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Writer: Torstein Magnussen (Writer's signature)
Faculty supervisor: Ingebret Fjelde	
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Abstract

Wettability is one of the most important parameters of the reservoir, and to understand it is therefore of high importance (Donaldson & Alam, 2008). A sandstone reservoir can have a complexed mineralogy and each sandstone is unique in its complexity. It is therefore important to understand how the wetting of each mineral can be altered, so the best possible injection brine can be designed.

The effect of chemical enhanced recovery can be tested on a core in the lab (Rajapaksha et al., 2014). For these tests to represent the reservoir as accurately as possible the conditions must be the same. However the cores are often stored in contact with the atmosphere which is an oxidizing environment in contrast to the reduced state of the reservoir. By storing the core in contact with oxygen some iron containing minerals may be oxidized to ferric ions and create a ferric ion coating. These ferric ions can have a negative effect on the chemicals and thereby undermined the performance of the chemical flooding. A study by Rajapaksha et al (2014) proposes a new restoration method to reduce the ferric ions to ferrous ions and remove them by injecting sodium dithionite, EDTA and sodium bicarbonate.

EDTA as used in the restoration method has been proposed as a chemical for enhanced recovery (Mahmoud, Attia, & Al-Hashim, 2017). To enhance the recovery, EDTA chelates cations from the injected brine and formation water. As this disturbs the rock-brine equilibrium, the rock releases cations that changes the surface to a more water-wet condition.

The flotation method was used to test how these chemicals and ferric ions affect the wettability of glauconite, hematite and goethite.

First the effect of adding Fe^{3+} to the brine was tested on glauconite. The results showed more oil-wet particles if the total acid number of the oil was high enough. EDTA had surprisingly the same effect on glauconite and increased the concentration of oil-wet particles. Although it reduced the concentration of oil-wet particles for both hematite and goethite. The restoration chemicals had a reducing effect on the concentration of oil-wet particles for glauconite. However the effect of the restoration chemicals was significant in the hematite and goethite samples which changed from 100w% oil-wet in a Fw to under 10w% oil-wet in the restoration brine.

More tests can be done to further understand why EDTA increased the concentration of oil-wet particles. The EDTA concentration can be increased and the effect of pH can be further tested in a more alkaline solution.

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Abbreviations

CEOR	Chemical enhanced recovery
DW	Diluted water
EDTA	Ethylenediaminetetraacetic acid
Fw	Formation water
IFT	Interfacial tension
TAN	Total acid number
TBN	Total base number
SWAG	water-alternating-gas injection

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1 Introduction

The oil production from a reservoir will decline as pressure declines, to prevent this sea water injection can be applied as pressure support. Seawater injection is a success due to its abundance offshore and its low cost (Green & Willhite, 1998). However seawater has a low viscosity leading to a low macroscopic sweep efficiency and scaling due to the different ion composition in sea water and formation water. As a field matures the production of water increases until the production becomes uneconomical and the field is shut down. To prolong the life of a field, chemical enhanced recovery (CEOR) methods can be implemented. When a CEOR method is implemented, the purpose is to sweep as large a volume as possible and reduce the residual oil saturation to a minimum (Green & Willhite, 1998). In the North Sea the most common EOR method is water-alternating-gas (SWAG) injection where water injection and gas injection is performed alternately (Awan, Teigland, & Kleppe, 2008). If the mobility control of water is insufficient polymers can be used to thicken the water and displace more oil on a macroscopic scale than sea water (Green & Willhite, 1998). To reduce the residual oil saturation, surfactants can be used to lower the surface forces between water and oil. Surfactants have a hydrophobic and a hydrophilic part which creates micelles in water, these micelles can adsorb oil and form a water oil micro emulsion that mobilises the oil. Another method to enhance the microscopic recovery is to inject a low salinity brine, a low salinity brine also reduces the scaling in the reservoir (Austad, 2013; Chilingar, Mourhatch, & Al-Qahtani, 2008).

The effect of these injection fluids can be tested on a core plug from the reservoir (Rajapaksha et al., 2014). When the core plug is taken out of the reservoir it is effected by oxygen in the atmosphere where ferrous ions Fe^{2+} is oxidized to ferric ions Fe^{3+} . To produce lab result that represents the reservoir, the plug must be restored back to its initial reservoir state, hence reduce the ferric ions to ferrous ions and remove them. A restoration procedure was proposed by Rajapaksha et al 2014 where they used sodium dithionite to reduce the surficial ferric iron in a reservoir core and EDTA to remove the iron whereas sodium bicarbonate was used to buffer the solution in an alkaline pH.

Earlier this year EDTA was investigated as a CEOR method used in seawater as an alternative to the low salinity injection (Mahmoud et al., 2017). The results from the core flooding showed higher oil production when EDTA was added to seawater then a low salinity flooding.

The objective of this thesis will be to learn more about how glauconites affinity for oil can change by changing the components of the brine. Several different brines will be used among the chemicals in the proposed restoration method and the CEOR method.

Two ferric iron minerals hematite (Fe_2O_3) and goethite ($FeOOH$) will also be tested to see the direct effect on the surficial minerals.

First a literature study to get an insight in how wetting works and why it is so important.

Then the results of the flotation experiment is presented.

The flotation method simulates the history of the reservoir in very short time where formation water and mineral is aged at reservoir temperature before the mineral is only aged in oil and then the three phases altogether (Sohal, Thyne, & Søgaaard, 2016). The wetting is determined by how much of the initial mineral is left when the oil phase is removed.

In the end the results will be discussed and compared with previous knowledge before conclusions are made.

2 Theory

2.1 Origin of sandstones

The Norwegian continental shelf has its origin mainly from the igneous and metamorphic mountain range called the Caledonian (Haakon Fossen, Khani, Faleide, Ksienzyk, & Dunlap, 2016). This mountain range consists of many types of rock, however it is dominated by granite and metamorphic granite (Håkon Fossen, Pedersen, & Bergh, 2006). Granite is defined as shown in Figure 1, where plutonic rocks are classified by their quartz, alkali feldspar, and plagioclase content (Streckeisen, 1974). It is also common for granite to contain small amounts of mafic minerals such as biotite and amphibole, which contain iron. Rhyolite is the volcanic equivalent of granite, so it contains the same minerals but in smaller crystals due to rapid crystallization time (Streckeisen, 1980). These minerals break down into smaller particles (sediment) as sand and clay (Bjørlykke, 2015). These sediments are transported and deposited in different environments such as deltas, beaches, and deep marine clay. These deposits may play a part in a petroleum system as a reservoir rock like the BRENT delta or a source rock like Draupne (organic rich clay).

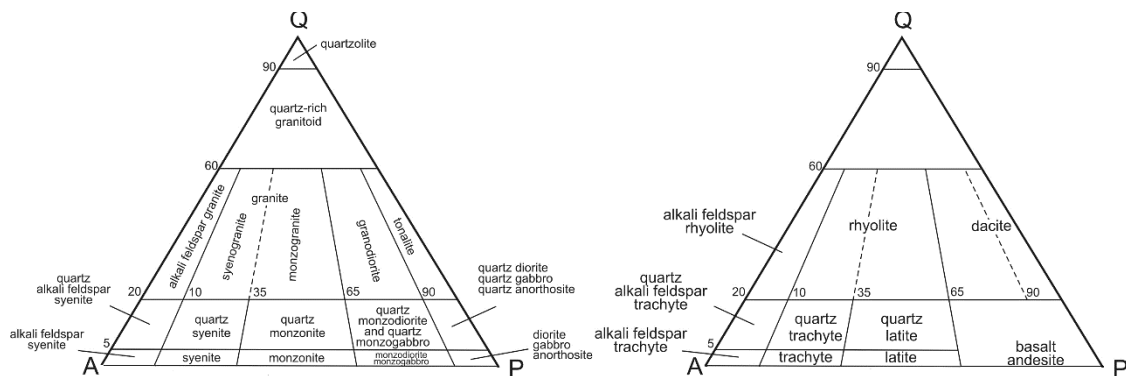


Figure 1. Left figure shows classification of plutonic rocks by quartz, alkali feldspar and plagioclase (Streckeisen, 1974). The right figure shows classification of volcanic rock by quartz, alkali feldspar and plagioclase (Streckeisen, 1980).

As these sediments formed clastic sedimentary rock, they can be classified again in several ways, Figure 2 shows the Pettijohn classification (Pettijohn, 1987). Pettijohn classified clastic sedimentary rocks by quartz, feldspar and lithic fragments. Lithic fragments are grains that contain more than one mineral or a fragment of a rock. This says something about the maturity of the rock. A high content of lithic fragment is interpreted as short sediment transport since these fragments are weak.

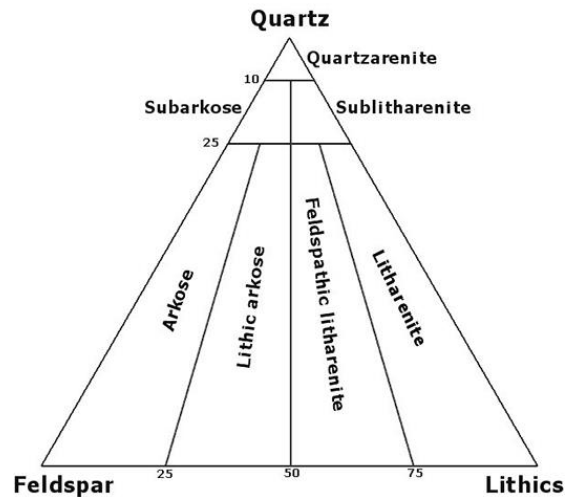


Figure 2. Pettijohn classification clastic sedimentary rock by quartz, feldspar and lithic fragments (Pettijohn, 1987).

2.2 Minerals

Minerals are naturally occurring homogenous solids, these solids can be characterised by chemical composition combined with optical methods (Demange, 2012). These mineral can be studied in a microscope to understand where the rock come from and what it has gone through.

2.2.1 Quartz

Quartz (SiO_2) is made up of silicone and oxygen and form a silicone-oxygen tetrahedra structure where each oxygen is shared by two tetrahedra (Anderson & Anderson, 2010). Quartz is mostly formed when magma cools slowly beneath the crust or rapidly from a volcanic eruption (Götze & Zimmerle, 2000). When the magma cools slowly quartz form a hard and brittle structure, 7 on Mohs scale. When it cools rapidly it becomes glass a non-crystalline amorphous mineral, meaning it has no repetitive order. Quartz is very common in sedimentary rocks since it is the second most common mineral in earth's crust, after feldspar. Due to its hard properties (resistant to erosion) many sandstone contain more quarts then feldspar.

2.2.2 Feldspar

Feldspar is an aluminosilicate mineral that contains calcium, sodium or potassium (*International Drilling Fluid (IDF) Clay chemistry*, 1982). There is more than 3000 known feldspar minerals species and they represent more than 50 % of earth's crust. Since feldspar is so abundant it is only natural to use it to classify rocks, it is therefore divided into two groups alkali feldspar and plagioclase. Due to its diversity it is defined as AT_4O_8 where $A=\text{K, Na or Ca}$ $T=\text{Si or Al}$. Weathered feldspar is also a common source for clay mineral.

2.2.3 Hematite

Hematite (Fe_2O_3) is one of the most common iron oxide in soils and rocks and has a blood red colour (Paterson, 1999). Hematite is a very stable iron oxide that has an octahedral structure.

2.2.4 Goethite

Goethite ($\alpha\text{-FeO(OH)}$) is yellow to orange iron oxide-hydroxide (Wigginton, Haus, & Hochella Jr, 2007). Goethite is a naturally occurring mineral which can form from weathering of iron-rich minerals. The goethite mineral can form as very small particles and are therefore usually found in natural water and sediments.

2.2.5 Carbonates

Carbonate minerals are made up of cations and carbonate CO_3^{2-} (Bjørlykke, 2015). Carbonate is formed when dissolved CO_2 reacts with water and forms carbonic acid (H_2CO_3) which again can react with Ca^{2+} to form calcite (CaCO_3). The Ca^{2+} source can be a product of weathered feldspar minerals. There are many forms of carbonate however limestone (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) are the most common. Carbonates are often a product of a living organism as reefs, shells and algae as coccolithophores. Dolomite is believed to form from magnesium-rich groundwater in limestone.

2.2.6 Clay minerals

Clays are the most abundant mineral on the surface of earth and cover about 75% of the surface (Bjørlykke, 2015). The name clay mineral refers to members of the hydrous aluminous phyllosilicates group and clay refers to the grain size of a sediment smaller than $3.9 \mu\text{m}$ in diameter (Worden & Morad, 2003). These clays are made up of tetrahedral and octahedral sheets see Figure 3 (Bjørlykke, 2015). In quartz the tetrahedral only contains Si^{4+} cations, however in clay it can also contain aluminium and iron cations. The tetrahedral sheet is attached to an octahedral sheet composed of 6 anions, oxygen and hydroxyl arranged around a cation. The clay mineral is classified by the different cations in the octahedral sites. If three valent cations occupy the octahedral sites the mineral is called dioctahedral since it takes two cations to provide six positive charges and trioctahedral for ferrous cations. Two mechanisms control the clay surface charge, the structure of the mineral and the charge from broken edges. Clay minerals in sedimentary rocks mainly come from metamorphic and volcanic rocks with minerals as mica (muscovite and biotite), and chlorite. Clay can also form after deposition (authigenic) by breaking down mica and feldspar

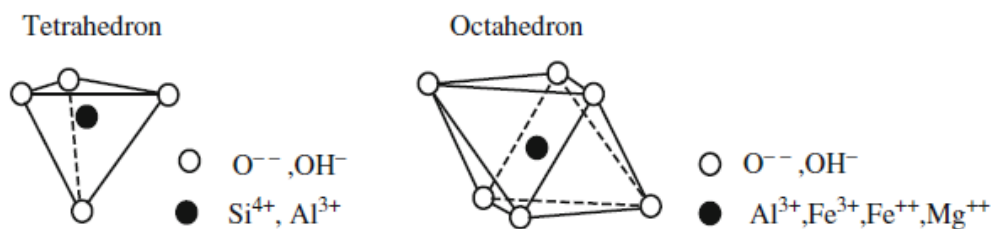


Figure 3. Tetrahedron and octahedron structure (Bjørlykke, 2015).

2.2.6.1 Chlorite

Chlorite has a 2:1:1 structure meaning an octahedral sheet with a tetrahedral sheet on both sides and between these structures a positive charged octahedral structure of cations and hydroxyl anions (Worden & Morad, 2003). Chlorite is an iron rich clay mineral and can be written as $(\text{Mg,Al,Fe})_{12}[(\text{Si,Al})_8\text{O}_{20}]$. Chlorite typically coat grains where crystals are attached perpendicular to the sand grains.

The porosity of reservoirs decline with increasing depth due to increased quartz cementation at higher temperatures (Ehrenberg, 1993). However reservoirs with grains coated with chlorite seems to have a porosity 10-15% higher than predicted.

2.2.6.2 Illite

Illite $(\text{Al,Mg,Fe})_{2-3}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ is one octahedral sheet between two tetrahedral sheet (2:1) and a layer of potassium between the structures to balance the substitution of silicon with aluminium in the tetrahedral sheet (Worden & Morad, 2003). The ionic bond in illite between potassium and oxygen is strong and prevents therefore illite to swell. Kaolinite can alter to illite in deep reservoir which can cause sever damages to permeability.

