

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

A Dissertation

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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.

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 oil-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 oil 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).

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.

rate of 1ml/min. Electron multiplier voltage was 1900v. Spectra were submitted to NIST library search for confirmation.

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; Israelachvili, 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;

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_{so}) and/or solid-water (γ_{sw}) IFTs.

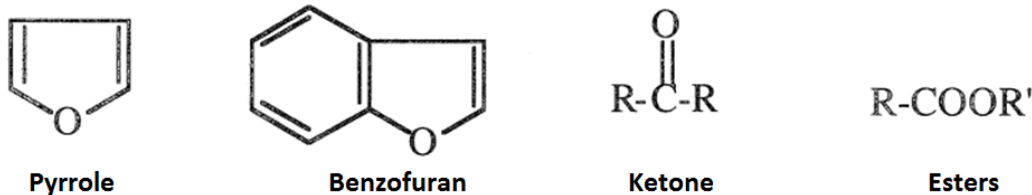


Figure 37: Structure of non-acidic oxygen compounds.

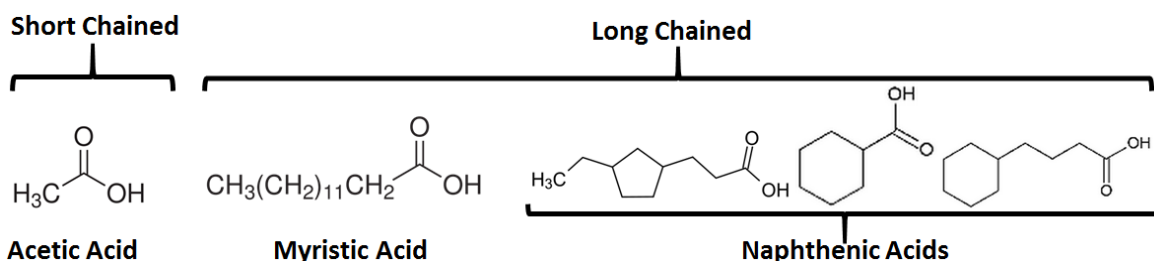


Figure 38: Structures of selected acidic oxygen compounds.

The tested oxygen SACs affected wettability differently. The long-chained oxygen SAC strongly shifted both the Berea and the carbonate rocks towards oil-wet. Similarly, 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.



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. $\text{solid CaCO}_3 + 2\text{RCOO}^- \rightarrow \text{solid Ca(RCOO)}_2$

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).



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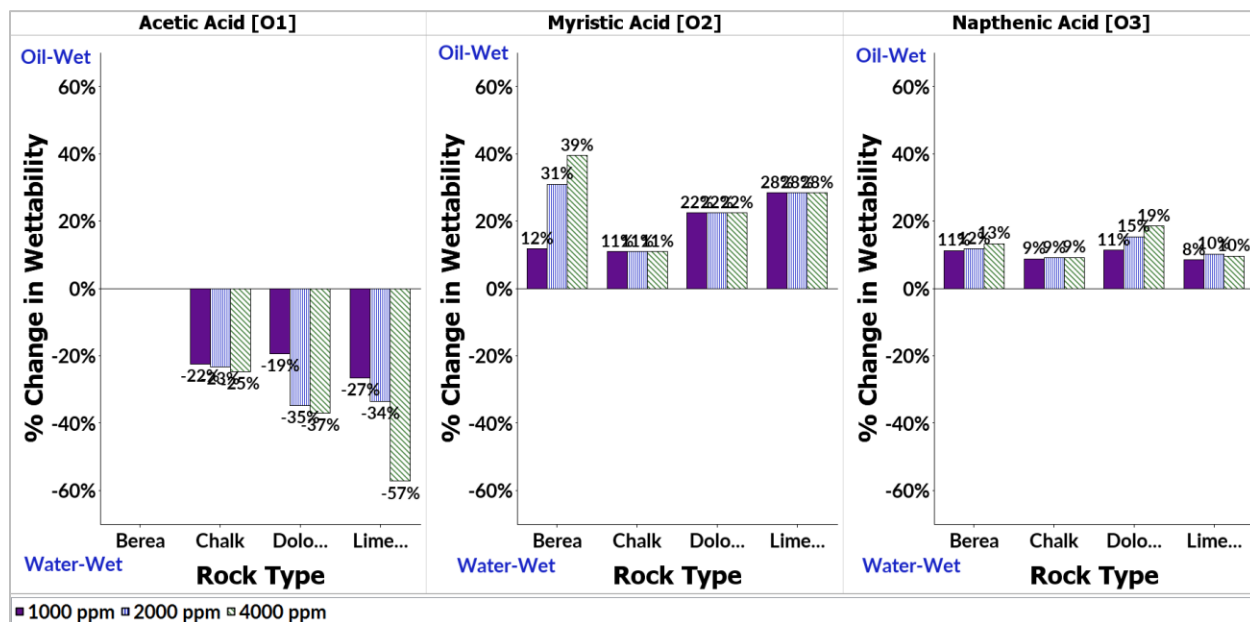


Figure 39: Effect of oxygen SAC on wettability in the presence of DI water at 70°C.

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.

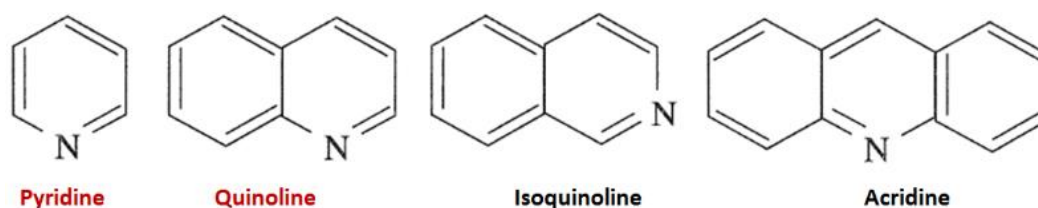


Figure 40: Examples of basic nitrogen SAC present in crude oil including pyridine and quinoline which are used as model compounds for the basic nitrogen class.

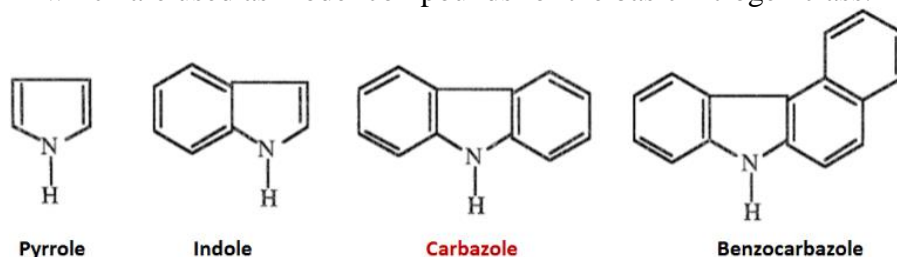


Figure 41: Examples of non-basic nitrogen SAC present in crude oil including carbazole, which is used as the model compound for the neutral nitrogen class.

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.

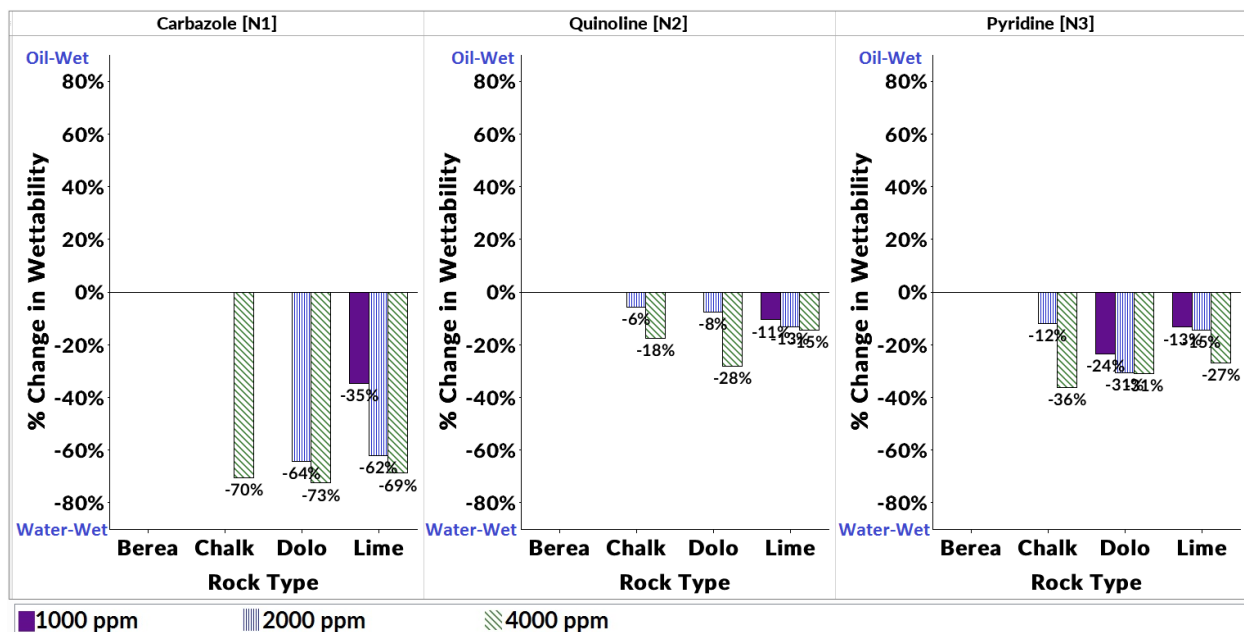


Figure 42: Effect of nitrogen SAC on wettability in the presence of DI water at 70°C.

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.

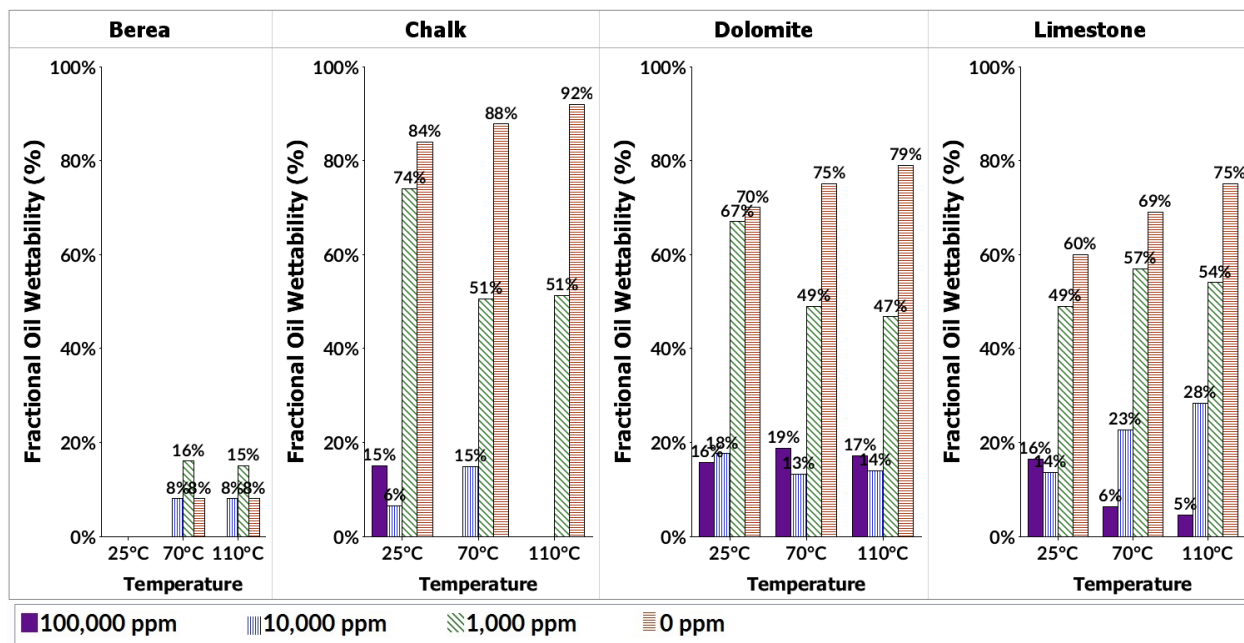


Figure 43: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70 and 110°C).

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 $\pm 5\%$ 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.

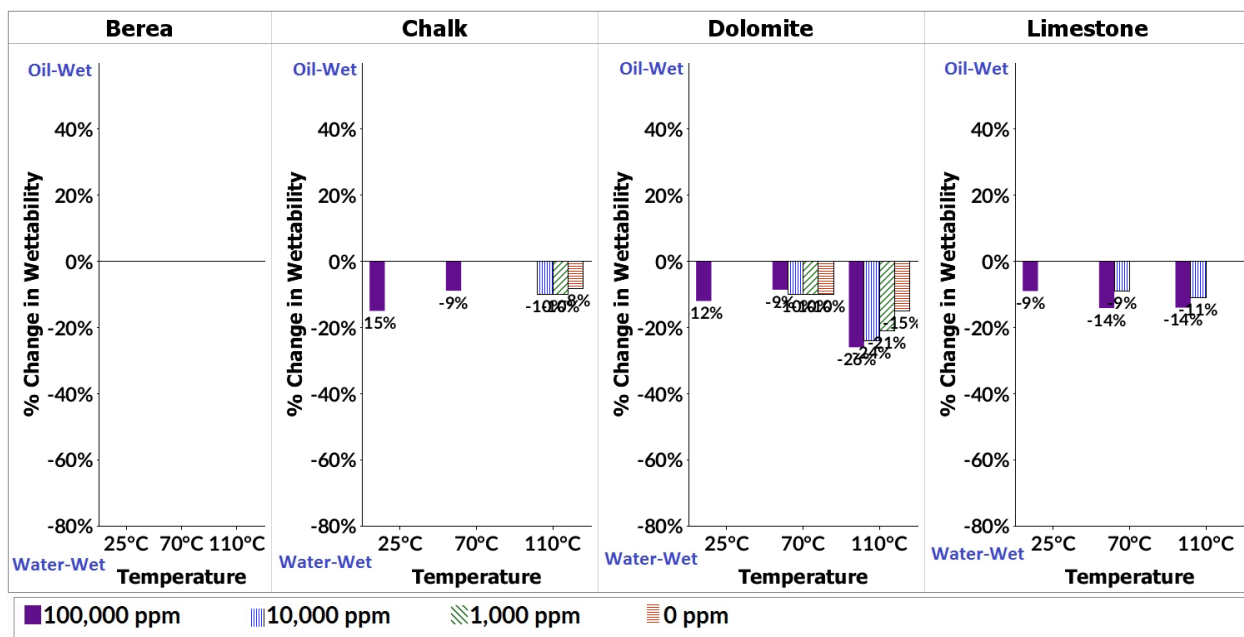


Figure 44: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using tetralin. Values below 5% are not displayed.

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.

