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ABSTRACT

For more than a decade the mechanism behind flooding with low salinity water have been studied and well documented as increased oil recovery method (EOR) in sandstone reservoirs. Recently Austad et. al.²⁷ proposed a new chemical wettability alteration mechanism showing increases in pH as the high saline water is displaced by low saline water is a key factor. Proposed mechanism discusses desorption of cations, Ca^{2+} from clay surface during flooding with water of low salt concentration. Local pH increase occurs near clay surface and saltwater since active cations (Ca^{2+}) are replaced by protons (H^+) from water. Desorption of the organic material is a result of quick reaction between OH^- and adsorbed basic and acidic material. Reservoir rocks becomes more water –wet and more oil is displaced toward the production well resulting in increased recovery.

This study attempts to evaluate adsorption of polar basic components onto sandstone minerals, and to understand the potential of each mineral in a wettability alteration process. Experiments are performed to determine adsorption amount of quinoline onto feldspar minerals and quartz. Experiments conducted under ambient temperature with three types of brines. Low salinity brine (1015 ppm), high salinity brine (30 000 ppm) and NaCl brine (36 000). End result shows adsorption is highly dependent on mineral size distribution in samples and pH. Increased adsorption is noted for low salinity compared to high salinity brine in feldspar mineral anorthite. The amount of adsorption of organic material in anorthite is comparable with clay mineral kaoliniteⁱⁱ. While for quartz adsorption was reduced with increased pH in low salinity brine.

NOMENCLATURE

θ_c	Contact angle
σ_{os}	Interfacial tension between the oil and solid.
σ_{ow}	Interfacial tension between the oil and water.
σ_{ws}	Interfacial tension between the water and solid.
AN	Acid number
BET	Brunauer – Emmet –Teller
BN	Base Number
CBR	Crude oil, Brine and Rock
CEC	Cation exchange capacity
DI	Deionized water
EOR	Enhanced oil recovery
FW	Formation water
HS	High salinity
HSFW	High salinity formation water
HSQ	High salinity quinoline
IFT	Interfacial tension
IOR	Improved Oil Recovery
K	Absolute permeability
k_{ro}	Relative permeability of oil
k_{rw}	Relative permeability of water
LS	Low salinity
LSFW	Low salinity formation water
LSQ	Low salinity quinoline
MIE	Multi -component ion exchange
NaClQ	Sodium chloride quinoline
NSO	Oxygen, Nitrogen and Sulfur
OOIP	Original oil in place
Pc	Capillary pressure
Ppm	Parts per million
SEM	Scanning Electron Microscope
TDS	Total Dissolved Solid
WAG	Water alternating gas
wt%	Weight percent

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1 INTRODUCTION

In a world with increasing demand for fossil fuel and simultaneously with a declining oil production, a new field has emerged, enhanced oil recovery. This allows increased oil recovery to become more and more attractive and relevant. Researchers trying hard to reach higher oil recovery, the best recoveries are currently around 40-50% of OOIP.

Enhanced oil recovery (EOR) is a common term of techniques that will increase the amount of oil produced. Flooding of salt water with manipulated chemical composition is one of the mechanisms which is called “Smart Water”. EOR is about to find the best, cheapest and easiest feasible technique on industrial scale to improve recovery by changing the injection water. By injecting water with low salt concentration into a sandstone reservoir, the chemical equilibrium at the established between formation water, oil and rock surface in the reservoir is changed and results in increased recovery. Mechanism behind this technique is very important and much researched.

1.1 Thesis objective

Mineral composition and surface reactivity of the rock material is central in initial wettability alteration. Sandstone consist mainly of three main minerals; quartz, feldspars and clay. Surface area of each mineral is different and will react contrarily. Polar organic components could be the anchor molecules which causes wettability alteration at the surface of the mineral. The main objective of the work is to analyze adsorption of the polar organic components onto the three main minerals of sandstones, to understand the potential of each mineral in a wettability alteration process with Smart Water.

2. THEORY

2.1 Hydrocarbon Recovery Mechanism

From the traditional view, hydrocarbon recovery is divided into three stages; primary, secondary and tertiary recovery. Where the primary and secondary targets mobile oil, the tertiary targets the immobile oil, which can't be recovered because of capillary forces and viscous forces.

All three recovery stages follow a natural progression, but not a chronological progression of oil production from the start to a point where it is no longer economically efficient to produce from the hydrocarbon reservoir. ^{1,2}figure 1³ shows a typical model over all stages of IOR with its source for production and recovery factor in percentage. In primary stage recovery takes advantage of the natural drive and/or artificial lift through a single wellbore. Water is injected in second stage recovery to provide pressure maintenance and immiscibly displace oil via one wellbore and produce oil from another. Tertiary recovery includes injection of miscible gasses, chemicals and thermal energy to provide additional recovery. ⁴

2.1.1 Primary recovery

In primary stage of production, the natural energy in the reservoir is the main source to replace oil into the production. 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. In this stage, approximately 10-30 % of the original oil in place (OOIP) is produced.² It is important to mention that in modern reservoirs implementation of secondary recovery by waterflooding at early stage of primary production before reservoir energy has been depleted.⁴

2.1.2 Secondary recovery

Production rate reduces as the stored energy is released and then the second stage takes over. Secondary oil recovery includes injection of water or gas to maintain reservoir pressure and displace oil. Injection of gas takes place at gas cap in order to maintain pressure or in oil column to displace oil immiscibly towards production wells.

Waterflooding doesn't generate a promising recovery due to reservoir heterogeneity well spacing and unfavorable mobility ratio which promotes the fingering of water through the more viscous oil^{1,5}. According to Castor et al.⁶ recovery factor is 60% of OOIP in a good quality sandstone and for unfavorable reservoir conditions recovery is as low as 20%.

2.1.3 Tertiary recovery/EOR

Since oil recovery doesn't follow a chronological order tertiary recovery has been classified as enhanced oil recovery (EOR)². It has been defined by Beviér⁷ as: "methods aimed at increasing ultimate oil recovery by injecting appropriate agents not normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers, in order to induce new mechanisms for displacing oil". Green and Willhite² divided EOR into four categories as presented in figure 1. Categories are injection of thermal energy, CO₂, miscible gas or chemicals. All these processes are aimed either to increase macroscopic or microscopic sweep efficiency by modifying equilibrium between the crude oil-brine-rock (CBR)⁸. Alternating wettability, interfacial tension (IFT), fluid viscosities and miscible flooding accomplish by modification of CBR. In this stage more than 50- 80% of the OOIP produced.

Injection of water or low salinity water can be characterized as an EOR method in sandstone and carbonate reservoirs. Lager et al.⁵³ have estimated an average of 14% increase in recovery with injection of low saline water. The main purpose of waterflooding is to maintain reservoir pressure, but in the last decade it has been proven that it also possesses a chemical impact in both sandstone and carbonate reservoirs. Chemically modify the wetting properties of the reservoir to a more water-wet and with this increase production, low salinity water is entitled as "Smart water "

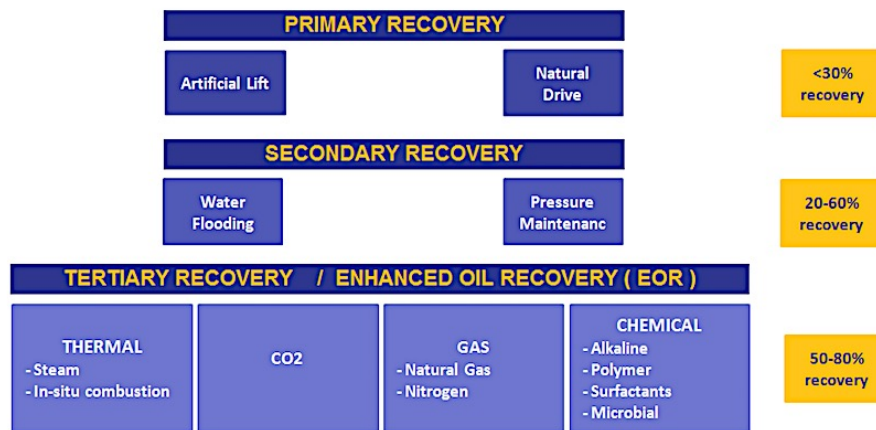


Figure 1: Illustration over stages of Improved oil recovery

2.2 Sandstone mineralogy

Sandstone reservoirs make up approximately 80% of global reservoirs and approximately 50% of global reserves. Giant fields can occur in a wide range of depositional environments. Sandstones are siliclastic sediments or sedimentary rocks indicate deposits composed of clasts of pre-existing rocks, minerals, organic materials and a cementing matrix of silt- or clay-size particles that binds the sand grains together⁹.

These clasts are result of both chemical and physical weathering of pre-existing rocks. They are transported and deposited as discrete bits and pieces by variety of erosional agents: wind, water and Ice¹⁴. The grain size and how well grains are sorted in rock indicates how far the sediments have been transported from its source¹⁰. The presence of various minerals in sedimentary rocks is important indicator of its source. Less stable minerals such as feldspars indicate short transport from its source, if the sedimentary rock indicates long transport from its source and contains feldspar, it means the weathering was not intense enough to produce kaolinite.

Over time will sediments consolidate with temperature and pressure. Under these conditions the deposited sediments undergo processes such as diagenesis and recrystallize to new minerals and cements. Sandstones with typically 35 to 10% porosity is solid rock reservoir produced by these geological processes.

2.2.1 Quartz

Quartz is the second common rock –forming mineral and one of the main components of sandstone, granites and metamorphic rocks.¹¹ Quartz is nearly pure silica with chemical name silicon dioxide [SiO_2]). Characterized by hardness of 7 and specific gravity of 2.65, and are colourless but impurities causes a variety of colours to be seen.^{12,13,14} As presented in figure 2, quartz crystal consists of Si-O tetrahedron as its building block with the silicon ions located in the centre and the oxygen ions located at the corners.¹⁵

In contrast to most minerals quartz crystallizes at a wide variety of temperatures in different geological environments. This characteristic gives its crystal structure and fluid inclusions useful aids in determining the temperature and conditions under which the reservoir rock formed.

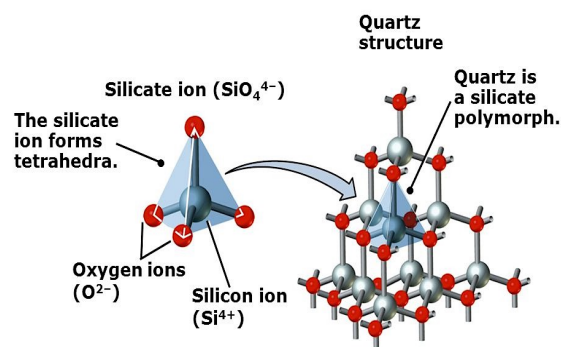


Figure 2: A central silica ion is surrounded by four oxygen atoms, forms a tetrahedron.¹³

According to the Caroll¹⁶ silt fraction of quartz ranging with size [2 – 63 μm] has a cation exchange capacity (CEC) of 0,6 cmol kg^{-1} , compared to clay fraction of quartz with size lower than 2 μm , has 5,3 cmol kg^{-1}

Iler¹⁷ described that silica particles have no charge at pH of 2, while up to pH of 6 the CEC increases because negative charges accumulate on particle surface. Furthermore, Welding et. al. reports that increase in quartz content decrease in CEC, surface area etc.

Quartz is of the important minerals in soil science, where silica minerals effect numerous environmentally essential soil properties. As an example, sandy quartz-rich soils are poor filters for contaminated systems because they have little surface area and ionic charge to adsorb pollutants.¹⁸ As previously mentioned, Carroll states that CEC increases in quartz with decreasing mineral size this is the same for adsorption. This statements will be tested in experimental part, where adsorption of polar basic component will be measured onto quartz minerals with different grains sizes.

2.2.2 Feldspars

Feldspars are the most widespread rock forming minerals in the earth's crust. They are essential elements in igneous rocks and metamorphic where the amount and type used for classification. Feldspar crystallized from magma as veins in both intrusive rocks and extrusive rock. They can also be formed as solid minerals, formed almost entirely of calcic plagioclase feldspar known as anorthosite. Feldspar can range from colorless to white and light gray, but there are also varieties that are brown, yellow, red, green and black. Comprises of two main groups¹⁹ :

- (i). Plagioclase Feldspars have composition between $\text{NaAlSi}_3\text{O}_8$ (albite) and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite)
- (ii). Alkali Feldspars have composition between KAlSi_3O_8 (orthoclase) and $\text{NaAlSi}_3\text{O}_8$ (albite)

The composition of the feldspars can be presented in a triangle in figure 3 where albite and anorthite are end-members of the Plagioclase group.²⁰

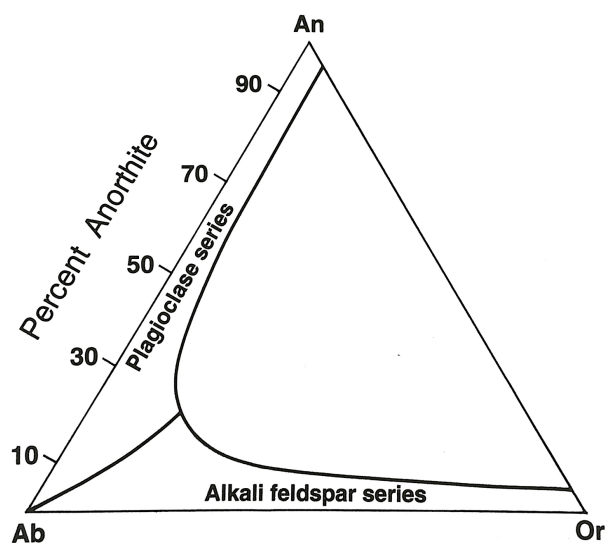


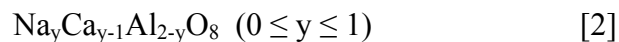
Figure 3: Triangle diagram showing the composition of plagioclase and alkali feldspars in term of three end members, anorthite (An), Albite (Ab) and orthoclase (Or).²⁰

Structures of the feldspars are organized in three-dimensional framework as in quartz (figure 2). Framework forms as each tetrahedron shares all its oxygen ions with other tetrahedral, Grontzinger and Jordan.¹⁴ Structures differ based on crystallization temperature.

Dr. Ribbe²¹ is one of the recognized researchers on feldspar mineral; he has built a systematic connection between the atomic structure and, how the atoms are arranged in feldspar. According to Dr. Ribbe²² feldspars are defined as aluminosilicates whose structures are organized of corner-sharing AlO_4 and SiO_4 tetrahedral linked in an endless three-dimensional network. Remark that there are several other minerals fit this description, according to Dr. Helen Megaw²³ it's the topology of the tetrahedral mineral framework that defines feldspars. General formula²² for alkali feldspar series that characterizes their chemistry is:



where A is divalent ions Ca^{2+} or Ba^{2+} for alkaline –earth feldspars and monovalent Na, K for alkali feldspars. T is tetrahedral cat ions (Al, Si) and O is oxygen. A complete range of compositions is observed in plagioclase feldspar series:



In order to understand feldspar relationships, it's important to differentiate them not only according to the chemical composition, but also according to structural state depending on the crystallization temperature. There is high temperature formation; mostly feldspars of igneous/plutonic/volcanic rocks and low temperature sedimentary formations. The variance between high- and low-structural state in feldspars includes lattice geometry with or without a change of symmetry, also the degree of ordering Al and Si atoms between individual tetrahedral sites.²⁴

Albite

Albite is a part of plagioclase feldspars with the chemical formula $\text{NaAlSi}_3\text{O}_8$ and composition of 0-10 % anorthite. Albite is one of the last feldspars to crystallize from magma, means it forms under low temperature and is s found nearer the surface. It can also form by low temperature alteration of volcanic and sedimentary rocks.

Anorthite

Anorthite is a part of plagioclase feldspars with chemical formula $\text{CaAl}_2\text{Si}_2\text{O}_8$ and composition 90-100 % Anorthite. Different plagioclase has altered ratio of sodium and calcium. Albite has the most sodium, while anorthite has the most calcium and the other minerals lies in between¹³. While albite forms under low temperature, anorthite generally forms in high temperature environments.

Microcline

The composition for alkali feldspars lies between alkali elements K^+ and Na^+ ; albite ($\text{NaAlSi}_3\text{O}_8$) and microcline (KAlSi_3O_8). Microcline has chemical formula KAlSi_3O_8 indicates that microcline is a potassium mineral with very little sodium, while orthoclase and sanidine involves the substitution of sodium for potassium. Formed under low temperature. Figure 4 shows an idealized crystalline structure of microcline: the red spheres represent oxygen atoms; silicon and aluminum atoms are within the $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, and the potassium charge-balancing cations are the blue spheres.²⁵

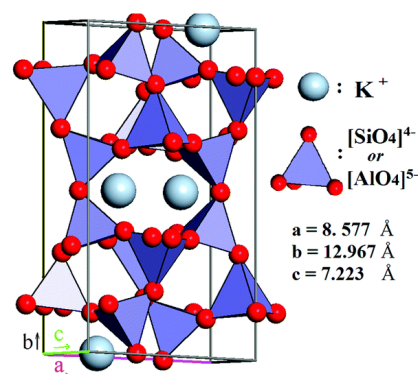


Figure 4: Idealized microcline structure

Major differences between these three alkali feldspars are the crystal structure, which depends on temperature of magma solidification, its cooling rate and geothermal history.^{25,26}

2.2.3 Clay

Clay minerals are the by-product of weathering of other rocks; found in nature with many different compositions, depends on its source rock. Purest kaolin is formed by the weathering of feldspar mineral and composed almost entirely of the mineral kaolinite. Clay also contains much fine sand and usually also calcium and iron precipitation. Clay minerals are the fine-grained particles with diameter less than $2\mu\text{m}$ have large surface area and high reactivity in reservoir. It's recognized by its unique characteristics as cation exchange material because of structural charge imbalance, either in silica or in the aluminum layer and also at the edge surfaces, causing a negative charge on the clay surface²⁷.

Silica (Si), Aluminum (Al) and water (H_2O) are the main elements in the clay minerals. In addition, the clay minerals contain a significant amount of iron (Fe), magnesium (Mg), and a minor amount of sodium (Na) and potassium (K). Figure 5 shows the different clay types, distinguished the way tetrahedral, the octahedral sheets are joined together to form 1:1, and 2:1 silicate layers, as well as the interlayers between them.²⁸

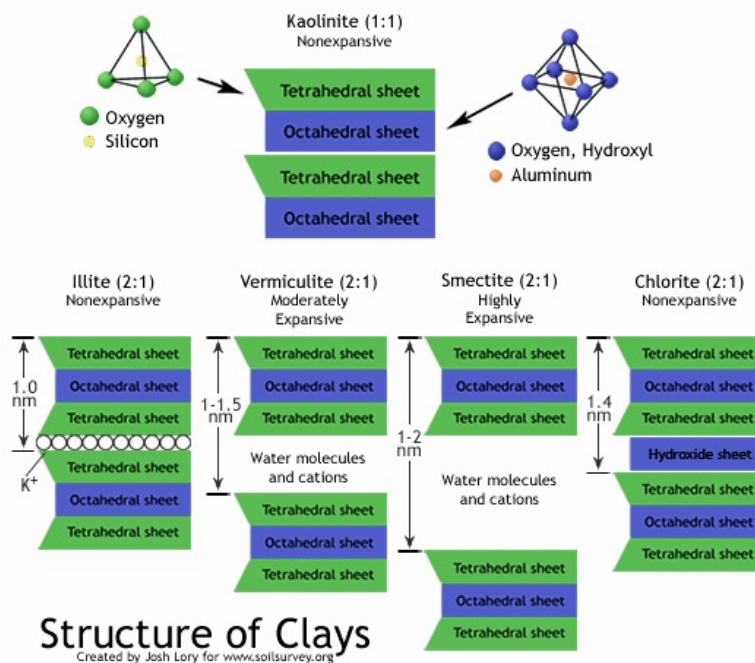


Figure 5: Clay structures

Clay minerals are sheets of tetrahedral silica and octahedral aluminum arranged into layersilicates, also referred to as phyllosilicates. The octahedral sheet consists of two planes of with a tightly packed oxygen (O^{2-}) or hydroxyl (OH^-) with either aluminum (Al^{3+}) or magnesium (Mg^{2+}) bonded with a six-fold coordinated octahedral structure.²⁹ There are five major groups of clay minerals in sandstones: kaolinite, illite, smectite and mixed layer varieties. Table 1 presents four major types of clay with its chemical composition and structural layer.

Table 1: General formulas for clay (Morad and Worden, 2003)³⁰

Kaolinite	Montmorillonite	Illite	Chlorite
$Al_2Si_2O_5(OH)_4$	$(Na, 0.5Ca)_{0.7}(Al, Mg, Fe)_4(Si, Al)_8O_{20}(OH)_{20} \cdot nH_2O$ (Smectite)	$K_y Al_4 (Si_{4-y} Al_y) O_{20} (OH)_4$, $y < 2$	$(Mg, Al, Fe)_{12} [(Si, Al)_8 O_{20}]$
2-layer clay	3-layer clay. Interlayer ions: H_2O , Ca	3-layer clay. Interlayer ions: K, OH, Fe, Mg	3-layer clay. Interlayer ions: OH, Mg

2.3 Mineral Cation Exchange Capacity and ion substitution

Cation exchange capacity (CEC) is often the result of:

- Isomorphous substitution of aluminum Al^{3+} for silicon Si^{4+} chemical substitution in the 4 fold coordinated tetrahedral sheet
- Isomorphous substitution of magnesium Mg^{2+} for aluminum Al^{3+} substitution in the 6 fold coordinated octahedral sheet.

