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The Role of Surface Active Compounds in Crude Oil on Reservoir Wettability.

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THE ROLE OF SURFACE ACTIVE COMPOUNDS IN CRUDE OIL ON RESERVOIR WETTABILITY

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the degree of
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in

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by
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

This study examines the role of crude oil's surface active compounds (SAC) in determining the reservoir wettability. Wettability describes the relative preference of a reservoir rock for oil or water. Wettability influences the distribution of fluids in a reservoir and the efficiency of oil recovery methods. Unfortunately, the chemical mechanisms controlling wettability in individual reservoirs remain hazy.

Wettability is conditional and is influenced by rock mineralogy, fluid chemistry, and temperature. An extensive experimental study was executed to understand the impact of naturally-occurring SACs typically found in crude oil, on the wettability of sandstone and carbonate rocks over a range of salinities and temperatures. To isolate the effects of individual SACs, this project used model oil mixtures of pure decane and SACs to represent the oleic phase. The four groups of SAC studied are: aromatic, oxygen-bearing, sulfur-bearing, and nitrogen-bearing SACs. Due to the large number of experiments in this study, standard wettability measurement methods were not used due their limitation of the time and expense it takes to run a single experiment. To overcome this barrier, we developed a measurement technique that was fast, reliable, and would serve as both a screening tool and provide quantitative results. This wettability measurement method is known as the modified flotation technique (MFT).

In the quest to determine why low salinity waterflooding is successful in increasing oil recovery in some reservoirs and not in others, this study found that it is crucial to accurately characterize crude oil, brine, and reservoir rock material. This allows one to effectively engineer injection water chemistry which would favorably alter wettability, and maximize oil recovery. The overall effect toward either oil-wet or water-wet conditions was observed to depend more on brine salinity than temperature. As salinity was decreased nitrogen SACs, non-acidic sulfur SACs, and the short chained oxygen SAC shifted the wettability of the carbonate rocks towards water-wet conditions. Long chained acids SACs, acidic sulfur SACs, and aromatics shifted the wettability of carbonates towards oil-wet conditions as brine salinity was decreased. This difference in SACs' reaction to salinity was proposed as one of the reasons why low salinity waterflooding is successful in some reservoirs and not in others.

CHAPTER 1. INTRODUCTION

To meet the global rising energy demand, the oil and gas industry is challenged to maximize oil recovery from the existing hydrocarbon reservoirs. The current global average field recovery from waterflooding is around 35%, leaving between 60 to 70% of oil in place (Shell, 2016). This represents a substantial opportunity for enhanced oil recovery (EOR) processes. EOR methods strive to mobilize crude oil by lowering the interfacial tension (IFT) and/or by altering wettability to a favorable wetting state. The concept of engineering and optimizing the injected water chemistry has proved to be a promising EOR technique popularly known as "low salinity waterflooding (LoSal™)" by BP (Lager et al., 2008), "designer waterflooding" by Shell (Ligthelm et al., 2011), "advanced ion management" by ExxonMobil (Gupta et al., 2009), "smart waterflooding" by (Yousef et al., 2011), and "ionically modified waterflooding" by Sohal et al., 2016).

In the last 2 decades, many experimental studies have been performed to investigate the recovery mechanisms governing low salinity waterflooding. Of the proposed mechanism, wettability alteration has garnered the most attention as the main mechanism controlling the success of low salinity waterflooding. Numerous publications have reported low salinity's success in increasing oil recovery in certain reservoirs (Sylte et al., 1988; Hallenbeck et al., 1991; Jadhunandan & Morrow, 1995; Tang & Morrow, 1997); as others, have reported small to negligible oil recovery improvements (Boussour et al., 2009; Cissokho et al., 2009; Thyne & Gamage, 2011; Al-Shalabi et al., 2014). This has prompted further studies to understand wettability and the mechanisms that control wettability alteration.

Wettability describes the relative preference of a reservoir rock for oil or water, and it is a product of the balance of surface forces between the interaction of oil and water with the surface of the rock. Depending on the specific interactions, the wettability of a system can range from strongly water-wet to strongly oil-wet. Degrees of wetting apply along the wettability continuum, and as shown in this study, the oil chemistry, water chemistry, rock morphology and mineralogy, and temperature govern where in the continuum the rock wettability lies. At a grain level, wettability is homogenous, meaning it is either water-wet or oil-wet. At a reservoir scale, wettability is heterogeneous or fractional-wet (Brown & Fatt, 1956). Fractional wettability states that portions of the rock are water-wet while others are oil-wet. The two forms of heterogeneous/fractional wettability are: mixed-wettability and speckled/spotted/dalmatian wettability. Salathiel (1973) proposed mixed-wettability where oil-wet surfaces form continuous paths through the larger pores, as the smaller pores remain water-wet and contain no oil. Speckled/spotted/dalmatian wettability refers to continuous water-wet surface encompassing areas of discontinuous oil-wet surfaces or vice versa (Morrow et al., 1986; Cuiec, 1991).

Knowing wettability is a key to understanding the distribution of fluids in a reservoir. In addition, it is also the key to engineering more effective and efficient oil recovery methods. However, wettability has proven to be a complicated geochemical problem due to the numerous reservoir parameters that control it. This problem is further exacerbated by standard wettability measurement methods being limited by the time (days to weeks) and expense it takes to run a single experiment. This presents a significant bottleneck for laboratory experiments. Therefore, the chemical mechanisms controlling wettability in individual reservoirs remain hazy.

My goals are to develop a wettability measurement technique that is inexpensive, rapid, and reproducible, and to use it to describe the role of oil surface active compounds (SAC’s) in determining wettability in carbonate and sandstone reservoirs.

CHAPTER 2. LITERATURE REVIEW

2.1. Oil-Rock Adhesion

Wettability represents a balance between cohesive and adhesive forces. In oil wetting of a rock in the presence of water, cohesive forces within the oil cause a drop to ball up and avoid contact with the rock surface (water-wet). Adhesive forces cause oil to spread across the rock surface (oil-wet). At the molecular level, electrostatic (and van der Waals) interactions likely control oil-rock adhesion (Dubey & Doe, 1993; Buckley et al., 1989). Electrostatic interactions are governed by aqueous chemistry, oil chemistry, rock mineralogy, and temperature. Electrostatic forces are caused by interaction between charged oil and mineral surfaces (Busireddy and Rao, 2004; Israelachvili, 2011). The oil surface is charged because polar molecules of nitrogen and oxygen are segregated at the oil-water interface. Mineral surfaces are charged because broken, unsaturated bonds hydrate at the mineral-water interface. Electrostatic interaction can either be repulsive, attractive, or a combination of both (Hirasaki, 1991). Historically, quantitatively linking electrostatics with wettability and oil recovery has been limited by three factors: (1) multiple electrostatic mechanisms can operate simultaneously preventing determination of the individual contributions, (2) experimental and field data from cores are the sum of chemical and physical processes, making it difficult to isolate the specific chemical role of surface charge; and lastly, (3) surface charge measurements on rocks have typically been measured using zeta potentials, which are not easily converted into mechanistic and predictive thermodynamic models (Brady et al., 2015).

SACs make up the charged sites at the crude oil-water interface and are the most likely to interact electrostatically with the rock surface, and control wettability and recovery. SACs are likely to be mostly nitrogen bases and carboxylic acids attached to non-polar hydrocarbon chains/rings. This project tests the newly developed wettability measurement technique by measuring the role of individual of SACs on oil adhesion to carbonate and sandstone minerals.

2.2. Surfaces Forces Influencing Rock-Oil-Brine Interaction

Derjaguin, Landau, Verwey, Overbeek (DLVO) theory suggests that the interaction forces between rock, oil, and brine have three components: (1) van der Waals forces, (2) structural forces, and (3) electrostatic interactions (e.g. Israelachivili, 2011).

2.2.1. van der Waals Forces

The van der Waals force acts between two materials and is typically attractive and results from polarization between the particles on the molecular scale. While this force is not as strong as electrostatic or hydrogen bonding interactions, it is always present. Gregory (1981) derived the expression below for the retarded London van der Waals attractive force acting on two parallel infinite plates

$$\mathbf{\Pi_{LVA}} = \frac{\mathbf{A\left(15.96\frac{h}{\lambda_{lw}}+2\right)}}{\mathbf{12\pi h^3\left(1+5.32\frac{h}{\lambda_{lw}}\right)^2}} \qquad \text{Equation 1}$$

where A is the Hamaker constant in an oil/water/solid system, h is the distance between the two plates, and λ_{lw} is the London wavelength. The van der Waals force can be characterized by the Hamaker constant of a particular solid-liquid-liquid system. A negative Hamaker constant indicates a repulsive field while a positive Hamaker constant indicates an attractive field (Busireddy & Rao, 2004). The Hamaker constant is a coefficient of the dependence of energy on distance and is strongly dependent on the materials in the system.

2.2.2. Structural Forces

Structural forces are short range interactions at a distance of less than 5 nm, whereas the van der Waals and electrostatic forces are long-range interactions. These forces result when two interfaces approach a distance of a few orders of molecular diameter. At this point, the continuum theories of attractive van der Waal's and repulsive double layer forces fail to describe surface interactions (Israelachivili, 2011). The effects of other short range forces, such as solvation, structural, and hydration forces, become the dominating force. Hydration forces dominate for brine/water systems. The expression below is used to calculate this force:

$$\Pi_S(h) = A_s e^{\left(-\frac{h}{h_s}\right)} \qquad \text{Equation 2}$$

where A_s is a constant, h_s is decay length, and as h is distance. There are two types of hydration forces: (1) Short range hydration forces which are typically observed in aqueous media. The decay length is usually about 0.4-3 nm (Busireddy & Rao, 2004). (2) Hydrophobic hydration forces are long-range forces between two similar surfaces. They also dominate when the surfaces are hydrophobic (no polar groups, or unsaturated bonds). The decay lengths are in the range of 2-32 nm.

2.2.3. Electrostatic Forces

Oil or mineral surface charge (Stern layer) is balanced by an outer layer of counterions (Gouy-Chapman layer). The surface charge plus counterions are termed the electric double layer (EDL) (Figure 1). When the oil and mineral double layers approach each other, electrostatic interaction will occur. When two charged bodies approach each other in a vacuum the interactions are governed by Coulomb's law. The electrical field near a charged surface decays approximately exponentially with a decay length called the Debye length that is inversely proportional to the square root of the electrolyte concentration. This force is estimated using the zeta (ζ) potential for the interfaces of the system, and is approximated by (Gregory, 1975)

$$\Pi_{DLR} = n_b k_B T \left(\frac{2\psi_{r1}\psi_{r2}\cosh(kh) - \psi_{r1}^2 - \psi_{r2}^2}{(\sinh(kh))^2}\right) \qquad \text{Equation 3}$$

$$\psi_{ri} = \frac{e\xi_i}{k_B T} \qquad \text{Equation 4}$$

where k is the reciprocal of the Debye-Huckle double layer length, n_b is the ion density of the bulk solution, and k_B is the Boltzmann constant.

2.2.3.1. Zeta Potential

Zeta potential is the electrostatic potential measured at the shear plane which is below the diffuse layer (Jaafar & Pourbasirat, 2011; Jaafar et al., 2014). Electrostatic potential arises from fluid flowing past the solid surface, due to the excess charges in the diffuse layer being dragged with the flow of the fluid (Hunter, 1981) (Figure 1).

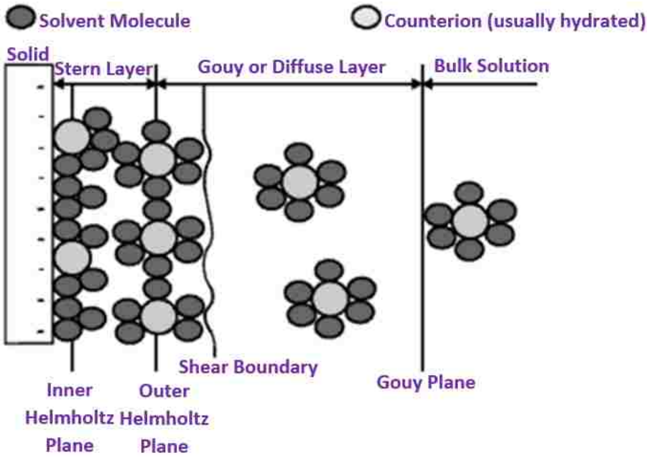


Figure 1: Electric double layer model (e.g. Davis et al., 1978).

The magnitude of the zeta potential gives an indication of the oil or mineral surface charge. The pH at which the total net charge is zero is known as the Zero Point of Charge (ZPC) or isoelectric point. The isoelectric point of sandstone and carbonate is pH ~ 3, and pH ~ 9, respectively, though the chemical composition of the bulk fluid can affect the latter value. The ZPC of crude oil is ~ pH 5 (e.g. Dubey & Doe, 1993). Below pH ~ 5, crude oil surfaces are positively charged because of the presence of nitrogen bases; above pH ~5 crude oil surfaces are negatively charged because of surface carboxylate groups. Electrostatically-driven oil adhesion results when the oil surface is cationic and the reservoir mineral surfaces are anionic, or when the oil surface is anionic and the reservoir mineral surfaces are cationic.

2.3. Parameters Influencing Oil-Rock-Brine Interaction

2.3.1. Rock Mineralogy

Originally, all reservoir rocks are water-wet. Sandstone and carbonate reservoirs are water-rich during burial. The ability of the different polar compounds to alter rock wettability depends, in part, on the rock type. Sandstone surfaces are typically anionic; limestone surfaces are typically cationic, though reservoir solution chemistry affects both (Brady et al., 2012). Sandstone reservoirs are made up of quartz, feldspar, oxide coatings, carbonates, and clays. Clay minerals will often dominate the reactive surface area seen by oil because of their smaller grain size, plate-like morphology, and much higher surface areas. Usually, they have negatively charged faces and positively charged edges when they get in contact with water. The negative surface charge of clays would be balanced by cations from solution, such as sodium ions, and by positively charged groups present at the oil-water interface, e.g. nitrogen bases (e.g. –NH+), and calcium-terminated carboxyls (e.g. –COOCa+). Electrostatic attraction between positively charged oil surface groups and negatively charged clay basal planes, is likely to control oil adhesion in sandstones containing clays such as illite or smectite (Brady et al., 2013). While the number of negatively charged basal plane clay groups is fixed by lattice composition, the abundance of charged oil surface groups depends upon the history of the oil and chemistry of the oil and the connate fluid (e.g. pH, brine salinity, brine composition). High numbers of nitrogen bases and calcium-terminated carboxyls groups should favor formation of electrostatic ‘‘bridges” and oil adhesion – that increases the degree of oil wetting (Alotaibi et al., 2011). Decreasing the numbers of nitrogen bases and calcium-terminated carboxyls groups should reduce oil adhesion, making the formation more water wet, resulting in greater oil mobility and recovery. Yukselen (2001) measured surface potential of kaolinite as a function of pH and concentration and concluded that as pH was increased zeta potential or surface charge became more negative. However, in the presence of divalent cations such as calcium and magnesium decreased the zeta potential.

The surface chemistry of carbonates is significantly more complex than that of sandstones. This is due to the presence of dolomite, Mg-rich calcites, clays, pyrite, and anhydrite (Ferno et al., 2011). Dissolution and/or precipitation into or from solutions does influence the surface chemistry of carbonate rocks (Hiorth et al., 2010). A study by Brady et al. (2012) found that the general controls of calcite’s surface charge to be: calcium and carbonate ions sorption largely determined the surface potential as opposed to hydrogen and hydroxide ions. Calcium ions were found to increase the surface charge of calcite as carbonate and sulfate ions decreased it.

2.3.2. Aqueous Chemistry

The pore water chemistry (pH, ion composition, and salinity) influences the oil and mineral surface charge, hence system wettability. The impact of water chemistry on wettability also depends on temperature. Enhanced oil recovery from sandstone and carbonates by modifying waterflood chemistry has been demonstrated by several groups (e.g. Lager et al., 2006; Zhang et al., 2006; Rezaei Doust & Puntervold, 2009). Brine composition and salinity do affect the surface charge of crude oil and reservoir rock and thus influencing the resultant wettability of the system (Brady et al. 2012). For example, sulfate, calcium, and magnesium ions can adsorb to the mineral surfaces, change the surface charge, and could potentially influence the ability of polar oil components to adsorb. Brine composition and salinity can influence the concentration of charged oil components at the oil-water interface. This could lead to an increase or decrease in the surface charge of oil. In addition, ions can make complexes with the polar part of the oil components, and this could change the solubility of the polar oil components in the oil phase.

2.3.2.1. Brine Salinity

In the past 10 years, several groups have carried out extensive research on the effect of brine salinity on wettability (Tang & Morrow, 1999; Lager et al., 2006; Zhang et al., 2006). This work was pioneered by Morrow's group at the University of Wyoming, where they have been studying the effect of low-salinity brines on wettability and thus oil recovery. These works have led the oil and gas industry to be conscious of the effects that injected water chemistry can have on oil recovery. Most research groups looking at this problem have reported that low salinity brines seem to favorably alter the wettability and increase oil production. However, there are a considerable number of research groups that have found that low salinity water injection does not have significant effects on oil recovery (Al-Shalabi et al., 2014). Thyne and Gamage (2010) evaluated the low salinity waterflooding effects in the fields in the Powder River Basin of Wyoming. They found no increase in recovery for the 26 fields where low salinity water was injected when they compared with the 25 fields where mixed water or formation water was injected. Among these 51 fields, the salinity of injected water was significantly reduced in 38 fields, whereas there was little reduction in salinity in the rest of 13 fields. There was no correlation observed between the salinity reduction and oil recovery factor. Boussour et al. (2009) conducted low salinity waterflooding experiments on a reservoir core sample and no increased oil recovery was observed. This project hypothesizes that the contradicting results can be attributed to the use of complex materials (e.g. crude oil and reservoir rock) while carrying out experiments that have a number of unknowns, and thus contradicting results.

2.3.2.2. Brine Composition

The presence of calcium, magnesium, and sulfate in water has been found to have profound effects on oil recovery in carbonate cores (Strand et al., 2006; Zhang et al., 2006, 2007; Zhang & Austad 2006). Zhang and Austad (2006) carried out a systematic study that investigated the impact of potential determining ions (calcium, magnesium, and sulfate) in chalk. Their study showed that when the concentration of sulfate was increased up to 4 times in injection water (seawater), oil recovery increased from 10% to about 50% original oil in place (OOIP). Similarly, when calcium concentration was increased from up to 4 times oil recovery also increased from 28% to 60% OOIP after 30 days of imbibition. Strand et al. (2006) observed that when temperature was increased the adsorption of sulfate also increased. They concluded that increase in adsorption of sulfate onto the chalk surface will reduce the positive charge, which decreased the affinity of calcium due to the less electrostatic interaction. In addition, they also investigated the relationship between calcium and magnesium at the chalk surface. It was found that at low temperature the affinity of calcium towards the chalk surface was higher than magnesium. However, at high temperature (130°C) magnesium has a higher affinity towards chalk than calcium. They interpreted the data as showing magnesium displacing calcium from the rock in a 1:1 reaction. However, it was not clear if the reaction constituted pure surface substitution or it was the formation of $MgCO_3$(s): $CaCO_3 + Mg^{2+} \leftrightarrow MgCO_3(s) + Ca^{2+}$. It was noted that the reactivity of magnesium towards the chalk surface increased dramatically as the temperature was increased beyond 70°C, which was observed to be the threshold for this substitution. This was explained as the small magnesium ion having a stronger hydration energy that makes it less reactive at low temperature. One explanation could be that sulfate, calcium, and magnesium adsorb to the pore surfaces, change the surface charge, and could thereby potentially influence the ability of polar oil components to adsorb. The effects of these divalent ions are illustrated in spontaneous imbibition experiments (Zhang et al., 2006, 2007). Hiorth et al. (2010) found some inconsistency with these conclusions. Their model predicted that increasing calcium concentration below 100°C increases oil recovery but above 100°C the effect is reversed. They attributed these inconsistencies to transport effects, where when "seawater-like" brine is spontaneously imbibed into the core at 70°C, sulfate is introduced to a large part of the core. When temperature is increased to 100°C sulfate can precipitate as anhydrite and lead to dissolution of the rock in order to supply more calcium to the system. However, when water is spontaneously imbibed into the core at high temperature (100°C), the brines with high calcium concentration can lose sulfate as anhydrite before the brines enter the core or very close to the border of the core. In this case, the impact of anhydrite precipitation would be reduced. The effect of rock dissolution is that a fresh water-wet surface is exposed. Lastly, ions in the aqueous solution can influence the concentration of charged oil components at the oil-water interface. This could lead to an increase or decrease in surface charge of oil. Ions can make complexes with the polar part of the oil components and this could change the solubility of the polar oil components in the oil phase.

2.3.2.3. Brine pH

Calcium ions present in the formation brine can influence the surface of the chalk to have a positive charge at pH less than 9 (Zhang et al., 2006). The positive charge of the chalk surface in the presence of calcium and magnesium ions has been confirmed by zeta potential measurements on a milled chalk in NaCl brine suspension.

2.3.3. Oil Chemistry

Oil chemistry plays a significant role in the wettability of a system. Acid number (AN) is the measure of acidic material in crude oil, as base number (BN) is that of basic material in the crude oil which is typically much higher than the AN (Puntervold et al., 2007). Carboxylic groups in naphthenic acids from the crude oil are the most strongly adsorbed material onto the rock surface and they may act as "anchor" molecules for other surface active components present in the crude oil (Standnes & Austad, 2003). When oil invades a chalk reservoir, the interface between oil and water become negatively charged due to partial dissociation of carboxylate groups (-COOH) present in crude oil, resulting in negatively charged carboxylates (-COO-). The resulting thin water film between the positively charged chalk surface and the negatively charged oil-water interface becomes unstable due to the negative disjoining pressure and the oil may contact the chalk surface. The carboxylates in the oil could adsorb onto the chalk surface and hence make the chalk less water-wet (Thomas 1993). Thus, (AN) could dictate the degree of water-wetness. The higher the AN, the more carboxylates have the possibility of adsorbing onto the chalk surface and decreasing the water wetting nature of the rock. Steric acid was also found to promote oil-wetness (Thomas et al., 1993; Karoussi and Hamouda, 2007).

Water wetness decreases as the AN increases. Puntervold et al. 2006, studied the impact of basic components on wetting properties of chalk by using oil with a constant AN of 0.5mg KOH/g oil and varying the AN/BN ratio in the range of 0.24 to 4.6. They used Benzyl Amine as their basic compound, and it was observed that the water wetness decreased as the content of base increased up to about 4 times the concentration of acid.

2.3.4. Temperature

Temperature has been found to play a significant role in determining wettability. Rao (1999) showed that in most cases, sandstone reservoirs become more oil-wet with increasing temperature, while most of the carbonate reservoirs become more water-wet. Schembre et al., (2006) suggested that the change in temperature that results when injected water is introduced into a reservoir causes the surface oil-wet fines to detach, leaving a clean, water-wet surface. One implication is that changes in wettability during water displacement of oil may differ from those during oil displacement of water. Using Rao’s conclusions and similar conclusions, Schembre’s conclusions may explain the wettability behavior in sandstones, where when temperature is decreased the systems becomes more water-wet, however, it does not explain the behavior found in carbonates. In addition, studies have shown that decarboxylation of carboxylic material takes place at elevated temperatures and this process could be catalyzed by the presence of carbonate (Shimoyama & Johns 1972). This process of decomposition decreases the acid number (AN) to base number (BN) ratio due to the decrease in AN and increases the oil-wetness of the system.

2.4. Wettability Measurement Methods

Anderson (1986) and Dixit et al. (2000) reviewed wettability measurement methods which include: oil-water contact angles, imbibition and forced displacement (Amott), the US Bureau Method (USBM), permeability/saturation relations, wire-line logs, imbibition rates, production performance, capillary pressure curves, relative permeability curves, microscope examination, flotation, nuclear magnetic resonance (NMR), displacement capillary pressure, dye adsorption, and capillary metric methods.

2.4.1. Flow Measurement Methods

The Amott and the USBM tests are the most commonly used quantitative methods for the assessment of wettability state (Amott, 1959; Donaldson et al., 1969; Sharma & Wunderlich, 1987). Both methods give the macroscopic average wettability of a rock-oil-brine system. The Amott method measures the amount of fluids spontaneously and forcibly imbibed by a rock sample (Figure 2). The USBM method is similar to the Amott method but considers the work required to do a forced fluid displacement. Both Amott and USBM do not give absolute wettability measurements, but they are regarded as an industry standard for comparing the wettability of core plugs. The core is usually considered water-wet when water is preferentially imbibed in the core, and oil-wet when oil is preferentially imbibed in the core. The core is considered neutral-wet when neither oil nor water is preferentially imbibed. This is assumed to indicate that equal portions of the surface have a preference for water or oil.

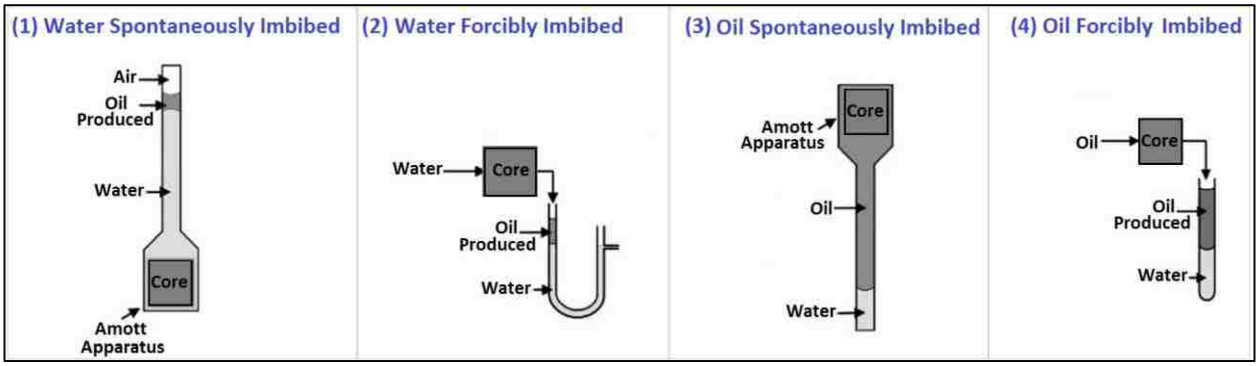


Figure 2: Schematic of Amott and USBM measurements.

2.4.2. Contact Angles Methods

Contact angle is a common measure of wettability and is most accurate when pure fluids and artificial cores are used. This method is the prefered method of measuring wettability since it is faster than the flow measurement methods. In addition, it has the added advantage of directly measuring wettability under reservoir conditions. As shown in Figure 3, the surface is considered water-wet when the contact angle is less than 75°, neutral-wet when 75°-105°, and oil-wet when greater than 105°.

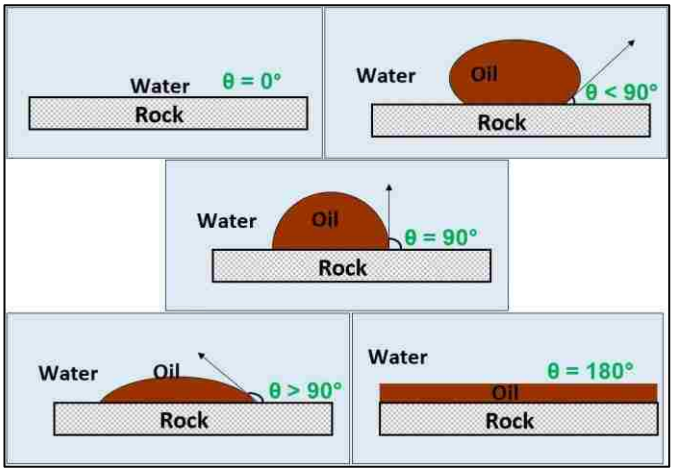


Figure 3: Schematic of sessile drop contact angle measurements

This method suffers from the hysteresis generated between the water-advancing and water receding angles. Anderson (1986) showed that contact angle hysteresis can be caused by the surface roughness, surface heterogeneity, and surface immobility on a macromolecular scale. In addition, this technique requires preparation of the coarse mineral sample by means of polishing and then cleaned using various solvents and leachants. All the above pretreatments of the mineral samples can be expected to affect the surface roughness as well as surface composition of the sample (Somasundaran, 1970; Kulkarni & Somasundaran, 1973, 1977). Smearing of the mineral surface by contaminants during polishing can also be of significant effect (Bangs, 1962). Wagner & Leach (1959) stated in their study that the removal of bituminous or organic coatings that have a governing role in imparting oi1-wettability to rock surfaces during polishing can also lead to misleading results that are not representative of the original samples. Equally important alterations in surface variations can produce changes in both the equilibrium contact angle and the nature of hysteresis that is important in determining the oi1 saturation. In 1956 Brown and Fatt suggested that the concept of a contact angle, as applied to reservoir rock, be abandoned. They made this suggestion due to the heterogeneous mineral composition of most reservoir rocks, each with a different surface chemistry and a different capacity to adsorb surface active materials from reservoir fluids. Furthermore, they stated that the operation of a contact angle in determining the form of a fluid-fluid interface is difficult to picture in the very complex geometry of a pore.

2.4.3. Flotation Method

Flotation processes have been routinely used for over a century in the mining industry (Nguyen, 2004). Flotation is a physicochemical process that is used to separate finely crushed solids based on their wettability. This wettability measurement method has long been considered as a qualitative method of measuring wettability in the oil and gas industry (Anderson, 1986).

Celik and Somasundaran (1980) studied the wettability of reservoir minerals by flotation and correlated the wettability results with data obtained for adsorption and zeta potential. Their study presented good correlation between mineral flotation and surfactant adsorption with both properties exhibiting a maximum near critical micelle concentration. Dubey and Doe (1993) used flotation to investigate the effect of acid and base numbers of crude oil on wetting characteristics. Wu et al. (2008) used flotation to study the wetting behavior and surfactant EOR in carbonates with model compounds.

Mwangi et al. (2013) developed a quantitative flotation technique known as Modified Flotation Technique (MFT). They used MFT to study the effect of rock mineralogy, brine salinity, surface active compounds commonly found in crude oil, and temperature. MFT proved to be a successful quantitative technique to rapidly test the influence of oil and brine chemistry on the wettability of sandstone and carbonate rocks at different temperatures. Sohal et al. (2016) studied the effects of ionic strength and composition of brine on chalk wettability at 23°C and 100°C. They also examined the role of potential scale forming ions (barium and strontium) in wettability alteration and restoration, and the correlations between IFT and wettability. They studied the effect of temperature on wettability and optimum wetting conditions for maximum oil recovery in carbonate reservoir system (Sohal et al., 2017). Haugen (2016) used a variation of the MFT to characterize the wettability alteration of five rocks in the presence of four brine and four oil types from a North Sea reservoir. He observed that quartz, K-feldspar, glauconite, and a North Sea outcrop sandstone rock were primarily water-wet for all brine-oil combinations. Muscovite showed both water-wet and oil-wet tendencies, depending on the brine-oil combination. Also, he demonstrated a clear correlation between the total acid number of the oil and calcium concentration of the brine for all minerals except quartz. Fjelde et al. (2017) used MFT to screen the potential for different injection water compositions to alter wettability to more water-wet. They found that screening of potential for available injection water compositions to alter the wettability to more water-wet can be carried out by a combination of flotation experiments with geochemical simulations. They proposed that this combination does also allow for possibility to determine whether direct adsorption or cation bridging is the dominating wetting mechanism.

2.5. Wettability of Sandstone Reservoirs

40-50% of the World's oil is in sandstone reservoirs. Sandstone reservoirs are made up of quartz and clays that are negatively charged under most conditions. Because of their strong negative charge, and their high surface area, clays tend to sorb cationic SAC components from crude oil. In the past decade, widespread attention has been given to low salinity waterflooding in sandstone reservoirs (e.g. Tang and Morrow, 1999; Morrow & Buckley, 2011; Winoto et al., 2012). Numerous experimental and field studies have demonstrated that modifying brine composition can result in significant improvement in oil recovery (10-30% of OOIP).

2.5.1. Low Salinity Waterflooding in Sandstone Reservoirs

The popularity of this technique is due to its: low cost, water availability, ease of application in the field, and its efficiency in displacing light to medium gravity crude oils. Evidence of enhancement in waterflood efficiency by injecting low-salinity brine has been observed in the laboratory and in the field on both carbonate and sandstone reservoirs (Robertson, 2010; Hadia et al., 2013; Aladasani et al., 2014; Myint & Firoozabadi, 2015). Gamage & Thyne (2011a) showed the advantages of using low salinity water injection in secondary mode compared to tertiary mode by producing 6 to 20% more oil during coreflooding experiments on sandstone cores.

2.5.2. Wettability Alteration Mechanisms in Sandstone Reservoirs

Several mechanisms have been proposed to explain the low salinity effect. All proposed low salinity waterflooding mechanisms invoke adhesion of oil SACs to the rock surface. Therefore, it is necessary to quantitatively measure, and ultimately understand, the role of SAC adhesion in order to make low salinity waterflooding predictive.

2.5.2.1. Effect of Fine Migration

Tang and Morrow (1999) proposed that the migration of fine particles, mainly kaolinite, might play a key role in the sensitivity of oil recovery to salinity. They concluded that a range of oil recovery and wettability observations could be explained by assuming that heavy polar components of crude oil adsorbed onto particles and pore walls to obtain mixed wetness. During aging, clay fines are partly in contact and exposed to crude oil, and the fines are then mixed-wet particles. The production of oil droplets on these clays would contribute in changing the system to a more water-wet system since the fines migration resulted in the exposure of the underlying surfaces that lead to an increase in water-wetness of the system. When high salinity brine is present, clays are undisturbed and retain their oil-wet nature leading to poorer displacement efficiency (Lager et al., 2006). When the clay particles encounter low salinity water, the clay particles will detach from the pore surface. Unfortunately, migration of clays can plug pore throats and reduce permeability with flowing fluid (Lever and Dawe, 1984).

On the other hand, numerous other experiments with low salinity have shown an increase in oil recovery but not observed fines migration. Several groups have reported an increase in oil recovery with no fine migration or significant permeability reductions observed during numerous low salinity corefloods (Lager et al., 2006; Zhang & Morrow, 2007). Valdya and Fogler (1992) reported that a gradual reduction in salinity kept the concentration of fines in the flowing suspension low, with formation damage minimized or totally avoided. On the other hand, Boussour et al., (2009) and Romero et al., (2014) reported no low salinity effect but with sand production in their experiments.

2.5.2.2. Effect of pH Variation

Tang and Morrow (1999) and McGuire et al. (2005) observed a pH increase by low salinity injection on Berea and North Slope field samples, respectively. McGuire et al. (2005) proposed that low-salinity mechanisms could be due to increased pH and reduced IFT similar to alkaline flooding. It has been proposed that this increase in pH is due to the exchange of hydrogen ions in water with adsorbed sodium ions (Mohan et al., 1993). Overall, a small change in bulk pH can impose a great change in the zeta potential of the rock. pH increase can cause organic materials to be desorbed from the clay surfaces (Austad, 2013).

2.5.2.3. Effect of Multicomponent Ion Exchange

Lager et al. (2006), proposed a Multicomponent Ionic Exchange (MIE) mechanism where divalent ions in pore water competed and displaced oil molecules from mineral surface exchange sites. Multivalent cations at clay surfaces are bonded to polar compounds present in the oil phase, thus forming organo-metallic complexes and promoting oil-wetness on rock surfaces. Meanwhile, some organic polar compounds are adsorbed directly to the mineral surface, displacing cations present at the clay surface and enhancing the oil-wetness of the clay surface. During the injection of low salinity brine, MIE will take place, removing organic polar compounds and organometallic complexes from the surface and replacing them with uncomplexed cations. The evidence of MIE was shown from an effluent analysis taken from a low salinity core flood in the North Slope. The analysis showed that the injected brine had a lower salinity than the connate water. The concertation of magnesium and calcium ions in the effluent samples decreased as more pore volumes of low salinity water was injected and dropped below the concentration of the injected brine. This indicated that the calcium and magnesium ions were adsorbed by the rock matrix. Sposito (1989) proposed eight mechanisms for adsorption of organic functional group on soil minerals (Table 9).

Table 1: Proposed mechanisms for adsorption of organic functional group (Sposito, 1989)

Adsorption Mechanisms	Organic Functional Groups
Protonation	Amino, heterocyclic N, carbonyl, carboxylate
Van der Waals Interactions	Uncharged organic units
Anion Exchange	Carboxylate
Hydrogen Bonding	Amino, carbonyl, carboxyl, phenolic OH
Cation Exchange	Amino, ring NK, heterocyclic N (aromatic ring)
Cation Bridging	Carboxylate, amines, carbonyl, alcoholic OH
Ligand Bridging	Carboxylate
Water Bridging	Amino, carboxylate, carbonyl, alcoholic OH

Of the eight proposed mechanisms, the four affected by possible cation exchange capacity in low salinity flooding are: cation exchange, cation bridging, ligand bridging, and water bridging.

2.5.2.4. Effect of Electric Double Layer

Lower salinity brines increase the thickness of the ionic double layer between the clay and oil interfaces. Ligthelm et al. (2009) suggested that the concentration of cations in the high salinity brine is sufficient to screen off the negative charge of the oil-water interface and the clay surface. This would result in the suppression of the electrostatic repulsion force. Therefore, the wettability of the rock in high salinity brine is less water-wet because polar components will adsorb onto the clay surface. Low salinity brines reduce the ability of the cations to screen off negative charges of the clay surface. The result is increased repulsive forces between the mineral surface and the oil-water interface, and expansion of the electrical double layer (RezaeiDoust et al., 2011). Frontiers BP, 2009, presented a hypothesis for low salinity effect in the presence of clay. The thickness of the double layer will increase with decreasing salinity. They suggested that the negatively charged clay particles produce a diffuse double layer where as the aqueous phase near clay is positively charged.

2.5.2.5. Chemical Low Salinity Mechanism

Austad et al. (2010) proposed that the following parameters play a major role in low salinity effects in sandstones: (1) rock mineralogy (e.g. clay properties, type, and quantity), (2) crude oil chemistry (e.g. SACs), and (3) aqueous chemistry (e.g. brine composition and pH). The suggested mechanism requires both polar components and active cations be initially adsorbed onto the clay (Austad et al., 2010). Different clays have different adsorption/desorption windows. For observing the low salinity effect, clay minerals with high cation exchange capacity appear to be favorable. Initially, there is a balanced adsorption onto the clay minerals of organic material, active cations and protons, preferentially at reservoir pH of about 5. An ordinary acid-base reaction that promotes desorption of organic material takes place between OH- and the adsorbed acid and protonated base. As the water wetness increases, the oil recovery is increased. Injection of low salinity brine will cause desorption of adsorbed cations which will increase the pH close to the water-clay interface because calcium is substituted by hydrogen ions on the clay surface. If the amount of adsorbed organic material is low and the adsorption of active ions is high, the low salinity EOR effect will be low as a result of the rock already being water-wet. As long as the low saline injected water has a concentration of active ions that are low enough to promote significant desorption from the clay surface, the composition of the injected low saline may not play an important role.

2.6. Wettability of Carbonate Reservoirs

Chilingar and Yen (1983) reported that of 161 carbonate rocks studied, 15% were strongly oil-wet, 65% were oil-wet, 12% were intermediate-wet, and 8% were water-wet. In fractured and low permeability carbonate reservoirs oil displacement from the matrix blocks by spontaneous imbibition of the injection fluid constitutes the main drive mechanism to obtain high oil recovery. However, the unfavorable wetting state of carbonates prevents spontaneous uptake of water (and expulsion of oil) into the matrix due to negative capillary pressure. Spontaneous imbibition of wettability-altering water into fractured reservoirs of chalk, limestone, and dolomite (carbonate reservoirs) is relatively inexpensive and therefore an important secondary oil recovery method. The technique appears to function quite well under water-wet to mixed-wet conditions (Thomas et al., 1987). To promote spontaneous imbibition into oil-wet carbonate matrices and achieve higher oil recoveries, the capillary pressure should be increased by altering the wettability of the rock surface to a more favorable water-wet state. This requires first understanding the link between SACs and wettability.

Carbonates have positively charged and weakly basic surfaces in brines near neutral pH (Anderson, 1986). Therefore, the rock-brine interface is positively charged while the oil-brine interface is negatively charged due to the carboxylic acids in the oil. The opposite charge between the oil/brine and mineral/brine surfaces results in an electrostatic attraction between the two interfaces, which tends to thin the brine film and can bring the oil in direct contact with the mineral surface (Hiraski et al. 2004).

2.6.1. Low Salinity Waterflooding in Carbonate Reservoir

One of the emerging EOR methods for wettability alteration in carbonate reservoirs is low salinity waterflooding. The effect of low salinity water injection in carbonate reservoir has not been as thoroughly investigated as sandstones. This is due to wettability alterations by low salinity waterflooding in sandstone reservoirs related to the presence of clay (Lager et al., 2006; Doust et al., 2009). Only a few field scale (i.e. Ekofisks and Valhall oil fields) low salinity waterflood projects have been reported (Sylte et al., 1988; Hallenbeck et al., 1991). Interest in modifying the water chemistry of injected water was stimulated by observation of unexpectedly high oil recoveries from injecting seawater in the fractured Ekofisk chalk reservoir of the North Sea (Sylte et al., 1988; Hallenbeck et al., 1991)

2.6.2. Wettability Alteration Mechanisms in Carbonate Reservoirs

Increase in oil recovery due to modified brine chemistry of injection water has attributed to wettability alteration in carbonates. The fundamental observations from the laboratory studies and field cases show that altering water chemistry increases oil mobility underflow and imbibition, which means wettability has been altered. Most the observed results attributed improved oil recovery to change of wettability to a more water-wet state (Yousef et al., 2010, 2011; Fathi et al., 2006; Zhang et al., 2006, 2007; Strand et al., 2006), or to a more mixed-wet state (Sharma et al., 2000; Agbalaka et al., 2008; Hazim et al., 2013). The wettability alteration mechanisms proposed are either by potential determining ions or by decreasing the total salinity of injected water. However, there is no consensus on a single main mechanism for the low salinity effect. This is due to the complex nature of the interaction between crude oil, brine, and rock, as wells as a number of conflicting observations from experimental studies. Therefore, either there are a number of mechanisms involved to increase the oil recovery by chemically modified water or the right mechanism has not yet been identified yet (Suijkerbuijk et al., 2012).

2.6.2.1. Effect of Multivalent Ions

Injecting low salinity with different electrolyte concentration than formation brine will disturb the equilibrium crude oil-rock-brine system. The variations in ionic concentration results in the substitution of divalent cations by the monovalent cations (Lager et al., 2006). In addition, the presence of divalent cations in the formation brine could bridge the rock and the crude oil. Theoretically, exchange with monovalent cations can release the crude oil from the rock surface, which alters the system to more water-wet thus increasing the recovery factor.

Zhang et al. (2007) determined the potential of multivalent ions to improve the oil recovery by changing chalk wettability in imbibition experiments. They observed that sulfate in the presence of NaCl was unable to change the wettability to improve spontaneous imbibition. However, if calcium or magnesium ions were present together with sulfate, improved spontaneous imbibition was observed. They proposed that sulfate from the imbibing seawater adsorbed onto the chalk surface and the positive charge is decreased. More calcium is then attracted to the surface due to lowered electrostatic repulsion. Calcium can then react with carboxylic groups and displace it from the surface. At high temperature, the process became more active and magnesium displaced the calcium bound to the chalk surface as well as from the carboxylate complexes. Strand et al. (2005) used chromatographic separation methods to show the adsorption of sulfate onto the chalk surface increases as the temperature increases without any precipitation of $CaSO_4$. They also observed improved oil recovery by co-adsorption of calcium and sulfate onto the chalk surface was more pronounced at higher temperatures. Shehata et al. (2014) and Mohanty et al. (2013) found that sulfate and magnesium ions are more effective than calcium to improve oil recovery. Gupta et al. (2011) recovered an additional 15% to 20% OOIP by adding borate and phosphate to seawater in coreflood experiments using Middle Eastern limestone. They found borate and phosphates are superior to sulfate to alter wettability to a more water-wet state.

2.6.2.2. Effect of Ionic Strength

Increase in oil recovery has been observed as the ionic strength of the injected water is reduced. Shehata et al. (2014) recovered more oil by deionized water in secondary recovery mode compare to seawater and attributed it to limestone and water interaction which increased the repulsive forces between crude oil component and rock surface. Hazim et al. (2013) recovered additional oil by injecting almost 40 to 200 times diluted versions of reservoir brine in water-wet reservoir cores and ascribed additional oil recovery to mixed-wet or intermediate-wet conditions contrary to Morrow and coworkers who attributed the additional recovery to water-wet conditions. Yousef et al. (2011) flooded carbonate reservoir cores with two and ten times diluted seawater and recovered a substantial amount of oil. They observed a decreasing trend in IFT correlated with decreasing the ionic strength of injected water.

2.6.2.3. Effect of Rock Dissolution

This mechanism proposes that the lower calcium concentration in low-salinity brine causes calcium carbonate from the rock to dissolve and establish equilibrium with the brine (Hiorth et al., 2010). When the calcium carbonate dissolves, the adsorbed oil components are removed and the rock surface is rendered water-wet. During the dissolution of carbonate, an excess of OH- will give increased pH. Gupta et al. (2011) found in Middle Eastern reservoir limestone coreflooding experiments that soft water dissolved a small amount of rock desorbing some of the oil and altering wettability towards a more water-wet state. Yousef et al. (2010, 2012) measured pore coupling in carbonate coreflooding experiments at reservoir conditions and found that the connectivity between micro and macro pores was attributed to microscopic dissolution of anhydrite. Hiorth et al. (2010) evaluated the rock dissolution concept through geochemical modeling and they concluded that chemical dissolution of calcite appears the controlling factor.

2.6.2.4. Effect of Electric Double Layer

The double layer theory describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion. When low salinity water is introduced to a crude oil-brine- rock system, the double layer of counter ions on mineral surfaces will expand when the salinity is lowered because of less suppressive force exerted by ions in solution. This is a function of brine salinity and composition. Divalent and trivalent ions compress the double layer more than monovalent ions (Hunter, 1988). However, a higher concentration of divalent ions in the electrical double layer will also increase the surface charge density. Takamura et al (1985) explained that increasing pH beyond the isoelectric point changes the solid/water interface from positive to negative. Since the charge at the water/oil interface is already negative repulsive electrostatic force emerge and thus expand the electrical double layer. Strand et al. (2005) observed that the wettability of carbonates is dictated by the stability of water film between the rock surface and the oil phase which is related to zeta potentials of the oil water and water rock interfaces. Fathi et al. (2010a) used seawater depleted in NaCl in order to provide calcium, magnesium, and sulfate ions easier access to approach the chalk surface. This change of ionic composition inside the electrical double layer increased imbibition rate and oil recovery. Yousef et al. (2012a, 2012b) used diluted seawater to change the carbonate cores surface charge to more negative values which lead to more water interaction and eventually alteration to the water-wet state, confirmed by zeta potential results and NMR study.

2.7. Summary

The goal of this project is to create a faster, cheaper, and more reliable wettability measurement method that more accurately identifies the chemical controls over oil-rock adhesion and wettability. Traditional methods are time-consuming, costly, and require considerable interpretation. Moreover, conventional wettability tests cannot distinguish heterogeneous wettability states. Developing a method to better understand wettability/oil-rock adhesion should ultimately lead to greater enhanced oil recoveries. Using the new method, systematic experiments to investigate the role of specific SACs on wettability were performed.

CHAPTER 3. EXPERIMENTAL METHODOLOGY

This section describes the materials and methods used to study the role of SACs on wettability as a function of rock mineralogy, brine chemistry, and temperature.

3.1. Materials

3.1.1. Rock Material

Three reservoir materials were considered: sandstone, shale, and carbonate. The three carbonates were Austin chalk, Indiana limestone, and Silurian dolomite. The four sandstones were Berea, Gray Berea, Kirby, and Bandera sandstone; the shale was Mancos shale. Experiments using Gray Berea, Kirby, Bandera, and Mancos shale focused on examining the effect of brine composition on sandstone, shale, and carbonate rocks. These results will be presented in a separate report. All rocks came from Kocurek Industries of Caldwell, TX. Each of the four rock samples were ground and sieved to five different sizes: <53 µm, 53-105 µm, 105-149 µm, 149-206 µm, and >206 µm as shown in Figure 4. This project used grain size distribution of 105-206 µm.

To avoid contamination, the mortar, pestle, and sieves were thoroughly cleaned using the following procedure: blast the equipment with 100 psi air under a fume hood until the loose powder is extracted, rinse with DI water, rinse with acetone, dry with air, crush a small amount of the rock of interest to fine powder and use the powder to scrub the surface of the equipment with intent for the powder to pick up any contamination stuck on the surface. Lastly, decant the potentially contaminated powder and the equipment is ready for use.

