductID=34).

2.2. Sandstones

2.2.1. Sedimentology and mineralogy

Sandstones are sedimentary rocks, and are usually deposited in high energy sedimentary environments such as flood plains, deserts, beaches and/or deltas. Sandstones are formed as a result of deposition of clastic material or detritus, and the building particles are products of erosion of older rocks of igneous, methamorphic or sedimentary origin. The building particles are also a result of weathering and fragmentation. The buried grains will go through digenesis, a cementation and compaction process of the grains, as a result of increasing overburden pressure and dissolved minerals (Nichols, 2009; Zolotuchin and Ursin, 2000).

The mineral quartz (SiO_2) is the most common mineral type in a sandstone reservoir. In addition to many other minerals, the sandstone may consist of mica, feldspar, lithic fragments, biogenetic particles and heavy minerals. Common cements in sandstone are silica, calcium carbonate, iron oxide and clay minerals (Zolotuchin and Ursin, 2000).

2.2.2. Clay minerals

Clay minerals are composed of silica, alumina, water, large amounts of iron and magnesium and smaller amounts of sodium and potassium (Morad and Worden, 2003). Clay materials are a main wetting mineral, because of their permanent negative surface charge and their wish of beeing neutral charged. Thus, clay minerals are important in order of achieving a possible wettability alteration.The clay minerals are attached to the sandstone grains as coating (Zolotuchin and Ursin, 2000). The four most common clays found in sandstone are Kaolinite, Illite/mica, Montmorillonite and Chlorite (IDF, 1982). On the edges of the unit cells, there is an unbalanced negative charge which will attract positively charged ions from the surrounding pore fluid and try to establish neutrality (Morad and Worden, 2003). The clay minerals can exchange cations adsorbed to the naturally negative charged external surfaces and between the layers of the clay structure (Hamilton, 2009). This ability is called the cation exchange capacity (CEC) and is a measure of the clay’s ability to attract and hold cations from a solution. The CEC defines “the quantity of exchangeable cations held by the clay at a given pH, usually pH 7” (Bergaya et al., 2006). The forces that attract and hold the cations in solution are electrostatic and van der Waals forces. Some cations will be adsorbed more strongly than other cations. The relative replacing power of a particular cation depends on its strength of binding.

The relative replacing power of cations at room temperature is believed to be (IDF, 1982):

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < H^+$$

The replacing power says that at an equal concentration of Ca^{2+} and K^+, Ca^{2+} will be more successful to displace K^+ from the clay surface, than K^+ will be to displace Ca^{2+} from the clay surface. It is possible for a cation with a low replacing power to replace a cation with high replacing power, if the concentration of the cation with low replacing power is sufficiently higher than the concentration of cation with high replacing power.

2.3. Polar components in crude oil

The polar components in the crude oil are believed to have acidic and basic properties, and are most suitable to adsorb onto reservoir minerals. Depending on the conditions, both anionic and the neutral form of the acid are able to adsorb onto reservoir minerals. The relative adsorption is depending on the pH, and the fraction of undissociated acid and protonated base will show a very similar variation with the pH variation of the solution (Austad et al., 2010). When the salinity of the injected fluid decreases at a given pH, increased adsorption of organic material onto the clay surface will occur (RezaeiDoust et al., 2011; Fogden et al., 2011; Burgos et al., 2002; Sandengen et al., 2011). If the pH of the initial formation water is alkaline (pH>7), less organic material will adsorb onto the clay surface. However, if the pH of the initial formation water is low, then it is possible to observe a low salinity EOR process when flooding with low salinity water since organic material may at low initial pH adsorb onto the clay surface. When pH< pKa, the protons compete with other cationic material for the negative sites on the clay, since the concentration of H^+ increases. When the pH is increased to 8-9, organic material will desorb from the clay surface, making the clay more water-wet (RezaeiDoust et al., 2011).

A basic polar component in crude oil is quinoline. Quinoline is in equilibrium with half at protonated form and half at neutral form, when pKa =4.8 (Viswanath, 1979). pKa value for both acids and bases are in the range of pH= 4,5 -5. The protonated form of quinoline increases when the pH decreases, and the neutral form of quinoline increases when the pH is increased (Hamsø., 2011). Master student Dagny Hamsø (Hamsø, 2011) at the University of Stavanger did an experiment on the adsorption of quinoline onto illite at high salinity and temperature.

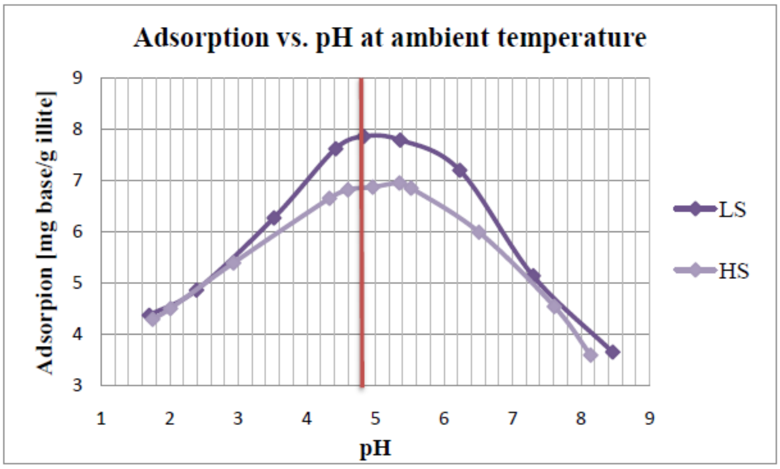


Figure.2.2. Adsorption of quinoline onto clay vs pH for HS and LS. Red line indicate pKa = 4,8. (Hamsø., 2011)

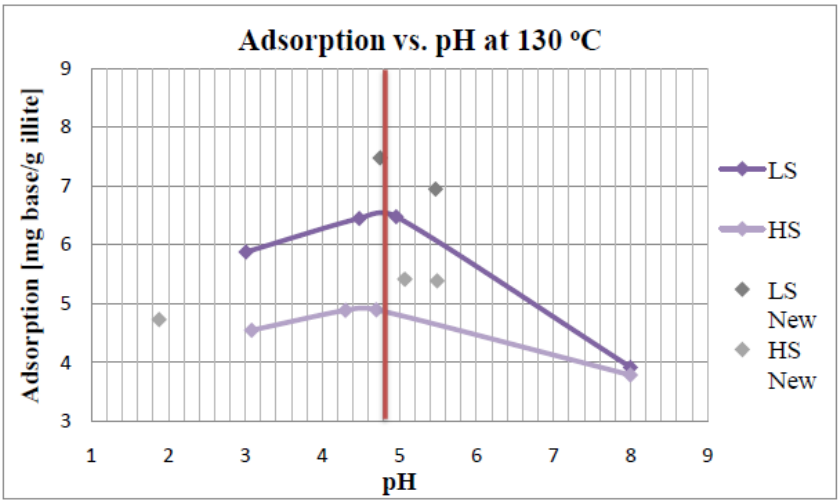


Figure.2.3. Adsorption of quinoline onto clay vs pH for LS and HS. Red line indicate pKa = 4,8. A Gray dot indicates a measurement done after the sample were equilibrated for a long time (Hamsø., 2011).

The adsorption of quinolone onto cleaned and protonated illite, was found by calculating the amount of adsorbed quinoline onto the clay surface. Figure.2.4 and Figure.2.5 shows the results of adsorption at ambient temperature and 130°C, with different pH values.

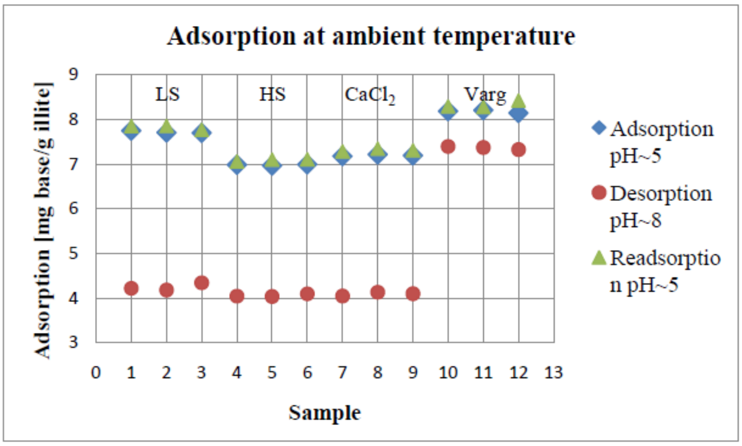


Figure 2.4: Adsorption of quinoline onto illite at ambient temperature using four different brines: LS, HS, pure CaCl2 and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure CaCl2 brine and sample 10-12 Varg formation brine (Hamsø, 2011).

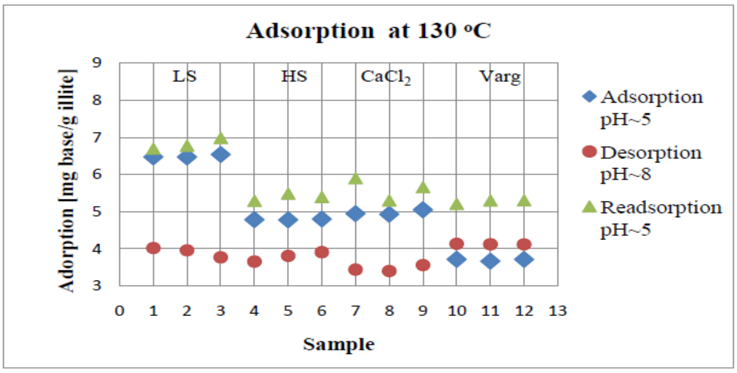


Figure 2.5: Adsorption of quinoline onto illite at 130 ºC using four different brines: LS, HS, pure CaCl2 and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure CaCl2 brine and sample 10-12 Varg formation brine (Hamsø, 2011).

The results shows that adsorption of quinoline onto illite is dependent on the pH. When the pH increases, the quinoline is desorbed from the clay surface and the process is reversible. The permanent negatively charged clay surface want to be neutral charged, and different cations present have to compete for the negative charged clay sites (Aksulu et al., 2012). The adsorption of Quinoline in the LS brine is higher than for the HS brine, and may be explained by the fact that there is a lower concentration of divalent ions, especially Ca^{2+}, in the LS brine. This will create less competition between the cations and the protonated quinoline, and hence more quinoline will be adsorbed onto the clay surface in LS brine compared to in HS brine. The adsorption of quinoline is lower at higher temperatures, since the reactivity of Ca^{2+} ions increases at higher temperatures (T<100°C).

An experiment done by Aksulu et al (Aksulu et al., 2012) shows that the pH gradient will decrease with higher temperatures. This coincide with increased reactivity of Ca^{2+} at higher temperatures, which will result in a smaller pH gradient when less organic material is desorbed from the clay surface.

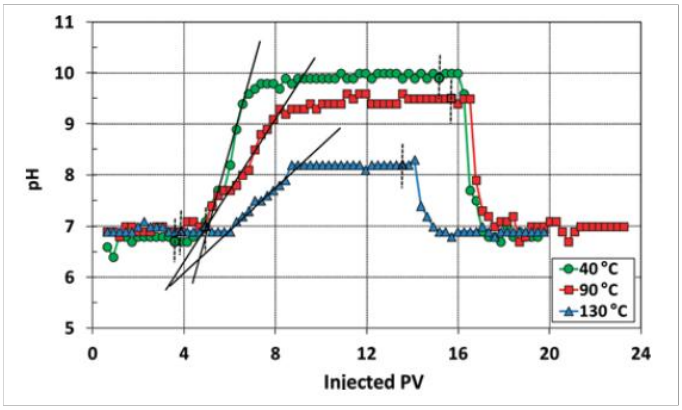


Figure.2.6. Change in effluent pH versus PV-injected fluid in core RC2 at 40, 90, and 130 °C. The brine flooding sequence was HS2−LS2−HS2. The switches of injection fluids are indicated by the dashed lines.The slopes of the pH change curves are indicated by the black lines (Aksulu et al., 2012).

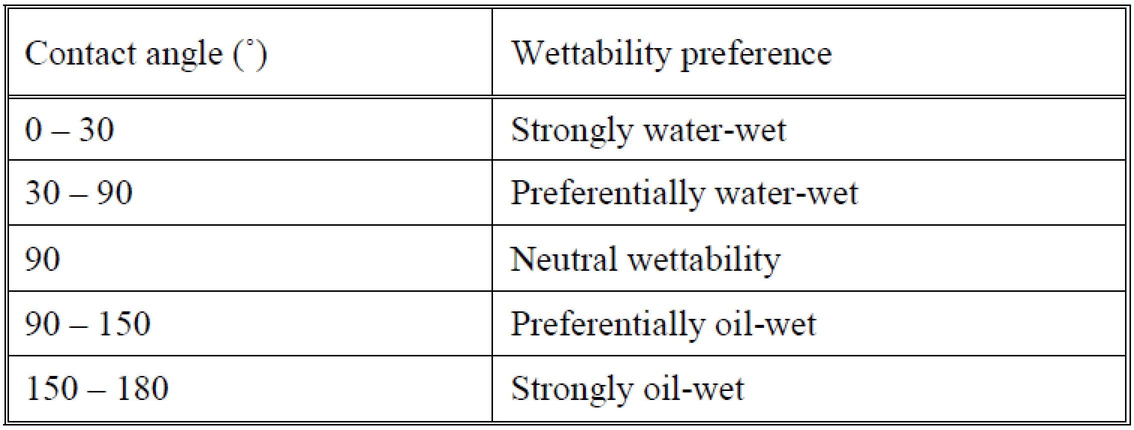
2.4. Wettability

Wettability is defined as ”the tendency of one fluid to spread or adhere to a solid surface in the vicinity of another immiscible fluid” (Craig, 1971).

“When two immiscible phases are in contact with a solid surface, one phase usually is attached to the solid more strongly than the other. The more strongly attracted phase is called the wetting phase “(Green and Willhite, 1998).

Wettability can also be defined as the fraction of the rock surface in a reservoir that is coated by adsorbed hydrocarbons, and it can be measured by measuring the contact angle between the rock surface and hydrocarbons. When the porous medium is completely oil wet, the porous medium is completely coated by hydrocarbons. The porous medium is completely water wet when the porous medium has no hydrocarbon coating (Ligthelm et al., 2009). The wettability in terms of contact angle may be classified as shown in table 2.1, where the phases are measured through the water phase (Zolotuchin and Ursin, 2000).

Table 2.1: Wettability expressed by contact angles (Zolotuchin and Ursin, 2000).



Contact angle (˚)	Wettability preference
0 – 30	Strongly water-wet
30 – 90	Preferentially water-wet
90	Neutral wettability
90 – 150	Preferentially oil-wet
150 – 180	Strongly oil-wet

For a static oil/water/solid system, as shown in eq.2.1, the mechanical equilibrium can be expressed by Young’s equation (Anderson, 1986b):

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos\theta \tag{2.1}$$

Where:

θ : Contact angle measured through the denser phase
σ_{os} : Oil-solid interfacial tension
σ_{ow} : Oil-water interfacial tension
σ_{ws} : Water-solid interfacial tension

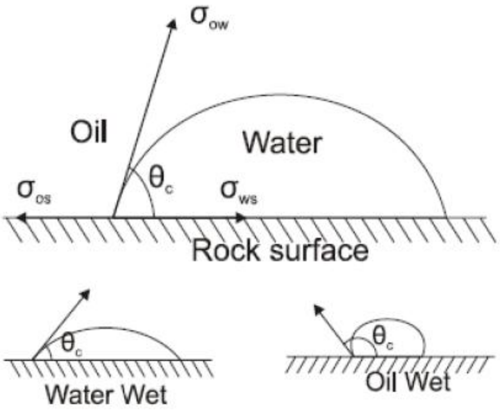


Figure 2.7: Contact angle measurement through water phase (Craig, 1971).

In a strongly water-wet system, the water will be in contact with most of the rock system and will occupy the smaller pores. The oil will be trapped in the center of the larger pores, and the residual oil will be trapped in disconnected globules in the middle, created by a snap-off mechanism. In strongly oil-wet systems, oil occupies the smaller pores and will be as a thin film covering the rock. The water will be located as droplets in the middle of the pores. (Anderson, 1986b).

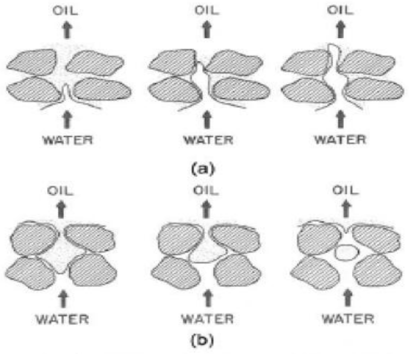


Figure.2.8: Displacement of oil by water. a)oil-wet rock, b)water- wet rock (Strand, 2005).

2.4.1. Factors affecting wettability

Due to variations in the mineralogy and pore structure, the wettability through a reservoir varies. It is the complex interactions between rock, brine and crude oil (COBR) which the wetting condition is dependent of. The wetting condition is also dependent on that the crude oil contains polar components.

Brine salinity, oil characteristics and temperature can alter the rock wettability in a sandstone reservoir (Alotaibi et al., 2010). If the temperature during water displacement or the temperature when aging the rock and crude oil is changed in the laboratory, wettability can be altered. Wettability can also be altered by changing the crude oil composition (Jadhunandan and Morrow, 1995). Many have also observed that the water composition have a great impact on wettability and oil recovery (Jadhunandan and Morrow, 1995,; Yildiz and Morrow, 1996,;Yildiz et al.,1999,; Tang and Morrow, 1997). It has been shown that the composition and the salinity of the brine are important factors in the stability of the water film. The water film is important in the wettability process, since the water film separates the charged surfaces (Buckley et al., 1998).

Clay is the main wetting mineral because of its permanent negative charge (Austad et al., 2010). Other important parameters behind the wettability alteration process in a reservoir are listed below (Strandnes, 2001):

- Molecules in the crude oil containing polar functional groups (Strandnes, 2001)

- Mineral composition and surface charge of the rock material (Anderson, 1986a; Buckley, 1989).

