

**AES/PE/14-20 Calcite dissolution behaviour during low salinity
water flooding in carbonate rock**

28/08/2014 Liselotte den Ouden



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Date : 28 August 2014

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TA Report number : AES/PE/14-20

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MASTER THESIS

Calcite dissolution behaviour during low salinity water flooding in carbonate rock

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Petroleum Engineering and Geosciences

August 2014

TU DELFT

Abstract

CITG

Petroleum Engineering and Geosciences

Master of Science

Calcite dissolution behaviour during low salinity water flooding in carbonate rock

by Liselotte den Ouden

Low salinity water flooding (LSF) has been proved to be a promising enhanced oil recovery method for sandstone reservoirs. The efficiency of LSF in carbonate reservoirs has not been proven completely yet, because there are still uncertainties about the LSF recovery mechanism in carbonate. From experimental studies, it was shown that wettability alteration, due to salinity reduction, is able to mobilize the remaining oil. Some studies attributed the wettability alteration by LSF to Calcite dissolution. Furthermore, Calcite dissolution can influence the salinity and pH of injected brines, and hence the oil recovery. However, there is a lack of experimental data on the Calcite dissolution effect of LSF in carbonate rock. The objective of this experimental study was to get a better understanding of the Calcite dissolution behaviour and how it might affect the oil recovery. Bulk and coreflood experiments have been performed; the experimental data was history matched with the use of PHREEQC. Calcite dissolution decreased with decreasing P_{CO_2} and increased with decreasing pH and increasing NaCl salinity from 500-2000PPM. Increasing the injection rate reduced the interaction time and therefore Calcite dissolution did not reach equilibrium in coreflood at high rates. Calcite dissolution from chalk matched with the Calcite dissolution from pure Calcite, while Calcium concentration in effluent from limestone was higher. The two-phase coreflood experiment confirmed that Calcite dissolution occurs as well if oil is present in the porous media, but showed lower values than in single-phase coreflood experiment. pH increased from 5-6 to 9.5 due to Calcite dissolution, which might have an effect on the rock and oil surface charges, and hence oil recovery improvement. The effluent of the two-phase coreflood showed that an emulsion was formed, which suggested formation of in-situ surfactants. From CT scans, micro-CT scans and material mass balance calculations an increase in porosity around 1% was observed. The increase in the total dissolved species due to Calcite dissolution was not significant, which will not harm LSF effect.

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Physical Constants

Avogadro's number	N_a	$6.022 \cdot 10^{23}$	mol^{-1}
Faraday constant	F	96485	$C\ mol^{-1}$
Gas constant	R	8.314	$J\ K^{-1}\ mol^{-1}$
Charge of electron	q_e	$1.602 \cdot 10^{-19}$	C

Symbols

γ_i	Activity coefficient	—
	Interfacial tension	$10^{-5} N/m$
ϵ	dielectric constant	$F m^{-1}$
$\frac{1}{\kappa}$	EDL thickness	m
σ_{DL}	EDL charge	$C m^{-2}$
θ	Contact angle	$0 - 180^\circ$
Ψ	Potential in EDL	V
Ψ_0	Potential at solid surface	V
Ω	Saturation state	—
c_o	Oil corey exponent	—
c_w	Water corey exponent	—
D	Diffusion coefficient	$m^2 s^{-1}$
ΔG_r^0	Standard Gibbs free energy	kJ
ΔG_r	Change in Gibbs free energy	kJ
I	Ionic strength	$mol l^{-1}$
k	Permeability	$Darcy$ or m^2
K	Rate constant	—
k_{roe}	Relative oil permeability	—
k_{rwe}	Relative water permeability	—
m_i	Molality	$mol l^{-1}$
P_c	Capillary pressure	Pa
P_{CO_2}	Partial pressure CO_2	Bar
r	Dissolution rate	$mol m^{-2} s^{-1}$
SI	Saturation index	—
S_w	Water saturation	—
T	Temperature	K
V_m	Molar volume	$m^3 mol^{-1}$
$[X_i]$	Concentration of species X_i	$mol m^{-3}$
z_i	Ionic charge	—
Z	Compressibility factor	—

Chapter 1

Introduction

Low Salinity Water Flooding (LSF) is a promising EOR method to improve the oil recovery for both sandstone and carbonate reservoirs. During LSF, brine with a low salinity, referred to as low sal, will be injected in the oil reservoir. For sandstone reservoirs a salinity below 5000 ppm is required to have an effect of the LSF on the oil recovery. The salinity is less restricted for LSF in carbonate reservoirs. However, the presence of Sulphate, Calcium and Magnesium is essential. In the case of conventional water flooding, seawater, formation water, aquifer water or river water is injected. Formation water of the reservoir can be up to 300,000 ppm and seawater has a salinity between 30,000-50,000 ppm. Seawater can be diluted to provide the low salinity brine, because of availability and therefore cost efficient. Secondly seawater contains Ca^{2+} , Mg^{2+} and SO_4^{2-} , which are important potential determining ions for LSF in carbonate rock.

Over 60% of proven oil reserves in the world are captured in carbonate reservoirs. Conventional water flooding in carbonate reservoirs often has not been successful, because of the oil wetting surface of the rock and the high fracture density. Fractures in a carbonate reservoir act as a thief zone, which can cause an early water break through. Secondly, due to the oil wet rock surface, the water imbibition in the oil bearing parts of the reservoir will be low. Therefore carbonate reservoirs will not be flooded sufficiently during conventional water flooding and the oil recovery will be insufficient. LSF might improve the the performance of waterflood for carbonate reservoirs, by wettability alteration. Wettability alteration towards more water wet rock surface will improve the water imbibition and the oil mobility. There is a high possibility that Calcite dissolution will occur during LSF in carbonate rock, which can enhance the pores connectivity, hence the sweep efficiency.

For sandstone porous media there is quite some knowledge about the mechanisms behind the incremental oil recovery as a result of LSF. The incremental oil recovery in sandstone is related to the release of negative charged oil droplets from positive charged clay particles [Al Shalabi et al. 2013]. These clay particles are lacking in Carbonate porous media. The suggested recovery mechanism for carbonates is wettability alteration [Aladasani et al. 2012; Yousef et al. 2011], due to ion exchange [Al Shalabi et al. 2013; Brady et al. 2012], electric double layer expansion [Alotaibi et al. 2011], Calcite dissolution [Hio 2008; Yousef et al. 2011; Zhang and Sarma 2012] and pH increase. Other mechanisms are in-situ surfactants generation, emulsion formation [Emadi and Sohrabi 2013; Mahzari and Sohrabi 2014], salting-in effect [RezaeiDoust et al. 2009] and fines migration [Zahid et al. 2012].

Several experimental and modelling studies are performed on LSF in carbonate rock. In chapter 2, a summary is given of these studies and their findings. Wettability alteration from oil wet to intermediate-water wet is proven to be the main contributor to the incremental oil recovery when the salinity of the injection fluid is lowered. The presence of Sulphate in the brine have been proven to be a wettability modifier in several studies [Hognesen et al. 2005; Al-Attar et al. 2013; Zhang and Sarma 2012; Zhang et al. 2007].

Calcite dissolution is claimed to have a positive effect on the incremental oil recovery by improving the connectivity [Yousef et al. 2011] or exposing a fresh, more water wet surface [Hio 2008]. Both findings are theoretically supported, not experimentally. There is a lack of experimental studies on the Calcite dissolution behaviour during LSF in carbonates.

The objective of this study is to get a better understanding of the calcite dissolution behaviour during LSF in carbonate rock and how it might effect the oil recovery. The effect of parameters, like pH, CO_2 , salinity, temperature and flow rate on the calcite dissolution need to be experimentally tested. One of the risk of calcite dissolution is formation of caves and sinkholes, which can lead to subsidence and collapse of facilities. Therefore an indication of this risk is needed, by studying the change in porosity due to LSF.

At first a set of bulk experiments is performed to obtain calcite dissolution behaviour at equilibrium. Followed up by single-phase and two-phase core flood experiment, to imitate the behaviour of calcite dissolution in porous media. The Calcite dissolution behaviour is matched with modelling data obtained with PHREEQC, a geochemical simulator. CT scans and micro-CT scans are made of the cores before and after the coreflood experiments, to study whether the calcite dissolution affects the porosity and connectivity.

Chapter 2

Literature Review

Low salinity flooding can enhance the oil recovery by mobilisation of remaining oil. The mobilisation is caused by wettability alteration, which can be induced by different LSF mechanism. In this chapter a summary of the knowledge on these mechanism is given, obtained from experimental, modelling and field studies.

2.1 Wettability

As mentioned before, wettability alteration mobilizes remaining oil in the reservoir. The wettability affects the capillary pressure and relative permeabilities, and therefore the oil recovery. This will be explained more extensively in the next section.

The rock surface has a wetting fluid and a non wetting fluid. The wetting fluid is attracted to the rock surface form a film on this surface. The non-wetting fluid is not attracted by the surface and will be able to flow more easily through the rock. The wettability is related to the contact angle between the fluid and the rock, which is related to the interfacial tensions at the interfaces. The Young equation (equation 2.1) describes this relation.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos(\theta) \quad (2.1)$$

Where γ_{SG} is the interfacial tension between the solid and the gas, γ_{SL} between the solid and the liquid and γ_{LG} between the gas and the liquid and θ is the contact angle. Interfacial tension (IFT) is the force that holds the interface between two immiscible phases together, given in dynes/cm. The IFT prevents invasion of the two phases into each other. Figure 2.1 illustrates the direction of the interfacial tensions and contact angle.

The wettability is related to the contact angle. $\theta = 0^\circ$ if a fluid is completely wetting, the fluid is spread out over the surface. $\theta = 180^\circ$ when a fluid is non-wetting, the fluid is not attracted to the surface. According to Anderson (1986) a distinction between the wettabilities can be made based on the contact angle of the water with the rock surface. For a water wet rock θ_w should be in between $0 - 75^\circ$, an

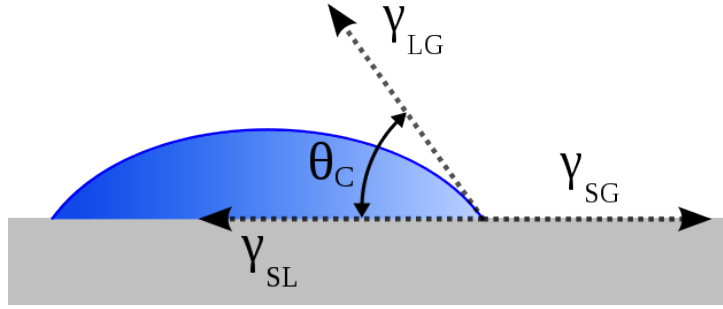


FIGURE 2.1: Contact angle and surface tensions according to Young's equation.

intermediate wetting state has a θ_w between $75 - 105^\circ$ and for an oil wet rock θ_w should be in between $105 - 180^\circ$. An oil wet rock surface behaves hydrophobic and a water wet surface behaves hydrophilic.

Initially, when the carbonates are deposited, the surface is still water wet. Due to ageing with the oil present in the reservoir, the rock surface will become more oil wet. The wettability of a rock depends on the Acid and Base number of the crude oil, mineralogy of the rock, composition and pH of the equilibrium brine and the temperature of the reservoir during the ageing. When the oil is migrated to the carbonate reservoir, the interface between water and the oil becomes negatively charged by forming Carboxylates, COO^- (equation 2.8). As a result the water film between the oil and rock surface becomes unstable, because of the positive charge at the rock/water interface and the negative charge at the oil/water interface. As a result the oil is attracted to the rock surface and the oil becomes the wetting phase [Punternvold et al. (2007)]. This process is influenced by the Acid and Base number of the crude oil. The higher the acidity of the oil, the higher the concentration of the Carboxylates. As a result more Carboxylates can adsorb on the carbonate rock surface and it becomes more oil wet.

2.1.1 Capillary Pressure

As mentioned before, the wettability affects the capillary pressure. The capillary pressure is the difference between the pressure of the non-wetting phase and wetting phase across an interface between two fluids.

$$P_c = P_{non-wetting} - P_{wetting} \quad (2.2)$$

The capillary pressure is a function of the contact angle θ and the interfacial tension γ (IFT):

$$P_c = \frac{2\gamma \cos(\theta)}{r} \quad (2.3)$$

Where r is the effective radius, like the pore radius. The capillary pressure is also a function of the saturation which is described by the Leverett J-function:

$$J(S_w) = \frac{P_c(S_w) \sqrt{k/\phi}}{\gamma \cos \theta} \quad (2.4)$$

Initially, carbonate reservoirs have a high negative capillary pressure when they are oil wet. This negative capillary pressure holds the oil in place. Alternation of the wettability to a more intermediate or water wet rock creates a less negative or even positive capillary pressure, which results in spontaneous water imbibition [Al Shalabi et al. 2013] and in an increase in the oil production. Imbibition is the process where the non wetting phase is pushed out by the wetting phase and the saturation of the wetting fluid increases. The drainage process is the other way around.

2.1.2 Relative Permeability

The relative permeability is also related to the wettability. Each phase (oil/gas/water) during two-phase flow in a porous medium has its own relative permeability, which is a fraction between 0 and 1. The relative permeability of a phase is a function of the saturation of the phase.

$$K_{rw} = K_{rwe} S_{we}^{n_w} \quad (2.5)$$

$$K_{ro} = K_{roe} (1 - S_{we}^{n_o}) \quad (2.6)$$

K_{roe} and K_{rwe} are the end point relative permeabilities, where the saturation of the other phase is at minimum. S_{we} is the effective water saturation.

If the rock is water wet, a water film is present between the rock and the oil phase. . In this way the oil flow is enhanced and has a larger K_{roe} . For an oil wet rock the water film is thinner or not present at all. The oil is attracted to the rock surface and therefore, the water phase flows easier and has a higher relative permeability.

2.2 LSF in Sandstone

Low salinity flooding in sandstone has been proven to be an promising enhanced oil recovery technique in sandstone. Lowering the salinity of the injection brine below 5000 ppm can enhance the recovery. The incremental oil recovery in sandstone is related to certain recovery mechanisms.

The surface of a sandstone rock is often covered by small clay particles. The surface of these clay particles have a negative charge. Bonds between the negative charged clay surface and negative charged oil surface can be formed by divalent cations, like Calcium and Magnesium. In this way oil sticks to the clay. [Seccombe et al. 2008]. LSF recovery mechanisms, like the expansion of the electric double layer (EDL) and ion exchange, can break these bonds and the oil will be mobilized [Lager et al. 2006]. This two mechanisms will be explained more extensively in section 2.3.3 and 2.3.5.

Another LSF recovery mechanism in sandstone is the change in the zeta potential. Lowering the salinity creates a more negative zeta potential solid/brine and oil/brine interfaces [Nasralla and Nasr-El-Din 2011]. Opposite signs cause repulsion forces between the two interfaces, which results in release of oil droplets from the rock surface.

2.2.1 LSF in Sandstone reservoirs, field studies

LSF has been proven to be an efficient EOR method from field studies as well. Low salinity flooding has been applied in the Minnelusa formation, an oil bearing sandstone. The Minnelusa formation is a clean sandstone, cemented with carbonate and anhydrite. In total 130 fields are producing from this formation, 55 of these fields are recovered by low salinity water flooding, 52 mixed salinity water flooding and 23 by formation brine flooding [Thy 2011]. The fields have been flooded up to 30 years. No increase in oil recovery was observed by Thy (2011), who performed a study on comparing the historical production data of the low salinity and the high salinity fields. Secondly, the water break through at the production wells was not influenced as well by the LSF.

Rob (2007) studied the historical production and injection data of three fields producing from the Minnelusa formation in the Powder River basin as well. The reservoirs are the West and North Semlek reservoir and the Moran reservoir. For the West Semlek field, the salinity of the initial formation water was 60,000 ppm and 10,000 ppm for the injection water. For the North Semlek field, the salinities were respectively 42,000 ppm and 3300 ppm. For the Moran field, the salinities were 128,000 ppm for the formation water and 8000 ppm for the injection water [Rob 2007]. The historical production data of the three field showed that the North Semlek and Moran field had a higher recovery rate and a lower salinity ratio than the West Semlek field. Rob (2007) observed a relation between the salinity ratio and oil recovery, but points out that this observation cannot be proven because of the lack of more field production and experimental data.

The Endicott field in Alaska has been flood with low salinity in the tertiary stage, after conventional water flooding. The Endicott formation consists of sandstone, deposited in a braided and meandering river system, and some discontinuous shales. Initially, the sandstone rock surface is intermediate wet. The remaining oil saturation after the high salinity waterflood was 41% and after the low salinity waterflood, 27% of the oil remained in the reservoir [Secombe et al. 2008]. These values were based on a single well chemical tracer test (SWCTT). So the LSF Pilot of the Endicott field had proven to be successful.

The LSF potential of the Snorre field has been tested with the use of a SWCTT as well. This field lies in the North Sea and its main reservoir layer is the Statfjord formation, a weakly water wet, fluvial sandstone [Skrettingland et al. 2010]. The residual oil obtained from the SWCTT did not show a significant change after injecting sequentially High salinity, Low salinity and again High salinity brine. Neither the Coreflood test, conducted in the laboratory, showed a significant LSF effect on the oil recovery [Skrettingland et al. 2010]. The low LSF potential of the Snorre field is due to the already optimal initial Wettability of the sandstone, according to Skrettingland et al. (2010).

The Omar field has been flooded with low salinity brine over 10 years in secondary recovery [Mahani et al. 2011]. From production data, a dual step water break through has been observed, which is indicated by Mahani et al. (2011) as an effect of wettability alteration from oil to water wet. An incremental oil recovery of 10-15% OIIP is created by the wettability alteration.

The Sijan field has been flooded by Low salinity water in tertiary recovery. Water with a salinity of 200,000 ppm was injected during the ten years of secondary flooding and water with a salinity of 500 ppm was injected during the tertiary flooding [Mahani et al. 2011]. According to Mahani et al. (2011)

the LSF flood is still immature and no low salinity water break through has occurred. No clear LSF response has been observed yet from this field. According to Mahani et al. (2011), this is probably due to the high contrast in salinities between the secondary and tertiary flooding, which creates significant mixing effect. This mixing of low salinity and high salinity brine inhibits the LSF effect.

2.3 LSF in Carbonates

Low salinity flooding is proven to be a sufficient method to create an incremental oil recovery in or after secondary recovery. Since 60 % of the proven oil reserves are present in Carbonate reservoirs, it is interesting to investigate the potential of LSF in carbonates. The recovery mechanisms of LSF in carbonates differ from LSF in sandstone, because of the difference in initial wettability and the lack of clay in carbonates.

2.3.1 Experimental methods on LSF

Several studies proved that LSF in carbonates can enhance the oil recovery. This is done by performing spontaneous imbibition tests, secondary and tertiary coreflood experiments.

Spontaneous imbibition tests give an insight on the initial wettability of the core and the potential wettability alteration. During spontaneous imbibition the fluid is sucked into the core by the capillary pressure, which is dependent on the wettability. An increase in the water imbibition rate indicates a more water wet rock surface. So the wettability alteration due to the LSF is reflected by the increase of the water imbibition rate and the accompanied oil recovery.

During secondary coreflood tests low salinity water is injected in an oil saturated core. During tertiary coreflood test, at first high salinity water is injected till the residual oil saturation is reached and the pressure is stabilized. At second, the low salinity brine is injected. In this way the mobilized remaining oil is due to the wettability alteration.

The capillary end effect should be taken into account for coreflood experiments with low flow rates in short cores. This feature does not occur on large cores or in the reservoir. The capillary end effect can be explained as a hold up of the wetting phase at the outlet of the core. A build up of the wetting phase takes place at the end of the core as a result of the discontinuity in the capillary pressure. The capillary pressure just outside the core is equal to zero, while just inside the core the $P_c > 0$. When this effect is not taken into account, data can be interpreted wrongly and calculation for saturations and relative permeabilities from pressure and production data will be incorrect. The incremental oil recovery will be due the increase in pressure drop, which overrules the capillary end effect. The oil held up at the outlet will be remobilized and produced.

According to Masalmeh et al. (2014) coreflood experiments with low injection rates are not representative for the field scale. For low rates and short cores the extra production, when the injection is switched to low salinity, can be due to the capillary end effect instead of an effect of LSF. Wettability alteration to more intermediate wet reduces the capillary pressure and the hold up at the end of the core will be produced. The capillary end effect is not present in the field and the incremental oil recovery will be

less than expected from experimental data. According to Masalmeh et al. (2014), it is better to start injecting high salinity brine at a low rate and increase the rate stepwise to overcome the capillary end effect. Subsequently the low salinity brine has to be injected at the higher rate as well. In this way the incremental oil recovery will be due to change of relative permeability instead of due to the capillary end effect.

For longer cores and higher flow rates the capillary end effect can be neglected, because of the higher pressure drop along the core. As a rule of thumb, if $\delta P_{core} \gg P_c$, then the capillary end effect can be neglected [Masalmeh et al. 2014].

Wettability alteration can be measured with the use of a Nuclear Magnetic Resonance tool (NMR). With the use of NMR the surface relaxation time can be measured (T_2), which depends on pore size distribution, porosity, permeability, pore fluids and wettability. The surface relaxivity gives a measure of the surface to enhance relaxation. The surface relaxivity is higher for the wetting fluid. In other words, the relaxation of the protons to the rock surface is higher for the wetting phase.

2.3.2 Wettability alteration during LSF in Carbonate

Wettability alteration as an effect of LSF in carbonate rock is proven by Yousef et al. (2011). Yousef et al. (2011) conducted different laboratory studies to investigate the potential of LSF in carbonates. They performed oil/brine/rock interaction tests and coreflood experiments with different composition and salinity. Coreflooding experiments were performed with several cores consecutive up to a length of 16.24 cm and 23.65 cm. The different brine salinities range from 57,670 - 600 ppm (Sea water - 2X diluted SW-10X Dil SW -20X Dil SW- 100X Dil SW). IFT and contact angle measurement are conducted at reservoir conditions to see the effect of LSF in carbonates on the capillary pressure.

High pressure/high temperature pendant drop measurements showed a reduction of the IFT with decreasing salinity. The IFT gradient is the largest at the higher salinities (FW, SW, 2X dil SW). The IFT is reduced when the salinity is reduced (10X, 20X, 100X Dil SW), however the reduction in the IFT is said to be insignificant between the low sal brines.

Contact angle measurement for the oil and injected brine were performed at reservoir conditions. Decreasing salinity showed a reduction in the contact angle, which indicated a wettability alteration towards more water-wet. The decrease in salinity from formation to sea water did not show any change in the contact angles, while this step showed the largest effect on the IFT. The low salinity brines (2X, 10X, 20X Dil SW) showed the largest change in the contact angle. Ten times diluted seawater showed a $\theta_o = 111^\circ$ and $\theta_w = 69^\circ$, which is already in the range on the water wetting state according to Anderson (1986). From these observations Yousef et al. (2011) concluded that the LSF in carbonate rock has a bigger impact on rock/fluid interactions (contact angle) than on fluid/fluid interaction (IFT).

Yousef et al. (2011) also performed two coreflood experiments injecting subsequently the five different brines (Sea water, 2X diluted SW, 10X Dil SW, 20X Dil SW and 100X Dil SW). Secondary recovery with seawater was continued till no more oil was produced. The rate was stepwise increased from 1, 2 to 4 cc/min for each injection cycle, to avoid the capillary end effect. This procedure is repeated for the tertiary recovery with subsequent cycles of decreasing salinity. An incremental oil recovery of 17.94 % and 19.52 % in the tertiary mode was observed by injection of 2, 10 and 20 times diluted SW.

Injection of 100X diluted seawater did not show a significant increase any more (0.00 %). Pressure data showed a decrease in the pressure drop along the core with decreasing salinity. Yousef et al. (2011) assert this pressure drop reflects a decreasing capillary pressure, which is in line with an alternation of the wettability to a more intermediate state.

Yousef et al. (2011) also observed the wettability alternation with the use of a Nuclear Magnetic Resonance tool (NMR). The measurements were done before and after the coreflood experiment to show the LSF effect. The NMR results showed a shift in the T_2 distribution before and after the LSF, which is indicated as an increase in the surface relaxivity due to LSF. Change of surface relaxivity can be an indication of wettability alteration.

Yousef et al. (2011) experimental results proved the wettability alteration as a result of LSF in carbonate rock. Several techniques (contact angle, Coreflood, NMR) were used to study the LSF effect, and all results showed the wettability alteration effect.

Aladasani et al. (2012) investigated the suitability and validity of LSF in carbonate reservoirs by matching their simulated results with published coreflood data of Yousef et al. (2011). From the data matching, Aladasani et al. (2012) concluded that the incremental oil recovery during LSF is caused by alteration of the wettability from oil wet to intermediate wet. As a result, the capillary pressure became less negative and the oil relative permeability increased, which resulted in the incremental oil recovery [Aladasani et al. 2012]. Alteration of wettability can be enhanced by potential determining ions to the brine.

Studies performed by Yousef et al. (2011) and Aladasani et al. (2012) proved that wettability alteration from oil wet to intermediate or water wet can enhance the oil recovery during LSF in carbonate rock. The wettability alteration can be an effect of several mechanisms, like ion exchange, electric double layer expansion and increase in pH.

2.3.3 Wettability alteration due to ion exchange

Ion Exchange can be seen as a replacement of Ions due to adsorption. Adsorption means the adhesion of atoms, ions or molecules from a fluid or solid on the adsorbent. In the case of a soluble solid, adsorption of particles occurs at both sides (solid and liquid). The adsorption can be seen as a replacement, ion exchange, and the degree of adsorption can be measured by the concentration changes in the fluid. The second case is the most applicable to LSF in carbonate reservoirs.

There can be made a distinguish between positive adsorption (attraction) and negative adsorption (repulsion). Electrostatic and Van der Waals adsorption forces are present in during attraction. The Van der Waals forces can be neglected in the case of repulsion, because of the high separation forces needed for repulsion.

The wettability of a rock surface can be altered due to ion Exchange. Most of the carbonate rock surfaces are oil wet, which means the surface charge of the rock and the oil are each other's anti-poles. At the limestone surface, $CaOH$ is exposed. At the oil surface a Carboxylic acid group, $COOH$, is exposed. These two molecules at the surfaces create the following bond [Brady et al. 2012]:

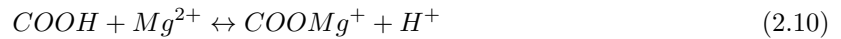
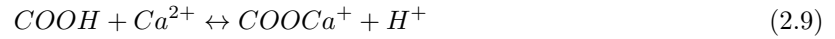




According to equation 2.7 and 2.8, the Carbonate rock surface has a positive charge and the oil surface a negative charge. In this way the oil is attracted to the rock surface. In other words, the carbonate rock is oil wet.

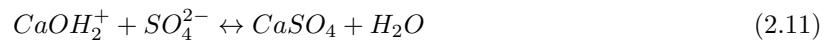
In order to create a more water wet rock surface, this bond needs to be taken apart. This is the desired effect of LSF on the rock surface by ion exchange. The surface charge of both the rock and oil surface can be altered by potential determining ions like Ca^{2+} , Mg^{2+} and SO_4^{2-} . These ions are only effective in the aqueous phase. The advantage of injecting (diluted) seawater is the presence of all these ions. In General the concentrations of these ions in seawater are: $[Mg^{2+}] = 4 [Ca^{2+}]$ and $[SO_4^{2-}] = 2 [Ca^{2+}]$.

Ca^{2+} and Mg^{2+} cations can alter the negative charge on the oil surface to a positive charge by forming Carboxylic bonds according to the following reactions [Brady et al. 2012].



In general, the Calcium-Carboxylic bonds are stronger than the Magnesium-Carboxylic bonds. By increasing the concentration of Ca^{2+} and Mg^{2+} cations in the brine, the number of $[-COO^-][>CaOH_2^+]$ can be reduced.

By adding Sulphate to the injection brine, the number of $[-COO^-][>CaOH_2^+]$ bonds can be reduced as well by creating a negative surface charge of the carbonate rock [Brady et al. 2012].



$$K = \frac{a[CaSO_4]a[H_2O]}{a[CaOH_2^+]a[SO_4^{2-}]\exp(-Z_cF\Psi/(RT))} \quad (2.12)$$

This type of ion exchange happens at the rock surface instead of the fluid surface.

In this way Sulphate improves the wettability alteration to more water wet due to adsorption on the carbonate surface [Hognesen et al. 2005]. The adsorption rate increases with temperature. However, the solubility of Anhydrite ($CaSO_4$) decreases with temperature as shown in figure 2.2.

Therefore, the efficiency of Calcium and Sulphate acting as a wettability modifier is reduced with increasing temperature. A significant amount of Anhydrite (200 ppm) is still soluble at temperatures below $150^\circ C$. Precipitation of $CaSO_4$ occurs at the limiting temperature and the Sulphate cannot act as a wettability modifier any more by adsorption on the carbonate surface. When Magnesium is added to the

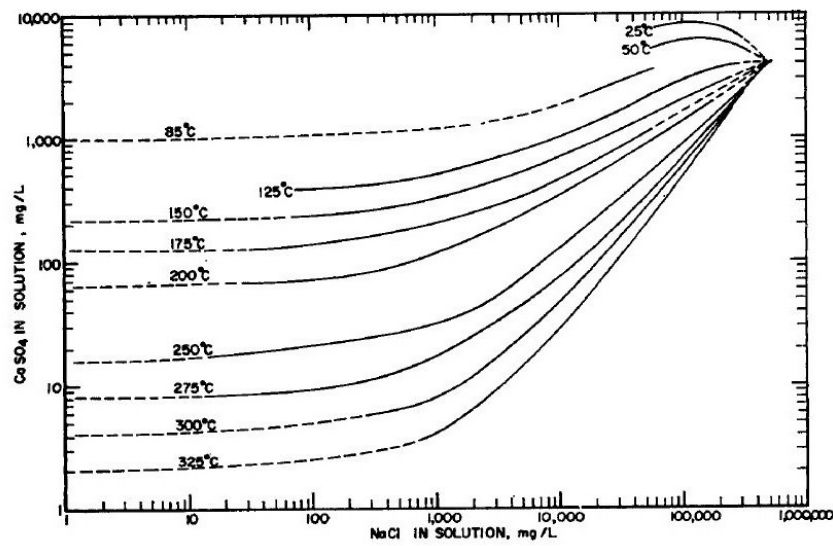
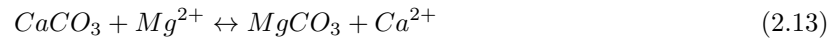


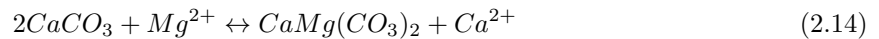
FIGURE 2.2: Solubility of Anhydrite in brine with temperature and salinity, Carlberg et al., (1973).

solution, the limiting temperature for $CaSO_4$ precipitation is raised [Zhang et al. 2007]. This is because SO_4^{2-} and Mg^{2+} form an ion pair in an aqueous solution, which increases with temperature.

Substitution of ions can also occur between Calcium and Magnesium at chalk surfaces at high temperatures [Punternold and Austad 2007].