Figure 4: Mortar and pestle were used to grind the rock samples and a series of sieves were used to separate the rock powder to different rock size distributions.

3.1.2. Oil

To isolate the effects of individual SACs, this project used model oils mixtures of pure decane and SACs to represent the oleic phase. Obviously, natural petroleum is a complex mixture of organic molecules that a model oil can only roughly approximate. But model oils are a useful means for isolating the effects of individual SACs on wettability. The four groups of SAC studied are: aromatic, oxygen-bearing, sulfur-bearing, and nitrogen-bearing compounds, and a natural condensate sample. Table 2 lists the nine SACs used in this study. Tetralin, a non-SAC aromatic compound labeled A1, was also used.

Table 2: Surface active compounds used in this study.

Surface Active Compounds (SAC)	Label	Chemical compound	Chemical Formula	MW (g/mol)
Oxygen-bearing SAC	O1	Acetic acid (short chain)	CH_3COOH	60.05
	O2	Myristic acid (long chain)	$CH_3(CH_2)_{12}COOH$	228.37
	O3	Naphthenic acids (long chain)	$C_7H_{10}O_2$	126.15

Table 2 cont'd

Surface Active Compounds (SAC)	Label	Chemical compound	Chemical Formula	MW (g/mol)
Sulfur-bearing SAC	S1	Dibenzothiophene	$C_{12}H_8S$	184.26
	S2	Di-n-Butyl Sulfide	$C_8H_{18}S$	146.29
	S3	1-Tetradecanethiol	$CH_3(CH_2)_{13}SH$	230.45
Nitrogen-bearing SAC	N1	Carbazole	$C_{12}H_9N$	167.20
	N2	Quinoline	C_9H_7N	129.16
	N3	Pyridine	C_5H_5N	79.10
Condensate	Cond	Condensate		
Non-reactive organic medium	Dec	Decane	$C_{10}H_{22}$	142.28

The condensate was supplied by a major oil company. This fluid is clear and its specific gravity, density, and viscosity at 22°C are 62°API, 0.7340 g/cm^3, and 1.0028 cp, respectively. The composition of the condensate is presented in Table 3. The condensate is a complex mixture composed mostly of alkanes as shown in the GC results in Figure A1 and Table A1.

Table 3: Compositional Analysis of Condensate.

Component	Carbon No.	Mole %	Weight %
Methane	C1	0.002	0.000
Ethane	C2	0.045	0.013
Propane	C3	0.896	0.377

Table 3: Cont'd

Component	Carbon No.	Mole %	Weight %
i-Butane	iC4	1.156	0.641
-Butane	nC4	3.580	1.984
i-Pentane	iC5	4.333	3.478
n-Pentane	nC5	5.590	3.846
Hexane	C6	12.722	10.455
Heptanes Plus	C7+	71.676	79.703
Total		100.000	100.000
Properties of Heptanes Plus (C7+) of condensate			
Mole %			71.7
Molecular Weight			116.5
Specific Gravity @ 60°F			0.76

3.1.3. Brine

To isolate the individual effects of brine composition on wettability, deionized water was used for baseline tests, then individual salts were added to make up chemically different brines (Table 4).

Table 4: Brine compositions (all in mg/L).

Salts	NaCl	$NaHCO_3$	$CaCl_2$	$MgCl_2$	Na_2CO_3	$NaSO_4$	$AlCl_3$	$FeCl_3$	Salinity
Brine 1 / DI	Deionized water								~ 0 ppm
Brine 2	900	10	30	30	-	30	-	-	1,000 ppm

Table 4: Cont'd

Salts	NaCl	$NaHCO_3$	$CaCl_2$	$MgCl_2$	Na_2CO_3	$NaSO_4$	$AlCl_3$	$FeCl_3$	Salinity
Brine 3	9,000	100	300	300	-	300	-	-	10,000 ppm
Brine 4	90,000	1,000	3,000	3,000	-	3,000	-	-	100,000 ppm
Brine 5	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	

3.2. Sample Preparation

3.2.1. Rock sample preparation

All rock samples used in the wettability measurement method Modified Flotation Technique (MFT) were ground and sieved to a fine powder. Dolomite samples used in the contact angle experiments were cut and polished to thin wafers. A mixture of 20% methanol and 80% chloroform was used in the Dean-Stark soxhlet system to clean the wafers prior to conducting the contact angle experiments.

3.2.2. Model oil preparation

Ten model oils were created by the addition of 2000 ppm of SAC to pure decane. Decane is considered non-surface reactive, is non-polar, and contains no SACs. Therefore, any observed change in wettability from that of the baseline decane is attributed to the added SAC. Condensate wettability was also tested.

3.3. Methods

3.3.1. Modified Flotation Technique

This project developed and used the modified flotation technique as wettability measurement method. This method is explained in detail in Chapters 4 and 5.

3.3.2. Dual Drop Dual Crystal Technique

The contact angle method used is the Dual Drop Dual Crystal (DDDC) method (Rao and Girard, 1996) depicted in Figure 5. DDDC was used to validate the MFT process (Section 5.4).

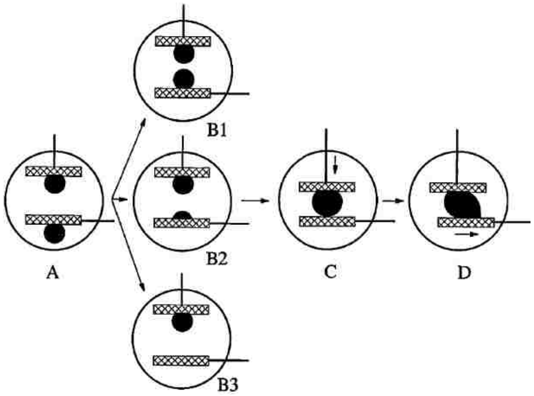


Figure 5: Schematic depiction of DDDC contact angle measurement method (Rao & Girard, 2006).

Two crude oil drops (**A**) are placed on two parallel polished rock surfaces held by horizontal and vertical arms of an optical cell. The water film between the crude oil sessile drops and mineral crystal surfaces is drained with the help of the buoyancy forces to attain adhesion equilibrium before measuring advancing and receding contact angles with respect to aging time. By turning the lower crystal upside down (**A → B**) there are three possible ways the oil drop could behave. In case **B1** the oil drop remains attached to the lower crystal due to adhesion, in case **B2** part of the oil drop floats away due to buoyancy, and in case **B3** the oil drop detaches cleanly from the lower crystal without leaving any oil on the surface. In case **B1** and **B2**, the upper crystal is lowered so that the two oil drops can mingle (**C**), In case **B3**, the upper crystal is brought down to interact with the surface where the oil drop from the lower crystal was previously situated. The advancing and receding contact angles are measured by shifting the lower crystal laterally (**D**). The water receding contact angle determines the spreading behavior of reservoir fluids; while the water advancing contact angle describes the wettability and rock/oil adhesion.

3.3.3. X-Ray Diffraction Technique

X-ray diffraction (XRD) was used to determine the mineral compositions of the rocks used in this project. XRD is used to identify the atomic and molecular structure of a crystal in which the crystalline atoms cause a beam of x-ray to diffract in specific directions. By measuring the angles and intensities of these diffracted beams, a three-dimensional picture of the density of electrons within the crystal is produced. The generated electron density is then used to determine the mean positions of the atoms in the crystal as well as their chemical bonds and various other parameters. This project used a Panalytical Empyrean XRD instrument shown in Figure 6. Sample preparation is crucial for accurate diffraction pattern and repeatability. Problems associated with poor sample preparation includes: graininess, micro-absorption, texture, sample height displacement, surface roughness, and sample transparency.

Figure 6: XRD instrument

Even though there is a sample preparation and loading procedure for the XRD, there are minor but crucial details that defer depending on the type of material one is testing. Therefore, it is important to conduct preliminary experiments to determine the most favorable parameters for good results such as ideal grain size distribution, sample loading (front end, back end, or side loading), etc. Table 5 lists the conditions used in the XRD measurements.

Table 5: XRD experimental conditions

X-Ray Diffractometer	Panalytical Empyrean
Loading	Side loading to avoid clay orientation
Sample size	105-206 microns
Temperature	Ambient

3.3.4. Gas Chromatograph Technique

Gas chromatography (GC) is a method of separating compounds with a high vapor pressure or a relatively low boiling point so that they are separated and detected in complex mixtures. Compounds are separated based on differences in their vapor pressures and their attraction to solid materials inside the GC. Because the vapor pressure of a given compound is a function of the intermolecular forces between molecules, GC takes advantage of differences in at least one of the properties of matter. In this project, the GC instrument was used to measure the composition of decane, the ten surface active compounds, and condensate. Each of the compounds was diluted in dichloromethane (DCM) solvent prior to running it on the GC instrument. No impurities were detected in the decane nor the ten surface active compounds samples. The GCMS samples were analyzed on a Varian CP-3800 gas chromatograph connected to a Varian Saturn 2200 Ion Trap mass spectrometer (Agilent). The samples were injected in splitless mode with a temperature program of: initial temp 40^{o} C, hold for 6min then increasing to 240^{o} C at a rate of 4^{o}/min, hold of 10min then ramping to 280^{o} at 20^{o}/min holding for 5min with total run time being 73min. Injector temperature was constant at 200^{o}. The carrier gas was helium at a constant flow rate of 1ml/min. Electron multiplier voltage was 1900v. Spectra were submitted to NIST library search for confirmation.

CHAPTER 4. MODIFIED FLOTATION TECHNIQUE FUNDAMENTALS

For over a century, flotation has been routinely used as a separation process (Perkins, 1921; Klassen, 1948a, 1948b; Whelan, 1956; Boutin and Wheeler, 1967). For a successful flotation process, the following criteria must be met: (1) wettability difference between the material of interest and the waste, and (2) the grain sizes need to fall in the range where surface forces can be dominant over gravitational forces. MFT is a flotation technique where water and oil are added to powdered rock, mixed and allowed to separate as illustrated in Figure 7.

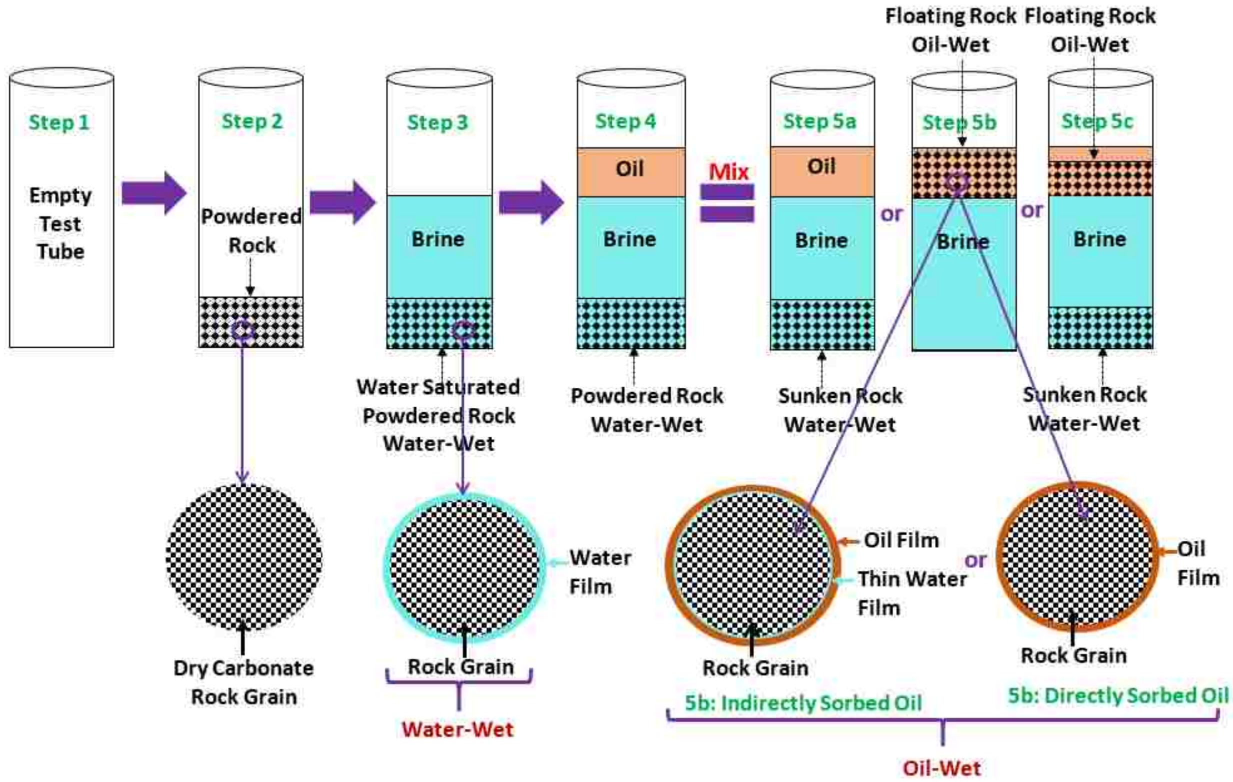


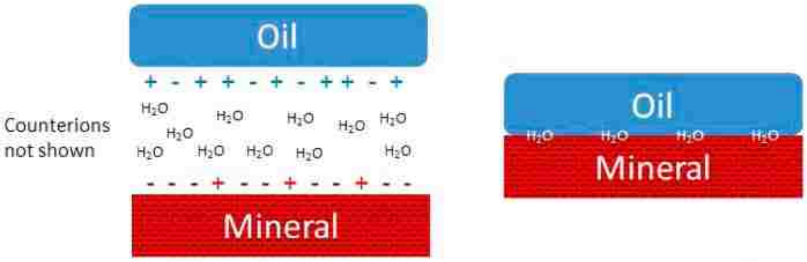
Figure 7: Detailed schematic depicting the MFT procedure.

The wetting of the solid grains results from the balance of surface forces between the interaction of the oil and water with the rock grain surface. The MFT procedure mimics the sequence of events in the creation of oil reservoirs. As shown in Step 3, all grains in the MFT procedure start out as water-wet and thus negatively buoyant since their density is greater than water. As oil is added (Step 4) and the rock, water, oil phases are thoroughly mixed, there are 3 possible results. If the geochemical conditions are such that the rock powder is: (1) water-wet, the grains will sink (Result 1a); (2) oil-wet, the grains will be suspended in the oil-phase (Result 1b); (3) fractional-wet, then a fraction of the rock will be suspended (oil-wet) in the oil-phase and the rest of the grains (water-wet) will sink (Result 1c). This separation process is what allows us to determine the wettability of the rock in an oil-water-rock system. Each portion of the rock is then dried and weighed to quantify oil adhesion. In this work the result is normalized to decane-rock adhesion to identify the wetting contribution of individual surface active compounds.

In 1956, Brown and Fatt proposed that the wettability of reservoir rock be stated in terms of the fractional internal surface area that is in contact with water or oil. All surfaces on which there is water are called water-wet; surfaces on which there is oil are called oil-wet. They proposed that fractional water wettability is a number which represents the fraction of the internal surface that is in contact with water. In MFT, this is the fraction of grains residing in the water phase. In addition, fractional oil wettability is then stated as a number which represents the fraction of the internal surface that is in contact with oil. In MFT, this is the fraction of grains residing in the oil phase.

In MFT, the rock grains are first exposed to water and aged for 2 days to allow for equilibrium conditions to be met (Figure 7). Solid particles carry an electrical charge when in contact with an aqueous phase, and its magnitude depends upon the surface chemistry of the solid and the solution chemistry of the aqueous phase (Kelebek, 1984). Once oil is introduced, the balance of surface forces between the grain surface and oil and water, determine which of the two immiscible fluids will adhere to the grain surface. If water adheres to the surface, then the grain is considered water-wet. Similarly, if oil adheres to the surface, then the grain is considered oil-wet.

Oil-wetness can be described by direct and indirect sorption of oil to the rock surface (Brady & Thyne, 2016), which refers to mechanism of wetting on the grain scale. Figure 7 is an illustration of the two oil-wet scenarios, direct and indirect sorbed oil. Direct adsorption of oil occurs if the attractive force is greater than the disjoining pressure. Solvent recovery methods such as surfactant flooding, are required to displace the directly adhered oil (Brady & Thyne, 2016). Indirect adsorption occurs when oil adheres loosely to the rock surface through a water film, and thus sensitive to the brine chemistry. To identify the causes of wettability alteration in carbonate rocks, Brady and Thyne (2016) coined the term functional wettability, which is a product of indirectly adsorbed oil. In their work, they focused on indirectly adsorbed oil, which makes up the largest fraction of non-free-phase original oil in place and can be influenced by waterflooding.



(a) Indirectly Sorbed Oil (b) Directly Sorbed Oil

Figure 8: Indirect and direct adsorption of oil on reservoir mineral surfaces (Brady & Thyne, 2016).

In this project, grains referred to as oil-wet describe oil adhering to the rock both directly and indirectly. This description of oil-wetness was selected since the synthetic oils used in this project are not expected to have enough of an attractive force to overcome the disjoining pressure and thus break the water film layer. Instead, the interaction between the oil and rock surface are through a thin film of water.

4.1. Flotation Requirements

Flotation is a well-known physicochemical process exploiting differences in surface properties of minerals which depend on wettability or hydrophobicity of particles (Perkins, 1921; Klassen, 1948a, 1948b; Whelan, 1956; Boutin & Wheeler, 1967). If the solid surface of the particles of interest is not hydrophobic (oil-wet) to begin with, a chemical agent is added to render the surface hydrophobic, thus causing the solid to adhere to the hydrophobic phase (oil). The hydrophobic particles then floats or remain in suspension while the hydrophilic (water-wet) particles sink (Swinburne and Rudorf, 1906; Wang & Peng, 2014). In the case of MFT, the wettability of the rock grains are a natural consequence of the solid interaction with oil and water.

Grain size plays a crucial role in the effectiveness of flotation processes since it determines which forces (region) are dominant in a given condition. The three possible regions that could be determined by grain size are: (1) The <u>colloidal region</u> where grain sizes are typically less than 5-10 microns. In this region, the Brownian motion becomes essential, but the gravity-induced capillary force is completely negligible. (Yoon, 2000; Danov & Kralchevsky, 2010). Collision between the particles resulting from Brownian motion can lead to perikinetic coagulation (Yoon, 2000). The properties of such suspensions strongly depend on the surface properties of the dispersed solid phase. Thus, the particles are always suspended in the fluid (e.g. bacteria or polymer in water) regardless of wettability. Therefore, flotation processes are ineffective in this region. (2) The <u>gravitation force dominant region</u> is a result of large particle sizes. In this region, the particles will always sink regardless of its wettability making flotation impossible (Rickard, 1916; Pryor, 1965; Yoon, 2000). (3) Between the colloidal and gravitational force region, there exist a <u>transitional region</u> where surface forces or gravitational forces can dominate depending on the wettability of the particle. In this region, flotation processes are effective in separating materials based on their wettability (Rickard, 1916; Pryor, 1965; Yoon, 2000). Numerous studies have shown that the successful exploitation of differences in surface properties to separate minerals requires the metallic ore particle size to be between 10 µm to 300 µm, and bituminous coal particle size to be between 10 µm to 6700 µm (Rickard, 1916; Ralston 1916; Pryor, 1965). Note that the range of grain size range eligible for flotation differs depending on the density of the grains. The higher the density the narrower the range. Flotation processes are ineffective for particles outside this range since they will fall in the colloidal or gravitational region.

A set of controlled visual experiments using glass beads, deionized water and decane were conducted to demonstrate wettability measurements in a gravitation force dominant region and in a transitional region. The colloidal region was not tested due to difficulty in attaining glass beads sizes less than 10 µm. The three glass beads sizes selected were: 88-149 µm, 425-600 µm, and 3000 µm. For each grain size, oil-wet and water-wet cases were examined. For the water-wet cases, the beads did not require any preparation prior to MFT experiments since the beads were made of glass and thus hydrophilic (water-wet). For the oil-wet cases, the beads were soaked in WD-40 for 15 minutes to render the surfaces hydrophobic before the MFT experiment.

As shown by Figure 9 and Figure 10, both 88-149 µm and 425-600 µm are in the transition region. In this region, the water-wet beads reside in the water-phase as the oil-wet beads float to the oil phase. The oil-wet glass beads float because the downward pull of gravity is insufficient to overcome the oil-wet adhesion to the oil phase. On the other hand, 3000 µm glass bead size was found to be in the gravitational force dominant region as shown by Figure 11. Regardless of the wettability, both the water-wet and oil-wet beads sink to the bottom of the beaker. Due to the large size, the pull of gravity is large enough to overcome the oil-wet beads adhesion to the oil phase.

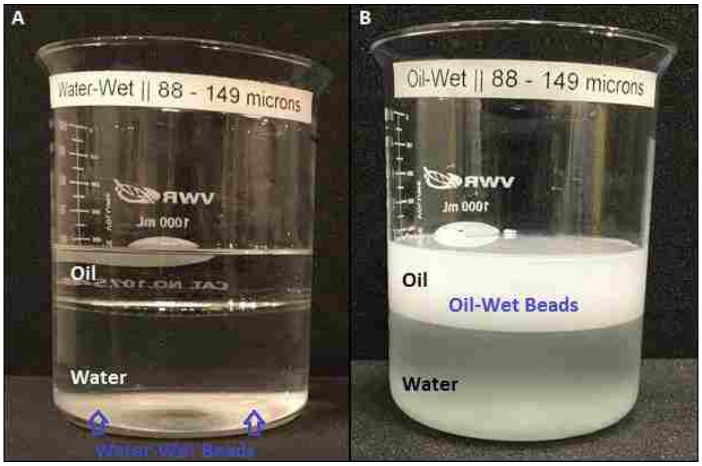


Figure 9: Results of water-wet and oil-wet 88-149 µm glass beads which are in the transitional region.

Figure 10: Results of water-wet and oil-wet 425-600 µm glass beads which are in transitional region.

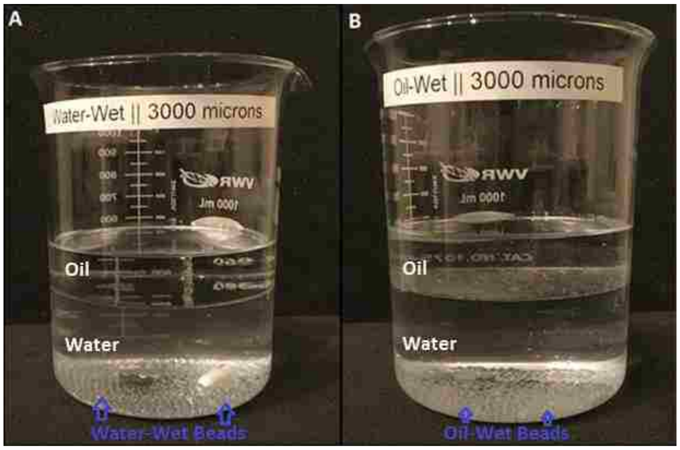


Figure 11: Results of water-wet and oil-wet 3000 µm glass beads which are in the gravitational force dominant region.

4.2. Flotation Fundamentals

Capillary forces play a crucial role in a variety of phenomena and appear whenever the particles distort the liquid interface. These forces are responsible for the adhesion between two solid bodies connected by a liquid bridge and for the flotation of denser particles at the free surface of a liquid, in a gravitational field. Theoretically, determining the strength of interaction forces between bodies at an interface requires solving the Young-Laplace equation, which describes the interface shape (de Gennes, 1985). Analytical solutions can only be obtained for highly symmetric situations or by using approximations. The most common approximation is the linearization of the Young-Laplace equation, valid when the interface slope is small. Several studies on the capillary interactions between different bodies have been done by Kralchevsky and co-workers (2000, 2001). They calculated the exact force for two cylinders and spheres numerically and compared it with the approximated formula. They concluded that for short distances between the particles the approximated formula underestimates the force considerably. In the case of floating spheres, they calculate the interaction by replacing the spheres with equivalent cylinders (Paunov, et al., 1993). Danov and Kralchevsky (2010) studied the interactions between particles at a fluid interface. In their work, they reviewed different kinds of lateral capillary forces and derived their expression.

4.2.1. Flotation Force Balance

The process of flotation combines fluid and particle mechanics, thin film theory, and surface science. This section presents a force balance analysis adopted from several publications (Bloom & Heindel, 1997; Pitois and Chateau, 2002; Emerson, 2007; Binks & Horozov, 2007). The stability of a floating particles in a fluid can be expressed by a dimensionless parameter analogous to the bond number (Bo') which gives the ratio of detachment forces ($\mathrm{F}_{\mathrm{detach}}$) to attachment forces ($\mathrm{F}_{\mathrm{attach}}$) (Schulze, 1984). The attachment force is the force that keeps the particle in the oil-water interface and it consists of the capillary force on the liquid side (F_{ca}) and hydrostatic pressure force (F_{hyd}). The detachment force is the force that is needed to detach the particle from the oil-water interface and it includes the weight of the particle ($F_g - F_b$), drag (F_d), and capillary force on the bubble side (F_σ).

$$Bo' = \frac{F_{detach}}{F_{attach}} = \frac{F_g - F_b + F_d + F_\sigma}{F_{ca} + F_{hyd}} \qquad \text{Equation 5}$$

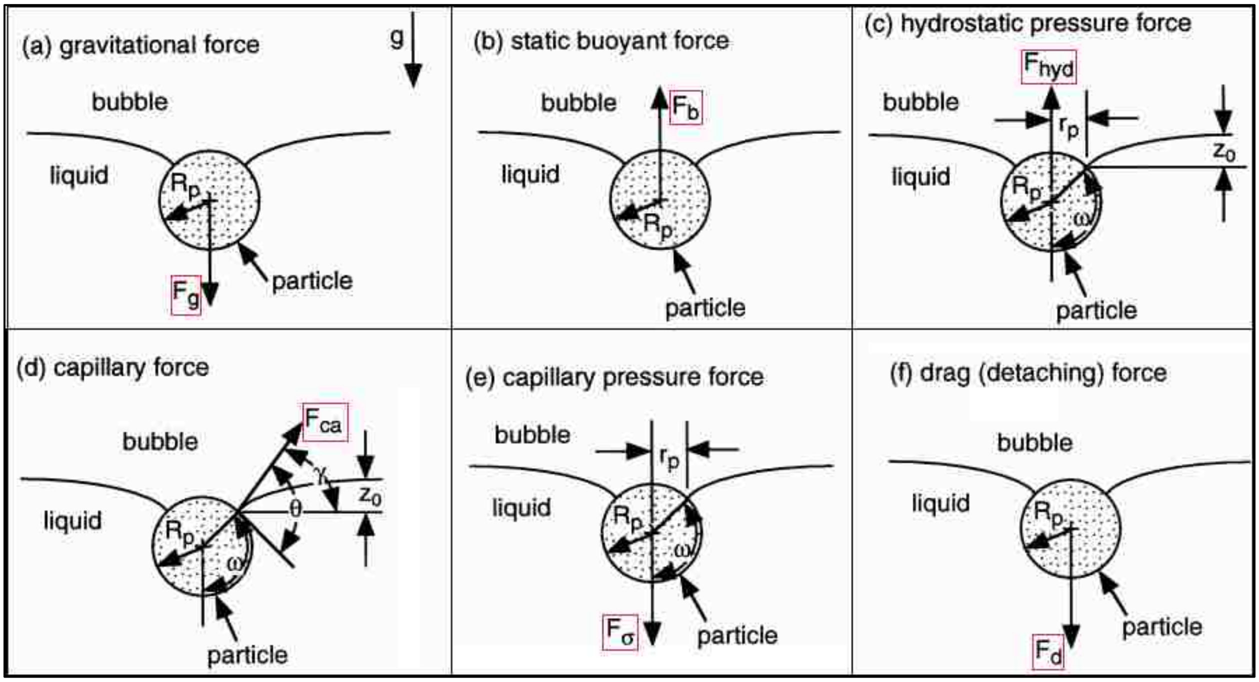


Figure 12: Forces acting on a bubble-particle aggregate (Bloom & Heindel, 1997).

- $F_g = \frac{4}{3}\pi R_P^3 \rho_P g$ Equation 6
- $F_b = \frac{\pi}{3} R_P^3 \rho_l g[(1-\cos(\omega))^2(2+\cos(\omega))]$ Equation 7
- $F_d = \frac{4}{3}\pi R_P^3 \rho_P a_c$ Equation 8
- $F_\sigma = \pi r_P^2 P_\sigma \approx \pi R_P^2 \sin^2(\omega)(\frac{2\sigma}{R_B} - 2R_B\rho_l g)$ Equation 9
- $F_{ca} = -2\pi R_P \sigma \sin(\omega)\sin(\omega+\theta)$ Equation 10
- $F_{hyd} = \pi R_P^2 \sin^2(\omega)(\rho_l g z_0)$ Equation 11

where a_c depends on both the structure and the intensity of the turbulent flow field, ω is the angle in the particle, θ is the contact angle, R_B is the bubble radius, R_P is the particle radius, ρ_l is the density of the liquid in a neighborhood of a bubble. Figure 13 illustrates the three-phase contact between the bubble, particle, and fluid regions, that corresponds to the above equations.

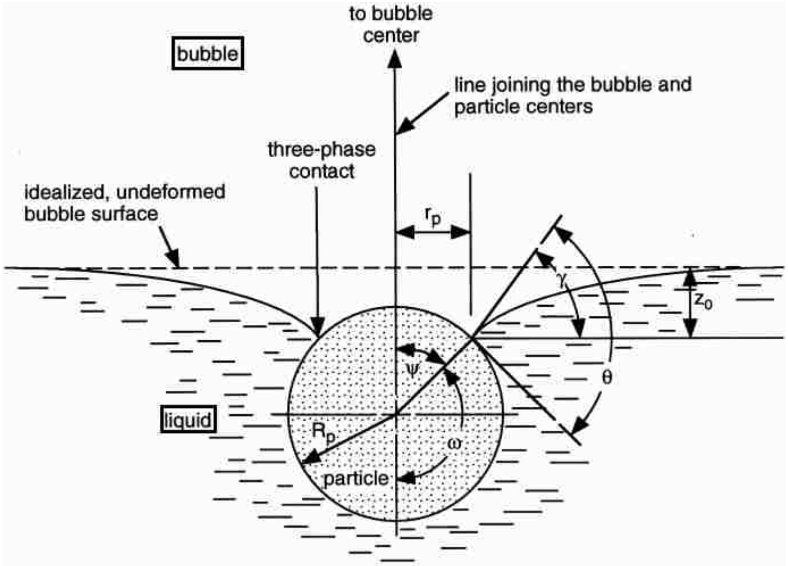


Figure 13: Three-phase contact between the bubble, particle, and fluid regions (Bloom & Heindel, 1997).

For a particle in the presence of oil and water (Figure 14), the following equations adopted from (Binks & Horozov, 2007) would apply.

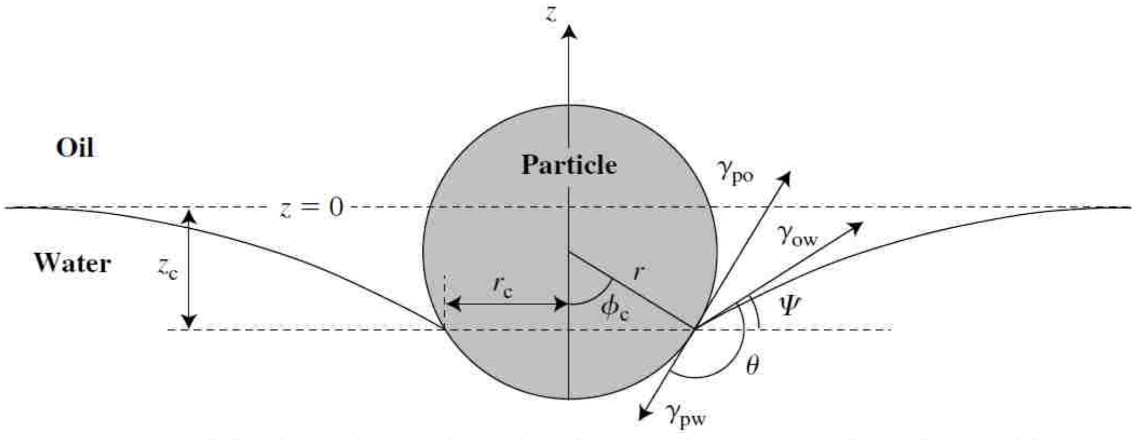


Figure 14: Heavy solid spherical particle with radius r and contact angle in the equilibrium at the oil-water interface levelled at z=0 far from the particle. The three-phase contact line with radius rc is depressed at the depth z_c below the zero level.

$$\mathrm{F_\gamma + F_P = \frac{4}{3}\pi\rho_P r^3 g}$$ Equation 12

$$\mathrm{F_\gamma} = -2\pi r\gamma_{ow}\sin(\varphi_c)\sin(\varphi_c + \theta)$$ Equation 13

$$\mathrm{F_P = \rho_w V_{pw} g + \rho_o V_{po} g - (\rho_w - \rho_o) g z_c} A_c$$ Equation 14

Where $\mathrm{F_\gamma}$ is the vertical capillary force, $\mathrm{F_P}$ is the Integration of the hydrostatic pressure distribution around the entire particle surface, γ_{ow} is interfacial tension between oil and water, the ρ_P, $\mathrm{\rho_w}$, $\mathrm{\rho_o}$ are the densities of the particle, water, and oil, respectively. $\mathrm{V_{pw}} = \frac{\pi r^3\left(2-3\cos(\varphi)+cos^3(\varphi)\right)}{3}$ and $\mathrm{V_{po}} = \frac{4}{3}\pi\mathrm{r}^3 - \mathrm{V_{pw}}$ are particle volumes immersed in water and oil, respectively. and $\mathrm{A}_c = \pi r^2\sin^2(\theta_\mathrm{C})$ is the area of the contact line. When $\mathrm{F_\gamma}$ and $\mathrm{F_P}$ are substituted into equation 12 the following force balance equation was derived.

$$\sin(\varphi_c)\sin(\varphi_c + \theta) = -\frac{\mathrm{B}}{6}\left[4\left(\frac{\rho_\mathrm{P}-\rho_\mathrm{o}}{\rho_w-\rho_\mathrm{o}}\right) - (1-\cos(\varphi_c))^2(2-\cos(\varphi_c)) + 3\frac{\mathrm{z_c}}{\mathrm{r}}\sin^2(\varphi_c)\right]$$

Equation 15

where $\mathrm{B} = \frac{(\rho_w-\rho_\mathrm{o})r^2}{\gamma_{ow}}$ is the dimensionless bond number. In the considered case of a heavy particle ($\rho_\mathrm{P} > \rho_w > \rho_\mathrm{o}$), $\mathrm{F_\gamma}$ must always act upwards, therefore, $\varphi_c + \theta \gg 180°$, $\varphi_c \leq 180°$. Hence the left-hand side of the equation is restricted in the range of $-1 \leq \sin(\varphi_c)\sin(\varphi_c + \theta) \leq 0$. The same should apply to the right-hand side of the equation.

If the particle is too big or dense, the bond number will be too large and cannot be solved. These particles are considered to be in the gravitational dominant region and will sink regardless of their wettability. For particles that are too small r approaching zero, the interfacial force, which varies linearly with r, dominates the buoyant weight of the particles which varies as r^2. In this limit, since $\frac{(\rho_w-\rho_\mathrm{o})r^2}{\gamma_{ow}} \to 0$, the right-hand side of equation 15 is zero and thus $\sin(\varphi_c + \theta) \approx 0$. Due to this, it has been understood that small particles can be suspended along fluid surfaces without causing significant interfacial deformation no matter how heavy they are. These particles are considered to be in the colloidal region which typically consists of particle less than 10 µm. Krahshesky, et al. (1992, 1993) reported that the lateral particle-particle attraction force, which arises due to interface deformation, is also insignificant when the particle diameter is smaller than 10 µm.

Krahshesky, et al. (1992, 1993, 2010) solved the Laplace equation for the interface shape using bipolar coordinates for a case where the meniscus slope and the particle size are small. This solution has provided expressions for calculating the capillary meniscus force between two vertical cylinders, two spheres partially immersed in a liquid layer and between a vertical cylinder and a sphere. Specifically, Kralchevsky and Nagayama (2000, 2001) have shown that the lateral force $\mathrm{F_l}$ acting on the particles of radii of R_1 and R_2 separated by distance L is equal in magnitude and opposite in sign and is given by

$$\mathrm{F_l} = -2\pi\gamma \mathrm{Q_1 Q_2 q} * \mathrm{K_1(qL)} \qquad \text{Equation 16}$$

where q is the inverse capillary length; γ is the liquid/fluid interfacial tension; $\mathrm{K_1(qL)}$ is the modified Bessel function of the second kind and first order, and $\mathrm{Q_1}$ and $\mathrm{Q_2}$ are capillary charges for floating particles that can be estimated from the following expression.

$$\mathrm{Q_i} = \frac{1}{6}\mathrm{q^2 R_i^3}(2 - 4\mathrm{D_i} + 3\cos(\alpha_\mathrm{i}) - \cos^3(\alpha_\mathrm{i})),\ (\mathrm{i} = 1, 2) \qquad \text{Equation 17}$$

where $\mathrm{D_i} = \frac{\rho_\mathrm{i} - \rho_\mathrm{II}}{\rho_\mathrm{I} - \rho_\mathrm{II}}$ and ρ_i, ρ_I, and ρ_II are the mass densities of the particle, lower (water) and upper (oil) fluid phases.

The interface surface becomes flatter with increasing distance from the particle. When a suspended particle is within the region of influence of another particle, it will move along the interface due to the lateral component of the interfacial force. The above static equilibrium analysis is useful for determining the parameter values for which the particles can remain trapped on two-fluid interfaces, as well as the sign and magnitude of forces that act between two suspended particles (Bloom & Heindel, 1997; Pitois and Chateau, 2002; Emerson, 2007; Binks & Horozov, 2007). To understand the actual motion of particles on the interface equations of motion must be solved. Since the governing equations are complex, the dynamic behavior of fluid particles is not well understood.

4.2.2. Wetting Forces in Flotation

The relative magnitude of intermolecular surface forces determines the wettability of the rock-oil-brine system (Anderson, 1986; Hirasaki, 1991; Israelachivili, 2011). The magnitude of these intermolecular surface forces is found to be significantly large when the thickness of aqueous wetting films squeezed between the bulk oil phase and reservoir rock surface becomes significantly small.

The wetting behavior of a liquid on a solid surface is determined by the difference between the cohesive interactions holding the liquid together and the adhesive interactions between the liquid and the solid (Schick, 1990; Israelachvili, 1992). The net effect of the interaction potentials on the wetting behavior are typically quantified by considering a liquid film of thickness on a solid surface. If the adhesive solid-liquid interactions are strong, the system can lower its free energy by increasing the distance between the two surfaces. This leads to a net repulsive force per unit area between the solid-liquid and liquid-vapor interfaces, which is called the disjoining pressure (de Feijter, 1988) and can be measured in experiment. Experimentally measured magnitude of surface forces in the form of adhesion energy per unit area is compared with either theoretically determined disjoining pressure using DLVO theory or using the concept of work of adhesion that relies on the theoretical determination of equilibrium (Young's) contact angle and its comparison with experimentally measured values of equilibrium (Young's) contact angle (de Gennes, 1985;

Israelachvili, 2011). An agreement between the experimental measurements and theoretically determined surface force-distance profile versus film thickness curves is sought for the development of accurate mathematical models to describe wettability of complex rock/oil/water systems at pore level. However, the experimental determination of surface force versus film thickness relationship using atomic force microscopy or surface force apparatus has only been reported at ambient conditions. The use of dead oil or pure hydrocarbons as oil phase in these types of experiments also limits the use of such measurements in determining the extent of rock/oil adhesion interactions at reservoir conditions.

There are several different ways to express the degree of wetting of a solid against liquids. Wetting has been described in terms of spreading coefficient shown in equation 18 (de Gennes, 1985; Somasundaran & Zhang, 2004; Israelachivili, 2011;)

$$S = \gamma_{\mathrm{so}} - \gamma_{\mathrm{sw}} - \gamma_{\mathrm{ow}} \qquad \text{Equation 18}$$

Where γ_{ow}, γ_{so}, and γ_{sw} are the interfacial tensions of the oil/water interface, the solid/oil interface (Figure 15), and the solid/water interface, respectively. When S is positive the spreading of oil occurs spontaneously.

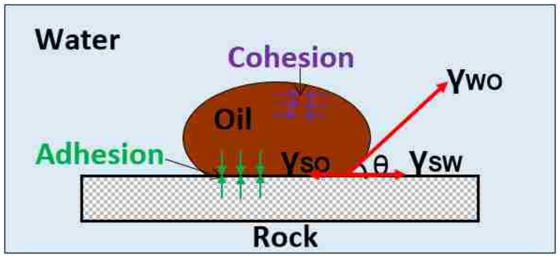


Figure 15: A schematic representation of contact angle in rock/oil/water (Solid/Liquid/Liquid) systems.

Since it is difficult to estimate γ_{so} directly, Young's equation was extended to understand the wettability phenomenon of rock/oil/water systems of petroleum engineering, by considering the equilibrium state at the point of three phase contact (Saini et al., 2008).

$\gamma_{\mathrm{so}} = \gamma_{\mathrm{sw}} + \gamma_{\mathrm{ow}}\cos(\theta)$ Equation 19

Where θ is the equilibrium contact angle. Similarly, Dupre's equation explains the change in free energy accompanying the replacement of unit area of solid-oil interface by solid-water interface.

$\Delta G = \gamma_{\mathrm{so}} - (\gamma_{\mathrm{sw}} + \gamma_{\mathrm{ow}})$ Equation 20

Thus, the displacement of water by the oil would happen when the solid-oil interfacial tension is higher than the combined interfacial tensions of solid-water and liquid-oil. Young's expression combined with Dupre's equation results in following expression.

$\Delta G = \gamma_{\mathrm{ow}}\,(\cos(\theta) - 1)$ Equation 21

Therefore, the change in free energy for three phase contact system depends of the particle's hydrophobicity, which is a function of contact angle (θ). The maximum negative change in free energy would occur for a perfect hydrophobic particle with a contact angle of 90°. However, equation 21 is valid for an equilibrium condition where all other forces are absent in the system.

As described by Celik and Somasundran (1980), solids in flotation will reside in the oil phase, water phase, or at the interface depending on the following criteria. If $\gamma_{\mathrm{so}} > \gamma_{\mathrm{sw}} + \gamma_{\mathrm{ow}}$, the solid will reside in the water phase, thus indicating water-wet or hydrophilic nature. If $\gamma_{\mathrm{so}} < \gamma_{\mathrm{sw}} + \gamma_{\mathrm{ow}}$, the solid will reside in the oil phase, thus indicating oil-wet or hydrophobic nature. If $\gamma_{\mathrm{ow}} > \gamma_{\mathrm{s0}} + \gamma_{\mathrm{sw}}$ or if none of the three interfacial tensions is greater than the sum of the other two, the solid will collect at the water-oil interface with a larger portion of the solid remaining on the water side of the interface if $\gamma_{\mathrm{sw}} > \gamma_{so}$ and θ is less than 90°, and on the oil side if the interface of $\gamma_{\mathrm{sw}} < \gamma_{so}$ and θ is greater than 90°.

These relationships show that all the three interfacial tensions play a role in determining the phase where the rock grain resides. Most of the researchers agree that changing the ionic composition of injected brine will affect the capillary forces in the core (Kilybay et al., 2017). However, none could provide a strong evidence that oil-water IFT (γ_{ow}) varied in an appreciable manner to influence oil-recovery. Yousef et al. (2011) observed a slight decrease in oil-brine IFT when brine salinity was decreased from formation water to sea water. However, oil-water IFT reduction was insignificant when the brines were diluted. Zheng (2012) also observed negligible change in oil-water IFT as brine salinity and composition variations. However, she did observe oil-water IFT changes when surfactants were introduced to the brine. Al Quraishi et al. (2015) conducted oil-water IFT measurements between oil and different brines at reservoir conditions. With decreasing brine salinity by dilution of up to 10 times, the oil-water IFT was reduced by about 6 units which is not significant enough to be a dominant mechanism for low salinity water flooding. Al-Harrasi et al. (2012) conducted laboratory experiments on low salinity waterflooding on carbonate rocks through spontaneous imbibition and core flooding experiments, and used brines with different dilutions of formation water (2-100 times dilution). These brines improved the oil recovery by 3–5% after injection of one pore volume of low salinity brine. From IFT studies, the authors found that there was little change in the oil-water IFT as brine salinity was varied. Therefore, they concluded that wettability alteration was the mechanism for improved oil recovery by low salinity waterflooding in carbonate rocks. Al-Attar et al. (2013) studied low salinity water injection with different values of salinity and concentration of calcium. They observed significant increase in oil recovery, up to 84% original oil in place, as salinity was decreased. Their contact angle studies showed that decreasing salinity shifted the wettability towards a more mixed wet state and not IFT change.

Based on the published research, oil-water IFT (γ_{ow}) does not change significantly as brine salinity is varied. Therefore, the changes observed due to brine salinity variations can be attributed to wettability change or the change in solid-oil (γ_{s0}) and/or solid-water (γ_{sw}) IFTs.

CHAPTER 5. TECHNIQUE DEVELOPMENT, REFINEMENT, & VALIDATION

This chapter details the development, refinement, and validation of the MFT. The MFT can be used to quickly measure wettability. Existing wettability methods are limited by the time and expense it takes to run a single experiment (days to weeks). This is a significant bottleneck for laboratory experiments and impedes progress toward better understanding the nature of petroleum adhesion due to the sheer number of measurements required. To overcome this barrier, we developed a measurement technique that was fast, reliable, and would serve as both a screening tool and provide quantitative results.

5.1. Development

Two flotation techniques in petroleum systems were identified in the literature: (1) Wu et al. (2008) and (2) Doe and Dubey (1993), referred to as Wu and D&D, respectively (Table 6). Both procedures give qualitative measures of wettability. The two main differences are that Wu's procedure dries the rock powder after it is aged in oil, while the D&D procedure ages the rock in brine prior to aging in oil and does not include the drying step.

Table 6: Comparison of the two published flotation experiment procedure by Wu et al (2008) and Dubey and Doe (1993). The asterisk (*) indicates the main differences in the two procedures.

Wu et al. (2008) Procedure	Dubey and Doe (1993) Procedure
• Age rock in oil for two days in a test tube • Decant the oil • Dry the remaining rock* • Add brine to the dried rock powder in test tube	• Age rock in brine for two days in a test tube* • Separate brine from rock and save the brine • Add oil in the test tube with rock grains • Age rock in oil for two days • Add the saved brine in oil-rock mixture • Stir the brine-oil-rock mixture

Table 6: Cont'd

Wu et al. (2008) Procedure	Dubey and Doe (1993) Procedure
• Stir the brine-oil-rock mixture • Take measurements after 2 hours	• Take measurements when the mixture settles.

Both procedures were tested for 24 different model oil-rock combinations (Table 7). It was observed that Wu's procedure rendered all rock types water-wet, while the D&D method indicated sandstone to be water-wet and the carbonates to be oil-wet. The D&D procedure was modified to add the drying step from Wu's procedure in order to test the effect of drying, and it was observed that both sandstone and carbonate rocks were rendered water-wet, that is no grains were floating. These results are denoted as D&D w/ drying in Table 7. In addition, when 2.5 ml oil was added at the end of Wu's procedure and the contents were vigorously stirred, the powdered limestone, chalk, or dolomite that had previously sunk to the bottom of the test tube floated in the oleic phase. This confirmed that the drying step unique to Wu's procedure is responsible for the difference between the procedures. We concluded that the true nature of the carbonate rocks under the tested conditions is oil-wet; however, the drying process is hypothesized to have destabilized the oil film around the grains or evaporated the SACs in the oleic phase thus rendering the originally oil-wet carbonate rock grains water-wet. Therefore, the D&D procedure is likely to be the most consistent and reliable of the two procedures because it avoids the drying process that shifts wettability and avoids potential evaporation of SAC in the model oil. Also, there is less chance of contamination in the D&D procedure because the test tubes are always closed.

Table 7: Effects of oil composition on wettability @ 70°C using Wu et al. (2008), Dubey and Doe (1993), and Dubey and Doe (1993) with drying step. WW represents water-wet conditions; OW is oil-wet.

Rock Type	Procedure	Aromatic A1	Oxygen O1	Sulfur S1	Nitrogen N1	Decane Dec	Condensate Cond
Berea	Wu	WW	WW	WW	WW	WW	WW
	D&D	WW	WW*	WW	WW	WW	WW
	D&D w/ drying	WW	WW	WW	WW	WW	WW
Chalk	Wu	WW	WW	WW	WW	WW	WW
	D&D	OW	OW	OW	OW	OW	OW
	D&D w/ drying	WW	WW	WW	WW	WW	WW
Limestone	Wu	WW	WW*	WW	WW	WW	WW*
	D&D	OW	OW	OW	OW	OW	OW
	D&D w/ drying	WW	WW	WW	WW	WW	WW
Dolomite	Wu	WW	WW*	WW	WW	WW	WW
	D&D	OW	OW	OW	OW	OW	OW
	D&D w/ drying	WW	WW	WW	WW	WW	WW
WW*: water-wet with a small fraction of rock displaying oil-wet behavior.							