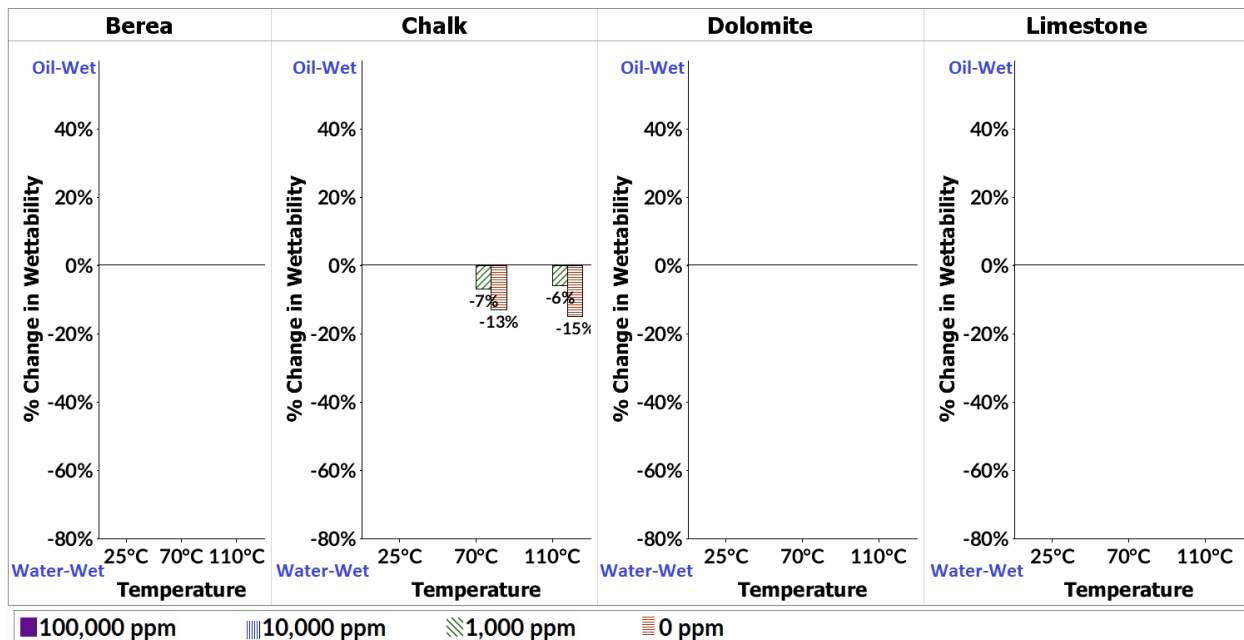


Figure 45: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using Dibenzothiophene (S1) SAC. Values below 5% are not displayed.

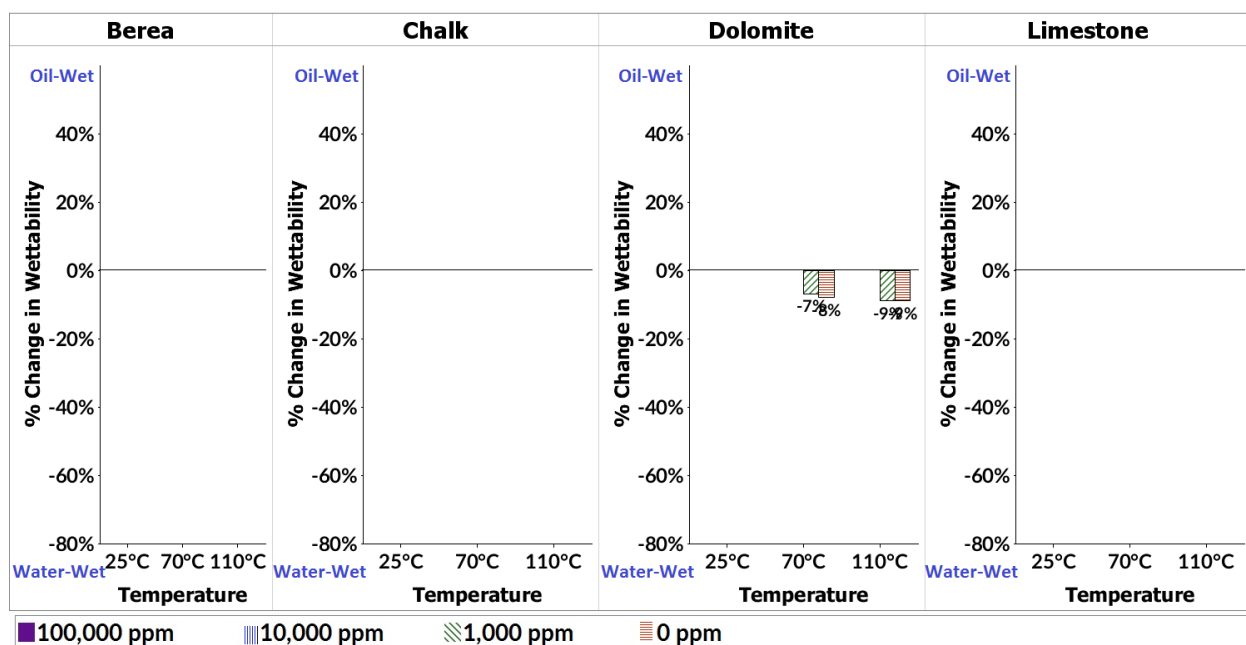


Figure 46: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using Di-n-butyl sulfide (S2) SAC. Values below 5% are not displayed.

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.

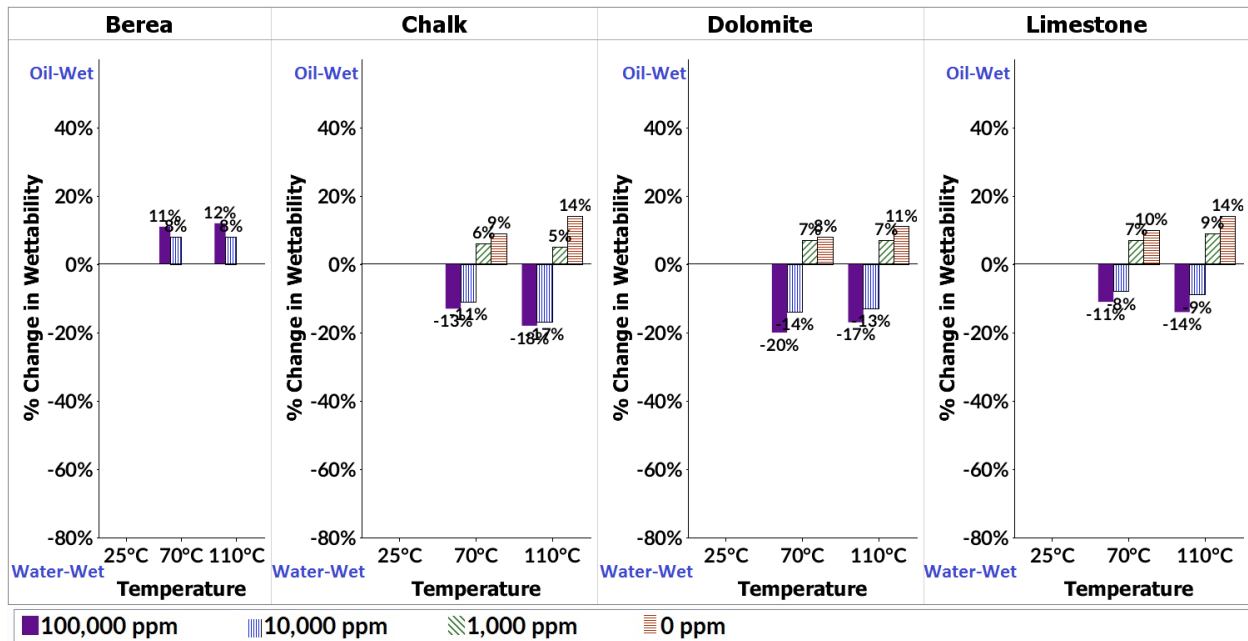


Figure 47: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using 1-tetradecanethiol (S3) SAC. Values below 5% are not displayed.

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.

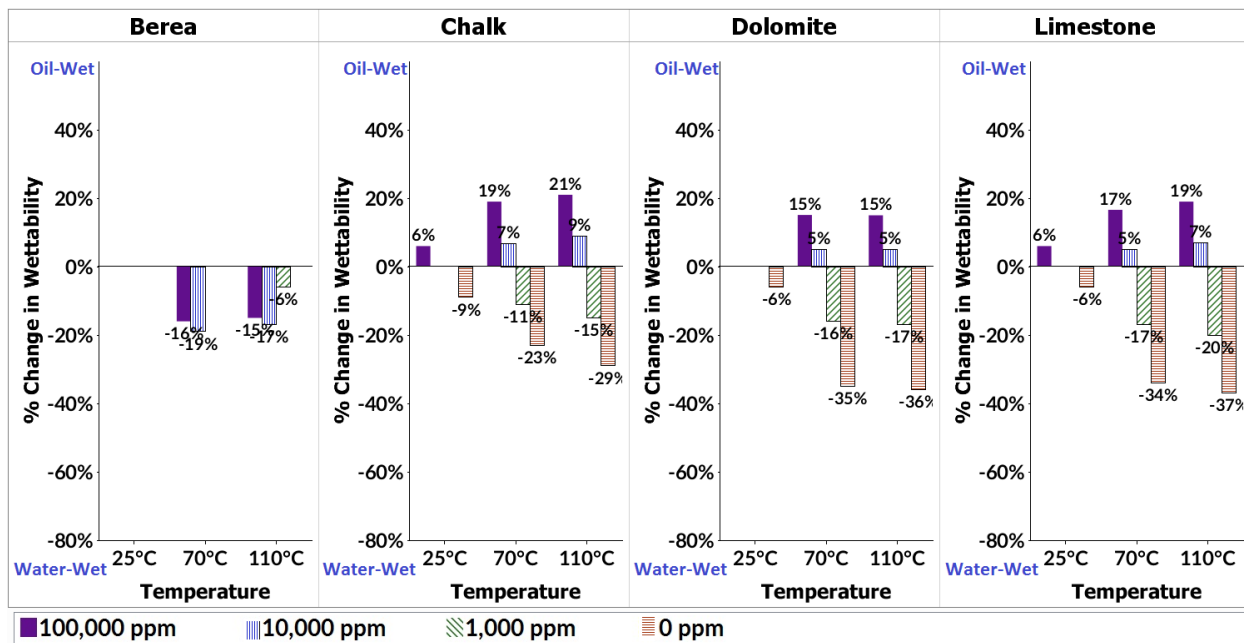


Figure 48: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid (O1) SAC. Values below 5% are not displayed.

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.

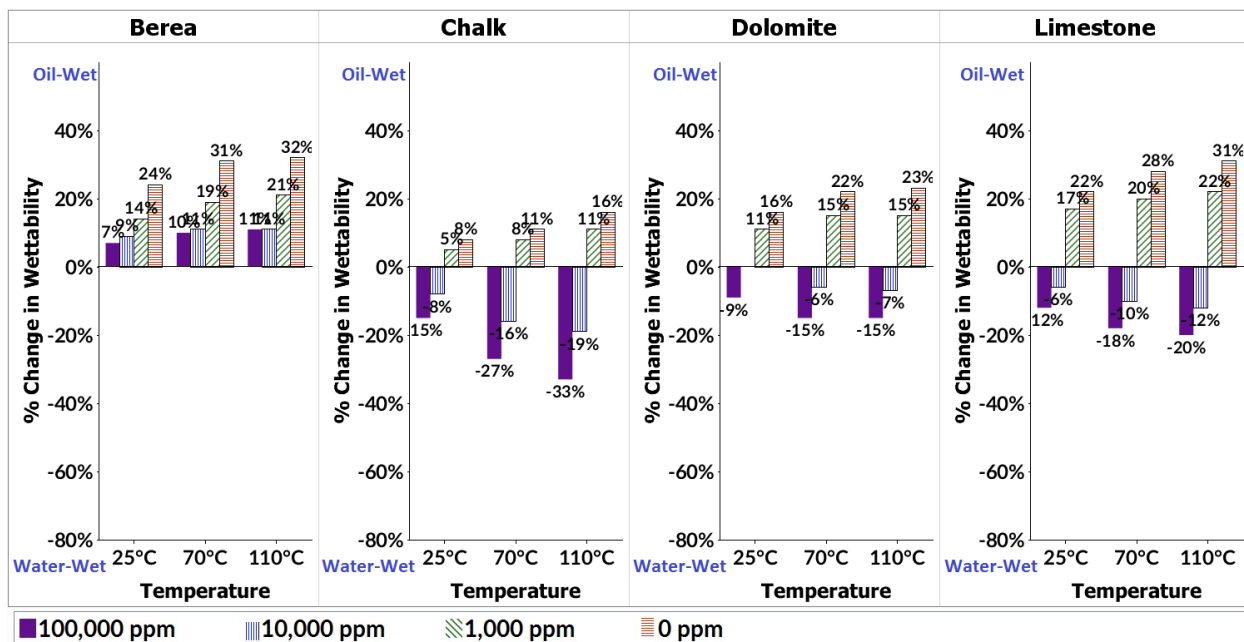


Figure 49: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using myristic acid (O2) SAC. Values below 5% are not displayed.

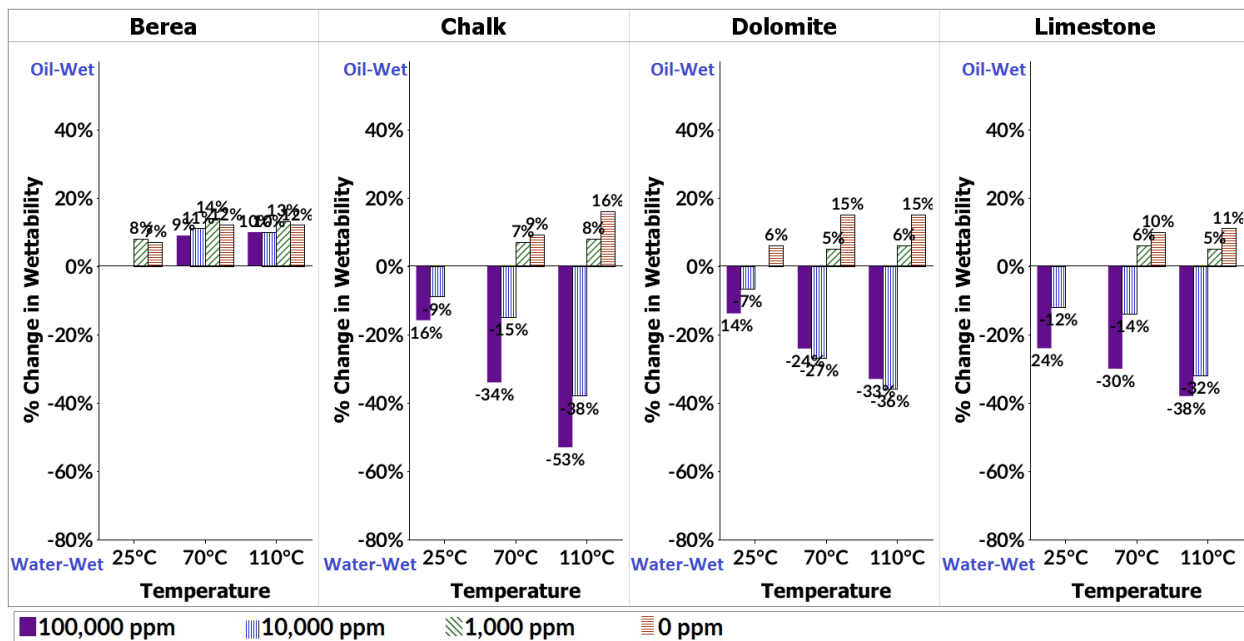


Figure 50: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using naphthenic acid (O3) SAC. Values below 5% are not displayed.

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.

