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UNIVERSITY OF STAVANGER

Characterization of Wettability Alteration by Flotation

A study by Preben Emil Haugen

6/15/2016

Abstract

Alterations in reservoir wettability are known to affect the oil production (1,2). The exact causes of alteration, and how much each of these causes alter wettability is what this study intends to examine.

The flotation method was used to examine how different brine and oil combinations affect the wettability of different sandstone minerals, and a rock from a clay rich sandstone reservoir in the North Sea. A total of 238 different samples were made to examine the effect all possible combinations of the following variables have on wettability:

- *oils:* three different stock tank oils (STO) from North Sea reservoirs, and N-decane
- *brines:* synthetic formation water (FW) from two North Sea reservoirs, synthetic sea water (SW) and low salinity water (LSW)
- *minerals:* quartz, K-feldspar, glauconite, muscovite and rock from a North Sea reservoir

In addition to this a few glauconite samples were prepared with a low concentration of three-valent Iron and Aluminum cations in the brine to examine how they affect wettability.

Quartz was found to be near 100% water-wet for all brine/oil combinations. K-feldspar, glauconite and rock from field #1 was found to primarily water-wet (>80% water-wet) for all brine/oil combinations. Muscovite showed both water-wet and oil-wet tendencies, depending on the brine/oil combination.

LSW came back with the most water-wet results, compared to the other brines, while samples aged in SW came back with similar wetting results as FW #1 and FW #2 in most cases.

The wettability results showed a clear correlation between the *total acid number* (TAN) of the oil and the Ca^{2+} concentration of the brine for all minerals except quartz. Samples aged in an oil with high TAN are more sensitive to the Ca^{2+} concentration of the brine, than samples aged in an oil with low TAN. If the samples are aged in a brine with a high Ca^{2+} concentration, the wettability is more sensitive to the TAN of the oil than if aged in a brine with a low Ca^{2+} concentration.

Fe^{3+} and Al^{3+} appears to have a similar effect as Ca^{2+}, only the effect can be observed at much lower concentrations.

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Abbreviations

IFT	Interfacial Tension
LSW	Low Salinity Water
SAC	Surface Active Compounds
STO	Stock Tank Oil
SW	Sea Water
TAN	Total Acid Number
TBN	Total Base Number

1 Introduction

The natural decline in oil production on the Norwegian Continental Shelf, and the fact that fewer new reservoirs are left to find is challenging the oil companies to find methods to extend production. This could be done using enhanced oil recovery methods like advanced water flooding (2). In short this alters the wettability of the reservoir by changing the chemical composition of the injection water. This is a study of what causes alterations in the wetting preferences of different minerals, and how large the effect of these causes are.

First, an in depth literature study in wettability is performed. This is done to investigate what wettability is, and to find out what type of brine and oil compositions that could cause alterations in the wettability of minerals.

secondly, the experimental procedures used in this study will be shown. The flotation method was used to study how four brines and four oils with different chemical compositions affect the wettability of four different minerals and a rock from a North Sea reservoir. In this method, crushed rock/mineral is first mixed with brine and aged in an oven for three days. After this phase is over, the brine is removed and stored for later use, and oil is added to the wet mineral before this mixture is aged in the oven for two days. Now the brine is poured back in, and the mixture is aged in the oven for another day. Finally the oil phase is removed along with the oil-wet particles floating in it and brine/mineral mixture is filtered, dried and weighed.

In the third part, the results of the flotation procedure will be discussed and compared with the literature study, and finally a conclusion will be presented.

2 Literature study

To properly describe fundamental reservoir properties such as relative permeability, interfacial tension and wettability, one must take the active forces in the system into account. These forces are the attraction between the individual elements present in the system. In a water/oil/solid system, the three present forces are the adhesive forces (tension) between oil and water, oil and rock, and water and rock (4). The surface forces, known as *interfacial tension* (IFT), are the first set of forces that should be considered, because wettability, capillary pressure and relative permeability are all depend on interfacial tension. See Figure 1 for a summary of how these reservoir properties are dependent on each other.

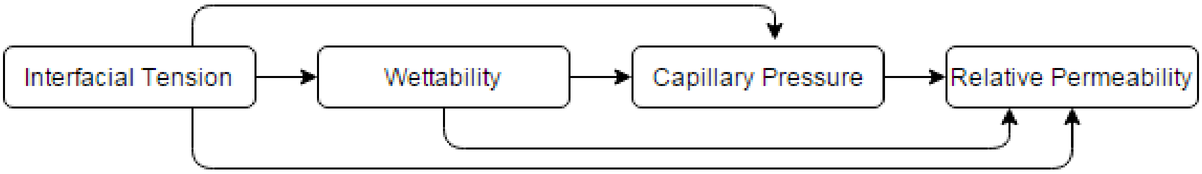


Figure 1: Dependence Summarization (4).

2.1 Interfacial Tension

In a system with two or more immiscible liquids, the term interfacial tension is used to describe the interfacial forces between them (4). The thickness of this interface is very small, and is usually about 1.0×10^{-9} m (6). To better understand IFT, imagine a system where the two immiscible fluids water and oil are present, see Figure 2 for illustration. A molecule that is far away from the interface is only surrounded by molecules of its' own kind. Since these molecules have the same charge, the molecule is pulled equally in all directions resulting in a net attraction equal to zero. A molecule that is at the interface is not totally surrounded by molecules with the same properties, and has forces of different magnitude acting upon it from the oil above and the water below. This imbalance of forces gives rise to interfacial tension (4). IFT has the dimensions of force per unit length. Even though IFT is a an entirely fluid- or interface-related property, and not a reservoir rock property it is discussed here since it has a high influence on other rock properties (see Figure 1), which in turn effect the total recovery of hydrocarbons (4).

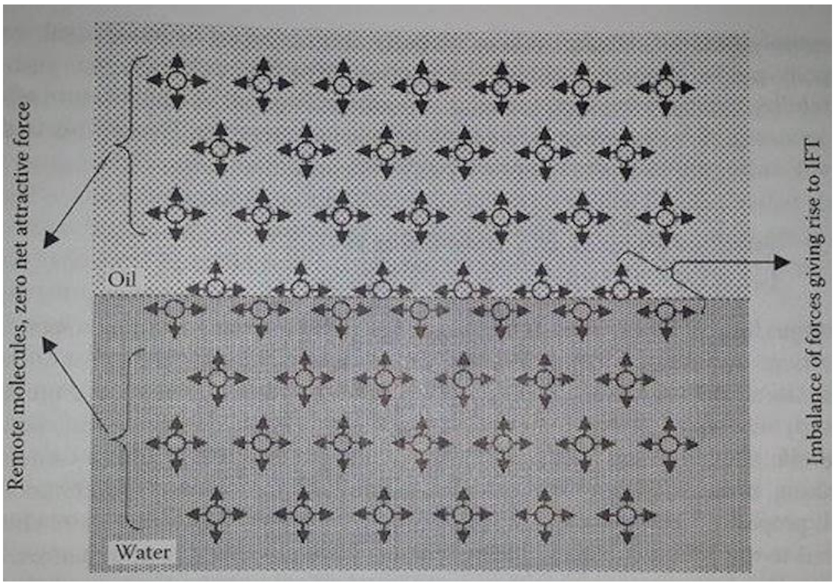


Figure 2: Interfacial tension between two immiscible fluids (4).

2.2 Wettability

2.2.1 Definition

According to Donaldson and Alam, wettability is defined as the relative adhesion of two fluids to a solid surface (7). If a porous media is surrounded by two immiscible fluids, wettability is the measure of how one of the fluids wet (spread or adhere to) the surface of that particular porous media. The exposed surface of the pores in the rocks consists of different minerals, which in turn have their own preferred affinity for water and oil. This means that for a system where we have a rock that is surrounded by both oil and water, the term wettability is the average wetting preferences of these minerals (7).

There are four different states of wettability that are recognized today: water-wet, fractional-wettability, mixed-wettability and oil-wet.

2.2.1.1 Water-wet System

The wettability of a flat and polished <u>single</u> mineral rock with a drop of water encapsulated by oil on it (see Figure 4), is said to be primarily water-wet when the contact angle between the rock and the water is less than 75^o (8). When the contact angle is between 75^o and 105^o the system is said to be neutrally-wet. This way of measuring wettability cannot be used to identify the wettability of a reservoir, because a reservoir is a porous media consisting of a mixture of different minerals. A porous media (consisting of <u>one or more</u> minerals) containing oil and water is said to be water-wet when 50% or more of the rock surface is wet by water (7), see Figure 3. At the *initial water saturation* (Sw_i) and *initial oil saturation* (Sw_o), water fills up the smaller pores and the dead end/cul-de-sac pores (4,8), and lays out as a coating on the surface of the larger predominantly water-wet pores (7). This results in droplets of oil, or oil globules being lodged in the larger pores as they are resting on the water coating. These oil globules can spread through two or more pores and may come into contact with the surface of the rock in areas where the mineral in place is predominantly oil-wet (7). This gives us a system where water is found as a continuous phase all through the system and the oil is found mainly as globules in the larger pores enclosed by water (7). If a water-wet rock is saturated with oil and then surrounded by water, the water will spontaneously imbibe into the rock and displace the oil until an equilibrium is reached. If the opposite is tested, oil will not imbibe into a water-wet rock (4,7).

2.2.1.2 Oil-wet System

The wettability of a flat and polished <u>single</u> mineral rock with a drop of water encapsulated by oil on it (see Figure 4), is said to be oil-wet when the contact angle between the rock and the water is more than 105^o (8). This way of measuring wettability cannot be used to identify the wettability of a reservoir, because a reservoir is a porous media consisting of a mixture of different minerals. A porous media (consisting of <u>one or more</u> minerals) containing oil and water is said to be oil-wet when 50% or more of the rock surface is wet by oil (7), see Figure 3. This is directly opposite to a water-wet system. At Sw_i and Sw_o, oil fills up the smaller pores and the dead end/cul-de-sac pores (5,8), and lays out as a coating on the surface of the larger predominantly oil-wet pores (7). This results in droplets of water, being lodged in the larger pores as they are resting on the oil coating. These water globules can spread through two or more pores and may come into contact with the surface of the rock in areas where the mineral in place is predominantly water-wet (7). This gives us a system where oil is found as a continuous phase all through the system and the water is found mainly as globules in the larger pores enclosed by oil (7). If an oil-wet rock is saturated with water and then surrounded by oil, the oil will spontaneously imbibe into the rock and displace the water until an equilibrium is reached. If the opposite is tested, water will not imbibe into an oil-wet rock (4,7,8).

2.2.1.3 Fractionally-wet System

A water/oil/solid system is said to be fractionally-wet when the preferential wetting of the pore surfaces is randomly distributed throughout the rock (7), see under mixed-wet in Figure 3. The random distribution of surface minerals with different chemical properties creates zones where the rock is either preferentially water-wet or oil-wet, which makes it so that there are no continuous oil networks through the rock (7).

2.2.1.4 Mixed-wet System

A mixed-wet system is a special type of fractional wettability, where both continuous oil-wet and continuous water-wet surfaces are found (9). In a heterogeneous mixed wet system like this, the smaller pores are water-wet and filled with water, while the larger pores are predominantly oil-wet and filled with oil (10). This gives us a system where the oil forms continuous phase as most of the larger pores are connected, while the water forms a continuous path through the smaller pores. Mixed-wet in Figure 3 is more representative of a fractionally-wet system. Mixed wettability is a condition that can occur when oil containing *surface active compounds* (SAC) invades a water-wet reservoir saturated with brines and displaces the water in the larger pores. The SAC will react with the surface of the rock and gradually displace the aqueous film, making the rock oil-wet in the larger pores (10). Oil will only enter the larger pores, because the capillary pressure for displacement of water in the smaller pores is too large (7).

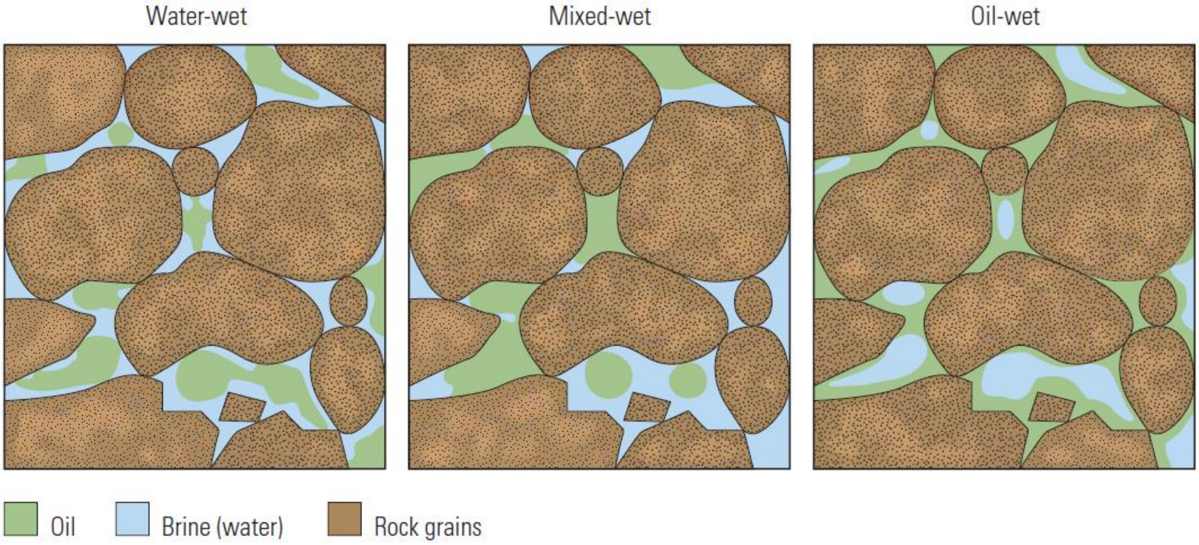


Figure 3: Types of wettability systems (11).

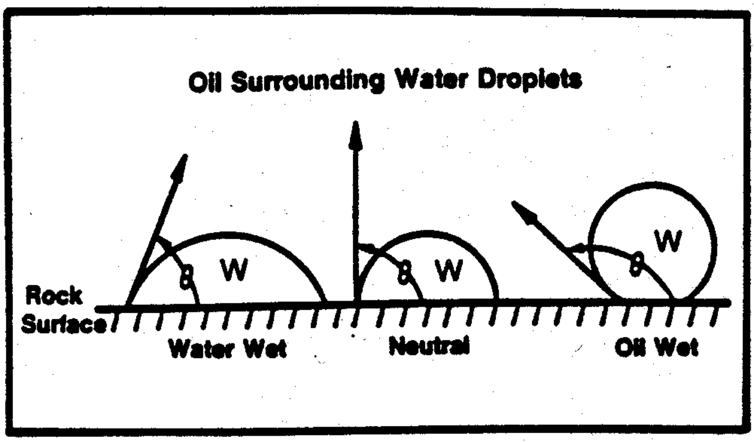


Figure 4: Contact angle of water droplets (8).

2.2.2 Methods used to Determine Wettability

There are two different groups of methods that can be used to measure the wettability of a water/oil/rock system: *qualitative* and *quantitative* (4). Qualitative methods uses other measurements such as capillary pressure curves or relative permeability curves to determine wettability. Quantitative methods use direct measurement, where the rock and reservoir fluids are used to determine the exact wettability of the system by giving the degree of water or oil wetness (4).

2.2.2.1 Qualitative Methods

The qualitative methods that will be discussed in this text are: flotation method, imbibition method and microscope examination. These are some of the most commonly used qualitative methods, and that is why they are mentioned here (12).

Flotation Method

The flotation methods come in different variations, and is in its simplest form only a glass container with oil, water and sand that is shaken to see what happens to the grains (12). If the system is strongly water-wet the grains will sink, and if the system is oil-wet the grains will float in the oil phase. The more advance versions involve several steps where the mineral is first aged in brine, then in oil, then the brine is poured back and the mixture is aged again before the oil is removed and the sample is filtered.

Imbibition Method

This method gives a quick but rough idea of the wettability without requiring any complicated equipment (12). Here a core at initial water and oil saturation is submerged in brine underneath a graduated cylinder, and the rate and amount of oil displaced by imbibed brine is measured. If the core is strongly water-wet a large volume of brine is quickly imbibed into the core, while in less water-wet cores a smaller amount of brine will imbibe and the rate will also be lower. If no brine is imbibed the core is either neutral- or oil-wet. The core is then driven to residual oil saturation before being submerged in oil underneath a graduated cylinder. The rate and amount of water displaced by imbibed oil is measured. If the core is strongly oil-wet a large volume of oil is quickly imbibed into the core, while in less oil-wet cores a smaller amount of oil will imbibe and the rate will also be lower. If no oil nor brine is imbibed the core is neutrally wet.

Microscope Examination

In this method the wettability is determined by examining flow on pore level (12). The structure of the residual oil and the changes in the location of the oil and water during flooding is described. In a strongly water-wet system the water surrounds the grains as a thin film, while oil is found either resting on this film, or as small spherical drops in the center of the pores. In a intermediate wet system both the oil and the water can found in contact with the rock surfaces and in the small pores. In a strongly oil-wet system the roles in the strongly water-wet system are reversed.

2.2.2.2 Quantitative Methods

The direct quantitative methods that will be discussed in this text are: contact angle measurement, the Amott test and the USBM method. These are the most widely used quantitative methods in the petroleum industry for measuring wettability (4).

Contact Angle Measurement

There are many methods that can be used to measure the contact angle, including sessile drops or bubbles, the tilting plate method, tensiometric method, vertical rod method, capillary rise method and cylinder method (12). The method that is most commonly used to measure the contact angle in the petroleum industry is the sessile drop method. In this method a drop of water is placed on a polished mineral surface (that is representative to the reservoir rock) in the presence of reservoir oil, a photograph is taken and the contact angle of the droplet is measured (4). If the surface is water wet the contact angle is low (between 0^o and 75^o), and the water easily spreads over the mineral surface. If the surface is oil wet the contact angle is high (between 105^o and 180^o) and the water droplet beads up. If the contact angle is measured to be between 75^o and 105^o the wettability of the surface is neutral (12). See Figure 4 for illustration. This procedure can also be done the other way around; a drop of oil is placed on the mineral surface in the presence of formation water, and the contact angle is measured (7).

Exactly how representative these results are of the actual reservoir rock wettability has been debated. In this method only polished mineral surfaces are used, which means that the roughness, complex geometry and heterogeneity of the reservoir rock is not taken into account when estimating the wettability of the reservoir (4,7). In 1970 it was shown by Morrow that the roughness and geometry of the rock affect the overall wettability of the rock (13). Since these polished mineral surfaces are not truly representative of all the properties of the reservoir rock, the Amott and USBM methods are considered more useful as they measure the average wettability of core samples (7). The main advantage of this method is that it is quick and cheap compared to the Amott and USBM methods (4).

Amott test

This wettability test was developed by Amott in 1951 (3), and is the wettability test that is most commonly used to determine the average wettability of core samples (4). In this test a core sample that has a residual oil saturation (achieved by force displacing the oil with water) is used. The size of the core samples vary, and they are either 1 or 1.5inches in diameter and length of the samples range from 2 to 3inches. The average wetting characteristics are then measured by performing four individual displacement operations (3):

1. Immerse the core sample into oil for 20 hours and observe the spontaneous imbibition of oil. Note the amount of water that has been displaced, if any, as V_{WS}.

2. Force displace the water in the core until a residual water saturation is reached by apply a high displacement pressure. The high displacement pressure can be obtained by using either a centrifuge or a displacement apparatus. Note the amount of water that has been displaced as V_{wf}.
3. Immerse the core sample into water for 20 hours and observe the spontaneous imbibition of water. Note the amount of oil that has been displaced, if any, as V_{os}.
4. Force displace the oil in the core until a residual oil saturation is reached. See number 2. for methods of forced displacement. Note the amount of oil that has been displaced as V_{of}.

The wettability of the core sample is determined as follows: The total volume of displaced water, $V_{wt} = V_{ws} + V_{wf}$. The total volume of displaced oil, $V_{ot} = V_{os} + V_{of}$. By using these values the displacement by oil ratio, δ_o, and displacement by water, δ_w, can be found.

$$\delta_o = \frac{V_{ws}}{V_{wt}} \tag{2.1}$$

$$\delta_w = \frac{V_{os}}{V_{ot}} \tag{2.2}$$

These equations shows the ratio of spontaneously displaced liquid to the total volume of displaced liquid, and they are used as wettability indices. These wettability indices can be used to determine the wetting preferences of the core sample, see

Table. A low value of δ_o (close to zero) indicates a weak oil-wetting preference, while a high value of δ_o (close to one) indicates a strong oil-wetting preference. The same applies to δ_w, a high value indicates a strong water-wetting preference while a low value indicates a weak water-wetting preference (1,5,10).

Table 1: Relationship between Wettability and Amott Wettability Indices (3).

Displacement Ratio	**Preferentially Water Wet**	**Neutral Wet**	**Preferentially Oil Wet**
δ_o	Zero	Zero	Approaching one
δ_w	Approaching one	Zero	Zero

Amott-Harvey Relative Displacement

Unlike in the Amott test, the procedure now begins by flooding the core with oil to achieve irreducible water saturation (4). For the Amott-Harvey relative displacement test, the sequence followed in the Amott test is reversed. First the core sample, which is now at irreducible water saturation is subjected to the spontaneous and forced displacement of oil by water, before it is subjected to spontaneous and forced displacement water by oil. based on the recorded volumes, the displaced water, and the displaced by oil ratios can now be calculated by eq. 2.1 and eq. 2.2. With these ratios the Amott-Harvey wettability index is calculated as follows:

$$I_{AH} = \delta_w - \delta_o \tag{2.3}$$

Table 2: Wettability classification based on the Amott-Harvey wettability index (4).

I_{AH}	Wettability
+0.3 to +1.0	Water wet
+0.1 to +0.3	Slightly water wet
-0.1 to +0.1	Neutral
-0.3 to -0.1	Slightly oil wet
-1.0 to - 0.3	Oil wet

U.S. Bureau of Mines (USBM) Method

This method was developed by Donaldson et al. in 1969 (14), and is among the most popular methods used to determine the average wettability of a core sample (4,7). A centrifuge apparatus is used throughout the whole test, see Figure 5 for illustration. First the irreducible water saturation of the core sample is established, and this is done by centrifuging the core under the displacing oil at high speeds. The oil forces the water out of the core, and the entire process is monitored and continued until an equilibrium is reached. At this stage no amount of water is displaced by the oil. The irreducible water saturation is then calculated by using either volume or mass balance (4,9,14).

The sample is now prepared at irreducible water saturation and the determination of the wettability can begin. It is time for the brine drive step. The core is now placed in a centrifuge where brine is the new displacing fluid and it is centrifuged at increasing speed steps until an effective pressure difference of -10 psi is reached between the displacing and displaced fluid. The effective pressure and water saturation are determined at each speed level (14). The brine drive step is now finished, and the core is placed in a centrifuge where oil is the displacing fluid. This is called the oil drive step and it is executed in the exact same manner as the brine drive step. The system is centrifuged at increasing speed steps until an effective pressure difference of 10 psi is reached. The water saturation and the effective pressure are calculated at each step (14). Note that the effective pressure has a positive value during the oil drive step, and a negative value during the water drive step.

The effective pressures for both the previous steps are now plotted against the water saturation see

Figure 6, and the area under these curves are used to calculate the USBM wettability index by using equation 2.4 (4).

$$I_{USBM} = \log\left[\frac{A_1}{A_2}\right] \tag{2.4}$$

Where:

I_{USBM} is the USBM wettability index

A_1 is the area under the oil curve

A_2 is the area under the brine curve

Since the areas under the curve represents the work required to displace the fluids, the ratio of the areas are used as a direct indicator of the degree of wettability. The fact that displacing a nonwetting fluid by a wetting fluid requires a smaller amount of energy than displacing a wetting fluid by a nonwetting fluid is what makes this whole method usable. Determining the wettability of the core sample is done as following; if the wettability index has value higher than 0 ($I_{USBM}> 0$) the core is water wet, if the value is near 0 the system is neutral wet, and if the value is lower than 0 ($I_{USBM}< 0$) the core is oil wet (14).

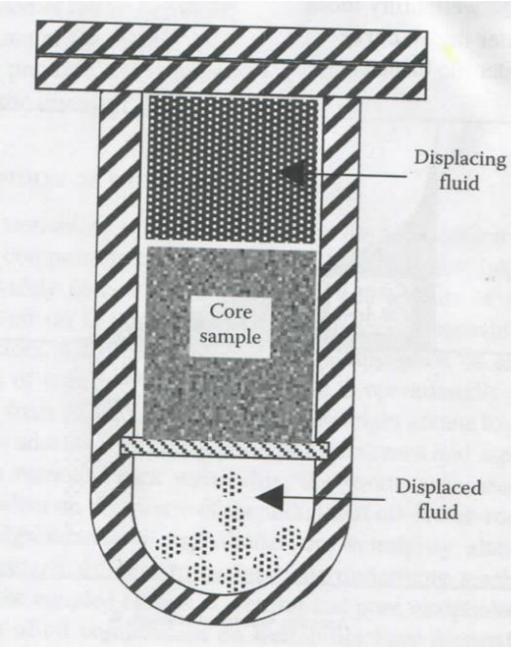


Figure 5: USBM centrifuge tube setup (4).

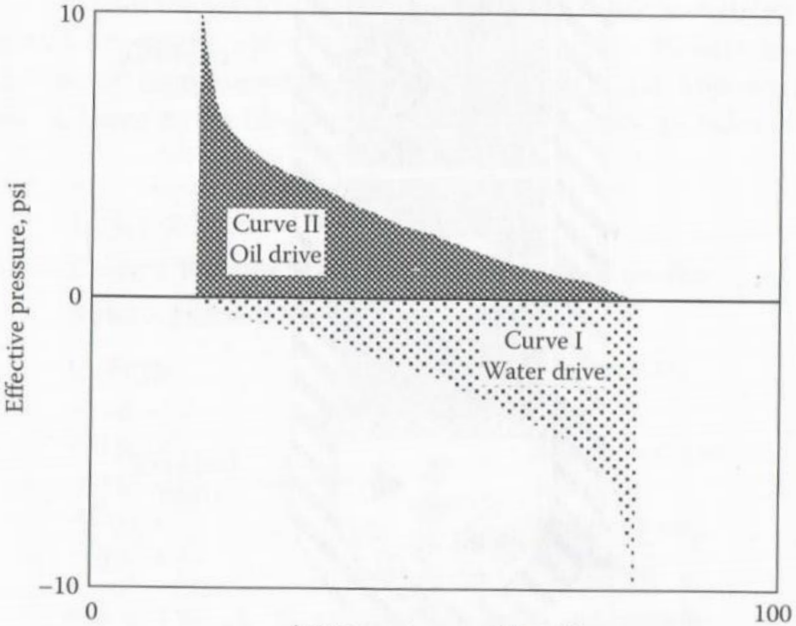


Figure 6: Plot of effective pressure versus average water saturation (4).

2.3 Capillary Pressure

2.3.1 Definition

Capillary pressure, P_c, is defined as the pressure difference across a curved interface between two immiscible fluids. The curvature of this interface is a direct result of the wetting preferences of the capillary walls (10). This pressure exists in a porous media whenever the pores are of capillary sizes and are saturated with two or more immiscible fluids (15). Capillary pressure has also been defined as the pressure differential between two immiscible fluids (that are occupying the same pores) which is caused by the interfacial tension between them that must be overcome to initiate flow (16).

Capillary forces in a porous media come as a direct result of the combination of IFT, wetting characteristics and pore sizes of the given system (4). Their presence can cause hydrocarbon entrapment (17)and they play a major role when it comes to the flow of immiscible fluids though a porous media (18). For a drop of oil or a bubble of gas to be able to flow through a small diameter pore it must first overcome the critical entry pressure, or capillary pressure (17). If we want a globule of oil to flow through a 0.01μm diameter pore that is completely wet by water and the oil-water IFT is 25mN/m, it would require a pressure in access of 1480 psi (4).

2.3.2 Capillary Pressure Curves

There are many different methods that can be used to measure capillary pressure, and in all of them the measurement of capillary pressure is confined to imbibition and drainage. In the imbibition process the saturation of the wetting fluid is increased, and in the drainage process the saturation of the wetting fluid is decreased from a maximum value (100%) to a irreducible value by increasing the capillary pressure from zero to a value so high that if further increased no more wetting fluid would have been displaced. The wetting fluid saturation recorded in both of the processes are then plotted against the capillary pressure, see Figure 7 (4,9).

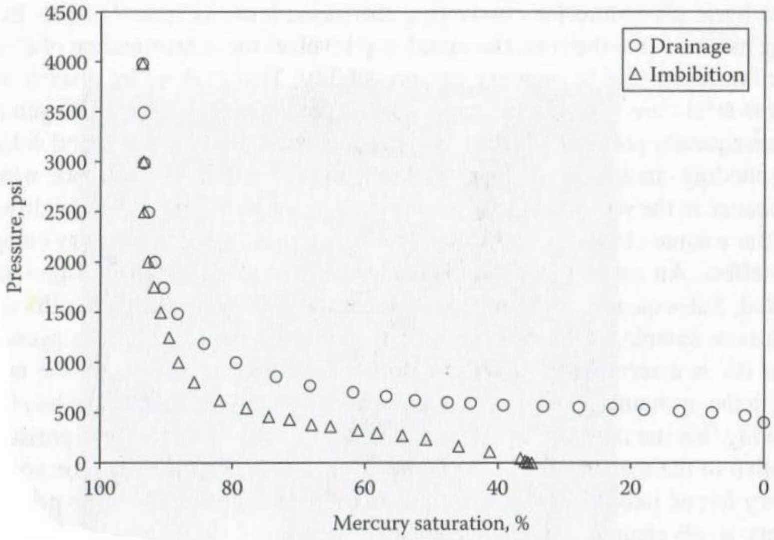


Figure 7: Capillary Pressure Curve (4).