The main modification of the MFT from the D&D procedure was measuring the mass of rock added to the test tube at the start of the experiment, and measuring the mass of water-wet grains at the bottom of the test tube at the end of the experiment. This allows us to calculate the mass of oil-wet grains by difference. This modification transforms the D&D procedure from a qualitative to quantitative wettability measurement method. The original MFT procedure is illustrated in Table 8 and Figure 7.

Table 8: Original Modified Flotation Technique (MFT) Procedure

Step 1. Crush rock to specified grain size e.g. 53 microns.

Step 2. Age 0.2 grams of rock in brine for 2 days.

Step 3. Separate brine from rock, measure pH, and save it for later reuse.

Step 4. Age wet rock in oil for 2 days and stir the mixture every 12 hours.

Step 5. Add the saved brine in the oil-rock mixture.

Step 6. Vigorously stir and allow for mixture to settle for 24 hours.

Step 7. Measure the results

   7.1. Decant the floating rock-oil mixture, measure pH, and decant the aqueous solution

   7.2. Thoroughly dry the sunken rock grains and weight it.

   7.3. Mass of water-wet grains = measured weight

   7.4. Mass of oil-wet grains = 0.2 grams - measured weight

5.2. Refinement

To improve the MFT, a series of refinements in the experimental procedures were made.

5.2.1. Scale-Up Refinement

The objective of this study was to identify the ideal mass of rock powder for the MFT. The initial procedure used 0.2 grams of rock sample, 3 ml of oil, and 10 ml of brine. It was observed that slight perturbations in the experiments (e.g. oil-wet grains sticking to the side of the test tube during the final weight measurement) introduce variability in the results due to the small mass of rock powder used. Therefore, three weights (0.2, 0.5, and 1 gram) of rock powder were tested with the goal of reducing variability in the results. In addition, the volume of oil was also proportionally scaled to the mass of rock (0.5grams and 1 gram).

It was hypothesized that the larger the rock mass, the less sensitive the results would be to slight weight changes/perturbations, e.g. oil-wet grains stuck on the test tube walls when the floating rock-oil mixture is evacuated. The results of the three tested weights are shown in Figure 16. The results of the smallest rock mass (0.2 grams) varied significantly due to its greater sensitivity to changes in weight. Experiments using 0.5 grams gave better precision in the case of Berea and chalk. Surprisingly, experiments using 1 gram of rock mass had low precision probably because of improper scaling of oil and water due to the limitation in test tube volume. This is likely due to the large quantities of oil-wet grains that would be stuck on the test tube walls. Note that regardless of the mass of rock tested, limestone and dolomite results have large deviations. This was also attributed to the considerable fraction of oil-wet grains that were observed sticking to the walls of the test tubes after the oil-phase was evacuated (Step 7.1). These results indicated a need for further procedure refinements that are described in the next section.

Further Procedure Refinements

Recall that 0.5 grams of rock mass gave better results for both Berea and Chalk. But significant quantities of oil-wet dolomite and limestone grains stuck to the test tube walls after the oil-wet phase was evacuated, hence the results lacked precision. Presumably using a larger rock mass would decrease the sensitivity of the MFT analysis to error in the rock mass. For this reason, the MFT procedure was modified to use a relatively high rock powder mass of 1 gram. Again, the variation in the 1.0 gram results shown in Figure 16 was caused by improper upscaling of brine and oil volumes. It was realized later that only upscaling of the oil volume was necessary with the higher mass of rock powder. The purpose of the brine is to initially wet the rock prior to its exposure to oil, hence large quantities are not needed. On the other hand, an increase in oil volume ensures that there is enough oil volume for 100% of rock powder to float if it is completely oil-wet. Therefore, in the refined MFT the brine volume was reduced from 10 ml to 5 ml and the oil volume was increased from 5 ml to 15 ml. MFT results measured after this modification are shown as **M1** in Figure 17.

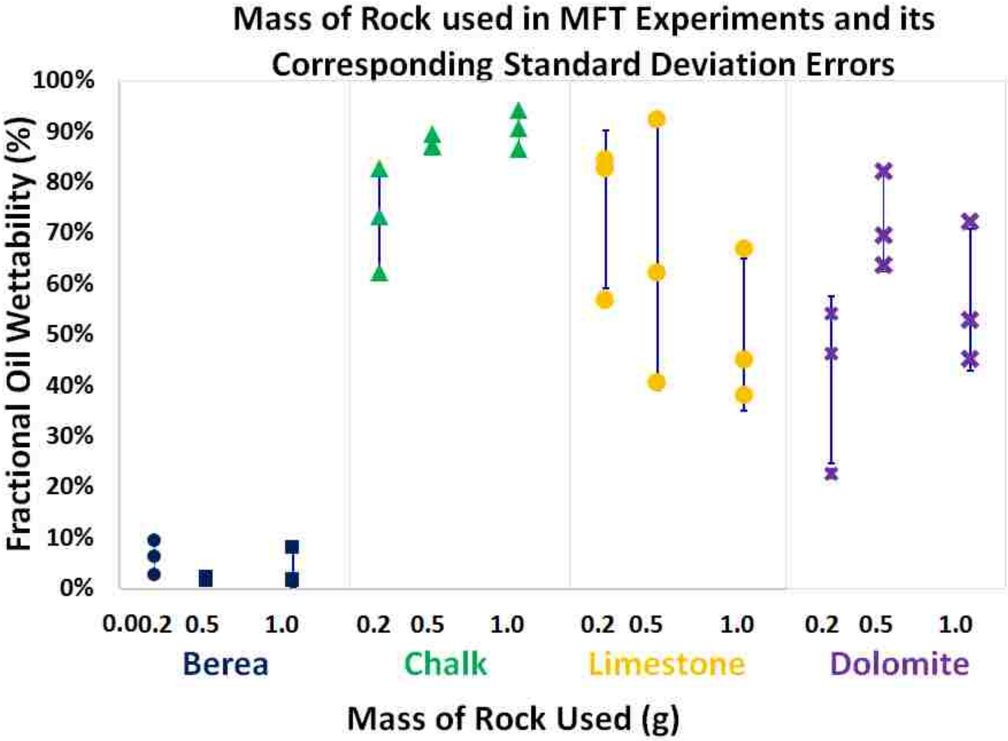


Figure 16: Test rock samples of 0.2, 0.5, and 1 grams of Berea, chalk, limestone, and dolomite with the goal of reducing variability in measurement.

Further tests showed that MFT reproducibility required consistent mixing and removal of fluid from the test tube prior to drying water-wet rock. Improved MFT precision from consistent mixing and fluid removal is shown in Figure 17 (**M2**).

Lastly, the process of decanting the brine and floating rock-oil mixture was optimized. After the brine was removed, oil-wet rock was observed to often stick to the test tube walls. A ‘rinse” step was then added, where brine was added to the test tube so that oil-wet rock powder would float.

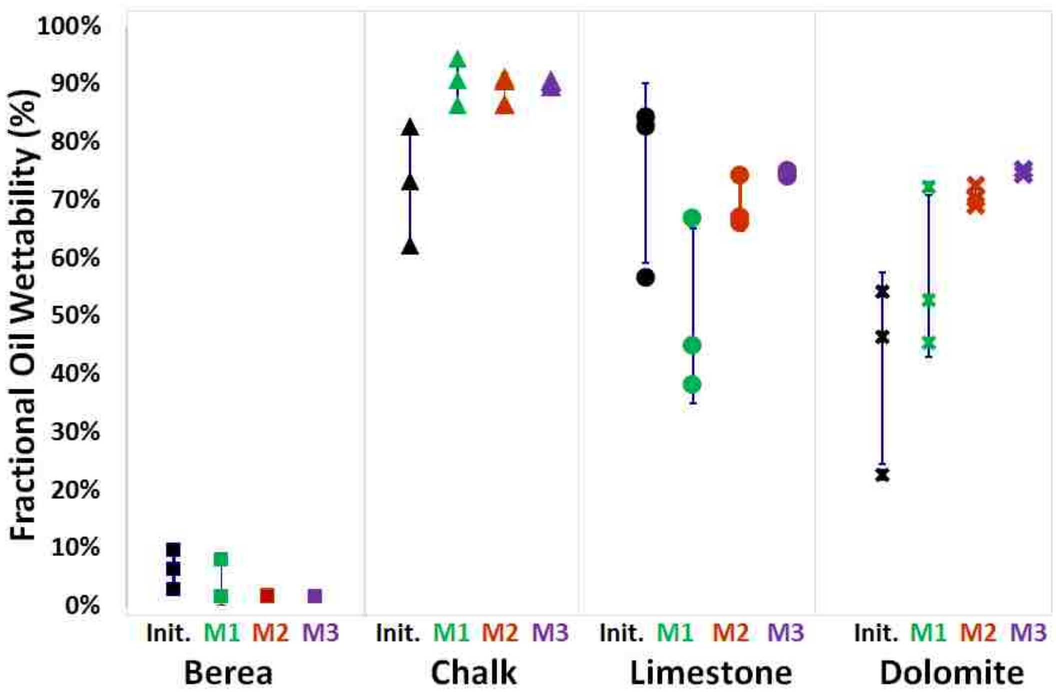


Figure 17: Different modifications (M1, M2, and M3) made to the procedure and their improvements on the precision of wettability when using 1 gram of Berea, chalk, limestone, and dolomite.

In some instances, rock grains were coagulated by the oil phase and dropped to the bottom of the test tube. These assemblages are noticeable because they lay on top of the water-wet rock grains without mixing. If the mixture was re-stirred the assemblage would remain suspended for some time in the oil phase, but would ultimately fall to the bottom of the test tube. To address this problem, a ‘rinse and repeat’ step was added to the procedure. This entails adding brine to the test tube to clean its walls and also provide a medium for the oil wet grains to float on and thus be evacuated from the test tube. This modification improved the precision of the results as indicated by **M3** in Figure 17. The refined MFT procedure that resulted from the described modifications is outlined in Table 9.

Table 9: Refined MFT Procedure

Step 1. Crush rock to specified grain size. 54-105μm/149-205μm grain size were used in this project

Step 2. Add 1.0 gram of rock in a test tube. (M1)

Step 3. Add 5 ml of brine in the test tube, thoroughly mix, and age for 2 days.

Step 4. Age wet rock in oil for 1 day and stir the mixture every 12 hours.

Step 5. Add the saved brine in oil-rock mixture.

Step 6. Vigorously stir mixture several times every 8-12 hours then allow for it to settle for 24 hours. (M2)

Step 7. Measure the results

  Step 7.1. Decant the floating rock-oil mixture, measure pH, and decant the aqueous solution.

  Step 7.2. Add brine to dislodge the oil-wet grains stuck on the sides of the test tube and decant the brine. (M3)

  Step 7.3. Thoroughly dry the sunken rock grains and weight it.

  Step 7.4. Mass of water-wet grains = measured weight

  Step 7.5. Mass of oil-wet grains = 1.0 gram - Mass of water-wet grains

5.2.2. Effect of Grain Size on MFT Results

A series of tests were conducted to determine the effect of grain size on the MFT wettability results. The three grain size distributions tested were: < 53 μm, 54-105 μm, and 105-206 μm for Berea, chalk, limestone, and dolomite. Each experiment was repeated 3 times to measure precision. As shown in Figure 18 rock grain size does not affect wettability results for chalk, limestone, and dolomite. However, Berea does vary with grain size. The smaller the Berea grain size the higher is the percentage of rock measured to be oil-wet, which is refered to as fractional oil wettability. This is due to higher clay content in the lower grain size, as shown in the X-Ray diffraction results in Figure 19. The higher the clay content of a rock, the higher the fraction of rock that is measured to be oil-wet using the MFT procedure.

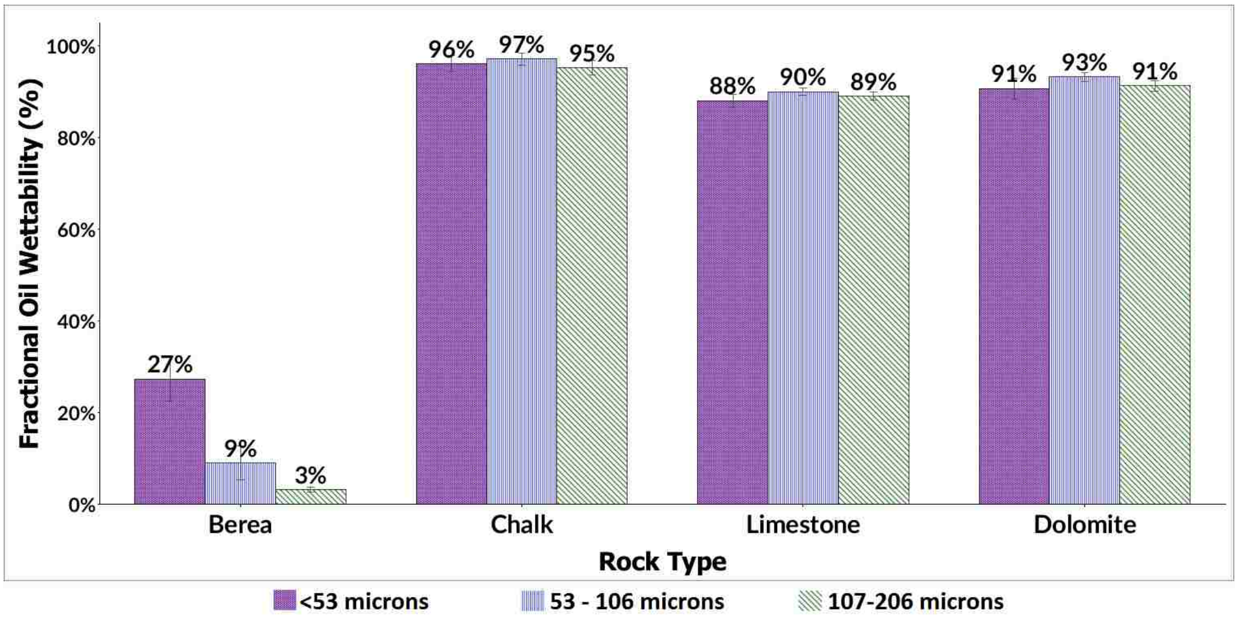


Figure 18: Effect of grain size on wettability at 70°C.

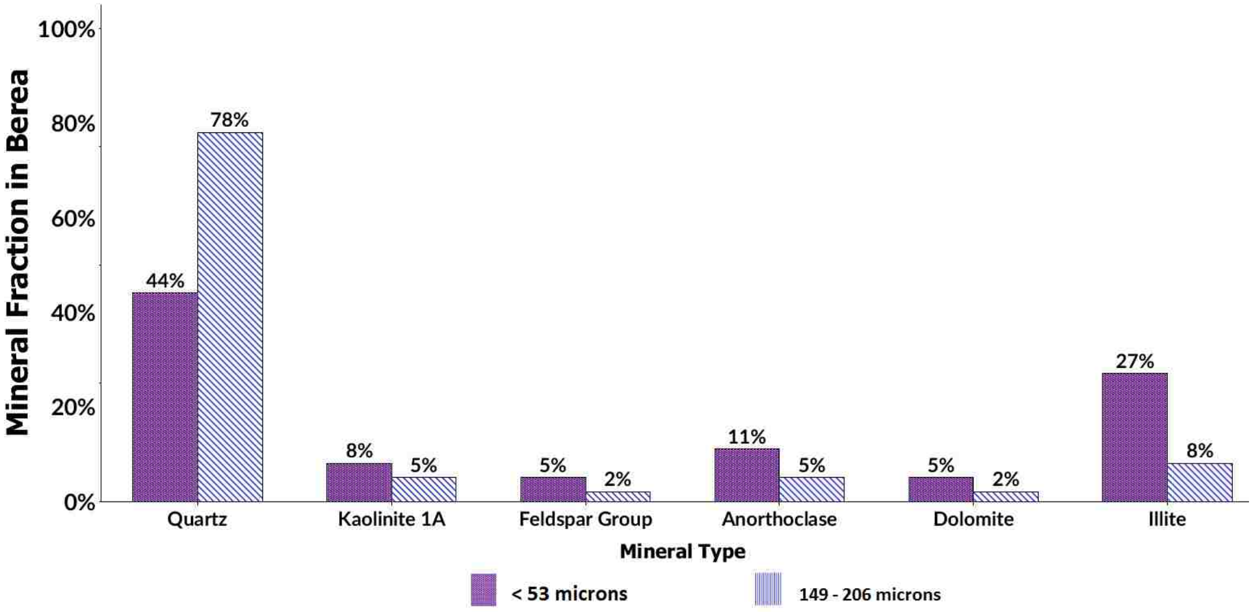


Figure 19: Comparison of mineralogy of <53 μm and 149-206 μm Berea samples.

5.2.3. Rock-Oil-Brine Aging Time Investigation

The objective of this study was to determine the optimal oil-brine-rock aging time for the MFT. Decane, condensate, and 4 model oils were tested. The 4 model oils were prepared by mixing decane with 2000 ppm of surface active compound: Tetralin (**A1**), Myristic acid (**O2**), Di-n-butyl sulfide (**S2**), and Quinoline (**N2**). Three temperatures were tested, 25°, 70°, and 110°C. The four aging periods tested were: 6 hours, 1 day, 2 days, and 14 days.

Figure 20 shows the effect of aging time on wetting of Tetralin SAC in the presence of DI water on Berea, chalk, limestone, and dolomite at 25°, 70°, and 110°C. MFT results were independent of aging time after 1 day. A similar trend was observed in the rest of the experiments (Figure A2 to Figure A5), except for the case of Berea + Myristic acid (Figure 21).

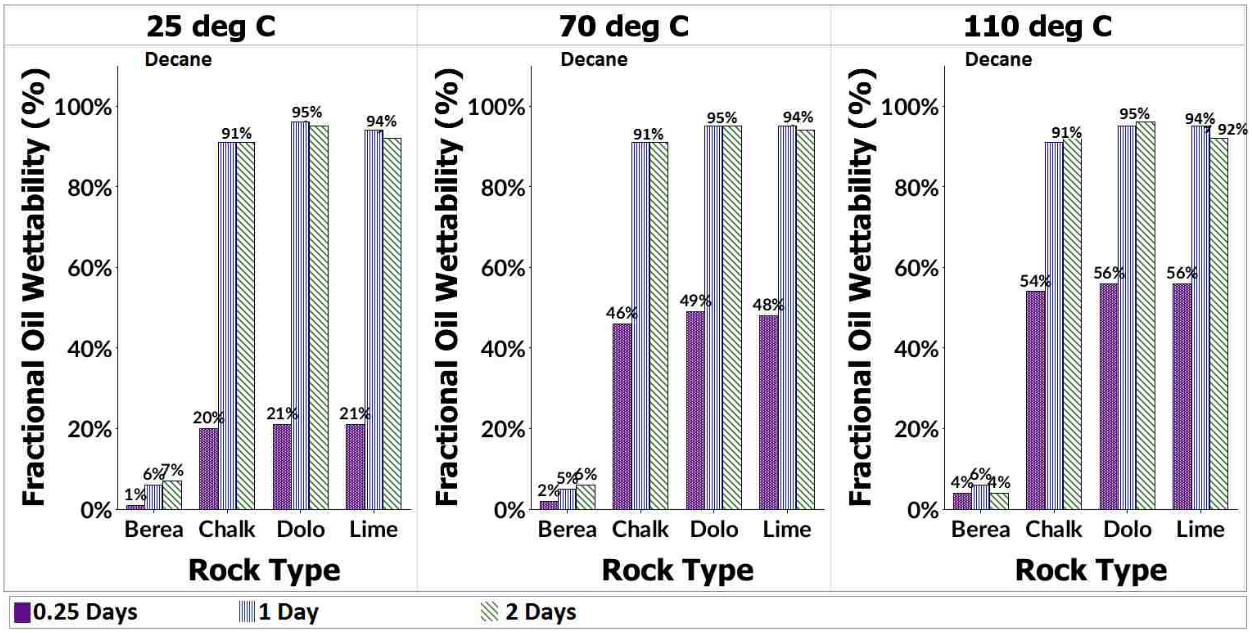


Figure 20: 6 hrs, 1 day, and 2 days aging time for 2000 ppm Tetralin at 25°C, 70°C, & 110°C.

Additional experiments were conducted to determine the ideal aging period for Berea when myristic acid is present (Figure 22). Six aging periods were tested and it was found that the ideal aging time for myristic acid was 2 days. Therefore, all subsequent MFTs used 2 days as the aging time. The required aging time may ultimately vary for different rock-fluid systems. One advantage of the MFT procedure is that it can quickly test and determine the appropriate aging period of the oil-rock-fluid system of interest.

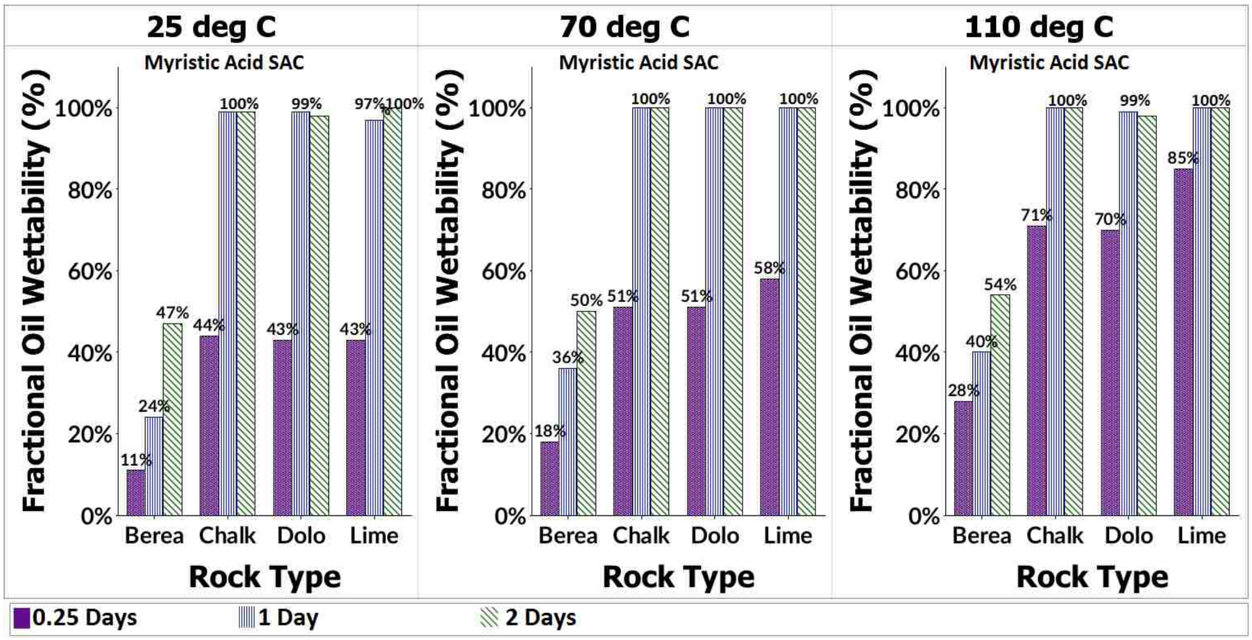


Figure 21: Aging time periods for Myristic acid (oxygen SAC) for Berea, chalk, limestone, and dolomite.

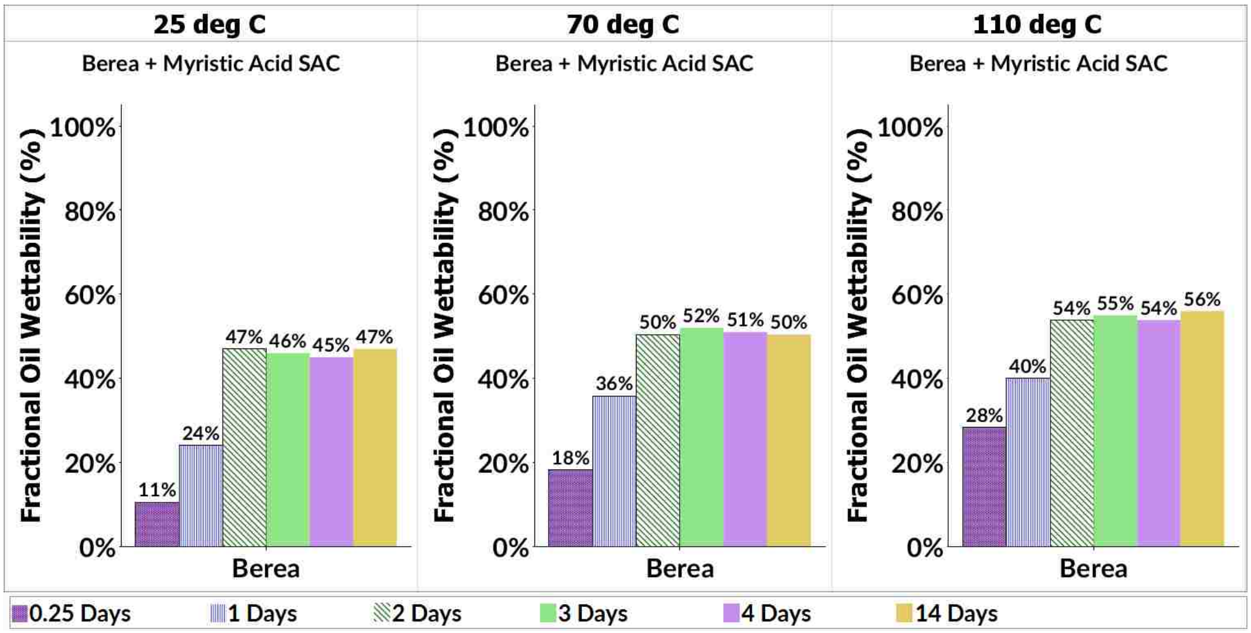


Figure 22: Aging time periods for Myristic acid (oxygen SAC) for Berea.

5.3. Rock Mineralogy Characterization

This study was divided into two parts. The first set of experiments focused on measuring the baseline mineralogy of Berea, chalk, dolomite, and limestone rocks. The second set of experiments examined the differences in the mineralogy of the fraction of rock that is oil-wet versus that which is water-wet.

5.3.1. Baseline Test

Baseline results of the four rock types were acquired by: crushing each rock to powder form, sieve to 149-206 microns, and then followed by XRD measurements. Each sample was tested twice to ensure the accuracy and repeatability of results. Table 10 outlines the XRD results for sandstones and carbonates. The three carbonate rocks were found to be primarily composed of a single mineral as illustrated Figure A7 to Figure A9. Therefore, in a case where wettability differences are measured within the same sample, it can be inferred that it is not due to the heterogeneity of the rock mineralogy. Fractional wettability in a reservoir may be caused by variations in cementation, interconnected porosity, surface area, and so on. Berea is made up of both quartz and clays (Figure A6) and is the focus of the more extensive wettability analysis below.

Table 10: XRD baseline results of Berea, chalk, limestone, and dolomite

Rock Type	Minerals					
Berea sandstone	Quartz: 67%	Illite: 21%	Kaolinite: 3%	Anorthoclase: 5%	Feldspar Group: 2%	Dolomite: 2%
Austin chalk	Calcite: 98%	Other: 2%				

Table 10: Cont'd

Rock Type	Minerals	
Indiana limestone	Calcite: 99%	Other: 1%
Silurian dolomite	Dolomite: 98%	Other: 2%

5.3.2. Composition of Oil-Wet versus Water-Wet Berea Samples

The second part of this study examined the differences in rock mineralogy between the fraction of Berea sample that is oil-wet versus that is water-wet. Following the MFT experiment, the oil-wet and water-wet fractions of each sample were separated and gently dried at 40^{o}C. XRD analyses of the two fractions were then conducted.

Berea MFT wettability measurements were conducted using deionized water at 70°C and the oleic phase was varied by using: decane, decane + 2000 myristic acid, and condensate (Table 11). Again, decane was selected because it is typically used as the baseline oil that SAC results can be compared to. Myristic acid and condensate were selected because they were the only oils (including naphthenic SAC oil) that materially altered the wettability of Berea.

Table 11: Berea MFT Wettability results.

Oil type	Decane Neutral	Decane + 2000 ppm Myristic Acidic	Condensate Natural Oil
Oil-wet	8%	21%	26%
Water-wet	92%	79%	74%

Neutral Oil Results

Berea in the presence of decane and DI water was found to be 92% water-wet and 8% oil-wet. The water-wet fraction of the sample was mainly quartz with a small fraction of feldspar (Figure 23). The oil-wet sample collected was too small to make XRD measurements. So the XRD data of the water-wet sample was used to infer the likely identity of the oil-wet minerals. This was accomplished by using the baseline fractions (Table 10 and Figure A6) and making the assumption that 100% of the Quartz and Feldspar is water-wet. Therefore, their fractions were eliminated from the baseline thus allowing for the clay fractions to be recalculated. Figure 23 compares the baseline sample with the water-wet and oil-wet samples. These results match with what has been observed in nature where quartz and feldspar are typically water-wet, but clays and carbonates are typically oil-wet (Tang and Morrow, 1999a; Abdallah et al., 2007; Morrow and Buckley, 2011).

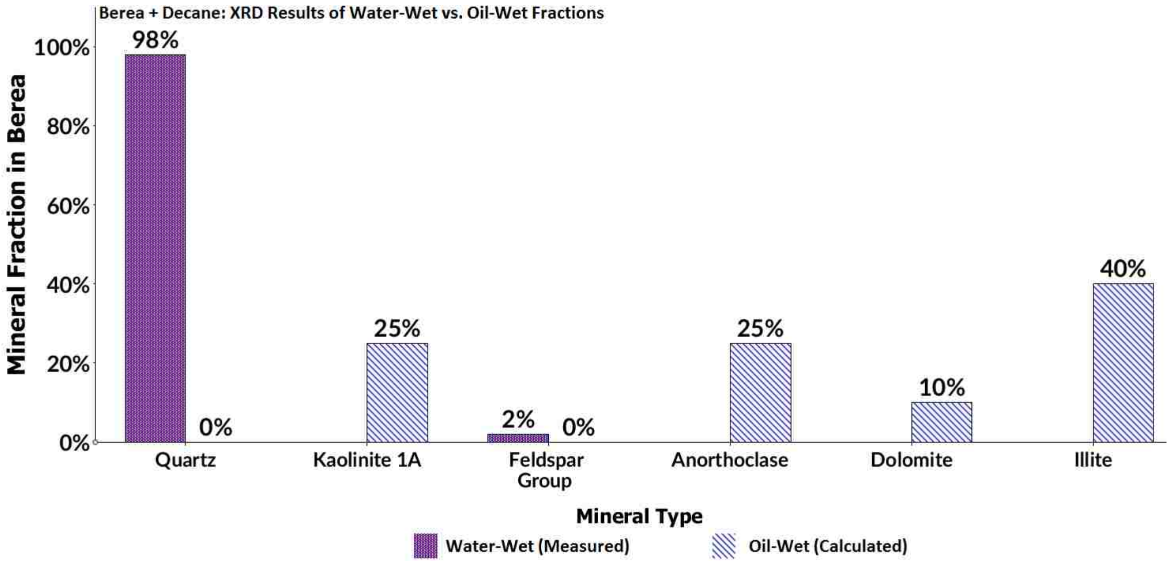


Figure 23: Comparison of Berea XRD measured and calculated mineralogy results.

Acidic and Condensate Oil Results

As illustrated by Figure 24, the Berea water-wet fraction in contact with Decane+Myristic Acid and Condensate is almost all quartz. But the Berea oil-wet fraction in Decane+Myristic Acid and Condensate also contains quartz, but a much higher fraction of clays. Unlike decane, it is evident that both condensate and myristic acid SAC interact with quartz.

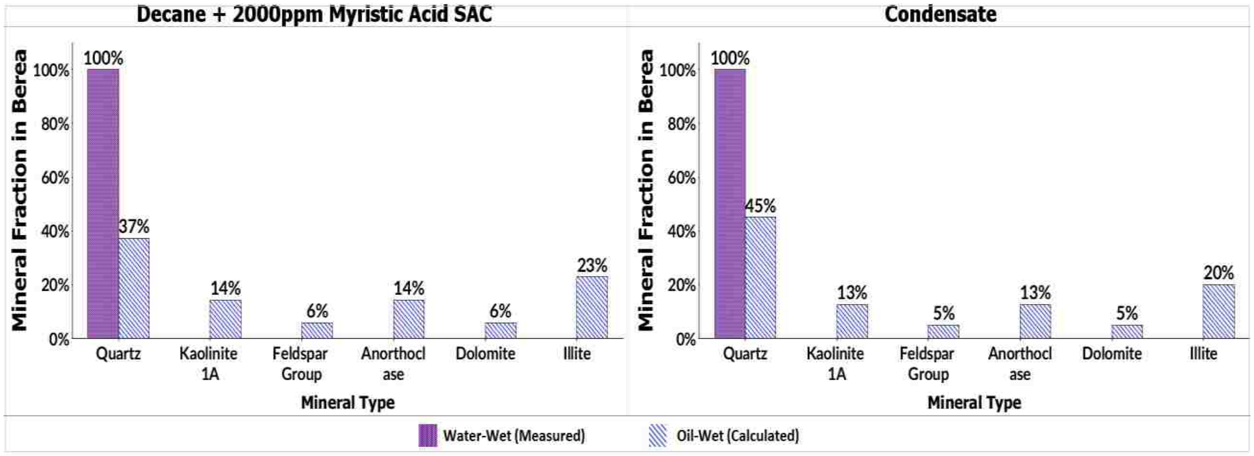


Figure 24: The difference in composition between the settled rock fractions vs. floating rock fraction of decane + 2000 ppm myristic SAC and condensate oil.

5.4. MFT Validation

A useful validation of the MFT is to compare its trends with those of another measure of wettability, for example, DDDC contact angles. Table 12 maps DDDC and MFT outputs to wettability classifications. Table 13 shows DDDC contact angle-measured wettability of Yates oil in contact with Silurian dolomite (Kasmaei and Rao, 2014) as a function of sulfate concentrations in Yates Brine.

Table 12: Contact angle and MFT outputs and wettability.

Contact Angle Wettability Classification	Contact Angle Result Interpretation (Anderson, 1986)	MFT Wettability Classification	MFT Result Interpretation % rock that is oil-wet
Strongly water-wet	0~55º	Strongly water-wet	0-15%
Weakly water-wet	55~75º	Water-wet	15-45%
Intermediate-wet	75~115º	Intermediate-wet	45-55%
Oil-wet	115 ~ 135º	Oil-wet	55-85%

Strongly oil-wet	135 ~ 180º	Strongly oil-wet	85-100%

Table 13: Contact angle and MFT results on the effect of varying sulfate on wettability

Sulfate Concentration (g/l)	NaCl Concentration (g/l)	DDDC Contact angle (º)	**DDDC Wettability Result**	MFT (% Rock that is Oil-Wet)	**MFT Wettability Result**
0 g/l	4.74	160°	**Oil-wet**	100%	**Oil-wet**
1.1g/l (1x increase)	3.64	148°	**Oil-wet**	96%	**Oil-wet**
2.2g/l (2x increase)	2.54	145°	**Oil-wet**	84%	**Oil-wet**
4.4 g/l (4x increase)	0.34	138°	**Oil-wet**	82%	**Oil-wet**
10.8 g/l (10x increase)	0	94°	**Intermediate**	76%	**Intermediate**

In order to maintain the same salinity, the concentration of NaCl (sodium chloride) was decreased as the concentration of $NaSO_4$ (sodium sulfate) was increased. Figure 25 depicts the wettability results where both the contact angles (DDDC) and % of rock that is oil-wet (MFT) decreased. In other words, the oil-wetting of dolomite by Yates oil declined with the increase in sulfate concentration thus rendering the system (rock-water-oil) more water-wet. More importantly, the MFT results accurately quantify the shift in wettability similar to the trend shown by the DDDC contact angle measurements.

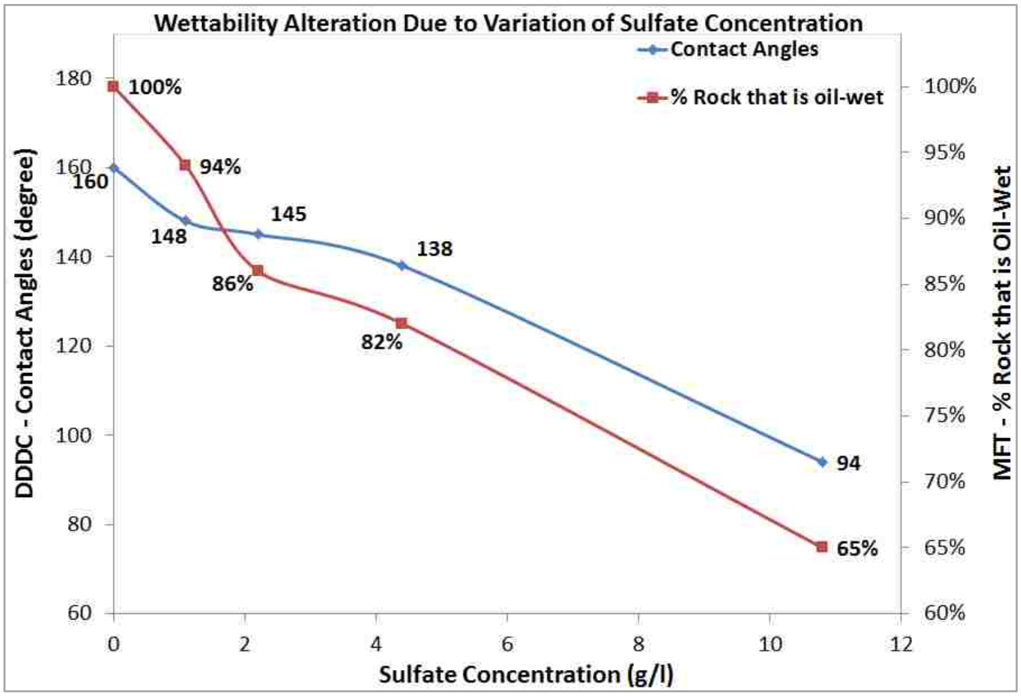


Figure 25: Comparison between contact angle and MFT results of wettability alteration due to the variation of sulfate concentration.

To gain further validation of the MFT, eight additional rock-oil-brine systems were examined by DDDC and MFT (Table 14). In the case of Berea-decane-DI water, both techniques observed strongly water-wet conditions. Also, both techniques show that Berea becomes slightly more oil-wet when condensate is used as the oleic phase. In addition, both dolomite and limestone are observed to be oil-wet when in the presence of Yates oil and Yates brine. DDDC and MFT differ for: dolomite-decane-DI water, dolomite-condensate-DI, and limestone-decane-DI water. DDDC contact angle results indicate that the three systems are strongly water-wet, while the opposite (oil-wet) is observed in the MFT case. This highlights one of the unique features of the MFT procedure. In the MFT procedure, rock samples are crushed to powder, which increases the surface area of the rock significantly. In the absence of ions in the brine, the dipole moment that exists in the carbon-hydrogen bonds of decane interacts with the large surface area of the rock. This interaction between the dipoles of decane and the large surface area of dolomite and limestone result in the oil-wet MFT results. The same is true for the dolomite-condensate-DI water case.

However, as the brine salinity is increased (Yates brine case) dolomite becomes more water-wet because the weak interaction between decane and the rock surface is replaced by stronger electrostatic interactions between the oil and the rock surface. Note that these weak interactions are not observed in the case of Berea-decane-DI water system. This is likely because the surface of dolomite and limestone has a positive charge rather than the negative charge of the clays and quartz in Berea (Buckley et al., 1989; Buckley, 2001; Hiorth et al., 2001). This suggests the interaction is between the positive surface and negative portion of the dipole in decane. Only the MFT can capture these weak interactions, unlike e.g. contact angle experiments.

Table 14: Contact angle and MFT results on the effect of varying salinity on wettability.

Rock - Oil – Brine System	DDDC Contact Angle θa, deg	DDDC Wettability Result	MFT (% Rock that is Oil-Wet)	MFT Wettability Result
Berea - Decane - DI water	~ 0°	Water-wet	5%	Water-wet
Berea - Condensate - DI water	63°	Water-wet	20%	Water-wet
Dolomite - Decane - DI water	**~ 0°**	**Water-wet**	**93%**	**Oil-wet**
Dolomite - Decane - Yates brine	~ 0°	Water-wet	53%	Intermediate-wet
Dolomite - Yate oil - Yates brine	164°	Oil-wet	100%	Oil-wet
Dolomite – Condensate – DI water	**~ 0°**	**Water-wet**	**98%**	**Oil-wet**
Limestone - Decane - DI water	**~ 0°**	**Water-wet**	**90%**	**Oil-wet**
Limestone - Yate oil - Yates brine	135°	Oil-wet	100%	Oil-wet

CHAPTER 6. ROLE OF SURFACE ACTIVE COMPOUNDS ON RESERVOIR SANDSTONE AND CARBONATE WETTABILITY

MFT results are used below to describe the role of oil SAC in determining wettability in carbonate and sandstone reservoirs. Electrostatic models describing measured wettability are proposed on the basis of the mineralogy of the rocks, model oils, and water used.

6.1. Establishing Baseline Conditions of All 4 Rock Types

Baseline conditions were acquired by measuring the wettability of each rock in the presence of decane and deionized water (Figure 26).

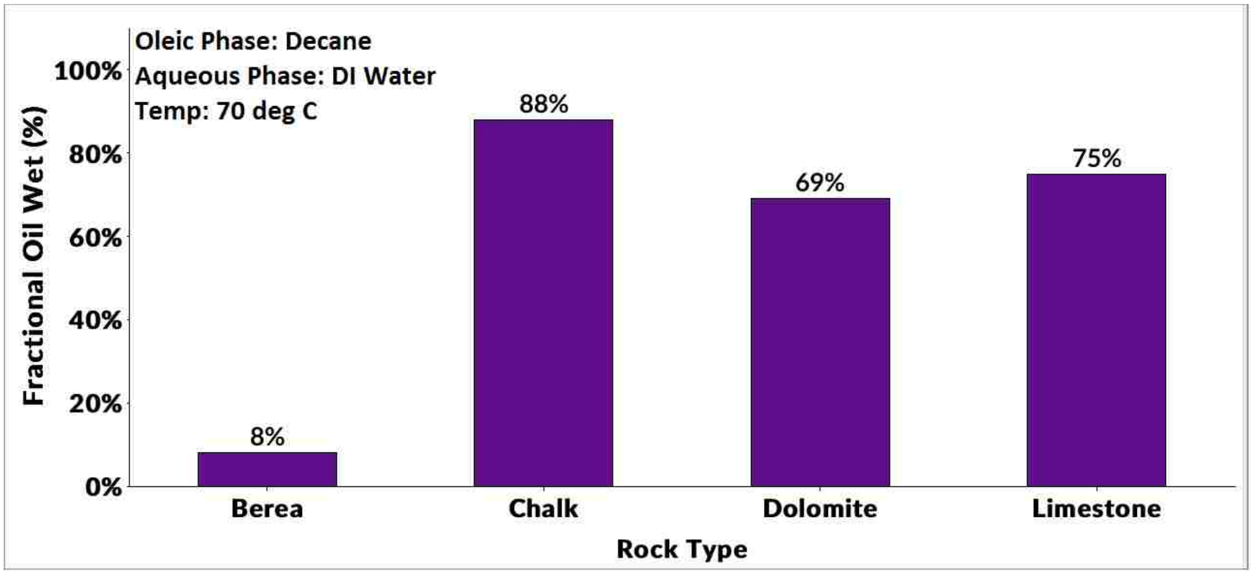


Figure 26: Initial conditions set by decane + rock + deionized water at 70°C.

Decane is an alkane hydrocarbon with the chemical formula of $C_{10}H_{22}$ with 75 structural isomers. A dipole moment exists between the carbon and hydrogen atoms of decane which creates a weak polar charge. In the presence of DI water, this charge is strong enough to interact with the opposite charge on the rock surface. The effect of the presence of salt will be discussed in Chapter 7.

Berea would be considered water-wet since 92% of the rock fraction is water-wet (quartz and feldspar) and 8% is clay. The 8% fraction of Berea floating is a result of the weak polar charge in decane interacting with the charge on the clay minerals.

The carbonate rocks are predominately oil-wet. Note that MFT procedure ages the rock in water prior to introducing it to the oleic phase. Therefore, the starting wettability is usually water-wet and the presence of the oleic phase may or may not foster interaction with the rock surface. As observed in Figure 26 decane binds to a large fraction of the carbonate rocks, 88% of Austin chalk ($Ca_{0.845}Mg_{0.155}CO_3$), 75% of Silurian dolomite ($CaMg(CO_3)_2$), and 69% of Indiana limestone ($CaCO_3$). The observed decane binding to carbonate rocks is a result of the dipole moment of decane interacting with the positive charge carbonate rock surfaces. These interactions are weak, however, once salinity is increased stronger electrostatic forces become more prevalent as shown in Section 7.1.

6.2. The Effect of SAC Concentration on Wettability

Three SAC concentrations (1000 ppm, 2000 ppm, 4000 ppm) were tested at 70°C. DI water was used as the aqueous phase. The results of these experiments are grouped by rock type, where each graph reports the percent change of wettability for each of the nine SACs, Tetralin, and condensate. The percent change in wettability is calculated by normalizing the wettability result of each SAC and condensate to that of decane. A positive change in wettability denotes an increase in the fraction of rock that is oil-wet. A negative change denotes an increase in the fraction of rock that is water-wet. Results in the region of $\pm 5\%$ are considered as analytical uncertainty and thus normalized to zero.

Figure 27 illustrates the effect of SAC concentration on the wettability of Berea in the presence of DI water at 70°C. Only condensate and the long-chained oxygen SAC have an effect on wettability, shifting it toward oil-wet. As the concentration of myristic acid (O2) is increased, a larger fraction of Berea becomes more oil-wet. In contrast, condensate and naphthenic acid also shift the wettability of Berea towards oil-wet; however, the shift in wettability was the same for all concentrations.

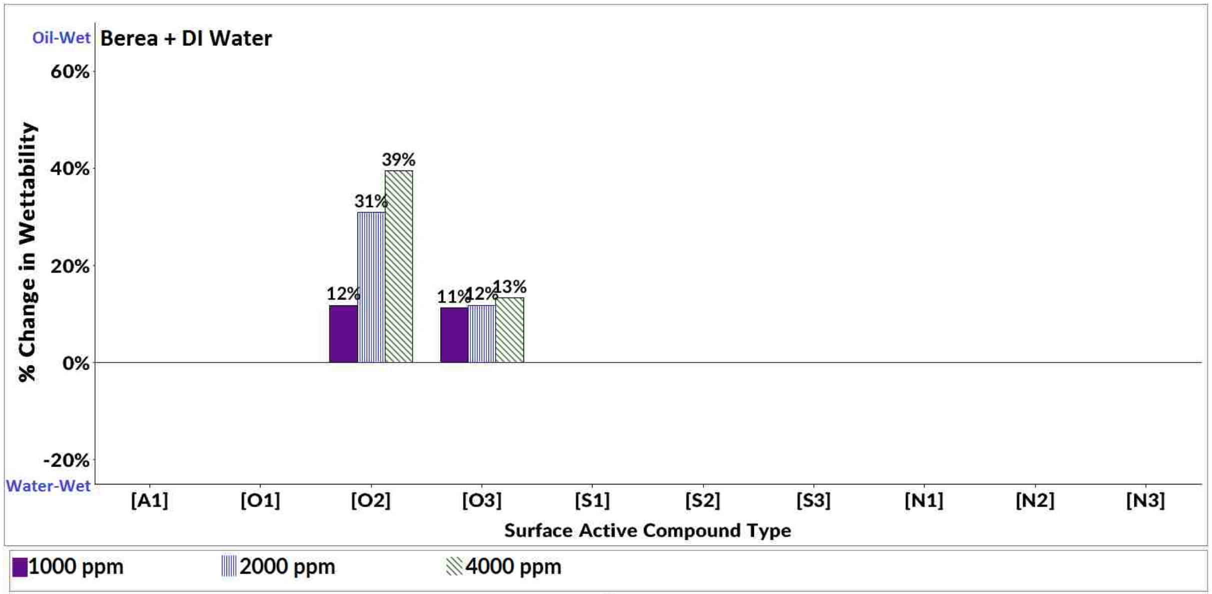


Figure 27: The effect of SAC concentration on the wettability of Berea sandstone.