Or Calcite is changed into dolomite:



According to Punternold and Austad (2007), the substitution rate of Calcium atoms by Magnesium atoms increases with temperature. This can be observed by an increase in the Calcium concentration and decrease in Magnesium concentration in the effluent with temperature. Because the Magnesium atom is much smaller than the Calcium atom, the carbonate rock becomes weaker as a result of the substitution reaction. This phenomenon is also observed by Zhang et al. (2007).

Hognesen et al. (2005) performed two-phase spontaneous imbibition test in outcrop chalk cores and reservoir limestone cores, both initially oil wet. The tests are performed at temperatures of 70 – 130°C, at a back pressure of 10 bar and with three different brines: Seawater (SW), Seawater without Sulphate (SW-0s) and seawater with three times the initial Sulphate concentration (SW-3s). The salinity of the brines was kept constant at a TDS of 33,390 ppm. Tests based on chromatographic separation showed an increase of affinity of Sulphate to the chalk rock surface with increasing temperature. With the use of chromatographic separation tests the wettability index (WI) can be determined. A WI of 1 represent a completely water wet rock surface and a WI of 0 represent a complete oil wet rock surface.

Spontaneous imbibition experiments with the chalk showed an increase in recovery from 22 % to 45 % when the temperature was raised from 90 to 130 °C. The first imbibition cycle was performed with SSW-0s, which gave a recovery of 6-7%. When changing the brine to SW-3s, oil recovery increased directly to 60 %. The same experiment was conducted at 90 to 110 °C. After 40 days an oil recovery of 18 % was obtained at 90 °C and 23-24 % at 110 °C.

Hognesen et al. (2005) study showed an increase of oil recovery from spontaneous imbibition tests with Sulphate concentration and temperature. The increase of brine imbibition and accompanied oil recovery is due to a wettability alteration to a more water wet rock surface. The results of Hognesen et al. (2005) showed that Sulphate is a wettability modifier for carbonate rock at higher temperatures. The injected brines have a relative high salinity of 33,390 ppm, which shows that Sulphate can act a wettability modifier in high salinity brine as well.

The impact of Sulphate, Calcium and Magnesium on the wettability alteration in chalk outcrop cores (L=7 cm. D=3.7cm) is studied by Zhang et al. (2007) by performing coreflood experiments, spontaneous imbibition tests and zeta potential measurements. The tests were run at temperatures of 23, 40, 70, 100 and 130 °C and at a back pressure of 6 and 10 bar for the coreflood and imbibition experiments respectively. Seawater with changing ionic composition of Ca^{2+} , Mg^{2+} and SO_4^{2-} was used for the experiments. The Ionic strength for all the brines was held constant with adding NaCl.

From the Zeta potential measurements it was concluded that both Calcium and Magnesium are potential determining ions towards the chalk surface. From competitive adsorption tests was concluded that Calcium has a bigger affinity towards the chalk surface at room temperature. However, the affinity of Magnesium towards the chalk surface was greatly increased at 130 °C and the Calcium concentration in the effluent increased with 50-60 %. This is explained in Zhang et al. (2007) by the substitution process of Ca^{2+} by Mg^{2+} at the rock surface. This substitution process is very sensitive to the temperature.

Spontaneous imbibition test did not show a significant oil production with seawater containing only SO_4 at 70 and 100 °C. When Ca^{2+} and Mg^{2+} were added to the brine, a sudden increase in oil displacement occurred. Therefore Sulphate is said to be a wettability modifier not by itself, but in a combination with Ca^{2+} and Mg^{2+} . Zhang et al. (2007) also concluded that Mg^{2+} can act as a wettability modifier in presence of SO_4^{2-} at high temperatures ($T > 100 - 130$ °C). Ca^{2+} is said to be a more efficient wettability modifier in presence of SO_4^{2-} at lower temperatures ($T < 70 - 100$ °C). This is because of the solubility of $CaSO_4$ drastically decreases at temperatures above 100 °C.

From the experiments of Zhang et al. (2007) it was concluded that seawater can act as a wettability modifier, because of the presence of the surface potential determining ions Ca^{2+} , Mg^{2+} and SO_4^{2-} . Sulphate acts together with Calcium and Magnesium to alter the Wettability and the efficiency increases with temperature. As remark is made about the reactivity of chalk, which is much higher than of recrystallized limestone. Therefore the results obtained are difficult to extend to limestone reservoirs.

History matching of recently published coreflooding experiments by Yousef et al. (2011) with the use of the UTCHEM simulator was performed by Al Shalabi et al. (2013). The UTCHEM simulator is a 3D multi phase, transport and chemical flooding simulator. The results from this study revealed that the main mechanism behind the incremental oil recovery due to LSF in carbonate rock is the wettability alteration. The Wettability effect was simulated by two methods. From the data they concluded that

wettability alteration occurred by changing the surface potential due to ion exchange. Al Shalabi et al. (2013) also claimed that wettability alteration can occur as an effect of calcite dissolution at the rock surface. By tuning the relative permeability parameters, it was observed that the k_{rwe} and k_{roe} are sensitive to the LSF effect. The k_{roe} was the most influenced of all parameters and increased when the rock became more water wet.

Coreflood experiments with Limestone cores from the Bu Hasa Field (Abu Dhabi) were performed by Al-Attar et al. (2013), using dilutes versions (5000 and 1000 ppm) of seawater and two field injection brines. The two field injection brines are from the Um-Eradhuma field (UER) and the Simsim field (SIM). The coreflood experiments were conducted at room temperature and at a constant injection pressure of 7 Bar. The length of the cores was in between 7.090 and 7.272 cm.

5000 ppm UER water gave the highest oil recovery (84.5 %), 1000 ppm gave the highest oil recovery (74.4 %) for the SIM water. There is no significant increase of recovery when seawater is diluted to 5000 ppm. However there are no experiments performed by Al-Attar et al. (2013) with diluted seawater below 5000 ppm, while this might be the salinity boundary for LSF in carbonates.

The effect of Ca^{2+} and SO_4^{2-} was studied by running coreflood experiments with different composition. A Sulphate concentration of 47 ppm gave the highest oil recovery (87.2 %), but increasing this concentration to 69.7 ppm gave a negative effect on the recovery. So there has to be an optimum Sulphate concentration for each low salinity brine to have a positive effect on the oil recovery. The lowest Calcium concentration in the 5000 ppm brine gave the highest recovery.

According to Al-Attar et al. (2013), increasing the Calcium concentration in a low salinity brine has a negative effect on the oil recovery. However, the effect of Calcium together with Sulphate on the oil recovery was not tested by Al-Attar et al. (2013).

Data of the change of the contact angle with time is obtained with the use of image analysis software. Comparison of the contact angle measurements and the coreflooding data indicated that an increasing contact angle can increase the oil recovery, which can be interpreted as alternation to an intermediate wetting state. Intermediate wettability creates low capillary pressures, which can be in favor for the oil production.

There is no significant change in the contact angle between the pure and diluted seawater of 5000 ppm, which is consistent with almost no incremental oil recovery when flooding with 5000 ppm seawater. An increasing SO_4^{2-} concentration, increased the contact angle. At the 69.7 ppm Sulphate concentration, the opposite effect was observed for the contact angle, again consistent with coreflood data.

Al-Attar et al. (2013) study indicates that an increasing Sulphate concentration, alters the wettability to an intermediate wetting state, which contributes to the incremental oil recovery. Wettability alteration and incremental oil recovery is observed up to an optimal Sulphate concentration.

Zhang and Sarma (2012) performed LSF coreflood experiments in tertiary mode in carbonate reservoir cores with a length of 7.5-9.3 cm and a diameter of 3.8 cm. In the secondary mode seawater was injected till the residual oil S_{or} was reached, in order to see clearly the LSF effect. At 70 °C diluted seawater (1/2 SW, 1/10 SW, 1/40 SW) was injected sequentially at a flow rate of 0.3 cc/min. When the oil production stopped and the pressure was stabilized, the injection was switched to a lower salinity

brine. Coreflood experiments were also conducted at reservoir conditions with a temperature of 120 °C, back pressure of 200 bar and injecting formation water (1/4.61 FW and 1/100 FW) with a flow rate of 0.25 ml/min. Wettability monitoring tests were performed at a temperature of 90 °C by taking pictures of droplets on core plates, which were aged by oil to obtain oil-wet surfaces. Spontaneous imbibition tests were performed at 70 °C with sub sequential seawater and 1/40SW.

From the results of coreflood experiments at 70 °C, it was observed that lowering the salinity was more effective on the oil production than increasing the Sulphate concentration and at 120 °C both features showed the same potential. The stabilized pressure slightly increased with decreasing salinity, while viscous forces should decrease with decreasing salinity. According to Zhang and Sarma (2012), the pressure build up was accompanied with the incremental oil production. The total incremental oil production at 70 °C from the LSF are 16.93 % and 5.64 %. The lower production during the LSF in the second core was said to be due micro fractures in the core. The total oil production from tertiary LSF was higher for 120 °C (25.04% and 26.13%). So the incremental oil recovery as a result of LSF is very sensitive to the temperature [Zhang and Sarma 2012]. Secondly, the pressure drop along the core is larger for higher temperatures, which is explained by the Zhang and Sarma (2012) as an effect of mineral dissolution which creates blockage of pore throats and fiercer brine/rock interaction.

From the spontaneous imbibition tests an incremental oil recovery of 4.59 % was observed with first imbibing SW, which was followed by 1/40SW and created an extra recovery of 18.36 %. It was concluded that lowering the salinity creates a more water wet rock surface. However, the incremental oil recovery took 50 days to be obtained, which means the alteration takes time according to Zhang and Sarma (2012).

The pictures from the wettability monitoring test showed that increasing Sulphate concentration in the brine creates a less oil wet rock surface, while Ca^{2+} and Mg^{2+} showed an insignificant effect on the wettability. However, the change of the wettability occurred faster when these two cations plus SO_4^{2-} were present in the brine. So there might be a relation between the concentrations of Ca^{2+} and Mg^{2+} and the concentration of SO_4^{2-} on the wettability alteration effect. Lowering the salinity of seawater by dilution also had a positive effect on the wettability alteration towards water wet.

According to Zhang and Sarma (2012) the main mechanisms behind the incremental oil recovery are wettability alteration and fines migration. The wettability alteration was induced by salinity reduction of the injection brine and the presence of Sulphate in the brine together with Calcium and Magnesium. The fines migration due to mineral dissolution was explained by the increase of the pressure drop along the core accompanied with the incremental oil recovery. Both effects increased with increasing temperature.

Still it needs to be accounted for the capillary end effect, since the incremental oil recovery is accompanied by the increase in pressure drop. However, the length of the cores might be large enough that the initial pressure drop already would overrule the capillary end effect and the incremental oil recovery can be attributed to the fines migration.

Sulphate, in combination with Calcium and Magnesium, is proved to be a wettability modifier from several experimental studies [Zhang et al. 2007, Hognesen et al. 2005, Al-Attar et al. 2013, Al Shalabi et al. 2013, Zhang and Sarma 2012]. Zhang and Sarma (2012)] also claims that the migration of fines has a positive effect on the oil recovery as well.

2.3.4 Fines Migration

When the salinity of the brine in a reservoir lowers due to LSF, fines can be released from the surface. These fines can be clay particles released from the surface, which mainly occurs during LSF in sandstone. In Carbonate rock the release of fines can be due to mineral dissolution. These fines will be transported along the oil/water interface.

For sandstone, the release of the clay particles can mobilize the oil, which is bonded to the clay. The migrating fines can block pore throats and induce formation damage [Lemon et al. 2011]. In this way the flow will go through non swept areas and the sweep efficiency will be enhanced. On the other hand, reduction of the permeability can occur due to plugging of pore throats. Fines migration often can be recognized as an increase in the pressure drop from coreflood pressure data.

Experiments with sequential injection of various diluted brines in carbonate plugs were performed by Zahid et al. (2012). Three limestone reservoir core plugs from the Middle East were used, with lengths of 3.81, 4.48 and 5.58 cm. Low sal (LS-2, LS-10, LS-20) injection was performed in the tertiary mode, after seawater injection. The injection rate for each cycle was set at 0.1 cc/min and increased to 0.5 and 1.0 cc/min, with a back pressure of 5 bar and a confining pressure of 30 bar.

From the coreflood experiments conducted by Zahid et al. (2012) flooding with diluted seawater did not result in a significant incremental oil recovery at room temperature. At a temperature of 90 °C an incremental oil recovery of 19% in total was observed when injecting diluted seawater in the tertiary phase. For the lowest salinity brine (LS-20) a raise in recovery of only 1.28 % was observed.

Unlike Yousef et al. (2011), no shift in the surface relaxation time T_2 was observed after LSF in the carbonate plugs at both temperatures. Concentration measurements were done for the effluent of the coreflood experiment. A constant production of Ca^{2+} was observed at room temperature and 90 °C, which is probably due to calcite dissolution.

For both temperatures an increase in pressure drop along the core with decreasing salinity was observed, while a decrease in pressure drop is expected when switching to low salinity brine. The increase in pressure drop is a result of fines migration according to Zahid et al. (2012). However, it is not proved that the fines migration contributes to the incremental oil recovery. The increase in pressure drop can overrule the capillary pressure and the hold up at the end of the core will be produced. So the incremental oil recovery is due to the increase in pressure drop and can not be attributed to the fines migration.

According to Tang and Morrow (1999), the stripping of the clay particles from the rock surface is related to the expansion the electric double layer, which is related to the decrease in the salinity. This LSF effect is mainly present in sandstone reservoirs, but the expansion of the EDL can occur during LSF in carbonates as well.

2.3.5 Electric double layer expansion and fines migration

During ion exchange between a charged surface and an electrolyte solution, an electric double layer (EDL) is formed [Overbeek 1971]. Electrolytes are ions from salts in solution, like Na^{2+} , Ca^{+} and Mg^{+} .

This EDL consists of the remaining free ions, which are not adsorbed on the charged surface, but are attracted to the surface. Therefore, the concentration of ions in this layer is higher than in the solution. The magnitude of the double layer conductivity varies with the concentration of the electrolyte and depends on the type of ion [Winsauer and McCardell 1953].

According to the Stern model, there is a region between the solid surface and diffusive layer where the ions are highly attracted to the surface and therefore are not moving. This Stern layer comprises the EDL and has a certain width δ [Overbeek 1971]. The Stern capacity is only dependent on the surface charge of the solid. In the diffusive layer the ions are less attracted to the surface and therefore can move. The capacity of the diffusive layer is also dependent on the electrolyte concentration.

Figure 2.3 illustrates the electric double Layer. From left to right, the charged surface, Stern Layer and the diffusive part of the EDL are illustrated in this figure. The solution/bulk fluid, which is not shown in the figure, is present on the right side of the diffusive layer.

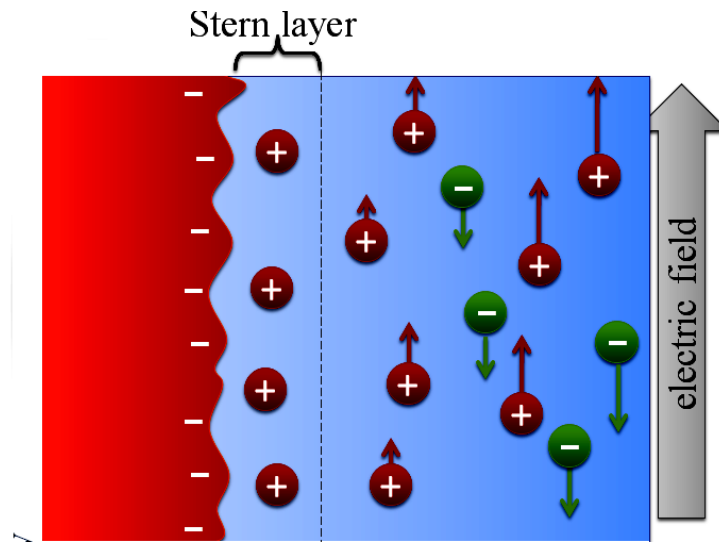


FIGURE 2.3: Electric double layer.

The charge of the EDL is equal and opposite to the charge of the exchanging surface. The EDL charge can be calculated from The Gouy-Chapman double layer equation [Appelo and Postma 2005].

$$\sigma_{DL} = \sqrt{8 \frac{RT}{\epsilon}} m_{i,\infty} \sinh\left(\frac{F\Psi_0}{2RT}\right) \quad (2.15)$$

Where $m_{i,\infty}$ is the concentration of ion i at infinite distance from the surface, in the electric neutral solution, Ψ_0 the surface potential ($x = 0$). The thickness of the EDL can be determined using the Debye length equation:

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon RT}{2(N_a q_e)^2 I}} \quad (2.16)$$

The thickness of the EDL increases as the concentration and the ionic strength of the bulk solution decrease and if the temperature increases. The repulsion forces between the oil and the rock surface

increase due to the EDL expansion, which mobilizes the oil and releases mineral particles or clay particles from the rock surface. Therefore, the EDL expansion can cause wettability alteration and fines migration.

2.3.6 Wettability alteration due to change in Zeta Potential

A shear plane is created between the diffusive layer (moving ions) and the stern layer (stagnated ions). At this plane a potential is created as product of repulsion forces and attractive Van der Waals forces. This is named the zeta potential, which is measurable. The zeta potential is a function of the surface charge of the solid and the nature of the surrounding medium [Johnson et al. 2010].

The surface charge is strongly pH dependent, because H^+ and OH^- are potential determining ions in many solids [Alotaibi et al. 2011]. Figure 2.4 shows the effect of pH on the oil and calcite surface charge, according to PHREEQC. The graph shows that an increase in pH creates a more negative surface charge for both oil and calcite.

A fluid is wetting if the sign of the rock surface charge equals the sign of fluid's surface charge. So the oil is the non-wetting phase for low and high pH, and oil is the wetting phase for intermediate pH, according to figure 2.4.

The Point of Zero Charge (PZC) is the pH value at which the surface charges alters from positive to negative charge. From literature, this point is 9.2 for Limestone and 7.4 for Dolomite. The PZC for a surface at certain conditions and interfaces can be calculated with the use of PHREEQC. Figure 2.4 shows a PZC of 5.5 for oil and 8.5 for calcite.

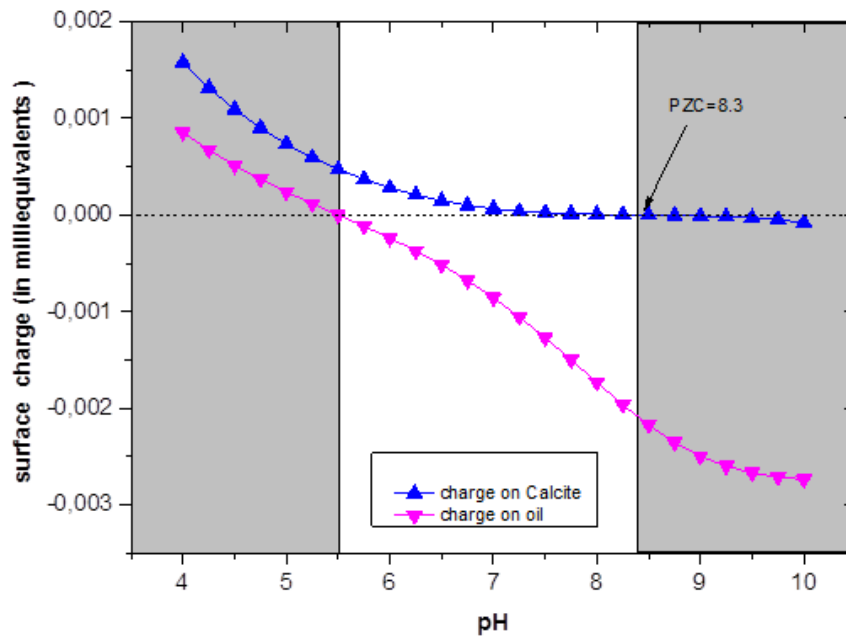


FIGURE 2.4: Charge of oil and Calcite surface with pH, 10,000 ppm NaCl, 50 °C, PHREEQC.

Alotaibi et al. (2011) studied the electrokinetic characteristics of dolomite and limestone particles in low salinity brine (0.2 g rock powder in 50 cm^3 brine) at temperatures of 25 °C and 50 °C. The zeta potential at the brine/rock interface was measured by a phase-analysis light scattering technique. The

surface charge of the particles was measured over a pH range of 3 to 12 (adjusted with HCl or NaOH). The particles were mixed with three different brines: Aquifer water (AQW), seawater (SW) and 50 % diluted AQW.

The rock surface charge was lower for the same pH if Calcium was removed from the brine, while Na^+ had an insignificant effect. Increasing the temperature created a more negative surface charge. This effect was mainly present for the limestone particles. Lowering the salinity of the brine created a more negative surface charge as well.

Wettability alteration can occur as a result of creating more negative surface charges. The surface charge of an oil phase is in general negative. So creating a more negative limestone surface results in repulsion forces between the oil and rock surface, which means oil is the non-wetting phase. The study of Alotaibi et al. (2011) showed that lowering the salinity by EDL expansion can cause wettability alteration of the Carbonate rock surface towards more water wet. Secondly, increasing the temperature of the brine and adding Ca^{2+} created a more water wet carbonate surface as well.

Al-shalabi et al. (2014) used the geochemical simulators PHREEQC as well to model the recovery mechanism behind LSF in carbonates by matching with published experimental data. The PHREEQC model was assumed to be more reliable than the UTCHEM simulator, because the activity coefficient model is included in the PHREEQC model [Al-shalabi et al. 2014]. Al-shalabi et al. (2014) pointed out that the wettability alteration is the main contributor to the incremental oil recovery during LSF. With the use of PHREEQC Al-shalabi et al. (2014) investigated if the surface charge and/or rock surface dissolution are the cause of wettability alteration.

Solid species analysis through the core had been modelled and compared with the experimental production data of Yousef et al. (2011). The modelling data showed that precipitation and dissolution mainly occurred at the entrance of the core (0.1 dimensionless distance). The successive injection of seawater dilutions showed a trend of calcite precipitation and anhydrite and dolomite precipitation at the entrance. Al-shalabi et al. (2014) claimed that mainly Anhydrite ($CaSO_4$) dissolution occurs during LSF, but is not the main contributor to the wettability alteration. The main contributor is the change of the surface charge as a function of the pH, which expands the EDL and therefore alters the wettability which contributes to the incremental oil recovery [Al-shalabi et al. 2014]. An increase in pH lowered the surface charge, which gets negative if the PZC is exceeded.

2.3.7 Calcite dissolution

Calcite dissolution is expected when low salinity brine is injected into a Carbonate rock, because of the low initial Calcium saturation in the brine. When this occurs, a new fresh surface is exposed, which has not been aged with the crude oil. Therefore, this new surface will be less oil wet, which is favourable for the oil production.

Secondly, due to dissolution a change in the porous structure can occur and the connectivity between the pores can be enhanced. As a result, the permeability and sweep efficiency might be increased. Calcite dissolution can induce fines migration as well.

NMR data of Yousef et al. (2011) showed a damped T_2 signal as a result of the LSF, which is an indicator for a improved connectivity between micro (small T_2) and macro pores (large T_2). This is probably due to calcite dissolution as a result of injecting low salinity brine. The NMR data is just an indicator and the effect of the calcite dissolution on the incremental oil recovery cannot be proven with this data.

Hio (2008) created a thermodynamic geochemical model for the seawater- CO_2 - $CaCO_3$ system to calculate the surface potential of a rock in equilibrium with seawater, which is high sal. With the model Hio (2008) tried to find a relationship for the wettability alteration with the changes in surface potential and with Calcite dissolution. Spontaneous imbibition tests of seawater into outcrop Chalk cores were used for history matching. For the aqueous chemistry the pH is assumed to be constant and the $P_{CO_2} = 10^{-3.5}$.

From their calculations they could not find a clear relation between the wettability alteration and change in the surface potential. The temperature dependency of the wettability alteration, related to the increase of the imbibition rate, is much stronger than the temperature dependency of the zeta potential. However, they pointed out that the Calcite dissolution has the right temperature dependency regarding to wettability alteration. The Calcite dissolution would mainly occur along the intergranular contacts, according to Hio (2008). The surface energy is assumed to be lower at these contacts because of the stress and therefore dissolution rate can be higher. Secondly they referred to enhanced dissolution. The organic acids (Carboxylic material) present in the oil are adsorbed to the rock surface and disturb the Calcite surface, which would enhance the dissolution process. This enhanced dissolution has a higher potential for oil with a high AN, i.e. lower pH. They pointed out that their theory is encouraging, but gives no proof. If their theory would be correct, LSF is interesting for carbonate reservoirs.

However, Austad et al. (2009) questioned the findings of Hio (2008). The relation between the Calcite dissolution and the incremental oil recovery is based on numerical modelling, but there is no empirical proof.

According to Austad et al. (2009) the composition of the brine at equilibrium conditions in the model is false, because no displacement of the formation water is assumed. From most of the experimental research it is observed that, in presence of Sulphate, the oil production increases with the Calcium concentration. However, the Calcite dissolution decreases when the Calcium concentration is increased. These two statements together are in contradiction with the findings of Hio (2008). Secondly, from experiments it is also observed that no incremental oil recovery occurs when only Sulphate is present and Calcium is not, while dissolution should increase in the absence of Calcium. The third objection to the theory of Hio (2008) is the substitution of Calcium by Magnesium which creates an incremental oil recovery. As a result, the Calcium concentration in the effluent increases, which would reduce the Calcite dissolution process.

Austad et al. (2009) gave three good reasons to disagree on the theory that oil recovery is enhanced by calcite dissolution when injecting seawater into chalk cores. However, both researches are based on seawater which is high salinity brine. It is not known if these observations are applicable to the low salinity brine injection.

2.3.8 LSF effect on the Oil-brine interface

From literature is observed that LSF affects the rock-fluid interface, for both sandstone and carbonate rock, by wettability alteration, fines migration and calcite dissolution. However, LSF can also effect the oil-brine interface by formation of in-situ surfactants, emulsion formation and the salting-in effect. This features can occur during LSF in sandstone and carbonates.

2.3.8.1 In-situ surfactants

An increase in pH can cause a reaction with the acidic components present in the oil, which can enhance the formation of in-situ surfactants. An Alkaline flooding behaviour can occur by lowering the IFT between oil and water. According to citetAl-Attar2013, the rise in pH is an effect of calcite dissolution and cation exchange during LSF.

The residual oil in a reservoir or core is a function of the capillary pressure. The Capillary pressure is a function of the inter facial tension according to equation 2.3. So reduction of IFT decreases the capillary pressure and therefore lowers the residual oil saturation.

According to Al-Attar et al. (2013), the IFT and the pH are not responsible for the incremental oil recovery due to LSF in carbonate rock, because no clear correlation between the incremental oil recovery and the IFT or pH was observed.

2.3.8.2 Micro dispersions

An emulsion is a mixture of two or more phases that are initially immiscible, like oil and water. Oil and water are able to mix due to the formation of water micro dispersions in the oil phase. Oil contains natural surfactants like Carboxylates and Sulphate [Emadi and Sohrabi 2013]. Surfactants have a hydrophobic tail and a hydrophilic head. Reverse micelles are formed in the oil phase, with a water droplet in the centre. Figure 2.5 shows an illustration of a reverse micelle.

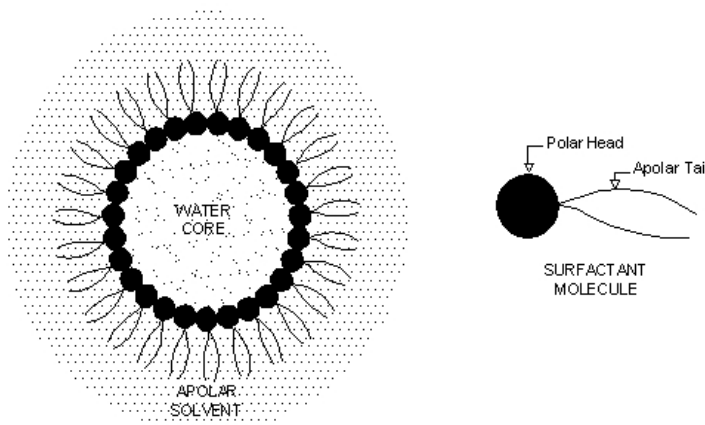


Figure 1: Reversed micelle structure.

FIGURE 2.5: Reverse Micelles.

Emadi and Sohrabi (2013) performed high pressure mixed wet micromodel tests, to investigate the LSF effect. The model is a 2D pore structure attached on a glass plate. When the low salinity brine got in contact with the oil, a large number of micro dispersions were formed at the oil/water interface within the oil phase. These micro dispersions were not formed when interaction of oil with High salinity water occurred.

The micro dispersions results in an incremental oil recovery according to Emadi and Sohrabi (2013) in two ways: wettability alteration and swelling of connate water droplets. As a result of the micro dispersions the oil surface charge alters and therefore the balance between repulsion and attraction forces between oil/water and rock/water interface, which results in a wettability alteration. Swelling of connate water droplets happens when the micro dispersions in the oil move coalescence with the connate water. The swelling pushes the trapped oil out of the dead end pore.

Further investigation on the formation of micro dispersions as a result of LSF, which can be a cause of wettability alteration and oil mobilization, was done by Mahzari and Sohrabi (2014). Fluid characterisation tests (ESEM, FTIR, Karl Fischer Titration) were performed with five different types of crude oil, interacted with brines with various salinities.

Spontaneous formation of micro dispersions was observed for all the crude oils, when salinity of the brine was lowered to 2000ppm. With the formation of the micro dispersions a change in the oil composition was detected for all the crude oils. This change in composition was due to the attachment of some of the oil molecules on the water molecules according to Mahzari and Sohrabi (2014). The amount of formed micro dispersion differed per type of crude oil, but no clear relationship could be found between crude oil properties and micro dispersion formation.

There was a slightly increase of micro dispersion formations with temperature observed. This last observation makes the micro dispersion theory as a recovery mechanism into doubt. At high temperatures, a significant incremental oil recovery was observed in several coreflood and spontaneous imbibition test [Hognesen et al. 2005, Zahid et al. 2012, Zhang and Sarma 2012].

2.3.8.3 Salting-in effect

The solubility of organic material in water can increase when salinity decreases, this is called the salting in effect. The opposite is called the salting out effect, when the solubility of organic material in water drastically decreases when the salinity increases.

Organic molecules are hydrophobic, but when solved in water, a structure is formed around the hydrophobic parts by hydrogen bonds. In this way the organic material is soluble in water. Inorganic ions like Calcium, Magnesium and Sodium break up the water structure around the organic molecules and therefore the solubility decreased when the concentration of these ions increased [RezaeiDoust et al. 2009].

The salting in effect is affected by the ionic strength. Therefore, divalent ions have a bigger impact than monovalent ions. Increasing the solubility also contributes to the desorption of organic material from the rock surface.

2.4 LSF in Carbonate reservoirs, field studies

From experimental studies has been observed that injecting low salinity water in carbonates can enhance the oil recovery, most likely by wettability alteration towards a more water wet rock surface. The first field pilots of LSF in carbonate rock have been performed.

The wettability alteration due to ion exchange in the field has been studied by Austad et al. (2005). High salinity seawater injection has been successful for the Ekofisk field in the North Sea, starting in 1988. The oil bearing layers of this reservoir are the Tor Formation (lower part reservoir) and the Ekofisk Formation (upper part of the reservoir). Both formations are chalks.