It's normally independent of pH, while it can depend on the concentration of cations, the properties of the anion and cation, and the properties of the clay mineral.²⁸ The idealized combination of the tetrahedral and octahedral sheets creates structure with overall charge balance, as is normally the case in crystals, see figure 6 below.²⁹

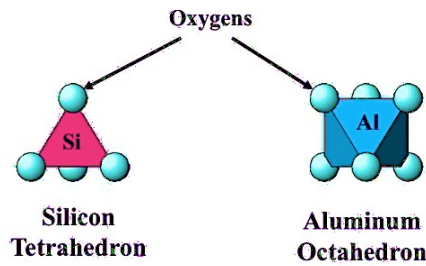
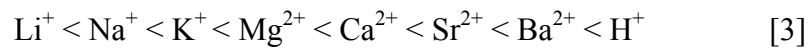


Figure 6: Structure of tetrahedron and octahedron

As observed in figure 6, in the tetrahedral layer Si^{4+} may be replaced by Al^{3+} , and in octahedral layer Al^{3+} replaced by Mg^{2+} , which together with the oxygen O^{2-} ions, results in a structure with a negative charge deficiency. This produces a crystal surface with a net negative charge, which in the reservoir attracts hydrated cations as well as organic functional groups. Clay minerals as part of multi-mineralic grains are responsible for most of the exchange capacity of sand and siltstones, as well as shales/claystones/mudstones. At low pH values, the H^+ relative strength of cations adsorbed (when present in equal concentration) by clays is as follows:



The amount of positively charged ions the clay is capable of adsorbing is called CEC. CEC is measured in chemical equivalent of base adsorbed at pH 7. It's expressed in milli-equivalents (meq) per 100 g of dry clay³⁰. CEC is one of the fundamental factors affecting low salinity waterflooding, as suggested by Austad et.al.²⁷

It's reported by Kennedy³¹ that CEC increases as grain size decrease. The CEC of sand fraction (63 μm - 1mm) ranges from about 0.3 to 13 meq per 100 g, and of silt fraction (4 - 63 μm) from about 4 to 30 meq per 100 g. As mentioned before according to Carroll³² silt fraction of quartz ranging with size (2 – 63 μm) has a cation exchange capacity (CEC) of 0,6 meq per 100 g and in clay fraction of quartz with size lower than 2 μm , has 5,3 meq per 100 g. Cation-exchange capacity commonly increases as grain size decreases, but this relation is empirical and not yet sufficiently researched. It is important to mention that ion exchange in clays and other minerals is also dependent on the crystalline structure of the mineral, and the chemical composition of any solution in contact with the mineral surfaces.¹⁶

2.4 Wettability

Wettability is defined by Craig (1971)³³, as “the tendency of one fluid to spread or adhere to a solid surface in the presence of other immiscible fluids” The wetting preferences influence many aspects of reservoir performance, such as relative permeability’s, capillary pressure, irreducible water saturation Making wrong assumption of wettability in reservoir will lead to irreversible reservoir damage. Although a number of factors are involved, rock wettability is thus shown to reflect considerable influence on the manner in which oil is displaced; if the rock is water preferentially water –wet, water displacement will be much more efficient than gas displacement.³⁴ Wettability characteristic essentially establishes position, flow and distribution of fluids in reservoirs at pore level. It will also affect core analysis, where capillary pressure, relative permeability, water injection pattern and tertiary recovery will be changed.

When two immiscible liquids are present in a solid surface, one liquid can either expand over whole surface or form small drops on the surface.³⁵ The stronger attached phase is called wetting phase. In reservoir we can find 3 types of wetting properties as its can be seen in figure 7; water–wet, oil –wet and mixed –wet.

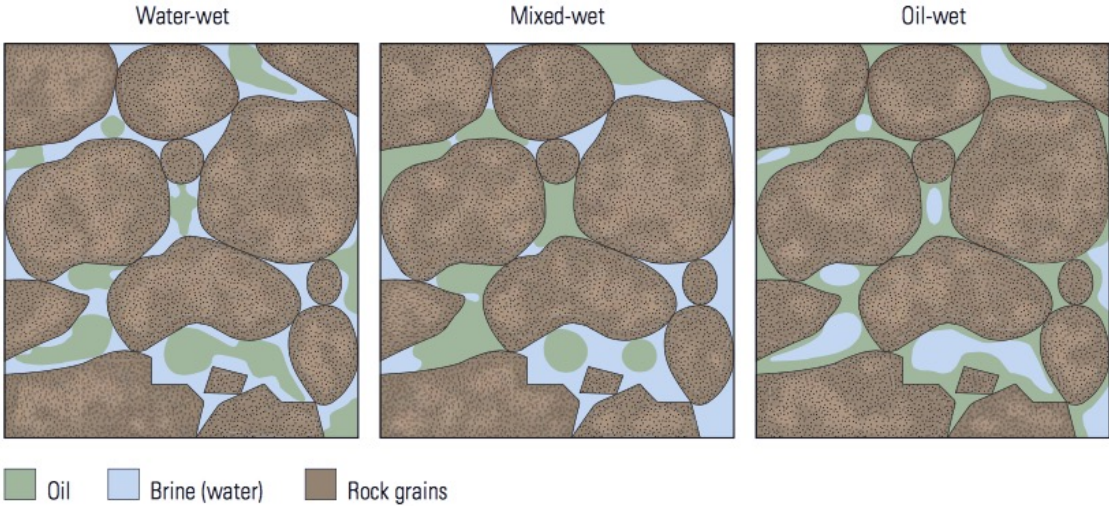


Figure 7: Wettability in pores (Schlumberger 2007)

In water –wet; water occupies completely smallest pores and is present as thin film covering grains, while oil droplet is in the middle surrounded by water. In oil –wet; oil occupies smallest pores and is present as thin film covering grains, while water droplet is in the middle surrounded by oil. In mixed –wet; surface is either water –wet or oil –wet due to variation of the chemical properties of mineral. The smallest pores are occupied by water, while the larger pores are occupied by oil.

Contact angle (θ_c) separates the different phases into water–wet, oil–wet and Neutral –wet as presented in figure 8. In static equilibrium liquid/water/ solid can be found by the Young’s equation².

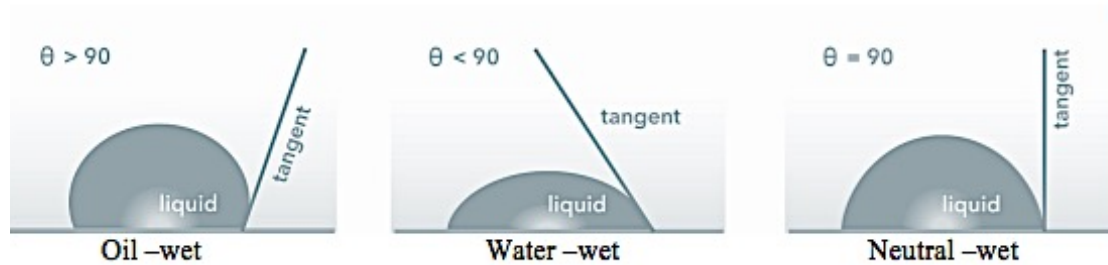


Figure 8: Correlation between interfacial tension and contact angle

$$\sigma_{ow} * \cos\theta = \sigma_{os} - \sigma_{ws} \quad [4]$$

Where:

σ_{ow} : Interfacial tension between the oil and water.

σ_{os} : Interfacial tension between the oil and solid.

σ_{ws} : Interfacial tension between the water and solid.

θ_c : Contact angle

Table 2: Wettability expressed by contact angles

Contact angle (°)	Wettability preference
0 - 30	Strongly water –wet
30 - 90	Water –wet
90	Neutral wettability
90 - 150	Oil –wet
150 - 180	Strongly oil –wet

There are several wettability measurement methods have been developed for determining wettability in the system both quantitatively and qualitatively. Quantitative wettability methods are Amott test, U.S. Bureau of Mines (USBM) and Contact angles. Qualitatively wettability methods are wettability directly measured from on rock sample using reservoir fluid.

2.5 Wettability alteration

Reservoir rocks are highly heterogeneous due to the variation in porosity, permeability, mineralogy and wettability. Numerous factors affect the total wettability of sandstones; among the important parameters are composition of crude oil, formation brine composition, initial water saturation, reservoir temperature.⁴⁰ Essentially wetting condition depends on the interactions which have been established during millions of years.

- Mineral Type

Mineral composition and surface charge of the rock material is central in wettability alteration. Sandstone consist mainly of three main minerals; quartz, feldspars and clay. Surface area of each mineral is different and will react contrarily. Clay has the highest surface area, following feldspars and quartz.³⁶

Clay >> Anorthite > Microcline > Albite > Quartz

All minerals can exhibit ion exchange behavior to some degree, as different ions exchange sites at the surfaces can be formed by chemical substitution, as well as the presence of unhealed broken chemical bonds by mechanical fracturing. Minerals with fixed charge, such as the clays, have high degrees of ion exchange. According to Austad et al.²⁷ clay minerals are also the main wetting factor in sandstone because of their extremely large and charged surface areas, which are strongly adsorbed by polar organic compound of crude oil. While feldspar and quartz will get negative charge at relevant pH.³⁶ Reported by Neadeau³⁷ type of clay (Kaolinite, Chlorite, Illite or Montmorillonite) have different cation as well as anion exchange capacity, which will affect wettability in their distinctive ways.

Experiments conducted by Aksulu et. al.⁵¹ shows that the presence of anhydrite in the rock will decrease the size of pH gradient and rate of desorption of divalent ion Ca^{2+} .

- Oil composition

Primary all reservoirs are believed to be strongly water –wet and as oil occupies in to the reservoir, over time certain polar components change the wettability by adsorption to to the surface rock.⁴⁰

Crude oil consists of complex combination, more importantly, it has been reported that elements like asphaltene and resin have the ability to change the wettability of initially water-wet rocks. These heavy polar molecules contain oxygen, nitrogen and sulfur, NSO compounds and are acidic and basic in nature. The acid/base interactions are important for the charge of both the rock/brine and brine/oil interfaces.³⁸

- Formation brine chemistry

Initial pH, salinity composition and concentration of divalent and other multivalent in brine can increase, decrease or change the surface charge of the rock. In case of decrease of salinity in the residual water the rock surface gets more water-wet and have a significant effect on the recovery.

Recently suggested mechanism by Austad et. al.²⁷ approaching the effect of pH increase due water- clay interactions, where desorption of multivalent cations occurs as LS brine enters in to the reservoir rock. This mechanism has been verified by earlier research, that acidic/basic and adsorption/desorption of organic material is pH dependent.

- Reservoir temperature

Increases in temperature affects both interactions between oil, brine and solid due to kinetics, consequently improving both adsorption and desorption. For example, as temperature increases IFT between oil and brine increases, rock surface behaves more water –wet and increase in solubility of wettability altering compounds in the crude oil. At the same time increase in temperature decreases pH gradient and desorption rate.⁵¹

- Reservoir Pressure

Depending on oil composition and temperature, some oil will experience asphaltene destabilization as the pressure decreases and approaches the onset asphaltene precipitation.

- Initial water saturation

As mentioned previously, primarily reservoirs are believed to be strongly water –wet. The initial water film separate polar crude oil components from interact with rock surface. It has been reported by several researchers that there is a certain range of initial water saturation which gives lowest residual oil saturation by waterflooding.

3. SMART WATER FLOODING

Wettability alteration of reservoir is of great importance in low salinity flooding, if there is to be seen any effect of low salinity the reservoir must be mixed –wet. Initially there is a chemical equilibrium between the crude oil, brine and the rock, which have been established during millions of years.^{43,39} The wetting condition depends due to this complex interaction, including crude oil composition, temperature, pressure, brine chemistry and pH.^{40,41}

Current studies confirm that smart or low salinity waterflooding gives widely distinctive oil recoveries by altering the initial wetting between crude oil, brine and rock (CBR). Increase in recovery can be achieved when CBR – system was slightly water-wet.^{42,43} It has also been suggested and reported by many researchers that the alteration of composition of the water can have a significant impact on wettability and oil recovery.^{44,45,46}

According to Tor Austad⁴³ Smart water is chemically alteration of the injected fluid in such a way that the change in equilibrium of the initial CBR interactions will modify the initial wetting condition. It has a positive effect on the capillary pressure and relative permeability, and results in increased recovery. Smart water can be acknowledged as tertiary recovery since extra oil is recovered after applying secondary water flood with FW. Smart water can simply be made by modifying the ion composition of injected water, its environmental friendly and cheap. Salt contents in smart water ranges from 1000-5000 ppm and it is basically having a small amount of salts compared to formation water FW.

Different mechanism have been suggested during the past years and the smart water effect is possibly a result of combination of processes interacting together, each with its specific contribution⁴⁷.

Some of the most relevant proposed mechanism are:

- Migrations of fines by Tang and Morrow⁵²
- Multi-ion exchange (MIE) by Lager et. al.⁵³
- Extension of the electrical double layer by Ligthelm et al.⁴⁸
- Alkaline flooding by McGuire et al.⁴⁹
- Salting –in Effect by RezaeiDoust et al.⁵⁴

- Wettability alteration due to local pH Increase at rock surface by Austad et. al²⁷

3.1 Migrations of fines

Tang and Morrow⁵² reported that when injecting low salinity brine, clay fragments (fines) in the produced water were observed on Berea sandstone cores. The study as well shows permeability reduction and a sharp increase in pressure drop. Migration of fines may result from unconsolidated or unstable formation, or from incompatible fluids that liberates fine particles. The authors concluded that when clay minerals come in contact with low salinity brines shown in figure 9, causes oil droplets on these clays to discharge and contribute to more water –wet system. From the field experiment they concluded that enhanced oil recovery could be archived without fine migration.

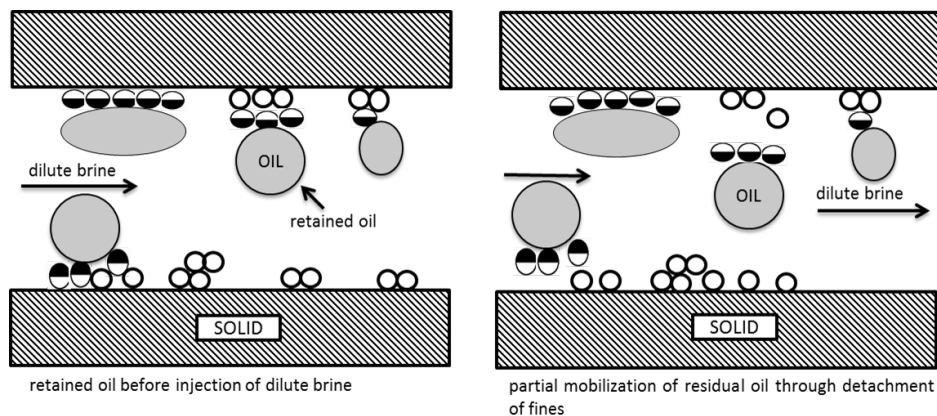


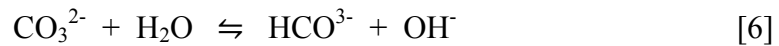
Figure 9: Detachment of clay particles and mobilization of oil.

According to Skauge et al.⁵⁰ mobilization of fines will block pore throats and might divert the flow of water towards the unwept area. This will result in increase of total oil recovery by improving the microscopic sweep efficiency.⁴⁷

3.2 Alkaline flooding

McGuire observes from North Slope field samples an increases in pH in low salinity waterflooding similar to alkaline flooding. In addition, experiments conducted by Tang and Morrow on Berea sandstones detected a pH increases by low salinity injection. Increases of the pH in reservoir can give improved recovery by surfactant flooding and interfacial tension reduction.

Lager et al. explains pH increases by carbonate dissolution and cation exchange. Carbonates are present as a cementing material in sandstone rocks, dissolution is dependent on the amount of carbonate in rock. By introducing low salinity water in reservoir following chemical reaction takes place.



Increases of OH^- as presented in equation 6 and 7 causes the pH to increases.

3.3 Multi -Component ion exchange (MIE)

Multi -component ion exchange is defined by Lager et al.⁵³ “is the basis of geochromatography and involves the competition of all the ions in pore water for the mineral matrix exchange sites”. Multi ionic exchange between mineral surface and low salinity water flooding causing to desorb organic material and causing increased oil recovery. Multi ionic exchange increases water wetness of clay minerals and cations acting as bridge between negatively charged clay minerals and carboxylic material.

Experimental study conducted by Lager et al., observation made that the brine injected and the connate water had similar Mg^{2+} concentrations. There were detected decrease of Mg^{2+} in concertation of effluent, showing that Mg^{2+} was adsorbed by the rock matrix. Similar study by BP and Harriot Watt University shows a slighter reduction in Ca^{2+} concentration. Following results Lager et. al. suggested that the oil recovery is caused by competition of all the ions in

the brine for ionic exchange with the rock surface during the brine flooding. Figure 10 shows suggested mechanisms of organic matter adsorbed onto clay mineral.

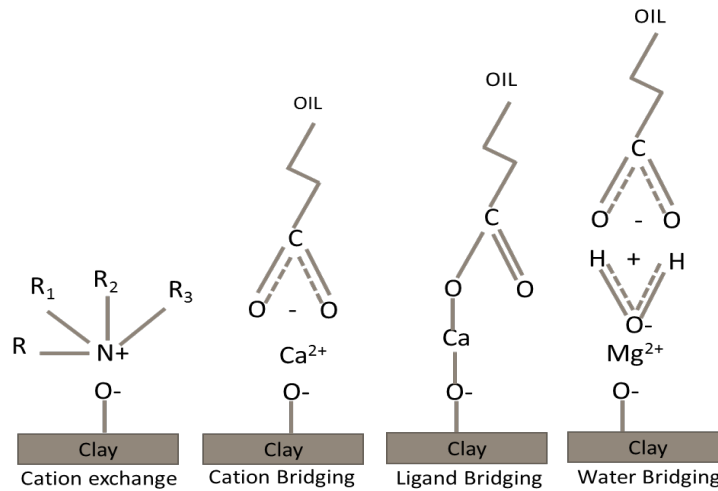


Figure 10: Attraction between clay surface and crude oil by divalent cations.

3.4 Double –layer effects

Lowering the salinity in brine, the concentration of ions relative to the initial formation brine is reduced. Multivalent cations such as Ca^{2+} and Mg^{2+} will act as bridge between negatively charged oil and the clay minerals creating a double layer. Ligthem et. al.⁴⁸ concluded decreases in low salinity injection will increase the ionic double layer between the clay and oil interfaces and might result in desorption of organic material. This desorption will increase the water wetness of the reservoir and increase the oil recovery.

3.5 Salting –in effect

The solubility of organic material in water is dependent by formation of water structure around the hydrophobic part due to hydrogen bonds between water molecules. As it can be observed from figure 11, water molecules have the ability to build water structure around the hydrophobic tail of the organic molecules, hydrogen bonding increases with decreasing salt concentrations. This increases the solubility of the material and result desorption of material.

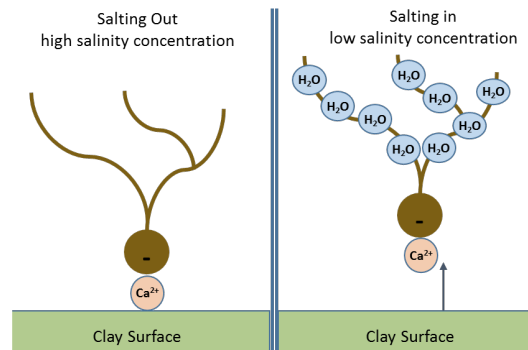


Figure 11: Illustration of the mechanisms Salting –out and Salting –in.

Salting –in effect is defined as decrease in salt below a critical ionic strength will increase the solubility of organic material in the aqueous phase and desorption of carboxylic material. Salting –out is referred to decreased solubility of organic material by increased in salinity. Cations such as Ca^{2+} , Na^{+} and Mg^{2+} break up the water structure around the organic molecule, and decreases the solubility.⁵⁴

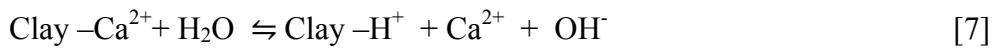
3.6 Wettability alteration due to local pH Increase at rock surface

Based on experiments conducted by Austad et. al. in 2010 new chemical mechanism was suggested that can explain the increases in recovery in low salinity floods. Mechanism clarifies desorption of initially adsorbed cations from clay surface with pH increases of the water. Following parameters will affect the mechanism²⁷:

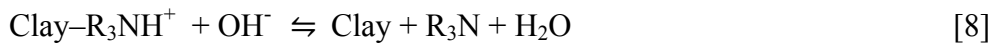
- Clay properties and amount present in the rock
- Polar components in the crude oil, both acidic and basic
- The initial formation brine composition and pH

- Improved of water wetness of the clay minerals

Initially both basic and acidic organic material are attached to clay surface with cation ion Ca^{2+} . An equilibrium of CBR system already existing at reservoir condition, which is supported by, pH, temperature, pressure etc. Equilibrium of CRB system will be disturbed by low salinity brine diluted in Ca^{2+} . As illustrated in figure 12, due to reduction of Ca^{2+} in injected brine an exchange between adsorbed cations Ca^{2+} in the clay surface desorbs. To balance the charges proton ions H^+ from water adsorb to clay surface. Following chemical reaction takes place:



Following chemical reactions in local increases in pH are the cause of desorption of the organic material from clay:



As illustrated in figure 12 desorption of basic material occurs as in equation 8 and in lower part desorption of acidic material as in equation 9 and are sensitive to pH changes. Hence, desorption of primarily adsorbed cations from the clay surface is the key process in the pH increase of the water. This is concluded with an increases in pH are required to removed adsorbed organic material.²⁷

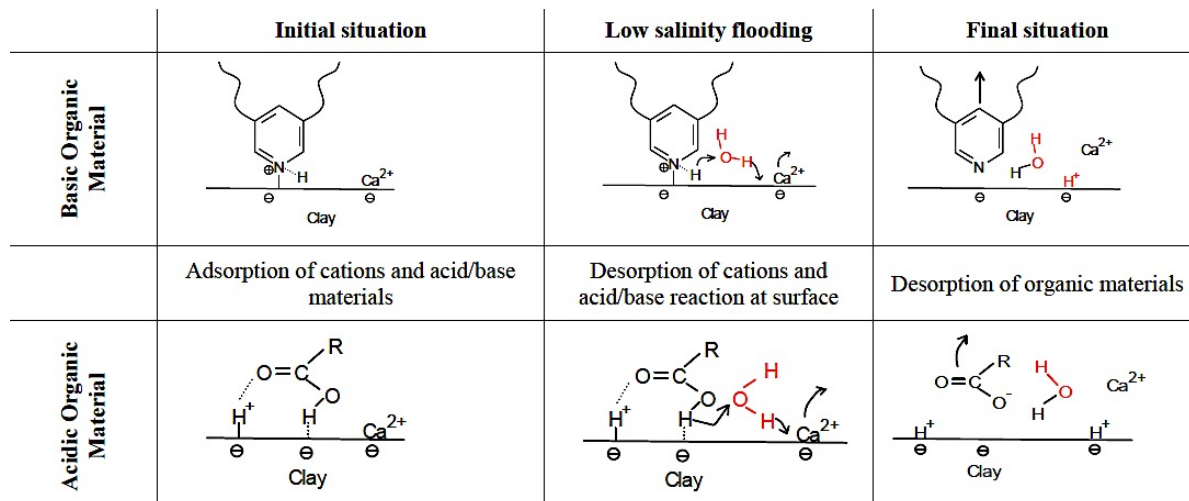


Figure 12: Proposed mechanism for low salinity EOR effects.

