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B.S. Thesis

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The Effects of Surface-Active Chemicals on Wettability of Conventional and
Unconventional Formations.

B.S.E Thesis

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2022-2023

Approval

We certify that we have read the thesis submitted by titled **“The Effects of Surface-Active Chemicals on Wettability of Conventional and Unconventional Formation.”** and that in our combined opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Bachelor in Science and Engineering.

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Declaration

I hereby declare that all information, documents, analysis and results in this thesis have been collected and presented according to the academic rules and ethical guidelines of Palacky University, Olomouc. I also declare that as required by these rules and conduct, I have fully cited and referenced information and data that are not original to this study.

Yousif H. AL-SHAAYA

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Day/Month/Year

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Yousif H. AL-SHAAYA

Abstract

This study investigates how surface-active chemicals (SAC) in crude oil impact the wettability of reservoirs. Wettability refers to a reservoir rock's relative susceptibility for oil or water. Both the efficiency of oil recovery procedures and the distribution of fluids in a reservoir are affected by the wettability of the reservoir. Unfortunately, it is yet unknown how chemical agents regulate the wettability of certain reservoirs. Temperature, fluid chemistry, and rock mineralogy all influence the wettability of a substance. An experiment was done to determine the impact of naturally occurring SACs, usually found in crude oil, on the wettability of sandstone and carbonate rocks at a range of salinities and temperatures. In this experiment, pure decane and SACs were combined to simulate the oleic phase in order to identify the effects of certain SACs. The four SAC groups being studied are aromatic, oxygen-containing, sulfur-containing, and nitrogen-containing SACs. According to this study, it is essential to describe crude oil, brine, and reservoir rock exactly in order to comprehend why low salinity waterflooding boosts oil recovery in some reservoirs but not others. This enables the efficient modification of injection water chemistry to increase oil recovery and improve wettability. Overall impacts toward either oil-wet or water-wet conditions were shown to be more reliant on temperature than brine salinity. As salinity decreased as a result of nitrogen SACs, non-acidic sulfur SACs, and short-chained oxygen SACs, the wettability of carbonate rocks moved toward circumstances where they were wet with water. extended-chain acids SAC As the salinity of the brine decreased, SACs, acidic sulfur SACs, and aromatics modified the wettability of carbonates to oil-wet conditions. It was postulated that differences in how SACs respond to salt are one of the reasons why low salinity waterflooding works in certain reservoirs but not in others.

Annotation

Tato studie zkoumá, jak povrchově aktivní chemikálie (SAC) v ropě ovlivňují smáčivost uložišť. Smáčivost se týká relativní náchylnosti horniny na ropu nebo vodu. Jak účinnost postupů získávání ropy, tak distribuce kapalin v nádrži jsou ovlivněny smáčivostí uložiště. Bohužel dosud není známo, jak chemické látky regulují smáčivost některých uložišť. Smáčivost látky ovlivňuje teplota, chemismus kapalin a minerální složení hornin. Byl proveden experiment s cílem určit, jak přirozeně se vyskytující SAC, které jsou obvykle přítomny v ropě, ovlivňují smáčivost pískovcových a karbonátových hornin za různých hodnot salinity a teploty. V tomto experimentu byl zkombinován čistý dekan a SAC, které simulují ropnou fázi, k identifikaci účinků určitých SAC. Čtyři studované skupiny jsou: aromatické SAC a SAC obsahující kyslík, síru a dusík. Podle této studie je nezbytné přesně popsat surovou ropu, solanku a okolní horninu, abychom pochopili, proč zaplavení nízkosalinitní vodou podporuje těžbu ropy na některých ložiscích a na jiných ne. To umožňuje účinnou modifikaci chemie vstříkované vody pro zvýšení regenerace ropy a zlepšení smáčivosti. Ukázalo se, že celkové dopady na podmínky smáčivého ropy nebo vody jsou více závislé na teplotě než na slanosti solanky. Pokud se slanost snížila v důsledku dusíkatých SAC, nekyselých sirných SAC a kyslíkatých SAC s krátkým řetězcem, smáčivost karbonátových hornin se posunula směrem ke stavu, kdy byly mokré vodou. Kyseliny s prodlouženým řetězcem SAC Jak slanost solanky klesala, SAC, kyselé sirné SAC a aromatické látky modifikovaly smáčivost uhličitánů na podmínky mokra olejem. Bylo zjištěno, že rozdíly v tom, jak SAC reagují na sůl, jsou jedním z důvodů, proč zaplavování s nízkou slaností funguje v některých nádržích, ale ne ve všech.

