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Dagny Håmsø

Abstract

Laboratory tests, as well as field tests, have shown that low salinity water flooding in sandstone reservoirs can improve the water wetness of the rock and thereby increase the oil recovery. Many mechanisms have been suggested in the last decades but none of these mechanisms are completely accepted and research is still going on. Austad et al. (2010) have recently suggested a new chemical mechanism based on a local increase in pH at the clay surface. By injecting low salinity brine a local pH increase at the clay surface will result in desorption of organic material.

Former research on low salinity has mainly been performed on temperatures below 100 °C.

In this connection experimental adsorption/desorption measurements on illite are carried out, both at ambient temperature and at 130 °C. The clay was taken from the Rochester formation in New York in the form of green shale containing about 85 % illite. Quinoline was used as model basic material with a concentration of 0,01 M. Four different brines were used, 1000 mg/l (LS), 25000 mg/l (HS), 25000 mg/l pure $CaCl_2$ and 201 000 mg/l Varg formation brine. The results clearly indicate that adsorption/desorption of basic organic material is strongly pH dependent. When the pH increased, initially adsorbed quinoline was desorbed from the clay surface and the process was reversible. The amount of active cations, especially Ca^{2+}, seems to play a role where adsorption decreases as concentration of Ca^{2+} increases. Adsorption/desorption measurement performed at 130 °C clearly indicate that the water-wetness of the clay is improved due to lower adsorption. At higher temperature it is believed that the active ions have a stronger affinity towards the clay surface. As the concentration of Ca^{2+} is increased, the adsorption decreases.

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1. Introduction

Improving the oil recovery by manipulating the brine composition has been a subject of study the last decades. Laboratory tests, as well as field tests, have shown that low salinity water flooding in sandstone reservoirs can improve the water wetness of the rock and thereby increase the oil recovery. Many mechanisms have been suggested, but none of these mechanisms are completely accepted and researches are still going on. Austad et al. (2010) have recently suggested a new chemical mechanism based on a local increase in pH close to the clay surface. By injecting low salinity brine the pH will increase and result in desorption of organic material.

This master's thesis will provide experimental work to determine adsorption/desorption of quinoline onto illite both at ambient temperature and at 130 °C. The thesis starts with general theory that provides background for understanding the results. Experimental methods and materials used will also be presented. Finally, the results are presented together with a discussion. The results will be compared with dynamic experiments done by PhD student Alireza RezaeiDoust and Bachelor student Kim Flatråker on outcrop sandstone cores that contains mostly illite and some chlorite.

2. Theory

2.1 Oil recovery

Oil production is generally divided into three stages; primary recovery, secondary recovery and tertiary recovery.

Primary recovery is the technical easiest method by taking the advantage of the natural energy stored in the reservoir. Drive mechanism for the natural energy sources are solution-gas drive, gas-cap drive, natural water drive, expansion of fluid and rock, gravity drainage, and a combination of these mechanisms (Green and Willhite, 1998). In this stage, approximately 10-30 % of the original oil in place is produced.

When natural drive mechanism drops off, secondary recovery takes place. Injection of water and/or gas are the most common methods. Water and gas will provide pressure support as well as water will displace oil to the well (Green and Willhite, 1998). In this stage, normally 30-50 % of the original oil in place is produced.

Tertiary recovery takes place when secondary recovery becomes uneconomical. Injection of miscible gases, chemicals, and/or thermal energy will then provide a further increase in recovery. This method can result in a change in the fluid properties and increase the mobility of the oil. Since oil production does not always occur in this chronological order, it is more common to refer tertiary recovery as EOR (Enhanced Oil Recovery). Another concept is IOR (Increased Oil Recovery), which includes EOR in addition to e.g. reservoir characterization, improved reservoir management, and infill drilling (Green and Willhite, 1998).

Water injection is the most common form of secondary recovery. The main purpose of water injection is to maintain the pressure, but during the last decades it has been proven that water also have a chemical effect both in sandstone and carbonate. The water can provide a wettability modification towards a more water-wet condition and increase the oil recovery. Thus, water injection can be characterized as an EOR method.

2.2 Sandstone

About one-fourth of the world's sedimentary rocks are sandstone. It is a clastic sedimentary rock composed primarily of sand-sized particles (Hyne, 2006). During deposition, other minerals such as feldspars, carbonate rocks and clay minerals will be entrained. With the passage of time, the sand will be buried with increasing confining pressure and temperature. Under these conditions, the deposited minerals can undergo digenetic changes and recrystallize as new minerals (IDF, 1982).

2.2.1 Clay minerals

Clay minerals are the end-product of mechanical and chemical disintegration. They are transported to the basins as suspension in flowing water. Due to the negatively charged surface, they will easily adsorb cations from the seawater, get lumpy and deposit relatively quick (Presvik, 2005).

Clay mineral is defined as different types of mineral groups that are members of the hydrous aluminous phyllosilicates. In sedimentary petrology the term clay mineral is often mixed with the term clay. Clay is a term that only describes the particle grain size that is less than 3,9 μm.

Clay minerals have a sheet-like structure where the building blocks are either tetrahedral or octahedral as shown in Figure 2-1 below.
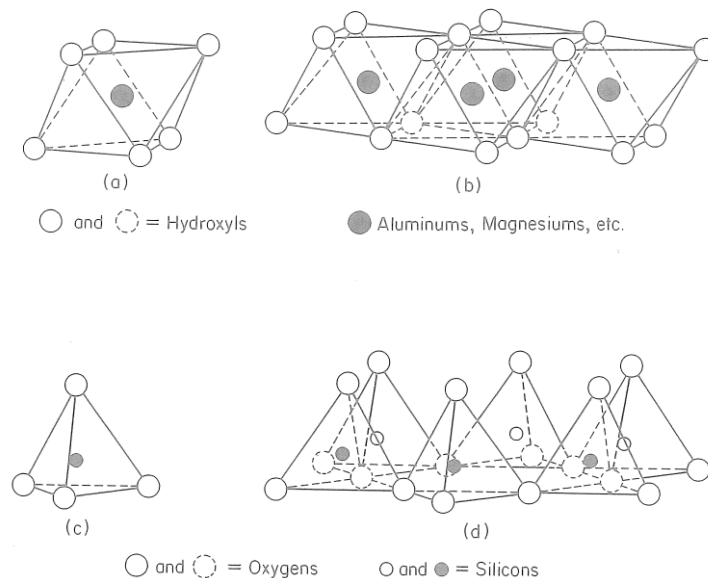

Figure 2-1: Single octahedral unit (a), sheet structure of the octahedral units (b), single silica tetrahedron (c), sheet structure of the tetrahedron units (d) (Blatt et al., 2008).

The layers are connected together into planer layers by sharing oxygen ions between Si or Al ions. Tetrahedral is a Si^{4+} ion or in some cases Al^{3+} surrounded by four O ions. Octahedral are close packing of six anions, dominantly oxygen, but may also include hydroxyl ions in some cases. The small hole in the center is normally occupied by Si or an Al ion. To ensure charge balance, other cations such as iron, calcium, magnesium and potassium are required in the clay structure to make charge balance (Worden and Morad, 2003).

A combination of these layers can make different types of clay minerals. In sandstone reservoirs the most common clay minerals are: kaolin, illite, chlorite, smectite and mixed-layers varieties.

Kaolin has a 1:1 structure connected by O-H-O bonds, which means alternately one tetrahedral layer and one octahedral layer with the chemical formula $Al_2Si_2O_5(OH)_4$ (Worden and Morad, 2003). The strong hydrogen bonding prevents the clay from swelling. Kaoline is normally found in marine deposits and it is a common weathering product of feldspars under acidic conditions. During burial, kaoline can be formed into illite and chlorite as shown in Figure 2-2 (IDF, 1982).

Illite has a 2:1 structure, alternately two tetrahedral layers and one octahedral layer connected by O-K-O bonds. The chemical formula for illite is $K_yAl_4(Si_{8-y},Al_y)O_{20}(OH)_4$., were y is significantly less than two (Worden and Morad, 2003). Illite is formed in temperate climates with moderate rainfall and is therefore common in marine deposits and especially in ancient sediments (IDF, 1982). During burial illite will have an increasing crystallisation (Tucker, 2001).

Chlorite has a 2:1:1 structure which means two tetrahedral layers and one octahedral layer that are negatively charged balanced by an interlayer of a positively charged octahedral layer (Newman, 1987). The general formula for chlorite is $(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$ (Woden and Morad, 2003). Chlorite tends to be associated with older sediments. During deep burial of smectite and kaolinite, chlorite can be formed (Tucker, 2001).

Smectite has the same structure as illite, but less binding by K^+. The interlayer also contains water and cations from the last aqueous medium smedrite was in contact with. The general formula for smecite is $(0.5Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4*nH_2O$. Smecite is a result of volcanic ash falling into a marine environment and it is associated with shallow burial. With

increasing age and depth, smectite will alter into illite, chlorite and kaolinite. Normally smectite is not found in older sediments than Jurassic (IDF, 1982).

Mixed-layer clay mineral is a result of a combination of different mineral layers in a single structure (Worden and Morad, 2003).
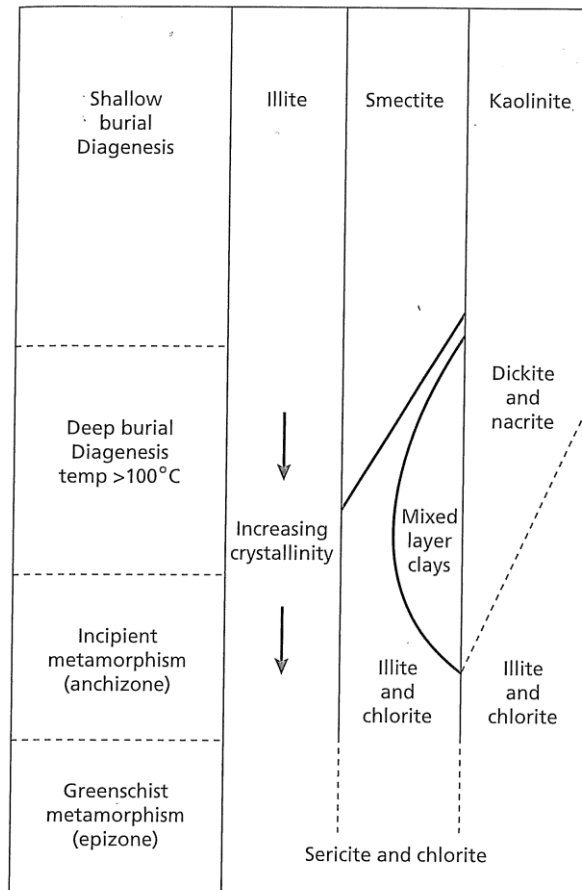

Figure 2-2: Illustrating the changes of clay minerals with increasing depth of burial and into metamorphism (Tucker, 2001).

2.2.2 Cation exchange capacity

Cations that are adsorbed to the unit-layer surface may be exchanged with other cations that are in contact with the clay. These cations are called the exchangeable cations. The quantity of cations per unite weight of clay is reported as the cation exchange capacity (CEC) and it is expressed in milliequivalents per 100 g of dry clay. The CEC of montmorillonite is within the range of 80 – 150 meq/100g. Illite and chlorite is about 10 – 40 meq/100g and for kaolinite 3-10 meq/100g.

The different ions have different attractive forces for the exchange site as listed below in decreasing preference from left:

$$H^+ > Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > NH^{4+} > Na^+ > Li^+ \tag{1}$$
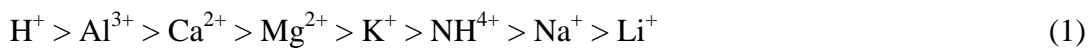
These ions have different solubility-to-temperature relationships and with increasing temperature the replacing power may be different. Also the relative concentration of each cation can affect the cation-exchange preference (MI, 1998).

2.3 Wettability

The first serious studies of the wettability were performed by the world's largest E & P Company, former known as the Arabian-American Oil Company, now known as Saudi Aramco. These studies took place in the late 1980's as a 7-year long project to understand the wetting properties in one of the world's largest oil field.

Wettability plays an important role in recovery of oil in petroleum reservoirs. The term wetting is defined as the fluid ability to spread or adhere to solid surface in the presence of an immiscible fluid. In petroleum context one distinguishes between four types of systems; water-wet, fractional-wettability, mixed-wettability and oil-wet.

In a water-wet system, more than 50 % of the rock surface is wet by water. The smallest pores are filled with water and in the largest pores the water exist as a film on the pore wall and oil as a droplet in the middle. Oil-wet system is opposite of water-wet system, meaning that the smallest pores are filled with oil and in the largest pores the oil exist as a film on the pore wall and water as a droplet in the middle. A fractional-wettability system is defined when the surface is either water-wet or oil-wet due to variety of chemical properties of the minerals. In a system with mixed-wettability, the smaller pores are wetted and saturated with water and the

larger pores are wetted and saturated by oil. This will occur if the oil contains surface active components, the oil can gradually displace the connate water film in the larger pores, but in the smaller pores the threshold capillary pressure will be too high for the oil to enter (Donaldson and Alam, 2008).
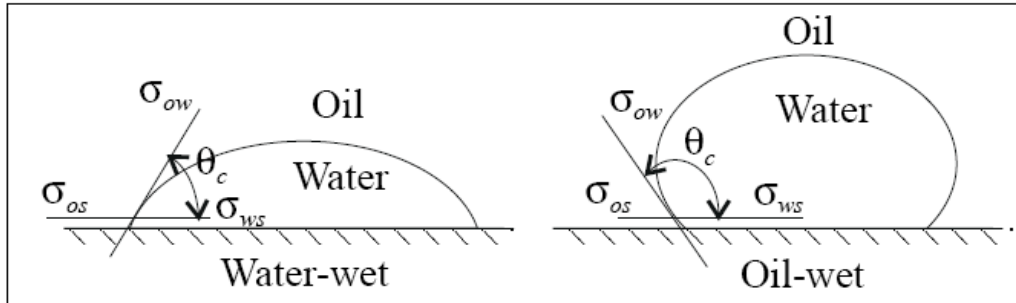
Figur 2-3: Relation between interfacial tension and contact angle in a water-wet and oil-wet system (Zolotukhin and Ursin, 2000).

A quantitative and illustrative way to determine the wettability is to measure the contact angle (θ) between the rock surface and the two immiscible fluids as shown in Figure 2-3. The contact angel refers to the fluid with highest density, in this case water, when equilibrium between the system is oil-wett. The relation between the three interfacial tensions and the contact angle is known as the Young-Dupré equation (Zolotukhin and Ursin, 2000):

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow}\cos\theta \quad , \tag{2}$$

where σ_{os} is the tension between oil/solid, σ_{ws} is the tension between water/solid and σ_{ow} is the tension between oil/water.

2.4 pH

The definition of pH is the negative logarithm to hydrogen ion concentration and it is measured in mol per liter.

At 25 ºC the product for water is given by $[H^+] \cdot [OH^-] = 10^{-14}$. When the temperature increases, the pH will decrease for the same system. At 125 ºC the product for water is then given by $[H^+] \cdot [OH^-] = 10^{-12}$. It means that at 125 ºC neutral water will have pH 6. This is important to take into account when evaluating a deep reservoir with high temperature (Bjørlykke, 2001).

2.5 Quinoline

Quinoline is a hetercyclic aromatic organic compound with general formula C_9H_7N and the molecular weight is 129,161 g/mol. At pKa = 4,8 the quinoline is at equilibrium with half at protonated form and half in neutral form (Viswanath, 1979):

$$C_9H_7N + H^+ \leftrightarrow C_9H_8N^+ \tag{3}$$

The concentration of the two forms of quinoline is highly dependent of the pH in the solution. When the pH in the solution decreases the protonated form of quinoline is increased and when the pH increases the neutral form of quinoline is increased.

2.6 Low Salinity mechanism

Experimental work and field tests have shown that the oil recovery can be enhanced by injecting low salinity water. As listed below, many mechanisms for low salinity flooding have been suggested the last 10 years:

- Migration of fines
- Microscopically diverted flow
- Impact of alkaline flooding
- Multi-component ion exchange (MIE)
- Double-layer expansion
- Local pH variation

None of these mechanisms are completely accepted and research is still going on.
It may be a combination of different mechanisms acting together.

2.6.1 Migration of fines

Migration of fines is a suggested mechanism by Tang and Morrow (1999). They believed that the crude oil adheres to the fine particles. During low salinity water flooding some of the oil will be produced together with the fine particles due to expansion of the electrical double-layer. Part of the oil will be trapped and remain adhered to the fine particles as droplets as shown in Figure 2-4. This will lead to a wettability modification towards a more water-wet condition and increase the oil recovery. The main forces that play an important role for the fine particles to be removed from the rock surface are a balance between mechanical and colloidal forces. Mechanical forces involve capillary forces between the crude oil/fines and

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viscous forces. Colloidal forces between the fines will depend on the van der Waals attractive forces and the electrostatic repulsion.
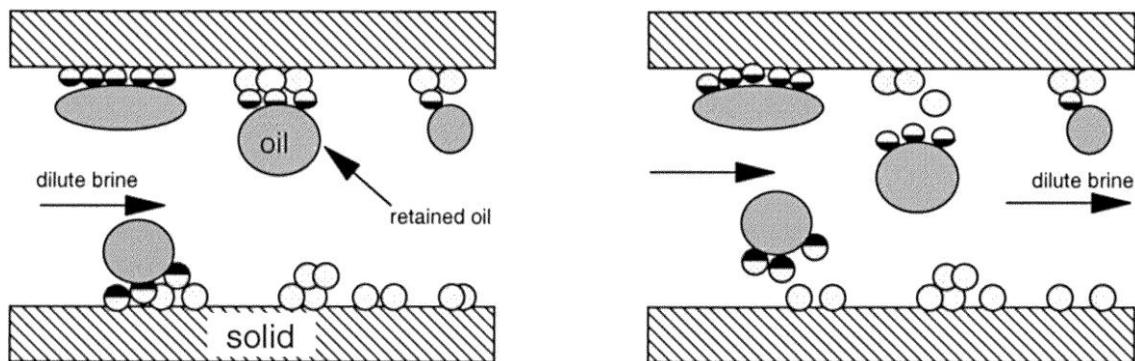
Figure 2-4: The first figure shows retained oil before low salinity flooding and the second figure shows mobilized oil detached to the fines during low salinity flooding (Tang and Morrow, 1999).

Tang and Morrow (1999) stated some conditions for low salinity based on experimental work. The oil must contain polar components as no effect has been observed by using refined oil. Initial water saturation is needed as no effect has been observed by saturating the core with 100 % oil.

Experimental work also showed reduction in permeability. This is believed to be caused by blocking of the pore throat with fines (Tang and Morrow, 1999).