Aksulu et al⁵¹ studied this mechanism by researching the adsorption of basic polar organic material onto clay mineral illite. With various range of pH for LS brine and HS brine as presented in figure 13. Observation confirms that there is a strong dependence of pH and adsorption of base onto illite. Figure 13 shows that there is higher adsorption with LS brine compared to HS brine.

Further Austad et. al. observed desorption of both basic and acidic crude oil occurs at the range of pH 5-6 to 8-9. This confirms that an increase in pH number will desorb cations, which results in discharge of organic components from rock surface.

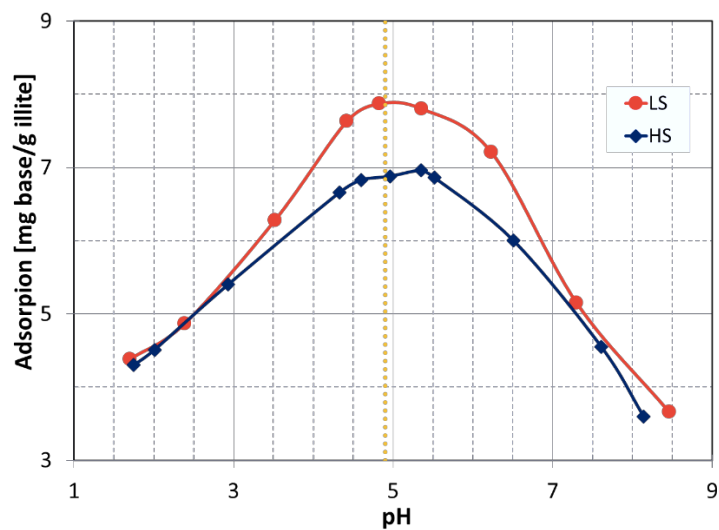


Figure 13: Adsorption of basic oil components vs pH at ambient temperature.

3.7 Condition for low salinity effects

Several proposed condition has been suggested by researchers based on experimental work. Austad²⁷, Tang and Morrow⁵², Lager et al.⁵³ listed condition for low salinity effect as follows^{54,43}:

- Porous medium
 - Clay must be present and type of clay may effect differently
 - Pu et. al (2008)⁵⁵ have observed low salinity effect in sandstones containing dolomite crystals.
- Oil
 - Must contain polar components (Acid/Basic)
- Formation water
 - Must contain divalent cations, i.e. Ca^{2+} , Mg^{2+}
- Low salinity injection fluid
 - Salinity 1000 and 2000 ppm
 - 5000 ppm have also given results
- Produced water
 - For non-buffering system, pH slightly increases with 1-3 units
 - It has not been verified that an increase in pH is needed to observe low salinity effects.
- Permeability decrease
 - Increases/decrease of pressure have been observed over the core by switching form high to low salinity, may reveal change in permeability
- Temperature
 - According to the earlier studies there haven't been fixed any temperature limitations to observe low salinity effects.
 - Recent study performed by Aghaeifar et al. (2015)⁵⁶ shows that the LSE decreases with increase temperature.

3.8 Feldspar contribution

Latest study conducted by Strand et. al.⁵ investigates influence of plagioclase minerals on pH of formation water, initial wetting condition of reservoir and pH increases as the HS is exchanged by the LS water. This study concludes that plagioclases such as albite as well as microcline with alkali metals Na⁺ and K⁺ can substitute with protons, H⁺. This influences the initial pH, it can rise above 7 if the salinity of the FW water is moderate. As an example, albite contributing with its substituting cation Na⁺ which gives a more alkaline solution according to the following reaction:



High pH makes the rock more water-wet, preventing polar components in crude oil to adsorb on to charged reservoir surfaces. The adsorption of acidic and basic components from hydrocarbon to clay minerals decreases⁵. High formation water salinity will suppress the pH below 7, which can result in mixed –wet wettability, thus significantly lower salinity EOR effect can be observed when HS water is displaced by LS water.

Experiments carried out by Skrettingland et. al.⁵⁷ on cores from Snorre field with FW 35 000 ppm and Ca²⁺ concentration five times higher than sea water. Result in very small low salinity EOR effect, only 2% OOIP recovered. High pH was determined in the produced water showing pH around 10. The increases of pH have as well been observed by Reinhorltdsen et. al⁵⁸ from the same core. It shows that Snorre field has high content of plagioclase, approximately 35%. Advance investigation by Strand et al.⁵ shows that plagioclase minerals have a buffering effect at moderate salinity brine.

Quan et. al⁵⁹ reports after core flooding experiment in XiFeng oil field that low salinity waterflooding is a promising technology to improve oil recovery for reservoirs with high plagioclase mineral. Quan et. al⁵⁹ performed experiments on samples containing high amount plagioclase ranging 20-25 wt%. Study showed an increase in oil recovery by 15% of OOIP for LS waterflooding. Experiments performed with FW 60 000 ppm and initial pH 6.5. pH of the effluent was measured 9.5 an increase with 3 pH units. Clearly in this case plagioclase contributed to increase in pH when high salinity formation water was replaced by low salinity

formation water. This indicates that salinity in FW was slightly high to maintain the pH below 7.

Concluding from these works that occurrence of feldspars can have both positive and negative effect on recovery depending on the salinity of the formation water. In case of Snorre field with FW 35 000 ppm gave only 2% recovery, while in XiFeng field with FW 60 000 ppm resulted in an increase of 15 % recovery of OOIP.

Recently, master student Andrew Wealⁱ studied pH development in sandpacks using feldspar minerals. The result for feldspar mineral, anorthite is presented in figure 14. pH increases each time LS (1000 ppm) is injected, at highest pH is almost 11 at temperature 90 °C. Observed from the results pH increases with temperature until 90 °C. pH at temperature 130°C less than ambient temperature. When FW (100 000ppm) water is introduced in sandpack pH decreases. The result is similar to the investigation done by Strand et. al. on influence of plagioclase minerals on pH of formation water, pH increases as the HS is exchanged by the LS water.

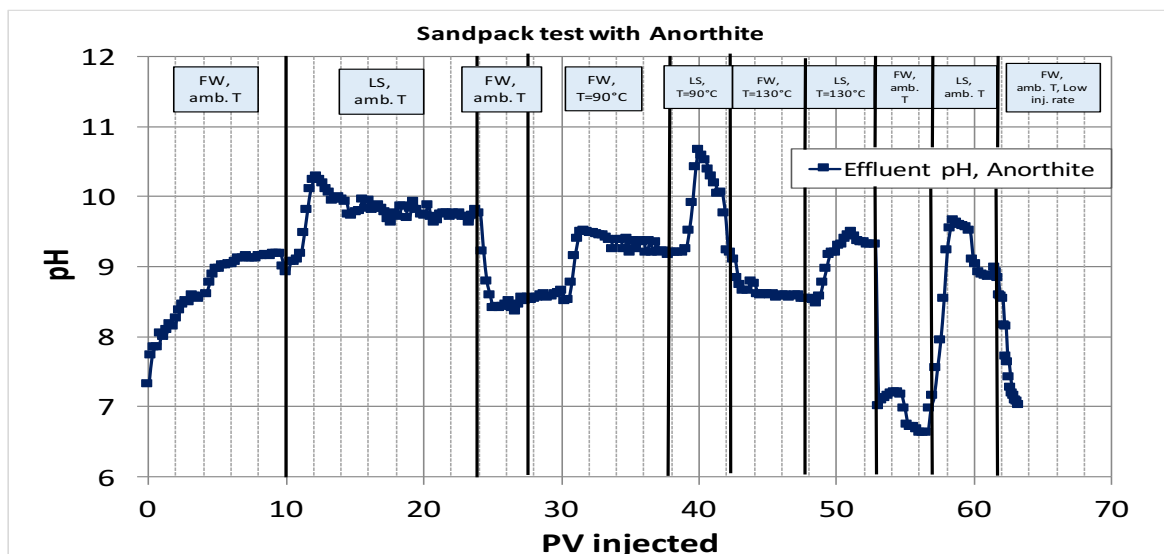


Figure 14: pH change in sandpack when HS is exchanged by LS.

ⁱ Master' Thesis "pH development in sandpacks through smart water using feldspar minerals"

4. Experimental

Polar oil components could be the anchor molecules which causes wettability alteration at the surface of the mineral. In this thesis adsorption experiments are performed on quartz and feldspars, such as albite, anorthite and microcline. This section describes performed experiments to investigate adsorptions of quinoline onto the minerals. The experiments have been conducted under ambient temperature, performed methods in addition to the used materials and equipment is presented in this part of the thesis.

4.1 Materials

4.1.1 Minerals

Quartz

Quartz is known to be one of the most stable minerals and are expected to have very low adsorptive capacity of polar organic component. It is provided by Sibelco Company previously known as North Cape Mineral and is 98 % pure silica from Norway.

Feldspars

Experiments have been conducted on three most common minerals of feldspars such as Albite, Anorthite and microcline. The minerals have been provided by *WARD'S Natural Science*. Albite is from Bancroft and microcline from Madawaska, Ontario, Canada. While Anorthite is from Grass valley, California, USA.

4.1.2 Brines

Reagent salts was provided by Merck *Schuchardt OHG*. Brines was synthetically prepared by dissolving required amount of salts in DI –water. The brine composition and the amount salts used is given in the table 3 and table 4, below.

Table 3: Amount of salts in brines

Salts	LS		HS		NaCl	
	g/l	mole/l	g/l	mole/l	g/l	mole/l
NaCl	0,798	0,0137	20,750	0,355	30,00086	0,5133
MgCl ₂ *6H ₂ O	0,348	0,0017	9,050	0,045	-	-
CaCl*2 H ₂ O	0,255	0,0017	6,620	0,045	-	-

Table 4: Ion composition

Ions	LS		HS		NaCl	
	g/l	mole/l	g/l	mole/l	g/l	mole/l
Cl ⁻	0,728	0,0205	18,938	0,5342	22,123	0,624
Mg ²⁺	0,042	0,0017	1,082	0,0445	-	-
Na ²⁺	0,314	0,0137	8,162	0,3551	14,345	0,624
Ca ²⁺	0,069	0,0017	1,805	0,0450	-	-
TDS [ppm]	1 150		30 000		36 500	
Ionic strength	0,024		0,624		0,624	

4.1.3 Quinoline

Quinoline is used as polar basic component in the experimentations. It is a nitrogen containing heterocyclic Polycyclic aromatic hydrocarbons (PAH) whose weakly basic N-atom is protonated to cationic form under acidic condition.⁶⁰ It has molecular formula C₉H₇N, molecular weight 129,161 g/mole and density 1.1 g/cm³. The pK_a of quinoline is measured to be 4,87, indicating that this compound will moderately occur in the protonated form and cations typically attract to organic carbon and clay more strongly than their naturally counterparts.⁶¹

Quinoline (>90%) is provided by *Merck Schuchardt OHG*. Required amount of quinoline with pK_a =4.87 was measured and dissolved approximately in 400 ml distilled water (DI) in a 500 ml volumetric flask. The pH was adjusted to 5, and put for 24 hours in stirring. Outcome is quinoline stock solution with concentration of ~ 0,07M and density 1.0005 g/cm³. As mentioned in part (2.3) fraction of protonated base increases as the pH of the solution decreases below the pK_a value and reaches 100% around pH 3,5⁶².

4.2 Equipment

To perform the experiment, following equipment was used as displayed in figure 15- 20:

-was used as sample container



Figure 15: glass container 10 [ml]

- pH meter was used to measure and adjust pH



Figure 16: Mettler Toledo pH meter

- analytical balance used to weight experimental materials



Figure 17: Mettler Toledo AB104 balance

- Rotator used to mix samples



Figure 18: Stuart SB3 rotator

- Spectrophotometer was used to measure absorbance



Figure 19: Shimadzu UVmini-1240 spectrometer.



Figure 20: Shimadzu UV-1700 PharmaSpec UV-VIS spectrometer.

4.3 Experimental procedures

Adsorption of quinoline onto the sandstone minerals are measured stage by stage over a series of workstations which is described in this section.

4.3.1 Milling

Minerals were milled with the grinding device *Retsch PM100*, 40 g mineral and 35 ml chemical additives such as DI –water and methanol was placed in grinder with 12 metal balls. Rate was adjusted to 600 rpm in 1 minute intervals for a total of 7 minutes. Dried for 48 hours at 80 °C. For alternative procedure for comparison the minerals were also milled by hand with a mortar and pestle into various grain sizes without any chemical additives.⁶³

4.3.2 Brunauer – Emmet –Teller

Brunauer –Emmet –Teller (BET)⁶⁴ is commonly recognized as surface area analysis assumes that adsorption occurs by multilayer formation, and the number of adsorbed layers is infinite at the saturation pressure.

Based on BET theory *Micromeritics Tristar 2* was used for determining of the specific surface area of a material by measuring physical multilayer adsorption of non-corrosive gas on solid surface. In this case nitrogen and helium gas was used by measuring adsorption of gas molecules on the surface of the minerals at given pressure.

4.3.3 Scanning Electron Microscope

Milled minerals was photographed with Scanning Electron Microscope (SEM)⁶⁵, *Zeiss Gemini Supra 35VP* for closer look at the sizes distribution of mineral surface. SEM is one of the most important beam technology inventions and constantly been developed since 1960s. Scanning high resolutions image of samples' surface. In order to prevent erosion prior to scanning, samples were prepared with *Emitech K550*, vacuumed and coated with palladium in argon gas environment.

4.3.4 Calculation of surface area from SEM Images

Surface area calculated from SEM images.⁶⁶This was achieved by drawing a red line across the picture, as displayed in figure 21. Every particle that crossed the line was measured with respect to its diameter. If they are equant grains, then only one measurement is made, but if they are non-equant then the maximum and minimum diameters are measured. It's important to measure the maximum and minimum diameter to understand the material, because pronounced cleavage in feldspars can result in high aspect ratios compared to quartz grains which are more equant.

From SEM images it is important for statistical analysis to have a minimum 30 particles for homogeneous and 100 particle measurements for heterogeneous samples. It is also very important is the particles are selected randomly to ensure that the data are representative of the entire sample, hence the use of a red line on the image to guide the particle measurement data acquisition. All calculation are performed in excel and results are plotted as surface area [μm^2] versus percentage [%] particles. Excel sheets will be presented in appendix A.1 and the plots in result section.

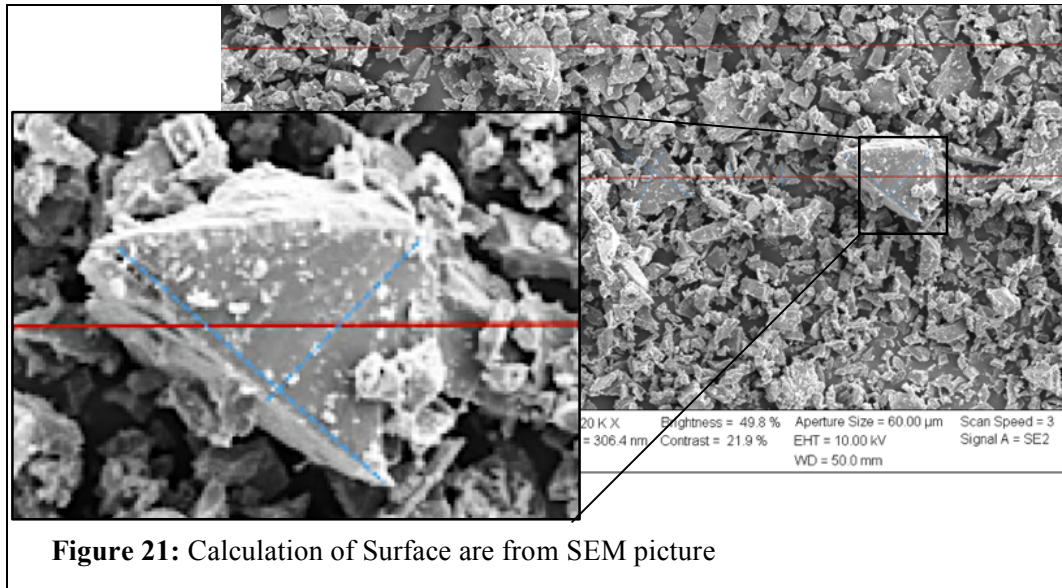


Figure 21: Calculation of Surface are from SEM picture

4.3.5 Sedimentation of particles

Mineral preparation comprises separation of fine fraction from coarser material. Settling is used to remove the fine fraction which has been created by the milling process and altered the material properties differently than expected. By performing settling for each mineral sample, this also results in more homogenous mineral/particle size distributions.

Settling is a process by which rock particles settle to the bottom of a liquid, water and form a sediment. In settling, the particles are separated from the fluid by gravitational forces acting on the particles. The settling time is calculated according to Stokes' law for the required size fraction. The procedure illustrated in figure 1 is repeated 3 time and the settled particles were dried for 48 hours in 80 °C.

This process may not be a problem for mud rocks but for sandstones separation procedure by Hardy & Tucker, (1998) should be followed⁶⁷.

Initially pre-treatment of minerals is required to remove impurities like carbonates by adding weak acid to prevent damage to clay minerals, which have not been done in this thesis⁶⁷.

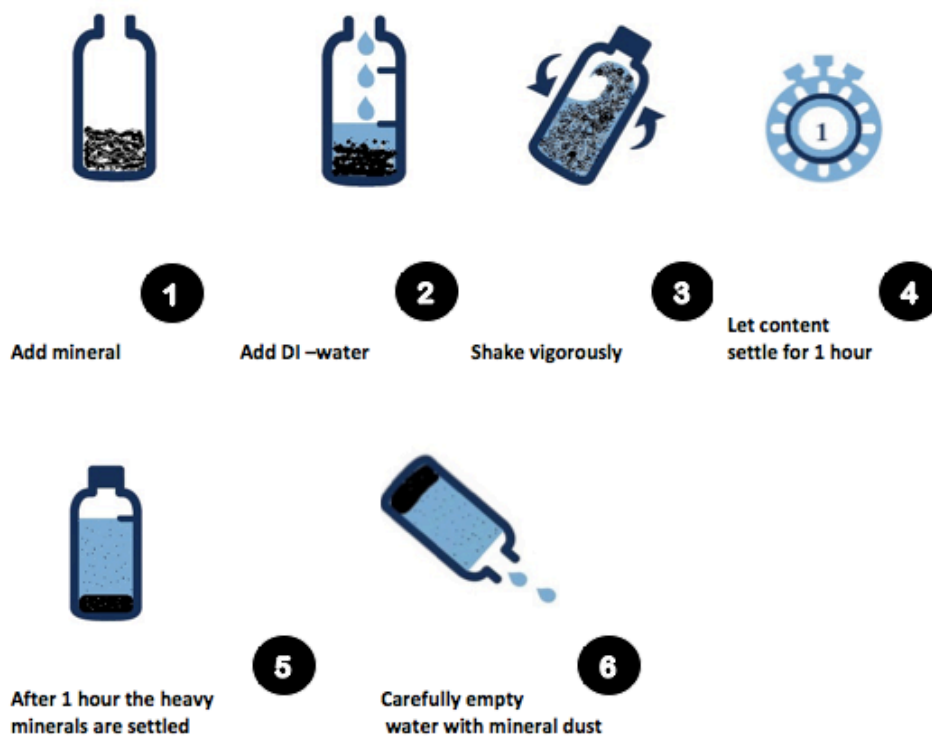


Figure 22: Illustration of settling process

4.3.6 Brine filtration

The brines were mixed and put for stirring more than 1 hour for LS, HS, NaCl and 24 hours for LSQ, HSQ and NaClQ. Filtered with a 0.22 μ m filter to remove particles and vacuumed to remove dissolved gas. Figure 23 illustrates filtration setup.

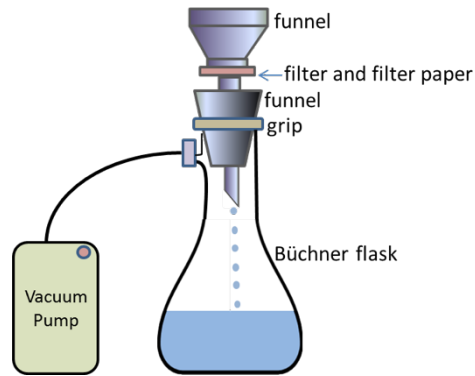


Figure 23: Brine filtration setup illustration

4.3.7 Density measurement

Densities for brines and brine – quinoline were measured by device *DMA 4500 Anton Paar Density Meter*. Before each measurement the device was cleaned by injecting 1-time white sprite and 2-times DI –water. The result for measured densities are presented in table 5.

Table 5: Measured densities

Solutions	[g/cm ³]
HS	1,0205
LS	0,9992
NaCl	1,0194
Q	1,0005
HSQ	1,01757
LSQ	0,99935
NaClQ	1,01667

4.3.8 pH measurement

pH is abbreviation for potential hydrogen and is expressed in chemistry as a numeric scale to specify the acidic or basicity of a solution. pH is equivalent to to the negative logarithmic value of the hydroxonium ion $[H_3O^+]$ concentration in aqueous solution:

$$pH = -\log [H_3O^+] \quad [11]$$

In an acidic solution the concentration of hydroxonium ion $[H_3O^+]$ is higher than the concentration of OH^- ion. A neutral solution has $pH = 7$ at $25^\circ C$. High concentration of the hydroxonium ion indicates that it has pH lower than 7 and if opposite the pH is higher than 7.

METTLER TOLEDO pH meter was used to measure and adjust pH in quinoline and samples. pH meter was calibrated frequently and initially cleaned with DI –water before taking any measurement to avoid unpredicted error.

4.4 Adsorption measurements

4.4.1 Absorbance

Absorbance wavelength was determined by measuring the maximum absorbance of 0,01 M quinoline in spectrometer in range of 100 -700 nm, the peak was determined in 312,5 nm. Device such as Shimadzu UV-1700 PharmaSpec UV-VIS and Shimadzu UVmini-1240 spectrophotometer was used.

