



Faculty of Science and Technology

MASTER'S THESIS

Study program/ Specialization: Petroleum technology/ reservoir engineering	Spring semester, 2013 Open
Writer: Tale Tryggeseid Meling (Writer's signature)
Faculty supervisor: Aksel Hiorth External supervisor(s):	
Title of thesis: Geochemical modeling of low salinity core flooding	
Credits (ECTS): 30	
Key words: Low-salinity, EOR, increased oil recovery, wettability, PHREEQC, surface ion exchange	Pages: 68 + enclosure: 23 Stavanger, 17.06.2013 Date/year

Abstract

Extensive research the last decades has shown that lowering the salinity and ionic composition of injection water can improve the oil recovery. The mechanisms that cause the interaction between low-salinity water and the crude oil/brine/rock system to give favorable reservoir conditions are not clearly understood. This is needed in order to scale up the low salinity water injection and optimize the process on a field scale. Many different mechanisms have been proposed, but none have been accepted among all researchers. This might be because there is not a single mechanism at work, but several.

The purpose of this master thesis is to analyze some of the published experimental results by the use of geochemical models, in order to get a better understanding of what is happening during a low salinity core flood. The textural changes (precipitation and dissolution) and ion exchange processes that happen within the cores during these corefloods have been quantified. Results found in this thesis indicate that low-salinity water will induce significant quartz dissolution that could explain the increased oil recovery in sandstones when injecting low-salinity water. Results also show a correlation between increased oil recovery and multivalent cation exchange in sandstones when diluted seawater is used as the low-salinity brine. No correlation is found between mineral dissolution or multivalent cation exchange and increased oil recovery in carbonates when diluted versions of seawater are used as the low-salinity brine.

Acknowledgments

I would like to express my gratitude towards my supervisor, Aksel Hiorth, for his guidance and advices during the work on this thesis, and for answering all my questions.

I am also thankful to my fellow students at Faculty of Science and Technology for discussions both off and on the subject.

Further I want to thank my family and friends, for all their support and for keeping me motivated and happy during my studies. Finally I would like to thank Eivind for his excellent support during the work on this thesis.

Nomenclature

[x]	Activity of specie x
COBR	Crude oil/brine/rock
w_c	Weight of core
EOR	Enhanced oil recovery
F_w	Formula gram weight
G	Gibbs free energy for a reaction
H	Enthalpy
i	Ion
I	Ionic strength
IAP	Ion activity product
K	Equilibrium constant/Solubility product
kgw	Kilogram water
LSE	Low-salinity effect
LSW	Low-salinity water
m	molal concentration
MIE	Multicomponent ion exchange
NCS	Norwegian continental chelf
OOIP	Original oil in place
OOIC	Original oil in core
R	Gas constant
SI	Saturation index
T	Temperature
wt%	weight percent
z	Charge number
\tilde{a}	Empirical ion size parameter
γ	Individual activity coefficient
θ	Contact angle
Ω	Saturation state

Contents

Abstract.....	II
Acknowledgments	III
Nomenclature	IV
Contents	V
1 Introduction.....	1
2 Review of recovery of oil due to changes in brine composition	5
2.1 Wettability alteration caused by rock dissolution	8
2.2 Wettability alteration caused by changes in adsorbed components.....	9
3 Theory	11
3.1 Wettability	11
3.2 Fluid rock interactions	13
3.2.1 Law of mass action	13
3.2.2 Activity.....	14
3.2.3 Ionic strength.....	14
3.2.4 Calculation of saturation condition	15
3.2.5 Calculation of equilibrium constants.....	16
3.2.6 Calculation of equilibrium constants at different temperatures.....	18
4 Interpretation of coreflood results by the use of PHREEQC.....	19
4.1 Impact of injection-water salinity and ionic content on oil recovery in carbonates	20
4.1.1 Mineralogy	23
4.1.2 Precipitation and dissolution.....	26
4.1.3 Exchanger composition	35
4.2 Impact of injection-water salinity and ionic content on oil recovery in sandstones.....	38
4.2.1 Mineralogy	41
4.2.2 Precipitation and dissolution.....	43
4.2.3 Exchanger composition	49
5 Results and discussion	53
6 Conclusions	59
References.....	60
Appendix A Examples of manual solubility calculations	63
A.1 Calcite in pure water; system not connected to the atmosphere	63
A.2 Calcite in pure water; system connected to the atmosphere	71

Appendix B	Databases in PHREEQC.....	73
Appendix C	Examples of solubility calculations in PHREEQC.....	77
C.1	Calcite in pure water; system not connected to the atmosphere	77
C.2	Calcite in pure water; system connected to the atmosphere	82
Appendix D	PHREEQC input files	84

1 Introduction

Since 1971, when petroleum production started on the Norwegian continental shelf (NCS), a total of 6 billion sm^3 oil equivalents have been produced and sold. This corresponds to 44% of the total resources on the NCS estimated by the Norwegian Petroleum Directorate's (NPD) base. This estimate also includes undiscovered resources, and it increased from 13.1 to 13.6 billion sm^3 oil equivalents in 2012 (Alvedal and Melberg, 2013). Figure 1-1 shows an overview of oil resources in the 25 largest producing fields on the NCS. These resources can be divided into three groups; produced volumes, remaining reserves and resources that will remain in the ground after planned shutdown.

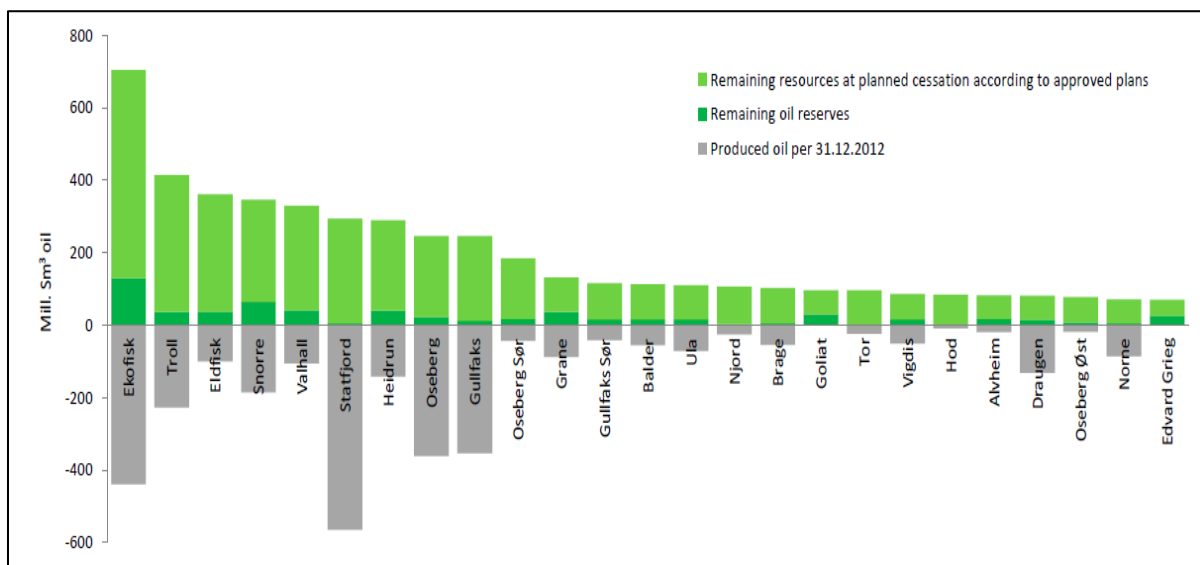


Figure 1-1: Distribution of oil resources in the 25 largest producing fields on the NCS (Alvedal and Melberg, 2013).

Figure 1-1 shows that resources of considerable size will remain in the ground after planned shutdown. The expected average oil recovery factor for producing fields on the NCS today is approximately 46% (Alvedal and Melberg, 2013). This means that more than half of the resources will be left behind. If the recovery factor at the ten largest oilfields on the NCS increases to 70%, the oil produced would correspond to what two new “Ekofisk-fields” would produce (Åm, 2010).

If more resources are to be produced, oil recovery operations must modernize. History has proven that research on new technology can make it possible to produce more resources than expected. In the 1980's, extensive research showed that water injection in chalk was beneficial and it was implemented at Ekofisk. Ekofisk had an expected recovery factor of 17-18% in 1972, which has today grown to 52.5%, mainly caused by the use of water injection ("Norsk olje og gass", 2012).

From an economical perspective, there are enormous values related to these resources. Ola Borten Moe (2013), oil and energy minister in Norway, states that if the recovery factor on the NCS is increased with even just one percent, it will represent an additional value of 360 billion NOK in gross income.

Improvement of the recovery factor on a producing field can be done by using increased oil recovery (IOR) methods. The most common methods on the NCS are increasing the number of wells, water- and/or gas-flooding. The two latter are also known as secondary recovery methods and have historically been looked at as a way to maintain reservoir pressure and physically displace oil towards producers. Water-flooding has been central on the NCS since the 1980's and gas-flooding since the 1970's (Åm, 2010). Compared to oil recovery by pressure depletion alone, water- and gas-flooding have proven to be very successful. However, there are still substantial oil resources left which seems not to be recovered by the use of these methods alone.

Most of the oil left behind in the reservoirs is immobile. To mobilize this oil, reservoirs need to be flooded with more advanced injection fluids that would release more oil, often referred to as enhanced oil recovery (EOR) methods. In addition to reservoir energy supplement, these fluids are meant to interact with the reservoir's crude oil/brine/rock (COBR) system and create favorable reservoir conditions so that the immobile oil is released. EOR methods have not been commonly used on the NCS so far, and there is therefore a great potential of extracting more oil with the use of such methods (Åm, 2010). Examples of EOR methods are injection of water added surfactants or polymers, water-alternating gas (WAG), foam-assisted water-alternating gas (FAWAG), CO₂ gas and low-salinity water.

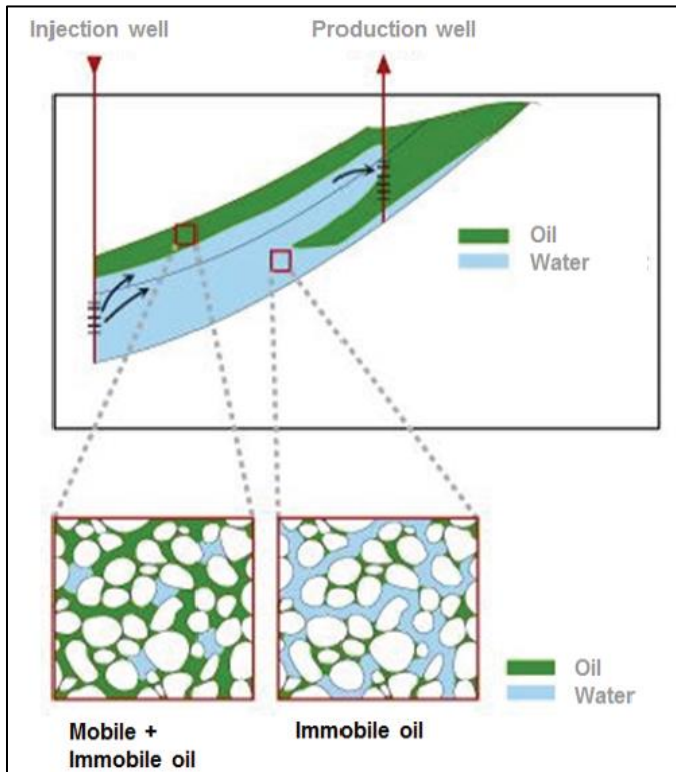


Figure 1-2: Recovery obtained with water-flooding - immobile oil is left behind (Åm, 2010).

Substantial increased oil recovery is obtained by the use of WAG at fields on the NCS, i.e. Statfjord, Snorre and Gullfaks. WAG can give an incremental recovery of 5-10% compared to water-flooding. There are several other fields at the NCS where it can be beneficial to implement WAG. There is also a great potential in FAWAG, where also foam is included. This method was tested at the Snorre field in 1990's with successful results. Water added surfactants as injection fluid has also been field tested at Gullfaks and Oseberg, where increased oil recovery was observed (Åm, 2010).

However, most of the EOR methods have not been field tested on the NCS. It requires large investments that most oil companies have not been willing to risk. According to director in NPD, Bente Nyland (2013), it seems that most oil companies prefer to invest in drilling exploration wells rather than investing in already producing fields. The director of NPD states that one of the most important tasks for them today is to contribute to an increased recovery at existing fields. To do this they have decided to establish a research center for increased recovery. The aim is to develop knowledge and technology so that the recovery factor at the NCS increases. There is also a hope for an increased collaboration between the industry and the research environments so that new solutions can be implemented as quickly as possible.

One of the EOR methods that require more research is injection of low-salinity water (LSW). In both laboratory experiments and field tests performed at fields in other countries, there has been observed an increase in oil recovery when injecting LSW. Research has shown that the interactions between LSW and the COBR system can create favorable wetting conditions so that immobile oil is released. Most experiments and tests so far have been on the effect LSW has on sandstones, but today there are many research groups who study the effect it has on carbonates. Results from these experiences and tests also look promising (Yousef et al., 2012). Laboratory investigation has also shown that a combination of LSW and surfactants or polymers give positive results (Skauge, 2012).

Injection of LSW is not necessarily the most promising EOR method (Åm, 2010), but there are several reasons why many research groups are trying to figure out if it works as an EOR method, and why. Most important, the costs are relatively low, especially at offshore installations. No expensive chemicals need to be added to the water. Water can be taken from the seawater surrounding the platforms, but a desalination unit is required if the seawater is too saline. BP and its partners have decided to invest in a desalination unit for the Claire Ridge Development project (Bjørsvik, 2012). Clair Ridge is sandstone reservoir in the North Sea on the British sector, and BP estimates to collect 42 million additional barrels of oil compared to salty seawater injection. The investment in the desalination unit represent less than 2% of the project costs, but is estimated to generate more than 6% of additional production.

However, the mechanisms that cause the interaction between LSW and COBR to give favorable reservoir conditions is not clearly understood. There are many different mechanisms proposed, but none have been accepted among all researchers. Finding the mechanisms will make it able to know in which type of reservoirs it will be beneficial to inject LSW, and more oil companies might be willing to invest in such a project.

2 Review of recovery of oil due to changes in brine composition

Extensive research the last decades has shown that tuning the salinity and ionic composition of injection water can affect COBR interactions and create favorable reservoir conditions (Yousef et al., 2012). In both laboratory experiments and field tests, there has been observed an increase in oil recovery when injecting LSW. In 1997 Tang and Morrow published results from their laboratory investigation on Berea sandstones where it was found that oil recovery increases with a decrease in salinity of injection water. Since then, many laboratories and organizations have been doing similar investigations on cores from different reservoirs. Webb et al. (2004) published a paper which described a log-inject-log field test designed to identify whether a positive effect caused by LSW could be observed within the near well region of a reservoir. These results were in line with previous laboratory tests from other fields, and it showed a 25-50% reduction in residual oil saturation when flooding with low salinity brine. This was the first field evidence of reduction in residual oil by LSW injection (Morrow and Buckley, 2011). Since then there has been done more field tests, many with promising results. LSW has been tested both as a secondary mode and as a tertiary mode. As a secondary mode when it is injected after primary recovery and as a tertiary mode when it is injected after injection of water with higher salinity. Positive results were observed in both modes (Morrow and Buckley, 2011).

Besides studying the effect LSW has on oil recovery, the most discussed topic between research groups today is what happens in the reservoir rock when low salinity water is injected which causes the increased oil recovery. This is known as the low salinity effect (LSE). There are many different recovery mechanisms proposed, but none of them have been accepted as “the one consistent mechanistic explanation” among all researchers (Morrow and Buckley, 2011). A reason why it is difficult to find the mechanism is probably a result of the use of different rocks and oils in the experiments and the variation in test procedures. Also, the complexity of minerals, crude oils, aqueous-phase compositions and the interactions among all these phases contribute to confusion. The LSE has been observed in a variety of circumstances, which suggest that there is more than one mechanism that causes it (Morrow and Buckley, 2011). In some laboratory and field studies the LSE has not been observed. It is important to find the mechanisms one believes causes the LSE, and find what conditions the mechanisms are linked to. By doing this it will be easier to know for which reservoirs it will be economically beneficial to inject LSW.

The most frequently suggested cause of increased recovery by LSW is wettability alteration of rock surface towards a more water-wet rock surface, both in sandstones and carbonates. The concept of wettability will be explained in chapter 3.1. When the rock surface becomes more water-wet, oil is released from rock surface. The evidence for change in wettability in investigations is often indirect, such as from changes in relative permeability curves or centrifuge capillary pressures. The most direct measure of wettability of rocks is the rate of spontaneous imbibition of the wetting fluid (Morrow and Buckley, 2011). Many research groups believe that this is the dominant mechanism for increased oil recovery. But among these there are different opinions of what exactly causes the rock surface to become more water-wet. Most experiments and tests so far have been concerning the effect LSW have on sandstones, but today there are many research groups who study the effect it has on carbonate reservoirs. Results from these experiences and tests also look promising.

For sandstones it is by many believed that wettability alteration of clay minerals in the rock causes increased oil recovery. There are many mechanisms proposed for causing wettability alteration of clay minerals when low-salinity water is injected. Some of these mechanisms are fines migration (Tang and Morrow, 1999), pH increase leading to interfacial tension reduction (McGuire et al., 2005), cation exchange between the mineral surface and the invading brine (Lager et al., 2008), expansion of electrical double layers (Ligthelm et al., 2009) and local pH variation (Austad et al., 2010). All these mechanisms are linked to the presence of clays. Lager et al. (2008) stated that the mechanism they proposed explained why the LSE does not seem to work on carbonate reservoirs.

Since many researchers have claimed that clay minerals are necessary to observe a LSE, LSW has not been expected to cause increased oil recovery in carbonates because of the lack of clay in most carbonates. However, in 2010 Put et al. published results from a laboratory study where reservoir cores without significant clay content was flooded with LSW, both sandstones and carbonates. Carbonate was also found in the sandstones used. The results showed an increase in oil recovery, and the mechanism could not be linked to clay. Dissolution of anhydrite and release of dolomite crystals and other fine embedded minerals was observed, and it was this mechanism that was proposed to cause the rock surface to become more water wet and therefore an increase in oil recovery.

Hiorth et al. (2010) published a paper where it was investigated how water chemistry affects surface charge and rock dissolution in pure calcium carbonate rock by applying a chemical model. They found that the surface potential changes are not able to explain changes in oil recovery, but that mineral dissolution seems to be the controlling mechanism leading to wettability alteration and increased oil recovery.

Yousef et al. (2011) presented results from a laboratory coreflooding study conducted using carbonate cores which was done to investigate the impact of salinity and ion composition on oil recovery. Their results showed that substantial oil recovery beyond conventional waterflooding can be achieved by lowering the salinity and ionic content of the injection-water. Gupta et al. (2011) presented their results from a combination of carbonate coreflood experiments and simulations which showed that modification of injection water composition can significantly increase oil recovery. The key mechanism for the substantial recovery was proposed to be wettability alteration towards a more water-wet condition of both research groups. Gupta et al. (2011) suggested that rock dissolution and/or surface ion exchange could be the reason for the altered wettability. The idea of surface ion exchange is that ions in the injection-water are adsorbed by the rock and negatively charged oil components are released

As for sandstones, changes in rock wettability in carbonates are believed to cause the increased oil recovery. What interactions that cause these changes are however discussed. As mentioned, rock dissolution and surface ion exchange has been proposed. In 2012 Zahid et al. suggested migration of fines and dissolution of rock material as possible mechanisms. In 2013 Al-Shalabi et al. matched oil recovery and pressure drop data for both first and second coreflooding experiments of Yousef et al.'s (2010) by the use of UTCHEM. They concluded that wettability alteration occurs by rock dissolution and/or surface change.

It has also been proposed that injection of seawater rather than any other type of water in chalk reservoirs will increase the oil recovery (Austad et al., 2008). They propose that surface active components in seawater, like Ca^{2+} , Mg^{2+} and SO_4^{2-} , has the capability to change rock surface charges. The mechanism proposed is a surface-charge alteration which will cause the bond between negative oil components and the rock surface to deteriorate, and oil components will be released.

2.1 Wettability alteration caused by rock dissolution

It has been suggested by Hiorth et al. (2010) that rock dissolution can change the wettability and perhaps even cause pore collapse that could expel oil in reservoir rocks. This can be done if dissolution takes place where the oil is adsorbed; then the oil can be liberated from the rock. If adsorbed oil components are removed from the rock surface, the rock surface will be more water-wet. Hiorth et al. illustrated the dissolution mechanism for a carbonate rock, shown in figure 2-1 and 2-2.

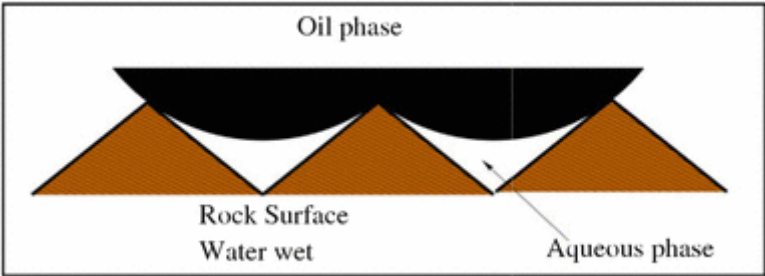


Figure 2-1: Illustration of a section of the pore space, before any dissolution reaction. The surface is rough and oil is attached where there is a large curvature and the water film is broken (Hiorth et al., 2010).

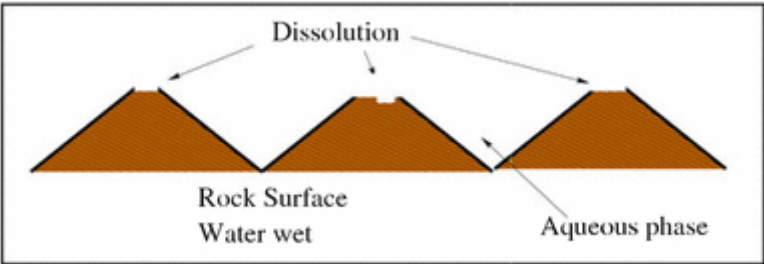


Figure 2-2: Dissolution of the chalk surface has taken place where the oil was attached, and new water-wet rock surface has been created (Hiorth et al., 2010)

2.2 Wettability alteration caused by changes in adsorbed components

The ion exchange theory refers to adsorption of ions from the injection water and desorption of negatively charged oil components on the rock surface.

At the rock surface there are naturally occurring exchange sites. The composition of an exchanger is affected by the ions in the water it is surrounded by. Under steady-state chemical conditions, the composition will be in equilibrium with the resident groundwater. If there is a change in the water composition, the exchanger readjusts its composition in order to reach equilibrium. Ions in the pore water compete for the mineral exchange site, and the natural exchangers display different selectivity for different cations. An exchanger may completely alter the concentrations in the water. I.e. if an exchanger is surrounded by water dominated by Ca^{2+} and HCO_3^- , the cation exchanger is dominated by adsorbed Ca^{2+} . If another type of water with other cations intrudes, there will be an exchange of cations (Appelo and Postma, 2005).

Lager et al. (2008) suggested multicomponent ion exchange (MIE) as the mechanism which causes the wettability alteration in sandstones during LSW flooding. It has been observed during waterfloods, where water less saline than the connate water has been injected, that some cations in the less saline water “stay” in the reservoir. This indicated that the “disappeared” cations had been strongly adsorbed by the rock matrix.

On an oil-wet clay surface, multivalent cations will bond to polar compounds in the oil phase forming organo-metallic complexes. At the same time, some organic polar compounds will be adsorbed directly to the mineral surface, enhancing the oil wetness of the clay surface (Lager et al., 2008). During injection of low salinity brine, an exchange of multivalent cations will take place, removing organic polar compounds and organo-metallic complexes from the surface and replacing them with uncomplexed cations. These should then result in a more water-wet surface, resulting in an increase in oil recovery (Lager et al., 2008)

For carbonates, surface ion exchange is proposed as the mechanism causing increased oil recovery by wettability alteration, when injecting water with specific composition of ions. Austad et al. (2005) suggested a chemical mechanism for the wettability alteration happening when seawater is injected into a carbonate reservoir. Initially, chalk surface is positively charged due to the high concentration of Ca^{2+} in the formation water, while the interface between oil and gas is negatively charged due to the content of carboxylic acid in the crude oil. SO_4^{2-} in the seawater will adsorb on the positively charged chalk surface, which will lead to removal of negatively charged carboxylic material present in oil.

Austad et al., (2007) stated that surface active components in seawater, like Ca^{2+} , Mg^{2+} and SO_4^{2-} will play an important role both regarding wettability modification and rock mechanics. Experiments showed that adsorption of Ca^{2+} onto the chalk surface increased during the adsorption of SO_4^{2-} . The relative affinity of Ca^{2+} and Mg^{2+} towards the chalk surface at different temperatures was studied. At temperatures below 70°C , Ca^{2+} appeared to be more strongly adsorbed to the chalk surface compared to Mg^{2+} . At temperatures over 70°C , Mg^{2+} substituted Ca^{2+} on the chalk surface. A chemical mechanism for the wettability modification was proposed. The mechanism is illustrated in figure 2-3. The adsorption of SO_4^{2-} onto the chalk surface will decrease the positive charge of the surface, which causes excess of Ca^{2+} to be close to the surface. Ca^{2+} will react with the negatively charged carboxylic group, and some carboxylic material is removed from the chalk surface. At high temperatures, Mg^{2+} also becomes active, and in the presence of SO_4^{2-} it is proposed that Mg^{2+} is able to replace Ca^{2+} at the chalk surface and it is also expected that Mg^{2+} can displace the Ca^{2+} bonded to carboxylate groups.