For the Ekofisk Formation, no correlation could be found between the imbibition rate and the porosity. Secondly, the real oil recovery of 60 % is much higher than the expected 44 % from laboratory tests [Austad et al. 2005]. This is probably due to the wettability alteration of the Ekofisk formation to a more water wetting state as a result of the surface potential determining ions Ca^{2+} , Mg^{2+} and SO_4^{2-} present in the seawater.

The study of Yousef et al. (2012) on the first two LSF field trial in carbonate revealed that knowledge obtained from experimental studies could be replicated to the field scale. Single-well-chemical-tracer test were performed to measure the residual oil for each injection water type. A reduction of the residual oil due to LSF has been observed from both field trials. From the field data Yousef et al. (2012) confirmed that LSF in carbonates has a great potential to be an efficient EOR method.

2.5 Conclusion

From this literature review was observed that the LSF is a promising EOR method for carbonate reservoirs as well. From both experimental studies and field studies an incremental oil recovery was observed when the salinity of the injection water was reduced. However, there are still a lot of uncertainties about the LSF effects and how this can contribute to the oil recovery. One of the carbonate LSF effects is calcite dissolution. No solid prove was obtained from studies that the dissolution can enhance the oil recovery. Secondly, there is a lack of experimental data on this topic. More knowledge is needed on the Calcite dissolution behaviour during LSF in carbonate rock in order to get a better understanding how it might can affect the oil recovery.

Chapter 3

Theory on Calcite Dissolution

3.1 Mineralogy of Carbonates

Carbonate rock is a type of sediment consisting mainly of Calcium Carbonate ($CaCO_3$). There are mainly three different types of carbonate rock minerals, which are Calcite ($CaCO_3$), Dolomite ($CaMg(CO_3)_2$) and Aragonite ($CaCO_3$). These minerals can form three types of carbonate rock. The most common is limestone, which consists mainly of Calcite and Aragonite; dolostone or dolomite rock, which mainly consists of the Dolomite mineral and chalk, which is composed of Calcite and is a soft and porous carbonate rock [Appelo and Postma 2005].

Dolomite originally is deposited as Calcite. Due to flooding of Magnesium rich groundwater the Calcite mineral is altered to Dolomite. The Dolomite mineral has a slightly higher hardness and is less reactive with cold acidic solution compared to Calcite. Dolomite differs also in the structure from Calcite. The Calcium and Magnesium ions are positioned in an alternating order in the crystal structure.

Aragonite minerals are composed of $CaCO_3$ as well, but differ in the crystal shape. This is called a polymorph, meaning same chemistry but different structure. The crystal structure of Aragonite falls within in the Orthorhombic system, while the Calcite crystal falls within the Trigonal system. Aragonite is the main component of organic species, like coral and shells. Aragonite is unstable and can convert easily into Calcite mineral. If Aragonite is heated up to 400°C , it spontaneously changes into Calcite. So in the geological time while buried, most of the Aragonite changes into Calcite.

The three carbonate minerals also differ in density. Calcite has a density of 2.71 g/cm^3 , Dolomite 2.85 g/cm^3 and Aragonite 2.95 g/cm^3 . This chapter is mainly focussed on Calcite dissolution. Calcite dissolution is the most stable form of $CaCO_3$ and therefore most common mineral in carbonate rock.

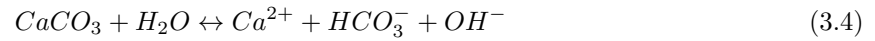
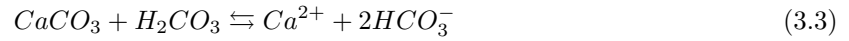
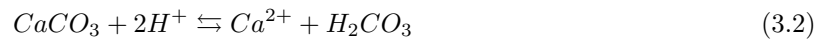
3.2 Calcite Dissolution

Dissolution of Calcite happens when in contact with a liquid. Calcite dissolution happens in two ways: with Kinetics and at Equilibrium. The Kinetic part of Calcite dissolution determines how fast the

dissolution process reaches equilibrium. This is affected by Temperature, pH, type of solution and specific surface area. At a certain time equilibrium is reached and kinetics do not play a role for the calcite dissolution.

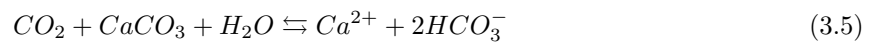
At equilibrium the properties of the fluid do not change with time. The concentration of the different species in the fluid is determined by the equilibrium constants. If changes occur in the concentration of species, temperature, pressure, pH, equilibrium is disrupted and Kinetics will take over again until a new equilibrium has been established.

The following equilibria can be established during Calcite dissolution:



According to equation 3.1 and 3.2, hydrogen consumption occurs during Calcite dissolution. Which is in coherence with a decrease of hydrogen in the fluid and this results in an increase of the pH. Equation 3.1 is the dominating process for $pH < 3.5$, Equation 3.3 for $3.5 < pH < 7$ and Equation 3.4 for $pH > 7$.

Dissolution of Calcite increases when the presence of Carbon Dioxide (CO_2) increases. The dissolution equilibria with CO_2 in the system is:



$$K = \frac{[Ca^{2+}][HCO_3^-]^2}{P_{CO_2}} = 10^{-6.0} \quad (3.6)$$

So when the CO_2 pressure increases, the concentration of Calcium and Bicarbonate increases as well to obtain equilibrium. This means that Calcite dissolution favours from increasing CO_2 pressure. CO_2 becomes aqueous when in contact with water and can form carbonic acid, $2H_2CO_3$ [Appelo and Postma 2005], and lowers the pH of the fluid. $H_2CO_3^* = CO_{2(aq)} + H_2CO_3$.

The effect of temperature on the solubility of Calcite is studied by Coto et al. (2012). Figure 3.1 shows that the solubility decreases significantly with temperature.

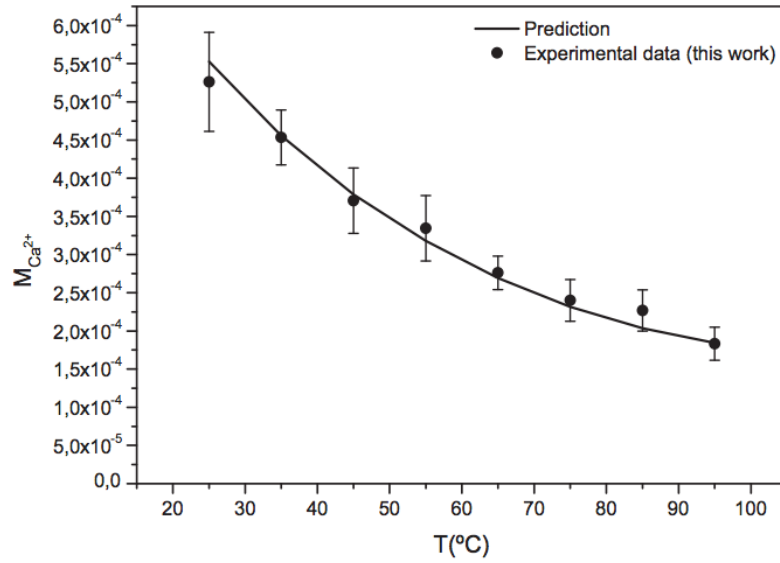


FIGURE 3.1: Solubility of Calcite with temperature, Coto et al. (2012).

3.2.1 Kinetics

The dissolution rate r at Kinetics is often reported in the following form:

$$r = \left(\frac{A}{V}K\right)(1 - \Omega)^n = \frac{dm_{Ca^{2+}}}{dt} \frac{1}{A} \quad (3.7)$$

Where Ω is the saturation state, A is the exposed Calcite surface area, V is the volume of the solution, K is the rate constant and n is the order of the reaction. For diluted solutions, which is the case in LSF, n is said to be $1/2$ [Morse and Arvidson 2002]. P_{CO_2} is the saturation state of CO_2 .

In the case of a high A/V ratio, the solid dominates and the reaction will be surface controlled [Morse and Arvidson 2002]. A system of loose grains mixed with a fluid has a higher A/V ratio than a system where fluid flows through a consolidated porous medium, like LSF in carbonate rock. The dissolution rate r is proportional to A/V and therefore it is assumed that the Calcite dissolution process during LSF requires some time to reach the equilibrium state.

The saturation state Ω is the ratio between the Ion Activity Product (IAP) and the solubility product (K_{SP}).

$$\Omega = \frac{IAP}{K_{SP}} \quad (3.8)$$

The saturation index SI is the log of the saturation state Ω :

$$SI = \log\left(\frac{IAP}{K_{SP}}\right) \quad (3.9)$$

K_{SP} is the product of the ion activities at equilibrium state and IAP is the product of the actual measured activities. The solubility product of Calcite is given by equation 3.10.

$$K_{SP} = (\gamma_{Ca^{2+}} m_{Ca^{2+}})(\gamma_{CO_3^{2-}} m_{CO_3^{2-}}) \quad (3.10)$$

The solubility product of Calcite is $3.36 \cdot 10^{-9}$ and of Aragonite is $6.0 \cdot 10^{-9}$ at 25 °C. A higher K_{SP} means a higher solubility of the mineral. If the $IAP = K_{SP}$, the solution is in equilibrium and when $IAP < K$, the solution is under saturated and dissolution will occur. For a dissolution process, the saturation state Ω should be below 1.

The activities of different inorganic carbonate species are a function the pH and the P_{CO_2} and can be calculated with the following equations: [Appelo and Postma 2005]:

$$\log(a_{H_2CO_3^*}) = \log(P_{CO_2}) - 1.5 \quad (3.11)$$

$$\log(a_{HCO_3^-}) = -6.3 + \log(a_{H_2CO_3}) + pH \quad (3.12)$$

$$\log(a_{CO_3^{2-}}) = -16.6 + \log(a_{H_2CO_3}) + 2pH \quad (3.13)$$

The Calcite dissolution is governed by the three equations 3.1/3.2 (k_1), 3.3 (k_2) and 3.4 (k_3) plus the backward precipitation process (k_4). Therefore the dissolution rate can be defined as:

$$r = k_1 a_{H^+} + k_2 a_{H_2CO_3^*} + k_3 a_{H_2O} - k_4 (a_{Ca^{2+}} + a_{HCO_3^-}) \quad (3.14)$$

The rate constants are a function of the temperature in Kelvin [Appelo and Postma 2005]:

$$\log k_1 = 0.198 - 444/T \quad (3.15)$$

$$\log k_2 = 2.84 - 2177/T \quad (3.16)$$

$$\log k_3 = -5.86 - 317/T \text{ for } T \leq 298K \quad (3.17)$$

$$\log k_4 = -1.1 - 1737/T \text{ for } T > 298K \quad (3.18)$$

When the pH and P_{CO_2} are known, the concentrations of the different carbonate species in solution can be calculated with the use of equations 3.11, 3.12 and 3.13. The different rate constants can be calculated as shown in equations 3.15-3.18. When the rate constants are known, the Calcite dissolution rate can be calculated according to equation 3.14. Finally, the change of Ca^{2+} in the solution with time can be calculated, which represents the Calcite dissolution rate.

3.2.1.1 Rate Controlling Mechanisms

When a fluid flows through a porous medium, there can be made a distinctions between the solution at the surface and solution in the bulk. Morse and Arvidson (2002) divided the kinetic dissolution process in different steps:

1. Diffusion of reactants through the bulk solution to the calcite surface
2. Adsorption of the reactants on the solid surface
3. Migration of reactants on the surface to an active site, which is called dislocation
4. The chemical reaction between the adsorbed reactants and solid. Bonds are broken and formed and hydration of ions occurs
5. Migration of the reaction products away from the reaction site
6. Desorption of the products into the solution
7. Diffusion of products away from the surface to the bulk solution

If step 1 and/or 7 are the limiting factor for the Calcite dissolution, the reaction is a diffusion controlled processes. If step 2 and 6 are the limiting factor, the dissolution is surface controlled.

If a reaction is diffusion controlled, there is a difference in the ion concentration, pH and P_{CO_2} in the bulk solution and at the surface. The activities of the ions, present in the carbonate system during Calcite dissolution, are dependent on the near surface pH and P_{CO_2} .

Diffusion controlled dissolution mainly occurs in the beginning of the process, when the equilibrium of Calcite dissolution has not been reached yet. When the equilibrium has been reached, the Calcite dissolution is surface controlled. There is a transition region between the diffusion and surface controlled dissolution.

If the reaction is diffusion controlled, the rate is linear with the saturation state Ω . If the reaction is surface controlled this relation is not linear. Carbonate dissolution is in general surface controlled, unless there is a high degree of disequilibrium [Morse and Arvidson 2002].

For moving solutions, which is the case for injection of low salinity brines, the advection transport is faster than the molecular diffusion, unless the injection rate is reduced to a certain value. So the flow rate through the core needs to be low enough to reach the equilibrium state. Otherwise the Calcite dissolution will be limited by to the diffusion of ions, like H^+ and CO_2 , which are needed for the process. According to Sanford et al. (1989), the reduction of Calcite dissolution due to a fluid velocity occurs from $v = 1m/day$ (figure 3.2), which is $3.2ft/day$ in field units.

The presence of inhibitors on Calcite dissolution can be present in natural waters, like seawater. These inhibitors can be Magnesium, Strontium, Barium, metal ions, Silica, organics, Sulphate, Phosphate and Calcium itself. The influence of these inhibitors at the Calcite surface increases significantly with increasing saturation state Ω [Morse and Arvidson 2002].

The inhibiting effect of Phosphate and Sulphate increases with the Calcium and Magnesium concentration in the solution as well. This is explained by Morse and Arvidson (2002) as an effect of the adsorption of Ca^{2+} and Mg^{2+} on the Calcite surface. As a result the Zeta potential will increase, and accompanied the co-adsorption of Sulphate and Phosphate on the Calcite surface, which inhibits the Calcite dissolution. Metals ions have a great inhibitory effect on Calcite dissolution, because they can adsorb on the surface as well and block or prevent the interaction between the brine and the Calcite surface molecules.

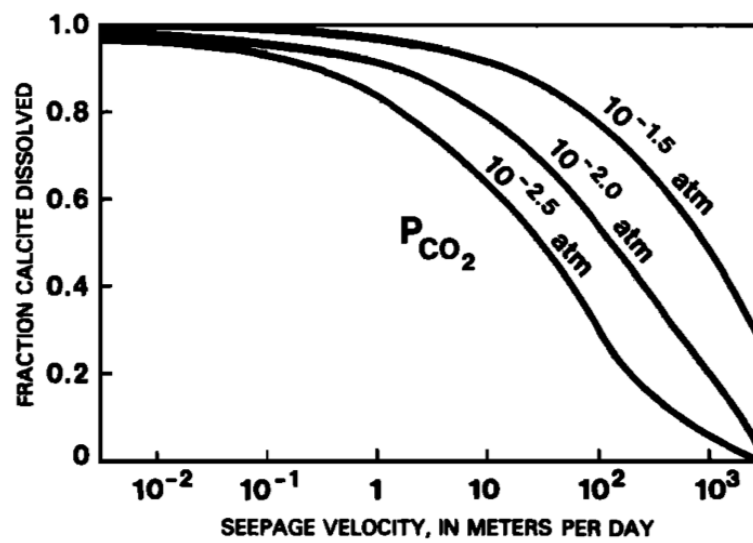


FIGURE 3.2: Kinetics effects on mixed waters for various groundwater velocities, Sanford et al. (1989).

3.2.2 Effect of pH on Calcite dissolution

According to Appelo and Postma (2005), the molecule $H_2CO_3^*$ dominates in the solution at a $pH < 6.3$, at a $pH > 10.3$ Carbonate (CO_3^{2-}) is dominant and in between Bicarbonate (HCO_3^-). The relation between the pH and the concentration of the different carbonate species is shown in figure 3.3.

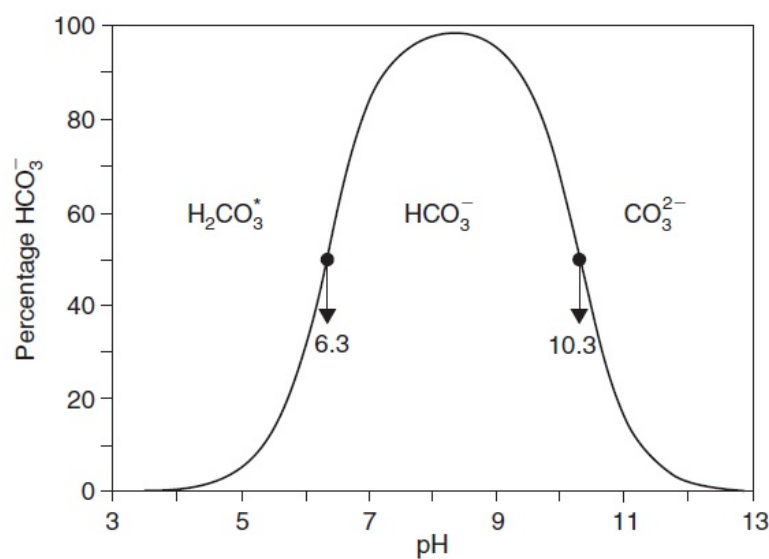


FIGURE 3.3: Aqueous carbonate species as function of pH, Appelo(2005), p180.

The effect of the pH on the Calcite dissolution has been investigated by Adh (2009) by numerical simulations. They assume that Calcite dissolution is influenced by both transport (Diffusion) and surface reaction process. Simulation results showed that the dissolution rate increases with decreasing pH. This can also be explained with the equilibrium equation of Calcite dissolution.

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[H^+]} = 10^{1.85} \quad (3.19)$$

According to the equilibrium condition of equation 3.19, Calcite dissolution favours from a higher Hydrogen concentration in the fluid. The decreasing pH showed an incremental change in the concentrations of H^+ , Ca^{2+} and H_2CO_3 and a decrease in the concentrations of CO_3^{2-} , HCO_3^- and $CaCO_3$ in the simulation results of Adh (2009). This observation is in line with figure 3.3 from Appelo and Postma (2005).

As explained before in this chapter, there are three regions distinguished. Where equation 3.1 is the dominating process for $pH < 3.5$, equation 3.3 for $3.5 < pH < 7$ and equation 3.4 for $pH > 7$.

According to Appelo and Postma (2005) in the first region below a pH of 3.5 the dissolution rate is more influenced by the rotation rate/flow rate and dependent on the pH. In the second region the dissolution rate is more influenced by the CO_2 pressure and less dependent on pH. In the third region the rate becomes independent of the pH and only depending on the CO_2 pressure.

Sjoberg and Rickard (1984) studied the temperature and pH dependency of Calcite dissolution in aqueous KCl solutions. Experiments were performed with a rotating disc apparatus. A distinction is made by them as well between three pH regions. At $25^\circ C$ a H^+ dependent region for $pH < 4$, a transition regime between $4 < pH < 5.5$ and a H^+ independent region for $pH > 5.5$. These boundaries move to higher pH values for lower temperatures. The H^+ dependent region is controlled by mass transfer, which is also explained by Appelo and Postma (2005), but sets the boundary at a lower pH value of 3.5.

Figure 3.4 gives a schematic overview of the different pH regions and temperature effect in the Calcite dissolution process.

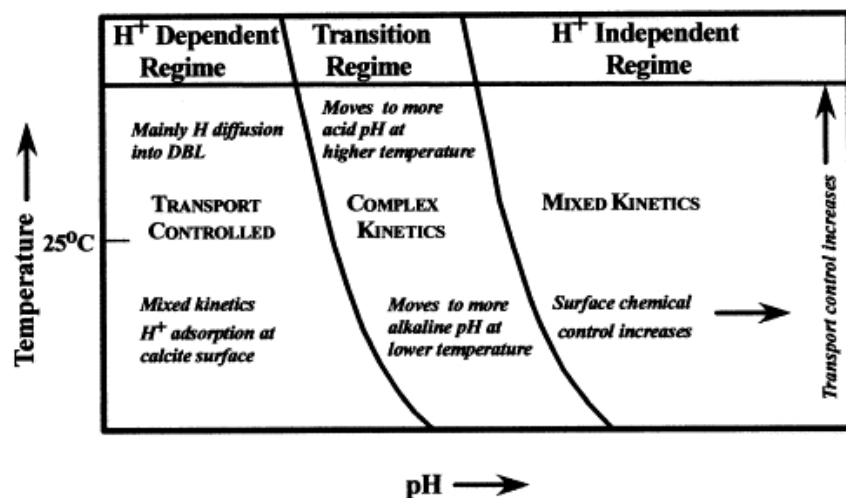


FIGURE 3.4: pH dependency of Calcite dissolution, Morse and Arvidson (2002).

3.2.2.1 Low pH regime

For the low pH regime ($pH < 4$), the Calcite dissolution is proportional to the H^+ concentration and the dissolution is transport controlled. The two limiting processes on the dissolution rate are diffusion

of H^+ from the bulk solution through the DBL to the surface and diffusion of reaction productions from the surface through the DBL to the bulk solution. The diffusion rates are assumed to be independent of the P_{CO_2} [Berner and Morse 1974]. According to Sjöberg and Rickard (1984) the dissolution rate is proportional to the H^+ concentration with a power of 0.9.

$$R_T = k'_T [H^+]^{0.9} \quad (3.20)$$

Equation 3.20 shows that the dissolution rate is not fully dependent on the H^+ diffusion, but also on the diffusion of the reaction products from the surface to the bulk solution and the formation of $CO_2(aq)$ at the surface. The diffusion coefficient of H^+ is 2-3 times higher than the diffusion coefficient of Ca^{2+} and the different carbonate species.

If the pH of the bulk solution decreases, the diffusion rate of H^+ through the DBL increases, and as a result the H^+ concentration at the surface will increase. So a lower pH for the bulk solution causes a lower pH at the surface. The concentrations of the reaction products at the surface increase as well with lower bulk pH. The chemical reaction rate constant k_C is very high for the low pH regime. However, the reaction rate is still limited by the diffusion of the reaction products away from the surface into the bulk solution. Therefore there is a slight difference between the reaction products concentrations at the surface and the equilibrium values of the products. The chemical surface reaction has a significant high rate to keep up the product concentrations at the surface, while diffusion of the products into the bulk solution takes place.

3.2.2.2 Transition zone

For a pH between 4 and 5.5 the Calcite dissolution dependency on the H^+ concentration varies. In this zone there is a transition from H^+ in-dependency to H^+ dependency. When the H^+ ions penetrate the diffusion boundary layer (=DBL) and at first reach the Calcite surface, there is a transition to H^+ dependency. The penetration of H^+ through the DBL in the H^+ independent regime is negligible and in the H^+ dependent regime the H^+ ions reach the surface.

The value of the pH at which the transition occurs can differ per system. It is depended on the nature of the Calcite surface, of the bulk solution and of the hydrodynamics of the system [Sjöberg and Rickard 1984]. As the initial Calcium concentration in the bulk solution increases, the transition pH increases as well. For most of the subsurface water flow, like LSF, there is a low flow rate and an a certain initial Calcium concentration. Therefore a wide pH range of the H^+ depended zone is assumed for Calcite dissolution during LSF.

3.2.2.3 Intermediate to high pH regime

For $pH > 5$ the Calcite dissolution is independent of the H^+ concentration. The H^+ independent region is more dependent on the ionic strength of the solution and characterized by mixed kinetics: Product diffusion through the boundary layer and first order surface chemical reactions.

When the temperature increases the diffusion control increases and when the temperature decreases the surface chemistry control increases. So for low temperatures the Calcite dissolution is mainly chemically controlled. The H^+ concentration at the surface is much lower than in the bulk solution and CO_3 is the dominant carbonate species. The reaction rate of the Calcite dissolution in the H^+ independent region is $\propto \sqrt{[Ca^{2+}][CO_3^{2-}]}$.

3.2.3 Activity and Activity Coefficient

As explained before, the saturation state Ω is a function of the ion activities (equation 3.8 and 3.8). The ion activity $a[i]$ is related to the concentration and the activity coefficient γ of the ion i . The activity is dimensionless.

$$a[i] = m_i \gamma_i \quad (3.21)$$

The activity coefficient is related to the ionic strength I , temperature and the ion charge z_i . The Debye-Hückel equation for the activity coefficient for salinities with a ionic strength up to 0.1 [Appelo and Postma 2005]:

$$\log \gamma_i = -\frac{A(T)z_i^2\sqrt{I}}{1 + \bar{a}B(T)\sqrt{I}} \quad (3.22)$$

Which can be simplified to the Güntelberg method:

$$\log \gamma_i = -\frac{0.5z_i^2\sqrt{I}}{1 + \sqrt{I}} \quad (3.23)$$

$A(T), B(T)$ are temperature dependent constants and $\bar{a}$ is the empirical ion-size parameter, which is between $2 - 11 \cdot 10^{-10}m$. $\bar{a}$ is $6 \cdot 10^{-10}m$ for Calcium [Appelo and Postma 2005]. This relation for γ is only valid for solutions with $I < 0.1$.

For even lower salinities ($I \leq 0.01M$) the Debye-Hückel method is altered to:

$$\log \gamma_i = -A(T)z_i\sqrt{I} \quad (3.24)$$

The ionic strength $I[mol/m^3]$ of a solution is defined as:

$$I = \frac{1}{2} \sum_i z_i^2 [X_i] \quad (3.25)$$

The ionic strength of seawater is around 0.9 mol/l and the ionic strength of low salinity water is below 0.1. The relation between the ionic strength and ionic activity according to equation 3.21 and 3.22 is shown in figure 3.5. For Ca^{2+} the activity coefficient decreases with the ionic strength I for $I \leq 0.2M$.

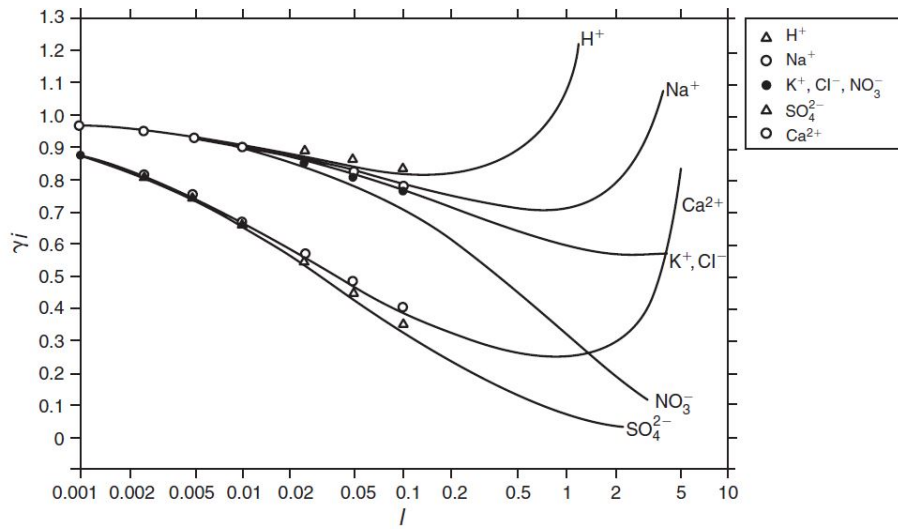


FIGURE 3.5: Activity coefficient versus the ionic strength for different species [Appelo and Postma 2005].

3.2.4 Thermodynamics

The Calcite dissolution equilibrium reactions are controlled by Thermodynamic parameters, like the Gibbs free energy. The Gibbs free energy G gives the direction of a chemical reaction, which is in this case of Calcite dissolution or precipitation.

A general reaction is given by:



The change in Gibbs free energy is:

$$\Delta G_r = \sum_{Products} \Delta G_r - \sum_{Reactants} \Delta G_r \quad (3.27)$$

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (3.28)$$

Or with the rate constant k :

$$\Delta G_r = \Delta G_r^0 + RT \ln k \quad (3.29)$$

Where ΔG_r^0 is the standard Gibbs free energy. The standard free Gibbs energy, or the Gibbs free energy of formation, gives the amount of energy needed for the formation of 1 mole of the material at standard conditions. The ΔG_r^0 of Calcite is -1129.30 KJ/mol [Wenk and Bulakh 2004].

If $\Delta G_r > 0$ the reaction proceeds to the left, if $\Delta G_r = 0$ the reaction is at equilibrium, and if $\Delta G_r < 0$ the reaction proceeds to the right. So in the case of Calcite dissolution, the change in the Gibbs energy should be smaller than zero.

In the Kinetic region the dissolution rate is very dependent on the change in Gibbs energy. Far from equilibrium $\Delta G < -12 \text{ KJ/mol}$ and near equilibrium $-1.7 \text{ KJ/mol} < \Delta G < 0$ [Xu et al. 2012].

The equilibrium constant is dependent on the Standard Gibbs free Energy and Temperature. This relation is at equilibrium when:

$$\ln K_{eq} = -\frac{\Delta G_r^0}{RT} \quad (3.30)$$

The change in Gibbs free energy is also a function of the Saturation state Ω , which is a function of the ion activities and Solubility Product (equation 3.8).

$$\Delta G_r = RT \ln \Omega \quad (3.31)$$

Implementing equation 3.31 in equation 3.7, we get:

$$r = \frac{A}{V} k (1 - e^{\Delta G/RT})^n \quad (3.32)$$

Chapter 4

Materials and Methods

4.1 Brines

Two types of experiments were performed to study the Calcite dissolution behaviour by LSF, bulk and coreflood experiments. Both the bulk experiment and the coreflood experiment are performed with various diluted versions of seawater and NaCl solutions. The composition of formation water (FW), seawater (SW), 5 times diluted seawater, 25 times diluted seawater and diluted artificial seawater (Dil ASG) are given in table 4.1. All the brines are prepared with de-mineralized water and reagent-grade chemicals.

Ions [mg/L]	Seawater	25Dil SW	Dil.ASG	2000ppm NaCl	500ppm NaCl
Na+	13404	536	87	787	197
K+	483	19	4	-	-
Mg2+	1618	65	2	-	-
Ca2+	508	20	1	-	-
Sr2+	17	1	0	-	-
Cl-	24141	967	143	1213	303
SO42-	3384	135	2	-	-
HCO3-	176	7	2	-	-
TDS	43731	1751	241	2000	500
I (mol/L)	0.869	0.035	0.004	0.034	0.009

TABLE 4.1: Composition of the various Brines.

4.2 Bulk Experiments

The purpose of the bulk experiment is to study the effect of temperature, salinity, composition of the brine and pH on the behaviour of Calcite dissolution in brine. The aim of the bulk experiment is to reach the calcite dissolution equilibrium state at different conditions.

4.2.1 Material

The following materials and equipment is used for the experiment:

1. Chalk, limestone or pure Calcite crystals
2. Oven
3. Magnetic stirrer
4. pH Meter (SD = 0.136)
5. High Performance Liquid Chromatography (HPLC)

4.2.2 Procedure

For each bulk experiment 5 gram of grounded carbonate rock material was added to 500 mL brine in a glass jar. A 5 mL sample was taken before adding the rock to the brine and the initial pH was measured. The brine containing the grounded rock was subsequently shaken, rested for 10 minutes, pH was measured and a sample taken. The jar was put on a magnetic stirrer and after each hour, the solution was rested for 10 minutes and again the pH was measured and a sample taken. The samples were filtered to remove the small fines. The Calcium concentration of the samples was measured with the use of HPLC.