Figure 28 shows the effect of SAC concentration on the wettability of Austin chalk. The long-chained oxygen SAC, myristic acid (O2) and naphthenic acid (O3), increase the oil-wetness of chalk. However, the short-chained oxygen SAC has the opposite effect, increasing the water-wetness of chalk. As the concentration of sulfur SAC dibenzothiophene (S1) increased, chalk became more water-wet. Di-n-butyl sulfide (S2) slightly shifted the wettability towards water-wet at 4000 ppm, but lower concentrations had a negligible effect on wettability. 1-Tetradecanethiol (S3) slightly shifted wettability to oil-wet as the concentration was increased. All nitrogen SACs shifted wettability towards water-wet especially at 2000 ppm and 4000 ppm. Carbazole (N1) significantly shifted the baseline oil-wet system to strongly water-wet.

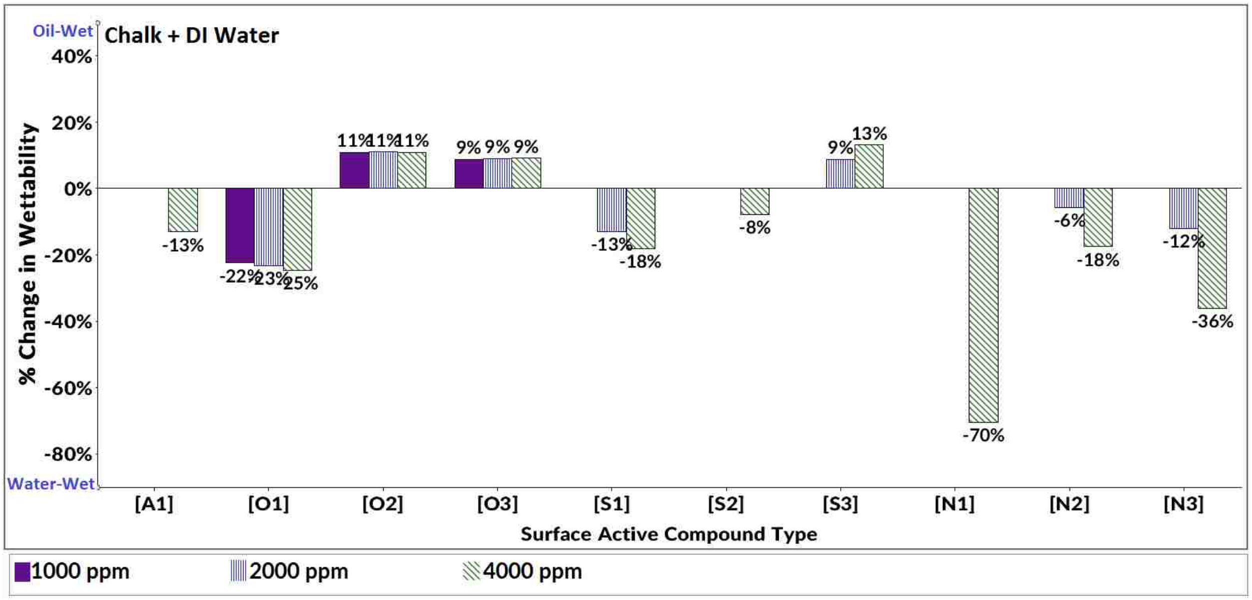


Figure 28: The effect of SAC concentration on the wettability of Austin chalk.

Figure 29 illustrates the effect of SAC concentration on the wettability of Silurian dolomite. Similar to chalk, long-chained oxygen SAC compounds increased the oil-wetness of dolomite; but short-chained oxygen SAC increased the water-wetness of the rock. The sulfur SACs, dibenzothiophene (S1) and Di-n-butyl sulfide (S2) slightly shifted the wettability of dolomite towards water-wet at higher concentrations. However, 1-Tetradecanethiol (S3) had an opposite effect, causing the system to become more oil-wet at 2000 ppm and 4000 ppm. All nitrogen SACs shift the wettability of dolomite towards water-wet especially at 2000 ppm and 4000 ppm. Carbazole (N1) shifted the wettability of dolomite from oil-wet to strongly water-wet at 2000 ppm and 4000 ppm. The two higher concentration of Quinoline (N2) slightly shifted the wettability of dolomite towards water-wet. All three Pyridine (N3) concentrations caused a significant shift in the wettability of dolomite towards water-wet.

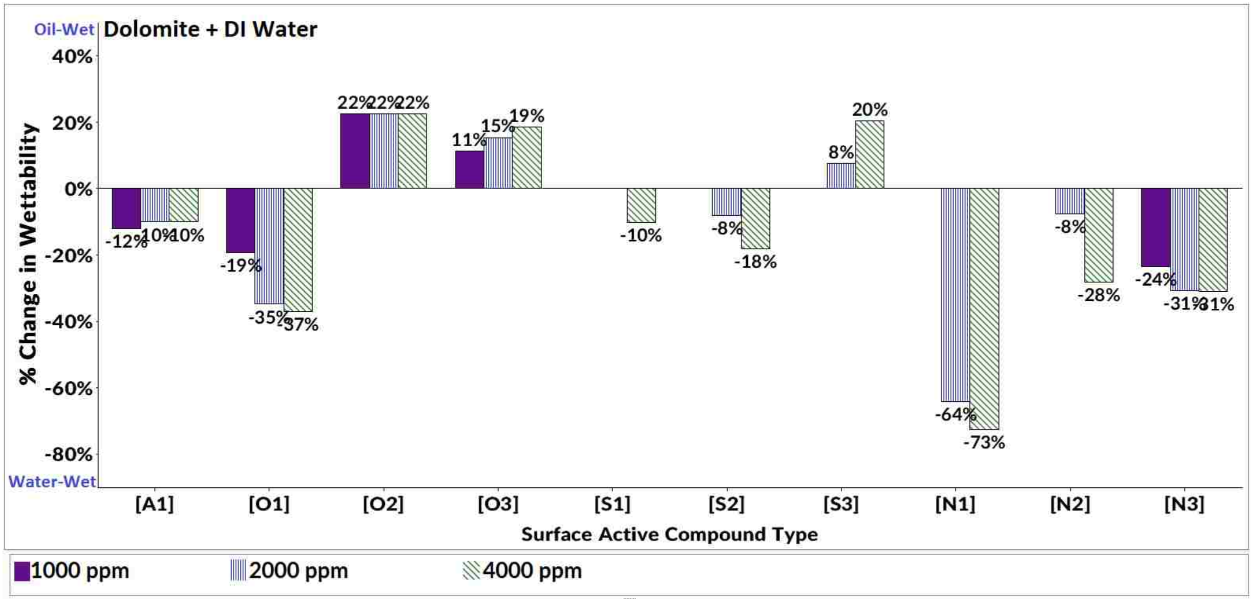


Figure 29: The effect of SAC concentration on the wettability of Silurian dolomite.

Figure 30 shows the effect of SAC concentration on the wettability of Indiana limestone. Similar to dolomite and chalk long-chained oxygen SAC shifted Indiana limestone wettability towards oil-wet and short-chained SAC shifted Indiana limestone wettability towards water-wet. Sulfur SACs, dibenzothiophene (S1) and Di-n-butyl sulfide (S2) slightly shifted the wettability of dolomite towards water-wet at 4000 ppm. 1-Tetradecanethiol (S3) had the opposite effect; the system became more oil-wet at 2000 ppm and 4000 ppm. All nitrogen SACs shifted limestone wettability towards water-wet at 2000 ppm and 4000 ppm. Carbazole (N1) shifted the wettability of limestone from oil-wet to strongly water-wet at all concentrations. Quinoline (N2) and Pyridine (N3) produced a significant shift in limestone wettability towards water-wet.

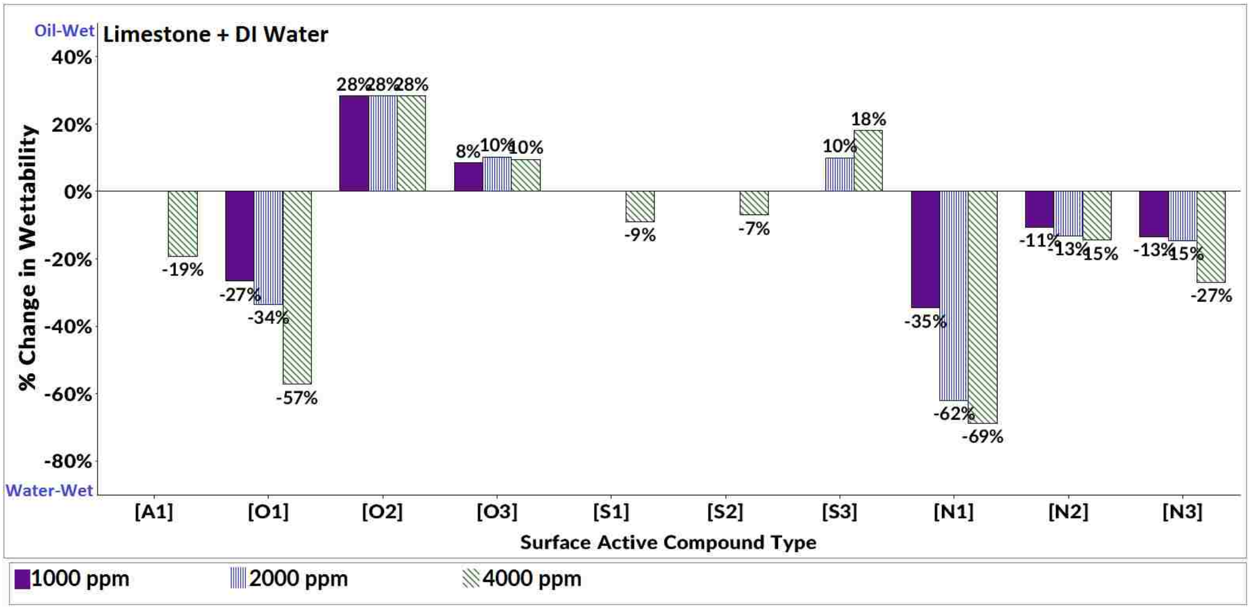


Figure 30: The effect of SAC concentration on the wettability of Indiana limestone.

To summarize, long-chained organic acids shift the wettability of all 4 rock types towards oil-wet. The short-chained organic acids had no effect on Berea's wettability but shifted the wettability of the 3 carbonate rocks towards water-wet. Sulfur SACs had no effect on Berea wettability. Dibenzothiophene (S1) and Di-n-butyl sulfide (S2) slightly shift the wettability of the carbonate rocks towards water-wet, especially when present at high concentrations. 1-Tetradecanethiol (S3) has the opposite effect on the wettability. Section 6.3.2 provides a more detailed discussion of why different sulfur SAC have different effects on wettability. Lastly, the tested nitrogen SACs had no effect on Berea wettability but shifted the wettability of the carbonate rocks towards water-wet. These results also highlight that SAC sensitivity to concentration is a function of rock mineralogy. For example, in the case of Berea, all SAC with the exception of the long-chained acids had no effect on wettability regardless of the increase in SAC concentration. Naphthenic acid was the only SAC that showed sensitivity to concentration. Myristic acid shifted the wettability of a 100% of the rock towards oil-wet at the lowest concentration (1000 ppm) tested, therefore, sensitivity to concentration could not be determined. On the other hand, these results also show the dynamic nature of carbonate rock-oil-water systems. To a certain extent, all SACs did shift the wettability of the carbonate rocks, especially at 4000 ppm. For example, as the concentration of acetic acid (O1), non-acidic sulfur compounds (S1 & S2), and the nitrogen SACs were increased, the carbonate rocks become more water-wet. For carbonate rocks, it is difficult to tell the sensitivity of the long-chained acids to concentration, since these acids shifted the rock to fully oil-wet at the lowest concentration.

6.3. A Detailed Examination of the Structure of SAC on Wettability.

One of the motivations behind this study is to provide information that may be used to help decipher the wettability alteration mechanisms. Using chemically well-understood materials (model oils and deionized water), and well-characterized rocks, should allow possible wettability controls to be identified. The wettability controls discussion below is organized by oleic phase chemistry.

6.3.1. Aromatic compound and its effect on wettability

Aromatic compounds are naturally present in crude oil and are made of 1-4 fused rings and rarely more. They are almost never present as peri-condensed rings or linear fused rings.

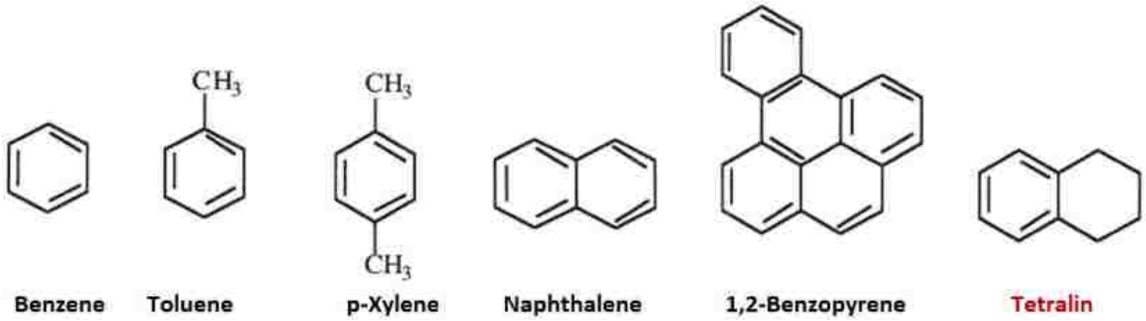


Figure 31: Examples of aromatic compounds present in crude oil including Tetralin, which is used as the model compound for the aromatic class.

Recall that Berea is water-wet in the presence of DI water and decane. The addition of Tetralin to decane did not shift Berea wettability, suggesting the lack of Tetralin-Berea surface interactions. This may be because Tetralin only has a dipole moment just like decane. On the other hand, Tetralin apparently slightly shifted the wettability of the three carbonate rocks towards water-wet, especially at 4000 ppm. Recall that baseline wettability for carbonates is oil-wet. The presence of Tetralin in decane, especially at higher concentrations, apparently disrupts the weak interactions between decane and the three carbonate rocks thus shifting wettability towards water-wet. Tetralin slightly shifts the wettability of dolomite at all three concentrations but shows no change with concentration.

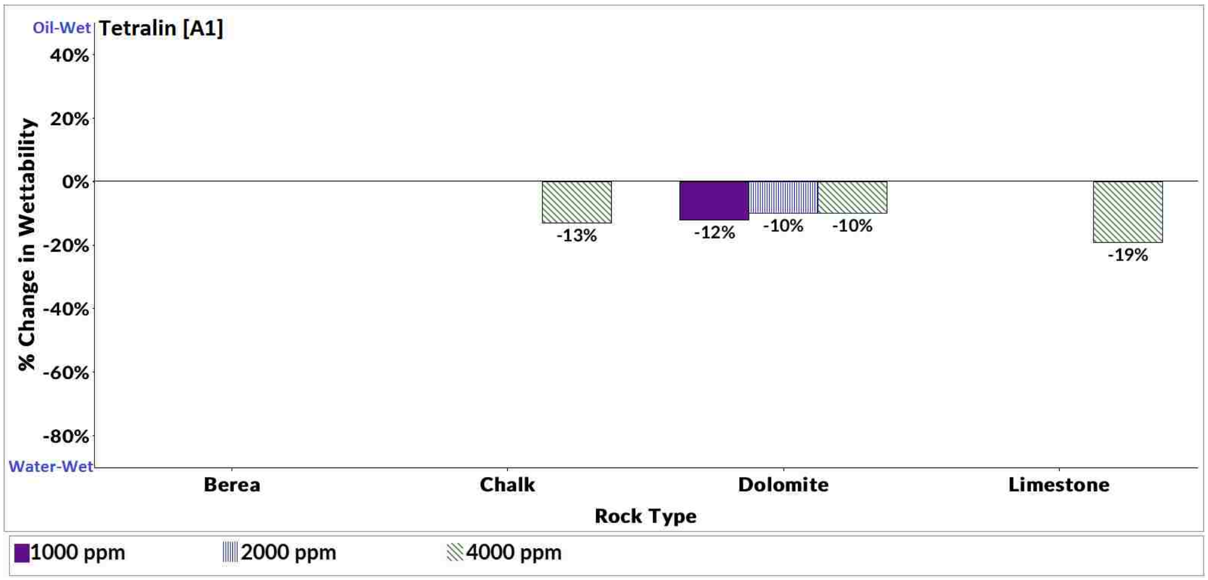


Figure 32: Effect of Tetralin on wettability in the presence of DI water at 70°C.

6.3.2. Sulfur SAC and its effect on wettability

Sulfur in crude oils is mainly present in the form of organosulfur compounds. Hydrogen sulfide is the only important inorganic sulfur compound found in crude oil. Organosulfur compounds can either be classified as acidic or non-acidic. Examples of acid and non-acidic SAC are shown in Figure 33. Figure 34 illustrates the structure of the three sulfur SACs selected for this project; two were non-acidic and one was acidic.

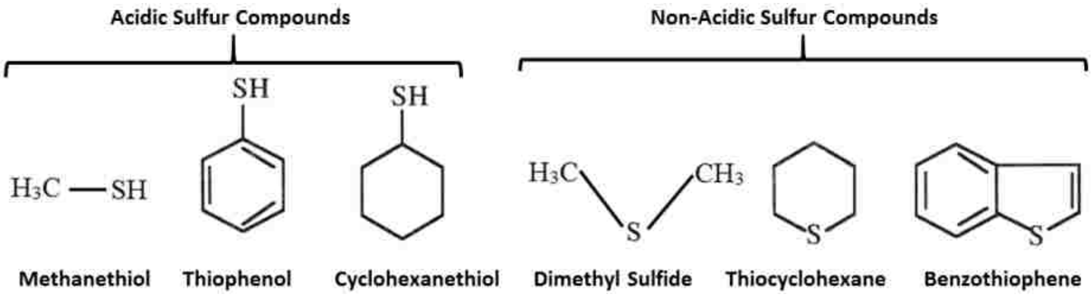


Figure 33: Examples of acid and non-acidic sulfur compounds.

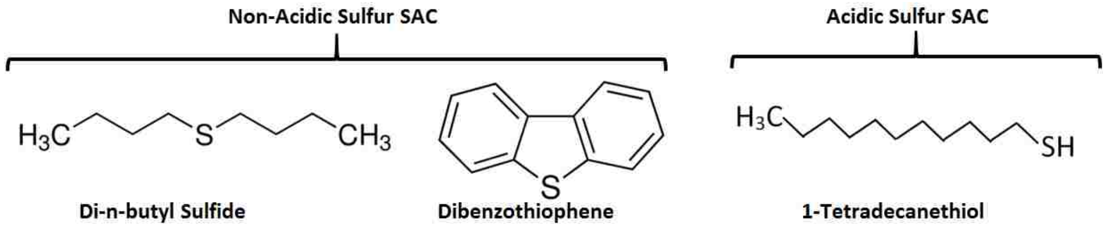


Figure 34: Structure of sulfur compounds used as sulfur SAC model compound.

Sulfur SACs did not alter the wettability of Berea. The non-acidic sulfur SACs slightly shifted the wettability of chalk, dolomite, and limestone towards water-wet, especially at higher concentrations. This similar trend was also observed when Tetralin (aromatic compound) was tested. Both non-acid SACs and Tetralin have dipole moments caused by: carbon-sulfur bonds in the case of non-acidic SACs, and carbon-carbon bonds in the case of Tetralin. I hypothesize that even though these dipole moments are slight, at higher concentrations of the SAC, their polarity is enough to disrupt the weak polar interactions of decane and the carbonate rock.

The opposite was observed for the acidic sulfur SAC 1-tetradecanethiol that slightly shifted the wettability of the carbonate rocks towards oil-wet. This behavior is similar to what was observed for the long-chained oxygen SAC. Deprotonated thiol groups are hypothesized to coordinate to positively charged carbonate surface groups to increase oil wetness by the reactions below. The shift towards oil-wetness is small because thiols are only weak acids; hence they are not fully deprotonated in the test fluids.

$$\text{Calcite\_Ca}^{+} + \text{Decane\_CH}_3(\text{CH}_2)_{13}\text{S}^{-} \rightarrow \text{Decane\_CH}_3(\text{CH}_2)_{13}\text{SCa\_Calcite} \qquad \text{Equation 22}$$

$$\text{Dolomite\_Ca}^{+} + \text{Decane\_CH}_3(\text{CH}_2)_{13}\text{S}^{-} \rightarrow \text{Decane\_CH}_3(\text{CH}_2)_{13}\text{SCa\_Dolomite} \qquad \text{Equation 23}$$

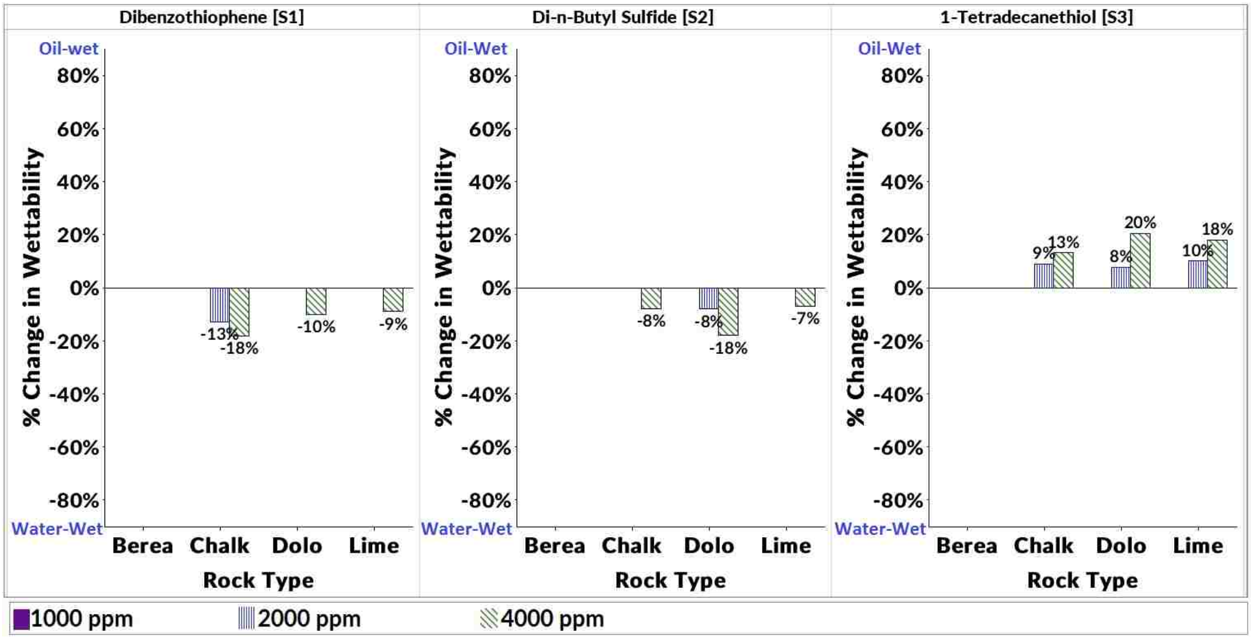


Figure 35: Effect of sulfur SAC on wettability in the presence of DI water at 70°C.

6.3.3. Oxygen SAC and its effect on wettability

Most oxygen compounds found in crude oils are weakly acidic e.g. carboxylic acids, cresylic acid, phenol, and naphthenic acid. Examples of acidic and non-acidic oxygen SAC are shown in Figure 36 and Figure 37. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain. Since acidic oxygen compounds have long been identified as wettability altering compounds, three of them were tested; their structures are illustrated in Figure 38.

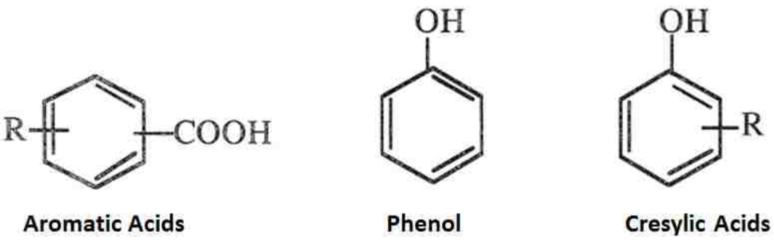


Figure 36: Structure of acidic oxygen compounds.

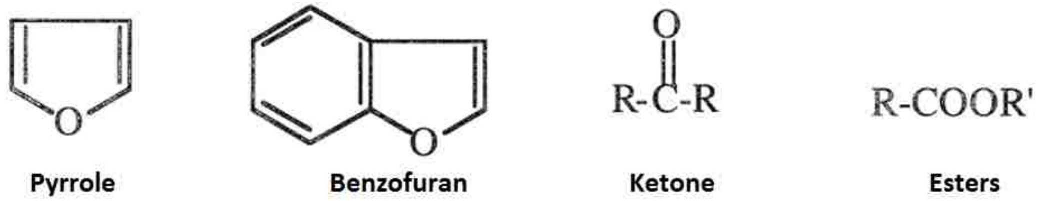


Figure 37: Structure of non-acidic oxygen compounds.

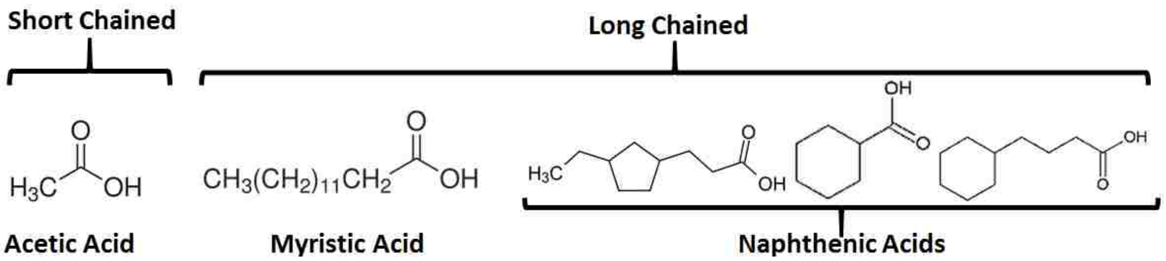


Figure 38: Structures of selected acidic oxygen compounds.

The tested oxygen SACs affected wettability differently. The long-chained oxygen SAC strongly shifted both the Berea and the carbonate rocks towards oil-wet. Similarily, Benner and Bartell (1941) reported that naphthenic acid displaced water to form a contact angle of 106° measured through water phase on calcite. Morrow et al. (1973) found that octanoic acid (0.1 molar in decane) gave a contact angle of as high as 145° on dolomite. We proposed electrostatic interaction responsible for the oil-wet shift for carbonates is indicated below where myristic acid and naphthenic acids are represented as RCOOH. Organic acids are hypothesized to give a stronger oil-wet shift than acidic sulfur SAC because they are stronger acids hence are more deprotonated under the experimental conditions.

$$\text{Calcite\_Ca}^{+} \quad + \quad \text{Decane\_RCOO}^{-} \quad \rightarrow \quad \text{Decane\_RCOOCa\_Calcite} \qquad \text{Equation 24}$$

$$\text{Dolomite\_Ca}^{+} \quad + \quad \text{Decane\_RCOO}^{-} \quad \rightarrow \quad \text{Decane\_RCOOCa\_Dolomite} \qquad \text{Equation 25}$$

In a flotation study by Fuerstenau and Miller (1967), they proposed a similar electrostatic reaction as Equation 5 and 6 between the fatty acids and calcite as follows. $\text{solid CaCO}_3 \quad + \quad 2\text{RCOO}^{-} \quad \rightarrow \text{solid Ca(RCOO)}_2$

What is not clear is why long-chained SACs made Berea more oil-wet. Berea clays should be negatively charged similar to the deprotonated organic acids, therefore unlikely to interact electrostatically. Perhaps the organic acids sorbed to positively charged clay edge sites, or were linked by Ca^{++} bridges to anionic clay basal planes. Lastly, note that while the organic acid-driven shift in Berea wettability towards oil-wetness is large in a relative sense, the overall degree of oil-wetness achieved is small because baseline Berea wettability is so water-wet to begin with.

Acetic acid, a short-chained acid, shifted carbonate wettability towards water-wet, but had no effect on Berea wettability. Acetic acid is more soluble in water than in oil. An explanation for the acetic acid effect on carbonate wettability is that acetic acid partitioned into the aqueous phase, then coordinated to cationic calcite surface sites, preventing them from otherwise coordinating with decane (see reaction below).

$$\text{Calcite\_Ca}^{+} + \text{Water\_CH}_3\text{COO}^{-} \rightarrow \text{Water\_RCOOCa\_Calcite}$$ Equation 26

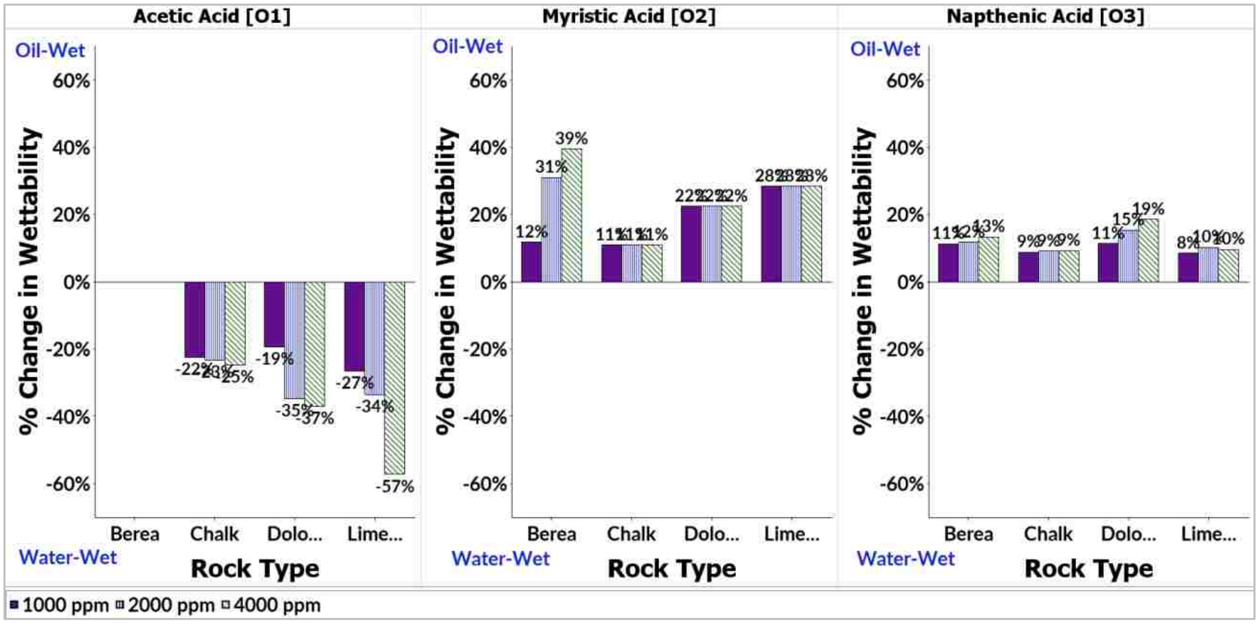


Figure 39: Effect of oxygen SAC on wettability in the presence of DI water at 70°C.

6.3.4. Nitrogen SAC and its effect on wettability

Nitrogen compounds are subdivided into two categories: (1) pyridinic forms that are considered basic nitrogen compounds, and (2) pyrrolic forms which are known as neutral, or non-basic, nitrogen compounds (Robbins and Hsu, 1999). The nitrogen content in most crude oils is low and does not exceed 0.1 wt. %. In some heavy crudes, however, the nitrogen content may reach up to 0.9 wt. % (Matar and Hatch 2001). Nitrogen compounds are more thermally stable than sulfur compounds and accordingly, are concentrated in heavier petroleum fractions and residuals.

Figure 40: Examples of basic nitrogen SAC present in crude oil including pyridine and quinoline which are used as model compounds for the basic nitrogen class.

Figure 41: Examples of non-basic nitrogen SAC present in crude oil including carbazole, which is used as the model compound for the neutral nitrogen class.

The three nitrogen SACs tested did not alter Berea wettability, but shifted carbonate wettability towards water-wet. Carbazole, the non-basic nitrogen SAC, had the biggest effect on wettability. The lack of a wettability shift of the nitrogen bases when contacting Berea is likely due to the fact that, at the pH of the Berea experiments (pH ~ 7), quinoline and pyridine will largely be uncharged and unlikely to interact electrostatically with charged Berea clay surfaces, since quinoline and pyridine pKa's are respectively, 4.9 and 5.2. The calcite experiments likely had an even higher pH, pH ~ 8, where even fewer cationic nitrogen bases are exposed at the model oil surface. The shift towards water-wetness of the nitrogen bases may be due to be a dipole effect. Note that carbazole, which has no positive charge, has the largest effect on water-wetting.

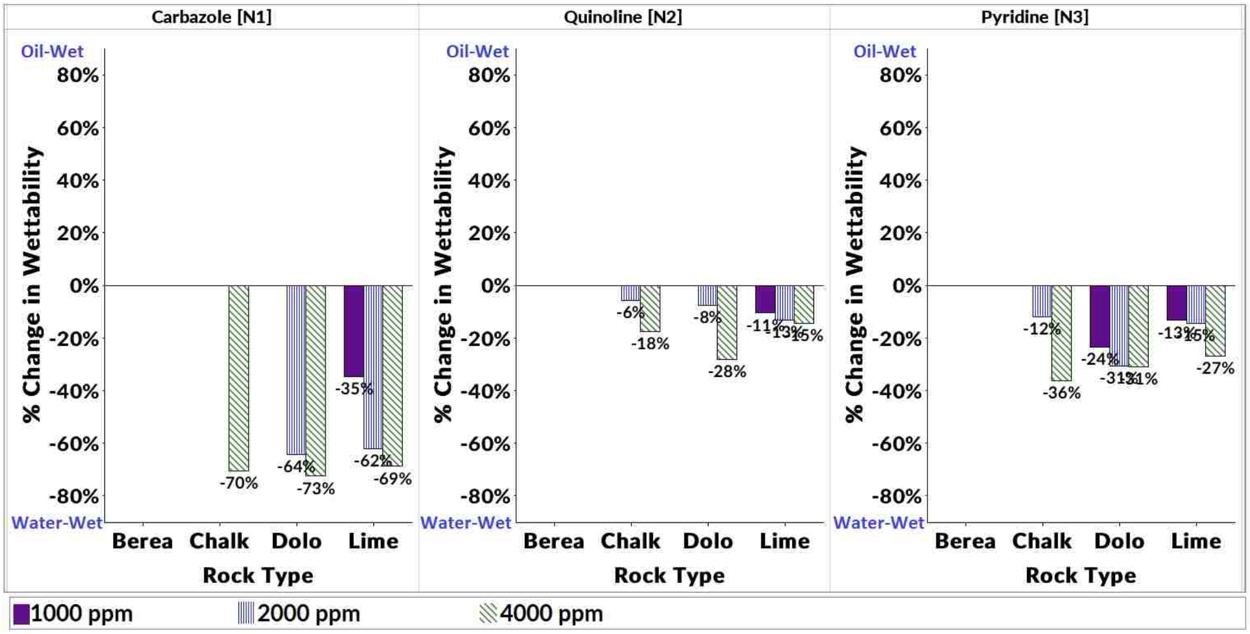


Figure 42: Effect of nitrogen SAC on wettability in the presence of DI water at 70°C.

CHAPTER 7. EFFECTS OF BRINE SALINITY, TEMPERATURE, AND SURFACE ACTIVE COMPOUNDS ON WETTABILITY

Brine chemistry has been shown to experimentally affect the stability of water films and the sorption of organic oil components on mineral surfaces (Tang and Morrow, 1999; Hiorth et al., 2001; Winoto et al., 2012). This can be attributed to its ability to change the charge on the rock surface and affect the rock wettability, which could lead to increase/decrease in oil recovery. In certain cases, lowering of brine salinity has been found to enhance oil production (Tang and Morrow, 1999; Lager et al., 2006; Zhang et al., 2006). Subsequently, temperature has been found to play a significant role in determining wettability. Rao (1999) showed that in most cases, sandstone reservoirs become more oil-wet with increasing temperature, while most of the carbonate reservoirs become more water-wet. This study examines the effect of brine salinity and temperature on the wettability of sandstone and carbonate rocks. Four brine salinities (0, 1000 ppm, 10,000 ppm, 100,000 ppm (Table 4)) were tested at 25°C, 70°C, and 110°C.

7.1. Baseline Wetting

Figure 43 shows the fraction of rock mass that is oil-wet in decane. As noted earlier Berea has little electrostatic interaction with decane because decane has only a weak dipole charge. The limited interaction is only apparent in water with few ions, i.e. distilled water. In the case of carbonate rocks, the interaction between surface and decane is larger at low salinity, but rapidly declines as salinity increases from 1,000 ppm and 10,000 ppm. These results suggest that lower salinity brines promote oil-wet conditions in carbonate rocks. The data also show that the degree of decane wetting in all three carbonate rock types is not very sensitive to temperature variations. Examining the data for limestone we see that changing salinity significantly changes wettability between 1000 and 10,000 ppm, but there is little change as salinity is further increased to 100,000 ppm. Increasing salinity does shift the wettability of the rock surface to decane towards water-wet.

At low salinity, the decane weak dipole moment can interact with the charged carbonate surfaces. At higher salinity, the ionic species with stronger dipole moments dominate the interactions with rock surfaces. Dilution of brine salinity increases oil-rock adhesion for decane, and probably for other alkanes, thus driving the wettability towards oil-wet. However, this effect is only significant at very low salinities. Therefore, as noted by other researchers the presence of acids and bases (SAC) are required to observe the low salinity effect since the aliphatic component appears to have very limited interaction at reservoir salinities.

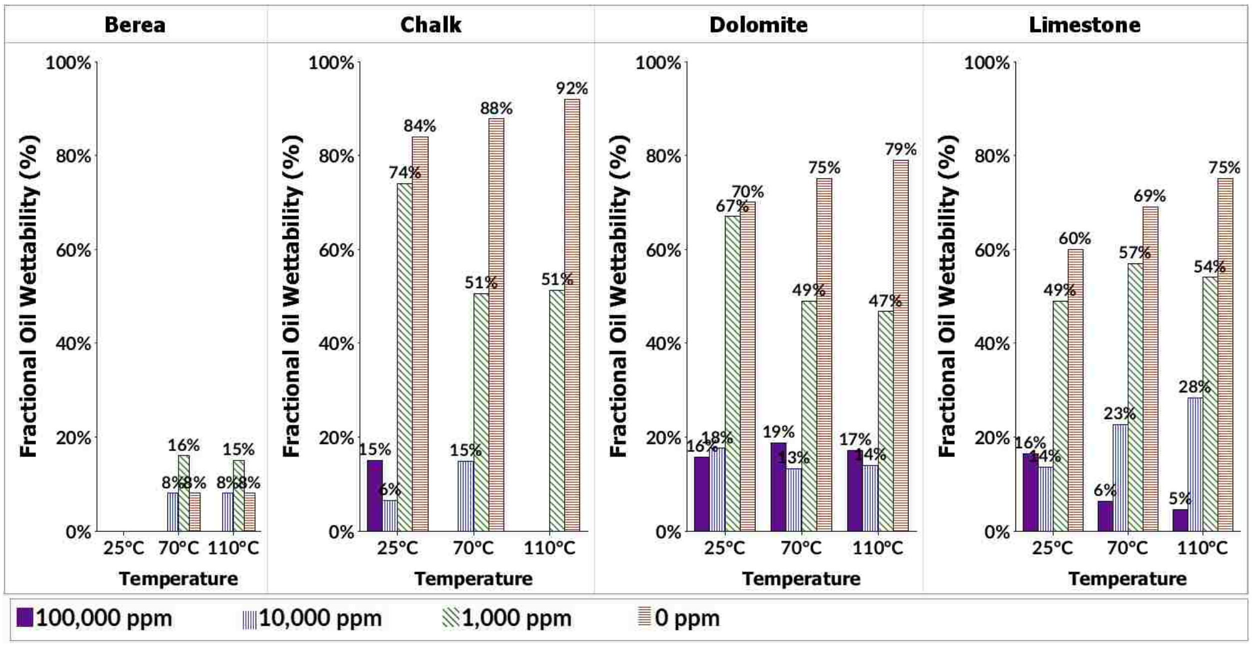


Figure 43: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70 and 110°C).

7.2. Effect of Salinity and SACs on Sandstone and Carbonate Wettability

The effect of SACs and Tetralin on wettability is examined as a function of brine salinity (0, 1000 ppm, 10,000 ppm, 100,000 ppm) and temperature (25°C, 70°C, and 110°C). The 10 model oils used are created by adding 2000 ppm of SAC to decane. Again, the percent change in wettability is calculated by normalizing the wettability result of each SAC and condensate to that of decane. Results in the region of ±5% are considered within analytical uncertainty and thus normalized to zero.

7.2.1. Aromatic

Berea is water-wet in the presence of DI water and decane. Tetralin shifted the wettability of the three carbonate rocks towards water-wet as brine salinity was increased (Figure 44). The amount of shift was different for each carbonate with dolomite wettability being the most sensitive to Tetralin.

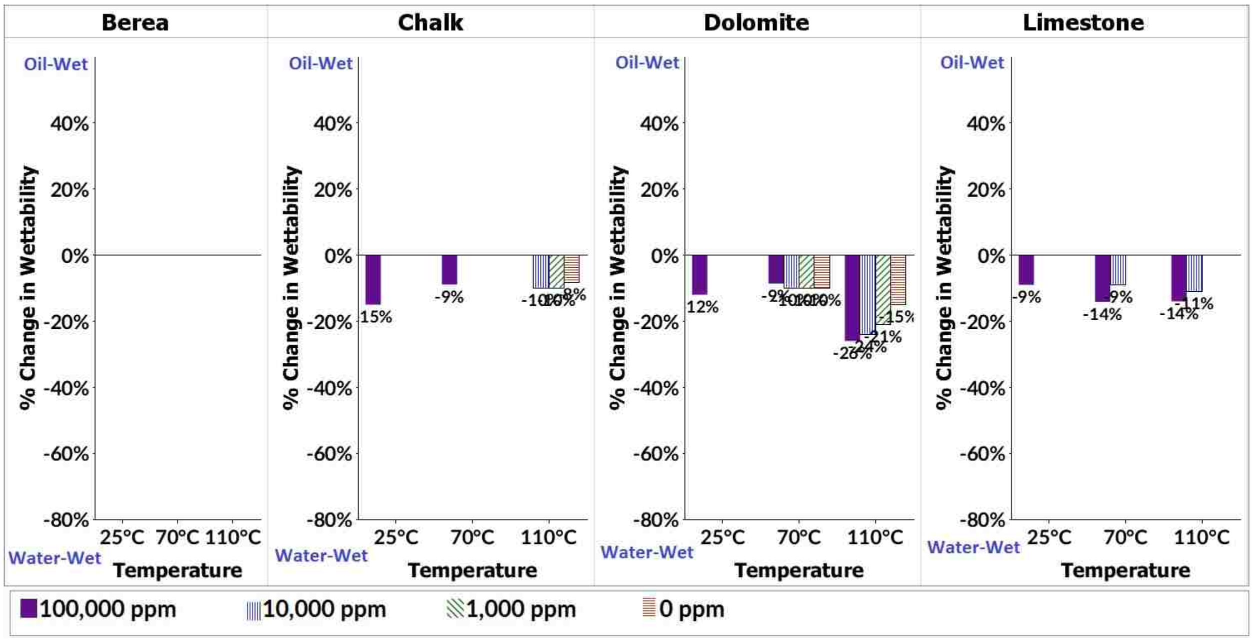


Figure 44: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using tetralin. Values below 5% are not displayed.

The effect of temperature was small with small changes in the impact of Tetralin increasing at higher temperature. Dolomite wettability showed the most temperature sensitivity. Salinity also has little effect on the wettability with Tetralin. The largest salinity effect is for dolomite where decreasing salinity increases the oil-wetting. In sum, the weak baseline Tetralin-carbonate interaction is somewhat enhanced with decreasing salinity shifting wettability to more oil-wet was greatest for dolomite, less so for chalk and limestone.

7.2.2. Sulfur SAC

The non-acidic sulfur SACs S1 and S2 (Dibenzothiophene and Di-n-butyl sulfide) did not change the Berea and carbonate wettability from the water-wet baseline as salinity and temperature increased (Figure 45 and Figure 46). The only exceptions were small shifts toward more water-wet for chalk with Dibenzothiophene and dolomite with Di-n-butyl sulfide.

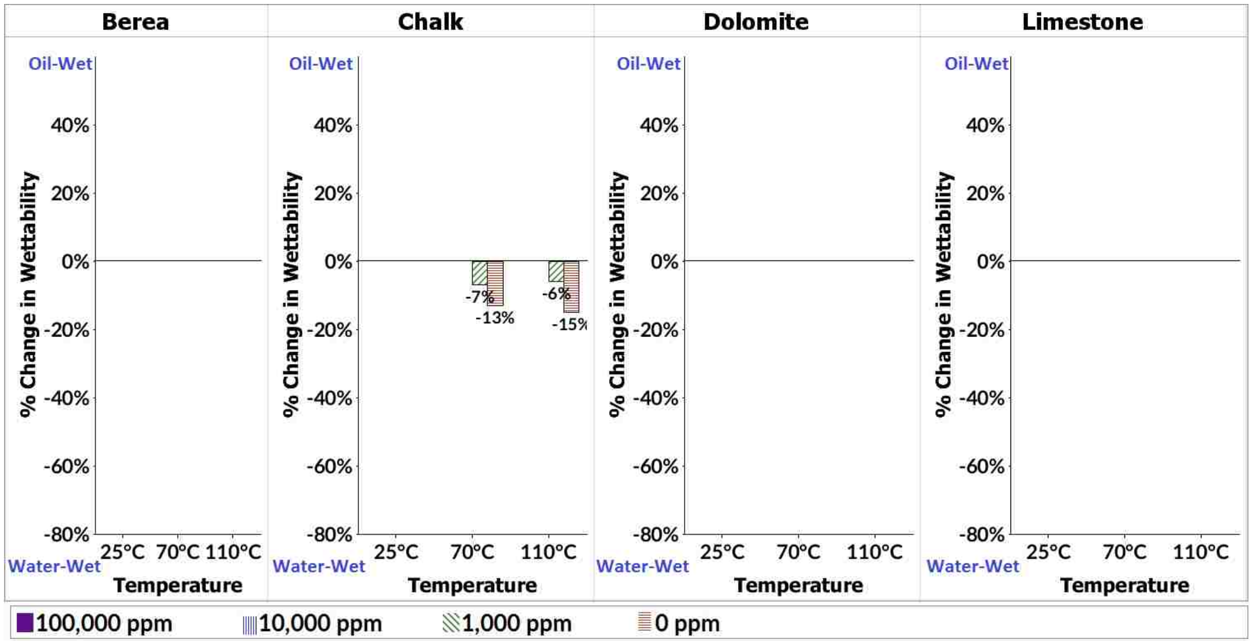


Figure 45: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using Dibenzothiophene (S1) SAC. Values below 5% are not displayed.

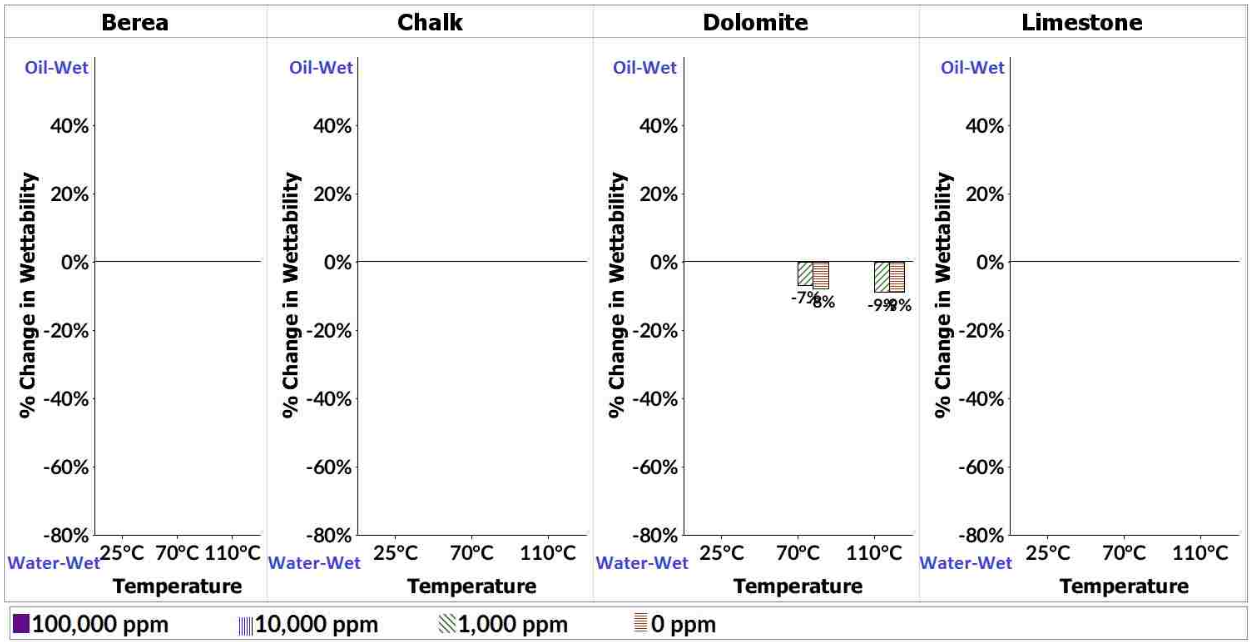


Figure 46: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using Di-n-butyl sulfide (S2) SAC. Values below 5% are not displayed.