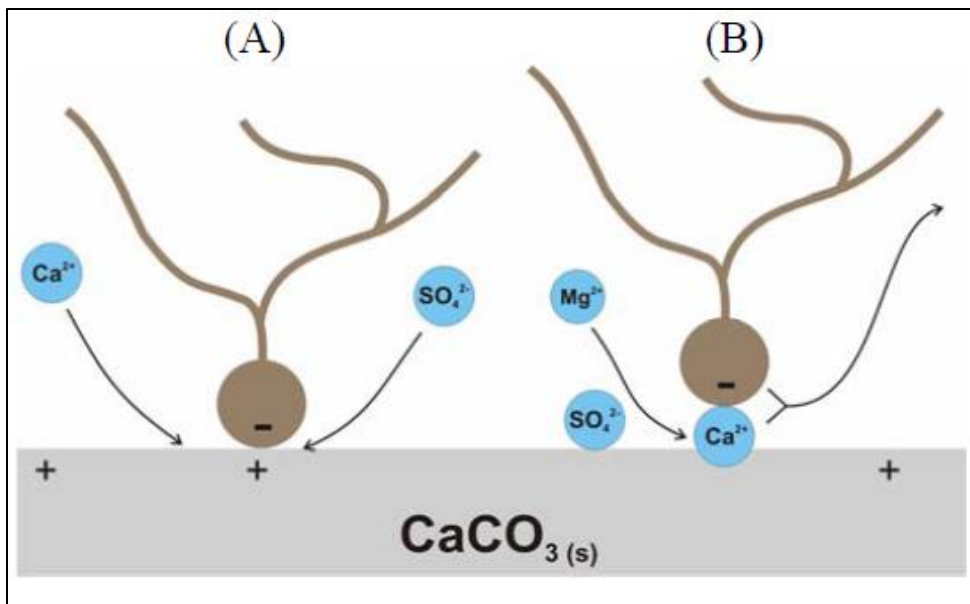


Figure 2-3: A: Proposed mechanism when mainly Ca^{2+} and SO_4^{2-} are active at lower temperatures. B: Proposed mechanism when Mg^{2+} and SO_4^{2-} are active at higher temperatures (Austad et al., 2007).

3 Theory

3.1 Wettability

The most frequently suggested cause of increased recovery by LSW and seawater flooding in chalk is wettability alteration of rock surface towards a more water-wet rock surface. Therefore the concept of wettability within petroleum sciences will be reviewed.

Fluid distributions and the general relative permeability characteristics in a reservoir rock reflect the balance between cohesive and adhesive forces. Molecules of one fluid are attracted to another fluid by an electrostatic force generally referred to as cohesion; the basic property of this is interfacial tension. The molecules of each fluid are to some degree attracted to the molecules of an adjoining solid by an electrostatic force called adhesion. In a reservoir, where there is more than one fluid present, the most adhesive fluid sticks preferentially to the solid's surface. This fluid is called the wetting fluid (Zolotukhin and Ursin, 2000). Wettability of a solid can be defined as the tendency of one fluid to spread on, or adhere to, a solid's surface in the presence of a second immiscible fluid (Forrest and Craig, 1971).

The wettability of a reservoir rock can be estimated quantitatively by measuring the contact angle between the liquid-liquid's, or liquid-gas', interface and the solid's surface. This is called the wetting angle and it reflects the equilibrium between the interfacial tension between the two fluids and their individual adhesive attraction to the solid. The angle is measured on the denser fluids' side of the interface. If the measured angle is smaller than 90° , the denser fluid is the wetting phase. If oil is this denser fluid, the rock is classified as oil-wet. If the angle is larger than the 90° , the less dense fluid is considered to be the wetting phase (Zolotukhin and Ursin, 2000). If water is this less dense fluid, the rock is classified as water-wet. The wettability of rocks' pore walls by fluids depend upon the chemical composition of the fluids and the mineral composition of the rock.

Most reservoirs are neither strongly water nor oil-wet, but fall in between the two extremes. In an oil-water system the porous media can be classified according to the oil-water contact angle:

Table 3-1: Wettability classification based on contact angle (Anderson, 1986)

0°	<	θ_{ow}	<	75°	water-wet
75°	<	θ_{ow}	<	105°	intermediate-wet
105°	<	θ_{ow}	<	180°	oil-wet

If the $\theta_{ow} = 90^\circ$, the rock is defined as neutral-wet. When a rock is neutral-wet it has no clear preference for either oil or water.

Laboratory experiments have proved that rock wettability affects oil displacement, hence the residual oil saturations (Zolotukhin and Ursin, 2000). An example of the effect on saturations is shown in figure 3-1, which shows residual oil saturations in a strongly water-wet and strongly oil-wet rock. As the figure shows, if a rock is water-wet, there will be less residual oil than if the rock is oil-wet. If it is oil-wet the oil prefers to stick to the rock and it flows less easy compared to water.

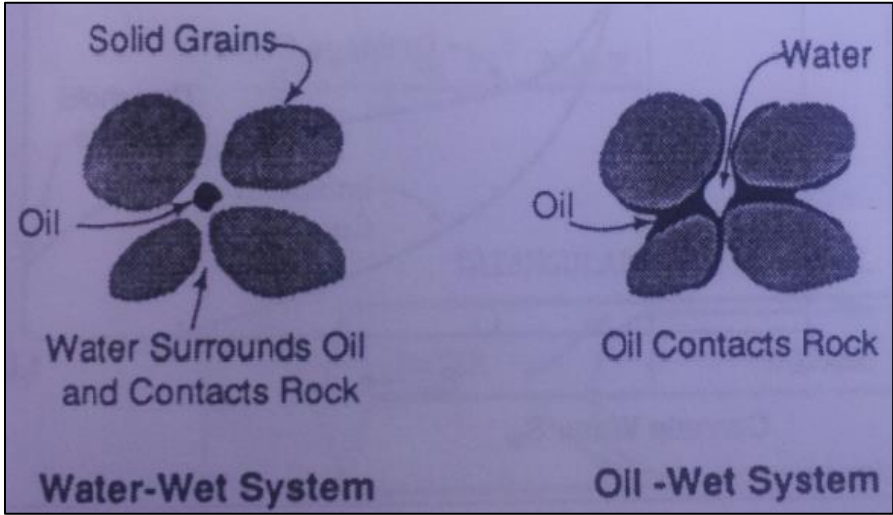


Figure 3-1: Residual oil saturations in a water-wet system and in and oil-wet system (Green and Willhite, 1998)

A wettability alteration towards a more water-wet system will give a lower residual saturation, hence increased oil recovery.

3.2 Fluid rock interactions

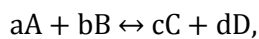
When water is injected into a reservoir, it will tend to equilibrate with the reservoir rock minerals, and minerals might dissolve or precipitate. These reactions might impact the wetting condition of the reservoir rock, and could potentially explain the LSW effect. Therefore there will be a review of the basic in this section.

All minerals, except for native elements, oxides and hydroxides, are salts. So when performing solubility calculations it is the solubility of salts that is being calculated. A salt may remain in solution or precipitate as a solid depending on its solubility. The solubility of a substance in water is the concentration of the substance in the water that is in equilibrium with the substance at the pressure and temperature of interest (Misra, 2012).

Water is an effective solvent because of its high dielectric constant. The dielectric constant of a solvent is a measure of its capacity of its molecules to prevent recombination of the charged solute particles. The high dielectric constant arises from the dipolar nature of the water molecules which causes the solute ions to be hydrated, thus reducing the probability of the solute ions to recombine. Since the dissolved ionic species are charged particles, the aqueous solutions are electrolyte solutions (Misra, 2012).

3.2.1 Law of mass action

Equilibrium will often be attained when a mineral is in contact with water, and the reactions can be written as follows:



where the capital letters is chemical symbols which express the chemical species involved in the reaction, and the non-capital letters is numbers which express the numeric relationship between the chemical species.

The distribution of the species at equilibrium is given by:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}. \quad (3.1)$$

These equations are based on the law of mass action. K is the equilibrium constant and the bracketed quantities “[]” denote activities. The law of mass action is applicable to any type of reaction and it is fundamental in solubility calculations. These equations should be written for all the reactions that will occur in the system that is being studied. Activities of pure solids and H_2O in dilute solutions are always considered to be one (Appelo and Postma, 2005).

3.2.2 Activity

Activity may be defined as the effective concentration. Electrolyte solutions are in general nonideal, and the activity of dissolved aqueous specie is not equal to its concentration in the solution, but it is a function of both concentration and the individual activity coefficient. In thermodynamics the activity is expressed as a fraction to a standard state. Molal concentration is written in terms of molality (mol/kgw), and the consistency between activity and molal concentration for aqueous solutes is as follows:

$$[i] = \frac{\gamma_i m_i}{m_i^0} = \gamma_i m_i, \quad (3.2)$$

where $[i]$ is the activity of the ion i , γ_i is the dimensionless individual activity coefficient, m_i is the concentration expressed in molality and m_i^0 is the standard state which causes the activity to be dimensionless. As γ_i approaches 1, the solution approaches ideal behavior. For a very dilute solution $\gamma_i = 1$ and $[i] = 1$.

3.2.3 Ionic strength

The electrostatic forces between the charged solute species in an aqueous electrolyte solution depend on the charges of the species and the total concentration of the species. Both these factors are included in the ionic strength of an aqueous solution. Ionic strength is a relation useful in comparing solutions of different compositions because the electrical effects of the interactions of the various charged ions present are taken into consideration. Because of these interactions, activity coefficients of aqueous ions cannot be estimated indirectly. Ionic strength was a concept introduced by G. N Lewis and M. Randall in 1921 for calculation of activity coefficients, and it is calculated by the formula

$$I = \frac{1}{2} \sum \frac{m_i}{m_i^0} z_i^2 = \frac{1}{2} \sum m_i z_i^2, \quad (3.3)$$

where m_i is the concentration expressed in molality, z_i is the charge number of ion i and m_i^0 is the standard state which causes also the ionic strength to be dimensionless. The ionic strength does not include any contribution from neutral molecules (Misra, 2012).

For dilute electrolyte solutions with ionic strengths lower than 0.1, the Debye-Hückel equation is used to calculate the individual activity coefficient for solutes:

$$-\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + \hat{a}_i B \sqrt{I}}, \quad (3.4)$$

where A and B are temperature and pressure dependent constants, \hat{a}_i is the empirical ion-size parameter of the ion i , z_i is the charge number of ion i , and I is the ionic strength.

3.2.4 Calculation of saturation condition

Sometimes the state of saturation is unknown in the systems of water and minerals studied. If the activities of the ions in the system are known the IAP, the ion activity product, can be calculated. IAP is the analogue product of activities to the solubility product K (Appelo and Postma, 2005). I.e., when gypsum is put in water, one can calculate the state of saturation: The activities at equilibrium give the solubility product:

$$K = [\text{Ca}^{2+}][\text{SO}_4^{2-}].$$

The activities of the ions in the system where the state of saturation is unknown, give the ion activity product:

$$\text{IAP} = [\text{Ca}^{2+}][\text{SO}_4^{2-}].$$

The saturation condition may be expressed as the ratio between IAP and K, the saturation state Ω :

$$\Omega = \frac{\text{IAP}}{K}. \quad (3.5)$$

When $\Omega = 1$ the system is in equilibrium, $\Omega > 1$ indicates supersaturation and $\Omega < 1$ subsaturation. Supersaturation suggests that there are more ions in the solution than what it would have been at equilibrium, and precipitation of the mineral is expected. Subsaturation suggests that there are fewer ions in the solution than what it would have been at equilibrium, and dissolution of the mineral is expected (Appelo and Postma, 2005).

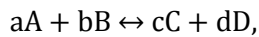
For large deviations from equilibrium, a logarithmic scale can be useful. This is given by the saturation index SI:

$$\text{SI} = \log(\Omega). \quad (3.6)$$

When $\text{SI} = 0$ the system is in equilibrium, $\text{SI} < 0$ suggests subsaturation and $\text{SI} > 0$ supersaturation.

3.2.5 Calculation of equilibrium constants

For the general equation:



one may write

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}, \quad (3.7)$$

where ΔG_r is the change in Gibbs free energy (kJ/mol) of the reaction, ΔG_r^0 is the standard Gibbs free energy of the reaction and equal to ΔG_r when each product or reactant is present at unit activity at a specified standard state, R is the gas constant and T is the absolute temperature. The prefix Δ is used because energy can be measured only as relative amounts (Appelo and Postma). The direction which the reaction will proceed is indicated by ΔG_r :

$\Delta G_r > 0$ the reaction proceed to the left (precipitation);

$\Delta G_r = 0$ the reaction is at equilibrium;

$\Delta G_r < 0$ the reaction proceed to the right (dissolution).

In the case of equilibrium the equation reduces to:

$$\Delta G_r^0 = -RT \ln K \quad (3.8)$$

This equation allows calculation of the equilibrium constant for any reaction from tabulated data of ΔG_f^0 for dissolved substances, minerals, and gases. ΔG_f^0 is the free energy of formation, and is tabulated for different species in thermodynamic tables (Appelo and Postma, 2005). Tabulations are normally given for 25°C and 1 atm pressure. ΔG_r^0 is calculated from:

$$\Delta G_r^0 = \sum \Delta G_f^0_{\text{product}} - \sum \Delta G_f^0_{\text{reactant}} \quad (3.9)$$

If one were to calculate the solubility product for calcite at 25°C (298.15 K), this can be done by the use of Gibbs free energies at 25°C. The values are given by Appelo and Postma:

$$\Delta G_f^0_{\text{CaCO}_3} = -1128.8 \text{ kJ/mol}$$

$$\Delta G_f^0_{\text{Ca}^{2+}} = -553.6 \text{ kJ/mol}$$

$$\Delta G_f^0_{\text{CO}_3^{2-}} = -527.8 \text{ kJ/mol}$$

For the reaction, $\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$, we may write:

$$\Delta G_r^0 = \Delta G_f^0_{\text{Ca}^{2+}} + \Delta G_f^0_{\text{CO}_3^{2-}} - \Delta G_f^0_{\text{CaCO}_3} = 47.4 \text{ kJ/mol}$$

$$\Delta G_r^0 = -RT \ln K = -8.314 \times 10^{-3} \times 298.15 \times 2.303 \log K = -5.708 \log K$$

$$\log K = \frac{47.4}{-5.708} = -8.30.$$

3.2.6 Calculation of equilibrium constants at different temperatures

Groundwater is generally not found at the standard conditions of 25°C and 1 atm pressure. The temperature variation has great effect on the value of the mass action constant. Variation of mass action constants with temperature are usually calculated with the Van't Hoff equation:

$$\frac{d \ln K}{d T} = \frac{\Delta H_r}{RT^2}, \quad (3.10)$$

where ΔH_r is the heat lost or gained by the chemical system; the change in enthalpy. For exothermal reactions, ΔH_r is negative and heat is gained. For endothermal reactions, ΔH_r is positive and heat is lost. ΔH_f^0 is listed for different species in thermodynamic tables, and ΔH_r^0 is calculated from:

$$\Delta H_r^0 = \sum \Delta H_f^0_{\text{product}} - \sum \Delta H_f^0_{\text{reactants}} \quad (3.11)$$

Usually, ΔH_r^0 is constant within the range of a few tenths of degrees and there we can integrate Van't Hoff equation:

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H_r^0}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (3.12)$$

Using this equation makes it possible to calculate the equilibrium constant at other temperatures than 25°C (Appelo and Postma)

If one were to calculate the solubility product of calcite at 10°C, this can be done by the use of formation enthalpies. The values are given by Appelo and Postma:

$$\Delta H_f^0_{\text{CaCO}_3} = -1206.9 \text{ kJ/mol}$$

$$\Delta H_f^0_{\text{Ca}^{2+}} = -542.8 \text{ kJ/mol}$$

$$\Delta H_f^0_{\text{CO}_3^{2-}} = -677.1 \text{ kJ/mol}$$

For the reaction, $\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$, we may write:

$$\Delta H_r^0 = -542.8 \text{ kJ/mol} + (-677.1 \text{ kJ/mol}) - (-1206.9 \text{ kJ/mol}) = -13.0 \text{ kJ/mol}$$

Since the value is negative, this means that the reaction is exothermal; the system heats up when calcite dissolves. Equation 2.12 is used to find the solubility product of calcite at 10°C, remembering that $\log K$ of calcite at 25°C is -8.30.

$$\begin{aligned} \log K_{10} &= \frac{\Delta H_r^0}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \log K_{25} = \frac{-(-13.0)}{2.303 \times 8.314 \times 10^{-3}} \left(\frac{1}{298.15} - \frac{1}{283.15} \right) + (-8.30) \\ &= -8.18. \end{aligned}$$

4 Interpretation of coreflood results by the use of PHREEQC

There has been done a lot of research on low-salinity water as an injection fluid. The purpose of this study is to go through some of the investigations, explain what has been done and then use PHREEQC to interpret some of the core floods. The purpose is to quantify the textural changes (precipitation and dissolution) and the exchanger composition changes that happen within the core during these corefloods, and investigate if there are any correlations with oil recovery. For the interested reader, we have in Appendix A performed analytical geochemical calculations for a brine in equilibrium with calcite and CO₂ in the atmosphere. In Appendix C, we explain how to use PHREEQC, and demonstrate that we can get similar results with PHREEQC as for the examples discussed in Appendix A.

4.1 Impact of injection-water salinity and ionic content on oil recovery in carbonates

Saudi-Aramco has initiated a research program called “SmartWater Flood”, where the goal is to investigate the potential of increasing oil recovery by tuning the injection-water properties.

Yousef et al. (2011) performed an investigation on the impact of salinity and ionic content of injection-water on oil recovery from carbonate reservoirs. They investigated the potential for increased oil recovery and possible reasons for why the oil recovery increases when altering the salinity and ionic content of injection-water.

To do this they performed a coreflooding study, a recovery mechanism study and also used a laboratory NMR instrument to study the impact of injection-water chemistry on carbonate rock samples. Core plugs were cut out from cores chosen from a carbonate reservoir and live oil recombined from an oil/gas separator was used in this study. Different brines were prepared from distilled water and reagent grade chemicals so that they had the same composition as field water. Composition of field connate water and seawater was found through geochemical analysis of field water. Several diluted versions of seawater were also prepared. The effect of salinity and ion composition on density and viscosity of brines was measured at reservoir temperature.

To investigate the potential of increased oil recovery they performed two coreflooding studies, where the salinity and ionic composition of the injection-water was altered during the floods. The objective of the second coreflood was to validate the result in the first coreflood.

The results found were that by injecting water with lower salinity and ionic content after injecting seawater, give an additional oil recovery of 18-19%. When injecting twice and 10 times diluted seawater the biggest percentage of additional oil recovery was observed.

To mobilize residual oil during a waterflood, a reduction in capillary forces is required. Capillary force is a function of fluid/fluid and fluid/rock interactions. To measure these interactions, IFT between oil and different salinity slugs and contact angle between the rock and different salinity slugs was measured in the recovery mechanism study. The results found were that injection of different diluted slugs has an insignificant impact on the fluid/fluid interactions, but a significant impact on the rock wettability. This suggests that injection of different salinity slugs changes rock wettability towards a water-wet state, and thus a higher oil recovery.

To investigate the impact of injection-water chemistry on the rock samples, a NMR instrument measured the rock sample before and after the coreflood. The conclusion of these measurements was that the salinity and ionic composition has a significant impact on the carbonate rock surface relaxation and connectivity among different pore systems. The five different salinity slugs of seawater were injected one after another, starting with regular seawater and ending with 100-times-diluted seawater. There were two core flooding experiments, four core plugs were flooded in the first experiment and six core plugs in the second experiment. A summary of the coreflooding experiments are given in table 4-1 and 4-2 and shown in figure 4-1 and 4-2. The additional oil recovery was 7 to 8.5% with twice diluted seawater, 9 to 10% with 10 times diluted seawater, 1 to 1.6% with 20 times diluted seawater, all in terms of OOIC (original oil in core). No additional oil recovery was observed with 100 times diluted seawater.

Table 4-1: Summary of the first coreflood experiment (Yousef et al., 2011)

Slug Type	Phase Type	Oil Recovery (% OOIC)	Residual Oil Saturation, Sor (% PV)
Regular Seawater	Secondary	67.04	29.5
Twice Diluted	Tertiary	6.99	23.3
10 Times Diluted	Tertiary	9.12	15.1
20 Times Diluted	Tertiary	1.63	13.5
100 Times Diluted	Tertiary	0.00	13.5
Final		84.97	13.46
The Slug of Regular Seawater	Secondary	67.00	29.5
Different-Salinity Slugs of Seawater	Tertiary	17.94	13.5

*PV = 36.82 cm³, OOIC = 32.82 cm³, Average Swi = 10.44%

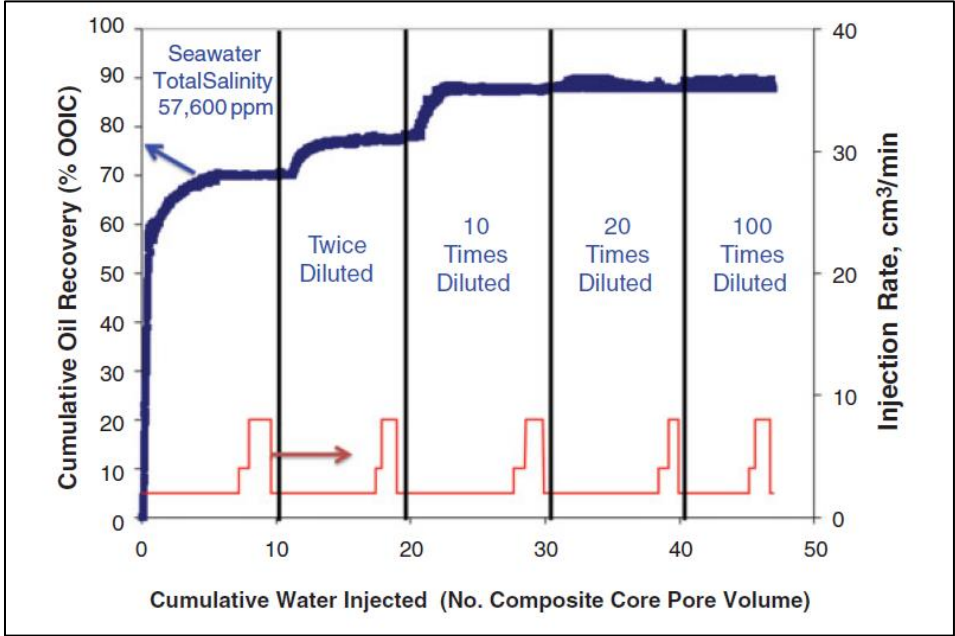


Figure 4-1: Oil recovery curve of the first coreflood experiment. The blue curve represents the amount of oil produced in terms of OOIC through all injected salinity slugs of seawater. The red curve represents the injection-rate profile implemented during the coreflood experiment (Yousef et al., 2011).

Table 4-2: Summary of the second coreflood experiment (Yousef et al., 2011)

Slug Type	Phase Type	Oil Recovery (% OOIC)	Residual Oil Saturation, Sor (% PV)
Regular Seawater	Secondary	74.12	22.1
Twice Diluted	Tertiary	8.48	14.9
10 Times Diluted	Tertiary	9.95	6.4
20 Times Diluted	Tertiary	0.95	5.4
100 Times Diluted	Tertiary	0.00	5.4
Final		93.65	5.43
The Slug of Regular Seawater	Secondary	74.12	22.1
Different-Salinity Slugs of Seawater	Tertiary	19.53	5.4

*PV = 63.42 cm³, OOIC = 54.28 cm³, Average Swi = 14.4%

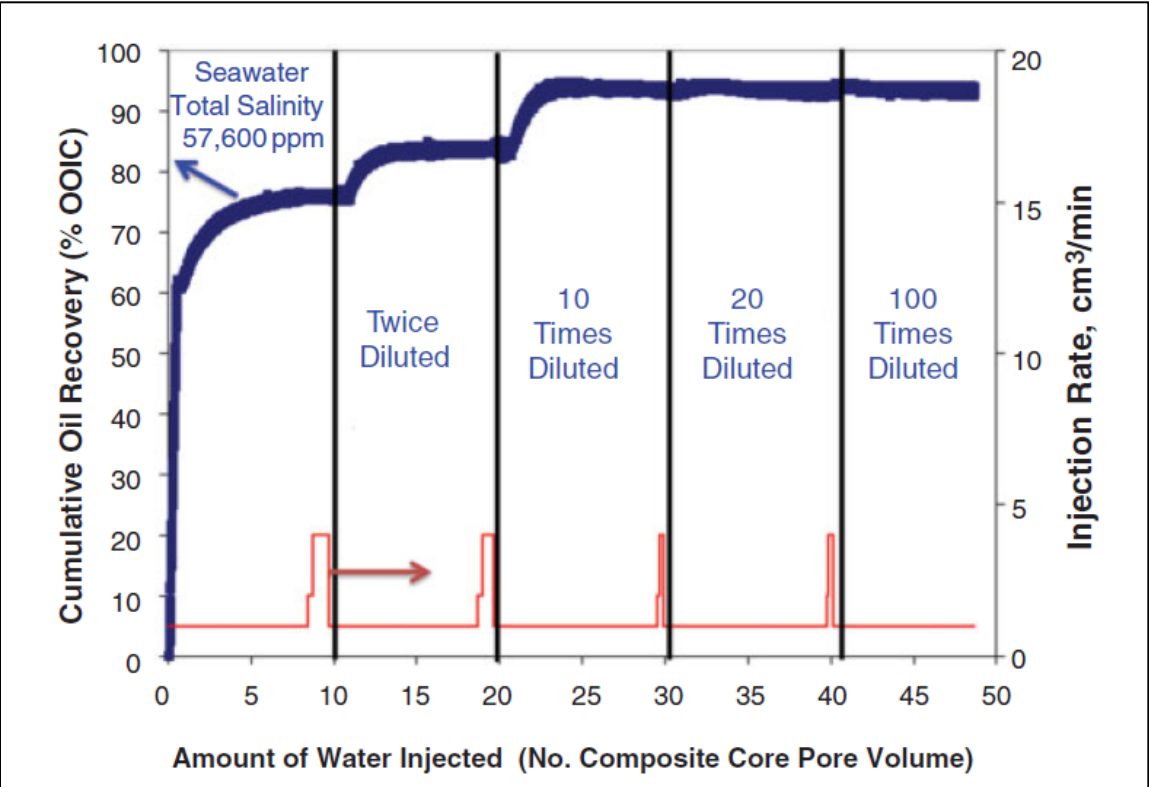


Figure 4-2: Oil recovery curve of the second coreflood experiment. The blue curve represents the amount of oil produced in terms of OOIC through all injected slugs of seawater, and the red curve represents the injection-rate profile implemented during the coreflood experiment. (Yousef et al., 2011)

4.1.1 Mineralogy

Which minerals that are present in the rock need to be known before one can find if there has been any dissolution or precipitation of minerals. One of the rock samples from the targeted carbonate reservoir was crushed to determine the main rock components. X-ray diffraction (XRD) technique was used to identify the chemical composition of the crushed materials. The components identified were calcite (80%), dolomite (13%), anhydrite (6%) and quartz (less than 1%) (Yousef et al., 2011)

The chemical composition of the field connate water is also given. The brine was prepared from distilled water and reagent grade chemicals on the basis of geochemical analysis of field water samples. This chemical composition of the field connate water can give an idea whether the chemical composition of the rock given, is correct. The field connate water has been in contact with the rock for such a long time that one can assume that the water is equilibrated with all minerals present in the rock.

The chemical concentrations for the field connate water used in this investigation (Yousef et al., 2011) are listed in table 4-3.