2.2.6.3 Glauconite

Glauconite is clay mineral found in several petroleum reservoir around the world. In the North Sea, Siri canyon holds several glauconite bearing fields as Nini and Cecilia (Hossain, Mukerji, Dvorkin, & Fabricius, 2011). Glauconite can form under normal marine salinity with the necessary components present and reducing conditions. A high organic content and slow sedimentation rate is also preferred (Cloud Jr, 1955).

Glauconite has a 2:1 structure as illite with about the same amount of potassium between the crystals (Weaver & Pollard, 1973). Ferric iron is five times more abundant in the octahedral sites then in illite. Ferrous iron is also more abundant in glauconite than illite. It is this variation in ferric and ferrous iron that gives glauconite its green colour.

2.2.6.4 Kaolinite

Kaolinite $(\text{Al}_2\text{SiO}_2\text{O}_5(\text{OH})_4$ has a 1:1 structure of one octahedral and one tetrahedral (Bjørlykke, 2015). This structure is very stable at low temperatures although at higher temperatures (at 130 °C) kaolinite will convert to illite if potassium is available. Sea water injection can dissolve feldspar and mica to form kaolinite which can reduce the permeability.

2.3 Interfacial tension

If two fluids are immiscible they will create an interface only a few molecules in thick that separates the fluids (Donaldson & Alam, 2008). The molecules away from the interface have an attractive force towards another in all direction (cohesion). However a molecule at the interface has less attractive molecules in one direction, the molecule therefore pulls harder on the surrounding molecules creating a membrane of molecules with stronger bonds. The molecules in the membrane are also pulled by an inward force to reduce the surface area by creating a spear. The interfacial tension (IFT) σ is defined as the normal force F acting on the surface per unit length of the surface $F/L=\sigma$ (Green & Willhite, 1998). Figure 4 shows a water drop emerged in oil, due the density difference the water drop rests on the horizontal solid surface. As mention before the interfacial tension between oil and water (σ_{ow}) pulls the molecules towards the centre like the water- solid IFT (σ_{ws}), however the oil-surface IFT (σ_{os}) pulls the molecules away from the centre, hence eq 1.

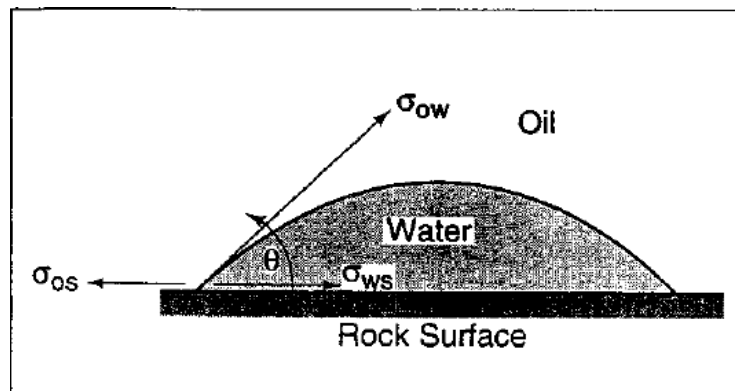


Figure 4. A water drop on a rock surface surrounded by oil. The angel θ measured in the wetting phase describes the wetting (Green and Willhite (1998)

$$\sigma_{os} - \sigma_{ws} = \sigma_{ow} \cos\theta \quad (\text{Eq. 1})$$

For a water drop to adhere to the surface the adhesive forces must be greater than the cohesive forces (Donaldson & Alam, 2008). Figure 5 shows two examples where oil or water adhere to a capillary surface and displaces the other phase. The phase with the highest affinity for the surface will curve the interface inwards as seen in Figure 5, the angle θ of this curvature is related to the IFT between oil and water (σ_{ow}) as seen in eq 2. Where r is the radius of the capillary and g is the gravitational constant $980 \frac{cm}{s^2}$, h is the fluid height defined in Figure 5, ρ_w and ρ_o is the water and oil density and θ is the angle measured from the wetting phase.

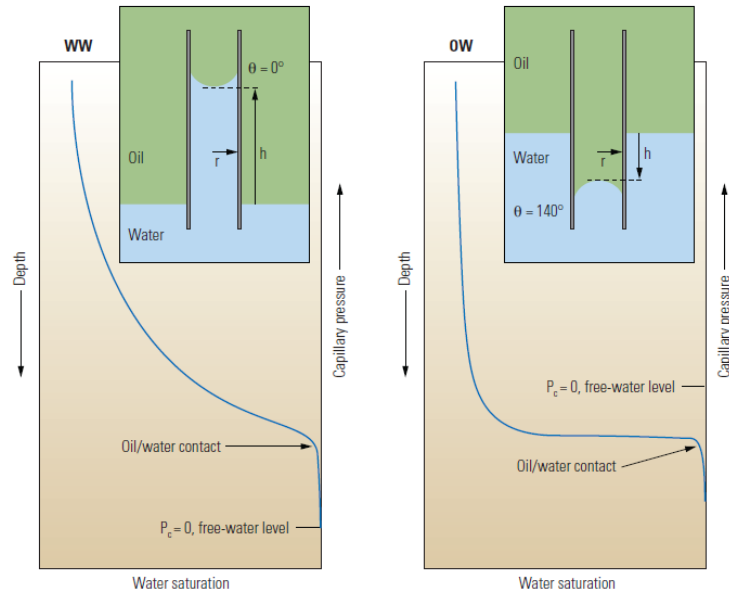


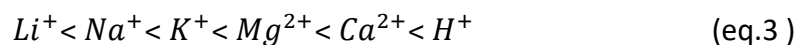
Figure 5. Illustration of how IFT can be measured and how it effects the distribution of the oil saturation vs depth (Abdallah et al., 2007).

$$\sigma_{ow} = \frac{rgh(\rho_w - \rho_o)}{2\cos\theta} \quad (\text{Eq. 2})$$

2.4 Wettability

Wettability is the preference a solid surface has for a liquid to adhere or spread on its surface (Abdallah et al., 2007). Why fluids adhere or not to a solid surface can mainly be explained by opposite electrical forces acting between the fluid and solid (Austad, 2013). In a calcium carbonate reservoir the surface is positively charged due to the abundance of calcium ions. Crude oil commonly contain some carboxylic acid that deprotonate to carboxylate anions which have a negative charge that can adhere to the positive surface hence making it oil-wet.

In contrast to carbonates, sandstone has a more complex mineralogy and contains a various amount of clay (Bjørlykke, 2015). Clays have a permanent negative charge and therefore act as cation exchangers and the affinity of the cations towards the surface is as shown in eq 3.



Cations as calcium at the clay surface can act as a bridge between the clay and negative carboxylate ions for the oil to adhere to the surface.

An oil wet system is when the majority of the rock surface is prefer to be wetted by oil, and similarly for a water-wet system (Donaldson & Alam, 2008). The wetting phase will occupy the small pores and the majority of the surface of the rock. To say that a rock or a reservoir is oil-wet or water-wet is a very un-accurate statement. A sandstone for example with a high complexity of minerals that are heterogeneously distributed in the reservoir will have large variations in wettability.

2.4.1 Wettability of glauconite

A special core analysis program was performed on a North Sea field containing 18-30 % glauconite (Thomas, Ringen, & Rasch, 2003). The glauconite was observed in a thin section as round pellets, flakes due to altered mica and as coating on grains. Glauconite was estimated to have a 40 % internal porosity, the properties of this porosity was investigated with an environmental scanning electron micro-scope. The glauconite was observed with potassium chloride crystals indicating that the internal porosity contained water. When they allowed water to condensate on the rock, water drops was absent on the glauconite surface indicating that the glauconite imbibed the water and is therefore water-wet.

2.5 Capillary pressure

In a capillary tube with two immiscible fluids the pressure difference over the interface is defined as the capillary pressure see (eq 4) (Donaldson & Alam, 2008).

$$P_c = P_o - P_w \quad (\text{Eq.4})$$

$$P_c = \frac{2\sigma_{ow}\cos\theta}{r} \quad (\text{Eq.5})$$

Equation 5 explains how the capillary pressure is influenced by IFT and the radius of the capillary (pore throat). Figure 6 shows how the wetting of the reservoir effects the capillary pressure curves which again controls the distribution and flow of the fluids in the reservoir. In a capillary system as a reservoir displacement is described by two systems, drainage and imbibition. Drainage is when the wetting phase is displaced by the non-wetting phase and imbibition is when the non-wetting phase is displaced by the wetting phase. In a water-wet system the capillary pressure needs to reach a threshold pressure to enter the reservoir and increasingly higher capillary pressure is needed to further displace the water until the irreducible water saturation S_{wi} . If the pressure is reduced water will be spontaneously imbibed into the reservoir, although to reach the irreducible oil saturation S_{or} pressure must be applied as water injection.

However in an oil-wet system some oil is imbibed into the reservoir before more pressure is needed to displace more water. Although if the pressure is reduced from S_{wi} the water does not spontaneously imbibe into the rock and pressure is needed to force the oil out. What Figure 6 doesn't illustrate is that the irreducible water saturation is lower for oil-wet then for a water-wet system.

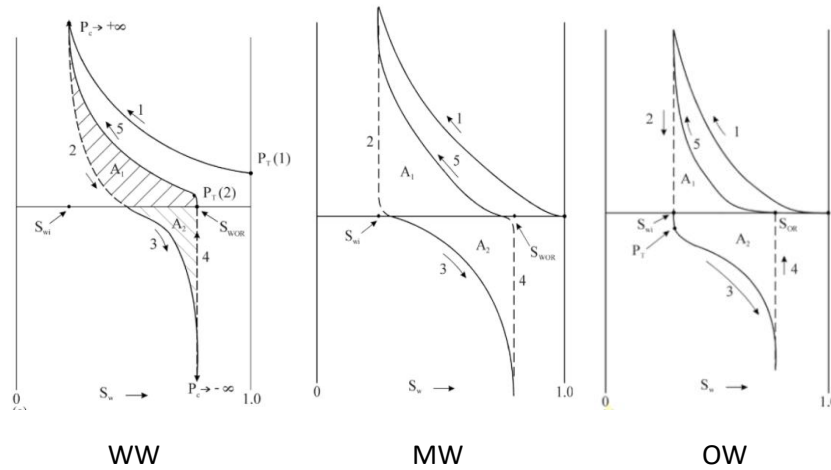
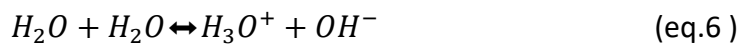


Figure 6. Capillary pressure on y axis and oil saturation on x axis. Left figure is water-wet, in the middle mixed wet and to the right an oil-wet system. The horizontal line in the middle is $P_c=0$.

2.6 Acid-base chemistry

Water chemistry is an important part of reservoir chemistry (Snoeyink & Jenkins, 1980). Water is a dipole molecule where the oxygen has a negative dipole moment and the hydrogen forms a positive dipole moment. The polarity attracts water to other polar components and itself through hydrogen bonds. This polarity makes water a good solvent for other polar components, oils are non-polar and do not mix with water. When an ion enters the water, water surrounds the ion. As an example, Cl^- would be surrounded by the positive hydrogen side of the water molecule. The number of water molecules surrounding the ion is called hydration number and is different for each ion type. The hydration of an ion is strongly affected by temperature, ionic strength and the ionic concentration of the water.

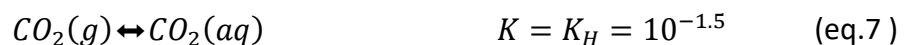
Water is also amphoteric which means it can act as a base and an acid (Snoeyink & Jenkins, 1980). This means it can receive or give away an H^+ ion. Since water can act as an acid and a base, it undergoes auto ionization as shown in equation 6.



This process affects the pH in the water, as the temperature rises the pH decreases as the concentration H_3O^+ increases.

2.6.1 Buffer

CO_2 is an important component in the acid-base system in the formation water (Snoeyink & Jenkins, 1980). CO_2 may originate from different processes as respiration, dissolution from atmosphere and dissolution of carbonate bearing minerals. The carbonate system acts as a buffer of pH shown in eq.7 to 10 below.





2.7 Oil components

Crude oil is a mixture of small volatile to very large non-volatile hydrocarbons compounds (Fingas, 2011). Crude oil mainly contain carbon and hydrogen (hydrocarbons), although oils may also contain amounts of sulphur, nitrogen, oxygen and salts. A common classification of oils is SARA saturates, aromatics, resins and asphaltenes. The saturate group contains mainly alkanes which are straight-chain, branched-chain or cyclo-alkanes where the carbons have maximum number of hydrogen (saturated). The aromatic compounds are composed of at least one benzene ring, a hex structure with two double bonds that floats around the ring. The smaller polar components are called resins, the charge comes from bonding with inorganic molecules as sulphur, nitrogen and oxygen. The larger polar compounds are asphaltenes.

There is no doubt that oil has an effect on the reservoir rock wettability, however which components that influences the wettability the most is unclear (Dandekar, 2013). Non-polar hydrocarbon components like alkanes, cycloalkanes and aromatic components is the main constituents of a reservoir oil, since these components are non-polar they are not believed to affect the wettability. Many studies show that acid-base numbers, the concentration of asphaltenes and its ability to solve the asphaltenes has a significant influence on rock wettability (Buckley, Liu, Xie, & Morrow, 1997). A poor asphaltene solvent usually has a high API gravity, the asphaltenes are less likely to stay in solution if the temperature or pressure decrease.

Qi and Wang (2013) studied the effect of aging time and the asphaltene/toluene ratio with different brines. The study was made by measuring the contact angle on a quartz surface. The results showed a correlation between an increased asphaltene concentration and an increasing oil-wet surface. The study also showed that the aging time had a significant effect up to 3 days of aging. When they tested the different brines with different metal cations, the divalent metal ion like calcium clearly increased the oil wetness of the quartz. They suggested that the metal cations compressed the diffused double layer surrounding the quartz particle, this would lower the electrostatic repulsion and favour adsorption of polar components like asphaltenes (Qi, Wang, He, Li, & Xu, 2013).

Fjelde (2014) investigated the retention of polar oil components with different brine composition and different base/acid ratio in the oil. When a crude oil with low base/acid ratio was used, the retention of polar components changed with different brine composition but same saline concentration. The retention increased with higher

concentration of divalent cations adsorbed on the clay surface. This retention indicates that carboxylic groups in the oil bonded with divalent cations on the clay surface. When the concentration of acidic components was reduced (higher base/acid ratio), the retention of polar components became insensitive to brine composition. The retention for the treated crude oil (highest base/acid ratio) was higher than for the original crude (lowest base/acid ratio), the retention was also found to be insensitive to brine salinity. The high retention for the treated crud is believed to be related to direct adsorption of basic components on the clay surface (Fjelde, Omekeh, & Sokama-Neuyam, 2014).