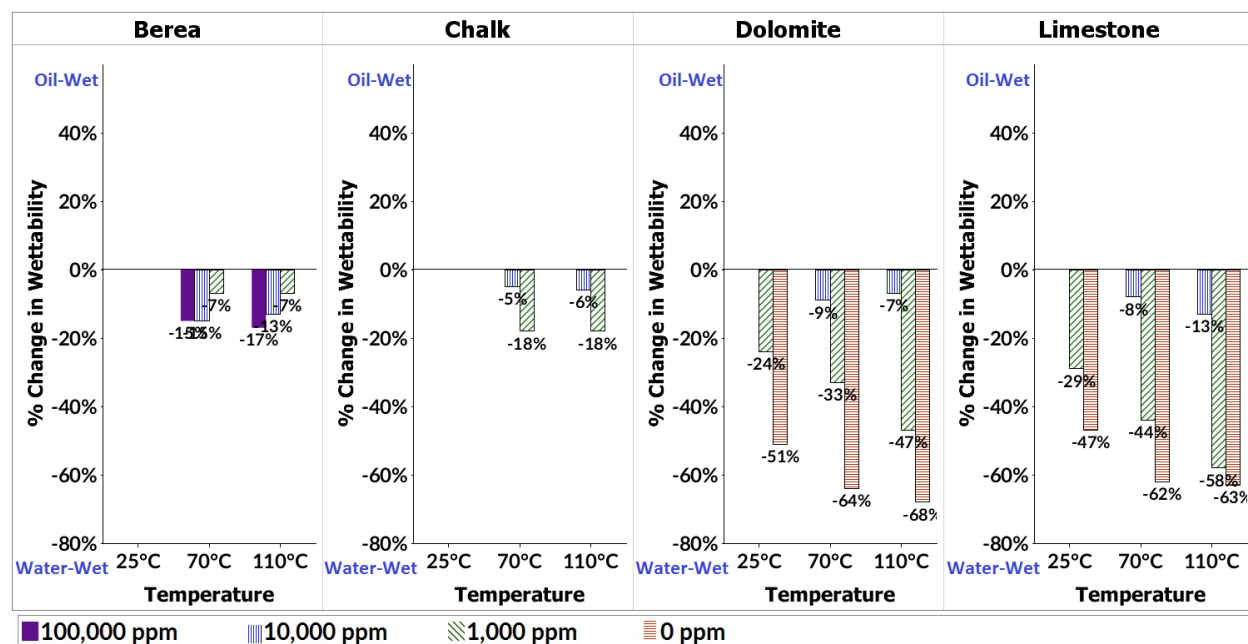


Figure 51: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using carbazole (N1) SAC. Values below 5% are not displayed.

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.

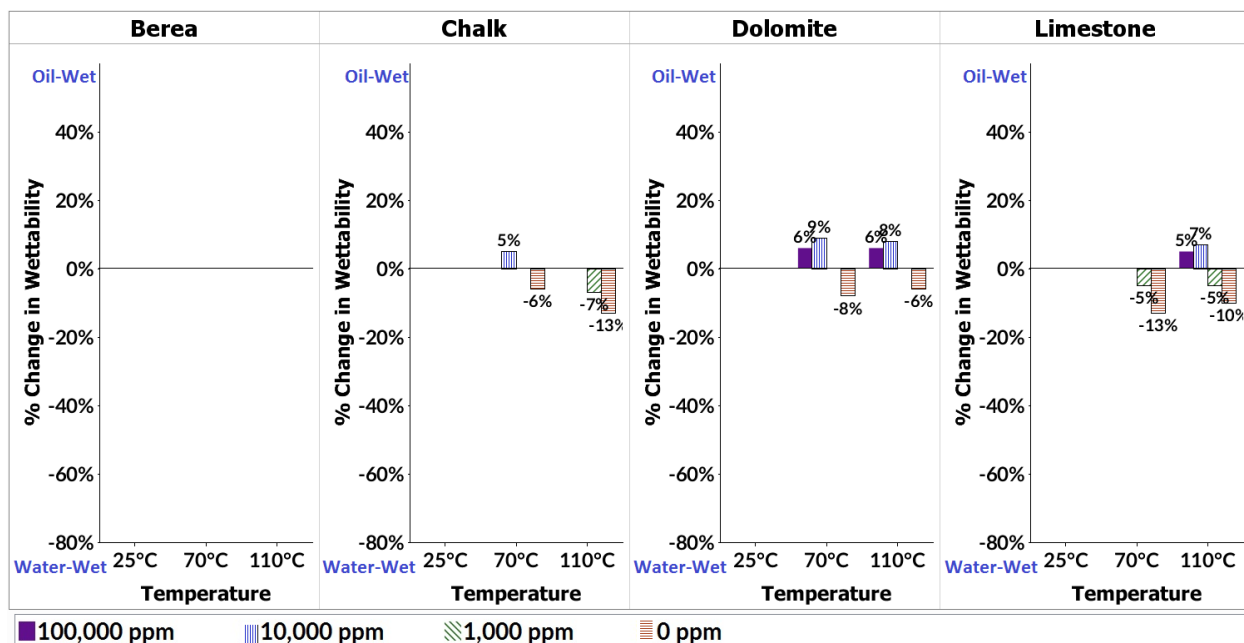


Figure 52: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using quinoline (N2) SAC. Values below 5% are not displayed.

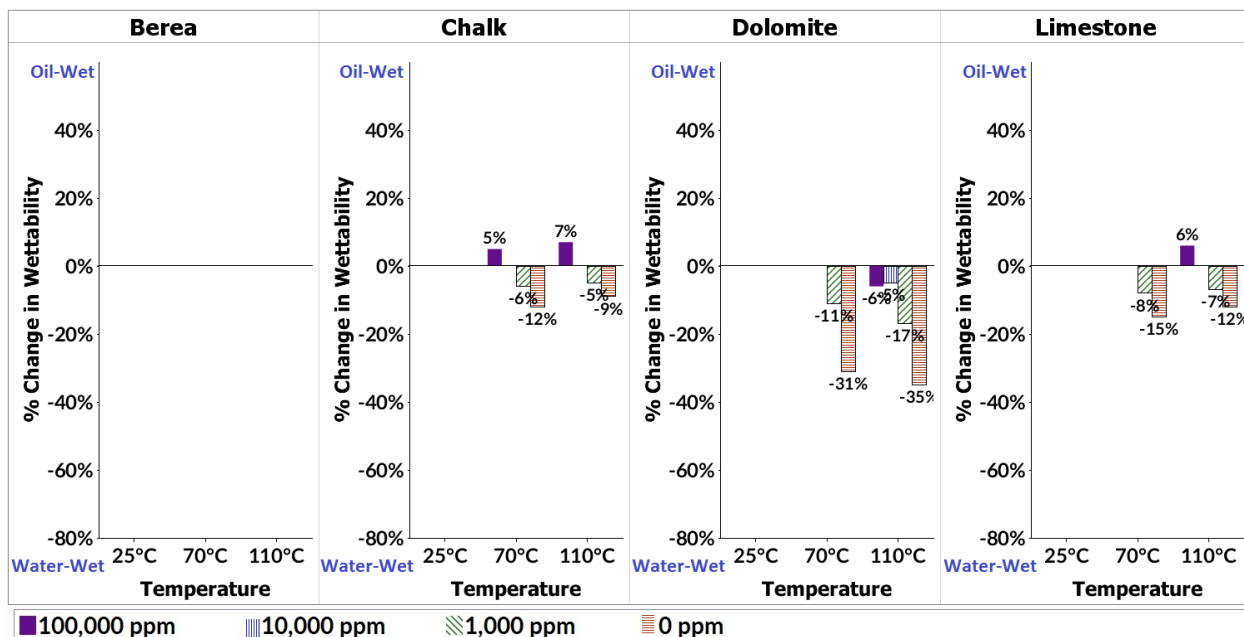


Figure 53: Experimental measurement of wettability for the four rock types at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using pyridine (N3) SAC. Values below 5% are not displayed.

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 extent 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.

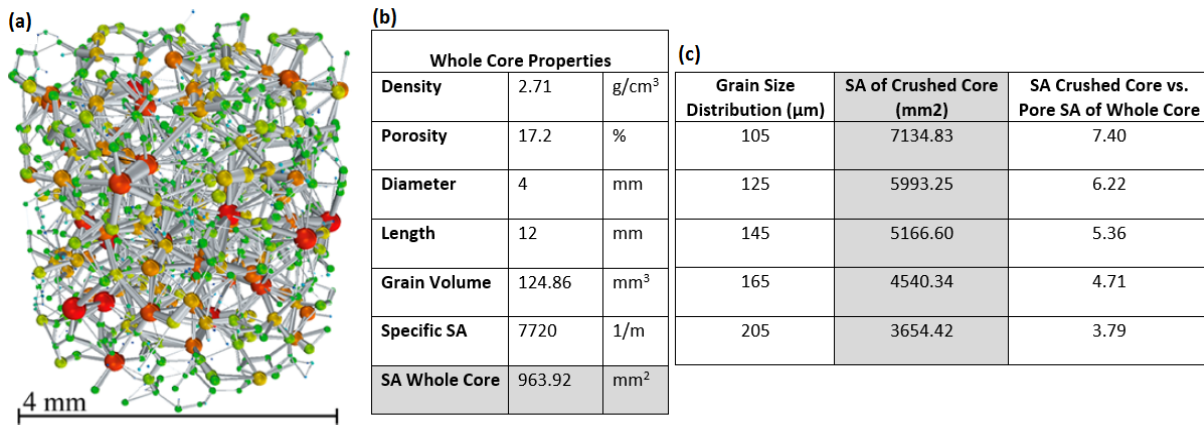


Figure 54: (a) Pore surface network representation of Ketton carbonate extract from micro-CT images (Menke et al., 2015) and (b) its given properties. (c) gives the calculated surface area values of the core if it was crushed to the given grain size distribution and the ratio of the total surface area 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 $\pm 5\%$ 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.

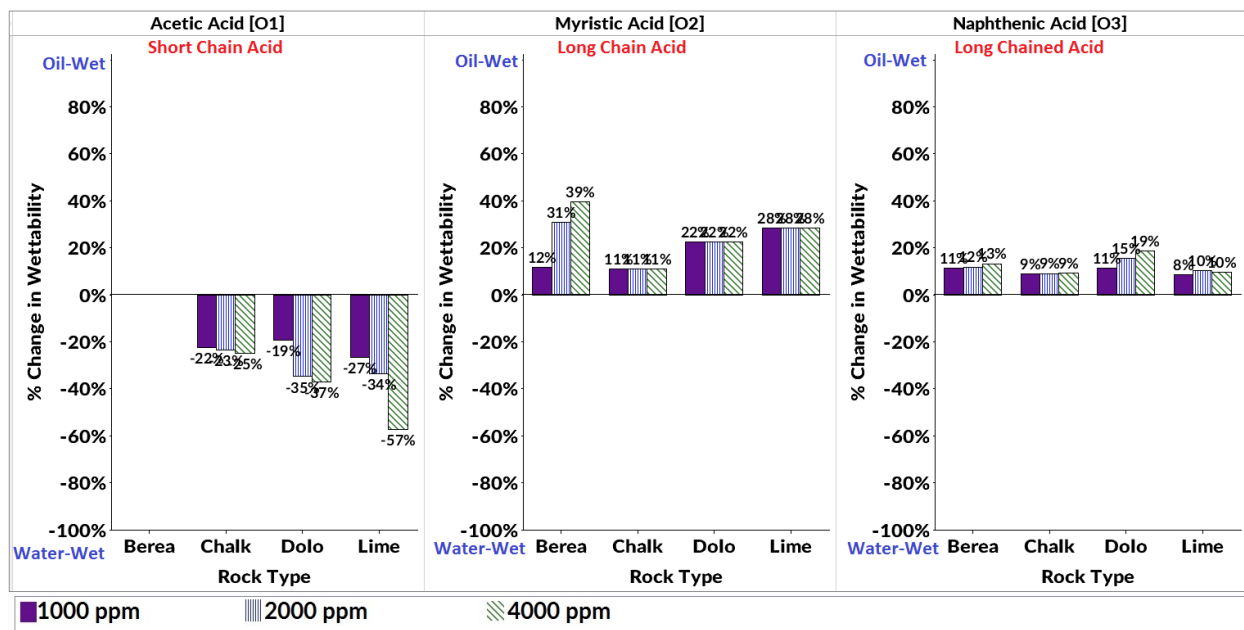


Figure 55: Experimental measurement of wettability for the four rock types at 0 ppm TDS and 70°C when using oxygen SACs at 3 concentrations (1000, 2000, 4000 ppm). Values below 5% are not displayed.

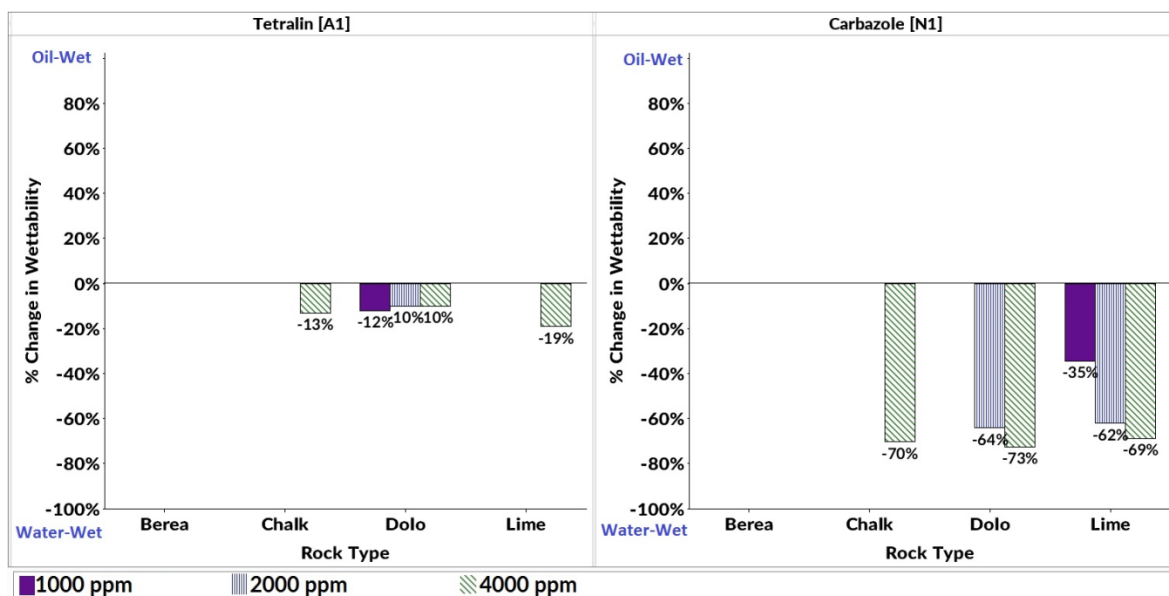


Figure 56: Experimental measurement of wettability for the four rock types at 0 ppm TDS and 70°C when using non-basic and non-acidic SACs. Values below 5% are not displayed.

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.