2.6.2 Microscopically diverted flow

Skauge et al. (2010) have been working on colloidal dispersion gel (CDG) as an EOR method, providing sweep improvement in reservoirs with unfavorable mobility ratio. The porous media is a complex structure with different sizes both for pore bodies and throats. A solution with particles flowing through the porous media containing particles that have a size that is equal or larger than the pore throats, the particles are getting trapped, so called straining. Another trapping mechanism that is more complicated than straining and the main factor for microscopic diversion is log-jamming. Particles can block pores larger than the particle size due to mass difference between particles and the solvent. Water molecules will accelerate faster than the particles resulting in a reduction in the pore throats diameter that will slowly lead to blocking. The blocking will cause a pressure buildup that will force the water to flow in the smaller pores with residual oil and thereby improve the sweep efficiency. The same

explanation can be used for fine migration suggested by Tang and Morrow (1999), where the fines slowly will block the pore throats (Skauge et al., 2010).

2.6.3 Impact of alkaline flooding

McGuire et al. (2005) suggested that the low salinity mechanism is a similar phenomenon as those found in alkaline flooding and surfactant flooding. Alkaline flooding is a known EOR process in which alkaline chemicals such as sodium hydroxide are injected into the reservoir. These chemicals react with the acidic oil components and forms surfactants which lead to a reduction in the interfacial tension, spontaneous emulsification and change in wettability (Hyne, 2006). When the concentration of magnesium and calcium is high in the formation water, alkaline flooding may lead to precipitation of $Ca(OH)_2$ and $Mg(OH)_2$. McGuire et al. (2005) believed that the observed increase in pH after low salinity water flooding is due to generation of surfactants from the residual oil. Hydroxyl ions are generated due to reaction with the surface when the low salinity water is injected. They reported an increase in pH from 7-8 range up to a pH of 9 or slightly above. At lower salinities in the injection water, a higher pH was obtained and thereby higher recovery. Divalent cations like calcium and magnesium presented in the brine will precipitate the surfactant during a high salinity flooding and prevent an increased recovery. This issue will be reduced when the low salinity water is injected and the surfactants will be effective (McGuire et al., 2005).

2.6.4 Multicomponent ion exchange

Multicomponent ionic exchange (MIE) is the basis of equilibrium that occurs during the geological time. It involves the composition of all the ions in the formation water for the mineral matrix exchange sites. Lager et al. (2007) reported 8 mechanisms based on experimental work where each mechanism will depend on the type of organic matter and the clay surface. Half of these mechanisms; cation exchange, ligand bonding, cation bridging and water bridging they thought would be possible during low salinity water flooding (Lager et al., 2007). From experimental work and from a single field test, Lager et al. (2008) observed significant reduction of the Mg^{2+} concentration in the produced water. They also reported a constant injectivity index (bbl/psi) during the field test which means that migration of fines is most likely excluded. The field test also showed just a small change in the pH during the low salinity test (Lager et al., 2008).

2.6.5 Double-layer expansion

Ligthelm et al. (2009) explained the low salinity mechanism as a result of expansion of the electrical double-layer. Negatively charged clay minerals that acts as colloid particles are detached to the pore wall. Multivalent cations like Ca^{2+} and Mg^{2+} present in the formation water acts like a bridge between the negatively charged oil and the clay surface. By reducing the brine salinity, especially reduction of the concentration of multivalent ions, leads to an expansion of the electrical double-layer. The electrostatic repulsion between the oil and clay particles increases and when the electrostatic repulsion exceeds the binding forces in the bridge, the oil components will desorb from the clay surface (Ligthelm et al., 2009).

2.6.6 Local pH variation

Austad et al. (2010) suggested that the low salinity effect is due to a local increase in pH close to the clay surface. They summarized important parameters based on observed experimental work that will play an effect on low salinity:

- ➢ Clay properties, type of clay and the amount present in the rock.
- ➢ Polar components in the crude oil, both acidic and basic.
- ➢ Composition and pH of the initial formation brine.
- ➢ The enhanced oil recovery during low salinity water flooding is assumed to be a result of improved water wetness of the clay minerals present in the rock.

At initial condition, both acidic and basic organic materials are adsorbed onto the clay surface together with inorganic cations especially Ca^{2+}, from the formation water. The chemical equilibrium that is formed during geological time will depend on the actual reservoir conditions regarding pH, temperature, pressure etc. Normally the pH of the formation water is 5 or less due to dissolved CO_2 and H_2S. When injecting a low salinity brine with a much lower ion concentration than the formation water, the initial equilibrium is disturbed. As a result, desorption of cations, especially Ca^{2+}, occur. To re-stabilize the equilibrium, H^+ from the water is adsorbed to the clay surface as illustrated by the following equation using Ca^{2+} as an example:

$$\text{Clay-}Ca^{2+} + H_2O = \text{Clay-}H^+ + Ca^{2+} + OH^- \tag{4}$$

The local increase in pH leads to a reaction between adsorbed basic and acidic material that is very sensitive to change in pH as illustrated by following two equations:

$$R_3NH^+ - \text{Clay} + OH^- = \text{Clay} + R_3N + H_2O \tag{5}$$

RCOOH - Clay + OH⁻ = Clay + RCOO⁻ + H₂O   (6)
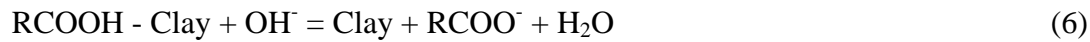
The suggested mechanism is illustrated in Figure 2-5 below (Austad et al., 2010).
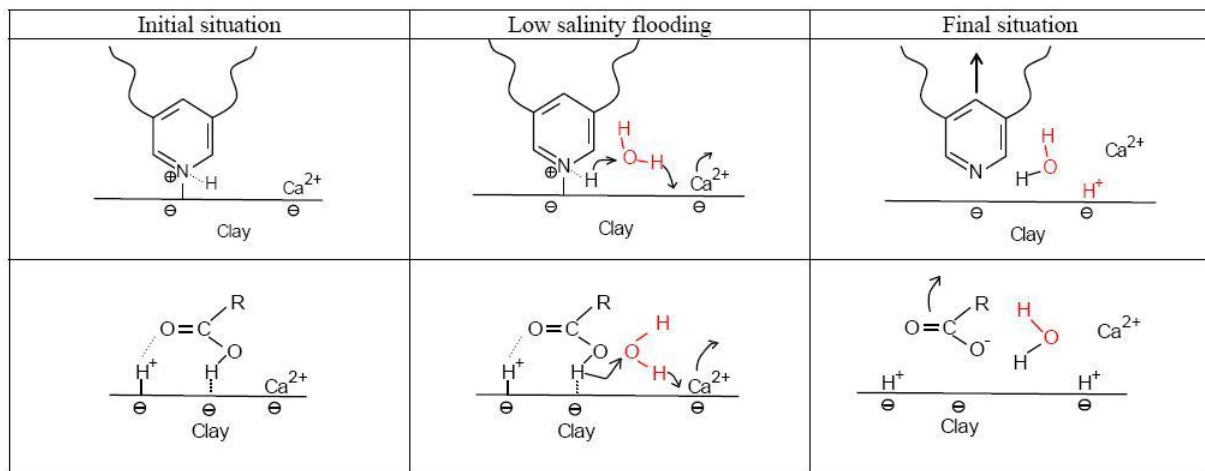
Figure 2-5: Illustrate initial and final condition after low salinity water flooding. The topmost row shows desorption of basic material and the lower row shows desorption of acidic material (Austad et al., 2010).

RezaeiDoust et al. (2011) reported that that the low salinity effect was independent of the ion composition of the LS fluid as long as the ionic strength was the same and low enough. The experimental work was performed on outcrop cores that contained about 10 wt% clay, with the highest fraction of illite and some chlorite. Four different cores where used, aged with the same formation water and oil. NaCl, $CaCl_2$, KCl and $MgCl_2$ where used as LS fluid with the same ionic strength of 0,0171 M. After injecting 4 PV of formation water, the pH varied between 6 and 7. When switching to LS brines, the pH in the effluent increased 1 to 3 pH units as the LS fluids displaced the formation water. The lowest increase was observed for the LS brine containing Ca^{2+} due to buffering effect. The highest increase was observed for the LS brine containing Na^+ due to lowest affinity towards the clay surface, thus more H^+ can replace the desorbed cations. For all the LS brine the increase in pH was high enough to improve the recovery between 7, 4 and 7, 7 % OOIP.

As mentioned, the pH of the formation water in a reservoir is normally 5 or less due to dissolved CO_2 and H_2S. Laboratory experiments using stabilized crude oils could give a lower EOR potential due to a higher initial pH and less adsorbtion of acids and bases. RezaiDoust et al. (2011) verified this by doing two experiments, one reference core with stabilized crude oil and one core with the same crude oil saturated with 6 bar of CO_2.

Due to a lower viscosity for the CO_2 saturated crude oil the reference core had 5 % lower recovery after secondary water flooding.

When injecting LS brine, the recovery increased 7 % for the reference core and 16 % for the core with CO_2 saturated crude oil. The pH increased about 3 pH units for the reference core and 2 pH units for the core containing CO_2 saturated crude oil. CO_2 have a buffering effect on the pH given by the equation 7:

$$CO_2 + H_2O \leftrightarrow [H_2CO_3] \leftrightarrow H^+ + HCO_3^- + OH^- \leftrightarrow H_2O + HCO_3^- \qquad (7)$$
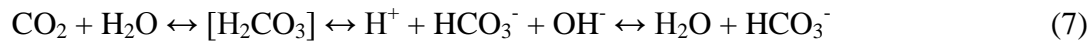
The equilibrium is moved to the right as the pH increase. Thus, observing tertiary low salinity effect depends on the pH of the formation brine.

Another parameter that also could influence the low salinity effect is the value of the acid number (AN) and base number (BN) in the crude oil. A crude oil with high AN (low BN) showed the same low salinity effect as the crude oil with high BN (low AN). The acidic oil resulted in a more water wet condition which indicates that basic material in the crude oil interacts more strongly onto the negatively charged clay minerals. For both crude oils the pH in the effluent for the tertiary recovery increased about 1,5 pH units.

Low salinity effect have also been observed by diluting the formation water and also by replacing the high salinity formation water by a new high salinity water containing low concentration of ions that are active towards the clay surface. In fact, 40000 ppm NaCl solution can act as low salinity brine when using 25000 ppm $CaCl_2$ brine as the formation brine. This confirms that the low salinity effect is not directly linked to the salinity, but rather the concentration of the active ions towards the negative charged clay surface, especially Ca^{2+} (RezaeiDoust et al., 2011).

3. Materials and experimental procedure

In this section the materials that are used in the experiments are presented and the experimental procedures are briefly described.

3.1 Materials

3.1.1 Clay

Illite clay was taken from the Rochester formation in New York and delivered from Ward´s Natural Science Establishment in the form of green shale containing about 85 % illite. Bachelor student Bjørnar Høie crushed the shale into smaller bits and milled it into powder. About 92 % of the illite particles had a diameter of 2 µm or less.

3.1.2 Quinoline

Quinoline > 97 % was delivered by MEARCK. Quinoline is slightly solvable in water at ambient temperature. The quinoline was dissolved in distilled water and the pH was adjusted to ~5 using HCl. The quinoline solution had a concentration of ~0,07 M. After sample preparation, the concentration of quinoline is equal to ~0,01 M.

3.1.3 Brines

The ion compositions in Table 3-1 where added to distilled water and mixed with a magnetic stirrer until the salts were dissolved. Then filtrated trough 0,22 µm to remove any particles.

Table 3.1: ion composition

Ion	30000 ppm	CaCl$_2$ brine	Varg X brine
Cl$^-$ [mol/l]	0,534	0,5406	4,030
Mg^{2+} [mol/l]	0,045		0,164
Ca^{2+} [mol/l]	0,045	0,2703	0,613
Na$^+$ [mol/l]	0,355		2,384
K$^+$ [mol/l]			0,058
Ba^{2+} [mol/l]			0,008
Sr^{2+} [mol/l]			0,009
Ionic Strength	0,624	0,811	4,824
TDS [ppm]	30 000	30 000	230 000

3.2 Equipment

To perform the experiment, different equipments were used as listed below:

- ➤ Gas sealed HT- sample glasses, seen in Figure 3-3.
- ➤ Mettler Toledo pH-meter, Figure 3-1.
- ➤ Shimandzu UV-1700 Spectrophotometer, Figure 3-2.
- ➤ Stuart SB3 rotator, Figure 3-3.
- ➤ Hettich Universal 1200 centrifuge, Figure 3-4.

Figure 3-1:Mettler Toledo pH-meter.
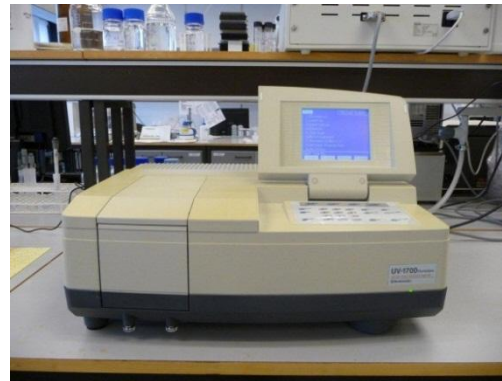
Figure 3-2: Shimandzu UV-1700 Spectrophotometer.

Figure 3-3: Stuart SB3 rotator

Figure 3-4: Hettich Universal 1200 centrifuge.

3.3 Experimental procedure

The experimental procedure was prepared in order to mimic earlier static experiments done by PhD student Alireza RezaeiDoust.

3.3.1 Absorbance wavelength for quinoline

For determination of the absorbance wavelength for quinoline, a 0,01 M quinoline solution in distilled water was made. The absorbance was measured in the range of 190 – 500 nm by using shimandzu UV-1700 spectrophotometer. The peak absorbance wavelength was found to be 312,5 nm.

3.3.2 Calibration curve

A 0,01M quinoline solution in LS brine was made, diluted 20 times and absorbance was measured in the pH range of 3-5. The absorbance was found to be stable at pH slightly below 4. Hence, pH~3,35 was used in absorption measurements.

The quantitative method used to measure the concentration of a sample with unknown concentration was from absorption of a sample with known concentration as illustrated in Figure 3-5 below.
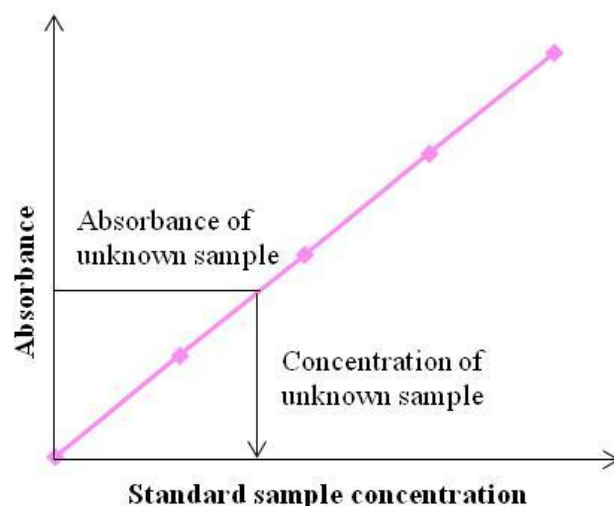

Figure 3-5: Calibration curve method illustration (redrawn from Shimadzu Corporation, 2001).

Calibration curves were made with a 0,01 M quinoline solution in both LS and HS brines. The solutions were diluted in the range 40 – 1000 times with constant pH~3,35.

3.3.3 Calculation of adsorbed quinoline

Before measuring the adsorption, the samples were centrifuged in a Hettich Universal 1200 centrifuge for 20 min at 2500 rpm to separate the clay particles. 50 µl of the liquid phase was pipetted out, diluted ~100 times and absorbance was measured. By using the quadratic equation obtained from the calibration curve, the amount of adsorbed quinoline onto the clay surface was found.

An example for calculating the amount of adsorbed quinoline onto the clay surface is shown in appendix 8.2.

3.3.4 Sample preparation

The samples were prepared in 18 ml gas sealed HT-sample glasses. In each sample, 1g illite (~ 10 wt %) was mixed with 7,8 ml brine solution and then rotated for 2 hours in a Stuart SB3 rotator. After rotation, 1,3 ml 0,07 M quinoline was added giving a 0,01 M concentration in the samples and then rotated for 24 hours.

Adsorbance was measured in 3 steps:

- ➢ Step 1: pH~5
- ➢ Step 2: pH~8 (or 9)
- ➢ Step 3: pH~5

At ambient temperature

At each step, the pH was adjusted with HCl or NaOH, preferably 5 M to minimize the amount of volume added. For checking the pH in the liquid phase, the samples were first centrifuged for 20 min at 2500 rpm to separate the clay particles and the pH was then measured in the liquid phase by using a Mettler Toledo pH-meter. When the pH was stable for 24 hours (except for initial test 2), 50 µl of the liquid phase was pipetted out, diluted ~100 times, pH was reduced to ~3, 35 and absorbance was measured.

At 130 °C

The sample preparation performed at 130 °C was done in the same way as ambient temperature. But before measuring the absorbance, the samples were rotated in a heating chamber for 24 hours. The pH was measured at ambient temperature and the results represent the pH value before aging.

<u>Initial test 2</u>

Based on initial test 1 for the LS brine, the first step for adjusting the pH~5, 88 µl 5 M HCl was added to the samples, rotated for 24 hours and absorbance and pH was measured. To increase the pH, 45 µl 5 M NaOH was added to the samples, rotated for 24 hours and absorbance and pH was measured. For readsorption, 45 µl 5 M HCl was added rotated for 24 hours and again, absorbance and pH was measured.

3.3.5 Cleaning illite

The milled illite was cleaned and protonated for possible divalent cations on the clay surface and precipitated salt. 100 g illite was dissolved in 500 ml distilled water and pH was reduced to ~3 by adding 5 M HCl until stable pH. Then the solution was centrifuged for 20 min, to separate the clay particles. New fresh distilled water was added to the clay and pH was again adjusted to ~3 and then centrifuged. Fresh distilled water was then added alternately with centrifuging until the pH was ~5. The clay was then dried at 90 ºC until stable weight.

3.3.6 Chemical analyses

A Dionex ICS-3000 ion chromatograph (IC) was used for measuring the ion composition of water samples. In order to be within the detection range for the IC, the water samples were diluted to an expected ion concentration of ~0,05 mM, and filtrated to remove any impurities and placed into 1,5 ml glasses. The IC measure the concentration of both anions and cations present in the samples.

4. Results and discussion

In this section all the result are presented followed by a discussion. The results will also be compared with dynamic experiments done by PhD student Alireza RezaeiDoust and Bachelor student Kim Flatråker.