Haugen (2016) tested the effect of di and three-valent cations on glauconite with the flotation method (Haugen, 2016). The study showed that ferric iron and aluminium cations altered the wettability to more oil wet at much lower concentration than divalent calcium. Although 50 ppm of ferric ions increased the concentration of oil-wet particles in a TAN as low as 0.1mgKOH/g. The same oil was tested with 50 ppm aluminium without any change in wettability, the TAN was raised to 0.381mgKOH/g and still no change in wettability. However when the concentration of aluminium was raised to 500 ppm the concentration oil-wet particles increased significantly.

2.8 Brine composition

Over millions of years the chemical equilibrium between the fluid and rock has been established (Austad, 2013). Today most reservoirs are flooded to improve recovery by stabilising the pressure above the bubble point and displacing the crude oil by viscous forces. If the injection brine has a different composition than the formation brine it will disturb the established equilibrium. To reach a new chemical equilibrium minerals may precipitate and reduce the permeability, it may also change the wetting of the reservoir to preferentially more water-wet.

To inject a low salinity brine has been observed to reduce the residual oil saturation and prevent scaling (Austad, 2013). A sandstone reservoir has a complicated mineral composition, this makes it difficult to fully understand the chemistry and mechanisms at play. There are many different hypotheses that explain the low salinity effect: Migration of fines, extension of the electrical double layer and multi-ion exchange (Rezaeidoust, Puntervold, & Austad, 2011).

For the low salinity brine to work some conditions must be met, the sandstone needs to contain clay minerals, the oil must contain polar components and a formation water containing divalent cations as Ca^{2+} (Rezaeidoust et al., 2011; Tang & Morrow, 1999). RezaeiDoust, Puntervold and Austad (2011) tested low saline injection on a sandstone core and discovered the following. When the injected fluid changed from high to low salinity the pH of the effluent increased by several pH units. When they added CO_2 to a basic crude oil to lower the pH of the formation water, the EOR effect of low saline brine was doubled. This increased effect is explained by increased amount of adsorbed polar

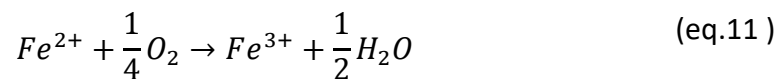
oil component to the clay surface due to a lower pH. The low salinity effect was the same on oils with high acid number 1.82(mg KOH/g) and high base number and 1.72(mg KOH/g). This result indicates adsorption of both basic and acidic oil components.

Aksulu (2012) tested the adsorption of quinoline (basic component) onto illite in high and low saline water in a pH range of 3-8 (Aksulu, Håmsø, Strand, Puntervold, & Austad, 2012). The experiment showed a higher adsorption in low salinity than high salinity, this indicates that low salinity is not changing the wettability itself. The low salinity effect is believed to be related to an increase in pH. When they flooded the cores with high salinity to low salinity with different temperatures, the pH gradient decreased with increasing temperature. An increasing in pH is believed to be related to desorption of Ca^{2+} , this should mean that Ca^{2+} desorption from the clay surface is an exothermic process.

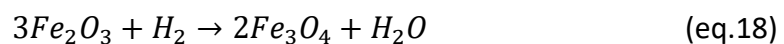
Plagioclase in the reservoir rock can give a pH above 7, if the formation water has a moderate salinity (Strand et al., 2014). This results in a water wet formation and no low salinity effect. A high salinity formation water with a pH below 7 resulting in a mixed wet system, plagioclase can contribute to a higher pH as the high salinity water is displaced by low salinity water. This would give a significant low salinity effect. This confirms that the low salinity effect is related to a pH increase.

2.9 Redox reactions

In a redox reaction one chemical species gains electrons and another species loses electrons (Boye, 2009). An example is a reaction between ferric iron and oxygen, where oxygen is reduced and ferric iron is oxidized eq.17.



Hematite which has ferric iron can be reduced to magnetite under high pressure and temperatures eq 18 (Mnrrnws, 1976).



The oxidation number for ions is usually the same as the charge or valence (Boye, 2009). As an example Cl^- , Ca^{2+} and Fe^{3+} has the oxidation numbers -1, 2+ and 3+. In covalent bonds, the oxidation number is decided from the electron negativity. In hydrochloric acid (HCl), for example, chlorine has an electronegativity of 3.0 and hydrogen has 2.1, which means chlorine pulls harder on the electron. Therefore, in hydrochloric acid, hydrogen gets the oxidation number of +1 and chlorine has -1 and is therefore reduced by hydrogen.

Redox potential measures the ability of a chemical species has to acquire electrons, or being reduced (Boye, 2009). This potential is measured in volts and the more positive it gets the higher the potential of being reduced.

A reservoir is normally in a reduced state, since microorganisms consume oxygen and deplete the reservoir for oxygen.

The redox potential can be calculated with Nernst equation (eq 18):

$$E_h = E^\circ + \frac{RT}{nF} \ln \frac{A_{ox}}{A_{red}} \quad (\text{eq.12})$$

Hence, the redox potential is dependent on:

- E_h =potential
- E° =Standard oxidation potential
- R= Universal gas constant
- T=Temperature in Kelvin
- n= number of electrons involved in the chemical reaction
- F=Faraday constant (96.484 absolute coulombs)
- A ox= activity of oxidized form of ions
- A red= activity of reduced form of ions

The activity of the ions is affected by the pH through formation of complexes and precipitation of solid (John David Hem & Cropper, 1959).

2.10 Solubility of Iron

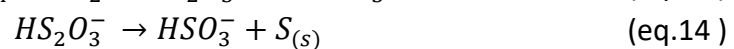
As mentioned before iron is a common metal in earth's crust, only aluminium is more abundant (J. D. Hem & Cropper, 1952). Iron occurs in sedimentary rocks as trivalent Fe^{3+} and divalent Fe^{2+} . The ferric form has a very low solubility and is therefore quickly redeposited as oxides and hydroxides. The solubility of Fe^{2+} and Fe^{3+} is very pH dependent as the solubility increases with decreasing pH however the pH of natural water is not very low. Ferric ions in natural water commonly form ferric hydroxide $\text{Fe}(\text{OH})_3$. Ferric hydroxide is a weak base and will ionize as $\text{Fe}(\text{OH})_2^+$, FeO^+ , $\text{Fe}(\text{OH})^{2+}$, and Fe^{3+} . Ferric iron also forms inorganic complexes with fluoride, chloride, phosphate, sulphate and carbonate ions. Ferrous iron is less strong in its complexing properties as ferric iron. Ferrous iron form ferrous hydroxide $\text{Fe}(\text{OH})_2$ which is a stronger base than ferric hydroxide. Ferrous hydroxide can ionize into $\text{Fe}(\text{OH})^+$ and the more common Fe^{2+} (John David Hem & Cropper, 1959).

2.11 EDTA

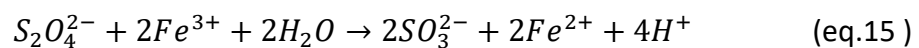
A low salinity brine has been reported to increase the oil recovery in several sandstones (Austad, Rezaeidoust, & Puntervold, 2010). Instead of removing the cations as Ca^{2+} and Mg^{2+} Mahmoud et al 2017 tested the effect of adding EDTA to seawater. EDTA or ethylenediaminetetraacetic acid is a chemical compound that can chelate metal ions as calcium, magnesium and iron (Mahmoud et al., 2017). The results from core flooding with EDTA/seawater showed an additional recovery compared to seawater and low salinity. They also measured the zeta potential which revealed a more negative surface charge for the EDTA/seawater than for the seawater and low salinity brine. This indicates that the wettability was altered to a more water-wet state. However they also reported a low IFT between the EDTA/seawater and the crude oil used in the experiment. Although the crude-brine IFT was further reduced when they increased the pH from 10.7 to 12.2. The recovery was also increased with increasing pH which they relate to an increased chelation ability of metal ions which altered the wettability.

2.12 Restoration

Reservoir cores are usually stored under oxidizing condition compared to reducing reservoir condition (Rajapaksha et al., 2014). This can change the mineralogy and the results of chemical EOR tests. Iron-containing minerals can have surficial ferrous iron that can be oxidized under storage to ferric ions. The ferric ions can degrade polymers and increase surfactant adsorption. The ferric ions are more positively charged and therefore bind more strongly to negatively charged oil components as carboxylic acid. This would result in a more oil-wet system. To restore the rock sample back to reservoir condition, sodium dithionite can be used as a reducing agent. Unfortunately sodium dithionite is unstable at temperatures above 65 C°. Sodium dithionite removes very little surface ferric ions alone and it decomposes to elemental sulphur in acidic water (eq. 13) (eq. 14).



Although in a neutral to alkaline solution thiosulphate ($S_2O_3^{2-}$) ions are less likely to produce elemental sulphur (Varadachari, Goswami, & Ghosh, 2006). However dithionite can reduce ferric ions to soluble ferrous ions (eq. 15).



To avoid formation of solid like FeS and F_2S_3 EDTA can be used as a complexing agent and bind with the ferrous ions to improve dithionite as a dissolution agent (Rajapaksha et al., 2014). Since the reduction of ferric ions produce H^+ (eq.15) a buffer as bicarbonate is needed to keep the solution alkaline.

This chemical was tested by Rajapaksha et al (2014) to restore core samples containing iron rich minerals as Siderite, Ankerite and Pyrite. They report the method to improve polymer transport and reduce polymer and surfactant retention.

2.13 Flotation

Flotation is a simple lab experiment to characterize the wettability of minerals (Sohal et al., 2016). The experimental setup of flotation mimics the history of a reservoir in a very short time. The setup involves of aging the mineral with a brine then remove the brine to age the oil with the mineral. As the previously removed brine is added back the hydrophobic particles (oil-wet) will float while the hydrophilic particles (water-wet) will sink. In the end the oil phase is removed with the oil-wet particle. The water-wet particles are filtered dried and weighed to find the weight % oil-wet particles lost.

This method is an opportunity to easily test the wetting of minerals or reservoir rocks and how it is effected by brine and oil composition, IFT and temperature (Sohal et al., 2016). The method cannot calculate the increased recovery due to change in wettability. However wettability as ben found strongly related to recovery.

3 Methods

3.1 Materials

3.1.1 Minerals and chemicals

Glauconite

Hematite (Fe_2O_3)

Goethite ($\alpha\text{-FeO(OH)}$)

EDTA ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2$)

- Purity 99%

Iron (III) chloride (FeCl_3)

Sodium bicarbonate (NaHCO_3)

Sodium dithionite ($\text{Na}_2\text{H}_2\text{S}_2\text{O}_4$)

- $\text{Cl}^- < 0.01\%$
- $\text{Fe} < 0.002\%$
- $\text{Na}_2\text{CO}_3 < 10\%$

3.1.2 Brine

Two different brines Fw1 and Fw2 in **Feil! Fant ikke referansekinden.** and *Table 2* where used as a base to make other brines.

Table 1. Composition of Fw1, ppm= $\frac{mg}{l}$

1000 ml	Fw1				
Salt	Mass (g)		Ion	ppm	(m*mole)/l
Na ₂ SO ₄	0.13		Na ⁺	30489	1326.2
Na ₂ SO ₄	0.13		K ⁺	220	5.6
KCl	0.42		Ca ²⁺	5929	147.9
MgCl ₂ *6H ₂ O	3.55		Mg ²⁺	424	17.5
CaCl ₂ *2H ₂ O	21.75		Cl ⁻	53636	1660.8
			SO ₄ ²⁻	88	0.9

Table 2. Fw2. Composition of Fw2, ppm= $\frac{mg}{l}$.

1000 ml	Fw2				
Salt	Mass (g)		ion	ppm	(m*mole)/l
NaCl	40.6		Na ⁺	16136	701.9
CaCl ₂ *2H ₂ O	10.71		K ⁺	278	7.1
MgCl ₂ *6H ₂ O	4.86		Ca ²⁺	2920	72.9
KCl	0.53		Mg ²⁺	581	23.9
Na ₂ SO ₄	0.51		Sr ²⁺	198	2.3
SrCl ₂ *6H ₂ O	0.44		Ba ²⁺	6	0.04
BaCl ₂ *2H ₂ O	0.01		Cl ⁻	29241	899.9
			SO ₄ ²⁻	345	3.6

Several other brines where made from the two base brines. The pH of these brines and their pH after aging with the mineral are presented in Table 4, Table 5 and Table 6. The table also shows what was done in each project and the order they were produced.

3.1.3 Oil

Two different oils where used to test the effect of different total acid numbers Table 3. STO 1 was chosen since it originates from a glauconite rich reservoir. As a references n-Decane was used due to its non-polar properties.

Table 3. Oils used with different total acid number (TAN) and total base number (TBN)

Oil	TAN(mgKOH/g oil)	TBN(mgKOH/g oil)
STO 1	<0.1	1.9
STO 2	2.9	0.95
n-Decane	0	0

3.2 Brine preparation

1. De-ionised water and a magnet is added to volumetric flask and placed on a magnetic stir plate.
2. A desired amount of salt is weight in on a pallet and added to the de ionised water, the remaining salt is flushed down with more de ionised water.
3. When all desired salt is added to the solution and the flask is topped of with de-ionised water, the solution is left to dissolve the salts helped by a rotating magnet for about one hour.
4. The brine is now filtered through a 0.45 μm filter paper to remove undissolved salts, the brine is now ready for use.
5. Only FeCl_3 was added after filtration due to loss of iron oxides in the filter paper.

3.3 Flotation procedure

1. First the mineral is added to a small bottle with 53 μm mesh lid, the mineral is sieved through the mesh with aid of a shaker.
2. 0.200 g of sieved brine is added to a 20.0 ml test tube
3. The selected brine is now added to the 10.0 ml mark.
4. The test tube is now shaken with a shaker and placed in the oven to age for 48 hours at reservoir temperature.
5. 4 ml of the brine aged with mineral is removed for pH measurement.
6. The remaining water phase is now removed with a pasteur pipette and added to the 4 ml brine used for pH measurement.
7. 3 ml of stock tank oil is added to the test tube with mineral and shaken, the sample is then left to age at reservoir temperature for 48 hours.
8. The removed brine in step 5 and 6 is now added back with the oil and mineral. This mixture is shaken and placed in the oven to settle at reservoir temperature for 24 hours.
9. The 3 phase volumes mineral, brine and oil are now measured. The particles floating at the top with the oil phase is considered oil wet and the accumulated mineral at the bottom considered water wet.
10. The oil phase is removed with a pasteur pipette
11. If oil still remain on the test tube wall, the test tube is filled to 10 ml mark with brine and 3 ml of n-Decane.
12. The sample is left in the oven for one hour before it is shaken and left in the oven at reservoir temperature for 24 hours.
13. The n-Decane is removed with the remaining crude oil.
14. This proses is repeated until all the crude oil has been removed from the test tube.
15. If all the crude oil, n-Decane and oil wet particles are removed the sample is ready to be filtered through a 0.22 μm filter paper.

16. Two samples of 10 ml of each brine is also filtered to later compensate for extra weight from salt on the filter paper.
17. The filter papers are placed in the oven to dry. The filter papers are weighed regularly until the weight is stable.

3.4 pH-meter

1. The pH (pHm 92 lab pH meter) meter is first calibrated in the expected pH range, below or above pH 7. A minimum calibration accuracy is set to 95 %.
2. The electrode is cleaned with de-ionised water and dried with a paper towel between each sample.
3. The electrode is cleaned and placed back in a pH 4 buffer.