- Brine salinity and concentration of divalent and other multivalent ions (Buckley, 1996).

- Capillary pressure and thin film forces, disjoining pressure (Hirasaki, 1991).

- Water solubility of polar oil components (Anderson, 1986a).

- The ability for the oil to stabilize heavy components (Al-Maamari and Buckley, 2000).

- Temperature, pressure and initial water saturation (Al-Maamari and Buckley, 2000; Jadhunandan and Morrow, 1995).

2.5. **Conditions for low salinity effects** (Austad et al., 2010)

Systematic experimental work done by Tang and Morrow (1999) represents most of the listed conditions for low salinity effect, but some points has also been taken from the work by Lager et al. (Lager et al., 2007; Lager et al., 2008a).

- Porous medium
  - – Sandstones.
    - • Low salinity effects have not been documented in pure carbonates, but Pu et al. have observed low salinity effects in sandstone containing dolomite crystals (Pu et al., 2008).
  - – Clay must be present in the reservoir to obtain improved recovery by low salinity flooding
    - • The type/properties of clay may play a role and the amount present in the rock: - the clays recognized as important are: kaolinite, illite, smectite, and chlorite. Increased clay content can give greater response to low salinity flooding (Lee et al., 2010). In earlier studies the most important clay was kaolinite.
- The combination of crude oil/brine/rock is very complex, and the right combinations can be essential for improved recovery.

- Oil must contain polar components (i.e. acids and bases)
    - There has not been showed any effects by using refined oil free from polar components.

- Formation brine, FW,
    - Formation water must contain divalent cations, i.e. Ca^{2+}, Mg^{2+} (Lager et al., 2008a)
    - Initial FW must be present
    - Efficiency is related to initial water saturation, Swi

- Low salinity injection fluid
    - The salinity is usually between 1000-2000 ppm, but effects have been observed for salinity ranging from 150 ppm to 5000 ppm.
    - It appears to be sensitive to ionic composition (Ca^{2+} vs. Na^{+})

- Produced water
    - For a non-buffered system, the pH of the effluent water usually increases about 1-3 pH units when injecting the low salinity fluid.
    - It has not been verified that increase in pH is needed to observe low salinity effects. In some cases a change in pH has been observed in the effluent, indicating a chemical interaction of the injected brine or the rock with the connate brine. But in other cases, especially with low initial pH, minor pH changes are observed and the pH does not reach the levels normally associated with either wettability change or low interfacial-tension mechanism of caustic flooding.
    - Production of fines has been detected in some cases, but there has also been observed low salinity effect without production of fines. (Lager et al., 2008a)

- Permeability decrease
    - Usually an increase in pressure drop over the core occurs when switching to the low salinity fluid, which may be related to migration of fines or formation of an oil/water emulsion.
    - There is a lack of experimental evidence to say that observed low salinity effects are accompanied by permeability reduction.
    - Waterflood experiments have been performed without any variation in end point relative permeability data between high and low salinity water floods, under both secondary and tertiary flood conditions (Webb et al., 2008).

- Temperature

    - There appears to be no temperature limitations to where low salinity effects can be observed. Most of the reported studies have, however, been performed at temperatures below 100 °C.

2.6. Proposed low salinity mechanisms

Martin (1959) observed increased recovery of heavy oil by injecting fresh water into sandstone reservoir. He suggested that emulsification and effects of clay swelling were possible reasons for the increased recovery. Later, Bernard (1967) did laboratory tests on oil recovery. He concluded that oil recovery of mineral oil was caused by swelling of clays and/or dispersion, together with a pressure drop, when fresh water or 1000 ppm NaCl was injected. Many other more recently examples have been reported for low salinity brine injection for both core floods and for field tests (Webb et al., 2004 and 2005; Lager et al., 2006; McGuire et al., 2005; Zhang and Morrow, 2006). Most of the experiments on coreflooding have documented increased oil recovery in both secondary and tertiary process (Zhang et al., 2007; Agbalaka et al., 2008), and sometimes only for one of the processes (Zhang and Morrow, 2006). Improvements of oil recovery in tertiary mode have also in some studies never been observed (Rivet et al., 2010).

Although the main mechanism for low salinity improved oil recovery is still debated, there have been some proposed mechanisms.

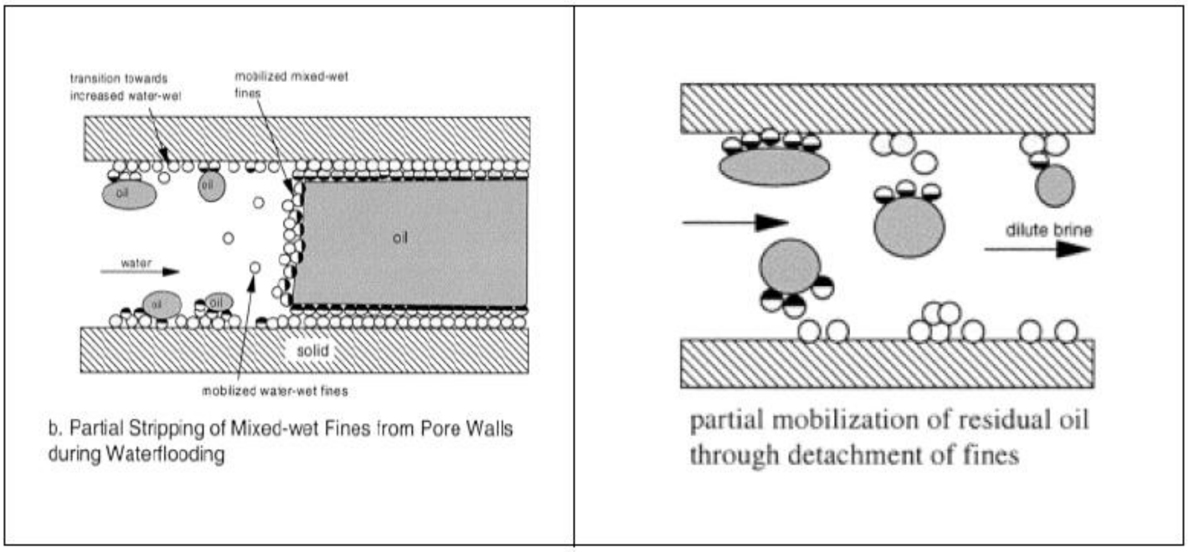
The proposed mechanisms are:

- Fines migration
- pH effects
- Multi-component ion exchange (MIE)
- Salting in
- Double layer effects
- Low salinity mechanism proposed by Austad et al.

2.6.1. Fines migration

Tang and Morrow (1999) found out that fines were being eluted during low salinity waterfloods on Berea core samples. They associated it with clay production, mainly Kaolinite in effluents. Tang and Morrow (1999) suggested a theory based on the release of mixed-wet clay particles from pores. During aging, clay fines are partly in contact and exposed to crude oil, and the fines are then mixed-wet particles. The production of oil droplets on these clays would contribute in changing the system to a more water wet system, since the fines migration resulted in exposure of the underlying surfaces that lead to an increase in water-wetness of the system.

When high salinity brine is present, clays are undistributed and retain their oil wet nature leading to poorer displacement efficiency (Lager et al., 2006). When the clay particles come in contact with low salinity water, the clay particles will detach from the pore surface. Figure 2.9. Fines migration is also associated with permeability reduction and formation damage, as a result from plugging of pore throats by fine mobilization with flowing fluid (Lever and Dawe, 1984).



b. Partial Stripping of Mixed-wet Fines from Pore Walls during Waterflooding

partial mobilization of residual oil through detachment of fines

Figure 2.9: Schematic of fines migration mechanism (Tang and Morrow, 1999).

DLVO (Deryaguin-Landau-Verwey-Overbeek) theory of colloids, have explained the well known phenomenon of fines migration. The two main competitive colloidal forces that attach clay particles to the pore surface are electrostatic repulsion forces and Van der Walls attractive forces (DLVO theory). The permeability reduction occurs if the ionic strength of the injected brine is equal or less than the critical flocculation concentration (CFC). CFC is strongly dependent on the concentrations of the divalent cations such as Mg^{2+} and Ca^{2+} (Khilar et al., 1990; Kia,1987).

Skauge et al. (2008) proposed a new explanation of partial mobilization of fines, where the released clay particles will block pore throats and divert the flow of low salinity brine into non-swept pores. This will increase the microscopic sweep efficiency and increase the total oil recovery. This explanation for increased oil recovery is not necessarily improved by altering the wettability of the rock, but rather by improving the microscopic sweep efficiency (RezaeiDoust, 2011).

Contradicting results:

Numerous of other experiments with low salinity have shown an increase in oil recovery, but has not observed fines migration. BP did not record any fines migration in several low salinity experiments performed in both reduced conditions and reservoir conditions, even though they recorded an increase in oil recovery (Lager et al., 2006). Morrow has more recently together with Zhang et al (2007) and Pu et al (2008) presented low salinity waterflooding experiments without observing fines migration. Boussour et al. (2009) did a low salinity waterflooding experiment on a reservoir core sample. No increased oil recovery was observed despite a significant fine production in effluents, Figure.2.10.

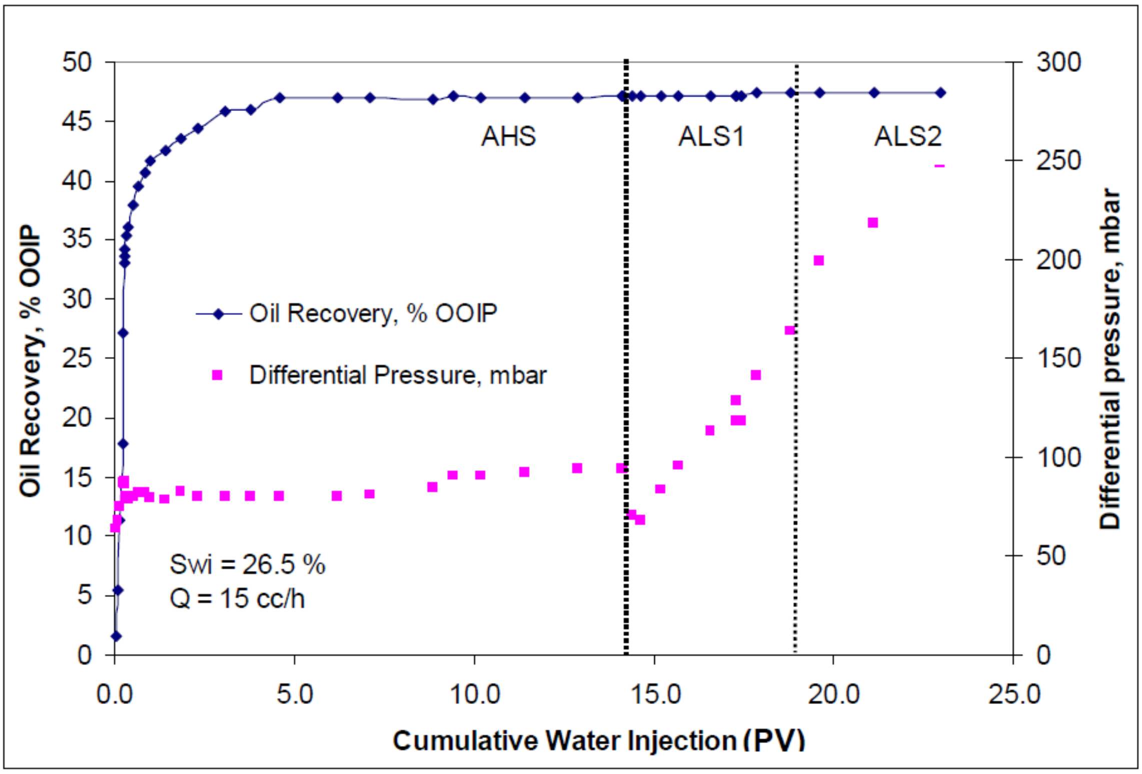


Figure 2.10: Response to low salinity brine in tertiary mode for reservoir core A. (Boussour et al., 2009)

By this, they explicitly conclude that fine mobilization is not responsible for the increase in oil recovery by low salinity (Boussour et al., 2009).

Zhang et al (2007) and Pu et al (2008) observed no fines migration, but a significant increase in pressure drop associated to the increased oil recovery. Their explanation is based on the analysis proposed by Mason and Morrow (1991) of capillary wetting liquid in triangular pore shapes. The explanation of Zhang et al (2007) and Pu et al (2008), is that fines that have been detached from low salinity flooding will form clay or mineral stabilized lamellas that generate a transient resistance to the brine flow in the pore causing a significant increase in pressure drop. However, when additional oil recovery is observed, permeability reduction is not in fact systematic, as Lager et al (2006) proposed (Boussou et al., 2009).

Other observations from experiments are in contradiction with increased pressure drop when increased oil recovery is observed. Boussour et al (2009) observed increased pressure drop without any increased oil recovery, Fig.2.10. Boussour and Cissokho et al (2009) also observed rise in pressure drop without any increased oil recovery.

These results indicates that when low salinity injection is performed, particle release and flow diversion are not the key parameters that control increased oil recovery (Lager et al., 2008b; Boussou et al., 2009).

Tang and Morrow (1999) had a theory that partial release of kaolinite that is attached to the crude oil could increase the oil recovery by low salinity brine injection, and may be a mechanism for increased oil recovery by low salinity brine.

However, Cissoko et al (2009) reported a 10% increase of OOIP by injecting low salinity brine into sandstone cores that contained illite and chlorite, but where free for kaolinite. This shows that kaolinite may not be essential for increased oil recovery, as concluded earlier (Cissoko et al., 2009).

2.6.2. pH effects

PH increase is in numerous laboratory test associated with dilute brine injection. Tang and Morrow (1999) observed a pH increase by low salinity injection on Berea sandstones and McGuire et al (2005) observed a pH increase on North Slope field samples.

The pH increase could be explained by: carbonate dissolution and cation exchanges (Lager et al., 2006). The dissolution reactions are dependent on the amount of carbonate present in the rock.

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \tag{2.2}$$

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \tag{2.3}$$

During the dissolution of carbonate, an excess of OH^- will give increased pH. Cation exchange will occur between clay minerals and the invading low salinity brine. An exchange of H^+ in the liquid phase with cation previously adsorbed at the mineral surface, will lead to a decrease of H^+ concentration inside the liquid phase. This could also result in a pH increase.

Reservoir oil that contain CO_2, will act as a pH buffer. It has also been observed a proton buffering, where crude acidic components and mineral oxides will release H^+ (Lager et al., 2006).

McGuire et al (2005) proposed that low salinity injection and alkaline flooding behaved in a similar way. The IFT between the reservoir oil and water is reduced by low salinity water injection (Morrow et al., 1998; Tang et al., 1997) like it is by alkaline flooding.

Contradicting results:

Other experiments come in conflict with this theory. Lager et al (2006) did an experiment in a North Sea reservoir where the crude oil had a very low acid number (AN< 0.05). According to the literature a high AN (AN>0.2) is needed to generate enough surfactants to induce wettability reversal and /or emulsion formation (Ehrlich and Wygal, 1977). Lager et al (2006) reported an increase in oil recovery on an experiment with a pH < 7, instead of a high pH (pH > 9). He also concluded that there could not be found any correlations between crude oil Acid Number and increased oil recoveries, shown in Figure 2.11.

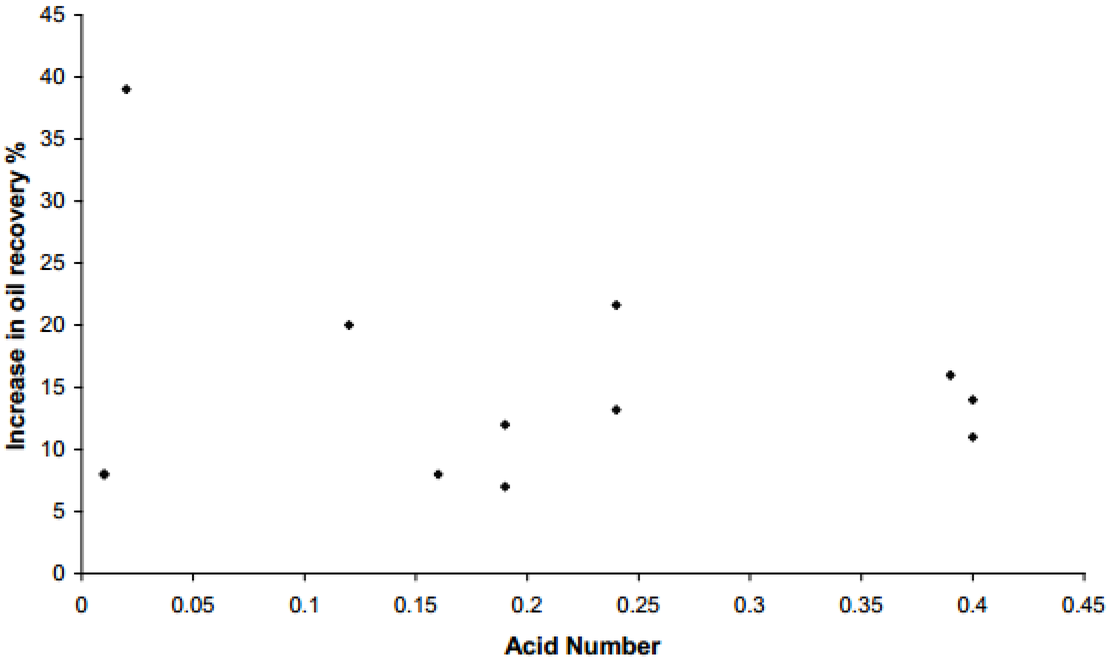


Figure 2.11: Lack of correlation between acid number and the increase in oil recovery due to low-salinity waterflood. (Lager et al., 2008)

Zhang et al (2007) reported that they only observed a slight rise in pH for most of the reservoir cores, and even observed a decrease in pH for one of the cores. Pu et al (2008) did also report a small increase in pH at experiments performed on Tensleep cores with increased oil recovery. Boussour et al (2009) did the same observation on waterfloods on reservoir samples. There have also been reported experiments where the pH have increased significantly, but no increased oil recovery was observed (Cissokho et al., 2009).