4.1 Calibration curve

A 0,01 M quinoline solution in LS brine was diluted 20 times and absorbance at 312,5 nm was measured in the pH range from 3-5 as shown in Figure 4-1. The absorbance increased with decreasing pH and became constant at pH slightly belowe 4. Hence, the calibration curves were made only for pH~3,35.
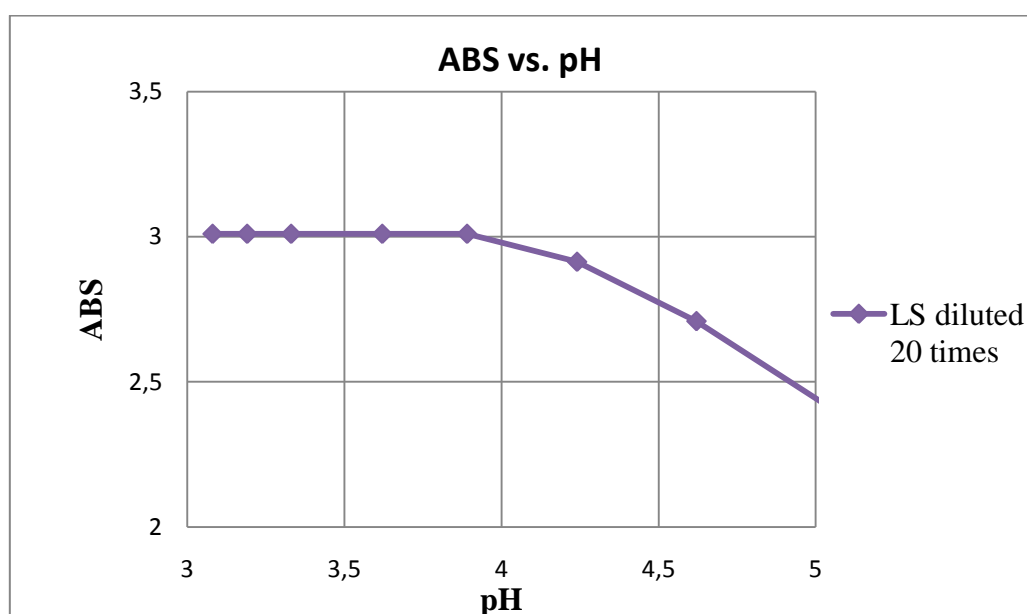
Figure 4-1: ABS vs. pH for LS brine diluted 20 times.

The calibration curves for quinoline in brine solution were made as described in Section 3.3.1. A 0,01 M quinoline solution in LS and HS brine was prepared. The samples were diluted 40-1000 times, pH was reduced to 3,35 and absorbance was measured. As shown in Figure 4-2, the calibration curves for both LS and HS were the same.
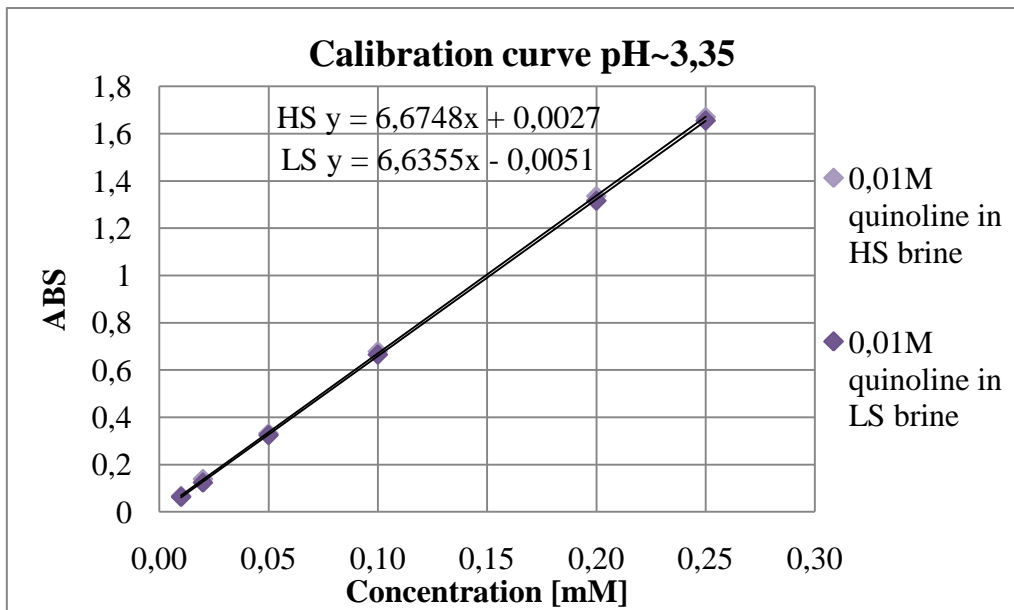
Figure 4-2: Calibration curve for high and low salinity with pH~3,35.

4.2 Initial tests

The object of these experiments was to verify earlier results of quinoline adsorption onto illite at ambient temperature done by RezaeiDoust et al. (2011). The amount of HCl and NaOH needed to adjust the pH to 5 and 9 in the solutions was registered.

4.2.1 Initial test at ambient temperature with constant pH

The samples were prepared as described in Section 3.3.4. The experiments were performed on uncleaned illite at ambient temperature. All the samples were prepared with 10 wt% illite dissolved in brine with a 0,01 M quinoline concentration. Two different brines were used, 1000 mg/l (LS) and 25000 mg/l (HS). The pH in the samples was adjusted and verified constant for 24 hours before the measurement. The pH was difficult to stabilize in all the steps indicating a buffer effect in the samples. The results are presented in Figure 4-3 below.
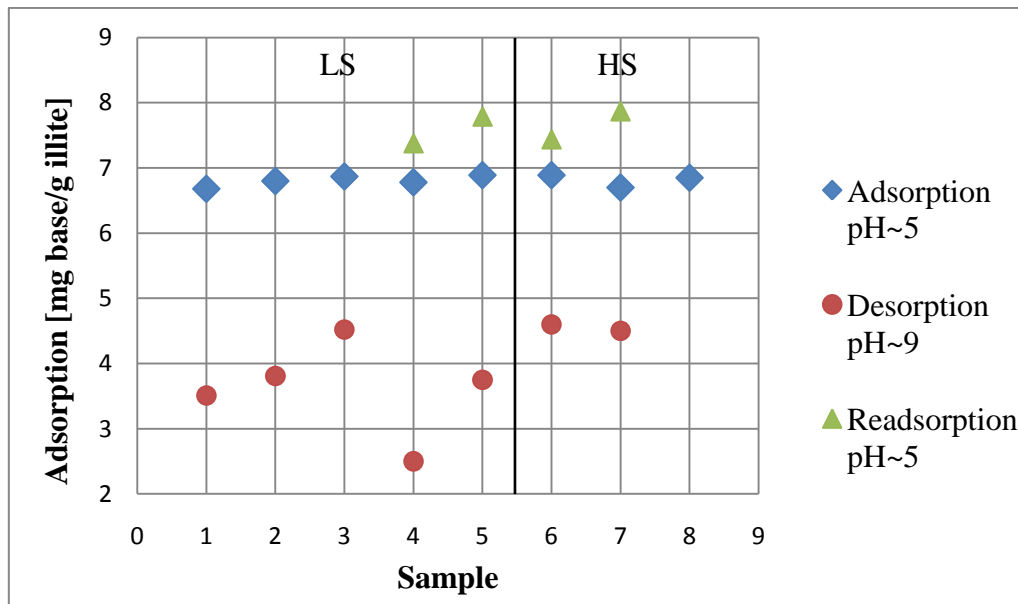
Figure 4-3: Adsorption of quinoline onto uncleand illite at ambient temperature using LS and HS brines. Sample 1-5 represent the LS brine and sample 6-8 the HS brine.

Sample 1-5 represent the LS brine and sample 6-8 the HS brine. In all the samples, about 6,9 mg of the initial quinoline is adsorbed to the clay surface at pH~5. By increasing the pH to 9, more than 2 mg quinoline is desorbed from the clay surface. When decreasing the pH back to 5, the quinoline is reabsorbed. There is a large spread in result for the samples at pH~9.

At pH~9, precipitation of $Mg(OH)_2$ could occur:

$$Mg^{2+} (aq) + 2OH^- (aq) \leftrightarrow Mg(OH)_2 (s) \tag{8}$$
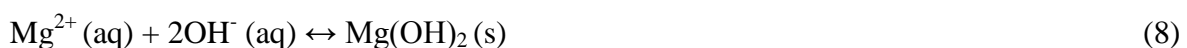
Since the OH$^-$ concentration in the samples is much lower than the Mg^{2+} concentration this reaction is not easy to detect. An ion analysis of sample 7 was performed and the results are presented in Table 4-1. The Ca^{2+} concentration in the brine solution increased from 0,0375 M to 0,0642 M which is more than 41 % of initial Ca^{2+} concentration in the sample. The Mg^{2+} concentration decreased from 0,0375 M to 0,0359 M, which is a small reduction of about 4 %. It is likely to believe that the increase in Ca^{2+} concentration is due to impurities in the clay from divalent cations on the clay surface and precipitated salts. The small decrease in Mg^{2+} concentration could be explained by precipitation of Mg(OH)$_2$.

Tabel 4-1: Concentration of calcium and magnesium before and after sample preparation in HS brine at pH~9.

Ion	Initial concentration [M]	Concentration after adjusted to pH~9 [M]	Change in concentration [%]
Ca2+	0,0375	0,0642	41,6
Mg2+	0,0375	0,0359	4,2

The whole adsorption tests for both LS and HS took a lot of time to perform due to pH variation. When a small amount of HCl or NaOH was added, the pH in the samples increased rapidly and then decreased back to a level slightly above the initial level. Due to this issue, it was decided to perform a new test where the known amount of HCl and NaOH for the LS brine was added to see how the results differ.

4.2.2 Initial test with same volume of NaOH and KCl added at ambient temperature

Based on the amount of HCl and NaOH added in each step in the initial test 1, a second test was performed as described in Section 3.3.4. The experiments were performed on uncleaned illite at ambient temperature. All the samples were prepared with 10 wt% illite dissolved in brine with a 0,01M quinoline concentration. Four different brines were used, 1000 mg/l (LS), 25000 mg/l (HS), 25000 mg/l pure $CaCl_2$ and 201 000 mg/l Varg formation brine.

In the first step when adjusting the pH to 5, 88 µl 5 M HCl was added to the samples, rotated for 24 hours and absorbances and pH were measured. To increase the pH to 9, 45 µl 5 M NaOH was added to the samples, rotated for 24 hours and absorbance and pH were measured. For readsorption, 45 µl 5 M HCl was added to the samples, rotated for 24 hours and again absorbance and pH were measured. The results are presented in Figure 4-4 below where sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure $CaCl_2$ brine and sample 10-12 Varg formation brine.
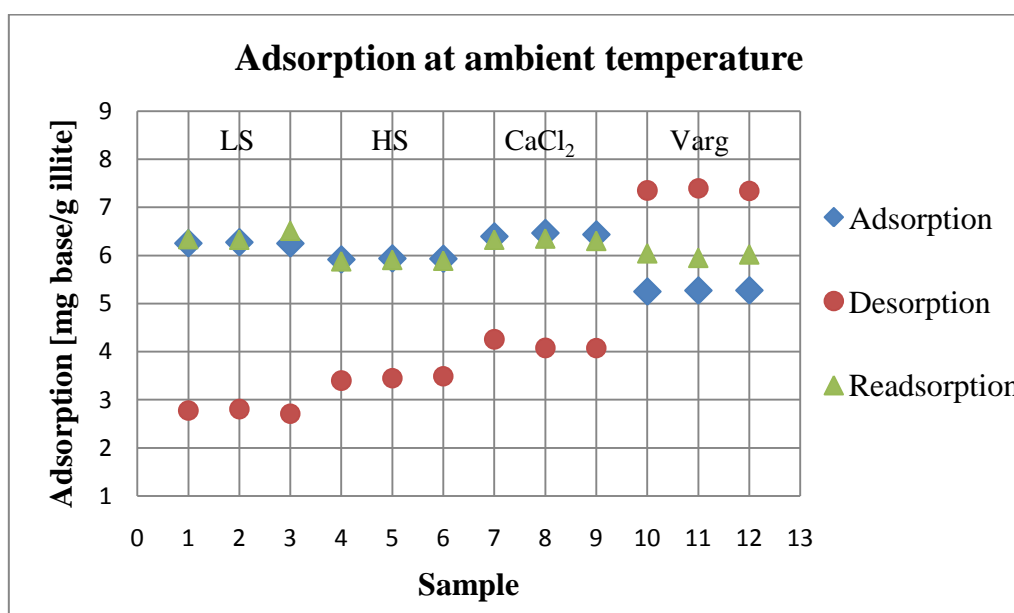
Figure 4-4: Adsorption at ambient temperature using four different brines: LS, HS, pure $CaCl_2$ and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure $CaCl_2$ brine and sample 10-12 Varg formation brine.

Table 4.2: Average pH for each step at ambient temperature.

	LS	HS	CaCl₂	Varg
Adsorption pH	5,03	4,90	4,74	4,15
Desorption pH	8,40	8,06	7,80	7,32
Reabsorption pH	4,85	5,00	4,61	4,43

About 6 mg of quinoline in the solution is adsorbed to the clay surface at pH~5 in all solutions at ambient temperature. Increasing the pH to ~9, the desorption of quinoline decreases as a function of both, pH and salinity. When the pH is reduced back to ~5, readsorption of quinoline is observed almost to the same level as initial value.

4.2.3 Initial test with same volume of NaOH and KCl added at 130 ˚C

Sample preparation at 130 ℃ was done in the same way as ambient temperature, but before measuring the absorbance, the samples were rotated in a heating chamber for 24 hours. The results are presented in Figure 4-5 below where sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure CaCl$_2$ brine and sample 10-12 Varg formation brine.
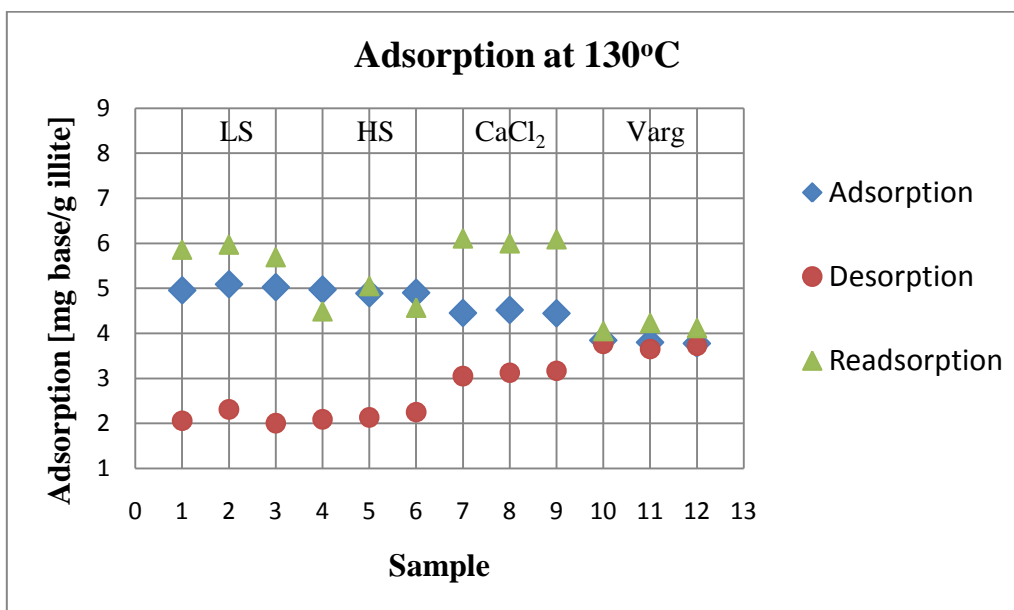
Figure 4-5: Adsorption at 130 ℃ using four different brines: LS, HS, pure CaCl$_2$ and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure CaCl$_2$ brine and sample 10-12 Varg formation brine.

Table 4-3: Average pH for each step at 130 ℃.

	LS	HS	CaCl$_2$	Varg
Adsorption pH	5,02	4,92	4,43	4,05
Desorption pH	6,48	6,07	5,93	5,79
Reabsorption pH	4,18	4,02	3,44	3,13

Adsorption at 130 ℃ shows a different trend in adsorption at pH~5 compared to ambient temperature. When the salinity increases the adsorption decreases. When the pH was

increased to ~9, the amount of desorbed quinoline from the clay surface decreases as the salinity increases. Readsorption ended up at almost the same level as initial.

For each sample at both temperatures the pH should first be 5, then 9 and back to 5 again. As shown in Table 4-2 and 4-3, the pH in the samples varied a lot. This makes it difficult to compare the results. The more saline brine, the longer it takes before the system is in equilibrium. Another parameter that affects the result is the impurities in the clay.

4.3 Cleaning process

The milled illite was cleaned as described in Section 3.3.5. Two times the clay was dissolved in distilled water and the pH was reduced to 3. Then, fresh distilled water was added alternately with centrifuging until the pH was 5. Samples of the cleaning water were analyzed on the ion chromatograph and the results of the four different waters are shown in Figure 4-6.
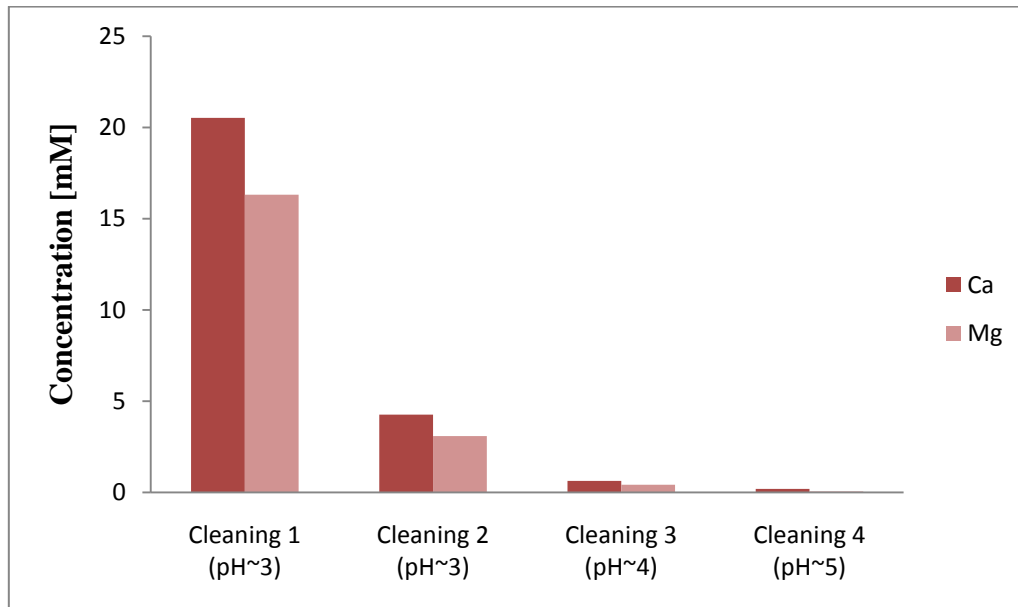
Figure 4-6: Concentration of Ca^{2+} and Mg^{2+} from cleaning process step 1 to 4.