The saturation end points on the drainage and imbibition curves are some of the most notable features of the entire plot. From these we can read the final saturation level of the wetting fluid, and the corresponding capillary pressure. The irreducible wetting phase saturation is equal to the connate water saturation level in the reservoir after oil has migrated in and an equilibrium between gravity and capillary forces is reached. As we can see from the plot in Figure 7 a certain pressure must be reached before the non-wetting fluid can start to displace the wetting fluid, and this is known as the displacement or threshold pressure (19).

Another important aspect is the apparent difference between the drainage and imbibition curves, which is there due to a phenomenon called capillary hysteresis. Different mechanisms for capillary pressure hysteresis have been proposed; Anderson identified contact angle hysteresis as a possible cause (20), another proposed mechanism is the ink-bottle effect (21).

The relationship between capillary pressure and permeability should also be noted. A decrease in permeability results in an increase in capillary pressure for an equal saturation level (4).

2.4 Relative Permeability

2.4.1 Definition

To define *relative permeability*, the definition of *absolute permeability* and *effective permeability* must first be established (4). The absolute permeability of a porous rock can only be found if it is 100% saturated by a single fluid. Permeability is a flow property, and can therefore only be characterized by conducting flow experiments. It should also be mentioned that permeability is a property of the rock alone, and not of the fluid flowing through it. Absolute permeability has been variously defined, and among these definitions we have:

- The measure of specific flow capacities of a rock
- The ability to flow or transmit fluids through a rock that is fully saturated with a single-phase fluid
- The proportionality constant *between the fluid flow rate and the applied pressure*

Absolute permeability is also expressed mathematically in Darcy's law, noted as k, see eq. 2.5.

$$Q = -\frac{k}{\mu} A \frac{dP}{dL} \tag{2.5}$$

Where:

- Q is the flow rate (m^3/s)
- k is the absolute permeability (m^2)
- μ is the fluid viscosity (N s/m^2)
- A is the cross-sectional area the fluid is flowing through (m^2)
- dP is the difference between up- and downstream pressure (N/m^2)
- dL is the length of the porous medium the fluid is flowing through (m)

Since most reservoirs contain at least two immiscible fluids, a reservoir containing only a single phase fluid seldom exist (4). As we have two or more immiscible fluids flowing in the reservoir the concept of effective permeability of each fluid is used instead of absolute permeability. Amyx et al. stated in their book on petroleum reservoir engineering that laboratory studies established that effective permeability is a function of prevailing fluid saturation, the wetting characteristics and the geometry of the pores (4). For this reason it is necessary to specify the fluid saturation when defining the effective permeability.

Because of the many possible combinations of saturations a porous medium can contain, test data are usually summarized and reported as relative permeability. This is normally done in the form of a relative permeability curve (see section2.4.2 Relative Permeability Curves. Relative permeabilities are either given as a percentage or fraction, and they are normally expressed by the ratio of effective permeability to absolute permeability (see equation 2.6), or by the ratio of the actual effective permeability to the initial effective permeability (the latter is the most common in relative permeability curves). The mathematical expression for relative permeability is as follows:

$$k_r = \frac{k_e}{k} \tag{2.6}$$

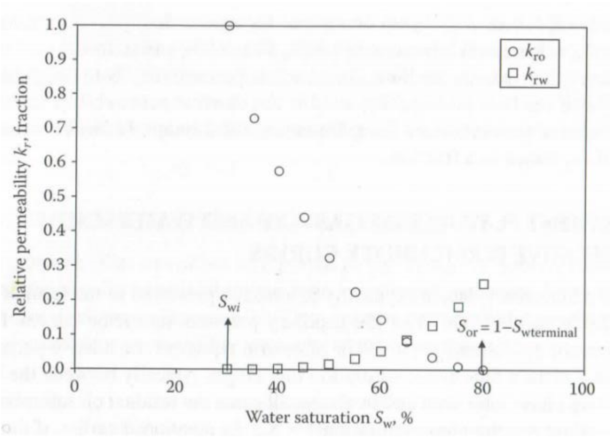
Where:

- k_r is the relative permeability, either for gas, oil or water (dimensionless)
- k_e is the effective permeability, either for gas, oil or water (mD or D)
- k is the base permeability and is either absolute permeability or initial effective permeability (mD or D)

2.4.2 Relative Permeability Curves

The data from relative permeability measurements are usually given as plots of the relative permeability curves (4). These curves show the relative permeability (y-axis) plotted against the fluid saturation (x-axis), and they usually range from the irreducible saturation of the wetting phase to the residual oil saturation. From this point on we will take a closer look at the relative permeability curves from two two-phase systems, respectively one oil-water and one gas-oil system, see Figure 8 and Figure 9. Both plots use the effective permeability of oil at initial water saturation as the base permeability, which means that the relative permeability of oil at S_{wi} equals one, and is gradually reduced to zero as the oil saturation is decreased.

For an oil-water relative permeability curve the y-axis represents the relative permeability of the present fluids as a fraction, while the x-axis represents the water saturation in percent (4). In a system like this we start at the irreducible water saturation, (the rest of the porous media is saturated with oil), and water is injected which decreases the oil saturation and in turn increases the water saturation. This process is continued until the residual oil saturation is reached. When the residual oil saturation is reached the relative permeability of oil will be equal to zero, since the oil phase is now immobile. See Figure 8 for illustration of a oil-water relative permeability curve.



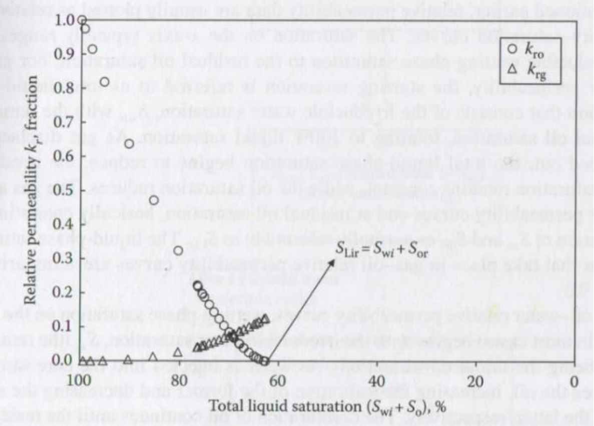


Figure 8 (left side): Oil-water relative permeability curve.
Figure 9 (right side): Gas-oil relative permeability curve.

For a gas-oil relative permeability curve the y-axis represents the relative permeability of the present fluids as a fraction, while the y-axis represents the total liquid saturation (S_{wi} + S_o) in percent (4). Just as for the oil-water system, the gas-oil relative permeability curves start at the irreducible water saturation, with the remainder of the fluid as oil. As the gas injection process is carried out, the total liquid saturation decreases. The water saturation stays the same, which means that the oil saturation alone is being decreased. This process is carried out until the residual oil saturation is reached. At this point the relative permeability of the oil is equal to zero as the phase is now immobile. On a gas-oil relative permeability curve this point is known as S_{Lir}, and is equal to the summation of S_{wi}, and S_{or}.

2.5 Petroleum Reservoir Rocks

In the present study minerals most commonly found in sandstone reservoirs will be examined (22), and that is why there will be no information on carbonate reservoirs in this chapter.

2.5.1 Sandstones

Around 50% of all petroleum reservoirs are sandstone reservoirs, and outside of the Middle East the percentage is even higher (22). Sandstones consists largely of sand grains that are between 0.06 and 2mm in diameter, however they also contain some amounts of rock with smaller grain sizes like silt and clay. See Figure 10 for a four-component diagram where it is possible to distinguish between clay, and sand grains which consists of quartz, feldspar and rock fragments (22). The larger grains are mainly quartz (silica tetrahedron) and feldspar which have a negatively charged surface (23, 24, 25). These minerals do not dissolve in water (22). By "clay minerals" we usually mean sheet silicates consisting mainly oxygen, silicon, aluminum, magnesium iron and water (22). Clay minerals are basically flat flakes causing them to have surface area of several hundred m^2/g (22). The smaller clay grains are negatively charged colloids which in turn are surrounded by positively charged cations. If smaller cations like calcium and magnesium get close to the surface of the clay the negatively charged clay particles become largely neutralized causing the clay particles to cling together (26). If these clay minerals are exposed to acidic solutions the hydrogen ion in the acid may be absorbed by the clay, while the cations originally holding the clay particles are released into the solution (26). Clay minerals are highly adsorptive of water, and tend to swell when in contact with LSW than water with a high salt concentration (26). If clay come in contact with LSW some of the cations holding the clay particles together may go out into the solution, causing swelling (26).

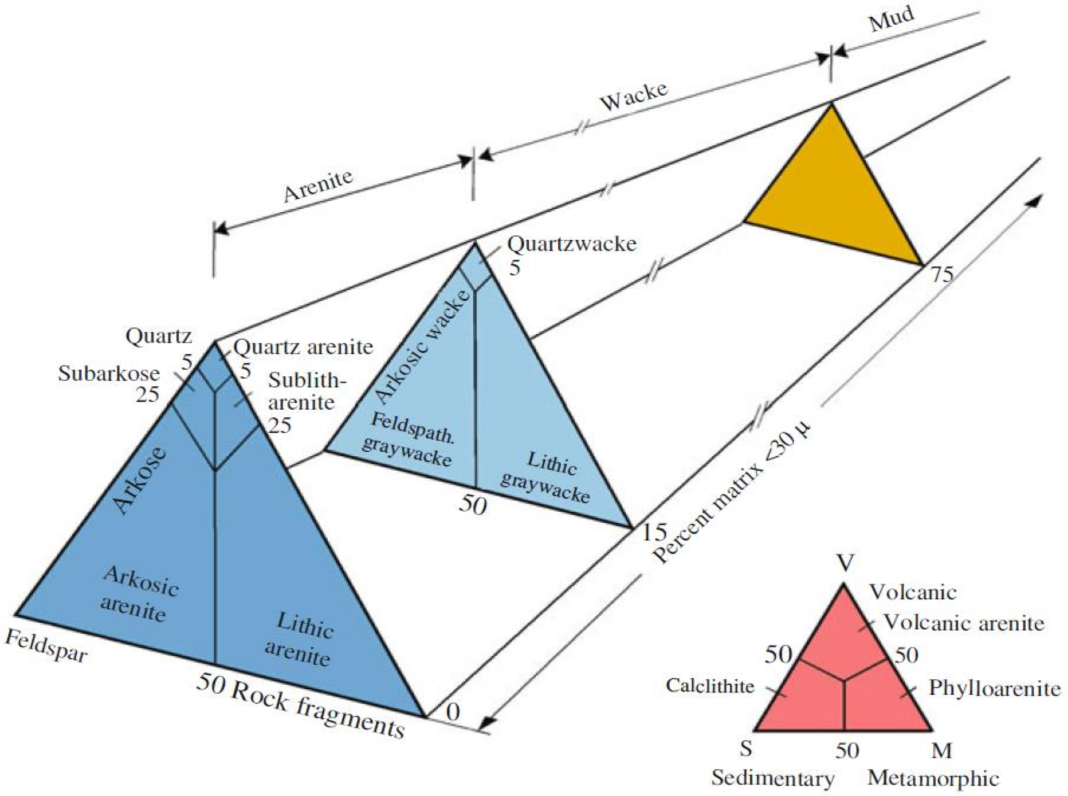


Figure 10: Classification of sandstones (22).

2.6 Petroleum Reservoir Fluids

In this study, only oil and brine, not gas, will be used, and that is why there will be no information on gas in this chapter.

2.6.1 Oil

Reservoir oils are mostly made up of hydrocarbon molecules like alkanes, alkenes, napthenes and aromatics (4). These are non-polar molecules with zero charge. In addition to hydrocarbons, oil also contain some nitrogen, oxygen, sulfur, asphaltenes and polar components like carboxylic acids. It is the concentration of the polar components and asphaltenes that affect wettability the most.

2.6.2 Formation Water

Formation water is the water found in the petroleum reservoirs, and is mostly a mixture of water and various dissolved salts (4). These dissolved salt cause the presence of various cations (sodium, calcium, magnesium, potassium and iron) and anions (chloride, sulfate and carbonate). The salt concentration of different formation waters have been found ranging from 200-300'000ppm. It is the concentration of the calcium and ferric cations that seem to affect wettability the most.

2.7 Factors Affecting the Wettability

The characteristics of the reservoir fluids and the properties of the reservoir rock are the primary factors affecting the reservoir wettability (4). In addition to this, reservoir pressure, temperature, and the location of fluid contacts also affect the reservoir wettability. However, there are many uncertainties as to how much these various factors actually affect the reservoir wettability. These variables will not be discussed further as they will not be used as variables in the flotation procedure. Temperature could be altered, but will in this study remain constant.

2.7.1 Oil Composition

Oil composition clearly affects the reservoir wettability, but exactly which components affect the wettability the most is not clear. However most scientists agree that the presence and amount of asphaltenes and polar components has a clear effect on the reservoir wettability. In the absence of a water film between the rock and the oil, the effect is attributed to the adsorption of asphaltenes onto the rock surface (4, 27). In the presence of water the effect is attributed to di- and three-valent cations to act as cation bridges between polar oil components and the negatively charged mineral particles (27). It is hard to evaluate the underlying mechanisms by studying core samples because of the internal structure of the rock (surface minerals and shape of pores pace) (27). Studies on the effect asphaltenes have on the wettability of smooth solid surfaces shows that their presence tends to alter the wettability towards more oil-wet (27, 28, 29, 30, 31). The following studies where examined to find out how brine composition affect wettability:

Liu and Buckley (1997) studied the effect asphaltenes has on the wettability of borosilicate glass that has been aged in four different crude oils (28). The study showed that the adsorption of asphaltenes altered the contact angle from 50^o – 70^o and all the way up to 170^o.

Al-Maamari and Buckley examined how the precipitation of asphaltenes affected the wettability of muscovite mica by aging freshly cleaved plates in an oil and heptane mixture (29). Heptane act as an asphaltene precipitant in the solution. The plates were frequently removed and contact angle for decane/water/aged mica was measured. Over time the wettability was altered from water-wet to oil-wet.

Rayes et al. looked at the effect asphaltenes has on the wettability of a Libyan and Hungarian oil field (30). The study showed that the asphaltenes altered the wetting angle from around 40^o-60^o and all the way up to 120^o. The asphaltenes completely altered the wettability of the reservoir from water wet to oil wet.

Tang and Morrow studied the effect aging, displacement temperatures and brine/oil composition has on the wettability of Berea sandstone (31). They found that removal of light components from the crude oil increased the water wetness, and addition of alkanes to the crude oil reduced the water wetness.

Liu and Buckley (1998) studied the main mechanisms of oil/brine/rock interactions and found that the following two dominate in the absence of water (27):

- Polar interactions between the asphaltenes and the solid dominate when a water film between the oil and the solid is absent. They found that the type of clay and its exchangeable cations along with the nitrogen content of the oil and the solvent in which the polar components are dissolved are some variables that affect the adsorption onto clay minerals in the absence of water.
- The ability of the crude oil to act as a solvent for the asphaltenes it contains play a major role in the oil/rock interactions. The poorer the oils ability to act as a solvent for the asphaltenes, the more oil-wet the conditions get.

In the presence of water they also found that polar components in the oil also has a clear effect on the wettability, if the water contains Ca^{2+} cations. This alters the rock towards more oil-wet due to Ca^{2+} acting as a cation bridge between the negatively charged rock and the polar components of oil.

From the previous studies it can be concluded that the presence of asphaltenes in the oil alters the wettability of different minerals towards more oil-wet, especially if the oil act as a poor solvent for the asphaltenes. Polar components in the oil also alter the wettability towards more oil-wet, but only if the water contains cations that can act as cation bridges between the negatively charged rock and the polar components of oil.

2.7.2 Brine Composition

The chemistry or composition of brines has been shown to be an influencing factor when it comes to reservoir wettability (31, 32, 33, 34, 35, 36). Especially the salt concentration has been shown to affect the system wettability. The following studies where examined to find out how brine composition affect wettability:

Tang and Morrows' study also showed that a decrease in salinity along with an increase in temperature during the course of oil displacement from the core samples resulted in a transition towards a more water-wet state for the Berea sandstone (31).

Fjelde et al. looked at the effects low salinity water has on the oil production and tried to describe the interactions between cations in brines of low and high salinity for a sandstone reservoir with high clay content. The core samples they used were first prepared with formation water and then aged in crude oil at initial water saturation (S_{wi}). When the cores were ready they were either flooded by 1) formation water, seawater and low salinity water in succession, or by 2) LSW directly from S_{wi}. Among other things, they found that the LSW altered the wettability of the rock to less water-wet and the high salinity formation water kept the water-wet conditions. (33)

Rao and Vijapurapu studied the effect of brine dilution on spreading and wettability of a dolomite rock (34). They found that diluting the brine (both Yates and synthetic brine) with deionized water decreased the IFT between water and oil, and changed the wettability from its' initial oil-wet state to intermediate-wettability.

Al-Aulaqi et al. examined how changes in temperature and brine salinity alter the wettability of a rock(sandstone)/water/oil system (35). They found that reducing the salinity of a brine with monovalent cations shift the wettability of the system towards a more water-wet state.

Mwangi et al. studied the wettability of sandstone and carbonate-oil-brine systems by flotation (32). They found that chalk is water wet when the brine has a high salinity level (100000 mg/L), but when the brine has a low salinity level (<10000 mg/L) chalk displays oil-wet conditions. The Berea sandstone displays water-wet conditions both when the salinity of the brine is high and low. The study also showed that the addition of two surface active compounds (SAC) had an impact on the wettability of chalk. The addition of acetic acid seemed to render chalk water-wet for all brine salinities, especially the low ones. Adding long chained fatty acids (Naphthenic acids) seemed to shift the wettability towards oil-wet, especially when the brine had a higher salinity level.

Rayapaksha et al. found that the presence of ferric (Fe^{3+}) cations in the brine can alter the wettability of the rock towards a more oil-wet state (36).

From the previous studies it can be concluded that LSW alters the wettability of sandstones (quartz) and dolomite towards a more water-wet state compared to brines with a higher salinity. Fjelde et al. found a different result for reservoir rock with a high clay content. Here LSW altered the wettability towards a more oil-wet state, from the previous water-wet state experienced with the high salinity formation water. Liu and Buckley (1998) found that high concentrations of Ca^{2+} alters the wettability towards a more water-wet state if the oil has high concentration of polar components. Mwangi et al. came to the same conclusion when they added long chained fatty acids (polar components) to the oil. High salinity water alter the wettability towards a more oil-wet state compared to low salinity water. The wettability of samples aged in brine with a high salinity level appear to be more sensitive to concentration of polar components in oil. The wettability of samples aged in oil with a high concentration of polar components appear to be more sensitive to the salinity of the brine. The interaction between oil/cation/rock appears to have a large effect on wettability.

3 Experimental Procedure

In this study a total of 11 series of wettability experiments were run over the course of 19 weeks. In these series of experiments the goal was to use materials that are found in real oil reservoirs, and measure how the mineral wettability is affected by using different oils and brines. The flotation method was used to determine the wettability of every possible combination of oil, brine and mineral (except for plagioclase and pyrite) used in this experiment. In addition to using LSW, SW FW #1 and FW #2, a few glauconite samples will also be aged in brines with Fe^{3+} and Al^{3+} cations to see how they affect wettability.

3.1 Experimental Methods

3.1.1 Preparation of Brine

Reference: Personal consultation (5).

1. Find the desired volumetric flask (usually 1000ml) and fill half of it with distilled water.
2. Gently slide an appropriately sized magnet down into the flask by holding it at an angle and place the flask on a magnetic stir plate
3. Calculate the amount of salt needed to make up the brine, weigh it in on a measuring plate and pour it into the volumetric flask. Wash remaining grains off the measuring plate with distilled water to make sure all of salts are added to the solution. Make sure the magnetic stir plate is turned on and the magnet is rotating.
4. Repeat step 3 until all of the desired salts are added.
5. Add distilled water until the solution is just below the calibration mark, put a lid on the flask, and let it stir for about one hour to make sure he salts are dissolved.
6. Remove the flask from the stir plate and use a magnet on the outside of the glass to remove the magnet inside the flask.
7. Add distilled water until the solution just reaches the calibration mark etched on the neck of the flask.
8. Filter the brine trough a 0.45µm filter paper to remove any undesired debris or undissolved salts that may be in it.
9. Pour the brine into a storage flask, put a lid on it, mark it with date, name and content, and store it properly until needed.

3.1.2 Preparation of Rock or Mineral Sample

Reference: Personal consultation (5).

1. Find the desired rock or mineral, and crush it with a mortar until it has become as fine-grained as possible.
2. Weigh the fine-grained sample before filtering it through a 53µm mesh with the aid of a shaker.
3. Weigh the filtered sample, put it into a storage bottle, put a lid on it, mark it with date, name and content, and store it properly until needed.
4. Repeat step 1-3 until the desired number of samples have been prepared.

3.1.3 Flotation Procedure

Reference: Personal consultation (5).

1. Crush the desired amount of mineral(s) or rock sample with a mortar, and sieve it through a 53µm mesh with the aid of a shaker.
2. Weigh and note the mass both the sieved and unsieved material.

3. Add 0.2000g of the sieved material to a 20ml graded test tube along with 10ml of prepared brine, formation water, or seawater and place a lid on top to prevent the water from evaporating. Remember to mark the test tube with date, name and content.
4. Shake the test tube with a shaker and age it in an oven at reservoir temperature for 72 hours.
5. Take the test tube out of the oven when the aging process is complete, and leave it to cool for 15 minutes. Take the lid off and remove the brine from the mixture with a Pasteur pipette and save it for later use. Make sure that the sedimentation particles are not removed, as this can interfere with the results.
6. Measure the pH of the removed brine with an electrode and compare it to the pH of the SFW.
7. Add 3ml of STO to the test tube now containing only wet mineral, place the lid back on top and shake it.
8. Put the mixture along with the saved brine back in the oven and age it for 48 hours at reservoir temperature. Stir the mixture once in the morning and once in the evening with a shaker.
9. Take the test tube out of the oven when the aging process is complete. Take the lid off, add the brine solution that was removed in step 5., and place the lid back on top.
10. Shake the mixture with a shaker, put it back in the oven and leave it to settle for 24 at reservoir temperature.
11. Take the test tube out of the oven when the aging process is complete, and leave it to cool for 15 minutes. Take a picture of the sample and measure the volume of oil and water contained in the mixture. Take the lid off, remove the oil phase with a pipette, and put the lid back on.
12. Put the test tube back in the oven for 1 hour to heat it up, allowing the oil remaining on the wall of the test tube to drain back down on top of the water phase.
13. If there is a substantial amount of oil-wet grains stuck on the test tube glass wall the following steps should be taken to remove them:
    - Add brine until the total volume of fluid in the test tube is equal to 10ml.
    - Add 3.0ml of N-decane to the mixture and place a lid on top.
    - Place the test tube in the oven for one hour to allow it reach test temperature.
    - Take it out from the oven, stir it, put it back in the oven and leave it for 24 hours.
    - Take the test tube out of the oven, leave it to cool for 15 minutes and remove the N-decane as done with the oil in stage 12-13.
    - Repeat step 14 if necessary.
14. When the oil and the oil-wet particles are sufficiently removed the remaining mixture of brine and sediments is filtered through a 0.22µm filter paper to separate the water-wet particles from the brine. Spray distilled water into the test tube and shake it to make sure all of the particles are removed. Remember to weigh the filter paper before use.
15. Three filter papers have only brine and distilled water through them. These filter papers act as a reference for how much weight is added to the filter papers by filtration of water and brine alone. The average increase in weight after these filter papers have been dried is then subtracted from the weight of the mineral samples.
16. Put the filter paper with the water-wet rock on into the oven and leave it to dry for 4 days before weighing it the first time. Put the samples back in the oven and weigh them again the next day to see if the weight is consistent.
17. Calculate the mass of oil- wet and water-wet material.

3.1.4 Use of pH-meter

Reference: Personal consultation (37).

1. Inspect the electrode to see if there are any air bubbles in the ball at the bottom of the. If present grab the wire 20 - 25cm from the top of the electrode swing it around a few times. Repeat until the air bubbles are no longer present.
2. Make sure the solution inside electrode is supersaturated with KCl (KCl crystals are clearly present). If not, add KCl until the crystals are clearly visible at the bottom of the electrode.
3. Calibrate the pH-meter for pH interval that is to be measured, either acidic $pH < 7.0$ or basic $pH > 7.0$. Make sure the accuracy of the calibration is above 92.0% or an error message will occur in the display, and the calibration will have to be redone.
4. Clean the electrode with distilled water, and carefully wipe of the water with a paper towel.
5. Lower the electrode into the solution that is to be measured*, and leave it there until the STAB (stabilized) indicator in the display has stopped blinking and the pH value is stable.
6. Note down the pH value as it is seen in the display and gently lift the electrode out of the solution.
7. Repeat step 4-6 until all the pH measurements are taken.
8. Clean the electrode with distilled water, and carefully wipe of the water with a paper towel.
9. Cover the tiny hole near the top of the electrode with tape (this is to prevent the water from evaporating), and place it in the buffer with $pH = 4.0$.

* *Make sure the solution hold the same temperature that the pH-meter is calibrated for (room temperature).*

3.1.5 Use of Spectrophotometer to Determine Fe^{3+} Concentration

Reference: College of Science at UC (38).

1. Prepare four 1.0ml standard solutions with a an increasing concentration of Fe^{3+} and note the concentration of each solution
2. Find and mark the solution(s) with the unknown Fe^{3+} concentration with name, number and date.
3. Take out 1.0ml from each solution with a pipette, and add it to a test tube. Mark each test tube with date, name and content.
4. Turn on the spectrophotometer.
5. Add 4.0ml of 2.0M thiocyanate to each solution and shake well.
6. Set the spectrophotometer to measure at wavelength of 447nm.
7. As close as possible to 15 minutes after adding thiocyanate, fill up the cuvette with one solution and measure the absorbance with the spectrophotometer.
8. After the measurement has been taken, gently remove the cuvette from the spectrophotometer, clean it and add the next solution.
9. Repeat step 7 and 8 until the absorbance of each solution has been measured.
10. Prepare a graph with $[Fe^{3+}]$ (in ppm) as the horizontal axis and absorbance as the vertical axis, and plot the results obtained from the standard solutions.
11. Identify the point on the graph which corresponds to the absorbance of the unknown iron sample(s), and draw a vertical line to the horizontal axis to determine the concentration.
12. If the absorbance value of the unknown iron sample is greater than that of the standard sample with the highest iron concentration, the unknown sample must be diluted to a

concentration lower than that of the standard sample, and the absorbance must be measured again.

13. Turn off the spectrophotometer.

3.2 Materials

In these series of experiments the goal was to use materials that are found in real oil reservoirs, and measure how the mineral wettability is affected by using different oils and brines. The materials used here were chosen as they make up the most part of two different oil fields in the North Sea, Field #1 and Field #2 (5).

3.2.1 Minerals

The following minerals were chosen for this experiment as the make up roughly 95% of field #1 and field #2, and among them are sandstone and clay minerals with different properties.

Quartz

Quartz or silica (SiO_2) is a transparent to gray insoluble (in water) oxide mineral, that is hard (7 on Mohs scale), dense (if pure: 2.65s.g.) and brittle, and it is the second most common mineral on the earth's surface (39, 40). This mineral makes up roughly 70% of both field #1 and #2, making them sandstone reservoirs (5). Quartz is known to be primarily water-wet (32). It was chosen for this experiment as it is the most abundant mineral in both reservoirs.

K-feldspar (Orthoclase)

K-feldspar or potassium feldspar refers to a number of minerals in the feldspar group that contains potassium (41), and in this case it is crushed orthoclase ($KAlSi_3O_8$) that is being used (5). It is a white to grey silicate mineral, that is hard (defining mineral for 6 on Mohs scale), dense (2.55-2.63s.g.) brittle (41) and insoluble in water. The feldspar mineral group which this mineral is a part of is the most abundant mineral group in the earth's crust (42). Orthoclase is known to be primarily water-wet (43). It was chosen for this experiment as it is one of the most abundant minerals in both Field #1 and Field #2.

Plagioclase (Albite)

Plagioclase refers to a series of tectosilicate minerals in the feldspar group (44), and in this case it is crushed Albite ($NaAlSi_3O_2$) that is being used (5). It is a white to grey silicate mineral that is hard (6-6.5 on Mohs scale), dense (2.6-2.63s.g.), brittle and insoluble in water (45). Plagioclase is known to be primarily water-wet (5). It was chosen for this experiment because it has similar properties to K-feldspar, as well as being almost as abundant.

Glauconite

Glauconite $(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$ (46) is a predominantly water-wet clay mineral that is usually distributed as pellets (47). This phyllosilicate is green in color, has a low hardness (2 on Mohs scale) is very dense (2.40-2.95s.g.) and it is insoluble in water (46). In 2014 a group of scientist at IRIS found that adhesion of oil to glauconite particles was dependent on pH and brine content. They saw that adhesion of acidic groups was particularly sensitive to the presence of calcium in the brine, while the adhesion of basic groups was insensitive to brine composition (48). Clementz has also found that clay minerals have their wettability altered from water-wet to neutral-wet by adsorbing petroleum heavy ends (49). It was chosen for this experiment because it is the most abundant clay mineral in both Field #1 and Field #2.

Muscovite

Muscovite or common mica ($KAl_3Si_3O_{10}(OH)_2$) is a clay mineral that is reported to have both intermediate and water-wet behavior (43, 50). This is a phyllosilicate mineral of aluminum and potassium, which has a white and almost silver like color. It has a low hardness (2-2.25 on Mohs scale), a high density (2.76-3.00s.g.), is elastic and it is insoluble in water (51). It was chosen for this experiment because it is one of the most abundant clay minerals in both Field #1 and Field #2.