These experimental evidences show that there is no direct relationship between pH observed in the effluent and increased oil recovery (Lager et al., 2008). However, pH may affect adsorption /desorption of carboxylic material onto clay (RezaeiDoust et al., 2009a).

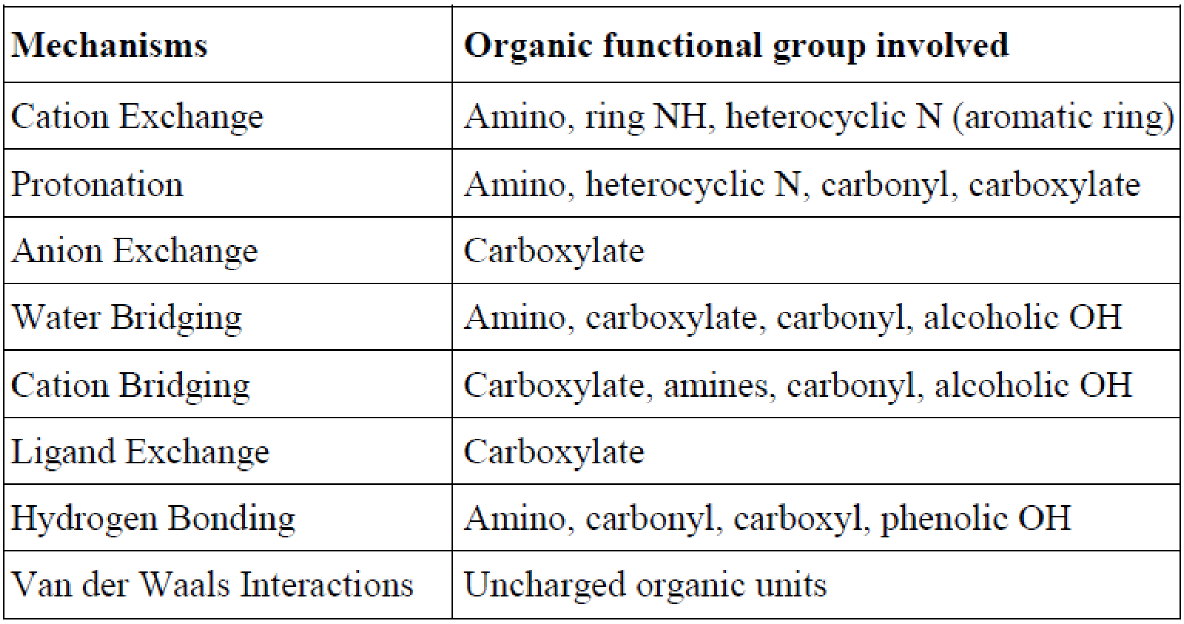
2.6.3. Multi-component ion exchange (MIE)

Multi-component ion exchange "is the basis of geochromatography and involves the competition of all the ions in pore water for the mineral matrix exchange sites" (Lager at al., 2008b).

The evidence of MIE was shown from an effluent analysis taken from a low salinity core flood of the North Slope. The analysis showed that the injected brine had a lower salinity than the connate water. The concentration of Mg^{2+} and Ca^{2+} in the effluent samples decreased as more PV's was injected and dropped below the concentration of the injected brine. This indicated that the Ca^{2+} and Mg^{2+} where adsorbed by the rock matrix. Heriot Watt university also reported same results for two different floods performed at the same system.

Sposito (1989) proposed eight mechanisms for adsorption of organic functional group on soil minerals.

Table 2.2: Adsorption mechanisms of organic compounds onto clay minerals (Sposito, 1989)



Mechanisms	**Organic functional group involved**
Cation Exchange	Amino, ring NH, heterocyclic N (aromatic ring)
Protonation	Amino, heterocyclic N, carbonyl, carboxylate
Anion Exchange	Carboxylate
Water Bridging	Amino, carboxylate, carbonyl, alcoholic OH
Cation Bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligand Exchange	Carboxylate
Hydrogen Bonding	Amino, carbonyl, carboxyl, phenolic OH
Van der Waals Interactions	Uncharged organic units

Four of the eight mechanisms proposed by Sposito (1989), where affected by possible cation exchange capacity in low salinity flooding. The mechanisms were cation exchange, water bridging, cation bridging and ligand bridging/bonding, Fig.2.12.

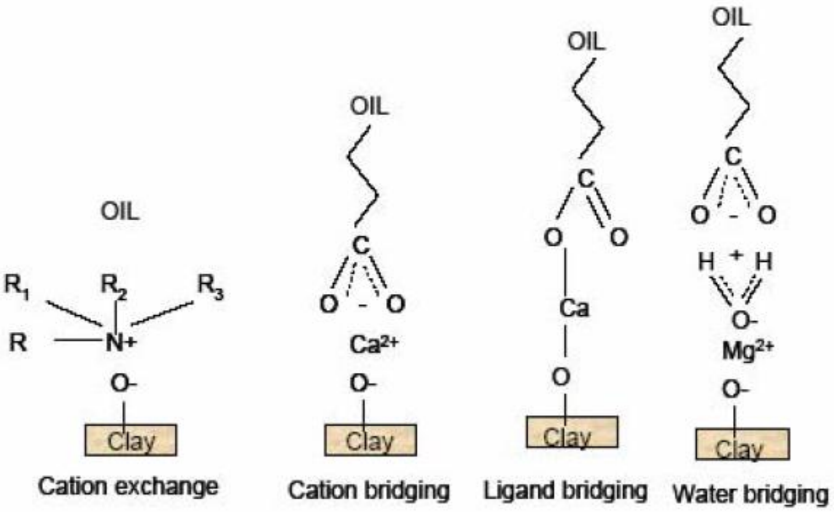


Figure 2.12: Attraction between clay surface and crude oil by divalent cations (Lager et al., 2008b).

Polar components in the crude oil can adsorb onto the clay (Lager et al., 2006):

- by forming an organo-metal complex where the polar components in the crude oil adsorb onto the clay surface by multivalent cations

or

- by direct adsoption of the polar components onto the clay by displacing the most labile cations at the clay surface.

Between the negatively charged clay surface and the negatively charged oil molecules, divalent cations will act as bridges (Buckley et al., 1998; Seccombe et al., 2008).

Multi-component ion exchange (MIE) will take place between adsorbed crude oil components, the clay mineral surface and the cations in the brine, when low salinity brine that contain low concentrations of Mg^{2+} and Ca^{2+} are injected. Divalent cations from the injected brine will exchange with either cationic organic complexes or with bases, due to the change in ionic equilibrium. The clay surface will become more water-wet as a result of the removal of polar organic compounds and organo-metallic complexes from the clay surface. This will increase the oil recovery. It was also suggested that the double layer related to the MIE mechanism will expand and facilitate desorption of oil from the clay, when low salinity brine is injected. The system will then become more water-wet, which can lead to increased oil recovery (RezaeiDoust, 2011).

Contradicting results:

The MIE mechanism is based upon the theory that in order to exchange cations connected to the clay surface and cause desorption of polar compounds, there must be a low concentration of divalent cations in the injected low salinity brine (RezaeiDoust, 2011). Cissokho et al (2009) performed low salinity floods containing no divalent ions, which resulted in increased oil recovery when switching to the low saline brine free for divalent ions. This result has also been reported by others (Ligthelm et al., 2009; Zhang et al., 2007).

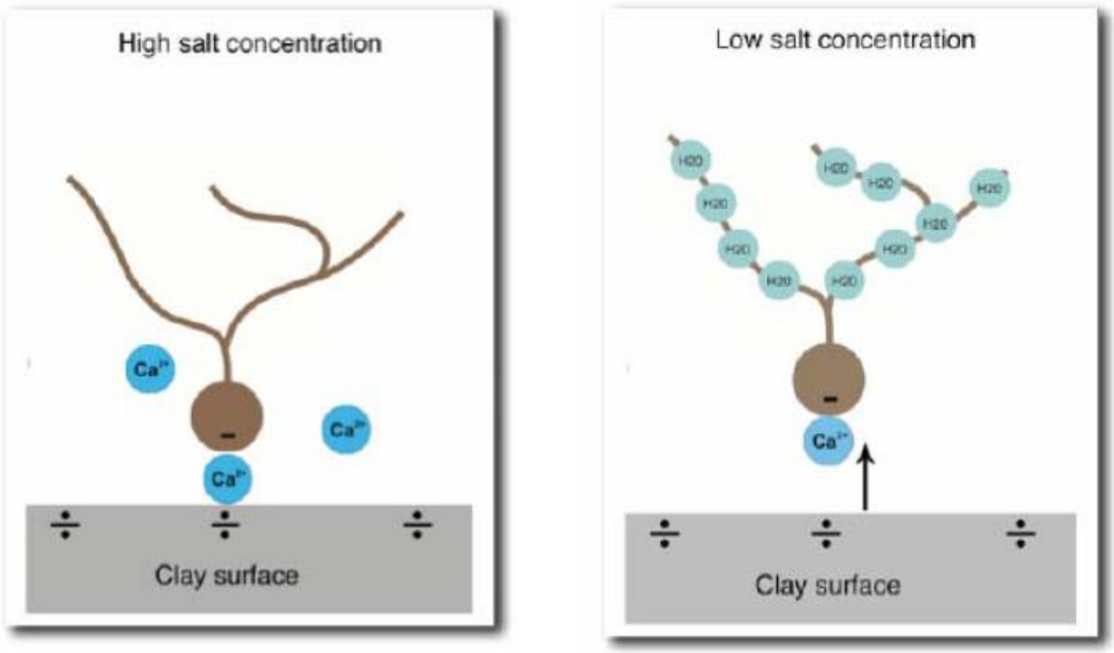
Cissokho et al (2009) also indicated that both the presence and amount of divalent cations, may not be an optimization parameter for increased oil recovery by low salinity flooding.

Austad et al (2010) also explained that the change in the concentration of Mg^{2+} could be caused by precipitation of $Mg(OH)_2$, and not necessarily an MIE process. $Mg(OH)_2$ will precipitate as a result of a local pH increase in the injected low salinity brine. The local alkalinity will decrease with the precipitation of $Mg(OH)_2$ and may have an impact on the desorption of the organic material from the clay surface.

2.6.4. Salting in

Austad et al. (2008) proposed the salting-in effect, as a proposal for the low salinity mechanism. They proposed that salting in and salting out effects are related to the changes in the solubility of organic polar components in the aqueous phase. A structure that will be created by hydrogen bonds around the non polar part of the organic compound in water, will solvate the organic material in water. The solubility is decreased by the breakage of the structure around the organic molecules, by inorganic ions such as Ca^{2+}, Mg^{2+} and Na^{2+} (RezaeiDoust et al., 2009a).

When injecting brine with different salinity than the original formation water, the termodynamical equilibrium will be changed, and the solubility of organic polar compounds in water will be affected by the salinity and ionic composition. Figure.2.13.



(a) (b)

Figure 2.13: System containing crude oil components, Ca^{2+}-ions in the water and clay. a) Salting-out effect, b) Salting-in effect.

Salting- in and salting-out effects are well known in the chemical literature (Li et al, 1997; RezaeiDoust et al, 2009a).

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

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

Contradicting results:

The salting-in mechanism was tested out by Austad et al. (2010) by performing adsorption and desorption studies of quinoline onto kaolinite. No significant difference between high salinity and low salinity condition in the desorption process were observed, Fig.2.14.

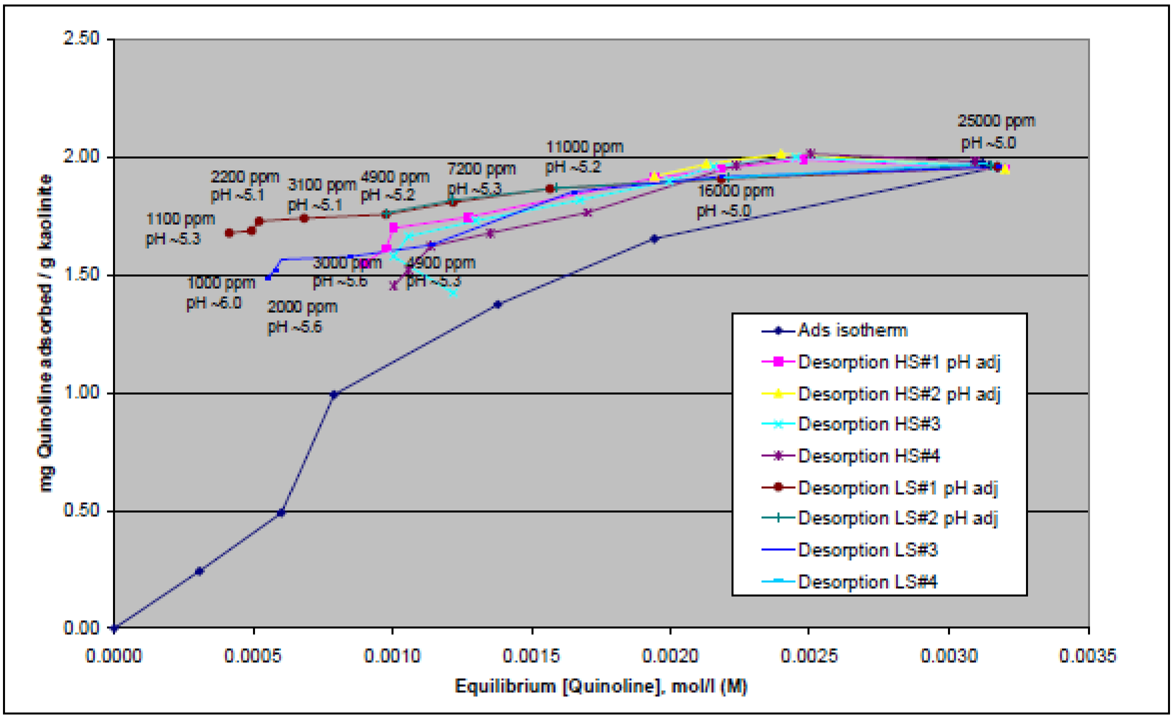


Figure 2.14: Desorption of quinoline from kaolinite at high and low salinity at room temperature. pH adj signifies that pH was attempted adjusted to ~5, in the remaining samples pH ran freely (Austad et al., 2010).

The proposed salting-in effect mechanism was rejected since it did not show expected results, and was used as a working hypothesis which later resulted in a new and different suggested mechanism for low salinity effect. The new suggested low salinity mechanism is presented later in this chapter.

2.6.5. Double layer effects

Ligthelm et al (2009) suggested that some of the cations in the low salinity brine could screen off the negative charges of the oil and clay, as the DLVO theory explains. They suggested that this would explain the increased oil recovery by low salinity brine injection.

The double layer effect explains that decrease in salinity will increase the thickness of the ionic double layer between the clay and oil interfaces. Ligthelm et al (2009) suggested that the amount of cations in the high saline brine is sufficient to screen off the negative charge of the oil/water interface and the clay surface, which will cause a suppression of the electrostatic repulsion force. The mineral surface zeta potential will be reduced, since the high saline brine reduces the negative electrical potential at the slipping plane. The wettability of the rock in high saline brine is less water wet, because polar oil components will adsorb onto the clay by forming organo-metallic complexes.

The ability of the cations to screen off negative charges on the clay surface is reduced when low salinity brine is injected into the reservoir. The result is increased repulsive forces between the mineral surface and the oil/water interface, and expansion of the electrical double layer. At a given salinity, oil will desorb from the surface because the repulsive forces between the mineral surface and the oil phase increase above the binding force for the organo-metallic complexes (RezaeiDoust, 2011).

The result is a release of organic material and altering of the wettability when injection of low salinity brine is performed (Ligthelm et al., 2009).

Frontiers BP, 2009, suggested a hypothesis for low salinity effect in the presence of clay, where the negatively charged clay particles produce a diffuse double layer. When the diffuse double layer are in a aqueous phase and near the clay, it will be positively charged (Abdulrazag et al., 2011), Figure 2.15.

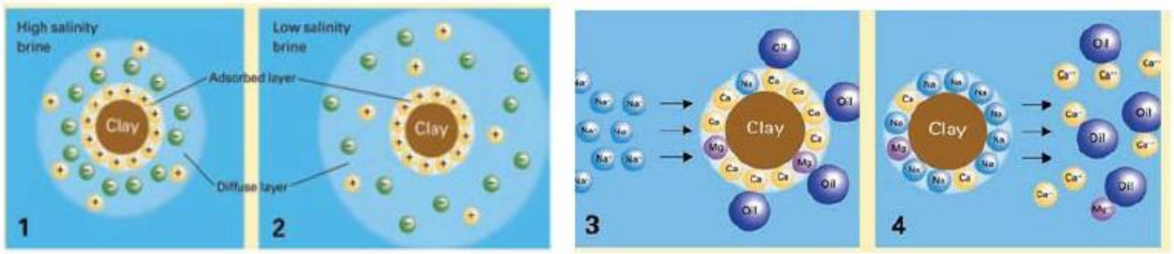


Figure 2.15: Formation of double layer by negatively charged clays, Frontier BP.

The thickness of the double layer will increase with decreasing salinity (ionic strength). As the medium becomes more water wet, the oil relative permeability will increase as a result of the water molecules within the double layer are “quasi-crystalline” or rigid. However, if hardness, such as Mg^{2+} and/or Ca^{2+},is present in the system, negatively charged oil surface can bind with the clays via an intermediate, such as divalent cations (Abdulrazag et al., 2011).

Ligthelm et al (2009) explained from an experiment that was performed that the increased oil recovery was believed to be solely related to the expansion of the electrical double layer, and concluded that the contribution of the double layer was higher than the contribution of the cation exchange mechanism (Ligthelm et al., 2009).