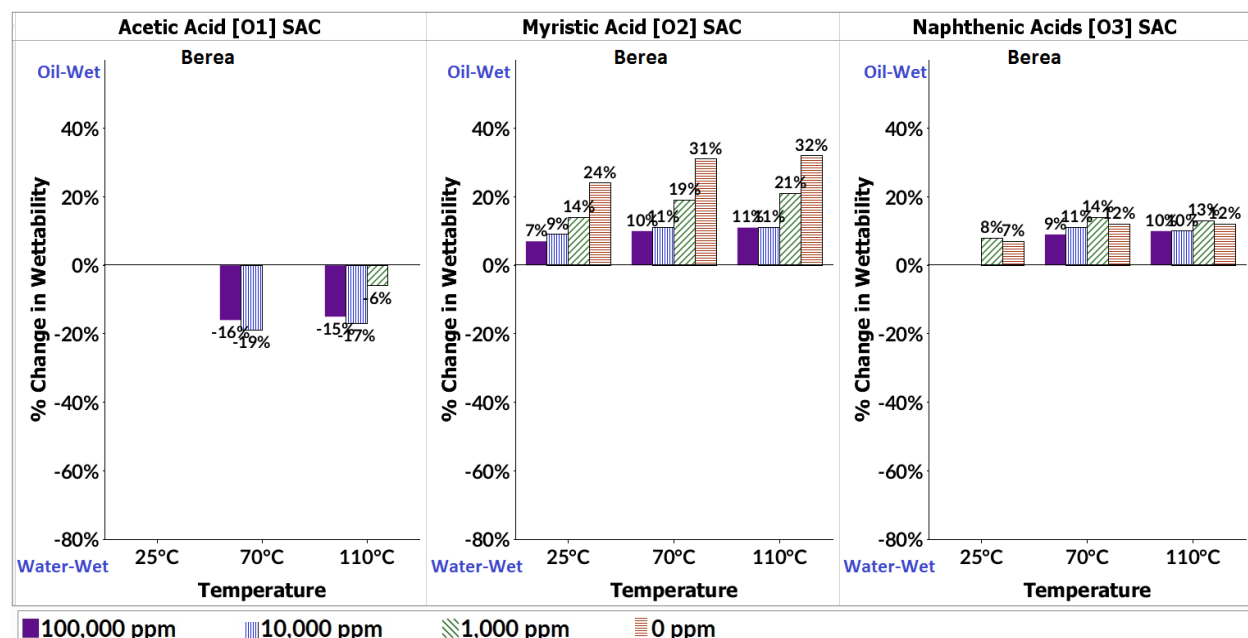


Figure 57: Experimental measurement of wettability for Berea at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using oxygen SACs. Values below 5% are not displayed.

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.

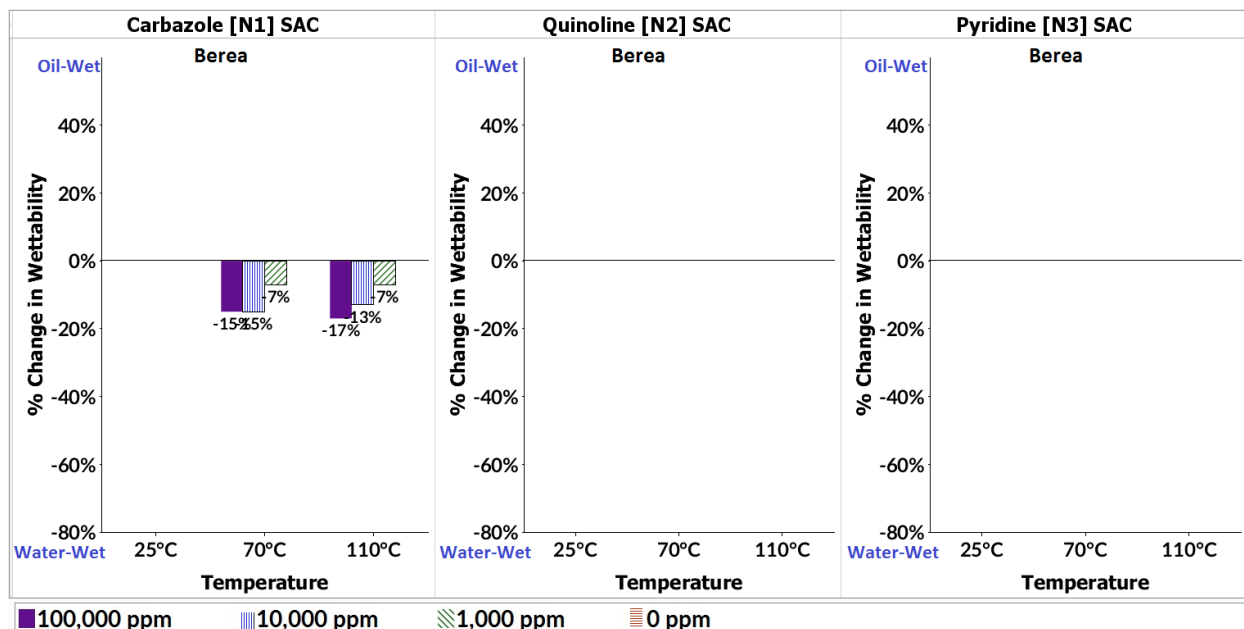


Figure 58: Experimental measurement of wettability for Berea at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using nitrogen SACs. Values below 5% are not displayed.

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.

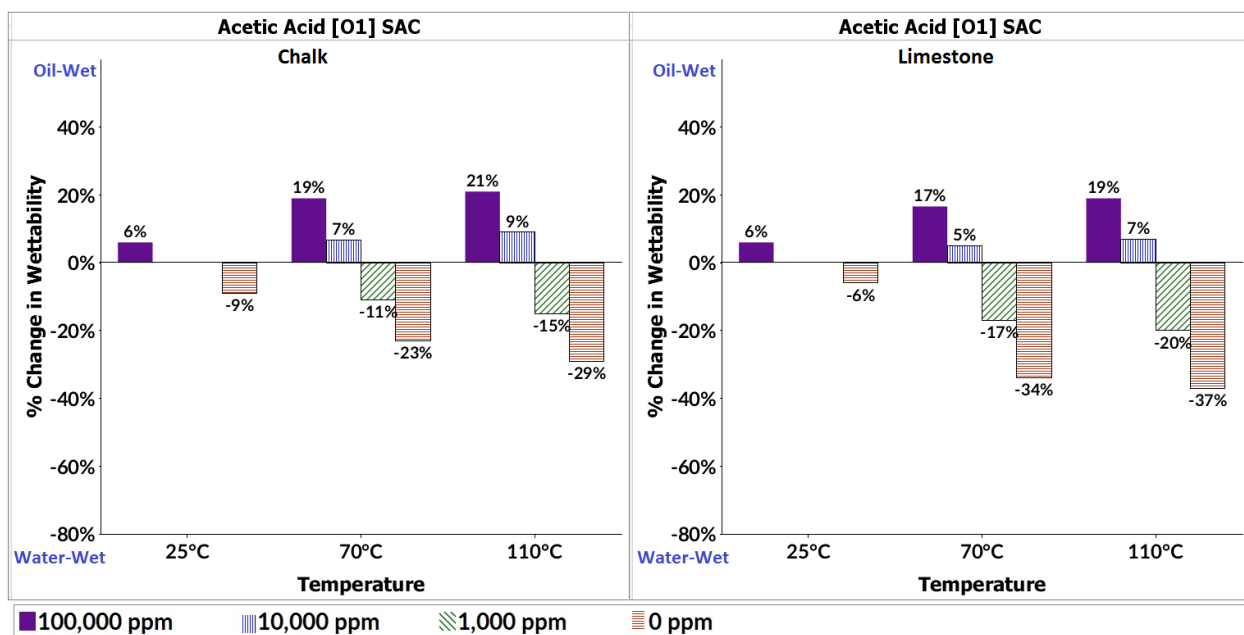


Figure 59: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid SAC. Values below 5% are not displayed.

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, 10,000 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.

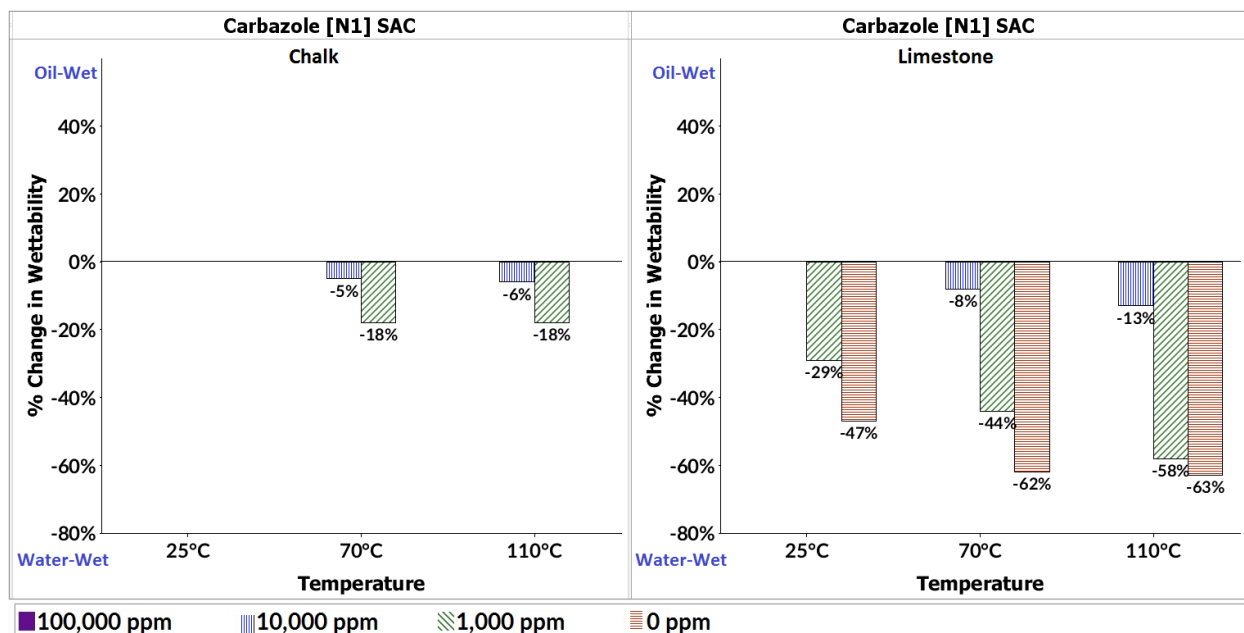


Figure 60: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using carbazole SAC. Values below 5% are not displayed.

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.

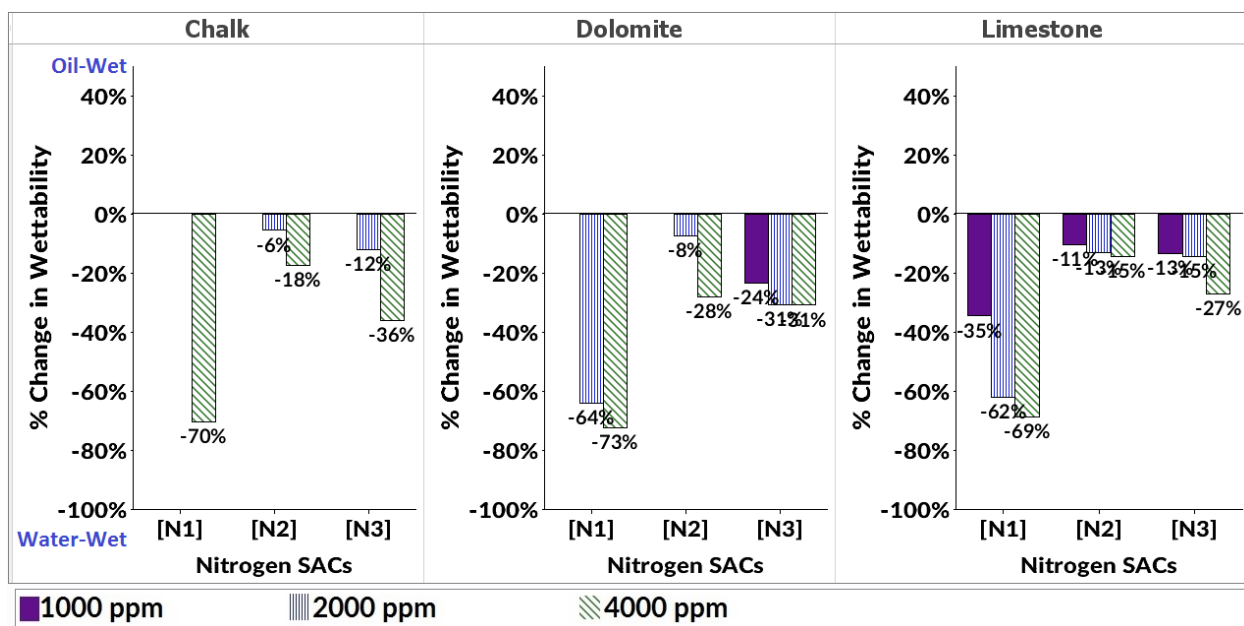


Figure 61: Experimental measurement of wettability for the carbonate rocks at 0, 2000, 4000 ppm of nitrogen SACs and 70°C. Values below 5% are not displayed.

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).

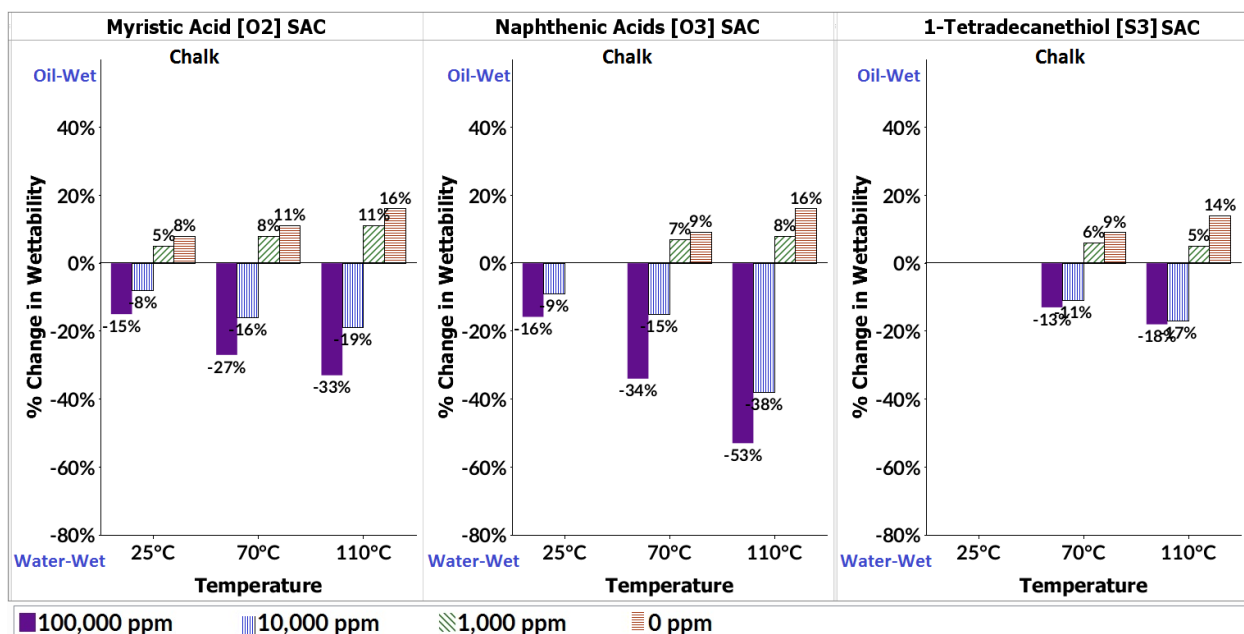


Figure 62: Experimental measurement of wettability for chalk at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using long-chained oxygen SACs and acidic sulfur acidic SAC. Values below 5% are not displayed.