The ion analysis showed high concentration of calcium and magnesium, but also traces of sulfate, lithium, ammonium and potassium. The results from Ca^{2+} and Mg^{2+} are presented in Figure 4-6. The calcium and magnesium concentration after the first step in the cleaning process was ~20 mM and ~16 mM respectively. After the fourth cleaning step only ~0,2 mM calcium and ~0,06 mM magnesium was left in the cleaning water.

Similarities in the adsorption at pH~5 for LS and HS in the initial test 1 can be explained with high amount of Ca^{2+} and Mg^{2+} in the clay. The LS brine, which initially had a concentration of 1,7 mM for both calcium and magnesium, actually contained a much higher concentration.

4.4 pH scan on cleaned illite

The variation of adsorption with pH was done for both LS and HS brine at ambient temperature and at 130 ºC. The samples were prepared as described in Section 3.3.2. All the samples were prepared with 10 wt% illite dissolved in brine with a 0,01 M quinoline concentration. Two different brines were used, 1000 mg/l (LS) and 25000 mg/l (HS). The pH in the samples was adjusted and verified constant for 24 hours before the measurement.

4.4.1 pH scan at ambient temperature
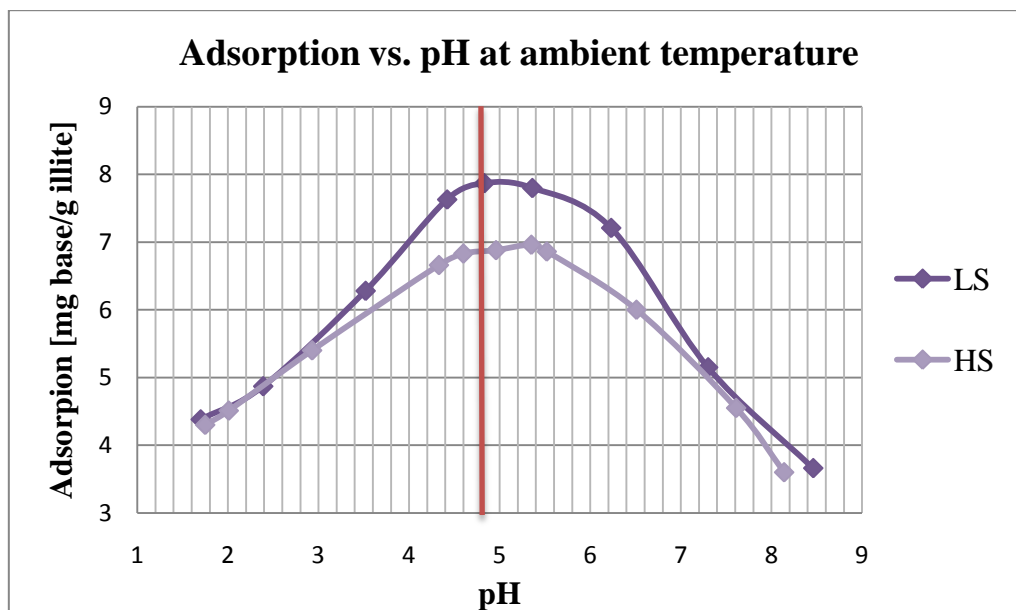
Figure 4-7: Adsorption vs. pH at ambient temperature for LS and HS brine. Red line indicate pKa = 4,8.

The vertexes for the LS and HS brine system in Figure 4-7 at ambient temperature are almost at the pKa-value for the quinoline in both brines. At pH below the pKa-value the adsorption of quinoline to the clay surface decreases, even though the concentration of protonated quinoline increases. H^+ is the ion with highest affinity towards the clay surface as shown in Section 2.2.2 by Equation 1 and the adsorption of quinoline decreases with increasing H^+ concentration.

At pH above the pKa-value, less quinoline is adsorbed to the clay surface. The concentration of the neutral form of quinoline increases as the pH increases. Hence, less quinoline will adsorb to the clay surface.

4.4.2 pH scan at 130 °C

Adsorption at 130 °C was done in the same way as ambient temperature, but before measureing the absorbance, the samples were rotated in a heating chamber for 24 hours. During the test, the spectrophotometer failed and some of the samples were then equilibrated for a longer time before testing. This resulted in a higher adsorption than expected as indicated with gray dots in Figure 4-8 below. Hence, the main curves are made with measurements from the first series of tests and the points at pH~8 are taken from measurements in Section 4.5.2.
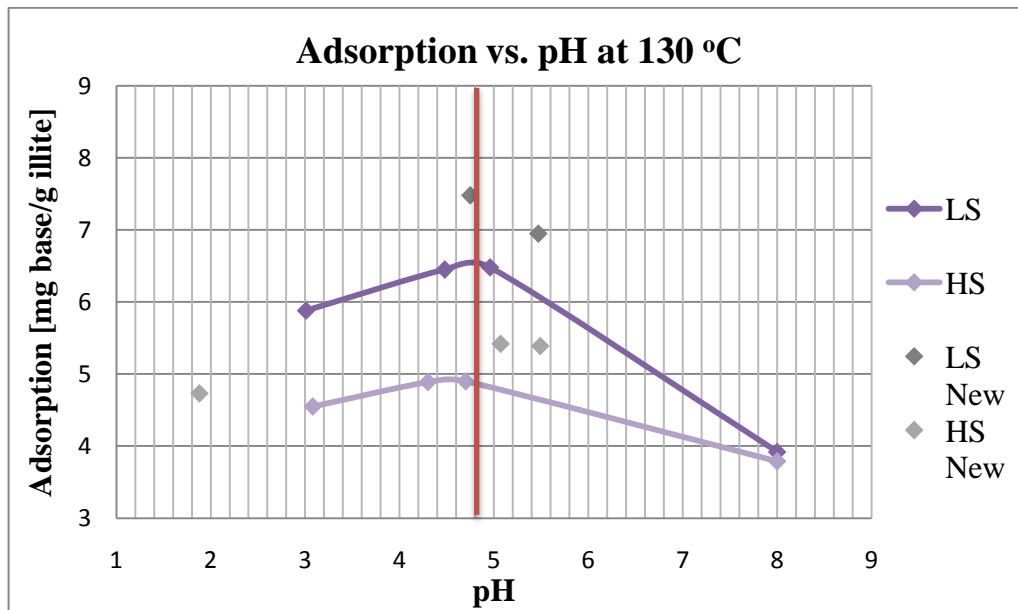
Figure 4-8: Adsorption vs. pH at 130 °C for LS and HS brine. Red line indicate pKa = 4,8. A Gray dot indicates a measurement done after the sample were equilibrated for a long time.

The two vertexes in Figure 4-8 are almost at pKa-value for the quinoline in both brines. The LS brine have a maximum adsorption of 6,5 mg quinoline per gram illite and HS have a maximum of 4,9. At pH below and above the pKa-value, quinoline is desorbed from the clay surface as described earlier. With increasing H^+ concentration, less protonated quinoline is adsorbed to the clay surface. At pH above the pKa-value the adsorption of quinoline decreases with increasing pH due to less protonated quinoline.

The adsorption at 130 °C is less than the adsorption at ambient temperature. At high temperature the reactivity of Ca^{2+} increases resulting in a less adsorption of quinoline.

4.5 Adsorption of quinoline onto cleaned illite

The milled illite was cleaned and protonated as described in Section 3.3.5. All the samples were prepared with 10 wt% illite dissolved in brine with a 0,01 M quinoline concentration. Clay solution with four different brines was used, 1000 mg/l (LS), 25000 mg/l (HS), 25000 mg/l pure $CaCl_2$ and 201 000 mg/l Varg formation brine. The pH was adjusted and verified constant for 24 hours before the absorbance was measured.

4.5.1 Adsorption at ambient temperature

Figure 4-9 shows the results at ambient temperature. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure $CaCl_2$ brine and sample 10-12 Varg formation brine.
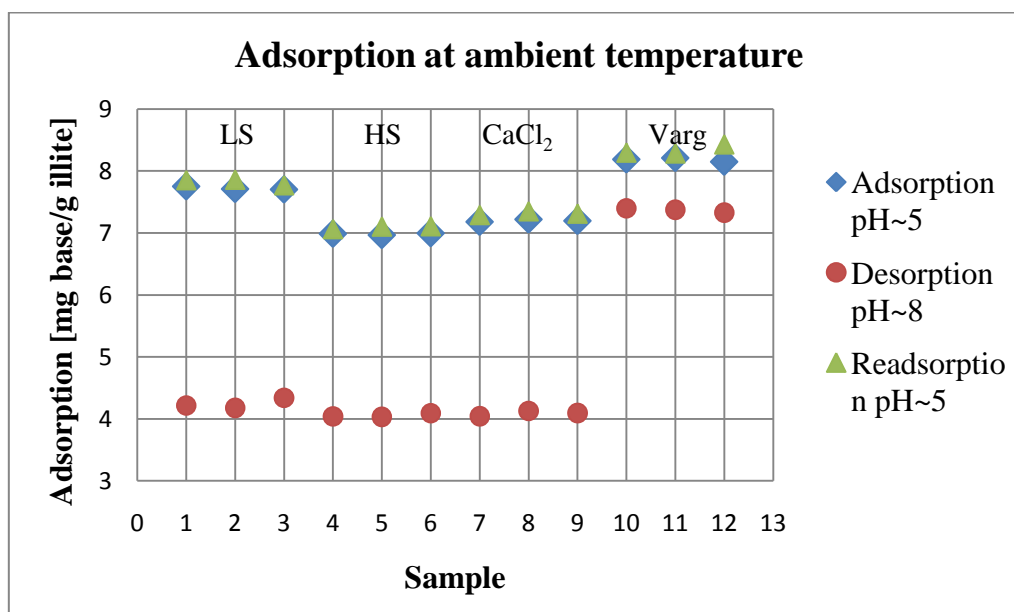
Figure 4-9: Adsorption of quinoline onto illite at ambient temperature using four different brines: LS, HS, pure $CaCl_2$ and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure $CaCl_2$ brine and sample 10-12 Varg formation brine.

<u>LS brine</u>

The adsorption of quinoline at pH~5 for the LS brine was 7,7 mg per gram illite, which is 65,5 % of initial quinoline in solution. With an increase in pH to 8, quinoline was desorbed from the clay surface. Only 4,3 mg of quinoline is adsorbed to the clay surface at this step. Reducing the pH back to 5 gave a readsorption of quinoline to the initial value. The adsorption/desorption is a reversible process.

HS brine

The adsorption of quinoline at pH~5 for the HS brine was 7,0 mg per gram illite, which is 59,3 % of initial quinoline in solution. The pH was then increased to 8, resulting in only 4,1 mg adsorbed quinoline onto the clay surface. Also the HS shows a reversible adsorption process when decreasing the pH back to 5.

Pure CaCl$_2$ brine.

The adsorption of quinoline at pH~5 for the CaCl$_2$ brine was 7,2 mg per gram illite, which is 61,2 % of initial quinoline in solution. By increasing the pH to 8, about 3,1 mg quinoline was desorbed from the clay surface. A reversible adsorption process was obtained when decreasing the pH back to 5.

Varg formation brine

The adsorption of quinoline at pH~5 for the Varg formation brine was 8,2 mg per gram illite, which is 69,6 % of initial quinoline in solution. A pH equilibrium was not possible to obtain at pH~8. Most likely precipitation of Ca(OH)$_2$ occurs due to high Ca^{2+} concentration in the brine. Due to this issue, the adsorption was measured at pH~7,5. At this step, only 0,8 mg quinoline is desorbed from the clay surface. A reversible adsorption process was obtained.

The results clearly indicate that adsorption of quinoline onto illite is strongly pH dependent. Quinoline is desorbed from the clay surface as the pH increases and the process is reversible.

At pH~5, the adsorption of quinoline in the LS brine is about 6,2 % higher than for the HS brine. This can be explained by lower concentration of divalent cations, especially Ca^{2+}, in the LS brine and thereby less competition between the cations and the protonated quinoline. The CaCl$_2$ brine has virtually the same adsorption as the HS brine at this step. The adsorption for the Varg formation brine is not fully understood so far. At pH~8, the concentration of the neutral form of quinoline is dominated due to reaction between OH$^-$ and R$_3$NH$^+$ as illustrated by Equation 5 in Section 2.6.6. Hence, desorption of quinoline from the clay surface occurs and it is therefore likely to believe that the neutral form of quinoline has a low affinity towards the clay surface. When the pH was reduced back to 5, the concentration of H$^+$ increases and the concentration of the protonated form of quinoline increases. The results confirms that the adsorption/desorption is a reversible process at ambient temperature.

4.5.2 Adsorption at 130 °C

Figure 4-10 shows the results at 130 ºC. Sample preparation at 130 ºC was done in the same way as ambient temperature, but before measuring the absorbance, the samples were rotated in a heating chamber for 24 hours. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure $CaCl_2$ brine and sample 10-12 Varg formation brine. The pH change before and after aging is shown in Table 4.4.
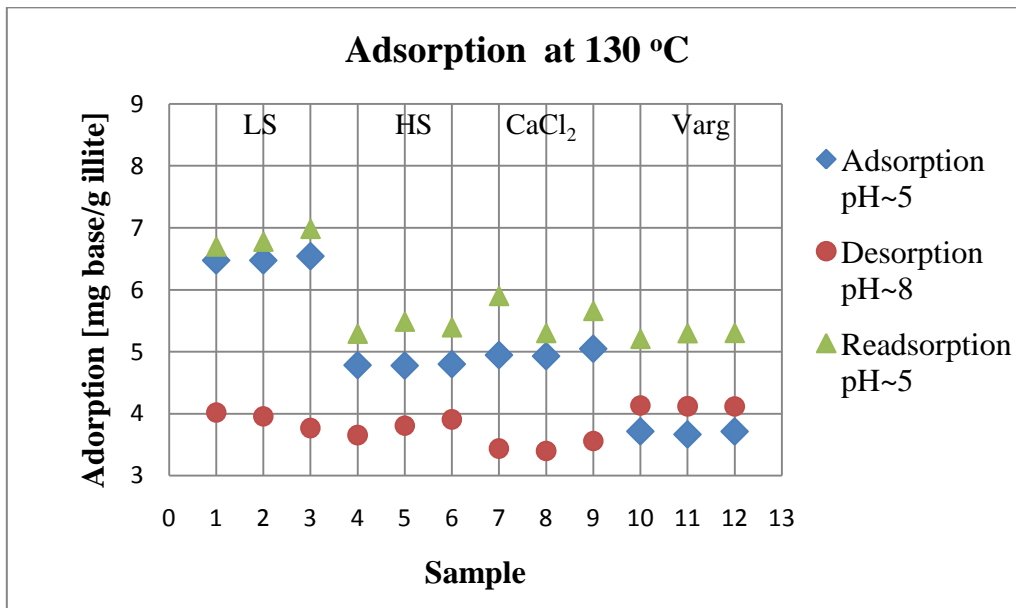

Figure 4-10: Adsorption of quinoline onto illite at 130 ºC using four different brines: LS, HS, pure CaCl2 and Varg formation brine. Sample 1-3 represent LS brine, 4-6 HS brine, 7-9 pure CaCl2 brine and sample 10-12 Varg formation brine.

Tabel 4-4: pH before and after aging at 130 ºC at each step.

	LS	LS After aging	HS	HS After aging	CaCl₂	CaCl₂ After aging	Varg	Varg After aging
Adsorption pH	4,96	4,24	4,92	4,24	4,94	4,31	4,98	4,18
Desorption pH	7,98	6,21	8,06	5,67	7,93	6,10	7,50	6,23
Reabsorption pH	4,91	5,00	5,01	5,11	5,03	5,10	5,05	5,36

LS brine

The adsorption of quinoline at pH~5 for the LS brine was 6,5 mg per gram illite, which is 55,2 % of initial quinoline in solution. With an increase in pH to 8, approximately 2,8 mg of initial adsorbed quinoline is released from the clay surface. A reversible process is observed when the pH was decreased back to 5.

HS brine

The adsorption of quinoline at pH~5 for the HS brine was 4,8 mg per gram illite, which is 40,7 % of initial quinoline in solution. By increasing the pH to 8, the adsorption decreased to 3,8 mg. About 5,4 mg quinoline was adsorbed to the clay surface when the pH was reduced back to 5.

Pure $CaCl_2$ brine

The adsorption of quinoline at pH~5 for the $CaCl_2$ brine was 5,0 mg per gram illite, which is 42,3 % of initial quinoline in solution. The adsorption of quinoline was decreased to 3,5 mg when the pH was adjusted to 8. When reducing the pH back to 5 the quinoline is reabsorbed from the clay surface, but there is a gap in adsorption between 5,3 and 5,9 for the three samples. A small leakage was visually observed in sample 7 and 9. Adsorption measurement was done twice for this step with good repeatability.

Varg formation brine

The adsorption of quinoline at pH~5 for the Varg formation brine was 3,7 mg per gram illite, which is 31,4 % of initial quinoline in solution. Also for these samples, the pH was adjusted to ~7,5 due to precipitation of $Ca(OH)_2$. At pH~7,5 , the adsorption increased with 0,4 mg. When the pH was decreased back to 5, the adsorption increased to 5,3.

At temperature above 100 °C the reactivity of the active ions, especially Ca^{2+}, became more active. Compared to ambient temperature, the adsorption is much lower which responds to a more water-wet system. The difference in adsorption for the LS brine and Varg formation brine which contain a high concentration of Ca^{2+} is 2,8. This support that Ca^{2+} is an even more important parameter at high temperature. When the pH is increased, quinoline is desorbed from the clay surface as explained in Section 4.5.1. Also at high temperature the process is reversible, but the adsorption increases more in the last step compared to ambient temperature. As seen in Table 4-4, the pH before and after aging in the last step is smaller compared to the first step. It is likely to believe that after the last step, the system is more at equilibrium than the first step due to longer heating time. The gap between the first and last step increases as the concentration of Ca^{2+} increases. The more Ca^{2+} in the solution, the longer it takes before the system is in equilibrium due to competition between Ca^{2+} and protonated quinoline.