Contradicting results:

The double layer effect is explained by the bridging of Ca^{2+} between the clay and oil, which both have negatively charged interfaces (Anderson, 1986a; Sposito, 1989;Arnarson and Keil, 2000; Buckley et al., 1998; Lager et al, 2006; Lager et al. 2008b). However, it is not necessary with a bridge of divalent cations, since polar oil components can adsorb onto clay minerals without a bridge of divalent cations (Austad et al., 2010).

2.6.6. Proposed chemical low salinity mechanism (Austad et al., 2010)

Austad et al. (2010) have assumed that the following parameters play a major role in observing low salinity effects in sandstones: (Austad et al., 2010)

- Clay properties/type and the amount present in the rock
- Polar components in the crude oil, both acidic and basic.
- The initial formation brine composition and pH.
- It is further assumed that the EOR effect of low salinity flooding is caused by improved water wetness of the clay minerals present in the rock.

From the formation water with a high Ca^{2+} concentration, both basic and acidic organic materials are adsorbed onto the clay together with inorganic cations, especially Ca^{2+} (Austad et al., 2010). Due to dissolution of sour gases like CO_2 and H_2S, the pH of the reservoir formation water is low, even less than 5.

$$CO_2 + H_2O \rightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (2.4)$$

$$H_2S \rightarrow H^+ + HS^- \qquad (2.5)$$

When low saline water, with lower concentration of ions than the initial formation brine, is injected into the reservoir, the equilibrium of the interactions between the brine and rock are disturbed. A net desorption of cations, especially Ca^{2+}, could take place. Protons, H^+, from the water close to the clay surface will adsorb onto the clay to compensate for the loss of cations. A local pH increase will then be created close to the clay surface as shown in Eq.2.6 for Ca^{2+}(Austad et al., 2010).

$$\text{Clay-}Ca^{2+} + H_2O = \text{Clay-}H^+ + Ca^{2+} + OH^- + \text{heat} \qquad (2.6)$$

Since the proton-transfer reactions (acid/base reactions) are very fast, desorption of active cations from the clay surface is the key reaction to create alkalinity which will initiate the wettability alteration. Desorption of the active cation Ca^{2+} is shown in eq.2.6.

Equations 2.7 and 2.8 show the local pH increase close to the clay surface, which will cause reactions between the adsorbed basic and acidic material.

$$\text{Clay -}NHR_3^+ + OH^- = \text{Clay} + R_3N + H_2O \qquad (2.7)$$

$$\text{Clay- }RCOOH + OH^- = \text{Clay} + RCOO^- + H_2O \qquad (2.8)$$

To obtain low salinity effects, it is necessary with presence of active clay minerals (Austad et al., 2010)

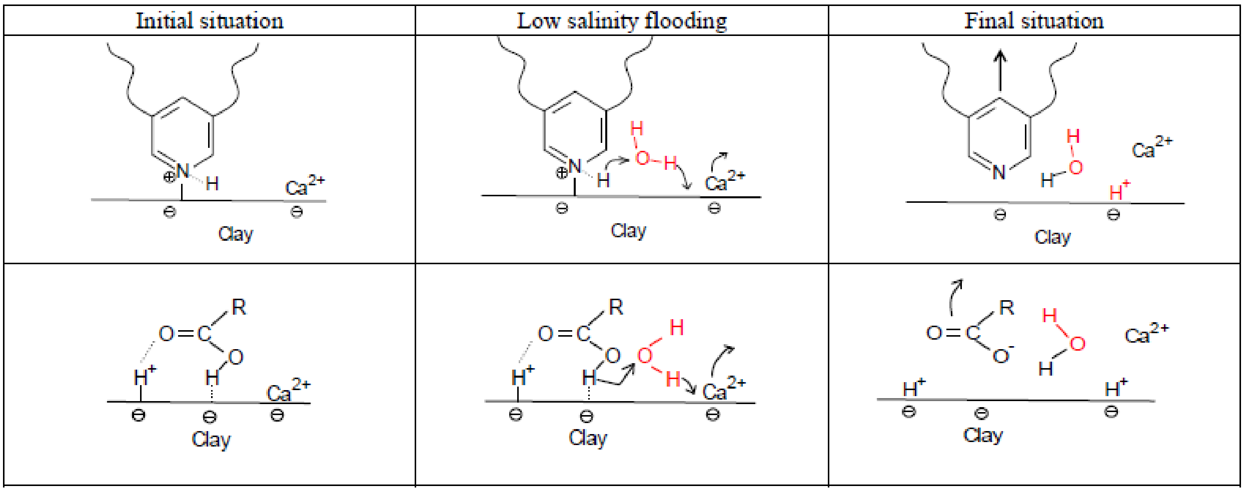


Figure 2.16: Proposed mechanism for low salinity EOR effects. Upper: Desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5 (Austad et al., 2010).

Adsorption of cations

The proton, H^+, has the strongest affinity towards the clay surface. The concentration of Na^{2+} , Ca^{2+} and Mg^{2+} found in initial formation water are usually much lower than the concentration of H^+ found in initial formation water. Acidic and basic material are co-adsorbed onto the clay together with the active cation Ca^{2+} when the system is at reservoir conditions with a pH buffered formation water close to pH 5. The mechanism of ion exchange is mainly linked to the edge surfaces for kaolinite and chlorite. The lattice substitutions are assumed to be the main mechanism for illite/mica and montmorillonite (Austad et al., 2010). Kaolinite shows a strong selectivity for Ca^{2+} over Na^{2+}, but montmorillonite only show a very small selectivity of Ca^{2+} over Na^{2+} (Kleven and Alstad, 1996). Illite/mica is believed to show a more similar selectivity of montmorillonite than kaolonite. This shows that the selectivity characteristics of different cations vary for different clays. The cations in the formation water must be able to compete with basic and acidic organic matter and H^+ for the adsorption sites on the clay surface. The formation water of a reservoir rock containing kaolinite and chlorite, should show a high concentration of Ca^{2+}, while a reservoir rock containing mostly montmorillonite and/or illite/mica may show low salinity effects even without divalent cations present in the initial formation water (Austad et al., 2010).

Local pH changes

"A local increase in the pH at the water-clay interface that is needed to desorb the organic matter, will only take place if desorption of cations occur" (Austad et al., 2010).

Without a pH buffer such as CO_2, a sudden pH increase of the produced water is always noticed when clay minerals are present and the formation water contain active ions like Ca^{2+} (Austad et al., 2010). A sudden desorption of active cations is the reason for increase in pH, shown by eq.2.6.

Substitution of Ca^{2+} by H^{+}, increases the pH close to the clay surface and causes a fast desorption of basic and acidic material by proton transfer, shown in eq. 2.7 and eq.2.8. The pH of the effluent is to some extent dependent on the composition of the injected brine. The pH may only have a small increase, if the presence of divalent cations in the injected fluid will create complex formation of the type seen in eq.2.9

$$Ca^{2+} + OH^{-} = [Ca \cdots OH]^{+} \qquad (2.9)$$

In a pH buffered system, the effluent pH may not show any increase at all. However, it has been described in the literature that the activity of H^{+} in the bulk solution, described by pH measurements, may be different from the activity close to interfaces between water and minerals (Baily et al., 1968). Thus, low salinity effects may still be observed in a pH buffered system, since a local pH increase at the clay surface will still occur and cause desorption of organic material from the clay surface.

During a low salinity flooding without pH buffering, a typical change in pH of the effluent may be from 6.5 to 8 as shown in Figure.2.17.

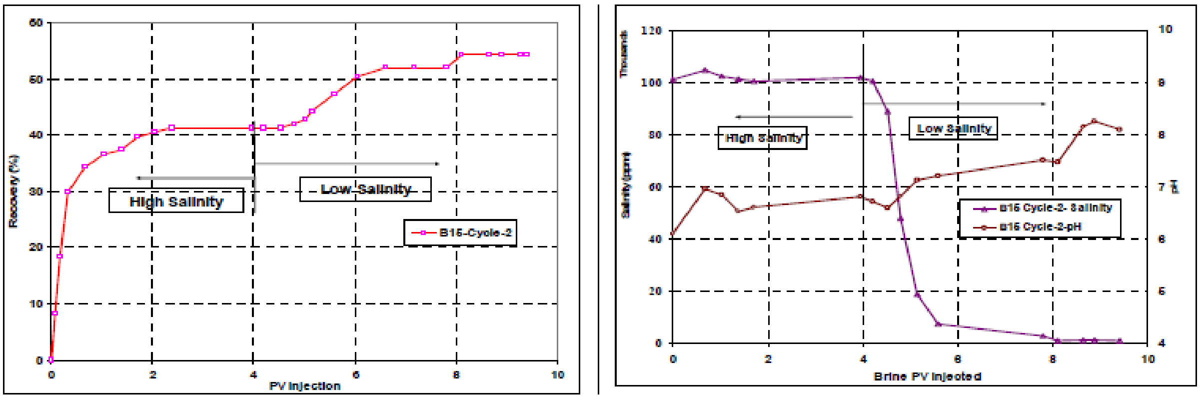


Figure 2.17: Left: A typical tertiary low salinity EOR effect. Right: Change in pH and salinity vs. flooded pore volumes (Austad et al. 2010).

An experiment done by Lager et al (2008b) showed a decrease in the concentration of multivalent cations in the effluent from core floods, especially a decrease in the concentration of Mg^{2+}. The change in concentration of Mg^{2+} do not need to be a MIE process as stated by Lager et al (2008), but could rather be precipitation of $Mg(OH)_2$ as a result of a local pH increase in the injected low saline water. The local alkalinity will decrease when $Mg(OH)_2$ is precipitated, and may have an impact on the desorption of organic material on the clay surface (Austad et al.,2010).

Criteria for optimal low salinity EOR effects

The suggested mechanism requires both polar components and active cations to be initially adsorbed onto the clay (Austad et al., 2010). For observing low salinity effect, clay minerals with high cation exchange capacity appear to be favorable.

The AN and BN in the crude oil give a good quantitative indication of the content of active polar components in the crude oil. For a crude oil with high AN and low BN, the wetting conditions are different, than for a crude oil with low AN and high BN. Basic components could also be able to adsorb onto negatively charged silica, when the oil has low AN and high BN.

The properties of the formation water determine the pH and the amount and composition of divalent cations, for a given crude oil and reservoir rock. A balanced initial adsorption of active cations, protons and organic material onto the clay surface could result in an optimal low salinity increased oil recovery. If the amount of adsorbed organic material is low and the adsorption of active ions is high (which could give a larger increase in pH during low salinity flooding due to desorption), the low salinity EOR effect will be low as a result of the rock already being to water-wet. The initial pH will play an important role for optimal initial adsorption conditions of specific active ions, if the concentrations of the active ions are above a certain level (Austad et al., 2010). As long as the low saline injected water has a concentration of active ions that are low enough to promote significant desorption from the clay surface, the composition of the injected low saline may probably not play an important role.

The suggested new chemical mechanism for tertiary low salinity EOR effect proposed by Austad et al. (2010) can be summarized as (taken from Austad et al., 2010):

- Initially there is a balanced adsorption onto the clay minerals of organic material, active cations and protons, preferentially at reservoir pH of about 5.
- Injection of low salinity brine will cause desorption of adsorbed cations, which will increase the pH close to the water-clay interface because Ca^{2+} is substituted by H^+ on the clay surface.
- An ordinary acid-base reaction, which promotes desorption of organic material, takes place between OH^- and the adsorbed acid and protonated base. The water wetness increases and increased oil recovery is observed.
- Different clays have different adsorption/desorption windows.

3. Experimental work

3.1. Materials

3.1.1. Core

One preserved sandstone reservoir core from the Yme field, Yme #23, was selected for the experiment. Yme is a sandstone oil reservoir located in the south-eastern region of the North Sea, with Talisman Energy Norge AS as operator. Sea water has already been injected into the reservoir. More details about Yme are found in appendices A.1. The core was taken from well 9/2-7S at a depth of 3917.88 m. The content of clays had been measured with X-ray diffraction analysis (XRD) by Talisman Energy. The core contained most kaolonite, some illite/mica and a smaller content of chlorite as shown in Table.3.1. The complete XRD-analysis is found in appendices A.2. The core had a smooth surface and the edges were cut until the cores got a cylindrical shape. The dimensions and other core properties are given in Table 3.2. It is assumed that the clay content of the core is somewhere between the given depths, since the core is taken in between the given depths.

Table.3.1: Clay content of Yme core

Depth [m]	Illite/mica [%]	Kaolinite [%]	Chlorite [%]
3917.75	7.4	9.6	1.5
3918.00	6.0	7.0	0.8

Table 3.2: Core properties

Core	L [cm]	D [cm]	V_b [cm^3]	W_s [g]	W_d [g]	W_f [g]	PV [cm^3]	Φ [%]	Sw_i [%]
Yme#23	5.72	3.78	64.13	151.79	141.69	143.93	9.817	15.307	20

Where:

L = Length of core [cm]

D = Diameter of core [cm]

V_b = Bulk volume of core [cm^3]

W_s = Weight of core 100 % saturated with Yme 5x diluted FW [g]

W_d = Weight of dry core [g]

W_f = Final weight of core after desiccator [g]

PV = Pore volume of core [cm^3]

Φ = Porosity of core [%]

Sw_i = Initial water saturation [%]

3.1.2. Crude oil

Reservoir crude oil from the Yme field was used in the experiment. The crude oil was sentrifuged for 50 minutes and then filtrated with a 2 µm filter paper by using a vacuum pump, to remove any solid and particles in the oil. The stabilized crude oil was saturated with CO_2 at 6 bars. The reservoir initially contains sour gases like CO_2 and H_2S. CO_2 will dissociate from the crude oil into the FW and reduce the initial pH which could affect the adsorption of polar components. By saturating the crude oil with CO_2, the wetting properties in the core would be as close to reservoir conditions as possible.

3.1.2.1. Asphaltene content

A known amount of crude oil without CO_2 was diluted in heptane [1:40] which will result in precipitation of any asphaltene. The diluted crude oil was then filtered through a 0.22µm filter paper using a vacuum pump. Asphaltene residue will then be left on the filter paper. The amount of asphaltene in the stable crude oil was found by subtracting the weight of the filter paper with and without the asphaltene residue.

The amount of asphaltene per 100ml was then calculated from the following equation:

$$Asphaltene\ content\ \left[\frac{g}{100ml}\right] = \frac{W_{asphaltene}}{V_{oil}} \cdot\ 100 \qquad (3.1)$$

Where:

$W_{asphaltene}$: Weight of filtrated asphaltene [g]
V_{oil} : Volume of filtrated oil [ml]

Eq.3.1 was used to calculate the amount of asphaltene in the crude oil. The calculated value is shown in Table.3.3.

Table 3.3: Asphaltene content

Filtrated asphaltene [g]	Filtrated crude oil [ml]	Asphaltene content in crude oil [g/100ml]
0.2372	20.227	1.173

3.1.2.2. CO_2 in crude oil

CO_2 was mixed into the stabilized Yme crude oil. The stabilized crude oil was contained in a recombination cell, with a tubing connected to a CO_2 container pressurized at 6 bars. The gas was transferred slowly into the recombination cell containing oil. The recombination cell was then shaked to dissolve the CO_2 into the oil. The pressure of the piston cell gradually increased without exceeding the saturation pressure of 6 bars. All experiment with crude oil was conducted at a pressure of 10 bars to avoid two phase flow of oil and gas.

Table 3.4: Properties of Yme crude oil without CO_2

AN (20°C) [mg KOH/g]	BN (20°C) [mg KOH/g]	Density (20°C) [g/cm^3]
0.25	1.17	0.85182

Table 3.5: Properties of Yme crude oil with CO_2

Density (23°C) [g/cm^3]
0.852

3.1.2.3. Volume correction: Thermal expansion and gas liberation

Volumetric expansion in oil due to temperature and pressure changes can be explained by thermal expansion and gas liberation (when the oil contains gas). The difference in oil volume at reservoir conditions and at atmospheric conditions can be described by the shrinkage factor.

Figure 3.1: The setup for measuring the shrinkage factor of oil at 110° C and 23°C.

The crude oil saturated with CO_2 in the recombination cell was displaced with distilled water into the mass flow meter CMFS 010 by Micro Motion. The mass flow meter temperature was set to 110°C, with a pressure of 10 bars. The density of the oil at 10 bars and 110°C was measured. The oil was injected from the recombination cell and through the mass flow meter at low rate. The oil was then displaced through the back pressure valve and into a glass, and the amount of oil was calculated. The density of the oil at 10 bars and 23°C was measured.

The shrinkage due to a temperature drop, thermal shrinkage, is calculated from the following equation:

$$Shrinkage_{thermal\ expansion} = 1 - \frac{\rho_{110°C,10\ bar}}{\rho_{23°C,10\ bar}} \qquad (3.2)$$

Where:

$\rho_{110°C,10\ bar}$: Density of oil at 110°C and 10 bar [g/cm^3]

$\rho_{23°C,10\ bar}$: Density of oil at 23°C and 10 bar [g/cm^3]

At 23°C, an exact amount of crude oil was flashed to atmospheric conditions. Weight and density of the flashed oil is then used to calculate the volume. Gas liberation, due to a pressure drop, is calculated from the following equation:

$$Shrinkage_{\ Gas\ liberation} = \frac{V_{Atm}}{V_{BP}} = 1 - \frac{W_{oil}/\rho_{oil}}{V_{fl}} \qquad (3.3)$$

Where:

V_{BP} : Volume back pressure [ml]

V_{Atm} : Volume atmosphere [ml]

W_{oil} : Weight of oil [g]

P_{oil} : Density of oil [g/cm^3]

V_{fl} : Volume of oil flashed [ml]

The total shrinkage factor for the oil (from the recombination cell to the glass) is calculated from the following equation:

$$\text{Shrinkage factor} = \text{Shrinkage}_{\text{thermal expansion}} + \text{Shrinkage}_{\text{Gas liberation}} \qquad (3.4)$$

Table 3.6: Properties for calculation of the shrinkage factor.

$\rho_{110°C,10\ bar}$ [g/cm^3]	$\rho_{23°C,10\ bar}$ [g/cm^3]	$weight\ of\ oil$ [g]	$density\ of\ oil, 1\ atm$ [g/cm^3]	$volume\ flashed$ [ml]
0.764	0.848	7.0423	0.852	8.626

Equations 3.3-3.4 were used to calculate the shrinkage factor. The calculated values are shown in table 3.7.