4.4.2 Calibration curve

For calibration curve 4 samples were prepared with brine – quinoline solution as stated in table 6. For preparing 0,01M high salinity quinoline brine (HSQ) 1,3 ml of quinoline was mixed 7,96 ml HS brine. Samples were diluted in range 100-1000 with DI – water pH ~3. References were prepared in the same way consisting of brines and DI – water pH ~3 solution with the same range of dilution. Absorbance was measured in spectrophotometer and plotted versus concentration.

Table 6: Preparation of HSQ, LSQ and NaClQ

Brine	HSQ		LSQ		NaClQ	
Solution	Q	HS	Q	LS	Q	NaCl
Amount [ml]	1,3	7,96	1,3	7,79	1,3	7,95

4.4.3 Sample preparation and adsorption calculation

For adsorption analysis each sample was prepared by measuring 10 wt% mineral powder mixed with 90 wt% brine – quinoline 0.01 M solution. Adjusted pH with HCl and NaOH in range of 3-10 and they were rotated 24 hours with rotation speed 25-30 rotation per minute [rpm]. Then samples were centrifuged at 2500 [rpm] for 20 min. Supernatant was extracted to another sample glass, and 25 [μ l] was pipetted out and diluted 200 times with 4.975 g of DI – water pH ~3.

Excel sheet was used to calculate adsorption of quinoline onto mineral from quadratic equation obtained from calibration curve. The results reported as [mg] base adsorbed per [g] of mineral and plotted versus pH. All calculation is presented in Appendix A.2

4.5 Error test

Experimental work was started with chaotic result which was the background for searching for uncertainties in material, equipment and procedures. In this section all additional experiments and changes which have been done will be presented.

4.5.1 Repeatability test

The experiment was performed on unsettled microcline, since this mineral showed fewer unchanging values from previous analysis. Samples were prepared as described in section 4.4.3. There were 9 identical samples prepared with 10 wt% microcline dissolved in 90 wt% of 0,01M LSQ solution. pH in the sample was adjusted to 4,85 by adding 10 μ l HCl and

after 24 hours it increased to 5,20. Calculation was performed in excel program presented in Appendix A.7.

4.5.2 Time test

The aim of this test is to confirm if the adsorption of polar oil components is time depended. Samples was made according to section 4.4.3, and centrifuged for 20 min right after it was vigorously shaken. Absorbance was measured and put for 3 hours in rotation. Then it was again centrifuged and absorbance measured. Finally, it was rotated for 24 hours and absorbance was measured for the last time.

4.5.3 Acid test – for carbonate minerals

Formation of gas was observed during adjusting pH for feldspar samples. In search of which feldspars was forming gas, acid test was carried out. Illustrated in figure 24, desired amount of each pulverize feldspar was put in a test glass and droplet of HCl acid was added.

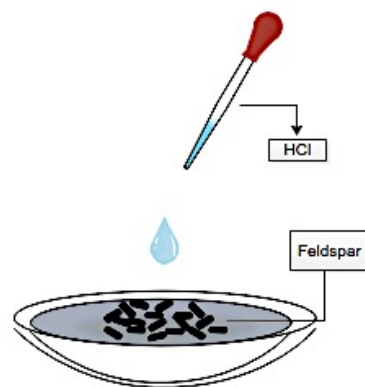


Figure 24: Illustration of acid test

5. RESULTS

Waterflooding of oil reservoirs has long been performed for pressure support and for oil displacement. The water is usually following the higher permeable zones, or fractures, from the injector to the producer, also influenced by the initial wetting preference of the rock surface. Injecting Smart Water that is different from the formation water into the reservoir will disturb the established chemical equilibrium and interactions will take place between the oil, water and rock. Research has shown that the injected water composition may be modified to alter the wettability of the rock towards a more water-wet state, thus creating positive capillary forces, and water can move into previously unswept pores and improve oil recovery due to improved sweep efficiency.

The initial wetting may be water-wet, oil-wet or mixed wet, and to be able to enhance oil recovery by wettability alteration with Smart Water, the reservoir must be mixed-wet to some extent. The objective of this thesis is to investigate how sandstone minerals (clay, feldspar and quartz) are influenced by adsorption of polar organic components from the oil.

Experimental procedure initially was established according to the previous experiments which has been conducted by several PhD, master and bachelor students on clay minerals. In this thesis the same procedure was followed on feldspars and quartz minerals. The minerals were milled, the brines were prepared and used in the same way which were used for clay. In this section the results are presented in chronological order, according to the experimental stages, which have been performed. The results are compared with the results of Guvnor Oline Frafjordⁱⁱ who has tested adsorption on to Kaolinite, Yngve Andersenⁱⁱⁱ who has observed pH changes in feldspars.

ⁱⁱ Bachelor's thesis "Wettability and low salinity EOR effects in sandstone reservoir. Adsorption of polar compound onto Kaolinite clay"

ⁱⁱⁱ Bachelor's thesis "Smart Water in Sandstone Reservoirs. Contribution of Feldspar Minerals to pH."

5.1 Calibration of spectrophotometer

Preparation of calibration curve are described in section 4.4.2. Samples were diluted in range 100-1000 with DI – water pH ~3. References were prepared in the same way consisting of brines and DI – water pH ~3 solution with the same range of dilution. Maximum absorbance was measured in spectrophotometer at 312,5 nm and plotted versus concentration.

Spectrophotometric device has two cuvettes in, one for reference and one for the sample. First device is set to auto zero, the cuvette with the sample and reference are diluted with deionized water with a pH ~3 so that the weight of fluids in total are almost exactly 5g. Four samples with LS, HS of NaCl was plotted against the concentration at different dilution. The calibration curve are linear curves, with three lines which points lie on, see figure 25. On the basis of these three linear lines we get three linear equations that help us to calculates concentrations when we know absorbance of the samples.

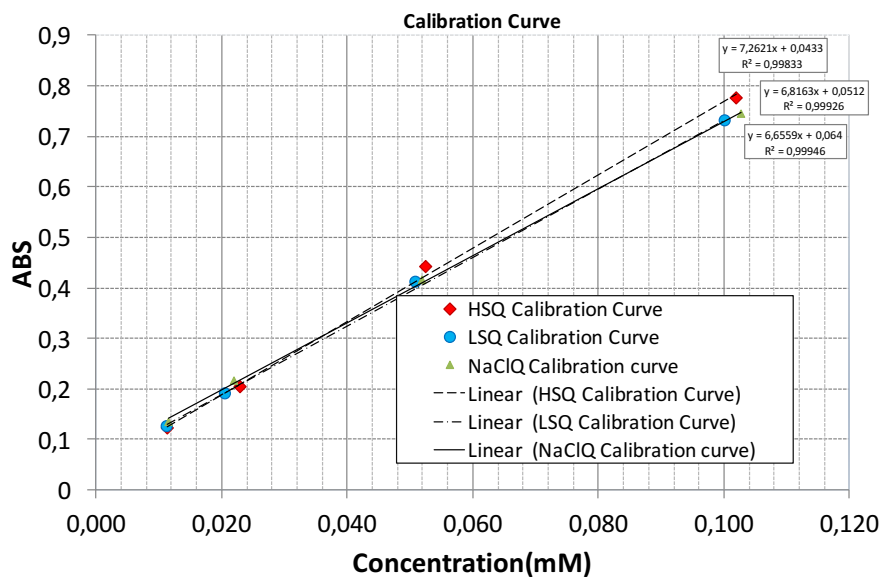


Figure 25: Calibration curve of spectrophotometer

5.2 Preliminary test

Plagioclase has impact in reservoir pH where the cation such as Na^+ and K^+ contribute with increases in pH by exchanging with H^+ from injected brine. This effect have been confirmed by several researchers such as Strand⁵, Quan⁵⁹, Skrettingland⁵⁷ and Reinhorltdsen⁵⁸.

Before starting to measure absorbance of quinoline onto plagioclase, pre-elementary test was carried out in order to confirm the possibility to supress the pH in brine –quinoline solution with plagioclase. One sample from each brine and mineral were prepared according to section 4.4.3 with 0.01M quinoline solution in LS, HS and NaCl brines. Table 7 shows modification of sample with albite. As presented in table 7, HCl was added and pH was reducing as amount of HCl increases with 25,60,105, 120 μl . At the end pH of samples were measured after rotating for 40 minutes and overnight. Table shows result over modification of pH of albite with three different brines. Observed from table below pH did not increase significantly after rotation.

Table 7: pH modification of brines with albite by adding HCl

<i>LSQ</i>		<i>HSQ</i>		<i>NaClQ</i>	
HCl [μl]	pH	HCl [μl]	pH	HCl [μl]	pH
initial	7,64	initial	7,0	initial	7,82
25	6,34	25	6,25	25	6,34
60	6,03	60	5,90	60	5,87
105	4,37	105	4,40	105	4,29
120	4,20	120	4,00	120	4,01
40 min.	4,43	40 min.	4,06	40 min.	4,20
24h	4,79	24h	4,10	24h	4,32

5.3 Adsorption of quinoline onto feldspars milled in methanol

Performed numerous experiments to verify if adsorption of polar components onto feldspars are pH and salinity dependent. Feldspar minerals milled with methanol according to the section 4.3.1 a 45 g feldspar milled with 35 ml methanol. Surface area determined by BET method as described in section 4.3.2. Feldspars photographed in SEMⁱⁱⁱ, figure 26 for closer observation of the size distribution. From the scale in figure 26 we can organise the particle size in a range of 1-10 μm , particle dust can be observed which might be less than 1 μm . These small particles are difficult to quantify by the naked eye and can impact BET surface area. In table 8 surface area for feldspars are presented where albite has the highest surface area, followed by microcline and anorthite.

Table 8: BET surface area of feldspar minerals

Feldspar	BET Surface area [m^2/g]
Albite	5,214
Microcline	4,661
Anorthite	3,265

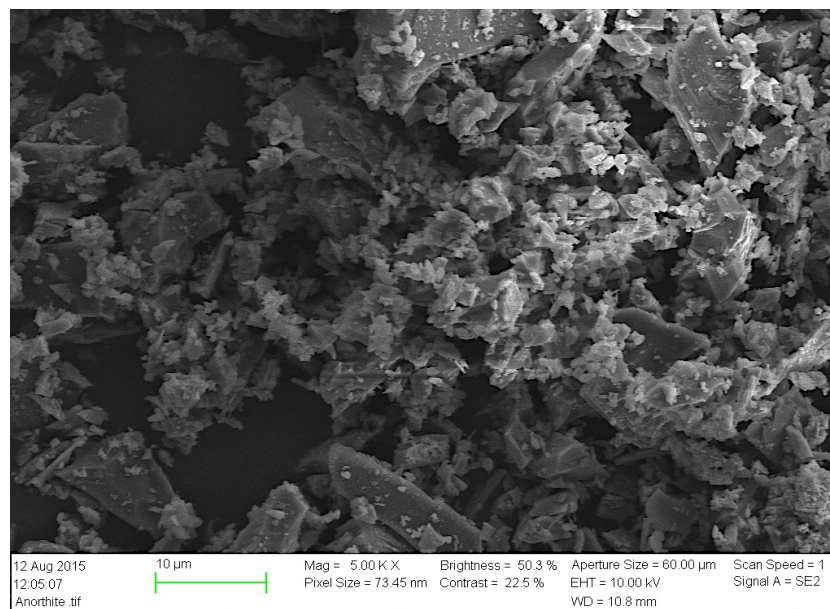


Figure 26: SEM image of anorthite milled in methanol

Test samples was prepared according to section 4.4.3 with 0.01M quinoline solution in LS, HS and NaCl brines and pH was adjusted to 3,5 and 7. Each experiment consisted of 27 samples; 9 samples for each minerals consisting with 3 different salinities and 3 different pH. Adsorption for all three feldspars was analysed several times at ambient temperature and plotted versus pH. In figure 27 and 28 plot of anorthite are presented from experimet 1 and 2. Plot of albite and microcline are presented in Appendix A5 and A6.

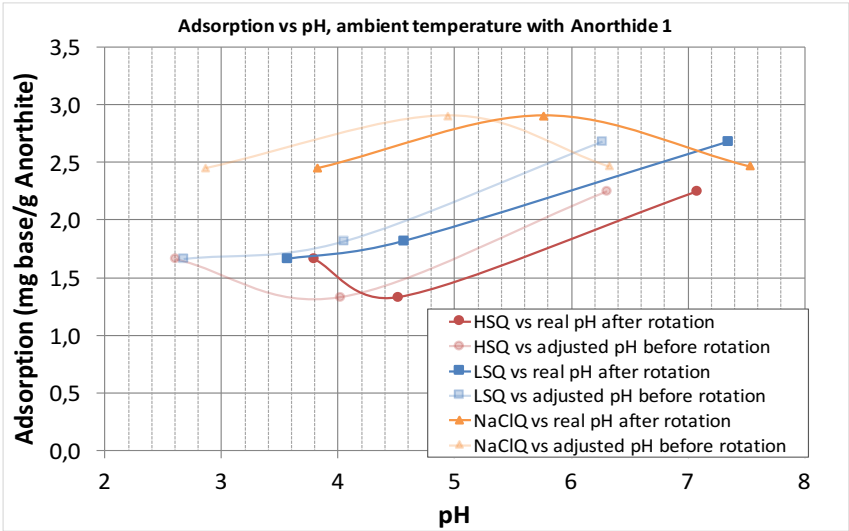


Figure 27: Adsorption of quinoline onto anorthite from experimet 1.

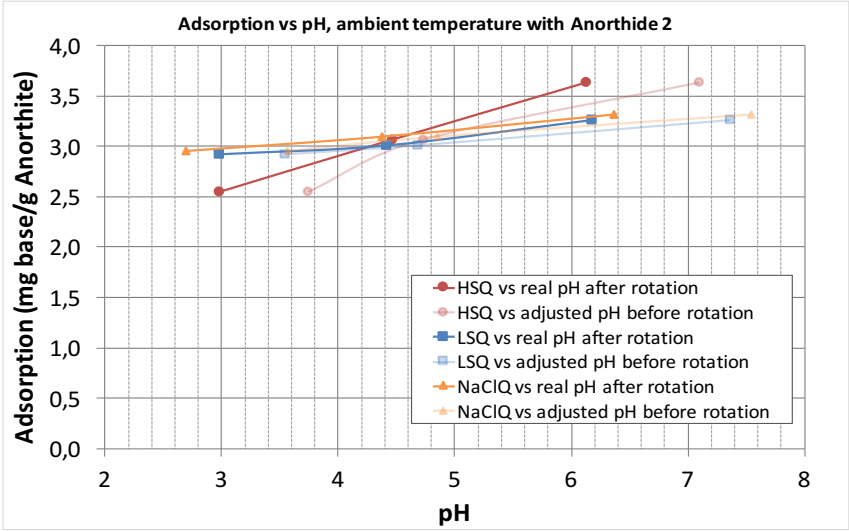


Figure 28: Adsorption of quinoline onto anorthite from experimet 2.

Results from both these tests are very chaotic and unpredictable. There is no clear trend to be seen, similar results are observed for both albite and microcline. Adsorption gap for anorthite is 1,5-3 mg base/anorthite, for albite is greatest 0 – 3.5 mg base/albite and microcline is between 0,5 – 2,5 mg base/microcline. Average adsorption is very high in all three minerals, up to 3 [mg base/feldspar]; it can be compared with clay mineral kaolinite valuesⁱⁱ.

The experiment was repeated several times before we become certain that there must be some significant uncertainties with either used equipment's, chemicals or preparation procedure.

5.4 Search for uncertainties

All experiments contain uncertainties. Apart from error contributed by human, used minerals and salts contain impurities, equipment used during experiments contain error connected to their calibrated range.

Unpredicted and chaotic results from both experiments in all minerals confirms that there must be something inaccurate either with the spectrophotometer device, preparation procedure or with feldspar treatment. These uncertainties were the background for testing new methods, performing error calculation, preparing minerals in different way in order to get adequate results.

5.4.1 Absorbance with new spectrophotometric device

Initially search for uncertainty started with replacing spectrophotometric device which measure the absorbance in solution. Spectrophotometer device model *Shimadzu UV-1700 PharmaSpec UV-VIS* was reported to have been inaccurate and was fixed before Christmas. It was replaced with *Shimadzu UVmini-1240*, see pictures in section equipment 4.2. Calibration curve was made for new device according to section 4.4.2. Adsorption was plotted versus equilibrium pH. As in figure 25 calibration curve for new spectrophotometer showed the same values for all their brines, similar to the calibration curve of previous device. This indicates that there is nothing wrong with device. Further, absorbance for feldspar was measured in new device.

The samples were prepared in the same order as explained in section 4.4.3 without NaCl brine due to a lack of time. Result for anorthite with new device are shown in figure 29. Observed

from figure 29 chaotic decreasing adsorption for anorthite, which is completely vice versa from previous results (figure 27-28). The results for albite and microcline are presented in appendix B-1. The adsorption result of two other feldspar minerals were completely inconsistent with the fits Spectrometer. With these results conclusion was deducted that there is nothing wrong with the devices and search for new inaccuracies has to be continued.

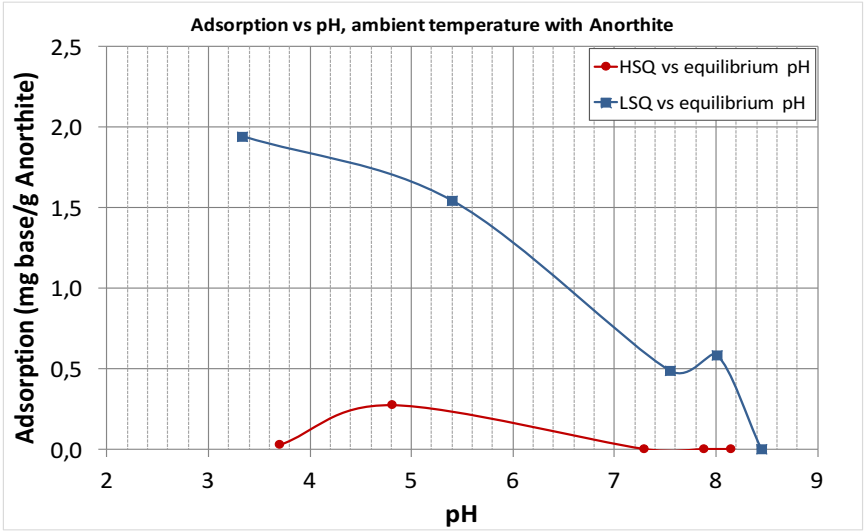


Figure 29: Adsorption of quinoline onto Anorthite with new spectrophotometric device

5.4.2 Improving procedure

The decisions for improving procedure emerged during sample preparation when gas formation was noticed in sample containing albite. Observation of gas was made during suppressing the pH by adding hydrochloric acid to the brine samples containing albite.

Quinoline evaporation

Following the observation made above, we assumed that probably quinoline might evaporate by adding hydrochloric acid into the samples and this could decrease the adsorption. Evaluation was made to perform Time Test. Time Test was performed only for samples containing albite according to section 4.5.1. The aim for the Time Test was to see if quinoline adsorption decreased with time. As shown in table 9, 9 samples were prepared with HS brine and 3 equal samples for each pH.

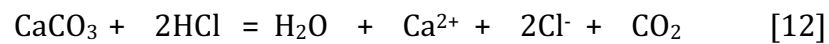
Absorbance of samples of each pH was measured at 3 different times; at first right after the samples were prepared, and then 3 hours and 24 hours of rotation. Calculation from each sample are presented in table 9, comparing the values from distinctive time there isn't any sign of decreasing adsorption. Where the maximum adsorption for all distinctive times are ~3 mg base/g albite. From these results conclusions were withdrawn that quinoline is not evaporated and adsorption doesn't reduce with time.

Table 9: Time dependent adsorption of quinoline onto albite

<i>Nr.</i>	<i>Sample</i>	<i>Albite [g]</i>	<i>Brine/Q[g]</i>	<i>pH adjusted</i>	<i>pH after 24 hours</i>	<i>ABS</i>	<i>Adsorption [mg base/g albite]</i>
1	1 - 1	1,0015	9,0008	3,01	-	0,3484	2,00
2	1 - 2	1,0015	9,0008	3,01	-	0,3057	3,44
3	1 - 3	1,0015	9,0008	3,01	3,69	0,3218	2,92
4	2 - 1	1,0006	9,0002	4,98	-	0,3627	1,53
5	2 - 2	1,0006	9,0002	4,98	-	0,3187	2,95
6	2 - 3	1,0006	9,0002	4,98	5,92	0,3203	2,93
7	3 - 1	1,0005	9,0003	6,95	-	0,3070	3,12
8	3 - 2	1,0005	9,0003	6,95	-	0,3232	2,85
9	3 - 3	1,0005	9,0003	6,95	7,36	0,3129	3,10

Test of CaCO₃ impurities in feldspars

Acid test is a well-known test for geologist to verifying the presence of carbonate minerals. Carbonate minerals are unstable in contact with hydrochloric acid. When gas is formed on a sample, carbone dioxide gas produced and following reaction occurs:



Experiment was carried out as described in section 4.5.2 to confirm which feldspar contains calcite. As shown in figure 30, desired amount of feldspar powder was put in glass test and droplet of hydrochloric acid was added. As it can be seen, small bobbles develop when acid is dropped at albite.

This is one of the confirmation that the experimental procedures are correct and there must be something with the mineral. If we conclude that the chaotic results in albite are outcome of contained impurities in albite, the question rises about the other two minerals which gives the same chaotic values.