The conducted bulk experiments are shown in table 4.2.

Exp nr.	Brine	T [°C]	Initial pH	Material	Vacuum
1	Dil ASG	22	6.73	Chalk	No
2	25 x Dil SW	22	6.84	Chalk	No
3	2000 ppm NaCl	22	5.43	Chalk	No
4	1000 ppm NaCl	22	5.49	Chalk	No
5	500 ppm NaCl	22	5.60	Chalk	No
6	2000ppm NaCl	22	5.44	Chalk	No
7	1000ppm NaCl	22	5.44	Chalk	Yes
8	2000ppm NaCl	22	6.22	Calcite	Yes
9	2000ppm NaCl	22	5.82	Chalk	Yes
10	2000ppm NaCl	22	5.84	Limestone	Yes
11	25 Dil SW	22	7.47	Chalk	Yes
12	25 Dil SW	22	8.22	Limestone	Yes
13	2000ppm SW	50	6.16	Limestone	Yes
14	25 Dil SW	22	3.05	Limestone	Yes
15	500ppm	22	6.09	Limestone	Yes

TABLE 4.2: Performed Bulk experiments.

For experiment 14, the initial pH was lowered with a droplet of a 10% HCl solution, which does not change the brine composition significantly. Experiment 7 till 15 were conducted at CO_2 free environment. During the experiment the jar was connected to a vacuum pump and stirred.

4.3 Core Flood Experiment

The purpose of the coreflood experiment was to mimic the LSF in a reservoir by injecting low sal brine into a small core of carbonate rock. Several coreflood experiments were performed at different conditions regarding to salinity, composition and pH of the brine, different temperatures and injection rates.

4.3.1 Material

The following equipment was used for the coreflood experiment:

1. Pump
2. Oven
3. Core holder
4. Core: D= 38mm en L= 50mm
5. Pressure transducer (Pressure range is -3 to 3 bar, Accuracy of 0.1 mbar)
6. Back pressure: 7 Bar
7. Data-acquisition box
8. Fraction collector
9. Computer
10. pH Meter (SD=0.136)
11. High Performance Liquid Chromatography (HPLC)
12. Density meter, Bronkhorst

Sketches of the setup are shown in figure 4.1 and 4.2.

4.3.2 Procedure

The following procedure was applied for the single-phase coreflood experiments:

- At first, a CT scan of the dry core was performed
- The core was vacuumed for 24 hours using a vacuum pump
- Brine was injected at a velocity of 1 ft/day and the back pressure was set at 7 Bar. The total pressure drop over the core was recorded during the experiment. The density and temperature before and after the flow through the core was measured during the high temperature coreflood experiments.

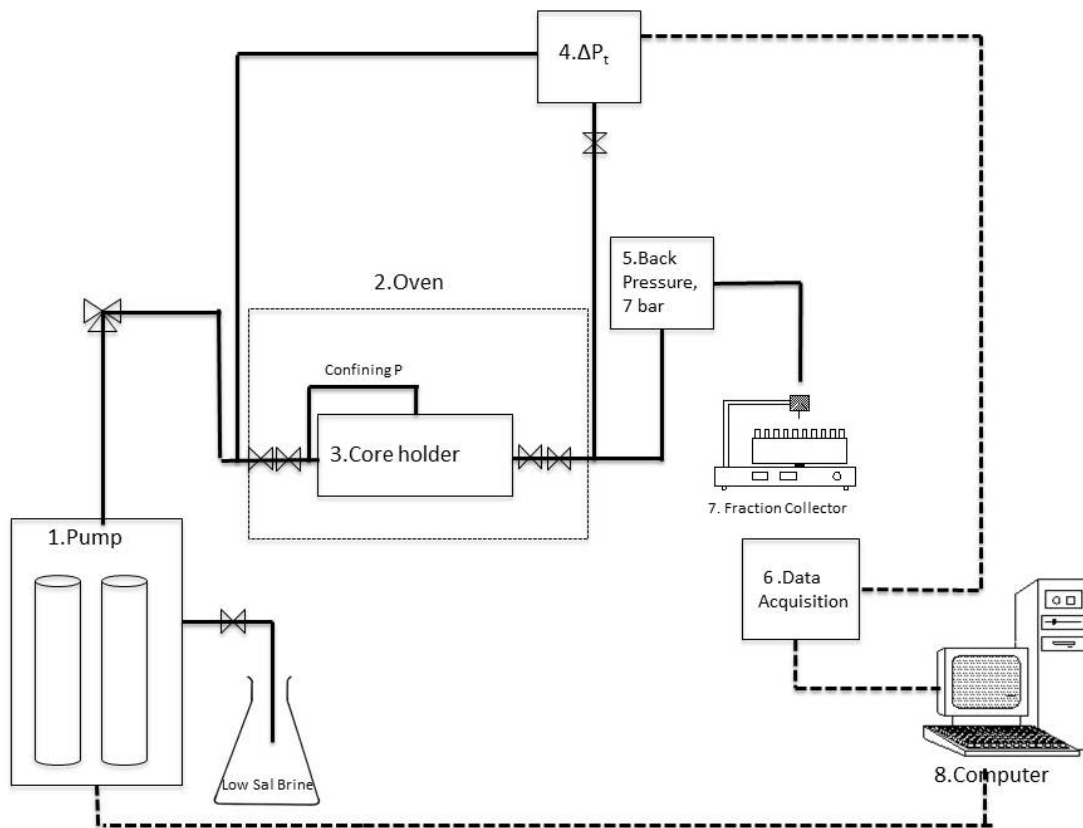


FIGURE 4.1: Sketch of the set up of the coreflood experiment at room temperature.

- The Effluent was collected by a fractional collector. Samples were taken of approximately 5 ml, pH and Calcium concentration of the effluent was measured.
- After the experiment the core was CT scanned within the core holder. The core holder was shut in, in order to keep the brine in the core and to prevent precipitation.
- The pH and Calcium concentration of the effluent was measured.

The following procedure was applied for the two-phase coreflood experiments:

- The core was vacuumed for 24 hours using a vacuum pump
- High salinity brine (10,000 ppm NaCl) was injected at 1 ft/day rate and the back pressure was set at 35 Bar. 10 Pore Volumes of high salinity brine was injected in order to remove undesired ions that might be present due to the drilling fluid.
- Six pore volumes of crude oil was injected with increasing rate; 0.4, 0.8, 1.2, 1.6 and 2.0 cc/min. The flow was top down.
- The oil saturated core was shut in for a week at 50 °C and at a back pressure of 35 Bar, to age the sample with the crude oil.

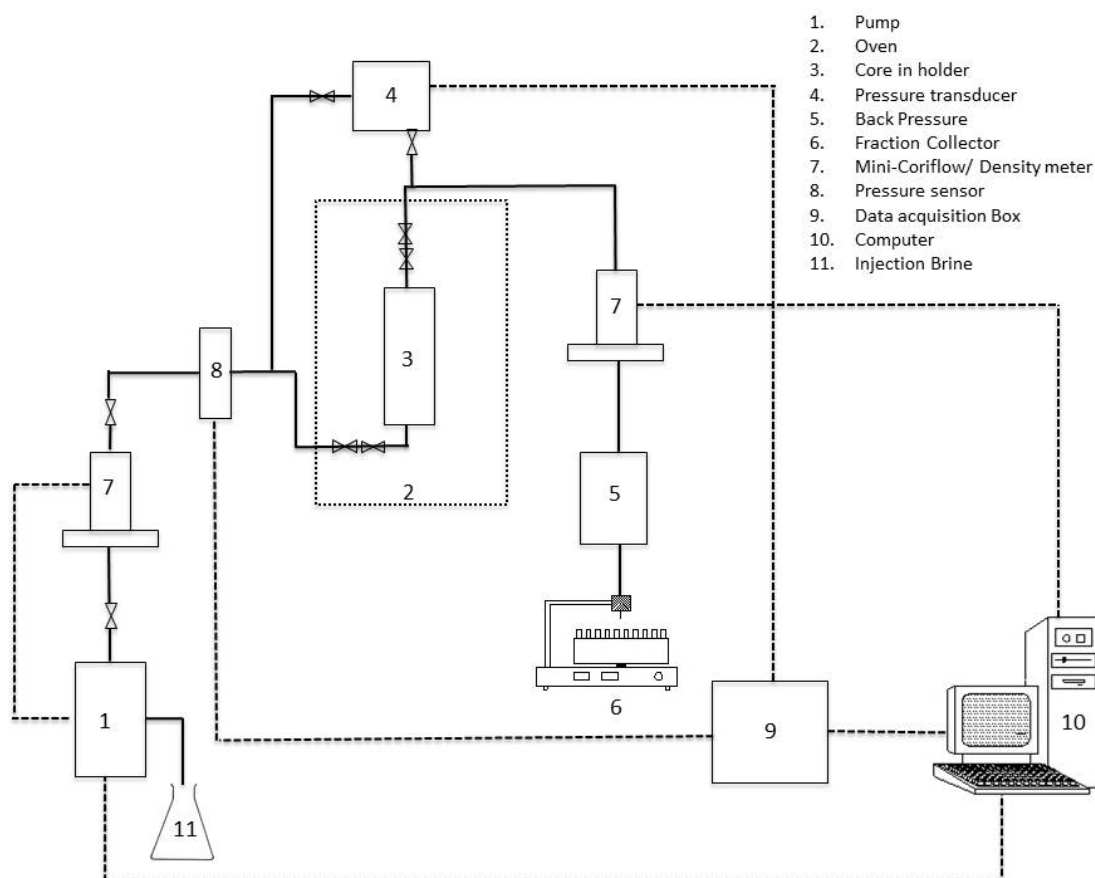


FIGURE 4.2: Sketch of the set up of the coreflood experiment at high temperature.

- After the shut in period, injection of low salinity brine was started with 1 ft/day, the flow was bottom up and back pressure was set at 7 Bar.
- The total pressure drop over the core was recorded during the experiment. The density and temperature before and after the flow through the core was measured as well.
- The effluent was collected by a fractional collector. Samples were taken each 5 ml approximately.
- The pH and Calcium concentration of the effluent was measured.

The properties of the used Crude oil are listed in table 4.3. TAN is the total acid number and TBN is the total basic number. The number indicates the quantity of acid/basic components in the oil. A crude oil has high acidity if the $\text{TAN} > 0.5 \text{ mg KOH/g oil}$.

4.3.3 Core preparation

Different core samples with different mineralogy were used for the coreflood experiment.

The chalk core of the first coreflood experiment was from an outcrop block of 'Limburg Mergel', which is Marl in Dutch. Limburg Mergel is a chalk, which consist of 99.9 % CaCO_3 , deposited in the Cretaceous. So the name of Marl is inappropriate, because the chalk has a very low clay content. The chalk consists

Property		Crude Oil
Density (60 °C)	[g/cm ³]	0.79
IFT	[mN/m]	27
API	[°API]	41.6
Viscosity (60 °C)	[cp]	1.68
TBN	[mg KOH/g oil]	<0.1
TAN	[mg KOH/g oil]	0.17
Cloud point	[°C]	33
Maximum Pour point	[°C]	18

TABLE 4.3: Properties of Crude Oil.

of small chalk skeletons and chalk mud, which were deposited on the bottom of the Cretaceous sea. The fossil remains are from marine organisms, like algae, small foraminifera, shells and ammonites. Most of the skeletons consist of Aragonite. However, in the Limburg chalk due to compaction, Aragonite is converted to calcite, with low magnesium content. This is because Aragonite is an unstable form of calcium carbonate. Further, the chalk consist of very small amount of Limonite and Silica. The matrix of the chalk is very fine and has a light yellow color.

Estailades limestone from a reservoir is used for the limestone cores. The Estailades limestone can be found in the South of France. The Estailades is deposited in the Cretaceous as well and consist of > 95% of Calcite. The limestone composes of algae grains with a size of 0.7-1 m, cemented by calcite [Guen et al. 2007].

The cores were drilled and a thin layer of heat resistant glue covers the surrounding surface. The core was dried in an oven for two days. The properties of the plugs used in this study are given in table 4.4.

Core	Material	Length [mm]	Diameter [mm]	Porosity [%]	PV [ml]
1	Chalk	50	38	47	26.65
2	Limestone	50	25	29	7.36
3	Limestone	50	38	29	16.44

TABLE 4.4: Dimension and Petrophysical parameters of the Cores.

4.3.4 Permeability Tests

Permeability tests were performed for the chalk and limestone cores. The pressure difference was measured for the different injection rates and plotted against each other in figure 4.3. With the use of Darcy's law the permeability can be determined from the slope. The calculated permeabilities from the permeability test are shown in table 4.5.

Core	Length [m]	Area [m ²]	Porosity [%]	Permeability [mD]
Chalk	0.05	$1.134 \cdot 10^{-3}$	47	518
Limestone	0.05	$1.134 \cdot 10^{-3}$	29	66

TABLE 4.5: Permeability determined from permeability test

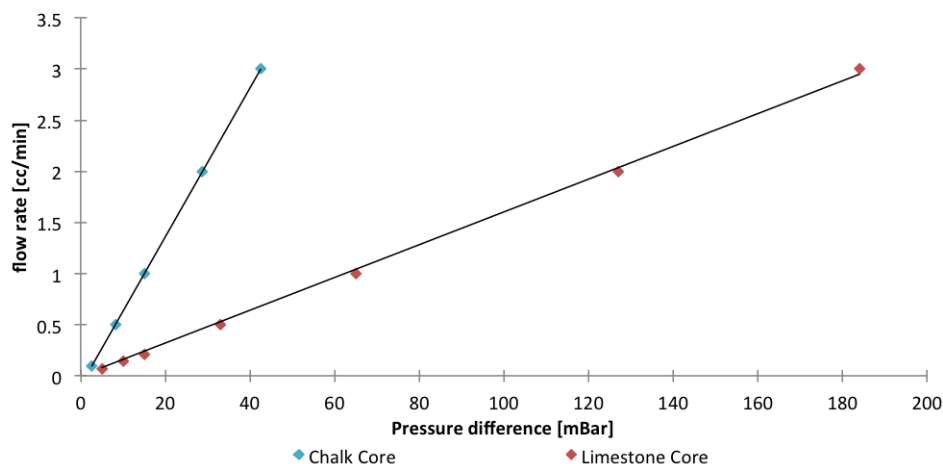


FIGURE 4.3: Permeability test of the chalk core and limestone core.

4.4 Scanning Electron Microscope and X-ray Diffraction

The Scanning Electron Microscope (SEM) was used for the chalk and limestone samples to study the present elements in the rock material. Table 4.6 shows the weight percentage of the elements found in the chalk and limestone samples. Figure 4.4 and 4.5 show the images of the chalk and limestone sample where the SEM measurement has been made.

Element	Chalk	Limestone
Carbon C	15.93 %	33.59 %
Oxygen O	40.20 %	30.01 %
Natrium Na	-	0.50 %
Magnesium Mg	0.47 %	0.44 %
Aluminium Al	0.25 %	0.27 %
Silicon Si	0.51 %	0.40 %
Sulfur S	-	0.23 %
Kalium K	-	0.34 %
Calcium Ca	41.58 %	33.34 %
Iron Fe	1.07 %	0.89 %

TABLE 4.6: Results of SEM in Weight Percentage.

The SEM results shows that there is mainly Calcite present in the samples ($CaCO_3$). In both the samples there is also Magnesium, Iron, Silica and Aluminium detected, which can be interpreted as presence of clays. The most common clay minerals are:

- Kaolinite: $Al_2Si_2O_5(OH)_4$
- Illite: $(K, H_3O)(Al, Mg, Fe)_2(Si, Al)_4O_{10}[(OH)_2, (H_2O)]$
- Chlorites: $(Fe, Mg, Al)_6(Si, Al)_4O_{10}(OH)_8$
- Smectite: $Ca_{0.17}(Al, Fe, Mg)_2(Si, Al)_4O_{10}(OH)_2.nH_2O$

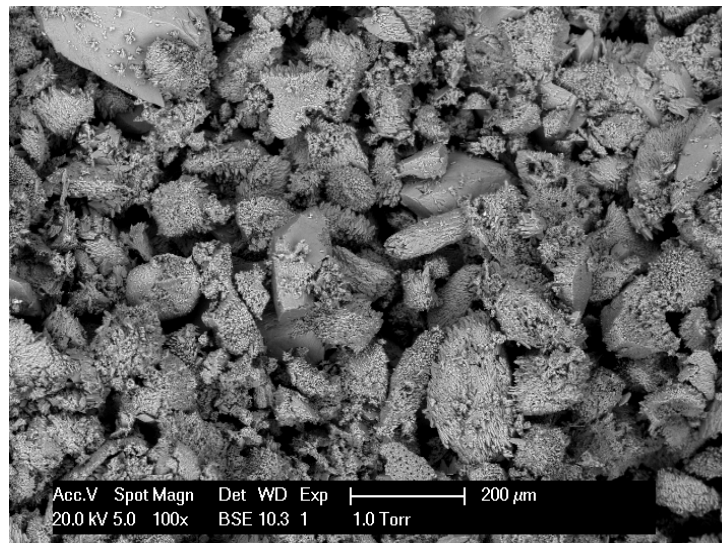


FIGURE 4.4: Photograph of chalk, SEM data

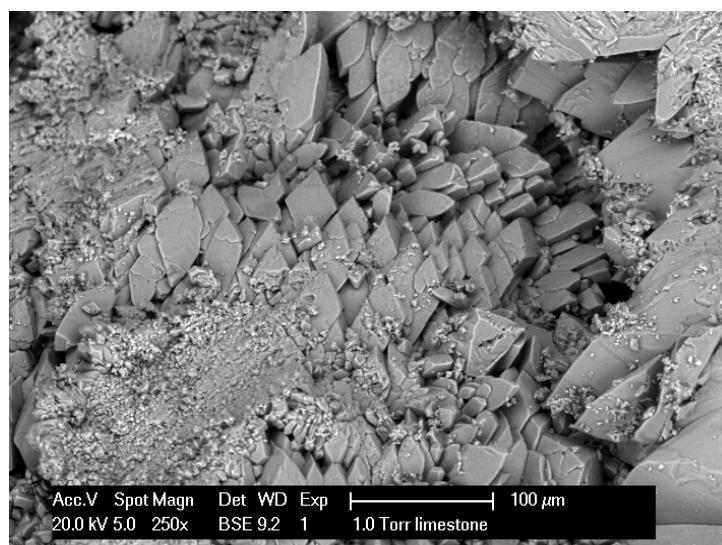


FIGURE 4.5: Photograph of limestone, SEM data

X-ray diffraction (XRD) technique was used as well to detect the present elements in the chalk and limestone samples. The results of the XRD are shown in table 4.7. No clay minerals are present according to the XRD analysis.

Sample	Compound
Chalk	$Ca(84.5\%), Mg(15.5\%), CO_3, Si, O_2$
Limestone	$Ca(97.0\%), Mg(3.0\%), CO_3$

TABLE 4.7: Results of XRD in Weight Percentage

4.5 PHREEQC Modelling

PHREEQC is a software which can perform aqueous geochemical calculations, like equilibrium reactions between solutions and different phases regarding to dissolution/precipitation, ion exchange, surface complexes and kinetics.

The kinetic model for Calcite dissolution was used to match the experimental data. An initial solution had to be determined by giving the composition, pH and temperature. The solution can be equilibrated with a certain P_{CO_2} , to set the amount of CO_2 present in the brine. For the CO_2 -free system, the solution was not equilibrated with a certain P_{CO_2} .

For the kinetics of calcite dissolution a reaction rate is obtained, as shown equation 3.7. In the PHREEQC model A/V and the exponent n are input parameters. For the Bulk experiment A/V was set 80, which means there is a relatively much surface area is open for dissolution. For the coreflood experiment A/V is much lower, because less surface area open for dissolution and it will take longer to reach the equilibrium state. A/V was set 5 for the coreflood experiment model and n was set at 0.67 (Appelo, 2005) for both models. The amount of moles initial moles m_0 in the solution is dependent on the brine and the amount of available reactant m for the bulk experiment was set at 0.05 mol (=5 gram Calcite). The amount of available reactant m for the coreflood experiment was set at default, which is 1.0 mol of Calcite. The injection rate in the PHREEQC model is set by adjusting the time needed for the brine to pass through the whole core.

After a certain time, the equilibrium state is reached. The concentrations of the different species at equilibrium is based on mole balance equations and activities(Equation 3.21). In this study, the matching between experimental and PHREEQC modelling data is focused on the the Calcium concentration at equilibrium.

Chapter 5

Results Bulk Experiments

Several Bulk experiments have been performed to obtain the Calcite dissolution equilibrium state for different brines at different conditions. The objective was to investigate the effect of different parameters on Calcite dissolution equilibrium; the following parameters were examined:

1. Brine composition and salinity
2. Temperature
3. CO_2
4. pH
5. Type of carbonate material

5.1 Composition and salinity effect

Bulk experiments have been performed with 500, 1000 and 2000 ppm NaCl and chalk or limestone at room temperature and atmospheric pressure. Figure 5.1 shows the Calcium concentration in the solution versus time for the three experiments. Initially there was no Calcium present in the brines, so the Calcium content of the brine during the whole experiment was due to mineral dissolution from the chalk powder.

The data in figure 5.1 shows that the Calcium concentration increased to a value of 0.6 mmol/l within 10 minutes, for all the three brines and the concentration remained constant up to 500 minutes. This shows that Calcite dissolution reaches equilibrium in a short period of time of ten minutes.

Figure 5.2 shows the experimental data together with the PHREEQC modelling data. The experimental and PHREEQC modelling data did not identically match. From the experimental data it is not observed that the dissolution in the 2000 ppm NaCl is higher than in the 500 ppm NaCl solution. The PHREEQC data shows that the Calcite dissolution increases with salinity for the NaCl solutions from 500 to 2000 ppm. For the 500 ppm NaCl solution the experimental data the Calcium concentration is 0.10 mmol/l

higher than PHREEQC data. The experimental data of the 2000 ppm NaCl solution shows a 0.08 mmol/l lower Calcium concentration than the PHREEQC data.

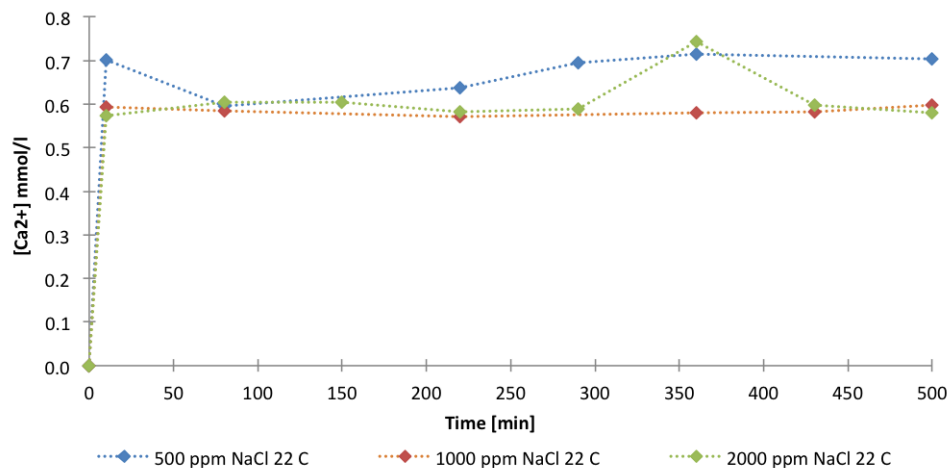


FIGURE 5.1: Calcium concentration in the NaCl solution versus experiment time, atmospheric conditions, chalk.

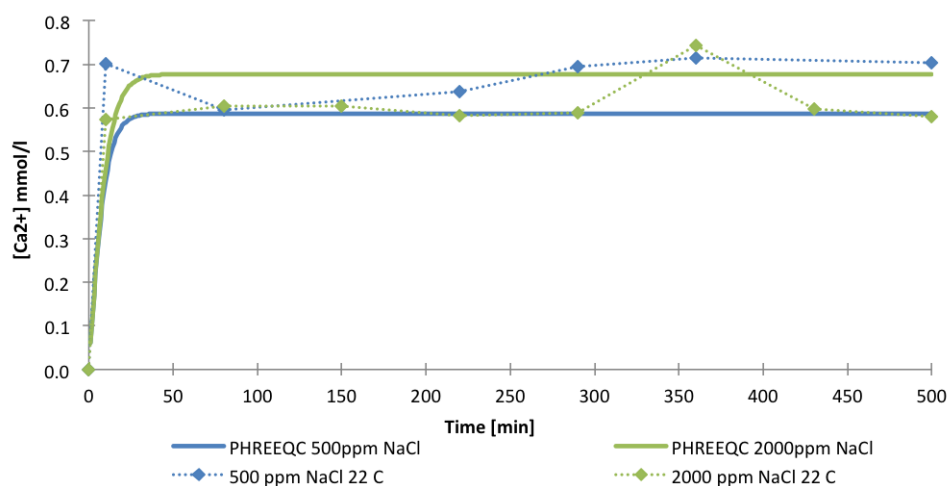


FIGURE 5.2: Calcium concentration in the NaCl solution versus experiment time, atmospheric conditions, chalk, experimental + PHREEQC data.

Figure 5.3 shows the data of bulk experiments conducted with grounded chalk core and PHREEQC modelling results at atmospheric conditions. Two different brines were used; 500 ppm NaCl and DilASG. The difference between the brines is the composition, given in table 4.1, and the salinity. The total salinities of the brines are respectively 500 and 240 ppm. The initial Calcium concentration in the brines was subtracted from the concentration of the effluent, so the data shows the Calcium concentration due to Calcite dissolution.

The experimental data shows that the Calcite dissolution at equilibrium for the 500 ppm NaCl solution is around 0.70 mmol/l. The Calcite dissolution equilibrium value for the Dil ASG is around 0.52 mmol/l. The Calcium concentration due to Calcite dissolution is higher in the 500 ppm NaCl solution, because initial no Calcium is present. Secondly, the slightly higher Calcium concentration in the 500 ppm solution

can be due to the higher salinity as well. The increase in Calcite dissolution at equilibrium is also confirmed by the PHREEQC data.

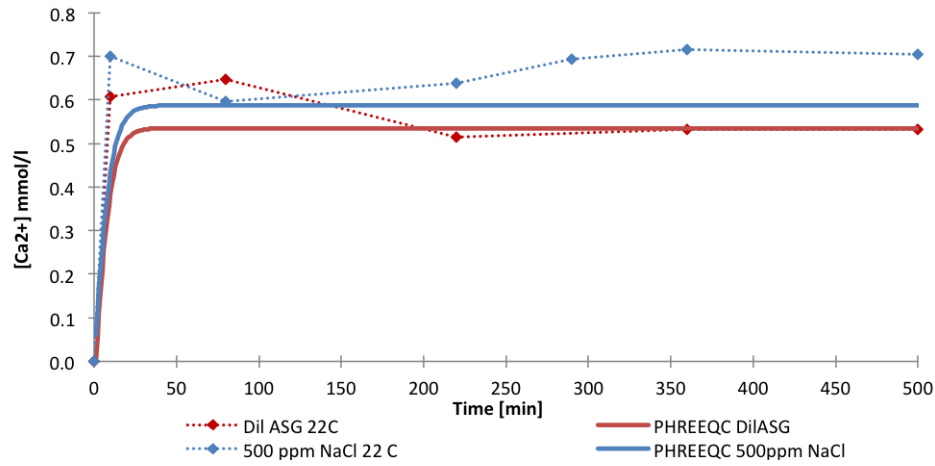


FIGURE 5.3: Calcium concentration in the brine versus experiment time, 22 °C, CO_2 -free conditions, chalk, experimental +PHREEQC data.

Figure 5.4 shows the data of two bulk experiments performed at room temperature and CO_2 -free environment with limestone powder. The experimental data shows that the Calcite dissolution at equilibrium increases with salinity at CO_2 -free environment as well. This observation is also confirmed by the PHREEQC modelling data. However, both experimental data sets show a higher Calcium concentration for both salinities than expected from pure Calcite according to the PHREEQC data.

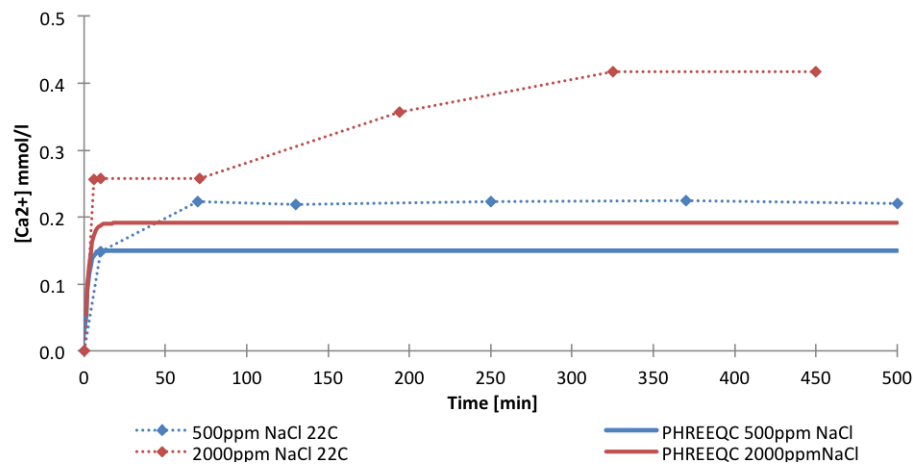


FIGURE 5.4: Calcium concentration in the brine versus experiment time, 22 °C, CO_2 -free environment, limestone, experimental +PHREEQC data.

Figure 5.5 shows the data of the bulk experiment performed with chalk and the PHREEQC data at room temperature and CO_2 -free environment. Two different brines were used; 2000 ppm NaCl and 25 times diluted seawater (=25Dil SW). The total salinities of the brines are respectively 2000 and 1750 ppm. So the main difference between the brines is their composition, which is given in table 4.1. The diluted seawater has an initial Calcium concentration of 0.40 mmol/l, which is subtracted from the measured effluent concentration.

The experimental data shows that there is almost no difference between the Calcite dissolution equilibrium value for the two brines despite their difference in composition. From the PHREEQC modelling data a more significant difference in concentration is expected. There was a fair match between the experimental and PHREEQC data for the 2000 ppm NaCl.

The initial Calcium concentration of the brine does not show an effect on the Calcite dissolution in the experimental data, but the effect is observed in the PHREEQC data.

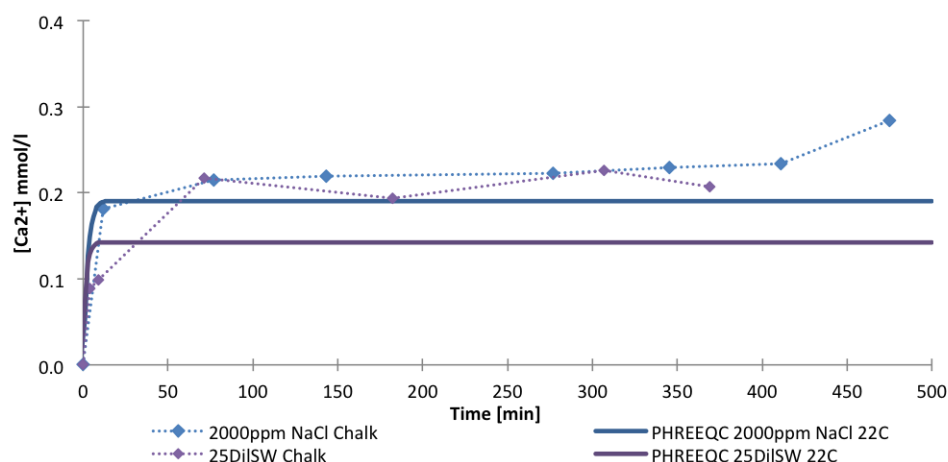


FIGURE 5.5: Calcium concentration in the brine versus experiment time, 22 °C, CO_2 -free environment, chalk, experimental + PHREEQC data.