Table 3.7: Calculated Shrinking factor.

Shrinkage $_{\text{Thermal expansion}}$	Shrinkage $_{\text{Gas liberation}}$	Shrinkage factor	Shrinkage factor [%]
0.099	0.042	0.141	14.1

2.1.1. Brines

The brines used in the experiment where synthetic Yme formation water (FW), synthetic seawater (SW) and 50 times diluted synthetic seawater ($d_{50}SW$) as low salinity water. The brines where prepared by using distilled water and reagent grade chemicals. The compositions of the brines are shown in Table.3.8.

Table 3.8: Composition of Brines used

	Yme FW		**SW**		**$d_{50}SW$**	
Salt	m, g/l	mole/l	m, g/l	mole/l	m, g/l	mole/l
NaCl	111,92	1,915	23,38	0,400	0,468	
Na_2SO_4	-	-	3,41	0,024	0,068	
$NaHCO_3$	-	-	0.17	0,002	0,003	
KCl	2,43	0,033	0,75	0,010	0,015	
$MgCl_2$ x $6H_2O$	16,24	0,080	9,05	0,045	0,18	
$CaCl_2$ x $2H_2O$	94,12	0,640	1,91	0,013	0,04	
$BaCl_2$ x $2H_2O$	1,60	0,007	-	-	-	
$SrCl_2$ x $6H_2O$	2,19	0,011	-	-	-	

Table 3.9: Ione composition of brines

Iones	**Yme FW (mole/l)**	**SW (mole/l)**	**$d_{50}SW$ (mmole/l)**
Cl^-	3,417	0,5251	10,503
Mg^{2+}	0.080	0,0445	0,891
Ca^{2+}	0,640	0,0130	0,259
Na^+	1,915	0,4501	9,002
K^+	0,033	0,0101	0,201
Ba^{2+}	0,007	-	-
Sr^{2+}	0,008	-	-
HCO_3^-	-	0,0020	0,040
SO_4^{2-}	-	0,0240	0,480
TDS [g/l]	195,68	33,39	0,668

Table 3.10: Brine properties

Brine	Density [g/cm^3]	Salinity [ppm]
Yme FW	1.13985	195 680
Yme 5xFW	1.0288	39136
SW	1.024	33 390
d_{50}SW	1.024	668
1000 ppm NaCl	0.999	500
Distilled water	0.9982	0

The complete table is found in appendices A.2.

3.2. Experimental procedure

3.2.1. Core cleaning

The preserved core was mounted in a Hassler core holder with a confining pressure of 33 bars from a N_2 container. The injection took place at room temperature (23°C). The core was first injected with about 4 PV of kerosene to displace any oil from the core. Then the core was cleaned by injected with series of 4 PV toluene and methanol, until the effluent was clear. Toluene will displace the oil and the organic materials in the core. Since toluene is a clear fluid, the core is considered cleaned for crude oil when the effluent becomes clear. The methanol injected will remove the brine (salt and water) inside the core. After the cleaning, 4 PV's with 1000 ppm NaCl solution was injected into the core to remove the remaining salt and formation water. The core was then put in a heating chamber at 90°C for drying and the dry weight was measured.

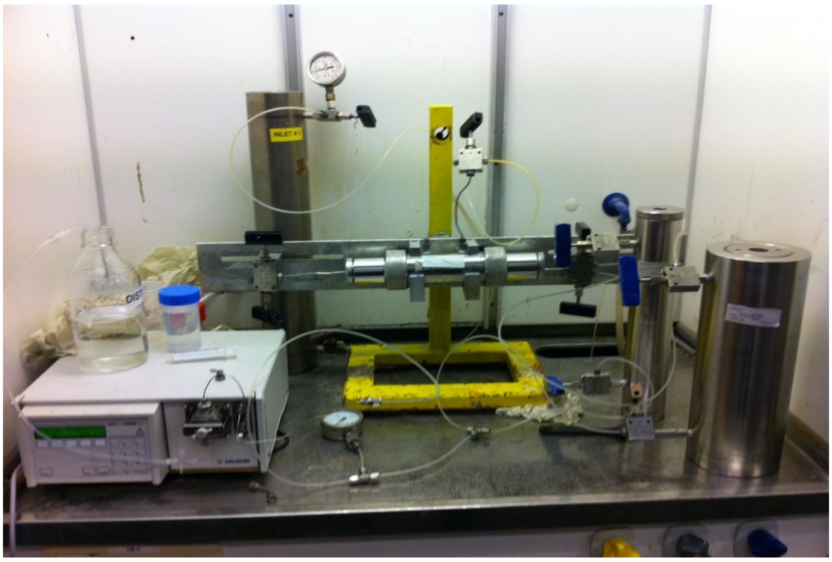


Figure 3.2: Core cleaning setup.

3.2.2. Initial water saturation, dessicator technique

The dried and cleaned core was put in a vacuum cell; setup is shown in Figure 3.4. When vacuum was achieved, the core was saturated with 5x diluted Yme FW. The pore volume was calculated from eq.3.5:

$$PV = \frac{W_s - W_d}{\rho_{5xFW}} \qquad (3.5)$$

Where:

PV : Pore volume of core [cm^3]

W_s : Saturated weight of core [g]

W_d : Dry weight of core [g]

ρ_{5xFW} : Density of 5 times diluted Yme formation water [g/cm^3]

Figure 3.3: Vacuum cell

The core was then put into a dessicator, Figure 3.4, with silica gel to establish 20% initial water saturation. The silica gel will only adsorb the water molecules leaving the salt behind in the core.

Figure 3.4: Dessicator to establish initial water saturation.

Eq.3.6. was used to calculate the desired and final weight of the core when the water saturation would be 20 %.

$$W_f = W_d + (PV \cdot 0.20 \cdot \rho_{FW}) \qquad (3.6)$$

Where:

W_f : Final weight of core [g]

W_d : Dry weigth of core [g]

PV : Pore volume of core [cm^3]

ρ_{FW} : Density of Yme formation water [g/cm^3]

The weight of the core was measured several times, until the core reached its desired weight and 20 % water saturation was established.

The porosity of the core was determined from eq.3.7:

$$\phi = \frac{PV}{V_b} \cdot 100 \qquad (3.7)$$

Where:

ϕ : Porosity of core [%]

PV : Pore volume of core [cm^3]

V_b : Bulk volume of core [cm^3]

3.2.3. Oil saturation and aging of core

The core was mountered in a Hassel core holder with a confining pressure of 30 bars. The core holder, core and inlet and outlet tubings where vacuumed for 10 minutes. Then the core where saturated with crude oil and pressurized to 10 bars. The core was then flooded with 2 PV of the CO_2- saturated oil in each direction with a rate of 0.1 ml/min with a back pressure of 10 bars to ensure one phase flow.

The core saturated with crude oil was aged in the core holder at Yme the reservoir temperature 110°C for 14 days and with a back pressure of 10 bars.

3.2.4. Core flooding with FW, SW and d_{50}SW

The aged core was first flooded with Yme formation water in a secondary stage. The oil and water production was monitored in a burette at ambient conditions. The effluent of the produced water was sampled and the density and the pH were measured. When the oil recovery plateau was achieved, and the pH and density of the produced water stabilized, the injection fluid was changed. The injected water was changed to synthetic sea water and the core was flooded in a tertiary stage. When the pH and salinity of the effluent was constant, seawater diluted 50 times (d_{50}SW) was injected.

The injection rate was 0.027 ml/min, which is 4 PV per day. The displacement temperature was Yme reservoir temperature of 110°C. The experiment was conducted at a pressure of 10 bars, with a back pressure of 10 bars and confining pressure of 30 bars.

The amount of produced oil was recorded. The pH and density was measured, and the total dissolved salt (TDS) was calculated from the density. The complete test data are reported in appendices A.3.

The flooding setup consisted of one Gilson 307 pump, piston cells for the individual injection brines, a Hassler core holder mounted into an oven, piston cells, a measuring burette, a temperature measurer and a computer. Figure.3.5 and Figure 3.6.

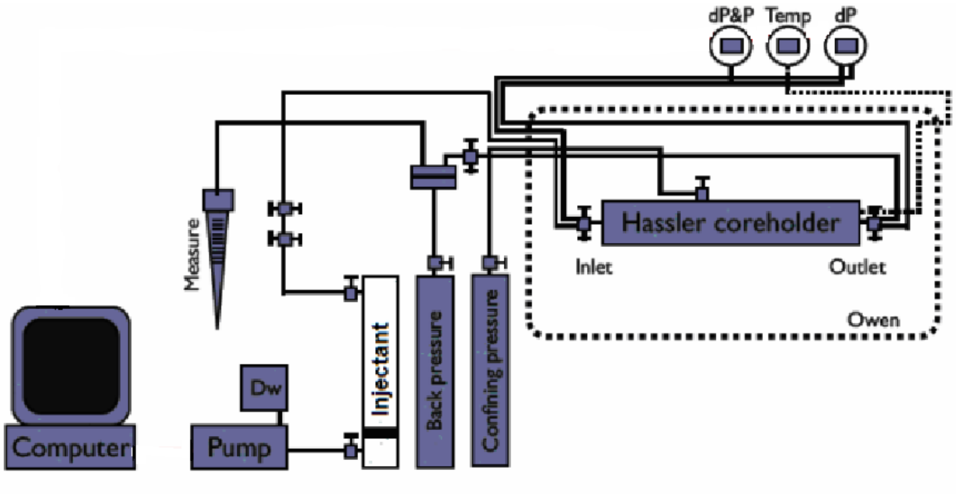


Figure 3.5: Schematic figure of the flooding system (Austad et al., 2010)

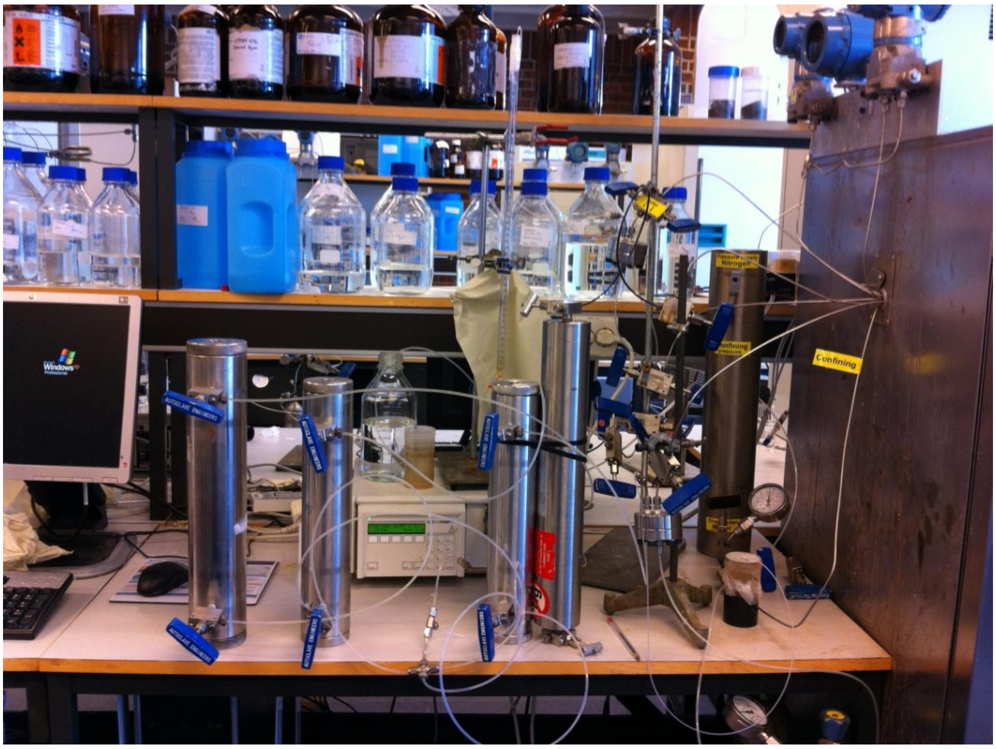


Figure 3.6: Setup for flooding. The piston cells seen from the left contained Yme FW, SW, d_{50}SW and oil saturated with CO_2.

A plot of oil recovery versus injected pore volumes of brine is presented in the result chapter.

The recovery factor was calculated from the following equation:

$$R = \frac{V_{prod}}{OOIP} \cdot 100 \tag{3.8}$$

Where:

R = Oil recovery factor [%]

V_{prod} = Volume of oil produced [ml]

OOIP = Original oil in place [ml]

3.2.5. Chemical analysis

Effluent samples were collected during the waterflooding of Yme FW, SW and d_{50}SW. After the waterflooding was finished, a chemical analysis was performed on the effluent samples. SW was used as external standard. All the samples were diluted 200 times, and then chemical analysis was performed on an IC (Ion Chromatograph) device, which recorded peaks for both anions and cations. From the peaks the concentration of ions were calculated based on the external standard. The amount of ions in the effluent was compared with the amount of ions in the injected brines in order to determine if there had been any changes in ion concentration due to dissolution of minerals, adsorption or desorption.

Figure 3.7: To the left; machine to perform dilutions of sample tests. To the right; IC (Ion Chromatograph) for performing chemical analysis of sample tests.

Results are presented as injected PV versus the concentration of Ca^{2+} and SO_4^{2-} in mmole/liter. The complete results from the IC are found in appendices A.4.

3.2.6. Measurement of pH

The pH was measured using a Mettler Toledo ph-meter at ambient temperature.

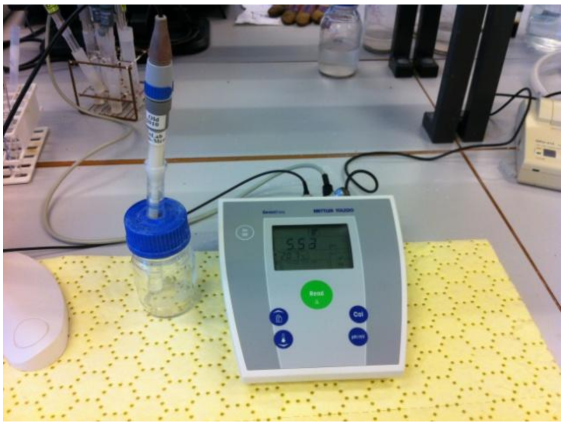


Figure 3.8: A Mettler Toledo pH-meter.

A plot of effluent pH versus effluent salinity is presented in the results.

3.2.7. Measurement of density

The density of the oil and brine was measured at a temperature of 20°C using a densitometer, DMA 4500 from Anton Paar, shown in figure 3.9. The tube was cleaned with white spirit and acetone before injecting oil and brine into the densitometer. White spirit removes oil, while acetone adsorbs water and dissolves white spirit. It was important that no air bubbles were injected into the densitometer together with the fluid, since this could lead influence the density measurement. The density of the 5x diluted Yme FW was used to calculate the pore volume and the porosity of the core, while the density of the brine was used to calculate the amount of salinity/total dissolved salt (TDS) in the effluent brine after flooding.

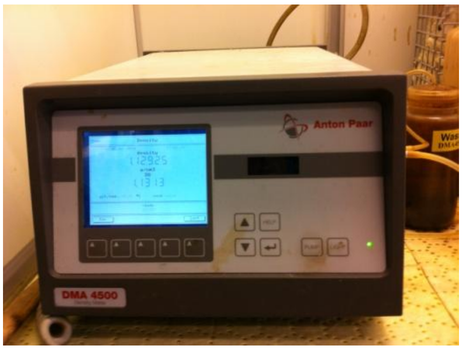


Figure 3.9: Measurement of density by a densitometer.

3.2.8. Calculation of effluent salinity

The effluent salinity was calculated from the density of the effluent brine. Known values of the densities of Yme FW and distilled water was used. Salinity of a mixture between these two brines could be determined by using a linear fit and the following equation:

$$TDS_e = TDS_{FW} - \frac{(\rho_{FW} - \rho_e)}{(\rho_{FW} - \rho_{DW})} \cdot TDS_{FW} \qquad (3.9)$$

Where:

TDS_e: Total dissolved solid of effluent brine [ppm]

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

ρ_{FW}: Density of Yme FW [g/cm^3]

ρ_e: Density of effluent brine [g/cm^3]

ρ_{DW}: Density of distilled water [g/cm^3]

4. Results

The core from the Yme field, Yme #23, was first cleaned from reservoir fluids and salt, and then an initial water saturation of 20% was established in the core. The core was then saturated with Yme crude oil that was saturated with CO_2, and aged for 14 days at Yme reservoir temperature of 110°C. After the aging was complete, the core was flooded with formation water, sea water and 50 times diluted sea water. The injection rate of the individual brines was 4 PV per day at a temperature of 110°C. Oil recovery was recorded. Density, pH and ion composition was measured from the produced water.

Formation water was the first brine that was injected into the core. There was a piston like displacement to about 55 % oil recovery. Then, both oil and water was produced. The oil recovery reached a plateau of 65 % after 5 PV of FW had been injected into the core. The oil recovery versus injected PV is shown in Figure.4.1. The pH and the salinity of the effluent versus injected PV is shown in Figure 4.2. The pH of the first produced water in the core was 5.6, and increased to pH = 6, during the injection of formation water. The salinity of the effluent of formation water increased from initial 141500 ppm to 179000 ppm, which is close to the salinity of Yme FW (195 680 ppm). The concentration of Ca^{2+} in the effluent when FW was injected (630mmole/l), is close to the concentration of Ca^{2+} in Yme FW (640 mmole/l). The concentration of SO_4^{2-} in the effluent was about 2-3mmole/l, compared to no SO_4^{2-} present in the FW. Figure 4.3.

No additional oil recovery was recorded when the injection fluid was changed to seawater. Figure.4.1. SW was injected after 7 PV’s of injected FW. The pH of the effluent increased gradually from 6 to 6,8 during injection of seawater. However, the pH gradient is not very steep and it takes 3 PV’s for the pH to increase. The salinity of the effluent decreased during the injection of SW, but the gradient of the salinity decrease is not very steep. Figure.4.2.The concentration of Ca^{2+} and SO_4^{2-} in the effluent is about the same as the concentration of Ca^{2+} and SO_4^{2-} in the injected seawater. Figure.4.3.