Pyrite

Pyrite or iron sulfide (FeS_2) is a sulfide mineral. It has a gold like color, has a high hardness (6-6.5 on mohs scale), is very dense (4.9-5.2s.g.), very brittle and it is insoluble in water (52). This mineral is found to be water-wet by the use of the sessile drop method (53). It was chosen for this experiment because of its high iron content.

Reservoir Rock from Field #1

This is crushed and sieved rock from a sandstone oil reservoir in the North Sea, with a clay content of about 13% of the weight of the bulk sample (33). Before being used in this experiment the rock was cleaned by Soxhlet extraction with methanol and toluene and then dried. It was chosen for this experiment as it is the original reservoir rock from field #1, and also so that the results from the pure mineral samples can be compared to a more complex combination of minerals.

3.2.2 Brine

Four different synthetic brines were used in these experiments to examine the effect brine composition and salt concentration has on mineral wettability. At first synthetic formation water from the two North Sea reservoirs were used, and secondly synthetic seawater and low salinity water were used since these are brines that are often being used as injection water. The composition of LSW is decided by a low salinity plant. The exact composition of each brine was given to me by Fjelde (5).

Formation Water Field 1

Table 3: Salt Concentration of Formation Water from Field #1.

SALT	Concentration in Reservoir (g/l)	Synthetic FW Concentration (g/l)
NaCl	**77.40**	**77.40**
Na_2SO_4	**0.13***	**-**
KCl	**0.42**	**0.42**
$MgCl_2·6H_2O$	**3.55**	**3.55**
$CaCl_2·2H_2O$	**21.75**	**21.75**
$SrCl_2·6H_2O$	**2.25**	**2.25**
pH		**5.72-5.77**

**$SrSO_4$ is supersaturated at room conditions, so Na_2SO_4 is removed since FW #1 has a lower concentration of Na_2SO_4 than it has of $SrCl_2·6H_2O$* (5).

Formation Water Field 2

Table 4: Salt Concentration of Formation Water from Field #2.

SALT	Concentration in Reservoir (g/l)	Synthetic FW Concentration (g/l)
NaCl	40.60	40.60
Na_2SO_4	0.51*	0.51
KCl	0.53	0.53
$MgCl_2{\cdot}6H_2O$	4.86	4.86
$CaCl_2{\cdot}2H_2O$	10.71	10.71
$SrCl_2{\cdot}6H_2O$	0.44	0.44
$BaCl_2{\cdot}2H_2O$	0.01	0.01
pH		5.62-5.66

**No precipitation of $SrSO_4$ was observed here, so both Na_2SO_4 and $SrCl_2{\cdot}6H_2O$ were used.*

Seawater

Table 5: Salt Concentration of Seawater.

SALT	Original SW Concentration (g/l)	Synthetic SW Concentration (g/l)
NaCl	23.38	23.38
Na_2SO_4	3.41	3.41
$NaHCO_3$	0.17	0.17
KCl	0.75	0.75
$MgCl_2{\cdot}6H_2O$	9.05	9.05
$CaCl_2{\cdot}2H_2O$	1.91	1.91
pH		7.98-8.02

Low Salinity Water

Table 6: Salt Concentration of Low Salinity Water.

SALT	Original LSW Concentration (g/l)	Synthetic LSW Concentration (g/l)
NaCl	10.17	10.17
$CaCl_2{\cdot}2H_2O$	0.11	0.11
pH		5.71-5.73

Other

Thiocyanate solutions

Two different thiocyanate solutions were prepared, a 0.1M solution and a 2.0M solution. They were made by adding sodium thiocyanate to distilled water. These solutions were used to determine the concentration of Fe^{3+} ions in some experimental samples, since thiocyanate forms a blood red complex with these ions (37). The following reaction takes place:

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow [FeSCN]^{2+}_{(aq)}$$

Three-valent iron and aluminum solutions

For experiment nr. 6 and nr. 11 brine containing three-valent iron and aluminum was needed to examine the impact they have on the wettability of glauconite. These solutions were prepared by adding iron(III)chloride and aluminum(III)chloride tetrahydrate to FW #1 and FW #2, making a total of eight different solutions. For experiment nr. 6 four 0.02M (1117ppm and 539ppm) solutions were made. The effect of much lower concentrations of three-valent iron and aluminum was examined in experiment nr. 11, and this time four 50ppm solutions were made.

Table 7: Salt Concentration of three-valent Aluminum and Iron Solutions.

Solution	FW	Salt	Concentration	
	Type	**Type**	**Molar**	**ppm**
1	**FW #1**	$FeCl_3$	**0.02**	**1117**
2	**FW #1**	$AlCl_3\cdot 4H_2O$	**0.02**	**539**
3	**FW #2**	$FeCl_3$	**0.02**	**1117**
4	**FW #2**	$AlCl_3\cdot 4H_2O$	**0.02**	**539**
5	**FW #1**	$FeCl_3$	$9.01\cdot 10^{-4}$	**50**
6	**FW #1**	$AlCl_3\cdot 4H_2O$	$1.85\cdot 10^{-3}$	**50**
7	**FW #2**	$FeCl_3$	$9.01\cdot 10^{-4}$	**50**
8	**FW #2**	$AlCl_3\cdot 4H_2O$	$1.85\cdot 10^{-3}$	**50**

In addition to this four other Iron(III)chloride solutions were prepared and they had the following concentrations: 10ppm, 25ppm, 50ppm and 100ppm. They were used to make a scale for the spectrophotometer, so that the unknown Fe^{3+} concentration of some experimental samples could be determined. Iron(II)sulfate solutions with a concentration of 50ppm and 500ppm were also made for an oxidation experiment. They were made by dissolving an Iron(II)sulfate heptahydrate salt in distilled water.

3.2.3 Oil

Four different types of oils were chosen to examine the effect of oil chemistry on the wettability. All except one are from North Sea reservoirs. STO #1 and STO #2 were chosen because they come from the reservoirs as the mineral selection was based upon. STO #3 comes from a different North Sea reservoir, and it is being used to find the impact higher acidity has the wettability. N-decane ($C_{10}H_{22}$) is an alkane hydrocarbon that is being used as a reference, since it does not contain any SAC.

Table 8: Properties of oil used in these experiments (5).

Oil	TAN	TBN
STO #1	<0.1	1.9
STO #2	0.38	2.3
STO #3	2.9	0.95
N-decane	0	0

3.3 Experimental Setup

3.3.1 Flotation Experiment

For this study 11 series of experiments were run with a total of 238 different samples. One series of experiments took roughly 1-2 weeks complete. It was set up so that each mineral would be matched with every brine and every oil (see Table 9), and aged in the oven at 80°C. There would be at least two matching duplicates of each sample, and for two samples to match the difference in weight in the oil phase would have to be less than 1% of the total weight of the mineral sample. If the difference was between 1-2%, one new sample was later created to confirm which of the previous samples was correct, and if the difference was more than 2% two new samples were made to confirm the wetting preference of the mineral.

Table 9: Number of samples made of each combination.

	Quartz				**Muscovite**				**K-feldspar (Orthoclase)**			
	Brine				**Brine**				**Brine**			
Oil	FW #1	FW #2	SW	LSW	FW #1	FW #2	SW	LSW	FW #1	FW #2	SW	LSW
STO #1	5	2	5	2	2	2	2	2	4	2	4	7
STO #2	2	2	3	4	2	2	2	2	2	2	4	4
STO #3	2	2	2	2	2	2	2	2	2	2	2	2
N-decane	5	2	2	2	2	2	2	2	4	2	4	2
	Rock from Field #1				**Plagioclase (Albite)**				**Pyrite**			
	Brine				**Brine**				**Brine**			
Oil	FW #1	FW #2	SW	LSW	FW #1	FW #2	SW	LSW	FW #1	FW #2	SW	LSW
STO #1	2	2	3	2	4							
STO #2	2	2	2	2		2				3		
STO #3	2	2	2	2								
N-decane	2	2	3	3	2	3				2		
	Glauconite											
	Brine											
Oil	FW #1	FW #2	SW	LSW	FW #1 50ppm Fe^{3+}	FW #1 50ppm Al^{3+}	FW #2 50ppm Fe^{3+}	FW #2 50ppm Al^{3+}	FW #1 1117 ppm Fe^{3+}	FW #1 539 ppm Al^{3+}	FW #2 1117 ppm Fe^{3+}	FW #2 539 ppm Al^{3+}
STO #1	3	2	4	2	2	2			2	2		
STO #2	2	2	2	4			2	2			2	2
STO #3	2	2	2	2								
N-decane	4	2	3	2								

For every mineral except for plagioclase and pyrite a full set of experiment were set up. Only a few samples were made with pyrite and plagioclase, since there was not enough of them to complete a full set of experiments. These experiments were set up so that only formation water and stock tank oil from the same reservoir and FW/N-decane would be mixed, and the results would later be compared. There was only enough pyrite to test it for one reservoir, so the reservoir containing the most pyrite was chosen. The glauconite samples aged in three-valent aluminum and iron ions were set up so that only formation water and stock tank oil from the same reservoir would be mixed. See appendix A for an overview of each series of experiments.

3.3.2 pH-Experiment

After the second series of experiments was completed one could see that there was a wide variation in the results from the pH-measurements from some of the duplicate samples. The largest span in pH of any two duplicate samples was from 4.24 to 8.98 (experiment 2, sample 5 and 8). This should not occur since those samples were supposed to be identical in every way. They contained the same brine and the same mineral, and they were all carefully prepared to avoid contamination. A wide variation in pH should be avoided, because pH can have an effect on wettability (48), thus rendering the samples useless for comparison. It was suspected that the variation in pH could be caused by contaminated test tubes or corks, so a series of experiments were set up to find out. 10 test tubes identical to the ones used in the flotation experiment were filled with 10ml of LSW and aged in the oven for three days before the brine was poured over into non graded test tubes and aged in the oven for two more days, just like in the flotation experiment. When the aging process was over the non graded test tubes were removed from the oven and left to cool for an hour before the pH was measured. A second experiment was performed to confirm the findings from experiment one, only here distilled water was used instead of LSW, and the rubber insulation in the corks used on the non graded test tubes was swapped out for brand new insulation pads lined with teflon. Some of the samples were aged in room temperature to see if temperature had effect on pH.

Table 10: Setup of pH-experiment.

Sample	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10
Series	1	1	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2
LSW	x	x	x	x	x	x	x	x	x	x										
Distilled water											x	x	x	x	x	x	x	x	x	x
Teflon Insulation											x	x	x	x	x	x	x	x	x	x
Aged in the oven	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				

3.3.3 Oxidation Experiment

Two iron(II)sulfate solutions with an Fe^{2+} concentration of 50ppm and 500ppm were aged in the oven at 80°C and two identical solutions were aged at room temperature to examine how temperature affect the oxidation of Fe^{2+} to Fe^{3+}. If this oxidation takes place at high temperature, it shows that it is possible for this oxidation to occur at reservoir conditions. This means minerals that can release Fe^{2+}, as well as minerals that can release Fe^{3+} into the present FW can have an effect on the wettability of the reservoir rock (36). This is because iron(III) oxides can bind more strongly to the polar components of oil and act as cation bridges between the oil and the charged clay minerals (54).

4 Results

4.1 Flotation Experiment

The most convenient way to present the results was to graphically display the wettability of each mineral by itself, and then compare them later. The results are plotted as columns, and each column represents one sample. The vertical axis represents how many percent of the total weight of the sample is found in the oil phase, and on the horizontal axis one can see what type of brine is being used. What type of STO that is being used is displayed in the legend on the right side of the plot. Two duplicates were made of each sample to see if they came back with similar results. The duplicates are displayed as a columns along with the average of the two. The accuracy of the method is estimated to be ± 1W%. For the minerals that are showing a pattern in wettability alteration, different types of plots are being used to try and explain these patterns. See appendix A for a spreadsheet overview of the results from each series of experiments.

4.1.1 Quartz

By examining the wettability results seen in Figure 11 it is clearly confirmed that quartz is primarily water-wet, since the sample that is <u>the least water-wet</u> is still 96% water-wet. By giving the plot in Figure 11 a quick glance, it might seem like there is a lot of variation in the wettability results of quartz, but keep in mind that the vertical axis (the one where wettability is plotted) only goes up to 4,5%. In Figure 12 the vertical axis goes up to 16% and it becomes clear that the variation between the different samples is very small. This makes it hard to find a clear pattern among the wettability results. As expected, one can still see that LSW seems makes the sample more water-wet compared to the other brines (31, 35). For the N-decane samples the wettability was expected to be close to 100% water-wet, and that seems to be the case also (32). The N-decane sample that came back as the <u>least</u> water-wet was still around 99% water-wet, and with an accuracy of ± 1W% this shows that the samples aged in N-decane are basically 100% water-wet. Mixing SW and N-decane came back with results saying that more than 100% of the total mass of the sample was left in the water-phase. This cannot be true, since the mineral samples could not have gained weight during the aging process, they could however have been contaminated during the drying process. During this process the samples are stored in an oven and they are not covered, so some dust particles may have landed on them, thus slightly increasing the weight. Another explanation could be that an error was made while weighing in the mineral sample in the test tube, or simply while weighing in the filter paper before filtration.

There seem to be no distinct differences in wettability when the samples that are aged in the same brine but in different STOs are compared. The wettability never vary more than 2,5% if the previous comparison is done. That is barely above the accuracy of the method (± 1W%). If the samples that are aged in the same STO but different brines are compared the largest difference in wettability is just under 3%. Again it is just barely above the accuracy of the method.

The overall impression is that quartz is near 100% water-wet. Other than that the samples aged in LSW and the samples aged in N-decane seems to be slightly more water-wet than the other samples, no clear correlation is found in the wettability alteration of quartz when samples aged in different STO's or different brines are compared.

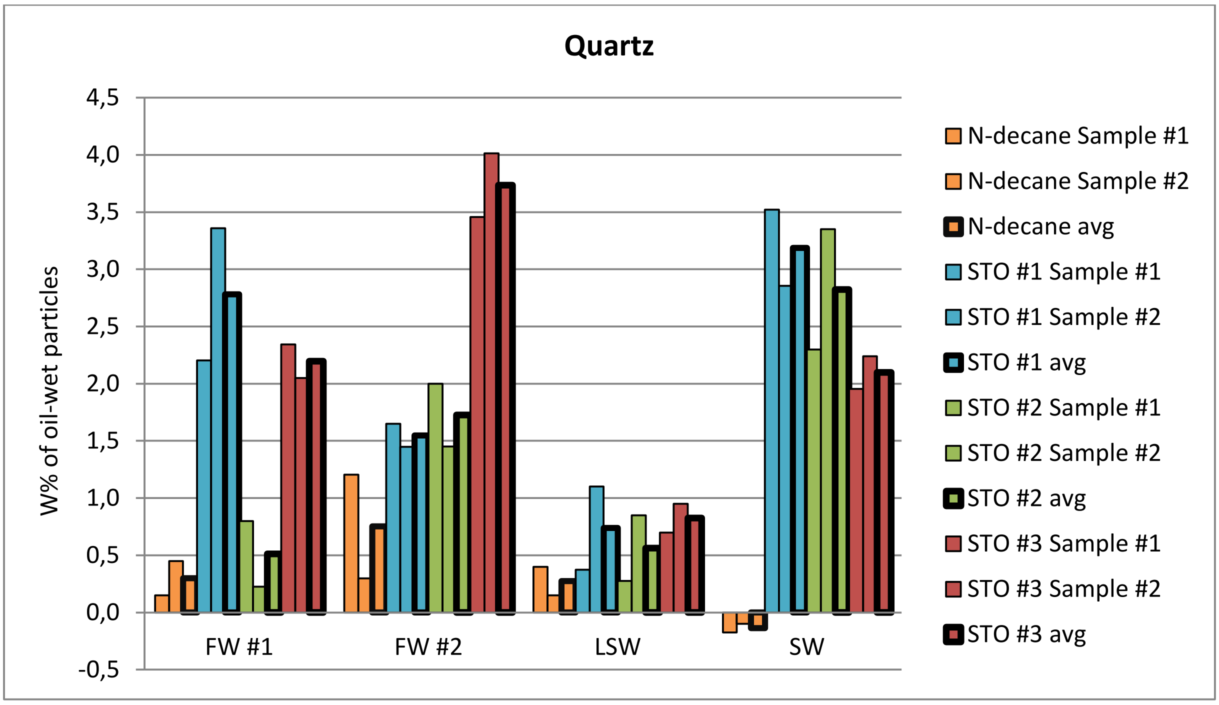


Figure 11: Wettability results of quartz.

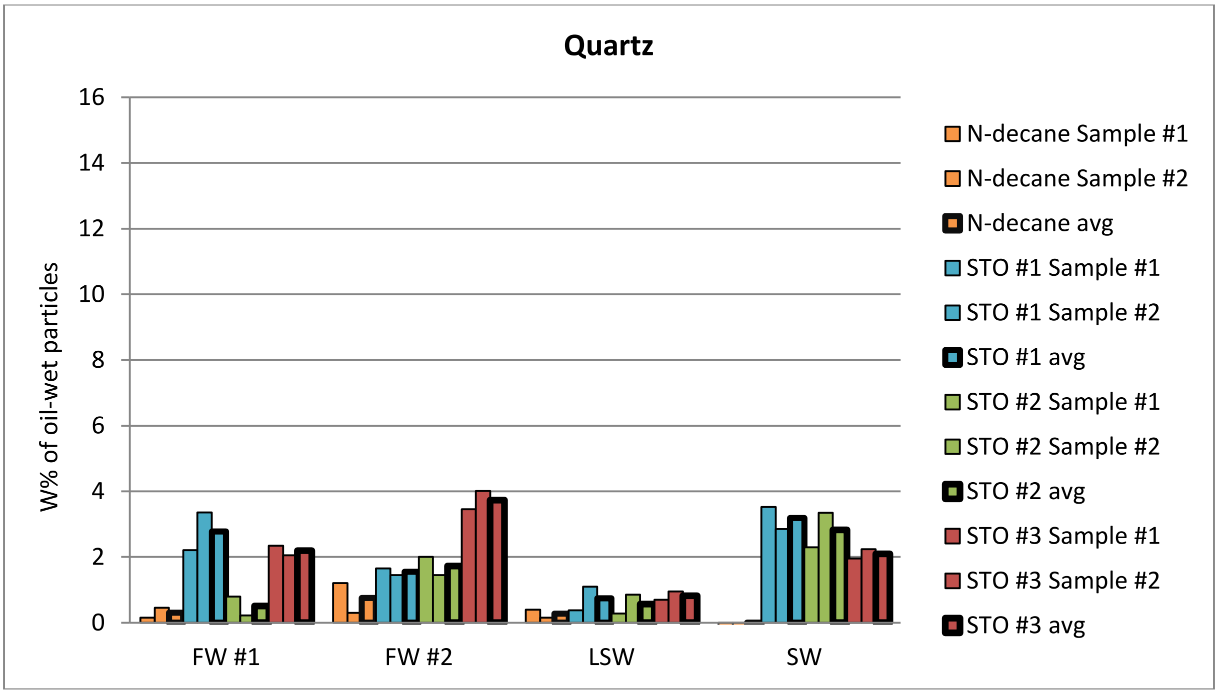


Figure 12: Wettability results of quartz.

To examine the wettability results of the other minerals, different plots were used to see if there was a correlation between wettability and TAN, and wettability and the Ca^{2+} concentration of the brine. This will not be done for quartz because the overall variation in the wettability is so low that it would not make sense to do it here.

4.1.2 K-feldspar

By examining the wettability results seen in Figure 13 it is clearly confirmed that K-feldspar is primarily water-wet. It still more oil-wet than quartz, since the K-feldspar sample that is the most oil-wet is still more than 14% oil-wet, compared to only 4% oil-wet for quartz. In contrast to quartz there seems to be a pattern in the wettability alteration of K-feldspar.

No clear pattern seems to emerge if samples that are aged in the same brine but different STOs are compared. If the samples that are aged in the same STOs but different brines on the other hand, are compared a pattern emerges for the samples aged in STO #3. The wettability results from the samples that are aged with STO #3 (oil with high TAN) seem to be dependent on concentration of Ca^{2+} in the brine, see the blue line in Figure 14. The wettability seems to go toward more water-wet as the Ca^{2+} concentration decreases. Fjelde et al saw the same in their experiment with glauconite and reservoir rock (48). The wettability of the samples aged in STO #1, STO #2 and N-decane (oil with low TAN) does not seem to be dependent on the Ca^{2+} concentration of the brine. This is also in accordance with what Fjelde et al saw in their experiment with glauconite and reservoir rock.

The wettability results of K-feldspar have also been plotted against the total acid number of the STOs to see if a pattern emerged, see Figure 15. From this plot it appears that the wettability of the samples aged in FW #1 (yellow line), a brine with high Ca^{2+} concentration seems to go towards more water-wet as TAN decreases. The samples that are aged in brines with a low Ca^{2+} concentration (FW #2, SW and LSW) does not seem to be dependent on the TAN of the oil it is mixed with.

The samples that are aged in oil and formation water from the same reservoir are compared to the samples that are aged in oil from the same reservoir and SW or LSW. This is done to examine how injection water might affect the wettability of a reservoir with high K-feldspar content and oil/formation water with similar properties to the ones found in field #1 and Field #2. If the wettability of the samples aged in STO #1 and FW #1 are compared with the samples aged in STO #1 and SW an increase from 5% oil-wet and up to 12% oil-wet is observed. If the same comparison is done for the samples aged in STO #1 and LSW, a decrease from 5% oil-wet to 3% oil-wet is observed. Using SW as injection water instead of LSW might alter the wettability of the rock towards more oil-wet, if these results are true. This could cause reduction in production in a field with oil similar to STO #1, formation water similar to FW #1 and a high concentration of K-feldspar.

Comparing the samples aged in STO #2 and FW #2 with the samples aged in STO #2 and SW show no significant change in wettability (less than 1%). If the same comparison is done for the samples aged in STO #2 and LSW, a reduction from 12% oil-wet to 6% oil-wet is observed. If these results are true, using SW as injection water might not alter the wettability of the rock, but using LSW could lower the wettability towards more water-wet. This means that using LSW as injection water in a field with oil similar to STO #2, formation water similar to FW #2 and a high K-feldspar content could cause an increase in oil production due to the alteration towards more water-wet conditions.

Another thing worth noticing is that all samples mixed with N-decane as well as all samples mixed with LSW seem to be very water-wet (all but two samples are more than 95% water-wet).

The overall impression is that K-feldspar is primarily water-wet, but it is still more oil-wet than quartz. The wettability of the samples aged in STO #3 are clearly dependent on the Ca^{2+} concentration in the brine, where lower Ca^{2+} concentration results in K-feldspar being more water-wet. The TAN of the oils does not seem to have a direct impact on wettability if the formation water does not have a high Ca^{2+} concentration. If samples with the same oil and different brines are compared, SW seems to keep the wettability on the same level or increase it towards more oil-wet for all comparisons except for the sample aged in STO #3 and FW #1. In this case the high TAN of the oil and the high Ca^{2+} concentration in the brine makes the sample more oil-wet compared to the one aged in STO #3 and SW. Samples aged and LSW are the most water-wet if compared to other brines. This is true for all samples except for the ones aged in N-decane and the one aged in FW #1 and STO #2.

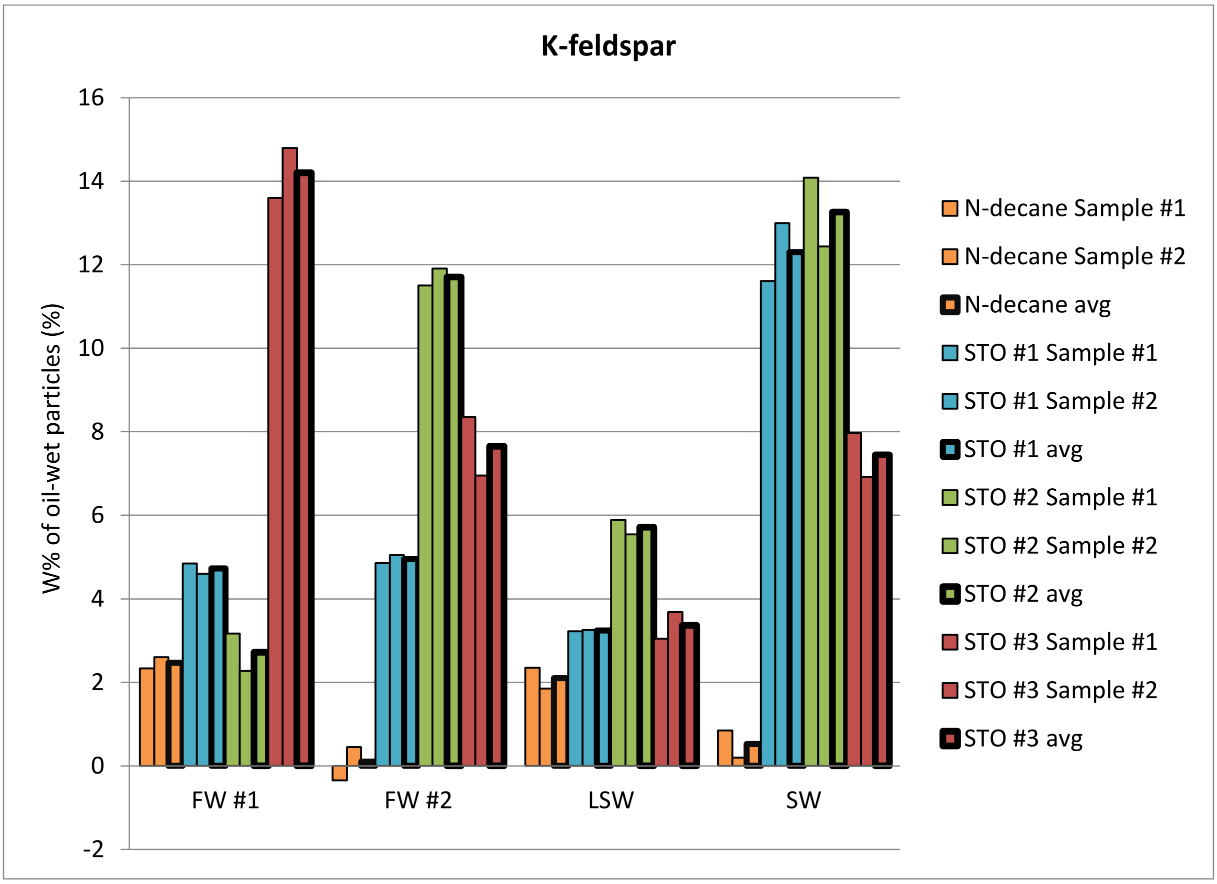


Figure 13: Wettability results of K-feldspar.

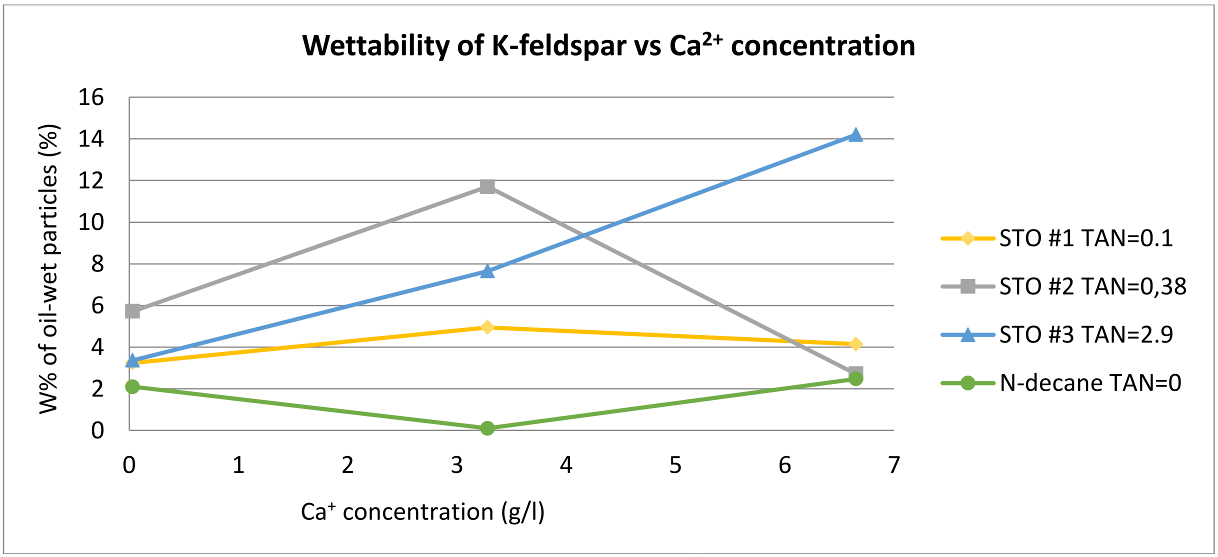


Figure 14: Wettability of K-feldspar vs Ca^{2+} concentration in the brine.