The acidic sulfur SAC (S3) 1-tetradecanethiol had a stronger impact on wettability. This acidic sulfur SAC shifted Berea towards water-wet at lower salinity. The effect was opposite carbonates where lowering salinity made the rock more oil-wet. These effects were observed at 70 and 110°C, but there was no salinity effect at 0 and 1000 ppm and 25°C for Berea or any of the carbonates (Figure 47). In the carbonates the acidic sulfur shifted wettability towards oil-wet at lower salinity. All three carbonates had very similar responses in magnitude of shift. Temperature had a threshold effect in the sense that there was no effect at 25°C, but a measurable effect at 70 and 110°C. However, there was no significant increase in effect between 70 and 110°C.

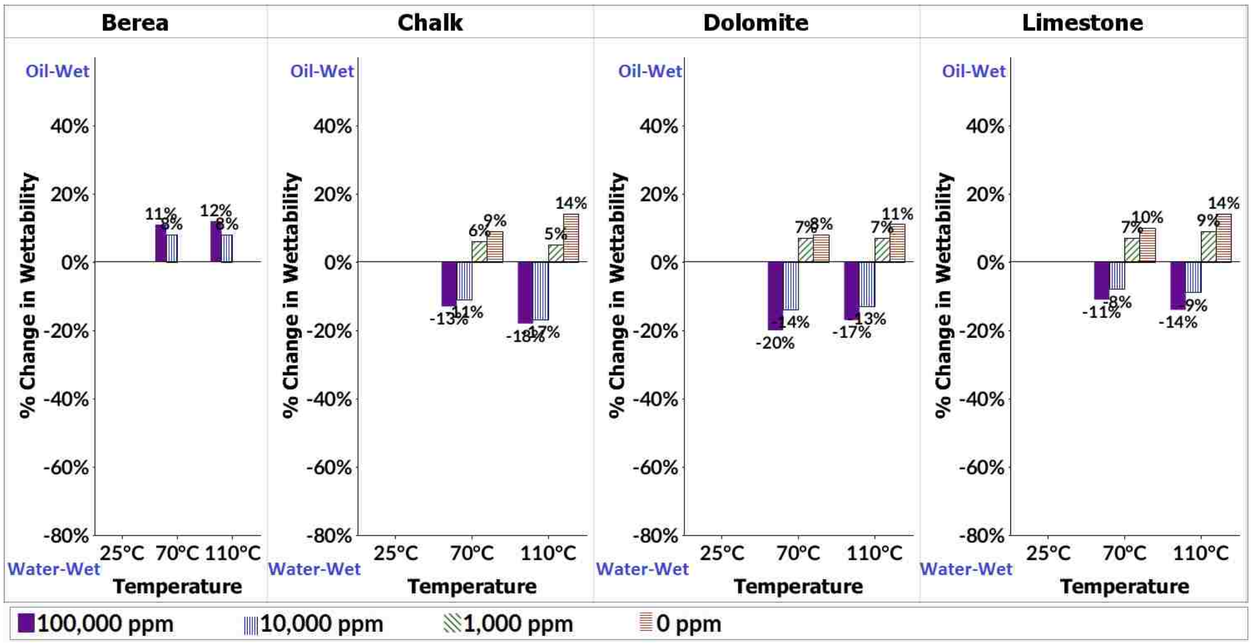


Figure 47: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using 1-tetradecanethiol (S3) SAC. Values below 5% are not displayed.

7.2.3. Oxygen SAC

Acetic acid (O1) had a significant effect on wettability for all the rock types tested. Acetic acid shifts Berea towards water-wet at 70 and 110°C as the salinity declines. There is no effect at 25°C or in distilled water. Decreasing salinity during waterflood would shift the wettability to more water-wet. The impact of acetic acid (acetate at experimental pH) is greater in the carbonate rocks. Carbonate rocks shift from water-wet at higher salinity and to oil-wet at low salinity and the amount of shift with salinity is similar for all three rocks. There is little to no effect on wettability at 25°C, but acetate has about the same effect at 70 and 110°C.

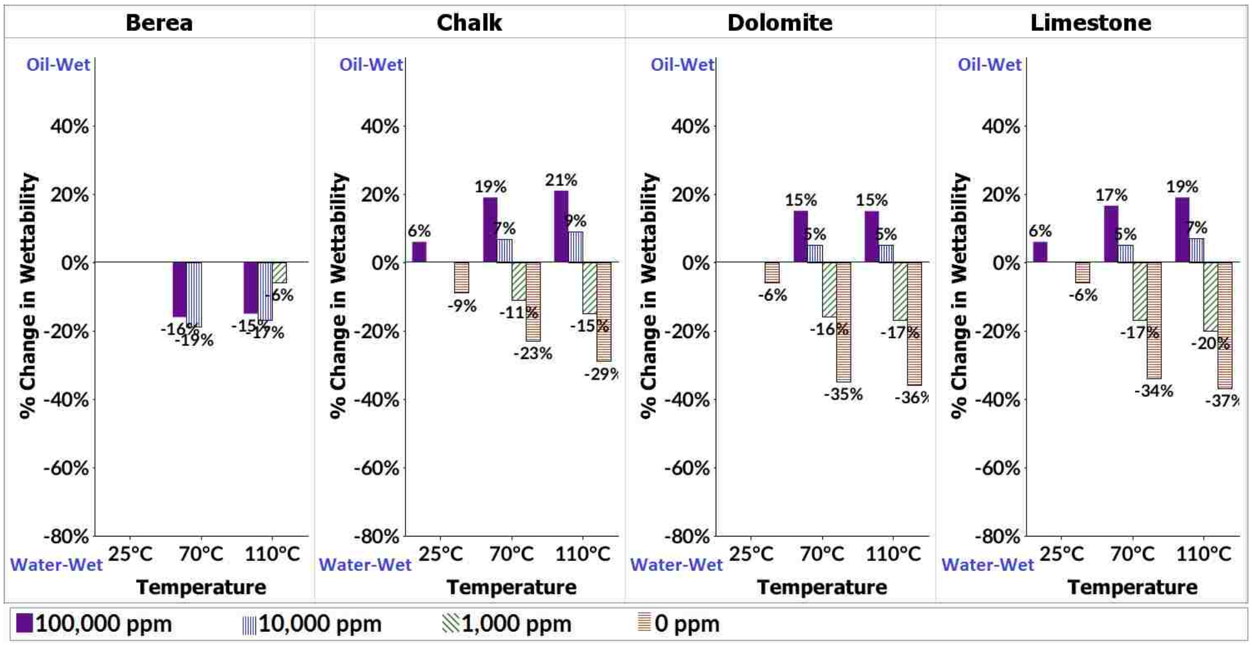


Figure 48: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid (O1) SAC. Values below 5% are not displayed.

The long-chain acids O2 and O3 (myristic acid and naphthenic acid) also have a significant effect on both Berea and the carbonates. In the sandstone, both acids shift the wettability towards oil-wet as the salinity declines. The myristic acid effect is greatest at high temperature (110°C), but only slightly less at 25 and 70°C. The effect is slightly enhanced at higher temperatures (Figure 47). The salinity effect is greater for the carbonates, with the largest shift for limestone, followed by dolomite and finally chalk. There was some increase of the effect with temperature, but it was minor. Naphthenic acid has the same effect as myristic on Berea wettability increasing oil-wetting. However, effect is not sensitive to salinity or temperature. The carbonate rocks show the same pattern of shifting towards oil-wet with lower salinity. The effect is greatest for chalk, followed by limestone and dolomite. The data show less change in wettability with salinity at lower temperature. This may be a result of sulfate coordinating with the positive carbonate surface group, thus shifting the charge of the rock surface to negative that would repel the negatively charged oil at reservoir salinity. As salinity is lowered the rock surface is more positive and the negatively-charged oil is attracted.

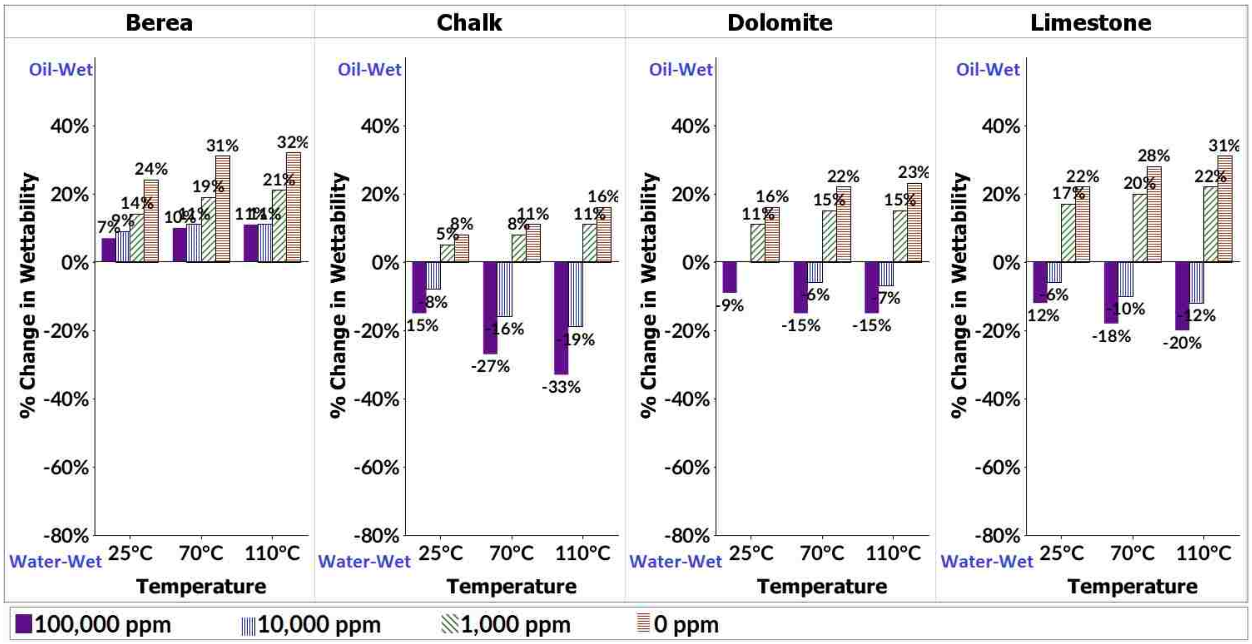


Figure 49: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using myristic acid (O2) SAC. Values below 5% are not displayed.

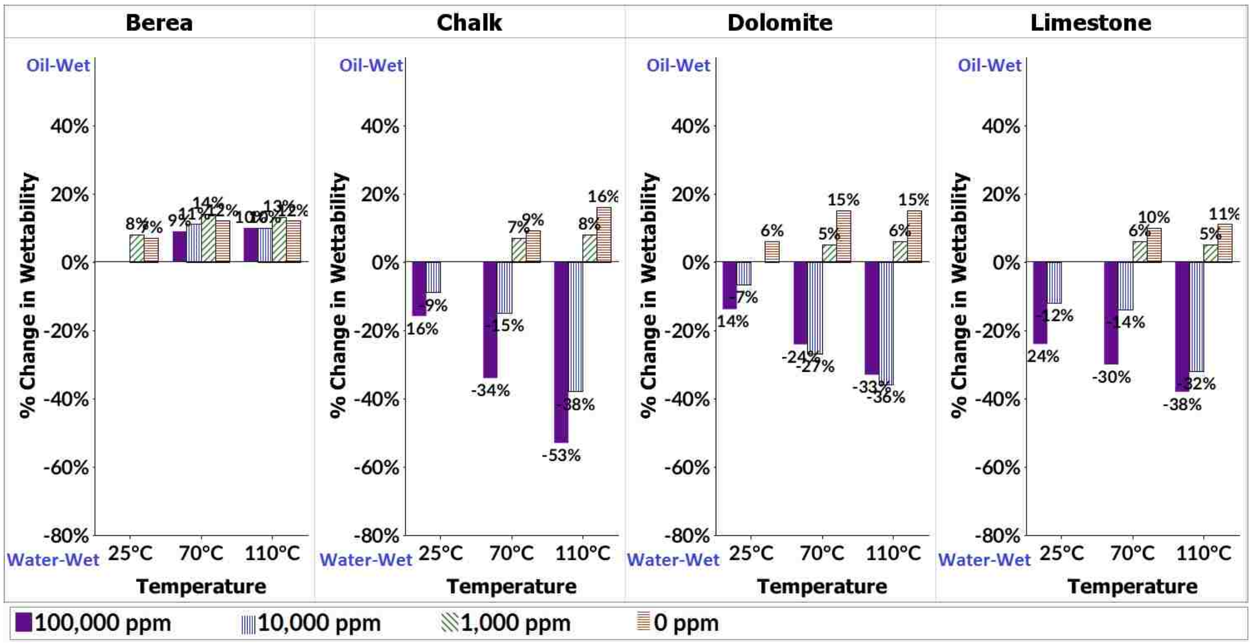


Figure 50: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using naphthenic acid (O3) SAC. Values below 5% are not displayed.

7.2.4. Nitrogen SAC

Carbazole, the non-basic nitrogen SAC (N1), shifted Berea slightly towards oil-wet with decreasing salinity and temperature (Figure 51). The carbonates had the opposite pattern with all three rocks becoming much more water-wet with decreasing brine salinity. There was a small temperature effect with greater shift with salinity at higher temperature. The amount of shift with salinity was large for limestone and dolomite, but much smaller for chalk.

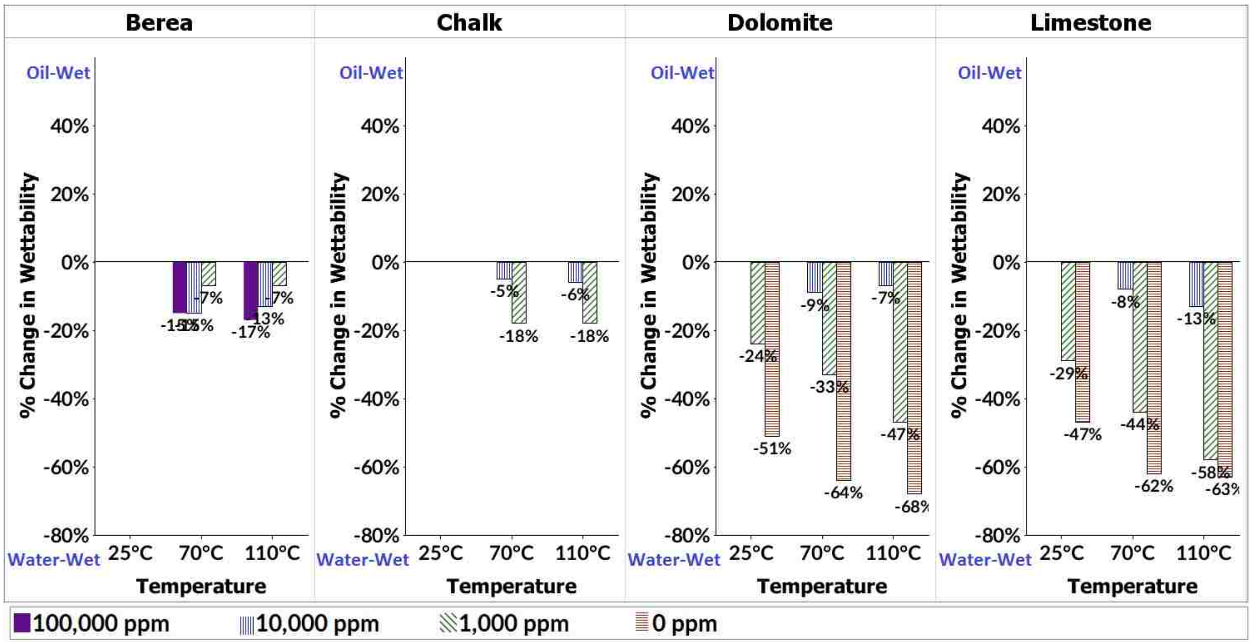


Figure 51: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using carbazole (N1) SAC. Values below 5% are not displayed.

The basic nitrogen SAC N2 and N3 (quinoline and pyridine) did not change the wettability of Berea regardless of salinity and temperature (Figure 52 and Figure 53). They also had little effect on the carbonate rocks; possibly due to the reduction of dipole interaction as salinity is increased. The pH of the experiments means most of the basic nitrogen is uncharged. The greatest effect was in dolomite at 110°C. Lowering salinity significantly increased water wetting. The effect was greatest at 110°C and less at 70°C. There was no effect at 25°C. The same pattern was observed for limestone and chalk, but the change with salinity was less.

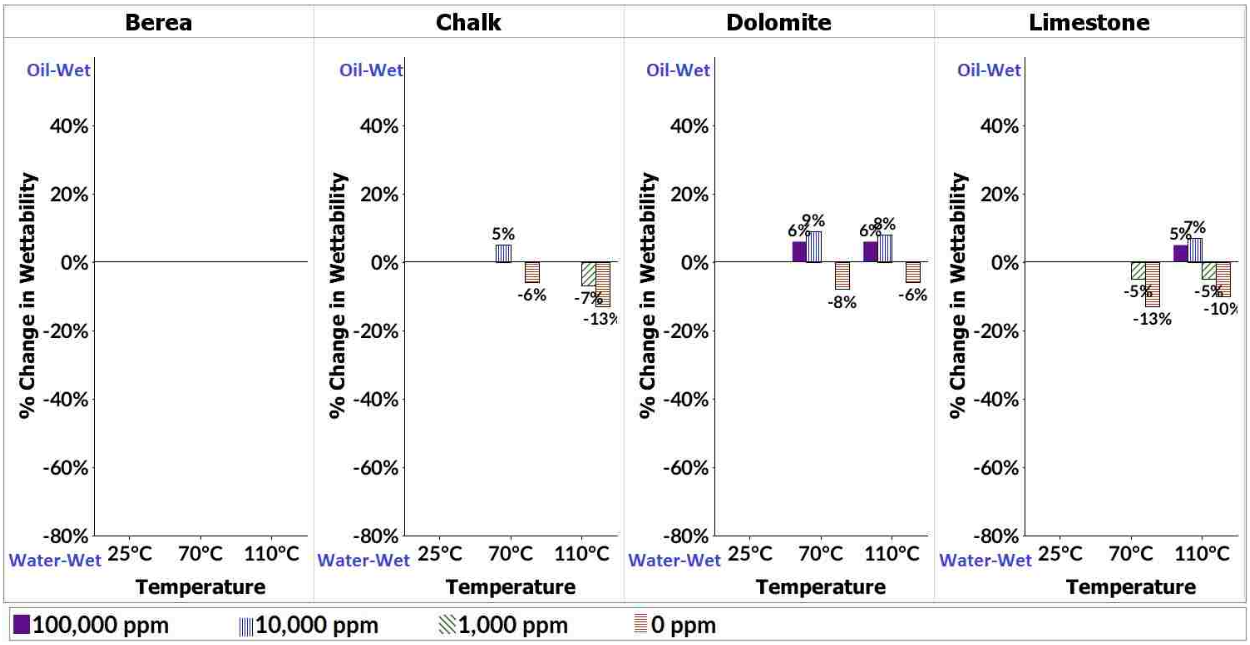


Figure 52: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using quinoline (N2) SAC. Values below 5% are not displayed.

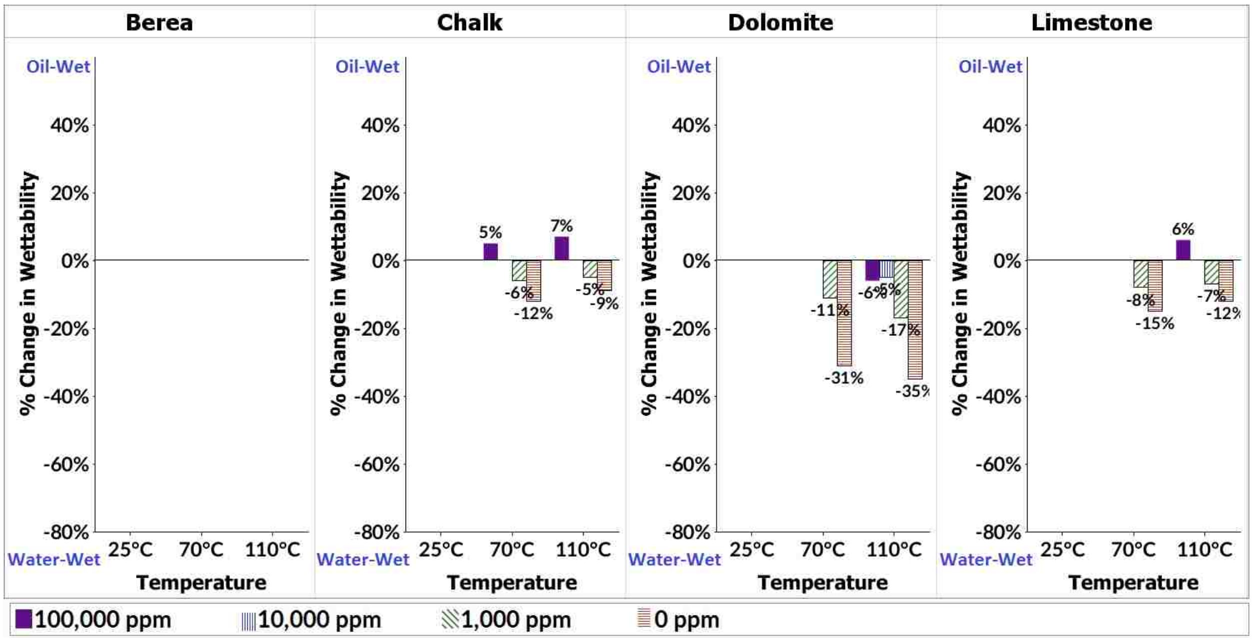


Figure 53: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using pyridine (N3) SAC. Values below 5% are not displayed.

CHAPTER 8. DISCUSSION

8.1. MFT

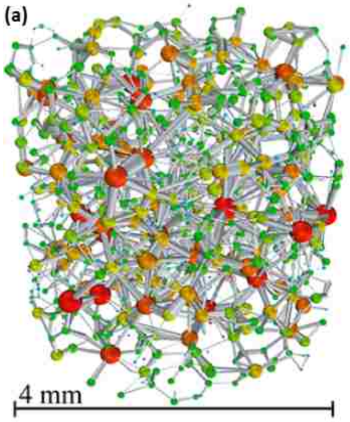
An accurate determination of the reservoir wettability leads to an effective selection of the most suitable EOR method for the reservoir of interest. Proposed mechanisms responsible for the increase in oil recovery by ionically modified waterflooding, and to a certain extend processes such as surfactant flooding and caustic flooding are attributed to wettability alteration. Several wettability measurement methods have been developed, however, they all have limitations: contact angle measurements lack natural surface roughness and geometry, and flow-based tests like Amott-Harvey, USBM and spontaneous imbibition take months and do not give absolute wettability measurements. In addition, traditional methods for the measurement of wettability are time-consuming and usually require expensive equipment. This dissertation details the development of the MFT method and its use in studying the effects of surface active compounds (SAC) on wettability for variations in rock mineralogy, brine chemistry, and temperature. MFT is the application of the well-established flotation process that has been routinely used for over a century in the mining industry to petroleum systems. Flotation has been recognized as a non-quantitative technique for wettability measurement (Anderson, 1986). The modified flotation technique is quantitative and uses core material or cuttings, saving valuable cores for traditional experiments. The technique measures wettability at the grain scale directly and is very sensitive, fast and easy to use. This work has shown that MFT can serve as a screening tool to estimate the wettability alteration potential of brines in a short time with high precision. MFT can also differentiate the impact of potential determining ions and salinity on wettability alteration that is hard to measure by other means.

MFT is an excellent tool for measuring heterogeneous wettability. None of the standard wettability measurement methods have the ability to directly measure heterogeneous wettability.

MFT accomplishes this by physically separating the hydrophobic (oil-wet) rock grains from the hydrophilic (water-wet) rock grains. This allows one to further investigate differences between the oil-wet versus water-wet rock grains. For example, XRD experiments can be performed on the either fraction to examine differences in mineralogy. The Berea results (Section 0) showed there was a mineralogical difference between the oil-wet samples that were clay-rich versus the water-wet samples that were quartz-rich. Heterogeneous wettability in a reservoir is typically attributed to variations in the rock properties such as: cementation, surface area, etc. MFT allows further investigation of the differences in the rock properties of the oil-wet versus the water-wet fraction on the grain scale.

Compared to other standard wettability measurement methods, MFT has the added advantage of directly examining the rock-fluid interactions between fluids and the rock surface. Wettability is a geochemical property, and flotation interrogates the rock-fluid interactions at the grain scale, by directly by looking at the chemical reactions. Contact angles do give direct wettability measurements, however, only a minimal surface area is examined. Therefore, numerous experiments would be needed in order to get a more representative wettability of the rock sample. Amott and USBM do not give absolute wettability measurements since wettability is estimated from flowing fluid through a core sample. The MFT technique facilitates examination of the rock-fluid interactions by crushing the rock to small grain sizes (105 to 205 microns), and thus promoting maximum surface contact with the oil and brine. Therefore wettability measurements are much faster.

Figure 54 shows the difference between the surface area of a whole core sample and a crushed core sample. The core property data was acquired from a dynamic 3D pore scale imaging study where the properties of a Ketton Carbonate core were calculated from a micro-CT scan image and compared to experimental data (Menke et al., 2015). We compare the whole core's pore surface area to the total surface area of the grains if the whole core were to be crushed to 105-205 microns grains. As shown, the total surface area of the crushed core is 3.8 to 7.4 times larger than the pore surface area of the whole core. Therefore, a wettability result by MFT (using the crushed core sample) would be a product of the fluids interacting with 3.8 to 7.4 times more rock surface area, than an Amott/USBM method using the whole core.



(b)

Whole Core Properties		
Density	2.71	g/cm^3
Porosity	17.2	%
Diameter	4	mm
Length	12	mm
Grain Volume	124.86	mm^3
Specific SA	7720	1/m
SA Whole Core	963.92	mm^2

(c)

Grain Size Distribution (μm)	SA of Crushed Core (mm2)	SA Crushed Core vs. Pore SA of Whole Core
105	7134.83	7.40
125	5993.25	6.22
145	5166.60	5.36
165	4540.34	4.71
205	3654.42	3.79

Figure 54: (a) Pore surface network representation of Ketton carbonate extract from micro-CT images (Menke et al., 2015) and (b) its given properties. (c) gives the calculated surface area values of the core if it was crushed to the given grain size distribution and the ratio of the total surface area of crushed core versus pore surface area of the whole core.

8.1.1. MFT Limitations

Similar to the standard wettability measurement methods, MFT cannot determine the exact wettability of an entire oil field with a single measurement. However, due to the ease in conducting numerous experiments at once, MFT can help construct a clearer picture of the reservoir wettability faster, provided with reservoir material from different parts of the reservoir and field. MFT cannot simulate reservoir pressure conditions which can play a role in controlling the formation water pH which can have an effect on wettability.

The purpose of this project was to examine the impact of SACs on reservoir sandstone and carbonate rocks. To accomplish this task, outcrop rocks were used instead of the pure minerals.

Similar to reservoir rocks, outcrop rocks are natural and contain several minerals. Unlike reservoir rocks, outcrop rocks are typically clean and do not contain crude oil and other contaminants that arise from coring and plugging. The use of outcrop material eliminated the need for core cleaning process which is complex and can introduce artifacts. All MFT experiments were made in a narrow range of pH which is not representative of the reservoir pH. This project recommends future experiments to be conducted in the reservoir pH range where the impact of SACs can be studied at reservoir conditions. There are analytical uncertainties up to +/-5 as shown by the raw data section in Appendix C. Results in the region of ±5% are considered as analytical uncertainty and thus normalized to zero.

8.2. Effects of Surface Active Components on Wettability

In the last 2 decades, the level of investigation in the optimization of injected brine chemistry (e.g. low salinity flooding, smart waterflood, etc.) has drastically increased (Morrow and Buckley, 2011). This form of EOR changes the surface properties of the reservoir rock, favorably altering wettability and subsequently increasing oil recovery. However, this EOR method has not succeeded in improving oil recovery in certain reservoirs (Boussour et al., 2009; Cissokho et al., 2009; Thyne & Gamage, 2011; Al-Shalabi et al., 2014). This has led to further studies on understanding the chemical controls that govern wettability. This includes developing a good understanding of the components of reservoir rock, brine, and crude oil that play a role in intermolecular interactions. With this understanding, an effective formulation of injected water chemistry that favorably alters wettability and thus increases oil recovery can be customized for the reservoir of interest. This project placed focus on understanding the influence of crude oil's surface active compounds (SAC) on the rock-oil-brine wettability.

In wettability studies, crude oil is typically characterized by its total acid number (TAN), total base number (TBN), and asphaltene content (Thomas, 1993; Dubey & Doe, 1993; Buckley, 1996). TAN and TBN specify the quantity of acidic and basic compounds, respectively, present in crude oil. This project took a more in-depth look at the oil content by examining individual SACs and their effect on wettability. We observed differences in SACs interactions with respect to salinity and temperature for acid, basic and sulfur components of oil. For example, we observed that long chain acids (myristic acid and naphthenic acid) have the tendency to promote oil-rock adhesion, while short chain acids (acetic acid) promoted water-wetness to the rock (Figure 55). This could explain contradicting results on wettability and/or oil recovery when testing crude oil with similar TAN or TBNs, but not accounting for the specific components of the TAN or TBN. Also, we observed geochemical conditions where non-acidic and non-basic SACs had the ability to shift the wettability of carbonate rocks (Figure 56) showing that just TAN and TBN may not be sufficient to fully understand the experimental results.

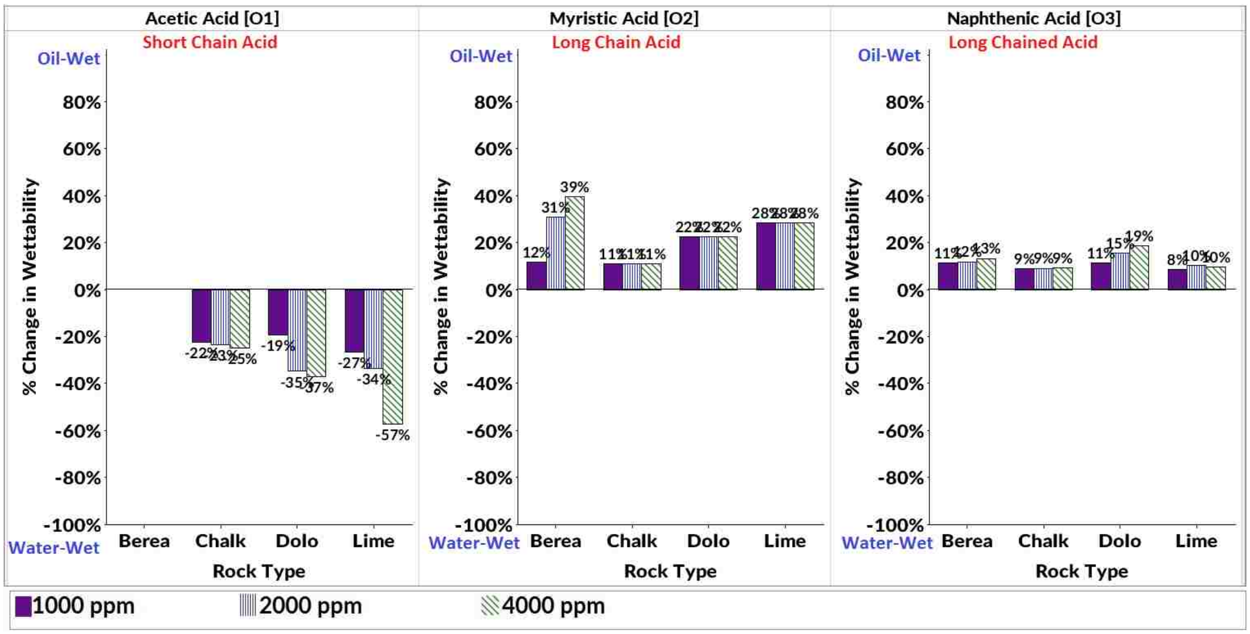


Figure 55: Experimental measurement of wettability for the four rock types at 0 ppm TDS and 70°C when using oxygen SACs at 3 concentrations (1000, 2000, 4000 ppm). Values below 5% are not displayed.

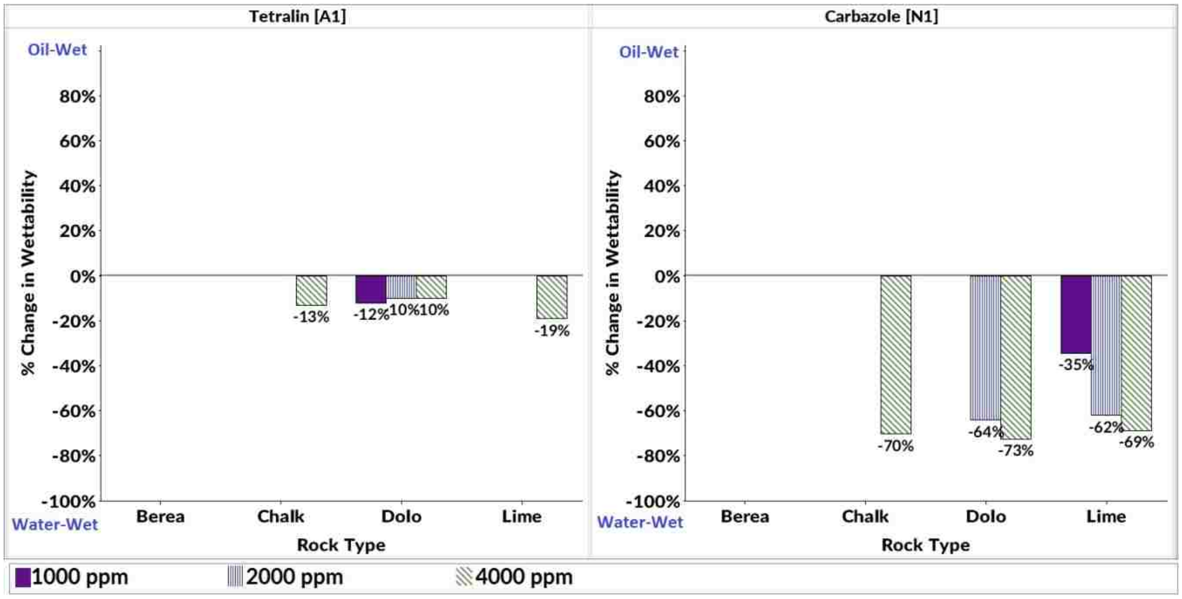


Figure 56: Experimental measurement of wettability for the four rock types at 0 ppm TDS and 70°C when using non-basic and non-acidic SACs. Values below 5% are not displayed.

Therefore, this work concludes that TAN/TBN values on their own are not sufficient to reliably predict the nature of wettability. These values only give a measure of the amount of acid/base in a sample and not the specific quantities of acidic/basic compounds or their affinity to either adhere or repel from the rock. In addition, non-acidic and non-basic SACs with the ability to shift wettability are not accounted for. This observation has also been made in corrosion chemistry where numerous groups have reported that TAN/TBN values cannot be relied upon to predict corrosion (Kane et al., 1998; Babaian-Kibala, et al., 1999; Ayello et al., 2010). This is because it is possible to have two oils with the same TAN values, but one has high levels of corrosive acids (e.g. naphthenic acids) while the other has much lower levels of the same corrosive acids. Therefore, to accurately characterize crude oils and capture relevant information needed to reliably predict wettability, we recommend crude oil testing that captures the major SACs present in the crude oil and their respective quantities. With this information, a comprehensive study can be conducted to link SACs to their ability to either promote or depress oil-rock adhesion under different geochemical conditions. This approach would further the effort of building accurate wettability prediction models by providing more accurate information on wetting parameters of crude oil.

The pH of the experiments is a critical factor in interpreting and applying the results. As discussed earlier, wettability is the result of electrostatic interactions between the oil and rock surface. The MFT experimental solutions had final pH values between 7 and 8, while reservoir pH is typically 5 to 6. The polar components present in the oil phase are ionized depending on the pH value. The ionization of basic material results in positively charged crude oil components; while the ionization of acidic material results in negatively charged crude oil components (Cuiec, 1975).

8.2.1. Sandstone

Similar to what has been published (Anderson, 1986), Berea was generally found to be water-wet in this study (Figure 26). The SACs that had a significant effect on Berea's wettability as salinity and temperature were varied are: acetic acid (O1), myristic acid (O2), naphthenic acids (O3), 1-Tetradecanethiol (S3), and carbazole (N1).

The acid SAC's will have a negative charge at experimental pH and should be able to strongly interact with rock surfaces. Of the SACs tested on Berea, only the long-chained acids promoted oil-rock adhesion, which decreased as salinity was increased (Figure 57). On the other hand, the short-chained acid tested, slightly shifted Berea towards water-wet with increasing salinity and temperature (Figure 57). A clear distinction observed was that the long-chained acids promoted oil-wetness as the short-chained acids either promoted water-wetness or had no effect on the rock wettability. Therefore, considering the parameters tested, long-chained acids are the most important in shifting the wettability of Berea and by extrapolation, other sandstones. Multiple groups have reported that the wettability of sandstone changed to more oil-wet conditions at higher acid numbers (Skauge et al., 1999; Shabib-Asl et al., 2015). Based on the results of this project, I would hypothesize that the significant amounts of the acids present in their crude oil were long-chained acids with a strong affinity to adhere to the sandstone rock surface.

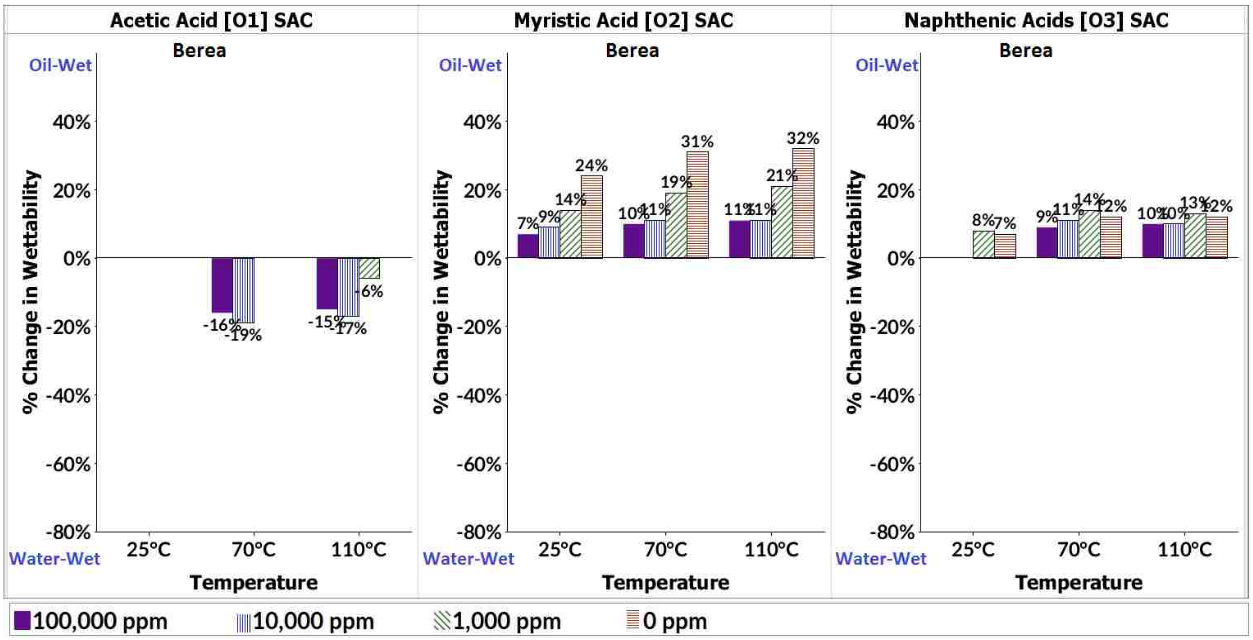


Figure 57: Experimental measurement of wettability for Berea at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using oxygen SACs. Values below 5% are not displayed.

Skauge et al., (1999) and Shabib-Asl et al., (2015) observed that crude oils with high base numbers promoted water-wet conditions. In this study, we examined the effect of both basic and non-basic nitrogen SACs. The Berea samples examined were initially water-wet, and with the introduction of nitrogen SACs the wettability remained water-wet (Figure 27). Changes in salinity are not observed to have any effects on the wettability of Berea in the presence of the base nitrogen SACs. However, the non-basic nitrogen SAC did shift the wettability of Berea towards water-wetness as salinity was increased (Figure 58). It appears that temperature was not a significant parameter in the relationship between the basic SACs and Berea. In interpreting this data, we have to consider that the nitrogen bases are neutral species at the experimental pH, and have dipole moments rather than charge. This may account for the apparent lack of effect on wettability in the data. The non-basic nitrogen SAC did have an effect that is greater with higher salinity and temperature. This SAC is uncharged and would not contribute to TBN, yet has an effect on wettability.

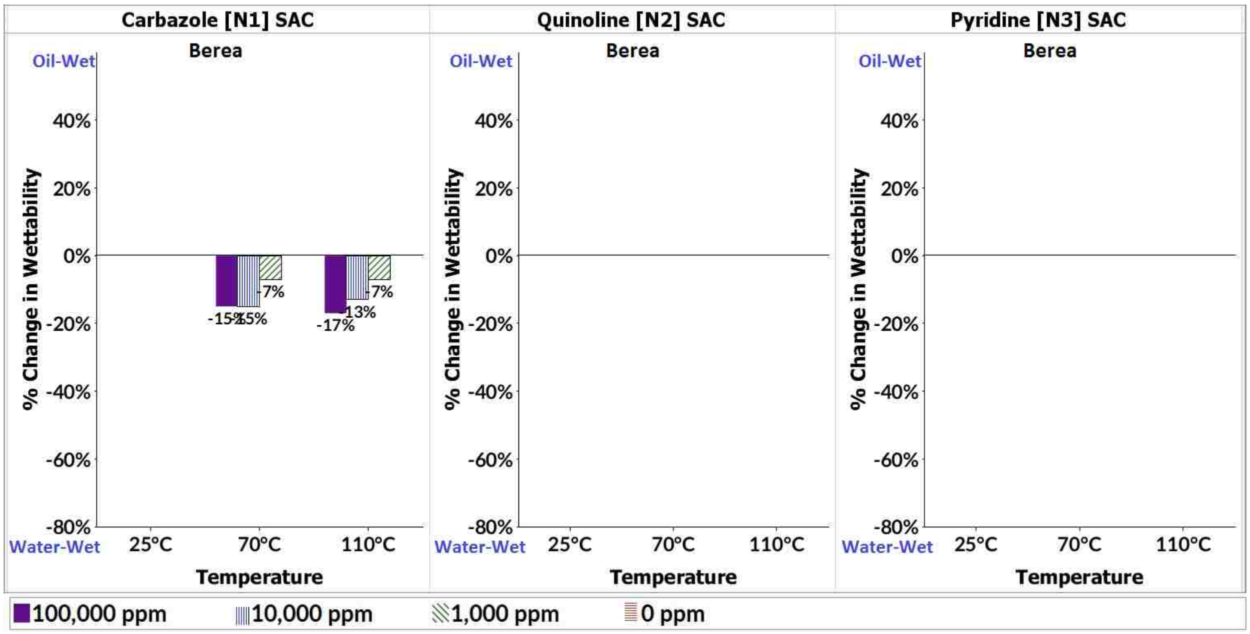


Figure 58: Experimental measurement of wettability for Berea at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using nitrogen SACs. Values below 5% are not displayed.

All in all, we observe that at the geochemical conditions tested, oxygen SACs play a more significant role in shifting the wettability of Berea than the other SACs. To have a better understanding of how these SACs would shift wettability in a typical reservoir, we recommend repeating these experiments using reservoir pH conditions and examining the impact of the basic SACs.

8.2.2. Carbonates

The three carbonates examined in this project were found to be predominantly oil-wet (Figure 26), the same as other authors (Treiber et al., 1972; Chilingar & Yen, 1983). The SACs that had a significant effect on the carbonates' wettability as salinity and temperature were varied are: tetralin, acetic acid (O1), myristic acid (O2), naphthenic acids (O3), 1-Tetradecanethiol (S3), carbazole (N1), quinoline (N2), and pyridine (N3).

For the most part, the three carbonates examined displayed similar trends in wettability change as a function of SAC type, salinity, and temperature. However, the degree of oil-adhesion due to brine salinity, SAC, and/or temperature varied from one carbonate rock to another. Figure 59 and Figure 60 illustrate the effect of two SACs on the wettability of chalk and limestone, respectively.

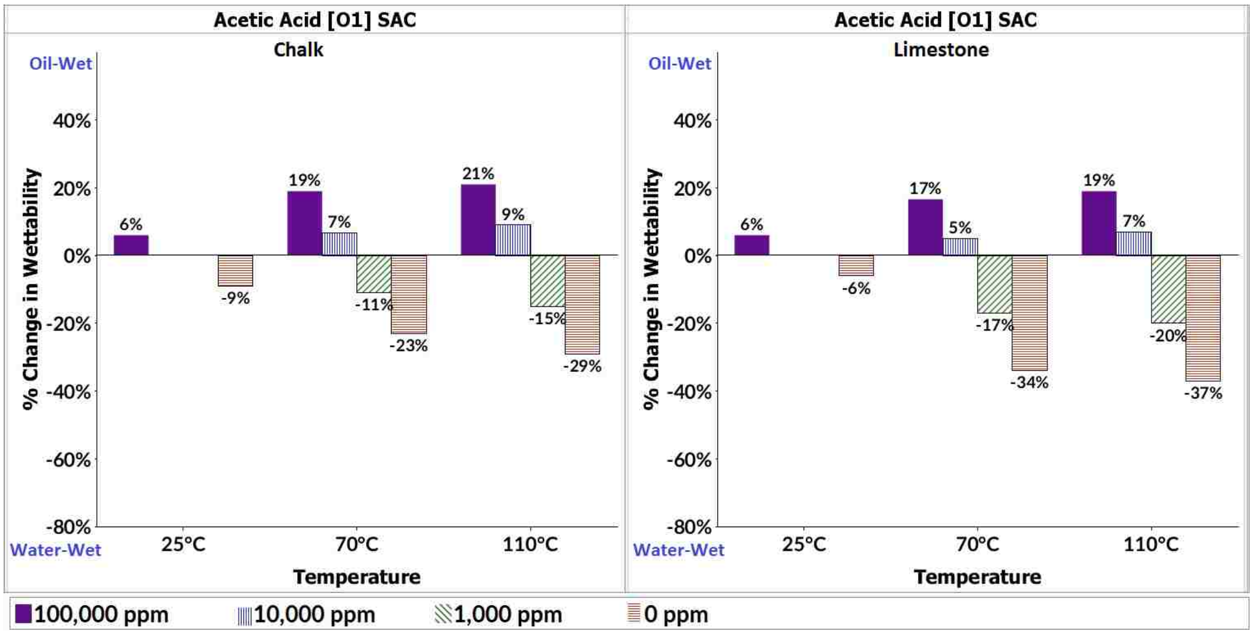


Figure 59: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid SAC. Values below 5% are not displayed.

As shown, the wettability trend produced by the two SACs is similar between the carbonate rocks. However, there are variations in the degree at which each SAC impacts the wettability of the two rocks. For example, acetic acid shifted the wettability of both carbonate rocks in a similar fashion and degree (Figure 59). Carbazole slightly shifted the wettability of chalk towards water-wetness at 1000 ppm and 10,000 ppm brine salinities and at the higher temperatures (70°C and

110°C). However, carbazole significantly shifted the wettability of limestone at 0 ppm, 1000 ppm, and 10,000 ppm for the three temperatures examined (Figure 60). All in all, we conclude that care must be taken when generalizing the wettability behavior of carbonate, sandstone, or shale rocks.