3.5 Fe³⁺ concentration determined by spectrophotometer

1. Prepare four samples with increasing concentration of Fe³⁺.
2. Add 1.0 ml of each solution to a 10.0 ml test tube
3. Add 4.0 ml of 2.0 M thiocyanate to each test tube and shake the sample.
4. Fill the cuvette and measure the absorbance at a wavelength of 447 nm.
5. It is important that each sample is measured 15 minutes after thiocyanate is mixed in with the sample.
6. When the four samples has been measured a graph can be made, Fe³⁺ ppm vs absorbance.
7. From the trend line in this plot other unknown samples can be determined.
8. The unknown samples should always be in the same range as the known samples.

4 Results

The results from the flotation experiments will be presented graphically in column diagrams where each sample is presented as a column. The height of each column represents the weight percent of oil-wet mineral lost to the oil phase. The yellow columns represent an average of the previous duplicate samples. Whereas the n-Decane or n-C₁₀ is represented with a red contour around on each column. The brine composition and oil type is represented in the legend.

At the end of the results the brine pH before and after aging with a mineral and its percent oil-wet mineral is presented in a table.

4.1 Flotation results

4.1.1 Glaucosite

4.1.1.1 Formation water

From the results presented in Figure 7 glaucosite is clearly water-wet. The n-C₁₀ reference samples represents loss of mineral without polar crude components and are about 2w% for glaucosite in Fw1. The Fw1/STO1 samples is about 5w% oil-wet which is significantly higher than for the n-C₁₀ indicating that glaucosite is affected by the crude. Glaucosite was also slightly affected by an increase in the total acid number TAN and increased from 5w% for STO1 to 6w% for STO2. The lower saline brine Fw2 was aged in STO2 to see how glaucosite is affected by a lower cation concentration. The result was 3.5w% for Fw2/STO2 which is lower than Fw1/STO1 and Fw1/STO2. This shows that a lower cation concentration is a dominating factor since Fw1/STO1 samples was more oil-wet then Fw2/STO2.

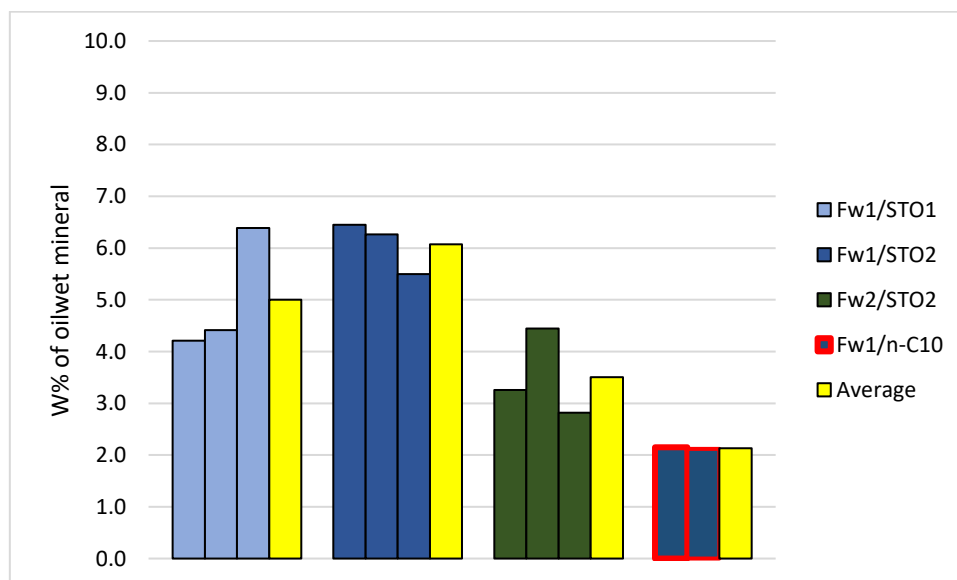


Figure 7. Glaucosite. Flotation results where Fw1, Fw2, STO1 and STO2 were used, the average of each series are in yellow.

4.1.1.2 Ferric ion

Figure 8 presents glauconite aged in brines where Fe^{3+} is added to Fw1 and Fw2. The ferric ions was added to the brine after filtration except for the Fw1/ Fe^* /STO1 samples, this resulted in a loss of Fe^{3+} , the concentration was determined by a spectrophotometer to be 12ppm (Figure 9). Another special case is the Fw1/ H^+ +OH/ Fe /STO1 where HCl was added to make Fe^{3+} more soluble when the brine is shaken with the glauconite, after the samples was shaken an equal amount of NaOH was added.

Some small variations can be observed in the STO1 samples from Figure 8 where the 12ppm Fe^{3+} samples have the highest weight percent of oil-wet particles. It is worth mentioning that Fw1/ Fe /STO1 samples where aged in a brine with pH 2.5 while the other samples where aged in a pH of 6 (Table 4, Table 5, Table 6). With this in mind the different results with STO1 seems to be linked to pH as the samples aged in low pH are less oil-wet. The Fw1/ Fe /STO1 samples are actually not affected by adding Fe^{3+} to the brine when comparing with Fw1/STO1. However the Fw1/ Fe /STO2 samples are clearly the most oil-wet as seen in Figure 8 the same effect as seen with Fw1/STO2 only now the difference is greater. As for the Fw2/ Fe /STO2 samples no effect is observed by adding Fe^{3+} to the brine as only 2.4w% of the mineral was oil-wet.

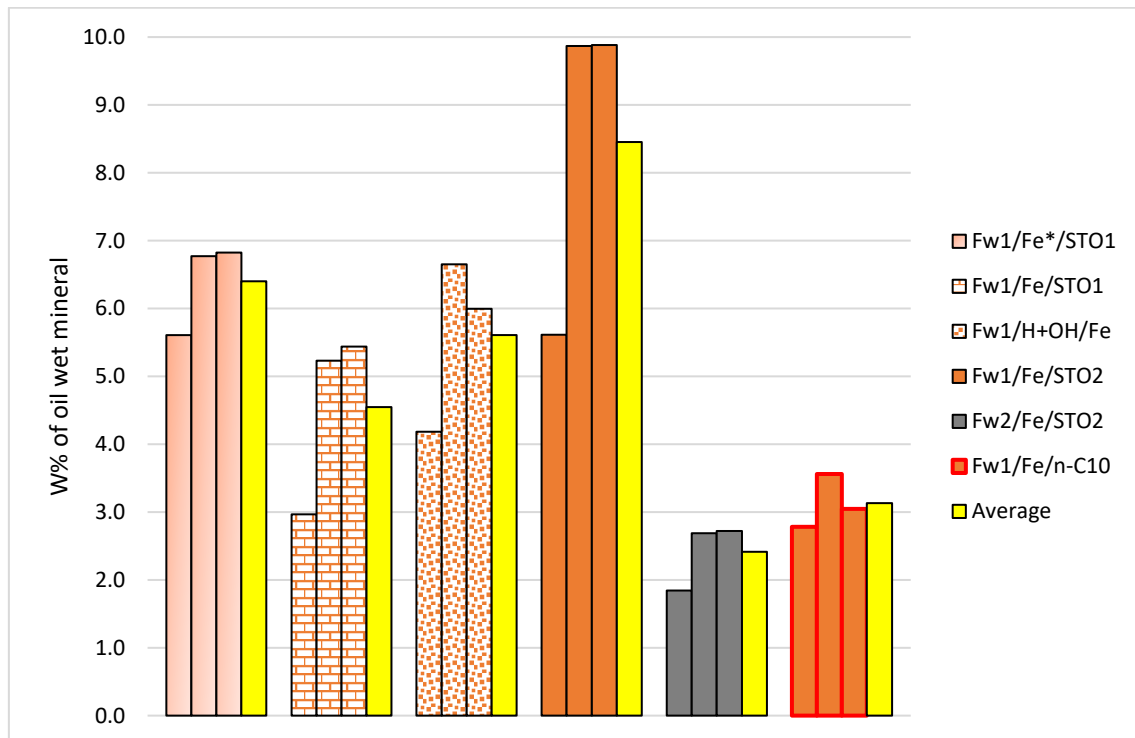


Figure 8. Glauconite. Flotation results where 50 ppm of Fe^{3+} is added to Fw1 and Fw2, the exception is Fe^* where 12 ppm is used. Two different oils where used STO1 and STO2. For Fw1/H+OH/ Fe HCl was added to the brine and shaken then the same amount of mole NaOH was added and then shaken, this happened before brine and mineral is aged.

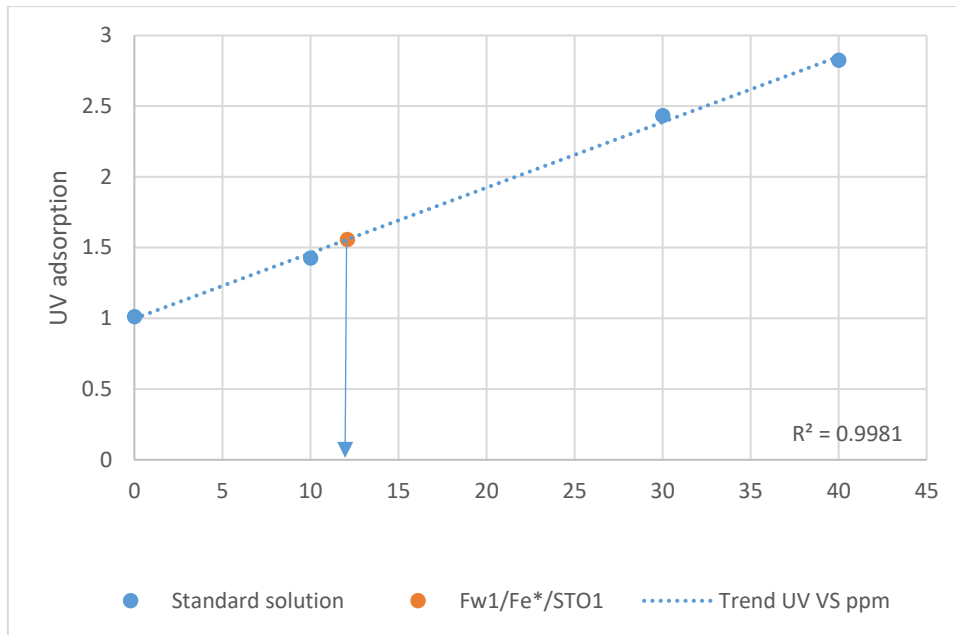


Figure 9. Spectrophotometer. The adsorption of four standard solution where plotted to find the concentration of the filtered brine.

4.1.1.3 EDTA

Figure 10 presents glauconite aged in Fw1 and Fw2 with added 16.9 m mole/l EDTA and 1.69 m mole/l EDTA*. Glauconite is increasingly oil-wet with decreasing EDTA concentration when aged in FW1 and STO1. However when 16.9 m mole/l EDTA is added to Fw1/STO2 the w% of oil-wet particles is 11%. This shows a significant effect of increasing the TAN in the crude when EDTA is mixed in with Fw1. As for the Fw2/EDTA/STO2 samples glauconite is as oil-wet as the n-C₁₀ samples. The pH for each brine before aging was: Fw1/EDTA*/STO1 (6.4), Fw1/EDTA/STO2 (7.0), Fw1/EDTA/STO2 (5.4) and 5.9 for Fw2/EDTA/STO2.

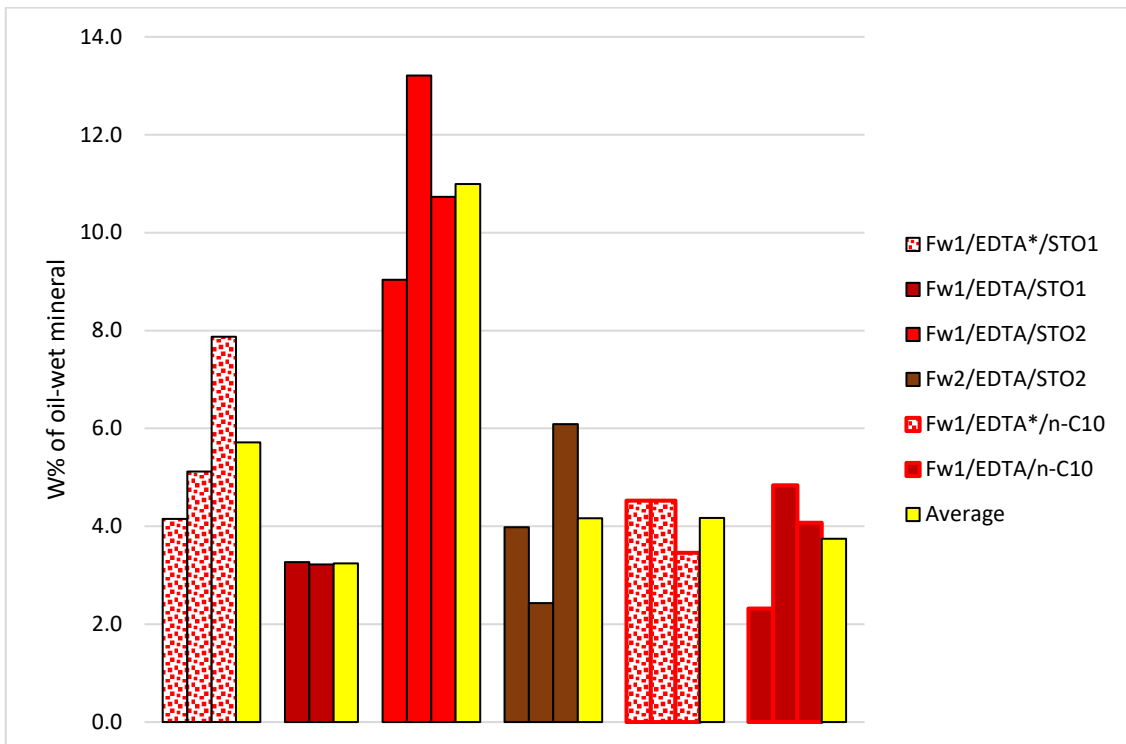


Figure 10. Glauconite. Flotation results where Fw1 and Fw2 has a 16.9 m mole/l of EDTA concentration. Two oils where used STO1 and STO2. EDTA* is a ten times lower EDTA concentration of 1.69 m mole/l.

4.1.1.4 EDTA/Fe³⁺

In Figure 11 both 16.9 m mole/l EDTA and 50ppm Fe³⁺ is added to Fw1 and Fw2. The results in Figure 11 are very similar to those in Figure 10. The Fw1/EDTA*/Fe/STO1 samples are slightly more oil-wet then Fw1/EDTA/Fe/STO1 which is the same effect seen when 50 ppm Fe³⁺ was not added. Hence a reduction in EDTA concentration increased the amount of oil-wet particles. The Fw1/EDTA/Fe/STO2 was about 10.4w% oil-wet which is about the same as for Fw1/EDTA/STO2 and Fw1/Fe/STO2. This can mean that the STO2 is limiting factor since the oil wetness was not further increased when both EDTA and Fe³⁺ was added to the brine. Although one cannot rule out that EDTA and Fe³⁺ had an effect on each other that limited a higher concentration of oil-wet particles.