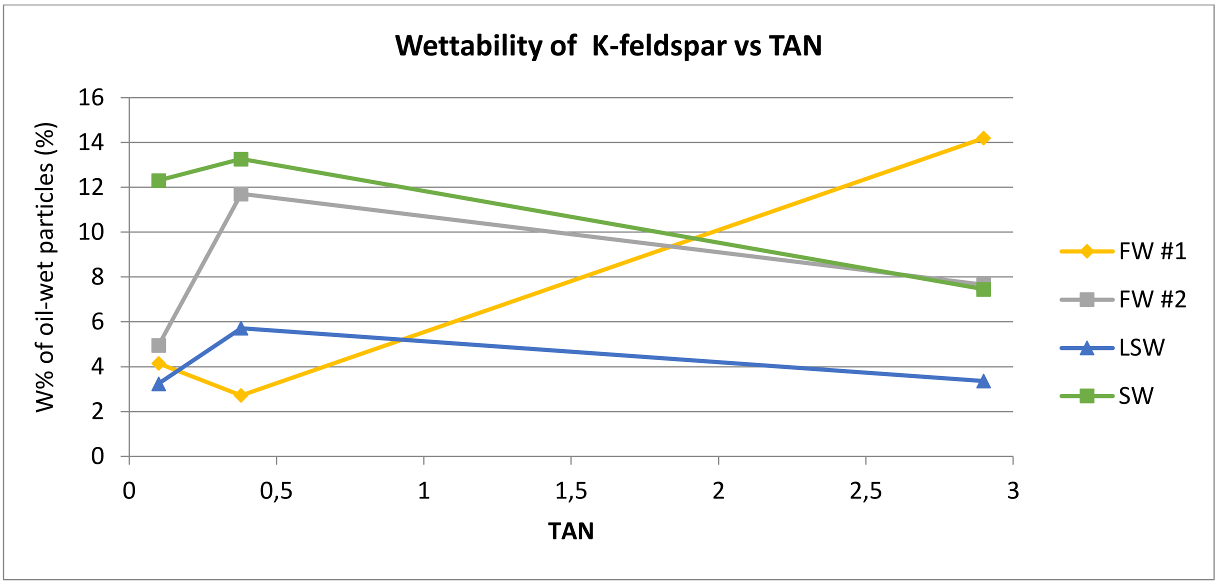


Figure 15: Wettability of K-feldspar vs TAN.

4.1.3 Plagioclase (albite)

Since there was not enough plagioclase to prepare a full set of experiments it is difficult to say how the different brines and the different oils affect the wettability of plagioclase, based on these results (see Figure 16). Once this data is set-up against the wettability data from K-feldspar, a pattern seems to emerge, see Figure 17. The data from the plagioclase samples combined with the results from K-feldspar seems to suggest that plagioclase might have similar wettability properties as K-feldspar. By examining Figure 17 it can be seen that the plagioclase and K-feldspar samples that are mixed with the same brine and the same oil have very similar wettability results. There is less than 1.5% in difference between samples that are subjected to the same variables. Based on these data here and the fact that they are both members of the feldspar mineral group it appears that plagioclase might have similar wettability properties as K-feldspar, but more research is needed to make sure.

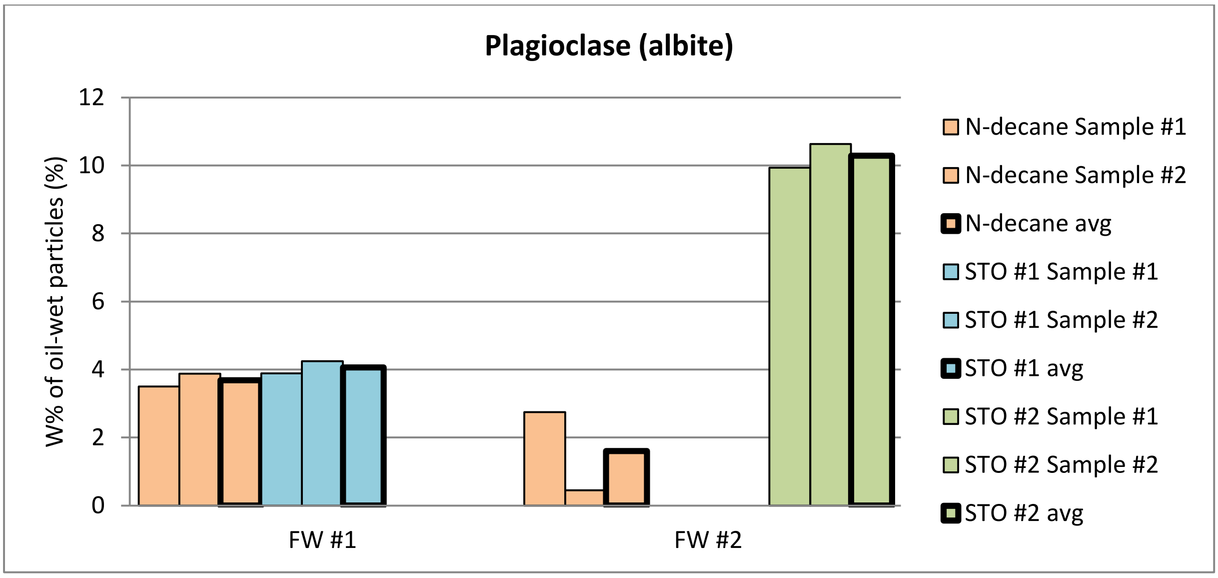


Figure 16: Wettability results of plagioclase.

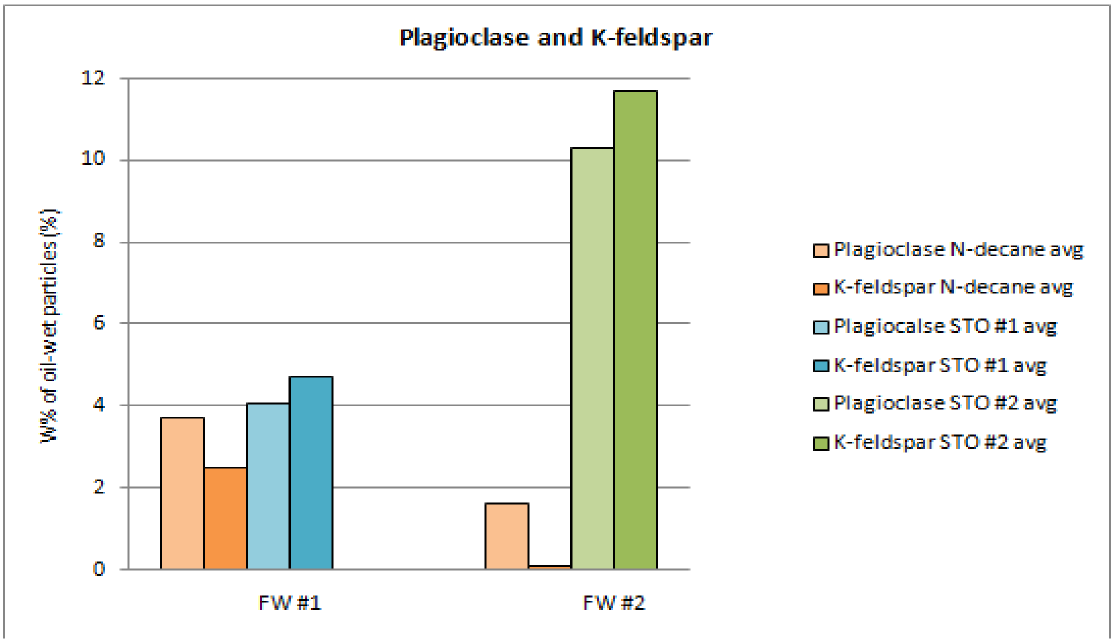


Figure 17: Wettability results of plagioclase and K-feldspar combined.

4.1.4 Glauconite

By examining the wettability results showed in Figure 18 it is clearly confirmed that glauconite, like the prior minerals is primarily water-wet. It still less water-wet than quartz, since the glauconite sample that is the least water-wet is 84% water-wet, compared to 96% water-wet for quartz. In contrast to quartz, and similar to K-feldspar there seems to be a pattern in the wettability alterations of glauconite.

Comparing samples aged in the same brine but in different STOs give the following results: A small variation in wettability is observed if the samples aged in STO #1 are compared to samples aged in STO #2. This variation in wettability is less than 2%, which is bellow the accuracy of this method, so more research is needed to verify these results. When the samples aged in STO #3 are compared to the samples aged in other STOs, the wettability changes towards more oil-wet. This is true for all samples, except the ones aged in LSW.

Changing the FW while keeping the STO on the other hand seems to have a larger impact on the wettability of glauconite. Just like for K-feldspar, the wettability results of the samples that are aged with STO #3 (oil with high TAN) seems to be linked to the calcium concentration in the brine. A reduction in the Ca^{2+} concentration of the brine seems to leave glauconite more water-wet. This can be seen as the blue line in Figure 19 where the wettability of glauconite is plotted against the Ca^{2+} concentration of the brine. Fjelde et al saw the same in their experiment with glauconite and reservoir rock (48). For the samples aged in STO #1, STO #2 and N-decane (oils with low TAN) oil-wetness appears to increase slightly when Ca^{2+} concentration goes from zero to around 3.3 g/l, before decreasing again as the Ca^{2+} concentration in the brine increases further.

The wettability results of glauconite have also been plotted against the total acid number of the STOs to see if a pattern emerged, see Figure 20. The wettability of the samples aged in FW #1 (yellow line) a brine with a high Ca^{2+} concentration, appears to be highly correlated to the TAN number of the oil. A lower TAN seems to result in glauconite being more water-wet. A similar pattern emerges for the samples aged in FW #2 and SW (brines with a low concentration of Ca^{2+}) as well, but the change in wettability is just below 2%. This means that the accuracy of this method is not good enough to determine if the wettability of the samples aged in FW #2 and SW really are dependent on the TAN of the oil or not. More research is needed to confirm. The wettability of the samples aged in LSW does not seem to be dependent on the TAN of the oil.

The samples that are aged in oil and formation water from the same reservoir are compared to the samples that are aged in oil from the same reservoir and SW or LSW. This is done to examine how injection water might affect the wettability of a reservoir with high glauconite content and oil/formation water with similar properties to the ones found in field #1 and Field #2. If the wettability of the samples aged in STO #1 and FW #1 are compared with the samples aged in STO #1 and SW an increase from 3% oil-wet and up to 6% oil-wet is observed. If the same comparison is done for the samples aged in STO #1 and LSW, no significant difference (less than 1%) is observed. Using SW as injection water instead of LSW might alter the wettability of the rock towards more oil-wet, if these results are true. This could cause reduction in production in a field with oil similar to STO #1, formation water similar to FW #1 and a high concentration of glauconite.

Comparing the samples aged in STO #2 and FW #2 with the samples aged in STO #2 and SW show a decrease from 9% oil-wet to 7% oil-wet. If the same comparison is done for the samples aged in STO #2 and LSW, a reduction from 9% oil-wet to 6% oil-wet is observed. The accuracy of this method is too low to determine if one of these brines are preferred as injection water over the other, because the results show a mere 1% difference in wettability. Both of these brines might slightly alter the wettability towards more water-wet for a reservoir with high glauconite content, and oil and formation water similar with similar properties to what is found in field #2.

Another thing worth noticing is that all samples mixed with N-decane as well as all samples mixed with LSW seem to be very water-wet (all but two samples are more than 96% water-wet).

The overall impression is that Glauconite is primarily water-wet, but it is still more oil-wet than quartz. STO #2 appears to slightly alter the wettability towards more oil-wet compared to N-decane and STO #1, but this cannot be confirmed because the accuracy of this method is too low. STO #3 also seems to slightly alter the wettability towards more oil-wet, but the accuracy of this method is too low to confirm this for all samples except for the ones aged in FW #1. The wettability of the samples aged in STO #3 are clearly dependent on the Ca^{2+} concentration in the brine, where lower Ca^{2+} concentration results in glauconite being more water-wet. The TAN of oil also seems to affect the wettability of glauconite samples aged in brines containing Ca^{2+}. The effect seems to be greater the higher the Ca^{2+} concentration of the brine is.

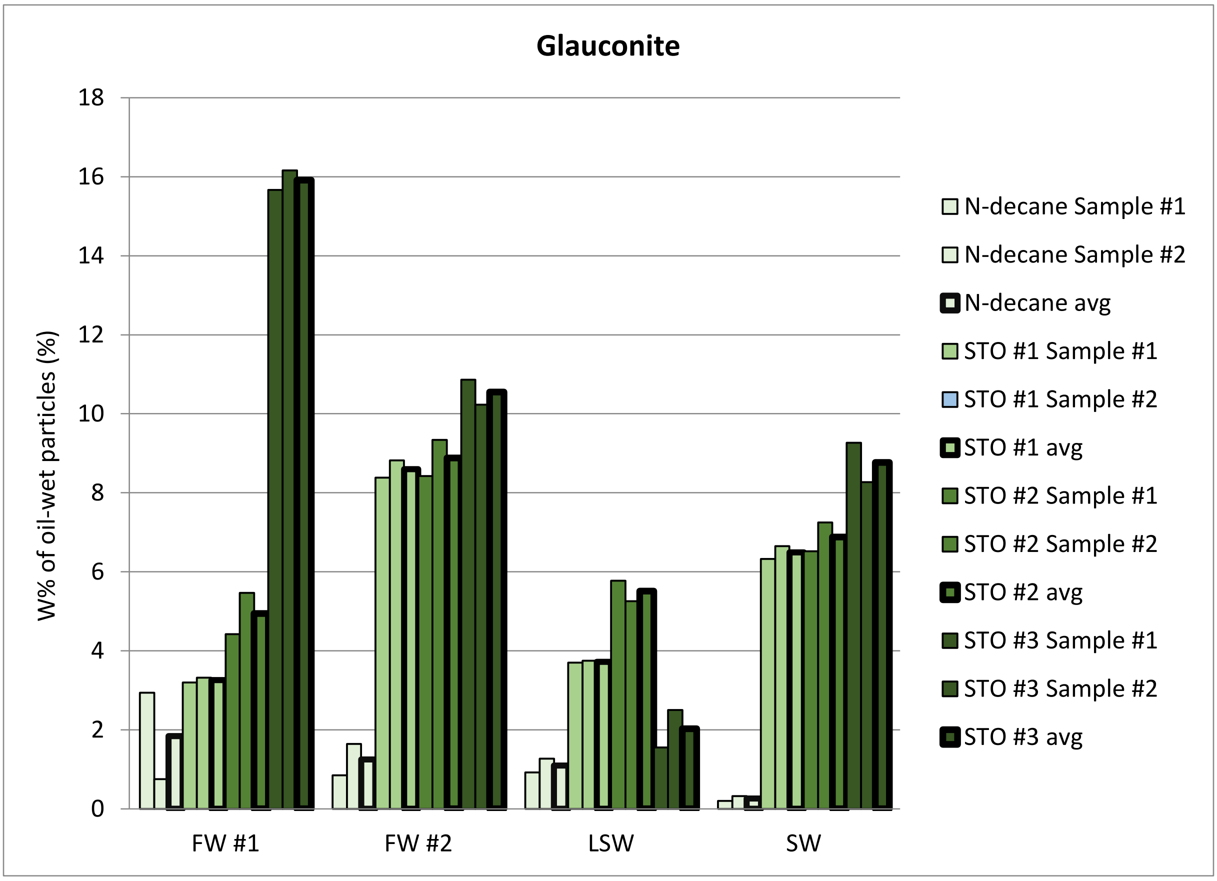


Figure 18: Wettability results of glauconite.

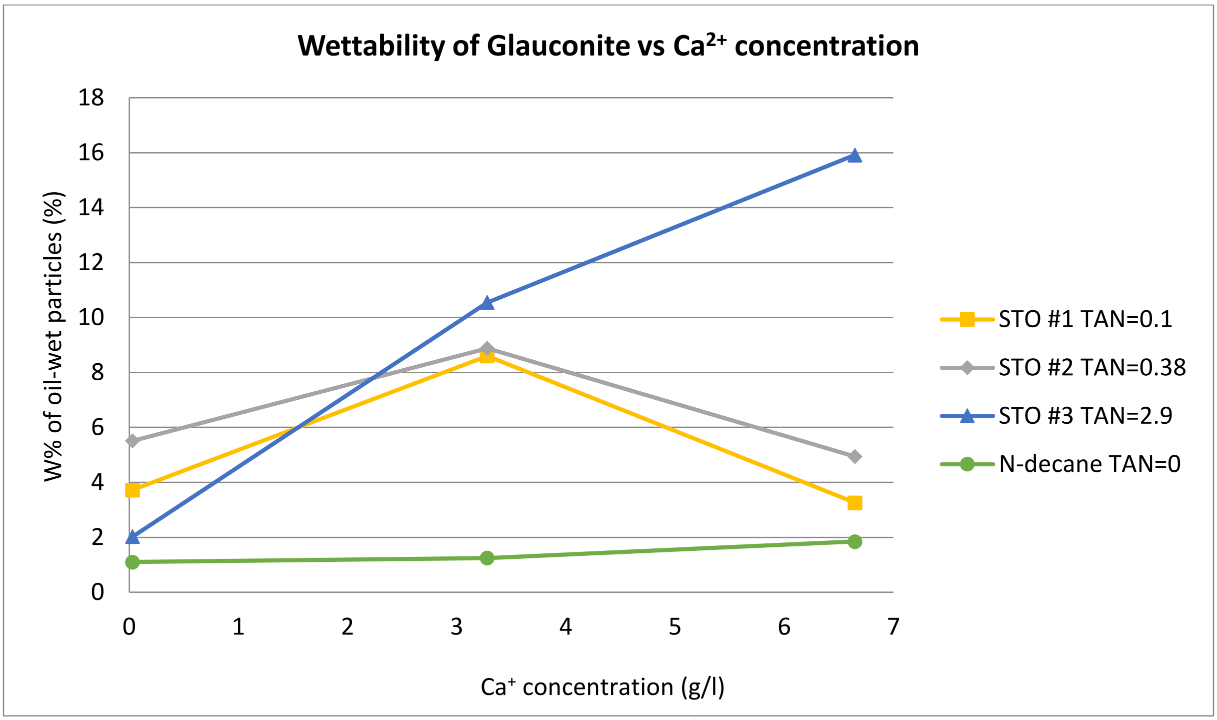


Figure 19: Wettability of glauconite vs Ca^{2+} concentration in the brine.

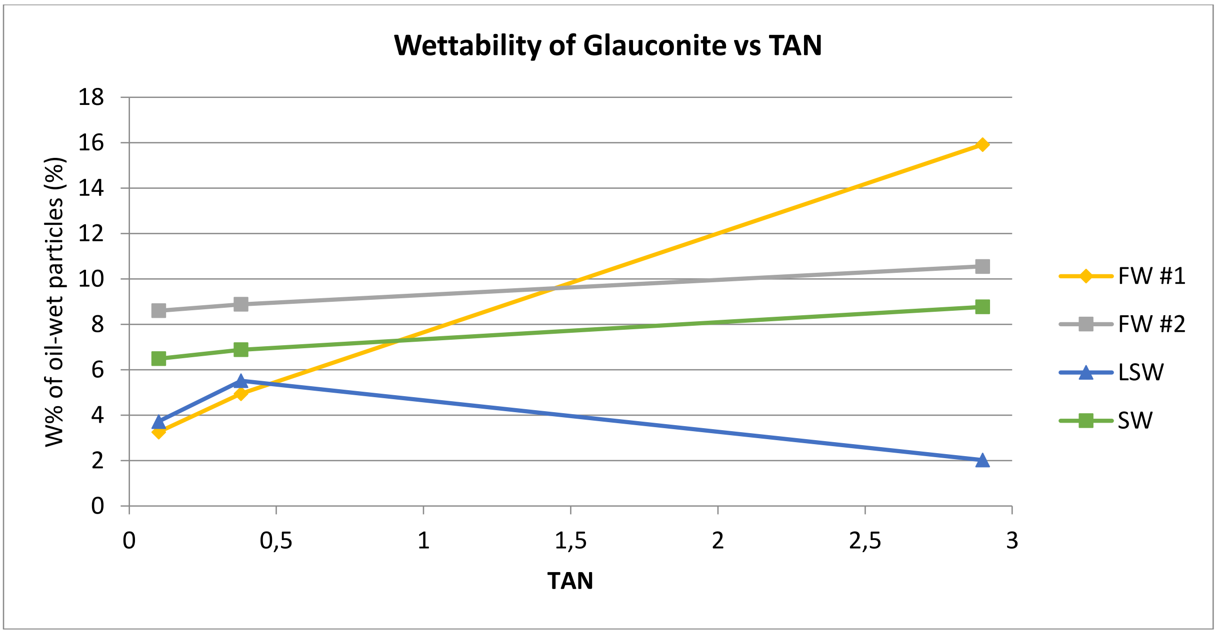


Figure 20: Wettability of glauconite vs TAN.

Glauconite aged with three-valent ions in the brine

The effect three-valent ions have on the wettability of clay minerals like glauconite was also examined. This was done by adding Al^{3+} and Fe^{3+} to the brine before aging it with glauconite. First samples with unrealistically high concentrations (1117ppm and 539ppm) of Fe^{3+} and Al^{3+} were created to see if such concentrations would have a noticeable effect on the wettability of glauconite. Later on more realistic concentrations (50ppm) were tested. The reason this concentration was chosen, was that the brine the pyrite samples were aged in were tested for Fe^{3+} and came back positive with a concentration of 25-40ppm. This concentration was determined by the use of a spectrophotometer, see Figure 21 for the results. It was decided to use a Fe^{3+} concentration that was a little higher high than the one found in the pyrite samples in case some other minerals could also contribute to the Fe^{3+} concentration. Fe^{3+} was expected to have an impact on wettability (36, 54), but how much this concentration of Al^{3+} would affect the wettability was unknown. They were both expected to alter the wettability of glauconite towards more oil-wet because they are three-valent cations, and they could act as cation bridges between the negatively charged clay minerals and carboxylic acids in the oil (36, 54).

By examining the wettability results plotted in Figure 22 it is obvious that brine containing three-valent cations have a large impact on the wettability results compared to regular brine. In this figure the wettability of the samples aged in high and low concentrations of Al^{3+} cations are represented by light and dark green columns, while the samples aged in high and low concentrations of Fe^{3+} cations are represented by light red, dark red and blue columns. In the samples aged with a high concentration of Fe^{3+} cations, rust ($Fe(OH)_3$) precipitation was observed (eq 5.1) see , and HCl was added just before filtering to dissolve the rust particles (eq 5.2).

$$Fe^{3+} + 3H_2O \rightleftharpoons \mathrm{Fe(OH)_3} + 3\mathrm{H}^+ \tag{5.1}$$

$$HCl(aq) \rightarrow H^+ + Cl^- \tag{5.2}$$

By adding HCl the brine gets a high concentration of hydrogen cations, thus forcing the equilibrium seen in eq. 5.1 to the left resulting in the dissolution of rust particles. In a worst case scenario all of the Fe^{3+} ions precipitate out as rust, and it is this scenario that is used to calculate the amount of HCl needed dissolve the rust particles. See Appendix B for calculations. HCl can also cause glauconite dissolution, and three glauconite samples were aged with FW #1 containing different amounts of HCl to see if there was any correlation between the amount of HCl added and the amount of dissolved glauconite. There was a clear correlation, and the results were plotted as markers along with a linear trendline, see Figure 23. This trendline was then used to correct the samples containing HCl for dissolution of glauconite. In a worst case scenario very little rust is precipitated and all of the HCl added to the brine/glauconite mixture causes glauconite to dissolve. For this scenario we can use the trendline equation to find just how much could possibly be dissolved by the HCl, and withdraw that from the oil-wet phase. This is represented as the dark red columns in Figure 22.

From the results plotted in Figure 22 it is clear that the presence of Al^{3+} and Fe^{3+} makes the glauconite samples more oil-wet. Low concentrations of Al^{3+} does not seem to have significant impact on the wettability of glauconite, but low concentrations of Fe^{3+} on the other hand does. Comparing the samples aged in STO #1 and FW #1 to the ones aged in STO #1 and FW #1 containing 50ppm Al^{3+}, glauconite has its oil-wetness increased from 3% to 7%. If the same comparison is done for the samples aged in STO #2 and FW #2 there is no observable change in wettability (<1%). This shows how little low concentrations of AL^{3+}

affect the wettability of glauconite. Comparing the samples aged in STO #1 and FW #1 with the samples aged in STO #1 and FW #1 containing 50ppm Fe^{3+}, glauconite has its oil-wetness increased from 3% to 14%. If the same comparison is done for the samples aged in STO #2 and FW #2, glauconite has its oil-wetness increased from 9% to 15%. These results shows that even low concentration of Fe^{3+} cations have a significant effect on the wettability of quartz.

Higher concentrations of both Fe^{3+} and Al^{3+} cause a significant impact on the wettability of glauconite. Fe^{3+} still affects the wettability of glauconite more than Al^{3+}, but that might be because the Fe^{3+} concentration is more than twice as high as the Al^{3+} concentration. If the samples with a high concentration of Al^{3+} are compared to the ones without aluminum we can see an increase in oil-wetness from 3% - 19% for FW #1/STO #1 mixture and from 9% - 24% for FW #2/STO #2 mixture. High concentrations of Fe^{3+} has an even larger impact on the wettability of glauconite. Comparing the samples with a high concentration of iron to the ones without iron we can see an increase in oil-wetness from 3% - 33% for the FW #1/STO #1 mixture and from 9% - 32% for FW #2/STO #2 mixture. The actual oil-wetness might be even higher since these values are corrected for the maximum possible dissolution of glauconite. The wettability changes caused by the high concentrations of these three-valent cations are not representable for reservoir conditions, because the concentration of these cation is too high. The lower concentrations on the other hand are representable for reservoir conditions, thus showing the effect such concentrations of Fe^{3+} and Al^{3+} can have on the wettability of a reservoir with a high clay content..

From these results it is clear that even low concentrations of Fe^{3+} has an observable effect on the wettability of glauconite, and higher concentrations of this cation has an even larger effect on wettability. Low concentrations of Al^{3+} does not seem to have an observable impact on the wettability of glauconite, but higher concentrations do. The tendency for glauconite to be more oil-wet in the presence of these three-valent cations could be due to the fact that the positively charged ions act as cation bridges between the negatively charged clay particles and the hydrophilic head found on acidic substances in oil.

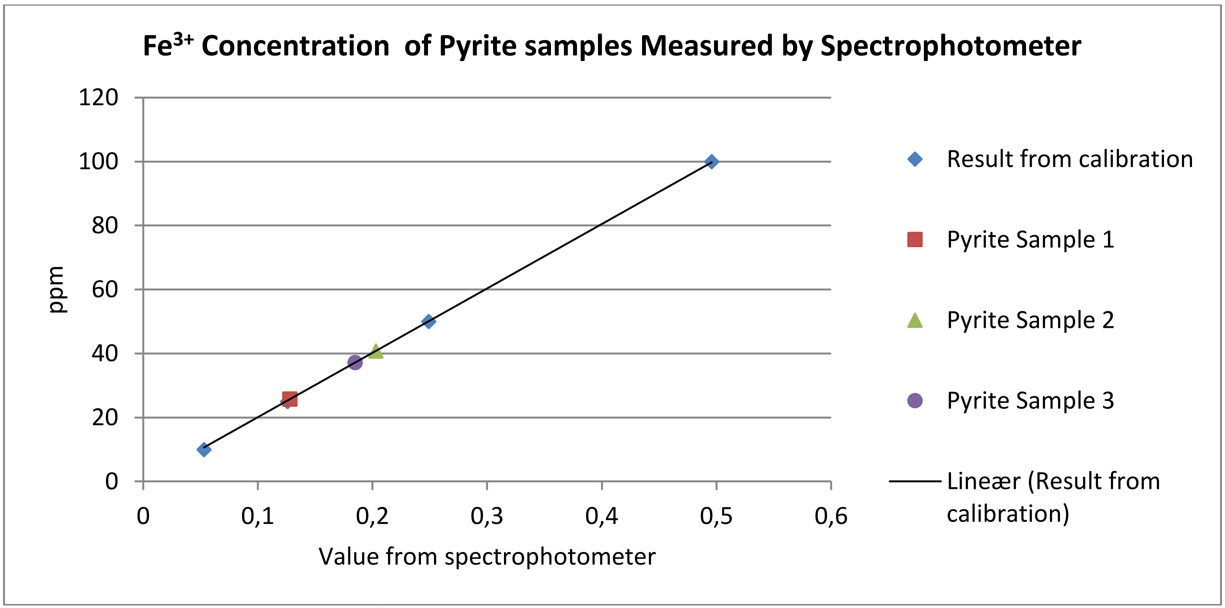


Figure 21: Fe^{3+} concentration measured by spectrophotometer.