The amount of Calcite that dissolved in the brine increased when the total salinity of NaCl increased from 500 to 2000 ppm. From the experimental data no influence of the initial Calcium concentration on the Calcite dissolution was observed. However, it is expected that less Calcite would dissolve when Calcium initially is present in the brine. This expectation is confirmed by the PHREEQC modelling.

5.2 Temperature effect

Figure 5.6 shows the experimental and PHREEQC data of two bulk experiments performed with chalk in 2000 ppm NaCl at atmospheric conditions. One of the experiments was performed at room temperature and one at 50 °C.

The Calcite dissolution equilibrium value at room temperature is at 0.60 mmol/l and 0.28 mmol/l at 50 °C. The PHREEQC showed a fairly good match with the experimental data. The $\log P_{CO_2}$ in the PHREEQC model was set at -3.5 for the room temperature data and -4.5 for the 50 °C data. Both the Experimental and PHREEQC data show that for atmospheric conditions Calcite dissolution decreases when temperature increases.

The same experiments as the previous were performed with 1000ppm NaCl solution. The experimental and PHREEQC data is shown in figure 5.7. The Calcite dissolution equilibrium value for the 1000 ppm NaCl solution. at room temperature is at 0.60 mmol/l and at 50 °C the Calcium concentration is fluctuating around 0.30 mmol/l.

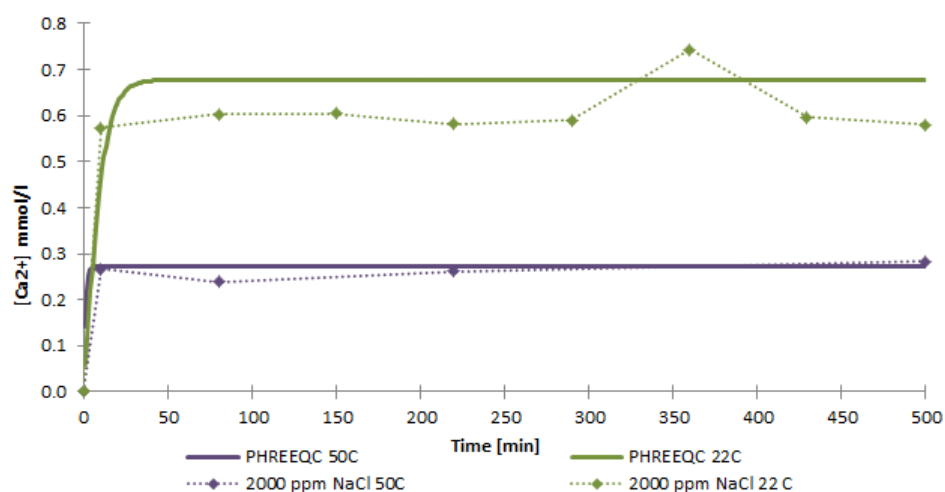


FIGURE 5.6: Calcium concentration in 2000 ppm NaCl solution versus experiment time, 22 – 50 °C, atmospheric pressure, chalk, experimental + PHREEQC data.

The same $\log P_{CO_2}$ was set the same for each temperature as in the 2000 ppm PHREEQC model. The experimental data and PHREEQC data show a good agreement for the Calcite dissolution at room temperature. The PHREEQC data for the Calcite dissolution at 50 °C is 0.05 mmol/l lower than some experimental data points. However, the trend of this data set shows a decrease Calcite dissolution when temperature was increased, atmospheric conditions.

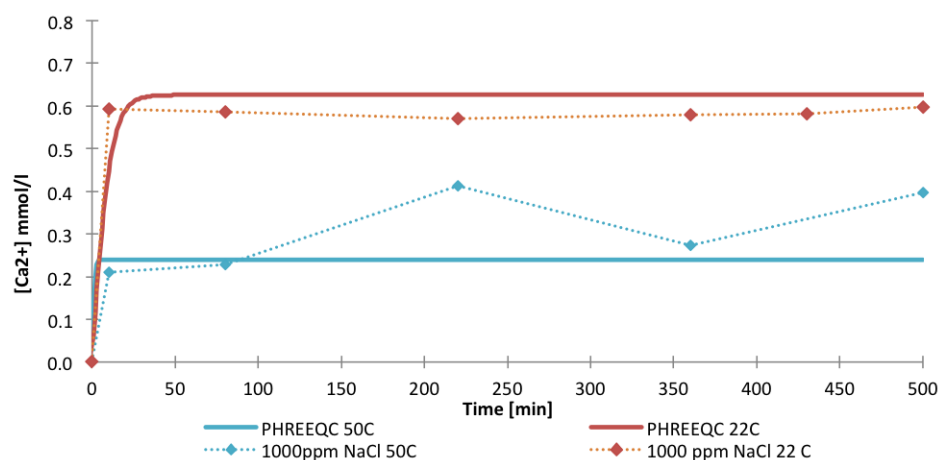


FIGURE 5.7: Calcium concentration in 1000 ppm NaCl solution versus experiment time, 22 – 50 °C, atmospheric pressure, chalk, experimental + PHREEQC data.

Figure 5.8 shows the experimental and PHREEQC data of two bulk experiments performed with 2000 ppm NaCl, limestone powder, CO_2 -free conditions at 22 and 50 °C.

The experimental data shows that the Calcite dissolution at equilibrium decreased with temperature. The experiment at 22 °C reached a constant Calcium concentration of 0.40 mmol/l and the experiment at 50 °C a constant Calcium concentration of 0.21 mmol/l. The PHREEQC data shows that the effect of temperature on the Calcite dissolution is the other way around, i.e. Calcite dissolution increases with temperature.

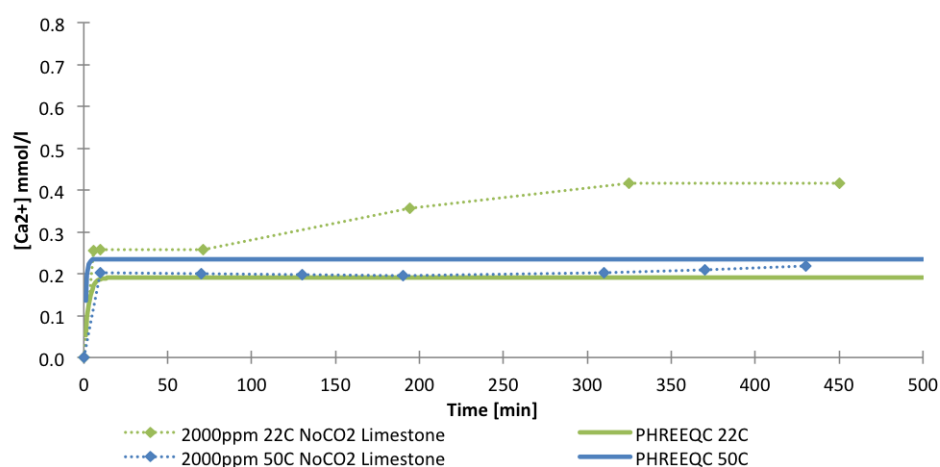


FIGURE 5.8: Calcium concentration in 2000 ppm NaCl solution versus experiment time, 22 – 50 °C, CO_2 -free conditions, limestone, experimental + PHREEQC data.

Calcite dissolution decreases with temperature at atmospheric pressure. The PHREEQC data was matched to the experimental data by adjusting the P_{CO_2} . At CO_2 -free conditions the effect of temperature on the Calcite dissolution is not clear. The Experimental and PHREEQC data showed contradictory results.

5.3 CO_2 effect

Figure 5.9 shows the data of bulk experiments performed with 2000 ppm NaCl and Chalk at room temperature. One of the experiments is conducted at atmospheric pressure and one at a CO_2 -free environment.

The Calcite dissolution at atmospheric pressure, where CO_2 is present, had an equilibrium value at 0.60 mmol/l of Calcium. For the experiment where no CO_2 is present in the system, the solution had a Calcium concentration of 0.22 mmol/l at equilibrium. The PHREEQC data plotted in figure 5.9 shows the same effect of CO_2 on the Calcite dissolution; the PHREEQC and experimental data showed a good match. The experimental and PHREEQC data both show that the Calcite dissolution decreased drastically when CO_2 was removed from the system.

Figure 5.10 shows the data of bulk experiments at 50 °C with 2000 ppm NaCl at CO_2 -free and atmospheric pressure. The Calcium concentration in the solution at equilibrium for the atmospheric pressure was 0.3 mmol/l and 0.22 mmol/l when CO_2 was absent. So more Calcite got dissolved when CO_2 was present in the system.

The PHREEQC data shown in figure 5.10 showed the same relation between CO_2 and Calcite dissolution and for both the experiments the PHREEQC data matched the experimental data. However, it should be taken into account that one of the experiments was performed with chalk and one with limestone.

Calcite dissolution was largely influenced by the CO_2 content of the system. At higher temperatures, the effect of CO_2 on the Calcite dissolution is less significant. This is probably due to the lower P_{CO_2} in the brine at atmospheric pressure at higher temperatures.

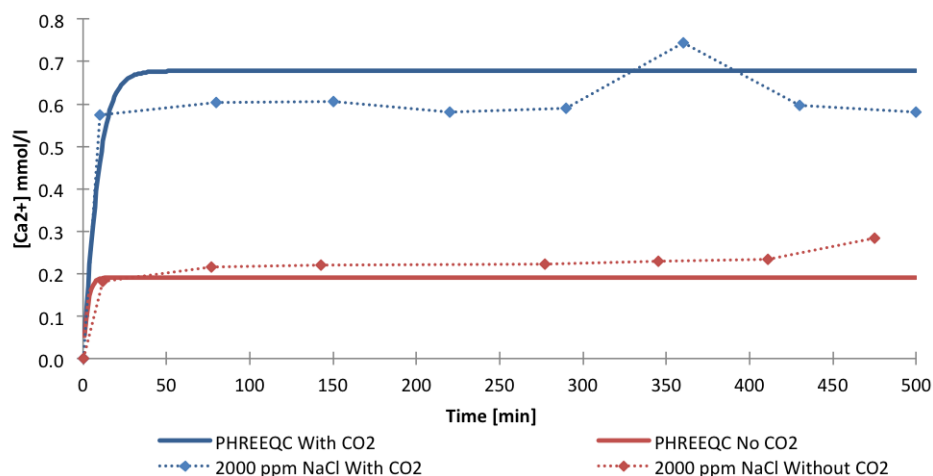


FIGURE 5.9: Calcium concentration in 2000 ppm NaCl solution versus experiment time, 22 °C, atmospheric pressure and CO_2 -free conditions, chalk, experimental + PHREEQC data.

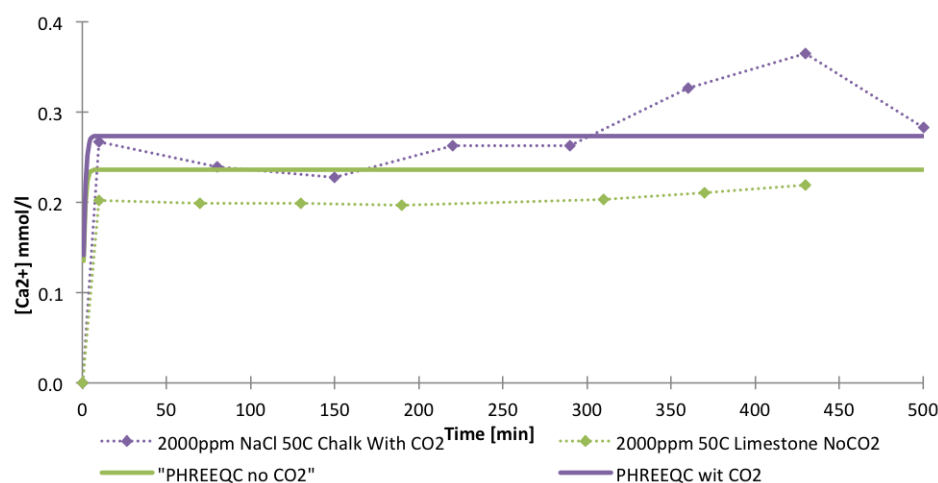


FIGURE 5.10: Calcium concentration in 2000 ppm NaCl solution versus experiment time, 50 °C, atmospheric pressure and CO_2 -free conditions, experimental + PHREEQC data.

5.4 pH effect

Figure 5.11 shows the experimental and PHREEQC data of two bulk experiments, performed with 25 times diluted seawater with different pH. For both the experiments, limestone powder was added to low salinity brine, at room temperature and CO_2 -free conditions. The data, as shown in figure 5.11, represents the Calcium concentration due to Calcite dissolution. The initial Calcium concentration is subtracted from the measured Calcium concentration.

The amount of Calcite dissolved in the low pH brine was three times higher and reached a Calcium concentration of 0.7 mmol/l at equilibrium. The Calcium concentration in the brine with a pH of 7 was 0.2 mmol/l at equilibrium. So Calcite dissolution increased significantly when the pH was lowered. The PHREEQC data showed the same effect of the pH on the Calcite dissolution. There was a small difference of 0.1 between the measured pH and the pH as input for the PHREEQC model, but this can be within the error of the pH meter, which has a standard deviation of 0.136.

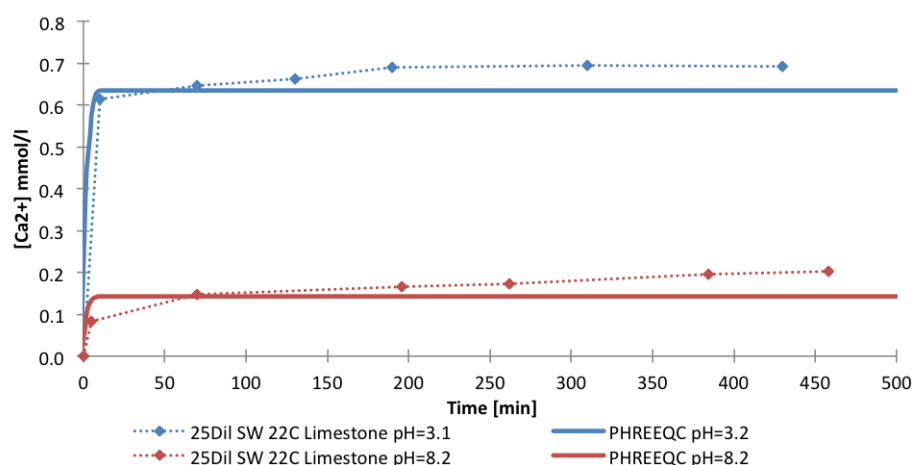


FIGURE 5.11: Calcium concentration in 25Dil SW versus experiment time, 22 °C, CO_2 -free conditions, limestone, different pH.

From both experimental and PHREEQC data, it was observed that Calcite dissolution at equilibrium increases with decreasing pH.

5.5 Effect of different carbonate material

Bulk experiments have been performed with 2000 ppm NaCl, at room temperature and CO_2 -free conditions, but with different carbonate material; chalk, limestone and pure Calcite crystals. The data of these bulk experiments together with the PHREEQC data, are plotted in figure 5.12. In PHREEQC it is not possible to model the Calcite dissolution with different types of carbonates. The PHREEQC data shows the Calcite dissolution from pure Calcite mineral.

The experiments with chalk and Calcite crystals showed the same Calcium concentration of 0.22 mmol/l at equilibrium. The experiment performed with limestone had a higher Calcite dissolution with a Calcium concentration of 0.42 mmol/l at equilibrium. The data of the experiments with chalk and Calcite crystals showed a good match with the PHREEQC data. More Calcite got dissolved from limestone compared to the two other experiments and PHREEQC data.

Figure 5.13 shows the experimental and PHREEQC data of bulk experiments conducted with 25Dil SW at room temperature and CO_2 -free conditions. Two types of carbonate material have been added to the brine: chalk and limestone.

The Calcite dissolution from the chalk and limestone reached approximately the same equilibrium value with a Calcium concentration of 0.2 mmol/l, while in the 2000 ppm NaCl more Calcite from the limestone got dissolved than from chalk. The PHREEQC shows a lower Calcium concentration of 0.14 mmol/l at equilibrium compared to the experimental data for the 25Dil SW, at the same conditions.

The Calcite dissolution from chalk equals the dissolution from pure chalk crystals in the NaCl solution. Secondly the data of bulk experiments with chalk matched the PHREEQC data. More Calcite got dissolved from the limestone powder in the NaCl solution, compared to chalk and pure Calcite. However, in the 25 times diluted seawater the Calcite dissolution from chalk and limestone is equal.

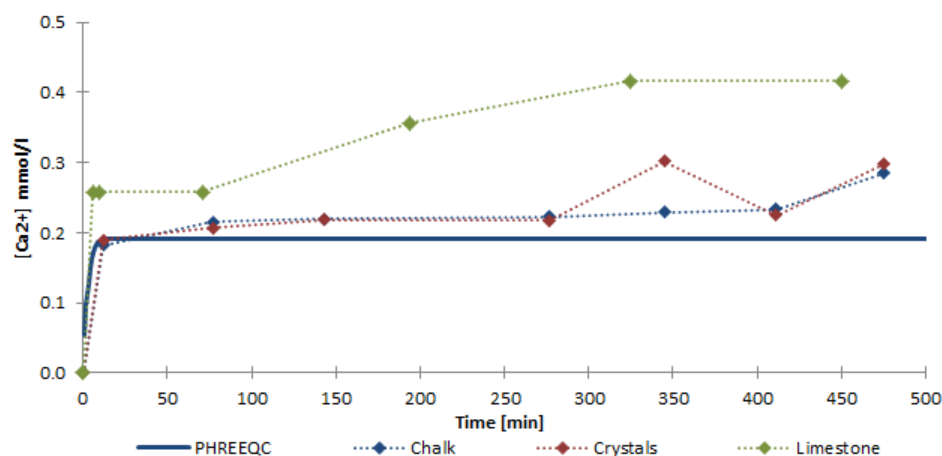


FIGURE 5.12: Experimental and PHREEQC $[Ca^{2+}]$ data of bulk experiment, 2000 ppm NaCl, 22 °C, CO_2 -free conditions.

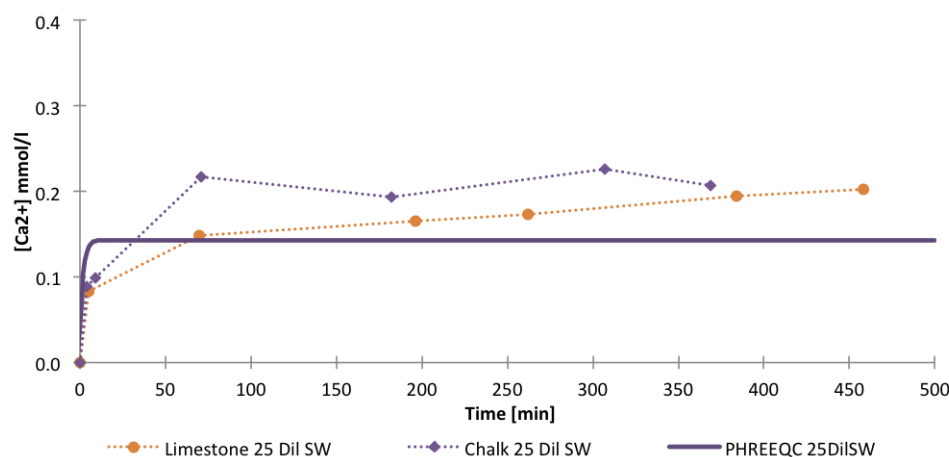


FIGURE 5.13: Experimental and PHREEQC $[Ca^{2+}]$ data of bulk experiment, 25Dil SW, 22 °C, CO_2 -free conditions

5.6 pH data

Figures 5.15 and 5.15 give the pH data of bulk experiment performed with 2000 ppm NaCl and low pH 25Dil SW at room temperature and closed to CO_2 . The PHREEQC data is plotted with the experimental data in both figures. The pH increased rapidly from 5.5 to 9.8 within 10 minutes for the 2000 ppm NaCl experiment. The same pH value is observed from the PHREEQC modelling data. The pH of the bulk experiment performed with low pH brine increased from 3.1 to 8.9 within 10 minutes. PHREEQC results showed a lower pH value than the experimental data, but shows a significant increase in pH in a short time as well.

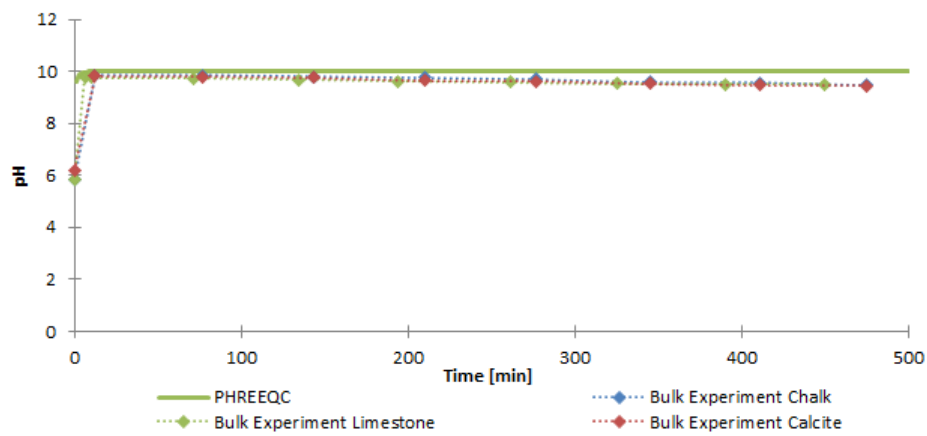


FIGURE 5.14: Experimental and PHREEQC pH data of bulk experiment, 2000 ppm NaCl, 22 °C, CO_2 -free conditions.

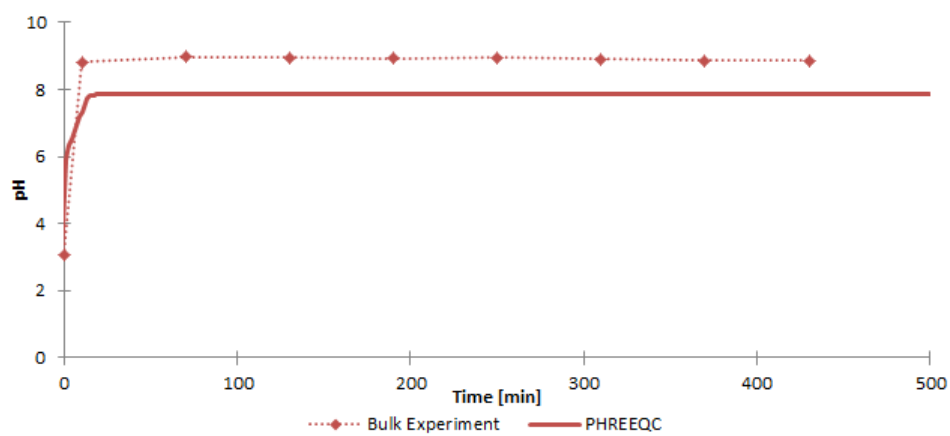


FIGURE 5.15: Experimental and PHREEQC pH data of bulk experiment, 25Dil SW with pH=3.1, 22 °C, CO_2 -free conditions.

Chapter 6

Results Single-phase Coreflood Experiments

Coreflood experiments have been performed with injecting low sal brines with different composition, salinity, pH at different temperatures and rates. The objective of the coreflood experiments was to study whether Calcite dissolution equilibrium will be reached during the low salinity flooding and what the significance is of the increase in porosity. The following parameters on calcite dissolution were examined as well:

1. Brine composition and salinity
2. Temperature
3. pH
4. Type of carbonate material
5. Injection rate

6.1 Injection sequence

Figure 6.1 shows the sequence of injection of the first coreflood experiment with chalk at room temperature. Figure 6.2 shows the sequence of injection of the second coreflood experiment with limestone at room temperature. Figure 6.3 shows the sequence of data of the third coreflood experiment with limestone at a temperature of 50 to 80 °C. The coreflood data will be discussed more extensively in the next sections of this Chapters.

6.2 Drilling fluid impurities

The coreflood experimental data in figure 6.1, 6.2 and 6.3 show a high Calcium concentration peak up to 2.00 mmol/l during the first injected pore volumes. This concentration peak is an experimental artefact.

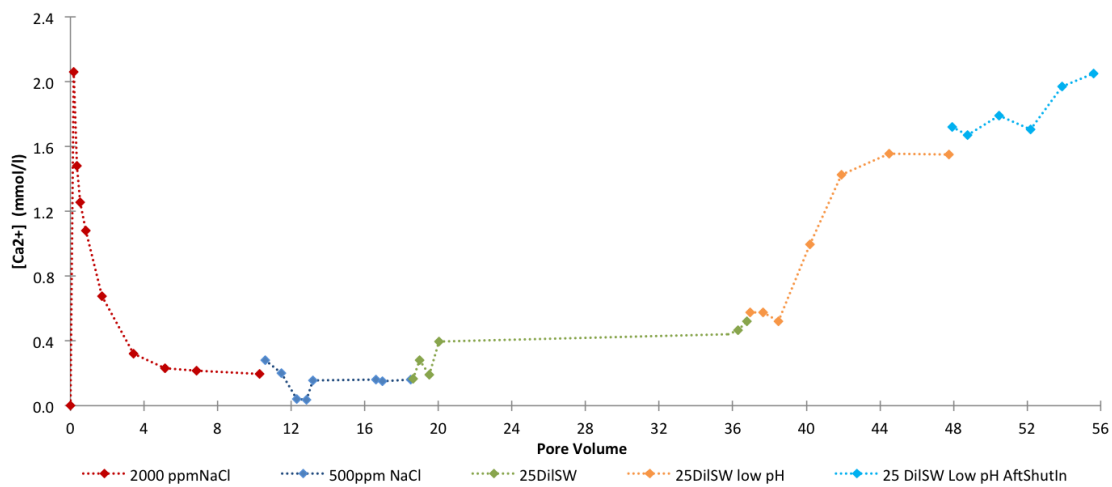


FIGURE 6.1: Calcium concentration of the effluent, chalk core, 22 °C.

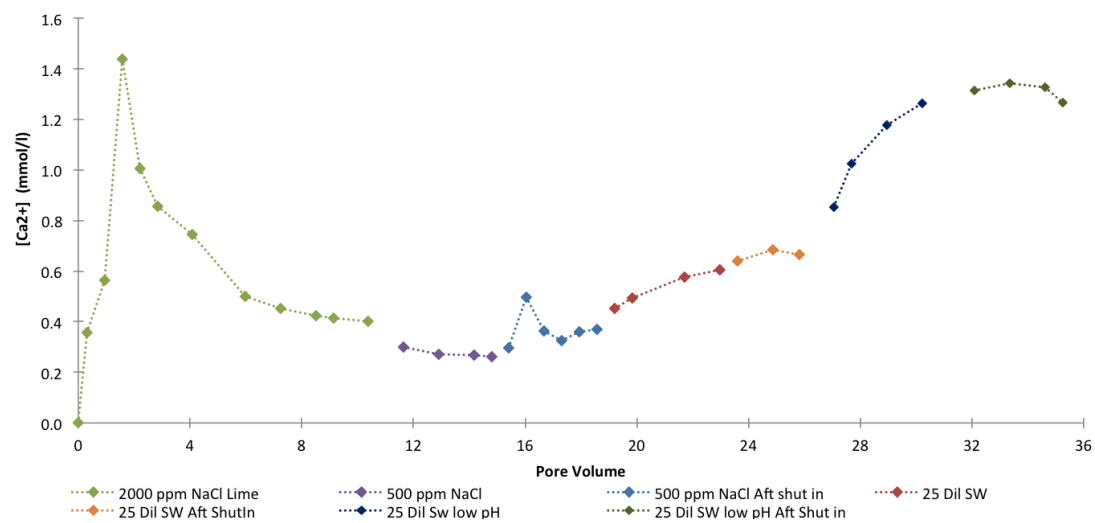


FIGURE 6.2: Calcium concentration of the effluent, limestone core, 22 °C.

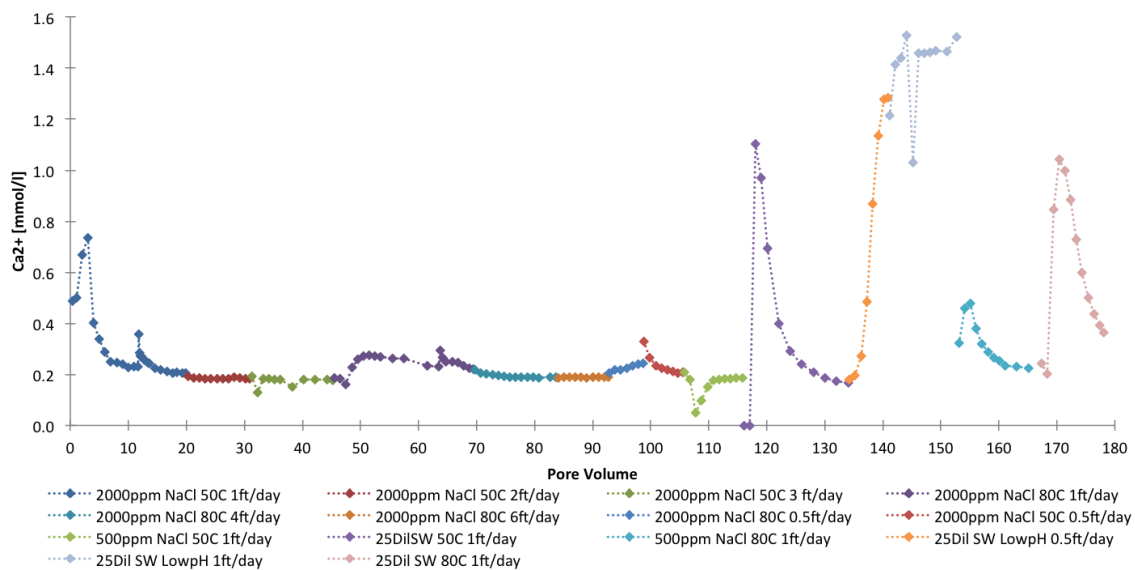


FIGURE 6.3: Calcium concentration of the effluent, limestone core, 50 – 80 °C.

During the drilling of both the chalk and limestone core, tap water was used as a cooling liquid. The cores were oven-dried after the drilling. During the drying period, the ions present in the tap water have been precipitated. These ions dissolved in the injected brine during the coreflood experiment. Therefore the effluent of the first pore volumes injected had a higher calcium concentration than the equilibrium value. The concentration of Calcium, Potassium and Magnesium in the used tap water is listed in table 6.1.

	Calcium [mmol/l]	Potassium [mmol/l]	Magnesium [mmol/l]
Tap Water	1.52	0.14	0.24

TABLE 6.1: Calcium, Potassium and Magnesium concentrations in tap water.