Punternvold 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.

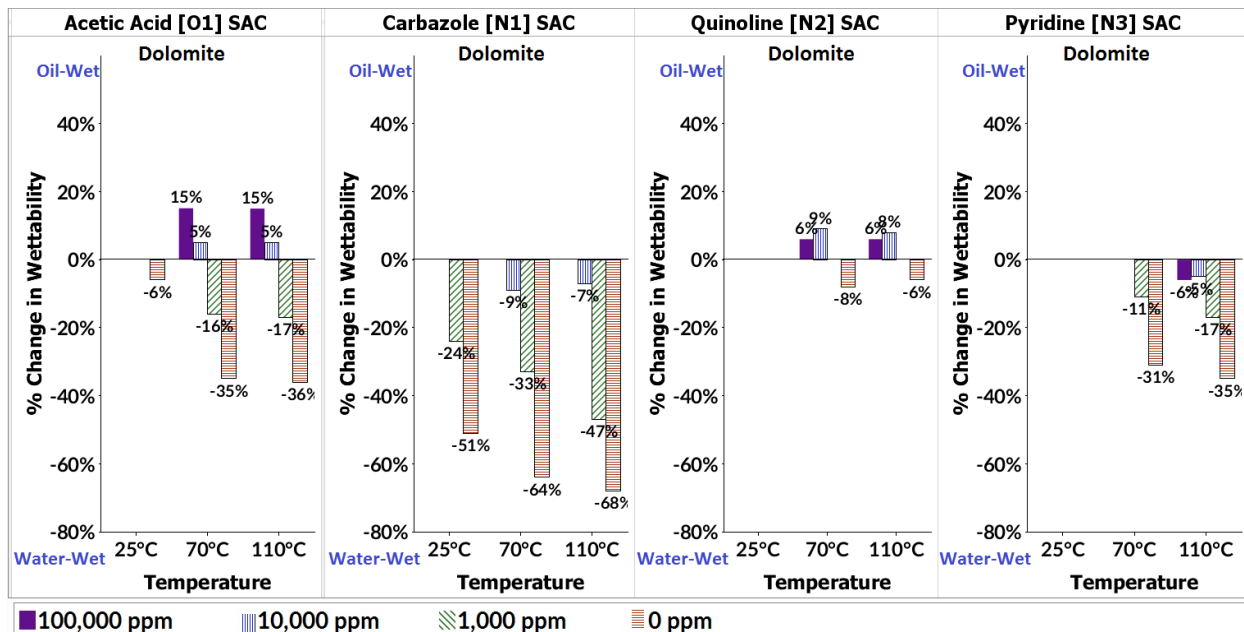


Figure 63: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid SAC and nitrogen SACs. Values below 5% are not displayed.

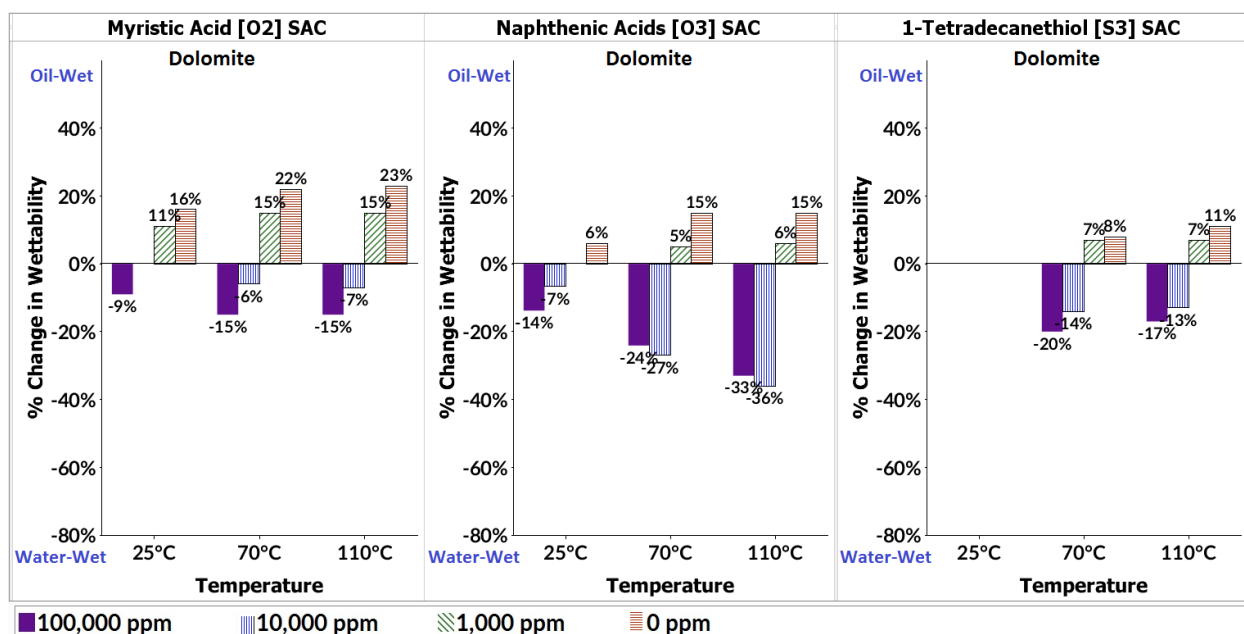


Figure 64: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using long-chained oxygen SACs and acidic sulfur acidic SAC. Values below 5% are not displayed.

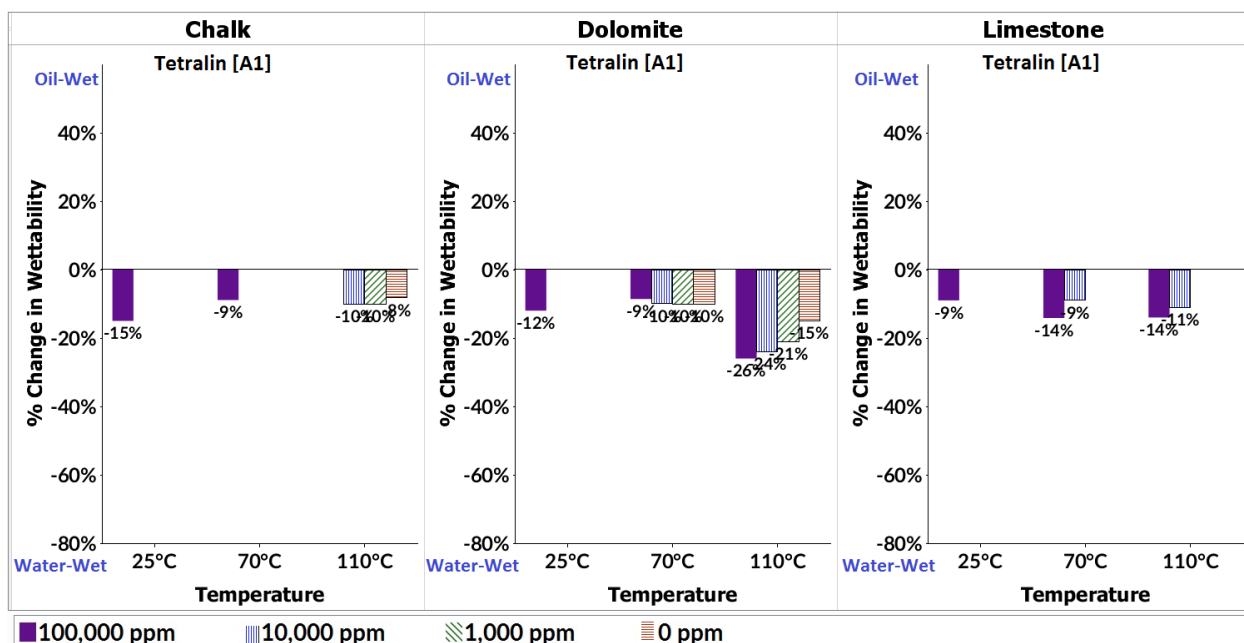


Figure 65: Experimental measurement of wettability for the carbonate rocks at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using tetralin. Values below 5% are not displayed.

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.

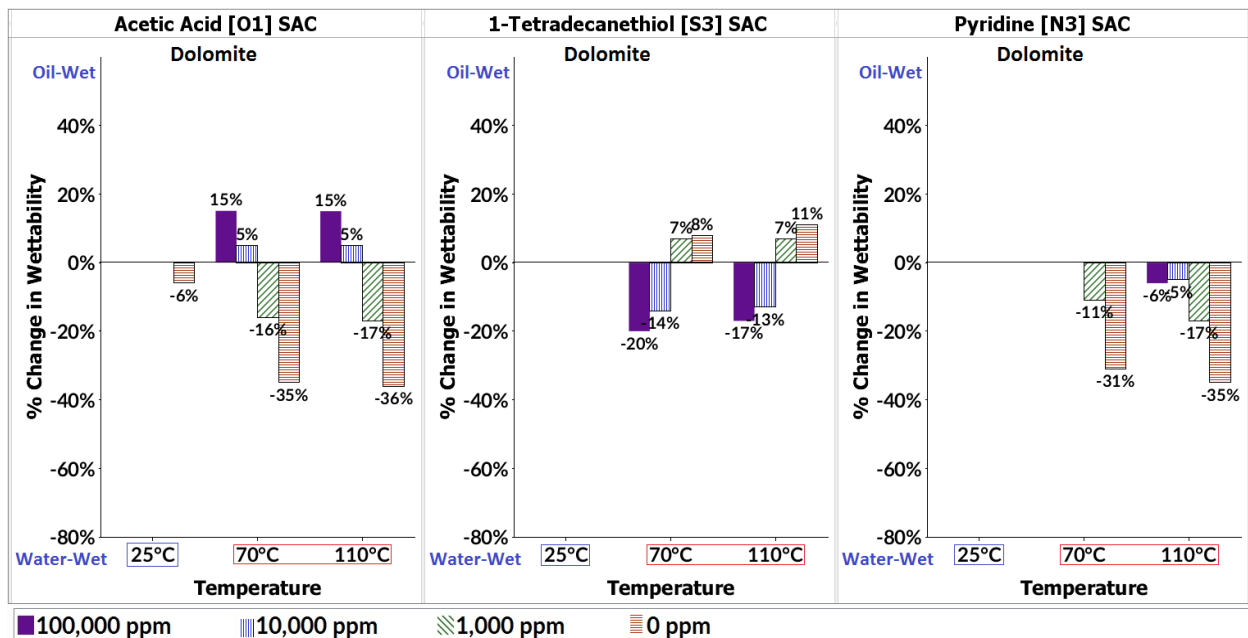


Figure 66: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid, 1-Tetradecanethiol, and pyridine SACs. Values below 5% are not displayed.

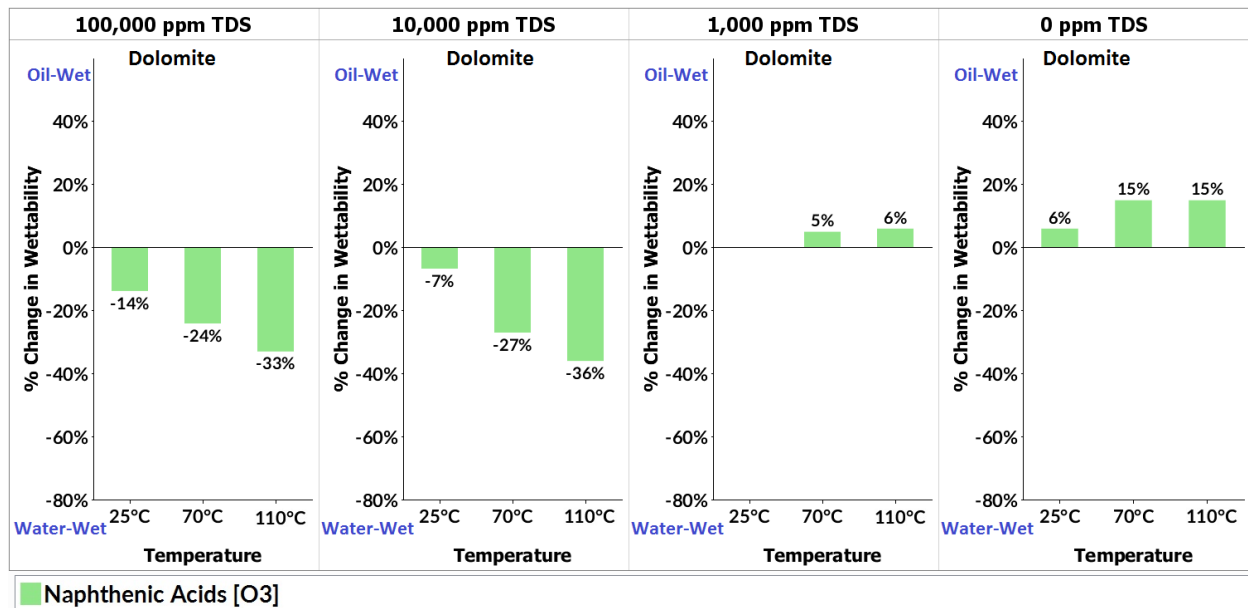


Figure 67: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and three temperatures (25, 70, 110°C) when using naphthenic acids SAC. Values below 5% are not displayed.

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.