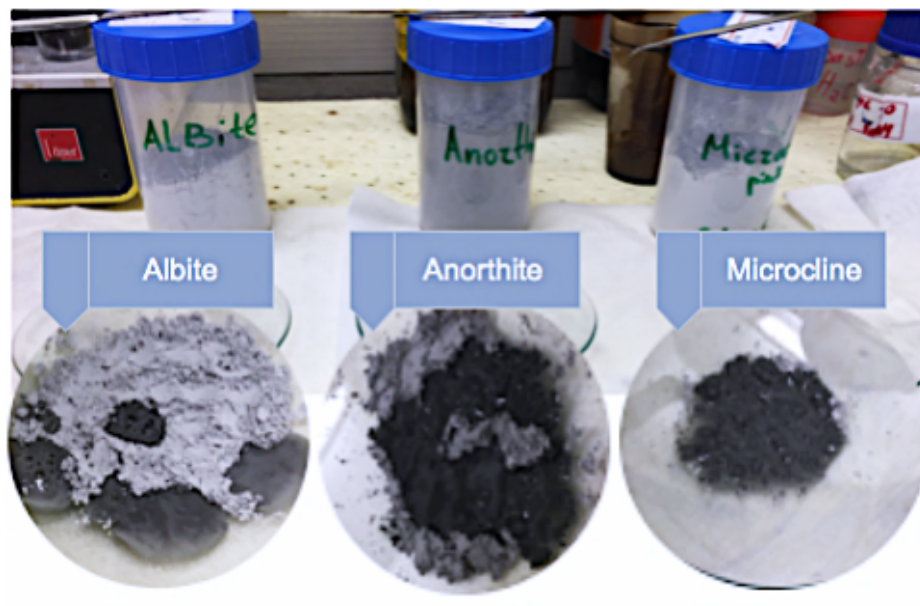


Figure 30: Gas production observed in sample to the left, albite.

5.4.3 Reversibility test

Samples with pH 8 and 9 was prepared according to the section 4.4.2. for each mineral. After 24 hours of rotation pH was measured and had slightly increased. The object of this test was to check behavior of feldspars at high pH and expected reduced adsorption. The result showed still chaotic but increased adsorption for all three minerals as it is shown in figure 29. Adsorption is highest for albite, followed by anorthite and microcline. Conclusion deducted from this chaotic result with no trend that the minerals does not correspond according to the theory.

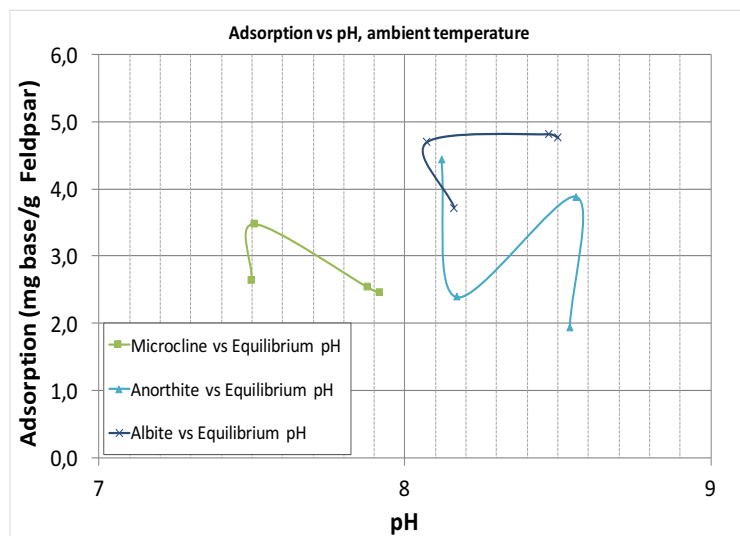


Figure 31: Adsorption of quinoline onto feldspar minerals at high pH

5.4.4 Test reproducibility of quinoline adsorption

As mentioned before uncertainties in minerals, salts, equipment and human error can affect the results. Repeatability is conducted to measure absolute and relative error contributed by all uncertain parameters. The experiment was performed on unsettled microcline, since this mineral showed fewer unchanging values from previous analysis. Samples were prepared as described in section 4.4.3. There were 9 identical samples prepared with 10 wt% microcline dissolved in 90 wt% of 0,01M LSQ solution. pH in the sample was adjusted to 4,85 by adding 10 μ l HCl and after 24 hours it increased to 5,20. Calculation was performed in excel program presented in Appendix A.

A plot of the average error value is presented in figure 32, where relative error for LSQ are determined 8,53%. Adsorption amount are varying from one compared to the other sample. Apart from the human error the samples are made almost identically. The error is relatively high; results in figure 32 confirms the chaotic result which have been achieved earlier.

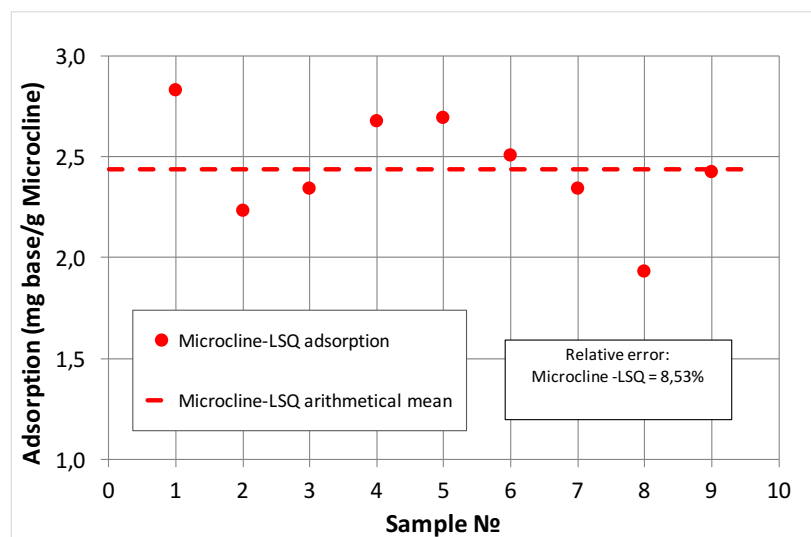


Figure 32: Adsorption of quinoline onto microcline with LSQ at pH 5, ambient temperature

Reproducibility of quinoline absorbance of the analytical method was as well teste. The samples are prepared according to the same procedure as for calibration curve without any contact with the minerals. Samples were diluted in range of 100-1000, in here the absorbance of dilution rate 200 is presented with known concentration, figure 33. Observed from figure below absorbance in five samples are almost parallel, this means that the chaotic result obtained in previous section are due to the mineral in the sample and not the experimental method.

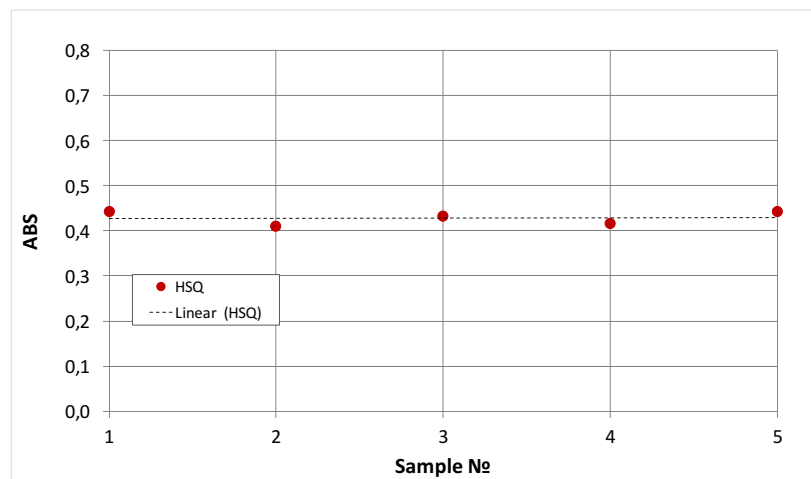


Figure 33: Absorbance analysis with HSQ sample with dilution 200

This leave us questioning the mineral composition and the milling procedure, as stated before the minerals were milled with methanol. Thought emerged if methanol might have affected the reactivity of the mineral. The composition for each mineral has been determined by BSc student Yngve Andersonⁱⁱⁱ. He performed ion composition analysis and concludes that the minerals are relatively pure for albite and microcline, only in anorthite the amount of Na^+ was too high compared to Ca^{2+} for being pure anorthite. Even this finding does not resolve the chaotic result in pure minerals compared to anorthite which is considered containing impurities.

SEM image of anorthite milled in methanol from figure 26 shows highly heterogeneous size distribution and small minerals elements as dusty particles. This observation led us to examine the size distribution and its impact on the results.

5.5 Mineral treatment

We can assume based on results from section 5.4.2 and 5.4.4 that there is nothing wrong with spectrophotometric device and experimental procedure. On the basis of size distribution observed in SEM image, figure 26. A suspicion thought emerged if feldspar milled in methanol might have impact on adsorption results by increasing surface area. In this section evaluation of mineral treatment have been conducted. First the minerals were dry grinded with mortar and pestle into fine powder. Then the adsorption was measured on dry grinded feldspar minerals. Next feldspar minerals were machine milled in DI-water. Then new adsorption was measured for feldspar milled in DI –water.

5.5.1 Hand milling with mortar and pestle

Initially feldspars have been milled in methanol as explained in section 4.3.1, the reason for milling with methanol was to prevent altering the chemical structures. Methanol was as well recommended by distributor. It's assumed that it might have affected the mineral and increased the reactive sites and the surface area. Decided to hand mill the minerals without any additives to see what kind of impact it has.

From logical point of view, the adsorption should decrease since the quantity of the bigger particle sizes are higher than dusty particles, which have been seen in machine milled feldspars.

Surface area of albite was determined with BET to be 0,293 m²/g and photographed with SEM to see the size distribution. Figure 33 shows SEM image of hand milled albite, as it can be observed the particle size is quite high in range of 10 – 450 µm. There can as well be seen particle dust which is covering the bigger particles.

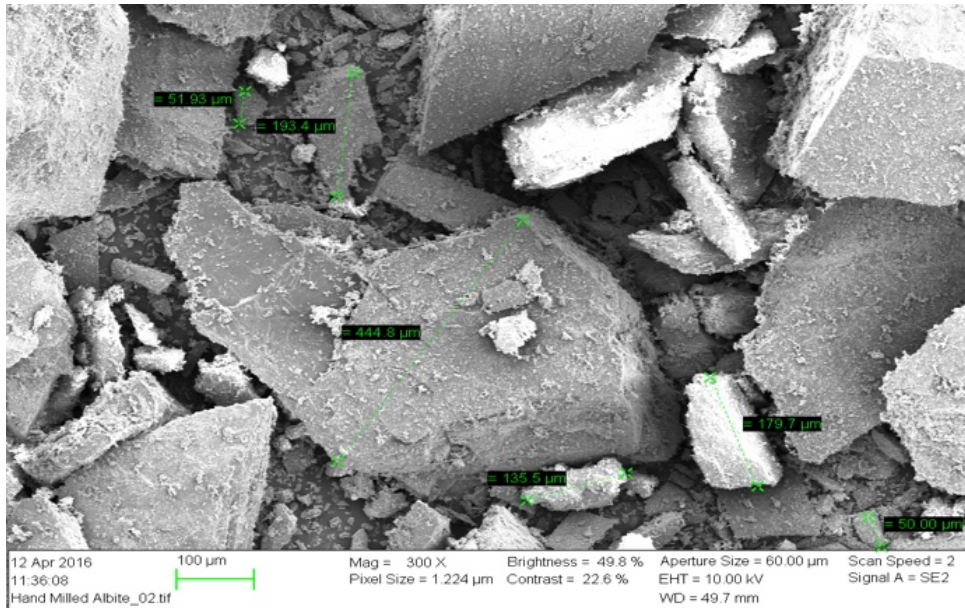


Figure 34: SEM image of hand milled albite, dry milled with mortar and pestle.

Adsorption of polar organic components onto hand milled albite is presented in figure 35. It shows unpredictably value opposite to machine milled. Observed similar result for microcline and anorthite, presented in appendix B1. The reason might be high particle size heterogeneity and the dusty elements observed from SEM picture above. This result leads us to try to archive a more homogenous particle distribution and see if stable result is possible.

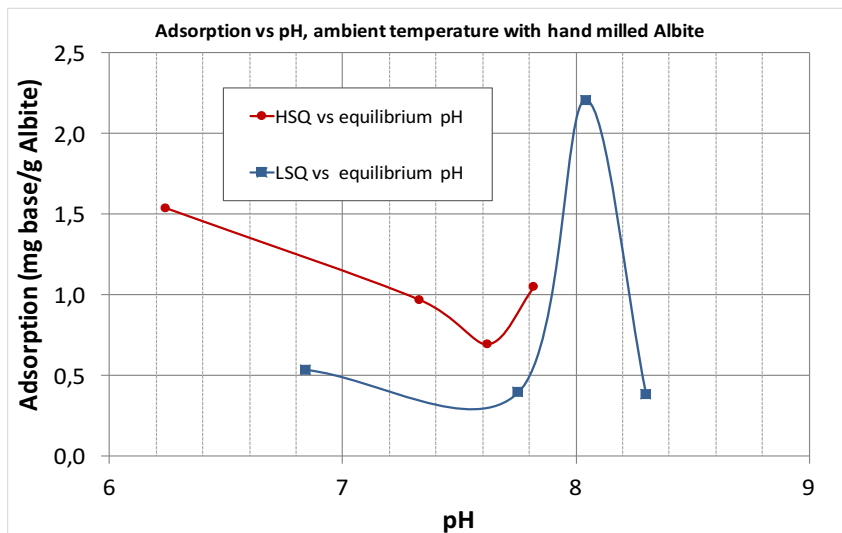


Figure 35: Adsorption of polar organic components onto hand milled albite.

5.5.2 Anorthite milled in DI –water

Initially feldspars have been milled with methanol as explained in section 4.3.1, the reason for milling with methanol was to maintain the initial reactivity. Thought emerged if methanol might have affected the reactivity of the mineral and it could be the reason for unstable result. Anorthite was milled in DI-water and was put for drying for 48 hours in 80 °C oven.

Samples was prepared as previously, adsorption was measured and result are presented in figure 36. Unfortunately, the result didn't change, only adsorption has slightly decreased, but still chaotic and unpredictable results with no trend. This leave us with the last suspicion about of the impact the heterogeneity and dusty elements which is observed on the bigger mineral grains from SEM image of hand milled albite.

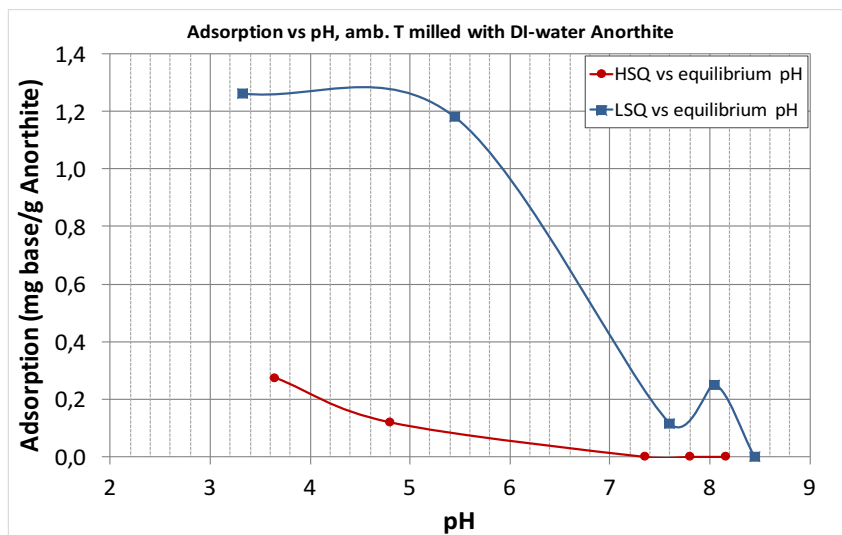


Figure 36: Adsorption of polar organic minerals onto Anorthite milled with DI-water

5.6 Sedimentation of anorthite

According to the previous observation, assumption was deduced that there might be a problem with the heterogeneity of the mineral grain size and the fine dusty elements that have been noticed in SEM picture in figure 34. This problem was solved by performing separation process according to the section 4.3.5. Since lack of time sedimentation process was performed for only anorthite milled in water and methanol. Figure 22 illustrates how sedimentation process is performed. Desired particles size is calculated from Stokes' law and the settling time is determined. Settling process used to separate fine fraction that has been created by the mechanical milling process and altered the material properties differently than expected. By performing settling for each mineral, this leads to a more representative and homogenous mineral samples. After the settling the mineral samples were placed in an 80 °C oven for drying.

A preliminary test was performed on two equal samples for each brines to observe if the adsorption values are comparable. This test gave a positive respond. Then experiment was performed on settled minerals with the sample preparation described in section 4.4.3 for HSQ and LSQ brine. Results are presented below in figure 37 and 38.

The results show clear trend which is depended of pH. This means adsorption of quinoline onto milled anorthite with particle sizes above 2 m gives consistent and reproducible results. The adsorption increased with increasing pH and then decreased again for LSQ in both figures below. Highest adsorption observed in low salinity brine, was in line with the adsorption observed for clay type, kaoliniteⁱⁱⁱⁱⁱⁱ. The slightly difference are the minor adsorption for anorthite milled in methanol compared to milled in DI-water, which is neglectable. From these result we can assume that milling with additives like methanol and DI-water does not necessarily change adsorption surface in feldspar minerals

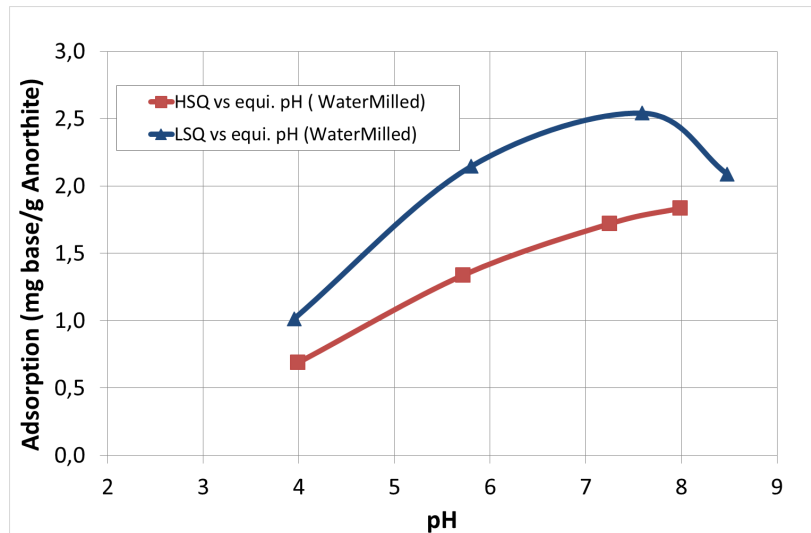


Figure 37: Anorthite, milled in water and small particles are removed by settling.

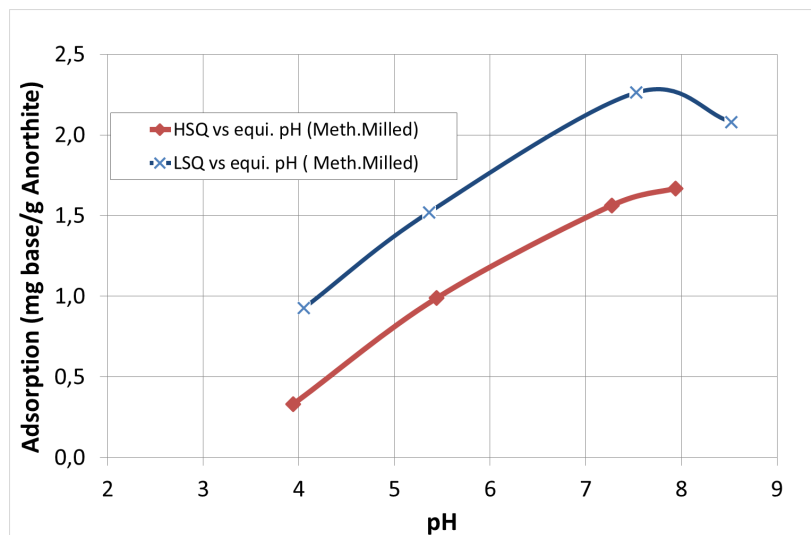


Figure 38: Anorthite, milled in methanol and small particles are removed by settling

From result in figure above, assumption can be deducted about the cause of the chaotic values in feldspar compared with more stable values for clay can be milling procedure. Minerals react differently according to their mineral structure. Feldspars are more brittle than clays, it gets more grounded and the result are mineral dust particles which is very reactive, probably as a result of the very large number of broken chemical bonds on their surfaces.

The reason why the hand milled albite has adsorbed much more than machine milled is because of uneven particle distribution, because every time we do not get representative particles in each sample.

5.7 Grain size analysis of anorthite

According to result in section 5.1, 5.3 and 5.4 adsorption are very depending on mineral grain size by its degree of heterogeneity. How homogeneous and how heterogeneous is the particle size impact the results. In this section surface area measured by BET and calculated from SEM images are presented. The result is predictable according to the results obtained in previous sections, high surface area will contribute to better adsorption. Table 11 shows a reduction in surface area after performing settling, since there is less fraction of small particles. The particle size reduction can be explained due to heterogeneity mineral powder after milling, BET surface area can vary within 2-3 m²/g, or by performing separation process.

Table 10: Surface Area by BET

Mineral	Sedimentation	Additives	BET, [m²/g]
Albite	✘	Methanol	5,214
Anorthite	✘	Methanol	3,265
Microcline	✘	Methanol	4,661
Hand Milled Albite	✘	✘	0,293
Anorthite	✓	Methanol	1,723
Anorthite	✓	Water	3,139

5.7.1 Surface Area and Particle size analysis

In this part I have tried to look closer in to particle size and surface area of the feldspar, anorthite. The mineral was machine milled in water and methanol according to the milling procedure in section 4.3.1. Amount of 40 g of the mineral and 35 ml chemical additive such as methanol or DI –water placed in a grinder with 12 metal balls.

Settling of the mineral powder performed according to the sedimentation as described in section 4.3.5. The aim of particle size sedimentation is to get more homogeneous, stable and reproducible sample. Which is more representative of the minerals in reservoir.

Calculating of surface area by SEM, as described in section 4.3.4, a representative particle was measured randomly and the surface area was determined by the calculation performed in excel sheet. For determining the surface area, it's actually important to measure the minimum and the maximum diameter since feldspar has higher aspect ratio.

The real problem for determining the surface area by SEM is the dusty mineral particles, which are impossible to quantify. Dusty mineral particles could be healed by heating in longer period, for example two weeks in 95 °C. In this way dust minerals would dissolve and re-precipitate be freshly grown particle surfaces, similar to diagenetic minerals. The grown minerals would have less unsatisfied charges. While in this case mineral used are milled with a grinder, it will break many mineral bonds, and the unsatisfied charges increases.