Table 4-3: Conversion of concentrations of field connate water from ppm to mol/kgw

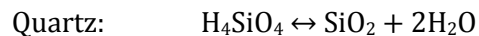
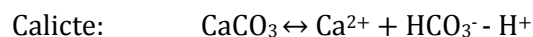
Ions	Concentration (ppm)	Gram formula weight (g/mol)	Concentration (mol/kgw)
Na ⁺	59491	22.99	2.588
Ca ²⁺	19040	40.08	0.475
Mg ²⁺	2439	24.31	0.1003
SO ₄ ²⁻	350	96.07	0.00364
Cl ⁻	132060	35.45	3.725
CO ₃ ²⁻	0	60.01	0
HCO ₃ ⁻	354	61.02	0.005801

Conversion from parts per million to molality is done with the relation:

$$\text{molality} = \frac{\text{ppm}}{\text{gram formula weight}} \times 10^{-3} \quad (4.1)$$

According to the components identified by Yousef et al. one can assume that when the connate water is in contact with the formation, the water will be in equilibrium with calcite, dolomite, anhydrite and quartz. The composition of the field connate water also suggest this since Ca²⁺ is a component in calcite, dolomite and anhydrite, Mg²⁺ is a component in dolomite, and SO₄²⁻ is a component in anhydrite. Since there is some quartz present, one should also assume that the field connate water contains some Si⁴⁺. Why this has not been included is unknown.

These relations yield at equilibrium:



The density of the connate water was measured to be 1.1083 g/cm³ at reservoir temperature of 212°F (100°C). In PHREEQC one can put the given concentrations of sodium, chloride and bicarbonate, while calcium, magnesium, sulfate and silicon is forced in equilibrium with respectively calcite, dolomite, anhydrite and quartz. PHREEQC will then calculate the ionic composition of the water, shown in table 4-4. If that composition is similar to the one given by Yousef et al. we have found the right mineralogy, since it is expected that field connate water is in equilibrium with the minerals it has been surrounded of.

Table 4-4: Ionic composition given by PHREEQC and Yousef et al., and the ratio between.

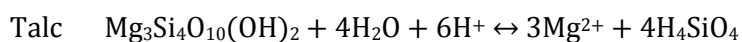
Ions	Ionic composition given by PHREEQC (mol/kgw)	Ionic composition used by Yousef et al. (mol/kgw)	Ratio
Na ⁺	2.588	2.588	1
Ca ²⁺	0.3440	0.475	0.72
Mg ²⁺	0.2300	0.1003	2.29
SO ₄ ²⁻	0.00327	0.00364	0.9
Cl ⁻	3.725	3.725	1
CO ₃ ²⁻	0	0	
Si ⁴⁺	0.0002542	0	
HCO ₃ ⁻	0.005801	0.005801	1

There are differences between the concentrations predicted of PHREEQC compared to what was given in the geochemical analysis used by Yousef et al. The biggest difference is in magnesium. The saturation indices of the field connate water may also indicate something about the chemical composition of the rock. When the saturation index to a mineral is larger than zero, precipitation of the mineral is expected.

Saturation indices	
Phase	SI
Anhydrite	0.00
Aragonite	-0.10
Calcite	0.00
Chalcedony	-0.20
Chrysotile	-2.27
CO2(g)	-0.21
Dolomite	-0.00
Gypsum	-0.58
H2(g)	-18.21
H2O(g)	-0.01
H2S(g)	-55.32
Halite	-1.03
O2(g)	-26.39
Quartz	0.00
Sepiolite	-4.44
Sepiolite(d)	-8.91
SiO2(a)	-0.84
Sulfur	-42.06
Talc	1.81

Figure 4-3: Saturation indices given by PHREEQC when the field connate water is equilibrated with calcite, dolomite, anhydrite and quartz.

As observed in figure 4-3, precipitation of talc ($Mg_3Si_4O_{10}(OH)_2$) is expected. Therefore it should be assumed that there is talc in the rock. At equilibrium this relation yields:



If the problem is run one more time in PHREEQC, and magnesium is forced in equilibrium with talc instead of dolomite, a chemical composition of water more alike the one given in the paper is found, shown in table 4-5.

Table 4-5: Second ionic composition given by PHREEQC, ionic composition used by Yousef et al., and the ratio between.

Ions	Ionic composition given by PHREEQC (mol/kgw)	Ionic composition used by Yousef et al. (mol/kgw)	Ratio
Na ⁺	2.588	2.588	1
Ca ²⁺	0.4878	0.475	1.03
Mg ²⁺	0.08417	0.1003	0.8391
SO ₄ ²⁻	0.001829	0.00364	0.5
Cl ⁻	3.725	3.725	1
CO ₃ ²⁻	0	0	
Si ⁴⁺	0.0002542	0	
HCO ₃ ⁻	0.005801	0.005801	1

The concentration of sulfate is more unlike than the first run, but the concentrations of calcite and magnesium is much more alike. There are no saturation indices larger than zero in this run. Therefore it will from now on be assumed that the minerals present in this rock are calcite, talc, anhydrite and quartz.

4.1.2 Precipitation and dissolution

When flooding a reservoir with injection water, the reactions between the minerals and injection water will move towards equilibrium. In this case, the major minerals present are assumed to be calcite, talc, anhydrite and quartz. Through the use of PHREEQC one can force the injection water in equilibrium with these minerals to observe what happens with the concentration of the ions in the water. These changes will tell if there has been any dissolution or precipitation of minerals.

The composition of the injection waters tested in this study is given in table 4-6 (Yousef et al, 2011).

Table 4-6: Ionic composition of seawater and diluted versions given in ppm.

Ions	Seawater (ppm)	Twice diluted seawater (ppm)	10 times diluted seawater (ppm)	20 times diluted seawater (ppm)	100 times diluted seawater (ppm)
Na ⁺	18300	9150	1830	915	183
Ca ²⁺	650	325	65	32.5	6.5
Mg ²⁺	2110	1055	211	105.5	21.1
SO ₄ ²⁻	4290	2145	429	214.5	42.9
Cl ⁻	32200	16100	3220	1610	322
CO ₃ ²⁻	0	0	0	0	0
HCO ₃ ⁻	120	60	12	6	1.2

Table 4-7: Ionic composition of seawater and diluted versions converted to mmol/kgw

Ions	Gram formula weight (g/mol)	Seawater (mmol/kgw)	Twice diluted seawater (mmol/kgw)	10 times diluted seawater (mmol/kgw)	20 times diluted seawater (mmol/kgw)	100 times diluted seawater (mmol/kgw)
Na ⁺	22.99	796	398	79.6	39.8	7.96
Ca ²⁺	40.08	16.2	8.1	1.62	0.81	0.162
Mg ²⁺	24.31	86.8	43.4	8.68	4.34	0.868
SO ₄ ²⁻	96.07	44.65	22.3	4.465	2.23	0.4465
Cl ⁻	35.45	908.3	454.2	90.83	45.42	9.083
CO ₃ ²⁻	60.01	0	0	0	0	0
HCO ₃ ⁻	61.02	1.97	0.98	0.197	0.098	0.0197

Densities of the different injection waters were measured at reservoir temperature and were given in the paper (Yousef et al., 2011):

Table 4-8: Densities of seawater and diluted versions

	Seawater	Twice diluted seawater	10 times diluted seawater	20 times diluted seawater	100 times diluted seawater
Density (g/cm ³)	1.0152	0.9959	0.9812	0.9782	0.9779

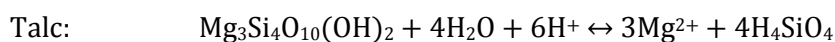
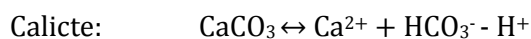
The different versions of seawater will now, through the use of PHREEQC, be forced in equilibrium with calcite, talc, anhydrite and quartz. The amount of the different minerals is unknown. As long as the amount given in PHREEQC is big enough, it will be able to quantify the textural changes that happen within the core. In this case 100 moles of each mineral was used. If 1000 moles was used instead of 100 moles, the difference of ions in the water would be exactly the same.

After equilibrating seawater with the minerals, changes in the seawater are observed, shown in table 4-9.

Table 4-9: Changes in ionic composition of seawater when equilibrated with minerals.

Ions	Seawater (mol/kgw)	Seawater equilibrated with minerals in PHREEQC (mol/kgw)	Difference (mol/kgw)
Na ⁺	0.796	0.7963	0.0003
Ca ²⁺	0.0162	0.03228	0.01608
Mg ²⁺	0.0868	0.05018	-0.03662
SO ₄ ²⁻	0.04465	0.01978	-0.02487
Cl ⁻	0.9083	0.9086	0.0003
CO ₃ ²⁻	0	0	0
HCO ₃ ⁻	0.00197	0.04293	0.04096
Si ⁴⁺	0	0.0006518	0.0006518

Through the use of equilibrium equations one can find the difference in minerals based on the difference in concentration of the ions in the water.



Changes in concentration of Ca^{2+} effect both calcite and anhydrite, changes in Si^{4+} effect both quartz and talc, changes in SO_4^{2-} effect anhydrite and changes in Mg^{2+} affect talc. The equations below can give the differences in different minerals based on the differences of the different ions:

$$\begin{aligned} \Delta\text{Calcite} &= -\Delta\text{Ca}^{2+} - \Delta\text{Anhydrite} = -0.01608 - 0.02487 &= -0.04095 \text{ mol/kgw} \\ \Delta\text{Anhydrite} &= -\Delta\text{SO}_4^{2-} &= 0.02487 \text{ mol/kgw} \\ \Delta\text{Quartz} &= -\Delta\text{Si}^{4+} - 4*\Delta\text{Talc} = -0.0006518 - (4*0.01219) &= -0.04949 \text{ mol/kgw} \\ \Delta\text{Talc} &= -\Delta\text{Mg}^{2+}/3 &= 0.01221 \text{ mol/kgw} \end{aligned}$$

PHREEQC also give the difference in moles of minerals, given in table 4-10.

Table 4-10: Differences in minerals when seawater is equilibrated with the minerals

Mineral	Difference (mol/kgw)
Calcite	-0.04095
Anhydrite	0.02488
Quartz	-0.0495
Talc	0.01221

As observed, the difference found theoretically is the same as the one PHREEQC finds. From now on the differences in mineral will be read in PHREEQC. It will be assumed that the weight of the core, w_c , is 1 kg, and the amount of water is also 1 kg. To find the difference in weight percent the following equation is used:

$$\Delta\text{wt}\% = \frac{\Delta\text{mineral} \times F_w}{w_c} \times 100\% , \quad (4.2)$$

where $\Delta\text{wt}\%$ is the difference expressed in weight percent, $\Delta\text{mineral}$ is the difference observed in mol/kgw, F_w is the minerals formula gram weight expressed in gram/mol and w_c is weight of core expressed in gram. The difference in weight percent for minerals when equilibrated with seawater is shown in table 4-11.

Table 4-11: Difference in minerals converted from mol/kgw to wt%

Mineral	$\Delta\text{Mineral}$ (mol/kgw)	F_w (g/mol)	Difference (g/kgw)	$\Delta\text{wt}\%$
Calcite	-0.04095	100.085	-4.098	-0.4098
Anhydrite	0.02488	136.136	3.3870	0.3387
Quartz	-0.0495	96.11	-4.75	-0.475
Talc	0.01221	379.272	4.6309	0.463

This can be understood as when 1 kg of seawater is flooded through a 1 kg core, there will be dissolution of calcite and quartz, and precipitation of anhydrite and talc. This procedure will now be done for all the diluted versions of seawater.

Table 4-12: Mineral differences presented in wt% for all versions of seawater when equilibrated with the minerals

	Seawater Δ wt%	Twice diluted Δ wt%	10 times diluted Δ wt%	20 times diluted Δ wt%	100 times diluted Δ wt%
Calcite	-0.4098	-0.245	-0.071	-0.04134	-0.0112
Anhydrite	0.3387	0.103	-0.0513	-0.06495	-0.07292
Quartz	-0.475	-0.283	-0.082	-0.04866	-0.0177
Talc	0.463	0.272	0.073	0.03982	0.00917

Negative values represent dissolution of minerals; positive values represent precipitation of minerals. Dissolution and precipitation of the different minerals will be presented graphically as a function of the ionic strengths and oil recovery observed with the different versions of seawater in figure 4-5 – 4-12. The ionic strength is calculated in PHREEQC and the oil recovery is an average of the recoveries observed in the first and the second coreflood (Yousef et al., 2011).

Table 4-13: Ionic strength and oil recovery observed for each version of seawater.

	Seawater	Twice diluted seawater	10 times diluted seawater	20 times diluted seawater	100 times diluted seawater
Ionic strength	1.041	0.5246	0.1066	0.05371	0.01102
Cumulative oil recovery % (OOIC)	70.6	78.3	87.9	89.1	89.1

The consistency between the ionic strength of each version of seawater and the oil recovery observed with each version of seawater is presented in figure 4-3. It is almost linear, except when no additional oil recovery is observed when changing from 20 times diluted seawater to 100 times diluted seawater.

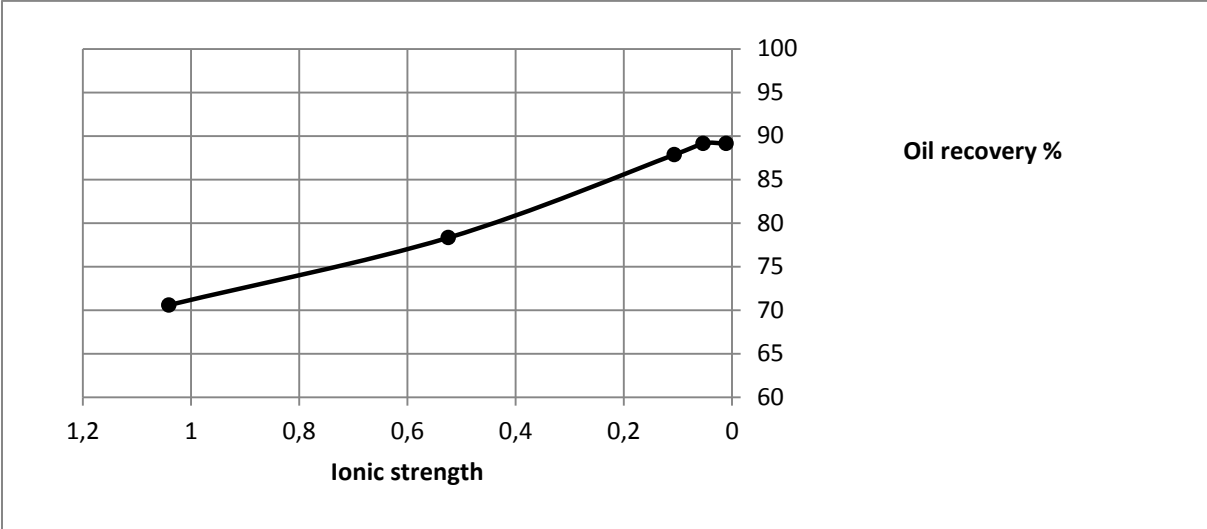


Figure 4-4: Consistency between ionic strength and observed oil recovery for each version of seawater

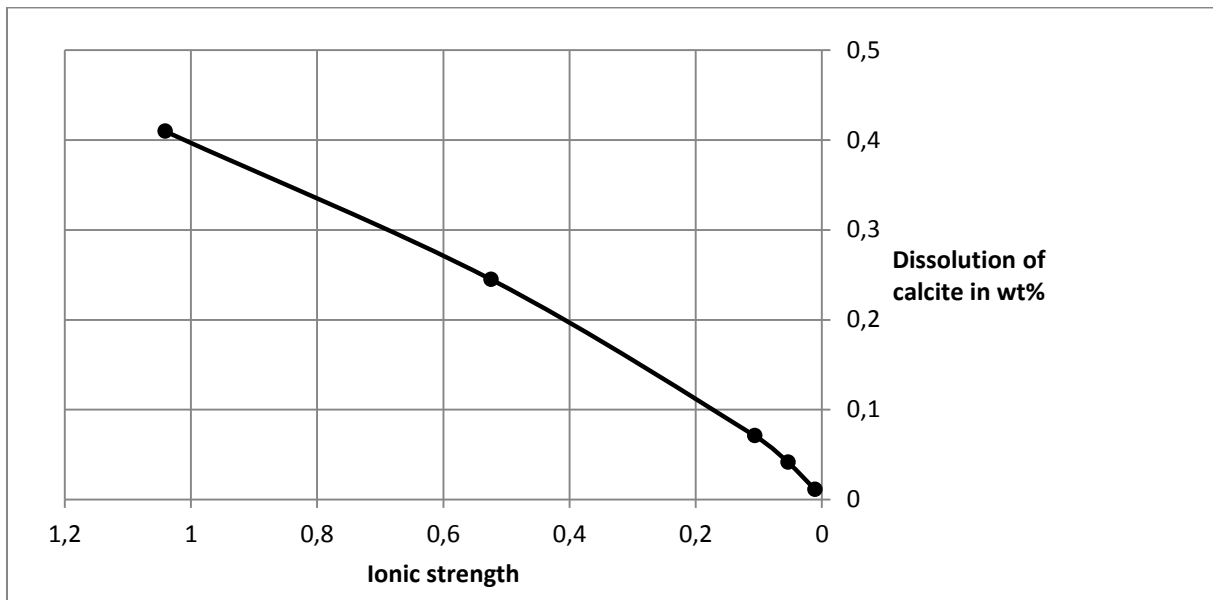


Figure 4-5: Dissolution of calcite is observed when equilibrated with each type of diluted seawater. The biggest amount of dissolved calcite is observed when seawater is equilibrated with seawater. The amount decreases as the ionic strength decreases (as the salinity decreases).

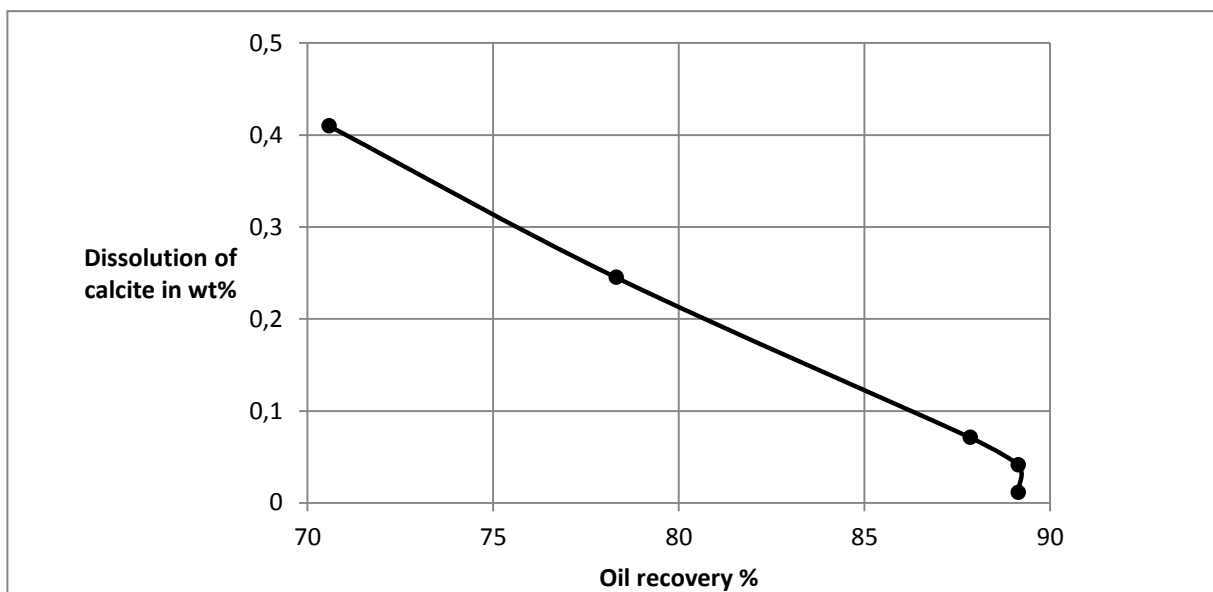


Figure 4-6: When changing from seawater to twice diluted seawater, an additional oil recovery of 7.7 % is observed and dissolution of calcite decreases. When changing from twice diluted to 10 times diluted seawater, an additional oil recovery of 9.6% is observed and dissolution of calcite decreases. When changing to 20 times and 100 times diluted seawater, little additional oil recovery is observed and the dissolution of calcite still decreases.

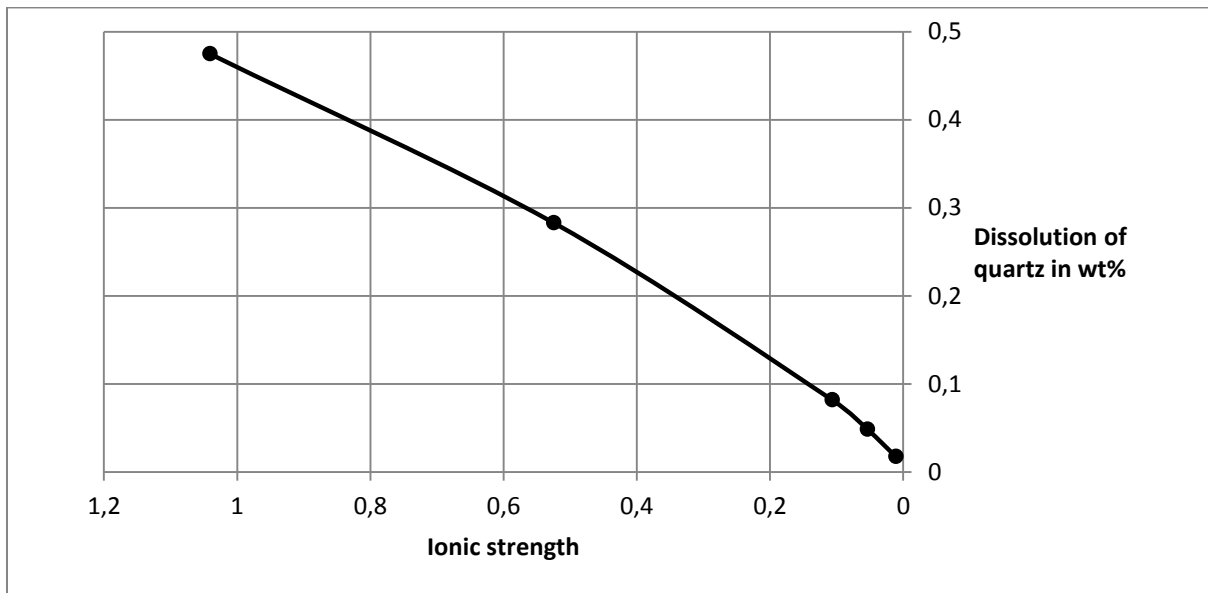


Figure 4-7: Dissolution of quartz is also observed when equilibrated with each type of diluted seawater. The biggest amount of dissolved quartz is observed when seawater is equilibrated with seawater. The amount decreases as the ionic strength decreases (as the salinity decreases).

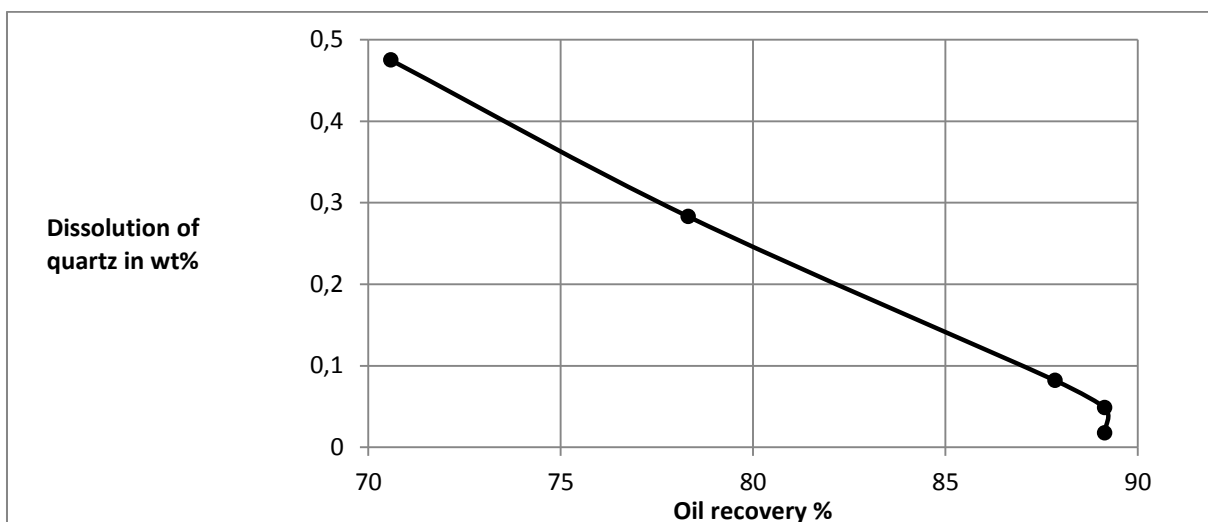


Figure 4-8: When changing from seawater to twice diluted seawater, an additional oil recovery of 7.7% is observed and dissolution of quartz decreases. When changing from twice diluted to 10 times diluted seawater, an additional oil recovery of 9.6% is observed and dissolution of quartz decreases. When changing to 20 times and 100 times diluted seawater, little additional oil recovery is observed and the dissolution of calcite still decreases.

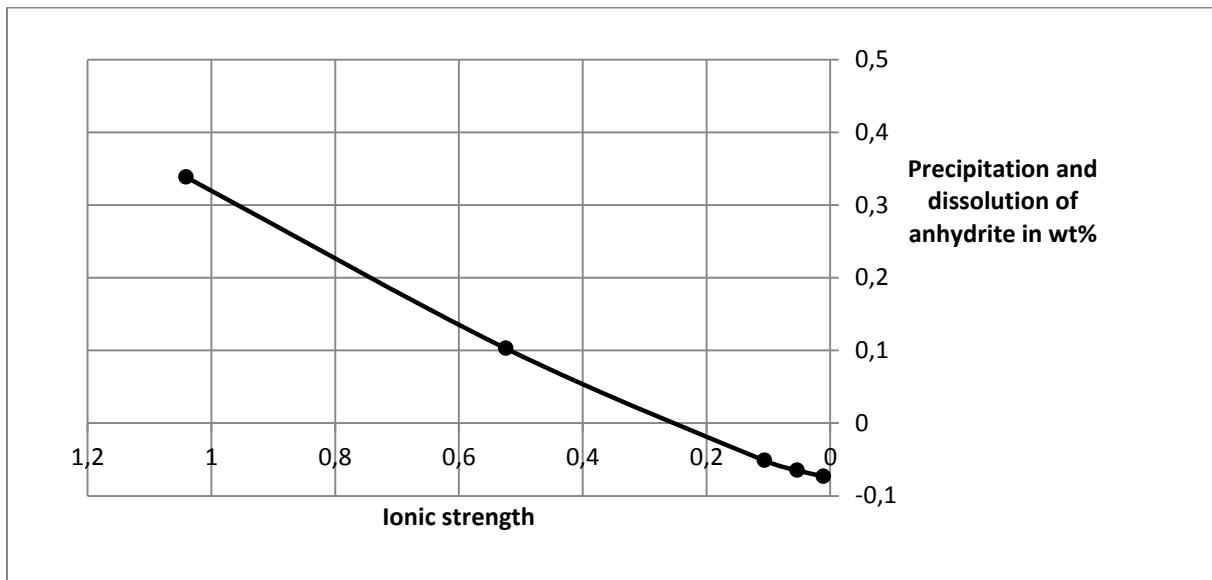


Figure 4-9: Anhydrite is first precipitated. Precipitation is observed when seawater and twice diluted seawater is forced in equilibrium with the minerals. The amount precipitated when the minerals are equilibrated with seawater is larger than when equilibrated with twice diluted seawater. When 10, 20 and 100 times diluted seawater is forced in equilibrium with the minerals, anhydrite is dissolved, here represented with negative values.