50 times diluted seawater was injected into the core after 19 PV’s had been injected. Any additional oil recovery was still not observed. Figure.4.1. There was a small pH increase in the effluent when d_{50}SW was injected. The pH gradient was small and less than the pH gradient when seawater was injected. The pH increased from 6,8 to 7,2. A small decrease in the salinity of the effluent was observed. Figure.4.2. The concentration of Ca^{2+} in the effluent was 5 mmole/l and the concentration of SO_4^{2-} was 3,4 mmole/l. The concentration in the initial 50 times diluted sea water was only 0.0259mmole/l Ca^{2+} and 0.480mmole/l SO_4^{2-}. This indicates that both calcium and sulfate had been dissolved from the core, indicating the precipitation of the mineral anhydrite, $CaSO_4$(s), in the core. Figure.4.3.

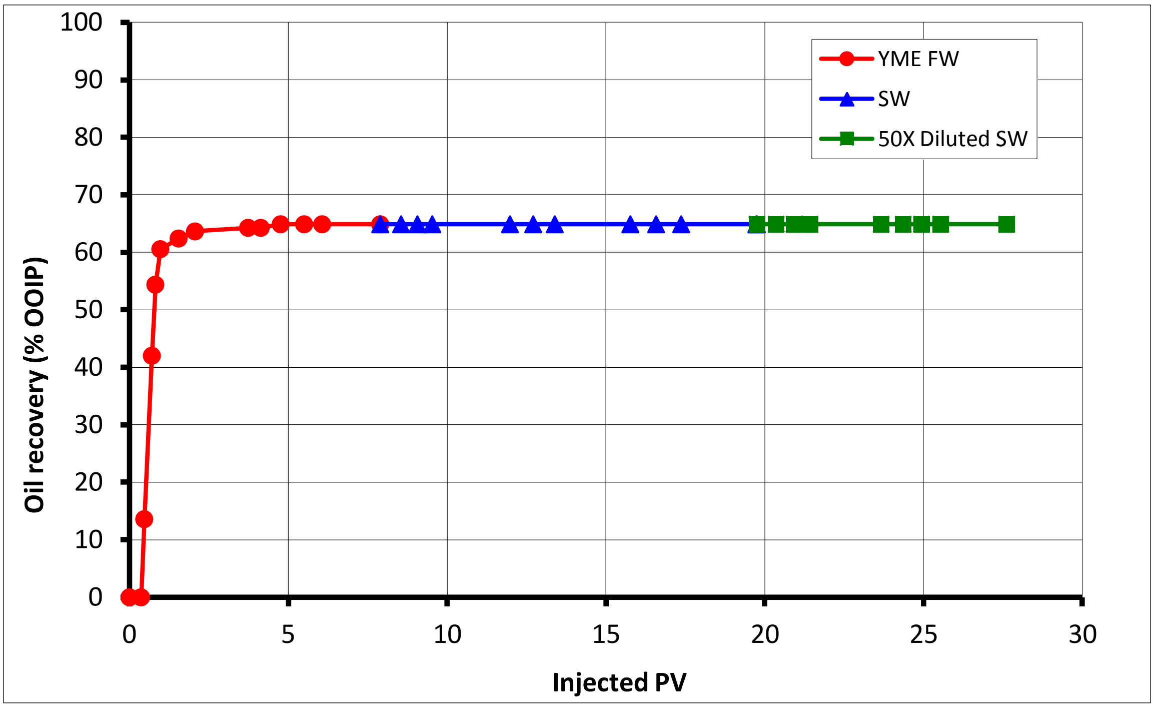


Figure 4.1: Oil recovery (% OOIP) versus injected PV, at reservoir temperature 110°C and constant injection rate of 4 PV per day.

The shrinking factor of thermal expansion and gas liberation has been taken into account in the results of %OOIP.

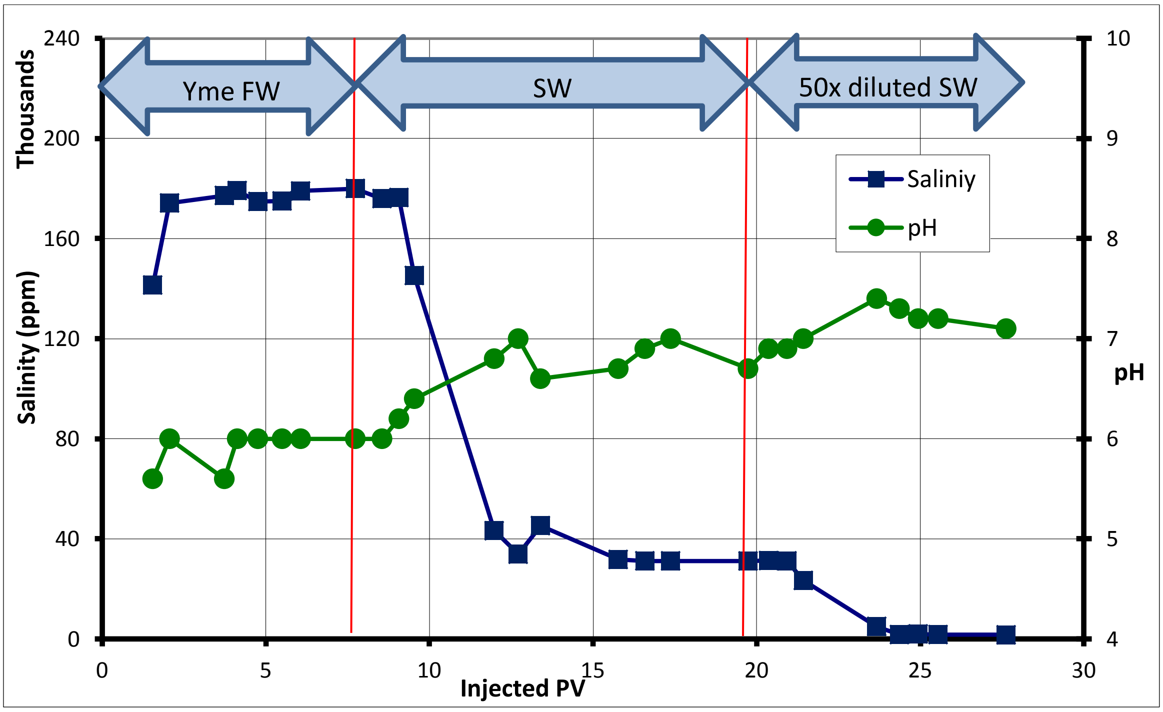


Figure 4.2: pH and salinity of the effluent versus injected PV.

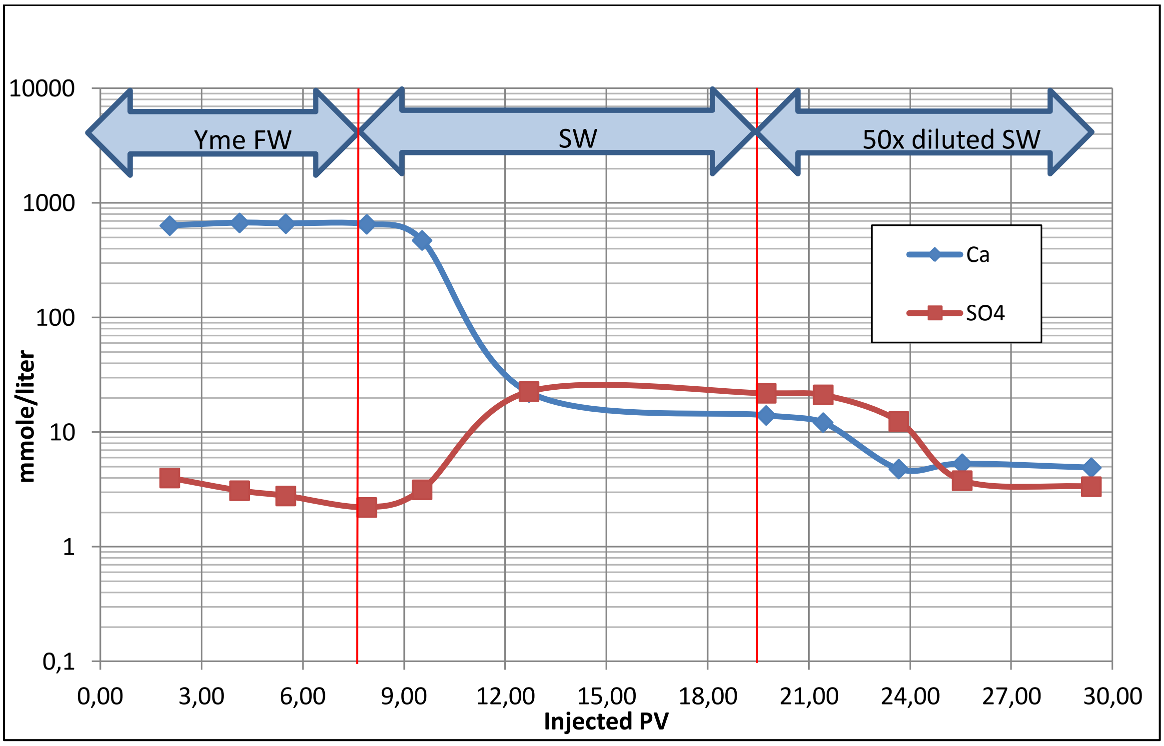


Figure 4.3: Dissolution of Ca^{2+} and SO_4^{2-} versus injected PV.

The complete data from the flooding experiment and the complete data of the pH and salinity of the effluent can be found in appendices A.3.The complete data and results from the chemical analysis can be found in appendices A.4.

5. Discussion

The criteria's for observing low salinity effects are as earlier mentioned; clay present, polar components in the crude oil, wettability alteration towards a more water-wet condition, low initial pH for adsorption of polar components and the Ca^{2+} gradient (Ca^{2+} in the FW compared to Ca^{2+} in SW and d_{50}SW). All these criteria coincide with the properties of the Yme core and it should therefore be possible to observe a low salinity effect from the Yme core.

The clay content in the Yme core was relatively high with about 16 wt% clay content (~ 7 wt% illite/mica, 8 wt% kaolinite, 1 wt% chlorite). The amount of acidic material in the Yme crude oil is moderate as seen from the acid number 0.25 mg KOH/g. The base number is high with 1.17 mg KOH/g. There should be enough polar components present in the crude oil to adsorb onto the clay surface, provided that the initial pH is low. The observed initial pH was low enough to promote adsorption of polar components onto the clay surface.

Since there is a significant difference in the concentrations in the active ions, especially Ca^{2+}, in the Yme formation brine (0,640 mole/l Ca^{2+}) and sea water (0,013 mole/l Ca^{2+}), sea water may act as a low salinity fluid itself. However, the oil recovery in Yme core #23 did not increase when the injection fluid was switched from formation water with high salinity to sea water with lower salinity. It may therefore not be possible to recover increased oil recovery after first flooding with seawater.

The pH of the effluent brine increased when switching from formation brine to seawater and then to the 50 times diluted seawater. Figure 4.2. The pH increase could be explained by active cations from the clay surface which are desorbed. From the water close to the clay surface, protons (H^+) may adsorb onto the clay and create a local pH increase to compensate for the loss of cations. The pH gradient when injecting low salinity water (d_{50} SW) is small and the pH changes are relatively slow. Adsorption of organic material onto the clay surface may create a less water-wet condition inside the core. When the initial pH is low and close to pKa values of the actrive compounds (pKa ~5), the adsorption of active polar oil components is at its maximum (Aksulu et al.,2012). In this experiment the initial pH was pH =5.6, and thus the maximum amount of active polar components in the crude oil should be adsorbed. At low capillary pressure and slightly water-wet conditions, maximum oil recovery can be reached (Morrow et al., 1998). When the high saline formation water is exchanged by the low saline water, active cations are desorbed from the clay surface due to desorption of organic material by a ordinary acid-base reaction (Austad et al., 2010). However, since the Yme formation brine is highly saline (about 200 000 pppm) the adsorption of organic material from the crude oil would most likely be small (Aksulu et al., 2012).

A rapid increase in pH due to desorption of active ions, is important for oil components to desorb from the clay surface (Austad et al., 2010). When active cations are desorbed from the clay surface, the pH will increase rapidly due to adsorption of H^+ onto the clay surface. Organic material will as a result of an increase in pH be desorbed from the clay surface. Because of mobilization of bypassed oil from the clay-rich areas, a new oil bank will be created. When the pH gradient is steep, more organic material will be desorbed from the clay surface.

CO_2, which was saturated in the crude oil to lower the pH of the formation brine, may have some buffering effects and may result in only a small pH increase when switching injection water. A pH increase may occur close to the clay surface, even though the pH gradient in the effluent is small (Austad et al., 2010). The pH changes close to the clay surface is not possible to monitore. The results of this experiment should not be explained by the measured pH, because of the buffering effects on the pH by CO_2.

Master student Silje Storås at the University of Stavanger, did a similar experiment with Yme core #22, which is taken from a depth of 3917.85m. It is assumed that the clay content in Yme #22 is about the same as the clay content in Yme #23. The procedure for the experiment with Yme #22 was the same as for Yme #23. The only difference in the experiment was that $CaSO_4$ was removed from the core after the core cleaning. Yme #22 was also flooded at Yme reservoir temperature of 110°C and with a constant rate of 4 PV per day (Storås, 2012).

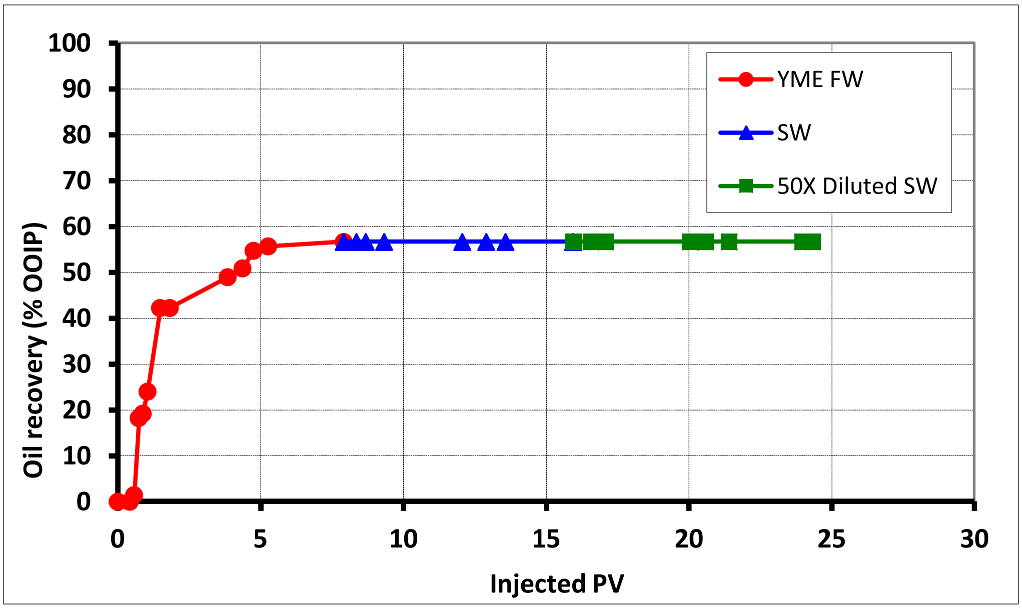


Figure 5.1: Oil recovery versus injected PV, at Yme reservoir temperature 110°C and constant injection rate of 4 PV per day (Storås, 2012).

From the graphs in figure.5.2, it is shown that Yme #23 had a more piston like displacement compared to Yme #22. The oil recovery in Yme #23 was almost 10 % of OOIP higher than the oil recovery in Yme #22, even though core #23 behaved more water-wet than core #22.The difference in oil recovery from the two cores indicates that the initial properties of the core after ageing are different. This was as expected, since $CaSO_4$ was removed from core #22.

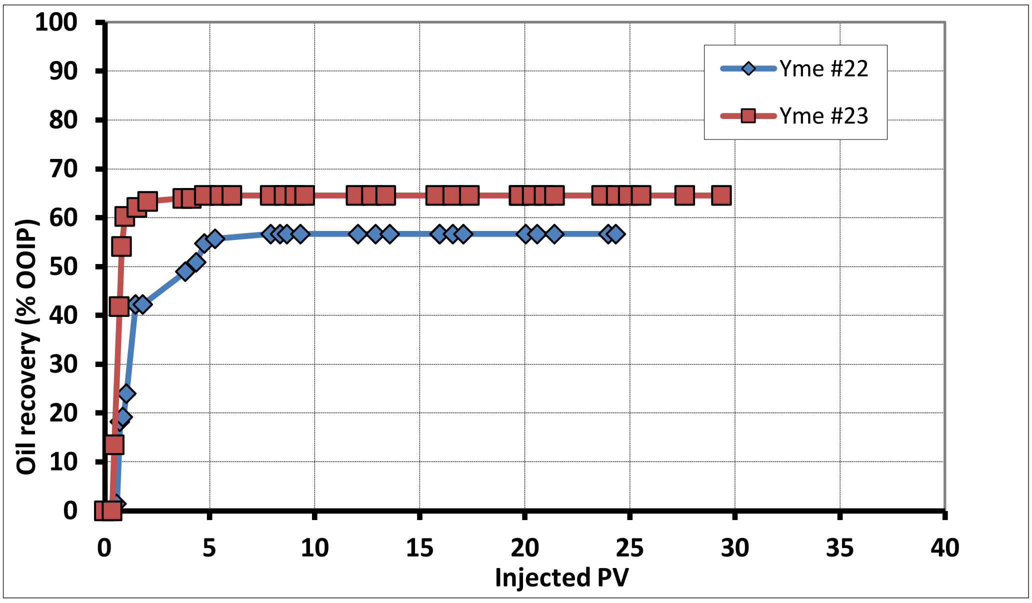


Figure 5.2: Comparison of Oil recovery (%OOIP) from Yme #22 and Yme #23 (Result for Yme #22 is taken from Storås, 2012).