4.6 Dynamic studies

Dynamic experiments were done by PhD student Alireza RezaeiDoust and Bachelor student Kim Flatråker. Two outcrop sandstone cores were used, B02 and B20, containing about 10 wt% clay, mostly illite and some chlorite. Crude oil that was used had a high BN of 1,78 and an AN of 0,12. The crude oil was saturated with CO_2 at 6 bar in order to mimic reservoir conditions. B02 was aged at 60 °C and water flooding was performed at 40 °C. Core B20 was aged and flooded at 130 °C. Both cores were initially flooded with a 100 000 ppm FW containing 1,54 M NaCl and 0,09M $CaCl_2$. A recovery plateau of ~47 % was reached after 4 and 8 PV injected. Then the brine was switched to low salinity water containing 0,003 M NaCl and 0,005 M $CaCl_2$. From Figure 4-11, one can see that the low salinity flooding increased the recovery from 47–62 % in both cores.
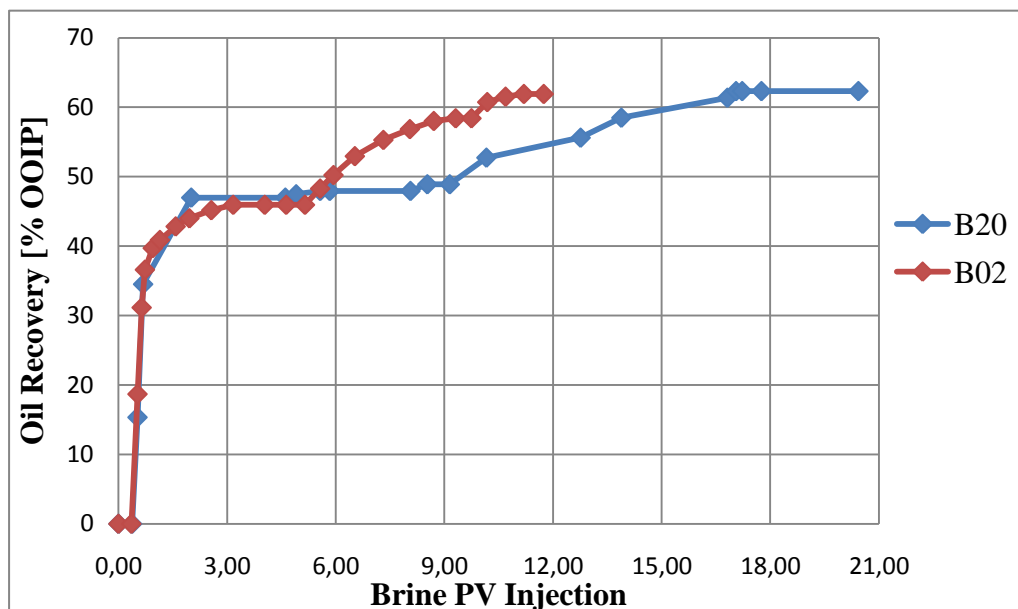
Figure 4-11: Tertiary low salinity effect with two different temperatures. B20 is aged and flooded at 130 °C and B02 is aged at 60 °C and flooded at 40 °C.

During the low salinity flooding, the pH of the effluent increased about 1 pH unit in both cores. This is in line with observation seen from the static experiments: when the pH is increased, organic material is desorbed from the clay surface. This is in line with the suggested mechanism by Austad et al. (2010).

The plateau of ultimate recovery with LS brine at 40 °C was reached after 6 PV injected compared to 9 PV injected for the experiment at 130 °C. This indicates an increased reactivity of Ca^{2+} ions towards the clay surface. The desorption of Ca^{2+} ions from the clay surface takes a longer time compared to lower temperatures.

5. Conclusions

➢ Adsorption of quinoline onto illite is dependent of pH, temperature and Ca^{2+} concentration.

➢ Adsorption of quinoline at pH~5 was significantly higher than adsorption at pH~8-9 both at ambient temperature and at 130 °C. The process was reversible.

➢ Below the pKa-value, adsorption of quinoline decreases as the pH decreases.

➢ Amount and type of divalent cations present in the brine will affect the amount of adsorbed quinoline.

➢ The adsorption of quinoline decreased with increasing Ca^{2+} concentration.

➢ Increase in temperature decreases the amount of adsorbed quinoline onto the clay surface.

6. Further work

The experimental work done in this thesis has given many interesting results that could be worth looking further into. Listed below, some thoughts on further work are presented.

➢ Redo adsorption measurement at high temperature with pressurized cell.

➢ Verify if the relative affinity of Ca^{2+} and Mg^{2+} towards the clay surface change as the temperature increases.

➢ Based on the results from illite at high temperature, there is a reason to believe that same trend will be observed for kaolinite and montmorillonite.

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8. Appendix

8.1 Calibration curve for LS and HS

Calibration curve 0,01 M quinoline 1000 mg/l pH~3,35

Dilution	Concentration [mM]	ABS
x1000	0,01	0,0631
x500	0,02	0,1240
x200	0,05	0,3246
x100	0,10	0,6655
x50	0,20	1,3167
x40	0,25	1,6558

Calibration curve 0,01 M quinoline 25000 mg/l pH~3,35

Dilution	Concentration [mM]	ABS
x1000	0,01	0,0667
x500	0,02	0,1385
x200	0,05	0,3312
x100	0,10	0,6787
x50	0,20	1,3359
x40	0,25	1,6704

8.2. Adsorption calculations for sample 5 initial test 1

Illite (m_{ill}): 1,0001 g
Brine (m_b): 7,8013 g
Quinoline (m_q): 1,3045 g
Molarity quinoline (C_q): 0,07 M
Molar mass quinoline (M_q): 129,16 g/mol
HCl/NaOH added ($m_{H/N}$): 0,095 g
Calibration curve: ABS = 6635,5x – 0,0051
ABS: 0,2683

Total amount liquid (m_{tot}) in the sample:
$m_{tot} = m_b + m_q + m_{H/N} = 9,2008$ g

Molarity of quinoline in the sample (M_{qs}):
$M_{qs} = m_q/m_{tot}*C_q = 0,01$ M

Molarity of quinoline in sample after stable pH (x):
$x = (ABS + 0,0051)/6635,5 = 4,120*10^{-5}$
Diluted 100 times → x = 0,00412

Percent quinoline in solution ($\%_{qs}$):
$\%_{qs} = (x/m_{qs})*100 = 41,55$ %

Percent quinoline adsorbed ($\%_{qa}$):
$\%_{qa} = 100 - \%_{qs} = 58,45$ %

Initially mol quinoline in sample (n_i) :
$n_i = (m_q/1000)*C_q = 0,0000913$ mol

Mol quinoline in sample after stable pH (n_s) :
$n_s = (m_{tot}/1000)*x = 3,79*10^{-5}$ mol

Mol quinoline adsorb to the clay surface (n_{ad}) :
$n_{ad} = n_i - n_s = 5,34*10^{-5}$ mol

→

Adsorption $= (n_{ad}*M_q*1000)/m_{ill} =$ **6,89 mg base/g illite**

8.3 Initial test 1

8.3.1 Sample 4

Illite: 1,0000 g

Brine (1167 mg/l): 7,8046 g

Quinoline 0,07 M, pH~4: 1,3027 g

Date	Measurement	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
25.jan	1						6,34	
	2	10	10				5,94	
	3	20	30				5,38	
	4	10	40				5,82	
26.jan	5	30	70				4,94	
27.jan	6						5,31	
	7	5	75				4,94	
28.jan	8						5,01	
31.jan	9						5,03	
01.feb	10		75				5,04	0,2747
02.feb	11				10	10	5,33	
	12				10	20	8,12	
03.feb	13						8,00	
04.feb	14			5		25	8,06	
07.feb	15						8,46	
08.feb	16			5		30	8,57	
09.feb	17						8,49	
10.feb	18				5	35	8,72	
11.feb	19						8,98	
14.feb	20						8,79	
15.feb	21				5	40	9,00	
16.feb	22						8,99	
17.feb	23						8,99	0,5104
21.feb	24	20	95				7,33	
22.feb	25	10	105				5,87	
23.feb	26	5	110				5,25	
24.feb	27	5	115				4,61	
28.feb	28						4,85	
01.mar	29						4,88	
02.mar	30						4,92	
03.mar	31						5,00	0,2363

8.3.2 Sample 5

Illite: 1,0001 g

Brine (1167 mg/l): 7,8013 g

Quinoline 0,07 M: 1,3045 g

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
25.jan	1		80	80				4,58	
26.jan	2							5,23	
	3		5	85				4,74	
	4							5,05	
27.jan	5							5,30	
	6		5	90				4,76	
28.jan	7							4,76	
31.jan	8							4,77	
01.feb	9							4,75	
02.feb	10				5		5	4,96	
03.feb	11							4,92	
04.feb	12							4,91	0,2683
07.feb	13					25	30	8,61	
08.feb	14				5		35	8,61	
09.feb	15							8,51	
10.feb	16					5	40	8,78	
11.feb	17					5	45	8,96	
14.feb	18							8,84	
15.feb	19					5	50	9,25	
16.feb	20							9,14	
17.feb	21							9,16	
21.feb	22	5		95				8,99	
22.feb	23							8,95	
23.feb	24							8,94	0,438
24.feb	25		30	125				6,92	
28.feb	26		5	130				6,42	
01.mar	27		5	135				5,62	
02.mar	28	5		140				5,57	
03.mar	29		5	145				5,03	
04.mar	30							5,07	
05.mar	31							5,16	
07.mar	32	5		150				4,98	
08.mar	33							5,06	
09.mar	34							5,11	0,2163

8.3.3 Sample 6

Illite: 1,0000 g

Brine (29167 mg/l): 7,8023 g

Quinoline 0,07 M: 1,3032 g

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
02.feb	1		85	85				4,89	
04.feb	2							5,07	
07.feb	3							5,31	
08.feb	4		5	90				4,79	
09.feb	5							4,82	
10.feb	6				5		5	4,88	
11.feb	7							4,92	
14.feb	8							4,86	
15.feb	9							4,93	
16.feb	10							4,89	
17.feb	11							4,89	0,2813
21.feb	12					30	35	8,11	
22.feb	13					10	45	8,44	
23.feb	14					5	50	8,52	
24.feb	15					5	55	8,43	
01.mar	16					5	60	8,23	
02.mar	17					5	65	8,45	
03.mar	18					5	70	8,54	
05.mar	19					5	75	8,67	
07.mar	20					5	80	8,86	
09.mar	21							8,65	
10.mar	22							8,70	0,4027
15.mar	23		40	130				7,71	
25.mar	24		10	140				7,43	
28.mar	25		10	150				6,60	
29.mar	26		5	155				5,00	
30.mar	27							5,04	
31.mar	28	5		160				5,12	
04.apr	29							5,12	0,2203

8.3.4 Sample 7

Illite: 1,0004 g

Brine (29167 mg/l): 7,8023 g

Quinoline 0,07 M: 1,3049 g

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
02.feb	1		85	85				4,90	
03.feb	2							5,09	
07.feb	3							5,23	
08.feb	4		5	90				4,74	
09.feb	5							4,72	
10.feb	6				5		5	4,70	
11.feb	7							4,77	
14.feb	8				5		10	4,87	
15.feb	9							4,89	
16.feb	10							4,89	0,2920
17.feb	11					30	40	8,17	
21.feb	12					5	45	8,11	
22.feb	13					10	55	8,33	
23.feb	14					5	60	8,45	
24.feb	15					5	65	8,42	
01.mar	16					5	70	8,24	
02.mar	17					5	75	8,45	
03.mar	18					5	80	8,55	
05.mar	19					5	85	8,61	
07.mar	20					5	90	8,73	
09.mar	21					10	100	8,75	
10.mar	22							8,77	0,4081
15.mar	23		40	130				7,72	
25.mar	24		10	140				7,44	
28.mar	25		10	150				6,62	
29.mar	26		5	155				5,05	
30.mar	27							5,15	
31.mar	28							5,27	
04.apr	29	5		160				4,96	
05.apr	30	10		170				5,06	
06.apr	31							5,05	0,2164

8.3.5 Adsorption calculation initial test 1

Adsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3045	7,8022	7,8022		0,1	9,2067	0,010	1,0000	9,7975	5,02	0,2799	4,295E-05	0,00430	43,35	56,65	0,0000913	3,96E-05	5,17E-05	6,68
LS	2	1,3030	7,8042	7,8042		0,12	9,2272	0,010	1,0000	9,7787	4,91	0,2705	4,153E-05	0,00418	42,25	57,75	0,0000912	3,85E-05	5,27E-05	6,80
LS	3	1,3055	7,8025	7,8025		0,090	9,1980	0,010	1,0002	9,8076	4,95	0,2703	4,150E-05	0,00415	41,77	58,23	0,0000914	3,82E-05	5,33E-05	6,87
LS	4	1,3027	7,8046	7,8046		0,075	9,1823	0,010	1,0000	9,8210	5,04	0,2747	4,217E-05	0,00422	42,46	57,54	0,0000912	3,87E-05	5,25E-05	6,78
LS	5	1,3045	7,8013	7,8013		0,095	9,2008	0,010	1,0001	9,8040	4,91	0,2683	4,120E-05	0,00412	41,55	58,45	0,0000913	3,79E-05	5,34E-05	6,89
HS	6	1,3032	7,8023	7,6493		0,095	9,0475	0,010	1,0000	9,9527	4,89	0,2817	4,180E-05	0,00419	41,53	58,47	0,0000912	3,79E-05	5,33E-05	6,89
HS	7	1,3049	7,8023	7,6493		0,1	9,0542	0,010	1,0004	9,9497	4,89	0,2920	4,334E-05	0,00436	43,19	56,81	0,0000913	3,94E-05	5,19E-05	6,70
HS	8	1,3014	7,9569	7,8009		0,097	9,1993	0,010	1,0005	9,8090	5,03	0,2764	4,100E-05	0,00414	41,77	58,23	0,0000911	3,80E-05	5,30E-05	6,85

Desorption pH~9

Type	Sample	Q [g]	Brine [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3045	7,8022	7,8022		0,165	9,2717	0,010	1,0000	9,7355	9,02	0,4542	6,922E-05	0,00692	70,22	29,78	0,0000913	6,41E-05	2,72E-05	3,51
LS	2	1,3030	7,8042	7,8042		0,155	9,2622	0,010	1,0001	9,7454	8,95	0,4366	6,657E-05	0,00667	67,70	32,30	0,0000912	6,17E-05	2,95E-05	3,81
LS	3	1,3055	7,8025	7,8025		0,155	9,2630	0,010	1,0002	9,7455	8,96	0,3979	6,073E-05	0,00608	61,66	38,34	0,0000914	5,63E-05	3,50E-05	4,52
LS	4	1,3027	7,8046	7,8046		0,125	9,2323	0,010	1,0000	9,7730	8,99	0,5104	7,769E-05	0,00778	78,74	21,26	0,0000912	7,18E-05	1,94E-05	2,50
LS	5	1,3045	7,8013	7,8013		0,145	9,2508	0,010	1,0001	9,7562	8,94	0,4380	6,678E-05	0,00673	68,19	31,81	0,0000913	6,23E-05	2,91E-05	3,75
HS	6	1,3032	7,8023	7,8023		0,17	9,2755	0,010	1,0000	9,7319	8,70	0,4027	5,993E-05	0,00600	60,96	39,04	0,0000912	5,56E-05	3,56E-05	4,60
HS	7	1,3049	7,8023	7,8023		0,19	9,2972	0,010	1,0004	9,7149	8,77	0,4081	6,074E-05	0,00608	61,85	38,15	0,0000913	5,65E-05	3,48E-05	4,50

Readsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	4	1,3027	7,8046	7,8046		0,165	9,2723	1,0000	1,0000	9,73	4,97	0,2363	3,6380E-05	0,0036683	37,30	62,70	0,000091189	3,40131E-05	5,71759E-05	7,38
LS	5	1,3045	7,8013	7,8013		0,2	9,3058	1,0000	1,0001	9,70	5,11	0,2163	3,3366E-05	0,00333301	33,97	66,03	0,000091315	3,10163E-05	6,0298E-05	7,79
HS	6	1,3032	7,8023	7,6493		0,24	9,3455	1,0000	1,0000	9,67	5,12	0,2203	3,260E-05	0,0032696	33,50	66,50	0,0000912	3,06E-05	6,07E-05	7,84
HS	7	1,3049	7,8023	7,6493		0,28	9,3872	1,0004	1,0004	9,63	5,05	0,2164	3,202E-05	3,239E-03	33,28	66,72	0,0000913	3,04E-05	6,09E-05	7,87

8.4 Initial test 2

8.4.1 Adsorption calculation initial test 2 at ambient temperature

Adsorption pH-5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,306	7,8030	7,8030	0,0880	9,1916	0,010	1,0001	9,81	5,02	0,3015	0,00046	0,0046	46,81	53,19	0,000091	0,00004	0,00005	6,25
LS	2	1,310	7,8015	7,8015	0,0880	9,1905	0,010	1,0002	9,81	5,04	0,3000	0,00046	0,0046	46,64	53,36	0,000091	0,00004	0,00005	6,28
LS	3	1,316	7,8037	7,8037	0,0880	9,1933	0,010	1,0003	9,81	5,04	0,3013	0,00046	0,0046	46,87	53,13	0,000091	0,00004	0,00005	6,25
LS	4	1,301	7,9592	7,9592	0,0880	9,1912	0,010	1,0000	9,81	4,91	0,3242	0,00048	0,0049	49,67	50,33	0,000091	0,00005	0,00005	5,92
HS	5	1,300	7,9586	7,9586	0,0880	9,1905	0,010	1,0008	9,82	4,90	0,3202	0,00048	0,0049	49,44	50,56	0,000091	0,00004	0,00005	5,94
HS	6	1,301	7,9597	7,9597	0,0880	9,1917	0,010	1,0007	9,82	4,89	0,3229	0,00048	0,0049	49,51	50,49	0,000091	0,00004	0,00005	5,93
CaCl2	7	1,301	7,9354	7,9354	0,0880	9,1909	0,010	1,0006	9,82	4,72	0,2992	0,00045	0,0045	45,55	54,45	0,000091	0,00004	0,00005	6,40
CaCl2	8	1,309	7,9353	7,9353	0,0880	9,1916	0,010	1,0005	9,82	4,77	0,2948	0,00044	0,0045	44,98	55,02	0,000091	0,00004	0,00005	6,47
CaCl2	9	1,306	7,9348	7,9348	0,0880	9,1908	0,010	1,0003	9,82	4,73	0,2974	0,00044	0,0045	45,24	54,76	0,000091	0,00004	0,00005	6,44
VargX	10	1,310	9,0485	9,0485	0,0880	9,1894	0,010	1,0009	9,82	4,13	0,3668	0,00055	0,0055	55,34	44,66	0,000091	0,00005	0,00004	5,25
VargX	11	1,302	9,0522	9,0522	0,0880	9,1918	0,010	1,0001	9,81	4,17	0,3652	0,00054	0,0055	55,16	44,84	0,000091	0,00005	0,00004	5,27
VargX	12	1,317	9,0520	9,0520	0,0880	9,1931	0,010	1,0000	9,81	4,16	0,3672	0,00055	0,0055	55,19	44,81	0,000091	0,00005	0,00004	5,27