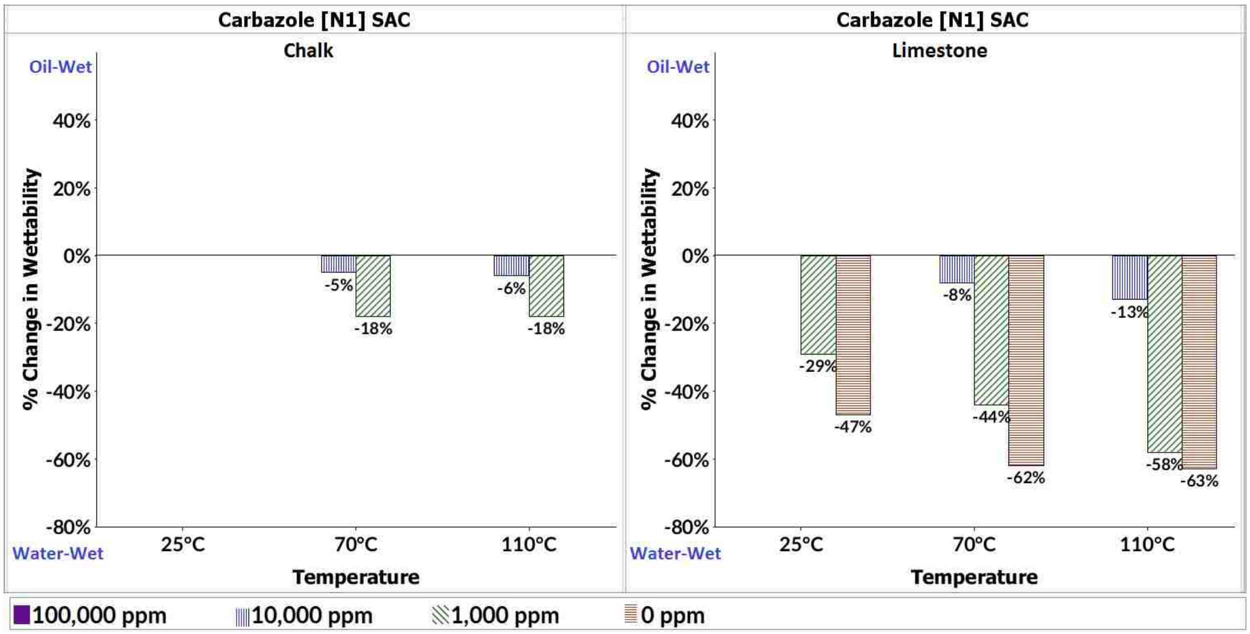


Figure 60: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using carbazole SAC. Values below 5% are not displayed.

In this work, we observed both basic and non-basic nitrogen SACs playing a major role in carbonate wetting, by increasing the water-wetness of the carbonate rocks, especially at higher concentrations. Puntervold et al. (2007) made a similar observation with natural bases, where she observed an increase in water-wetness as the basic material was increased.

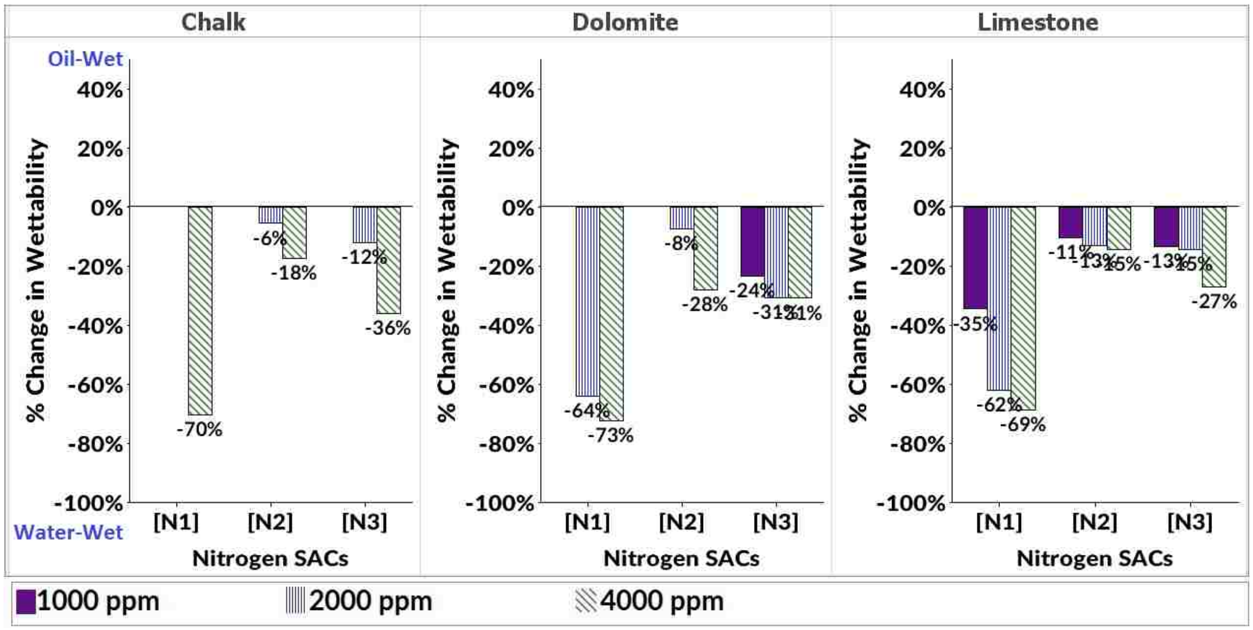


Figure 61: Experimental measurement of wettability for the carbonate rocks at 0, 2000, 4000 ppm of nitrogen SACs and 70°C. Values below 5% are not displayed.

Morrow et al. (1973) reported hydrocarbon containing sulfur SACs did not induce oil adhesion in either quartz or dolomite surfaces. Similarly, we found non-acidic sulfur compounds S1 and S2 did not induce oil adhesion in sandstone, and slightly shifted the wettability of the carbonate rocks towards water-wetness (Figure 35, Figure 45, Figure 46). On the other hand, we observed an opposite effect with long-chained oxygen SACs and acidic sulfur SAC; both promoted oil-rock adhesion (Figure 62). This effect was attributed to the bonding between the negatively charged acids ($RCOO^-$) and the positively charged sites on carbonate surfaces. Different groups have made similar observations and thus concluded that acids/oxygen SACs can play a significant role in the wetting of carbonates (Morrow et al., 1973; Speight, 1999, Standnes and Austad 2000a, Fathi et al., 2011).

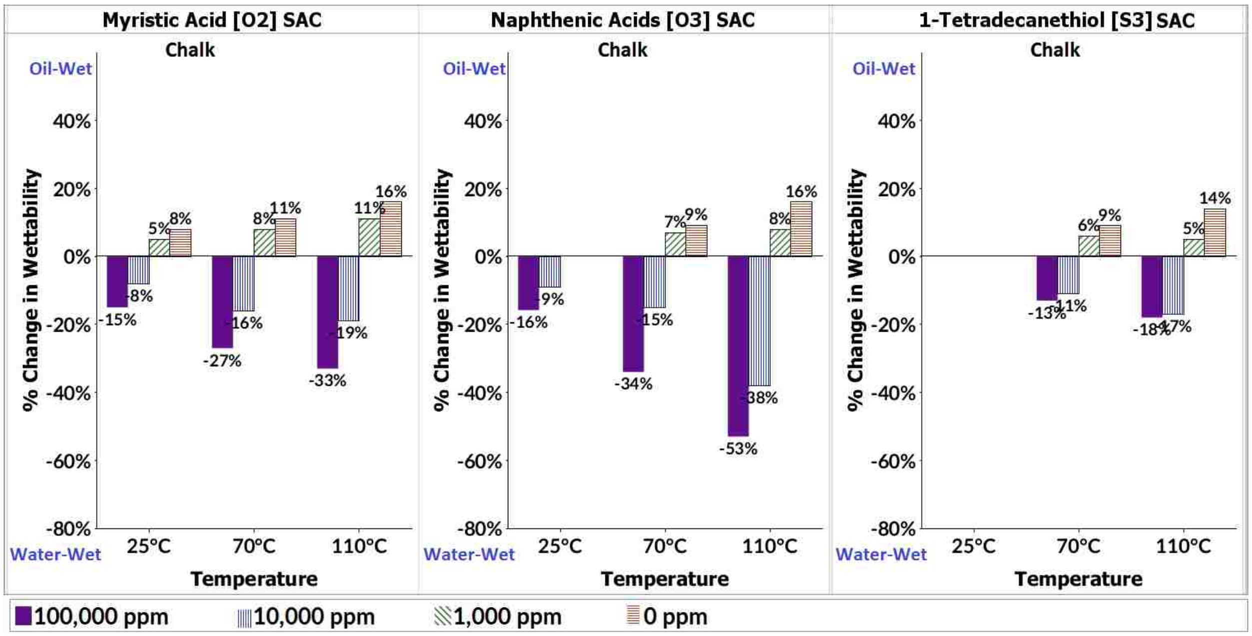


Figure 62: Experimental measurement of wettability for chalk at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using long-chained oxygen SACs and acidic sulfur acidic SAC. Values below 5% are not displayed.

Puntervold et al. (2007) suggested that an acid-base complex could be formed in the crude oil that to an extent made the acidic material less active towards the carbonate surface. Also, reservoir temperature has been found to decrease the acid number of crude oil due to the decarboxylation process at high temperatures (Shomoyama & Johns, 1972). Therefore, with these observations, one can hypothesize that the nitrogen SACs have more influence towards determining wettability than the oxygen SACs. This study found that the oxygen SACs play a major role in the wetting of carbonate rocks. However, only one of the three nitrogen SAC had a significant effect. This is assumed to be due to the lack of charge at experimental pH. To determine which of the two SAC groups has a larger influence on wettability, a systematic study is needed to examine the effects of combining long-chained oxygen SAC (acids) that promote oil-rock adhesion with nitrogen SAC (base) that promote water-wetness at reservoir pH values. This recommended study would highlight the synergetic effects of the two groups, but more importantly, help identify the key SACs that either promote or depress oil-rock adhesion.

The effect of four brine salinities (0 ppm, 1,000 ppm, 10,000 ppm, and 100,000 ppm) on the wettability of the carbonate and sandstone rocks was examined. Brine salinity was found to play a major role in the wettability of the carbonate rocks. With decreasing brine salinity, nitrogen SACs and the short-chained oxygen SAC shifted the wettability of the carbonate rocks towards water-wet conditions (Figure 63). On the other hand, long-chained acids SACs, acidic sulfur SACs, and aromatic compound shifted the wettability of carbonates towards oil-wet conditions as salinity declined (Figure 64, Figure 65). The degree of wettability alteration varied for each carbonate.

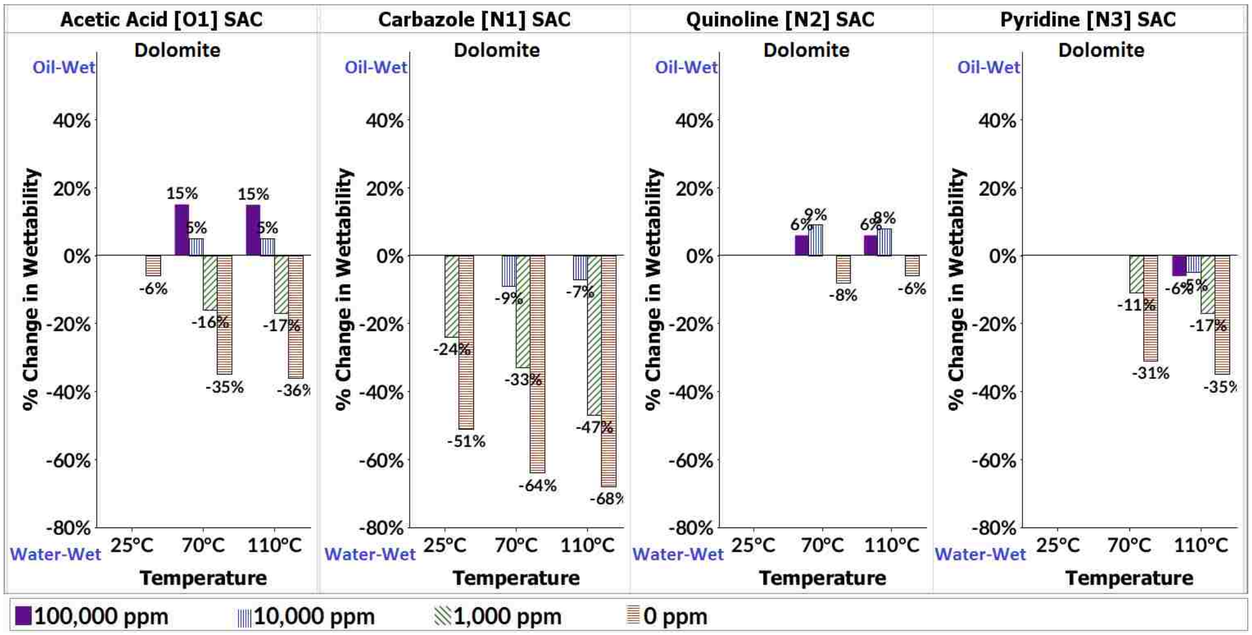


Figure 63: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid SAC and nitrogen SACs. Values below 5% are not displayed.

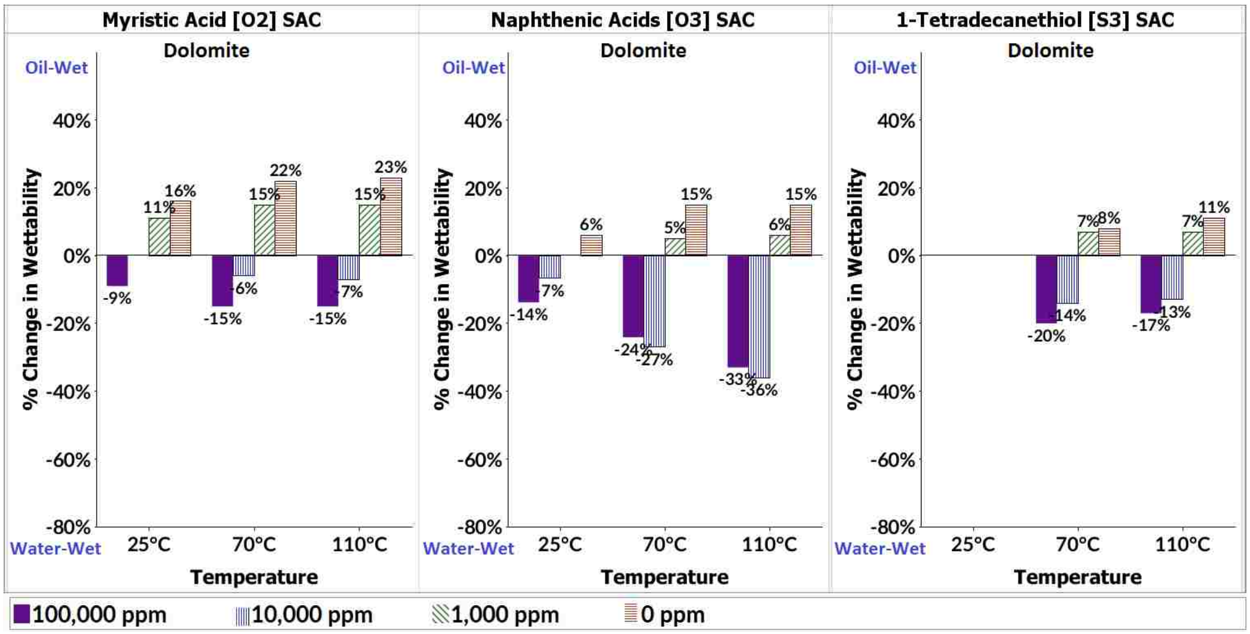


Figure 64: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using long-chained oxygen SACs and acidic sulfur acidic SAC. Values below 5% are not displayed.

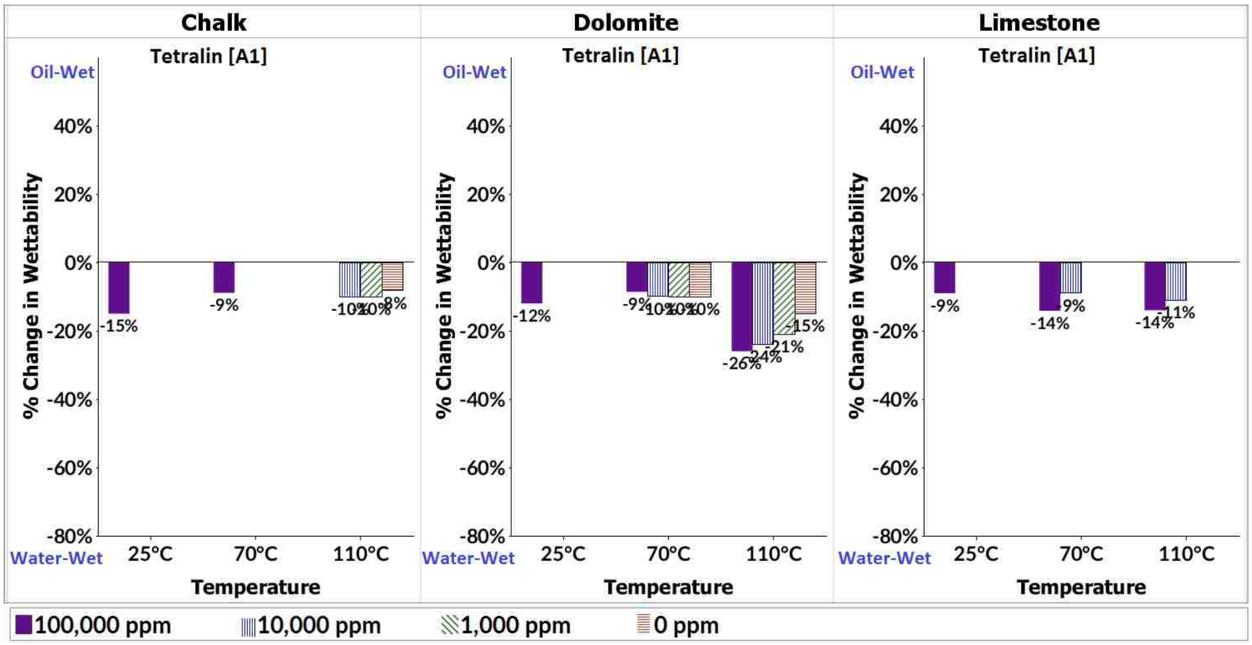


Figure 65: Experimental measurement of wettability for the carbonate rocks at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using tetralin. Values below 5% are not displayed.

These results give us a detailed understanding on how different SACs shift wettability with respect to brine salinity. Various published studies (Zhang and Austad 2006; Alameri et al. 2014) have reported positive improvement on oil recovery through low salinity waterflooding, and others (Hamouda et al., 2014; Gandomkar & Rahimpour, 2015) have reported small or negligible effects on recovery. Typically, the low salinity effect is probed by performing spontaneous imbibition and coreflooding experiments demonstrating additional oil recovery. The incremental oil released is typically attributed to wettability alteration of carbonate surfaces. A proposed explanation for the lack of low salinity effect in some reservoirs has been attributed to the lack of potential determining ions (e.g. Mg^{2+}, $Ca^{2+,}$ and SO_4^{2-}) in the injected brine (Austad et al., 2005; Al-Attar et al., 2013). This study proposes that the lack of low salinity effect may dependent on the crude oil having high levels SACs with minimum sensitivity to salinity change, and/or low levels of SACs with high sensitivity to salinity.

Temperature was found to play a role in the wettability of the carbonate rocks. Three temperatures were examined in this project, 25°C, 70°C, and 110°C. A significant difference in the wettability of the rocks was noticed between the low temperature (25°C) and higher temperatures (70°C, and 110°C) as shown in Figure 66. Of the SACs successful in shifting wettability, only a few were successful at 25°C. The degree of the wettability alteration was greater at the higher temperatures, but the difference in wettability between 70°C and 110°C was observed to be small.

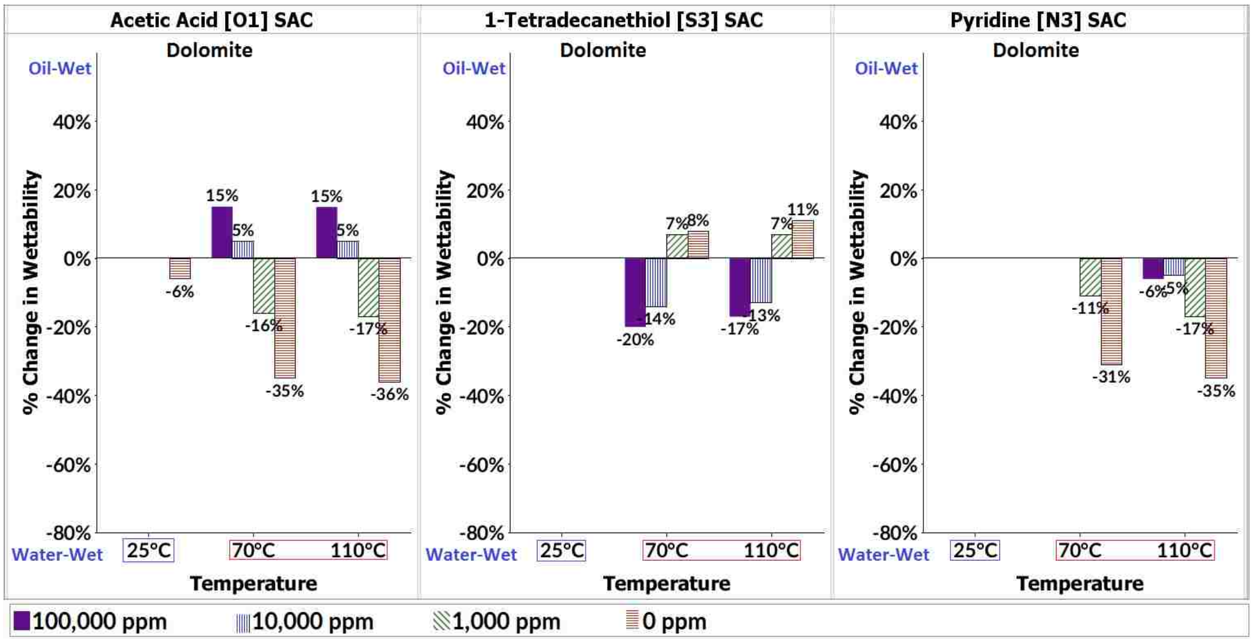


Figure 66: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid, 1-Tetradecanethiol, and pyridine SACs. Values below 5% are not displayed.

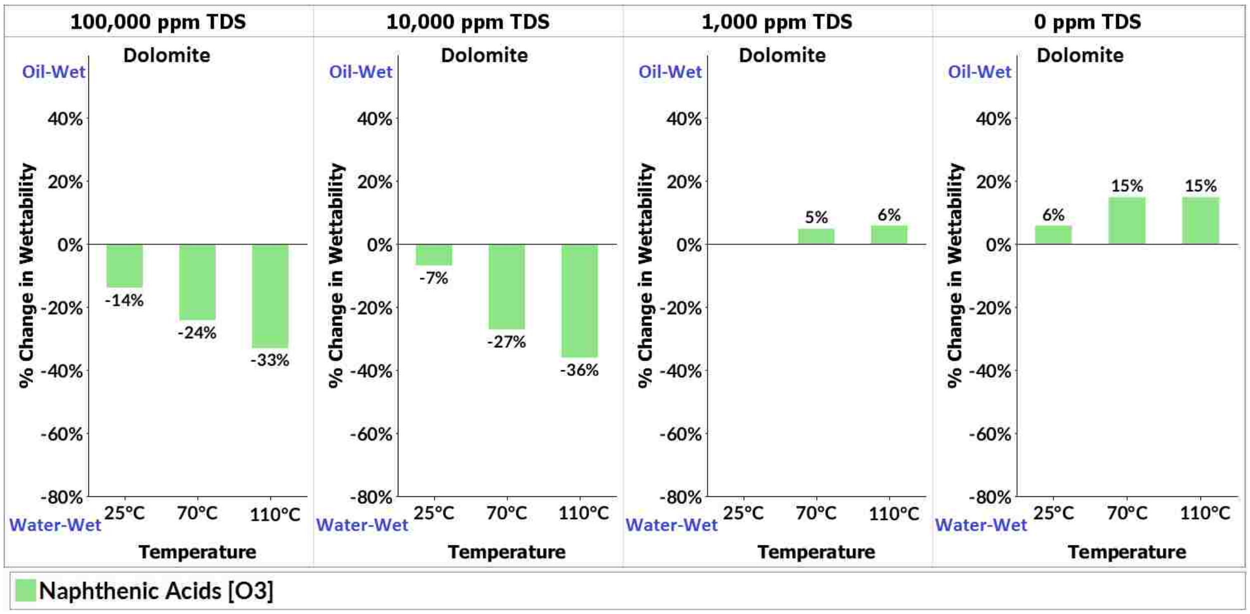


Figure 67: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using naphthenic acids SAC. Values below 5% are not displayed.

Several groups have observed that high-temperature carbonate reservoirs appear to be more water-wet compared to low-temperature reservoirs (Rao, 1996; Al-Hadhrami and Blunt, 2001; Schembre et al., 2006; Hamouda and Karoussi, 2008). However, in this study we found that while temperature accentuated the wettability effect of the SAC of interest on the rock, the effect toward either oil-wet (low salinities) or water-wet (higher salinities) depends more on salinity.

8.2.3. SACs Overview

This study has been successful in highlighting the role of SACs in shifting the wettability of Berea, chalk, dolomite, and limestone, as brine salinity and temperature are varied. We found that the overall effect toward either oil-wet or water-wet conditions depended more on brine salinity than temperature. This section focuses on SACs that shifted the wettability of the four rocks as the brine salinity was decreased from 100,000 to 10,000 ppm at 70 and 110°C. These conditions were selected because they are more representative of reservoir conditions. Graphs in this section display the wettability alteration values greater than 10% due to salinity change. These screening criteria show very few SACs were significant in controlling wettability as shown by Figure 68 to Figure 71. As shown in Figure 68, the SACs tested in this study did not significantly shift the wettability of Berea at these conditions. Of the SACs examined, oxygen SACs shifted the wettability of the carbonate rocks at varying degrees as brine salinity was decreased from 100,000 ppm to 10,000 ppm. At these conditions, chalk was found to be more sensitive to brine salinity variation as dolomite was the least sensitive. This information can be used in conjunction with TAN/TBN values to predict wettability.

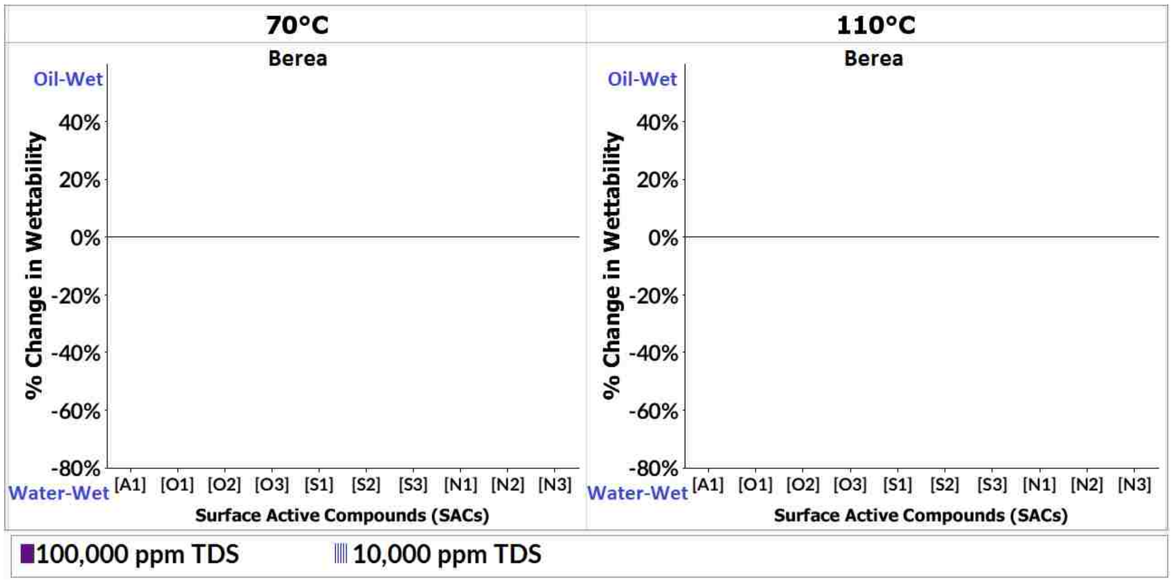


Figure 68: Experimental measurement of the SACs ability to change wettability of berea as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

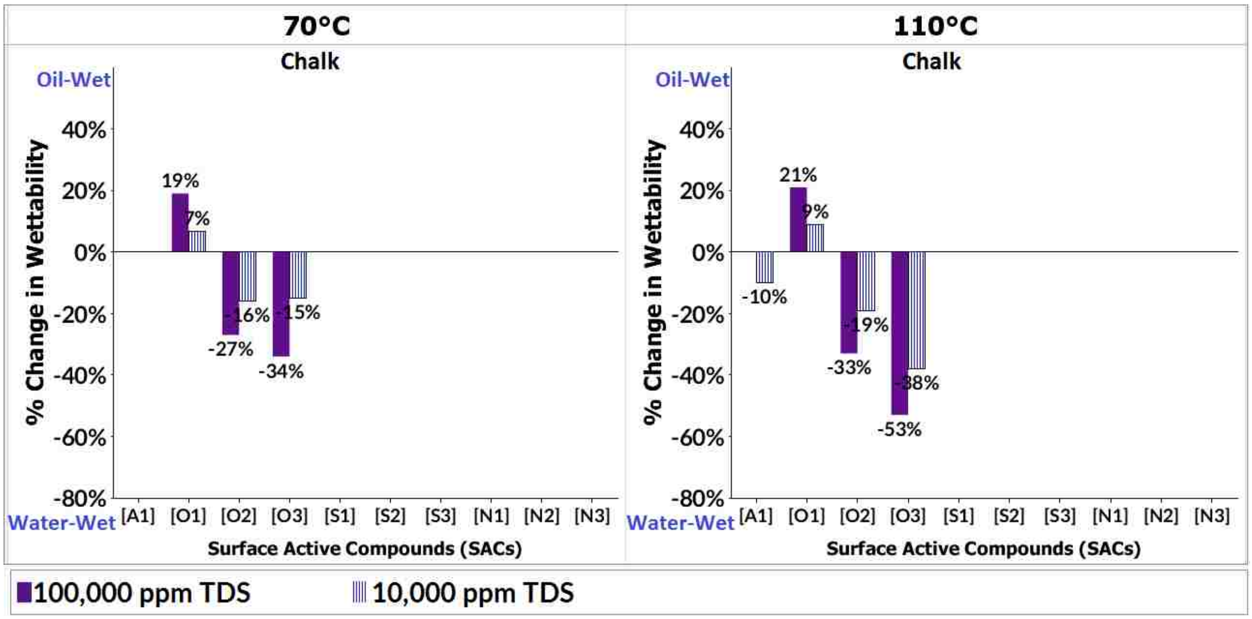


Figure 69: Experimental measurement of the SACs ability to change wettability of chalk as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

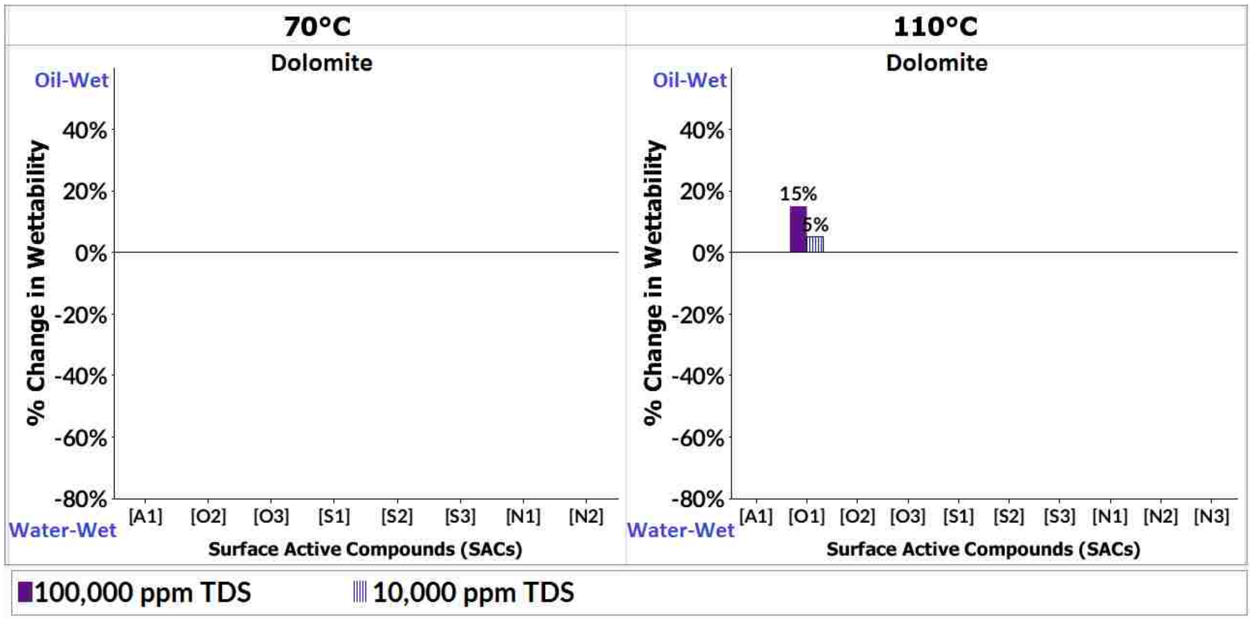


Figure 70: Experimental measurement of the SACs ability to change wettability of dolomite as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

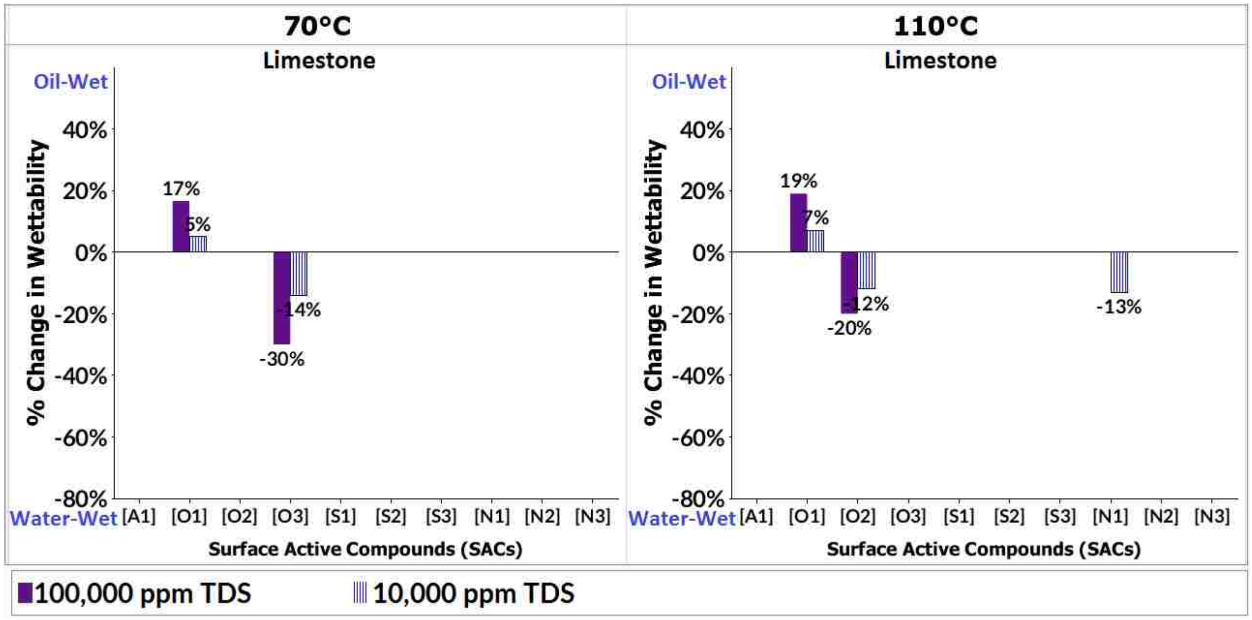


Figure 71: Experimental measurement of the SACs ability to change wettability of limestone as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

8.3. Wettability Revisited

Wettability is determined by the balance of surface forces between the interaction of oil and water with the surface of the rock. Depending on the specific interactions, the wettability of a system can range from strongly water-wet to strongly oil-wet. Degrees of wetting apply along the wettability continuum, and as shown in this study, the oil chemistry, water chemistry, rock morphology and mineralogy, and temperature govern where in the continuum the rock wettability lies. This study has prompted us to evaluate our understanding of wettability, and in this section, we share our thoughts, hypothesis, and conclusions regarding the subject.

8.3.1. Traditional wettability

Wettability has traditionally been classified into three categories: water-wet, neutral-wet, and oil-wet. The three wettability classifications are generally defined by the common wettability measurement methods, such as flow measurement (Amott and USBM) and contact angle methods. The flow measurement methods produce results (oil-wet, etc.) equivalent with a specified range of contact angle values. However, the correlation between these wettability measurements is not the best. This is probably attributed to the different scales that wettability is measured (Figure 72).

Both the Amott and USBM methods estimate the average wettability of a core by measuring the imbibition and displacement of oil and water (Anderson, 1986). The size of the core samples varies from 1 to 1.5 inches in diameter and 2 to 3 inches in length (Haugen, 2016). The rock is characterized as water-wet when water is preferentially imbibed in the core, which is assumed to indicate the rock's preference to the water phase rather than the oil phase. The rock is considered neutral-wet when neither oil or water are preferentially imbibed, which is assumed to indicate that equal portions of the rock surface have a preference for water or oil. Lastly, the rock is characterized as oil-wet when oil is preferentially imbibed into the core.

The contact angle method makes a direct wettability measurement of a small, flat, and polished rock surface that is suspended horizontally and encapsulated by water. The wettability measurement is based on the average wettability of the grains contacted by the drop of oil placed on the rock surface. The rock is said to be: water-wet when the contact angle between the rock and oil is less than 75°, neutral-wet when between 75° to 105°, and oil-wet when greater than 105°.

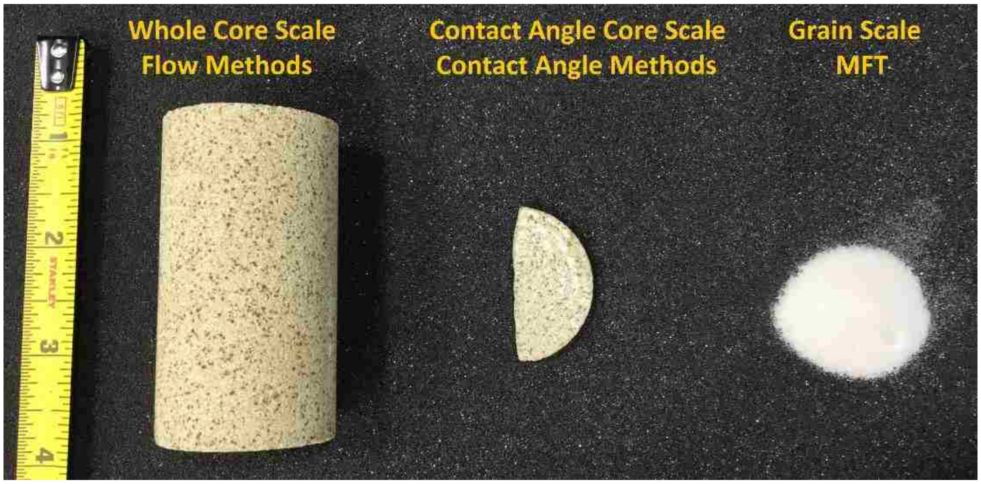


Figure 72: Different scales that wettability is measured by flow measurements (whole core scale), contact angles (contact angle core scale) and MFT (grain scale).

For the flow measurement methods, the fluids contact millions of grain surfaces, and an average wettability is calculated or estimated. This scale of measurement will be referred to as whole core scale (Figure 72). For contact angles, the drop of oil contacts at least several grains and an average wettability of those grains forming the polished surface is measured. This scale of measurement will be referred to as contact angle core scale (Figure 72). By crushing the core, MFT directly interrogates the rock-fluid interactions at the grain scale by looking at the chemical reactions. This scale of measurement will be referred to as grain scale (Figure 72). Therefore, if standard wettability measurement methods generally define wettability classifications, how do the different scales of measurement influence the definition and understanding of wettability?

8.3.2. Wettability: Scale of Measurement

The definitions of homogenous wettability states, water-wet and oil-wet, are consistent between flow measurements, contact angle, and MFT methods. At a core and grain scale level, water-wetness describes the preference of the rock to be in contact with water, thus having a film of water coating the rock grain surfaces. In a porous media, water exists as a continuous phase throughout the pore network as oil is a discontinuous phase consisting of globules in the larger pores surrounded by water (Donaldson & Waqi, 2006). On the other hand, when the system is preferentially oil-wet, the locations of water and oil in the rock are reversed from the water-wet case. Oil occupies the smaller pores and is in contact with most of the rock grain surfaces, whereas water resides as globules in the larger pores.

Researchers have also recognized that rocks can have a mixture of water-wet and oil-wet grains within the sample. Brown and Fatt (1956) proposed that the wettability of reservoir rock be stated in terms of the fractional internal surface area that is in contact with water or oil, fractional-wettability. The condition of heterogeneous/fractional wettability is described by terms such as: mixed wet, speckled, and dalmatian wettability. Mixed-wettability was introduced by Salathiel (1973) where he proposed that oil-wet surfaces form continuous paths through the larger pores, as the smaller pores remain water-wet and contain no oil. Therefore, since all the oil is contained in the larger pores, a small but finite oil permeability exists down to very low oil saturation. Salathiel proposed that this condition could occur during the original accumulation of oil in a reservoir if natural oil containing SACs displace connate water from the larger pores. Oil would not enter the smaller pores where the threshold capillary pressure for displacement of water is too large. Speckled/spotted/dalmatian wettability refers to continuous water-wet surface encompassing areas of discontinuous oil-wet surfaces or vice versa (Morrow et al., 1986; Cuiec, 1991).

These forms of heterogeneous wettability refer back to the measurements and apply to describing wettability at core scale. Both the contact angle and flow measurement methods do not have the ability to directly measure heterogeneous wettability. Flow methods do observe spontaneous imbibition of both fluids for mixed-wet rocks. The result (Amott/USBM index) classifies the rock as neutral wet (Donaldson & Waqi, 2006). MFT can directly measure heterogeneous wettability of a core, by physically separating the oil-wet rock grains from the water-wet rock grains. It may also be possible to have heterogeneous wettability at a grain scale level, where part of the grain is oil-wet, and another is water-wet. A controlled study similar to the glass beads experiments in section 4.1, could be undertaken where parts of a glass bead surface can be altered to simulate natural inclusions and variation in surface mineralogy and morphology.

In section 4.1, we established that grains in the surface force dominant range would float and reside in the oil phase if oil-wet, as the water-wet grains will sink and reside in the water phase. If both hydrophobic and hydrophilic beads were mixed to create heterogeneous surfaces, we expect that the fraction of beads that are oil-wet to float and the fraction that is water-wet to sink. As an extension of this, I hypothesize that if several hydrophobic and hydrophilic beads were clustered together to form a smooth flat surface, a measured contact angle of the heterogeneous surface would give an average wettability of the grains. Also, if the hydrophobic and hydrophilic glass beads were packed in a cylindrical tube to mimic a core, the flow measurement methods would give an average estimate of the wettability. If equal amounts of hydrophobic and hydrophilic grains were used, we hypothesize that contact angle and flow measurements would indicate neutral-wet conditions. However, depending on the arrangement pattern of the hydrophobic and hydrophilic grains, different patterns of wettability could be formed, e.g. mixed-wet or speckled wettability. We recommend testing these hypotheses as a way to accurately relate the microscale to macroscale wettability measurements. Since we measure numerous grains in flotation and aggregate the result, there should be an equivalence with the other macroscale measurements. Individual grains are not neutral wet. Depending on the geochemical condition present, the grain will show a degree of preference towards water or oil.

Lastly, we also recommend wettability discussions to include scale in order to provide context. As more work is done to further this area of research, there needs to be an application of the wettability knowledge gathered from the grain scale to the core scale, and how it helps us understand the reservoir scale wettability.

8.3.3. Wettability: Inherent vs. Situational Wettability

Another aspect of wettability established in this study is that it is not an inherent property of the rock surface to be water-wet or oil-wet. Instead, it is a function of the oil, water, rock, and temperature. These four parameters create a unique geochemical condition that produces a wettability state specific to it. Therefore, the wettability of a rock can vary from water-wet to oil-wet depending on the geochemical condition present. This makes wettability “situational” rather than an inherent characteristic of the rock.

Figure 73 illustrates four different salinity conditions for two SAC’s. The rock type used is dolomite and the temperature is 110°C. In the case of acetic acid, we observe that the SAC shifts the wettability of dolomite from oil-wet to water-water as salinity is decreased. This is an example of how salinity can influence wettability of a rock. However, if all conditions are kept the same and the SAC in the model oil chemistry is changed from acetic acid to myristic acid, we observe an opposite wettability trend as salinity is decreased. This shows how oil chemistry can influence the wettability of a rock.

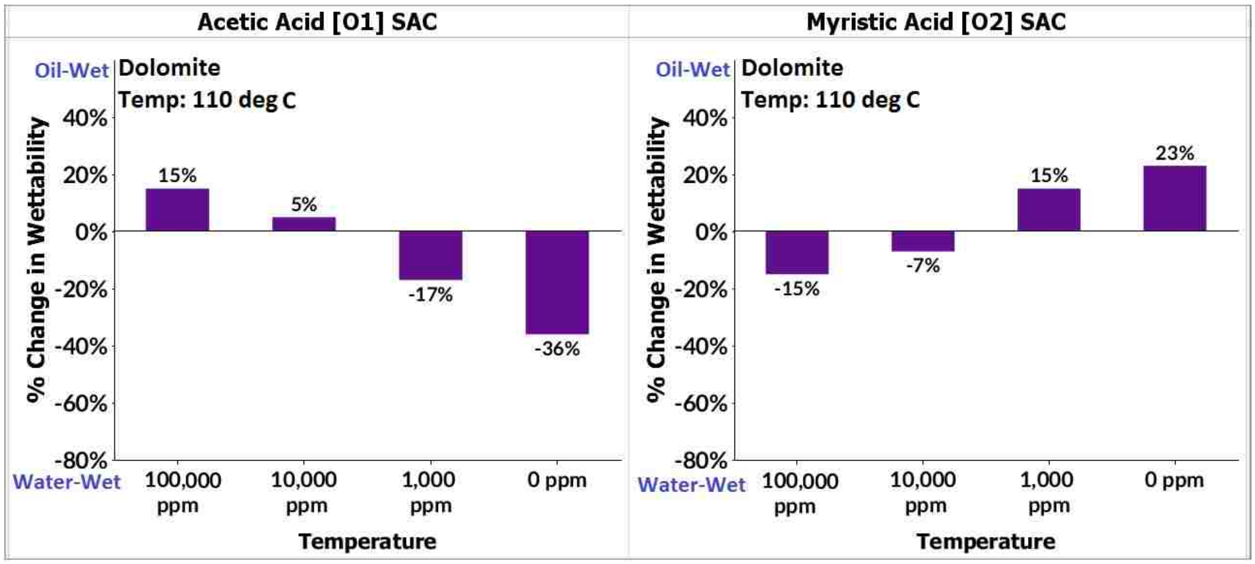


Figure 73: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and 110°C when using acetic acid and myristic acid SACs. Values below 5% are not displayed.

In Figure 74 brine salinity is held constant at 0 ppm and the temperature was varied from 25°C to 110°C. In the case of acetic acid, temperature does make a difference in the degree of wettability change. However, in the case of myristic acid, the effect of temperature on wettability is much less or negligible. This shows that temperature has the ability to influence the wettability of a rock.