The result of surface determined by BET method and by SEM calculation are presented in table 11. The difference is very small. As its observed from the SEM pictures the surface area is expected to reduce after settling for methanol milled anorthite. While for water milled anorthite the surface area has not changed drastically from unsettled anorthite which is 3,265 BET, [m²/g].

Table 11: Anorthite, surface area by SEM and BET

Mineral	Sedimentation	Additives	Surface area BET, [m ² /g]	Surface area SEM, [m ² /g]
Anorthite	✗	Methanol	3,265	3,675
Anorthite	✓	Methanol	1,723	1,408
Anorthite	✓	Water	3,139	3,097

Surface area was calculated by SEM according to section 4.3.4. This was archived by drawing a red line across the image and measured diameter of every particle that crossed that line. Average surface area for all 30 minerals that crossed the line was calculated and the result are presented with SEM pictures of the anorthite from different stages in figure 39-41.

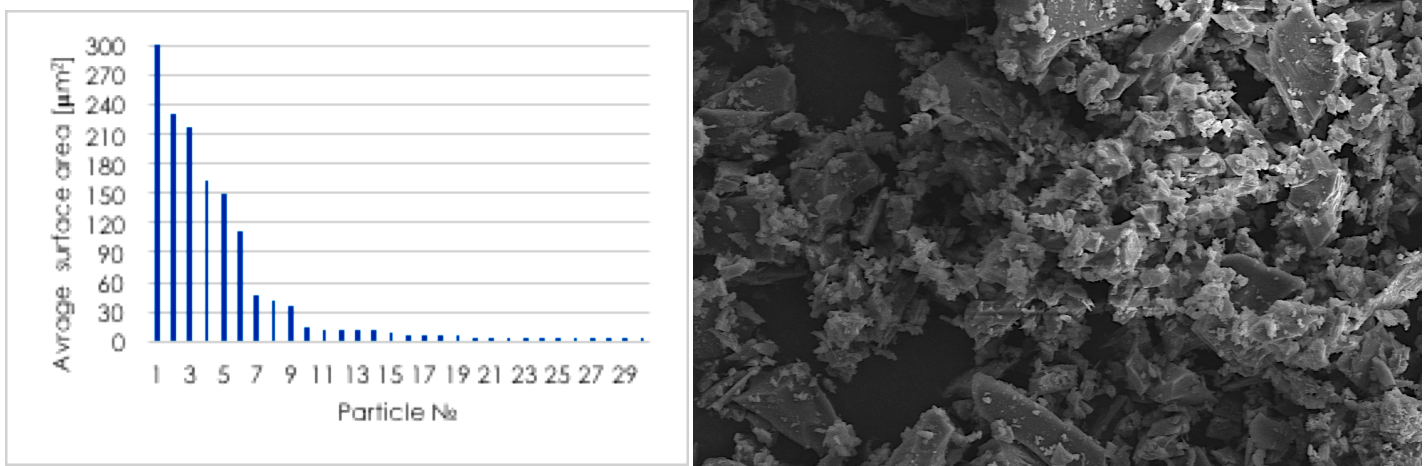


Figure 39: Anorthite –milled in methanol. Left: Plot of average surface area with particle number. Right: SEM picture of the mineral

To the left of figure 39 shows a plot of average surface area. This gives an overview of grain surface area in anorthite milled in methanol. It is plotted surface area [µm²] versus number of particles. Only 5/30 particles are higher than 50 µm, this makes 16% of the particles, the rest is less than 50 µm and even smaller as its impossible to measure the mineral dust that can be observed to the right of figure above. It is important to note the scale in each SEM images; in this picture the scale is 4 times bigger than the two below. This indicates the particle size are much smaller compared to settled anorthite in figure 40.

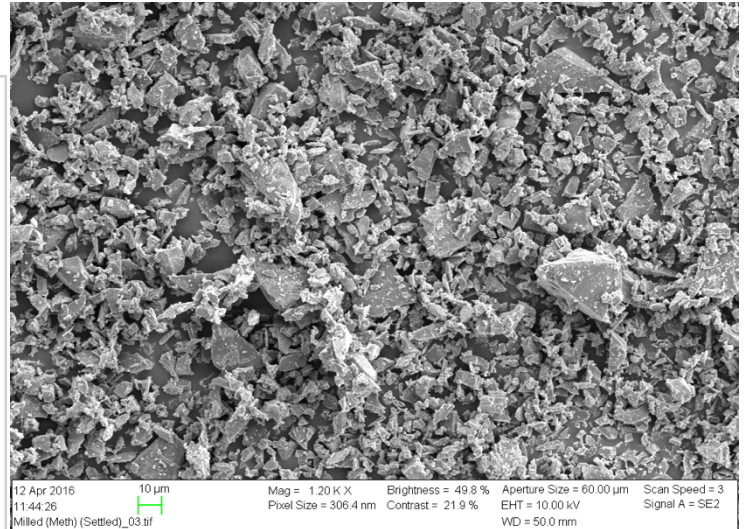
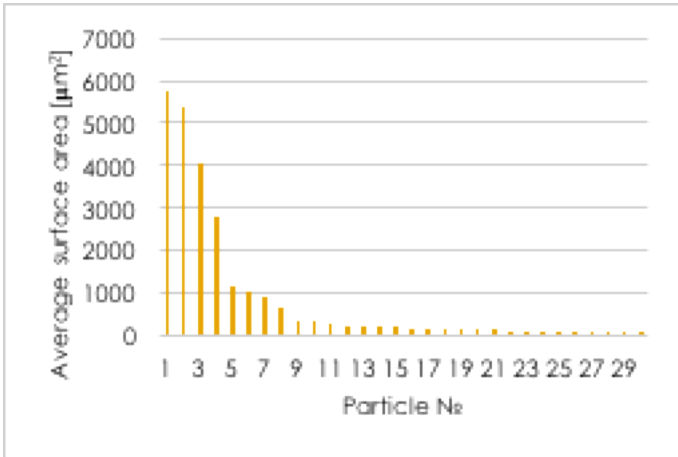


Figure 40: Anorthite –milled in methanol and settled in DI –water. Left: Plot of average surface area versus particle number. Right: SEM image of the mineral

To the left of figure 40 shows a plot of average surface area of the milled feldspar mineral, anorthite milled in methanol. Then the fine particles are removed by settling process. Plot gives an overview of grain surface area, it is plotted by surface area [μm^2] and particle number. Only 5/30 particles are larger than 1000 μm , this makes 16% of the grains, the rest is less than 1000 μm and in compared to the previous SEM picture it appearances much more clean, and the grains size are more clear seen. It's important to note the scale in each picture, in this picture the scale is 4 times less than SEM above. This indicates the particle size are much larger compared to unsettled anorthite in figure 30.

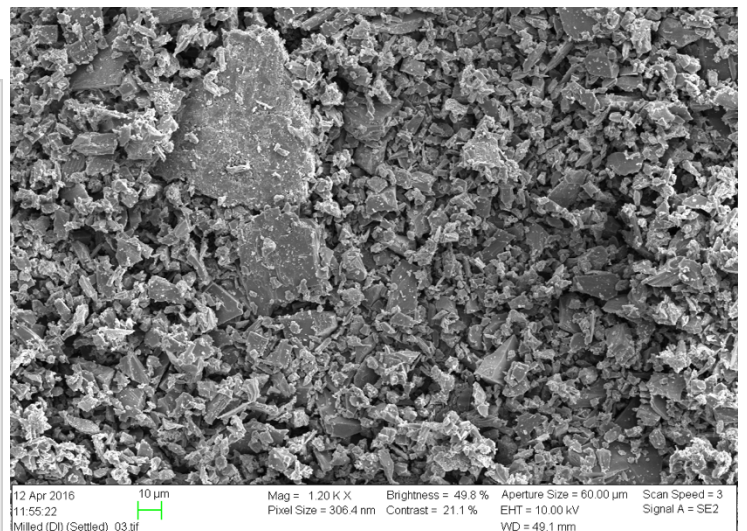
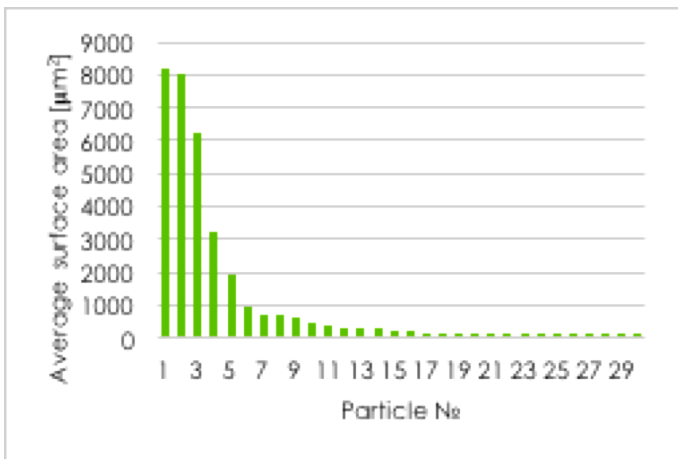


Figure 41: Anorthite –milled and settled in DI –water. Left: Plot of average surface area versus particle number. Right: SEM image of the mineral

To the left of figure 41 shows a plot of average surface area of the milled feldspar mineral, anorthite milled in DI–water. Then the fine particles are removed by settling process. Plot gives an overview of grain surface area, it is plotted by surface area [μm^2] and particle number. The grains in this case are rapidly varying and much more homogenous than figure 40 anorthite milled with methanol. Additives used for milling in methanol and water have different density, viscosity etc. this might be one the reasons for the difference in grain size.

5.8 Adsorption of polar organic components onto quartz

Polar organic components could be the anchor molecules which causes wettability alteration at the surface of the mineral. In this part of the thesis adsorption of the polar organic components are analyzed for the most stable mineral on earth, quartz. To understand what impact quartz mineral has on initial wettability of mineral surface. This section describes performed experiments to investigate adsorption of quinoline onto different grain size of quartz mineral. To reduce the relative error in the experimental analysis. Experimental in quartz and feldspar minerals were performed at the same time.

5.8.1 Machine-milled quartz in methanol

Quartz minerals was milled in methanol according to the 4.3.1 and dried in 80 °C oven. Then used without further preparation. Surface area was measured by BET method as described in section 4.3.2 and was found to be 2,784 m^2/g . Representative quartz sample was photographed in SEM for closer observation of the grain size, figure 42. As it can be observed from SEM image the size of particles varies significantly, from less than 1 μm (dust) up to 20 μm . This heterogeneity of particle size and the dust elements might affect the adsorption.

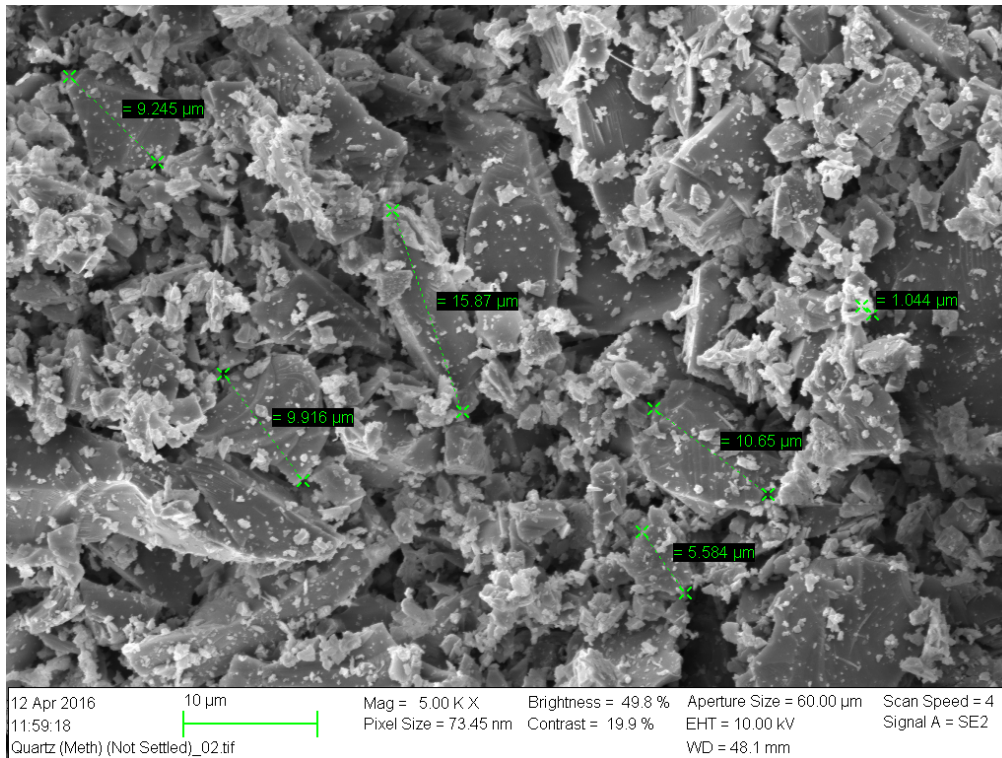


Figure 42: SEM image of quartz mineral milled in methanol.

Adsorption was measured by preparing samples according to the 4.4.3 with 0.01 M quinoline solution in LS and HS brines. Adjusting of pH was performed by adding HCl to suppress or NaOH to increase the pH. Samples were adjusted in range of 3-9, after 24 hours in rotation the pH slightly decreased. Adsorption was analysed at ambient temperature and plotted versus equilibrium pH. Adsorption results are presented in figure 43, as it can be observed the plots are chaotic, there is no trend to be seen between adsorption and pH. The chaotic result can be explained from SEM picture of quartz. As described earlier the mineral size of particles varies significantly, from less than 1 μm (dust) up to 20 μm. This heterogeneity of minerals can create a problem to observe stable results.

According to Caroll⁶⁸ silt fraction of quartz ranging with size [2 – 63 μm] has a cation exchange capacity (CEC) of 0.6 cmol kg⁻¹ and in clay fraction with size lower than 2 μm, has 5.3 cmol kg⁻¹. Iler 1979⁶⁹ described that silica particles have no charge at pH of 2, while up to pH of 6 the CEC increases because negative charges accumulate on particle surface.

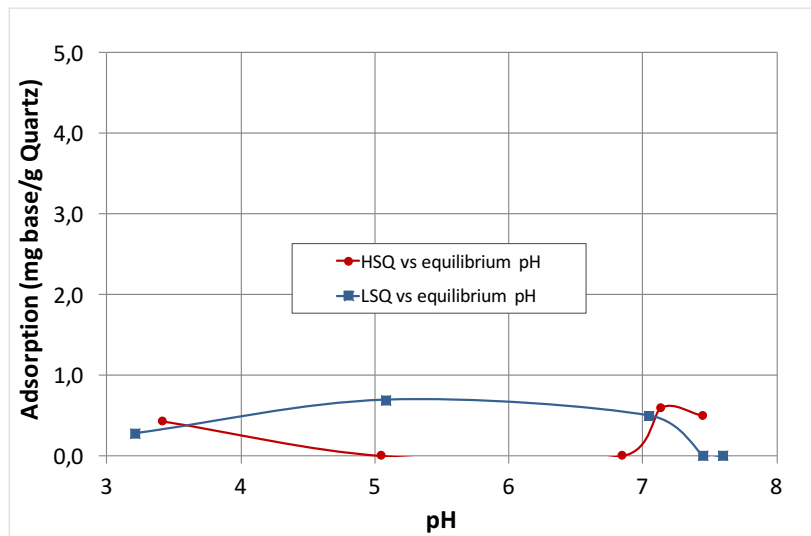


Figure 43: Adsorption of polar organic component on machine milled quartz with effect of pH

5.8.2 Repeatability test for quartz

Repeating from uncertainty measurements from section 5.2.3 uncertainties in minerals, salts, equipment and human error can affect the results. Repeatability is conducted to measure absolute and relative error contributed by all uncertain parameters.

The experiment was performed on quartz milled in methanol without sedimentation process and samples were prepared as described in section 4.4.3. There were 9 identical samples prepared with 10 wt% quartz dissolved in 90 wt% 0,01M LSQ solution. pH in the sample was adjusted to 4,90 by adding 10 μ l HCl and after 24 hours in rotation pH slightly increased to 5. Calculation was performed in excel program and a plot of the average value is presented in figure 44. Absolute error and relative error are determined to be 0,2862 base/g quartz and 6,98%. Error is relatively high; this confirms the chaotic result which have been achieved previously.

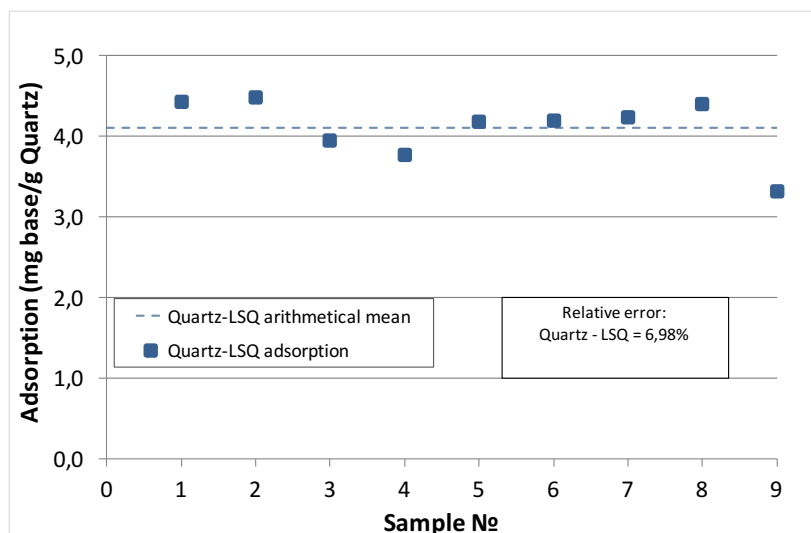


Figure 44: Adsorption of quinoline onto quartz milled in methanol at pH =5

The most remarkable values to notice are the high adsorption of quinoline onto quartz, which is surprising. According to Bowen's reaction series ⁷⁰quartz is one of the most stable mineral, in addition to being resistant chemically to most attacking solutions, its hardness and lack of cleavage helps it to resist many of other agencies of weathering. Fluid content, inclusions are common in quartz. May as well impact the adsorption. They typically range from 1 -10 μm to several millimeters in maximum dimension and are abundant. When trapped the composition of the aqueous fluid in the inclusions can range from 0 to 70 wt% NaCl.²⁴

The high adsorption in this case can be as well explained by the size distribution from SEM picture in figure 42. Nano particles like dust will have much higher surface area and will react distinctively according to the representative quantity added in each sample. Because every time we do not get representative particles in each analyzed sample.

It is important to mention that ion exchange in quartz and other minerals is also dependent on the crystalline structure of the mineral, and the chemical composition of any solution in contact with the mineral surfaces. Milling procedure might impact minerals. Quartz's are quite brittle, it gets more grounded and the result are mineral dusty/fluffy particles which is very reactive, probably as a result of the very large number of broken chemical bonds on their surfaces.

5.8.3 Increasing pH in LSQ quartz samples

Adsorption of polar organic components onto quartz are analyzed in high pH environment. The aim of this test was to see if the adsorption decreases by increasing pH. Four identical sample was prepared according to section 4.4.3 for low salinity quinoline brine (LSQ). Then the pH was adjusted to 8, after 24 hours in rotation pH slightly decreased to 7,5. Adsorption was measured in spectrophotometric device and results are plotted vs. number of samples.

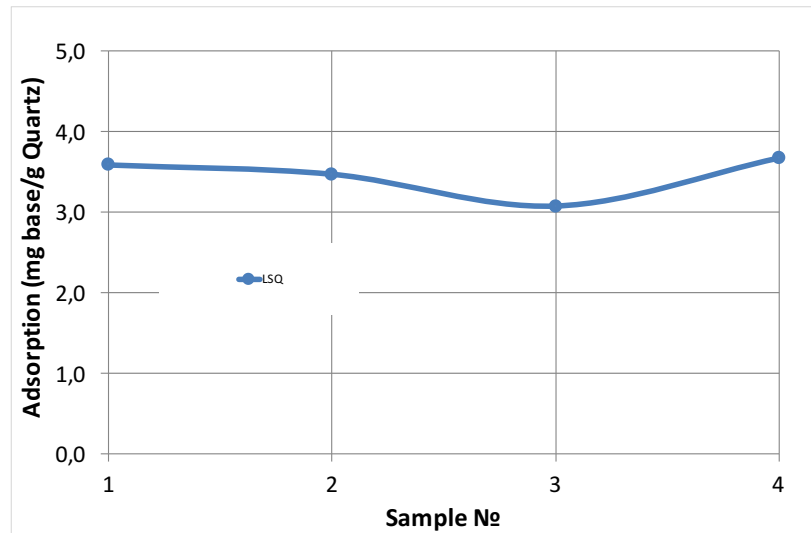


Figure 45: Adsorption of polar organic components onto quartz at pH =7,5

Result of quinoline adsorbed onto quartz in pH = 7,5 are presented in figure 45. Adsorptions are slightly decreased compared to pH =5. Assumption can be derived from these result that the adsorption of polar basic oil onto quartz might be dependent on pH similar to clay and feldspar minerals.

5.8.4 Coarse grained quartz

Quartz is known to be one of the most stable minerals and are expected to have very low adsorptive capacity of polar organic component. Coarse grained quartz is provided by Sibelco Company previously known as North Cape Mineral. Quartz was manufacture grounded, what kind of milling procedure is used is unknown. It is 98 % pure silica from Norway. Surface area was measured by BET method and photographed by SEM. In this section I have tried to analyze adsorption on different grains size than previous. Surface area of quartz was determined with

BET to be 0,216 [m²/g], compared to machine milled which is 2,784 [m²/g]. SEM image is presented in figure 46, scale is 100 mm which is ten times larger than machine milled. Observe from the image the grains are clean, ways to measure and dusty minerals are nonexistent. Probably dusty minerals are removed by some kind of process or the companies milling device gives more homogenous mineral grains.