Desorption pH-9

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,306	7,8030	7,8030	0,1330	9,2366	0,010	1,0001	9,77	8,45	0,4939	0,0000752	0,0075	76,40	23,60	0,000091	0,00007	0,00002	2,78
LS	2	1,310	7,8015	7,8015	0,1330	9,2355	0,010	1,0002	9,77	8,37	0,4901	0,0000746	0,0075	76,12	23,88	0,000091	0,00007	0,00002	2,81
LS	3	1,316	7,8037	7,8040	0,1330	9,2386	0,010	1,0003	9,77	8,38	0,4945	0,0000753	0,0076	76,97	23,03	0,000091	0,00007	0,00002	2,71
LS	4	1,301	7,9592	7,9592	0,1330	9,2362	0,010	1,0000	9,77	8,10	0,4672	0,0000696	0,0070	71,09	28,91	0,000091	0,00006	0,00002	3,40
HS	5	1,300	7,9586	7,9586	0,1330	9,2355	0,010	1,0008	9,78	8,05	0,4670	0,0000696	0,0070	70,62	29,38	0,000091	0,00006	0,00003	3,45
HS	6	1,301	7,9597	7,9597	0,1330	9,2367	0,010	1,0007	9,77	8,04	0,4640	0,0000691	0,0069	70,28	29,72	0,000091	0,00006	0,00003	3,49
CaCl2	7	1,301	7,9354	7,9354	0,1330	9,2359	0,010	1,0006	9,77	7,73	0,4255	0,0000633	0,0063	63,76	36,24	0,000091	0,00006	0,00003	4,26
CaCl2	8	1,309	7,9353	7,9353	0,1330	9,2366	0,010	1,0005	9,77	7,86	0,4320	0,0000643	0,0064	65,31	34,69	0,000091	0,00006	0,00003	4,08
CaCl2	9	1,306	7,9348	7,9348	0,1330	9,2358	0,010	1,0003	9,77	7,80	0,4305	0,0000641	0,0064	65,33	34,67	0,000091	0,00006	0,00003	4,08
VargX	10	1,310	9,0485	9,0485	0,1330	9,2344	0,010	1,0009	9,78	7,35	0,2483	0,0000368	0,0037	37,45	62,55	0,000091	0,00003	0,00006	7,35
VargX	11	1,302	9,0522	9,0522	0,1330	9,2368	0,010	1,0001	9,77	7,23	0,2452	0,0000363	0,0037	37,08	62,92	0,000091	0,00003	0,00006	7,40
VargX	12	1,317	9,0520	9,0520	0,1330	9,2381	0,010	1,0000	9,77	7,38	0,2501	0,0000371	0,0037	37,64	62,36	0,000091	0,00003	0,00006	7,34

Readsorption pH-5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,306	7,8030	7,8030	0,1780	9,2816	0,010	1,0001	9,72	4,68	0,2920	0,0000448	0,0045	46,10	53,90	0,0001	0,00004	0,00005	6,34
LS	2	1,310	7,8015	7,8015	0,1780	9,2805	0,010	1,0002	9,73	4,97	0,2950	0,0000452	0,0045	46,21	53,79	0,0001	0,00004	0,00005	6,33
LS	3	1,316	7,8037	7,8040	0,1780	9,2836	0,010	1,0003	9,73	4,89	0,2855	0,0000438	0,0044	44,65	55,35	0,0001	0,00004	0,00005	6,51
LS	4	1,301	7,9592	7,9592	0,1780	9,2812	0,010	1,0000	9,73	4,86	0,3192	0,0000489	0,0049	49,99	50,01	0,0001	0,00005	0,00005	5,88
HS	5	1,300	7,9586	7,9586	0,1780	9,2805	0,010	1,0008	9,73	5,13	0,3158	0,0000484	0,0049	49,70	50,30	0,0001	0,00005	0,00005	5,91
HS	6	1,301	7,9597	7,9597	0,1780	9,2817	0,010	1,0007	9,73	5,02	0,3170	0,0000485	0,0049	49,85	50,15	0,0001	0,00005	0,00005	5,89
CaCl2	7	1,301	7,9354	7,9354	0,1780	9,2809	0,010	1,0006	9,73	4,72	0,2921	0,0000448	0,0045	46,15	53,85	0,0001	0,00004	0,00005	6,33
CaCl2	8	1,309	7,9353	7,9353	0,1780	9,2816	0,010	1,0005	9,73	4,68	0,2990	0,0000449	0,0045	45,98	54,02	0,0001	0,00004	0,00005	6,35
CaCl2	9	1,306	7,9348	7,9348	0,1780	9,2808	0,010	1,0003	9,73	4,43	0,2950	0,0000452	0,0046	46,40	53,60	0,0001	0,00004	0,00005	6,30
VargX	10	1,310	9,0485	9,0485	0,1780	9,2794	0,010	1,0009	9,74	4,44	0,3086	0,0000473	0,0048	48,57	51,43	0,0001	0,00004	0,00005	6,04
VargX	11	1,302	9,0522	9,0522	0,1780	9,2818	0,010	1,0001	9,73	4,41	0,3141	0,0000481	0,0048	49,38	50,62	0,0001	0,00004	0,00005	5,95
VargX	12	1,317	9,0520	9,0534	0,1780	9,2831	0,010	1,0000	9,72	4,45	0,3110	0,0000476	0,0048	48,83	51,17	0,0001	0,00004	0,00005	6,02

8.4.2 Adsorption calculation initial test 2 at 130 °C

Adsorption pH-5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3004	7,8040	7,8040	0,0880	9,1924	0,010	1,0003	9,81	4,97	0,3728	0,000057	0,0057	57,85	42,15	0,000091	0,00005	0,00004	4,95
LS	2	1,3000	7,8033	7,8033	0,0880	9,1913	0,010	1,0005	9,82	4,88	0,3656	0,000056	0,0056	56,68	43,32	0,000091	0,00005	0,00004	5,09
LS	3	1,3001	7,8041	7,8041	0,0880	9,1922	0,010	1,0002	9,81	4,90	0,3696	0,000056	0,0057	57,24	42,76	0,000091	0,00005	0,00004	5,03
HS	4	1,3035	7,9595	7,8034	0,0880	9,1949	0,010	1,0002	9,81	4,79	0,3783	0,000056	0,0057	57,82	42,18	0,000091	0,00005	0,00004	4,97
HS	5	1,3014	7,9583	7,8023	0,0880	9,1917	0,010	1,0003	9,81	4,76	0,3826	0,000057	0,0058	58,45	41,55	0,000091	0,00005	0,00004	4,89
HS	6	1,3002	7,9562	7,8002	0,0880	9,1884	0,010	1,0006	9,82	4,75	0,3793	0,000057	0,0058	58,29	41,71	0,000091	0,00005	0,00004	4,90
CaCl2	7	1,3016	7,9339	7,8013	0,0880	9,1909	0,010	1,0003	9,82	4,44	0,4116	0,000061	0,0062	62,16	37,84	0,000091	0,00006	0,00003	4,45
CaCl2	8	1,3016	7,9335	7,8009	0,0880	9,1905	0,010	1,0003	9,81	4,35	0,4087	0,000061	0,0061	61,60	38,40	0,000091	0,00006	0,00003	4,52
CaCl2	9	1,3024	7,9342	7,8016	0,0880	9,1920	0,010	1,0003	9,81	4,49	0,4146	0,000062	0,0061	62,26	37,74	0,000091	0,00006	0,00003	4,44
VargX	10	1,3010	9,0528	7,8041	0,0880	9,1931	0,010	1,0000	9,81	4,06	0,4471	0,000067	0,0067	67,32	32,68	0,000091	0,00006	0,00003	3,84
VargX	11	1,3020	9,0487	7,8006	0,0880	9,1906	0,010	1,0001	9,81	4,07	0,4507	0,000067	0,0067	67,73	32,27	0,000091	0,00006	0,00003	3,80
VargX	12	1,3021	9,0499	7,8016	0,0880	9,1917	0,010	1,0004	9,82	4,03	0,4509	0,000067	0,0067	67,92	32,08	0,000091	0,00006	0,00003	3,77

Desorption pH-9

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3004	7,8040	7,8040	0,1330	9,2374	0,010	1,0003	9,77	6,47	0,5338	0,000081	0,0081	82,50	17,50	0,000091	0,00008	0,00002	2,06
LS	2	1,3000	7,8033	7,8033	0,1330	9,2363	0,010	1,0005	9,77	6,47	0,5197	0,000079	0,0079	80,33	19,67	0,000091	0,00007	0,00002	2,31
LS	3	1,3001	7,8041	7,8041	0,1330	9,2372	0,010	1,0002	9,77	6,51	0,5359	0,000082	0,0082	82,95	17,05	0,000091	0,00008	0,00002	2,00
HS	4	1,3035	7,9595	7,8034	0,1330	9,2399	0,010	1,0002	9,77	6,09	0,5446	0,000081	0,0081	82,26	17,74	0,000091	0,00008	0,00002	2,09
HS	5	1,3014	7,9583	7,8023	0,1330	9,2367	0,010	1,0003	9,77	6,09	0,5410	0,000081	0,0081	81,87	18,13	0,000091	0,00007	0,00002	2,13
HS	6	1,3002	7,9562	7,8002	0,1330	9,2334	0,010	1,0006	9,78	6,04	0,5317	0,000079	0,0080	80,86	19,14	0,000091	0,00007	0,00002	2,25
Ca	7	1,3016	7,9339	7,8013	0,1330	9,2359	0,010	1,0003	9,77	5,96	0,4886	0,000073	0,0073	74,08	25,92	0,000091	0,00007	0,00002	3,05
Ca	8	1,3016	7,9335	7,8009	0,1330	9,2355	0,010	1,0000	9,77	5,95	0,4840	0,000072	0,0072	73,44	26,56	0,000091	0,00007	0,00002	3,13
Ca	9	1,3024	7,9342	7,8016	0,1330	9,2370	0,010	1,0003	9,77	5,88	0,4823	0,000072	0,0072	73,11	26,89	0,000091	0,00007	0,00002	3,17
VargX	10	1,3016	7,9339	7,8013	0,1330	9,2359	0,010	1,0003	9,77	5,96	0,4886	0,000073	0,0073	74,08	25,92	0,000091	0,00007	0,00002	3,05
VargX	11	1,3016	7,9335	7,8009	0,1330	9,2355	0,010	1,0000	9,77	5,95	0,4840	0,000072	0,0072	73,44	26,56	0,000091	0,00007	0,00002	3,13
VargX	12	1,3024	7,9342	7,8016	0,1330	9,2370	0,010	1,0003	9,77	5,88	0,4823	0,000072	0,0072	73,11	26,89	0,000091	0,00007	0,00002	3,17

Readsorption pH-5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3004	7,8040	7,8040	0,1780	9,2824	0,010	1,0003	9,73	4,11	0,3203	0,000049	0,0049	50,15	49,85	0,000009	0,00005	0,00005	5,86
LS	2	1,3000	7,8033	7,8033	0,1780	9,2813	0,010	1,0003	9,73	3,92	0,3129	0,000048	0,0048	49,17	50,83	0,000009	0,00005	0,00005	5,97
LS	3	1,3001	7,8041	7,8041	0,1780	9,2822	0,010	1,0005	9,73	4,51	0,3289	0,000050	0,0051	51,56	48,44	0,000009	0,00005	0,00004	5,69
HS	4	1,3035	7,9595	7,8034	0,1780	9,2849	0,010	1,0002	9,72	3,88	0,3982	0,000061	0,0061	61,88	38,12	0,000009	0,00006	0,00003	4,49
HS	5	1,3014	7,9583	7,8023	0,1780	9,2817	0,010	1,0002	9,73	4,05	0,3663	0,000056	0,0056	57,06	42,94	0,000009	0,00006	0,00004	5,05
HS	6	1,3002	7,9562	7,8002	0,1780	9,2784	0,010	1,0006	9,73	4,13	0,3922	0,000060	0,0060	61,08	38,92	0,000009	0,00006	0,00004	4,57
Ca	7	1,3016	7,9339	7,8013	0,1780	9,2809	0,010	1,0006	9,73	3,47	0,3071	0,000047	0,0047	48,08	51,92	0,000009	0,00004	0,00005	6,11
Ca	8	1,3016	7,9335	7,8009	0,1780	9,2805	0,010	1,0000	9,73	3,40	0,3134	0,000048	0,0048	49,02	50,98	0,000009	0,00004	0,00005	6,00
Ca	9	1,3024	7,9342	7,8016	0,1780	9,2820	0,010	1,0003	9,72	2,95	0,3071	0,000047	0,0047	48,28	51,72	0,000009	0,00004	0,00005	6,09
VargX	10	1,3010	9,0528	7,8041	0,1780	9,2831	0,010	1,0000	9,72	2,95	0,4196	0,000064	0,0064	65,55	34,45	0,000009	0,00006	0,00003	4,05
VargX	11	1,3020	9,0487	7,8006	0,1780	9,2806	0,010	1,0001	9,73	3,23	0,4116	0,000063	0,0063	64,03	35,97	0,000009	0,00006	0,00003	4,23
VargX	12	1,3021	9,0499	7,8016	0,1780	9,2817	0,010	1,0004	9,73	3,21	0,4143	0,000063	0,0064	64,98	35,02	0,000009	0,00006	0,00003	4,12

8.5 pH scan for LS and HS

8.5.1 pH scan at ambient temperature

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3012	7,8005	7,8005	0,088	9,1897	0,010	1,0005	9,82	1,70	0,4070	0,00006	0,0062177	62,73	37,27	0,0000911	0,00006	0,00003	4,38
LS	2	1,3002	7,8005	7,8005	0,005	9,1057	0,010	1,0005	9,90	5,36	0,2178	0,00003	0,0033605	33,62	66,38	0,0000910	0,00003	0,00006	7,80
LS	2	1,3002	7,8005	7,8005	0,01	9,1107	0,010	1,0005	9,89	6,23	0,2509	0,00004	0,0038634	38,67	61,33	0,0000910	0,00004	0,00006	7,21
LS	3	1,3017	7,8024	7,8024	0,118	9,2221	0,010	1,0001	9,78	2,39	0,3783	0,00006	0,0057911	58,61	41,39	0,0000911	0,00005	0,00004	4,87
LS	4	1,3007	7,8003	7,8003	0,148	9,2490	0,010	1,0002	9,76	3,52	0,2981	0,00005	0,0045880	46,61	53,39	0,0000910	0,00004	0,00005	6,28
LS	5	1,3001	7,8001	7,8001	0	9,1002	0,010	1,0005	9,91	4,42	0,2273	0,00004	0,0035091	35,09	64,91	0,0000910	0,00003	0,00006	7,63
LS	2	1,3002	7,8005	7,8005	0,015	9,1157	0,010	1,0005	9,89	7,30	0,3641	0,00006	0,0056039	56,13	43,87	0,0000910	0,00005	0,00004	5,15
LS	6	1,3010	7,8009	7,8009	0,04	9,1419	0,010	1,0005	9,86	8,46	0,4489	0,00007	0,0068648	68,91	31,09	0,0000911	0,00006	0,00003	3,66
LS	4	1,3001	7,8001	7,8001	0,015	9,1152	0,010	1,0005	9,89	4,83	0,2131	0,00003	0,0032940	32,99	67,01	0,0000910	0,00003	0,00006	7,87
HS	1	1,3005	7,9570	7,8010	0	9,10148	0,010	1,0002	9,90	4,33	0,2904	0,00004	0,0043245	43,31	56,69	0,0000910	0,00004	0,00005	6,66
HS	1	1,3005	7,9570	7,8010	0,015	9,11648	0,010	1,0002	9,89	4,6	0,2800	0,00004	0,0041820	41,88	58,12	0,0000910	0,00004	0,00005	6,83
HS	2	1,3011	7,9560	7,8000	0,005	9,1061	0,01	1,0003	9,90	4,96	0,2784	0,00004	0,0041974	41,49	58,51	0,0000911	0,00004	0,00005	6,88
HS	3	1,3010	7,9588	7,8027451	0,02	9,12375	0,01	1,0007	9,88	2,93	0,3627	0,00005	0,00539517	54,05	45,95	0,0000911	0,00005	0,00004	5,40
HS	1	1,3005	7,9570	7,8010	0,02	9,12148	0,01	1,0002	9,88	5,35	0,2733	0,00004	0,00406918	40,77	59,23	0,0000910	0,00004	0,00005	6,96
HS	2	1,3011	7,9560	7,8000	0,015	9,1161	0,01	1,0003	9,89	6,51	0,3289	0,00005	0,00489718	49,02	50,98	0,0000911	0,00004	0,00005	6,00
HS	3	1,3010	7,9588	7,8027451	0,05	9,15375	0,01	1,0007	9,85	2,01	0,4117	0,00006	0,00613382	61,65	38,35	0,0000911	0,00006	0,00003	4,51
HS	3	1,3010	7,9588	7,8027451	0,08	9,18375	0,01	1,0007	9,83	1,75	0,4197	0,00006	0,00629178	63,45	36,55	0,0000911	0,00006	0,00003	4,30
HS	1	1,3005	7,9570	7,8010	0,03	9,13148	0,01	1,0002	9,87	5,52	0,2778	0,00004	0,00414762	41,60	58,40	0,0000910	0,00004	0,00005	6,86
HS	2	1,3011	7,9560	7,8000	0,02	9,1211	0,01	1,0003	9,88	7,61	0,4102	0,00006	0,00612548	61,34	38,66	0,0000911	0,00004	0,00004	4,55
HS	2	1,3011	7,9560	7,8000	0,03	9,1311	0,01	1,0003	9,87	8,14	0,4611	0,00007	0,00692485	69,43	30,57	0,0000911	0,00006	0,00003	3,60