Figure 6.4 shows the concentration of Calcium, Potassium and Magnesium of the effluent of the first pore volumes injected into a limestone core at 80 °C. The data shows that the concentration of Calcium, Potassium and Magnesium decreased when more pore volumes were injected. Concentrations of Magnesium and Potassium even go down to zero, which demonstrates that these ions are not present due to rock dissolution. It took at least eight pore volumes of injection fluid in this experiment to remove all the ions that precipitated from the drilling fluid.

Calcium remains in the effluent, due to Calcite dissolution. The Calcium concentration remained constant after 10 pore volumes, but the equilibrium value is 0.1 mmol/l higher than expected from the PHREEQC model. There might be some remaining Calcium ions present due to the drilling fluid.

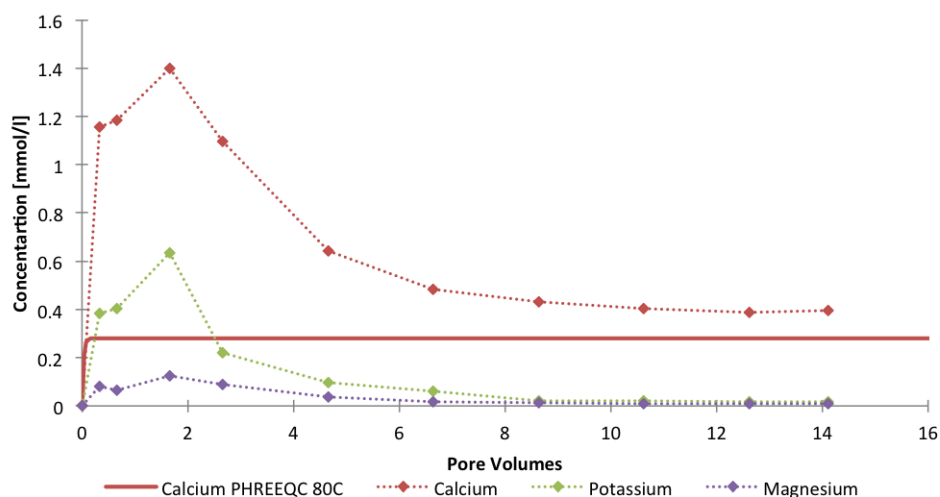


FIGURE 6.4: Calcium, Potassium and Magnesium concentration of the effluent, 2000 ppm NaCl, limestone core, 80 °C.

6.3 Composition and Salinity dependency

Figure 6.5 shows the data of coreflood experiments at 22 °C by injecting NaCl solutions into a chalk core. The high Calcium concentration peak for the first injected pore volumes due to the drilling fluid is not

shown in the figure, because it is not representative for the natural Calcite dissolution process.

The Calcium concentration in the 2000 ppm NaCl effluent remains constant at 0.2 mmol/l after 10 pore volumes injected. The Calcium concentration in the 500 ppm NaCl solution is 0.15 mmol/l at equilibrium. The Calcium concentration at equilibrium, obtained from the bulk experiments, has been plotted in the figure as well. From the bulk experiment the equilibrium concentration of 0.23 mmol/l Calcium is observed, which is slightly higher than the coreflood and PHREEQC data. The PHREEQC data shows the same equilibrium values as for the coreflood data and both show that the Calcite dissolution increases with increasing salinity, i.e. Ionic strength.

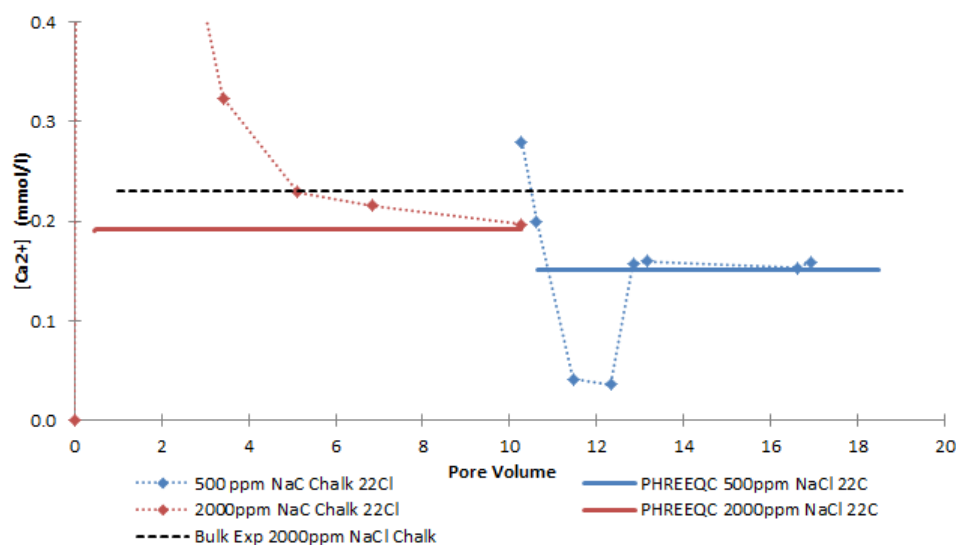


FIGURE 6.5: Calcium concentration of the effluent with injected pore volumes, 500 and 2000 ppm NaCl, 22 °C, chalk.

The same experiments have been performed on a limestone core. The experimental and PHREEQC data is shown in figure 6.6. The experimental data of the coreflood in the limestone core shows the same influence of the salinity in the calcite dissolution. The data from the bulk experiment shows a Calcium concentration of 0.42 mmol/l in the 2000 ppm NaCl solution. The coreflood data matched the bulk experiment data after 8 pore volumes injected, so it is assumed equilibrium has been reached for the 2000 ppm NaCl. However, the limestone coreflood and bulk data show for both salinities an almost 50% higher Calcium concentration compared to the chalk coreflood data and the PHREEQC data, which is also observed in the bulk experimental data in figure 5.12.

Figure 6.7 shows the data of a limestone coreflood injecting 2000 and 500 ppm subsequently, at a temperature of 50 °C. The Calcium concentration of the 2000 ppm NaCl effluent reached a constant value of 0.23 mmol/l before shut in, which matched the equilibrium value data according the PHREEQC model. After the shut in period of three days, the Calcium concentration increases to 0.38 mmol/l. Eventually the concentration decreased to a value of 0.21 mmol/l, which matched the equilibrium value obtained from the bulk experiment, but below the PHREEQC data. The Calcium concentration in the 500 ppm NaCl effluent reaches an equilibrium value of 0.18 mmol/l, which matched the PHREEQC data. Both the experimental and PHREEQC data show that at a temperature of 50 °C the amount of Calcite dissolved at equilibrium increases with salinity from 500 to 2000 ppm of NaCl solutions.

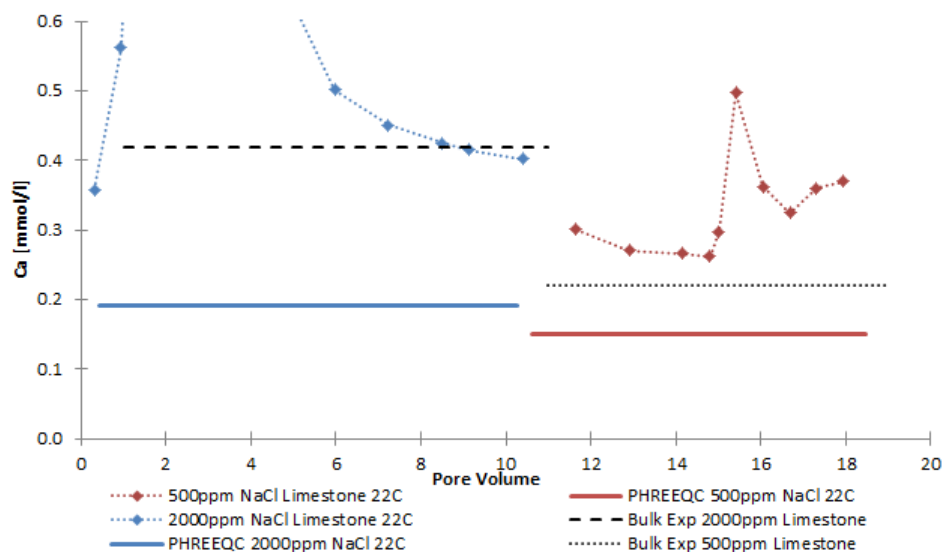


FIGURE 6.6: Calcium concentration of the effluent with injected pore volumes, 500 and 2000 ppm NaCl, 22 °C, limestone.

The effluent of the first pore volumes 500 ppm NaCl injected for both experiments at 22 °C and 50 °C had a Calcium concentration 0.03-0.05 mmol/l, which is below the equilibrium value. This decrease in Calcium concentration can be observed as a dip in the experimental data in figures 6.5 and 6.7. The 500 ppm NaCl solution is the second injected brine, after 2000 ppm NaCl, in both experiments. After the concentration dip Calcite dissolution equilibrium is established. A more extensive discussion on this concentration dip will be in section 8.1.

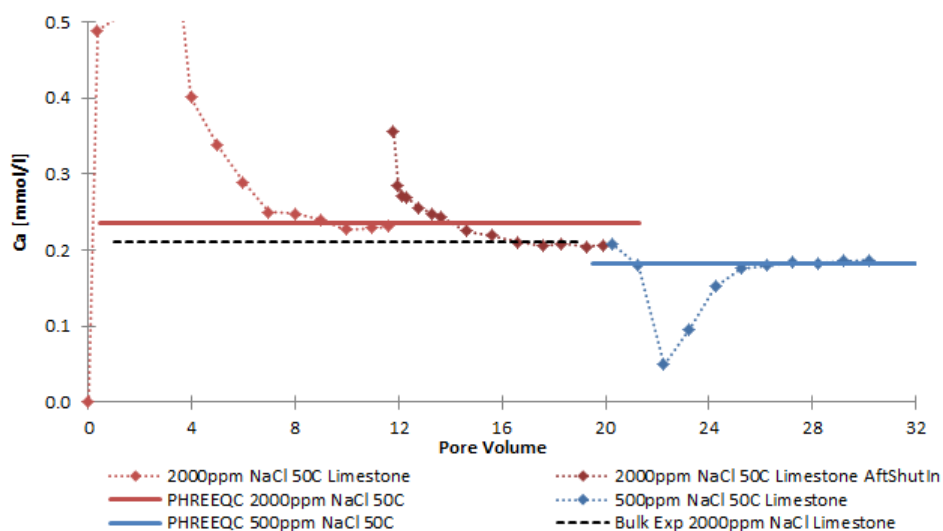


FIGURE 6.7: Calcium concentration of the effluent with injected pore volumes, 500 and 2000 ppm NaCl, 50 °C, limestone.

The same coreflood experiments have been performed at a temperature of 80 °C. The experimental and PHREEQC data is plotted in figure 6.8. The Calcium concentration in the 2000 ppm NaCl effluent remained constant at 0.28 mmol/l, which matched the PHREEQC data, and then decreased to a value of 0.23 mmol/l. After the shut in period the Calcium concentration increased to 0.30 mmol/l, but rapidly

decreased to a value of 0.23 mmol/l again. It seems that the equilibrium state can not be retained after it has been reached. The Calcium concentration in the 500 ppm NaCl effluent was relatively high for the first eight pore volumes injected but decreased to a constant value of 0.21 mmol/l. The high Calcium content for the first pore volumes is due to the previous injected brine, which had a low pH, as shown in figure 6.3. Before the 500 ppm NaCl solution was injected the core was flushed with distilled water, but a certain amount of $[H^+]$ ions remained and affected the Calcite dissolution for the first eight pore volumes injected. However, in the end the experimental and PHREEQC equilibrium value matched for the 500 ppm NaCl solution.

At 80 °C the same effect of Salinity on the calcite dissolution equilibrium value is observed.

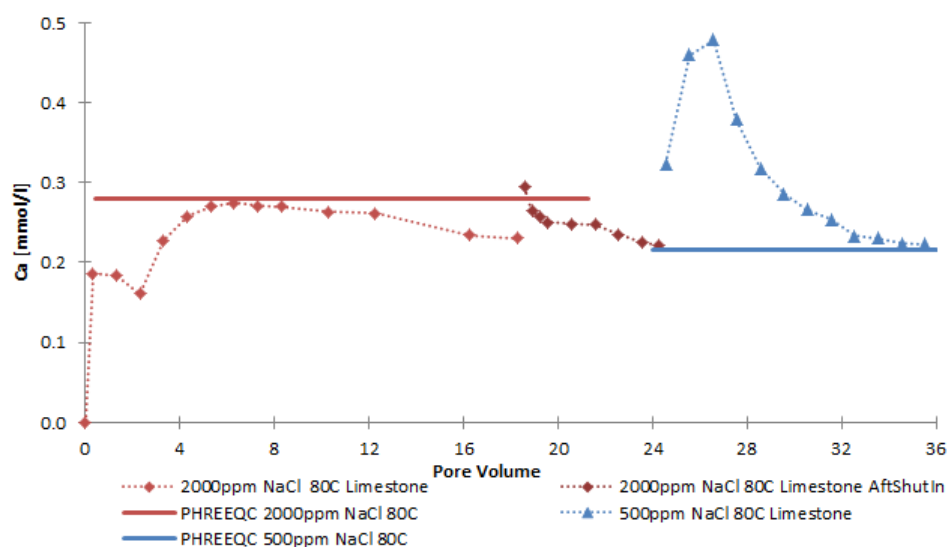


FIGURE 6.8: Calcium concentration of the effluent with injected pore volumes, 500 and 2000 ppm NaCl, 80 °C, limestone.

From experimental data, it was observed that less Calcite got dissolved at equilibrium when the salinity was decreased from 2000 to 500 ppm of NaCl solutions. This effect was observed at 22 °C, 50 °C and 80 °C. The PHREEQC data matched the experimental data for most cases and confirms the observation from the experimental data.

6.4 Temperature dependency

Figure 6.9 shows the coreflood data of coreflood experiments by injecting 2000ppm NaCl at 22 °C and 50 °C. The experimental data is from three different experiments; chalk core at 22 °C, limestone at 22 °C and limestone at 50 °C.

The experimental data of the chalk experiment at 22 °C showed a constant Calcium concentration of 0.20 mmol/l after eight pore volumes injected. This value matched with the equilibrium value obtained from the Bulk experiment of chalk at 22 °C in a CO_2 -free environment and the PHREEQC data. Again the Calcium concentration peak at the beginning is excluded from this figure, because it is not representative for the natural Calcite dissolution process. The equilibrium state might have been reached in region as

well, but is not visible due to the drilling fluid contamination. The experimental data of the limestone experiment at 22 °C indicates that equilibrium has been reached after seven pore volumes injected at a Calcium concentration of 0.40 mmol/l. This value matched with the equilibrium value obtained from the bulk experiment of limestone at 22 °C in a CO_2 -free environment.

The experimental data of the limestone experiment at 50 °C shows a constant Calcium concentration of 0.23 mmol/l after ten pore volumes injected. This value matched with the PHREEQC data of 2000 ppm NaCl at 50 °C. The core was shut in for three days with the purpose to reach the equilibrium state. After this shut-in period, injection is resumed, which data is light blue coloured. At first there is an increase in Calcium concentration from 0.23 to 0.36 mmol/l, which did not match with the concentration value at equilibrium obtained from bulk experiments and PHREEQC. This increase in dissolution might be from other minerals, like dolomite. This observation will be discussed more extensively in chapter 8. Hereafter, the Calcium concentration was decreasing gradually and reached a constant value of 0.21 mmol/l. This value matched with the equilibrium value obtained from the bulk experiment of limestone at 50 °C in a CO_2 -free environment.

So the Calcite dissolution from limestone decreased by 50 % when temperature was decreased from 22 °C to 50 °C. The Calcite dissolution from limestone at 50 °C was 0.03 mmol/l higher than from chalk at 22 °C, which experimental data both matched with the PHREEQC data. There was a fair match between the Bulk experimental data and Coreflood data for all the three experiments.

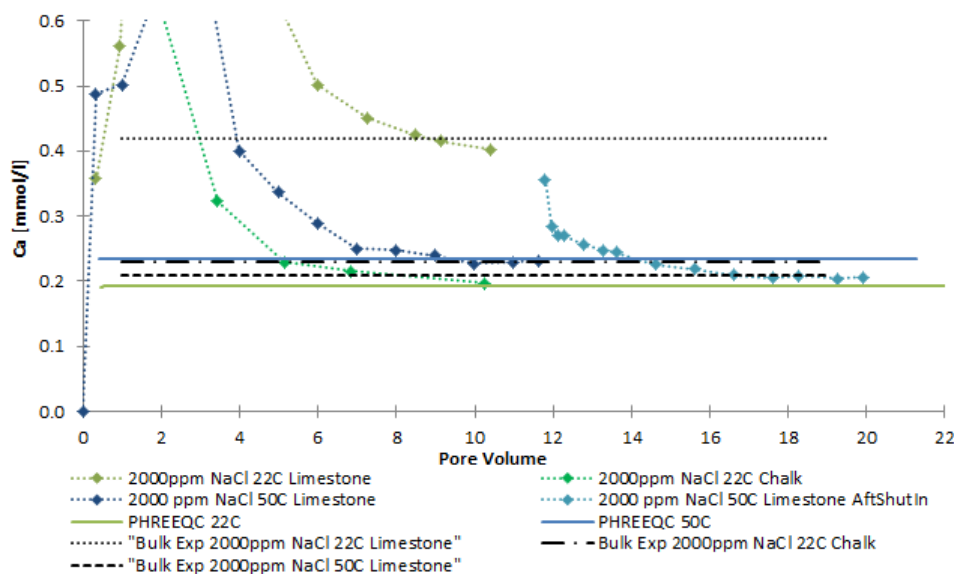


FIGURE 6.9: Calcium concentration of the effluent with injected pore volumes, 2000 ppm NaCl, 22 – 50 °C.

Figure 6.10 shows the coreflood data of coreflood experiments of injecting 2000ppm NaCl at 50 °C and 80 °C. The experimental data is obtained from the same limestone core.

The data of the limestone experiment at 50 °C indicates that equilibrium has been reached after ten pore volumes injected at a Calcium concentration of 0.23 mmol/l. This value matched with the PHREEQC data of 2000 ppm NaCl at 50 °C. After a shut-in period of three days injection was resumed, which data is light blue coloured. At first there was an increase in Calcium concentration from 0.23 to 0.36 mmol/l. This increase in dissolution might be from other minerals, like dolomite. This observation will be discussed more extensively in chapter 8. Hereafter, the Calcium concentration was decreasing gradually and reached a constant value of 0.21 mmol/l. This value matched with the equilibrium value obtained from the bulk experiment of limestone at 50 °C in a CO_2 -free environment.

mmol/l, which is approximately 60%. The Calcium concentration was decreasing gradually and reached a constant value of 0.21 mmol/l. This value matched with the equilibrium value obtained from the Bulk experiment of limestone at 50 °C in a CO_2 -free environment.

The experimental data of the limestone experiment at 80 °C reached equilibrium at 24 pore volumes injected at a Calcium concentration of 0.28 mmol/l. This value matched with the equilibrium value obtained from PHREEQC modelling data 80 °C in a CO_2 -free environment. The Calcium concentration did not remain constant and decreased to a value of 0.23 mmol/l. After a shut-in period of three days, injection was resumed. The first data points after shut-in had a 0.06 mmol/l higher Calcium concentration. Hereafter the value decreased to a value of 0.23 mmol/l again.

From the coreflood data a slightly increase in Calcite dissolution from limestone was observed when temperature was raised from 50 °C to 80 °C. This observation was confirmed by the PHREEQC data.

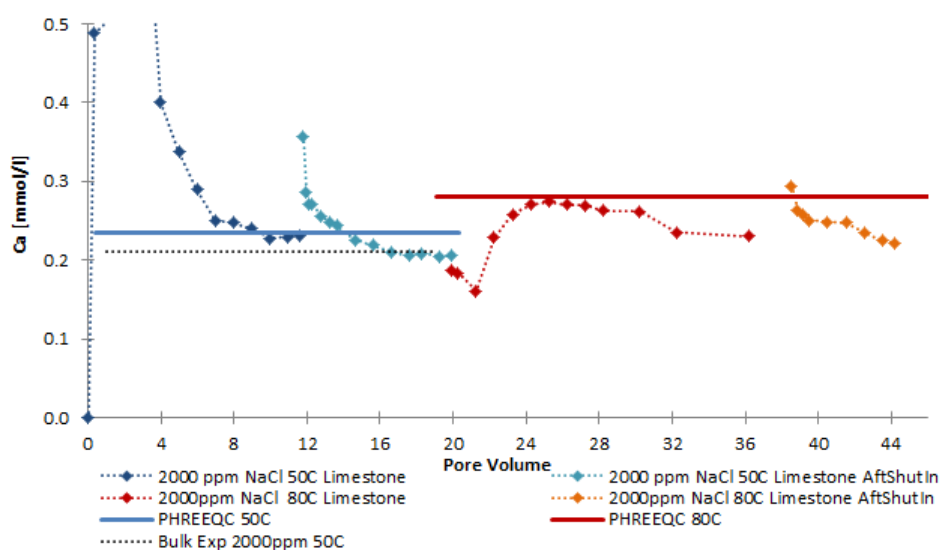


FIGURE 6.10: Calcium concentration of the effluent with injected pore volumes, 2000 ppm NaCl, 50 – 80 °C.

Figure 6.11 shows the experimental data of corefloods performed with 500 ppm NaCl at different temperatures. The experimental data is from three different experiments; chalk core at 22 °C, limestone at 22 °C and limestone at 50 to 80 °C. The calcium concentration in the effluent of the coreflood experiment with chalk at 22 °C reached an equilibrium value of 0.15 mmol/l. The Calcite dissolution from the limestone core was higher and reached a equilibrium value of 0.27 mmol/l. After five pore volumes injected the limestone core had been shut in for three days. When injection was resumed, a concentration peak was observed for the first two pore volumes. After the shut-in-period no new equilibrium has been established.

The data of the experiment conducted at 50 °C reached an equilibrium of 0.18 mmol/l of Calcium. When the temperature was raised to 80 °C the Calcium concentration increased to a constant value of 0.22 mmol/l. For the first pore volumes injected the calcium concentration was higher, because the 500ppm NaCl solution was injected after the low pH 25Dil SW solution. A new equilibrium needed to be established, which was reached after injecting 12 pore volumes of 500ppm NaCl.

The PHREEQC data in figure 6.11 matched the experimental data for all the three temperatures, except for the coreflood with limestone at 22 °C. The calcite dissolution from limestone decreased significantly when temperature was decreased from 22 °C to 50 °C. The Calcite dissolution from limestone at 50 °C was higher than from chalk at 22 °C, which both experimental data matched with the PHREEQC data. From the coreflood data a slightly increase in Calcite dissolution from limestone was observed when temperature was raised from 50 °C to 80 °C. Both equilibrium values obtained from coreflood data at 50 °C and 80 °C matched with the PHREEQC data.

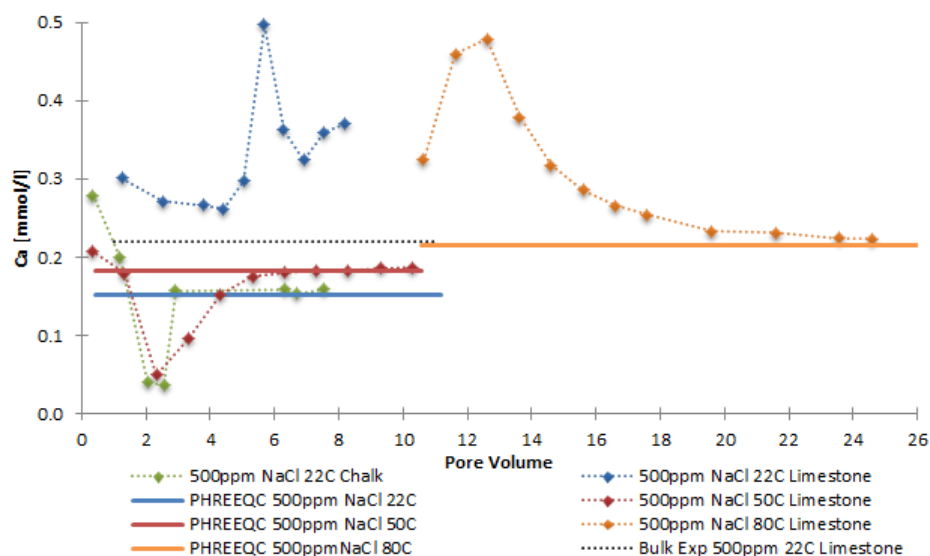


FIGURE 6.11: Calcium concentration of the effluent with injected pore volumes, 500 ppm NaCl, 22 – 80 °C.

From limestone coreflood experiments a decrease in Calcite dissolution from 0.40 to 0.23 mmol/l was observed when temperature was raised from 22 °C to 50 °C. An increase of 0.05 mmol/l in Calcite dissolution was observed when temperature was raised from 50 °C to 80 °C. The PHREEQC confirms the Calcite dissolution increase from 50 °C to 80 °C. However, PHREEQC data and Experimental data did not match for the limestone with a temperature increase from 50 °C to 80 °C. The PHREEQC and the chalk coreflood data at 22 °C did match.

6.5 pH dependency

Figure 6.12 shows the data of coreflood experiments performed at 22 °C by injecting 25Dil SW with three different pH values: 2.9, 7.2 and 10.4. In this figure the initial concentration of Calcium is subtracted from the measured concentration and the experiments are performed from the same limestone core.

The experimental data shows that more Calcite got dissolved in the solution with a pH of 2.9, with a Calcium concentration of 0.98 mmol/l at equilibrium. The least Calcite got dissolved in the brine with a pH of 10.4, for which the Calcium concentration remained constant at 0.04 mmol/l. The Calcium concentration due to Calcite dissolution for the brine with a pH of 7.2 had an equilibrium value of 0.21 mmol/l.

The experimental data shows that the Calcite dissolution increased significantly when the pH was lowered. The amount of calcite dissolved decreased when the pH was raised. Lowering the pH had a larger impact on the calcite dissolution compared to increasing the pH, because of the logarithm dependency of pH on the $[H^+]$ concentration.

The PHREEQC data showed the same effect of the pH on calcite dissolution. The experimental and PHREEQC data did not exactly match. For the high pH experiment, the Calcium concentration of the experimental data was 0.02 mmol/l lower than the PHREEQC data. For the medium pH data, the Calcium concentration of the experimental data was 0.05-0.10 mmol/l higher than the PHREEQC data. For the low pH data, the experimental and PHREEQC data matched. However the pH in the PHREEQC model was set 0.2 higher to be able to match with the experimental data. The difference in pH fits within the accuracy of the pH meter, which has a standard deviation of .136.

The equilibrium value obtained from the bulk experiments is plotted in the figure 6.12 as well. The pH of the brine of the bulk experiment was 3.1 and showed 0.3 mmol/l lower Calcium concentration. To be able to match with the PHREEQC, the pH was set at 3.2 in the model as shown in figure 5.11. The Equilibrium value obtained from the bulk experiment with medium pH brine showed a higher Calcium concentration than according the PHREEQC data, but still within the Calcium concentration of the coreflood data.

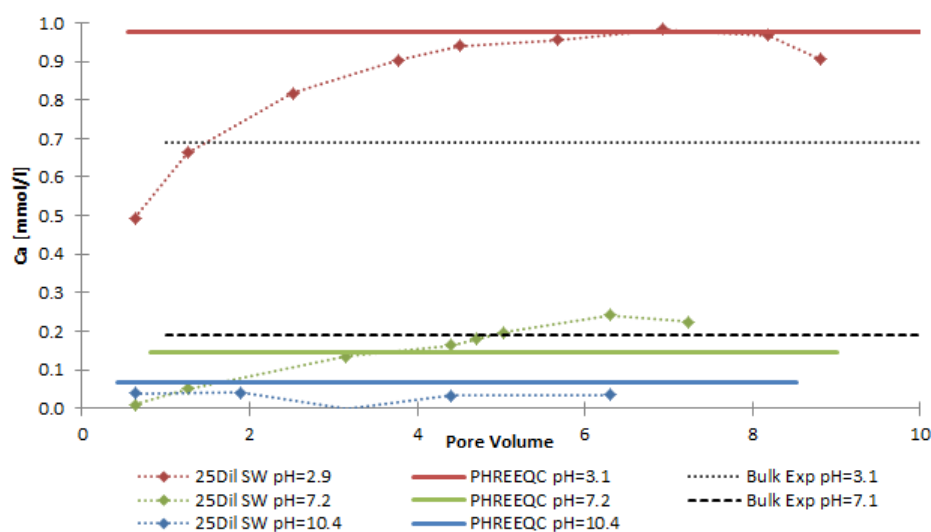


FIGURE 6.12: Calcium concentration of the effluent with injected pore volumes, 25Dil SW, 22 °C, limestone.

The experimental data of coreflood experiments conducted at 50 °C injecting 25Dil SW with different pH is shown in figure 6.13. This data is obtained from experiments in the same limestone core. The initial Calcium concentration of the brines is subtracted, so the data curves shows the Calcium concentration due to Calcite dissolution.

The fluid with a pH of 7.3 reaches equilibrium after 14 pore volumes injected with a concentration of 0.17 mmol/l, which matched the PHREEQC data as well. The fluid with a pH of 2.9 has a 1.35 mmol/l higher Calcium concentration than the experimental data with a pH of 7.3. The experimental data reaches an equilibrium value around 1.50 mmol/l after 14 pore volumes injected. The PHREEQC data gives a Calcium concentration of 1.54 mmol/l at equilibrium.

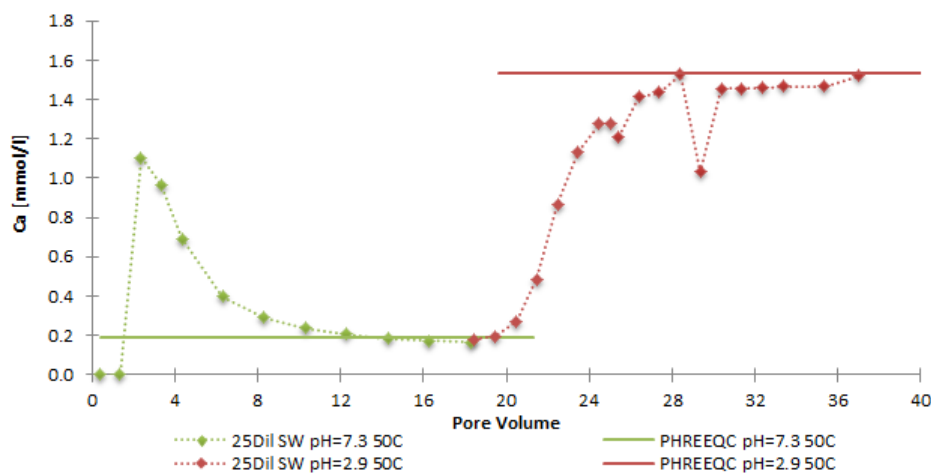


FIGURE 6.13: Calcium concentration of the effluent with injected pore volumes, 25Dil SW, 50 °C, limestone.