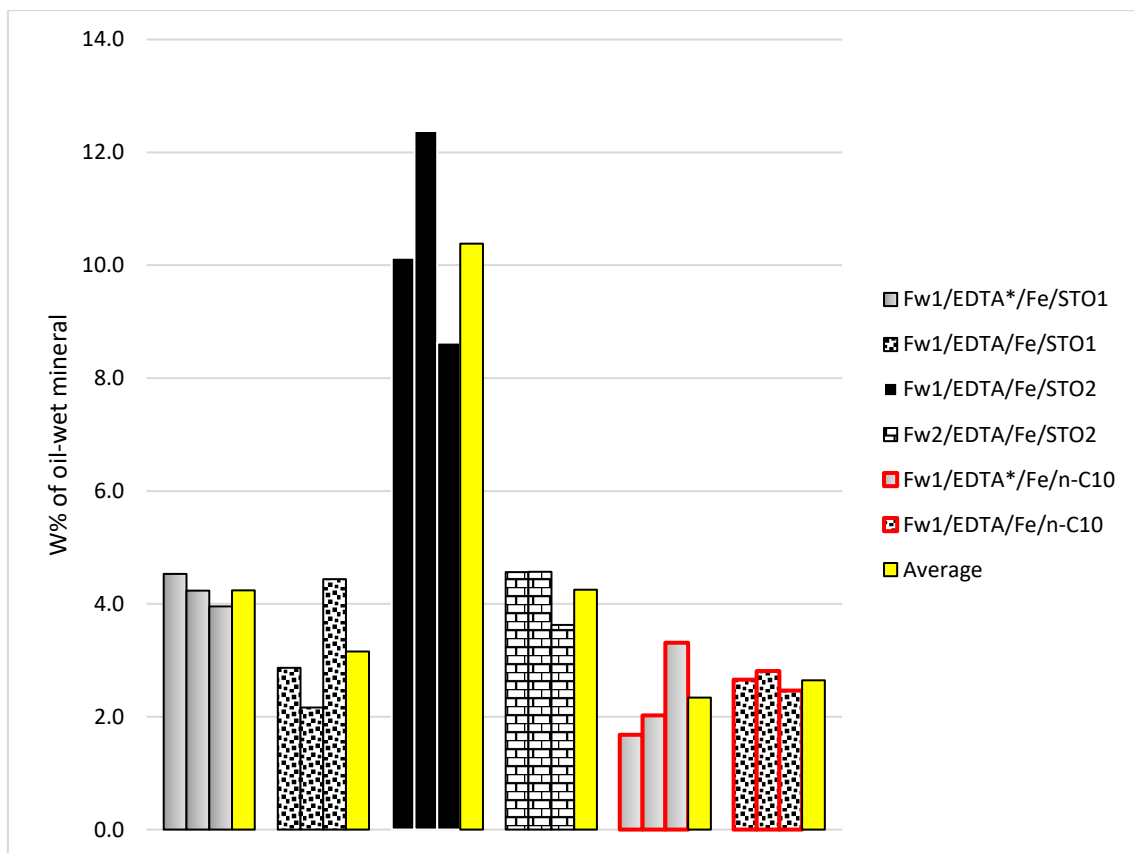


Figure 11. Glauconite. Flotation results where 50 ppm Fe³⁺ and 16.9 m mole EDTA or 1.69 m mole EDTA* is added to Fw1 and Fw2. Oils used are STO1 and STO2.

4.1.1.5 Summary of STO2

Figure 12 is a summary of the glauconite samples mentioned so far which have been aged in STO2. By observing Figure 12 it is obvious that Fw2 with a lower salinity has had a positive effect and represents the most water-wet samples. When the salinity was increased to Fw1, glauconite became more oil-wet. When Fe³⁺ was added to Fw1 and Fw2 the concentration of oil-wet particles increased further for Fw1 but not for Fw2. When EDTA was added to Fw1 the oil wetness increased to almost the double, only a small increase was observed for Fw2. When both Fe³⁺ and EDTA was added to Fw1 and Fw2 no further increase in oil-wet particles was observed.

The deviation of the glauconite samples in STO2 are plotted in Figure 13. The standard deviation of the glauconite samples resemble somewhat the Fe₂O₃ samples mostly in the 0.2-1.2 range.

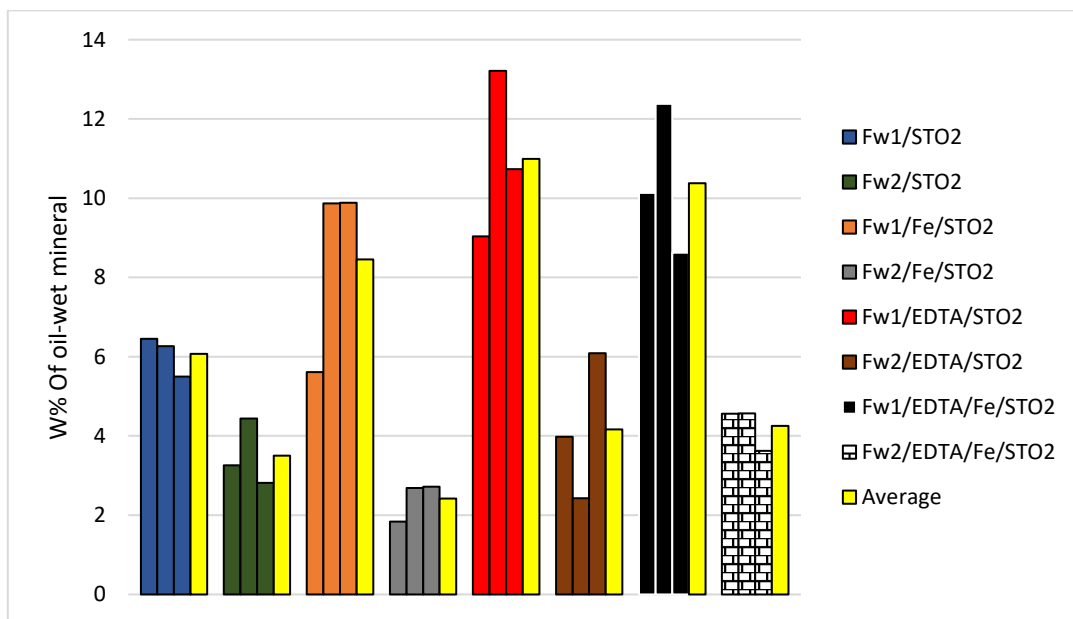


Figure 12. Glauconite STO2. A summary of glauconite aged in different brines and STO2.

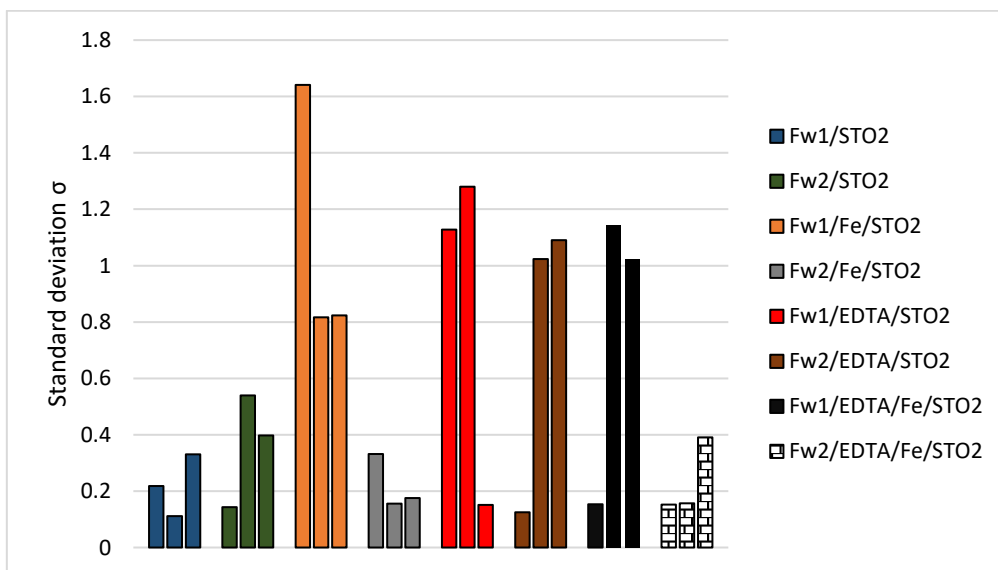


Figure 13. Glauconite STO2. The standard deviation of each sample in Figure 12.

4.1.1.6 pH effect

A correlation between pH after aging and the concentration of oil-wet particles is presented in Figure 14. The trend line indicates that glauconite is very sensitive to pH in the 6.8 to 7.3 range when aged in ST02. However an increase in the concentration of oil-wet particle seems correlate with an increased pH.

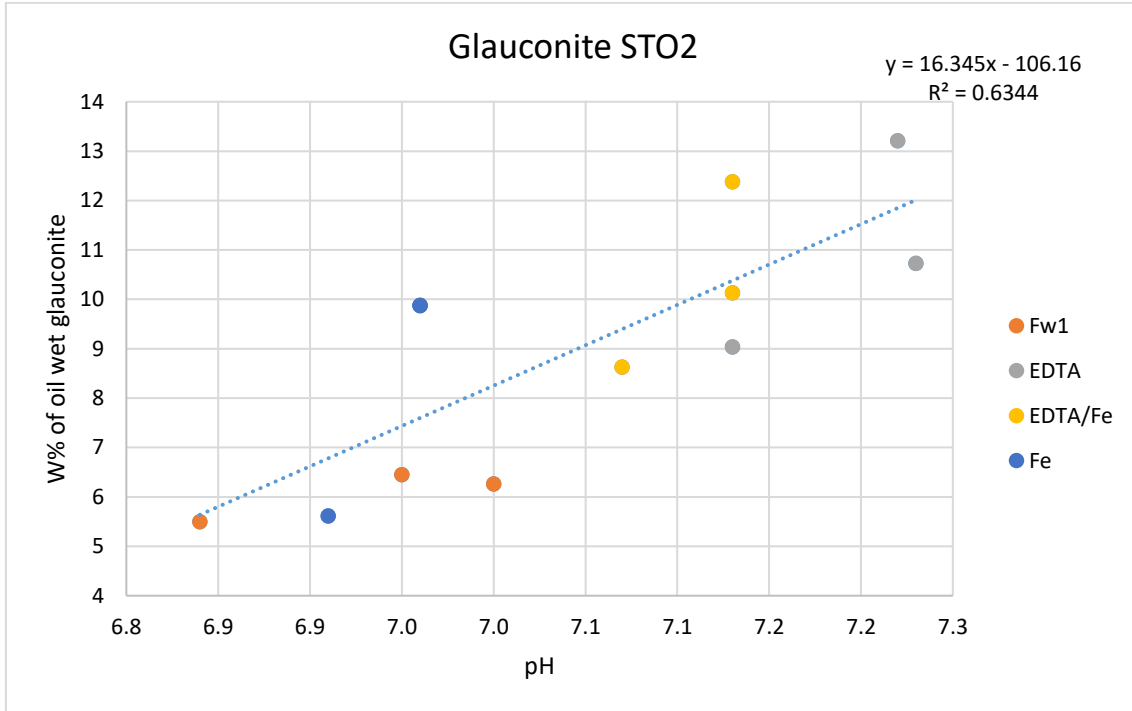


Figure 14. Glauconite w% vs pH. The plot shows pH vs w% oil-wet particles or the pH sensitivity of glauconite.

4.1.2 Hematite

From Figure 15 Fe_2O_3 is close to 100% oil-wet for STO1 and STO2. EDTA has clearly reduced the concentration of oil-wet particles for both Fw1/EDTA/STO1 and Fw1/EDTA/STO2. However the EDTA samples mixed with a lower TAN oil has a higher concentration of oil-wet particles, which is the opposite effect seen in the glauconite samples. Although the pH of the brines were not the same, the more oil-wet Fw1/EDTA/STO2 had a brine pH of 2.9 and the Fw1/EDTA/STO1 had a pH of 5.4.

The n-C₁₀ samples has a relatively high concentration of oil-wet particle of 18.3w% for Fw1/n-C₁₀ and 12.2w% for Fw1/EDTA/n-C₁₀. This is similar to what is seen in the crude oil samples.

The brine was observed changing colour from transparent to yellow when aged in EDTA, this is probably a result of EDTA dissolving some hematite.

The standard deviation for each sample is presented in Figure 16 where Fw1/EDTA/STO1 has the least stable results. No correlation in brine and deviation can be observed.

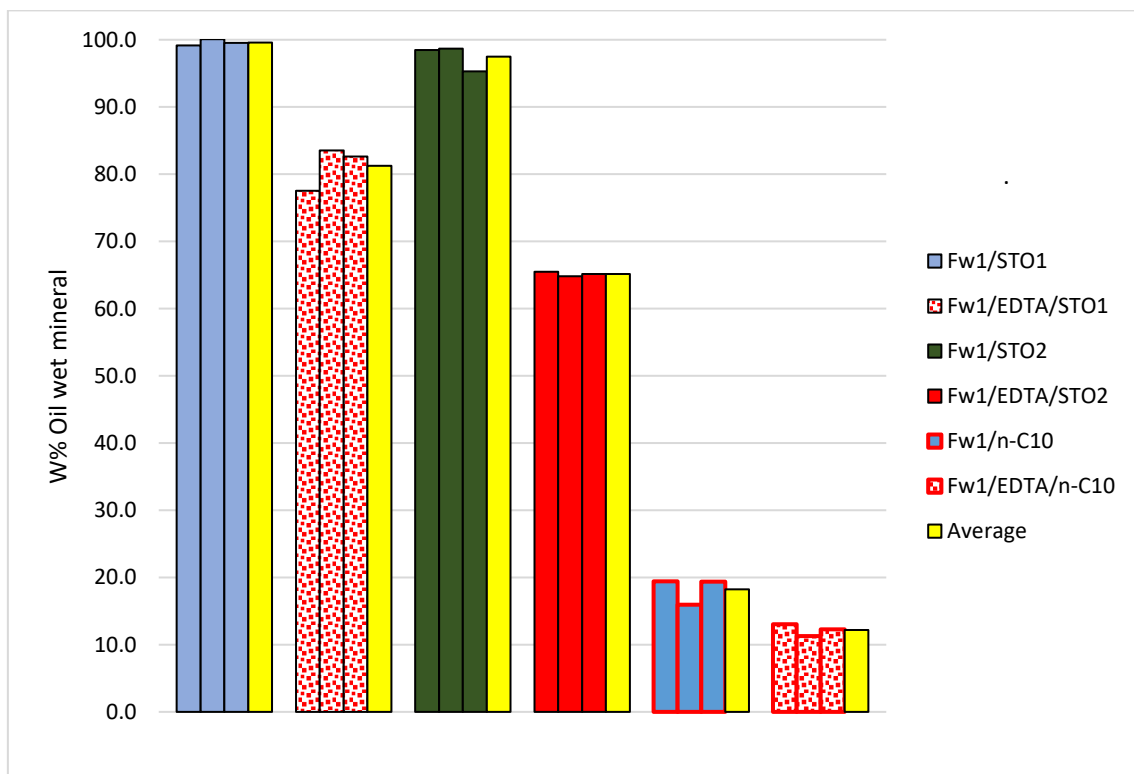


Figure 15. Hematite Fe_2O_3 . Flotation results where Fe_2O_3 is aged in Fw1, and Fw1 with 16.9 m mole EDTA. Two oils were used STO1 and STO2.