8.5.2 pH scan at 130 ºC

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	2	1,3004	7,8022	7,8022	0	9,1026	0,010	1,0002	9,90	4,48/3,67	0,2928	0,000045	0,004512	45,12	54,88	0,0000910	0,000041	0,000050	6,45
LS	3	1,3003	7,8002	7,8002	0,02	9,1205	0,010	1,0006	9,89	4,96/4,28	0,2902	0,000045	0,004474	44,83	55,17	0,0000910	0,000041	0,000050	6,48
LS	1	1,3005	7,8014	7,8014	0,02	9,1219	0,010	1,0003	9,88	3,01/2,65	0,3229	0,000049	0,004984	49,94	50,06	0,0000910	0,000045	0,000046	5,88
LS	1	1,3005	7,8014	7,8014	0,05	9,1519	0,010	1,0003	9,85	1,93/2,13	0,3336	0,000051	0,005119	51,46	48,54	0,0000910	0,000047	0,000044	5,71
LS	2	1,3004	7,8022	7,8022	0,04	9,1426	0,010	1,0002	9,86	4,75/4,60	0,2349	0,000036	0,003618	36,34	63,66	0,0000910	0,000033	0,000058	7,48
LS	3	1,3003	7,8002	7,8002	0,065	9,1655	0,010	1,0006	9,84	5,47/5,17	0,2637	0,000041	0,004060	40,88	59,12	0,0000910	0,000037	0,000054	6,95
HS	2	1,3002	7,9599	7,8038	0	9,1040	0,010	1,0006	9,90	4,30/3,50	0,3879	0,000058	0,005839	58,40	41,60	0,0000910	0,000053	0,000038	4,89
HS	1	1,3002	7,9565	7,8005	0,02	9,1207	0,010	1,0001	9,88	3,08/2,74	0,4064	0,000060	0,006114	61,27	38,73	0,0000910	0,000056	0,000035	4,55
HS	3	1,3008	7,9586	7,8025	0,02	9,1233	0,010	1,0004	9,88	4,70/3,95	0,3876	0,000058	0,005820	58,31	41,69	0,0000911	0,000053	0,000038	4,90
HS	2	1,3002	7,9599	7,8038	0,055	9,1590	0,010	1,0006	9,85	5,49/4,67	0,3517	0,000053	0,005377	54,12	45,88	0,0000910	0,000049	0,000042	5,39
HS	3	1,3008	7,9586	7,8025	0,04	9,1433	0,010	1,0004	9,86	5,07/4,34	0,3501	0,000053	0,005368	53,90	46,10	0,0000911	0,000049	0,000042	5,42
HS	1	1,3002	7,9565	7,8005	0,08	9,1807	0,010	1,0001	9,82	1,88/2,18	0,3878	0,000059	0,005922	59,73	40,27	0,0000910	0,000054	0,000037	4,73

8.6 Adsorption of quinoline onto cleaned illite

8.6.1 Adsorption at ambient temperature

				Sample 1					
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,45	
04.apr	2							4,53	
	3				15		15	4,87	
05.apr	4				5		20	5,00	
06.apr	5							5,06	0,2201
08.apr	6					10	30	7,13	
	7					5	35	8,31	
11.apr	8							7,88	
12.apr	9				5		40	8,02	
13.apr	10							8,04	0,4187
15.apr	11		15	15				4,88	
19.apr	12				*			4,92	
26.apr	13							5,00	0,2141

				Sample 2					
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,45	
04.apr	2							4,53	
	3				15		15	4,86	
05.apr	4				5		20	5,01	
06.apr	5							5,00	0,2213
	6					10	30	7,07	
	7					5	35	8,39	
11.apr	8							7,86	
12.apr	9				5		40	8,05	
13.apr	10							8,07	0,4094
15.apr	11		15	15				4,91	
19.apr	12				*			5,06	
26.apr	13							4,98	0,2115

				Sample 3					
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,43	
04.apr	2							4,53	
	3				15		15	4,89	
05.apr	4				5		20	5,02	
06.apr	5							5,00	0,2224
	6					10	30	6,87	
	7					5	35	8,19	
11.apr	8							7,71	
12.apr	9				5		40	7,88	
13.apr	10				*			8,02	0,4092
15.apr	11							4,86	
19.apr	12				*			5,08	
26.apr	13							4,95	0,2180

*Less than 5µl

				Sample 4					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,33	
04.apr	2							4,40	
	3				15		15	4,69	
05.apr	4				5		20	4,77	
	5				10		30	5,05	
06.apr	6							4,95	
07.apr	7							4,99	0,2719
08.apr	8					10	40	6,66	
	9					5	45	8,44	
11.apr	10							7,86	
12.apr	11				5		50	7,99	
13.apr	12							8,06	0,4358
15.apr	13		15	15				5,50	
19.apr	14	5		20				5,32	
26.apr	15	5		25				5,20	
27.apr	16	5		30				5,14	
28.apr	17	5		35				4,92	
02.mai	18							4,93	0,2661

				Sample 5					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,31	
04.apr	2							4,34	
	3				15		15	4,64	
05.apr	4				5		20	4,75	
	5				10		30	5,02	
06.apr	6							4,94	
07.apr	7							4,98	0,2745
08.apr	8					10	40	6,61	
	9					5	45	8,34	
11.apr	10							7,96	
12.apr	11							7,92	
13.apr	12							8,00	0,4358
15.apr	13		15	15				5,55	
19.apr	14	5		20				5,36	
26.apr	15	5		25				5,28	
27.apr	16	5		30				5,13	
28.apr	17	5		35				4,93	
02.apr	18							5,00	0,264

				Sample 6					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,33	
04.apr	2							4,33	
	3				15		15	4,64	
05.apr	4				5		20	4,74	
	5				10		30	5,00	
06.apr	6							4,93	
07.apr	7							4,95	0,2716
08.apr	8					10	40	6,64	
	9					5	45	8,41	
11.apr	10							7,98	
12.apr	11							7,93	
13.apr	12							7,97	0,4351
15.apr	13		15	15				5,50	
19.apr	14	5		20				5,32	
26.apr	15	5		25				5,26	
27.apr	16	5		30				5,17	
02.apr	17	5		35				4,94	0,2639

				Sample 7					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,36	
04.apr	2							4,32	
	3				15		15	4,54	
05.apr	4				5		20	4,65	
	5				10		30	4,93	
06.apr	6							4,83	
07.apr	7				5		35	4,99	
08.apr	8							5,01	0,2604
	9					15	50	7,56	
11.apr	10							7,21	
12.apr	11				5		55	7,35	
13.apr	12					5	60	8,74	
14.apr	13	5		5				8,20	
15.apr	14							8,10	
18.apr	15							8,10	0,4362
19.apr	16		15	20				5,12	
26.apr	17							5,15	
27.apr	18	5		25				5,04	
28.apr	19							5,01	
02.mai	20							5,02	0,2527

				Sample 8					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,37	
04.apr	2							4,34	
	3				15		15	4,63	
05.apr	4				5		20	4,73	
	5				10		30	4,94	
06.apr	6							4,87	
07.apr	7				5		35	5,03	
08.apr	8							5,09	0,2595
	9					15	50	7,62	
11.apr	10							7,22	
12.apr	11				5		55	7,37	
13.apr	12					5	60	8,78	
14.apr	13	5		5				8,21	
15.apr	14							8,12	
18.apr	15							8,10	0,4318
19.apr	16		15	20				4,93	
26.apr	17							5,01	
27.apr	18							5,04	
28.apr	19							5,00	
02.mai	20							5,07	0,2501

				Sample 9					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,41	
04.apr	2							4,30	
	3				15		15	4,58	
05.apr	4				5		20	4,67	
	5				10		30	4,96	
06.apr	6							4,89	
07.apr	7				5		35	5,07	
08.apr	8							5,04	0,2589
	9					15	50	7,41	
11.apr	10							7,16	
12.apr	11				5		55	7,34	
13.apr	12					5	60	8,70	
14.apr	13	5	5					8,19	
15.apr	14							8,08	
18.apr	15							8,10	0,4338
19.apr	16		15	20				5,22	
26.apr	17	5		25				5,09	
27.apr	18							5,20	
28.apr	19	5		30				4,97	
02.mai	20							5,02	0,2494

				Sample 10					
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
05.apr	1				50		50	4,96	
07.apr	2							4,97	0,2036
08.apr	3					10	60	6,69	
	4					5	65	7,82	
11.apr	5							7,29	
12.apr	6							7,21	
13.apr	7					5	70	7,70	
14.apr	8				5		75	7,63	
15.apr	9				5		80	7,63	
18.apr	10							7,71	
19.apr	11				10		90	7,66	
26.apr	12				10		100	7,43	
27.apr	13					5	105	7,84	
28.apr	14							7,75	
02.mai	15							7,51	
03.mai	16					5	110	7,83	
04.mai	17							7,82	
05.mai	18				5		115	7,68	
06.mai	19					5	120	7,93	
10.mai	20							7,58	0,2457
11.mai	21					30	150	8,36	
12.mai	22							8,15	0,2612
13.mai	23		20	20				7,46	
16.mai	24		10	30				7,20	
18.mai	25		10	40				6,61	
19.mai	26		10	50				5,93	
20.mai	27		5	55				5,53	
23.mai	28		5	60				5,34	
24.mai	29		5	65				4,75	
27.mai	30							4,99	
30.mai	31							5,04	
05.jun	32							5,19	
06.jun	33	5		70				5,09	
08.jun	34							5,06	0,1932

				Sample 11					
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							3,92	
04.apr	2							3,87	
	3				15		15	4,22	
05.apr	4				10		25	4,45	
	5				20		45	4,87	
06.apr	6				5		50	4,93	
07.apr	7							4,96	0,2014
08.apr	8					10	60	6,53	
	9					5	65	7,79	
11.apr	10							7,22	
12.apr	11							7,19	
13.apr	12					5	70	7,68	
14.apr	13				5		75	7,65	
15.apr	14				5		80	7,63	
18.apr	15							7,70	
19.apr	16				10		90	7,69	
26.apr	17				10		100	7,47	
27.apr	18					5	105	7,86	
28.apr	19							7,74	
02.mai	20							7,49	
03.mai	21					5	110	7,76	
04.mai	22							7,81	
05.mai	23				5		115	7,7	
06.mai	24					5	120	7,91	
10.mai	25							7,56	0,246
11.mai	26		5	5				7,01	
12.mai	27		5	10				6,89	
13.mai	28		10	20				6,19	
16.mai	29		5	25				6,02	
18.mai	30		5	30				5,41	
19.mai	31		5	35				4,93	
23.mai	32							5,12	
27.mai	33	5		40				5,15	
30.mai	34	10		50				4,82	
06.jun	35							4,95	
08.jun	36							4,99	0,1932

					Sample 12			
Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							3,97	
04.apr	2							3,88	
	3				15		15	4,24	
05.apr	4				10		25	4,44	
	5				20		45	4,87	
06.apr	6				5		50	4,94	
07.apr	7							4,98	0,2057
08.apr	8					10	60	6,78	
	9					5	65	7,94	
11.apr	10							7,32	
12.apr	11							7,27	
13.apr	12					5	70	7,72	
14.apr	13				5		75	7,69	
15.apr	14				5		80	7,65	
18.apr	15							7,73	
19.apr	16				10		90	7,71	
26.apr	17				10		100	7,43	
27.apr	18					5	105	7,88	
28.apr	19							7,78	
02.mai	20							7,49	
03.mai	21					5	110	7,77	
04.mai	22							7,85	
05.mai	23				5		115	7,73	
06.mai	24					5	120	7,92	
10.mai	25							7,51	0,2494
11.mai	26		5	5				7,06	
12.mai	27		5	10				6,95	
13.mai	28		10	20				6,24	
16.mai	29		5	25				6,03	
18.mai	30		5	30				5,49	
19.mai	31		5	35				4,97	
23.mai	32							5,24	
27.mai	33	5		40				5,23	
30.mai	34	10		50				4,94	
06.jun	35							5,08	
08.jun	36							5,09	0,1844

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS

8.6.2 Adsorption calculation ambient temperature

Adsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3021	7,8034	7,8030	0,0200	9,1251	0,010	1,0009	9,88	5,06	0,2201	0,000034	0,0034	34,11	65,89	0,0000911	0,000031	0,000060	7,75
LS	2	1,3005	7,8030	7,8030	0,0200	9,1235	0,010	1,0008	9,89	5,00	0,2213	0,000034	0,0034	34,40	65,60	0,0000910	0,000031	0,000060	7,71
LS	3	1,3002	7,8010	7,8010	0,0200	9,1212	0,010	1,0002	9,88	5,00	0,2224	0,000034	0,0034	34,49	65,51	0,0000910	0,000031	0,000060	7,70
HS	4	1,3024	7,9594	7,8010	0,0300	9,1357	0,010	1,0005	9,87	4,99	0,2719	0,000040	0,0041	40,65	59,35	0,0000912	0,000037	0,000054	6,99
HS	5	1,3023	7,9579	7,8019	0,0300	9,1342	0,010	1,0000	9,87	4,98	0,2745	0,000041	0,0041	40,84	59,16	0,0000912	0,000037	0,000054	6,97
HS	6	1,3025	7,9595	7,8034	0,0300	9,1359	0,010	1,0001	9,87	4,95	0,2716	0,000040	0,0041	40,60	59,40	0,0000910	0,000037	0,000054	6,99
Ca	7	1,3006	7,9366	7,8039	0,0350	9,1395	0,010	1,0007	9,87	5,01	0,2604	0,000039	0,0039	38,92	61,08	0,0000910	0,000037	0,000056	7,18
Ca	8	1,3012	7,9331	7,8005	0,0350	9,1367	0,010	1,0009	9,87	5,09	0,2595	0,000038	0,0038	38,60	61,40	0,0000911	0,000035	0,000056	7,22
Ca	9	1,3011	7,9353	7,8027	0,0350	9,1388	0,010	1,0008	9,87	5,04	0,2589	0,000038	0,0039	38,80	61,20	0,0000911	0,000035	0,000056	7,19
VargX	10	1,3013	9,0505	7,8022	0,0500	9,1535	0,010	1,0007	9,86	4,97	0,2036	0,000030	0,0030	30,38	69,62	0,0000911	0,000028	0,000063	8,19
VargX	11	1,3003	9,0484	7,8003	0,0500	9,1506	0,010	1,0005	9,86	4,96	0,2014	0,000030	0,0030	30,15	69,85	0,0000910	0,000027	0,000064	8,21
VargX	12	1,3007	9,0486	7,8005	0,0500	9,1512	0,010	1,0008	9,86	4,98	0,2057	0,000030	0,0031	30,67	69,33	0,0000910	0,000028	0,000063	8,15

Desorption pH~8

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3021	7,8034	7,8030	0,0400	9,1451	0,010	1,0009	9,86	8,04	0,4187	0,000064	0,0064	64,15	35,85	0,0000911	0,000058	0,000033	4,22
LS	2	1,3005	7,8030	7,8030	0,0400	9,1435	0,010	1,0008	9,87	8,07	0,4094	0,000062	0,0064	64,45	35,55	0,0000910	0,000059	0,000032	4,18
LS	3	1,3002	7,8010	7,8010	0,0400	9,1412	0,010	1,0002	9,86	8,02	0,4092	0,000062	0,0063	63,08	36,92	0,0000910	0,000057	0,000034	4,34
HS	4	1,3024	7,9594	7,8033	0,0500	9,1557	0,010	1,0005	9,85	8,06	0,4358	0,000065	0,0065	65,67	34,33	0,0000912	0,000060	0,000031	4,04
HS	5	1,3023	7,9579	7,8019	0,0450	9,1492	0,010	1,0000	9,85	8,00	0,4358	0,000065	0,0066	65,75	34,25	0,0000912	0,000060	0,000031	4,03
HS	6	1,3025	7,9595	7,8034	0,0450	9,1509	0,010	1,0001	9,85	7,97	0,4351	0,000065	0,0065	65,25	34,75	0,0000912	0,000059	0,000032	4,09
Ca	7	1,3006	7,9366	7,8039	0,0650	9,1695	0,010	1,0007	9,84	8,10	0,4362	0,000065	0,0065	65,59	34,41	0,0000910	0,000060	0,000031	4,04
Ca	8	1,3012	7,9331	7,8005	0,0650	9,1667	0,010	1,0009	9,84	8,10	0,4318	0,000064	0,0065	64,88	35,12	0,0000911	0,000059	0,000032	4,13
Ca	9	1,3011	7,9353	7,8027	0,0650	9,1688	0,010	1,0007	9,84	8,10	0,4338	0,000065	0,0065	65,17	34,83	0,0000911	0,000059	0,000032	4,09
VargX	10	1,3013	9,0505	7,8022	0,1200	9,2235	0,010	1,0007	9,79	7,58	0,2457	0,000036	0,0037	37,09	62,91	0,0000911	0,000034	0,000057	7,40
VargX	11	1,3003	9,0484	7,8003	0,1200	9,2206	0,010	1,0005	9,79	7,56	0,2460	0,000036	0,0037	37,25	62,75	0,0000910	0,000034	0,000057	7,37
VargX	12	1,3007	9,0486	7,8005	0,1200	9,2212	0,010	1,0008	9,79	7,51	0,2494	0,000037	0,0037	37,64	62,36	0,0000910	0,000034	0,000057	7,33

Readsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3021	7,8034	7,8030	0,0550	9,1601	0,010	1,0009	9,85	5,00	0,2141	0,000033	0,0033	33,23	66,77	0,0000911	0,000030	0,000061	7,85
LS	2	1,3005	7,8030	7,8030	0,0550	9,1585	0,010	1,0008	9,85	4,98	0,2115	0,000033	0,0033	33,09	66,91	0,0000910	0,000030	0,000061	7,86
LS	3	1,3002	7,8010	7,8010	0,0550	9,1562	0,010	1,0002	9,85	4,95	0,2180	0,000034	0,0034	33,88	66,12	0,0000910	0,000031	0,000060	7,77
HS	4	1,3024	7,9594	7,8033	0,0850	9,1907	0,010	1,0005	9,82	4,93	0,2661	0,000039	0,0040	39,98	60,02	0,0000912	0,000036	0,000055	7,06
HS	5	1,3023	7,9579	7,8019	0,0800	9,1842	0,010	1,0000	9,82	4,94	0,2640	0,000039	0,0039	39,66	60,34	0,0000912	0,000036	0,000055	7,11
HS	6	1,3025	7,9595	7,8034	0,0800	9,1859	0,010	1,0001	9,82	4,94	0,2639	0,000039	0,0039	39,61	60,39	0,0000912	0,000036	0,000055	7,11
Ca	7	1,3006	7,9366	7,8039	0,0900	9,1945	0,010	1,0007	9,82	5,02	0,2527	0,000037	0,0038	37,95	62,05	0,0000910	0,000035	0,000056	7,29
Ca	8	1,3012	7,9331	7,8005	0,0800	9,1817	0,010	1,0009	9,83	5,07	0,2501	0,000037	0,0037	37,46	62,54	0,0000911	0,000034	0,000057	7,35
Ca	9	1,3011	7,9353	7,8027	0,0900	9,1938	0,010	1,0008	9,82	5,02	0,2494	0,000037	0,0037	37,78	62,22	0,0000911	0,000034	0,000057	7,31
VargX	10	1,3013	9,0505	7,8022	0,2150	9,3185	0,010	1,0007	9,70	5,06	0,1932	0,000029	0,0029	29,42	70,58	0,0000911	0,000027	0,000064	8,30
VargX	11	1,3003	9,0484	7,8003	0,1700	9,2706	0,010	1,0005	9,74	4,99	0,1952	0,000029	0,0029	29,49	70,51	0,0000910	0,000027	0,000064	8,29
VargX	12	1,3007	9,0486	7,8005	0,1700	9,2712	0,010	1,0008	9,74	5,09	0,1855	0,000027	0,0028	28,25	71,75	0,0000910	0,000026	0,000065	8,43