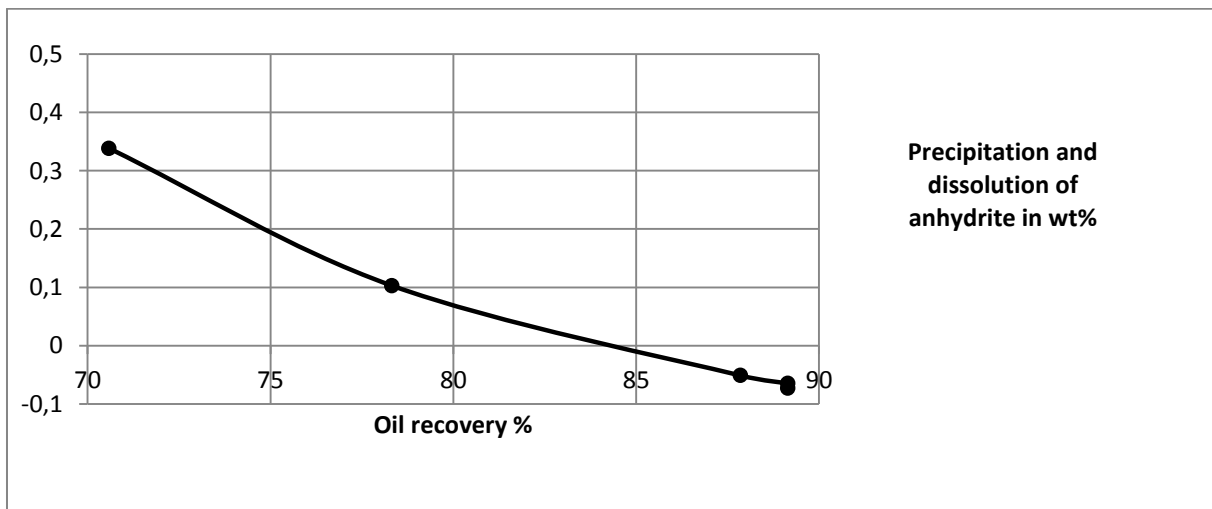


Figure 4-10: When changing from seawater to twice diluted seawater, an additional oil recovery of 7.7% is observed and precipitation of anhydrite decreases. When changing from twice diluted to 10 times diluted seawater, an additional oil recovery of 9.6% is observed and dissolution of anhydrite is observed. When changing to 20 times and 100 times diluted seawater, little additional oil recovery is observed and the dissolution of anhydrite increases.

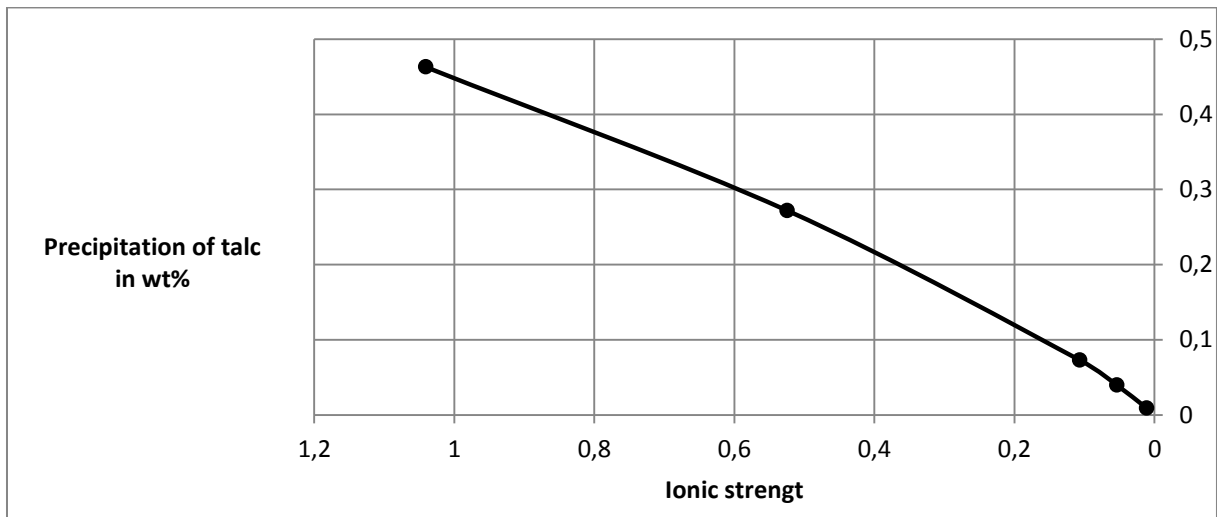


Figure 4-11: Talc is precipitated when the different versions of seawater are forced in equilibrium with the different minerals. The precipitation is at its highest when forced in equilibrium with seawater. The amount of talc precipitated decreases as the salinity decreases.

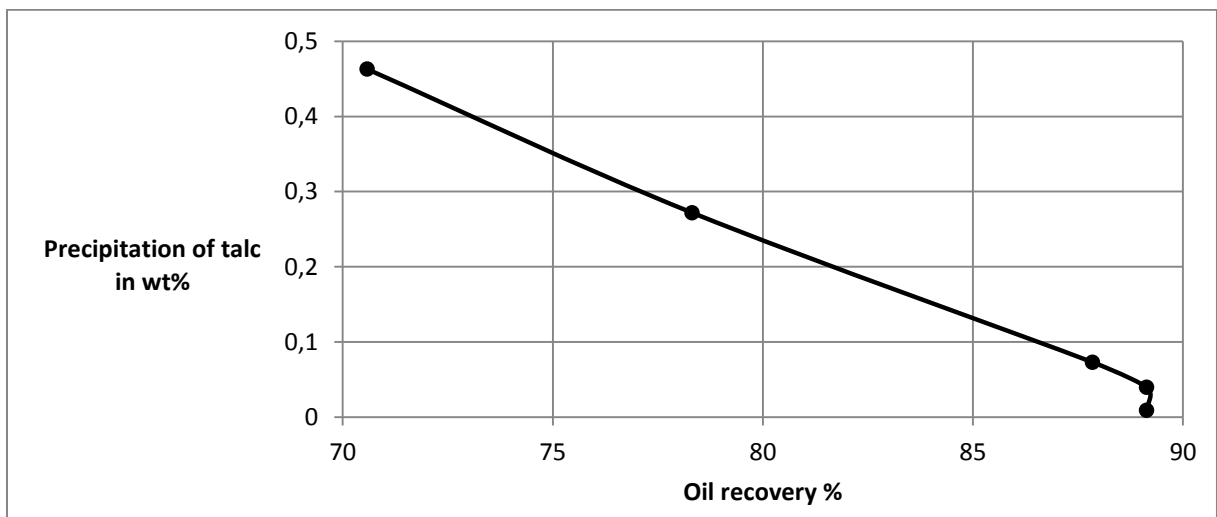


Figure 4-12: When changing from seawater to twice diluted seawater, an additional oil recovery of 7.7% is observed and precipitation of talc decreases. When changing from twice diluted to 10 times diluted seawater, an additional oil recovery of 9.6% is observed and precipitation of talc decreases. When changing to 20 times and 100 times diluted seawater, little additional oil recovery is observed and the precipitation of talc still decreases.

4.1.3 Exchanger composition

The water chemistry of injection water can change the rock surface, and the amount of adsorbed ions. Though the use of PHREEQC one can predict how the cation exchanger at the surface of the rock changes when it is forced in equilibrium with different brines.

First the different solutions are being equilibrated with the minerals, and then the exchanger is calculated. The exchanger gives the amount of exchangeable cations present. The size of the exchanger is assumed to be $X = 1.1e^{-3}$ mmol. If it was assumed to be smaller or larger, the difference between the different cations would still be the same.

Table 4-14: Cation exchanger composition when the different solutions are equilibrated with the minerals

	Field connate water	Seawater	Twice diluted seawater	10 times diluted seawater	20 times diluted seawater	100 times diluted seawater
Na ⁺ (%)	63.42	61.27	49.21	26.25	19.27	8.893
Mg ²⁺ (%)	3.635	28.56	37.65	55.06	60.50	69.11
Ca ²⁺ (%)	32.94	10.17	13.14	18.69	20.22	22.00

The changes in the exchanger composition are shown graphically in figure 4-13 as a function of the oil recovery observed with the different versions of water.

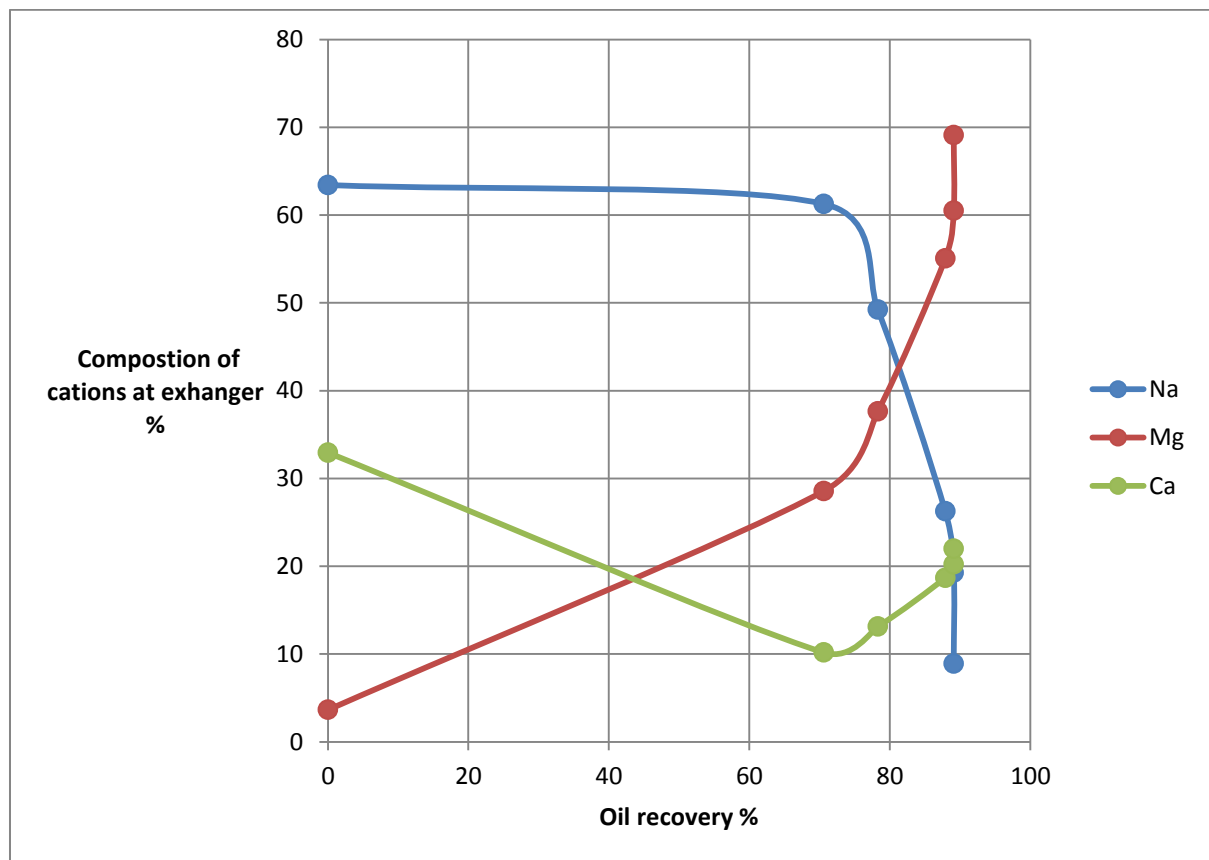


Figure 4-13: Concentration of N⁺, Ca²⁺ and Mg²⁺ at the exchanger versus observed oil recovery

When seawater is forced in equilibrium with the rock, there will be an exchange of cations at the surface; Mg^{2+} replaces Ca^{2+} . The amount of Na^+ stays almost constant. An oil recovery of 70.6 % was observed when injecting seawater in the core. When changing from seawater to twice diluted seawater, and from twice to 10 times diluted seawater, an additional oil recovery was observed. The amount of both Mg^{2+} and Ca^{2+} at the surface increases and the amount of Na^+ decreases. When changing to 20 and 100 times diluted seawater, little additional oil recovery is observed, still the amount of Mg^{2+} and Ca^{2+} increases and the amount of Na^+ decreases.

The exchanger composition is dominated by Na^+ when the rock is equilibrated with seawater and twice diluted seawater. It is dominated by Mg^{2+} when equilibrated with 10, 20 and 100 times diluted seawater.

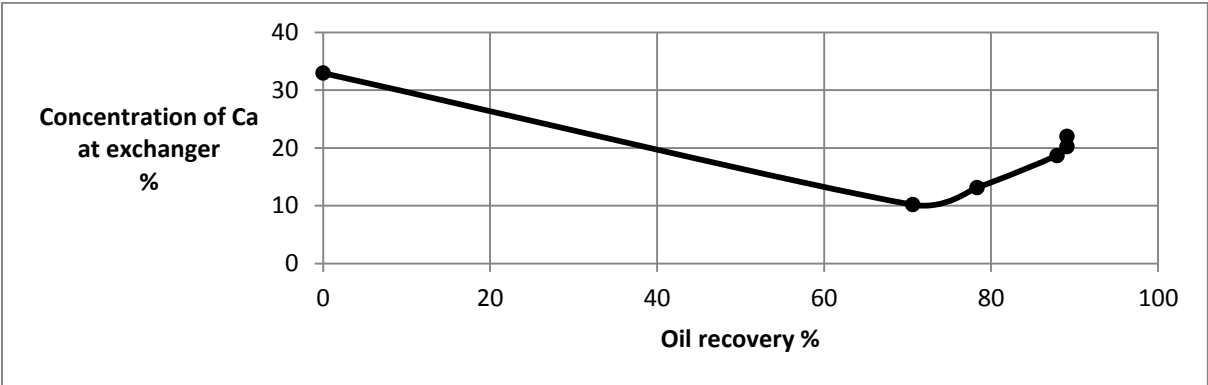


Figure 4-14: When forcing the minerals in equilibrium with seawater, the composition of Ca^{2+} at the rock surface decreases. An oil recovery of 70.6% is observed. When forcing minerals in equilibrium with diluted versions of seawater, the amount of Ca^{2+} at the rock surface increases.

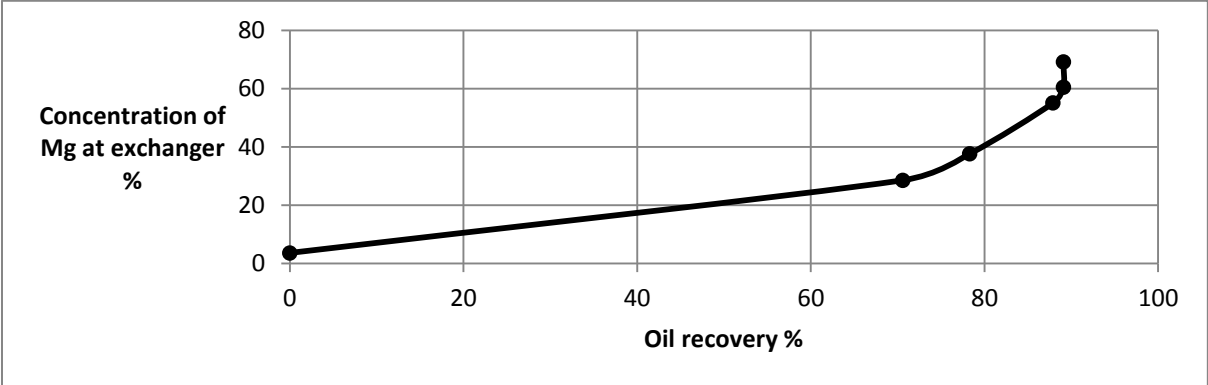


Figure 4-15: When forcing the minerals in equilibrium with seawater, the composition of Mg^{2+} at the rock surface increases. An oil recovery of 70.6% recovery is observed. When forcing minerals in equilibrium with diluted versions of seawater, the amount of Mg^{2+} at the rock surface increases even more.

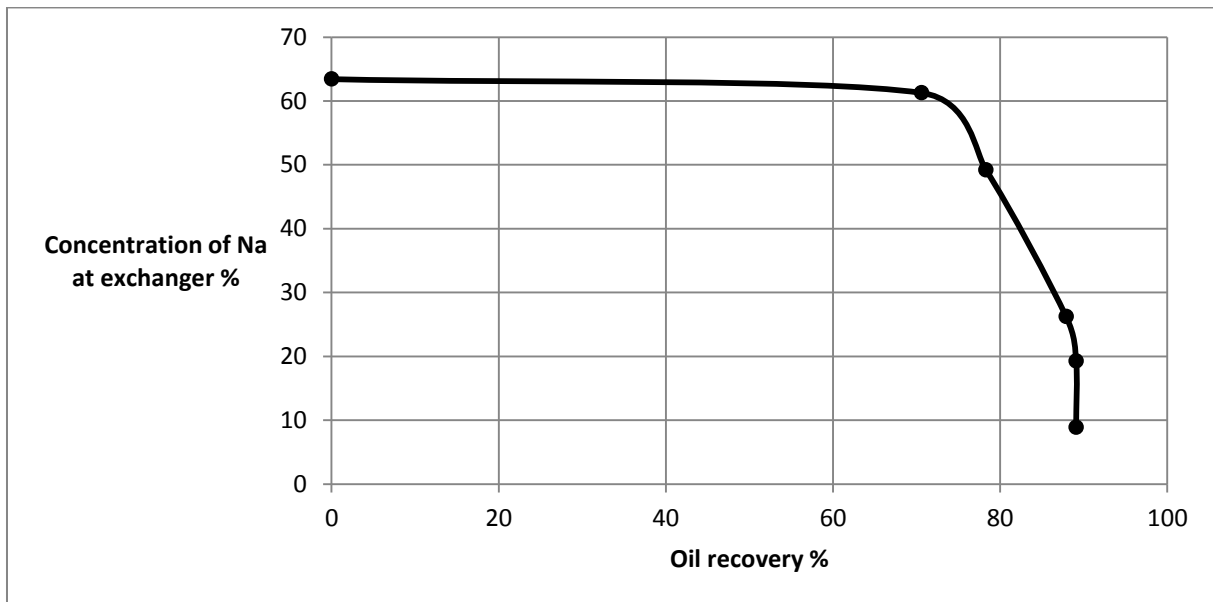


Figure 4-16: When forcing the minerals in equilibrium with seawater, the composition of Na⁺ at the rock surface stays constant. An oil recovery of 70.6% is observed. When forcing minerals in equilibrium with diluted versions of seawater, the amount of Na⁺ at the rock surface decreases.

4.2 Impact of injection-water salinity and ionic content on oil recovery in sandstones

In a paper published by RezaeiDoust et al. (2010), results from low salinity laboratory experiments on cores from an offshore field in the North Sea are discussed in relation to the recovery mechanism proposed by Austad et al. in 2010; local pH variation. The cores were taken from a sandstone reservoir, Varg, which had been flooded with seawater and the goal of the experiment was to find out if the oil recovery could increase by injecting diluted seawater as the low salinity water.

The six cores used in the experiment were mainly selected due to the clay content. Four of the cores had a clay content of approximately 16% and the two others 8%.

Synthetic brines were prepared based on compositions given by Talisman. For most of the floods, the cores were first flooded with formation water in a secondary process followed by 20 times diluted seawater in a tertiary process. Sulfate was excluded from the diluted seawater to avoid precipitation of BaSO_4 . For some cores diluted formation water (salinity of 31000 ppm) was used as high salinity water and 200 times diluted formation water (salinity of 1050 ppm) was used as low salinity water.

They found that the aging temperature was important for observing an additional oil recovery. When it was 90°C, a low salinity effect of about 6% of OOIP was observed when core flooding was performed at 60 and 130°C. The low salinity effect decreased from 6% to about 2% when the clay content of the core material decreased from 16 to 8 wt%.

The low salinity effect of 6% of OOIP was observed when two of the cores first were flooded with formation water, and secondly with 20 times diluted seawater. For one of the cores, there was observed an oil recovery of 44% when injecting formation water, and additional 6% when injecting 20 times diluted seawater, shown in figure 4-17. For the other core, there was observed an oil recovery of approximately 53% when injecting formation water, and additional 6% when injecting 20 times diluted seawater, shown in figure 4-18.

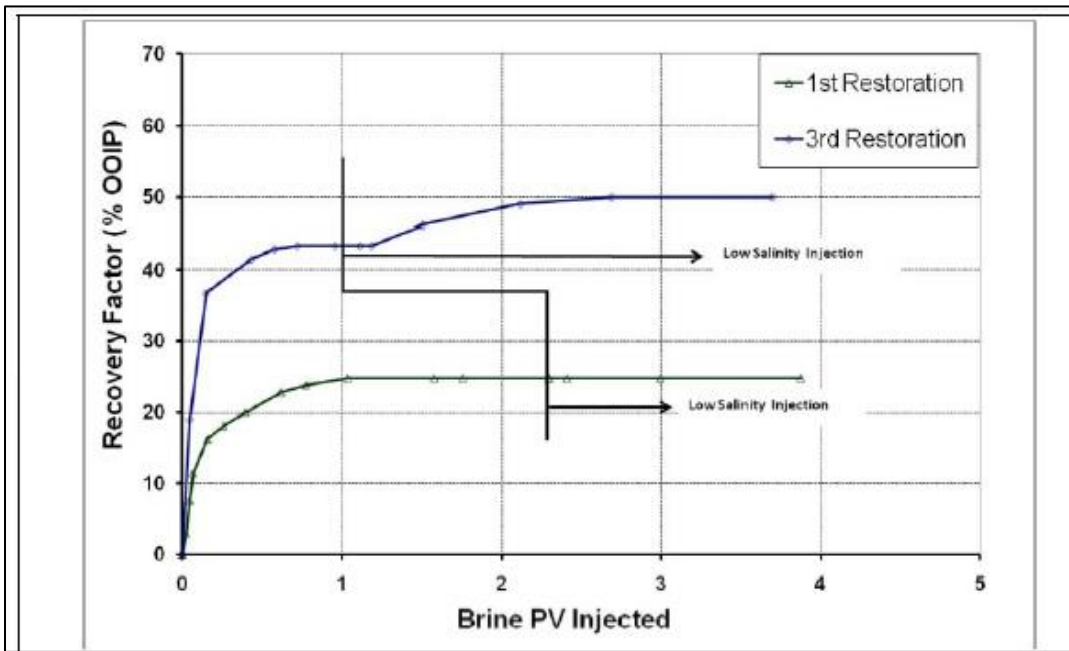


Figure 4-17: During the third restoration of Varg Core 1, the oil recovery increased from 44% using formation brine to 50% OOIP during the low salinity flood (RezaeiDoust et al., 2010)

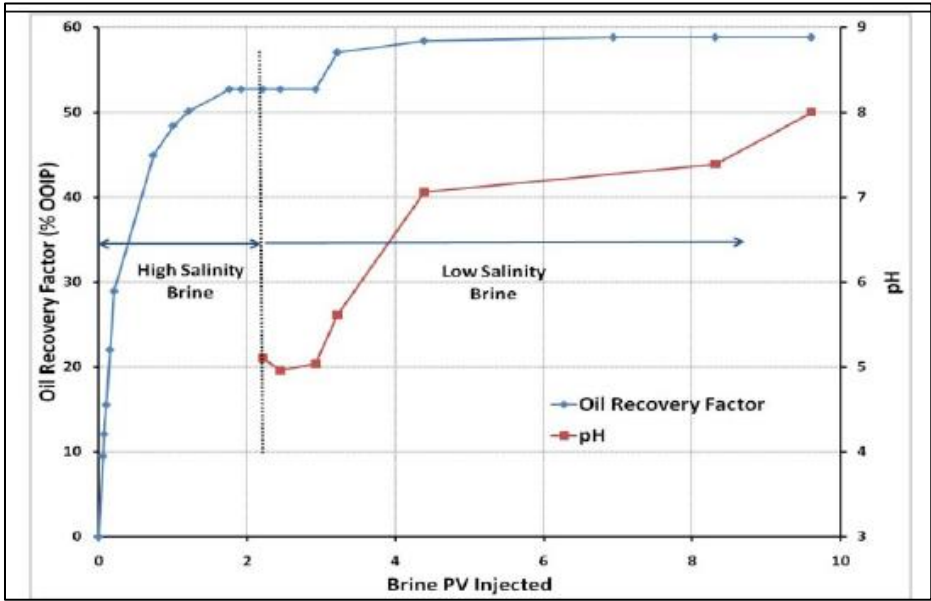


Figure 4-18: For Varg Core 2, the oil recovery increased from 53% using formation brine to 59% OOIP during the low salinity flood (RezaeiDoust et al., 2010)

The low salinity effect of 2% of OOIP was observed when two of the cores first were flooded with formation water diluted to 31000 ppm, and secondly with formation water diluted to 1050 ppm. For one of the cores, there was observed an oil recovery of 28% when injecting formation water diluted to 31000 ppm, and additional 2% when injecting formation water diluted to 1050 ppm. For the other core, there was observed an oil recovery of approximately 39% when injecting formation water diluted to 31000 ppm, and additional 2% when injecting formation water diluted to 1050 ppm. This is shown in figure 4-19:

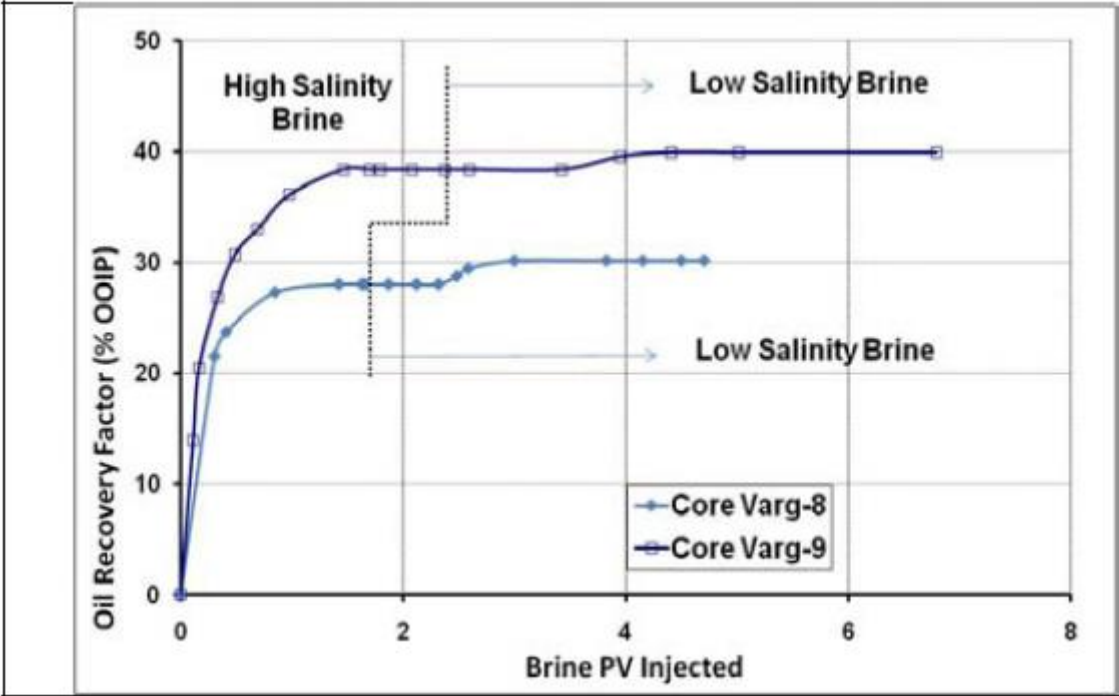


Figure 4-19: For Varg Core 8, the oil recovery increased from 28% using formation brine diluted to 31000 ppm to 30% OOIP during the low salinity flood. For Varg Core 9, the oil recovery increased from 39% using formation brine diluted to 31000 ppm to 41% OOIP during the low salinity flood (RezaeiDoust et al. (2010))

Two of the cores were first flooded with formation water, followed by seawater, and finally by low salinity water at 500 ppm. No low salinity effects were recorded when switching from FW to SW or by switching from SW to the low salinity water. Both aging and flooded were performed at 130°C, and this was suggested as a reason why no effect was observed.