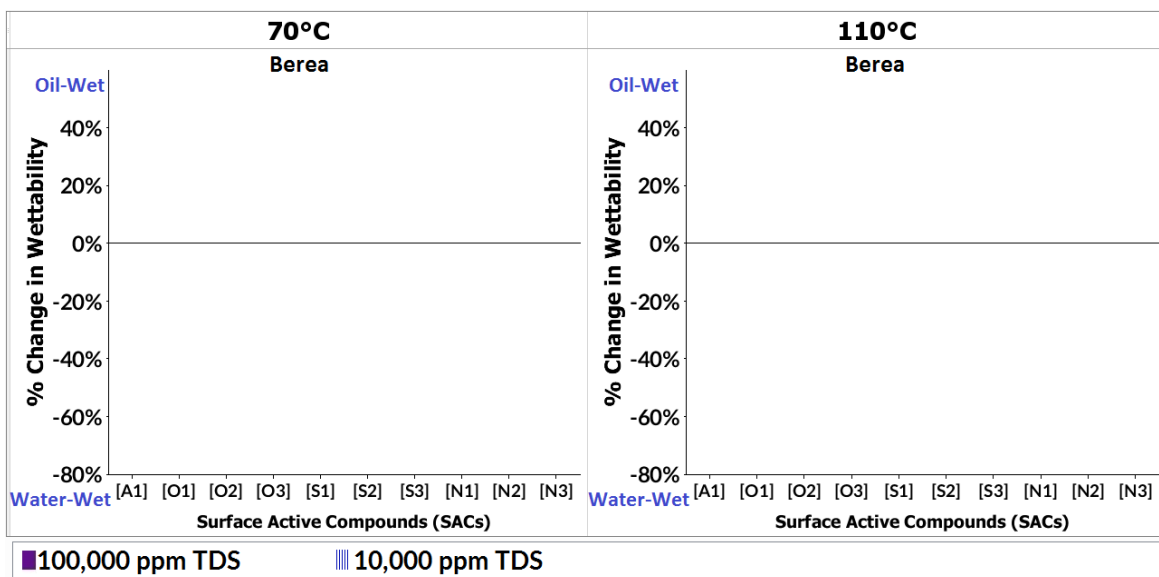


Figure 68: Experimental measurement of the SACs ability to change wettability of berea as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

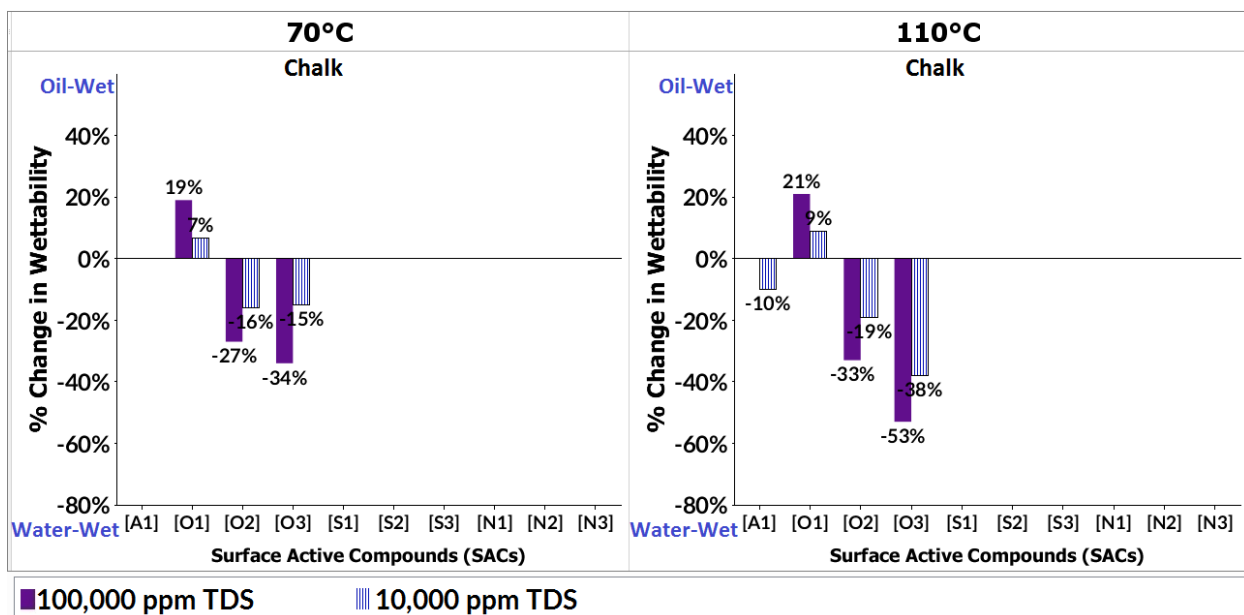


Figure 69: Experimental measurement of the SACs ability to change wettability of chalk as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

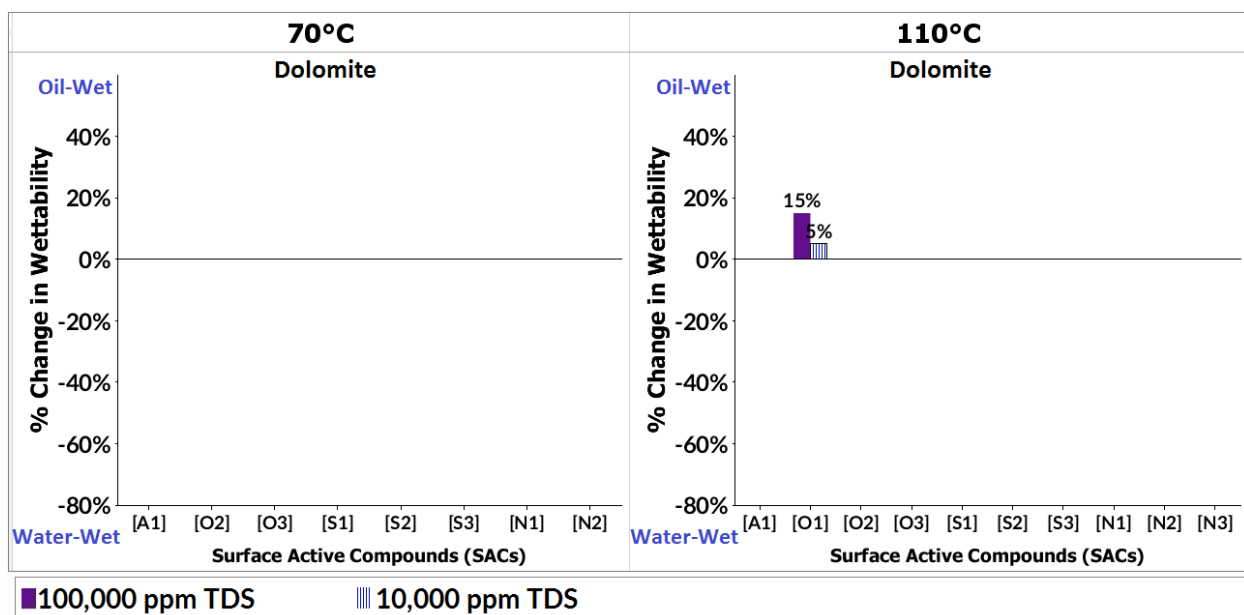


Figure 70: Experimental measurement of the SACs ability to change wettability of dolomite as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

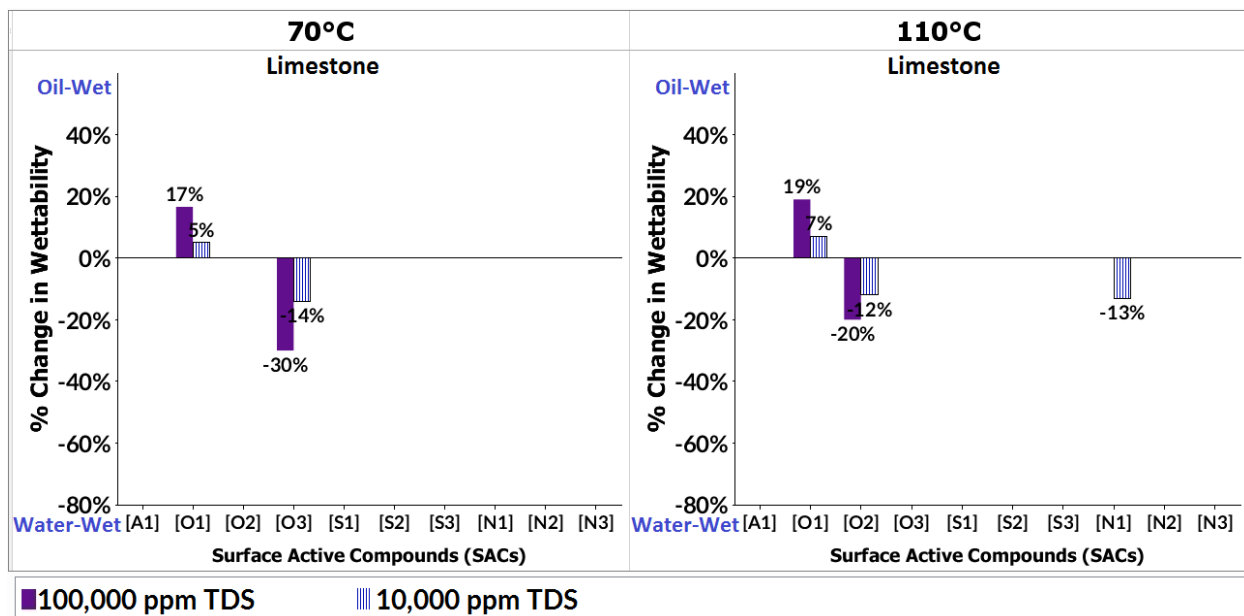


Figure 71: Experimental measurement of the SACs ability to change wettability of limestone as salinity is decreased from 100,000 to 10,000 ppm TDS at 70 and 110°C. Changes in wettability less than +/- 10% as salinity is decreased are not displayed.

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° .

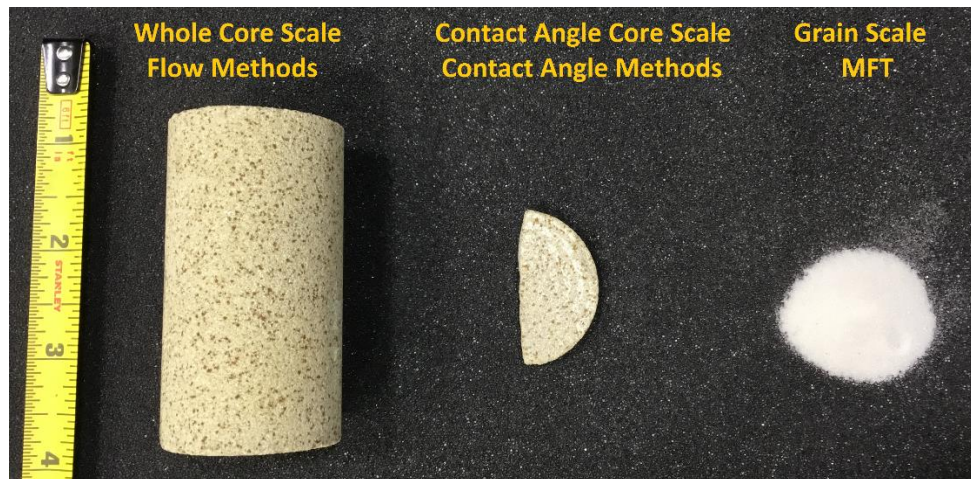


Figure 72: Different scales that wettability is measured by flow measurements (whole core scale), contact angles (contact angle core scale) and MFT (grain scale).

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.

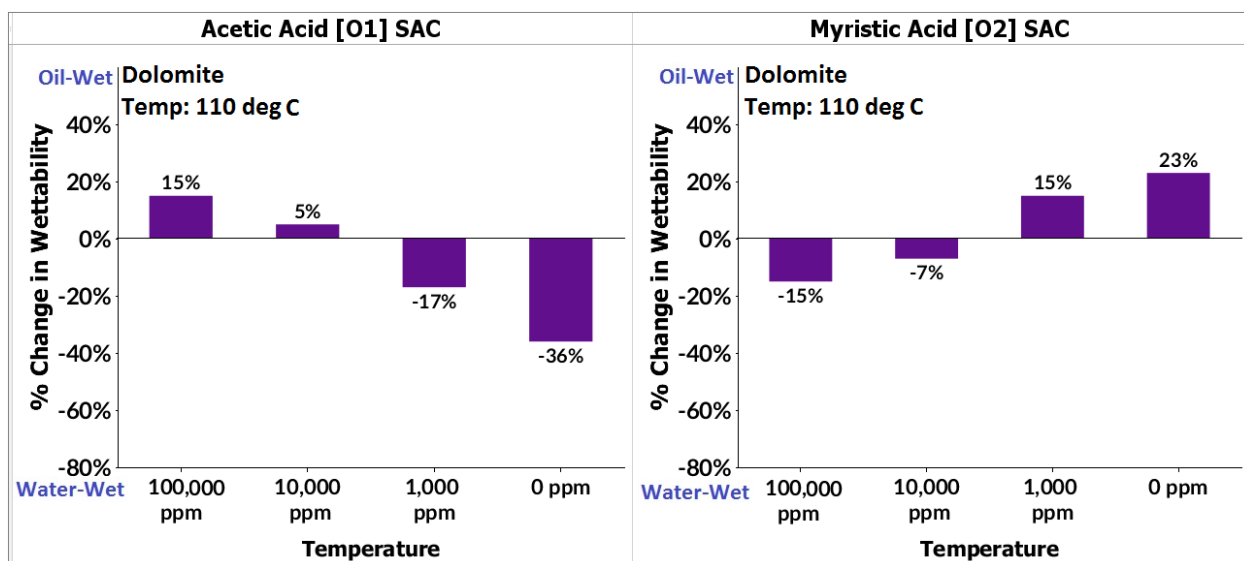


Figure 73: Experimental measurement of wettability for dolomite at 0, 1000, 10,000 and 100,000 ppm TDS and 110°C when using acetic acid and myristic acid SACs. Values below 5% are not displayed.

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.

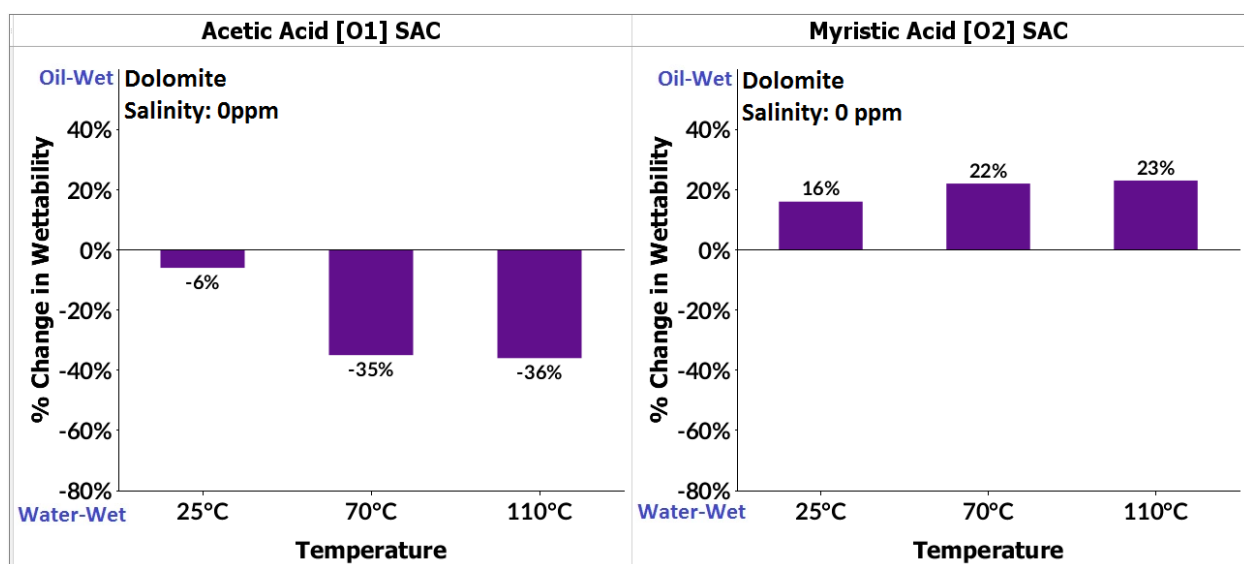


Figure 74: Experimental measurement of wettability for dolomite at 0 ppm TDS and three temperatures (25, 70, 110°C) when using acetic acid and myristic acid SACs. Values below 5% are not displayed.

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.