Figure 6.14 shows the experimental data of two coreflood experiment with low pH brine, but different temperature and different limestone cores. Again the initial concentrations are subtracted.

The fluid of the experiment conducted at 22 °C has a pH of 2.9 and reaches a constant calcium concentration of 0.98 mmol/l. The PHREEQC model gives a much higher calcium concentration at equilibrium under these conditions. However, if the pH is raised to 3.1 in the PHREEQC model it matched the experimental data. So an increase of 0.2 in the pH can decrease the calcite dissolution significantly, which is almost 50 % in this case. The PHREEQC curves with a pH of 2.9 show that Calcite dissolution at the low pH regime is minimally affected by the temperature. The pH impact on the Calcite dissolution overrules the temperature impact.

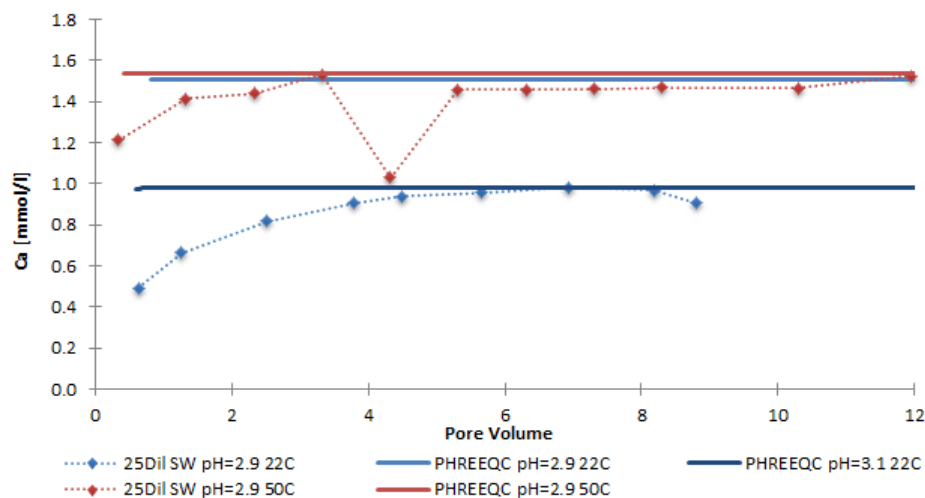


FIGURE 6.14: Calcium concentration of the effluent with injected pore volumes, 25Dil SW, 22 – 50 °C, limestone.

From the coreflood data it was observed that the Calcite dissolution increased significantly during the low salinity brine injection when the pH was lowered to 2.9-3.2. This was observed at 22 °C and 50 °C. The pH effect on the Calcite dissolution overruled the temperature effect.

6.6 Carbonate material dependency

2000 ppm NaCl solution has been injected in chalk and limestone cores with 1 ft/day at room temperature. The experimental data of the coreflood has been plotted in figure 6.15, together with the bulk and PHREEQC data. The bulk and coreflood data matched for both materials. From both the bulk and coreflood data it was observed that more Calcite dissolved from the limestone. The data of the coreflood experiment with chalk matched the PHREEQC data after 8 pore volumes injected.

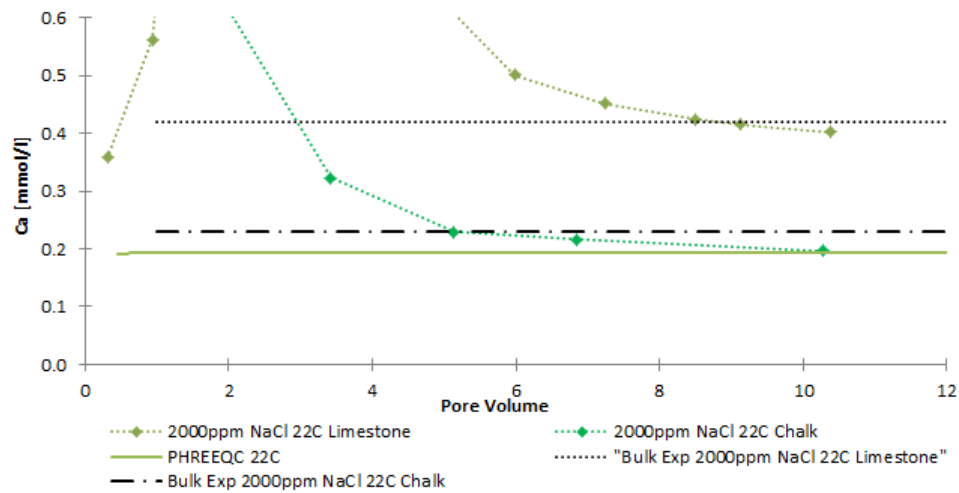


FIGURE 6.15: Calcium concentration of the effluent with injected pore volumes, 2000 ppm NaCl, 22 °C, chalk and limestone.

Figure 6.16 shows the data of coreflood experiments with 500 ppm NaCl injected into chalk or into limestone. Again, from the coreflood experiments it was observed that more Calcite got dissolved from the limestone than from chalk. Only the chalk data matched the PHREEQC data.

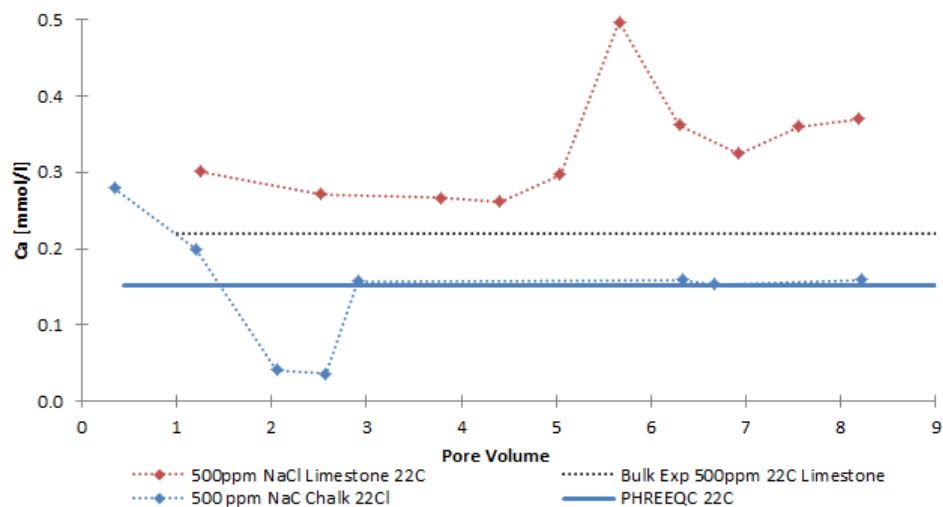


FIGURE 6.16: Calcium concentration of the effluent with injected pore volumes, 500 ppm NaCl, 22 °C, chalk and limestone.

From the data in figures 6.15 and 6.16 it was observed that the Calcite dissolution at equilibrium at room temperature was almost 50% higher from limestone than from pure Calcite (PHREEQC) and chalk. This observation was also made from the bulk experimental data.

6.7 Injection rate dependency

2000 ppm NaCl has been injected with different injection rates. Table 6.2 shows the applied injection rates and the corresponding time of the fluid in the core, i.e. the interaction time of between the brine and carbonate rock. The interaction time determines whether it is possible for the Calcite dissolution to reach equilibrium.

Velocity [ft/day]	Rate [ml/min]	Travel time through core [min]
0.5	0.035	470
1	0.07	235
2	0.14	117
3	0.21	78
4	0.28	59
6	0.42	39

TABLE 6.2: Different Injection Rates, pore volume = 16.44 ml.

Figures 6.17, 6.18 and 6.19 show the Calcium concentration data from the Kinetic PHREEQC model at different injection rates and temperatures.

The PHREEQC data showed that the fluid needed less time in the core to reach the equilibrium when the temperature was raised, while the Calcium concentration at equilibrium increased with temperature. According to the PHREEQC model, the fluid at 22 °C does not have enough time in the core to reach equilibrium with a velocity of 2, 3 or 4 ft/day. Equilibrium only can be reached with a velocity of 1 ft/day or less. The A/V ratio, where A is the exposed area and V the solution volume, was set 5 in the PHREEQC model. If this value would be increased in the model, the rate would increase as well. i.e. the reaction needs less time to reach the equilibrium state.

The PHREEQC data of the calcite dissolution at 50 °C shows that the fluid is able to reach equilibrium in the core with a velocity of 1, 2 and 3 ft/day. The interaction time between the fluid and rock is too short to reach equilibrium at 4 ft/day. The PHREEQC data in figure 6.19 shows that at 80 °C the fluid has enough time in the core to reach equilibrium with a fluid velocity of 6 ft/day.

Figure 6.20 shows the data the coreflood experiment performed with 2000 ppm NaCl at 50 °C, with different injection rates. The Calcium concentration at equilibrium according to the PHREEQC model and the bulk experiment are plotted as well in the figure. The data shows that the Calcium concentration of the brine injected with 1 ft/day matched with the PHREEQC data and with the bulk experimental data after the shut in. The effluent of the fluids injected at 2 and 3 ft/day had a significant lower Calcium concentration than the equilibrium values according to the PHREEQC model and the Bulk experiments. There is no significant change in Calcium concentration between 2 and 3 ft/day. The Calcium concentration of the fluid injected at 0.5 ft/day showed a higher Calcium concentration in the

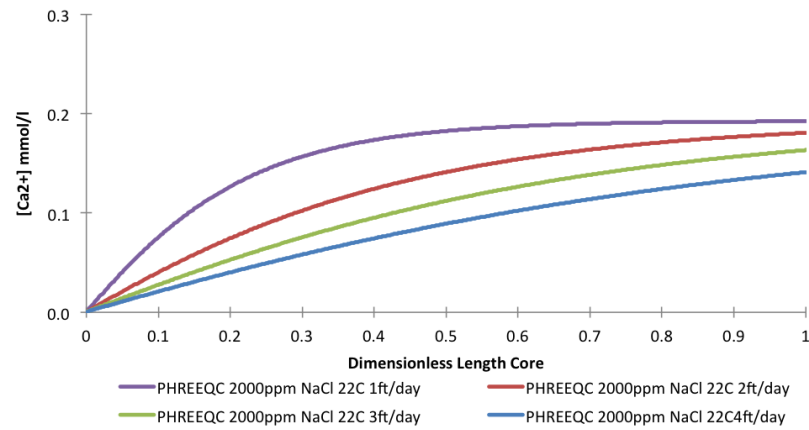


FIGURE 6.17: Calcium concentration of the fluid passing through the core, 2000 ppm NaCl, 22 °C.

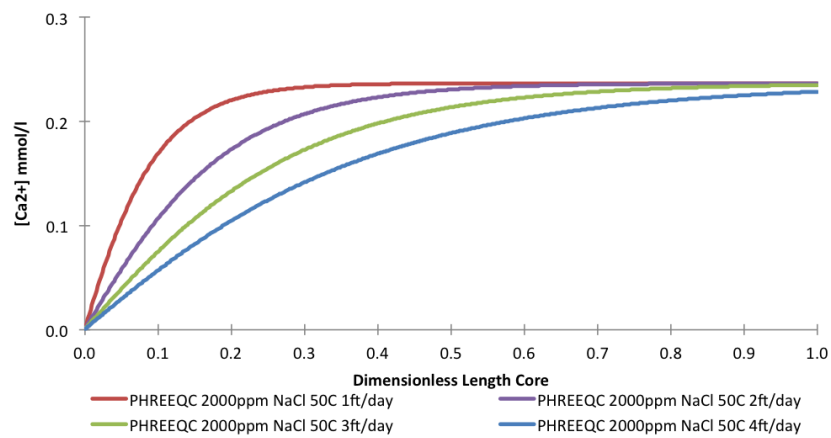


FIGURE 6.18: Calcium concentration of the fluid passing through the core, 2000 ppm NaCl, 50 °C.

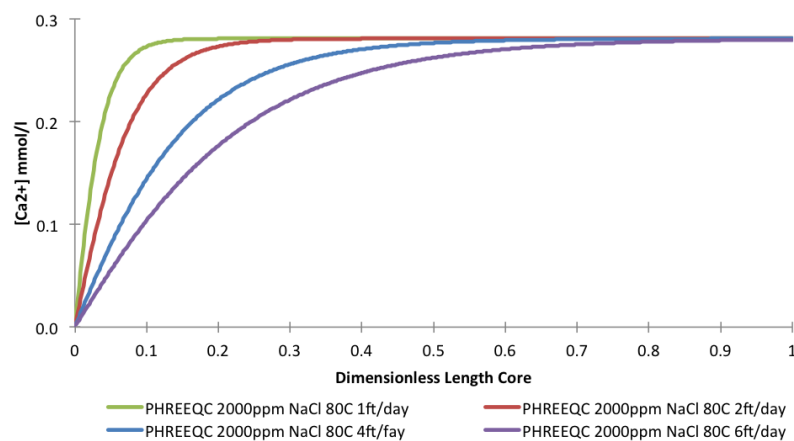


FIGURE 6.19: Calcium concentration of the fluid passing through the core, 2000 ppm NaCl, 80 °C.

beginning (45-48 pore volumes). This is due to the previous injection conditions of 2000 ppm at 80 °C, as shown in figure 6.3. A new equilibrium has been established for 0.5 ft/day at 50 pore volumes, there was no increase in Calcium concentration compared to the 1 ft/day data. This indicates that equilibrium has been reached at 1 ft/day as well.

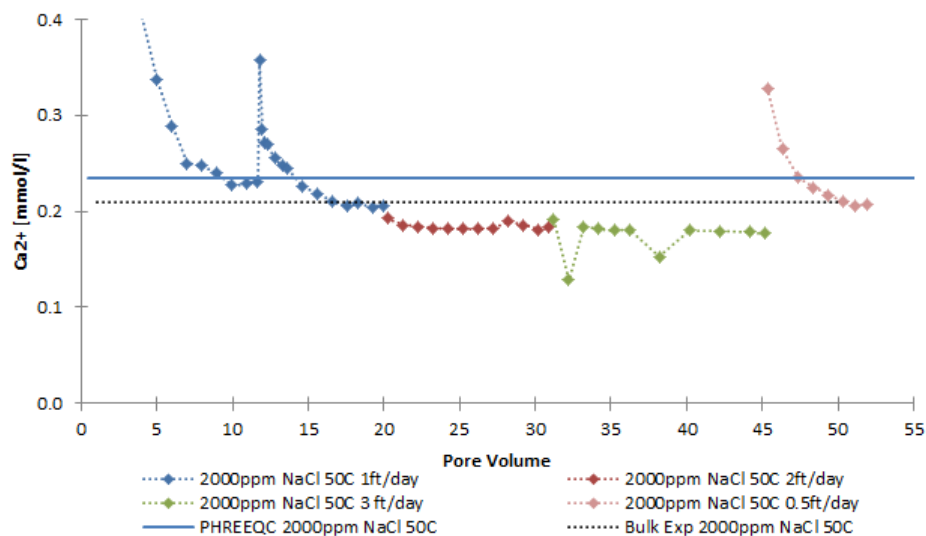


FIGURE 6.20: Calcium concentration of the effluent with injected pore volumes, 2000ppm NaCl , 50 °C, limestone.

Figure 6.21 shows the data of coreflood experiments with 2000ppm NaCl at 80 °C, with different injection rates as well. The data shows that with an injection velocity of 1 ft/day the Calcium concentration of the fluid reached the equilibrium value of the PHREEQC model. The fluids injected with a velocity of 4 and 6 ft/day did not reach the equilibrium value of to the PHREEQC model. The fluid injected with 0.5 ft/day did not match the equilibrium value of to the PHREEQC model as well. However, if the experiment had been continued for another 5 pore volumes, this equilibrium value probably would have been reached.

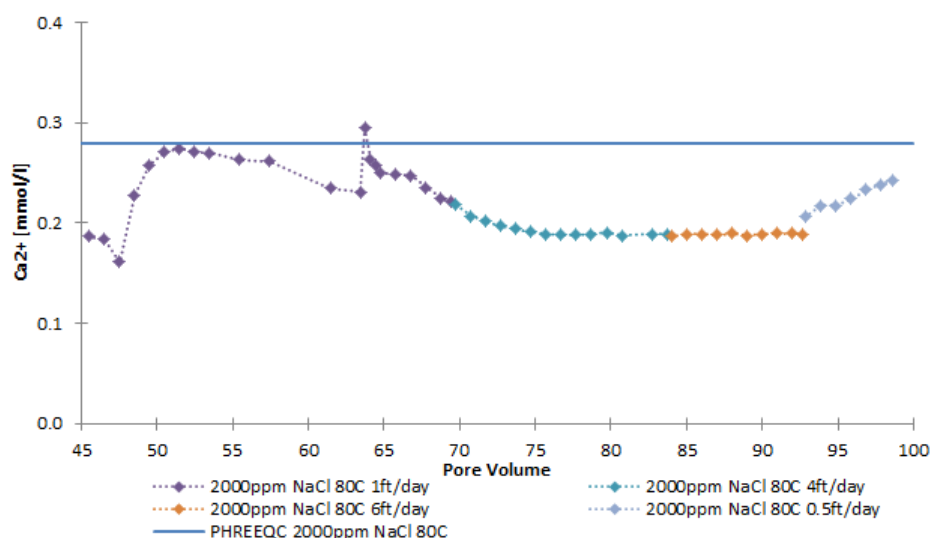


FIGURE 6.21: Calcium concentration of the effluent with injected pore volumes, 2000ppm NaCl , 80 °C.

PHREEQC and Experimental data showed that the injection rate influences the Calcite dissolution for the kinetic part of the process. The process needs a certain time to reach equilibrium. Therefore the interaction between the fluid and the carbonate core needs to last a certain time, which is influenced by the injection rate of the fluid. The time needed to reach Calcite dissolution equilibrium was reduced when the temperature was raised, according to the PHREEQC data. For the field, the effect of the injection rate on the calcite dissolution will be different. If the injection rate would be increased in the field, the Calcite dissolution will take place over a longer distance.

6.8 pH data

Figure 6.22 shows the pH data of the coreflood experiment performed with limestone at room temperature. The pH was measured of the effluent of different injection brines. For each brine the pH of the effluent was within the range of 7.5-8.0. This value is lower compared to the pH data of the bulk experiments and the PHREEQC model. This is because of CO_2 . The effluent samples are open to the atmosphere and therefore can be equilibrated with CO_2 . When CO_2 solved in a fluid carbonic acid, H_2CO_3 , was formed. As a result the pH was lowered. The pH of the fluid of the bulk experiment was measured concurrently as the sample was taken. The pH of the coreflood effluent was measured after 1-2 days, and therefore the fluid was able to equilibrate with CO_2 .

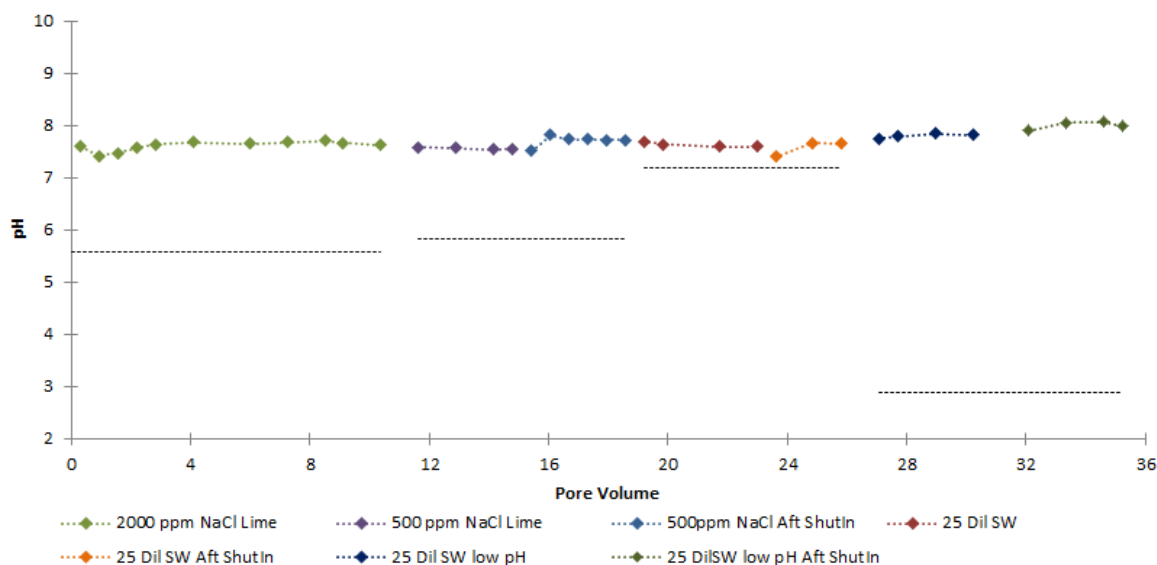


FIGURE 6.22: pH of the effluent with injected pore volumes, limestone , 22 °C.

6.9 Influence of Calcite dissolution on Porosity

CT scans and micro-CT scans were made of the rock to study the effect of Calcite dissolution on the porosity of the core.

CT scans were made of the dry core before the experiment, after 10 pore volumes injected and after 58 pore volumes injected. Each scan consists of 17 slices, with a separation of 3 mm. Of each slice an

average grey value was determined, using ImageJ, a Java based image processing software. The higher the grey value, the higher the density. The averaged grey value per slice is plotted in figure 6.23.

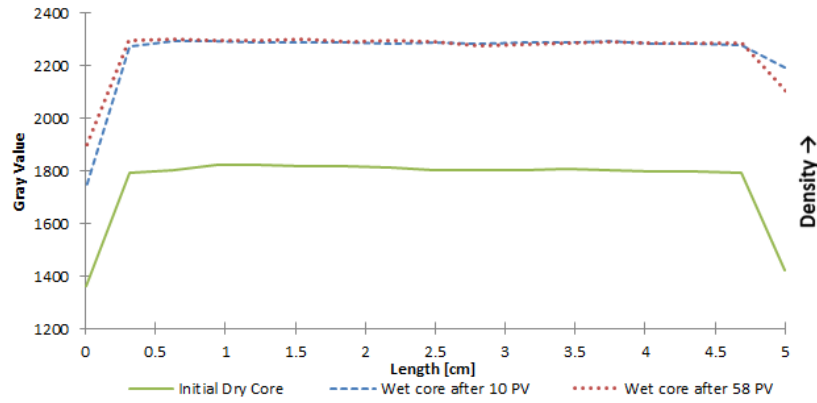


FIGURE 6.23: Grey value through chalk core.

The CT scan of the dry core shows relative low grey values. This is because of the core was not saturated with brine, which has a higher density than air. There was no significant difference in the density of the cores after 10 and 58 pore volumes injected.

There was a difference in density observed between the two scans at the inlet and outlet of the core. This is due to the beam hardening effect at the edge of the core, i.e. at the edge there is less attenuation. The beam hardening leads to artefacts in the processing of the image, which is clearly present in 6.23.

Micro-CT scans were made for the limestone core before and after the second coreflood experiment (figure 6.2) An image was made for the first 5 mm of the inlet of the core after injection. The reference image was made of another piece of rock, but drilled from the same block of limestone. Two images are shown in figure 6.24 and 6.25.



FIGURE 6.24: Micro CT scan of limestone core, before LSF.

From the figures no change in porosity or roundness of the particles was observed, i.e. no increase of the connectivity between the pores.

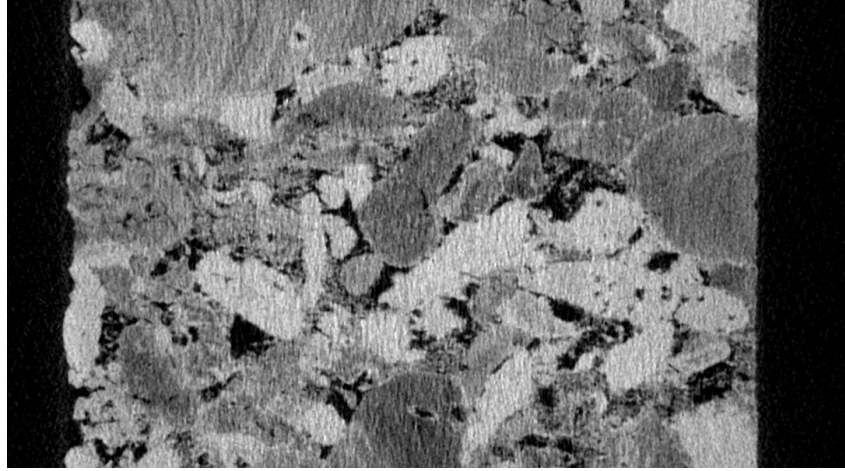


FIGURE 6.25: Micro CT scan at inlet limestone core, after LSF.

Porosity measurements have been performed with the use of ImageJ. This is done by setting a threshold of the grey to make a distinction between pores and grains. The porosity was determined by measuring the area percentage of the pores.

The measured porosities are listed in table 6.3. The limestone sample before the LSF had an average porosity of 8.59% with a standard deviation of 0.38%. The limestone sample after the LSF had an average porosity of 9.06% with a standard deviation of 0.65%. So the difference between the porosities is negligible when taking the standard deviations into account.

	Before experiment	After Experiment
Measurement	Porosity [%]	Porosity [%]
1	8.80	9.20
2	8.26	8.33
3	8.28	10.02
4	8.47	8.33
5	8.59	9.44
6	9.62	9.20
7	8.65	8.74
8	8.13	7.97
9	8.45	9.44
10	8.57	8.98
11	8.70	10.05
Average	8.59	9.06
SD	0.38	0.65

TABLE 6.3: Porosity measurement from micro-CT scans of limestone core, before and after LSF.

The change in porosity can also be calculated by a material mass balance. If we assume the equilibrium value of 2000 ppm NaCl at room temperature is 0.20 mmol/l and equilibrium is obtained during 60 pore volumes injected. One pore volume is 16.44 ml, then the amount of dissolved Calcite is:

$$60 \cdot 16.44 \cdot 10^{-3} \cdot 0.2 = 0.197 \text{ mmol of Calcium} = \text{mmol Calcite} \quad (6.1)$$

The molar mass of Calcite is 100.1 g/mol . So the amount of Calcite dissolved after 60 pore volumes of 2000 ppm NaCl injected is 19.74 mg . The density of Calcite is 2.711 g/cm^3 , which gives a volume of 0.054 cm^3 of Calcite. So the change in porosity over the whole core is 0.09%. This change in porosity is insignificant and therefore not detected by the CT scans.

Chapter 7

Results Two-phase Coreflood Experiments

7.1 Production Profile

Table 7.1 shows the oil and water saturations of the core before and after the experiment.

Saturations		
	Sw [%]	So [%]
Initial	9.40	90.60
End	58.5	41.50

TABLE 7.1: Water and oil saturations before and after the experiment.

Figure 7.1 shows the cumulative oil production of the two-phase coreflood experiment, injecting subsequently 2000 ppm NaCl, 500 ppm NaCl and low pH 25 times diluted seawater. Water break through occurred after 5.2 ml oil production, which is 35% of the OIIP. 39.60 % of the OIIP was produced after flooding with 2000 ppm NaCl at 1 ft/day, i.e. 0.07 cc/min. An incremental oil recovery of 3.69 % was observed when the injection rate was increased to 0.14 cc/min and another 2.52 % when the rate was increased to 0.21 cc/min. Lowering the salinity of the injection brine to 500 ppm NaCl did not increase the oil recovery. The total oil recovery was 45.81 % OIIP.

The wettability of the core can be determined from the production curve. For a water wet rock, there is relative little oil produced after water breakthrough. For a oil wet rock, water breakthrough occurs earlier and relative more oil is produced after. Figure 7.2 shows the cumulative oil production for the first five pore volumes injected. This curve indicates that the surface of the limestone core, used in the two-phase coreflood, was water wet.

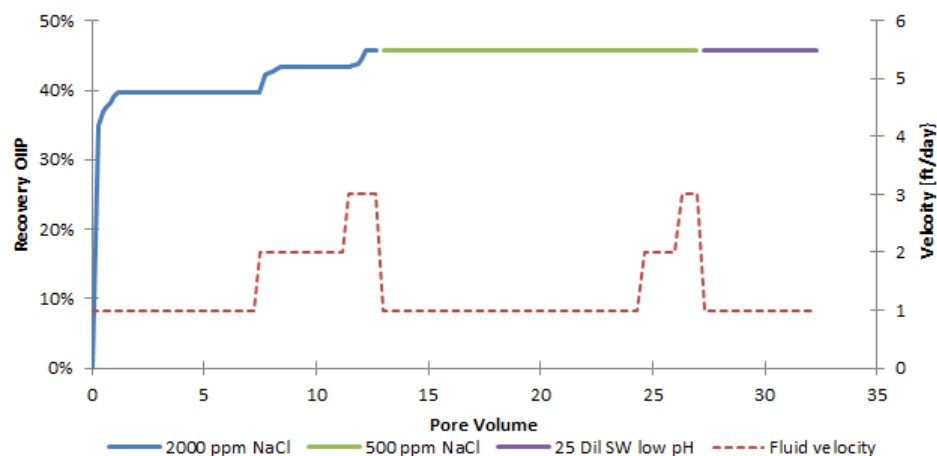


FIGURE 7.1: Cumulative oil production with injected pore volumes, 50 °C, 1-3 ft/day, limestone.

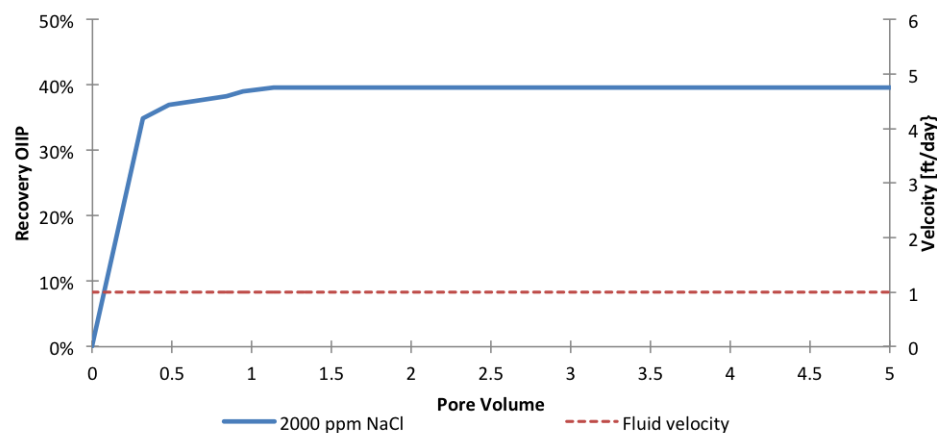


FIGURE 7.2: Cumulative Oil with injected pore volumes, 50 °C, 1-3 ft/day, limestone.

7.2 Calcite dissolution

Figure 7.3 shows the Calcium concentration of the effluent with the amount of low salinity brine pore volumes injected. The total Calcium concentration was due to dissolution, because initially there was no calcium present in the brine. Secondly, the unwanted ions present due to the drilling fluid were removed by injecting at least 10 pore volumes of the high salinity formation brine (10,000 ppm NaCl).

The Calcium concentration of the first pore volume injected is at 0.4 mmol/l. During this part of the experiment there was still oil produced. From 2 pore volumes injected on the Calcium concentration remained constant at 0.18 mmol/l in the 2000 ppm NaCl effluent. The Calcium concentration of the 500 ppm NaCl effluent is around 0.13 mmol/l. Calcite dissolution decreased when the salinity was reduced, which was observed from the single-phase coreflood as well.