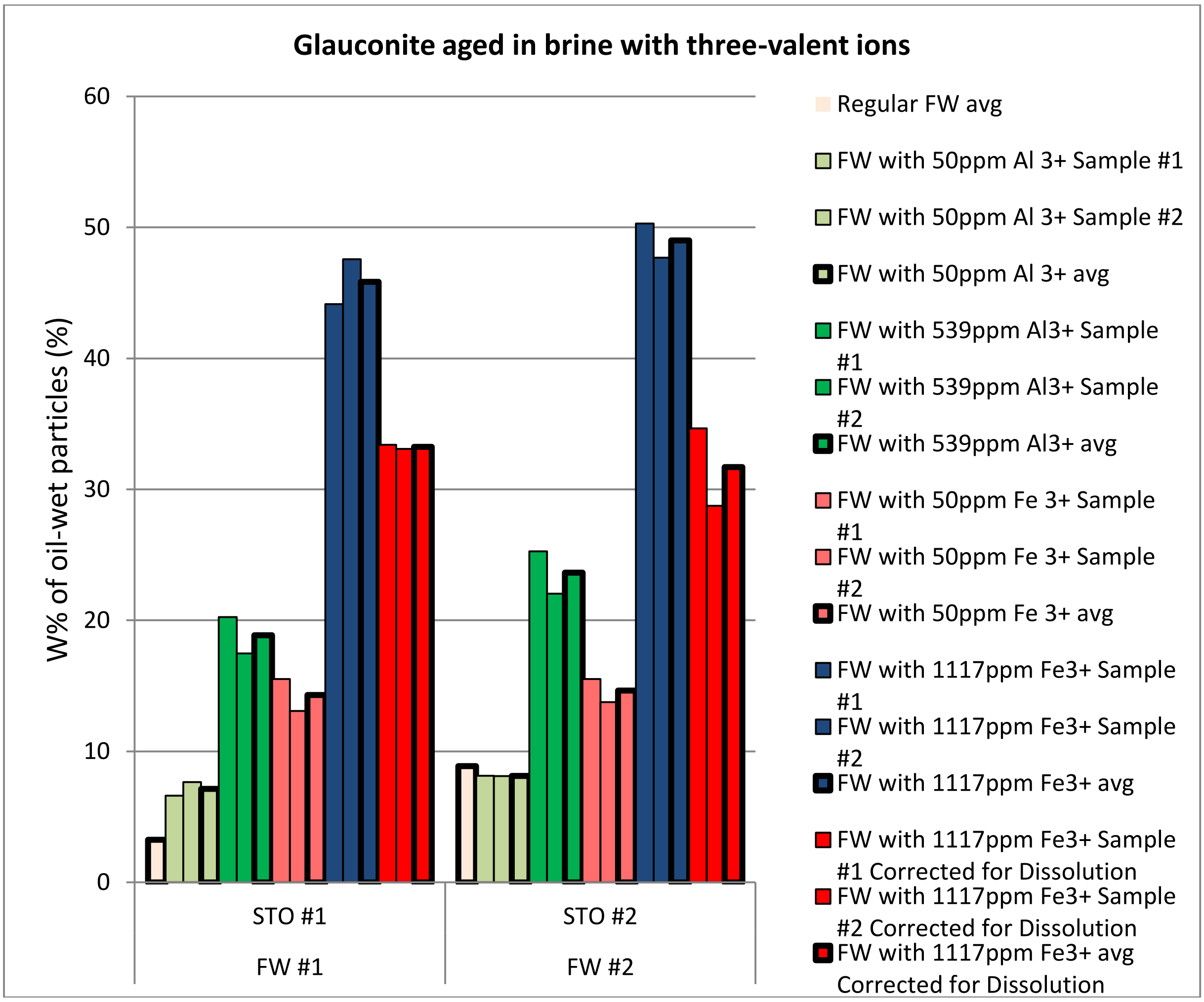


Figure 22: Glauconite aged in brine with three-valent ions.

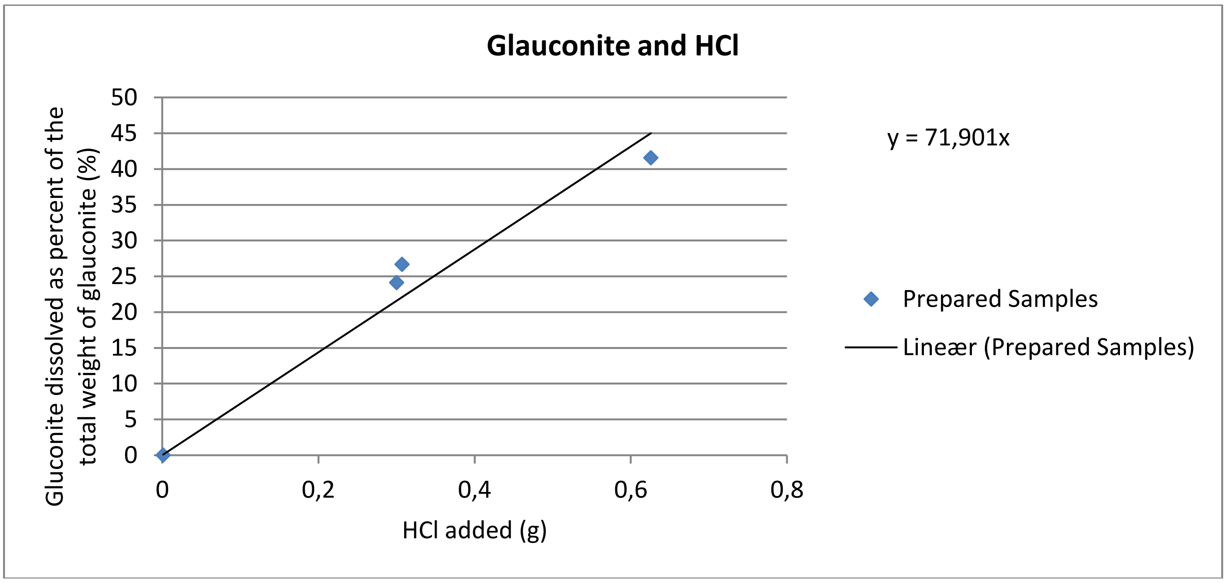


Figure 23: Dissolution of glauconite by HCl.

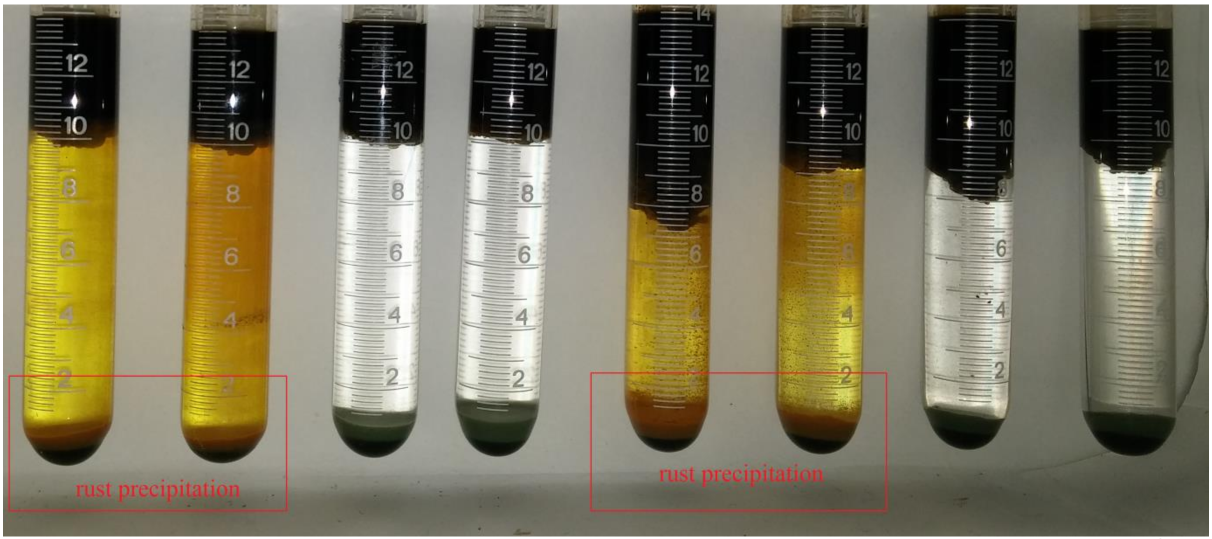


Figure 24: Rust precipitation in glauconite samples aged with high concentrations of Fe^{3+}.

4.1.5 Muscovite

By examining the wettability results showed in Figure 25 it can be seen that muscovite seems to be much less water-wet than the previous minerals. For the samples aged in STO the wettability range from 16% oil-wet to 98% oil-wet. Muscovite was expected to be more oil-wet than the other minerals, since previous experiments have shown that this mineral range from water-wet to intermediate-wet (43, 50). Similar to K-feldspar and glauconite, the wettability alteration of muscovite seems to follow a pattern.

Comparing samples aged in the same brine, but in different STOs give the following result: A decrease of about 5% in oil-wetness is observed when comparing the samples aged in STO #1 to the ones aged in STO #2. Samples aged in STO #3 are the most oil-wet, if compared to samples aged in the other oils. This is true for all samples.

If the samples aged in the same STO, but in different brines are compared the following pattern emerges: Samples aged in SW came back the most oil-wet of all by far, with two samples close to 100% oil-wet. Even the samples aged in N-decane came back close to 17% oil-wet. Since there are no SAC in N-decane, and the TAN/TBN=0 these samples should come back close to 100% water-wet. There were some emulsions close to the SW/N-decane contact, see Figure 26, and all the particles that were stuck in these emulsions were removed when the N-decane was removed. These results might also be caused by the brine forcing some of the K^+ cations in the interlayer space that are holding the tiny muscovite particles together to be released into the solution, thus causing the tiny layers to be released into the brine. These layers might be so small that they could have passed through the filter paper during filtration or caused the emulsions and get stuck in the oil phase. Samples aged in FW #2 came back the second most oil-wet, and all of the samples except for the ones aged in N-decane were 40-48% oil-wet. The samples aged in FW #1 came back the third most oil-wet, and this is true for all samples aged in STO except for the one aged in STO #3. The combination of high concentration of Ca^{2+} in the brine, and the high TAN of the oil resulted in a sample that was much more oil-wet than the others aged in FW #1. The samples aged in LSW came back the least oil-wet of all, with samples raging from 16-27% oil-wet for the ones aged in the different STOs, and close to 100% water-wet for the ones aged in N-decane.

Just like for K-feldspar and glauconite, the wettability results of the samples that are aged with STO #3 (oil with high TAN) seems to be linked to the calcium concentration in the brine. A reduction in the Ca^{2+} concentration of the brine seems to leave muscovite more water-wet. This can be seen as the blue line in Figure 27 where the wettability of muscovite is plotted against the Ca^{2+} concentration of the brine. Fjelde et al saw the same in their experiment with glauconite and reservoir rock (48). For the samples aged in STO #1, STO #2 and N-decane (oils with low TAN) oil-wetness appears to increase when Ca^{2+} concentration goes from zero to around 3.3 g/l, before decreasing again as the Ca^{2+} concentration in the brine increases further.

The wettability results of muscovite have also been plotted against the total acid number of the STOs to see if a pattern emerged, see Figure 28. In contrast to glauconite and K-feldspar, the same pattern emerges for every brine, not only for FW #1: When comparing samples aged in the oil with highest TAN to the samples aged in the oil with the second highest TAN the wettability is altered towards more water-wet. When comparing the samples aged in the oil with the second highest TAN to the one with the lowest TAN the wettability is altered towards more oil-wet. The wettability was not expected to be altered towards more oil-wet in the last comparison, because this has not happened to any of the other samples except for the K-feldspar samples aged in FW #1. In that case the change in wettability was less than the accuracy of this method.

The samples that are aged in oil and formation water from the same reservoir are compared to the samples that are aged in oil from the same reservoir and SW or LSW. This is done to examine how injection water might affect the wettability of a reservoir with high muscovite content and oil/formation water with similar properties to the ones found in field #1 and Field #2. If the wettability of the samples aged in STO #1 and FW #1 are compared with the samples aged in STO #1 and SW an increase from 36% oil-wet and up to 83% oil-wet is observed. If the same comparison is done for the samples aged in STO #1 and LSW, a decrease from 36% oil-wet to 22% oil-wet is observed. Using SW as injection water instead of LSW might completely alter the wettability of the rock from water-wet to oil-wet, if these results are true. This could cause reduction in production in a field with oil similar to STO #1, formation water similar to FW #1 and a high concentration of muscovite.

Comparing the samples aged in STO #2 and FW #2 with the samples aged in STO #2 and SW show an increase from 39% oil-wet to 75% oil-wet. If the same comparison is done for the samples aged in STO #2 and LSW, a reduction from 39% oil-wet to 16% oil-wet is observed. Using SW as injection water instead of LSW might completely alter the wettability of the rock from water-wet to oil-wet, if these results are true. This could cause reduction in production in a field with oil similar to STO #1, formation water similar to FW #1 and a high concentration of muscovite.

Another thing worth noticing is that all samples aged in N-decane seem to be near 100% water-wet, except for the ones where SW was the brine.

The overall impression is that muscovite is primarily water-wet since most of the samples are more than 50% water-wet, but the samples aged in SW are primarily oil-wet. STO #2 appears to slightly alter the wettability towards less oil-wet compared to STO #1. STO #3 seems to slightly alter the wettability towards more oil-wet compared to the other oils. The wettability of the samples aged in STO #3 are clearly dependent on the Ca^{2+} concentration in the brine, where lower Ca^{2+} concentration results in muscovite being more water-wet. The TAN of oil also seems to affect the wettability of all muscovite samples. Going from higher to lower TAN appears to results in more water-wet samples for all but the ones aged in the STO with the lowest TAN. Here the wettability seems to alter slightly towards more oil-wet.

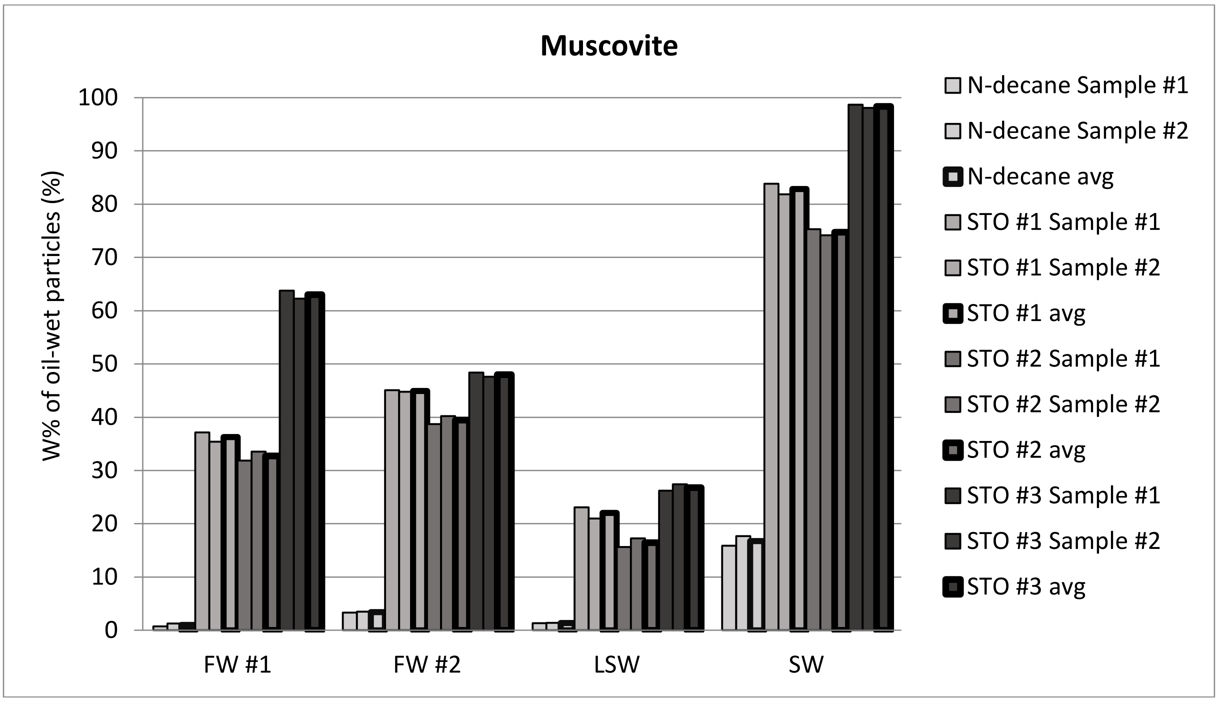


Figure 25: Wettability results of muscovite.

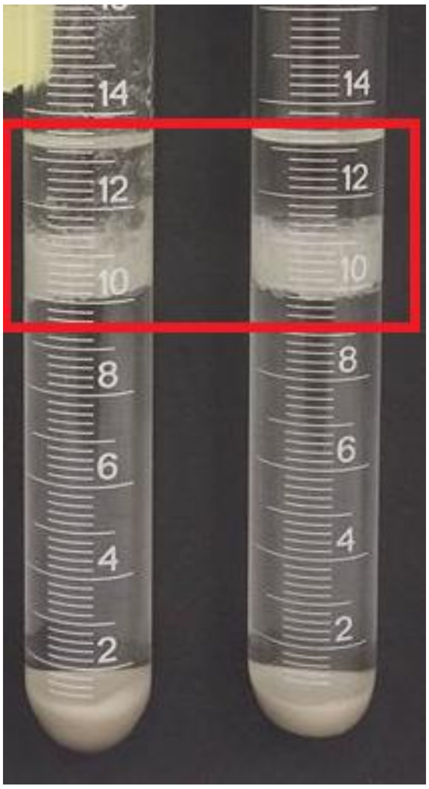


Figure 26: Emulsions near the oil/water contact.

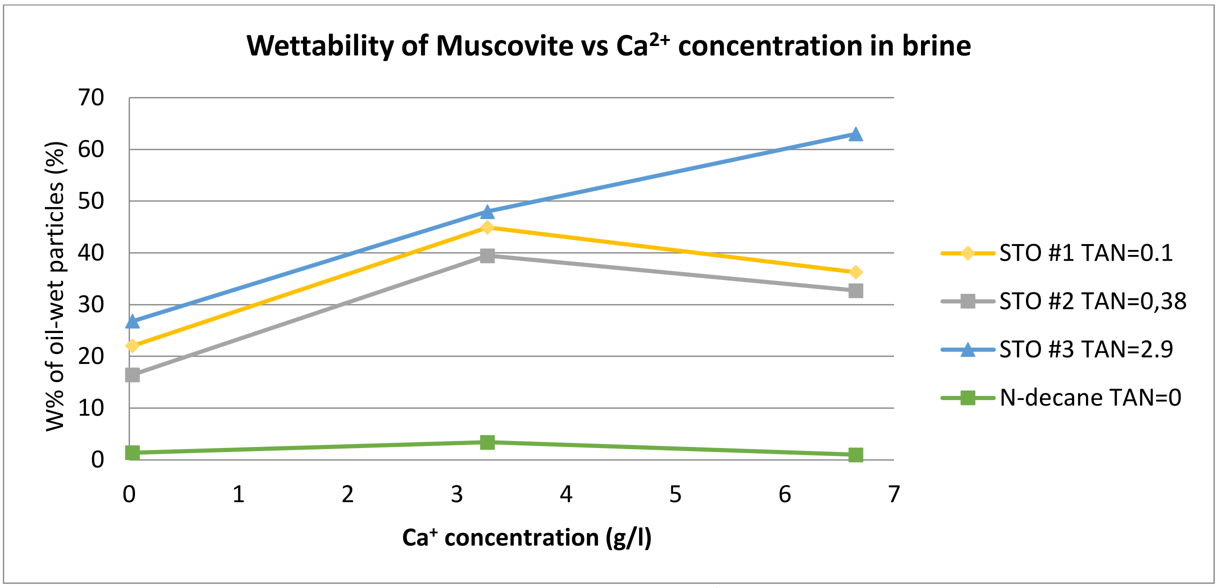


Figure 27: Wettability of Muscovite vs Ca^{2+} concentration in brine.

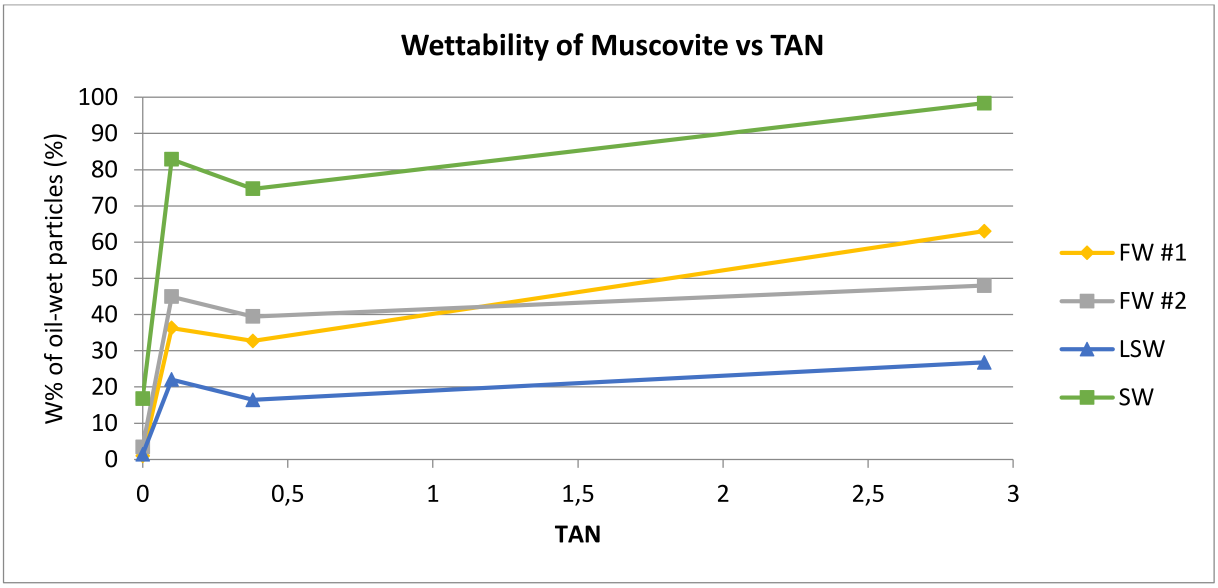


Figure 28: Wettability of muscovite vs TAN.

4.1.6 Pyrite

Only five pyrite samples were made and there was a lot of variation in the wettability results, see Figure 29, but it appears that pyrite is primarily oil-wet. The low number of samples and the large variation in the results makes it near impossible to say anything about how different brines and different oils affect the wettability of pyrite. The duplicates that were aged in N-decane came back with similar results, but they seem to suggest that pyrite is primarily oil-wet even when aged with N-decane. The results were 63% and 65% oil-wet. This should be impossible because N-decane is made up of non-polar decane without any SAC. Both of the samples aged in N-decane caused the oil to form a thick wax like substance with a lot of emulsions near the oil-water contact, see Figure 30. This might cause the tiny pyrite particles to get stuck in the thick oil phase even if the particles were expected to be found in the water phase, thus causing them to be removed along with the N-decane.

The first two duplicates that were aged in STO #2 came back with very different wettability results: 45% and 65% oil-wet. Judging by these results alone STO #2 makes pyrite more water-wet than N-decane, which should also be impossible. Just like in the samples aged with N-decane, the oil phase formed a thick wax like substance in the samples aged with STO #2 as well. A closer look at the samples aged in STO #2 revealed that pyrite samples covered in oil had fallen to the bottom of the test tube and formed "globules" after the brine had been added back to the mixture, see Figure 30. These globules appears to be oil-wet pyrite particles that have clumped together and become too dense to float. After N-decane had been added to help remove the last remains of STO #2, the oil phase had once again formed a thick wax like substance, see Figure 31. "Globules" of oil-wet pyrite were found at the bottom of the test tube this time as well, but they were not as large as before the N-decane was added. More pyrite particles appears to have gone into the oil phase. The third pyrite sample aged in STO #2 came back more than 90% oil-wet, and only very small oil-wet pyrite "globules" were found at the bottom of the test tube. It appears that pyrite is near 100% oil-wet when aged in STO #2 and FW #2, but the pyrite particles are too dense to float in the oil phase. This is not unlikely because pyrite is by far the most dense mineral used in these experiments, with a density of 4.9-5.2s.g.

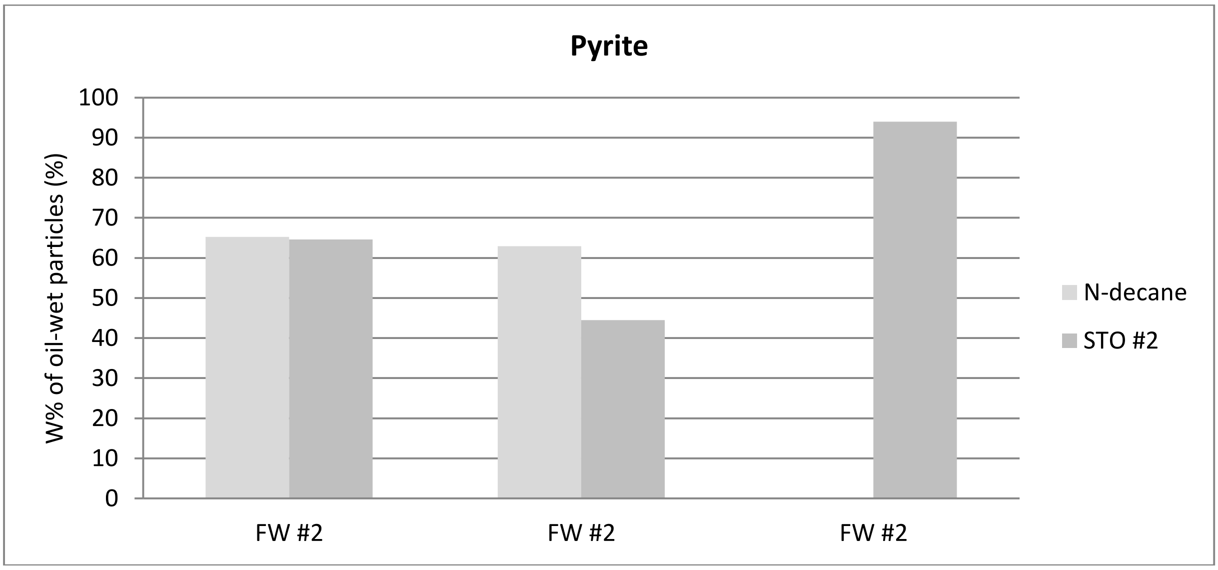


Figure 29: Wettability results of pyrite.

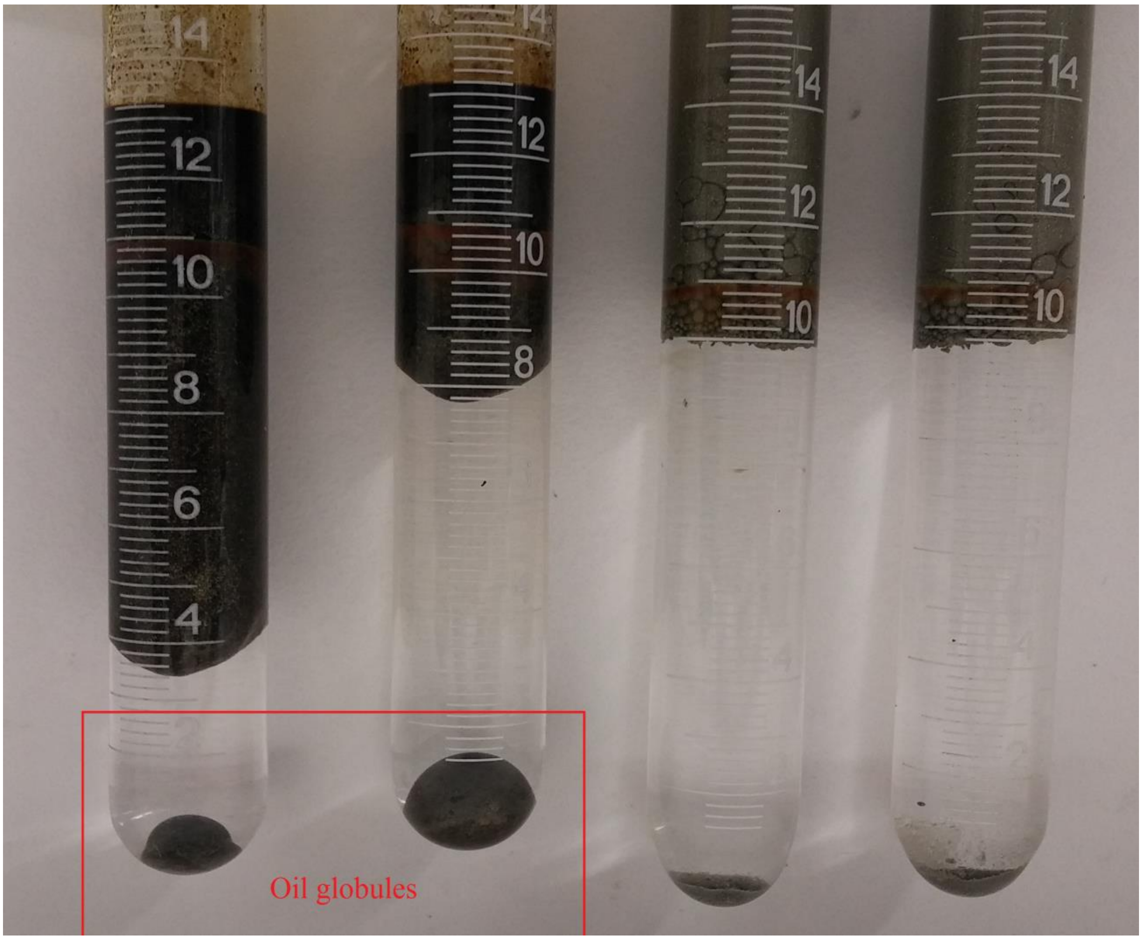


Figure 30: Pyrite aged in STO #2 on the left, and in N-decane on the right.

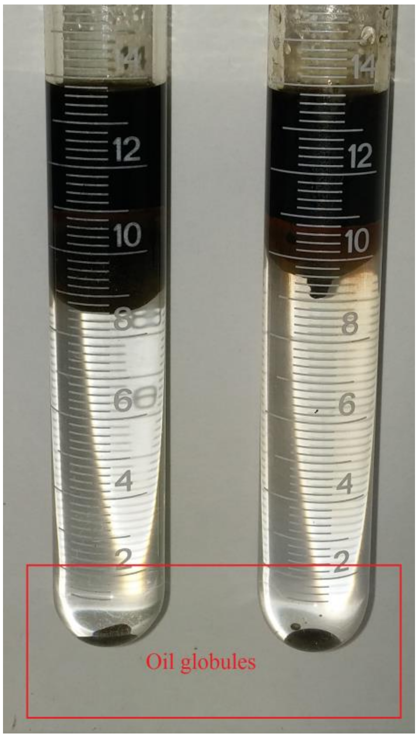


Figure 31: After N-decane had been added to remove STO #2.

4.1.7 Reservoir Rock from Field #1

By examining the wettability results showed in Figure 32 it is clearly confirmed that Rock from field #1, like K-feldspar and glauconite is primarily water-wet (33). It is still less water-wet than quartz, and more like K-feldspar and glauconite. Similar to all the previous minerals except for quartz, there appears to be a pattern in the wettability alterations of rock from field #1. This pattern appears to be very similar to the pattern found in the wettability alterations of glauconite, see Figure 33.