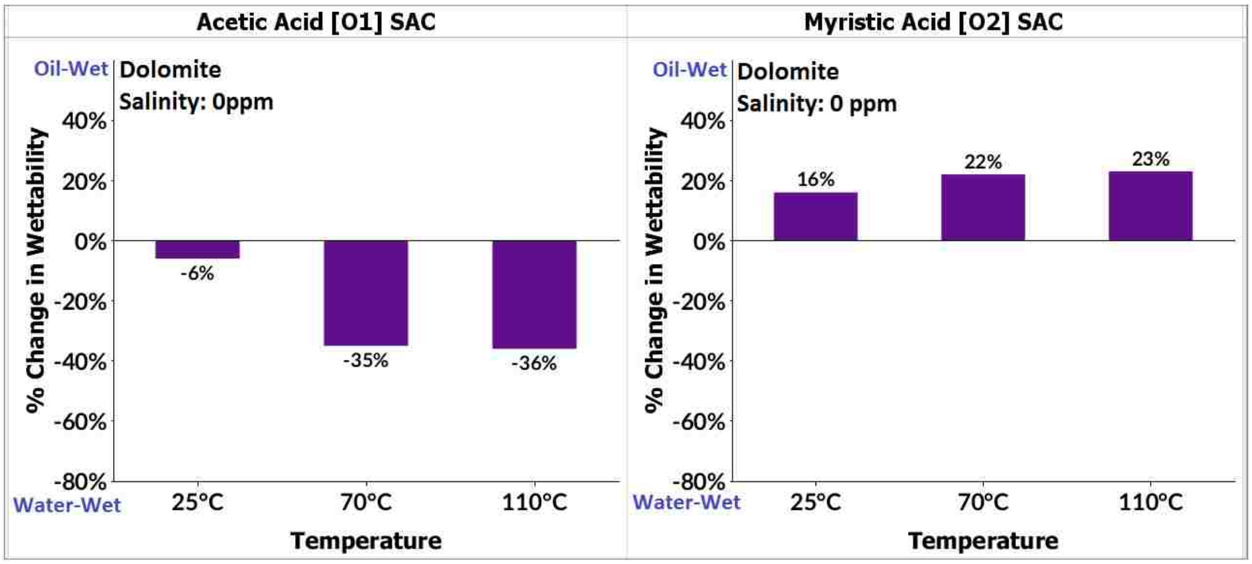


Figure 74: Experimental measurement of wettability for dolomite at 0 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid and myristic acid SACs. Values below 5% are not displayed.

At the start of this project, the standard convention of classifying the rock based on its mineralogy was used. Using this approach, we would assume that chalk and limestone would behave the same. During the course of this project, we have learned that the surface structure of the rock also plays a significant role. In Figure 75 we observe the change in wettability of chalk and limestone when salinity is varied at 110°C. As shown by XRD results, chalk and limestone are both composed of calcite. However, the two rocks have different morphologies. In the case of myristic acid, we observed the two rocks having a similar trend in wettability variation as salinity is decreased, where the wettability shifted towards oil-wet. However, the degree of change with salinity is somewhat different. In a similar fashion when the oil chemistry is changed by using carbazole in the model oil, the degree of shift in wettability of limestone towards water-wet at low salinities significantly greater than chalk. Thus, mineral morphology may play a significant role in wetting.

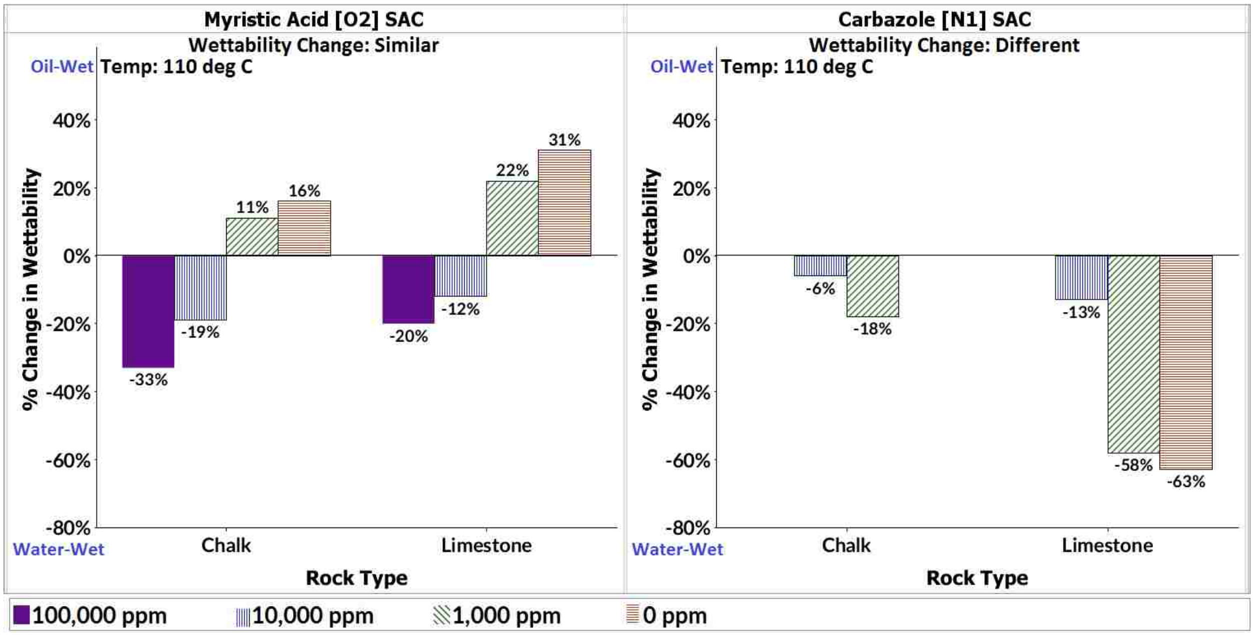


Figure 75: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and 110°C when using myristic acid and carbazole SACs. Values below 5% are not displayed.

Since MFT physically separates the oil-wet and water-wet rock grains, we recommend material (rock, oil, and water) analysis of the different fractions. We expect the careful examination of the rock properties such as composition, morphology and surface area using techniques such as micro-CT will reveal further insights that can help us better understand rock-fluid interactions and will help identify additional characteristics that influence wetting.

8.4. Field Application

The two major contributions of this project are: (1) the development of a wettability measurement technique (MFT) that is fast, reliable, and serves as an effective screening tool; and (2) a clearer understanding of the role of SAC in altering wettability at different geochemical conditions. This section explores how these contributions can be applied in the oil and gas industry.

8.4.1. Wettability Studies

8.4.1.1. Current Challenges in Studying Wettability

In petroleum engineering, wetting forces play a crucial role in determining the distribution and flow of reservoir fluids, and the effectiveness of oil recovery methods. Sophisticated wellbores, completions systems, and fracture networks can be implemented, however, their success and failure in achieving high oil recovery is a function of whether the rock’s wettability (rock-oil-brine interaction) is favorable, thus facilitating the flow of oil to the production well. Nevertheless, as significant as this parameter is, it has historically been assumed to be inherent rather than an easily manipulated parameter. This mindset has largely been a result of the following issues: (1) most petroleum engineers rarely consider wettability in their day to day work mainly because it is a parameter that is not measured in the field or used directly in most reservoir related calculations. (2) wettability is indirectly included in flow equations and reservoir simulations through relative permeability data which is influenced by multiple parameters. (3) lack of direct integration of wettability in fluid flow equations is largely due to the unclear understanding of the rock-oil-brine interactions. As shown in this project, wettability is influenced by the reservoir rock mineralogy and morphology, aqueous chemistry, oleic chemistry, and temperature. Each of these parameters can have many different variations in a specific reservoir thus resulting in a wide-range of geochemical conditions that can affect wettability. To examine the effects of these geochemical conditions on wettability, thousands of experiments are required. Unfortunately, standard methods are limited by the time and expense it takes to run a single experiment (days to weeks). This significant bottleneck for laboratory experiments has greatly hindered the progress toward better understanding the nature of wettability. To overcome this barrier, a wettability measurement technique that was fast, reliable, and would serve as both a screening tool and provide quantitative results would be needed. This led to the creation of MFT.

8.4.1.2. Wettability Studies using MFT

As of now, MFT and its variations have been used by several groups to study different aspects of wettability (Mwangi et al. 2013; Haugen et al., 2016; Sohal et al. 2016; Sohal et al. 2017; Fjelde et al., 2017). As shown by these studies, MFT can rapidly determine important parameters for further studies. Since this tool is fast, reliable, and easy to use, it lends itself to carrying out extensive systematic wettability studies that can examine the wettability of different rock types under different geochemical conditions. This can lead to the creation of extensive wettability libraries/databases that can be used to predict the rock’s wettability, and variations in wettability as geochemical conditions are modified. More importantly, these wettability libraries/databases would serve as important platforms in creating accurate and robust wettability prediction models.

In the quest to decipher the mechanism(s) that govern wettability, extensive systematic studies of well-characterized reservoir material (such as this project) are important. By changing one parameter at a time, we were able to identify the critical parameters and how their effect on wettability. The next step would be to postulate and test different theories of the mechanisms that dictated the shifts in wettability. For example, understanding how neutral compounds are able to shift wettability, or the differences between the short-chained and long-chained acid effect on wettability. Significant strides can be made to decipher these mechanisms by coupling the experimental data with geochemical modeling. Fjelde et al. (2007) used MFT to study the potential of injected water composition in shifting the wettability of reservoir sandstone rocks to more water-wet conditions. Their study found that combining flotation experiments with geochemical simulations was effective in screening the ability for injection water composition to alter wettability. They concluded that a combination of flotation experiments and geochemical simulations has the potential to determine whether direct adsorption or cation bridging are the dominating wetting mechanisms. Their results indicated that cation bridging to be the dominating wetting mechanism for their rock-oil-water system.

In summary, MFT is not meant to replace but rather complement the standard wettability measurement methods. MFT studies wettability at a grain scale whereas contact angles and flow measurement methods study wettability at a macroscale. These techniques working in coordination and leveraging their strengths would provide an invaluable synergy and insight to the inner workings of wettability. As a result, this would bring us closer to the ultimate goal of significantly improving oil recovery hydrocarbon reservoirs.

8.4.2. Ionically Modified Waterflooding

This study has shown that the success of ionically modified waterflood is dependent on knowing the details of oil, brine, rock, and temperature. The brine chemistry, rock mineralogy, and temperature can be characterized using current technologies. Regarding crude oil, this study recommends the development of an analytical process to identify and quantify surface active compounds in crude oils. Extensive characterization of reservoir material would significantly assist in engineering effective chemistry of the injection water that would optimize the oil recovery. This would also decrease/eliminate instances where this EOR process would not work. Due to the ease of measuring the wettability of numerous geochemical conditions using MFT, many brine chemistries can be tested. MFT can be used as a screening tool to narrow down a few brine chemistries that can be tested using standard wettability measurement methods and coreflooding experiments. Sohal et al. (2016) found that MFT can serve as a screening tool to estimate the wettability alteration potential of brines in a quick time frame and with high repeatability and is an excellent process to differentiate the impact of potential determining ions and low salinity on wettability alteration that is hard to measure otherwise. Fjelde et al. (2007) found that using MFT to screen injection brine composition is much less time consuming than standard experiments, and only a small amount of rock samples were required. They concluded by stating that the potential for the most promising injecting water compositions can then be further evaluated by core flooding experiments, including chemical analyses to study rock-brine interactions, injectivity, and oil recovery potential.

8.4.3. Surfactant Flooding

MFT can also be used as a tool to select surfactant type and concentration for surfactant flooding processes. MFT can also help determine the surfactant types and concentrations that would form emulsions. Surfactants increase oil recovery by lowering the interfacial tension (IFT) between oil and water and also altering wettability to a desirable state (water-wet). Many studies have been executed to understand how surfactants impact IFT, and the mechanisms involved are relatively well understood. However, the mechanisms that govern wettability alteration due to surfactant use are still not well understood. The effect of surfactants on wettability depends on how much is adsorbed to the rock, and how they are adsorbed. Surfactant adsorption on the rock and resultant wettability changes are determined mainly by the chemical structure and mix of the surfactants, surface properties of the rock, oil chemistry, nature of additives (e.g. polymers added), brine chemistry, and temperature. Rock mineralogy plays a crucial role in determining interactions between reservoir minerals and surfactants/polymers. Also, some of the rock minerals can be sparingly soluble causing surfactant precipitation and changes in wettability. Before surfactant flooding, many parameters must be determined in order to create an optimal surfactant flood. These parameters are: surfactant type and concentration determination, ideal injection brine chemistry, etc. This study suggests that the use of MFT as a screening tool to determine the most suitable parameters for coreflooding experiments to further study the selected parameters.

8.4.4. Core Cleaning Solvent Selection

Appendix B presents a core cleaning solvent analysis that can be used in the selection of solvent(s) used in the core restoration process. Core material is often cleaned to a strongly water-wet state, then aged with formation water and reservoir oil to build up the initial conditions that are representative of reservoir conditions (Shariatpanahi et al., 2012). The aging period is significant limiting the number of experiments that can be conducted. The time needed for equilibration to restore the original wetting condition for reservoir core samples is significant. MFT has the advantage of reducing the required aging time. The common procedure of wettability restoration is to clean the reservoir core sample to make it strongly water-wet thus mimicking the initial wetting condition before oil migrated into the reservoir (Cuiec, 1975; Anderson, 1986; Jadhunandan, 1990). Thereafter, oil is injected into the brine saturated core and aged. MFT eliminates this limitation by crushing the core, thus increasing the surface area of the rock promoting maximum contact with oil and brine. The aging experiments (section 5.2.3) highlight that the formation of the organic surface reactions are rapid for decane, condensate, and 4 model oils were tested in the presence of DI water on Berea, chalk, limestone, and dolomite at 25°, 70°, and 110°C. MFT results were independent of aging time after 1 day except for the case of Berea + Myristic acid that required a period of 2 days. Based on the results of this project we can conclude that the long (weeks to months) equilibration times during the aging process reported in the literature are mainly due to the rock structure limiting the rate of contact with all the surfaces.

Even though many studies have been carried out to find the most effective cleaning solvent, core cleaning remains mostly a trial and error process, where the selection of the best solvents to be used greatly depends on the experience with the particular rock. Standard wettability measurement techniques are limited in the time and expense it takes to run a single experiment. Therefore, an extensive core cleaning solvent selection analysis is impossible. For instance, toluene followed by methanol is commonly used to remove hydrocarbons including asphaltenes and adsorbed polar components. As shown in this project, rock mineralogy, brine chemistry, oil chemistry, and temperature will affect wettability, and thus the effectiveness of the cleaning solvent. Therefore, we propose MFT can be used to identify an effective cleaning solvent for the rock of interest with respect to brine, crude oil, and temperature used that minimizes or avoids alteration of wettability.

Lastly, the results of this study pose an interesting question of whether it is possible to restore the wettability of the core to its reservoir wettability. The natural flora/fauna/microbes found in the reservoir would be eliminated in the core cleaning process, and it is not possible restore these components. These organic constituents would contribute to the geochemical conditions that produce the reservoir wettability.

CHAPTER 9. CONCLUSION

The aim of this project was to develop a wettability measurement technique that is inexpensive, rapid, and reproducible, and to use it to describe the role of oil surface active compounds (SACs) in determining wettability in carbonate and sandstone reservoirs. This project details the development, validation, theory, and application of the modified flotation technique (MFT) for that study. MFT proved to be a successful quantitative technique that can rapidly test the influence of oil and brine chemistry on wettability on sandstone and carbonate reservoir material at different temperatures and salinity. The MFT procedure allows us to tackle one of the fundamental problems of petroleum engineering, which is the link between subsurface chemistry, wettability, and oil recovery. This novel wettability measurement method is fast, low cost, and produces not just quantitative wettability measurements but also allows physical separation of oil-wet and water-wet surfaces for more in-depth study. In addition, it gives us the ability to resolve the chemical controls over oil adhesion to reservoir minerals. This is a great advance that has the potential to move the field forward substantially and allow us to precisely tailor waterflood chemistries for maximal oil recovery.

MFT was used to study the effect of rock mineralogy (Austin chalk, Indiana limestone, Silurian dolomite, and Berea sandstone), aqueous chemistry (salinity), surface active compounds (SACs), and temperature. To isolate the effects of individual SACs, this project used model oils mixtures of pure decane and a single SACs to represent the oleic phase. The main conclusions drawn from this study were:

- In the case of Berea, only the long-chained oxygen acids shifted the wettability by promoting oil-rock adhesion that increased when the salinity was decreased. Therefore, of the SACs examined long-chained oxygen SACs were the most influential in shifting the wettability of Berea.

- In the case of carbonate rocks, short-chained oxygen SAC, non-acidic sulfur SACs, and nitrogen SAC’s promoted water-wet conditions as their concentration was increased. On the other hand, an opposite effect was observed with long-chained oxygen SACs and acidic sulfur SAC where they promoted oil-rock adhesion. Organic acids gave a stronger oil-wet shift than acidic sulfur SAC’s because they are stronger acids, hence are more deprotonated under the experimental conditions. Nitrogen and oxygen SACs had to have the greatest impact on carbonate wettability.
- Carbonates were also found to be more sensitive to salinity than Berea. In the case of carbonate rocks, as brine salinity was decreased nitrogen SACs and the short-chained oxygen SAC shifted the wettability of the carbonate rocks towards water-wet conditions. On the other hand, long-chained acids SACs, acidic sulfur SACs, and aromatics shifted the wettability of carbonates towards oil-wet conditions. This difference in SACs’ reaction to salinity was proposed as one of the reasons why low salinity waterflooding is successful in some reservoirs and not in others. Therefore, this study proposes that the lack of low salinity effect can also be attributed to a crude oil having high levels of oil-wet promoting SACs with minimum sensitivity to salinity change, and/or low levels of water-wet promoting SACs. Therefore, for IOR processes dependent on wettability alteration to be successful, it is important to have a detailed characterization of the crude oil as well as brine and rock mineralogy. This work recommends an additional characterization of crude oils where SACs can be identified and quantified based on their ability to promote oil-wetness or water-wetness.
- Temperature was found to play a role in the wettability of the carbonate rocks. A significant difference in the wettability of the rocks was noticed between the low temperature (25°C) and

higher temperatures (70°C, and 110°C). Most of the wettability alteration was at the higher temperatures and the difference between the 2 higher temperatures was small to negligible.

The two major aspects of wettability established in this study: microscale versus macroscale wettability, and inherent versus situational wettability. Traditionally, wettability classifications are generally defined by the common wettability measurement methods. These methods usually measure wettability at different scales. This has caused some confusion especially in defining heterogenous wettability, making a lot of the literature confusing. We have found that scale needs to be accounted for when discussing wettability. On a microscale (grain scale) wettability is homogenous. On a macroscale, wettability is heterogenous since it an average of all the grains wettability. MFT measures wettability on a grain scale (microscale) as contact angle and flow measurements estimate/calculate wettability on a macroscale. Since MFT measures numerous grains in flotation and aggregate the result, there should be an equivalence with the other macroscale measurements. Lastly, wettability is not an inherent property of the rock surface to be water-wet or oil-wet. Instead, it is a function of the oil, water, rock, and temperature. These four parameters create a unique geochemical condition that produces a wettability state specific to it. Therefore, the wettability of a rock can vary from water-wet to oil-wet depending on the geochemical condition present. This makes wettability “situational” rather than an inherent characteristic of the rock.

CHAPTER 10. RECOMMENDATION

The experimental work upon which this thesis is built has given many interesting results that would be worth looking further into. Below are some thoughts on proposed future work:

- We recommend developing an analytical process to identify and quantify surface active compounds in crude oils. Subsequently, these surface active compounds will be examined at different geochemical conditions, in order to create a database linking their ability to promote, depress or not affect the wettability of different rock types. The aim of this study would be to better characterize crude oils and provide useful and accurate information used in building accurate wettability prediction models.
- We found that both long-chained oxygen SACs and nitrogen SAC play an important role on the wettability of carbonate rocks. To determine which of the two SAC groups has a more significant influence on wettability, a systematic study is needed to examine the effects of combining long-chained oxygen SAC (acids) that promote oil-rock adhesion with nitrogen SAC (base) that promote water-wetness. This recommended study would highlight the synergetic effects of the two groups, but more importantly bring forth key SACs that either promote or depress oil-rock adhesion.
- This study did examine the effects of SACs on the wettability of sandstone and carbonate rocks in the presence of various brine salinities and temperature. We recommend furthering this study by examining the effect of SACs in the presence of: identified potential determining ions, various pH levels, different sandstone and shale rock types. We also recommend studying more than 3 SACs per chemical group.
- To have a better understanding of how these SACs would shift wettability in a typical reservoir, we recommend repeating these experiments using reservoir pH conditions and examining the impact of the basic SACs.

- It is possible to have heterogeneous wettability at a grain scale level, where part of the grain is oil-wet, and another is water-wet. A controlled study like the glass beads experiments in section 4.1, could be undertaken where parts of a glass bead surface can be altered to simulate natural inclusions and variation in surface mineralogy and morphology
- Experiments shows the relationship between grain scale and core scale experiments.
- A comprehensive injection water chemistry customization study is recommended using reservoir core, crude oil, and brine. This study would use MFT as a screening tool for the brine composition and salinity, and solvent(s) for cleaning the rock. Once MFT is used for selecting the optimal parameters, coreflood experiments can then be conducted to measure oil recovery. A continuation of this study would be the addition of surfactant to the injected water. For surfactant flooding studies, the surfactant type and concentration selection process can be time-consuming. MFT can satisfy this experimental gap by allowing numerous surfactant types and concentration to be rapidly tested.
- Lastly, we recommend the using the data generated in this project in a surface complexation model. A surface complexation model is a chemical model that describes the reactions occurring at the interface of mineral and solution and simulates the chemical equilibrium. The reactions lead to the formation of surface complexes that are ultimately responsible for the charges at the mineral surface and have specific equilibrium (stability) constants that are similar to reactions in the bulk solution. In the area of improved oil recovery, Brady et al. (2012) and Brady and Krumhansl (2013) have used this type of modeling to examine the proposed wettability alteration theories and to give insight into the primary oil (polar functional groups) and mineral coordination reactions leading to oil adhesion to clay and calcite.

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APPENDIX A: FIGURES AND TABLES

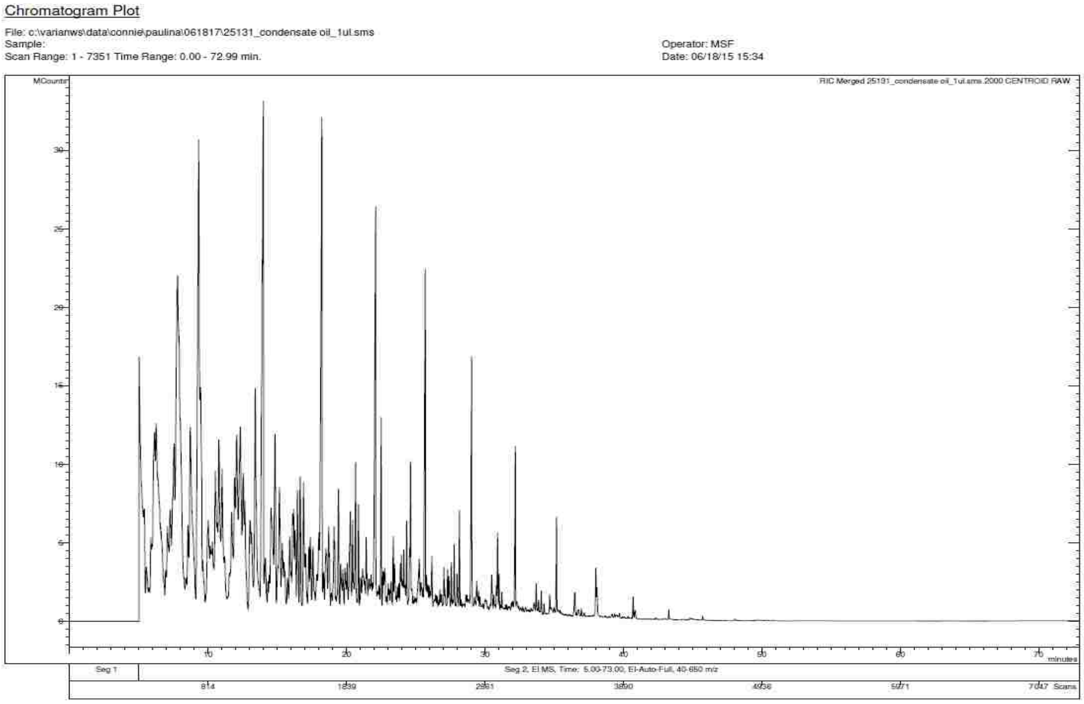

Figure A1: GC results of condensate oil.

Table A1: Condensate oil GC composition.

Name	Molecular Formula	Molecular Weight g/mol
1-ethyl-3-methyl-benzene	C_9H_{12}	120.19
1-ethyl-3-methylcyclohexane	C_9H_{18}	126.24
2,4-dimethyl-heptane	C_9H_{20}	128.26
1-methyl-2-propyl-cyclohexane	$C_{10}H_{20}$	140.27
2-methyl-trans-decalin	$C_{11}H_{20}$	152.28
hexyl-cyclohexane	$C_{12}H_{24}$	168.32
2,4,6-trimethyl-decane	$C_{13}H_{28}$	184.36
6-methyl-tridecane	$C_{14}H_{30}$	198.39
2,6,10-trimethyl-tetradecane	$C_{17}H_{36}$	240.47
Heptadecane	$C_{17}H_{36}$	240.48
2-cyclohexyl-dodecane	$C_{18}H_{36}$	252.48
Nonadecane	$C_{19}H_{40}$	268.52

Table A1: Cont'd

Name	Molecular Formula	Molecular Weight g/mol
10-methylnonadecane	$C_{20}H_{42}$	282.55
n-heptadecylcyclohexane	$C_{23}H_{46}$	322.61
3,5,24-trimethyl-tetracontane	$C_{43}H_{88}$	605.16
2-ethyl-1-decanol	$C_{12}H_{26}O$	186.33
2-butyl-1-octanol	$C_{12}H_{26}O$	186.33
2-hexyl-1-octanol	$C_{14}H_{30}O$	214.39
2-hexyl-1-decanol	$C_{16}H_{34}O$	242.44

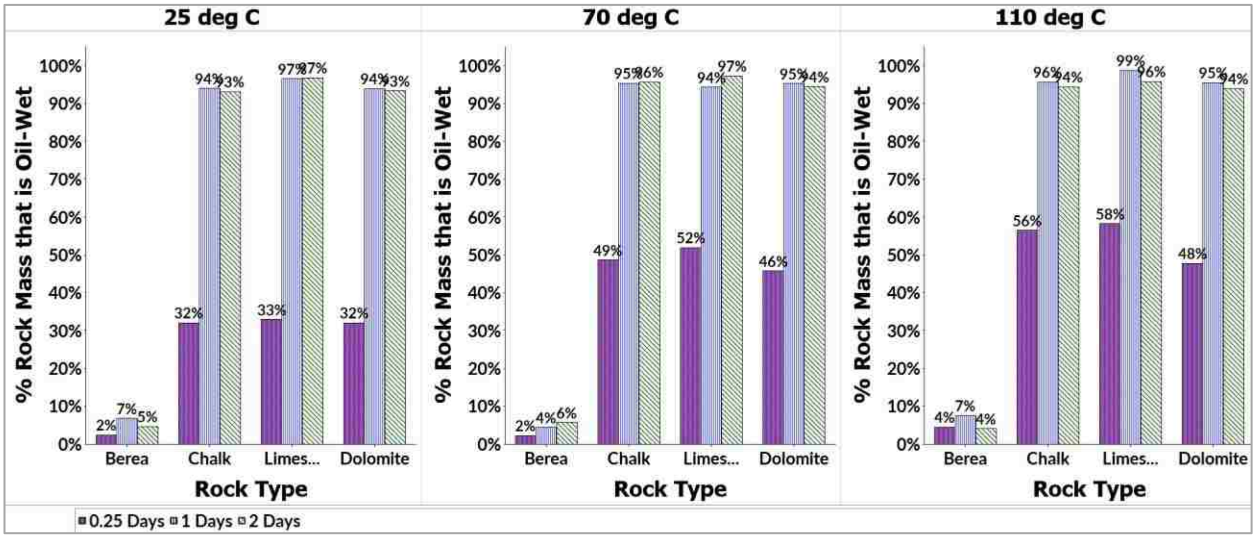

Figure A2: 6 hrs, 1 day, & 2 days aging time for decane at 25°C, 70°C, & 110°C.

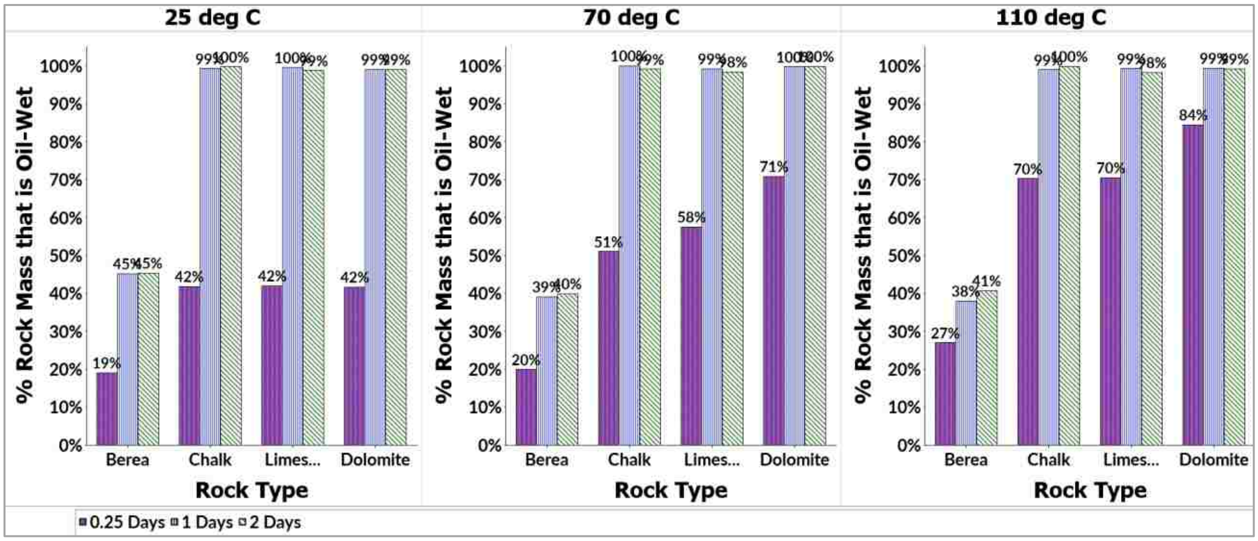

Figure A3: 6 hrs, 1 day, & 2 days aging time for condensate at 25°C, 70°C, & 110°C.

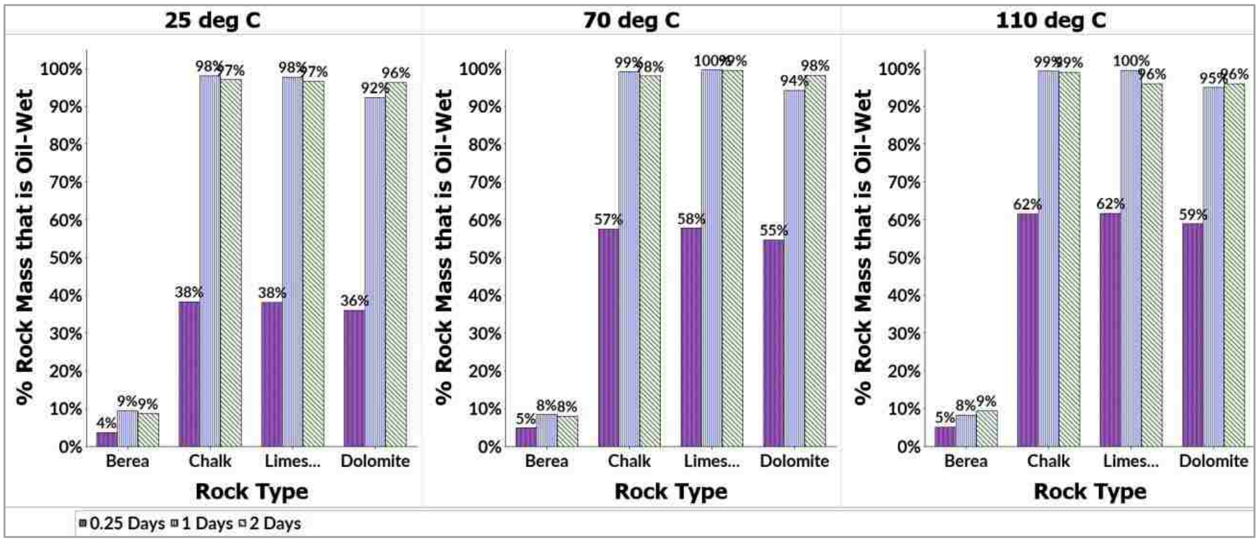

Figure A4: 6 hrs, 1 day, & 2 days aging time for decane +2000 ppm Di-n-butyl sulfide (sulfur SAC) and 2000ppm Quinoline (nitrogen SAC) at 25°C, 70°C, & 110°C.

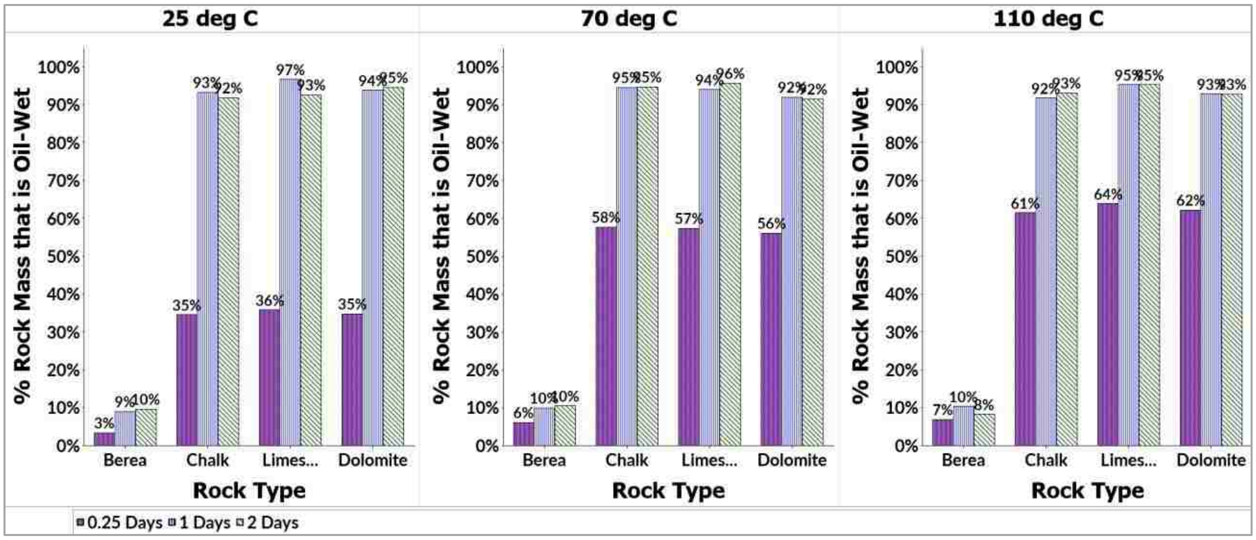

Figure A5: 6 hrs, 1 day, & 2 days aging time for decane +2000 ppm Quinoline (nitrogen SAC) at 25°C, 70°C, & 110°C.

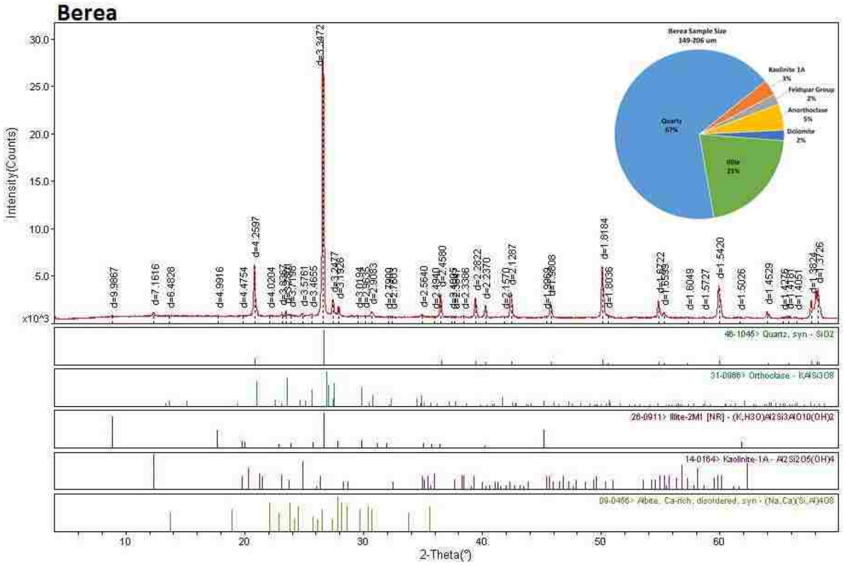

Figure A6: Sandstone Berea XRD mineralogy results.

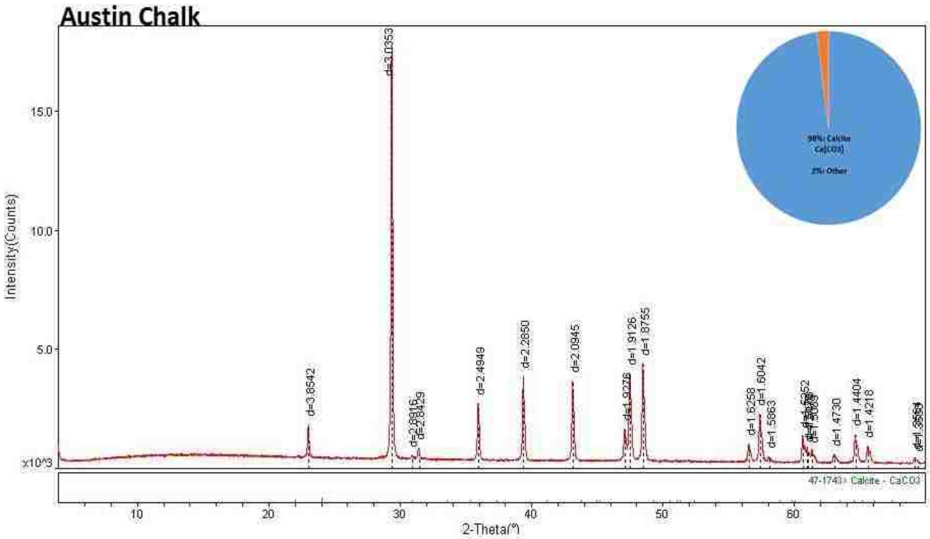

Figure A7: Austin chalk XRD mineralogy results.

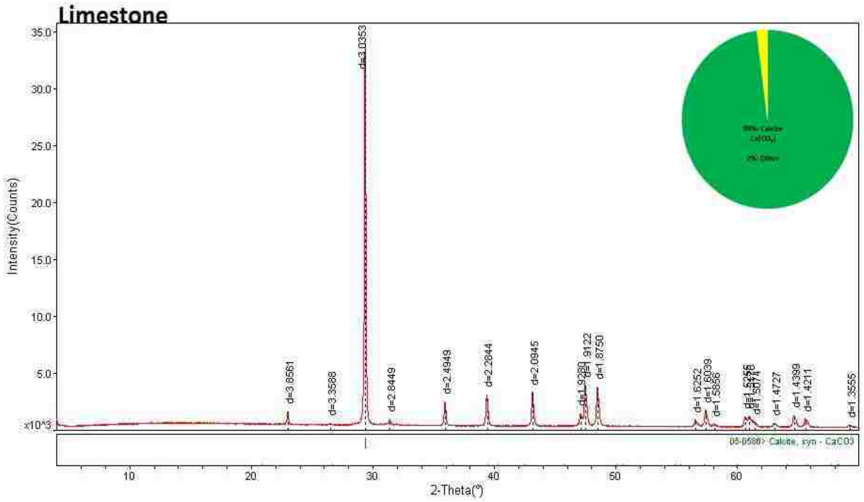

Figure A8: Indiana limestone XRD mineralogy results.

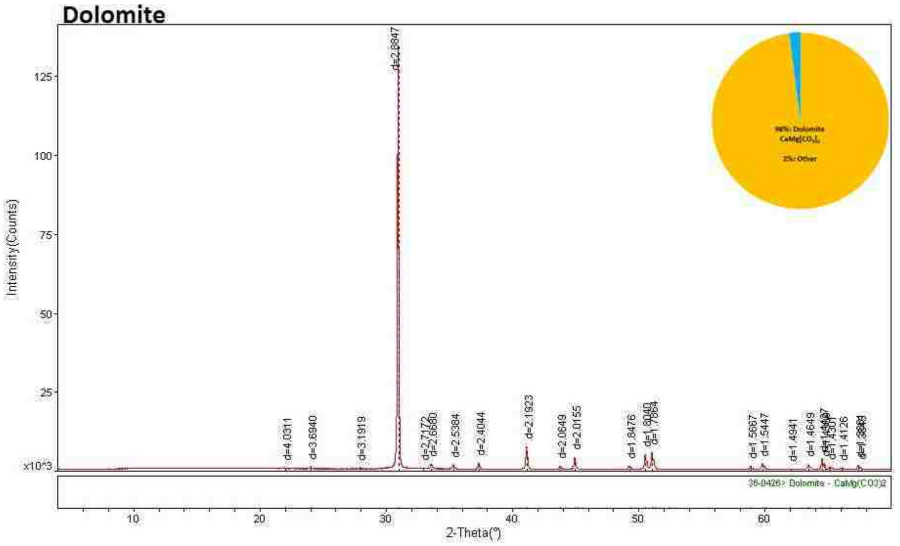

Figure A9: Silurian dolomite XRD mineralogy results.

APPENDIX B: CORE CLEANING SOLVENT ANALYSIS

Laboratory studies typically aim to simulate reservoir behavior by using parameters as close to the reservoir conditions as possible. Reservoir fluids (oil, brine, and gas), temperature, and pressure can be duplicated in the laboratory. However, it is difficult to know how well the core sample represents the original reservoir condition. Mud infiltration during the coring processes contaminates the cores and alters their native state due to the surfactant components in the oil-based muds that are typically used in the core extraction process. In addition, when cores are brought to the surface their interaction with atmospheric conditions can alter the wetting state due to the temperature drop, and pressure drop that may result in the evaporation of light components. In addition, air exposure may lead to oxidization of some of the active chemicals which may result in precipitation of polar components if present (Skopec, 1994). Lastly, core preparation techniques such as cutting, polishing, etc. may also introduce contaminants. Consequently, it is almost impossible to maintain the natural wetting state of core sample and thus cores have to be cleaned properly with solvents and try to restore their wetting state.

Even though many studies have been carried out to find the most effective cleaning solvent, core cleaning still remains mostly a trial and error process, where the selection of the best solvents to be used greatly depends on the experience with particular rocks. Cuiec (1975) and Gant and Anderson (1988) concluded that solvent mixtures work better than single solvents. Recommended solvent mixtures are: benzene/carbon disulphide, toluene/methanol, chloroform/methanol, and toluene/ethanol. Cuiec (1975) recommended acidic type solvents to clean sandstone rocks since they are known to have a surface of acid type (negative charge). The opposite was recommended for limestone that is known to have a basic type (positive charge) surface and thus basic solvents were observed to clean better. The core cleaning process is said to be successful when all the contaminants are removed from the surface of the rock leaving it strongly water-wet (Gant and

Anderson, 1988). The main challenge in core cleaning has typically been viewed as finding the most convenient solvent(s) that can dissolve all the organic compounds on the surface of the rock. However, when one thinks of this problem from a surface chemistry perspective several challenges arise. The solvent of choice may be effective in solubilizing the organic compounds present in the rock, however, what effect does the solvent have on the chemistry of the rock? Does the solvent(s) change the way the rock may interact with brine and/or water, thus wettability? This study examines the effect of three common cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone. Three model oil types were tested: decane, decane + acidic SAC, decane + basic SAC. The three common solvents selected are: toluene which is typically used to remove hydrocarbons, isopropyl alcohol (IPA) which is typically used as a dehydrating agent, and methanol/chloroform (20%/80%) mixture which is typically recommended for cleaning carbonate rocks.

A little over 100 MFT experiments were carried out to test the effect of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone. The percent change in wettability reported in the graphs is calculated by comparing the wettability of the cleaned rock by a particular solvent with the wettability of the fresh rock sample.

B1. Decane - DI water - Rock system

Figure B1 illustrates the effects of the selected cleaning solvents on the four rock types when decane is used. As observed, the three solvents did not affect the wettability of Berea, therefore, Berea remained strongly water-wet. In the case of chalk, IPA and toluene did not have an effect on wettability; however, the methanol/chloroform mixture shifted the wettability of chalk to more water-wet. All three solvents shifted the wettability of dolomite towards more oil-wet. Lastly, IPA shifted the wettability of limestone towards oil-wet; toluene did the opposite (water-wet), and the methanol-chloroform mixture did not have an effect on wettability.

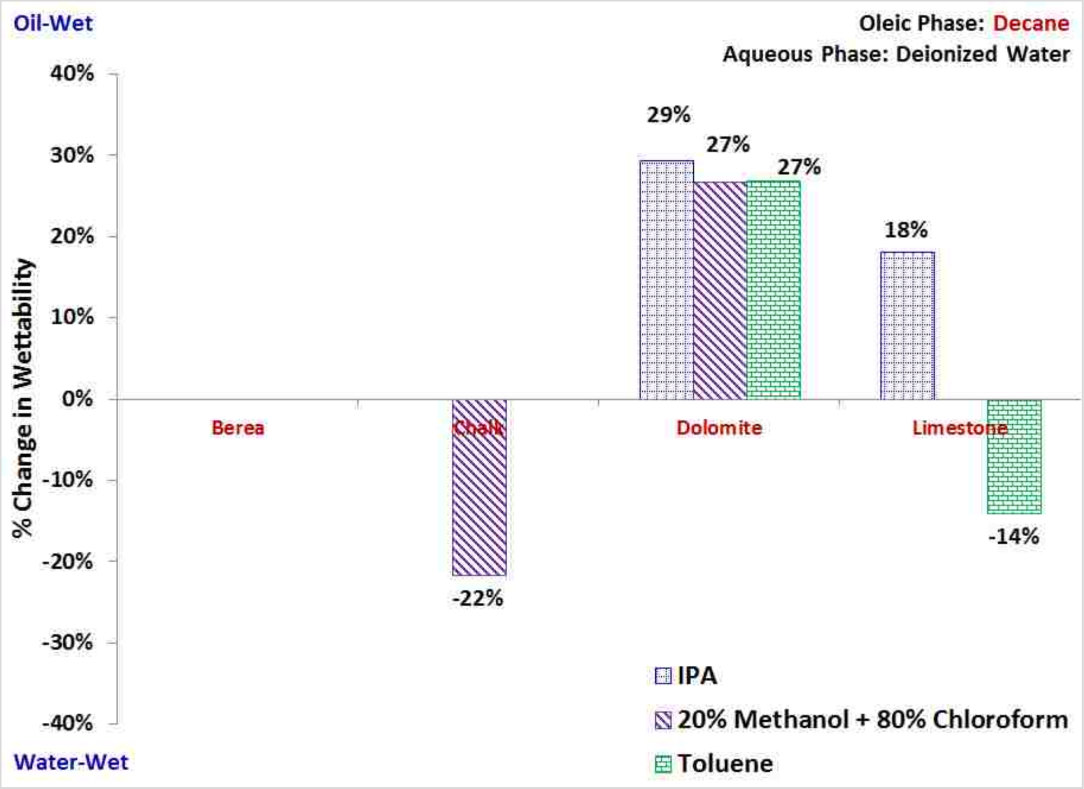

Figure B1: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of decane and DI water

Similar results were also observed when using DDDC contact angle measurement techniques. It was observed that in the presence of Yates oil and brine, dolomite rock crystal became extremely oil-wet (180°) after they were cleaned with the methanol-chloroform mixture. However, when the crystals were boiled in water instead of using the methanol-chloroform solvent, the measured contact angle was about 165° (less oil-wet). Solvents obviously have different effects on rock wettability, and the effect can differ even in rocks that are chemically similar, e.g. chalk, dolomite, and limestone.

B2. Decane + Basic SAC - DI water - Rock system

In this set of experiments, DI water was used as the aqueous phase and 4000 ppm of Quinoline was added to decane in order to simulate a basic type oil. The results are illustrated in

Figure B2 As previously discussed in section 6.3.4, Quinoline had no effect on Berea wettability: this result did not change when Berea was cleaned with the selected solvents. However, for all three carbonates the cleaning solvents behaved differently in the presence of a basic type oil.