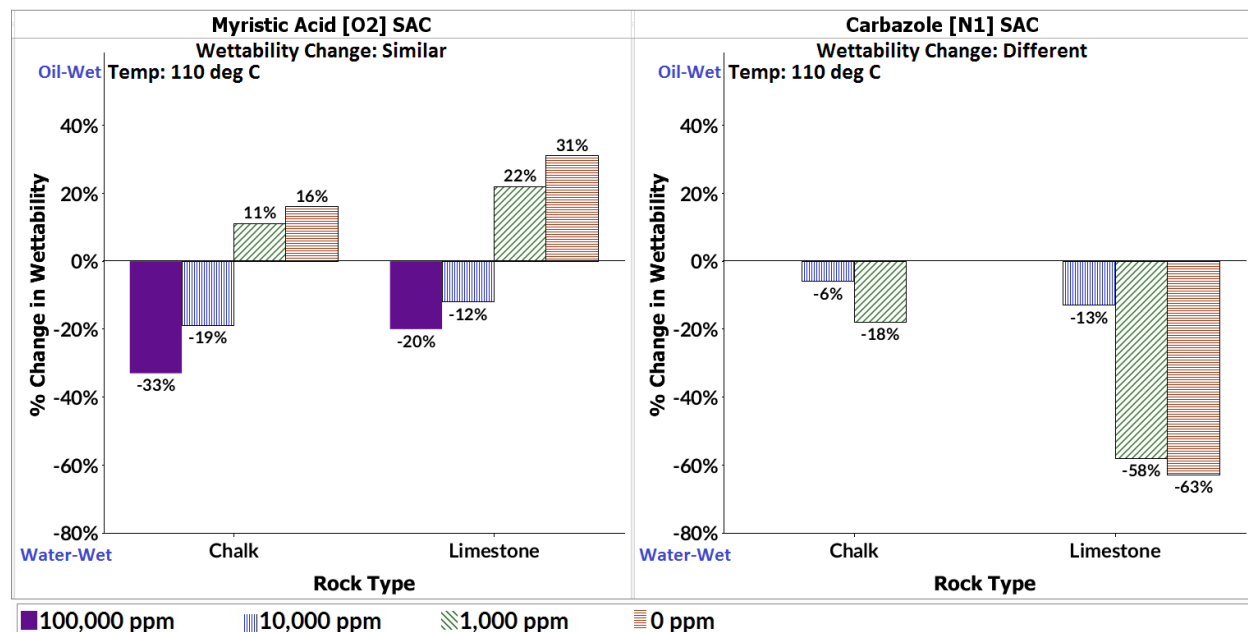


Figure 75: Experimental measurement of wettability for chalk and limestone at 0, 1000, 10,000 and 100,000 ppm TDS and 110°C when using myristic acid and carbazole SACs. Values below 5% are not displayed.

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 heterogeneous 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 homogeneous. On a macroscale, wettability is heterogeneous since it is 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

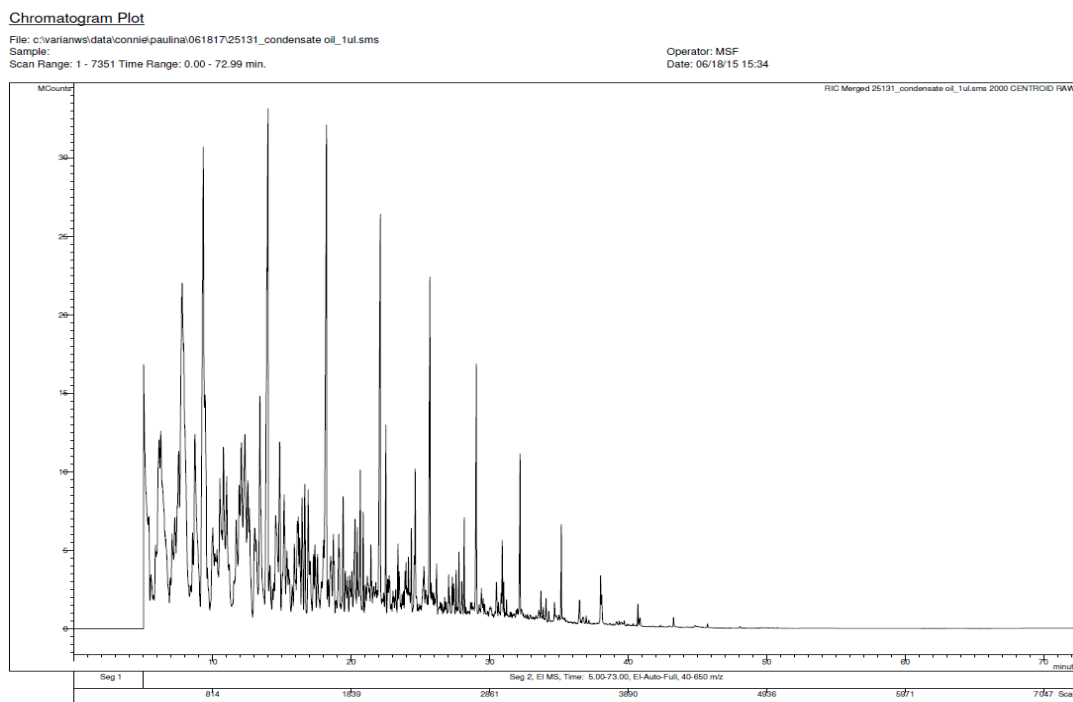


Figure A1: GC results of condensate oil.

Table A1: Condensate oil GC composition.

Name	Molecular Formula	Molecular Weight g/mol
1-ethyl-3-methyl-benzene	C ₉ H ₁₂	120.19
1-ethyl-3-methylcyclohexane	C ₉ H ₁₈	126.24
2,4-dimethyl-heptane	C ₉ H 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

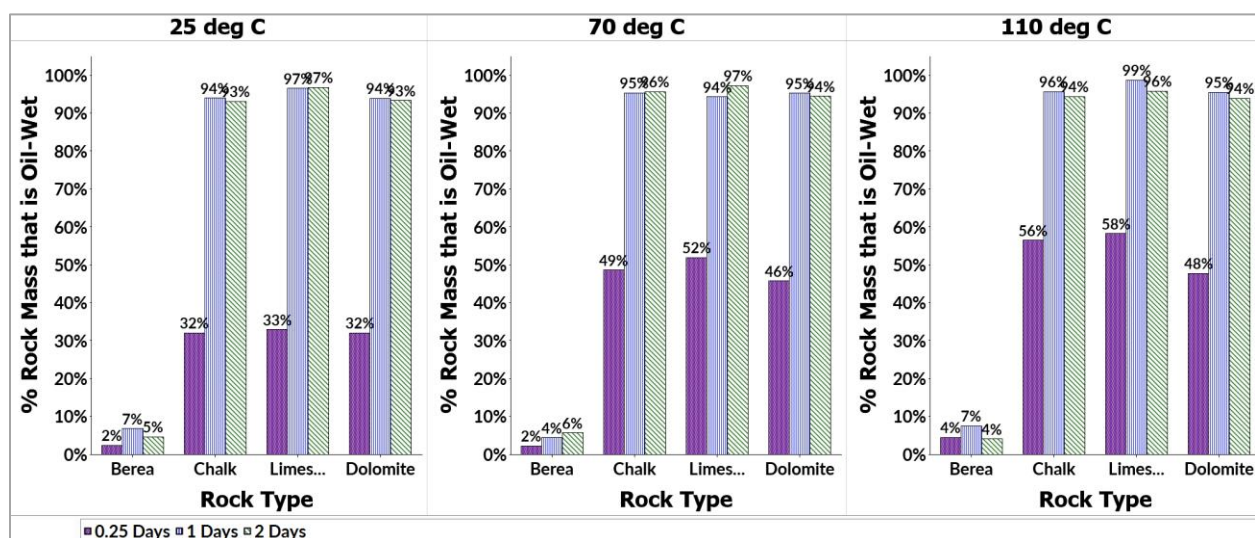


Figure A2: 6 hrs, 1 day, & 2 days aging time for decane at 25°C, 70°C, & 110°C.

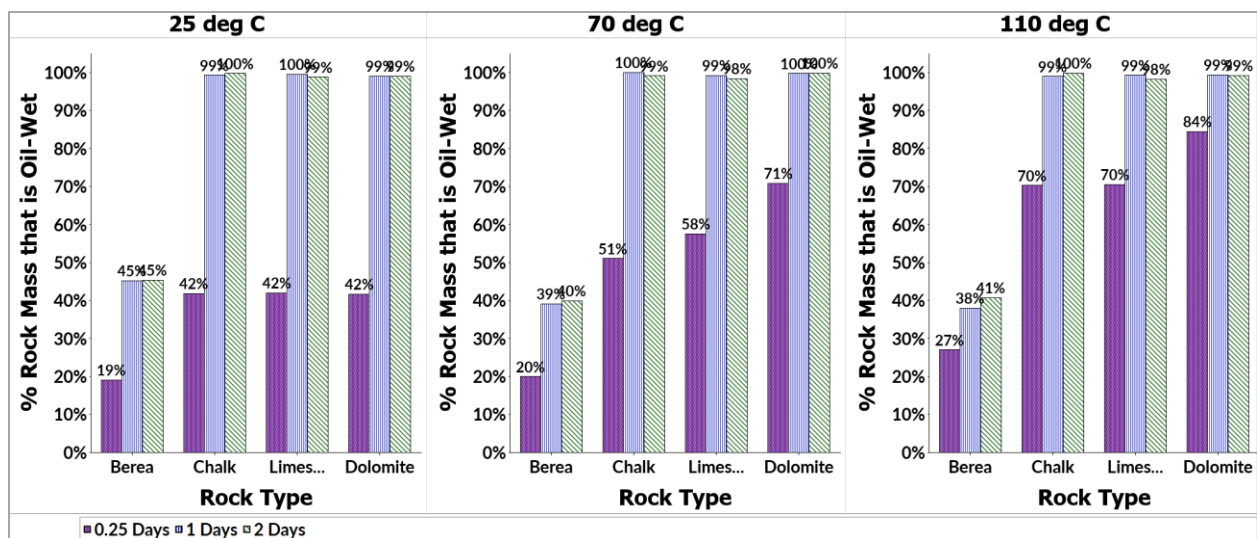


Figure A3: 6 hrs, 1 day, & 2 days aging time for condensate at 25°C, 70°C, & 110°C.

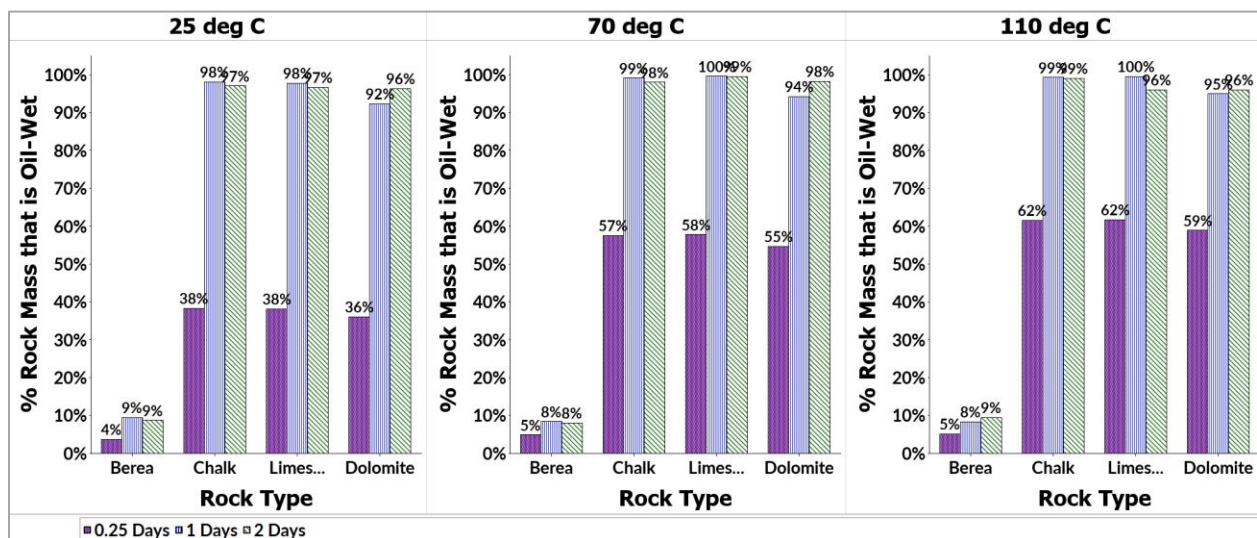


Figure A4: 6 hrs, 1 day, & 2 days aging time for decane +2000 ppm Di-n-butyl sulfide (sulfur SAC) and 2000ppm Quinoline (nitrogen SAC) at 25°C, 70°C, & 110°C.

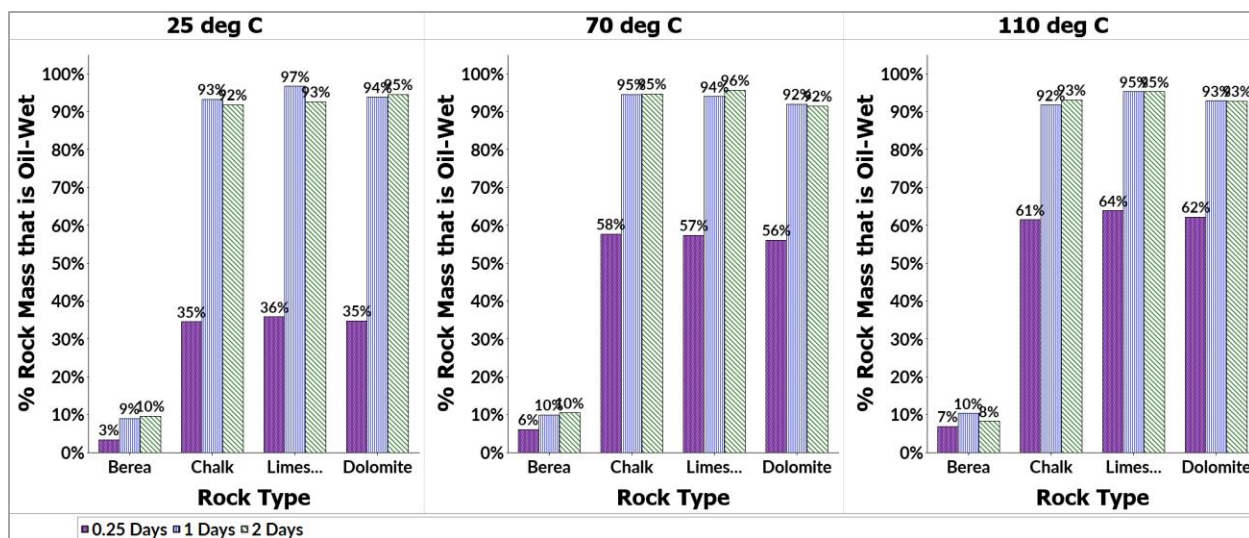


Figure A5: 6 hrs, 1 day, & 2 days aging time for decane +2000 ppm Quinoline (nitrogen SAC) at 25°C, 70°C, & 110°C.

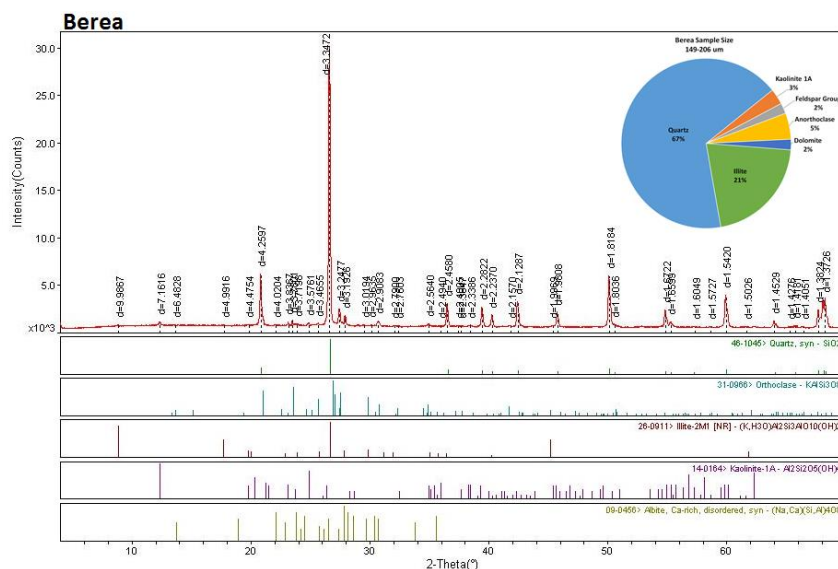


Figure A6: Sandstone Berea XRD mineralogy results.