The pH of the effluent in Yme #22 shows about the same results in salinity and pH for formation water, sea water and 50 times diluted sea water, as Yme #23.

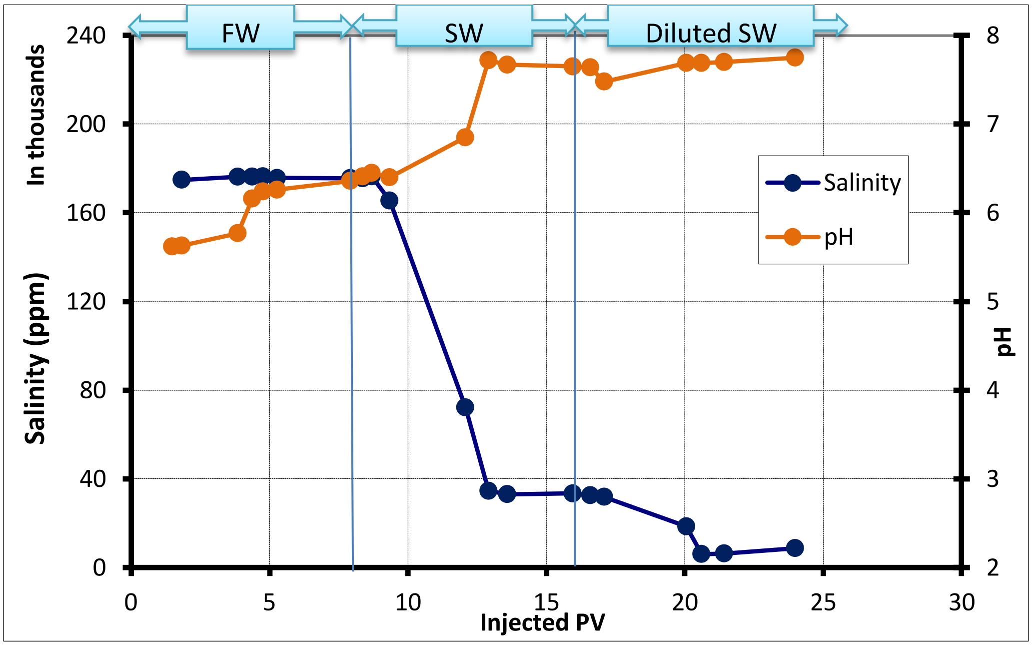


Figure 5.3: pH and salinity of the effluent from Yme #22 (Storås, 2012).

The mineral anhydrite, $CaSO_4(s)$, which was removed from Yme core #22, can affect desorption of Ca^{2+} from the clay surface when the mineral is dissolved. The dissolution of $CaSO_4$ can affect the pH increase that is important in order to obtain the wettability alteration. $CaSO_4$ was dissolved from Yme core #23 when 50 times diluted sea water was injected.

Austad et al (2010) suggested that the increase in pH when switching from high saline water to low saline water was related to the exothermic reaction shown in a previous equation, eq. 2.6.

The desorption of Ca^{2+} ions from the clay surface may be decreased in two ways when the equilibrium of eq.2.6. is moved to the left (Austad et al., 2012):

1. Supply of heat, i.e. increase in temperature
2. Supply of Ca^{2+} ions , i.e. dissolution of anhydrite, $CaSO_4$.

When the concentration of Ca^{2+} is reduced, i.e. when switching from high saline water to low saline water, the solubility of anhydrite will increase and the pH gradient will be reduced because of less desorption of Ca^{2+} in the core. The dissolution of anhydrite will increase with increasing temperature (Aksulu et al., 2012). This is supported by experimental results from Aksulu et al (Aksulu et al., 2012) shown in figure.5.4.

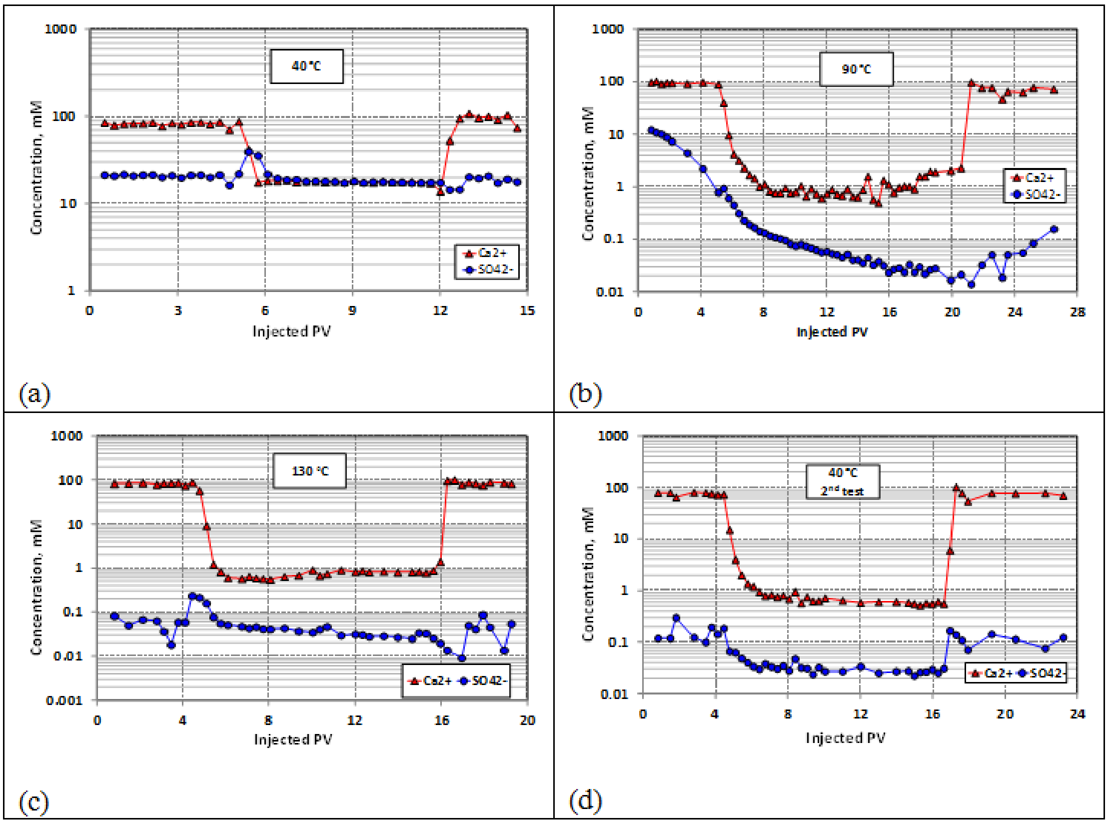


Figure 5.4: Concentration of Ca^{2+} and SO_4^{2-} in the effluent versus PV injected fluid into Core 2. The flooding sequence was HS-LS-HS in the order of increasing temperatures 40°C, 90°C,130°C and a second test done at 40°C (Aksulu et al., 2012).

No additional oil recovery was observed in either of the Yme cores, #22 and #23, when injecting low salinity water. The effect of anhydrite in this experiment was not an important parameter for not observing low salinity effect. This is confirmed by comparing the similar results from Yme #23 (containing anhydrite) with Yme core #22 (free for anhydrite).

A high temperature of 110°C may create an improved mobility ratio for the oil, by decreasing the viscosity of the oil. An improved mobility ratio would sweep a larger area inside the core, which could result in higher oil recovery. However, it has previous been experienced poor low salinity observations when the temperature was high (Aksulu et al., 2012).

The desorption process of different cations changes with temperature, due to solubility affects. Due to dehydration, the reactivity of Ca^{2+} and Mg^{2+} increases with increasing temperature. When the ageing temperature is high, increased reactivity of Ca^{2+} ions may reduce the adsorption of organic compounds onto the clay surface and the core stays water wet (RezaeiDoust et al., 2009b).

The Ca^{2+} ions may at high temperatures be strongly bonded to the clay surface. Hence, this will prevent the adsorption of organic material from the crude oil, and the wetting conditions in the core may therefore not be favorable for observing low salinity effect. In general, at high salinities and temperatures well above 100°C, the adsorption of polar components from the crude oil is significantly decreased. Boussour and Cissokho (2009) performed a study of injecting low salinity water after injecting formation brine. They concluded that the initial wetting state is controlled by the temperature and that the response of increased oil recovery was more positive at lower temperatures.

6. Conclusion

A core from the Yme field was tested for low salinity effects by flooding the core successively with Yme formation brine, sea water and 50 times diluted seawater. The crude oil was saturated with CO_2 to lower the pH of the formation water during ageing. The core was aged at reservoir temperature of 100°C and flooded with a constant rate of 4 PV per day. The main conclusions from the work are:

- The oil recovery by secondary displacement with formation water was 65% of OOIP for Yme core #23.

- No increased oil recovery was observed when injecting with sea water and 50 times diluted sea water.

- The pH gradient when switching from formation water to sea water and 50 times diluted sea water was small as expected, due to the buffering effects of CO_2 in the crude oil.
- A large amount of Ca^{2+} in the initial formation water may prevent adsorption of organic material from the crude oil, since there would be a competition between Ca^{2+} and polar components in the crude oil for the negative charged sites on the clay. This will not be favorable for observing low salinity effects.

- Dissolution of $CaSO_4$(s) may decrease the desorption process of Ca^{2+} from the clay surface. The presence of anhydrite in the core in this work was not an important factor.

- The ageing temperature may be important in the low salinity process, since the ageing temperature may alter the wettability. A high temperature may prevent adsorption of organic material to the clay surface.

- High temperatures ($T<100°$) may not be favorable for observing low salinity effect. The reactivity of Ca^{2+}increases with increased temperatures which will result in lower adsorption of organic material onto the clay surface, as a result of increased competition from Ca^{2+}.The desorption of Ca^{2+} from the clay surface would then decrease at high temperatures.

So, the main reason for why no additional oil recovery was observed would probably be high temperature and high concentration of Ca^{2+} in the initial formation water. This would result in a small adsorption of active polar components to the clay surface and a small desorption of polar components from the clay surface when the different brines were injected.

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8. Appendices

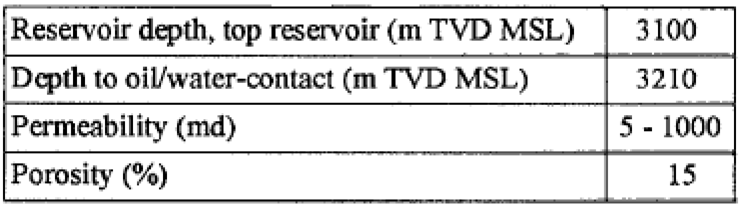
A.1 The Yme field

The Yme field lies in the south-eastern region of the North Sea, in blocks 9/2 and 9/5. It is located in the Egersund Basin at a water depth of 93 m. (www.offshore-technology.com/projects/ymeegersundbasin/)

January 1987, the field was discovered by Statoil. Statoil produced 56 million barrels (8.9 x 10^6 m^3) of oil in the time period 1996 to 2001. The field was abandoned in 2001, due to low oil prices. They produced about 15% of the oil originally in place. (www.en.wikipedia.org/wiki/yme_field)

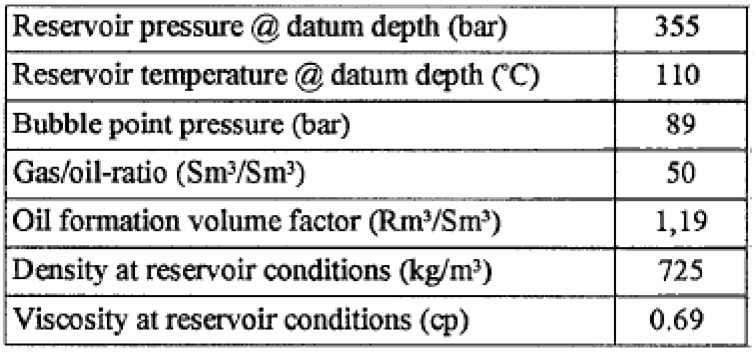
The two separate main structures in the Yme field, Gamma and Beta, consist of five deposits. (www.subseaiq.com/data/Project.aspx?project_id=873). The crude oil which was produced had high asphaltene content, a sulfur content of 0.17% mass and an API gravity of 38-39. The formation water contained dissolved NaCl of 190.000 ppm, which is a high salinity. The field also had low reservoir pressure and low dissolved gas content, which was a challenge. (www.en.wikipedia.org/wiki/yme_field)

Table A.1: Reservoir properties of Yme (Apeland et al., 1998)



Reservoir depth, top reservoir (m TVD MSL)	3100
Depth to oil/water-contact (m TVD MSL)	3210
Permeability (md)	5 - 1000
Porosity (%)	15

Table A.2: Fluid parameters for Yme oil (Apeland et al., 1998)



Reservoir pressure @ datum depth (bar)	355
Reservoir temperature @ datum depth (°C)	110
Bubble point pressure (bar)	89
Gas/oil-ratio (Sm^3/Sm^3)	50
Oil formation volume factor (Rm^3/Sm^3)	1,19
Density at reservoir conditions (kg/m^3)	725
Viscosity at reservoir conditions (cp)	0.69

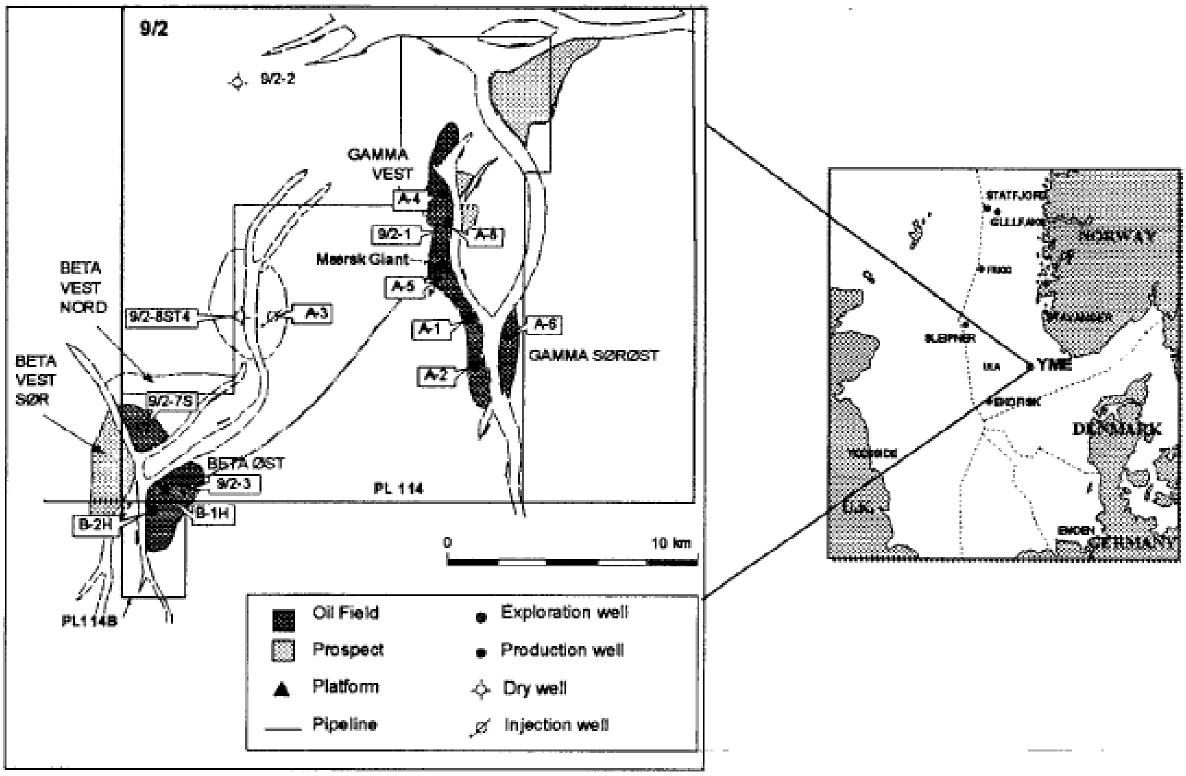


Figure A.1: Yme field location and area map (Apeland et al., 1998)

The Yme field is now operated by Talisman Energy, which is redeveloping the field. Talisman holds a 40% interest in the field, and the remaining interest is held by Bridge energy (20%), Lotus Exploration and Production (20%), Norske AEDC (10%) and Wintershall (10%). (www.offshore-technology.com/projects/ymeegersundbasin/)

Talisman decided in 2006 to produce oil by using water injection as the drive mechanism. Since the reservoir pressure is low, it will also be necessary with an artificial lift to lift the wells after water breakthrough.

Talisman expect that they will be able to produce about 60 billions of oil from the Yme field over the next ten years. The estimated production of the Yme field is set to a maximum of 40,000 bopd. (www.offshore-technology.com/projects/ymeegersundbasin/)

A.2 Compositions

Table A.3: Composition of synthetic Yme formation water.

Salt	**m [g/l]**	**m [mole/l]** (molar)
	228,49	
NaCl	111,92	1,915
Na_2SO_4	-	-
$NaHCO_3$	-	-
KCl	2,43	0,033
$MgCl_2$	7,605	
$CaCl_2$ (dry)	71,06	
$BaCl_2$	1,36	
$SrCl_2$	1,3	
$MgCl_2$ x $6H_2O$	16,24	0,080
$CaCl_2$ x $2H_2O$	94,12	0,640
$BaCl_2$ x $2H_2O$	1,60	0,007
$SrCl_2$ x $6H_2O$	2,19	0,011
Density (g/cm^3)	1,006	
Weight %	19,68	
TDS [g/l]	195,68	195,68
Ionic strength		4,152
Ions	**m [g/l]**	**m [mole/l]**
Cl^-	121,16	3,417
Mg^{2+}	1,94	0.080
Ca^{2+}	25,66	0,640
Na^+	44,03	1,915
K^+	1,27	0,033
Ba^{2+}	0,90	0,007
Sr^{2+}	0,72	0,008
HCO_3^-	-	-
SO_4^{2-}	-	-
	195,68	

Table A.4: Composition of synthetic Sea water.