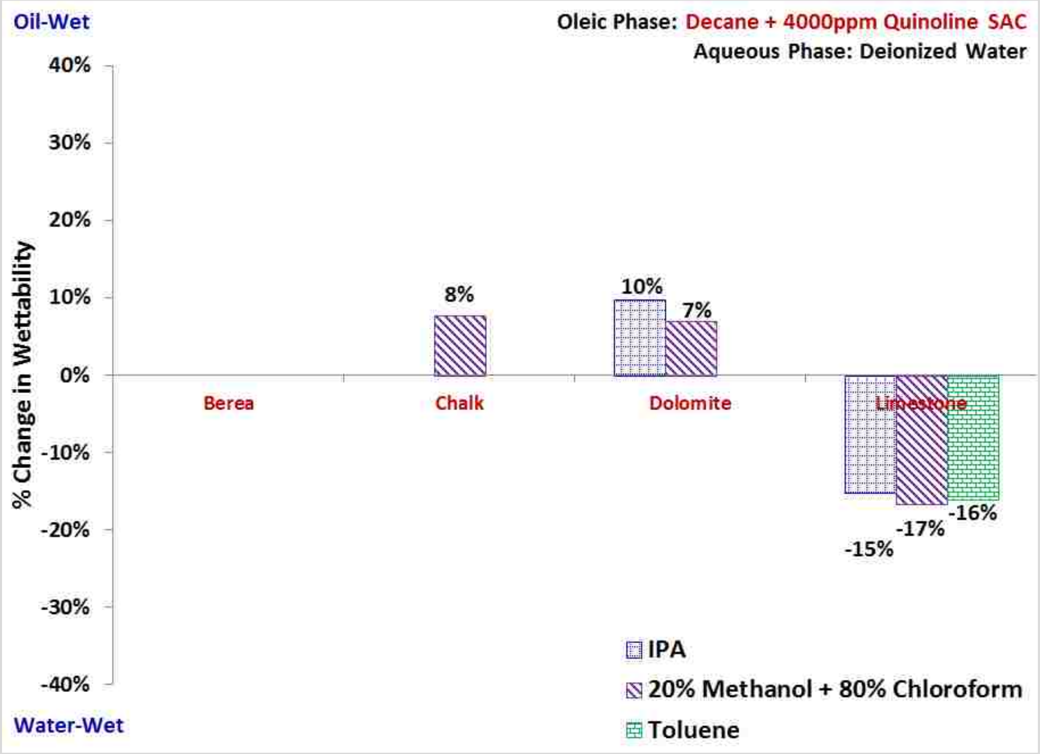

Figure B2: Effects of selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of decane + basic (quinoline) SAC and DI water.

As illustrated in Figure B2, IPA and toluene did not alter chalk wettability; but the methanol/chloroform mixture slightly shifted its wettability towards oil-wet. Note that previously when decane was used as the oleic phase, the methanol/chloroform mixture had the opposite effect on chalk where the wettability shifted towards water-wet. Similar to the previous case (decane-DI water-dolomite), both IPA and methanol-chloroform mixtures shift the wettability towards oil-wet but not as significantly as the decane case. Toluene had no effect on dolomite wettability when the oleic phase was basic, as opposed to the decane case where toluene shifted the wettability towards an oil-wet state. Lastly, all three solvents shifted the wettability of limestone towards water-wet.

Note that the effect of IPA and methanol-chloroform solvent on the wettability of limestone differs in the presence of decane verses decane + 4000ppm Quinoline.

B3. Decane + Acidic SAC - DI water - Rock system

In this set of experiments, DI water was used as the aqueous phase and 4000 ppm of myristic acid was added to decane to simulate an acidic oil. As previously discussed, myristic acid has a tendency to strongly interact with all four rock types, especially the carbonates. Carbonate wettability was unaffected by all three solvents. Toluene shifted Berea wettability towards oil-wet.

A subsequent set of experiments was conducted but using an acid SAC that did not bind as strongly to the rocks as myristic acid. In this set of experiments, DI water was used as the aqueous phase and 4000 ppm of naphthenic acid was added to decane. Similar to myristic acid, naphthenic acid is also a long-chained oxygen SAC that has a tendency to shift the wettability of the four rock types to oil-wet, however, not as strongly oil-wet as myristic acid does. Of the three solvents, toluene shifted Berea wettability towards oil-wet as seen in Figure B4. In the case of chalk, IPA and methanol/chloroform mixture shifted the wettability towards water-wet. All three solvents shifted dolomite wettability to oil-wet but not as significantly as the decane-dolomite-DI water case. Lastly, both IPA and methanol-chloroform mixture shifted the wettability of limestone towards oil-wet. Toluene did not have an effect on limestone in the presence of decane + 4000 ppm naphthenic acid.

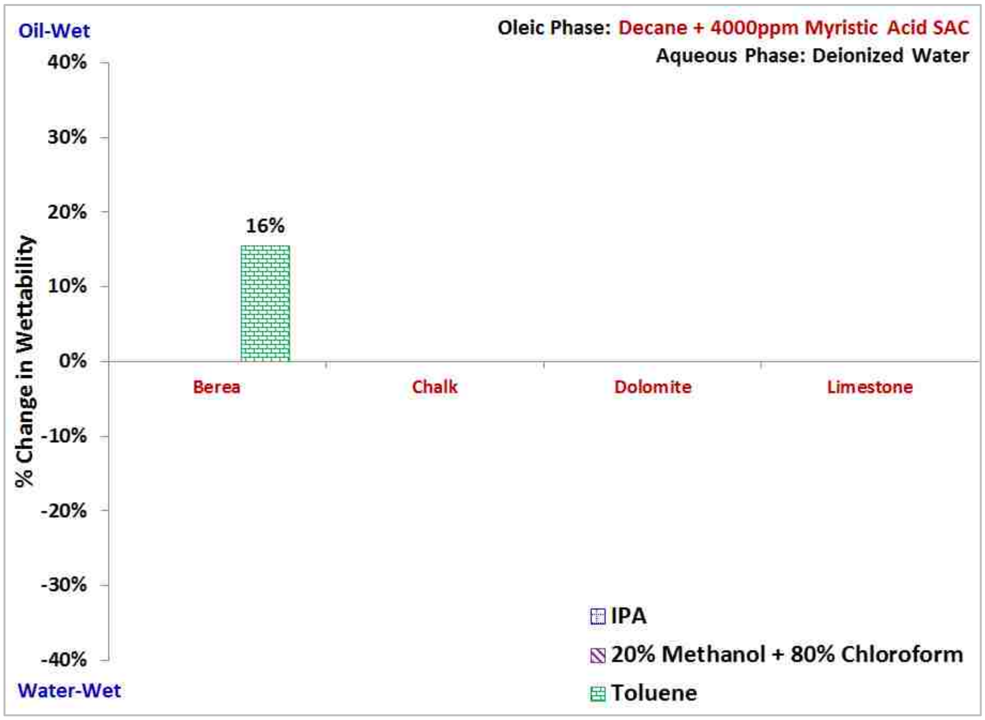

Figure B3: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of myristic acid.

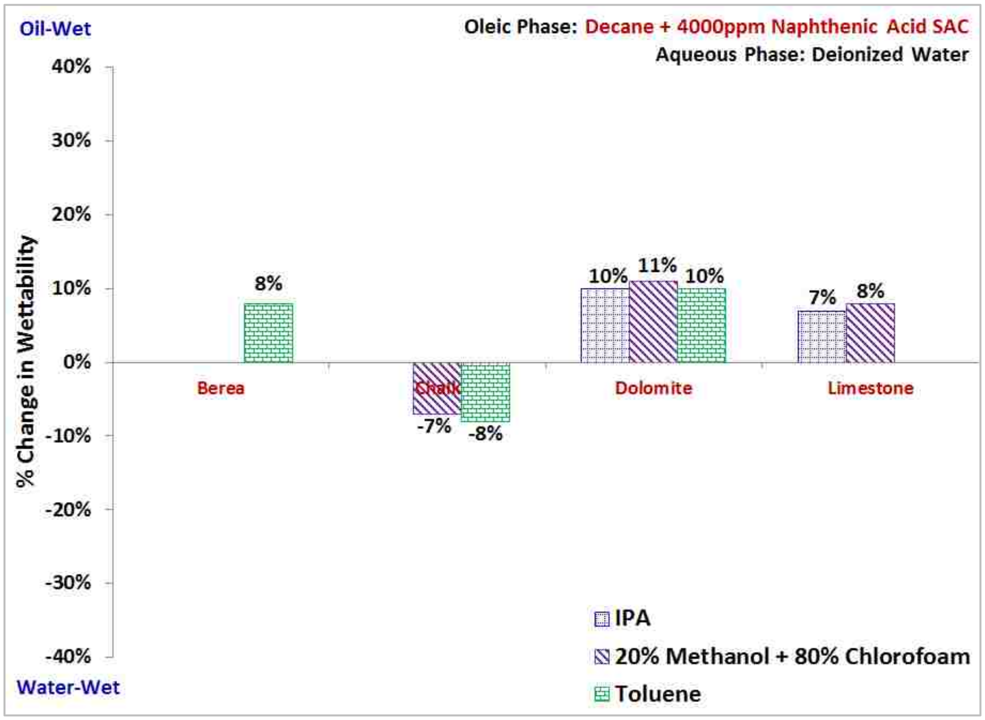

Figure B4: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of naphthenic acid.

In summary, the effectiveness of a cleaning fluid is a function of the rock mineralogy, oil-type, brine type, contaminant type, etc. A particular cleaning solvent might be effective in cleaning chalk and limestone, without altering wettability, however, this may might not be true for dolomite. Therefore, blanket statements about cleaning solvents being effective in cleaning ‘carbonates’ or ‘sandstone’ should not be made unless they have been tested for all applicable conditions. In addition, it was observed that a particular cleaning solvent may have different effects on a rock’s ability to interact with different oil-types. I therefore propose that the way to find the most appropriate cleaning solvent for a particular oil-brine-rock system is by testing different cleaning solvents. This can be a time-consuming process when using conventional wettability-measuring techniques: but it can be done very rapidly with the MFT. Prior to the coreflood experiment, a small section of the rock would be crushed and sieved to an ideal size. Several cleaning solvents of interested would then be tested and their wettability would be compared to that of a fresh sample. The cleaning solvent(s) displaying the least alteration of wettability compared to the fresh sample would then be used in core cleaning.

APPENDIX C: RAW DATA

Table C1: Raw data for 1000 ppm on wettability in the presence of 0 ppm TDS at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.3080	19.3180	4%	2%
	Chalk	20.2883	20.1783	89%	0%
	Dolomite	20.1915	19.9670	78%	2%
	Limestone	20.4107	20.1274	72%	4%
Tetralin [A1]	Berea	20.1340	19.1440	-3%	2%
	Chalk	20.1595	20.0295	-2%	1%
	Dolomite	20.0253	19.6808	-12%	0%
	Limestone	20.3375	20.0142	-4%	2%
Acetic Acid [O1]	Berea	20.4325	19.4725	0%	1%
	Chalk	20.3611	20.0269	-22%	5%
	Dolomite	20.5116	20.0936	-19%	2%
	Limestone	20.0572	19.5076	-27%	1%
Myristic Acid [O2]	Berea	20.1463	19.3037	12%	3%
	Chalk	20.2730	20.2722	11%	3%
	Dolomite	20.1293	20.1293	22%	2%
	Limestone	20.2626	20.2626	28%	2%
Naphthenic Acid [O3]	Berea	20.5037	19.6558	11%	5%
	Chalk	20.2626	20.2407	9%	1%
	Dolomite	20.1132	20.0016	11%	3%
	Limestone	20.1197	19.9213	8%	0%
Dibenzothiophene [S1]	Berea	20.2524	19.3024	1%	5%
	Chalk	20.3947	20.2447	-4%	3%
	Dolomite	20.4447	20.2102	-1%	0%
	Limestone	20.1435	19.8302	-3%	5%

Table C1: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.1360	19.1660	-1%	0%
	Chalk	20.1684	20.0584	0%	5%
	Dolomite	19.9589	19.7044	-3%	1%
	Limestone	20.2622	19.9789	0%	0%
1-Tetradecanethiol [S3]	Berea	20.2761	19.3461	3%	0%
	Chalk	20.3802	20.2402	-3%	2%
	Dolomite	20.5153	20.2508	-4%	5%
	Limestone	20.2855	20.0322	3%	1%
Carbazole [N1]	Berea	20.0370	19.0470	-3%	3%
	Chalk	20.0798	19.9498	-2%	3%
	Dolomite	20.1226	19.8781	-2%	4%
	Limestone	20.8775	20.2482	-35%	5%
Quinoline [N2]	Berea	20.1754	19.2154	0%	1%
	Chalk	20.7714	20.6214	-4%	4%
	Dolomite	20.4714	20.2169	-3%	3%
	Limestone	20.1864	19.7976	-11%	3%
Pyridine [N3]	Berea	20.1374	19.1574	-2%	3%
	Chalk	20.4050	20.2550	-4%	2%
	Dolomite	20.7413	20.2811	-24%	0%
	Limestone	21.1027	20.6857	-13%	3%

Table C2: Raw data for 2000 ppm on wettability in the presence of 0 ppm brine at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.8553	19.3180	8%	0%
	Chalk	20.7938	20.1783	88%	5%
	Dolomite	20.7770	19.9670	69%	1%
	Limestone	8.0000	20.1274	75%	1%
Tetralin [A1]	Berea	20.7252	19.7852	-2%	2%
	Chalk	20.0183	19.8583	-4%	0%
	Dolomite	20.2951	19.8846	-10%	3%
	Limestone	20.9166	20.6266	-4%	5%
Acetic Acid [O1]	Berea	20.5387	19.5887	-3%	2%
	Chalk	20.7446	20.3913	-23%	3%
	Dolomite	20.8549	20.1967	-35%	4%
	Limestone	20.3915	19.8062	-34%	4%
Myristic Acid [O2]	Berea	20.0390	19.4282	31%	1%
	Chalk	20.3543	20.3443	11%	5%
	Dolomite	20.4820	20.3966	22%	5%
	Limestone	20.4236	20.4570	28%	2%
Naphthenic Acid [O3]	Berea	20.3108	19.5086	12%	2%
	Chalk	20.0349	20.0053	9%	2%
	Dolomite	20.8855	20.7294	15%	4%
	Limestone	20.8905	20.7430	10%	2%
Dibenzothiophene [S1]	Berea	20.3731	19.4331	-2%	0%
	Chalk	20.6287	20.3787	-13%	0%
	Dolomite	20.5726	20.2226	-4%	3%
	Limestone	20.0987	19.8287	-2%	0%

Table C2: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.3670	19.4170	-3%	4%
	Chalk	20.4512	20.3312	0%	3%
	Dolomite	20.3715	19.9811	-8%	1%
	Limestone	20.2956	20.0456	0%	0%
1-Tetradecanethiol [S3]	Berea	20.3067	19.4067	2%	4%
	Chalk	20.9591	20.9274	9%	1%
	Dolomite	20.7736	20.5393	8%	0%
	Limestone	20.8081	20.6581	10%	1%
Carbazole [N1]	Berea	20.5716	19.6116	-4%	5%
	Chalk	20.6977	20.5577	-2%	1%
	Dolomite	20.8729	19.9210	-64%	5%
	Limestone	20.6677	19.7966	-62%	1%
Quinoline [N2]	Berea	20.8865	19.9465	-2%	3%
	Chalk	20.4730	20.2964	-6%	5%
	Dolomite	20.1173	19.7322	-8%	2%
	Limestone	20.1717	19.7890	-13%	0%
Pyridine [N3]	Berea	20.5236	19.5736	-3%	3%
	Chalk	20.1586	19.9186	-12%	4%
	Dolomite	20.5574	19.9406	-31%	0%
	Limestone	20.8790	20.4836	-15%	5%

Table C3: Raw data for 4000 ppm on wettability in the presence of DI water at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.8553	19.3180	5%	3%
	Chalk	20.7938	20.1783	89%	0%
	Dolomite	20.7770	19.9670	78%	5%
	Limestone	20.2578	20.1274	72%	4%
Tetralin [A1]	Berea	20.7252	19.7552	-2%	5%
	Chalk	20.0183	19.7785	-13%	2%
	Dolomite	20.2951	19.9702	-10%	2%
	Limestone	20.9166	20.4414	-19%	1%
Acetic Acid [O1]	Berea	20.5387	19.5687	-2%	3%
	Chalk	20.7446	20.3882	-25%	2%
	Dolomite	20.8549	20.2599	-37%	3%
	Limestone	20.3915	19.5355	-57%	3%
Myristic Acid [O2]	Berea	20.0390	19.4834	39%	0%
	Chalk	20.3543	20.3543	11%	1%
	Dolomite	20.4820	20.4820	22%	2%
	Limestone	20.4236	20.4236	28%	3%
Naphthenic Acid [O3]	Berea	20.3108	19.4933	13%	3%
	Chalk	20.0349	20.0181	9%	4%
	Dolomite	20.8855	20.8462	19%	4%
	Limestone	20.8905	20.7028	10%	2%
Dibenzothiophene [S1]	Berea	20.3731	19.4331	1%	0%
	Chalk	20.6287	20.3378	-18%	0%
	Dolomite	20.5726	20.2464	-10%	5%
	Limestone	20.0987	19.7253	-9%	5%

Table C3: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.3670	19.3770	-4%	1%
	Chalk	20.4512	20.2637	-8%	2%
	Dolomite	20.3715	19.9668	-18%	0%
	Limestone	20.2956	19.9422	-7%	3%
1-Tetradecanethiol [S3]	Berea	20.3067	19.3867	3%	4%
	Chalk	20.9591	20.9808	13%	5%
	Dolomite	20.7736	20.7526	20%	4%
	Limestone	20.8081	20.7048	18%	5%
Carbazole [N1]	Berea	20.5716	19.5816	-4%	4%
	Chalk	20.6977	19.8845	-70%	0%
	Dolomite	20.8729	19.9232	-73%	5%
	Limestone	20.6677	19.6966	-69%	5%
Quinoline [N2]	Berea	20.8865	19.8965	-4%	3%
	Chalk	20.4730	20.1885	-18%	5%
	Dolomite	20.1173	19.6112	-28%	5%
	Limestone	20.1717	19.7434	-15%	1%
Pyridine [N3]	Berea	20.5236	19.5336	-4%	5%
	Chalk	20.1586	19.6881	-36%	1%
	Dolomite	20.5574	20.0231	-31%	1%
	Limestone	20.8790	20.3255	-27%	4%

Table C4: Raw data for 2000 ppm of SAC on rock wettability in the presence of 100,000 ppm TDS brine at 25°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	21.1488	20.2288	0%	5%
	Chalk	21.1641	20.8941	-15%	1%
	Dolomite	20.9863	20.5563	-12%	4%
	Limestone	21.0656	20.7256	-9%	3%
Tetralin [A1]	Berea	20.8073	19.8473	-4%	4%
	Chalk	20.9572	20.8972	6%	0%
	Dolomite	21.1613	20.8513	0%	2%
	Limestone	21.0000	20.8100	6%	2%
Acetic Acid [O1]	Berea	20.7993	19.9493	7%	4%
	Chalk	20.7368	20.4668	-15%	2%
	Dolomite	20.5513	20.1513	-9%	5%
	Limestone	20.7862	20.4162	-12%	2%
Myristic Acid [O2]	Berea	20.3478	19.4578	3%	1%
	Chalk	20.6133	20.3353	-16%	4%
	Dolomite	20.5191	20.0711	-14%	1%
	Limestone	20.4015	19.9115	-24%	1%
Naphthenic Acid [O3]	Berea	20.5222	19.6022	0%	0%
	Chalk	20.4437	20.3237	0%	0%
	Dolomite	20.4060	20.1060	1%	1%
	Limestone	21.0022	20.8022	5%	2%
Dibenzothiophene [S1]	Berea	20.4235	19.5435	4%	3%
	Chalk	21.0051	20.9051	2%	0%
	Dolomite	21.2351	20.9451	2%	2%
	Limestone	20.5198	20.3098	4%	4%

Table C4: Cont’d

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.6224	19.7424	4%	4%
	Chalk	21.0068	20.8868	0%	5%
	Dolomite	21.0274	20.7374	2%	3%
	Limestone	20.4925	20.2925	5%	4%
1-Tetradecanethiol [S3]	Berea	20.7846	19.8746	1%	4%
	Chalk	20.4643	20.3943	5%	5%
	Dolomite	20.6832	20.4132	4%	5%
	Limestone	20.8094	20.5894	3%	2%
Carbazole [N1]	Berea	20.4343	19.5543	4%	2%
	Chalk	21.1765	21.0865	3%	5%
	Dolomite	20.9672	20.7072	5%	5%
	Limestone	20.7306	20.5306	5%	5%
Quinoline [N2]	Berea	20.5330	19.6330	2%	4%
	Chalk	20.6132	20.5032	1%	5%
	Dolomite	20.6926	20.4226	4%	0%
	Limestone	20.9860	20.7460	1%	0%
Pyridine [N3]	Berea	20.5531	19.6431	1%	0%
	Chalk	20.3823	20.2623	0%	0%
	Dolomite	21.1220	20.8620	5%	2%
	Limestone	20.8233	20.6233	5%	0%

Table C5: Raw data for 2000 ppm of SAC on rock wettability in the presence of 100,000 ppm TDS brine at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	21.5585	20.6285	-1%	3%
	Chalk	21.5370	21.3280	-9%	3%
	Dolomite	21.6919	21.2959	-9%	0%
	Limestone	21.1488	20.7573	-14%	2%
Tetralin [A1]	Berea	21.1641	20.0841	-16%	4%
	Chalk	20.9863	21.0563	19%	2%
	Dolomite	21.0656	20.9066	15%	1%
	Limestone	20.8073	20.7233	17%	0%
Acetic Acid [O1]	Berea	20.9572	20.1372	10%	5%
	Chalk	21.1613	20.7713	-27%	0%
	Dolomite	21.0000	20.5400	-15%	4%
	Limestone	20.7993	20.3693	-18%	3%
Myristic Acid [O2]	Berea	20.7368	19.9068	9%	1%
	Chalk	20.5513	20.0913	-34%	1%
	Dolomite	20.7862	20.2352	-24%	0%
	Limestone	20.3478	19.7978	-30%	1%
Naphthenic Acid [O3]	Berea	20.6133	19.7233	3%	0%
	Chalk	20.5191	20.4291	3%	3%
	Dolomite	20.4015	20.1415	5%	3%
	Limestone	20.5222	20.2822	1%	1%
Dibenzothiophene [S1]	Berea	20.4437	19.5537	3%	3%
	Chalk	20.4060	20.3060	2%	4%
	Dolomite	21.0022	20.7222	3%	5%
	Limestone	20.4235	20.1735	0%	2%

Table C5: Cont’d

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	21.0051	20.1951	11%	4%
	Chalk	21.2351	20.9851	-13%	5%
	Dolomite	20.5198	20.0098	-20%	5%
	Limestone	20.6224	20.2624	-11%	0%
1-Tetradecanethiol [S3]	Berea	21.0068	19.9368	-15%	1%
	Chalk	21.0274	20.9174	1%	5%
	Dolomite	20.4925	20.2025	2%	1%
	Limestone	20.7846	20.5746	4%	3%
Carbazole [N1]	Berea	20.4643	19.5843	4%	0%
	Chalk	20.6832	20.5832	2%	5%
	Dolomite	20.8094	20.5594	6%	4%
	Limestone	20.4343	20.1843	0%	1%
Quinoline [N2]	Berea	21.1765	20.3065	5%	0%
	Chalk	20.9672	20.8972	5%	5%
	Dolomite	20.7306	20.4206	0%	1%
	Limestone	20.5330	20.3330	5%	5%
Pyridine [N3]	Berea	20.6132	19.7232	3%	3%
	Chalk	20.6926	20.6026	3%	5%
	Dolomite	20.9860	20.6960	2%	0%
	Limestone	20.5531	20.3331	3%	5%

Table C6: Raw data for 2000 ppm of SAC on rock wettability in the presence of 100,000 ppm TDS brine at 110°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.3682	19.4082	-4%	1%
	Chalk	20.1676	20.0476	0%	2%
	Dolomite	19.9829	19.4129	-26%	0%
	Limestone	20.2071	19.8171	-14%	3%
Tetralin [A1]	Berea	20.0140	18.9440	-15%	0%
	Chalk	20.6201	20.7101	21%	3%
	Dolomite	20.4286	20.2686	15%	0%
	Limestone	20.5961	20.5361	19%	1%
Acetic Acid [O1]	Berea	20.2027	19.3927	11%	5%
	Chalk	19.9127	19.4627	-33%	4%
	Dolomite	19.7946	19.3346	-15%	1%
	Limestone	20.7276	20.2776	-20%	2%
Myristic Acid [O2]	Berea	20.1364	19.3164	10%	0%
	Chalk	20.5647	19.9147	-53%	1%
	Dolomite	20.0383	19.3983	-33%	1%
	Limestone	19.9527	19.3227	-38%	0%
Naphthenic Acid [O3]	Berea	20.4331	19.5231	1%	3%
	Chalk	20.1930	20.1130	4%	5%
	Dolomite	20.3884	20.1084	3%	0%
	Limestone	20.2845	20.0845	5%	5%
Dibenzothiophene [S1]	Berea	19.8354	18.9554	4%	2%
	Chalk	20.0017	19.9017	2%	0%
	Dolomite	20.3381	20.0481	2%	1%
	Limestone	19.8855	19.6855	5%	3%

Table C6: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.0753	19.2753	12%	1%
	Chalk	19.8398	19.5398	-18%	2%
	Dolomite	20.1592	19.6792	-17%	5%
	Limestone	20.0195	19.6295	-14%	3%
1-Tetradecanethiol [S3]	Berea	19.9415	18.8515	-17%	1%
	Chalk	20.0745	19.9945	4%	2%
	Dolomite	20.6386	20.3386	1%	4%
	Limestone	19.8153	19.6153	5%	1%
Carbazole [N1]	Berea	20.5834	19.6834	2%	2%
	Chalk	20.5615	20.4415	0%	5%
	Dolomite	20.1827	19.9327	6%	5%
	Limestone	19.9509	19.7509	5%	1%
Quinoline [N2]	Berea	19.8773	19.9573	100%	5%
	Chalk	19.8238	19.7738	7%	0%
	Dolomite	20.0537	19.6837	-6%	5%
	Limestone	20.2601	20.0701	6%	3%
Pyridine [N3]	Berea	20.2388	19.3288	1%	2%
	Chalk	20.2489	20.1489	2%	3%
	Dolomite	20.6160	20.3160	1%	2%
	Limestone	20.5945	20.3545	1%	4%

Table C7: Raw data for 2000 ppm of SAC on rock wettability in the presence of 10,000 ppm TDS brine at 25°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	19.6483	18.7283	0%	3%
	Chalk	19.2504	19.1304	0%	5%
	Dolomite	19.0686	18.7386	-2%	4%
	Limestone	19.7717	19.4717	-5%	2%
Tetralin [A1]	Berea	19.4705	18.5305	-2%	1%
	Chalk	19.6478	19.5278	0%	3%
	Dolomite	19.5141	19.2341	3%	1%
	Limestone	19.4426	19.2426	5%	0%
Acetic Acid [O1]	Berea	19.8648	19.0348	9%	2%
	Chalk	19.6837	19.4837	-8%	1%
	Dolomite	19.3584	19.0284	-2%	1%
	Limestone	18.9294	18.6194	-6%	0%
Myristic Acid [O2]	Berea	19.3821	18.4821	2%	1%
	Chalk	19.2398	19.0298	-9%	2%
	Dolomite	19.5387	19.1617	-7%	5%
	Limestone	19.0257	18.6552	-12%	4%
Naphthenic Acid [O3]	Berea	19.8850	18.9350	-3%	3%
	Chalk	19.7368	19.5868	-3%	2%
	Dolomite	19.4547	19.1247	-2%	0%
	Limestone	19.6615	19.3815	-3%	2%
Dibenzothiophene [S1]	Berea	19.7024	18.7724	-1%	5%
	Chalk	19.1774	19.0374	-2%	4%
	Dolomite	19.0177	18.6877	-2%	5%
	Limestone	19.0746	18.8146	-1%	4%

Table C7: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	19.5537	18.6337	0%	2%
	Chalk	19.2228	19.0828	-2%	3%
	Dolomite	18.9320	18.5820	-4%	0%
	Limestone	19.0360	18.7460	-4%	5%
1-Tetradecanethiol [S3]	Berea	19.5899	18.6199	-5%	3%
	Chalk	19.6783	19.5483	-1%	2%
	Dolomite	19.7265	19.4165	0%	0%
	Limestone	19.3963	19.0963	-5%	3%
Carbazole [N1]	Berea	19.7574	18.7874	-5%	1%
	Chalk	19.0906	18.9506	-2%	4%
	Dolomite	19.2570	18.9170	-3%	0%
	Limestone	19.7107	19.4607	0%	1%
Quinoline [N2]	Berea	19.7598	18.7898	-5%	3%
	Chalk	19.7349	19.5949	-2%	5%
	Dolomite	19.8828	19.5628	-1%	5%
	Limestone	19.2471	18.9671	-3%	0%
Pyridine [N3]	Berea	19.3643	18.4143	-3%	0%
	Chalk	19.5511	19.4011	-3%	3%
	Dolomite	19.8424	19.4824	-5%	3%
	Limestone	18.9017	18.6417	-1%	4%

Table C8: Raw data for 2000 ppm of SAC on rock wettability in the presence of 10,000 ppm TDS brine at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.3456	19.4156	-1%	4%
	Chalk	21.1707	21.0107	-4%	5%
	Dolomite	20.2221	19.8126	-10%	0%
	Limestone	20.9172	20.5772	-9%	1%
Tetralin [A1]	Berea	20.8441	19.7341	-19%	5%
	Chalk	21.1205	21.0685	7%	2%
	Dolomite	20.6875	20.4275	5%	4%
	Limestone	20.6615	20.4615	5%	3%
Acetic Acid [O1]	Berea	20.8098	19.9998	11%	4%
	Chalk	21.1035	20.8235	-16%	0%
	Dolomite	20.3433	19.9733	-6%	4%
	Limestone	20.6301	20.2801	-10%	0%
Myristic Acid [O2]	Berea	20.5648	19.7548	11%	5%
	Chalk	20.4932	20.2232	-15%	4%
	Dolomite	20.5159	19.9359	-27%	4%
	Limestone	21.0832	20.6932	-14%	0%
Naphthenic Acid [O3]	Berea	20.9844	20.0544	-1%	0%
	Chalk	20.5403	20.3703	-5%	0%
	Dolomite	20.3093	19.9693	-3%	1%
	Limestone	20.4867	20.2167	-2%	3%
Dibenzothiophene [S1]	Berea	20.2779	19.3279	-3%	4%
	Chalk	20.3580	20.2080	-3%	4%
	Dolomite	20.9617	20.6217	-3%	5%
	Limestone	20.6061	20.3361	-2%	3%

Table C8: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.6983	19.8583	8%	4%
	Chalk	20.5460	20.3160	-11%	0%
	Dolomite	21.1153	20.6653	-14%	5%
	Limestone	21.0586	20.7286	-8%	2%
1-Tetradecanethiol [S3]	Berea	20.3441	19.2741	-15%	2%
	Chalk	21.1495	20.9795	-5%	5%
	Dolomite	20.3268	19.9268	-9%	5%
	Limestone	20.4804	20.1504	-8%	5%
Carbazole [N1]	Berea	20.4955	19.5355	-4%	2%
	Chalk	20.5021	20.4321	5%	2%
	Dolomite	20.6208	20.4008	9%	2%
	Limestone	21.0758	20.7758	-5%	5%
Quinoline [N2]	Berea	20.4876	19.5376	-3%	0%
	Chalk	21.1740	21.0140	-4%	2%
	Dolomite	20.7749	20.4549	-1%	0%
	Limestone	20.9540	20.6640	-4%	3%
Pyridine [N3]	Berea	20.4218	19.4618	-4%	2%
	Chalk	20.9909	20.8709	0%	4%
	Dolomite	21.0733	20.7533	-1%	3%
	Limestone	21.1039	20.8439	-1%	5%

Table C9: Raw data for 2000 ppm of SAC on rock wettability in the presence of 10,000 ppm TDS brine at 110°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.6102	19.6602	-3%	5%
	Chalk	21.0845	20.8645	-10%	1%
	Dolomite	21.1483	20.5983	-24%	5%
	Limestone	20.8165	20.4565	-11%	5%
Tetralin [A1]	Berea	20.5411	19.4511	-17%	0%
	Chalk	21.1656	21.1356	9%	0%
	Dolomite	20.9011	20.6411	5%	2%
	Limestone	20.2258	20.0458	7%	5%
Acetic Acid [O1]	Berea	20.2421	19.4321	11%	2%
	Chalk	20.9819	20.6719	-19%	2%
	Dolomite	21.1909	20.8109	-7%	5%
	Limestone	21.1405	20.7705	-12%	0%
Myristic Acid [O2]	Berea	21.1926	20.3726	10%	0%
	Chalk	21.1106	20.6106	-38%	3%
	Dolomite	20.5785	19.9085	-36%	5%
	Limestone	20.2650	19.6950	-32%	2%
Naphthenic Acid [O3]	Berea	20.4969	19.5469	-3%	2%
	Chalk	20.7719	20.6019	-5%	4%
	Dolomite	21.0187	20.6987	-1%	0%
	Limestone	21.1523	20.9023	0%	5%
Dibenzothiophene [S1]	Berea	21.1009	20.1309	-5%	1%
	Chalk	20.2280	20.1080	0%	5%
	Dolomite	20.7060	20.3660	-3%	3%
	Limestone	21.0596	20.7996	-1%	3%

Table C9: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.8315	19.9915	8%	5%
	Chalk	21.1603	20.8703	-17%	3%
	Dolomite	21.0520	20.6120	-13%	4%
	Limestone	20.9743	20.6343	-9%	4%
1-Tetradecanethiol [S3]	Berea	21.1862	20.1362	-13%	3%
	Chalk	21.0623	20.8823	-6%	2%
	Dolomite	21.0781	20.6981	-7%	5%
	Limestone	20.9840	20.6040	-13%	4%
Carbazole [N1]	Berea	20.8785	19.9185	-4%	0%
	Chalk	20.6386	20.5286	1%	1%
	Dolomite	20.7722	20.5422	8%	0%
	Limestone	20.6435	20.4635	7%	5%
Quinoline [N2]	Berea	20.2855	19.3655	0%	5%
	Chalk	21.0756	20.9556	0%	5%
	Dolomite	20.9899	20.6299	-5%	5%
	Limestone	20.5316	20.2316	-5%	5%
Pyridine [N3]	Berea	20.6853	19.7553	-1%	4%
	Chalk	21.0093	20.8393	-5%	5%
	Dolomite	20.2631	19.9531	0%	2%
	Limestone	20.2392	19.9792	-1%	0%

Table C10: Raw data for 2000 ppm of SAC on rock wettability in the presence of 1,000 ppm TDS brine at 25°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.7728	19.8228	-3%	2%
	Chalk	21.2360	21.1160	0%	0%
	Dolomite	20.9617	20.6017	-5%	3%
	Limestone	20.6620	20.3820	-3%	2%
Tetralin [A1]	Berea	20.8733	19.9233	-3%	3%
	Chalk	21.1480	20.9880	-4%	1%
	Dolomite	21.2563	20.9363	-1%	4%
	Limestone	21.4760	21.1960	-3%	2%
Acetic Acid [O1]	Berea	20.5404	19.7604	14%	5%
	Chalk	20.9487	20.8787	5%	3%
	Dolomite	21.3265	21.1265	11%	1%
	Limestone	21.3615	21.2815	17%	2%
Myristic Acid [O2]	Berea	20.5492	19.7092	8%	3%
	Chalk	20.6948	20.5748	0%	4%
	Dolomite	20.7714	20.4514	-1%	3%
	Limestone	20.7530	20.4630	-4%	5%
Naphthenic Acid [O3]	Berea	21.4784	20.5284	-3%	0%
	Chalk	21.0613	20.9313	-1%	1%
	Dolomite	21.2195	20.8895	-2%	2%
	Limestone	21.4587	21.1887	-2%	1%
Dibenzothiophene [S1]	Berea	21.4701	20.5001	-5%	1%
	Chalk	20.9322	20.8122	0%	2%
	Dolomite	21.1452	20.7952	-4%	4%
	Limestone	20.6239	20.3639	-1%	3%

Table C10: Cont’d

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.6388	19.6788	-4%	0%
	Chalk	20.8073	20.6673	-2%	3%
	Dolomite	21.2967	20.9767	-1%	2%
	Limestone	21.0803	20.8203	-1%	0%
1-Tetradecanethiol [S3]	Berea	21.3630	20.4330	-1%	0%
	Chalk	20.7893	20.6493	-2%	5%
	Dolomite	21.0095	20.4595	-24%	0%
	Limestone	21.1568	20.6168	-29%	4%
Carbazole [N1]	Berea	21.4020	20.4820	0%	5%
	Chalk	20.5244	20.3644	-4%	4%
	Dolomite	20.6789	20.3389	-3%	2%
	Limestone	20.6689	20.4189	0%	3%
Quinoline [N2]	Berea	21.3724	20.4024	-5%	3%
	Chalk	21.4557	21.2857	-5%	3%
	Dolomite	20.7162	20.3562	-5%	2%
	Limestone	21.3083	21.0183	-4%	3%
Pyridine [N3]	Berea	21.3893	20.4193	-5%	1%
	Chalk	21.1879	21.0479	-2%	5%
	Dolomite	21.3706	21.0506	-1%	1%
	Limestone	20.5943	20.3343	-1%	2%

Table C11: Raw data for 2000 ppm of SAC on rock wettability in the presence of 1,000 ppm TDS brine at 70°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	21.3889	20.4689	0%	5%
	Chalk	21.4434	21.3134	-1%	2%
	Dolomite	21.6852	21.2752	-10%	2%
	Limestone	21.2578	21.0078	0%	5%
Tetralin [A1]	Berea	21.5053	20.5553	-3%	1%
	Chalk	21.4128	21.1828	-11%	2%
	Dolomite	21.4515	20.9815	-16%	0%
	Limestone	21.5313	21.1113	-17%	5%
Acetic Acid [O1]	Berea	21.6236	20.8936	19%	4%
	Chalk	21.2857	21.2457	8%	1%
	Dolomite	21.2878	21.1278	15%	4%
	Limestone	21.4800	21.4300	20%	2%
Myristic Acid [O2]	Berea	21.7711	20.9911	14%	0%
	Chalk	21.6814	21.6314	7%	3%
	Dolomite	21.4965	21.2365	5%	4%
	Limestone	21.6018	21.4118	6%	2%
Naphthenic Acid [O3]	Berea	21.1424	20.2324	1%	2%
	Chalk	21.5749	21.3849	-7%	1%
	Dolomite	21.3025	20.9625	-3%	1%
	Limestone	21.5138	21.2438	-2%	2%
Dibenzothiophene [S1]	Berea	21.5897	20.6297	-4%	5%
	Chalk	21.2343	21.1143	0%	2%
	Dolomite	20.9054	20.5254	-7%	2%
	Limestone	21.2160	20.9660	0%	0%

Table C11: Cont’d

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	21.6468	20.7468	2%	0%
	Chalk	21.1839	21.1239	6%	5%
	Dolomite	21.0421	20.8021	7%	0%
	Limestone	21.0218	20.8418	7%	4%
1-Tetradecanethiol [S3]	Berea	21.7895	20.7995	-7%	0%
	Chalk	21.5292	21.2292	-18%	3%
	Dolomite	21.7035	21.0635	-33%	5%
	Limestone	21.4889	20.7989	-44%	3%
Carbazole [N1]	Berea	20.9547	20.0247	-1%	4%
	Chalk	21.5350	21.4050	-1%	3%
	Dolomite	21.8116	21.4816	-2%	0%
	Limestone	21.2060	20.9060	-5%	5%
Quinoline [N2]	Berea	21.3570	20.4170	-2%	3%
	Chalk	21.5487	21.3687	-6%	2%
	Dolomite	21.8427	21.4227	-11%	3%
	Limestone	21.4164	21.0864	-8%	0%
Pyridine [N3]	Berea	21.3163	20.4163	2%	1%
	Chalk	21.6445	21.5245	0%	5%
	Dolomite	21.1569	20.8569	1%	1%
	Limestone	21.3782	21.1182	-1%	2%

Table C12: Raw data for 2000 ppm of SAC on rock wettability in the presence of 1,000 ppm TDS brine at 110°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.9508	20.0208	-1%	4%
	Chalk	20.6800	20.4600	-10%	1%
	Dolomite	20.3639	19.8434	-21%	4%
	Limestone	21.1060	20.8560	0%	3%
Tetralin [A1]	Berea	20.8106	19.8306	-6%	5%
	Chalk	20.9833	20.7133	-15%	1%
	Dolomite	20.2789	19.7989	-17%	1%
	Limestone	20.5937	20.1437	-20%	4%
Acetic Acid [O1]	Berea	20.4694	19.7594	21%	3%
	Chalk	20.5614	20.5514	11%	3%
	Dolomite	20.1804	20.0204	15%	1%
	Limestone	20.3618	20.3318	22%	4%
Myristic Acid [O2]	Berea	20.8817	20.0917	13%	2%
	Chalk	20.3640	20.3240	8%	1%
	Dolomite	20.5420	20.2920	6%	3%
	Limestone	20.9195	20.7195	5%	3%
Naphthenic Acid [O3]	Berea	20.5074	19.5974	1%	2%
	Chalk	20.8110	20.6310	-6%	2%
	Dolomite	20.4322	20.1022	-2%	0%
	Limestone	20.2286	19.9386	-4%	4%
Dibenzothiophene [S1]	Berea	20.3791	19.4491	-1%	0%
	Chalk	20.2557	20.1257	-1%	5%
	Dolomite	20.3973	19.9973	-9%	2%
	Limestone	21.0425	20.8025	1%	0%

Table C12: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.2127	19.3127	2%	5%
	Chalk	20.7990	20.7290	5%	3%
	Dolomite	20.2480	20.0080	7%	3%
	Limestone	20.6083	20.4483	9%	1%
1-Tetradecanethiol [S3]	Berea	20.8872	19.8972	-7%	2%
	Chalk	20.6912	20.3912	-18%	5%
	Dolomite	20.3225	19.5425	-47%	3%
	Limestone	20.9677	20.1377	-58%	0%
Carbazole [N1]	Berea	20.2267	19.3167	1%	2%
	Chalk	20.7197	20.5297	-7%	5%
	Dolomite	21.1076	20.7876	-1%	0%
	Limestone	20.4947	20.1947	-5%	5%
Quinoline [N2]	Berea	21.0315	20.1315	2%	1%
	Chalk	20.4541	20.2841	-5%	1%
	Dolomite	21.0253	20.5453	-17%	5%
	Limestone	20.3741	20.0541	-7%	4%
Pyridine [N3]	Berea	20.4814	19.5414	-2%	3%
	Chalk	20.7004	20.5504	-3%	5%
	Dolomite	20.8578	20.5378	-1%	5%
	Limestone	20.2646	20.0046	-1%	0%

Table C13: Raw data for 2000 ppm of SAC on rock wettability in the presence of 0 ppm TDS brine at 25°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	21.0102	20.1002	1%	5%
	Chalk	21.2860	21.1760	1%	4%
	Dolomite	21.6255	21.3455	3%	5%
	Limestone	21.1591	20.9291	2%	5%
Tetralin [A1]	Berea	21.4007	20.4907	1%	4%
	Chalk	21.8695	21.6595	-9%	3%
	Dolomite	21.4367	21.0667	-6%	3%
	Limestone	21.6097	21.2997	-6%	1%
Acetic Acid [O1]	Berea	21.3903	20.7103	24%	2%
	Chalk	21.6623	21.6223	8%	3%
	Dolomite	20.9395	20.7895	16%	4%
	Limestone	21.5695	21.5395	22%	2%
Myristic Acid [O2]	Berea	21.5097	20.6597	7%	3%
	Chalk	21.0935	20.9735	0%	5%
	Dolomite	21.0249	20.7749	6%	3%
	Limestone	20.9967	20.7267	-2%	0%
Naphthenic Acid [O3]	Berea	20.9660	20.0160	-3%	4%
	Chalk	21.6860	21.5160	-5%	4%
	Dolomite	20.9125	20.6025	0%	2%
	Limestone	21.7449	21.4549	-4%	5%
Dibenzothiophene [S1]	Berea	20.9210	19.9910	-1%	3%
	Chalk	21.0336	20.9136	0%	4%
	Dolomite	21.0425	20.7025	-3%	3%
	Limestone	21.2468	21.0368	4%	1%

Table C13: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.9081	20.0181	3%	0%
	Chalk	21.8290	21.7090	0%	4%
	Dolomite	21.2696	20.9996	4%	0%
	Limestone	21.8423	21.6023	1%	1%
1-Tetradecanethiol [S3]	Berea	21.2326	20.3226	1%	4%
	Chalk	21.8643	21.7643	2%	2%
	Dolomite	21.7062	20.8862	-51%	2%
	Limestone	21.8670	21.1470	-47%	2%
Carbazole [N1]	Berea	20.9276	19.9876	-2%	4%
	Chalk	21.3710	21.2410	-1%	2%
	Dolomite	21.2233	20.8833	-3%	1%
	Limestone	21.6518	21.3918	-1%	4%
Quinoline [N2]	Berea	21.3143	20.3543	-4%	2%
	Chalk	21.1629	20.9929	-5%	2%
	Dolomite	20.9699	20.6599	0%	0%
	Limestone	20.8921	20.6021	-4%	2%
Pyridine [N3]	Berea	21.7161	20.7561	-4%	2%
	Chalk	21.8534	21.7334	0%	4%
	Dolomite	21.4575	21.1375	-1%	5%
	Limestone	21.3892	21.1092	-3%	4%

Table C14: Raw data for 2000 ppm of SAC on rock wettability in the presence of 0 ppm TDS brine at 110°C. Each experiment was repeated at least 3 times and their standard deviation is reported.

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Decane	Berea	20.3913	19.4713	0%	2%
	Chalk	20.3093	20.1065	-8%	1%
	Dolomite	20.7644	20.3044	-15%	3%
	Limestone	20.9952	20.7452	0%	4%
Tetralin [A1]	Berea	21.0221	20.1021	0%	5%
	Chalk	20.8460	20.4360	-29%	5%
	Dolomite	20.6141	19.9441	-36%	1%
	Limestone	20.2889	19.6689	-37%	4%
Acetic Acid [O1]	Berea	20.8393	20.2393	32%	3%
	Chalk	20.1323	20.1723	16%	0%
	Dolomite	20.1279	20.0479	23%	3%
	Limestone	20.6683	20.7283	31%	2%
Myristic Acid [O2]	Berea	20.8559	20.0559	12%	4%
	Chalk	20.6574	20.6974	16%	0%
	Dolomite	20.7826	20.6226	15%	5%
	Limestone	20.6964	20.5564	11%	1%
Naphthenic Acid [O3]	Berea	20.6490	19.7390	1%	2%
	Chalk	20.7687	20.4987	-15%	0%
	Dolomite	20.1239	19.8139	0%	5%
	Limestone	20.3840	20.1040	-3%	1%
Dibenzothiophene [S1]	Berea	21.0188	20.1088	1%	1%
	Chalk	20.2303	20.0803	-3%	0%
	Dolomite	20.6807	20.2807	-9%	3%
	Limestone	20.2027	19.9127	-4%	1%

Table C14: Cont'd

Oil Chemistry (SAC)	Rock Type	Test Tube + Grain (g)	Test Tube (g)	Fractional Oil Wettability (%)	Standard Deviation (+/-)
Di-n-Butyl Sulfide [S2]	Berea	20.3596	19.4096	-3%	5%
	Chalk	20.2060	20.2260	14%	2%
	Dolomite	20.2165	20.0165	11%	4%
	Limestone	20.2206	20.1106	14%	0%
1-Tetradecanethiol [S3]	Berea	20.3193	19.3793	-2%	2%
	Chalk	20.7041	20.5641	-2%	1%
	Dolomite	20.8307	19.8407	-68%	1%
	Limestone	20.6604	19.7804	-63%	4%
Carbazole [N1]	Berea	20.1163	19.2063	1%	4%
	Chalk	20.3124	20.0624	-13%	3%
	Dolomite	20.5396	20.1696	-6%	5%
	Limestone	20.3070	19.9570	-10%	3%
Quinoline [N2]	Berea	20.7903	19.8403	-3%	5%
	Chalk	20.9342	20.7242	-9%	0%
	Dolomite	20.4657	19.8057	-35%	2%
	Limestone	20.2819	19.9119	-12%	5%
Pyridine [N3]	Berea	20.6838	19.7338	-3%	2%
	Chalk	20.5047	20.3447	-4%	4%
	Dolomite	20.4783	20.1283	-4%	4%
	Limestone	20.4565	20.1865	-2%	3%

APPENDIX D: VITA

Paulina Metili Mwangi was born and raised in Kajiado District, Kenya and Lynn, MA, USA to Simon Mwangi Ngachu and Jane Nyawira Mwangi. She completed her high school education at Lynn Classical High School, Lynn, MA. She acquired her Bachelors in Chemical Engineering with minors in Geology and American Sign Language from the University of Rochester, Rochester, NY in May 2008. She obtained her Masters of Science in Petroleum Engineering in the December 2010 from the Louisiana State University. She is currently a candidate for the degree of Doctor of Philosophy in Petroleum Engineering to be awarded in May 2017.