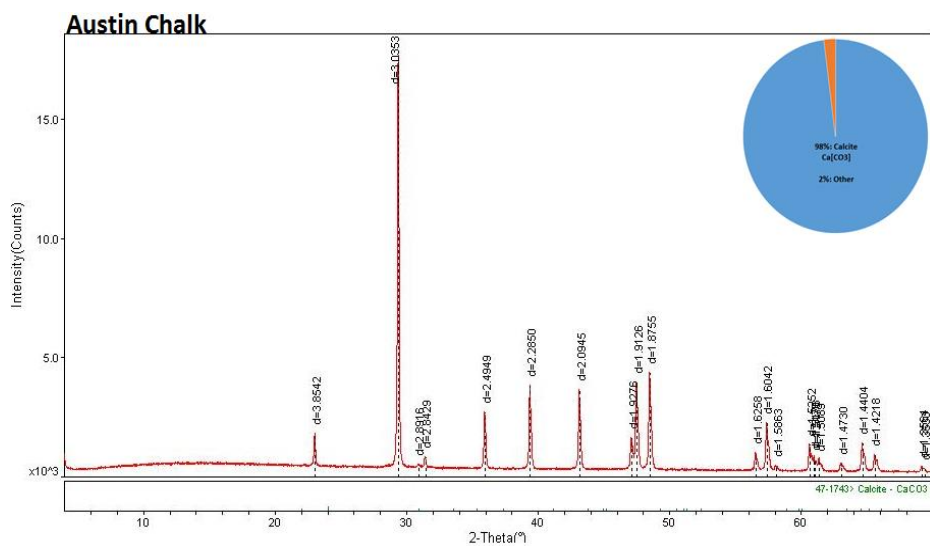


Figure A7: Austin chalk XRD mineralogy results.

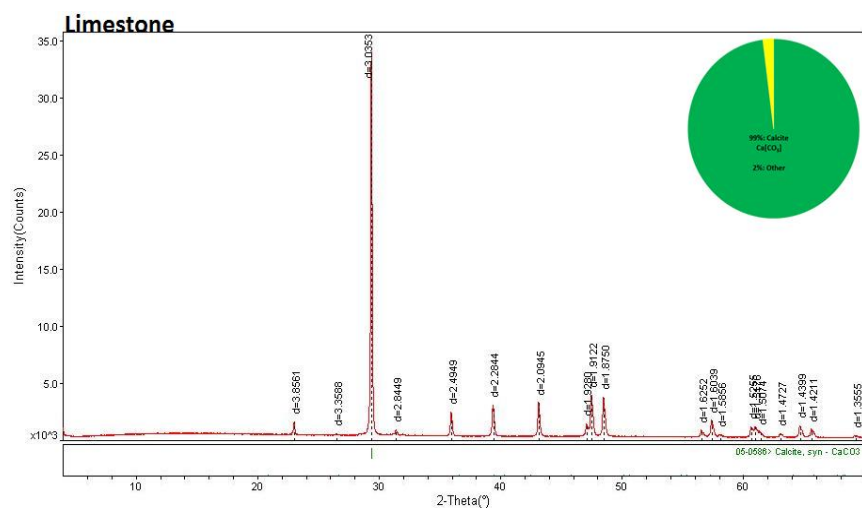


Figure A8: Indiana limestone XRD mineralogy results.

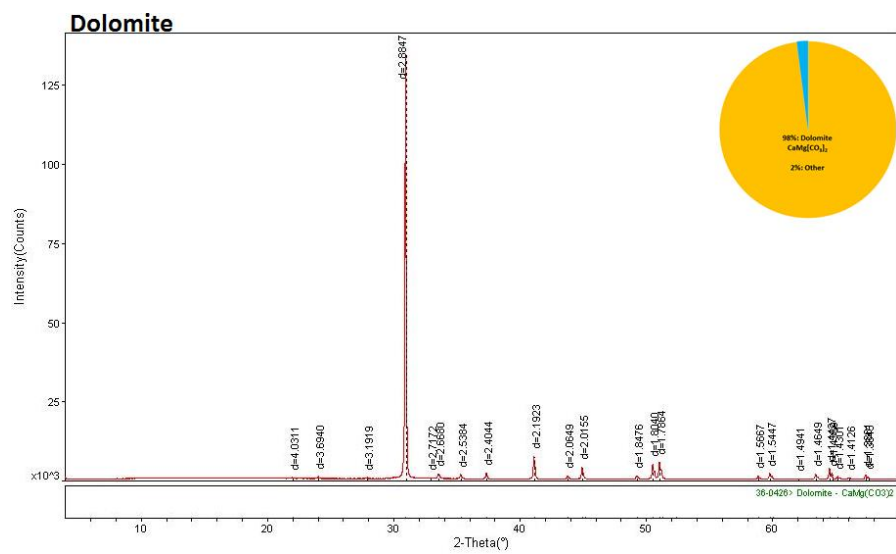


Figure A9: Silurian dolomite XRD mineralogy results.

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.

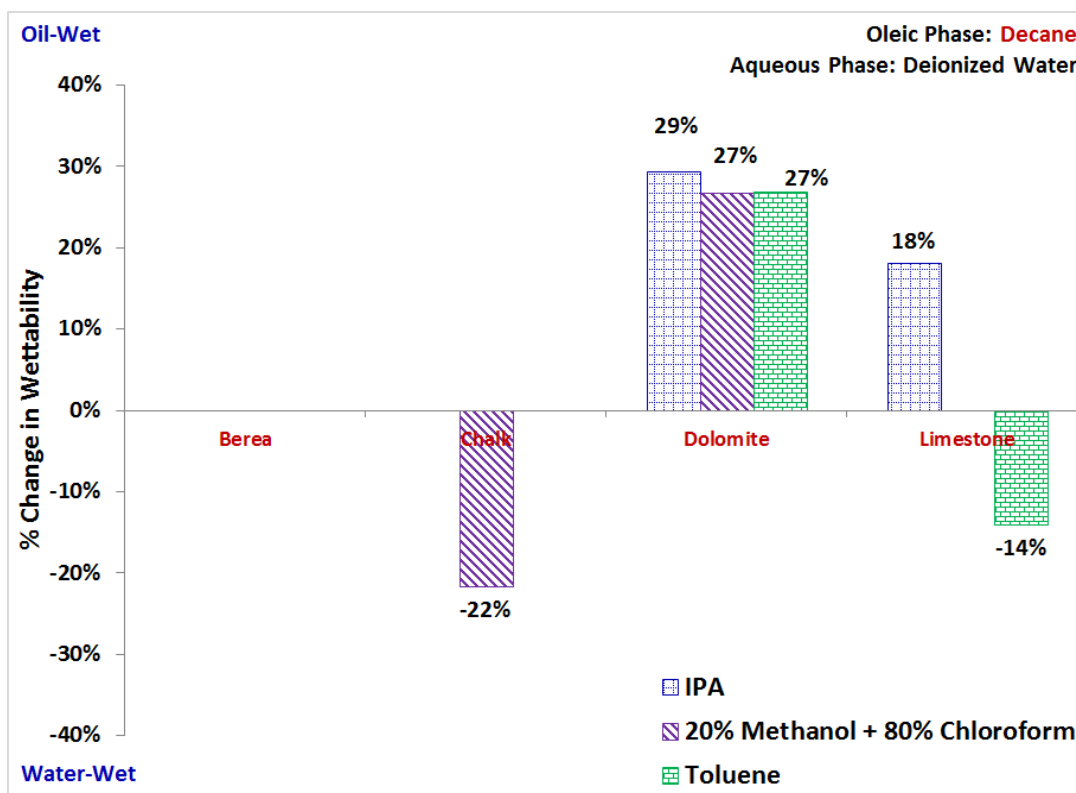


Figure B1: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of decane and DI water

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.

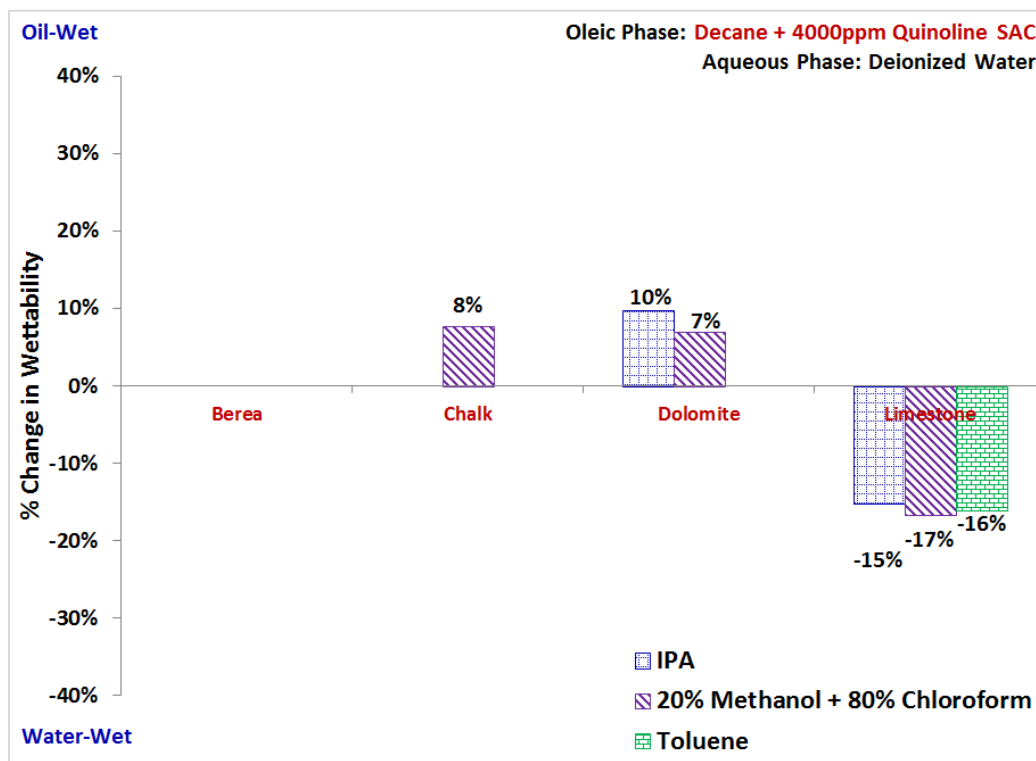


Figure B2: Effects of selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of decane + basic (quinoline) SAC and DI water.

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.

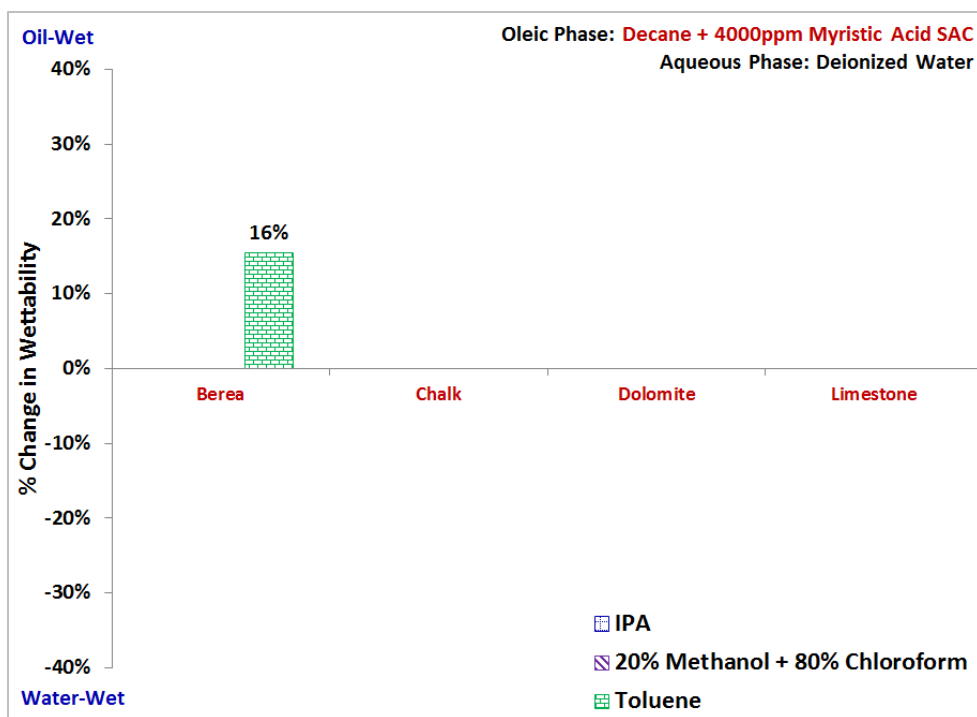


Figure B3: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of myristic acid.

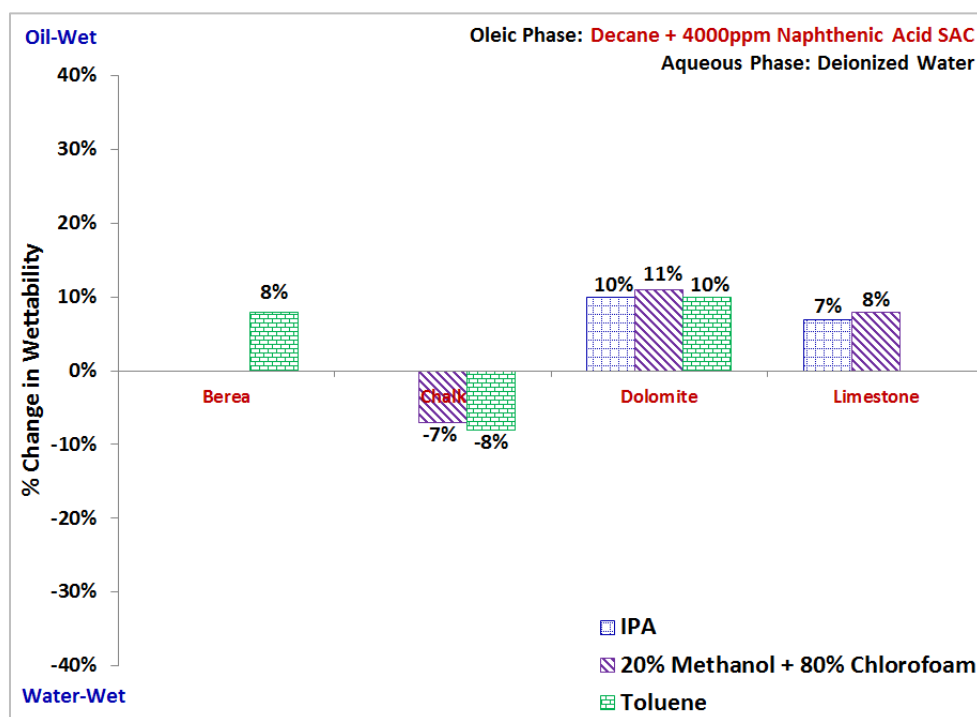


Figure B4: Effects of the selected cleaning solvents on the wettability of Berea, Austin chalk, Silurian dolomite, and Indiana limestone in the presence of naphthenic acid.

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 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 interest 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.