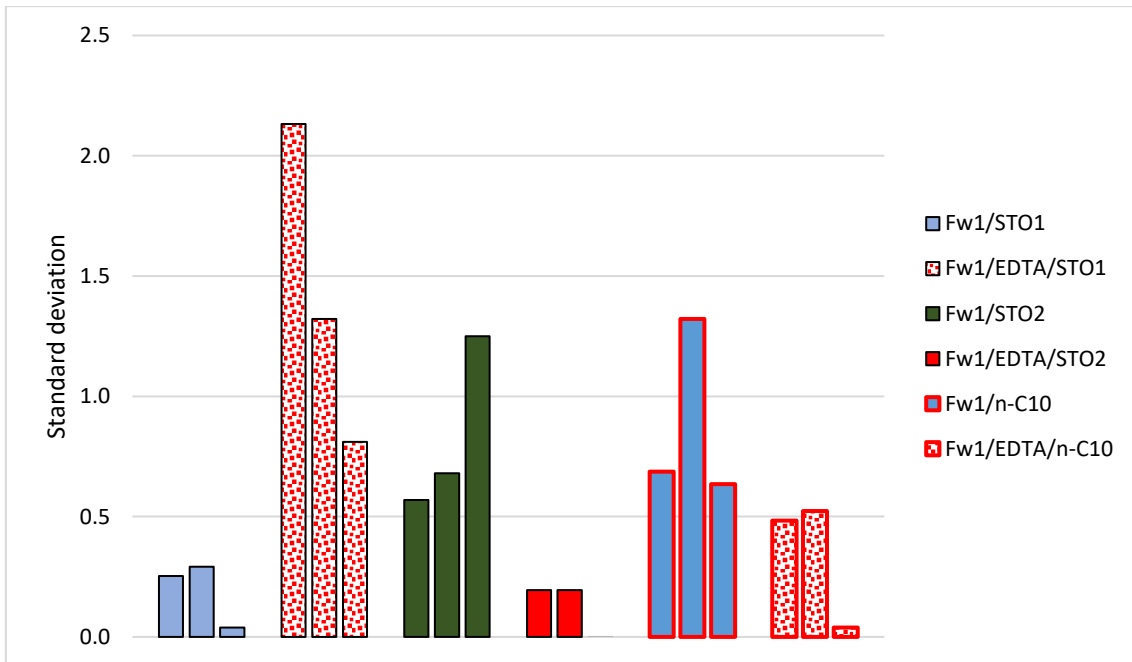


Figure 16. Hematite standard deviation. The figure shows the standard deviation of each sample in Figure 15.

4.1.3 Goethite

The results for FeOOH is in many ways similar to those for Fe₂O₃. The samples aged in STO1 or STO2 with Fw1 was 100% oil-wet. The EDTA in the brine reduced the concentration of oil-wet particle although no difference was observed between Fw1/EDTA/STO1 and Fw1/EDTA/STO2. The concentration of oil-wet particle was also higher than for hematite at about 91%.

The concentration of oil-wet particles is also higher for the n-C₁₀ samples where Fw1/n-C₁₀ is 51.9w% oil-wet and 28.1w% for Fw1/EDTA/n-C₁₀. The pH for each brine and sample after aging is presented in Table 4, Table 5 and Table 6.

The standard deviation for Fw1/n-C₁₀ is between 2.2 and 6.6, this is higher than any of the Fe₂O₃ samples. The FeOOH was observed to behave differently than the Fe₂O₃ when the oil and mineral was mixed alone, the volume expanded to about 13ml for FeOOH when Fe₂O had no volume change. FeOOH also had a stronger tendency to stick to the glass Figure 17.

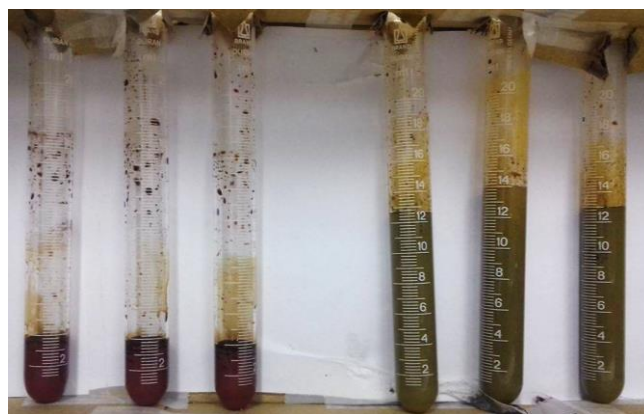


Figure 17. To the left Fe₂O₃ and FeOOH to the right, the image is taken after 48 hours of aging in STO1.

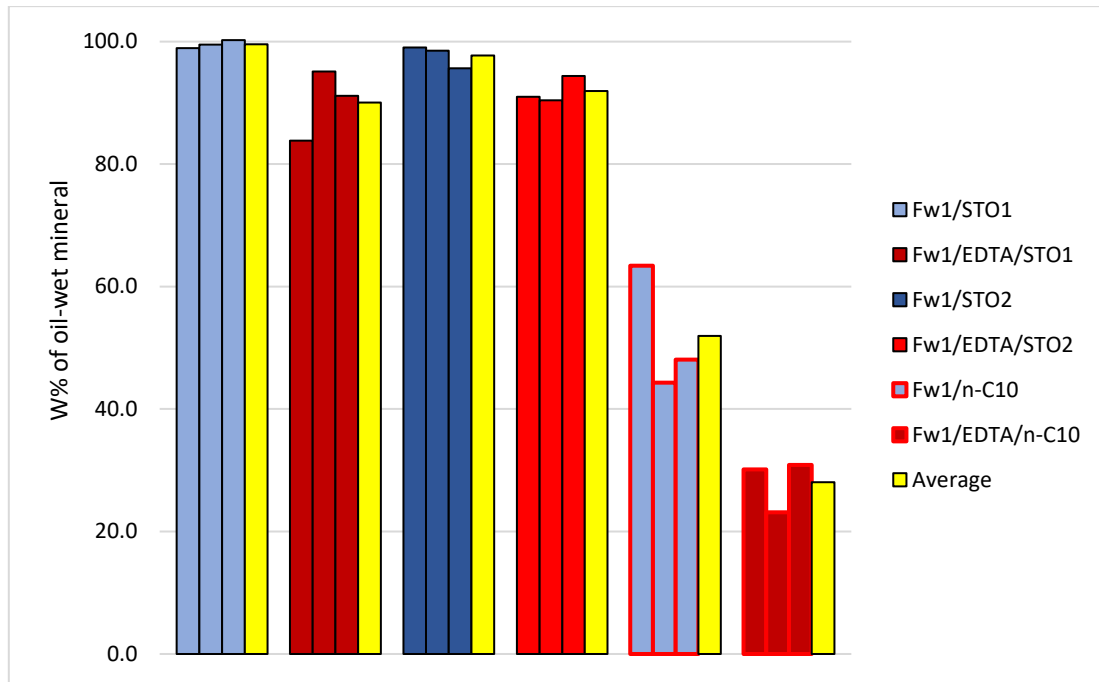


Figure 18. Goethite (FeOOH). Flotation results where iron hydroxide is aged in Fw1, Fw1 with 16.9 m mole EDTA. Two oils where used STO1 and STO2.

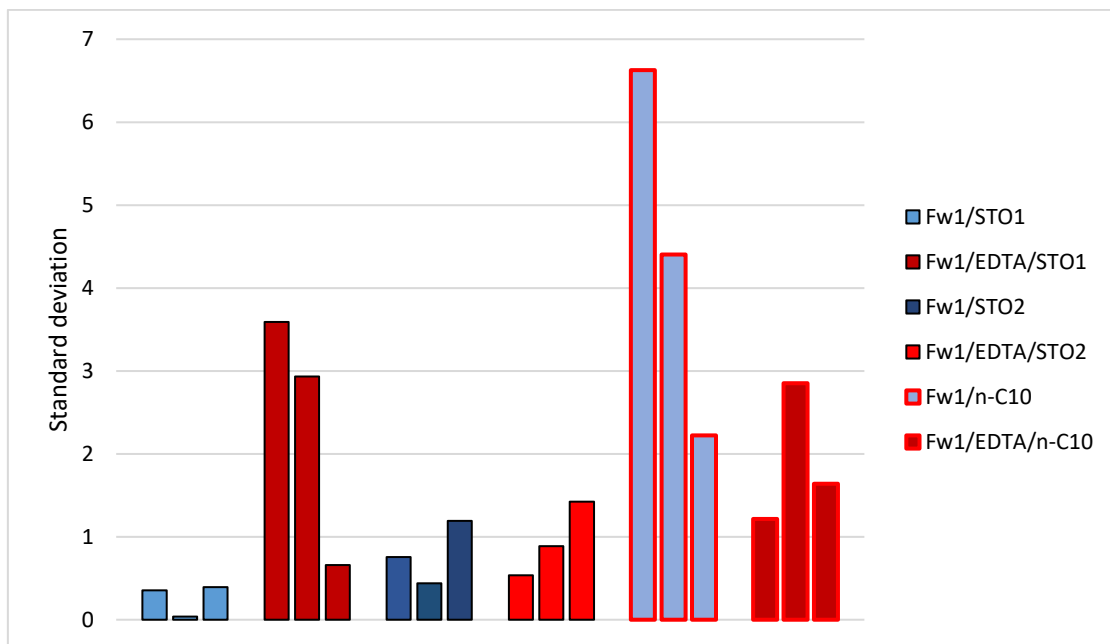


Figure 19. Standard deviation of FeOOH. The figure shows the standard deviation of each sample in Figure 18.

4.1.4 NaHCO₃/EDTA

In this chapter the effect of Fw1 with 16.9 m mole/l EDTA and 67.6 m mole/l sodium bicarbonate (NaHCO₃) has on glauconite, hematite and goethite aged in STO2. When the brine was prepared a white precipitation was observed most likely calcite (CaCO₃). This precipitate has resulted in some negative results although 10 ml of brine is always filtered and subtracted from the weight of the dried samples to compensate for the components in the brine. The samples are negative since more brine is added when the oil phase is removed and this has not been counted for. The pH for the brine used in this experiment was 5.8. There was also a deviation from the flotation procedure where the minerals was aged in the crude oil for 72 hours instead of 48 hours.

Although there is some uncertainties to this experiment the duplicate samples are fairly equal. Glauconite aged in STO2 and n-C₁₀ are close to similar indicating that the glauconite samples are not affected by the crude oil.

The Fe₂O₃ samples are about 90% oil-wet particles in STO2 and slightly negative in n-C₁₀. However the Fe₂O₃ has a higher concentration of oil-wet particles then Fw1/EDTA/STO2 (Figure 15).

The FeOOH samples in STO2 are about 48w% oil-wet. This is a reduction in oil-wet particles when comparing with Fw1/EDTA/STO2 (Figure 18).

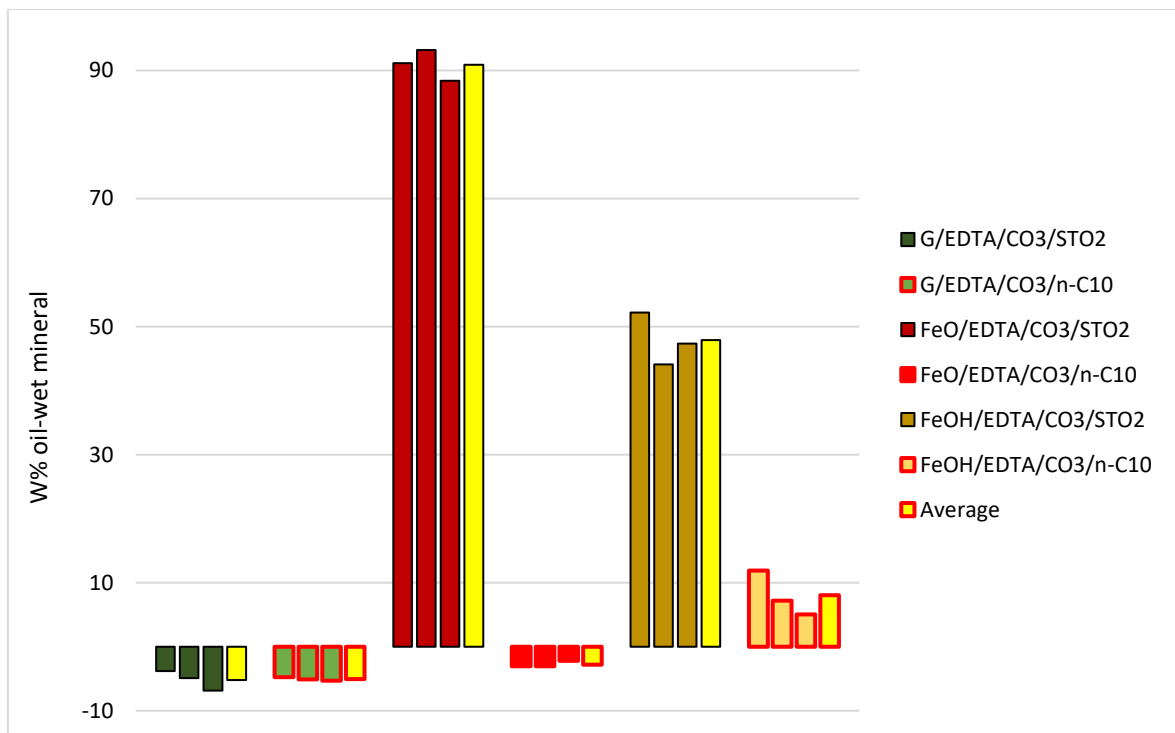


Figure 20. Glauconite, Hematite and Goethite aged in STO2.

4.1.5 Restoration

This experiment is performed without a formation water since the experiment in Figure 20 had problems with a precipitate. The chemicals are added directly to dilute water and all samples are aged in STO2.

Figure 21 shows the results for glauconite aged in several chemicals and a reference brine with only diluted water (DW). The samples were observed to change to a green colour indicating that some glauconite was dissolved.

The results show a high concentration of oil-wet particles for glauconite when only diluted brine is used at 19.5w%. This is higher than any of the previous glauconite samples aged in a formation brine. However the brine aged in EDTA/CO₃/S₂O₃ and CO₃ are the most water-wet at 9.4w% and 4.9w%. The EDTA and S₂O₄ is clearly the most oil-wet samples at 34.4w% and 30.9w%. There may be some correlation between brine pH and the concentration of oil-wet mineral. The pH for each brine: EDTA/CO₃/S₂O₄ (7.4), EDTA (4.7), CO₃ (8.5), S₂O₄ (4.4) and DW (6.1).