Comparing samples aged in the same brine but in different STOs give the following results: A small variation in wettability is observed if the samples aged in STO #1 are compared to samples aged in STO #2. This variation in wettability is less than 2% for all comparisons except for when SW is the brine. The accuracy of this method is to low to confirm this trend in samples aged in FW #1, FW #2 and LSW, so more research is needed to verify these results. When the samples aged in STO #3 are compared to the samples aged in other STOs, the wettability changes towards more oil-wet. This is true for all samples, except the ones aged in LSW.

Unlike the other minerals, the wettability of the rock from field #1 seems to slightly influenced by the Ca^{2+} concentration of the brine even when aged in oils with low TAN, see Figure 34. For the samples aged in STO #1 and STO #2 (yellow and grey line), a minor alteration towards more water-wet is observed when samples aged in FW #1, a brine with high Ca^{2+} concentration are compared to samples aged in FW #2, a brine with lower Ca^{2+} concentration. If the samples that are aged in FW #2 are compared to the samples aged in LSW a brine with no Ca^{2+} content a similar wettability alteration is observed. Samples aged in SW does not follow the same pattern. Samples aged in SW appears to have similar results as LSW when both are aged in STO #1, and similar to FW #1 when both are aged in STO #2.

Just like for the previous minerals, the wettability results of the samples that are aged in STO #3 (oil with high TAN) are more influenced by the calcium concentration in the brine than samples aged in the other oils. A reduction in the Ca^{2+} concentration of the brine seems to leave rock from field #1 more water-wet. This can be seen as the blue line in Figure 34 where the wettability of rock from field #1 is plotted against the Ca^{2+} concentration of the brine. Fjelde et al saw the same in their experiment with glauconite and reservoir rock (48).

The wettability results of rock from field #1 have also been plotted against the total acid number of the STOs to see if a pattern emerged, see Figure 35. The wettability of rock from field #1 appears to be connected to the TAN for all samples, except for the ones aged in LSW a brine without Ca^{2+}. A lower TAN seems to result in rock from field #1 being more water-wet. Just like the wettability of muscovite, the wettability of rock from field #1 aged in SW appears to be affected the most by a change in TAN, followed by FW #1 and FW #2. The wettability of the samples aged in LSW does not seem to be dependent on the TAN of the oil.

The samples that are aged in oil and formation water from the same reservoir are compared to the samples that are aged in oil from the same reservoir and SW or LSW. This is done to examine how injection water might affect the wettability of Field #1. If the wettability of the samples aged in STO #1 and FW #1 are compared with the samples aged in STO #1 and SW a decrease from 8% oil-wet to 6% oil-wet is observed. If the same comparison is done for the samples aged in STO #1 and LSW, a decrease from 8% oil-wet to 5% oil-wet is observed. Fjelde et al. saw an alteration towards more oil-wet when using LSW compared to FW #1 (33), this could be because different methods were used to measure wettability. The difference between the wettability alteration caused by LSW compared to SW are to small (1%) for this method to determine which would be better as injection water. Both seem to alter the wettability towards more water-wet.

If the reservoir in field #1 contained oil and formation water with similar properties as those found in field #2, the previous comparison might give the following result: If the wettability of the samples aged in STO #2 and FW #2 are compared with the samples aged in STO #2 and SW a decrease from 10% oil-wet to 9% oil-wet is observed. If the same comparison is done for the samples aged in STO #2 and LSW, a decrease from 10% oil-wet to 7% oil-wet is observed. Just like it was observed in the previous comparison with STO #1, the changes in wettability are very small here as well.

Another thing worth noticing is that all samples mixed with N-decane as well as all samples mixed with LSW seem to be very water-wet. All samples aged with N-decane are more than 98% water-wet, and the samples aged in LSW are at least 94% water-wet.

The overall impression is that rock from field #1 is primarily water-wet, but it is still more oil-wet than quartz. STO #2 appears to slightly alter the wettability towards more oil-wet compared to N-decane and STO #1, but this cannot be confirmed because the accuracy of this method is too low. STO #3 also seems to slightly alter the wettability towards more oil-wet for all samples but the ones aged in LSW, and here the increase in wettability is large enough to be confirmed by this method. The combination of high the TAN and the low Ca^{2+} concentration appears to alter the wettability towards more water-wet compared to the other oils, just like it did for glauconite. The wettability of rock from field #1 appears to be affected by the Ca^{2+} concentration of the brine for all of the oils. The lower the TAN of the oil was, the less rock from field #1 appeared to be affected by the Ca^{2+} concentration of the brine. Lower TAN still resulted in a more water-wet rock.

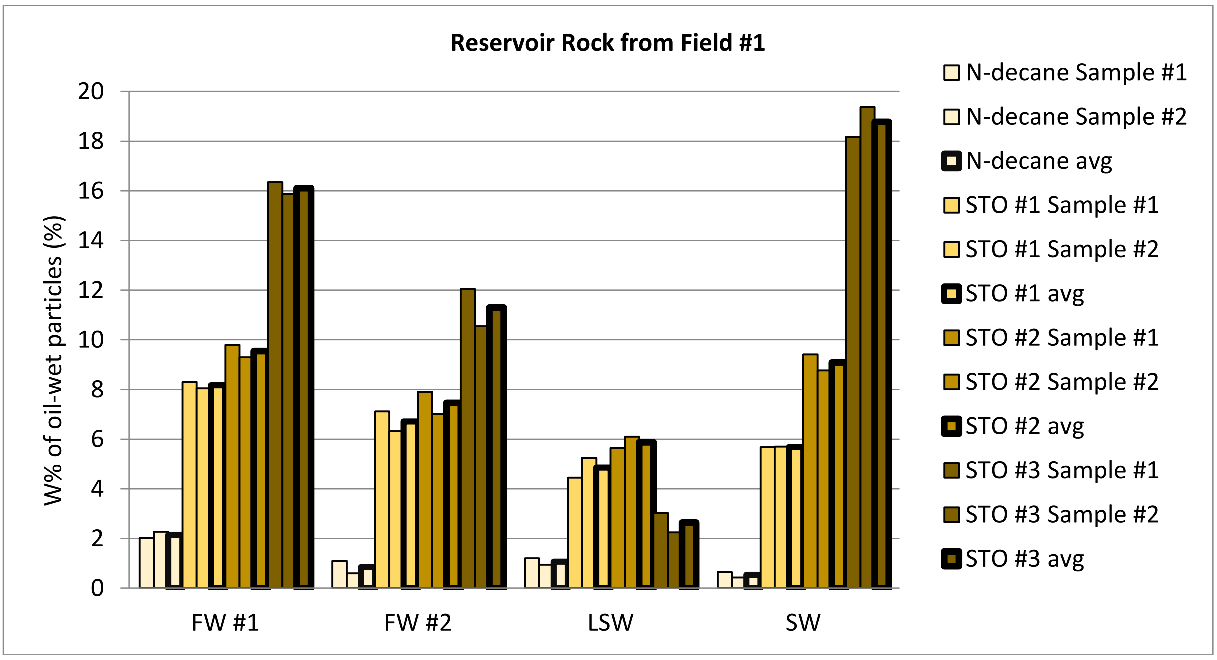


Figure 32: Wettability results of reservoir rock from field #1.

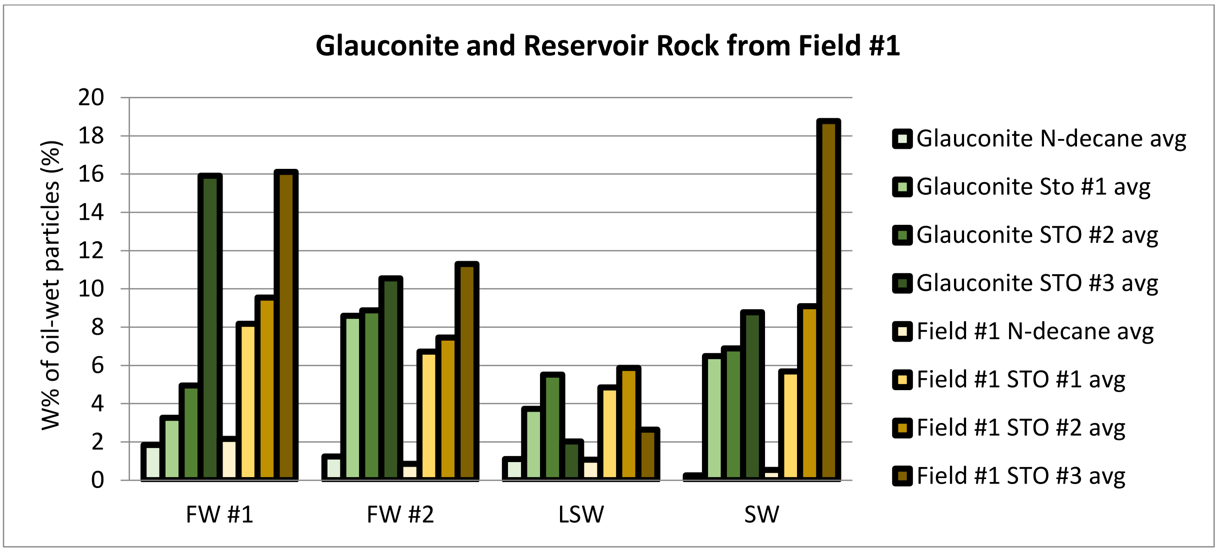


Figure 33: Wettability results of glauconite and rock from field #1 combined.

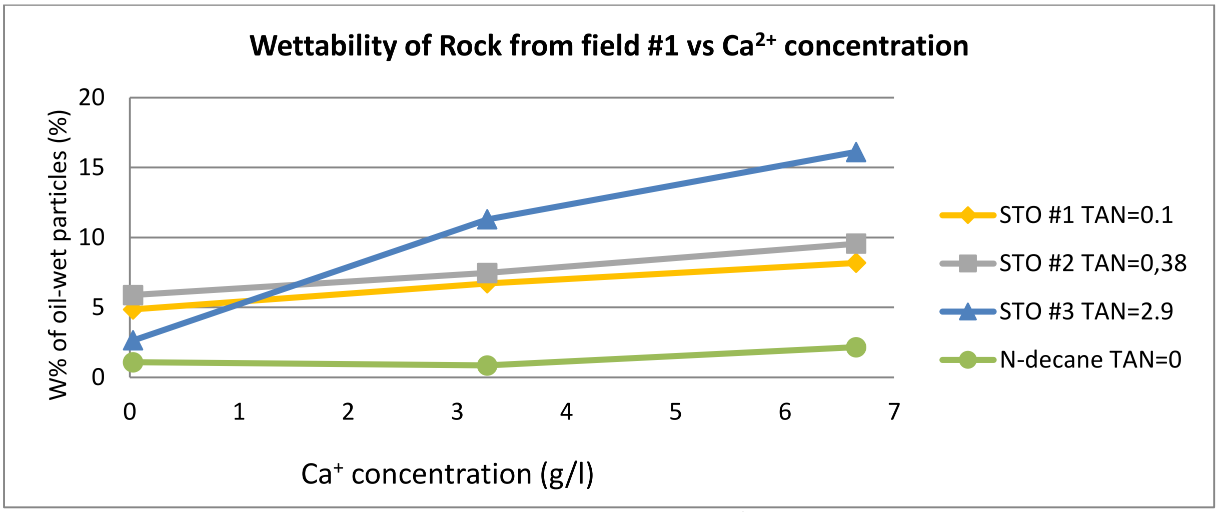


Figure 34: Wettability of rock from field #1 vs Ca^{2+} concentration in the brine.

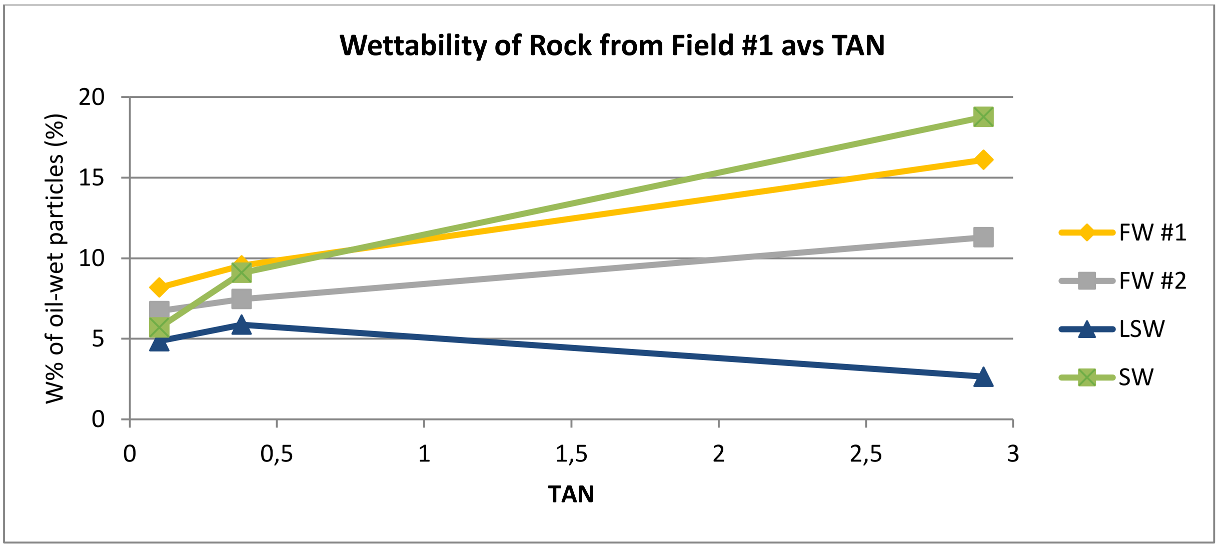


Figure 35: Wettability of rock from field #1 vs TAN of the oil.

4.1.8 Comparison of Wettability Results

Most of the minerals used in these experiments are primarily water-wet (see Figure 36), and the only exceptions are: A few brine/oil combinations turned muscovite oil-wet, while pyrite appears to be oil-wet for both the combinations that were created. Quartz is the most water-wet mineral used in these experiments, and came back highly water-wet for all oil/brine combinations. K-feldspar, glauconite and reservoir rock from field #1 have fairly similar wettability results, with only minor differences in wettability alteration. These are all primarily water-wet. Muscovite is the most oil-wet mineral that was tested for all oil/brine combinations. It is primarily water-wet for all oil/brine combinations except when aged with SW, and FW #1/STO #3. Only a few set of experiments were run on plagioclase (albite), and these result appears to suggest that plagioclase might have similar wettability properties as K-feldspar. Pyrite seems to be primarily oil-wet, but more research is needed to determine how brine and oil composition affect wettability alteration.

The wettability results of the minerals used in these experiments are clearly connected to the Ca^{2+} concentration of the brine. The higher the TAN of the oil is, the more the Ca^{2+} concentration of the brine appears to affect the wettability. Lower Ca^{2+} concentration results in more water-wet results. This is true for all samples where full series of experiments were run except for quartz. By examining the results plotted in Figure 37, it is clear that K-feldspar, glauconite, muscovite and rock from field #1 follow the same wettability alteration pattern when aged in STO #3. This figure shows that the wettability is clearly connected to the Ca^{2+} concentration in the brine when the TAN of the oil is high. For the samples aged in oils with a lower TAN a different pattern emerges. The wettability results of K-feldspar, glauconite and muscovite that are aged in oils with lower TAN is plotted against the Ca^{2+} concentration of the brine in Figure 38. From this figure it can be observed that going from a Ca^{2+} concentration of zero and up to 3.3g/l appears to alter the wettability towards more oil-wet, while a further increase in Ca^{2+} concentration actually appears to alter the wettability towards more oil-wet again. In both of these cases K-feldspar, glauconite and rock from field #1 have very similar wettability results. Muscovite appears to follow the same pattern, only it is much more oil-wet than the other samples.

The TAN number of the oil also appears to be connected to the wettability alteration of these minerals, especially if the Ca^{2+} concentration of the brine is high. The wettability results of K-feldspar, glauconite, muscovite and rock from field #1 aged in FW #1 (brine with high Ca^{2+} concentration) is plotted against TAN in Figure 39. By observing this figure it becomes clear that these minerals follow the same pattern: A reduction in TAN appears to alter the wettability of the samples towards more water-wet. Again we can see that K-feldspar, glauconite and rock from field #1 have very similar wettability results, while muscovite appears to follow the same pattern, only it is much more oil-wet than the other samples. For muscovite and rock from field #1 the same pattern also emerges if the Ca^{2+} concentration of the brine is lower, see Figure 40.

As expected, aging samples in LSW gives more or water-wet results if compared to samples aged in the other brines (31) (34) (35). Aging samples in N-decane also gives more water-wet results if compared to samples aged in other brines. In most cases the samples that are aged in N-decane are close to 100% water-wet. This is expected since N-decane does not have any SAC and the TAN/TBN=0.

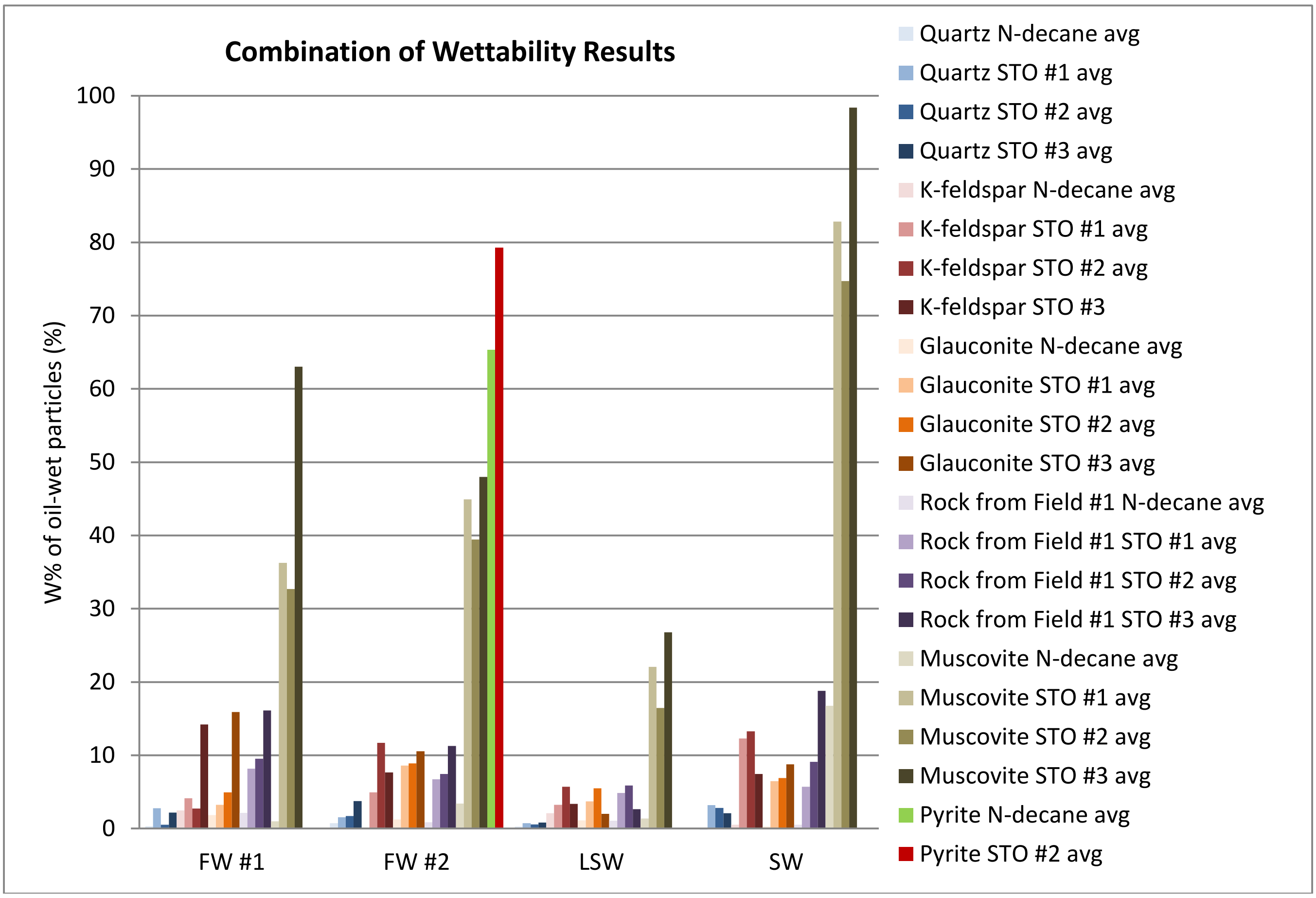


Figure 36: Combination of wettability results.

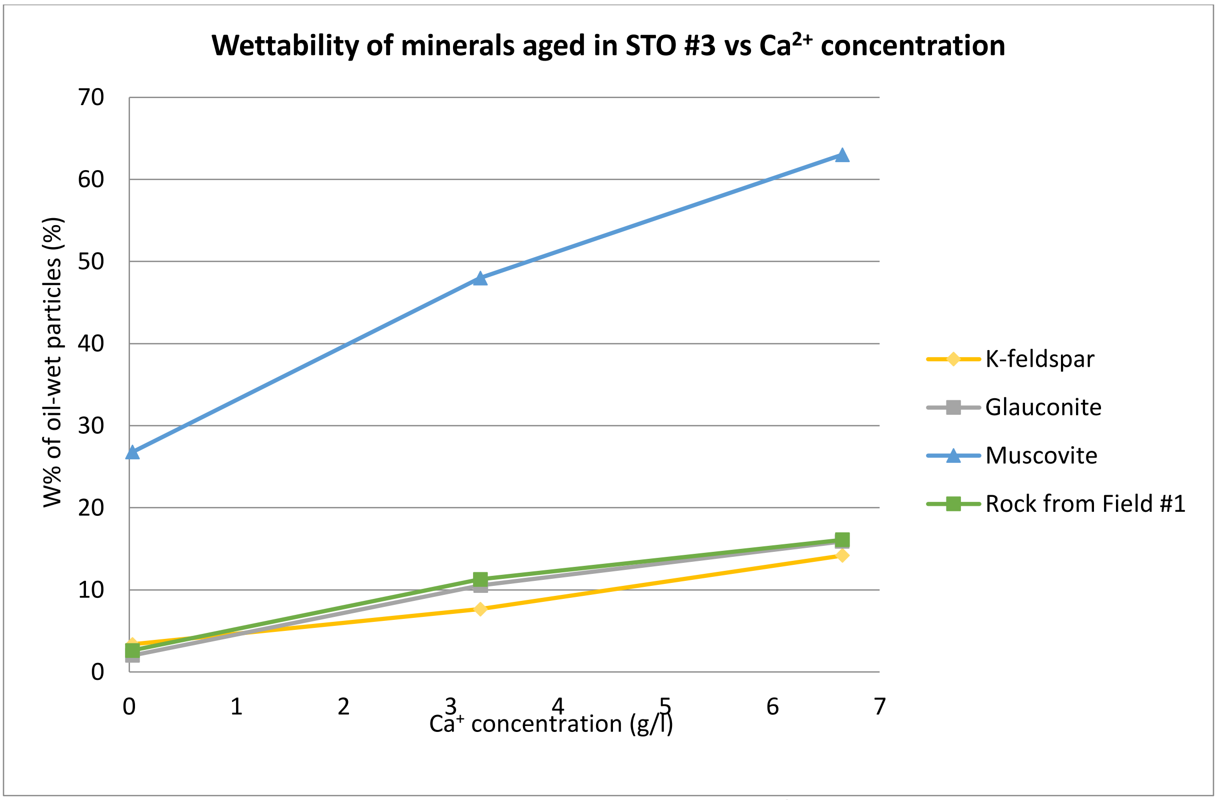


Figure 37: Wettability of minerals aged in STO #3 vs Ca^{2+} *concentration of the brine.*

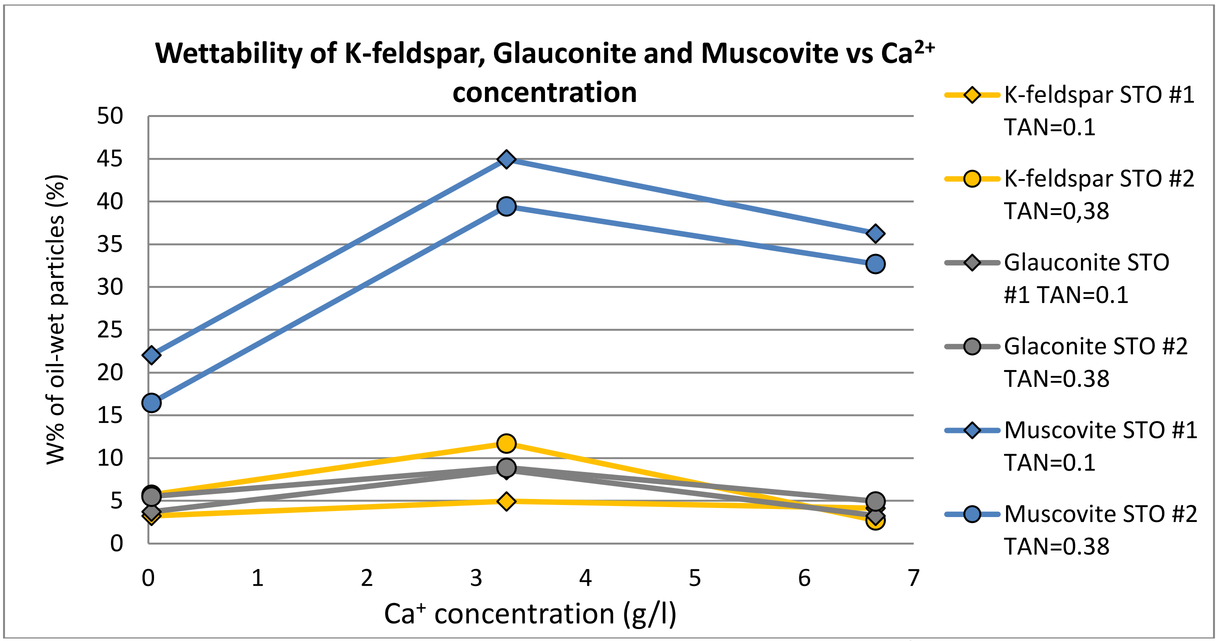


Figure 38: Wettability of K-feldspar, glauconite and muscovite vs Ca^{2+} concentration in the brine.

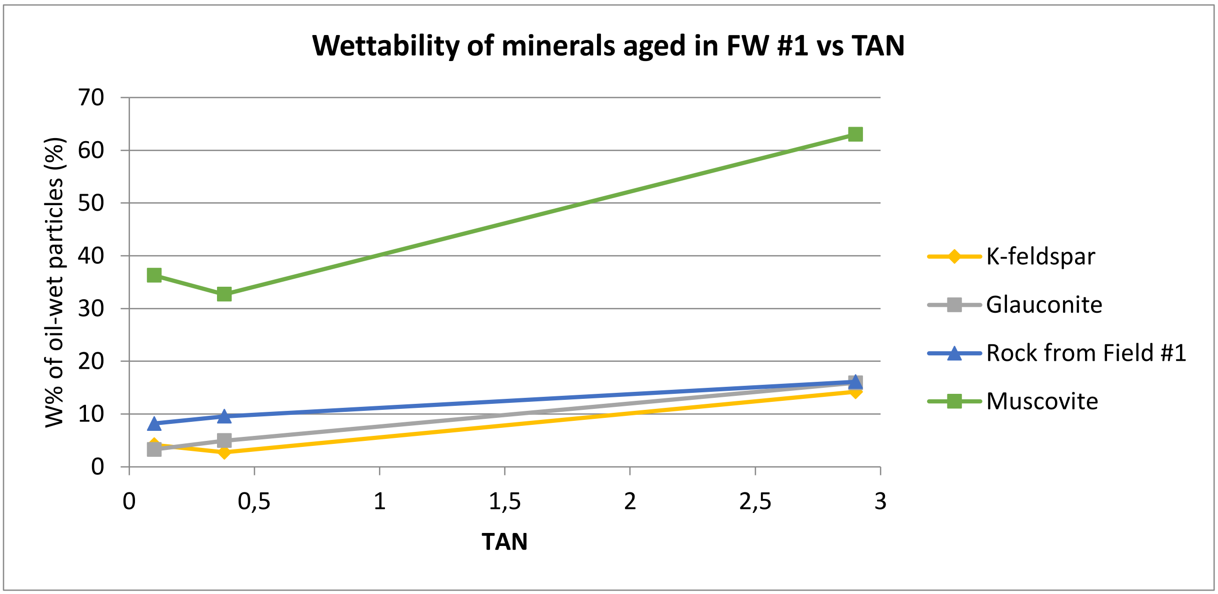


Figure 39: Wettability of minerals aged in FW #1 vs TAN.