4.2.1 Mineralogy

As no mineralogy was given by RezaeiDoust et al., we have to use the composition of the formation water to estimate the mineralogy of the reservoir rock. The composition of the formation water in the Varg formation is given, and this can give indications of which minerals that are present in the rock.

Table 4-15: Composition of Varg formation water and seawater (RezaeiDoust et al., 2010)

Salt	Varg Formation		Sea Water Brine	
	g/l	mol/l	g/l	mol/l
NaCl	121.9	2.09	23.38	0.4
Na ₂ SO ₄	0.0	0.0	3.41	0.02
NaHCO ₃	0.0	0.0	0.17	0.002
KCl	3.8	0.05	0.75	0.01
MgCl ₂ * 6H ₂ O	29.25	0.14	9.05	0.04
CaCl ₂ * 2H ₂ O	78.81	0.54	1.91	0.01
BaCl ₂ * 2H ₂ O	1.7	0.01	0.0	0.0
SrCl ₂ * 6H ₂ O	2.03	0.01	0.0	0.0

The composition of the salts in the formation water is given. To find the mineralogy of the rock, the composition of the different ions is needed. This conversion is done, and the ionic composition of formation water is given in table 4-16.

Table 4-16: Ionic composition of Varg formation water

Ions	Concentration (mol/l)
Na ⁺	2.09
Ca ²⁺	0.54
Mg ²⁺	0.14
SO ₄ ²⁻	0
Cl ⁻	3.54
Sr ²⁺	0.01
HCO ₃ ⁻	0
Ba ²⁺	0.01
K ⁺	0.05

The reservoir temperature given in the paper is 130°C. In the paper the amounts of clay are given. Clay minerals are based on Mg²⁺, Al³⁺ and Si⁴⁺, so it can be assumed that there is some Si⁴⁺ and Al³⁺ as well in the formation water and that they are neglected because of small amount.

When forcing magnesium in equilibrium with talc, aluminum with mica and silica with quartz, the composition of the water is the same as given. All the SI-indices are above zero.

Table 4-17: Ionic concentration given by RezaeiDoust et al. and PHREECQ when solution is equilibrated with talc, mica and quartz.

	Concentration (mol/l)	PHREECQ (mol/l)
Ions	2.09	2.09
Ca ²⁺	0.54	0.54
Mg ²⁺	0.14	0.14
SO ₄ ²⁻	0	0
Cl ⁻	3.54	3.54
Sr ²⁺	0.01	0.01
HCO ₃ ⁻	0	0
Ba ²⁺	0.01	0.01
K ⁺	0.05	0.05
Al ³⁺		0.00000001268
Si ⁴⁺		0.0004671

On the basis of this, the mineralogy of the rock will be assumed to be talc, quartz and mica.

4.2.2 Precipitation and dissolution

As for the formation water, the composition of the salts in the seawater is given. This composition need to be converted to ionic composition.

Table 4-18: Seawater composition

Salt	Seawater (mol/l)
NaCl	0.4
Na ₂ SO ₄	0.02
NaHCO ₃	0.002
KCl	0.01
MgCl ₂ *6H ₂ O	0.04
CaCl ₂ *2H ₂ O	0.01

Table 4-19: Ionic composition of seawater and 20 times diluted seawater

Ions	Seawater (mol/l)	20 times diluted (mol/l)
HCO ₃ ⁻	0.002	0.0001
Cl ⁻	0.53	0.0265
SO ₄ ²⁻	0.024	0.0012
Mg ²⁺	0.045	0.00225
Ca ²⁺	0.013	0.00065
Na ⁺	0.45	0.0225
K ⁺	0.01	0.0005

Table 4-20: Ionic composition in formation water and diluted versions of formation water:

Ions	Formation water (mol/l)	7 times diluted formation water (mol/l) (salinity of 31000 ppm)	200 times diluted formation water (mol/l) (salinity of 1050 ppm)
Na ⁺	2.09	0.298	0.01
Ca ²⁺	0.54	0.077	0.003
Mg ²⁺	0.14	0.02	0.0007
SO ₄ ²⁻	0	0	0
Cl ⁻	3.54	0.506	0.0177
Sr ²⁺	0.01	0.0014	0.00005
HCO ₃ ⁻	0	0	0
Ba ²⁺	0.01	0.0014	0.00005
K ⁺	0.05	0.007	0.00025
Al ³⁺	1.2 * 10 ⁻⁸	1.8 * 10 ⁻⁹	6.34 * 10 ⁻¹¹
Si ⁴⁺	0.0004671	6.67 * 10 ⁻⁵	2.34 * 10 ⁻⁶

The salinity of the different brines is different. Most saline is the formation water, followed by respectively 7 times diluted formation water, 20 times diluted seawater and, at last, 200 times diluted formation water as the least saline injection water. This yields when salinity is measured in ppm.

These brines will now, through the use of PHREEQC, be forced in equilibrium with talc, quartz and mica. This is done to find out if any changes in the chemical composition of the brines will occur when it is in contact with the minerals. These changes will tell if there has been either dissolution or precipitation of minerals.

Table 4-21: Mineral changes when formation water is equilibrated with the minerals.

Mineral	Difference (mol/kgw)
Mica	$5.954 * 10^{-12}$
Quartz	$-8.317 * 10^{-4}$
Talc	$2.079 * 10^{-4}$

It will be assumed that the weight of the core, w_c , is 1 kg, and the amount of water is also 1 kg. To find the difference in weight percent, equation 4.2 is used.

Changes in wt% when formation water is equilibrated with the minerals are given in table 4-22.

Table 4-22: Difference in minerals converted from mol/kgw to wt%

Mineral	Δ Mineral (mol/kgw)	F_w (g/mol)	Difference (g/kgw)	Δ wt%
Mica	$5.954 * 10^{-12}$	398.31	$2.37 * 10^{-9}$	$2.37 * 10^{-10}$
Quartz	$-8.317 * 10^{-4}$	96.11	0.08	0.008
Talc	$2.079 * 10^{-4}$	379.272	0.079	0.0079

This can be understood as when 1 kg of formation water is flooded through a 1 kg core, there will be dissolution of quartz and precipitation of talc and mica. This procedure will now be done for the rest of the waters. The differences in wt% of minerals when equilibrated with brine are tabulated in table 4-23.

Table 4-23: Mineral differences presented in wt% for all brines when equilibrated with the minerals

	Formation water Δ wt%	7 times diluted formation water Δ wt%	20 times diluted seawater Δ wt%	200 times diluted formation water Δ wt%
Mica	$2.37 * 10^{-10}$	$-9.86 * 10^{-7}$	$-2.84 * 10^{-6}$	$-4.44 * 10^{-6}$
Quartz	-0.008	-0.0137	-0.0156	-0.0151
Talc	0.0079	0.00167	0.000815	0.000208

Average oil recoveries observed when injecting the different brines is given in table 4-24.

Table 4-24: Average oil recoveries observed for the different brines

	Formation water	7 times diluted formation water	20 times diluted seawater	200 times diluted formation water
Oil recovery % of OOIP	48.5%	33.5%	54.5%	35.5%

The low salinity effect of 6% of OOIP was observed when two of the cores first were flooded with formation water, and secondly with 20 times diluted seawater. An average oil recovery of 48.5% was observed when injecting formation water. The dissolution/precipitation happening during these floods is shown in figures 4-20 – 4-22

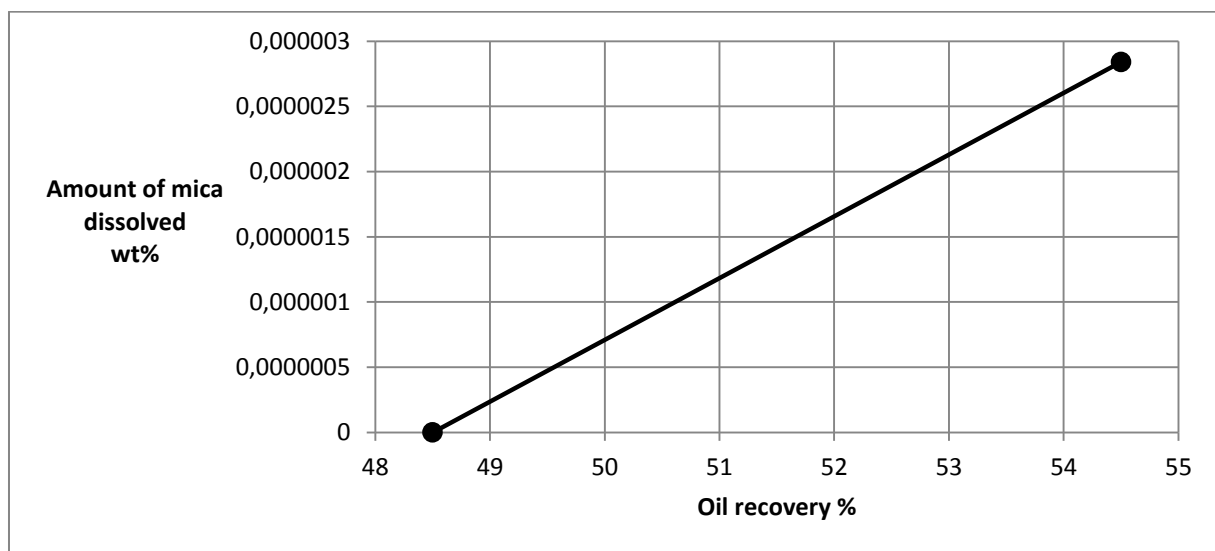


Figure 4-20: When the rock is equilibrated with formation water there will be precipitated a very small amount of mica. When it is equilibrated with 20 times diluted seawater there will be dissolved a small amount mica from the rock, and 6% more oil was observed recovered. The values are very small.

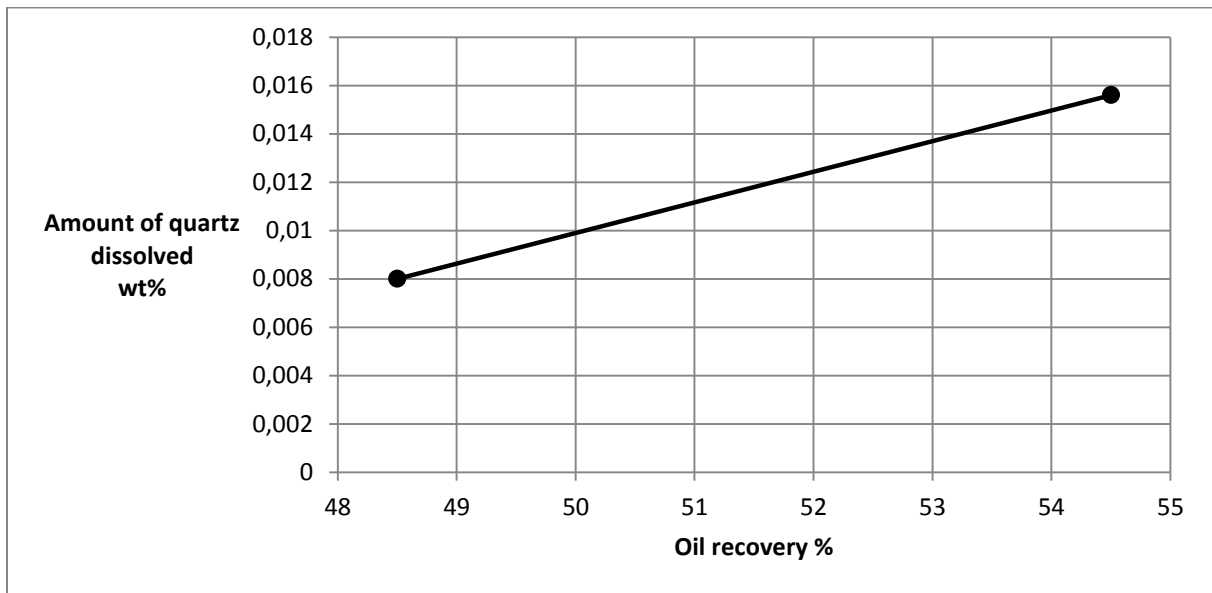


Figure 4-21: When the rock is equilibrated with formation water there will be dissolution of quartz. When it is equilibrated with 20 times diluted seawater, twice as much quartz will be dissolved, and 6 % more oil was observed recovered.

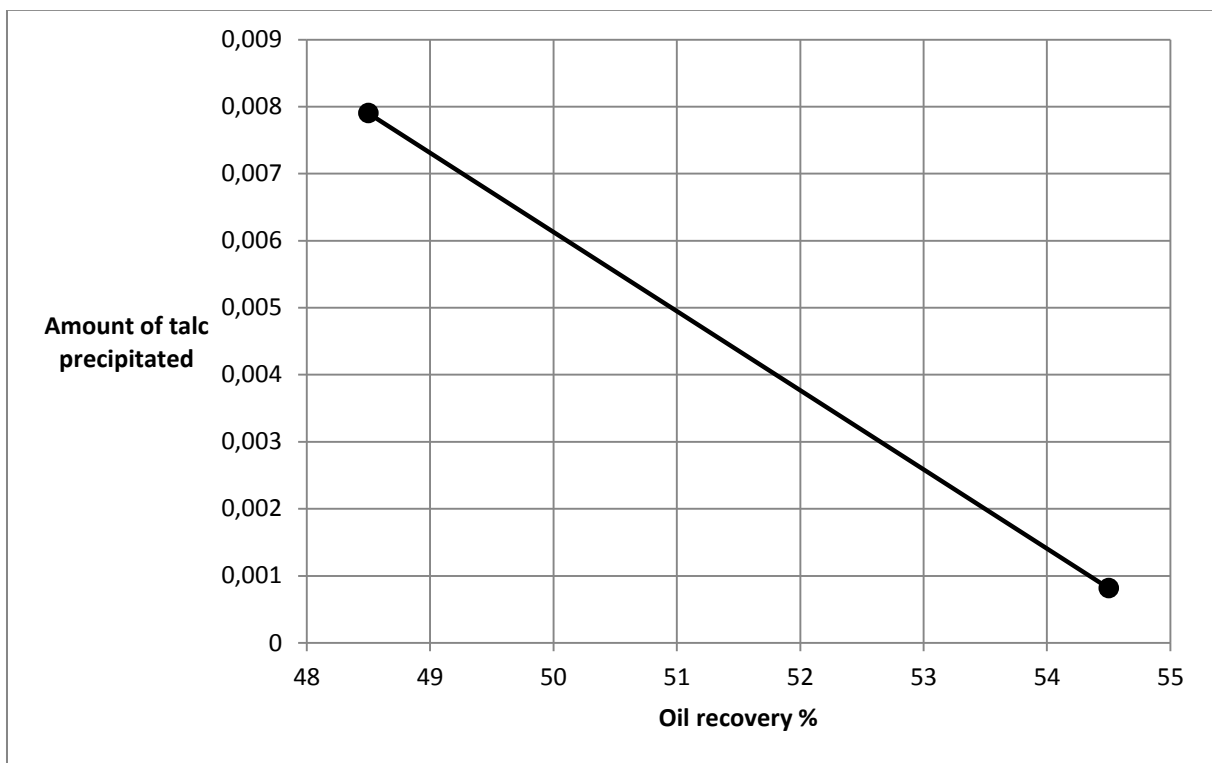


Figure 4-22: When the rock is equilibrated with formation water there will be precipitation of talc. When it is equilibrated with 20 times diluted seawater there will still be precipitation, but a smaller amount. 6 % more oil was observed recovered during this change of injection water.

The low salinity effect of 2% of OOIP was observed when two of the cores first were flooded with formation water diluted to 31000 ppm (7 times diluted formation water), and secondly with formation water diluted to 1050 ppm (200 times diluted formation water). An average oil recovery of 33.5% was observed when injection formation water diluted to 31000 ppm. The dissolution/precipitation happening during these floods is shown in figures 4-23 – 4-25.

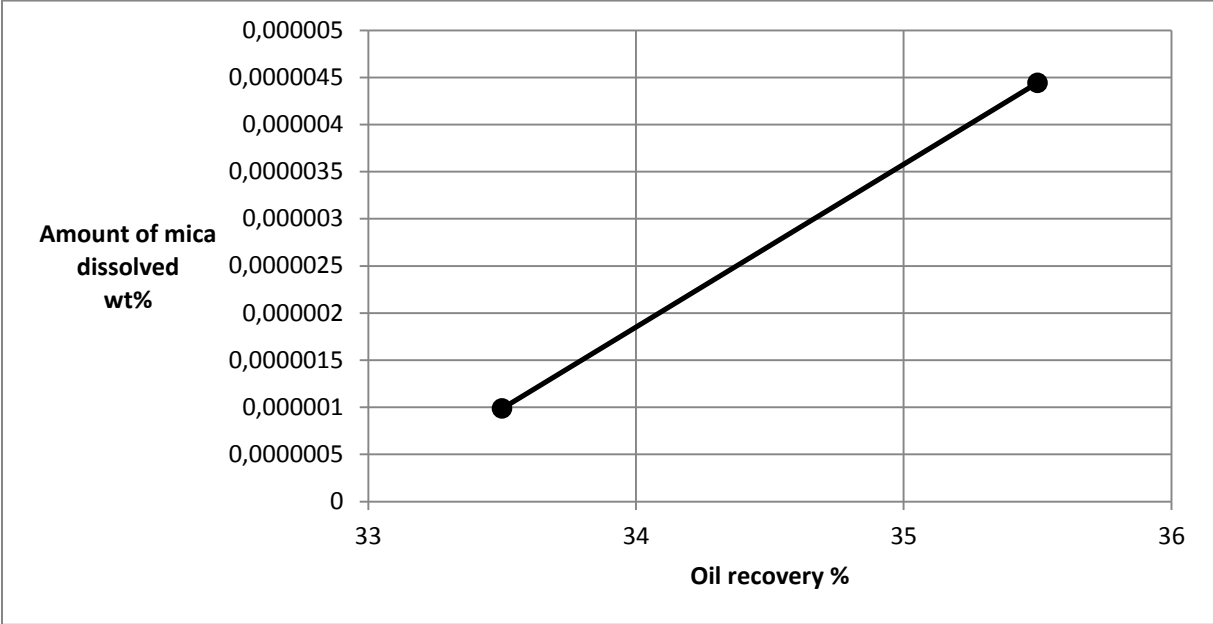


Figure 4-23: When the rock is equilibrated with 7 times diluted formation water, mica is dissolved. A bigger amount of mica is dissolved when equilibrated with 200 times dissolved formation water. During this change 2% more oil was observed recovered. The values are very small.

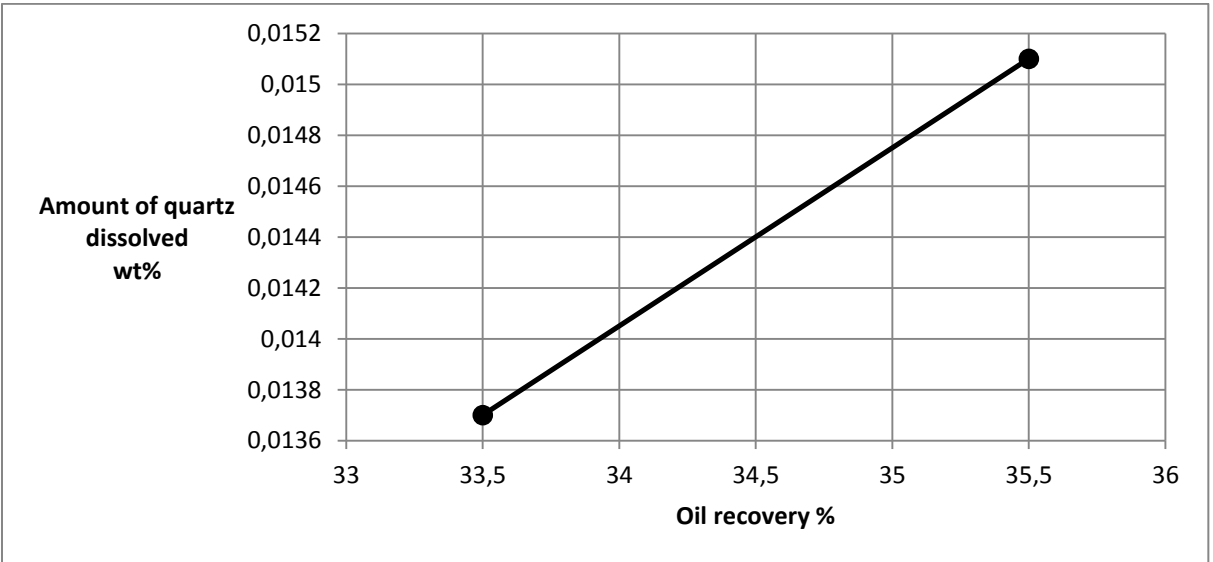


Figure 4-24: When the rock is equilibrated with 7 times diluted formation water, quartz is dissolved. A bigger amount of quartz is dissolved when equilibrated with 200 times dissolved formation water. During this change 2% more oil was observed recovered.

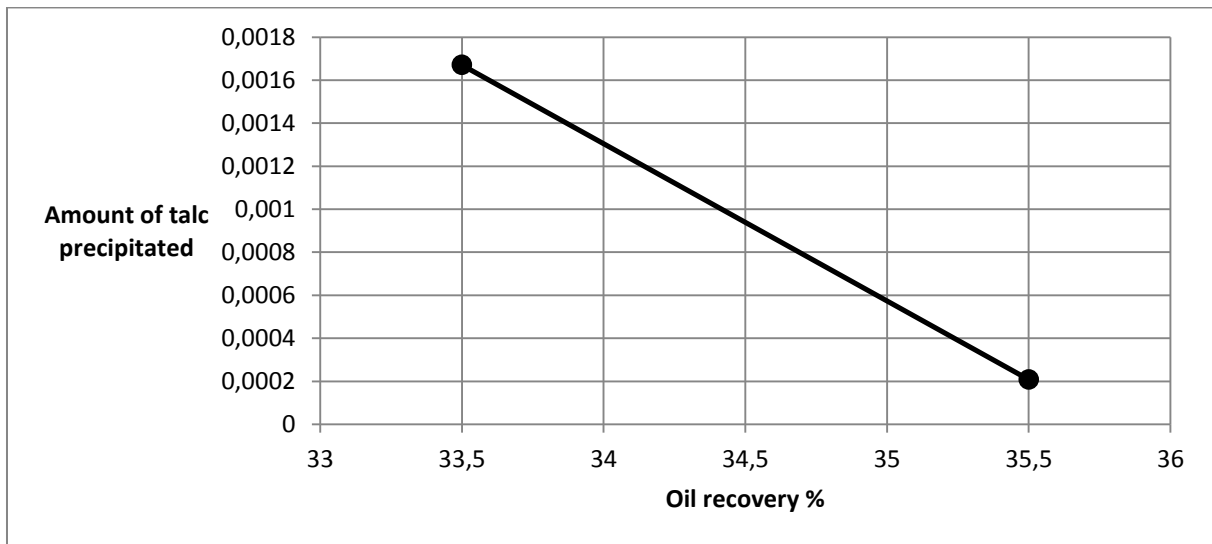


Figure 4-25: When the rock is equilibrated with 7 times diluted formation water, talc is precipitated. A smaller amount of talc is precipitated when equilibrated with 200 times dissolved formation water. During this change 2% more oil was observed recovered.

4.2.3 Exchanger composition

The exchanger composition of the rock when equilibrated with the different versions of brines is calculated by PHRREQC and it is tabulated in table 4-25.

Table 4-25: Exchanger composition when equilibrated with different versions of brines

	Formation water	7 times diluted formation water	20 times diluted seawater	200 times diluted formation water
Na ⁺ (moles)	48.75	23.14	13.49	4.47
Ca ²⁺ (moles)	39.49	62.42	29.84	80.60
K ⁺ (moles)	3.72	1.734	0.9507	0.3565
Mg ²⁺ (moles)	6.542	10.33	55.72	11.83
Sr ²⁺ (moles)	0.788	1.249	0	1.447
Ba ²⁺ (moles)	0.7095	1.125	0	1.303

Average oil recoveries observed when injecting the different brines is given in table 4-26.