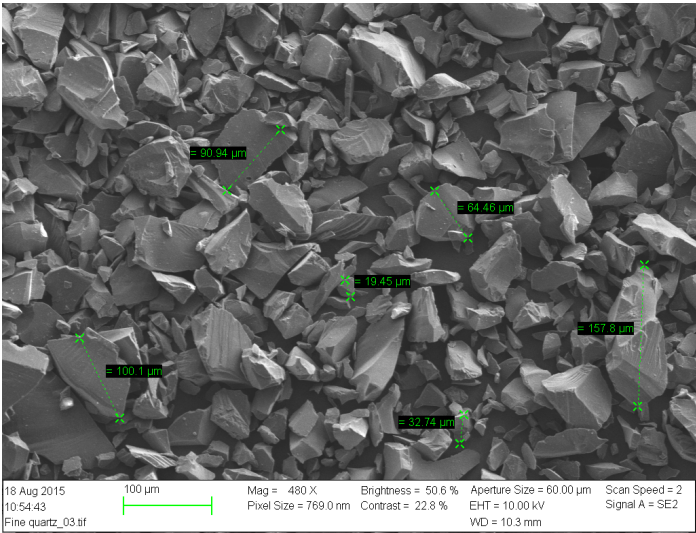


Figure 46: SEM image of coarse grained quartz.

In figure 47 result of coarse grained quartz is presented and it shows predictable adsorption. From logical point of view, the adsorption should decrease since the particles are ten times larger than machine milled. Neglecting the messy values in pH 7 to 8,5 there is approximately no adsorption. This range of grain size is most likely representative in reservoirs.

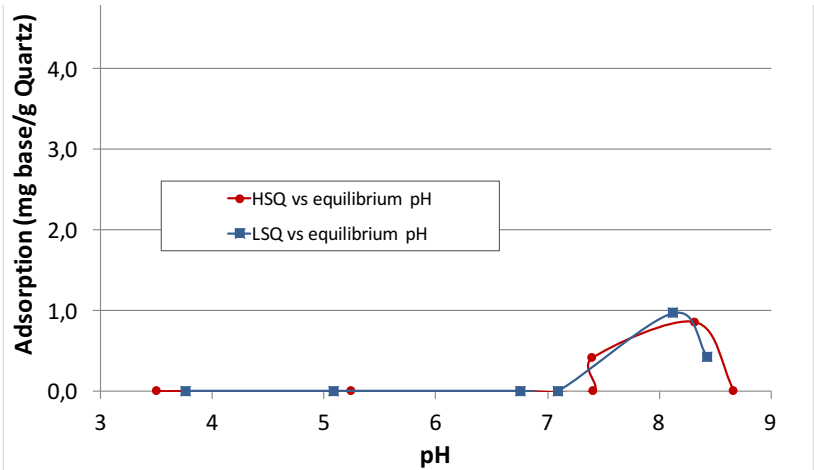


Figure 47: Adsorption of polar oil components on to hand milled quartz

6. DISCUSSION

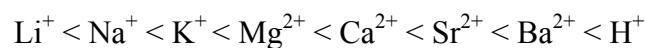
The initial wettability of reservoir are divided into water-wet, oil-wet or mixed wet, and to be able to enhance oil recovery by wettability alteration with Smart Water, the reservoir must be mixed-wet to some extent. The objective of this thesis is to investigate how sandstone minerals (clay, feldspar and quartz) are influenced by adsorption of polar organic components from the oil. How is the rock wetting affected?

The result in the beginning took an unusual turn, other than expected. I managed to get adequate result for the feldspar, anorthite. We learnt that adsorption of polar oil organic components is very depending on mineral size distribution. It's important to analyse size distribution of the sample and perform sedimentation process to get more homogeneous, stable and reproducible mineral grains.

In this part of the thesis the results of feldspar mineral, anorthite are discussed and compared with experimental results of Yngve Anderson. Our experiments are conducted on the same feldspar minerals.

6.1 Effect of different feldspar mineral

Anorthite is a part of plagioclase feldspars with chemical formula $\text{CaAl}_2\text{Si}_2\text{O}_8$ and composition 90-100 % Anorthite. It is known for being most reactive mineral amongst feldspar minerals. One of the explanation could be the the chemical composition, containing calcium ion which is charge balancing cations in anorthite. Well known CEC for clays the relative replacement power of cations towards the clay surface is considered to be:



All minerals can exhibit ion exchange behavior to some degree, as different ions exchange sites at the surfaces can be formed by chemical substitution, as well as the presence of unhealed broken chemical bonds by mechanical fracturing. Minerals with fixed charge, such as the clays, have high degrees of ion exchange. According to Austad et al²⁷. clay minerals are also the main wetting factor in sandstone because of their extremely large and charged surface

areas, which are strongly adsorbed by polar organic compound of crude oil. While feldspar and quartz will get negative charge at relevant pH. ³⁶

If we apply CEC for feldspars the relative replacement would be following:



Adsorption amount expected to change according to the cations in minerals. Anorthite containing divalent ion (Ca^{2+}) would adsorb more compared to microcline with monovalent ion K^+ and least adsorption in albite.

It is important to mention that ion exchange in clays and other minerals is also dependent on the crystalline structure of the mineral, and the chemical composition of any solution in contact with the mineral surfaces. ¹⁶Have to recall from theory part major differences between these three alkali feldspars are the crystal structure, which depends on temperature of magma solidification, its cooling rate and geothermal history. While albite and microcline forms under low temperature, anorthite generally forms in high temperature environments. This characteristic might as well respond differently when in contact with different brines.

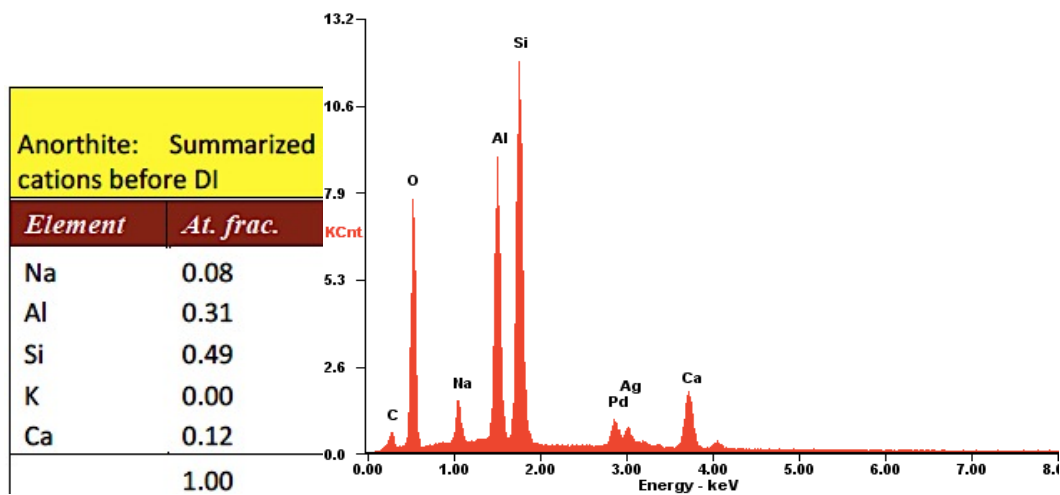


Figure 48: Anorthite, left: summarized cations before DI-water. Right: before DI-water histogram showing intensity vs. energy

Yngve Andersonⁱⁱⁱ determined ion composition on feldspar which is presented in figure 48. Anorthite shows large amount of Na^+ in pure anorthite 12% of Ca^{2+} and 8 % of Na^+ were

measured, the amount of Na^+ was too high for being pure anorthite. This means that the result that we have obtained from anorthite mineral are not 100% pure anorthite

6.2 Basic effects on feldspar minerals

Adsorption of quinoline was examined onto anorthite minerals milled in DI-water and methanol, then the small particles was removed by sedimentation process. The result are presented in figure 49.

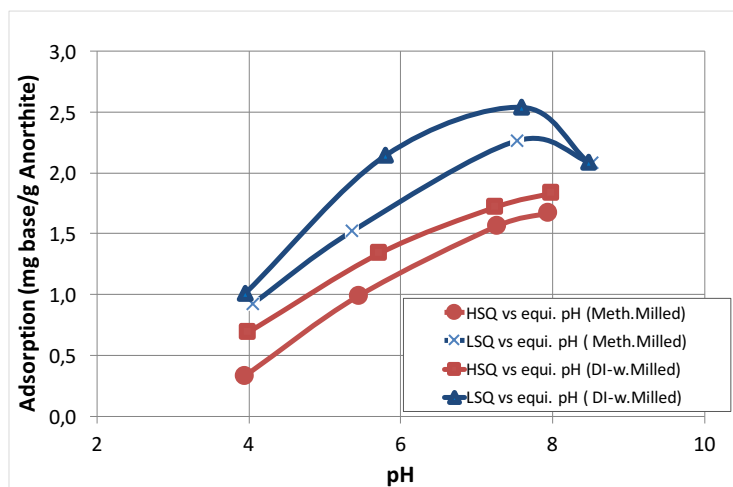
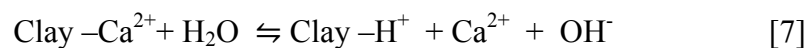


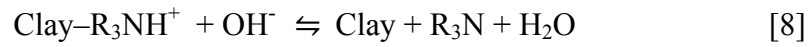
Figure 49: Adsorption of quinoline onto anorthite milled in methanol and DI-water.

The results clearly indicate that adsorption of quinoline onto Anorthite is strongly pH dependent, with difference in adsorption at different pH.

Adsorption can be explained by suggested mechanism for clay minerals in section 3.3 Desorption by pH increase, illustrated in figure 12. Due to reduction of Ca^{2+} in injected brine an exchange between absorbed cations Ca^{2+} in the clay surface desorbs. To balance the charges proton ions H^+ from water adsorb to clay surface. Following chemical reaction takes place:



Following chemical reactions in local increases in pH are the cause of desorption of the organic material from clay:



If we apply the same mechanism to anorthite with following reaction:

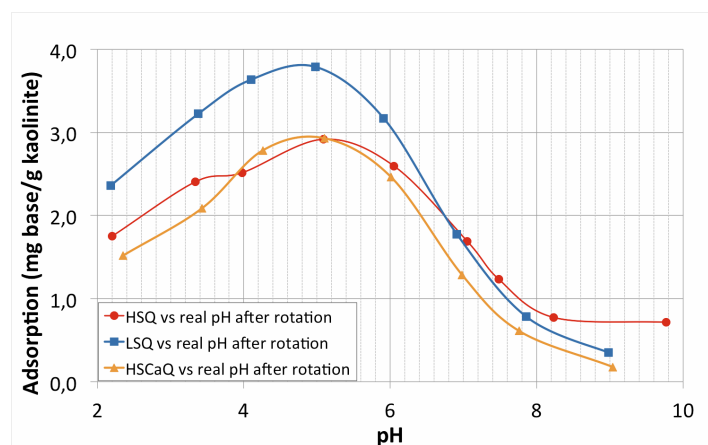
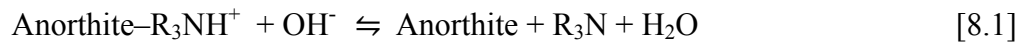
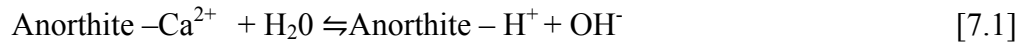


Figure50: Adsorption vs. pH at ambient temperature with low salinity, high salinity and CaCl brine. ⁱⁱ

Comparing the adsorption from figure 49 for milled and settled anorthite mineral, and figure 50 for kaolinite clay. The adsorption increased with increasing pH and then decreased again. Highest adsorption observed in low salinity brine, the results are in line with the adsorption observed for kaolinite clay.

7. CONCLUSION

Sandstone consist mainly of three main minerals; quartz, feldspars and clay. Surface area of each mineral is different and will react contrarily. Clay has the highest surface area, following feldspars and quartz.⁷¹

Clay >> Anorthite > Microcline > Albite > Quartz

Polar organic components could be the anchor molecules which causes wettability alteration at the surface of the mineral. The objective of the thesis is to verify any adsorption of the polar organic components onto quartz and feldspar minerals. The adsorption is compared and discussed with previous work performed on clays. Mineral composition and surface reactivity of the rock material is central in wettability alteration process observed in LS waterflooding.

All minerals can exhibit ion exchange behavior to some degree, as different ions exchange sites at the surfaces can be formed by chemical substitution, as well as the presence of unhealed broken chemical bonds by mechanical fracturing. Minerals with fixed charge, such as the clays, have high degrees of ion exchange. According to Austad et al.²⁷ clay minerals are the main wetting factor in sandstone because of their extremely large and charged surface areas, which are strongly adsorbed by polar organic compound of crude oil. While feldspar and quartz will get negative charge at relevant pH.³⁶ This study concludes that plagioclases such as Albite as well as microcline with alkali metals Na^+ and K^+ can in some cases substitute with protons, H^+ .

Feldspars minerals in sandstone reservoirs are mainly influencing reservoir pH. The initial reservoir pH dictates the initial wettability of the reservoir and CEC and ion substitution could contribute to pH increase and wettability alteration during smart waterflooding. Adsorption of polar organic components towards feldspar and quartz surfaces have been investigated. The CEC and surface area of feldspars and quartz mineral is less compared to clay minerals.

- It was difficult to get consistent results on quinoline adsorption in feldspar minerals anorthite, albite and microcline containing larger amount of particles less than $2\ \mu\text{m}$

- Adsorption of quinoline onto milled anorthite containing particle sizes above 2 μm gave consistent and reproducible results. The adsorption increased with increasing pH and then decreased again. Highest adsorption observed in low salinity brine, the results are in line with the adsorption observed for kaolinite clay.
- High adsorption of polar organic components was observed onto quartz samples containing larger amount of grains below 2 μm in low salinity brine with pH = 5. The adsorption was slightly reduced with increased pH = 7,5.
- In quartz samples with grain size larger than 2 μm , the adsorption was neglectable. This grainsize is more in line what we would expect in sandstone reservoirs.
- The experimental results confirm that the adsorption of polar organic components are very dependent on grain size and size distribution of the mineral samples. In real sandstone reservoir the mineral grain sizes of quartz and feldspars are much larger compared to clays, and the adsorption would most likely be significant lower than in the lab experiment.
- The experimental results confirm that better experimental procedures for mineral preparations are needed to get reproducible results.

8. FUTURE WORK

The experimental work done in this thesis has given many interesting results that could be worth investigating further into. Thoughts on further work are listed below:

- Repeat adsorption measurement for settled feldspars, albite and microcline at ambient temperature.
- Repeat adsorption measurement for settled quartz at ambient temperature.
- Repeat adsorption measurement at high temperature for both feldspar and quartz minerals

From the difficulties met at the experimental part of this thesis, it's important to get rid of the impurities before starting testing. Analyse size distribution of the sample and perform sedimentation process to get more homogeneous, stable and reproducible sample.

8.1 Purification of minerals

There is various purification method for different minerals, as an example the method of Tributh and Lagaly is designed to remove as many impurities as probable to acquire further "pure" clay mineral. However, the purified substance may still contain impurities like quartz etc. The purification procedure described according to Ammann ⁷² in five steps:

- First the carbonates are removed. Since calcium carbonate is barely soluble it may be a source of Ca^{2+} ions even if the clay was sodium saturated.
- Iron oxides are removed by a combination of reduction to Fe^{2+} and complexation with citrate ions.
- Organic material like humic acids are removed by oxidation with hydrogen peroxide.
- The $< 2 \mu\text{m}$ -fraction is obtained by sedimentation.
- Finally, the clay is dialyses until salt-free, freeze-dried and ground to powder.

8.2 Size analysis

It's important to take SEM and BET to analyze the particle size and surface area. If the mineral powder is highly heterogeneous it's essential to know what range of particle size, you want to work. According to archived particle size you can perform separation process as described section (4.4.3). Based on Stokes law you can calculate the desired size range. The aim of

particle size sedimentation is to get more homogeneous, stable and reproducible sample, which is more representative of the minerals in reservoir.

8.3 Maturing/aging of milled minerals

Dusty mineral particles can be healed by heating in longer period, for example two weeks in 95 °C. In this way dust minerals would dissolve and re-precipitate be freshly grown particle surfaces, similar to diagenetic minerals. The grown minerals would have less unsatisfied charges in compared to freshly machine milled minerals.

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10. APPENDIX

A. Calculation

A.1 Calculation of surface area from SEM

Measure particles as described in section 4.3.4 and insert the values in excel sheet.
Use the following values and formulas to determine mean and median surface area in [m²/g]:

- Mean = (maxD + minD)/2
- Volume = mean³
- Mass = Volume (density /10²)
- Surface area for each mineral = 6*mean²
- Median [part/g]= (1/2.49 mass pg) = 401606,4257 *10⁶ Part/g
- Surface area median = (401606,4257 Part/g * 122μm²*10⁶)/10⁹ = 48,995932 m²/g
- Mean [part/g]= (1/86.6 mass pg) = 11547,34411*10⁶ Part/g
- Surface area mean = (11547,34411Part/g * 122μm²*10⁶)/10⁹ = 1,408734 m²/g

Surface are determined from mean/average gives more realistic value than median.
Since in **median** only the mass of large values of particles contribute while in **mean** all particles contribute.

Scale 10mm = 10 μm

Density: 2,73 g/cm³

median	median	mean	mean
10 ⁶ Part/g	SA m ² /g	10 ⁶ Part/g	SA m ² /g
401606,4257	48,995932	11547,34411	1,408734

UiS IPT Particle Size Analysis										
PHN 20160425							Image: 03.tif		Sorted median	
Sample: Anorthite Milled (Meth) (Settled)										
Particle	max mm	min mm	max um	min μm	mean μm	max/min	volume μm ³	mass pg	SA um ²	mean μm
1	4	2	4	2	3	2,0	27,0	0,74	54	2
2	8	4	8	4	6	2,0	216,0	5,90	216	3
3	14	10	14	10	12	1,4	1728,0	47,17	864	3
4	6	4	6	4	5	1,5	125,0	3,41	150	3
5	2	2	2	2	2	1,0	8,0	0,22	24	4
6	7	5	7	5	6	1,4	216,0	5,90	216	4
7	5	3	5	3	4	1,7	64,0	1,75	96	4
8	30	22	30	22	26	1,4	17576,0	479,82	4056	4
9	9	6	9	6	8	1,5	421,9	11,52	338	4
10	8	5	8	5	7	1,6	274,6	7,50	254	5
11	5	3	5	3	4	1,7	64,0	1,75	96	5
12	30	30	30	30	30	1,0	27000,0	737,10	5400	5
13	5	4	5	4	5	1,3	91,1	2,49	122	5
14	5	4	5	4	5	1,3	91,1	2,49	122	5
15	9	3	9	3	6	3,0	216,0	5,90	216	5
16	5	3	5	3	4	1,7	64,0	1,75	96	6
17	6	2	6	2	4	3,0	64,0	1,75	96	6
18	7	5	7	5	6	1,4	216,0	5,90	216	6
19	4	2	4	2	3	2,0	27,0	0,74	54	6
20	4	2	4	2	3	2,0	27,0	0,74	54	7
21	36	26	36	26	31	1,4	29791,0	813,29	5766	8
22	22	6	22	6	14	3,7	2744,0	74,91	1176	8
23	25	18	25	18	22	1,4	9938,4	271,32	2774	11
24	6	4	6	4	5	1,5	125,0	3,41	150	12
25	7	3	7	3	5	2,3	125,0	3,41	150	13
26	20	6	20	6	13	3,3	2197,0	59,98	1014	14

27	4	4	4	4	4	1,0	64,0	1,75	96	22
28	5	4	5	4	5	1,3	91,1	2,49	122	26
29	13	8	13	8	11	1,6	1157,6	31,60	662	30
30	9	6	9	6	8	1,5	421,9	11,52	338	31
mean	11	7	11	7	9	2	3172	86,6	833	
<i>std</i>	9	7	9	7	8	1	7745	211	1553	

A.2 Preparation data for all brines

preparation of 0.01 M of HSQ: 1.3 Q+7.8 HS		
number of the sample	1	40,00
Q, g	1,30	52,03
HS, g	7,96	318,40
total, g	9,26	370,43
dens HSQ, g/cm3	1,01757	
total, ml	9,10	364,03

preparation of 0.01 M of LSQ: 1.3 Q+7.8 LS		
number of the sample	1	40,00
Q, g	1,30	52,03
LS, g	7,79	311,75
total, g	9,09	363,77
dens LSQ, g/cm3	0,99935	
total, ml	9,10	364,01

preparation of 0.01 M of NaClQ: 1.3 Q+7.8 NaCl		
number of the sample	1	40,00
Q, g	1,30	52,03
NaCl, g	7,95	318,06
total, g	9,25	370,08
dens NaClQ, g/cm3	1,01667	
total, ml	9,10	364,02

preparation of Reference HS: 1.3 DI + 7.8 HS		
number of the sample	1	15,00
DI (pH3), g	1,30	19,50
HS, g	7,96	119,40
total, g	9,26	138,90

preparation of Reference LS: 1.3 DI + 7.8 LS		
number of the sample	1	15,00
DI, g	1,30	19,50
LS, g	7,79	116,91
total, g	9,09	136,41

preparation of Reference NaCl: 1.3 DI + 7.8 NaCl		
number of the sample	1	15,00
DI, g	1,30	19,50
Ca, g	7,95	119,27
total, g	9,25	138,77

A.3 Calibration data for LSQ, HSQ and NaClQ

Calibration data for 0,01 [M] HSQ, pH~3

Dilution rate	Concentration [mM]	ABS
1000	0,01	0,1216
500	0,02	0,2042
200	0,05	0,4417
100	0,10	0,7764

Calibration data for 0,01 [M] LSQ, pH~3

Dilution rate	Concentration [mM]	ABS
1000	0,01	0,1248
500	0,02	0,1893
200	0,05	0,4097
100	0,10	0,7291

Calibration data for 0,01 [M] NaClQ, pH~3

Dilution rate	Concentration [mM]	ABS
1000	0,01	0,1337
500	0,02	0,2156
200	0,05	0,4153
100	0,10	0,7451

A.4 Calibration data for all three brines

Calibration data calculation for HSQ												
Total ml	Dilution rate	HSQ ml	ul HSQ	DI pH3 (gr) desired	DI pH3 (gr) real	HSQ (ul)	Total (gr)	ABS	Real dilution rate	pH	Desired conc., mM	Real conc., mM
5	1000	0,005	5	4,9950	4,9963	5	5,0020	0,1216	877,5		0,01	0,011
5	500	0,01	10	4,9900	4,9893	10	5,0008	0,2042	434,9		0,02	0,023
5	200	0,025	25	4,9750	4,9744	25	5,0006	0,4417	190,9		0,05	0,052
5	100	0,05	50	4,9500	4,9512	50	5,0022	0,7764	98,1		0,1	0,102

Calibration data calculation for LSQ

Total ml	Dilution rate	LSQ ml	ul LSQ	DI pH3 (gr) desired	DI pH3 (gr) real	LSQ (ul)	Total (gr)	ABS	Real dilution rate	pH	Desired conce., mM	Real conce., mM
5	1000	0,005	5	4,995	4,9947	5	5,0004	0,1248	877,3		0,01	0,011
5	500	0,01	10	4,99	4,9914	10	5,0017	0,1893	485,6		0,02	0,021
5	200	0,025	25	4,975	4,9759	25	5,0014	0,4097	196,1		0,05	0,051
5	100	0,05	50	4,95	4,9528	50	5,0029	0,7291	99,9		0,1	0,100

Calibration data calculation for NaClQ

Total ml	Dilution rate	NaClQ ml	ul NaClQ	DI pH3 (gr) desired	DI pH3 (gr) real	NaClQ (ul)	Total (gr)	ABS	Real dilution rate	pH	Desired conc., mM	Real conc., mM
5	1000	0,005	5	4,995	4,9952	5	5,0010	0,1337	862,2		0,01	0,012
5	500	0,01	10	4,99	4,9903	10	5,0013	0,2156	454,7		0,02	0,022
5	200	0,025	25	4,975	4,9751	25	5,0011	0,4153	192,4		0,05	0,052
5	100	0,05	50	4,95	4,9503	50	5,0017	0,7451	97,3		0,1	0,103

A.5 . Adsorption calculations sample nr. for Anorthite

Anorthite (mjll): 1,0001g BrineQ (mbq): 9,000 g

Molarity quinoline (Cq): 0,07 M

Molar mass quinoline (Mq): 129,16 g/mole HCl/NaOH added (mH/N): 0,095 g

Calibration curve: $ABS = 6635,5x - 0,0051$ ABS: 0,2683

Total amount liquid (mtot) in the sample: $mtot = mbq + mH/N = 9,2008$ g

Molarity of quinoline in the sample (Mqs): $Mqs = m_q/mtot * C_q = 0,01$ M

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

Diluted 100 times $\rightarrow x = 0,00412$

Percent quinoline in solution (%qs): $\%qs = (x/mqs) * 100 = 41,55$ %

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

Initially mole quinoline in sample (ni) $ni = (m_q/1000) * C_q = 0,0000913$ mole

Mole quinoline in sample after stable pH (ns) : $ns = (mtot/1000) * x = 3,79 * 10^{-5}$ mole

Mole quinoline adsorb to the clay surface (nad) : $nad = ni - ns = 5,34 * 10^{-5}$ mole

Adsorption = $(n_{ad} * M_q * 1000) / mjll = 2,2$ mg base/g Anorthite

A.6 Adsorption vs. pH data for HS brine with anorthite at ambient temperature.