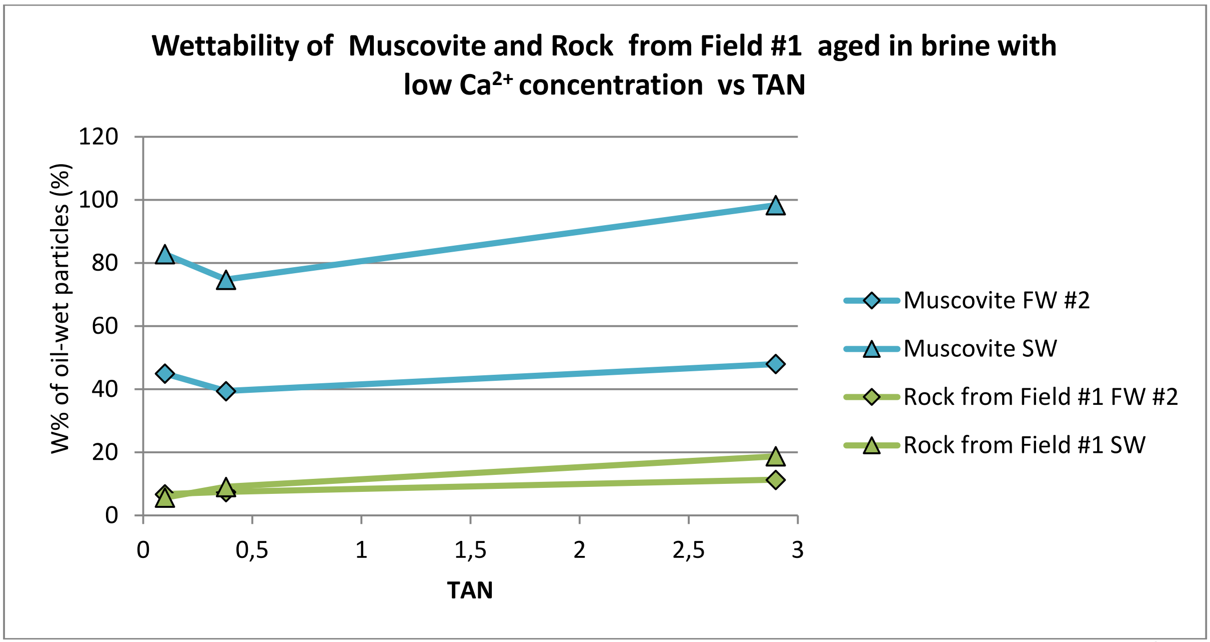


Figure 40: Wettability of muscovite and rock from field #1 aged in brine with a low Ca^{2+} *concentration vs TAN.*

4.2 pH-Experiment

From the first experiment two of the samples (#3 and #7) came back with results that were very different from the other 8 samples, see the blue columns lined with red inn Figure 41. These came back with a much lower pH (7 and 6), while the other 8 samples had a fairly consistent pH of 9,6-9,8. By examining the two samples that came back with a much lower pH further, it was discovered that the rubber insulation pads used in the corks was most likely contaminated. The insulation pads in the corks of sample #3 and #7 had turned black, while the other eight insulation pads had the original white color. It was decided to run a second experiment with brand new insulation pads that were lined with teflon. The second set of experiment confirmed that the large variation found in sample #3 and #7 were caused by contaminated insulation pads, because time all the samples came back with very similar results. Four samples were also aged at room temperature too see how the pH was affected. These four samples came back less basic than the ones aged in the oven at 80°C. After the second experiment was completed, it was decided to use brand new insulation pads in the corks to prevent the brine from being contaminated, and to keep the brine stored in the oven to prevent pH reduction.

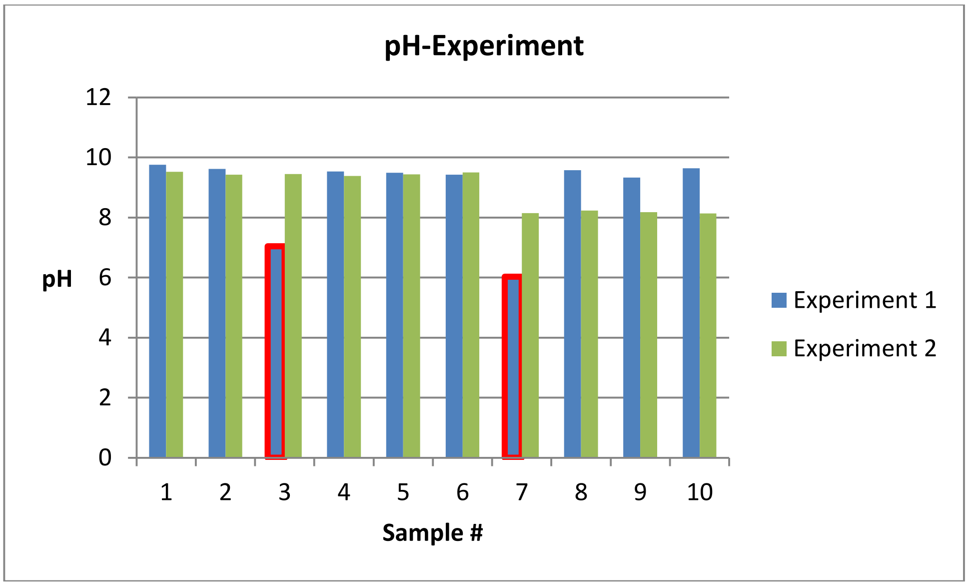


Figure 41: Results from pH measurements.

4.3 Oxidation Experiment

After two days of aging in the oven the both the sample with a 50ppm Fe^{2+} concentration and the sample with a 500ppm Fe^{2+} concentration showed that an oxidation had taken place. This can be seen by comparing the samples in Figure 42 to the ones in Figure 43. Low concentrations of Fe^{2+} turns the solution clear to light blue, while low concentrations of Fe^{3+} have a more orange/yellow color (55). Here it can clearly be seen that the color changes from clear to yellow and red. This means that Fe^{2+} has been oxidized to Fe^{3+}. Just to make sure the oxidation had taken place the spectrophotometer was used to find the exact Fe^{3+} concentration. It showed that the sample which originally contained a 50ppm Fe^{2+} solution now contained a 23ppm Fe^{3+} solution, and the sample that originally contained a 500ppm Fe^{2+} solution now contained a 241ppm Fe^{3+} solution. The samples that were aged at room temperature showed no change in color, so they were not measured for Fe^{3+} concentration by the spectrophotometer. The result from experiment suggest that the oxidation from Fe^{2+} to Fe^{3+} might occur at reservoir conditions. In a reservoir the pressure is much higher, and there is much less oxygen, which could affect the oxidation reaction seen in this experiment.

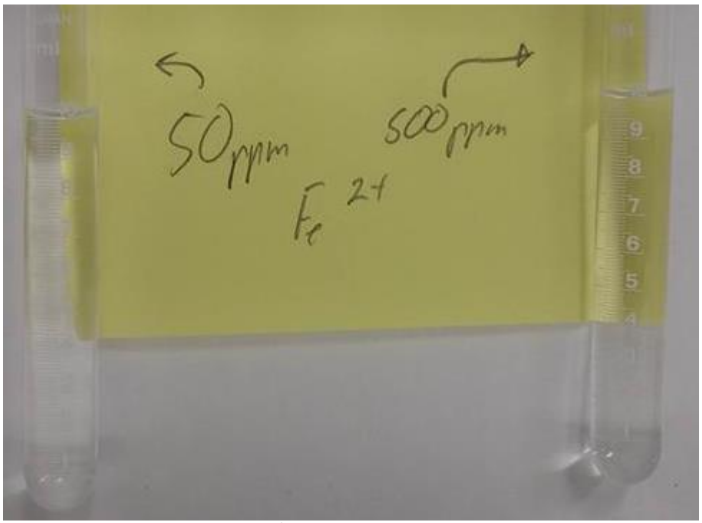


Figure 42: Fe^{2+} solutions before aging.

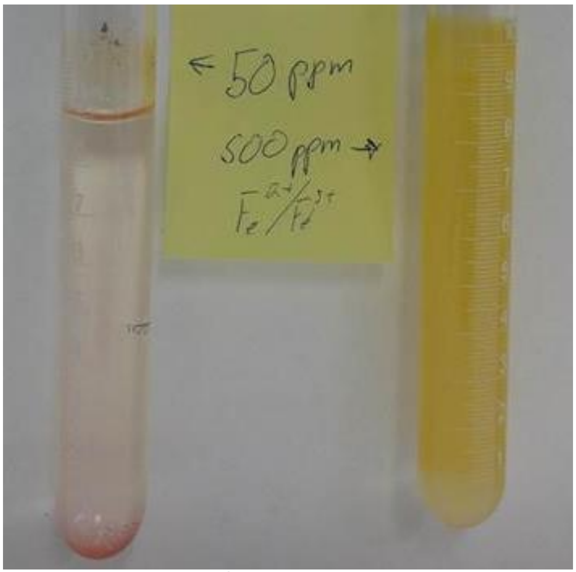


Figure 43: Fe^{2+} solutions after aging.

5 Discussion

5.1 Possible Causes of Error and How to Avoid them

Most of the duplicates made in these series of experiments came back with less than two percent variation in oil/water-wet particles, which is why the accuracy of the method is estimated to be ± 1%. A few duplicates came back with a larger variation than this, which was caused by either:

- *Contaminated equipment (test tube or cork).* Many of the test tubes in the lab have previously been used to perform experiments with polymers, and if some polymers are left in the test tube after they have been cleaned, it can affect the wettability results.
- *Spill or losses during filtration.* During filtration it is easy to lose some of the particles, either because they are stuck on the glass wall of the test tube or because they get stuck in or under the glass cup that contains the brine/mineral mixture during filtration.
- *Contamination during the drying process.* The samples can easily become contaminated during the drying process, because they are stored in an oven that is open and closed several times a day.
- *Mineral particles being removed during the brine removal phase*. After the samples have been aged in brine for three days, this brine is to removed and stored for later use. During this process the clay minerals are very easily agitated, and a small part of them could easily get removed with the brine. If this happens the particles that are removed are never aged with STO alone, which could affect the wetting preferences of these particles.
- *Incorrect weight of unused filter paper.* During this stage the unused filter papers are placed on a plastic weighing dishes. The filter papers are very static and are hard to place on the weighing dishes without the filter papers themselves flying off. The static charge on the surface of the filter papers make it hard to get an accurate reading of the weight of the filter paper. It takes a long time for the scale to stabilize while weighing them in.

If two duplicates came back with a variation in wettability that was larger than 2%, a new sample was made. The following measures are to be taken to reduce or eliminate the previous mentioned causes of variation:

- *Contaminated equipment (test tube or cork).* Make sure that there are no debris left on the inside of the test tube from previous use before using it. Inspect the cork to see if it has been thoroughly cleaned, so that it cannot contaminate the sample.
- *Spill or Losses during filtration*. Make sure to shake the brine/mineral mixture in the test tube well before pouring it into glass cup of the filtration device. This will cause mineral particles that are stuck on the wall to dislodge from the glass wall. If some particles are still observed on the wall of the test tube, pour in some distilled water and shake until all the particles are loose. To prevent particles from getting stuck on the glass cup of the filtration device, rinse the cup with distilled water during filtration.
- *Contamination during the drying process.* Cover up the samples while they are being dried in the oven, and use an oven that is not used for anything else than drying mineral samples to prevent it from being opened frequently.
- *Mineral particles being removed during the brine removal phase.* Be very careful not to agitate the mineral particles at the bottom of the test tube. If they

are agitated, put down the test tube and leave it until the particles have settled on the bottom before removing the rest of the brine.

- *Incorrect weight of unused filter paper.* Use a filter paper made of a non-static material if possible. If not, leave the filter paper and the weighing dish on the scale until it stabilizes. Note down the weight and take the weighing dish and filter paper off the scale. Put it back on the scale and wait until it stabilizes. If the value is the same as the one noted down earlier the weight is okay, if not repeat until you get the same results.

5.2 Discussion of Results

Most of the duplicates came back with similar wettability results and were not affected by any of the factors mentioned above. The wettability results appears to agree with what has been found in previous studies. Quartz was found to be near 100% oil-wet for all brine/oil combinations, which is in accordance with previous studies (32). K-feldspar, plagioclase, glauconite and rock from field #1 is found to be primarily water-wet, which is in accordance with previous studies (38, 47). Muscovite is found to be ranging from water-wet to intermediate-wet and to oil-wet, depending on the brine/oil combination. Previous studies have found this mineral to be ranging from water-wet to intermediate-wet (43, 50), but a different method were used to determine wettability which could explain the variation in results. Pyrite was found to be primarily oil-wet, and this is not in accordance with previous studies (53), different methods were used to determine wettability which could explain the variation in results.

If compared to samples aged in other brines, LSW will either alter the wettability towards more water-wet, or in cases where the wettability is close to 100% water-wet no significant change is observed. This is true for all samples aged in STO. This is also in accordance with previous studies on how LSW affect wettability (31, 34, 35). Fjelde et al. found LSW to alter the wettability of rock from field #1 towards more oil-wet (33). This is not in accordance with what has been found here. Different methods were used to determine wettability which could explain the variation in results.

SW appears to alter wettability towards more oil wet if compared to LSW, and slightly towards oil-wet if compared to FW #1 FW #1 for most combinations.

Low Ca^{2+} concentration in the brine appears to alter the wettability towards more water-wet if the oil has a high TAN number. Higher Ca^{2+} concentration in the brine appears to alter the wettability towards more oil-wet if the sample is aged in an oil with high TAN. This is in accordance with previous studies (33). These results are found to be true for K-feldspar samples, as well as the clay minerals and the reservoir rock. The effect could be caused by the Ca^{2+} ion acting as a cation bridge between the negatively charged mineral particles and the negatively charged head of the carboxylic acids in the oil. That would explain why the clay minerals, which have a larger surface area per gram than the other minerals are more affected by this than quartz and K-feldspar see Figure 37. It also explains the wettability correlation between a high concentration of Ca^{2+} ions and a high TAN, and a low concentration of Ca^{2+} ions and a low TAN.

If the negatively charged mineral is aged in a brine with a high Ca^{2+} concentration and an oil with high TAN there are a lot of Ca^{2+} ions which can act as cation bridges between the many charged carboxylic acids found in the oil and the negatively charged minerals. This causes more mineral particles to become oil-wet. If the negatively charged mineral is aged in a brine with a low Ca^{2+} concentration and an oil with low TAN there are much less Ca^{2+} ions and carboxylic acids present in the mixture. This means that there are less Ca^{2+} ions to act as cation bridges, and less carboxylic acids which can hold on to the Ca^{2+} ions and the negatively charged mineral particles, thus rendering the sample more water-wet. Figure 38 shows that samples aged in oils with low TAN are not affected by Ca^{2+} concentration as much as samples aged in oil with high TAN. The fact that some mineral samples aged in brine with a low Ca^{2+} concentration are also dependent on TAN (see Figure 40) is not in accordance with results found in previous studies (33). A possible cause for these differences in wettability results could be that two different methods were used to determine wettability.

From the glauconite samples aged in brine containing three-valent aluminum and iron it appears that both the Fe^{3+} and the Al^{3+} cation has a greater influence on wettability than the Ca^{2+} cations. A potential cause for this could be that the higher charge of the three-valent ions cause them to be more reactive than the divalent Ca^{2+} ion. Because of this, Al^{3+} and Fe^{3+} might be more effective as cation bridges than Ca^{2+}. This could explain why brines with low concentrations of AL^{3+} and Fe^{3+}, have a higher impact on wettability than brines with high concentrations of Ca^{2+}. A brine with a low concentration of Fe^{3+} greatly altered the wettability of glauconite towards more oil-wet even when aged in oils with low TAN (<0.1 and 0.38). For a sample aged in oil with a high TAN this effect could be even larger, and a brine with a low concentration of Al^{3+} might also alter the wettability towards more oil-wet, but more research is needed to confirm.

5.3 Application of this Method in the Oil Industry

This method might not be suitable to determine the exact wettability of an entire oil field because the wettability in different regions of the oil field may vary, and reservoir conditions like high pressure are not taken into account in this method. It may however be used as a quick screening method to help determine the chemical composition of the injection water. This method may also be used as a quick way to determine the wetting preferences in different layers of the reservoir, and to see if there are some major differences in wettability.

5.4 Proposal for Further Work

During this study a few areas where found to need some more research, and among them were:

- How low concentrations of Fe^{3+} and Al^{3+} in the brine affect wettability of a clay mineral if aged in an oil with high TAN vs low TAN.
- How Fe^{3+} and Al^{3+} affect the wettability of other minerals.
- How oil-wet clay minerals affect the wettability of a water-wet minerals like K-feldspar or quartz by mixing them together before aging.
- How different brine and oil composition affect wettability alteration of plagioclase.
- How different brine and oil composition affect wettability alteration of pyrite.

6 Conclusion

The wettability of the different minerals is not equally affected by changes in brine or oil composition. The wettability of quartz is nearly unaffected by changes in both oil and brine composition, and is rendered nearly 100% water-wet for all brine/oil combinations. K-feldspar, glauconite and rock from field #1 experience a greater variation in wettability than quartz when brine or oil composition is changed, but they are still primarily water-wet (>80% water-wet) for all brine/oil combinations. Of the minerals studied here, muscovite is the mineral whose wettability is most affected by changes in brine or oil composition. Changes in brine/STO composition can alter the wettability of muscovite from only 16% oil-wet and up to 98% oil-wet.

The wettability of the reservoir rock from field #1 is clearly more dominated by the low clay content (13%) than by the high quartz content (>70%). The pattern in wettability alteration caused by changes in brine/oil composition is very similar to the alteration pattern observed for glauconite, not for quartz. A possible cause for this could be that glauconite has a much higher area/gram than quartz, thus leaving glauconite more available to adhere to SAC in the oil.

LSW appears to alter the wettability towards more water-wet when compared the other brines for all but a few samples. There are a few samples where FW #1 gives >95% water-wet results and there is no observable change in wettability if the same samples are compared to samples aged in LSW. LSW always gives a more water-wet results than SW.

The chemical composition of the brine together with the TAN of the oil also appears to have an effect on the wettability. A variation in the concentration of Ca^{2+}, Fe^{3+} and Al^{3+} cations in the brine, along with varying TAN follows a clear trend in wettability alteration.

The wettability of samples aged in brine with a high Ca^{2+} concentration are clearly affected by changes in the TAN of the oil. As TAN increases the wettability is altered towards more oil-wet. The wettability of the samples aged in brine with a low Ca^{2+} concentration does not seem to be as sensitive to changes in TAN as the samples aged in brine with a high Ca^{2+} concentration. An increase in TAN when the Ca^{2+} of the brine is low only appears to alter the wettability of muscovite and rock from filed #1 towards more oil-wet, not the other minerals. TBN does not appear to have an impact on the wettability of samples used in this study.

The wettability of samples that are aged in an oil with high TAN are clearly affected by changes in the Ca^{2+} concentration of the brine. As the Ca^{2+} concentration increases the wettability is altered towards more oil-wet. The wettability of the samples that are aged in oil with low TAN does not seem to be as sensitive to changes in the Ca^{2+} concentration as the samples aged in oil with high TAN. An increase in Ca^{2+} concentration when TAN is low only appears to alter the wettability of rock from field #1 towards more oil-wet. The other minerals experience an alteration towards more oil-wet when the Ca^{2+} concentration is increased from 0g/l to 3.3g/l, and then the wettability is altered towards more water-wet as the Ca^{2+} concentration is further increased.

The presence of three-valent iron and aluminum cations in the brine has a similar effect on the wettability of glauconite as Ca^{2+}, only much lower concentrations are needed for the wettability alteration to take place. Fe^{3+} concentrations as low as 50ppm altered the wettability noticeably towards more oil-wet even when the sample was aged in an oil with TAN <0.1. Higher concentrations altered the wettability even more. At 50ppm Al^{3+} does not appear to have any effect on the wettability if the sample is aged in an oil with than <0.38, but at 500ppm the wettability alteration is substantial.

The flotation method is not suitable to precisely determine the wettability of a reservoir, but it can be used as a quick and easy way to indicate the wetting preferences in different areas of the reservoir. It can also be used as a screening tool to quickly indicate a suitable chemical composition of for injection water.

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Appendix A

In this appendix results from every experiment is shown. They are in chronological order. The samples marked in green are plotted as columns in chapter 4.

Abbreviations used in the Raw Data Tables

W_{m}	Weight of added mineral (g)
W_{Nfp}	Weight of new and unused filter paper (g)
$W_{\text{Dfp (1)}}$	Weight of the filter paper the first time it is weighed in (g)
$W_{\text{Dfp (2)}}$	Weight of the filter paper the second time it is weighed in (g)
$W_{\text{Dfp avg}}$	Average weight of dried filter paper (g)
W_{Cor}	Average weight of dried filter paper corrected for filtration debris (g)
$W_{\text{mineral w.p.}}$	Mineral weight in the water phase (g)
$W_{\text{mineral o.p.}}$	Mineral weight in the oil phase(g)
$\%W_{\text{mineral o.p.}}$	W% of oil-wet particles (%)

Experiment #1

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Quartz	FW #1	STO #1	0,2000	5,57	2,1628	2,3601	2,3600	2,3601	2,3595	0,1973	0,0027	1,37
2	Quartz	FW #1	STO #1	0,2000	6,33	2,1243	2,2990	2,2980	2,2985	2,2980	0,1742	0,0258	12,90
3	Quartz	FW #1	STO #1	0,1990	5,90	2,1442	2,3328	2,3322	2,3325	2,3320	0,1883	0,0107	5,38
4	Quartz	FW #1	N-decane	0,1990	6,36	2,1941	2,3778	2,3775	2,3777	2,3771	0,1836	0,0155	7,76
5	Quartz	FW #1	N-decane	0,1990	6,16	2,1612	2,3487	2,3488	2,3488	2,3482	0,1876	0,0115	5,75
6	Quartz	FW #1	N-decane	0,2020	6,82	2,2228	2,4062	2,4060	2,4061	2,4056	0,1833	0,0187	9,26
7	Glauconite	FW #1	STO #1	0,2000	7,00	2,1558	2,3486	2,3482	2,3484	2,3479	0,1926	0,0074	3,70
8	Glauconite	FW #1	STO #1	0,2000	7,00	2,1406	2,3342	2,3342	2,3342	2,3337	0,1936	0,0064	3,20
9	Glauconite	FW #1	STO #1	0,2020	7,05	2,1237	2,3190	2,3190	2,3190	2,3185	0,1953	0,0067	3,32
10	Glauconite	FW #1	N-decane	0,2000	7,05	2,0694	2,2636	2,2630	2,2633	2,2628	0,1939	0,0061	3,05
11	Glauconite	FW #1	N-decane	0,2000	7,06	2,1248	2,3135	2,3130	2,3133	2,3127	0,1885	0,0116	5,78
12	Glauconite	FW #1	N-decane	0,1990	7,06	2,1071	2,3004	2,3001	2,3003	2,2997	0,1932	0,0058	2,94
13	K-feldspar	FW #1	STO #1	0,2000	6,51	2,1110	2,3014	2,3012	2,3013	2,3008	0,1903	0,0097	4,85
14	K-feldspar	FW #1	STO #1	0,2010	6,52	2,2415	2,4333	2,4332	2,4333	2,4327	0,1918	0,0092	4,60
15	K-feldspar	FW #1	STO #1	0,1980	6,55	2,1850	2,3758	2,3756	2,3757	2,3752	0,1907	0,0073	3,69
16	K-feldspar	FW #1	N-decane	0,1990	6,66	2,1739	2,3636	2,3631	2,3634	2,3628	0,1895	0,0096	4,80
17	K-feldspar	FW #1	N-decane	0,2010	6,60	2,1998	2,3964	2,3958	2,3961	2,3956	0,1963	0,0047	2,34
18	K-feldspar	FW #1	N-decane	0,2000	6,48	2,0570	2,2510	2,2506	2,2508	2,2503	0,1938	0,0062	3,10

Experiment #2

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Quartz	SW	STO #2	0,2001	8,27	2,0527	2,2478	2,2486	2,2482	2,2477	0,1955	0,0046	2,30
2	Quartz	SW	STO #2	0,2000	8,24	2,1815	2,3745	2,3751	2,3748	2,3743	0,1933	0,0067	3,35
3	Quartz	SW	N-decane	0,2002	8,32	2,0576	2,2580	2,2583	2,2582	2,2576	0,2006	-0,0004	-0,17
4	Quartz	SW	N-decane	0,2001	8,22	2,1250	2,3247	2,3259	2,3253	2,3248	0,2003	-0,0002	-0,10
5	Quartz	LSW	STO #2	0,2001	4,24	1,9927	2,1922	2,1923	2,1923	2,1917	0,1996	0,0005	0,27
6	Quartz	LSW	STO #2	0,2003	4,90	2,2168	2,4059	2,4058	2,4059	2,4053	0,1891	0,0113	5,62
7	Quartz	LSW	N-decane	0,2001	4,92	2,1699	2,3685	2,3692	2,3689	2,3683	0,1990	0,0012	0,40
8	Quartz	LSW	N-decane	0,2000	8,98	2,0418	2,2414	2,2416	2,2415	2,2410	0,1997	0,0003	0,15
9	Glauconite	SW	STO #2	0,2000	7,71	2,0236	2,2128	2,2123	2,2126	2,2120	0,1890	0,0110	6,52
10	Glauconite	SW	STO #2	0,2001	7,70	2,1066	2,2924	2,2920	2,2922	2,2917	0,1856	0,0145	7,25
11	Glauconite	SW	N-decane	0,2001	7,76	2,0636	2,2638	2,2628	2,2633	2,2628	0,1997	0,0004	0,20
12	Glauconite	SW	N-decane	0,1999	8,05	2,0718	2,2677	2,2689	2,2683	2,2678	0,1965	0,0034	1,70
13	Glauconite	LSW	STO #2	0,2001	8,47	2,1108	2,2999	2,2988	2,2994	2,2988	0,1886	0,0115	5,77
14	Glauconite	LSW	STO #2	0,2000	8,33	2,0719	2,2645	2,2655	2,2650	2,2645	0,1931	0,0069	3,45
15	Glauconite	LSW	N-decane	0,2002	8,54	2,1605	2,3593	2,3584	2,3589	2,3583	0,1984	0,0018	0,92
16	Glauconite	LSW	N-decane	0,2001	8,91	2,1427	2,3404	2,3401	2,3403	2,3397	0,1976	0,0025	1,27
17	K-feldspar	SW	STO #2	0,2000	8,12	2,1429	2,3232	2,3270	2,3251	2,3246	0,1822	0,0178	8,90
18	K-feldspar	SW	STO #2	0,2002	8,12	2,0721	2,2421	2,2461	2,2441	2,2436	0,1720	0,0282	14,09
19	K-feldspar	SW	N-decane	0,2000	8,65	2,1602	2,3544	2,3554	2,3549	2,3544	0,1947	0,0053	2,65
20	K-feldspar	SW	N-decane	0,1999	8,09	2,1954	2,3839	2,3849	2,3844	2,3839	0,1890	0,0109	5,45
21	K-feldspar	LSW	STO #2	0,2003	9,08	2,1779	2,3632	2,3646	2,3639	2,3634	0,1860	0,0143	7,14
22	K-feldspar	LSW	STO #2	0,2002	8,46	2,1876	2,3794	2,3806	2,3800	2,3795	0,1924	0,0078	3,90
23	K-feldspar	LSW	N-decane	0,2000	9,09	2,1819	2,3769	2,3775	2,3772	2,3767	0,1953	0,0047	2,35
24	K-feldspar	LSW	N-decane	0,2001	8,61	2,2410	2,4369	2,4379	2,4374	2,4369	0,1964	0,0037	1,85

Experiment #3

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Quartz	LSW	STO #1	0,1999	8,86	2,2554	2,4542	2,4549	2,4546	2,4540	0,1992	0,0007	0,38
2	Quartz	LSW	STO #1	0,1999	9,59	2,2130	2,4106	2,4108	2,4107	2,4102	0,1977	0,0022	1,10
5	Glauconite	LSW	STO #1	0,2001	8,55	2,3653	2,5585	2,5575	2,5580	2,5575	0,1927	0,0074	3,70
6	Glauconite	LSW	STO #1	0,2002	8,51	2,3628	2,5556	2,5554	2,5555	2,5550	0,1927	0,0075	3,75
9	K-feldspar	LSW	STO #1	0,2002	8,96	2,3493	2,5379	2,538	2,5379	2,5374	0,18865	0,0116	5,77
13	Quartz	SW	STO #1	0,1999	8,34	2,3770	2,5663	2,5662	2,5662	2,5657	0,18925	0,0107	5,33
14	Quartz	SW	STO #1	0,2002	8,36	2,3713	2,5660	2,5658	2,5659	2,5653	0,1946	0,0056	2,80
17	Glauconite	SW	STO #1	0,2001	7,35	2,3406	2,5304	2,5293	2,5299	2,5293	0,1893	0,0108	6,33
18	Glauconite	SW	STO #1	0,2002	7,34	2,3300	2,5164	2,5148	2,5156	2,5151	0,1856	0,0146	6,65
21	K-feldspar	SW	STO #1	0,2002	8,11	2,3513	2,5284	2,5281	2,5283	2,5277	0,1770	0,0233	11,61
22	K-feldspar	SW	STO #1	0,1999	8,11	2,3847	2,5435	2,5440	2,5438	2,5432	0,1591	0,0408	13,00

Experiment #4

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Glauconite	FW #1	STO #2	0,2003	8,05	2,2698	2,4605	2,4620	2,4613	2,4607	0,1915	0,0088	4,42
2	Glauconite	FW #1	STO #2	0,2002	7,96	2,2553	2,4443	2,4448	2,4446	2,4440	0,1893	0,0110	5,47
3	Quartz	FW #1	STO #2	0,2000	7,90	2,2586	2,4573	2,4567	2,4570	2,4565	0,1984	0,0016	0,80
4	Quartz	FW #1	STO #2	0,2000	8,06	2,3161	2,5154	2,5159	2,5157	2,5151	0,1996	0,0005	0,23
5	K-feldspar	FW #1	STO #2	0,2002	8,03	2,2943	2,4882	2,4881	2,4882	2,4876	0,1939	0,0063	3,17
6	K-feldspar	FW #1	STO #2	0,2001	8,00	2,2531	2,4481	2,4492	2,4487	2,4481	0,1956	0,0046	2,27
8	K-feldspar	LSW	STO #1	0,2000	9,32	2,1441	2,3373	2,3380	2,3377	2,3371	0,1936	0,0064	3,22