Table 4-26: Average oil recoveries observed

	Formation water	7 times diluted formation water	20 times diluted seawater	200 times diluted formation water
Oil recovery % of OOIP	48.5%	33.5%	54.5%	35.5%

The changes in the exchanger composition are shown graphically as a function of the oil recovery observed with the different versions of water in figure 4-26 and 4-27.

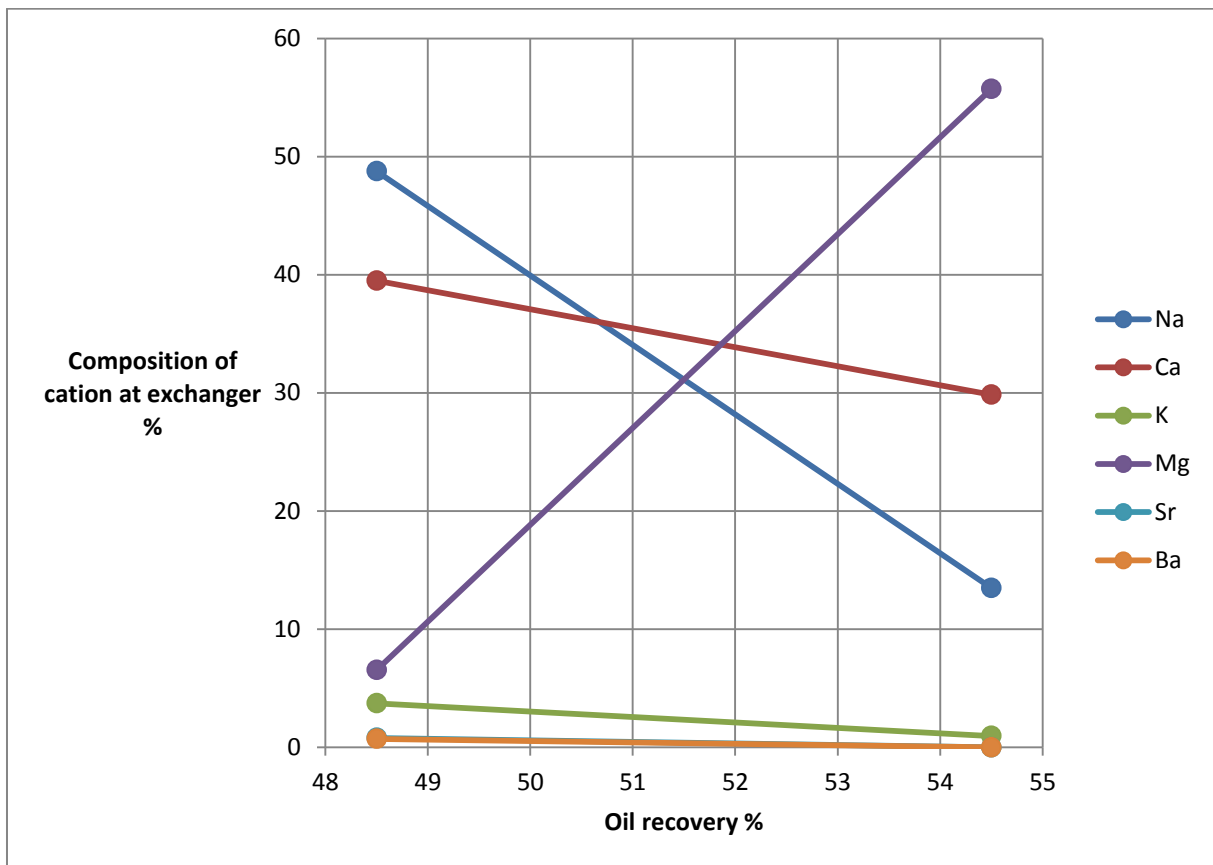


Figure 4-26: Concentration of Na⁺, Ca²⁺, K⁺, Mg²⁺, Sr²⁺ and Ba²⁺ at the exchanger versus observed oil recovery

Figure 4-26 illustrates the change in the exchanger composition when the minerals first are equilibrated with formation water, and secondly 20 times diluted seawater. 6 % more oil was observed recovered during this change of injection water. Surface changes from being Na⁺ and Ca²⁺ dominant, to being Mg²⁺ and Ca²⁺ dominant. Mg²⁺ replaces Na⁺ and Ca²⁺.

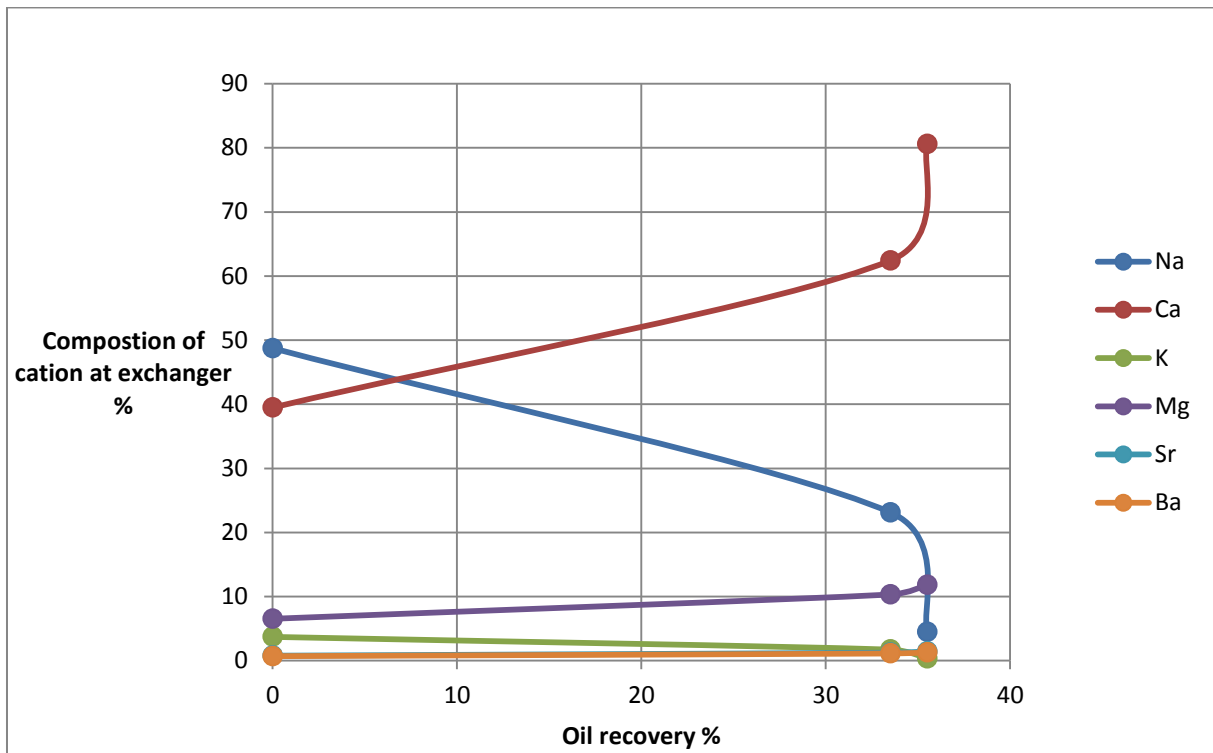


Figure 4-27: Concentration of Na⁺, Ca²⁺, K⁺, Mg²⁺, Sr²⁺ and Ba²⁺ at the exchanger versus observed oil recovery

Figure 4-27 illustrates the change in the exchanger composition when the minerals first are equilibrated with formation water, secondly with 7 times diluted formation water and at last, 200 times diluted formation water. Formation water is included because one can assume that formation water surrounds the rock before injecting the diluted versions. The two cores that were tested showed average oil recovery of 33.5% when 7 times diluted seawater was injected. For both cores, 2 % more oil was observed recovered when changing from 7 to 200 times diluted formation water. When the minerals are forced in equilibrium with 7 times diluted formation water, Ca²⁺ replaces Na⁺ at the rock surface. The concentration of rest of the cations stays small and constant. When equilibrated with 200 times diluted formation water, the concentration of Ca²⁺ increases and the concentration of Na⁺ decreases.

5 Results and discussion

The results found when the minerals in the carbonate cores used by Yousef et al. (2011) were equilibrated with seawater and different versions of seawater were:

- Calcite in the rock will dissolve. The amount of dissolved calcite decreases as the salinity of the injection water decreases.
- Quartz in the rock will dissolve. The amount of dissolved quartz decreases as the salinity of the injection water decreases.
- There will be precipitation of anhydrite when seawater and twice diluted seawater is injected into the rock. When 10, 20 and 100 times diluted seawater is injected, anhydrite will dissolve.
- There will be precipitation of talc. The precipitation decreases as the salinity of the injection water decreases.

The interesting transitions in the carbonate coreflood performed by Yousef et al. (2011) was when switching from seawater to twice diluted seawater and from twice diluted seawater to 10 times diluted seawater. When seawater was injected an average oil recovery of 70.6% was observed, when twice diluted seawater was injected an additional average of 7.7% oil recovery was observed and when 10 times diluted seawater was injected an average of 9.6% oil recovery was observed.

Based on these results, mineral dissolution does not explain the additional oil recovery observed with the use of twice and 10 times diluted seawater. The amount of dissolved calcite and quartz is at its highest when seawater is equilibrated with the minerals, it does not increase when diluted versions are equilibrated with the minerals. Dissolution of anhydrite is first observed when the minerals are equilibrated with 10 times diluted seawater. If dissolution of anhydrite should be considered as a reason for the increased recovery, dissolution should also been observed with twice diluted seawater. No dissolution of talc is observed.

The results found when the minerals in the sandstone cores used by RezaeiDoust et al. (2010) were equilibrated with formation water, diluted versions of formation water and diluted seawater were:

- Dissolution of mica increases as the salinity of the water decreases, but the values are so small that they should be neglected.
- Quartz will be dissolved. There will be an increase in the amount of quartz dissolved when minerals first are equilibrated with one type of water and secondly with water of lower salinity.
- Talc will be precipitated. There will be a decrease in the amount of talc precipitated when minerals first are equilibrated with one type of water and secondly with water of lower salinity.

A low salinity effect of 6% of OOIP was observed by RezaeiDoust et al. (2010) when two of the cores first were flooded with formation water, and secondly with 20 times diluted seawater. A low salinity effect of 2% of OOIP was observed when two of the cores first were flooded with formation water diluted to 31000 ppm and secondly with formation water diluted to 1050 ppm.

Based on these results, mineral dissolution can be an explanation of the low salinity effect observed as the salinity of the injection water changes. Both when diluted seawater and diluted formation water was used as the low saline brine, an additional oil recovery was observed and in PHREEQC an increase in dissolution of quartz was observed when equilibrating the minerals with the low saline fluid. This is in line with the suggestion made by Hiorth et al. (2010) that rock dissolution can change the wettability. If quartz is dissolved where oil is adsorbed, oil will be liberated from the rock.

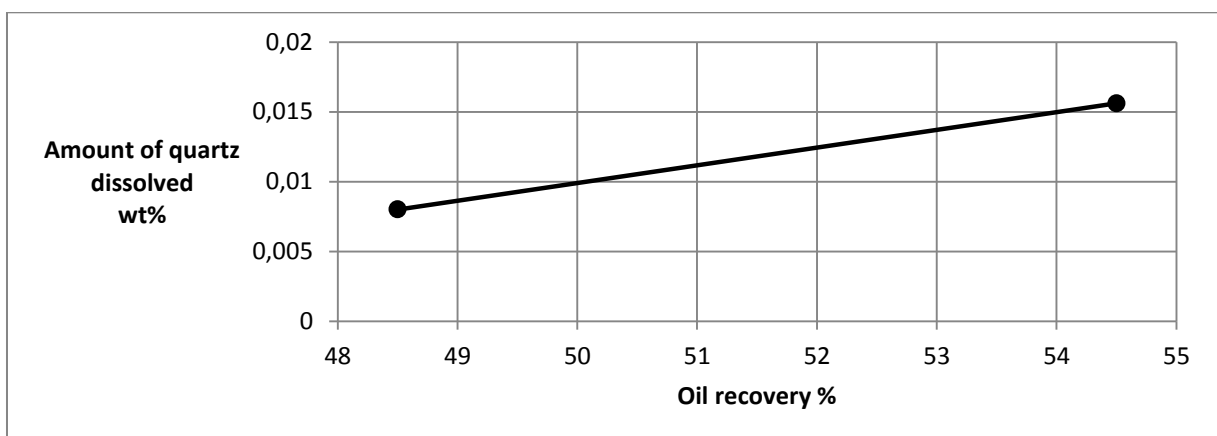


Figure 5-1: When the minerals present in the sandstone core used by RezaeiDoust et al. (2010) were forced in equilibrium with formation water followed by diluted seawater, an increase in dissolution of quartz was observed. When RezaeiDoust et al. (2010) injected formation water into Varg Core 1 & 2, followed by diluted seawater, and average increase in oil recovery of 6% was observed.

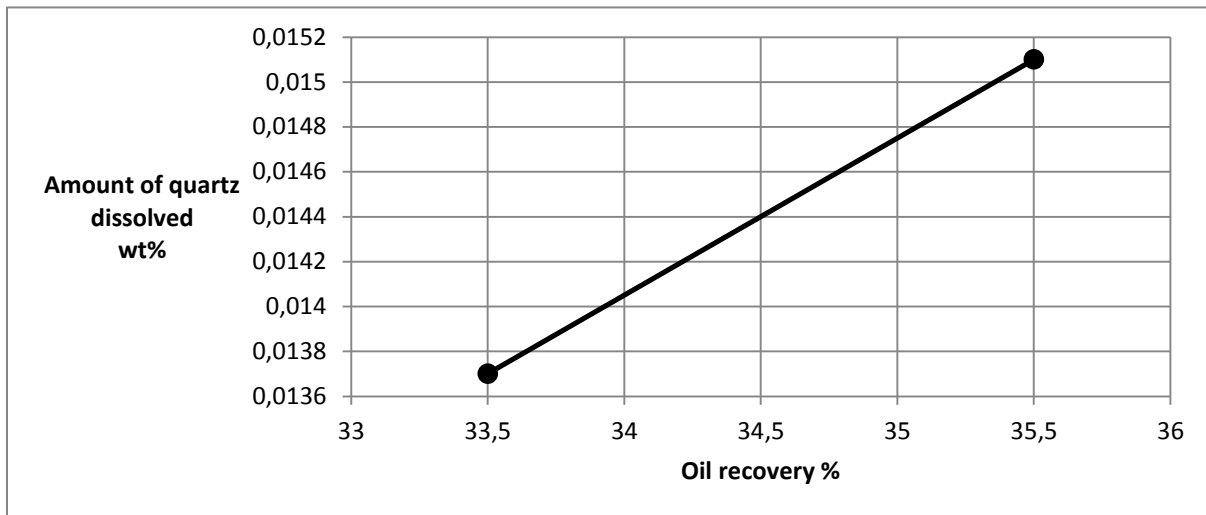


Figure 5-2: When the minerals present in the sandstone core used by RezaeiDoust et al. (2010) were forced in equilibrium with formation water diluted to 31000 ppm followed by formation water diluted to 1050 ppm, an increase in dissolution of quartz was observed. When RezaeiDoust et al. (2010) injected formation water diluted to 31000 ppm into Varg Core 8 & 9, followed by formation water diluted to 1050 ppm, and average increase in oil recovery of 2% was observed.

The increase in dissolution of quartz is larger when the 6% additional oil recovery is observed compared to the increase when 2 % additional oil recovery was observed, which also indicates quartz dissolution as a reason for the additional oil recovery.

The changes in exchanger composition when the minerals in the carbonate cores used by Yousef et al. (2011) were equilibrated with seawater and the different diluted versions were:

- when equilibrated with seawater, the concentration of Mg^{2+} increased while the concentration of Ca^{2+} decreased.
- when equilibrated with twice diluted seawater, the concentration of Mg^{2+} and Ca^{2+} increases, while the concentration of Na^{+} decreases
- when equilibrated with 10 times diluted seawater, the concentration of Mg^{2+} and Ca^{2+} keeps increasing, while the concentration of Na^{+} keeps decreasing
- when equilibrated with 20 and 100 times diluted seawater, the trend continues, the concentration of Mg^{2+} and Ca^{2+} keeps increasing while the concentration of Na^{+} decreases.

The oil recovery observed when injecting seawater could be explained by the exchange of cations observed in PHREEQC. It seems as Mg^{2+} replaces Ca^{2+} . This is in line with Austad et al.'s (2007) suggestion that seawater containing SO_4^{2-} causes this change in carbonates at temperatures over 70°C. Temperature used when conduction these results in PHREEQC was 100°C. Austad et al. (2007) suggested that Mg^{2+} displaces Ca^{2+} bonded to carboxylate groups present in oil, hence more oil is released. However, since the concentrations of both Mg^{2+} and Ca^{2+} increases when the minerals are equilibrated with diluted versions of seawater, results found in PHREEQC do not suggest cation exchange as an explanation for the low salinity effect observed.

The changes in exchanger composition when the minerals in the sandstone cores used by RezaeiDoust et al. were forced in equilibrium with formation water and secondly diluted seawater were:

- concentration of Na^+ , K^+ and Ca^{2+} decreased
- concentration of Mg^{2+} increasesd
- concentration of Sr^{2+} and Ba^{2+} is very small, and it stays constant

A low salinity effect of 6% of OOIP was observed by RezaeiDoust et al. (2010) when two of the cores were flooded with formation water followed by diluted seawater. An exchange of multivalent cations (Mg^{2+} replaces Ca^{2+}) is observed in PHREEQC when changing from formation water to diluted seawater, shown in figure 5-3. This is in line with Lager et al. (2008) suggestion that multivalent cation exchange can release additional oil components. On an oil-wet clay surface, multivalent cations will bond to polar compounds in the oil phase forming organo-metallic complexes. At the same time, some organic polar compounds will be adsorbed directly to the mineral surface, enhancing the oil wetness of the clay surface (Lager et at., 2008) During injection of low salinity brine, an exchange of multivalent cations will take place, removing organic polar compounds and organo-metallic complexes from the surface and replacing them with uncomplexed cations. These should then result in a more water-wet surface, resulting in an increase in oil recovery (Lager et al., 2008). However, it should be remembered that the ion exchange interactions PHREEQC describes the interactions between Mg^{2+} and Ca^{2+} with the surface, and not Mg^{2+} and Ca^{2+} bond with the surface and bond with the oil phase. But this is beyond the scope of this thesis to also include oil phase in the geochemical reactions.

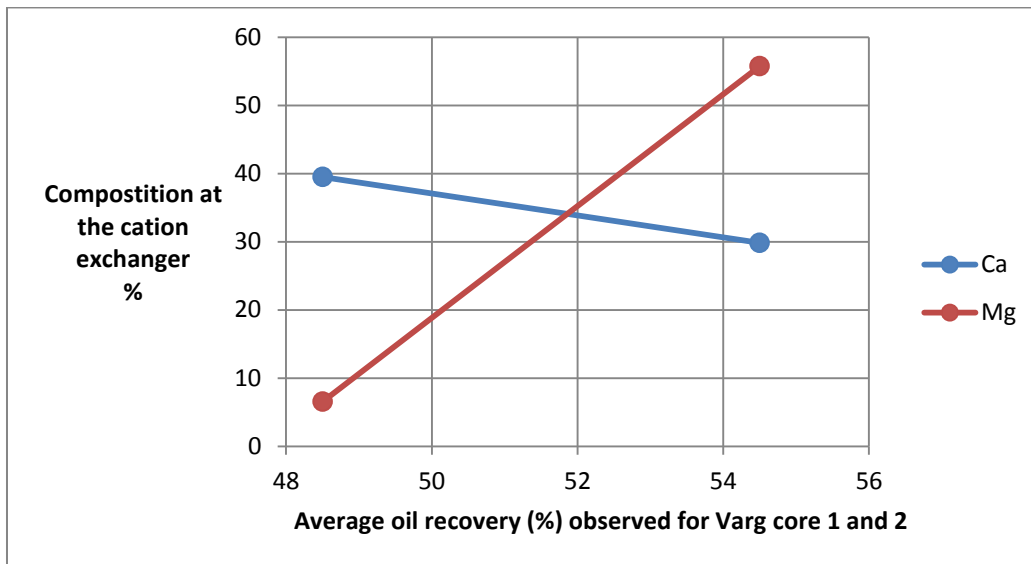


Figure 5-3: Ca^{2+} is replaced by Mg^{2+} when diluted seawater is used as the low saline brine.

The changes in the exchanger composition when the minerals in the sandstone cores used by RezaeiDoust et al. were equilibrated with formation water diluted to 31000 ppm followed by formation water diluted to 1050 ppm were:

- when equilibrated with formation water diluted to 31000 ppm, the concentration of Mg^{2+} and Ca^{2+} increases, while the concentration of Na^+ and K^+ decreases. The concentration of Ba^{2+} and Sr^{2+} is low and stays constant.
- when equilibrated with formation water diluted to 1050 ppm, the concentration of Mg^{2+} and Ca^{2+} keeps increasing, while the concentration of Na^+ and K^+ keeps decreasing. The concentration of Ba^{2+} and Sr^{2+} is low and stays constant.

Based on these results, multivalent cation exchange suggested by Lager at al. (2008), cannot explain the average oil recovery of 33.5% observed when injecting formation water diluted to 31000 ppm or the additional oil recovery of 2% that was observed when injecting formation water diluted to 1050 ppm.

The increase in dissolution of quartz in the sandstone observed when changing from high to low saline brine indicates that dissolution affects the increased oil recovery. However, more research is required before one can conclude that dissolution causes increased oil recovery. PHREEQC is not able to find out if rock dissolution occurs where the oil is adsorbed. When Hiorth et al. (2010) found that dissolution of calcite could have an effect on the rock wettability; they stated that a coupled scale model that could address where the dissolution inside the core takes place was needed for further investigations. In addition to this, results found did not indicate that dissolution lead to additional oil recovery in the carbonate corefloods performed by Yousef et al. (2011). With these results we can only conclude that mineral dissolution may be a cause of wettability alteration and increased oil recovery in sandstones.

The exchange of multivalent cations observed when sandstone minerals was equilibrated with diluted formation water followed by diluted seawater, indicates that cation exchange also affects the oil recovery in sandstones positively. However, this was not observed when using diluted formation water as the low saline brine. Therefore we can only conclude that results indicate that multivalent cation exchange affects the oil recovery in sandstones when diluted seawater is used as the low saline brine. More investigation is required before one can conclude that multivalent cation exchange is the mechanism leading to additional oil recovery with use of low salinity water. The results found in this thesis, give no information whether the released cations was bound to oil or not. More advanced modeling need to be done for that to be found.

There are several factors that possibly have affected the results found. PHREEQC was used to find the mineralogy of the cores by the use of formation water given in the papers of Yousef et al and RezaeiDoust et al. When formation water is brought from the reservoir to the surface it will go through changes that may affect the ionic composition of the formation water. Therefore there is a possibility that the mineralogy of the cores predicted by PHREEQC is not correct. Also, in the investigations studied, several cores were flooded, and average results of oil recovery observed were used. Potential differences between cores were not considered.

When doing calculations in PHREEQC, it was assumed that there is equilibrium between all species in the water and the minerals it is surrounding. No information is given of what happens before equilibrium is reached between the different species. Some reactions reaches equilibrium faster than others, and there might be dissolution or precipitation happening that cannot be shown.

6 Conclusions

Results found in this thesis does not give any clear answers of what causes the low salinity effect observed in the corefloods of Yousef et al. (2011) and RezaeiDoust et al. (2010). However, for some of the floods, results found in PHREEQC can indicate possible mechanisms.

Results found in PHREEQC showed correlation between dissolution of quartz and incremental oil recovery in sandstones. A model that can address where the dissolution inside the core takes place, and also include the oil phase is needed for further investigations.

We have found a correlation between multivalent cation exchange and incremental oil recovery in sandstones when seawater was used as the low salinity fluid. More advanced modeling, and experimental techniques is required if we are to find out whether the released cations was bound to oil or not. A correlation between multivalent cation exchange and incremental oil recovery was not observed when diluted formation water was used as the low salinity brine.

Mineral dissolution in carbonates as the mechanism leading to wettability alteration and increased oil recovery is questionable. Results can confirm Austad et al.'s (2007) suggestion that seawater containing SO_4^{2-} , causes Mg^{2+} to replace Ca^{2+} bonded to oil at temperatures over 70°C . This can however not explain the increased recovery observed when injecting diluted versions of seawater.

Results may also indicate that there are different mechanisms leading to additional oil recovery when flooding carbonates and sandstones with water of low salinity. This could also be the reason that there does not seem to be a consensus.

The work performed in this thesis clearly demonstrates that when injecting different brine chemistries through the cores, the brines induce changes in the rock texture and ion exchange. Further work should be to investigate which of these interactions are important for oil recovery. Possible ways of doing this would be to include oil components in the PHREEQC geochemical reactions or model the oil production curves with a Darcy scale model.

References

- Al-Shalabi, E. W., Sepehrnoori, K. and Delshad, M. (2013) *Mechanisms Behind Low Salinity Water Flooding in Carbonate Reservoirs*. Presented at SPE Western Regional & AAPG Pacific Section Meeting, 2012 Joint Technical Conference, April 19-25, 2013, Monterey, CA, USA.
- Alvedal, L. and Melberg, E. V. (2013) *Facts 2013 The Norwegian Petroleum sector*. Published at NPD's homepages: <http://www.npd.no/Publikasjoner/Faktahefter/Fakta-2013/>. [Read 04.06.2013]
- Anderson, W. G. (1986) *Wettability Literature Survey – Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability*. Journal of Petroleum Technology, 38 (10), 1125-1144.
- Appelo, C. A. J. and Postma, D. (2005) *Geochemistry, groundwater and pollution*. 2nd edition. London, CRC Press.
- Austad, T., RezaeiDoust, A. and Puntervold, T. (2010) *Chemical Mechanism of Low-Salinity Water Flooding in Sandstone Reservoirs*. Presented at SPE Improved Oil Recovery Symposium, 24-28 April, Tulsa, Oklahoma, USA.
- Austad, T., Strand, S., Høgnesen, E. J. and Zhang, P. (2005) *Seawater as IOR Fluid in Fractured Chalk*. Presented at SPE International Symposium on Oilfield Chemistry, 2-4 February 2005, The Woodlands, Texas.
- Austad, T., Strand, S., Madland, M. V., Puntervold, T. and Korsnes, R. I. (2007) *Seawater in Chalk: An EOR and Compaction Fluid*. SPE Reservoir Evaluation & Engineering, 11 (4), 648-654.
- Bjørsvik, B. T. (2012) *EOR er viktigst på lang sikt*. Article in Petromagasinet. Available at: <http://www.petro.no/petrono/arkiv/nyheter01/eor-er-viktigst-pa-lang-sikt/34722b51-3f4c-4388-a57c-3e8c4a456e62>. [Read 04.06.2013]
- Boye, N. C. (2006) *Kjemi og miljølære*. 3 utg. Oslo, Gyldendal Norsk Forlag AS.
- Brown, T. L., LeMay Jr., H. E., Bursten, B. E. and Murphy, C. J. (2009) *Chemistry: The central science*. 11th edition. Milan, Italy, Rotolito Lombarda S.p.A.
- Forrest, F. and Craig, Jr. (1971). *The Reservoir Engineering Aspects of Waterflooding*. SPE, Texas.
- Garrels, R. and Christ, C. L. (1965) *Solutions, minerals and equilibria*. Boston, USA, Jones and Bartlett Publishers.
- Green, D. W. and Willhite, G. P. (1998) *Enhanced oil recovery*. Volume 6. Texas, SPE Textbook Series.
- Gupta, R., Griffin Smith Jr., P., Hu, L., Willingham, T. W., Lo Cascio, M. L., Shyeh, J. J. and Harris, C. R. (2011) *Enhanced Waterflood Carbonate Reservoirs – Impact of Injection Water Composition*. Presented at SPE Middle East Oil and Gas Show and Conference, 25-28 September 2011, Manama, Bahrain.
- Hiorth, A., Cathles, L. M. and Madland, M. V. (2010) *The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability*. Springer.