8.6.3 Adsorption 130 °C

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
				Sample 1					
31.mar	1							4,45	
07.apr	2				20		20	4,95	
11.apr	3							4,93/4,25	0,2930
13.apr	4					15	35	6,97	
14.apr	5				10		45	7,24	
15.apr	6				10		55	7,69	
18.apr	7				5		60	7,87	
19.apr	8							7,80	
26.apr	9				5		65	7,73	
27.apr	10				5		70	8,12	
28.apr	11							8,1	
02.mai	12							7,94	
03.mai	13							7,96/6,23	0,4286
05.mai	14		5	5				5,47	
06.mai	15	10		15				4,96	
09.mai	16							5,15	
	17	5		20				4,93	
10.mai	18							4,91/5,00	0,2770

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
				Sample 2					
31.mar	1							4,45	
07.apr	2				20		20	4,95	
11.apr	3							4,96/4,22	0,2925
13.apr	4					15	35	6,86	
14.apr	5				10		45	7,18	
15.apr	6				10		55	7,63	
18.apr	7				5		60	7,82	
19.apr	8							7,84	
26.apr	9				5		65	7,78	
27.apr	10				5		70	8,14	
28.apr	11							8,1	
02.mai	12							7,98	
03.mai	13							7,99	0,4286
05.mai	14		5	5				5,54	
	15	10		15				5,1	
06.mai	16							5,14	
09.mai	17	*						4,92	
10.mai	18							4,91/5,02	0,2748

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
				Sample 3					
05.mai	1							4,54	
06.mai	2				20		20	5,02	
09.mai	3							4,99/4,17	0,2878
10.mai	4					17	37	7,57	
11.mai	5							7,18	
12.mai	6				5		42	7,55	
13.mai	7				5		47	7,65	
16.mai	8				5		52	7,79	
18.mai	9				5		57	7,97	
19.mai	10							7,99/6,17	0,4397
20.mai	11		5	5				5,21	
23.mai	12	5		10				4,97	
24.mai	13							5,12	
25.mai	14							5,15	
06.jun	15							5,14	
08.jun	16							4,92/4,99	0,2607

*Less than 5µl

Sample 4

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,32	
	2				30		30	4,93	
11.apr	3							4,96/4,26	0,3951
13.apr	4					15	45	6,55	
14.apr	5				10		55	6,99	
15.apr	6				10		65	7,26	
18.apr	7				10		75	7,62	
19.apr	8				10		85	7,93	
26.apr	9							7,61	
27.apr	10				10		95	8,14	
28.apr	11							8,10/5,70	0,4579
03.mai	12		5	5				4,88	
04.mai	13							4,93	
05.mai	14							5,01	
09.mai	15							5,12	
	16	5		10				4,94	
10.mai	17							4,88	
11.mai	18				*			5,05	
12.mai	19							5,09	
16.mai	20							5,05/5,12	0,3639

Sample 5

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,29	
	2				30		30	4,95	
11.apr	3							4,90/4,22	0,3975
13.apr	4					15	45	6,51	
14.apr	5				10		55	6,85	
15.apr	6				10		65	7,23	
18.apr	7				10		75	7,58	
19.apr	8				10		85	7,89	
26.apr	9							7,58	
27.apr	10				10		95	8,08	
28.apr	11							8,06/5,68	0,4452
03.mai	12		5	5				4,73	
04.mai	13							4,79	
05.mai	14				5		100	5,03	
09.mai	15							5,15	
	16	5		10				4,93	
10.mai	17							4,96	
11.mai	18							4,97	
12.mai	19							5,00	
16.mai	20							5,00/5,13	0,3494

Sample 6

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							4,30	
	2				30		30	4,96	
11.apr	3							4,91/4,24	0,3956
13.apr	4					15	45	6,27	
14.apr	5				10		55	6,60	
15.apr	6				10		65	7.00	
18.apr	7				10		75	7,32	
19.apr	8				10		85	7,69	
26.apr	9				5		90	7,51	
27.apr	10				10		100	8,05	
28.apr	11							8,03/5,64	0,4374
03.mai	12		5	5				4,76	
04.mai	13							4,81	
05.mai	14				5		105	5,02	
09.mai	15							5,12	
	16	5		10				4,90	
10.mai	17							4,93	
11.mai	18							4,95	
12.mai	19							5,01	
16.mai	20							4,98/5,07	0,3584

*Less than 5µl

				Sample 7					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,39	
	2				35		35	5,01	
12.apr	3							4,95/4,37	0,3873
14.apr	4					15	50	6,48	
15.apr	5					5	55	7,78	
18.apr	6				5		60	7,86	
19.apr	7							7,73	
26.apr	8				10		70	7,91	
27.apr	9							7,95	
28.apr	10							7,89	
02.mai	11				*			7,90	
03.mai	12							7,92/6,12	0,4678
05.mai	13		5	5				5,38	
06.mai	14	5		10				5,24	
09.mai	15	5		15				5,12	
	16	5		20				4,99	
10.mai	17							5,03/5,15	0,3296

				Sample 8					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
08.apr	1							4,35	
11.apr	2				35		35	4,95	
12.apr	3							4,96/4,31	0,3871
14.apr	4					15	50	6,53	
15.apr	5					5	55	7,76	
18.apr	6				5		60	7,93	
19.apr	7							7,69	
26.apr	8				10		70	7,93	
27.apr	9							7,93	
28.apr	10							7,87	
02.mai	11				*			7,96	
03.mai	12							7,96/6,08	0,4697
05.apr	13		5	5				5,40	
06.mai	14	5		10				5,20	
09.mai	15	5		15				5,12	
	16	5		20				5,00	
10.mai	17							5,05/5,15	0,3627

				Sample 9					
Date	**Measurement**	**1M HCl[µl]**	**5M HCl[µl]**	**Total HCl[µl]**	**1M NaOH[µl]**	**5M NaOH[µl]**	**Total NaOH[µl]**	**pH**	**ABS**
31.mar	1							4,33	
	2				35		35	4,96	
12.apr	3							4,90/4,25	0,3815
14.apr	4					15	50	6,43	
15.apr	5					5	55	7,58	
18.apr	6				5		60	7,76	
19.apr	7				5		65	7,77	
26.apr	8				10		75	7,88	
27.apr	9				*			8,13	
28.apr	10							8,11	
02.mai	11							7,93	
03.mai	12							7,91/6,10	0,4656
05.mai	13		5	5				5,38	
06.mai	14	5		10				5,20	
09.mai	15	5		15				5,16	
	16	5		20				4,97	
10.mai	17							5,01/4,99	0,3433

*Less than 5µl

Sample 10

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							3,93	
07.apr	2				50		50	4,90	
12.apr	3							4,81	
13.apr	4				5		55	5,03	
14.apr	5							5,01	0,4554
18.apr	6					20	75	7,13	
19.apr	7					5	80	7,68	
26.apr	8				10		90	7,39	
27.apr	9					5	95	7,93	
28.apr	10							7,83	
02.mai	11							7,5	
03.mai	12					5	100	8	
04.mai	13							7,96	
05.mai	14							7,69	
06.mai	15					5	105	7,99	
10.mai	16							7,63	
11.mai	17							7,51/6,22	0,4255
12.mai	18	20		20				4,31	
16.mai	19							4,57	
18.mai	20				5		110	4,69	
19.mai	21				5		115	4,91	
23.mai	22							5,00	
27.mai	23							4,98	
30.mai	24							5,02	
06.jun	25							5,06/5,36	0,3686

Sample 11

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							3,97	
07.apr	2				50		50	4,91	
12.apr	3							4,80	
13.apr	4				5		55	4,99	
14.apr	5							4,97	0,4568
18.apr	6					20	75	7,14	
19.apr	7					5	80	7,75	
26.apr	8				10		90	7,41	
27.apr	9					5	95	7,88	
28.mai	10							7,82	
02.mai	11							7,54	
03.mai	12					5	100	7,95	
04.mai	13							7,91	
05.mai	14							7,67	
06.mai	15					5	105	7,94	
10.mai	16							7,52	
11.mai	17							7,49/6,23	0,4276
12.mai	18	20		20				4,28	
16.mai	19				5		110	4,58	
18.mai	20				5		115	4,70	
19.mai	21							4,89	
23.mai	22							4,98	
27.mai	23							4,96	
30.mai	24							4,98	
06.jun	25							5,05/5,31	0,3618

Sample 12

Date	Measurement	1M HCl[µl]	5M HCl[µl]	Total HCl[µl]	1M NaOH[µl]	5M NaOH[µl]	Total NaOH[µl]	pH	ABS
31.mar	1							3,96	
07.apr	2				50		50	4,91	
12.apr	3							4,84	
13.apr	4				5		55	5,01	
14.apr	5							4,97/4,14	0,4541
18.apr	6					20	75	7,07	
19.apr	7					5	80	7,78	
26.apr	8				10		90	7,39	
27.apr	9					5	95	7,90	
28.mai	10							7,81	
02.mai	11							7,49	
03.mai	12					5	100	7,97	
04.mai	13							7,93	
05.mai	14							7,72	
06.mai	15					5	105	7,99	
10.mai	16							7,58	
11.mai	17							7,50/6,24	0,4294
12.mai	18	20		20				4,44	
16.mai	19							4,70	
18.mai	20						110	4,85	
19.mai	21				5		115	5,02	
23.mai	22							5,06	
24.mai	23							5,08	
27.mai	24							5,04	
06.jun	25							5,05/0,3629	0,3629

8.6.4 Adsorption calculation at 130 °C

Adsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3044	7,8010	7,8010	0,0200	9,1254	0,010	1,0003	9,88	4,93/4,25	0,2930	0,000045	0,0045	45,09	54,91	0,0000913	0,000041	0,000050	6,47
LS	2	1,3040	7,8012	7,8012	0,0200	9,1252	0,010	1,0000	9,88	4,96/4,22	0,2925	0,000045	0,0045	45,09	54,91	0,0000913	0,000041	0,000050	6,47
LS	3	1,3005	7,8009	7,8009	0,0200	9,1214	0,010	1,0000	9,88	4,99/4,17	0,2878	0,000044	0,0044	44,34	55,66	0,0000910	0,000040	0,000051	6,54
HS	4	1,3024	7,9577	7,9577	0,0300	9,1341	0,010	1,0008	9,87	4,96/4,26	0,3951	0,000059	0,0059	59,35	40,65	0,0000912	0,000054	0,000037	4,78
HS	5	1,3016	7,9572	7,9572	0,0300	9,1328	0,010	1,0004	9,87	4,90/4,22	0,3975	0,000059	0,0059	59,40	40,60	0,0000911	0,000054	0,000037	4,78
HS	6	1,3040	7,9588	7,9588	0,0300	9,1367	0,010	1,0000	9,87	4,91/4,24	0,3956	0,000059	0,0059	59,29	40,71	0,0000913	0,000054	0,000038	4,80
Ca	7	1,3006	7,9344	7,9344	0,0350	9,1374	0,010	1,0000	9,86	4,95/4,37	0,3873	0,000058	0,0058	57,94	42,06	0,0000910	0,000053	0,000038	4,95
Ca	8	1,3007	7,9343	7,9343	0,0350	9,1374	0,010	1,0000	9,86	4,96/4,31	0,3871	0,000058	0,0058	58,09	41,91	0,0000910	0,000053	0,000038	4,93
Ca	9	1,3032	7,9336	7,9336	0,0350	9,1392	0,010	1,0007	9,87	4,90/4,25	0,3815	0,000057	0,0057	57,13	42,87	0,0000912	0,000052	0,000039	5,05
VargX	10	1,3034	9,0480	7,8000	0,0500	9,1534	0,010	1,0003	9,85	5,01/4,25	0,3554	0,000058	0,0058	68,47	31,53	0,0000912	0,000062	0,000029	3,71
VargX	11	1,3035	9,0509	7,8025	0,0500	9,1560	0,010	1,0002	9,85	4,97/4,17	0,4568	0,000068	0,0069	68,90	31,10	0,0000912	0,000063	0,000028	3,66
VargX	12	1,3041	9,0496	7,8014	0,0500	9,1555	0,010	1,0000	9,85	4,97/4,14	0,4541	0,000068	0,0068	68,51	31,49	0,0000913	0,000063	0,000029	3,71

Desorption pH~9

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3044	7,8010	7,8010	0,0700	9,1754	0,010	1,0003	9,83	7,96/6,23	0,4286	0,000065	0,0066	65,90	34,10	0,0000913	0,000060	0,000031	4,02
LS	2	1,3040	7,8012	7,8012	0,0700	9,1752	0,010	1,0000	9,83	7,99/6,22	0,4286	0,000065	0,0066	66,44	33,56	0,0000913	0,000061	0,000031	3,96
LS	3	1,3005	7,8009	7,8009	0,0570	9,1584	0,010	1,0004	9,85	7,99/6,17	0,4397	0,000067	0,0068	67,93	32,07	0,0000910	0,000062	0,000029	3,77
HS	4	1,3024	7,9577	7,9577	0,1000	9,2041	0,010	1,0008	9,81	8,10/5,70	0,4579	0,000068	0,0068	68,93	31,07	0,0000912	0,000063	0,000028	3,66
HS	5	1,3016	7,9572	7,9572	0,1000	9,2028	0,010	1,0004	9,80	8,06/5,68	0,4452	0,000066	0,0067	67,63	32,37	0,0000911	0,000062	0,000029	3,81
HS	6	1,3040	7,9588	7,9588	0,1050	9,2117	0,010	1,0000	9,79	8,03/5,64	0,4374	0,000065	0,0066	66,85	33,15	0,0000913	0,000061	0,000030	3,91
Ca	7	1,3006	7,9344	7,9344	0,0700	9,1724	0,010	1,0000	9,83	7,92/6,12	0,4678	0,000070	0,0070	70,75	29,25	0,0000910	0,000064	0,000027	3,44
Ca	8	1,3007	7,9343	7,9343	0,0700	9,1724	0,010	1,0000	9,83	7,96/6,08	0,4697	0,000070	0,0071	71,10	28,90	0,0000910	0,000065	0,000026	3,40
Ca	9	1,3032	7,9336	7,9336	0,0750	9,1792	0,010	1,0007	9,83	7,91/6,10	0,4656	0,000069	0,0069	69,75	30,25	0,0000912	0,000064	0,000028	3,56
VargX	10	1,3034	9,0480	7,8000	0,1500	9,2534	0,010	1,0003	9,76	7,51/6,22	0,4255	0,000064	0,0064	64,92	35,08	0,0000912	0,000059	0,000032	4,13
VargX	11	1,3035	9,0509	7,8025	0,1500	9,2560	0,010	1,0002	9,75	7,49/6,23	0,4276	0,000064	0,0064	65,03	34,97	0,0000912	0,000059	0,000032	4,12
VargX	12	1,3041	9,0496	7,8014	0,1500	9,2555	0,010	1,0000	9,75	7,50/6,24	0,4294	0,000064	0,0064	65,08	34,92	0,0000913	0,000059	0,000032	4,12

Readsorption pH~5

Type	Sample	Q [g]	Brine [g]	Brine [ml]	HCl/NaOH [g]	Total [g]	Q [M]	Illite [g]	wt% illite [%]	pH	ABS	Q in solution [M]	x dilution [M]	Base in water [%]	Q adsorbd [%]	Initial mol [mol]	Mol Q [mol]	Mol ads [mol]	Adsorption [mg base/g illite]
LS	1	1,3044	7,8010	7,8010	0,0900	9,1954	0,010	1,0003	9,81	4,91/5,00	0,2770	0,000043	0,0043	43,18	56,82	0,0000913	0,000039	0,000052	6,70
LS	2	1,3040	7,8012	7,8012	0,0900	9,1952	0,010	1,0000	9,81	4,91/5,02	0,2748	0,000042	0,0042	42,51	57,49	0,0000913	0,000039	0,000052	6,78
LS	3	1,3005	7,8009	7,8009	0,0670	9,1684	0,010	1,0004	9,84	4,92/4,99	0,2607	0,0000	0,0040	40,58	59,42	0,0000910	0,000037	0,000054	6,98
HS	4	1,3024	7,9577	7,9577	0,1050	9,2091	0,010	1,0008	9,80	5,05/5,12	0,3659	0,000054	0,0054	55,01	44,99	0,0000912	0,000050	0,000041	5,29
HS	5	1,3016	7,9572	7,9572	0,1100	9,2128	0,010	1,0004	9,80	5,00/5,13	0,3494	0,000052	0,0053	53,35	46,65	0,0000911	0,000043	0,000043	5,49
HS	6	1,3040	7,9588	7,9588	0,1150	9,2217	0,010	1,0000	9,78	4,98/5,07	0,3584	0,000053	0,0054	54,23	45,77	0,0000913	0,000049	0,000042	5,40
Ca	7	1,3006	7,9344	7,9344	0,0900	9,1924	0,010	1,0000	9,81	5,03/5,15	0,3296	0,000049	0,0049	49,81	50,19	0,0000913	0,000045	0,000046	5,90
Ca	8	1,3007	7,9343	7,9343	0,0900	9,1924	0,010	1,0000	9,81	5,05/5,15	0,3627	0,000054	0,0054	54,90	45,10	0,0000910	0,000050	0,000041	5,30
Ca	9	1,3032	7,9336	7,9336	0,0950	9,1992	0,010	1,0007	9,81	5,01/4,99	0,3433	0,000051	0,0051	51,93	48,07	0,0000912	0,000047	0,000044	5,66
VargX	10	1,3034	9,0480	7,8000	0,1450	9,2484	0,010	1,0003	9,76	5,06/5,36	0,3683	0,000055	0,0055	55,78	44,22	0,0000912	0,000051	0,000040	5,21
VargX	11	1,3035	9,0509	7,8025	0,1450	9,2510	0,010	1,0002	9,76	4,96/5,31	0,3618	0,000054	0,0054	55,01	44,99	0,0000912	0,000050	0,000041	5,30
VargX	12	1,3041	9,0496	7,8014	0,1450	9,2505	0,010	1,0000	9,76	5,05/5,42	0,3629	0,000054	0,0054	55,00	45,00	0,0000913	0,000050	0,000041	5,31