The single-phase coreflood data is plotted in the figure as a reference. For both the injection brines, the Calcium concentration of the effluent is 0.03-0.05 mmol/l lower in the two-phase coreflood data. However, Calcite dissolution still occurs if there is oil present in the core.

The coreflood data indicates that the Calcite dissolution might favours from the oil. Calcite dissolution was higher when the oil was still produced. This can be due to the presence of the acid components in the oil. These components reduce the pH. From bulk and coreflood experimental data and PHREEQC data was observed that Calcite dissolution increases significantly when the pH is reduced.

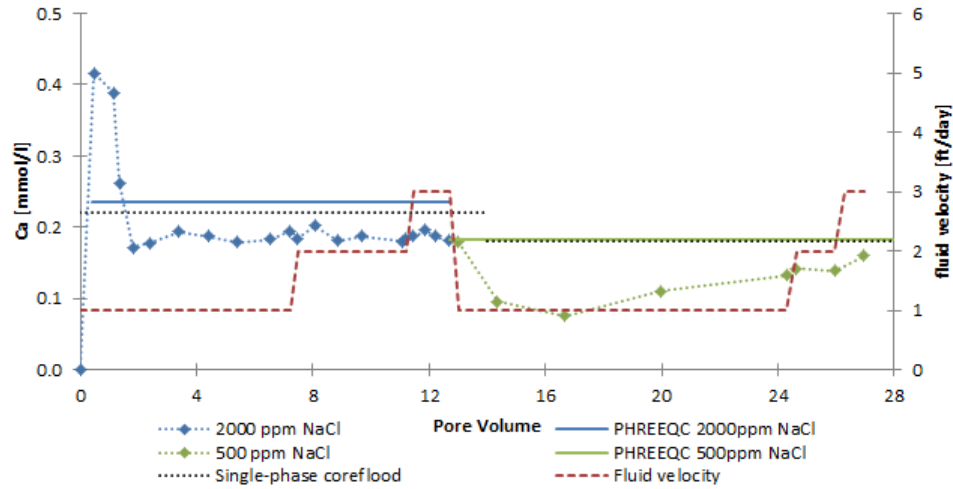


FIGURE 7.3: Calcium concentration of the effluent with injected pore volumes, 500-2000 ppm NaCl, 50 °C, 1-3 ft/day, limestone.

25 times diluted seawater with a pH of 2.9 was injected after the 500 ppm NaCl. The measured Calcium concentration of the effluent is shown in figure 7.4. The Calcium concentration in the figure is due to Calcite dissolution, because the initial concentration is subtracted. The pH had a significant effect on the Calcite dissolution for the two-phase experiment as well and almost reaches the same concentration as for the single-phase experiment.

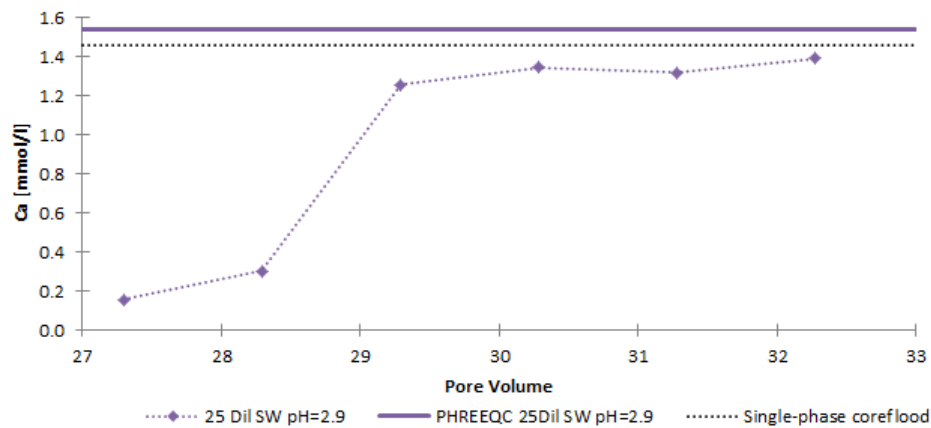


FIGURE 7.4: Calcium concentration of the effluent with injected pore volumes, 25Dil SW, pH=2.9, 50 °C, 1 ft/day, limestone.

7.3 Effluent

The effluent during both oil and water production was a thicker matter than the crude oil. Figure 7.5 shows a picture taken of the effluent and indicates that there was an emulsion formed. This might be an effect of the increase in pH due to the Calcite dissolution. The high pH brine can react with the acid components in the crude oil. As a result, in-situ surfactants can be generated, as explained before in chapter 2.



FIGURE 7.5: Sample of the effluent during both oil and water production, 2000 ppm NaCl, 50 °C, limestone core.

Chapter 8

Discussion

8.1 Effect of brine salinity on the Calcite dissolution

From both the bulk experiments and coreflood experiments was observed that the Calcium concentration at Calcite dissolution equilibrium is higher for the 2000 ppm NaCl solution than for the 500 ppm NaCl solution. This observation was confirmed by the PHREEQC modelling data.

The activity coefficient is related to the ionic strength, as shown in equation 3.22 and in figure 3.5. The ionic strength of the 2000 ppm NaCl solution is:

$$I = \frac{1}{2} \sum_i z_i^2 [X_i] = \frac{1}{2} (1^2 \cdot 0.0342 + 1^2 \cdot 0.0342) = 0.0342 \text{ mol/m}^3 \quad (8.1)$$

And the ionic strength of the 500ppm NaCl solution is:

$$I = \frac{1}{2} \sum_i z_i^2 [X_i] = \frac{1}{2} (1^2 \cdot 0.0086 + 1^2 \cdot 0.0086) = 0.0086 \text{ mol/m}^3 \quad (8.2)$$

Figure 3.5 shows that the activity coefficient $\gamma_{Ca^{2+}}$ is related to the ionic strength of a solution. This figure gives, with the calculated ionic strengths, a $\gamma_{Ca^{2+}}$ of 0.7 for the 500 ppm NaCl solution and 0.6 for the 2000 ppm NaCl solution.

The solubility product of Calcite, given in equation 3.10, is $3.36 \cdot 10^{-9}$. The solubility product is the product of the Ca^{2+} and CO_3 activities at equilibrium. The activity of an ion, is the product of the molar concentration and the activity coefficient of the ion. So when the activity coefficient $\gamma_{Ca^{2+}}$ decreases, the molal concentration m_{Ca} at equilibrium increases. The increasing ionic strength in the low salinity range, creates a lower $\gamma_{Ca^{2+}}$ and therefore a higher Solubility of Calcite.

From the PHREEQC model the same relation between ionic strength and solubility was observed. For 2000 ppm NaCl, at 22 °C and in a CO_2 -free environment, the $\gamma_{Ca^{2+}}$ is 0.52 at the equilibrium in the PHREEQC model. For 500 ppm NaCl at same conditions the $\gamma_{Ca^{2+}}$ is 0.68 at equilibrium. The $a_{Ca^{2+}}$ for 2000 and 500 ppm NaCl are respectively $9.68 \cdot 10^{-5}$ and $9.89 \cdot 10^{-5}$. Using equation 3.21, this gives

a Calcium concentration at equilibrium of 0.19 mmol/l for 2000 ppm NaCl and 0.15 mmol/l for 500ppm NaCl.

From the data of coreflood experiments with chalk at 22 °C and limestone at 50 °C (figures 6.5 and 6.7), a lower Calcium concentration was observed of 0.03-0.05 mmol/l. The dip is sudden after lowering the salinity from 2000 to 500 ppm NaCl. The occurrence of this sudden dip is suspected to be caused by ion exchange between negative charged clay and Ca^{2+} in the solution, which is present in the low salinity brine due to Calcite dissolution. Ion exchange is induced when the salinity of the brine is lowered [Lager et al. 2006].

The SEM data, shown in table 4.6, indicates that some clays are present at the rock surface. From XRD analysis no clays are suspected. However, XRD mainly detects the presence of elements in the bulk volume, while SEM detects the elements present at the rock surface. Clays might be present at the carbonate rock surface.

8.2 Effect of CO_2 on the Calcite dissolution

From bulk experiments was observed that Calcite dissolution is very dependent on the partial pressure of CO_2 ($=P_{CO_2}$). Equation 3.5 gives the equilibrium of Calcite with the presence of CO_2 . Equation 3.6 show that at a higher P_{CO_2} creates a higher Calcium molarity at equilibrium.

From bulk experiments at atmospheric pressure a Calcium concentration of 0.60 mmol/l was observed at room temperature. The PHREEQC model was fitted with the data model by setting the P_{CO_2} at $10^{-3.5}$. Using equation 3.6, the Calcium molarity at equilibrium can be calculated:

$$K = \frac{[Ca^{2+}][HCO_3^-]^2}{P_{CO_2}} = \frac{[X][2X]^2}{10^{-3.5}} = 10^{-6.0} [4X]^3 = 10^{-9.5} X = 0.43 \text{ mmol/l} \quad (8.3)$$

$$K = \frac{[Ca^{2+}][HCO_3^-]^2}{P_{CO_2}} = \frac{[X][2X]^2}{10^{-4.5}} = 10^{-6.0} [4X]^3 = 10^{-10.5} X = 0.20 \text{ mmol/l} \quad (8.4)$$

Equations 8.3 and 8.4 show that the Calcite dissolution at equilibrium increases with increasing P_{CO_2} .

In a system open to atmospheric CO_2 , the P_{CO_2} remains constant. There is a continuous supply of CO_2 while it is consumed during Calcite dissolution. In a CO_2 -free environment, there is no or little CO_2 present, which will be consumed and the CO_2 can not be replenished.

Before adding the Carbonate powder to the brine in the CO_2 -free bulk experiment, the jar with the brine had been connected to a vacuum pump for at least 12 hours, to create a CO_2 -free environment. During the experiment, the jar remained connected to the vacuum pump. Each hour, the jar was opened for the measurements and some CO_2 entered the system. Before starting the coreflood experiments, the total set-up had been connected to a vacuum pump in order to remove all the air from, with the removal of CO_2 accompanied. Therefore the Calcite dissolution during coreflood experiments is assumed to be in a CO_2 -free environment as well.

To match the PHREEQC data with the CO_2 -free bulk and the coreflood data, the CO_2 was not added to the brine in the model. Initially the brine does not contain CO_2 . However, at equilibrium CO_2 has a SI ($=\log P_{CO_2}$) of -6.28. This is because CO_2 is formed during the Calcite dissolution process. This indicates that the brines of the CO_2 -free bulk and the Coreflood experiments are not completely CO_2 free, but the solution has a very low CO_2 content at equilibrium.

Unlike the coreflood experiment, CO_2 is present in the field, due to biodegradation of organic material. Therefore, the Calcite dissolution at equilibrium in the field is considered to be higher than observed from the coreflood experiments. The amount of CO_2 present differs per reservoir.

8.3 Effect of pH on the Calcite dissolution

From bulk and coreflood experiments was observed that Calcite dissolution at equilibrium increased with decreasing pH. The pH is a function of the $[H^+]$ concentration as shown in figure 8.5. A lower pH means a higher $[H^+]$ concentration.

$$pH = -\log[H^+] \quad (8.5)$$

Equations 3.1 and 3.2 show that H^+ is consumed during the Calcite dissolution equilibrium. This equilibria are dominating in the low pH regime. Equation 3.3 is the dominating equilibria in the intermediate pH regime and equation 3.4 in the high pH regime. The higher the $[H^+]$ in the fluid, the higher the $[Ca^{2+}]$ in the fluid at equilibrium in the low pH regime. Table 8.1 shows the relation between the pH and Calcium concentration at equilibrium for the low pH regime.

pH	H^+ [mmol/l]	Ca^{2+} [mmol/l] eq.3.1	Ca^{2+} [mmol/l] eq.3.2
2.9	1.26	1.26	$6.29 \cdot 10^{-1}$
3	1.00	1.00	$5.00 \cdot 10^{-1}$
3.1	$7.94 \cdot 10^{-1}$	$7.94 \cdot 10^{-1}$	$3.97 \cdot 10^{-1}$
3.2	$6.31 \cdot 10^{-1}$	$6.31 \cdot 10^{-1}$	$3.15 \cdot 10^{-1}$
7.1	$7.94 \cdot 10^{-5}$	$7.94 \cdot 10^{-5}$	$3.97 \cdot 10^{-5}$
10.4	$3.98 \cdot 10^{-8}$	$3.98 \cdot 10^{-8}$	$1.99 \cdot 10^{-8}$

TABLE 8.1: pH values and the related Molarities.

The bulk experiment performed with a low pH brine at room temperature showed a Calcium concentration of 0.70 mmol/l at equilibrium. This concentration matches with the Calcium molarity at equilibrium according to equation 3.1 for a pH between 3.1-3.2. The coreflood experiment performed with a low pH brine at room temperature showed a Calcium concentration of 0.98 mmol/l at equilibrium, with matches with the Calcium molarity according to equation 3.1 for a pH between 3.0-3.1. The Coreflood experiment performed with a high pH brine (10.4) at room temperature showed a Calcium concentration of 0.04 mmol/l at equilibrium. This is higher than the Calcium molarity at equilibrium according to equation 3.1. This is because another equilibrium will establish at a high pH regime, shown in 3.4.

8.4 Effect of temperature on the Calcite dissolution

From bulk experiments at atmospheric conditions was observed that the Calcite dissolution decreased when the temperature is increased from 22 °C to 50 °C. The PHREEQC data is fitted to the experimental data by adjusting the P_{CO_2} . The P_{CO_2} was set at $10^{-3.5}$ Bar at 22 °C and was set at $10^{-4.5}$ Bar at 50 °C. This means the amount of CO_2 present in the brine decreased with temperature.

This can be explained by the decreasing solubility of CO_2 in the brine with temperature. Solubility of CO_2 in water with temperature has been investigated by Carroll et al. (1991). They observed a solubility of $0.704 \cdot 10^3$ mol CO_2 per 1 mol of water at 20 °C, $0.609 \cdot 10^3$ at 25 °C and $0.319 \cdot 10^3$ at 50 °C. Secondly, from literature is know that the solubility of Calcite decreased with increasing temperature, as shown in figure 3.1 [Coto et al. 2012].

From coreflood experiments was observed that the Calcite dissolution increased when temperature was raised from 50 °C to 80 °C. However, from literature [Coto et al. 2012] is observed that the solubility of Calcite decreases with temperature. From PHREEQC data was observed that in a CO_2 -free environment, the Calcite dissolution increases with increasing temperature from 22 °C to 80 °C .

The Solubility product of $CaCO_3$ (equation 3.10) in the PHREEQC model is $3.43 \cdot 10^{-9}$ at 22 °C and is $2.172 \cdot 10^{-9}$ at 50 °C. So the Solubility product decreases with temperature in the PHREEQC model, which is in contradiction with the increasing Calcium concentration at equilibrium with temperature.

The temperature also has an effect on the regions of pH dependency of Calcite dissolution, shown in figure 3.4. The pH of the 2000 ppm solution is at 5.5 for the coreflood experiments at 50 – 80 °C. This pH value is near the border of the Transition zone to the H^+ independent zone.

In the transition zone, the Calcite dissolution is partly dependent on the diffusion of H^+ from the bulk solution to the surface, where the dissolution reaction occurs. In the H^+ independent zone, the calcite dissolution is controlled by the surface. It might be that at a pH of 5.5, the dissolution process is within the transition zone. When the temperature is raised, the border shifts to a lower pH. So an increase in temperature may cause the dissolution process to be in the H^+ independent zone for a constant pH.

In the transition zone, the dissolution can be limited by the fluid velocity. If the velocity is too high, the H^+ might not have enough time to reach the surface. The Calcite dissolution is limited by the H^+ diffusion. When the process is within the H^+ independent zone, the Calcite dissolution is not dependent on the H^+ diffusion from the bulk solution to the surface, and therefore not limited by the flow rate.

This can be an explanation for the higher Calcium concentration at 80 °C. However, there is no significant increase in Calcite dissolution when the injection rate is decreased from 1 to 0.5 ft/day at 50 °C. If we assume that the previous explained theory is applicable to this situation, it is expected that the Calcite dissolution increased with decreasing flow rate at 50 °C. At a lower flow rate, the H^+ has more time to diffuse to the surface and the reaction is less or not limited.

8.5 Effect of flow rate on Calcite dissolution

From coreflood experiments was observed that Calcite dissolution decreased when the injection was rate increased. For a relative high flow rate, the Calcite dissolution will remain in the kinetic part of the process. The fluid does not have enough interaction time with the rock to be able to reach equilibrium. For a flow rate below a certain value, the Calcite dissolution process is able to reach equilibrium within the time that the fluid passes through the core.

From the PHREEQC data, shown in figures 6.17, 6.18 and 6.19, was observed that the dissolution rate r increased with temperature. The higher the dissolution rate, the less time needed for process to reach equilibrium. From the PHREEQC modeling data was observed, when A/V was set at 5, that this period of time is approximately 4 hours at 22 °C, 1 hour at 50 °C and half an hour at 80 °C.

The higher the temperature, the faster the particles are moving. As a result they collide with more energy. This gives more effective collisions per unit time and therefore the reaction rate increases. Secondly, the diffusivity increases with temperature. The H^+ ions are able to diffuse faster from the bulk solution to the surface and the consumption of H^+ is accelerated. As a result the dissolution is accelerated, and therefore the dissolution rate is higher.

For the field, an increasing injection rate would have a different effect on the Calcite dissolution. The fluid will establish equilibrium and the Calcite dissolution will take place over a longer distance from the injection well. For a low injection rate, like 1 ft/day, the Calcite dissolution will mainly take place in a short radius around the well.

8.6 Effect of Carbonate material on Calcite dissolution

From bulk experiments was observed that at 22 °C Calcite dissolution from chalk at equilibrium matched with the dissolution from pure Calcite. The dissolution from limestone was almost 50% higher. So there is an effect of mineralogy on the rock dissolution as well.

XRD data, given in table 4.7, showed that both the chalk and limestone samples contain Magnesium as well. This indicates that dolomite is present next to calcite. The chalk sample contains more Magnesium. Two different micro-ct scans are shown in figure 8.1 and 8.2. They show that there is a difference in the grey value for different grains. This difference in grey value indicates a difference in material. Taking the XRD data into account, the possible present minerals are Calcite ($CaCO_3$), Aragonite ($CaCO_3$) and Dolomite ($CaMg(CO_3)_2$).

The solubility product of Calcite is $3.4 \cdot 10^{-9}$ and of Aragonite is $6.0 \cdot 10^{-9}$ at 25 °C. Dolomite has a relative low solubility products, which is $9.84 \cdot 10^{-18}$ at 25 °C according to PHREEQC modelling data. The higher Calcite dissolution of the limestone experiments compared to pure Calcite can be due to the dissolution of both Calcite and Aragonite. According to Burton et al. (1987) the precipitation rate increases with temperature for Aragonite. Calcite precipitation rate increases as well with temperature, but the effect is less significant for Calcite. The increasing precipitation rate is proportional to a decreasing dissolution rate. At 50 °C and 80 °C there was a fair match between the limestone experimental data and PHREEQC data. This can be explained by the decrease of the Aragonite dissolution rate with temperature.

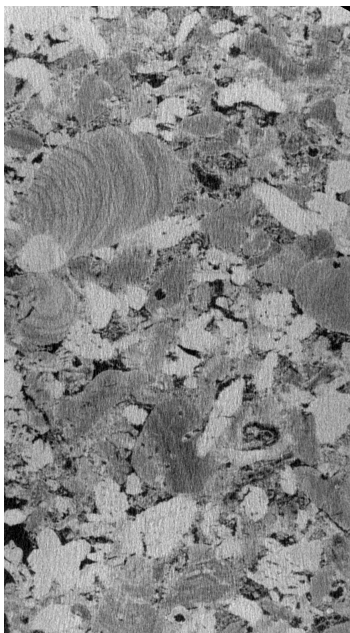


FIGURE 8.1: Micro CT scan, limestone.

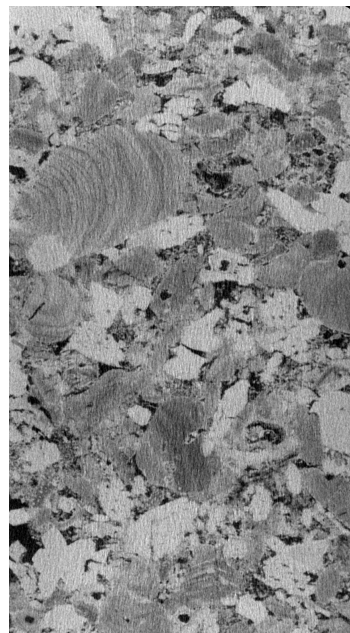


FIGURE 8.2: Micro CT scan, limestone.

8.7 Effect of shut-in during coreflood experiments

During the single-phase coreflood experiment, the core has been shut-in several times for three days, as shown in figure 6.7 and 6.8. This was done with the purpose to reach the Calcite dissolution equilibrium. However, the Calcium concentration increased above the value expected from bulk experimental data and PHREEQC modelling data.

As mentioned before, XRD data indicated that Dolomite is probably present in both the chalk and limestone core. From experiments we can conclude that Calcite dissolution occurs immediately if the rock interacts with the low salinity brine. However, dissolution of Dolomite is a slower process. Figure 8.3 shows the Calcium concentration due to Calcite and Dolomite dissolution according to the PHREEQC model. In the model, Dolomite dissolution has not been able to reach the equilibrium state even after three days, while Calcite dissolution reaches equilibrium within four hours. The HPLC data of the samples after the shut-in period did not show a Magnesium peak, so the dissolution of Dolomite is not confirmed by the experimental data.

8.8 pH of the effluent

From bulk and coreflood experimental data an increase of pH was observed. The pH of bulk experiment increased to a pH of 8.5-9.8 and the pH of the coreflood effluent had a pH of 7.5-8.0. However, the pH of the brine in the core is expected to be between 8.5-9.8 as well. This is because the pH of the effluent decreases when open to atmospheric CO_2 .

The increase of pH during Calcite dissolution is due the consumption of H^+ and CO_2 . If it is assumed that the pH of the brine in the carbonate core is between 8.5-9.8, due to Calcite dissolution, the wettability of the core can be effected.

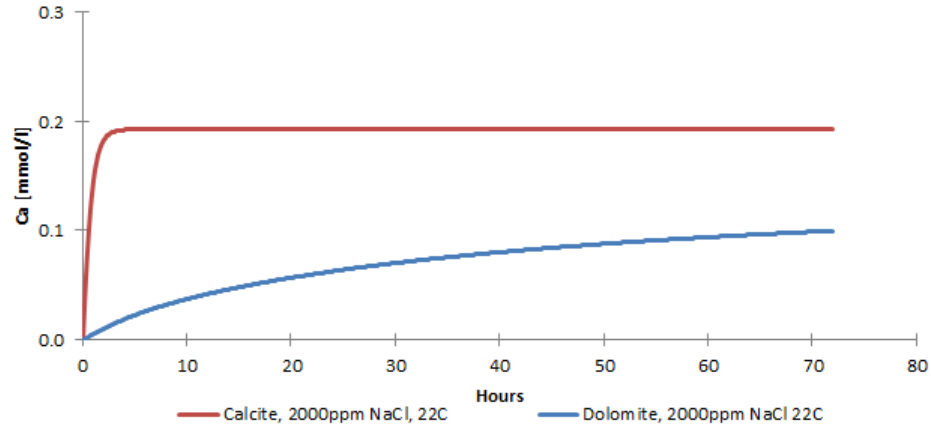


FIGURE 8.3: Calcium concentration due to Dolomite and Calcite dissolution in 2000 ppm at 22 °C, PHREEQC.

With PHREEQC, the surface charges of the oil and Calcite as a function of pH was modelled, equilibrated with 2000 ppm NaCl at 22 °C. The plot is shown in figure 8.4. The Calcite surface is assumed to be oil wet if the charges of the oil and calcite surface are of opposite signs (+/-), the surfaces will be attracted to each other. The rock is assumed to be more water wet when the surface of oil and Calcite have the same sign, due to repulsion forces.

If we assume the pH rises to 9.5, due to dissolution, both the calcite and oil surface will be negative charged. So the increase in pH can alter the wettability of the Calcite surface to more water wet.

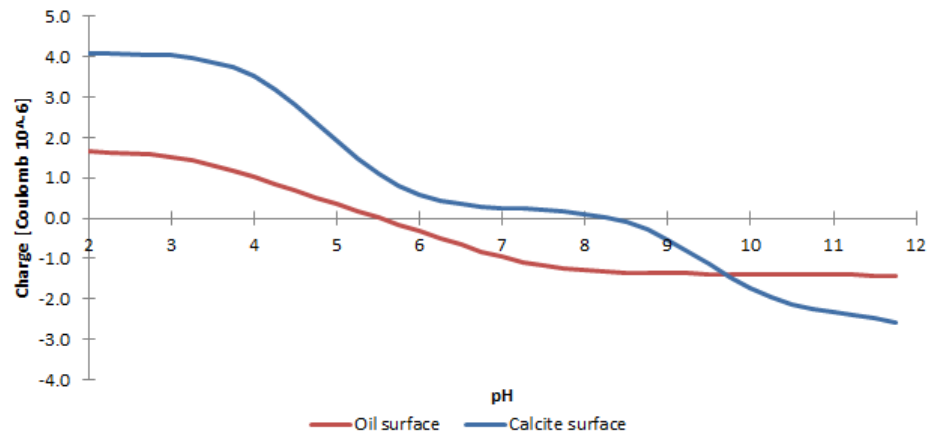


FIGURE 8.4: Surface Charge of Oil and Calcite with pH, 2000 ppm NaCl 22 °C, PHREEQC.

8.9 Effect of Calcite dissolution on porosity and connectivity

From CT scans and Micro CT scans, there was no change in porosity observed. Material mass balance calculations gave a porosity increase of 0.09% over the whole core. If we assume porosity mainly occurs in the first 5 mm, the increase in porosity is 0.91%. The increase in porosity was difficult to detect with the use of CT or Micro CT scans. Even if the change in porosity is assumed to be in the first 10% of the length of the core, like Al-shalabi et al. (2014), the increase in porosity is very small.

It was not feasible to measure the porosity with the use of the Micro CT scans, by adjusting a grey value threshold for the pores in an Image processing software. According to given data of the core in table 4.4, the porosity of the limestone should be at 29%, while the measured porosities from the Micro CT scans are within the range of 8-10%

The presence of small intra granular porosity might be the reason for this. Intra granular porosity is the porosity within grains. This type of porosity is often present in Carbonate rock, due to dissolution. This type of porosity is difficult to detect in a 2D image, obtained from Micro CT scans. However, it is assumed that this type of porosity is not affected by Calcite dissolution during core flooding, because it is excluded from the effective porosity.

It is expected that the risk of formation of caves and sinkholes during LSF in carbonate rock is low, because no significant increase in porosity is observed in this study.

8.10 Two-phase coreflood experiment

From the two-phase coreflood experimental data was observed that the Calcite dissolution occurred as well when oil and low salinity brine were present in the core. However, The Calcium concentration of the two-phase coreflood effluent was lower 0.03-0.05 mmol/l compared to the single-phase coreflood data, for both 500 and 2000 ppm NaCl. So the presence of oil can have an inhibitory effect on the Calcite dissolution, by reducing the specific surface. The oil covers parts of rock surface.

The production data indicated that the limestone core is intermediate to water wet. If the rock surface would be oil wet, the oil covers the rock surface and probably this will reduce the Calcite dissolution even more. It is expected that Calcite dissolution increases when the wettability is altered from oil wet to water wet.

8.11 Increase in salinity due to carbonate rock dissolution

Due to Calcite dissolution, the total dissolved species (TDS) in the low salinity brine increases. From this, the questions arises if this increase in TDS creates a risk for the LSF effect.

If we assume that 25 times diluted seawater (TDS=1751) is flooded at 80 °C and the Calcium concentration due to Calcite dissolution at equilibrium is at 0.3 mmol/l, then an amount 0.3 mmol of Calcite is dissolved per liter. The molar mass of Calcite is 100.1 g/mol, so the amount of dissolved Calcite in the low sal is 0.03 g/l, which is an increase of 30 ppm TDS. This increase in TDS will not be harmful for the desired effect of LSF.

Chapter 9

Conclusions and Recommendations

9.1 Conclusion

An experimental study was performed to get a better understanding of the Calcite dissolution behaviour during LSF in carbonate rock. Bulk experiments and coreflood experiments were performed, which data was matched with PHREEQC modelling data. The experiments were conducted at different conditions by changing various parameters in order to investigate the effect of these parameters on the Calcite dissolution. Based on the presented work, the following conclusions can be drawn:

- In the bulk experiments, Calcite dissolution reached equilibrium within ten minutes. For the single-phase coreflood experiments, this period of time is longer, because of the smaller specific surface available for dissolution and the presence of the mixing zone in the core when adjusting one of the parameters.
- Calcite dissolution requires a certain amount of time to reach the equilibrium state, which decreases with temperature. From the PHREEQC modeling data was observed, when A/V was set at five, that this period of time is approximately 4 hours at 22 °C, 1 hour at 50 °C and 0.5 hour at 80 °C.
- In the remaining oil saturation condition in the two-phase coreflood, Calcite dissolution was observed. The Calcium concentration due to dissolution in the presence of oil was lower than in the absence of oil, which indicates that the presence oil has an effect on Calcite dissolution.
- Calcite dissolution decreased with decreasing P_{CO_2} , decreasing salinity of NaCl solutions from 2000 to 500 ppm. Calcite dissolution increased when pH was decreased.
- Calcite dissolution at room temperature from chalk matched dissolution from Calcite crystal. However, Calcium concentration in the effluent of limestone experiments was 50% higher than expected from pure Calcite dissolution, which suggests that Calcite present in limestone has a different equilibrium condition or other minerals may have interacted with LSF and hence higher Calcium concentration. This indicates that mineralogy is important for the rock dissolution behaviour.
- The increase in the salinity of injected brines, due to Calcite dissolution will not harm the required salinity for the LSF to be effective.

- The pH of effluent increased from 5.5 to 9.8 due to Calcite dissolution, which can have an effect on the Calcite and oil surface charges.
- A viscous emulsion phase was observed in the two-phase coreflood effluent. It suggested the formation of in-situ surfactant.
- A maximal increase of 1% in porosity was observed, which is assumed to be insignificant to have an effect on pore connectivity or to create a risk for subsidence.
- The match between the experimental and modelling data proved that PHREEQC is a reliable geochemical simulator.

9.2 Recommendations

From this study a better understanding is obtained of the Calcite dissolution behaviour during LSF in carbonate rock. However, there are still some questions and observations unresolved.

- For the PHREEQC modelling, kinetics should be integrated in the fluid transport model in order to be able to see the effect of the mixing zone on the Calcite dissolution.
- Specific surface area measurements of the porous media are needed to be able to have an accurate input for the modelling.
- From this study was observed that mineralogy of the carbonate rock affects the rock dissolution. Therefore more knowledge is needed on the dissolution behaviour of the different carbonate minerals.
- The effect of increasing pH, due to Calcite dissolution, on the oil and carbonate rock surface charge needs to be studied more extensively.

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