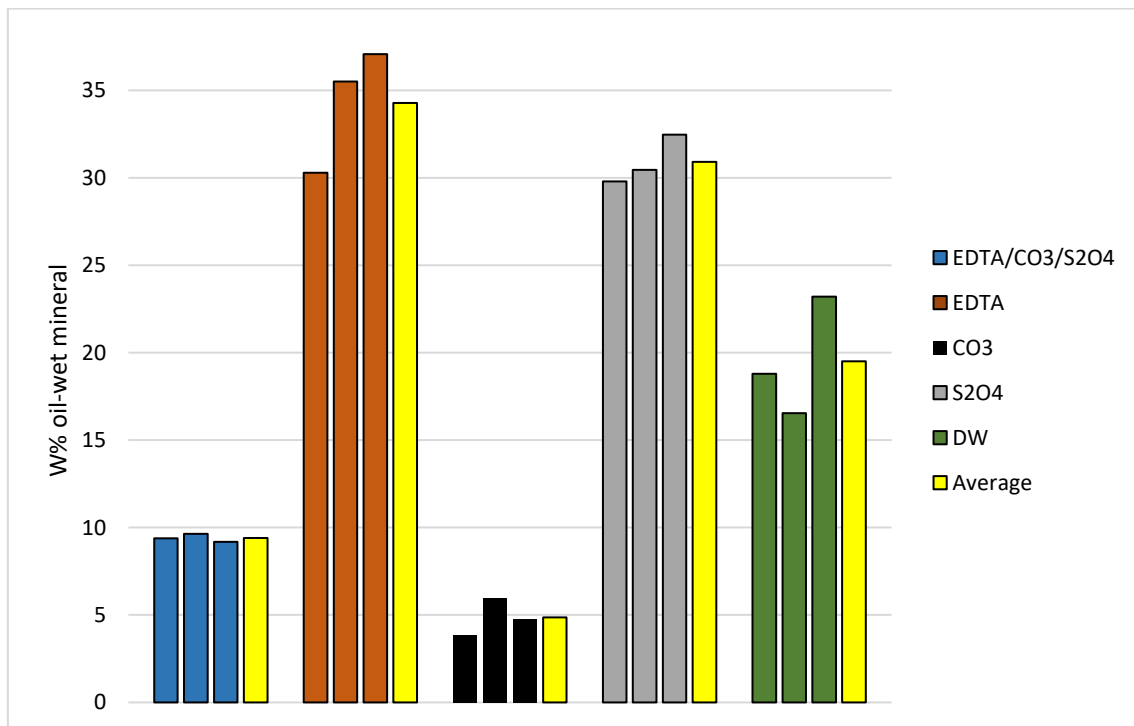


Figure 21. Glauconite STO2.

In Figure 22 Fe₂O₃ and FeOOH are aged in DW and EDTA/CO₃/S₂O₄, and STO2 is used for all samples. The results show that both mineral are 100% oil-wet in dilute water. When the minerals are age in EDTA/CO₃/S₂O₄ the concentration of oil-wet minerals are significantly reduced.

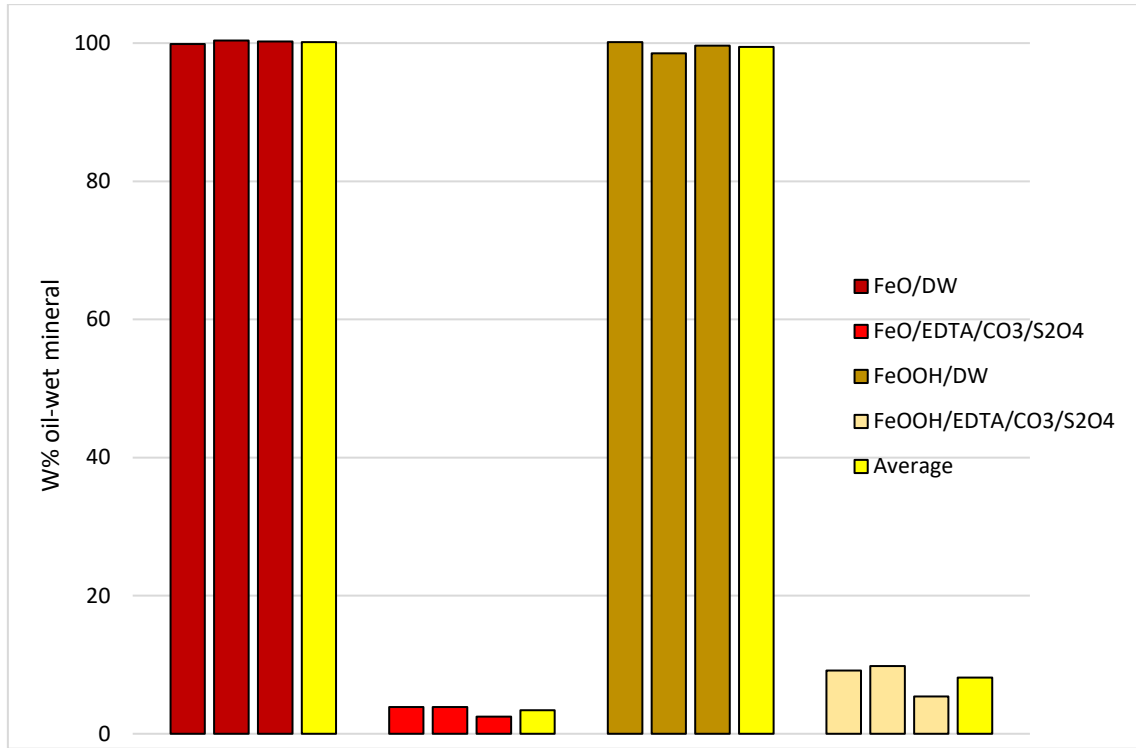


Figure 22. Fe₂O₃ and FeOOH in STO2

4.1.6 All samples

Table 4. Presents the pH before the brine is aged in the mineral, after the brine is aged for 48 hours with the mineral and the w% oil wet mineral for each sample. Fe=50ppm(mg/l) Fe³⁺, Fe*=12ppm(mg/l) Fe³⁺. EDTA=16.9 m mole/l, EDTA*=1.69 m mole/l. G=Glauconite, FeO=Hematite (FeO) and FeOH=Goethite (FeOOH). n-C₁₀=n-Decane a non-polar component.

ID	Brine pH before aging	pH after aging	W% oil-wet		ID	Brine pH before aging	pH after aging	W% oil-wet
Project 1					Project 3			
G/Fw1/STO1/S1	5.7	7.0	6.4		G/Fw1/Fe/EDTA*/STO1/S1	7.0	6.8	4.5
G/Fw1/STO1/S2	5.7	7.1	8.3		G/Fw1/Fe/EDTA*/STO1/S2	7.0	6.9	4.2
G/Fw1/STO1/S3	5.7	7.0	12.1		G/Fw1/Fe/EDTA*/STO1/S3	7.0	6.8	4.0
G/Fw1/n-D/S1	5.7	7.1	2.1		G/Fw1/Fe/EDTA*/n-D/S1	7.0	6.8	1.7
G/Fw1/n-D/S2	5.7	7.0	2.1		G/Fw1/Fe/EDTA*/n-D/S2	7.0	6.8	2.0
G/Fw1/Fe*/STO1/S1	5.8	5.4	5.6		G/Fw1/Fe/EDTA*/n-D/S3	7.0	6.8	3.3
G/Fw1/Fe*/STO1/S2	5.8	5.4	6.8		G/Fw1/Fe/EDTA/STO1/S1	7.1	7.1	2.9
G/Fw1/Fe*/STO1/S3	5.8	5.2	6.8		G/Fw1/Fe/EDTA/STO1/S2	7.1	7.1	2.2
G/Fw1/Fe*/n-D/S1	5.8	5.2	2.8		G/Fw1/Fe/EDTA/STO1/S3	7.1	7.2	4.4
G/Fw1/Fe*/n-D/S2	5.8	5.4	3.6		G/Fw1/Fe/EDTA/n-D/S1	7.1	7.1	2.7
G/Fw1/Fe*/n-D/S3	5.8	4.7	3.0		G/Fw1/Fe/EDTA/n-D/S2	7.1	7.1	2.8
Project2					G/Fw1/Fe/EDTA/n-D/S3	7.1	7.1	2.5
G/Fw1/STO1/S1	5.7	6.1	4.2		G/Fw1/EDTA*/STO1/S1	6.4	6.9	4.1
G/Fw1/STO1/S2	5.7	7.0	4.4		G/Fw1/EDTA*/STO1/S2	6.4	7.0	5.1
G/Fw1/STO1/S3	5.7	7.0	8.0		G/Fw1/EDTA*/STO1/S3	6.4	7.0	7.9
G/Fw1/n-D/S1	5.7	7.0	4.1		G/Fw1/EDTA*/n-D/S1	6.4	7.0	4.5
G/Fw1/n-D/S2	5.7	7.0	4.8		G/Fw1/EDTA*/n-D/S2	6.4	6.3	4.5
G/Fw1/n-D/S3	5.7	7.0	3.9		G/Fw1/EDTA*/n-D/S3	6.4	7.1	3.5
G/Fw1/Fe/STO1/S1	2.5	5.6	3.0		G/Fw1/EDTA/STO1/S1	7.0	7.2	3.3
G/Fw1/Fe/STO1/S2	2.5	5.5	5.2		G/Fw1/EDTA/STO1/S2	7.0	7.3	3.2
G/Fw1/Fe/STO1/S3	2.5	5.5	5.4		G/Fw1/EDTA/n-D/S1	7.0	7.3	2.3
G/Fw1/Fe/n-D/S1	2.5	5.1	4.3		G/Fw1/EDTA/n-D/S2	7.0	7.3	4.8
G/Fw1/Fe/n-D/S2	2.5	5.5	4.2		G/Fw1/EDTA/n-D/S3	7.0	7.3	4.1
G/Fw1/Fe/n-D/S3	2.5	5.5	5.0					

Table 5. Presents the pH before the brine is aged in the mineral, after the brine is aged for 48 hours with the mineral and the w% oil wet mineral for each sample. Fe=50ppm (mg/l) Fe³⁺. EDTA=16.9 m mole/l. G=Glaucinite, FeO=Hematite (FeO) and FeOH=Goethite (FeOOH). n-C₁₀=n-Decane a non-polar component.

ID	Brine pH before aging	pH after aging	W% oil-wet	ID	Brine pH before aging	pH after aging	W% oil-wet
Project 4				Project 5			
FeO/Fw1/STO1/S1	5.7	5.8	99.1	FeO/Fw1/STO2/S1	5.4	5.8	98.5
FeO/Fw1/STO1/S2	5.7	5.8	100.1	FeO/Fw1/STO2/S2	5.4	5.8	98.7
FeO/Fw1/STO1/S3	5.7	6.0	99.5	FeO/Fw1/STO2/S3	5.4	5.4	95.3
FeO/Fw1/n-D/S1	5.7	5.7	19.4	FeO/Fw1/EDTA/STO2/S1	5.4	6.2	65.5
FeO/Fw1/n-D/S2	5.7	6.0	16.0	FeO/Fw1/EDTA/STO2/S2	5.4	6.3	64.8
FeO/Fw1/n-D/S3	5.7	5.9	19.4	FeO/Fw1/EDTA/STO2/S3	5.4	6.3	65.1
FeOH/Fw1/STO1/S1	5.7	5.8	98.9	G/Fw1/STO2/S1	5.4	7.0	6.4
FeOH/Fw1/STO1/S2	5.7	5.8	99.5	G/Fw1/STO2/S2	5.4	7.0	6.3
FeOH/Fw1/STO1/S3	5.7	5.8	100.2	G/Fw1/STO2/S3	5.4	6.8	5.5
FeOH/Fw1/n-D/S1	5.7	5.9	63.4	G/Fw1/EDTA/STO2/S1	5.4	7.1	9.0
FeOH/Fw1/n-D/S2	5.7	5.8	44.3	G/Fw1/EDTA/STO2/S2	5.4	7.2	13.2
FeOH/Fw1/n-D/S3	5.7	5.9	48.1	G/Fw1/EDTA/STO2/S3	5.4	7.2	10.7
FeO/Fw1/EDTA/STO1/S1	2.9	5.4	77.5	G/Fw1/EDTA/Fe/STO2/S1	6.4	7.1	10.1
FeO/Fw1/EDTA/STO1/S2	2.9	5.4	83.5	G/Fw1/EDTA/Fe/STO2/S2	6.4	7.1	12.4
FeO/Fw1/EDTA/STO1/S3	2.9	5.4	82.6	G/Fw1/EDTA/Fe/STO2/S3	6.4	7.1	8.6
FeO/Fw1/EDTA/n-D/S1	2.9	5.3	13.0	G/Fw1/Fe/STO2/S1	6.0	6.9	5.6
FeO/Fw1/EDTA/n-D/S2	2.9	5.4	11.3	G/Fw1/Fe/STO2/S2	6.0	7.0	9.9
FeO/Fw1/EDTA/n-D/S3	2.9	5.3	12.3	G/Fw1/Fe/STO2/S3	6.0	7.0	9.9
FeOH/Fw1/EDTA/STO1/S1	2.9	4.0	83.8				
FeOH/Fw1/EDTA/STO1/S2	2.9	4.0	95.1				
FeOH/Fw1/EDTA/STO1/S3	2.9	4.3	91.2				
FeOH/Fw1/EDTA/n-D/S1	2.9	4.1	30.2				
FeOH/Fw1/EDTA/n-D/S2	2.9	4.1	23.1				
FeOH/Fw1/EDTA/n-D/S3	2.9	4.1	30.9				
G/Fw1/Fe/H+OH/STO1/S1	5.7	6.4	4.2				
G/Fw1/Fe/H+OH/STO1/S2	5.7	5.5	6.7				
G/Fw1/Fe/H+OH/STO1/S3	5.7	6.2	6.0				
G/Fw1/Fe/H+OH/n-D/S1	5.7	6.5	1.9				
G/Fw1/Fe/H+OH/n-D/S3	5.7	6.3	1.0				

Table 6. Presents the pH before the brine is aged in the mineral, after the brine is aged for 48 hours with the mineral and the w% oil wet mineral for each sample. Fe=50ppm (mg/l) Fe³⁺. EDTA=16.9 m mole/l. G=Glaucinite, FeO=Hematite (FeO) and FeOH=Goethite (FeOOH). n-C₁₀=n-Decane a non-polar component. CO₃=67.6 m mole/l sodium bicarbonate, Na₂SO₄= 16.9 m mole/l sodium dithionite