Experiment #5

#	Mineral	Brine	Oil	W_{m}	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Field #1	FW #1	STO #1	0,2004	7,69	2,1955	2,3792	2,3793	2,3793	2,3787	0,1838	0,0167	8,31
2	Field #1	FW #1	STO #1	0,2002	7,85	2,1774	2,3613	2,3617	2,3615	2,3610	0,1841	0,0161	8,04
3	Field #1	FW #1	N-decane	0,2000	7,95	2,1854	2,3796	2,3782	2,3789	2,3784	0,1935	0,0065	2,03
4	Field #1	FW #1	N-decane	0,2002	7,89	2,1441	2,3397	2,3398	2,3398	2,3392	0,1957	0,0045	2,27
5	Field #1	SW	STO #1	0,2001	7,67	2,1832	2,3694	2,3701	2,3698	2,3692	0,1866	0,0136	6,77
6	Field #1	SW	STO #1	0,1999	7,73	2,1469	2,3351	2,3358	2,3355	2,3349	0,1886	0,0114	5,68
7	Field #1	SW	N-decane	0,1998	7,83	2,1015	2,2969	2,2968	2,2969	2,2963	0,1954	0,0045	2,23
8	Field #1	SW	N-decane	0,2003	7,71	2,0701	2,2688	2,2694	2,2691	2,2686	0,1990	0,0013	0,65
9	Field #1	LSW	STO #1	0,2000	9,05	2,0982	2,2891	2,2895	2,2893	2,2888	0,1911	0,0089	4,45
10	Field #1	LSW	STO #1	0,1999	8,92	2,0736	2,2625	2,2635	2,2630	2,2625	0,1894	0,0105	5,25
11	Field #1	LSW	N-decane	0,2003	8,93	2,0795	2,2740	2,2752	2,2746	2,2741	0,1951	0,0052	2,60
12	Field #1	LSW	N-decane	0,2004	8,80	2,0614	2,2589	2,2599	2,2594	2,2589	0,1980	0,0024	1,20
13	Pyrite	FW #2	STO #2	0,2004	2,54	2,1082	2,1788	2,1795	2,1792	2,1786	0,0709	0,1295	64,60
14	Pyrite	FW #2	STO #2	0,2004	2,57	2,1423	2,2533	2,2537	2,2535	2,2530	0,1112	0,0892	44,51
15	Pyrite	FW #2	N-decane	0,2001	2,54	2,1142	2,1833	2,1841	2,1837	2,1832	0,0695	0,1306	65,27
16	Pyrite	FW #2	N-decane	0,1999	2,58	2,1062	2,1799	2,1808	2,1804	2,1798	0,0741	0,1258	62,91
17	Plagioclase	FW #1	STO #1	0,1998	8,40	2,1164	2,2849	2,2859	2,2854	2,2849	0,1690	0,0308	15,42
18	Plagioclase	FW #1	STO #1	0,2001	8,13	2,0985	2,2775	2,2786	2,2781	2,2775	0,1796	0,0206	10,27
19	Plagioclase	FW #1	N-decane	0,2000	8,14	2,0567	2,2495	2,2499	2,2497	2,2492	0,1930	0,0070	3,50
20	Plagioclase	FW #1	N-decane	0,1998	8,14	2,0327	2,2243	2,2252	2,2248	2,2242	0,1921	0,0077	3,88
21	Plagioclase	FW #2	STO #2	0,1997	7,95	2,0712	2,2506	2,2515	2,2511	2,2505	0,1799	0,0198	9,94
22	Plagioclase	FW #2	STO #2	0,1998	8,03	2,1361	2,3143	2,3150	2,3147	2,3141	0,1786	0,0213	10,64
23	Plagioclase	FW #2	N-decane	0,1998	8,30	2,1611	2,3527	2,3538	2,3533	2,3527	0,1922	0,0076	3,83
24	Plagioclase	FW #2	N-decane	0,2000	7,95	2,1355	2,3296	2,3304	2,3300	2,3295	0,1945	0,0055	2,75

Experiment #6

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Glauconite	FW #1 (Fe)	STO #1	0,2003	1,36	2,4600	2,5719	2,5723	2,5721	2,5714	0,1119	0,0884	44,13
2	Glauconite	FW #1 (Fe)	STO #1	0,1997	1,37	2,3733	2,4780	2,4784	2,4782	2,4775	0,1047	0,0950	47,57
3	Glauconite	FW #1 (Al)	STO #1	0,2000	3,12	2,1393	2,2988	2,2992	2,2990	2,2983	0,1595	0,0405	20,25
4	Glauconite	FW #1 (Al)	STO #1	0,2002	3,16	2,0933	2,2585	2,2589	2,2587	2,2580	0,1652	0,0350	17,48
5	Glauconite	FW #2 (Fe)	STO #2	0,1998	1,48	2,0621	2,1614	2,1618	2,1616	2,1609	0,0993	0,1005	50,30
6	Glauconite	FW #2 (Fe)	STO #2	0,2002	1,48	2,2247	2,3294	2,3298	2,3296	2,3289	0,1047	0,0955	47,70
7	Glauconite	FW #2 (Al)	STO #2	0,2003	2,96	2,2786	2,4283	2,4287	2,4285	2,4278	0,1497	0,0506	25,26
8	Glauconite	FW #2 (Al)	STO #2	0,2001	3,01	2,2797	2,4357	2,4361	2,4359	2,4352	0,1560	0,0441	22,04

Experiment #7

#	Mineral	Brine	Oil	W_{m}	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	%$W_{mineral}$ o.p.
1	Quartz	FW #1	STO #1	0,1996	7,60	2,3310	2,5262	2,5266	2,5264	2,5257	0,1952	0,0044	2,20
2	Quartz	FW #1	STO #1	0,1997	8,10	2,2265	2,4175	2,4179	2,4177	2,4170	0,1910	0,0087	3,36
3	Quartz	FW #1	N-decane	0,1999	7,57	2,3553	2,5566	2,5570	2,5568	2,5561	0,2013	-0,0014	0,15
4	Quartz	FW #1	N-decane	0,2003	8,00	2,3750	2,5666	2,5670	2,5668	2,5661	0,1916	0,0087	0,45
5	Quartz	SW	STO #1	0,1998	7,70	2,1426	2,2263	2,2267	2,2265	2,2258	0,0837	0,1161	58,11
6	Quartz	SW	STO #1	0,2000	7,55	2,1895	2,2898	2,2902	2,2900	2,2893	0,1003	0,0997	49,85
7	Quartz	SW	STO #2	0,2006	8,10	2,0481	2,2481	2,2485	2,2483	2,2476	0,2000	0,0006	0,30
8	Quartz	LSW	STO #2	0,1995	8,75	2,1207	2,3171	2,3175	2,3173	2,3166	0,1964	0,0031	1,55
9	Glauconite	FW #1	N-decane	0,2003	7,92	2,1895	2,3883	2,3887	2,3885	2,3878	0,1988	0,0015	0,75
10	Glauconite	SW	STO #1	0,2003	7,52	2,1442	2,3119	2,3123	2,3121	2,3114	0,1677	0,0326	16,28
11	Glauconite	SW	STO #1	0,2001	7,28	2,0802	2,2500	2,2504	2,2502	2,2495	0,1698	0,0303	15,14
12	Glauconite	SW	N-decane	0,2004	7,39	2,1681	2,3704	2,3708	2,3706	2,3699	0,2023	-0,0019	0,32
13	Glauconite	LSW	STO #2	0,1997	8,62	2,1131	2,3007	2,3011	2,3009	2,3002	0,1876	0,0121	6,06
14	K-feldspar	FW #1	STO #1	0,2004	7,81	2,1458	2,3333	2,3337	2,3335	2,3328	0,1875	0,0129	6,44
15	K-feldspar	FW #1	N-decane	0,1995	8,18	2,1402	2,3345	2,3349	2,3347	2,3340	0,1943	0,0052	2,61
16	K-feldspar	SW	STO #1	0,2002	7,67	2,1691	2,2677	2,2681	2,2679	2,2672	0,0986	0,1016	50,75
17	K-feldspar	SW	STO #1	0,2000	7,74	2,4092	2,4598	2,4602	2,4600	2,4593	0,0506	0,1494	74,70
18	K-feldspar	SW	STO #2	0,1994	7,80	2,3928	2,5674	2,5678	2,5676	2,5669	0,1746	0,0248	12,44
19	K-feldspar	SW	N-decane	0,1996	7,99	2,4506	2,6485	2,6489	2,6487	2,6480	0,1979	0,0017	0,85
20	K-feldspar	LSW	STO #1	0,2001	8,51	2,0642	2,0760	2,0764	2,0762	2,0755	0,0118	0,1883	94,10
21	K-feldspar	LSW	STO #1	0,2002	8,48	2,0871	2,2691	2,2695	2,2693	2,2686	0,1820	0,0182	9,09
22	K-feldspar	LSW	STO #2	0,2004	8,49	2,2241	2,4127	2,4131	2,4129	2,4122	0,1886	0,0118	5,89
23	Quartz	LSW	STO #2	0,2001	8,15	2,0430	2,2414	2,2418	2,2416	2,2411	0,1986	0,0015	0,75

Experiment #8

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Quartz	FW #1	STO #3	0,2005	6,20	2,3870	2,5828	2,5832	2,5830	2,5823	0,1958	0,0047	2,34
2	Quartz	FW #1	STO #3	0,2001	6,40	2,3450	2,5410	2,5414	2,5412	2,5405	0,1960	0,0041	2,05
3	Quartz	FW #2	STO #3	0,1996	6,16	2,2724	2,4651	2,4655	2,4653	2,4646	0,1927	0,0069	3,46
4	Quartz	FW #2	STO #3	0,1993	6,07	2,1938	2,3851	2,3855	2,3853	2,3846	0,1913	0,0080	4,01
5	Quartz	SW	STO #3	0,1995	7,79	2,2389	2,4345	2,4349	2,4347	2,4340	0,1956	0,0039	1,95
6	Quartz	SW	STO #3	0,2008	7,95	2,3152	2,5115	2,5119	2,5117	2,5110	0,1963	0,0045	2,24
7	Quartz	LSW	STO #3	0,2002	7,03	2,1692	2,3680	2,3684	2,3682	2,3675	0,1988	0,0014	0,70
8	Quartz	LSW	STO #3	0,2000	6,87	2,3452	2,5433	2,5437	2,5435	2,5428	0,1981	0,0019	0,95
9	Glauconite	FW #1	STO #3	0,2004	7,10	2,0940	2,2630	2,2634	2,2632	2,2625	0,1690	0,0314	15,67
10	Glauconite	FW #1	STO #3	0,2005	7,06	2,2318	2,3999	2,4003	2,4001	2,3994	0,1681	0,0324	16,16
11	Glauconite	FW #2	STO #3	0,1997	7,10	2,1412	2,3192	2,3196	2,3194	2,3187	0,1780	0,0217	10,87
12	Glauconite	FW #2	STO #3	0,1994	7,14	2,1850	2,3640	2,3644	2,3642	2,3635	0,1790	0,0204	10,23
13	Glauconite	SW	STO #3	0,2007	7,75	2,2130	2,3951	2,3955	2,3953	2,3946	0,1821	0,0186	9,27
14	Glauconite	SW	STO #3	0,1995	7,38	2,1797	2,3627	2,3631	2,3629	2,3622	0,1830	0,0165	8,27
15	Glauconite	LSW	STO #3	0,1994	7,83	2,2087	2,4050	2,4054	2,4052	2,4045	0,1963	0,0031	1,55
16	Glauconite	LSW	STO #3	0,2000	7,84	2,1196	2,3146	2,3150	2,3148	2,3141	0,1950	0,0050	2,50

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
17	Glauconite	FW #1 + HCl		0,1997		2,2777	2,4576	2,458	2,4578	2,457067	0,1799	0,0198	9,91
18	Glauconite	FW #1 + HCl		0,2001		2,2974	2,4734	2,4738	2,4736	2,472867	0,176	0,0241	12,04
20	K-feldspar	FW #1	STO #3	0,2007	6,17	2,1015	2,2749	2,2753	2,2751	2,2744	0,1734	0,0273	13,60
21	K-feldspar	FW #1	STO #3	0,2007	6,45	2,1671	2,3381	2,3385	2,3383	2,3376	0,1710	0,0297	14,80
22	K-feldspar	FW #2	STO #3	0,1999	7,03	2,1943	2,3775	2,3779	2,3777	2,3770	0,1832	0,0167	8,35
23	K-feldspar	FW #2	STO #3	0,2000	6,85	2,1567	2,3428	2,3432	2,343	2,3423	0,1861	0,0139	6,95
24	K-feldspar	SW	STO #3	0,1994	7,59	2,1723	2,3558	2,3562	2,356	2,3553	0,1835	0,0159	7,97
25	K-feldspar	SW	STO #3	0,2007	7,65	2,2482	2,4350	2,4354	2,4352	2,4345	0,1868	0,0139	6,93
26	K-feldspar	LSW	STO #3	0,1999	7,81	2,2300	2,4178	2,4182	2,418	2,4173	0,1878	0,0121	3,05
27	K-feldspar	LSW	STO #3	0,2005	8,02	2,2056	2,3927	2,3931	2,3929	2,3922	0,1871	0,0134	3,68

Experiment #9

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Glauconite	LSW	STO #2	0,1998	7,93	2,2539	2,4432	2,4436	2,4434	2,4427	0,1893	0,0105	5,26
2	Glauconite	FW #1 + HCl		0,1998		2,2404	2,3920	2,3924	2,3922	2,3915	0,1516	0,0482	24,12
3	Glauconite	FW #1 + HCl		0,2000		2,2246	2,3713	2,3717	2,3715	2,3708	0,1467	0,0533	26,65
4	Glauconite	FW #1 + HCl		0,2005		2,0128	2,1300	2,1304	2,1302	2,1295	0,1172	0,0833	41,55
5	Glauconite	FW #2	N-decane	0,2004	7,00	1,9951	2,1938	2,1942	2,1940	2,1933	0,1987	0,0017	0,85
6	Glauconite	FW #2	N-decane	0,2005	7,00	2,0343	2,2315	2,2319	2,2317	2,2310	0,1972	0,0033	1,65
7	Glauconite	FW #2	STO #1	0,2002	7,09	1,9972	2,1754	2,1758	2,1756	2,1749	0,1782	0,0220	8,38
8	Glauconite	FW #2	STO #1	0,2006	7,00	2,0287	2,2032	2,2036	2,2034	2,2027	0,1745	0,0261	8,82
9	Glauconite	FW #2	STO #2	0,2006	7,07	1,9925	2,1806	2,1810	2,1808	2,1801	0,1881	0,0125	8,42
10	Glauconite	FW #2	STO #2	0,2001	7,14	2,1330	2,3124	2,3128	2,3126	2,3119	0,1794	0,0207	9,34
11	K-feldspar	SW	STO #2	0,2006	7,53	2,1262	2,2832	2,2836	2,2834	2,2826	0,1570	0,0436	21,73
12	K-feldspar	SW	N-decane	0,1998	7,65	2,1776	2,3770	2,3774	2,3772	2,3765	0,1994	0,0004	0,20
13	K-feldspar	LSW	STO #1	0,1996	7,85	2,1691	2,3622	2,3626	2,3624	2,3617	0,1931	0,0065	3,26
14	K-feldspar	LSW	STO #2	0,2003	7,96	2,1469	2,3361	2,3365	2,3363	2,3356	0,1892	0,0111	5,54
15	K-feldspar	LSW	STO #1	0,1995	7,83	2,1455	2,3368	2,3372	2,3370	2,3362	0,1913	0,0082	4,11
16	K-feldspar	FW #2	N-decane	0,2000	6,81	2,0223	2,2230	2,2234	2,2232	2,2225	0,2007	-0,0007	-0,35

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	%$W_{mineral}$ o.p.
17	K-feldspar	FW #2	N-decane	0,2007	6,84	2,0415	2,2413	2,2417	2,2415	2,2408	0,1998	0,0009	0,45
18	K-feldspar	FW #2	STO #2	0,2000	6,85	2,0830	2,2600	2,2604	2,2602	2,2595	0,1770	0,0230	11,50
19	K-feldspar	FW #2	STO #2	0,1998	6,91	2,0665	2,2425	2,2429	2,2427	2,2420	0,1760	0,0238	11,91
20	K-feldspar	FW #2	STO #1	0,1997	6,68	2,0412	2,2312	2,2316	2,2314	2,2307	0,1900	0,0097	4,86
21	K-feldspar	FW #2	STO #1	0,2002	6,88	2,0511	2,2412	2,2416	2,2414	2,2407	0,1901	0,0101	5,04
22	Field #1	SW	STO #1	0,2001	7,54	2,0956	2,2843	2,2847	2,2845	2,2838	0,1887	0,0114	5,70
23	Field #1	SW	N-decane	0,1999	7,51	2,1167	2,3167	2,3171	2,3169	2,3162	0,2000	-0,0001	0,43
24	Field #1	LSW	N-decane	0,1998	8,40	2,1529	2,3508	2,3512	2,3510	2,3503	0,1979	0,0019	0,95
25	Quartz	SW	STO #1	0,1997	7,99	2,1269	2,3132	2,3136	2,3134	2,3127	0,1863	0,0134	3,52
26	Quartz	SW	STO #1	0,1997	7,97	2,1075	2,3015	2,3019	2,3017	2,3010	0,1940	0,0057	2,85
27	Quartz	FW #2	N-decane	0,1993	6,52	2,1244	2,3213	2,3217	2,3215	2,3208	0,1969	0,0024	1,20
28	Quartz	FW #2	N-decane	0,2005	6,27	2,0705	2,2704	2,2708	2,2706	2,2699	0,1999	0,0006	0,30
29	Quartz	FW #2	STO #2	0,2002	6,17	2,0820	2,2763	2,2767	2,2765	2,2758	0,1943	0,0059	2,00
30	Quartz	FW #2	STO #2	0,1997	6,25	2,0921	2,2889	2,2893	2,2891	2,2884	0,1968	0,0029	1,45
31	Quartz	FW #2	STO #1	0,2006	6,39	2,0848	2,2821	2,2825	2,2823	2,2816	0,1973	0,0033	1,65
32	Quartz	FW #2	STO #1	0,2004	6,17	2,1372	2,3347	2,3351	2,3349	2,3342	0,1975	0,0029	1,45

Experiment #10

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{minera}$ l o.p.
1	Muscovite	FW #1	STO #1	0,2001	6,07	2,0962	2,2220	2,2224	2,2222	2,2217	0,1260	0,0741	37,03
2	Muscovite	FW #1	STO #1	0,1999	6,21	2,1704	2,2995	2,2999	2,2997	2,2992	0,1293	0,0706	35,32
3	Muscovite	FW #1	STO #2	0,2008	6,45	2,1768	2,3217	2,3221	2,3219	2,3214	0,1451	0,0557	31,84
4	Muscovite	FW #1	STO #2	0,1999	6,21	2,1923	2,3171	2,3175	2,3173	2,3168	0,1250	0,0749	33,57
5	Muscovite	FW #1	STO #3	0,2000	6,13	2,1616	2,2341	2,2345	2,2343	2,2338	0,0727	0,1273	63,65
6	Muscovite	FW #1	STO #3	0,2009	6,17	2,2337	2,3095	2,3099	2,3097	2,3092	0,0760	0,1249	62,17
7	Muscovite	FW #1	N-decane	0,1997	6,30	2,1633	2,3616	2,3620	2,3618	2,3613	0,1985	0,0012	0,60
8	Muscovite	FW #1	N-decane	0,1996	6,24	2,0321	2,2292	2,2296	2,2294	2,2289	0,1973	0,0023	1,15
9	Muscovite	FW #2	STO #1	0,1998	5,80	2,0462	2,1479	2,1483	2,1481	2,1476	0,1019	0,0979	45,10
10	Muscovite	FW #2	STO #1	0,1998	6,31	2,0787	2,1776	2,1780	2,1778	2,1773	0,0991	0,1007	44,78
11	Muscovite	FW #2	STO #2	0,1997	6,32	2,0576	2,1880	2,1884	2,1882	2,1877	0,1306	0,0691	38,70
12	Muscovite	FW #2	STO #2	0,2005	6,22	2,0658	2,1777	2,1781	2,1779	2,1774	0,1121	0,0884	40,19
13	Muscovite	FW #2	STO #3	0,2003	6,32	2,0318	2,1352	2,1356	2,1354	2,1349	0,1036	0,0967	48,38
14	Muscovite	FW #2	STO #3	0,1998	6,49	2,0171	2,0793	2,0797	2,0795	2,0790	0,0624	0,1374	47,63
15	Muscovite	FW #2	N-decane	0,1995	6,34	2,0186	2,2115	2,2119	2,2117	2,2112	0,1931	0,0064	3,21
16	Muscovite	FW #2	N-decane	0,2001	6,33	2,0558	2,2489	2,2493	2,2491	2,2486	0,1933	0,0068	3,40
17	Muscovite	SW	STO #1	0,1999	7,66	2,0454	2,0777	2,0781	2,0779	2,0774	0,0325	0,1674	83,74
18	Muscovite	SW	STO #1	0,2000	7,66	2,0354	2,0717	2,0721	2,0719	2,0714	0,0365	0,1635	81,75
19	Muscovite	SW	STO #2	0,2007	7,67	2,1929	2,2284	2,2288	2,2286	2,2281	0,0357	0,1650	75,31
20	Muscovite	SW	STO #2	0,2006	7,66	2,2060	2,2799	2,2803	2,2801	2,2796	0,0741	0,1265	74,16
21	Muscovite	SW	STO #3	0,2001	7,65	2,0279	2,0306	2,0310	2,0308	2,0303	0,0029	0,1972	98,55
22	Muscovite	SW	STO #3	0,1998	7,67	2,1703	2,1741	2,1745	2,1743	2,1738	0,0040	0,1958	98,00
23	Muscovite	SW	N-decane	0,1994	7,65	2,3036	2,4714	2,4718	2,4716	2,4711	0,1680	0,0314	15,75
24	Muscovite	SW	N-decane	0,2000	7,65	2,1639	2,3286	2,3290	2,3288	2,3283	0,1649	0,0351	17,55

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
25	Muscovite	LSW	STO #1	0,2002	6,80	2,2552	2,3691	2,3695	2,3693	2,3688	0,1141	0,0861	23,11
26	Muscovite	LSW	STO #1	0,1995	6,76	2,3365	2,4941	2,4945	2,4943	2,4938	0,1578	0,0417	20,90
27	Muscovite	LSW	STO #2	0,2001	6,90	2,2638	2,4326	2,4330	2,4328	2,4323	0,1690	0,0311	15,54
28	Muscovite	LSW	STO #2	0,1999	6,84	2,2471	2,4025	2,4029	2,4027	2,4022	0,1556	0,0443	17,26
29	Muscovite	LSW	STO #3	0,2000	6,74	2,2991	2,4687	2,4691	2,4689	2,4684	0,1698	0,0302	26,20
30	Muscovite	LSW	STO #3	0,2000	6,70	2,2950	2,3802	2,3806	2,3804	2,3799	0,0854	0,1146	27,40
31	Muscovite	LSW	N-decane	0,1994	6,66	2,2778	2,4745	2,4749	2,4747	2,4742	0,1969	0,0025	1,25
32	Muscovite	LSW	N-decane	0,1998	6,69	2,2543	2,4513	2,4517	2,4515	2,4510	0,1972	0,0026	1,30
33	Pyrite	FW #2	STO #2	0,2003	2,81	2,1273	2,1394	2,1398	2,1396	2,1389	0,0121	0,1882	93,96
34	Plagioclase	FW #2	N-decane	0,1999	6,72	2,0851	2,2841	2,2845	2,2843	2,2836	0,1990	0,0009	0,45
35	Plagioclase	FW #1	STO #1	0,2006	6,34	2,1506	2,3434	2,3438	2,3436	2,3429	0,1928	0,0078	3,89
36	Plagioclase	FW #1	STO #1	0,2004	6,43	2,0477	2,2396	2,2400	2,2398	2,2391	0,1919	0,0085	4,24
37	Field #1	FW #1	STO #2	0,2000	7,09	2,2419	2,4217	2,4221	2,4219	2,4212	0,1798	0,0202	9,80
38	Field #1	FW #1	STO #2	0,1993	7,18	2,1963	2,3783	2,3787	2,3785	2,3778	0,1820	0,0173	9,30
39	Field #1	FW #1	STO #3	0,2010	7,15	2,2098	2,3767	2,3771	2,3769	2,3762	0,1669	0,0341	16,35
40	Field #1	FW #1	STO #3	0,1992	7,17	2,2614	2,4290	2,4294	2,4292	2,4285	0,1676	0,0316	15,86
41	Field #1	FW #2	STO #1	0,1996	7,35	2,2943	2,4797	2,4801	2,4799	2,4792	0,1854	0,0142	7,11
42	Field #1	FW #2	STO #1	0,1995	7,03	2,2490	2,4359	2,4363	2,4361	2,4354	0,1869	0,0126	6,32
43	Field #1	FW #2	STO #2	0,1998	7,37	2,2549	2,4369	2,4373	2,4371	2,4364	0,1820	0,0178	7,91
44	Field #1	FW #2	STO #2	0,1998	7,32	2,2703	2,4565	2,4569	2,4567	2,4560	0,1862	0,0136	7,02
45	Field #1	FW #2	STO #3	0,1994	7,36	2,2467	2,4221	2,4225	2,4223	2,4216	0,1754	0,0240	12,04
46	Field #1	FW #2	STO #3	0,1994	7,35	2,2296	2,4186	2,4190	2,4188	2,4181	0,1890	0,0104	10,55
47	Field #1	FW #2	N-decane	0,1995	7,34	2,3051	2,5024	2,5028	2,5026	2,5019	0,1973	0,0022	1,10

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
48	Field #1	FW #2	N-decane	0,1994	7,35	2,3400	2,5382	2,5386	2,5384	2,5377	0,1982	0,0012	0,60
49	Field #1	SW	STO #2	0,2003	7,58	2,3392	2,5109	2,5113	2,5111	2,5104	0,1717	0,0286	9,41
50	Field #1	SW	STO #2	0,1997	7,50	2,3913	2,5700	2,5704	2,5702	2,5695	0,1787	0,0210	8,77
51	Field #1	SW	STO #3	0,1997	7,54	2,3936	2,5610	2,5614	2,5612	2,5605	0,1674	0,0323	18,17
52	Field #1	SW	STO #3	0,2007	7,60	2,3687	2,5265	2,5269	2,5267	2,5260	0,1578	0,0429	19,38
53	Field #1	LSW	STO #2	0,2000	8,39	2,3789	2,5676	2,5680	2,5678	2,5671	0,1887	0,0113	5,65
54	Field #1	LSW	STO #2	0,2000	8,43	2,1164	2,3042	2,3046	2,3044	2,3037	0,1878	0,0122	6,10
55	Field #1	LSW	STO #3	0,1997	8,39	2,0715	2,2639	2,2643	2,2641	2,2634	0,1924	0,0073	3,03
56	Field #1	LSW	STO #3	0,2004	8,42	2,2914	2,4873	2,4877	2,4875	2,4868	0,1959	0,0045	2,25

Experiment #11

#	Mineral	Brine	Oil	W_m	pH-Brine	W_{Nfp}	$W_{Dfp\ (1)}$	$W_{Dfp\ (2)}$	$W_{Dfp\ avg}$	W_{Cor}	$W_{mineral}$ w.p.	$W_{mineral}$ o.p.	$\%W_{mineral}$ o.p.
1	Glauconite	FW #1 Fe	STO #1	0,1996	5,66	2,1372	2,3236	2,3240	2,3238	2,3233	0,1866	0,0130	6,51
2	Glauconite	FW #1 Fe	STO #1	0,1998	5,64	2,0614	2,2459	2,2463	2,2461	2,2456	0,1847	0,0151	7,56
3	Glauconite	FW #1 Al	STO #1	0,2002	3,74	2,1476	2,3165	2,3169	2,3167	2,3162	0,1691	0,0311	15,53
4	Glauconite	FW #1 Al	STO #1	0,2004	3,85	2,1083	2,2823	2,2827	2,2825	2,2820	0,1742	0,0262	13,07
5	Glauconite	FW #2 Fe	STO #2	0,2001	5,63	2,1234	2,3072	2,3076	2,3074	2,3069	0,1840	0,0161	8,05
6	Glauconite	FW #2 Fe	STO #2	0,1997	5,69	2,1596	2,3431	2,3435	2,3433	2,3428	0,1837	0,0160	8,01
7	Glauconite	FW #2 Al	STO #2	0,1998	3,82	2,1948	2,3636	2,3640	2,3638	2,3633	0,1690	0,0308	15,42
8	Glauconite	FW #2 Al	STO #2	0,1998	3,8	2,2302	2,4025	2,4029	2,4027	2,4022	0,1725	0,0273	13,66

Appendix B

Each sample has contained a total of 25ml of a 0.02M Fe^{3+} solution. We have a 12.39M HCl solution. Assuming all of the ferric ions have precipitated out as rust $Fe(OH)_3$, how much HCl is needed to dissolve the rust?

$$Fe^{3+} + 3H_2O \rightleftharpoons \mathrm{Fe(OH)_3} + 3\mathrm{H}^+ \tag{5.1}$$

$$HCl(aq) \rightarrow H^+ + Cl^- \tag{5.2}$$

From these equations we can see that three times as much HCl as there is rust present in the solution to dissolve all of the rust particles.

$$3 * 0.02\frac{mol}{liter} * 0.025\ liter = 1.5 * 10^{-3}mol$$

$$\frac{1.5 * 10^{-3}mol}{12.39mol} * 1liter = 1.21 * 10^{-4}liter = 0{,}121ml$$

From these calculations we can see that 0.121ml of the HCl solution is need to dissolve the rust particles if all the ferric ions have precipitated out as rust.