- Khan, M. I. and Islam, M. R. (2007) *The Petroleum Engineering Handbook: Sustainable operations*. Houston, USA, Gulf Publishing Company.
- Lager, A., Webb, K. J., Black, C. J. J., Singleton, M. and Sorbie, K. S. (2008) *Low Salinity Oil Recovery – An Experimental Investigation*. PETROPHYSICS, 49 (1).
- Ligthelm, D. J., Gronsveld, Hofman, J. P., Brussee, N. J., Marcelis, F. and van der Linde, H. A. (2009) *Novel Waterflooding Strategy By Manipulation of Injection Brine Composition*. Presented at EUROPEC/EAGE Conference and Exhibition, 8-11 June 2009, Amsterdam, The Netherlands.
- McGuire, P. L., Chatham, J. R., Paskvan, F. K., Sommer, D. M. and Carini, F. H. (2005) *Low Salinity Oil Recovery: An exciting New EOR Opportunity for Alaska's North Slope*. Presented at SPE Western Regional Meeting, March 30 – April 01, 2005, Irvine, California.
- Merkel, B. J. and Planer-Friedrich, B. (2008) *Groundwater geochemistry: a practical guide to modeling of natural and contaminated aquatic systems*. 2nd edition. Berlin, Springer-Verlag.
- Misra, K. C. (2012) *Introduction to geochemistry: Principles and Applications*. UK, Wiley-Blackwell.
- Moe, O. B. (2013) Statement done in press release: *Utlyser nytt forskningscenter for økt utvinning*. Available at: <http://www.regjeringen.no/en/dep/oed/press-center/press-releases/2013/utlyser-nytt-forskningscenter-for-okt-ut.html?id=714382>. [Read 04.06.2013]
- Morrow, N. and Buckley, J. (2011) SPE, University of Wyoming. *Improved Oil Recovery by Low-Salinity Waterflooding*. Journal of Petroleum Technology, 63 (5), 106-112.
- Norsk olje og gass (2012). Article at factpages: *Økt utvinning fra eksisterende felt*. Author unknown. Available at <http://www.norskoljeoggass.no/no/Faktasider/Okt-utvinning/>. [Read 10.06.2013]
- Nyland, B. (2013) *Store gevinster å hente*. Published at NPD's homepages: <http://www.npd.no/Templates/OD/Article.aspx?id=4622>. [Read 04.06.2013]
- Parkhurst, D. L. and Appelo, C.A.J. (1999) *User's guide to PHREEQC (version 2) – a computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical calculations*. Denver, Colorado, U.S Department of the Interior.
- Pu, H., Xie, X., Yin, P. and Morrow, N. R. (2010) *Low-Salinity Waterflooding and Mineral Dissolution*. Presented at SPE Annual Technical Conference and Exhibition, 19-22 September 2010, Florence, Italy.
- RezaeiDoust, A., Puntervold, T. and Austad T. (2010) *A discussion of the Low-Salinity EOR Potential for a North Sea Sandstone Fields*. Presented at SPE Annual Technical Conference and Exhibition, 19-22 September 2010, Florence, Italy.

Schlumberger Oilfield Glossary: Primary Production. Available at:

<http://www.glossary.oilfield.slb.com/en/Terms.aspx?LookIn=term%20name&filter=primary%20production>. [Read 22.05.2013].

Skauge, Arne (2012) *Økt utvinning på norsk sokkel*. Presentation available at: www.forskningsradet.no. [Read 12.06.2013]

Tang, G. Q and Morrow, N. R. (1997) *Salinity, Temperature, Oil composition, and Oil Recovery by Waterflooding*. SPE Reservoir Engineering, 12 (4), 269-276.

Tang, G. Q and Morrow, N. R. (1999) *Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery*. Journal of petroleum science & engineering, 24, 99-11.

Webb, K. J., Black, C. J. J. and Al-Ajeel, H. (2004) *Low Salinity Oil Recovery – Log-Inject-Log*. Presented at SPE/DOE Symposium on Improved Oil Recovery, 17-21 April 2004, Tulsa, Oklahoma.

Yousef, A. A., Al-Saleh, S. and Al-Jawfi, M. (2012) *Improved/Enhanced Oil Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic Content*. Presented at SPE Improved Oil Recovery Symposium, 14-18 april 2012.

Yousef, A. A., Al-Saleh, S., Al-Kaabi, A. and Al-Jawfi, M. (2011) *Laboratory Investigation of the Impact of Injection-Water Salinity and Ionic Content on Oil Recovery From Carbonate Reservoirs*. SPE Reservoir Evaluation & Engineering, 14 (5), 578-593.

Zahid, A., Shapiro, A. and Skauge, A. (2012) *Experimental Studies of Low Salinity Flooding Carbonate: A New Promising Approach*. Presented at SPE EOR Conference at Oil and Gas West Asia, 16-18 April 2012, Muscat, Oman.

Zhang, P. and Austad, T. (2005) *Waterflooding in chalk: Relationship between oil recovery, new wettability index, brine composition and cationic wettability modifier*. Presented at SPE Europepec/EAGE Annual Conference, 13-16 June 2005, Madrid, Spain.

Zolotukhin, A. B. and Ursin, J. R. (2000) *Introduction to Petroleum Reservoir Engineering*. Kristiansand, Høyskoleforlaget AS.

Åm, K. (2010). *Økt utvinning på norsk kontinentalsokkel*. Olje og Energidepartementet, Oslo.

Appendix A Examples of manual solubility calculations

A.1 Calcite in pure water; system not connected to the atmosphere

To gain an understanding of how to perform solubility calculations it may be preferable to look at specific examples. Knowing how to do manual solubility calculations is important to gain a basic understanding of the underlying principles. I will go through some examples in detail and show how to do this. The examples is taken from “Solutions, minerals and equilibria” written by Garrel and Christ in 1965.

The first example shows how to decide the solubility of calcite when pure calcite, CaCO_3 , is put in pure water, H_2O , with negligible gas present. It is assumed that there will be equilibrium between calcite and water, as well as internal equilibrium of all ionic species in the solution. Pure water is defined as water where reactive gases such as carbon dioxide, CO_2 , have been swept out. The temperature is assumed to be 25°C and the pressure 1 bar.

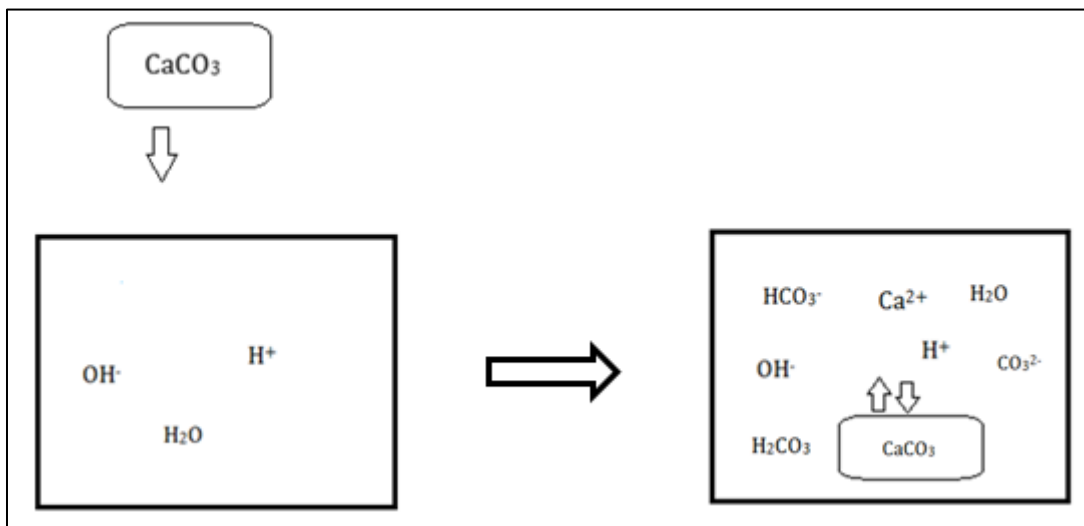
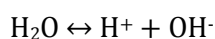


Figure A-1: Pure calcite is put in pure water

Pure water contains H_2O -molecules and the disassociated ions H^+ and OH^- . This is because one water molecule can donate a proton to another water molecule; a process which is called autoionization of water. H_2O -molecules react with each other to some degree and form equal amount of H^+ as OH^- . After some time H^+ -ions and OH^- -ions start to react with each other and form H_2O -molecules. After some time the amount of H_2O dissolved will equal the amount of H_2O formed. This is the definition of equilibrium, and the reaction can be written as follows (Brown et al., 2009):

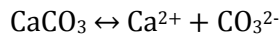


The distribution of species at equilibrium is given by the equilibrium constant:

$$K = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14.0} . \quad (A. 1)$$

The activity of H₂O is assumed to equal one. This can also be done in in dilute aqueous solutions. This constant is called the ion-product constant, K_w. It is applicable to any dilute aqueous solution and it is unaffected whether a solution is acidic or basic (Brown et al, 2009)

When calcite is placed in pure water there will be dissolved calcium ions, Ca²⁺, and carbonate ions, CO₃²⁻. When this reaction reaches equilibrium it can written as follows:



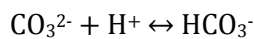
The distribution of species is given by the equilibrium constant:

$$K = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]} = 10^{-8.3} . \quad (A. 2)$$

CaCO₃ is a pure solid and the activity is therefore by definition considered to be one;

$$[CaCO_3] = 1.$$

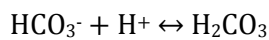
Some of the CO₃²⁻-ions dissolved will now combine with H⁺ in the water and form bicarbonate, HCO₃⁻. When this reaction reaches equilibrium it can be written as follows:



The distribution of species is given by the equilibrium constant:

$$K = \frac{[HCO_3^-]}{[H^+][CO_3^{2-}]} = 10^{10.3} . \quad (A. 3)$$

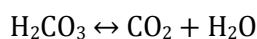
Some of the bicarbonate formed combines with H⁺ in the water and forms carbonic acid. When this reaction reaches equilibrium it is written as follows:



The distribution of species is given by the equilibrium constant:

$$K = \frac{[H_2CO_3]}{[H^+][HCO_3^-]} = 10^{6.4} . \quad (A. 4)$$

Some carbonic acid will break up into water and dissolved carbon dioxide. At equilibrium this reaction is written as follows:



In this example it is assumed that this is a saturated calcite solution in contact with excess calcite and that it is completely filling the container. Therefore the gas phase can be ignored, according Garrel and Christ.

The species of importance in this system is Ca^{2+} , CO_3^{2-} , HCO_3^- , H_2CO_3 , OH^- , H^+ , CaCO_3 and H_2O . The activity of H_2O and CaCO_3 is assumed to be one. The activities of Ca^{2+} , CO_3^{2-} , HCO_3^- , H_2CO_3 , OH^- and H^+ need to be found. The four equilibrium constants, A.1 – A.4, yield for this system.

Since there are six unknowns, there is a need for two more equations to solve all activities. The original water does not contain any carbonate species, so every carbonate specie in this solution must come from the calcite added. Since the calcite dissolve similar molal amount of calcium ions and carbonate ions it can be said that the molality of calcium in the solution must equal the sum of molalities of all species containing a carbonate ion. This can be expressed by writing a mass balance equation:

$$m_{\text{Ca}^{2+}} = m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{H}_2\text{CO}_3} \quad (\text{A.5})$$

Mass balance equations are fundamental in solubility calculations. Information about initial concentration of different species can give equations which will contribute to finding concentration of species in a system.

Another fundamental principle of solution chemistry is that positive and negative charges of the dissolved species in a solution must be equal to maintain electrical neutrality. The charge balance equation is written:

$$\sum_i z_i m_i = 0, \quad (\text{A.6})$$

where m_i is the molality and z_i is the charge of ion i . This equation is also fundamental in solubility calculations.

The sum of positive and negative charges in water must be equal, so the charge balance equation can be used for the solution:

$$2m_{\text{Ca}^{2+}} + m_{\text{H}^+} = 2m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} \quad (\text{A.7})$$

Now there are six equations to use and six unknowns to solve. A problem is that four of the equations are written in terms of activities while two are written in terms of concentrations. Another problem is that for the activity coefficients to be calculated, the ionic strength of the solution must be known, which requires knowledge of the concentrations, which is exactly what is trying to be solved.

A way to solve the problems is to perform an iteration procedure and do some assumptions. First it is assumed that the solution is ideal and that activities equals concentrations, in other words that $\gamma_i = 1$ for all species. When all the concentrations are calculated, the ionic strength of the solution can be calculated. With the ionic strength known, the individual activity coefficients can be calculated. If some of these differ from one, the concentrations should be calculated over again by using the calculated individual activity coefficients. With new values for concentration, the ionic strength should be calculated again to calculate new individual activity coefficients. This should be done repeatedly, until the approximations of concentrations show no appreciable differences.

A third problem is that solving six unknowns by using six equations will be very time consuming work. Simplifications are often very useful in chemical calculations, and any reasonable assumption can be made as long as the validity is tested afterwards.

Since both the carbonate ion and bicarbonate combines with H^+ , it is known that there is more OH^- in the system than H^+ . Since the concentration of OH^- will be relatively much larger than the concentration of H^+ , the molality of H^+ can be ignored in the charge balance equation. Neglecting terms is allowed in equations based on summations, which in this case would be the mass balance equation and the charge balance equation. Equation A.7 is now shortened down to:

$$2m_{Ca^{2+}} = 2m_{CO_3^{2-}} + m_{HCO_3^-} + m_{OH^-} \quad (A. 8)$$

Since there are more OH^- than H^+ , the solution must be basic; $pH > 7$.

Having an assumption about the pH, makes it possible to do an assumption about the carbonate species present. The sum of concentration of CO_3^{2-} , HCO_3^- and H_2CO_3 is constant. Based on this information and equilibrium constants A.3 and A.4, the amount of each carbonate specie present in a solution at a given sum can be found, for different pH-values. If the sum of the concentration of these three species is i.e. one, it can be written:

$$m_{CO_3^{2-}} + m_{HCO_3^-} + m_{H_2CO_3} = 1.$$

Now there are three equations and three unknowns, and the relative concentration of CO_3^{2-} , HCO_3^- and H_2CO_3 for different pH-values can be found, remembering that $pH = -\log[H^+]$. The result looks as follows:

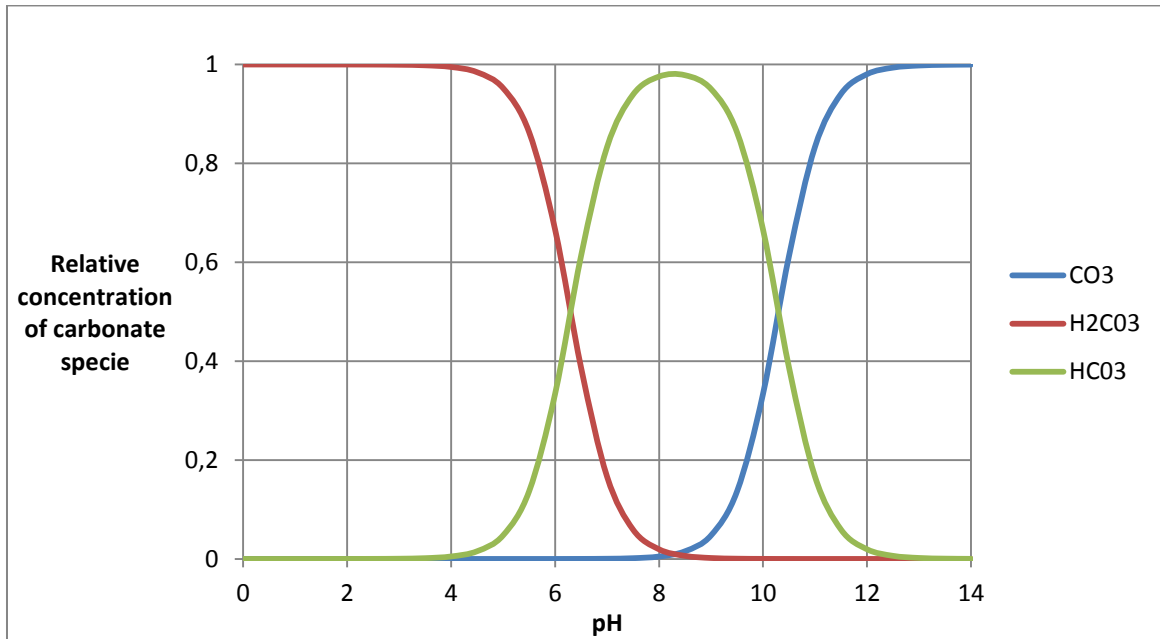


Figure A-2: Relative concentration of carbonate species at different pH-values.

According to this, when $\text{pH} > 7$, the concentration of carbonic acid, H_2CO_3 , is close to zero. When calculating the mass balance equation this value can be ignored, because it is so small relative to the other sizes involved.

Equation A.5 can now be written:

$$m_{\text{Ca}^{2+}} = m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} \quad (\text{A.9})$$

Multiplying equation (A.9) by two and subtracting from equation (A.8) give:

$$m_{\text{HCO}_3^-} = m_{\text{OH}^-} \quad (\text{A.10})$$

Expressing the four equilibrium equations, A.1 - A.4, in terms of m_{H^+} give the following equations:

$$m_{\text{OH}^-} = \frac{10^{-14.0}}{m_{\text{H}^+}} = m_{\text{HCO}_3^-}$$

$$m_{\text{CO}_3^{2-}} = \frac{10^{-24.3}}{(m_{\text{H}^+})^2}$$

$$m_{\text{Ca}^{2+}} = 10^{16} (m_{\text{H}^+})^2$$

$$m_{\text{H}_2\text{CO}_3} = 10^{-7.6} \text{ mol/kgw}$$

By using equation A.9, m_{H^+} can be calculated and then the other species' concentrations:

$$10^{16} (m_{H^+})^2 = \frac{10^{-24.3}}{(m_{H^+})^2} + \frac{10^{-14.0}}{m_{H^+}}$$

Using a solver in Microsoft Excel makes it possible to calculate m_{H^+} . Putting this value into the equilibrium equations makes it possible to calculate the other species' concentrations.

$$m_{H^+} = 10^{-9.95} \text{ mol/kgw}$$

$$m_{OH^-} = m_{HCO_3^-} = 10^{-4.05} \text{ mol/kgw}$$

$$m_{CO_3^{2-}} = 10^{-4.4} \text{ mol/kgw}$$

$$m_{Ca^{2+}} = 10^{-3.9} \text{ mol/kgw}$$

Now one has to start considering the error involved in assuming $[i] = m_i$. To calculate the activity coefficients we need to calculate the ionic strength, equation 3.3:

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} (10^{-9.95} \times 1^2 + 10^{-4.05} \times 1^2 + 10^{-4.05} \times 1^2 + 10^{-4.4} \times 2^2 + 10^{-3.9} \times 2^2) = 4.2 \times 10^{-4}$$

Knowing the ionic strength makes it possible to calculate the different individual activity coefficients by use of the Debye-Hückel equation, 3.4.

At 25°C the temperature dependent constants are $A = 0.5085$ and $B = 0.3201 \times 10^{-8}$.

The empirical ion-size parameter, \hat{a}_i , for the different ions is found from table A-1:

Table A-1: \hat{a}_i for the different ions (Garrel and Christ, 1965)

$\hat{a}_i \times 10^8$	Ion
2.5	Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Tl ⁺ , Ag ⁺
3.0	K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , NO ₃ ⁻
3.5	OH ⁻ , F ⁻ , HS ⁻ , BrO ₃ ⁻ , IO ₄ ⁻ , MnO ₄ ⁻
4.0-4.5	Na ⁺ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , HSO ₃ ⁻ , Hg ₂ ²⁺ , SO ₄ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻
4.5	Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻
5.0	Sr ²⁺ , Ba ²⁺ , Ra ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , WO ₄ ²⁻
6	Li ⁺ , Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺
8	Mg ²⁺ , Be ²⁺
9	H ⁺ , Al ³⁺ , Cr ³⁺ , trivalent rare earths
11	Th ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺

SOURCE: Adapted from I. M. Klotz, *Chemical Thermodynamics*. Englewood Cliffs, N.J., Prentice-Hall, 1950, p. 331.

Solving the Debye-Hückel equation give the following individual activity coefficients:

$$\gamma_{\text{Ca}^{2+}} = 0.91 = 10^{-0.04}$$

$$\gamma_{\text{CO}_3^{2-}} = 0.91 = 10^{-0.04}$$

$$\gamma_{\text{HCO}_3^-} = 0.98 = 10^{-0.0088}$$

$$\gamma_{\text{OH}^-} = 0.98 = 10^{-0.0088}$$

$$\gamma_{\text{H}^+} = 0.98 = 10^{-0.0088}$$

Since H_2CO_3 is a molecular specie the individual activity coefficient is one. The individual activity coefficients are close to one, so that is a sign that the approximation was pretty good.

The four equilibrium equations can now be written over again in terms of individual activity coefficients and molalities:

$$K = \frac{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{OH}^-} m_{\text{OH}^-}}{[\text{H}_2\text{O}]} = 10^{-14.0}$$

$$m_{\text{H}^+} m_{\text{OH}^-} = \frac{10^{-14}}{10^{-0.02}} = 10^{-13.98}$$

$$K = \frac{\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}} \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}}{[\text{CaCO}_3]} = 10^{-8.3}$$

$$m_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}} = \frac{10^{-8.3}}{10^{-0.08}} = 10^{-8.22}$$

$$K = \frac{\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}}{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}} = 10^{10.3}$$

$$\frac{m_{\text{HCO}_3^-}}{m_{\text{H}^+} m_{\text{CO}_3^{2-}}} = \frac{10^{10.3} 10^{-0.0088} 10^{-0.0088}}{10^{-0.0088}} = 10^{10.29}$$

$$K = \frac{m_{\text{H}_2\text{CO}_3}}{\gamma_{\text{H}^+} m_{\text{H}^+} \gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}} = 10^{6.4}$$

$$\frac{m_{\text{H}_2\text{CO}_3}}{m_{\text{H}^+} m_{\text{HCO}_3^-}} = 10^{6.4} 10^{-0.0088} 10^{-0.0088} = 10^{6.38}$$

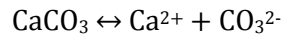
There are very small differences in these calculations, so the first estimated concentrations were close to the truth. Equation A.8 and A.9 still yields.

Equation A.9 in terms of m_{H^+} will now be slightly different:

$$10^{16.07} (m_{\text{H}^+})^4 = 10^{-24.29} + 10^{-14} m_{\text{H}^+}.$$

This will cause the equilibrium pH to be slightly lower, but the difference will be so small that the concentrations in the system can be assumed to be what we calculated them to be before considering the error involved in assuming activities to equal molalities.

The concentration of calcium in the water found was $10^{-3.9}$ mol/kgw. This means that there has been dissolution of calcite; there was no calcium in the water before the calcite was added. As observed in the reaction equation, 1 mol of calcite give 1 mol of Ca^{2+} and 1 mol of CO_3^{2-} :



If the amount of water in this example was given, one could have found the solubility of calcite. If one assume that there is 100 kg of water, then $10^{-3.9}$ mol/kgw * 100 kgw = $10^{-1.9}$ moles of calcite has dissolved in the water.

A.2 Calcite in pure water; system connected to the atmosphere

This example show how to decide the concentration of calcium in water, when a study is done on the equilibrium involved in a system where pure water contains calcite, and this system is connected to the atmosphere. The pH is arbitrarily determined and the ionic strength is given.

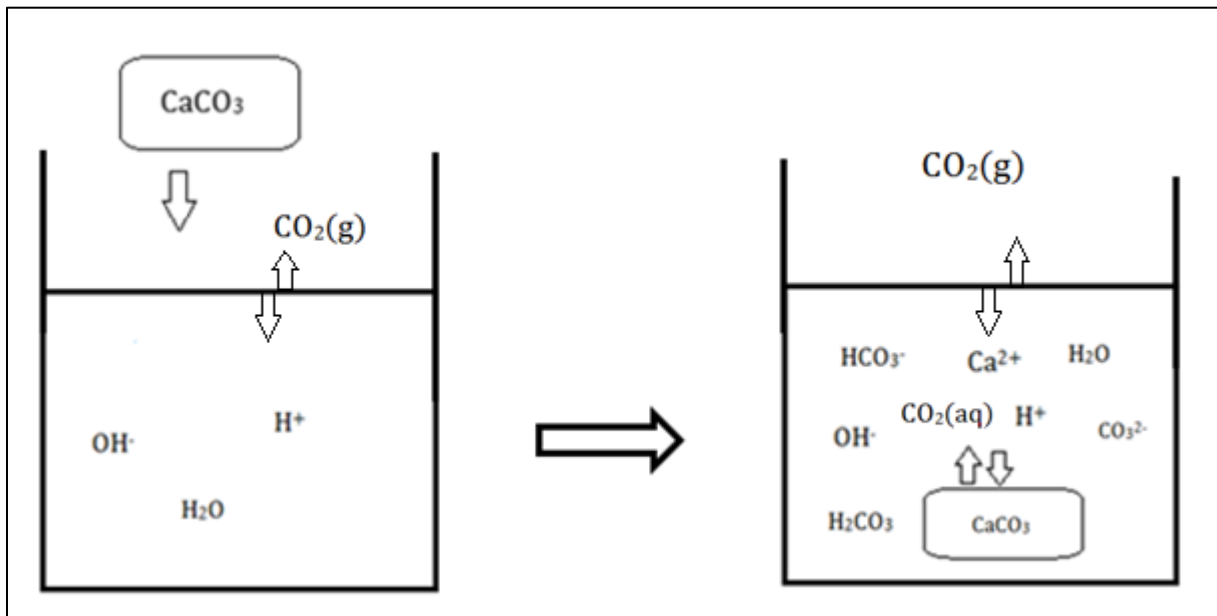
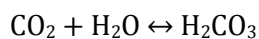
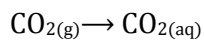


Figure A-3: Calcite is put water; system connected to the atmosphere.