Type	Sample	Anorthite [g]	Brine/Q [g]	Total (Anorthite**+B/Q) [g]	HCl* [g]	NaOH* [g]	Total liquid [g]	Q [M]	wt% K [%]	pH adjusted	pH after 24 hours
HS	1	1,0001	9,0006	10,0007	0,00005	0	9,00065	0,010	10,00	2,61	3,79
HS	2	1,0007	9,0005	10,0012	0,000025	0	9,000525	0,010	10,01	4,02	4,52
HS	3	1,0006	9,0006	10,0012	0	0	9,0006	0,010	10,00	6,31	7,08

Total ml	Dilution rate	Desired B/Q μl	DI pH3 desired gr	DI pH3 real gr	B/Q real gr	Total real gr	ABS	Real dilution rate	pH of sample for ABS(~3)
5	200	25	4,975	4,9751	0,0254	5,0005	0,3584	196,9	3,17
5	200	25	4,975	4,9756	0,0254	5,001	0,3690	196,9	
5	200	25	4,975	4,9750	0,0258	5,0008	0,3440	193,8	

Q in diluted solution*** [M]	Q in real solution*** [M]	Base in water [%]	Q adsorbd [%]	Initial Q**** [mol]	Final Q***** [mol]	Mol ads [mol]	Adsorption [mg base/g K]
0,04339	0,008542124	85,42	14,58	0,0000881968	0,0000753388	0,00001	1,66
0,04485	0,008830365	88,30	11,70	0,0000881958	0,0000778801	0,00001	1,33
0,04141	0,008025849	80,26	19,74	0,0000881968	0,0000707854	0,00002	2,25

*Under assumption that density of HCl/NaOH solution is 1 g/ml

**Anorthide

***Q in diluted solution taken from centrifuged A+B/Q sample after 24 hours

***Q in solution after cetrifuged A+B/Q sample after 24 hours

****Number of moles in initial solution (before rotation)

*****Number of moles in solution after 24 hours rotation

A.7. Error calculation for microcline and quartz with LSQ

Type	Sample	Microcline [g]	Brine/Q [g]	Total (M**+B/Q) [g]	HCl* [g]	NaOH* [g]	Total liquid [g]	Q [M]	wt% M [%]	pH adjusted	pH after 24 hours
LS	1	1,0001	9,0013	10,0014	0,00001	0	9,00131	0,010	10,00	4,85	5,13
LS	2	1,0003	9,0008	10,0011	0,00001	0	9,00081	0,010	10,00	4,81	5,13
LS	3	1,0004	9,0002	10,0006	0,00001	0	9,00021	0,010	10,00	4,81	5,14
LS	4	1,0006	9,0004	10,001	0,00001	0	9,00041	0,010	10,00	4,80	5,14
LS	5	1,0006	9,0012	10,0018	0,00001	0	9,00121	0,010	10,00	4,67	5,26
LS	6	1,0003	9,0009	10,0012	0,00001	0	9,00091	0,010	10,00	4,77	5,25
LS	7	1,0002	9,0006	10,0008	0,00001	0	9,00061	0,010	10,00	4,76	5,12
LS	8	1,0003	9,0003	10,0006	0,00001	0	9,00031	0,010	10,00	4,60	5,14
LS	9	1,0004	9,0005	10,0009	0,00001	0	9,00051	0,010	10,00	4,85	5,27

Total ml	Dilution rate	Desired B/Q μl	DI pH3 desired gr	DI pH3 real gr	B/Q real gr	Total real gr	ABS	Real dilution rate	pH of sample for ABS(~3)
5	200	25	4,975	4,9754	0,0253	5,0007	0,3180	197,7	
5	200	25	4,975	4,9751	0,026	5,0011	0,3431	192,4	
5	200	25	4,975	4,9755	0,0253	5,0008	0,3322	197,7	
5	200	25	4,975	4,9751	0,0251	5,0002	0,3203	199,2	
5	200	25	4,975	4,9751	0,0252	5,0003	0,3209	198,4	
5	200	25	4,975	4,9756	0,0251	5,0007	0,3252	199,2	
5	200	25	4,975	4,9756	0,0258	5,0014	0,3376	193,9	
5	200	25	4,975	4,9754	0,0252	5,0006	0,3431	198,4	
5	200	25	4,975	4,9753	0,0254	5,0007	0,3308	196,9	

Q in diluted solution*** [M]	Q in real solution*** [M]	Base in water [%]	Q adsorbd [%]	Initial Q**** [mol]	Final Q***** [mol]	Mol ads [mol]	Adsorption [mg base/g K]
0,03830	0,007569697	75,70	24,30	0,0000900761	0,0000681848	0,00002	2,83
0,04202	0,008082316	80,82	19,18	0,0000900710	0,0000727983	0,00002	2,23

0,04040	0,007985999	79,86	20,14	0,0000900650	0,0000719259	0,00002	2,34
0,03864	0,007697184	76,97	23,03	0,0000900670	0,0000693263	0,00002	2,68
0,03873	0,007684445	76,84	23,16	0,0000900751	0,0000692177	0,00002	2,69
0,03936	0,007842696	78,43	21,57	0,0000900721	0,0000706408	0,00002	2,51
0,04120	0,007987378	79,87	20,13	0,0000900690	0,0000719416	0,00002	2,34
0,04202	0,008338064	83,38	16,62	0,0000900660	0,0000750976	0,00001	1,93
0,04020	0,007913533	79,14	20,86	0,0000900680	0,0000712756	0,00002	2,43

Type	Sample	Quartz [g]	Brine/Q [g]	Total (Quartz**+B/Q) [g]	HCl* [g]	NaOH* [g]	Total liquid [g]	Q [M]	wt% Quartz [%]	pH adjusted	pH after 24 hours
LS	1	1,0008	9,0009	10,0017	0,000005	0	9,000905	0,010	10,01	4,86	5,00
LS	2	1,0006	9,0007	10,0013	0,000005	0	9,000705	0,010	10,00	4,86	5,00
LS	3	1	9,001	10,001	0,000005	0	9,001005	0,010	10,00	4,90	4,97
LS	4	1,0006	9,0003	10,0009	0,000005	0	9,000305	0,010	10,01	4,84	4,94
LS	5	1,0009	9,0002	10,0011	0,000005	0	9,000205	0,010	10,01	4,84	4,97
LS	6	1,0008	9,0007	10,0015	0,000005	0	9,000705	0,010	10,01	4,85	5,00
LS	7	1,0003	9,0008	10,0011	0,000005	0	9,000805	0,010	10,00	4,82	4,94
LS	8	1,0004	9,0007	10,0011	0,000005	0	9,000705	0,010	10,00	4,95	4,97
LS	9	1,0005	9,0008	10,0013	0,000005	0	9,000805	0,010	10,00	4,89	4,94

Total ml	Dilution rate	Desired B/Q µl	DI pH3 desired gr	DI pH3 real gr	B/Q real gr	Total real gr	ABS	Real dilution rate	pH of sample for ABS(~3)
5	200	25	4,975	4,9754	0,0257	5,0011	0,2743	194,6	
5	200	25	4,975	4,9751	0,0254	5,0005	0,2705	196,9	
5	200	25	4,975	4,9753	0,0256	5,0009	0,2880	195,3	
5	200	25	4,975	4,9751	0,026	5,0011	0,2969	192,4	
5	200	25	4,975	4,9752	0,0257	5,0009	0,2817	194,6	
5	200	25	4,975	4,9754	0,0255	5,0009	0,2795	196,1	
5	200	25	4,975	4,975	0,0255	5,0005	0,2786	196,1	
5	200	25	4,975	4,9752	0,0252	5,0004	0,2710	198,4	
5	200	25	4,975	4,9752	0,0256	5,0008	0,3065	195,3	

Q in diluted solution*** [M]	Q in real solution*** [M]	Base in water [%]	Q adsorbd [%]	Initial Q**** [mol]	Final Q***** [mol]	Mol ads [mol]	Adsorption [mg base/g K]
0,03182	0,006191643	61,92	38,08	0,0000900721	0,0000557694	0,00003	4,43
0,03125	0,006153102	61,53	38,47	0,0000900700	0,0000554210	0,00003	4,47
0,03385	0,006612382	66,12	33,88	0,0000900731	0,0000595597	0,00003	3,94
0,03517	0,006764733	67,65	32,35	0,0000900660	0,0000609273	0,00003	3,76
0,03292	0,006404892	64,05	35,95	0,0000900650	0,0000576857	0,00003	4,18
0,03259	0,006391157	63,91	36,09	0,0000900700	0,0000575652	0,00003	4,19
0,03246	0,006364478	63,64	36,36	0,0000900710	0,0000573255	0,00003	4,23
0,03133	0,006216522	62,17	37,83	0,0000900700	0,0000559922	0,00003	4,40
0,03659	0,007148065	71,48	28,52	0,0000900710	0,0000643834	0,00003	3,32

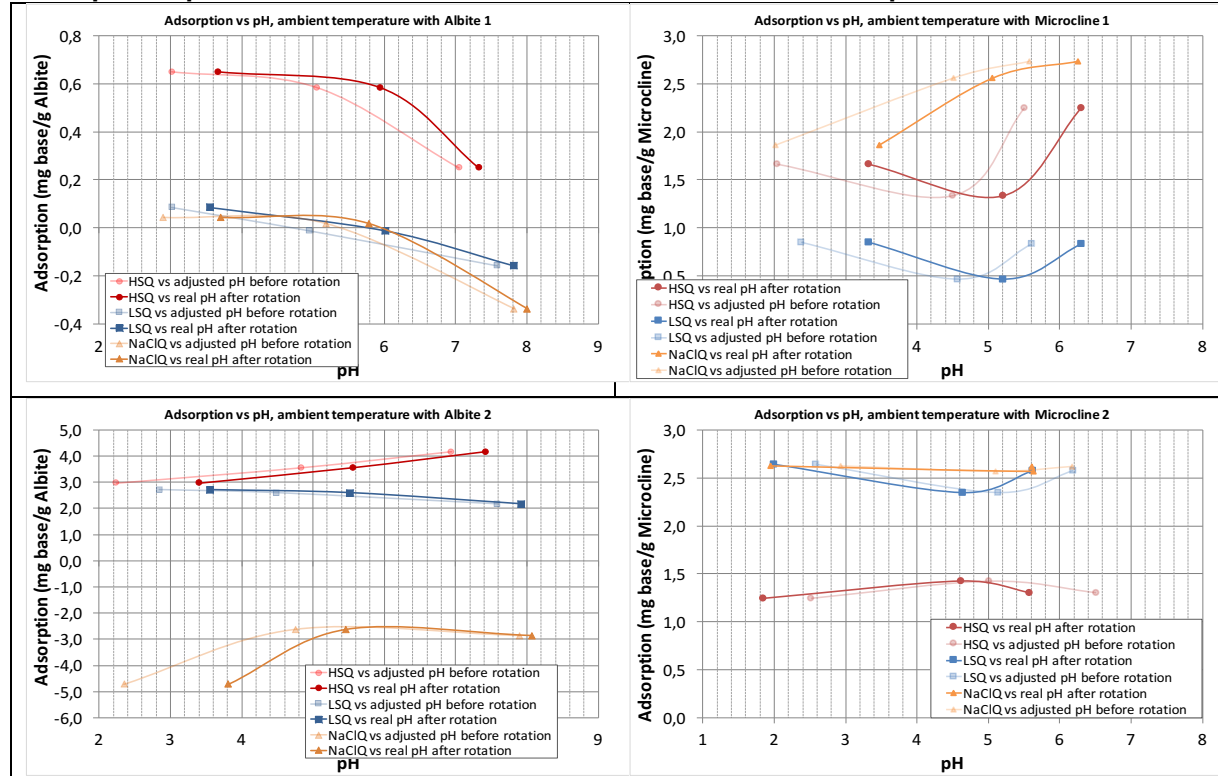
For plot	Arithmetical mean	
	Microcline	Quartz
0	2,44	4,1
9,5	2,44	4,10

Sample #	Error calculations					
	Arithmetical mean, mg base/g K		Deviations, mg base/g K		Absolut error, mg base/g Mineral	
	Microcline	Quartz	Microcline	Quartz	Microcline	Quartz
1	2,83	4,43	0,39	0,32	0,2084	0,2862
2	2,23	4,47	0,21	0,37		
3	2,34	3,94	0,10	0,16	Relative error,%	
4	2,68	3,76	0,24	0,34	Microcline	Quartz
5	2,69	4,18	0,25	0,08	8,53	6,98
6	2,51	4,19	0,07	0,09		
7	2,34	4,23	0,10	0,13		
8	1,93	4,40	0,51	0,30		
9	2,43	3,32	0,02	0,79		
Arithmetic mean	2,44	4,10				

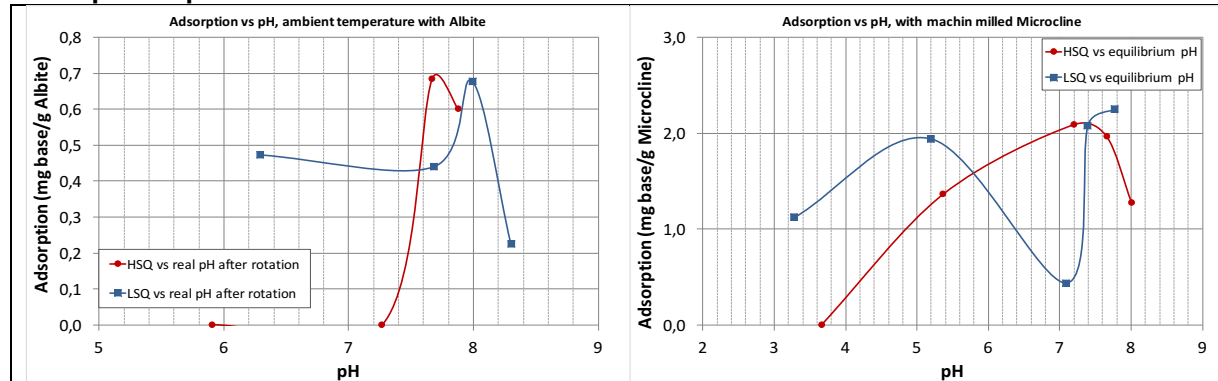
B. Plot of adsorption of quinoline onto minerals

B.1 Adsorption vs pH, at ambient temperature

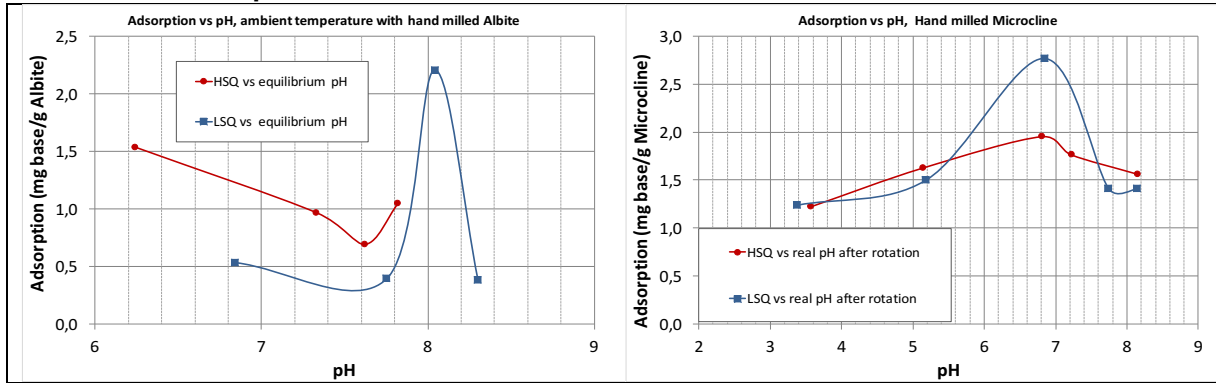
With spectrophotometric device Shimadzu UV-1700 PharmaSpec UV-VIS



With spectrophotometric device Shimadzu UVmini-1240

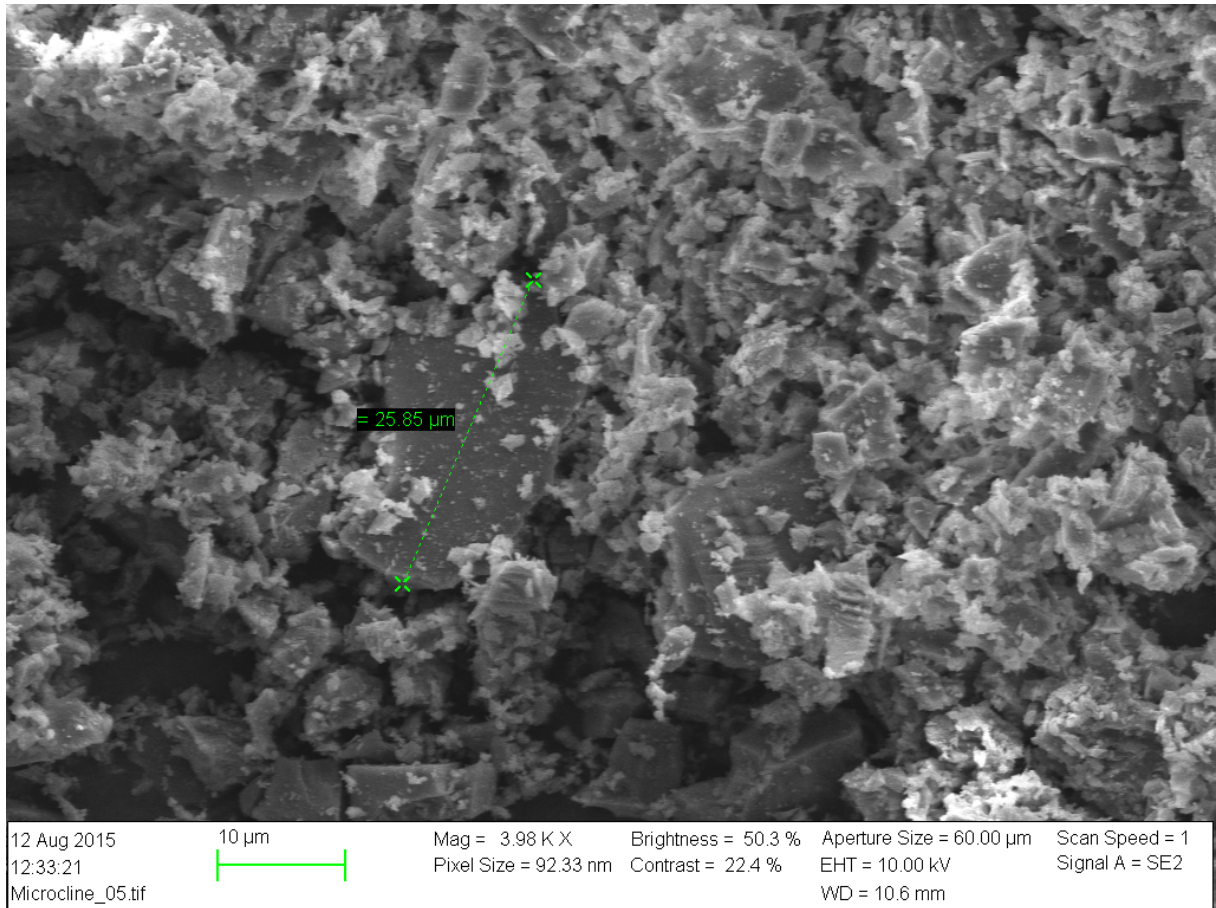


Hand milled feldspars



C. SEM images of albite and microcline

Microcline milled with methanol by Yngve Andersen



Albite milled with methanol by Yngve Andersen