ID	Brine pH before aging	pH after aging	W% oil-wet	ID	Brine pH before aging	pH after aging	W% oil-wet
Project 6				Project 8			
FeOH/Fw1/STO2/S1	5.5	5.5	99.0	G/EDTA/CO3/Na2SO4/STO2/S1	7.39	7.94	9.4
FeOH/Fw1/STO2/S2	5.5	5.5	98.5	G/EDTA/CO3/Na2SO4/STO2/S2	7.39	7.95	9.6
FeOH/Fw1/STO2/S3	5.5	5.6	95.7	G/EDTA/CO3/Na2SO4/STO2/S3	7.39	7.93	9.2
FeOH/Fw1/EDTA/STO2/S1	4.1	4.8	91.0	G/EDTA/STO2/S1	4.72	5.83	30.3
FeOH/Fw1/EDTA/STO2/S2	4.1	4.8	90.4	G/EDTA/STO2/S2	4.72	5.78	35.5
FeOH/Fw1/EDTA/STO2/S3	4.1	4.9	94.4	G/EDTA/STO2/S3	4.72	5.76	37.1
G/Fw2/STO2/S1	5.9	6.7	3.3	G/CO3/STO2/S1	8.5	8.66	3.8
G/Fw2/STO2/S2	5.9	6.9	4.4	G/CO3/STO2/S2	8.5	8.79	6.0
G/Fw2/STO2/S3	5.9	7.0	2.8	G/CO3/STO2/S3	8.5	9.66	4.8
G/Fw2/EDTA/STO2/S1	5.9	7.4	4.0	G/S2O4/STO2/S1	4.35	2.51	29.8
G/Fw2/EDTA/STO2/S2	5.9	7.4	2.4	G/S2O4/STO2/S2	4.35	2.43	30.5
G/Fw2/EDTA/STO2/S3	5.9	7.3	6.1	G/S2O4/STO2/S3	4.35	2.62	32.5
G/Fw2/EDTA/Fe/STO2/S1	6.1	7.2	4.6	G/DW/STO2/S1	6.07	8.77	18.8
G/Fw2/EDTA/Fe/STO2/S2	6.1	7.2	4.6	G/DW/STO2/S2	6.07	8.69	16.5
G/Fw2/EDTA/Fe/STO2/S3	6.1	7.3	3.6	G/DW/STO2/S3	6.07	8.65	23.2
G/Fw2/Fe/STO2/S1	5.9	6.9	1.8	FeO/DW/STO2/S1	6.07	6.9	99.9
G/Fw2/Fe/STO2/S2	5.9	6.9	2.7	FeO/DW/STO2/S2	6.07	6.91	100.4
G/Fw2/Fe/STO2/S3	5.9	7.0	2.7	FeO/DW/STO2/S3	6.07	6.89	100.2
ID	Brine pH before aging	pH after aging	W% oil-wet	FeO/STO2/EDTA/CO3/S2O4/S1	7.39	8.03	3.9
Project 7				FeO/STO2/EDTA/CO3/S2O4/S2	7.39	7.99	3.9
G/STO2/EDTA/CO3/S1	5.8	6.2	-3.8	FeO/STO2/EDTA/CO3/S2O4/S3	7.39	8.08	2.5
G/STO2/EDTA/CO3/S2	5.8	6.3	-4.9	FeOH/DW/STO2/S1	6.07	6.97	100.1
G/STO2/EDTA/CO3/S3	5.8	6.2	-6.8	FeOH/DW/STO2/S2	6.07	6.87	98.5
G/n-D/EDTA/CO3/S1	5.8	6.2	-4.8	FeOH/DW/STO2/S3	6.07	6.9	99.7
G/n-D/EDTA/CO3/S2	5.8	6.3	-5.1	FeOH/STO2/EDTA/CO3/S2O4/S1	7.39	8.09	9.2
G/n-D/EDTA/CO3/S3	5.8	6.2	-5.3	FeOH/STO2/EDTA/CO3/S2O4/S2	7.39	8.13	9.8
FeO/STO2/EDTA/CO3/S1	5.8	6.2	91.1	FeOH/STO2/EDTA/CO3/S2O4/S3	7.39	8.12	5.4
FeO/STO2/EDTA/CO3/S2	5.8	6.2	93.2				
FeO/STO2/EDTA/CO3/S3	5.8	6.3	88.4				
FeO/n-D/EDTA/CO3/S1	5.8	6.3	-3.1				
FeO/n-D/EDTA/CO3/S2	5.8	6.3	-3.1				
FeO/n-D/EDTA/CO3/S3	5.8	6.1	-2.2				
FeO/STO2/EDTA/CO3/S1	5.8	6.6	52.2				
FeO/STO2/EDTA/CO3/S2	5.8	6.6	44.1				
FeO/STO2/EDTA/CO3/S3	5.8	6.6	47.4				
FeO/n-D/EDTA/CO3/S1	5.8	6.7	11.9				
FeO/n-D/EDTA/CO3/S2	5.8	6.7	7.2				
FeO/n-D/EDTA/CO3/S3	5.8	6.6	5.1				

5 Discussion

5.1 Uncertainties in flotation

During a flotation procedure some mineral is lost in the process. Mineral lost in the process will lead to more oil-wet results. Even though the method is estimated to have an error of $\pm 1\%$, it is not always the case as seen in the results. These variations can come from:

- When the brine is removed after 48 hours of aging some mineral is removed and not aged alone with the crude oil. Some mineral is stuck at the glass wall in the pasteur pipettes.
- How many times the test tube is cleaned with n-Decane to remove oil and oil wet particles.
- A very fine grained mineral may float better than a coarser one.
- When the water-wet mineral is filtered some mineral is left on the glass that is pressed on to the filter paper. The glass is placed in the oven for the mineral to dry, then scraped off to the filter paper. This method is not optimum and will have some mineral loss.

These are errors that lead to more oil-wet results, they are also the most likely ones. Errors that lead to more water-wet results are: glass breaks of pasteur pipettes during brine removal and dust accumulating on the dried mineral in the oven.

5.2 Discussion of results

A significant amount of the duplicates came back with a higher uncertainty than the expected of ± 1 . No coherence between the brines was found in the standard deviation figures. Although the iron hydroxide samples had higher standard deviation especially for the n-Decane samples. This can come from a flocculation of the particles, were this seems to have the most effect on the iron hydroxide samples.

5.2.1 Glauconite

The main patterns in the results is that a high saline brine and a high TAN affects glauconite to become more oil-wet. This is in accordance with the hypothesis that polar components as carboxylic acid adheres to di- and tri-valent cations at the clay surface (Austad et al., 2010). Another major trend is the pH effect illustrated in Figure 14 where the w% oil-wet particles increased with increasing pH. The reason for this is most likely that the proton in carboxylic acids is not liberated from the molecule and less polar carboxylate ions are formed.

In Figure 7 the concentration of oil-wet particles increases when the total acid number is increased from Fw1/STO1 to Fw1/STO2. However when the salinity is lowered in Fw2/STO2 and the TAN is kept high the oil wetness drops, most likely due to a lack of di-valent cations to adsorb polar oil components.

As three valent iron is added to the brines as in Figure 8 no significant increase in oil wetness is observed when comparing Fw1/STO1 and Fw1/Fe/STO1. The explanation for this can be that the brine with Fe^{3+} had a very low pH at about 2.5 before the brine and mineral was aged. The pH after aging was around 5.5 indicating that the

mineral has acted as a base and adsorbed H^+ cation. This would prevent Fe^{3+} , Ca^{2+} and Mg^{2+} to be adsorbed at the glauconite surface, since the mineral surface has a higher affinity for H^+ . However Fw1/Fe/STO2 had a significant increase to about 9w%. To compare Fw1/Fe/STO1 and Fw1/Fe/STO2 is difficult due to the pH difference, this should be tested to see if it's a pH effect or a TAN effect. Although Fw1/STO2 and Fw1/Fe/STO2 had approximately the same pH, the increase in oil-wet particles can therefore be assumed to come from the Fe^{3+} in the brine.

When EDTA was added to Fw1 and Fw2 the wettability increased to an average of 11w% for Fw1/EDTA/STO2 which is even higher than for Fw1/Fe/STO2 at an average of 8.5w%. However the EDTA was expected to chelate the di- and tri-valent cations and reduce the concentration of available cations at the surface resulting in a higher concentration of water-wet particles. However if EDTA had dissolved some of the glauconite this would also affect the Fw1/n-C₁₀ samples which were low at 3.7w%. Although the mechanism behind the increase in oil-wet particles when EDTA is added is unclear. However the salinity is affecting it, as seen when the salinity is reduced in Fw2/EDTA/STO2 where the concentration of oil-wet particles is also reduced.

When 50 ppm Fe^{3+} was added to Fw1/EDTA and Fw2/EDTA no significant change in wettability was observed. 50 ppm iron is only 0.9 m mole this would only occupy a small part of the 16.9 m mole EDTA.

In Figure 14 the w% of oil-wet glauconite is plotted vs pH where the oil-wetness increases with increasing pH. The reason for this can be that the low pH results in more H^+ adsorbed at the surface reducing the number of divalent cations that can adhere and create cation bridging with carboxylate. The low pH will also reduce desorption of H^+ from carboxylic acid lowering the amount of polar components in the oil.

5.2.2 Hematite

In Figure 15 hematite is approximately 100% oil-wet for both Fw1/STO1 and Fw1/STO2. When EDTA is added to Fw1, iron oxide becomes less oil-wet for both STO1 and STO2. However Fw1/EDTA/STO2 lost about 15w% more than Fw1/EDTA/STO1 this may be a pH effect as the brine pH for STO1 was 2.9 and 5.4 for the STO2 samples. After aging the STO2 samples had a pH of about 6.2 and the STO1 samples had a pH of 5.6, therefore the STO1 samples adsorbed more H^+ ions affecting its wettability towards more oil-wet. However EDTA makes hematite less oil-wet also for the reference samples (n-C₁₀) indicating that other mechanisms than crud-brine-mineral interaction are affecting the results.

5.2.3 Goethite

Iron hydroxide is also 100% oil-wet for Fw1 in STO1 and STO2 as seen in Figure 18. Although the EDTA samples are about 10% lower for both STO1 and STO2, so no change in w% with different TAN. The reason for this w% loss can be that the EDTA reduces the polarity of the particle and reducing the flocculation.

No coherence in the brines was found in the standard deviation Figure 19 for iron hydroxide. The standard deviation was higher for iron hydroxide than for the two other

minerals especially for the n-Decane samples. This may come from flocculation of the particles or some effect of air reducing the density of the particles. There is also a difference in the n-Decane sample where Fw1/n-D is 24w% higher than Fw1/EDTA/n-D. This indicates again that EDTA reduces the flocculation of the iron hydroxide particles.

5.2.4 EDTA

EDTA was proposed as a chemical to increase recovery in formations with iron rich minerals (Mahmoud et al., 2017). However when EDTA is added to Fw1/STO2 the concentration of oil-wet particles increases (Figure 10). However when EDTA is added to the brines aged with hematite and goethite the concentration of oil-wet particles are reduced. Hence the effect of EDTA on goethite and hematite are the opposite for glauconite.

5.2.5 NaHCO₃/EDTA

Figure 20 shows the samples that were aged in Fw1 with EDTA and CO₃, these samples had problems with carbonate precipitation however they may still be of some use. The glauconite samples are negative, however the n-C₁₀ samples have the same value indicating that adding CO₃ has reduced the concentration of oil-wet particles when comparing with samples like Fw1/STO2 and Fw1/EDTA/STO2.

The hematite samples are most likely not affected by adding carbonate to the brine. However the goethite samples are lower than all other goethite samples aged in Fw and crude oil.

5.2.6 Restoration

In Figure 21 glauconite was not aged in any Fw only chemicals added to diluted water. Glauconite aged in DW and STO2 had an average of 19.5w% oil-wet particles. This is very high compared with all other glauconite samples aged in FW. This is unexpected since previously results show a reduced concentration of oil-wet particles when the salinity is reduced. However the brine samples aged in DW had a change in colour to glauconite green as if fine grained glauconite particles were suspended in the brine. These particles did not settle when aged for 48 hours, indicating that these are very small particles.

As for the glauconite samples aged in EDTA the concentration of oil wet particles was even higher than DW at 34.3w%. Previously glauconite concentration of oil-wet particles has not been very effected by adding EDTA in a brine with low salinity. However in Fw1/STO2 the concentration of oil-wet particles increased when EDTA was added the same effect is seen in DW.

The sodium dithionite samples were 30.9w% oil-wet slightly lower than the EDTA samples. These samples showed no change in the brine colour after ageing. Sodium dithionite can reduce ferric ions to ferrous which can reduce the concentration of oil-wet particles, a direct effect of this cannot be seen from these results. Although the sodium dithionite brine had a pH of 4.4 and it may have worked more efficiently in a more alkaline solution as it may precipitate as solid sulphur in an acidic environment (Rajapaksha et al., 2014).

The samples where all the chemical are added to the brine had an average w%

of 9.4 which is slightly higher than the CO₃ samples at 4.8w%. However the restoration brine EDTA/CO₃/S₂O₄ has reduced the concentration of oil-wet mineral when comparing with the DW samples. This may mean that the glauconite samples have some surficial ferric iron from exposure to the atmosphere. Although the CO₃ samples had an even lower concentration of oil-wet particles at 4.9w%.

The results from the hematite and goethite in Figure 22 are very similar with 100w% oil-wet particles in DW. However the EDTA/CO₃/S₂O₄ samples was 3.4w% for hematite and 8.1w% for goethite. These are the lowest concentration of oil-wet particles for both mineral in this thesis. This may mean that EDTA/CO₃/S₂O₄ can work as a good restoration mix for cores exposed to oxygen.

6 Conclusions

The wettability of glauconite is not significantly affected by adding 50ppm Fe^{3+} or EDTA when aged with STO1. When the TAN is increased to STO2, the effects of brine composition becomes more evident. Effects of brine composition on glauconite:

- Glauconite is 6w% oil-wet in Fw1/STO2
- The concentration of oil-wet particles increases when Fe^{3+} is added to Fw1/STO2.
- EDTA increases the concentration of oil-wet particles when EDTA is added to Fw1.
- When EDTA and Fe^{3+} are added to Fw1/STO2 the concentration of oil-wet particles does not increase further.
- An acidic brine lowers the concentration of oil-wet particles, contrary to the oil, where a higher TAN increases the concentration of oil-wet particles.
- Glauconite is water-wet when EDTA/ CO_3 is added to Fw1 and aged in STO2.
- When the EDTA/ CO_3 / S_2O_4 brine is aged with glauconite the concentration of oil-wet is reduced compared to glauconite aged in DW. This effect is likely to come from the reduction of surficial ferric ions.

Hematite is 100% oil-wet aged in Fw1 with STO1 and STO2.

- EDTA reduces the concentration of oil-wet particles for hematite.
- Hematite is not significantly affected when EDTA/ CO_3 is added to Fw1.
- Hematite is water-wet in the restoration brine EDTA/ CO_3 / S_2O_4 . The change from oil-wet to water-wet is assumed to come from the reduction of Fe^{3+} to Fe^{2+} by dithionite.

Goethite is 100% oil-wet when aged in Fw1 with STO1 and STO2.

- EDTA in Fw1 reduces the concentration of oil-wet particles.
- The concentration of oil-wet particles is reduced when EDTA/ CO_3 is added to Fw1.
- Goethite is water-wet in the restoration brine EDTA/ CO_3 / S_2O_4 . The change from oil-wet to water-wet is assumed to come from the reduction of Fe^{3+} to Fe^{2+} by dithionite.

6.1 Further work

More work should be done to further understand the wettability of glauconite, a few proposals for future work:

After this study it is not clear why EDTA increased the concentration of oil-wet particle in the glauconite samples. How the pH affects the behaviour of EDTA can be tested in a wider pH range.

The flotation method does not give an estimate on how the change in wettability will affect the production. The same brines can be tested on glauconite rich core samples to see if there is a correlation between residual oil saturation and concentration of oil-wet particles from flotation.

7 References

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