When CO₂ dissolves in water, gaseous CO_{2(g)} becomes aqueous CO_{2(aq)}, and some of this associates with water molecules to form carbonate acid, H₂CO₃. The reactions can be written as follows:



The carbonic acid will dissociate in water, and it will stepwise release two protons. The concentration of the dissolved carbonate species therefore depend on the pH of the solution.

The four equilibrium equations A.1 - A.4 are also valid for this system. Since the system is in equilibrium with the atmosphere there is a fifth equilibrium equation that yields:

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{[\text{P}_{\text{CO}_2}]} = 10^{-1.47}. \quad (\text{A. 11})$$

For gaseous species the activity is the same as partial pressure. It is known that in the atmosphere the partial pressure of CO₂ is approximately 10^{-3.5} bar. This makes it possible to calculate the activity of H₂CO₃.

$$[\text{H}_2\text{CO}_3] = 10^{-1.47} 10^{-3.5} = 10^{-4.97}$$

The pH is given to be 10, and the ionic strength 0.10.

Since pH is known, the activity of OH⁻ and H⁺ is also known; [OH⁻] = 10⁻⁴ and [H⁺] = 10⁻¹⁰. What we need to find out is the activity of HCO₃⁻, CO₃²⁻ and Ca²⁺. Using equations A.2 – A.4:

$$m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}} \gamma_{\text{CO}_3^{2-}} = 10^{-8.3}$$

$$\frac{m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{[\text{H}^+] m_{\text{CO}_3^{2-}} \gamma_{\text{CO}_3^{2-}}} = 10^{10.3}$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{H}^+] m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}} = 10^{6.4}$$

The activity coefficients can then be calculated using the Debye-Hückel equation, 3.4.

Then it is found that $\gamma_{\text{Ca}^{2+}} = 10^{-0.39}$, $\gamma_{\text{CO}_3^{2-}} = 10^{-0.43}$ and $\gamma_{\text{HCO}_3^-} = 10^{-0.11}$.

Putting these values in to the equations A.2 – A.4, makes it possible to calculate the concentrations.

$$m_{\text{HCO}_3^-} = \frac{[\text{H}_2\text{CO}_3]}{10^{6.4} \gamma_{\text{HCO}_3^-} [\text{H}^+]} = 10^{-1.26} \text{ mol/kgw}$$

$$m_{\text{CO}_3^{2-}} = \frac{m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{10^{10.3} \gamma_{\text{CO}_3^{2-}} [\text{H}^+]} = 10^{-1.24} \text{ mol/kgw}$$

$$m_{\text{Ca}^{2+}} = \frac{10^{-8.3}}{\gamma_{\text{Ca}^{2+}} m_{\text{CO}_3^{2-}} \gamma_{\text{CO}_3^{2-}}} = 10^{-6.24} \text{ mol/kgw}$$

The concentration of calcium found could also in this case give the solubility of calcite.

Appendix B Databases in PHREEQC

When a basic understanding of how to do manual solubility calculations is obtained, calculation of ion activities, ion molalities, saturation states and other hydrogeochemical calculations can be done in PHREEQC. As shown, manual solubility calculations requires much time since it often involves several iterations. PHREEQC has become the standard for doing these types of calculations. PHREEQC was developed for calculation of “real world” hydrogeochemistry and is a powerful tool for modeling data (Appelo and Postma, 2005).

The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces, but also includes the capability to model kinetic reactions with rate equations that are completely user-specified in the form of basic statements (Parkhurst and Appelo, 1999).

There are different thermodynamic databases distributed with PHREEQC. These are:

- iso.dat
- llnl.dat
- minteq.dat
- minteq.v4.dat
- phreeqc.dat
- pitzer.dat
- sit.dat
- wateq4f.dat.

Thermodynamic databases are the primary source of information of all geochemical modeling programs (Merkel and Planer-Friedrich, 2008). A database contains definitions of chemical species, complexes, mineral solubilities etc. which are needed to do the calculations. The need for different databases is that some elements, species or constant that are needed for a specific problem might be unavailable in one or more of the databases.

One of the databases; phreeqc.dat, will be explained to gain an understanding of what information may be found in a database, and how it is given. It contains definitions of chemical species, complexes, mineral solubilities etc. and can be viewed by clicking on the database tab. The database is structured by a number of keywords, each followed by chemical definitions and constants needed to do the calculations (Appelo and Postma, 2005).

The first keyword is SOLUTION_MASTER_SPECIES and defines the elements in solution. The first column gives the elements name. Elements with several redox levels may be repeated with the number of electrons lost. The second column lists the aqueous species that are used primarily in the speciation calculation. The third column gives the contribution of that species to the alkalinity. The alkalinity is defines as the amount of acid that is needed to bring the pH down to about 4.5. The next two columns give the chemical formula that is used to convert grams into moles, and the atomic weight of the element (Appelo and Postma, 2005).

SOLUTION_MASTER_SPECIES					
#	#element	species	alk	gfw_formula	element_gfw
#	Ca	Ca+2	0.0	Ca	40.08
	Mg	Mg+2	0.0	Mg	24.312
	Na	Na+	0.0	Na	22.9898
	K	K+	0.0	K	39.102
	Fe	Fe+2	0.0	Fe	55.847
	Fe(+2)	Fe+2	0.0	Fe	
	Fe(+3)	Fe+3	-2.0	Fe	
	Mn	Mn+2	0.0	Mn	54.938
# etc...					

The second keyword, SOLUTION_SPECIES, defines the various aqueous complexes. These are tabulated in the form of an association reaction, with log_k, the association constant. Changes of log_k with temperature are calculated from the reaction enthalpy delta_h or with an analytical expression. The different options to calculate the activity coefficient from the ionic strength are controlled by the parameter -gamma. For major ions the Truesdell-Jones equation is used, and the two parameters A and B follows -gamma. For minor ions the Debye-Hückel equation is used, and a is given as the first parameter following gamma. If the line -gamma is absent then the Davies Equation is used. For neutral species, like uncharged complexes and gases, PHREEQC uses $\log \gamma = 0.1I$ (Appelo and Postma, 2005).

SOLUTION_SPECIES					
H+ = H+		log_k	0.0		
		-gamma	9.0	0.0	
Ca+2 = Ca+2		log_k	0.0		
		-gamma	5.0	0.1650	
Ca+2 + CO3-2 = CaCO3		log_k	3.224		
		delta_h	3.545	kcal	
# etc...					

Keyword PHASES lists minerals and gases for which saturation indices are calculated. The equations are written as dissociation reactions, therefore log_k for dissociation reaction. The variation of log_k with temperature is again calculated from the reaction enthalpy or from an analytical expression.

```

PHASES
Calcite
  CaCO3 = CO3-2 + Ca+2
  log_k          -8.48
  delta_h        -2.297 kcal
  -analytic      -171.9065      -0.077993      2839.319      71.595
# etc...

```

Keyword "EXCHANGE-MASTER_SPECIES" followed by exchange half-reactions under keyword "EXCHANGE_SPECIES" follows next, which is necessary data if we are to calculate exchanger composition. The exchanger composition can be calculated by combining the mass action expressions with the mass balance for the sum of exchangeable cations.

```

EXCHANGE_MASTER_SPECIES
  X      X-
EXCHANGE_SPECIES
  X- = X-
  log_k  0.0

  Na+ + X- = NaX
  log_k  0.0
  -gamma 4.0      0.075

  Ca+2 + 2X- = CaX2
  log_k  0.8
  -gamma 5.0      0.165
# etc...

```

The last keywords in the database is "SURFACE_MASTER_SPECIES" followed by keyword "SURFACE_SPECIES". "SURFACE_MASTER_SPECIES" is the keyword used to define the correspondence between surface binding-site names and surface master species. «SURFACE_SPECIES» is the keyword data used to define a reaction and log K for each surface species, including surface master species (Parkhurst and Appelo, 1999).

```
SURFACE_MASTER_SPECIES
  Hfo_s  Hfo_sOH
  Hfo_w  Hfo_wOH

SURFACE_SPECIES

# strong binding site--Hfo_s,

  Hfo_sOH + H+ = Hfo_sOH2+
  log_k    7.29    # = pKa1,int

# weak binding site--Hfo_w

  Hfo_wOH + H+ = Hfo_wOH2+
  log_k    7.29    # = pKa1,int

# etc...
```

Appendix C Examples of solubility calculations in PHREEQC

C.1 Calcite in pure water; system not connected to the atmosphere

The example gone through in A.1 can be calculated in PHREEQC. It was the system where pure calcite was put in pure water, with negligible gas phase present. The concentration of the species in the water at equilibrium with calcite was calculated.

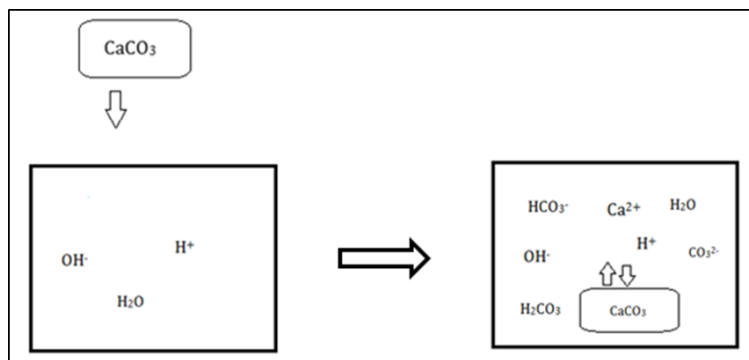


Figure C-1: Pure calcite put in pure water

With keyword `solution`, the initial water solution is specified. In this case it is pure water with $\text{pH} = 7$, $\text{density} = 1$ and the temperature is 25°C . This is written as follows:

```
SOLUTION 1
units      mmol/L
pH         7.0 charge    #default pH = 7.7 is an arbitrary number.
density    1.0          #density in kg/L, default = 1 kg/L.
temp      25.0         #temperature in degrees Celcius, default = 25°C.
pe         4.0         #pe = -log(electron activity), default = 4.
```

Information followed by “#” is not read by the code. By writing “`pH 7.0 charge`”, the code is going to adapt the PH to obtain charge balance for the final solution. Therefore one can say that 7.0 is an arbitrary number. If this was not pure water, the amount of other species present could have been added in solution.

A solution can be equilibrated with minerals assembled together in keyword `equilibrium phases`. In this case calcite is going to be equilibrated with the pure water. This is written as follows:

```
EQUILIBRIUM_PHASES 1
Calcite      0.0 100    # saturation index = 0, amount of calcite added = 100 mol.
```

The input file will look as follows:

```
SOLUTION 1
units      mmol/L
pH         7.0 charge      #default pH = 7.7 is an arbitrary number.
density    1.0            #density in kg/l, default = 1kg/L.
temp       25.0          #temperature in degrees Celcius, default = 25°C.
pe         4.0            #pe = -log(electron activity), default =4.
EQUILIBRIUM_PHASES 1
Calcite    0.0 100        # saturation index = 0, amount of calcite added = 100 mol.
END
```

The output file we get looks as follows:

```
Input file: C:\Users\Tale\AppData\Local\Temp\phrq0000.tmp
Output file: C:\Users\Tale\Desktop\Master\Problem1\case1.out
Database file: C:\Program Files (x86)\Phreeqc2\Databases\Phreeqc.dat
-----
Reading data base.
-----
SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
PHASES
EXCHANGE_MASTER_SPECIES
EXCHANGE_SPECIES
SURFACE_MASTER_SPECIES
SURFACE_SPECIES
RATES
END
-----
Reading input data for simulation 1.
-----
SOLUTION 1
units      mmol/L
pH         7.0 charge
density    1.0
temp       25.0
pe         4.0
EQUILIBRIUM_PHASES 1
Calcite    0.0 100
END
-----
Beginning of initial solution calculations.
-----
Initial solution 1.
-----Solution composition-----
Elements      Molality    Moles

Pure water

-----Description of solution-----
pH =          7.000    Charge balance
pe =          4.000
Specific Conductance (uS/cm, 25 oC) = 0
Density (g/cm3) = 0.99705 (Millero)
Activity of water = 1.000
Ionic strength = 1.001e-07
Mass of water (kg) = 1.000e+00
Total alkalinity (eq/kg) = 3.121e-18
Total carbon (mol/kg) = 0.000e+00
```

Total CO2 (mol/kg) =				0.000e+00		
Temperature (deg C) =				25.000		
Electrical balance (eq) =				-3.121e-18		
Percent error, 100*(Cat- An)/(Cat+ An) =				-0.00		
Iterations =				2		
Total H =				1.110124e+02		
Total O =				5.550622e+01		
-----Distribution of species-----						
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	
OH-	1.001e-07	1.001e-07	-7.000	-7.000	-0.000	
H+	1.001e-07	1.001e-07	-7.000	-7.000	-0.000	
H2O	5.551e+01	1.000e+00	1.744	-0.000	0.000	
H(O)	1.417e-25					
H2	7.087e-26	7.087e-26	-25.150	-25.150	0.000	
O(O)	0.000e+00					
O2	0.000e+00	0.000e+00	-42.081	-42.081	0.000	
-----Saturation indices-----						
Phase	SI	log IAP	log KT			
H2(g)	-22.00	-25.15	-3.15	H2		
H2O(g)	-1.51	-0.00	1.51	H2O		
O2(g)	-39.19	-42.08	-2.89	O2		

Beginning of batch-reaction calculations.						

Reaction step 1.						
Using solution 1.						
Using pure phase assemblage 1.						
-----Phase assemblage-----						
Moles in assemblage						
Phase	SI	log IAP	log KT	Initial	Final	Delta
Calcite	0.00	-8.48	-8.48	1.000e+02	1.000e+02	-1.227e-04
-----Solution composition-----						
Elements	Molality	Moles				
C	1.227e-04	1.227e-04				
Ca	1.227e-04	1.227e-04				
-----Description of solution-----						
pH =				9.910	Charge balance	
pe =				7.967	Adjusted to redox equilibrium	
Specific Conductance (uS/cm, 25 oC) =				37		
Density (g/cm3) =				0.99706	(Millero)	
Activity of water =				1.000		
Ionic strength =				3.848e-04		
Mass of water (kg) =				1.000e+00		
Total alkalinity (eq/kg) =				2.454e-04		
Total CO2 (mol/kg) =				1.227e-04		
Temperature (deg C) =				25.000		
Electrical balance (eq) =				5.510e-16		
Percent error, 100*(Cat- An)/(Cat+ An) =				0.00		
Iterations =				17		
Total H =				1.110124e+02		
Total O =				5.550658e+01		
-----Distribution of species-----						
Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	

OH-	8.316e-05	8.131e-05	-4.080	-4.090	-0.010
H+	1.258e-10	1.231e-10	-9.900	-9.910	-0.009
H2O	5.551e+01	1.000e+00	1.744	-0.000	0.000
C(-4)	0.000e+00				
CH4	0.000e+00	0.000e+00	-126.272	-126.272	0.000
C(4)	1.227e-04				
HCO3-	8.315e-05	8.132e-05	-4.080	-4.090	-0.010
CO3-2	3.386e-05	3.098e-05	-4.470	-4.509	-0.039
CaCO3	5.564e-06	5.565e-06	-5.255	-5.255	0.000
CaHCO3+	1.134e-07	1.110e-07	-6.945	-6.955	-0.010
CO2	2.251e-08	2.251e-08	-7.648	-7.648	0.000
Ca	1.227e-04				
Ca+2	1.169e-04	1.069e-04	-3.932	-3.971	-0.039
CaCO3	5.564e-06	5.565e-06	-5.255	-5.255	0.000
CaOH+	1.474e-07	1.441e-07	-6.831	-6.841	-0.010
CaHCO3+	1.134e-07	1.110e-07	-6.945	-6.955	-0.010
H(0)	2.496e-39				
H2	1.248e-39	1.248e-39	-38.904	-38.904	0.000
O(0)	5.352e-15				
O2	2.676e-15	2.676e-15	-14.572	-14.572	0.000
-----Saturation indices-----					
Phase	SI	log IAP	log KT		
Aragonite	-0.14	-8.48	-8.34	CaCO3	
Calcite	0.00	-8.48	-8.48	CaCO3	
CH4(g)	-123.41	-126.27	-2.86	CH4	
CO2(g)	-6.18	-7.65	-1.47	CO2	
H2(g)	-35.75	-38.90	-3.15	H2	
H2O(g)	-1.51	-0.00	1.51	H2O	
O2(g)	-11.68	-14.57	-2.89	O2	

End of simulation.					

Reading input data for simulation 2.					

End of run.					

The output can be divided into two parts. First shown is solution composition, solution description (in terms of pH, density, ionic strength, alkalinity etc), distribution of species and saturation indices for the solution before it is equilibrated with calcite. The second part starts with information about the phase the solution is to be equilibrated with, in this case calcite. Then, as for initial solution, it is shown solution composition, solution description, distribution of species and the solution when equilibrated with calcite.

The concentrations at equilibrium calculated manually was $m_{\text{OH}^-} = m_{\text{HCO}_3^-} = 10^{-4.05}$ mol/kgw, $m_{\text{CO}_3^{2-}} = 10^{-4.4}$ mol/kgw and $m_{\text{Ca}^{2+}} = 10^{-3.9}$ mol/kgw. The first approximation of m_{H^+} was $m_{\text{H}^+} = 10^{-9.95}$ mol/kgw, but it was concluded that the concentration probably was closer to $10^{-9.9}$.

The concentration at equilibrium calculated in PHREEQC is $m_{\text{OH}^-} = m_{\text{HCO}_3^-} = 10^{-4.08}$ mol/kgw, $m_{\text{CO}_3^{2-}} = 10^{-4.47}$ mol/kgw, $m_{\text{Ca}^{2+}} = 10^{-3.93}$ mol/kgw and $m_{\text{H}^+} = 10^{-9.9}$ mol/kgw. This is very similar results to the ones manually calculated. Some of the equilibrium constants used in PHREEQC is slightly different from the equilibrium equations used in chapter A.1 and A.2, and this might be the reason for the small differences. PHREEQC default assumes one kg of water. It therefore states that the molality of calcium in water equals the amount of calcite that has been dissolved.

These concentrations were calculated using the database phreeqc.dat. The calculations were done using all different databases to compare the results.

	manual	phreeqc	Iso	llnl	Minteq	minteq .v4	Pitzer	Sit	wateq 4f
m_{OH^-} (mol/kgw)	$10^{-4.05}$	$10^{-4.08}$	$10^{-4.07}$	$10^{-4.09}$	$10^{-4.08}$	$10^{-4.08}$	$10^{-4.05}$	$10^{-4.08}$	$10^{-4.08}$
$m_{\text{HCO}_3^-}$ (mol/kgw)	$10^{-4.05}$	$10^{-4.08}$	$10^{-4.08}$	$10^{-4.09}$	$10^{-4.08}$	$10^{-4.07}$	$10^{-4.05}$	$10^{-4.08}$	$10^{-4.08}$
$m_{\text{CO}_3^{2-}}$ (mol/kgw)	$10^{-4.4}$	$10^{-4.47}$	$10^{-4.47}$	$10^{-4.5}$	$10^{-4.46}$	$10^{-4.47}$	$10^{-4.42}$	$10^{-4.47}$	$10^{-4.47}$
$m_{\text{Ca}^{2+}}$ (mol/kgw)	$10^{-3.9}$	$10^{-3.93}$	$10^{-3.93}$	$10^{-3.95}$	$10^{-3.92}$	$10^{-3.93}$	$10^{-3.89}$	$10^{-3.93}$	$10^{-3.93}$
m_{H^+} (mol/kgw)	$10^{-9.}$ – $10^{-9.5}$	$10^{-9.9}$	$10^{-9.9}$	$10^{-9.9}$	$10^{-9.9}$	$10^{-9.89}$	$10^{-9.92}$	$10^{-9.9}$	$10^{-9.9}$

Table C-1: Concentrations given by different databases

All databases give very similar concentration of the species of interest. The database which gives results most similar to the ones manually calculates is pitzer. There are some elements and species that are unavailable in pitzer, which will be needed for later calculations. Therefore phreeqc will be chosen as the database for further calculations.

C.2 Calcite in pure water; system connected to the atmosphere

The second example was the equilibrium involved in the system where pure water contains calcite, and the system is connected to the atmosphere. The pH was arbitrarily determined to 10, and the ionic strength was given to be 0.10. The concentration of the calcium ion in the water was calculated. In the atmosphere the partial pressure of CO₂ is 10^{-3.5} bar.

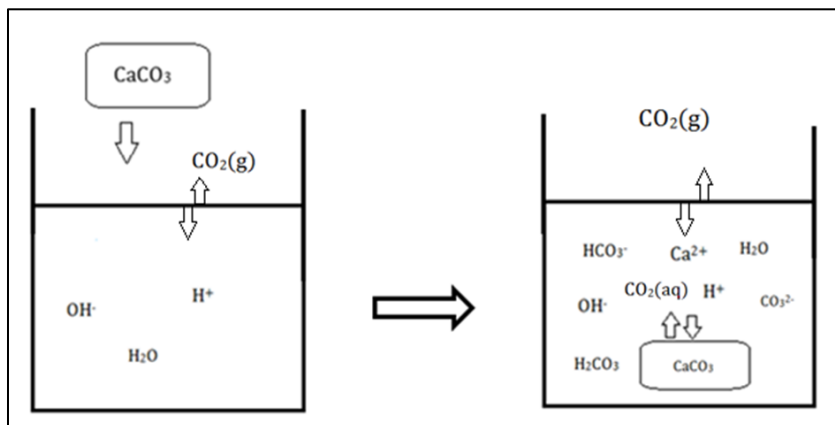


Figure C-2: Calcite put in pure water; system connected to the atmosphere

The problem is specified in the input file as follows:

```
SOLUTION 1
units      mmol/L
pH         10
density    1
temp       25
Ca         1e-4 Calcite 0.0 #adapt calcium ion to be in equilibrium with calcite, 1e-4 is a random value
C(4)      1e-4 CO2(g) -3.5 #adapt carbonate species to be in equilibrium with CO2, 1e-4 is a random value
END
```

The pure water is here being equilibrated with calcite and CO₂ in keyword "SOLUTION". This is because if it had been equilibrated in keyword "EQUILIBRIUM_PHASES" the pH would have changed. As seen, a solution can also be equilibrated with gases. The gas pressure can be varied, setting SI. The SI is equal to log(gas pressure/1 atm), and in the atmosphere the partial pressure of CO₂ is approximately 10^{-3.5} atm.

Parameters not mentioned in solution, is assumed by the code to have the default value. So in this case, *pe* is considered to be 4. Since the default value of density is 1, and the one for temperature is 25, it could have been left out in the input file. The concentration of the calcium ion found when this example was calculated manually was $m_{Ca^{2+}} = 10^{-6.24}$ mol/kgw. When calculated in PHREEQC the concentration found is $m_{Ca^{2+}} = 10^{-6.35}$ mol/kgw, which is almost 25% less than concentration found manually.

One reason can be differences between the equilibrium constants. Another one can be that the ionic strength is assumed to be 0.10 in the manual calculations, and calculations are done by using this value. This value cannot be given in the input file in PHREEQC and it is calculated to be 0.1681. This will lead to different individual activity coefficients which will give different values for concentration. In the description of solution we see that there is an electrical unbalance, which means that there is something wrong. This example is an example of a hypothetical condition, so it is not that important to focus on the difference in answer. This is shown as an example of how to find the concentration of a specie in a system where it is believed that equilibrium is already reached between minerals, water and the atmosphere.

Appendix D PHREEQC input files

```
SOLUTION 1
temp      100
density   1.1083
units     mmol/kgw
pH        7 charge      #adapt pH to electric neutrality
Na        2588
Ca        1 Calcite 0    #adapt calcium concentration to equilibrium with calcite
Mg        1 Dolomite 0  #adapt magnesium concentration to equilibrium with dolomite
S         1 Anhydrite 0 #adapt sulfate concentration to equilibrium with anhydrite
Si        1 Quartz 0    #adapt silicon concentration to equilibrium with quartz
Cl        3725
C(4)     5.801 as HCO3
END
```

Figure D-1: Input file when trying to find mineralogy. This example is from when I was trying to find out whether calcite, dolomite, anhydrite and quartz were present in the carbonate core or not.

```
SOLUTION 1
Temp      100
Density   1.0152
units     mmol/kgw
Na        796
Ca        16.2
Mg        86.8
S         44.65
Cl        908.3
C(4)     1.97 as HCO3
EQUILIBRIUM_PHASES 1
Calcite   0      100    #saturation index & amount
Talc     0      100    #saturation index & amount
Anhydrite 0      100    #saturation index & amount
Quartz   0      100    #saturation index & amount
END
```

Figure D-2: Input file when equilibrating solution with minerals. This example is from when I was equilibrating seawater with minerals present in the carbonate core.

```

SOLUTION 1
Temp          100
Density       1.1083
units         mmol/kgw
pH            7 charge
Na            2588
Ca            1 Calcite 0
Mg            1 Talc 0
S             1 Anhydrite 0
Si            1 as SiO2 Quartz 0
Cl            3725
C(4)         5.801 as HCO3
END

EXCHANGE 1
X              1.1e-3  # 1.1 mmol X- (assumed value)
-equilibrate  1        # equilibrate with SOLUTION 1
END

```

Figure D-3: Input file showing how to find the exchanger composition. This example shows how I found the exchanger composition of the carbonate core when it was surrounded by field connate water.

```

SOLUTION 1
temp          100
density       1.0152
units         mmol/kgw
Na            796
Ca            16.2
Mg            86.8
S             44.65
Cl            908.3
C(4)         1.97 as HCO3

EQUILIBRIUM_PHASES 1
Calcite       0        100
Talc          0        100
Anhydrite    0        100
Quartz        0        100
END

EXCHANGE 1
X              1.1e-3
-equilibrate  1
END

```

Figure D-4: Input file showing how to find the exchanger composition. This example shows how I found the exchanger composition of the carbonate core when the minerals were equilibrated with seawater.