Salt	**m [g/l]**	**m [mole/l]** (molar)
	38,67	
NaCl	23,38	0,400
Na_2SO_4	3,41	0,024
$NaHCO_3$	0.17	0,002
KCl	0,75	0,010
$MgCl_2$	4,24	
$CaCl_2$ (dry)	1,44	
$BaCl_2$	-	
$SrCl_2$	-	
$MgCl_2$ x $6H_2O$	9,05	0,045
$CaCl_2$ x $2H_2O$	1,91	0,013
$BaCl_2$ x $2H_2O$	-	-
$SrCl_2$ x $6H_2O$	-	-
Density (g/cm^3)	1,024	
Weight %	3,42	
TDS [g/l]	33,39	33,39
Ionic strength		0,657
Ions	**m [g/l]**	**m [mole/l]**
Cl^-	18,62	0,5251
Mg^{2+}	1,08	0,0445
Ca^{2+}	0,52	0,0130
Na^+	10,35	0,4501
K^+	0,39	0,0101
Ba^{2+}	-	-
Sr^{2+}	-	-
HCO_3^-	0,12	0,0020
SO_4^{2-}	2,31	0,0240
	33,39	

Table A.5: Composition of synthetic Sea water diluted 50 times.

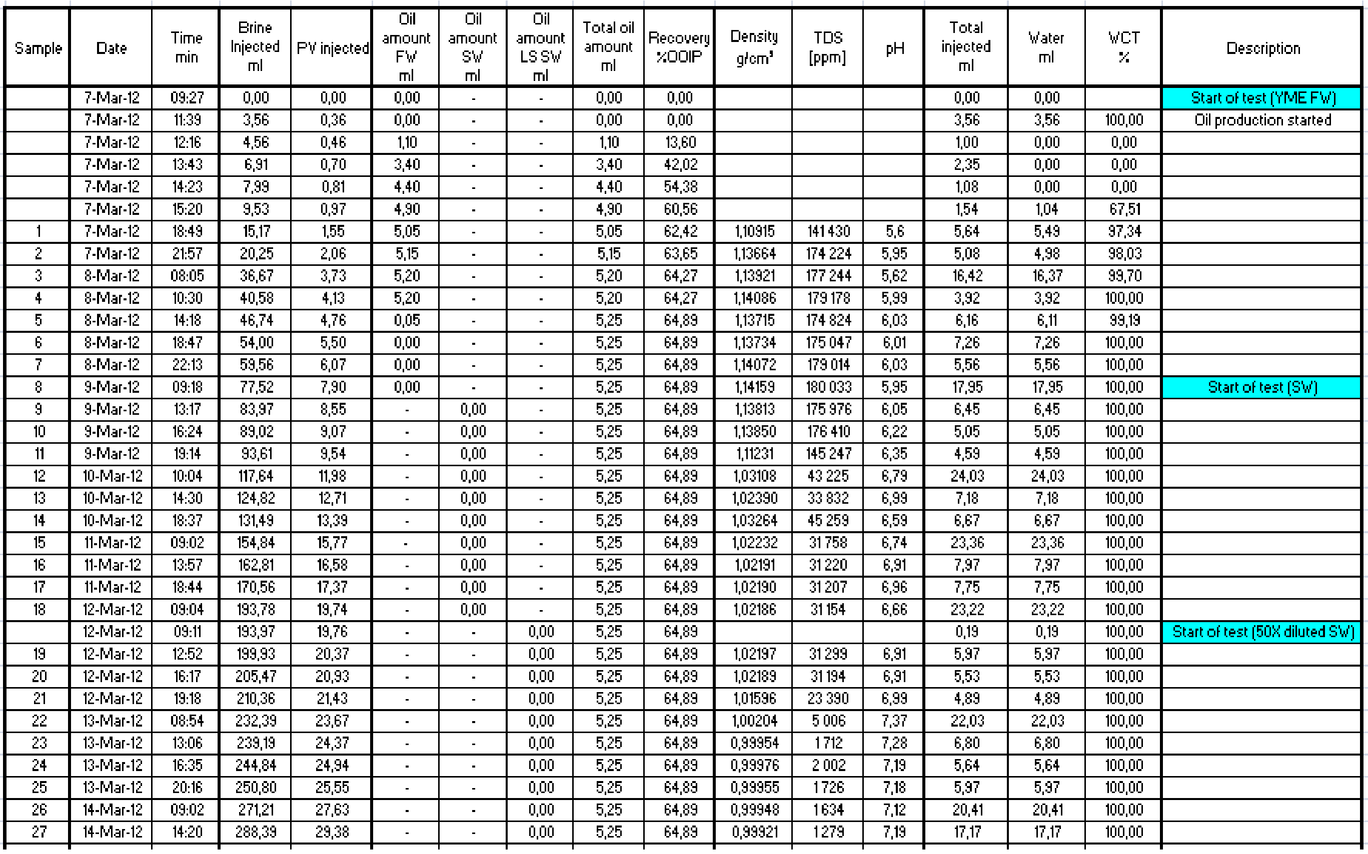
Salt	**m [g/l]**	**m [mole/l]** (molar)
	0,77	
NaCl	0,468	
Na_2SO_4	0,068	
$NaHCO_3$	0,003	
KCl	0,015	
$MgCl_2$	0,085	
$CaCl_2$ (dry)	0,029	
$BaCl_2$	-	
$SrCl_2$	-	
$MgCl_2$ x $6H_2O$	0,18	
$CaCl_2$ x $2H_2O$	0,04	
$BaCl_2$ x $2H_2O$	-	
$SrCl_2$ x $6H_2O$	-	
Density (g/cm^3)	1,024	
Weight %	0,07	
TDS [g/l]	0,668	0,668
Ionic strength		0,540
Ions	**m [mg/l]**	**m [mmole/l]**
Cl^-	372,3	10,503
Mg^{2+}	21,6	0,891
Ca^{2+}	10,4	0,259
Na^+	206,9	9,002
K^+	7,9	0,201
Ba^{2+}	-	-
Sr^{2+}	-	-
HCO_3^-	2,5	0,040
SO_4^{2-}	46,1	0,480
	667,80	

Table A.6: X-ray Diffraction Analysis for well 9/2-7S and Yme core #23.

Well	Depth (m)	Illite/Mica	Kaolinite	Chlorite	Quartz	K Feldspar	Plagioclase	Calcite	Dolomite	Pyrite	Total
9/2-7S	3917.75	7.4	9.6	1.5	68.5	1.6	9.3	0.3	0.9	0.6	100
9/2-7S	3918.00	6.0	7.0	0.8	76.3	2.9	5.3	1.1	-	0.6	100

A.3 Complete test data, main test

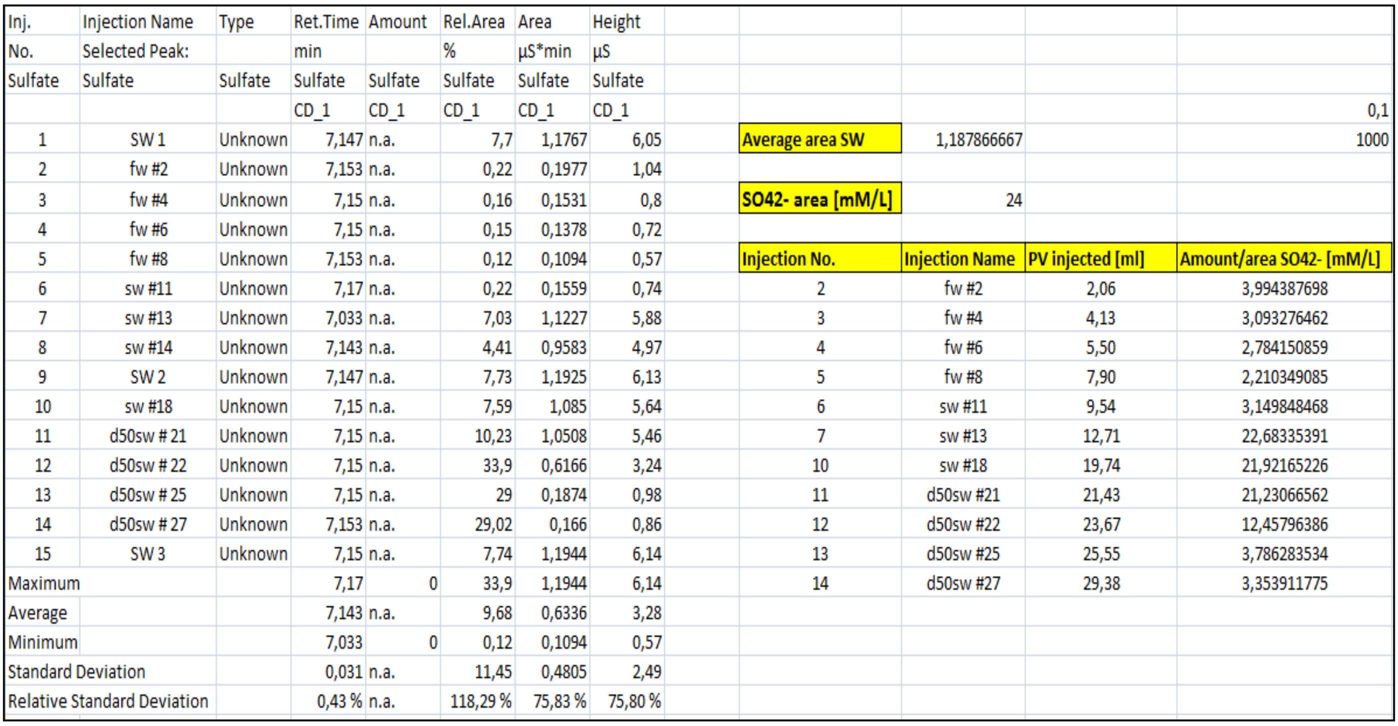
Table A.7: Flooding test data for Yme #23



Sample	Date	Time min	Brine Injected ml	PV injected	Oil amount FW ml	Oil amount SW ml	Oil amount LS SW ml	Total oil amount ml	Recovery %OOIP	Density g/cm^3	TDS [ppm]	pH	Total injected ml	Water ml	WCT %	Description
	7-Mar-12	09:27	0,00	0,00	0,00	-	-	0,00	0,00				0,00	0,00		Start of test (YME FW)
	7-Mar-12	11:39	3,56	0,36	0,00	-	-	0,00	0,00				3,56	3,56	100,00	Oil production started
	7-Mar-12	12:16	4,56	0,46	1,10	-	-	1,10	13,60				1,00	0,00	0,00	
	7-Mar-12	13:43	6,91	0,70	3,40	-	-	3,40	42,02				2,35	0,00	0,00	
	7-Mar-12	14:23	7,99	0,81	4,40	-	-	4,40	54,38				1,08	0,00	0,00	
	7-Mar-12	15:20	9,53	0,97	4,90	-	-	4,90	60,56				1,54	1,04	67,51	
1	7-Mar-12	18:49	15,17	1,55	5,05	-	-	5,05	62,42	1,10915	141 430	5,6	5,64	5,49	97,34	
2	7-Mar-12	21:57	20,25	2,06	5,15	-	-	5,15	63,65	1,13664	174 224	5,95	5,08	4,98	98,03	
3	8-Mar-12	08:05	36,67	3,73	5,20	-	-	5,20	64,27	1,13921	177 244	5,62	16,42	16,37	99,70	
4	8-Mar-12	10:30	40,58	4,13	5,20	-	-	5,20	64,27	1,14086	179 178	5,99	3,92	3,92	100,00	
5	8-Mar-12	14:18	46,74	4,76	0,05	-	-	5,25	64,89	1,13715	174 824	6,03	6,16	6,11	99,19	
6	8-Mar-12	18:47	54,00	5,50	0,00	-	-	5,25	64,89	1,13734	175 047	6,01	7,26	7,26	100,00	
7	8-Mar-12	22:13	59,56	6,07	0,00	-	-	5,25	64,89	1,14072	179 014	6,03	5,56	5,56	100,00	
8	9-Mar-12	09:18	77,52	7,90	0,00	-	-	5,25	64,89	1,14159	180 033	5,95	17,95	17,95	100,00	Start of test (SW)
9	9-Mar-12	13:17	83,97	8,55	-	0,00	-	5,25	64,89	1,13813	175 976	6,05	6,45	6,45	100,00	
10	9-Mar-12	16:24	89,02	9,07	-	0,00	-	5,25	64,89	1,13850	176 410	6,22	5,05	5,05	100,00	
11	9-Mar-12	19:14	93,61	9,54	-	0,00	-	5,25	64,89	1,11231	145 247	6,35	4,59	4,59	100,00	
12	10-Mar-12	10:04	117,64	11,98	-	0,00	-	5,25	64,89	1,03108	43 225	6,79	24,03	24,03	100,00	
13	10-Mar-12	14:30	124,82	12,71	-	0,00	-	5,25	64,89	1,02390	33 832	6,99	7,18	7,18	100,00	
14	10-Mar-12	18:37	131,49	13,39	-	0,00	-	5,25	64,89	1,03264	45 259	6,59	6,67	6,67	100,00	
15	11-Mar-12	09:02	154,84	15,77	-	0,00	-	5,25	64,89	1,02232	31 758	6,74	23,36	23,36	100,00	
16	11-Mar-12	13:57	162,81	16,58	-	0,00	-	5,25	64,89	1,02191	31 220	6,91	7,97	7,97	100,00	
17	11-Mar-12	18:44	170,56	17,37	-	0,00	-	5,25	64,89	1,02190	31 207	6,96	7,75	7,75	100,00	
18	12-Mar-12	09:04	193,78	19,74	-	0,00	-	5,25	64,89	1,02186	31 154	6,66	23,22	23,22	100,00	
	12-Mar-12	09:11	193,97	19,76	-	-	0,00	5,25	64,89				0,19	0,19	100,00	Start of test (50X diluted SW)
19	12-Mar-12	12:52	199,93	20,37	-	-	0,00	5,25	64,89	1,02197	31 299	6,91	5,97	5,97	100,00	
20	12-Mar-12	16:17	205,47	20,93	-	-	0,00	5,25	64,89	1,02189	31 194	6,91	5,53	5,53	100,00	
21	12-Mar-12	19:18	210,36	21,43	-	-	0,00	5,25	64,89	1,01596	23 390	6,99	4,89	4,89	100,00	
22	13-Mar-12	08:54	232,39	23,67	-	-	0,00	5,25	64,89	1,00204	5 006	7,37	22,03	22,03	100,00	
23	13-Mar-12	13:06	239,19	24,37	-	-	0,00	5,25	64,89	0,99954	1 712	7,28	6,80	6,80	100,00	
24	13-Mar-12	16:35	244,84	24,94	-	-	0,00	5,25	64,89	0,99976	2 002	7,19	5,64	5,64	100,00	
25	13-Mar-12	20:16	250,80	25,55	-	-	0,00	5,25	64,89	0,99955	1 726	7,18	5,97	5,97	100,00	
26	14-Mar-12	09:02	271,21	27,63	-	-	0,00	5,25	64,89	0,99948	1 634	7,12	20,41	20,41	100,00	
27	14-Mar-12	14:20	288,39	29,38	-	-	0,00	5,25	64,89	0,99921	1 279	7,19	17,17	17,17	100,00	

A.4 *Chemical analysis test data and results*

Table A.8: Chemical analysis data for Yme #23



Inj.	Injection Name	Type	Ret.Time	Amount	Rel.Area	Area	Height
No.	Selected Peak:		min		%	µS*min	µS
Sulfate	Sulfate	Sulfate	Sulfate	Sulfate	Sulfate	Sulfate	Sulfate
			CD_1	CD_1	CD_1	CD_1	CD_1
1	SW 1	Unknown	7,147	n.a.	7,7	1,1767	6,05
2	fw #2	Unknown	7,153	n.a.	0,22	0,1977	1,04
3	fw #4	Unknown	7,15	n.a.	0,16	0,1531	0,8
4	fw #6	Unknown	7,15	n.a.	0,15	0,1378	0,72
5	fw #8	Unknown	7,153	n.a.	0,12	0,1094	0,57
6	sw #11	Unknown	7,17	n.a.	0,22	0,1559	0,74
7	sw #13	Unknown	7,033	n.a.	7,03	1,1227	5,88
8	sw #14	Unknown	7,143	n.a.	4,41	0,9583	4,97
9	SW 2	Unknown	7,147	n.a.	7,73	1,1925	6,13
10	sw #18	Unknown	7,15	n.a.	7,59	1,085	5,64
11	d50sw # 21	Unknown	7,15	n.a.	10,23	1,0508	5,46
12	d50sw # 22	Unknown	7,15	n.a.	33,9	0,6166	3,24
13	d50sw # 25	Unknown	7,15	n.a.	29	0,1874	0,98
14	d50sw # 27	Unknown	7,153	n.a.	29,02	0,166	0,86
15	SW 3	Unknown	7,15	n.a.	7,74	1,1944	6,14
Maximum			7,17	0	33,9	1,1944	6,14
Average			7,143	n.a.	9,68	0,6336	3,28
Minimum			7,033	0	0,12	0,1094	0,57
Standard Deviation			0,031	n.a.	11,45	0,4805	2,49
Relative Standard Deviation			0,43 %	n.a.	118,29 %	75,83 %	75,80 %

			0,1
Average area SW	1,187866667		1000
SO42- area [mM/L]	24		
Injection No.	**Injection Name**	**PV injected [ml]**	**Amount/area SO42- [mM/L]**
2	fw #2	2,06	3,994387698
3	fw #4	4,13	3,093276462
4	fw #6	5,50	2,784150859
5	fw #8	7,90	2,210349085
6	sw #11	9,54	3,149848468
7	sw #13	12,71	22,68335391
10	sw #18	19,74	21,92165226
11	d50sw #21	21,43	21,23066562
12	d50sw #22	23,67	12,45796386
13	d50sw #25	25,55	3,786283534
14	d50sw #27	29,38	3,353911775