Keywords:

SACs: Surface active chemicals

EOR: Enhanced Oil recovery

PPM: Part-Per-Million

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List of Abbreviations

SACs: Surface active chemicals

EOR: Enhanced Oil recovery

PPM: Part-Per-Million

DDDC: Dual Drop Dual Crystal

CHAPTER I

Introduction

It is difficult for the oil and gas industry to maximize oil recovery from current hydrocarbon reserves in order to meet the rising global energy demand. Currently, the average worldwide field recovery by waterflooding is 35 percent, leaving 60 to 70 percent of the oil in place (Shell, 2016). This is a substantial opportunity for enhanced oil recovery (EOR) techniques. EOR technologies attempt to mobilize crude oil by lowering interfacial tension (IFT) and/or modifying wettability to a favorable wetting state. The concept of modifying and engineering the injected water's chemistry has emerged as a promising EOR technique, referred to by various names such as "low salinity waterflooding" (Lager et al., 2008), "designer waterflooding" by Shell (Ligthelm et al., 2011), and "advanced ion management" by ExxonMobil (Gupta et al., 2009). Wettability, which results from the equilibrium of surface forces between oil and water interactions with the rock's surface, describes the reservoir rock's relative preference for oil or water. Depending on the exact interactions, a system's wettability can range from being very water-wet to highly oil-wet. According to the findings of this study, oil chemistry, water chemistry, rock form and mineralogy, temperature, and degree of wetness all influence a rock's position on the wettability continuum. At the grain level, wettability is homogenous, meaning that it is either water-wet or oil-wet. Reservoir-scale wettability is heterogeneous or fractionally moist (Brown & Fatt, 1956). According to fractional wettability, a portion of the rock is oil-wet and the other portion is water-wet. Two forms of heterogeneous/fractional wettability are mixed and speckled/spotted/dalmatian wettability. Salathiel (1973) proposed mixed-wettability, in which oil-wetted surfaces constantly pass through larger pores while tiny pores remain water-wetted and oil-free. Speckled, spotted, or dalmatian wettability refers to continuously wet surfaces with patches of occasionally oil-moist surfaces, and vice versa (Morrow et al., 1986; Cuiec, 1991). Understanding the distribution of fluids inside a reservoir necessitates familiarity with wettability. It is also necessary for the development of more effective and efficient oil recovery methods. Wettability, however, has proven to be a hard geochemical issue due to the fact that it is governed by a multitude of reservoir parameters. Standard wettability measurement techniques are limited by the time (days to weeks) and expense (thousands of dollars) necessary to conduct a single experiment, which exacerbates the problem. This presents a considerable bottleneck for laboratory experiments. Consequently, it is unknown which chemical

mechanisms determine the wettability of certain reservoirs. Understanding how oil surface active chemicals (SACs) impact a reservoir's ability to retain water in carbonate and sandstone is the goal of this study.

CHAPTER II

Literature Review

2.1 Oil-Formation adhesion dynamic

Wettability is an indicator of the equilibrium between cohesive and adhesive forces. When oil is used to moisten a rock in the presence of water, cohesion forces inside the oil cause a drop to ball up and avoid contact with the rock surface (water-wet). Oil spreads across the rock's surface as a result of adhesive forces (oil-wet). Oil-rock adhesion is presumably regulated at the molecular level by electrostatic (and van der Waals) interactions (Dubey & Doe, 1993; Buckley et al., 1989). (Dubey & Doe, 1993; Buckley et al., 1989), Electrostatic interactions are governed by aqueous chemistry, petroleum chemistry, rock mineralogy, and temperature. The interaction of charged oil and mineral surfaces causes electrostatic forces (Busireddy and Rao, 2004; Israelachvili, 2011). (Busireddy and Rao, 2004; Israelachvili, 2011), Due to the separation of polar molecules of nitrogen and oxygen at the oil-water interface, the oil surface is charged. Mineral surfaces are charged because broken, unsaturated bonds hydrate at the mineral-water interface. The effects of electrical interaction might be either repellent, attractive, or both (Hirasaki, 1991). According to (Hirasaki, 1991), Three factors have historically made it difficult to establish a quantitative relationship between electrostatics and wettability and oil recovery: (1st) multiple electrostatic mechanisms can operate simultaneously, making it impossible to determine the individual contributions; (2nd) experimental and field data from cores are the sum of chemical and physical processes, making it difficult to isolate the specific chemical role of surface charge; and (3rd) surface charge measurement techniques have not been able to distinguish the chemical role of surface charge (Brady et al., 2015).

The charged sites at the crude oil-water interface, known as SACs, are what govern wettability and recovery by reacting electrostatically with the rock surface. SACs are composed mostly of nitrogen bases and carboxylic acids when they are connected to non-polar hydrocarbon chains or rings. This study evaluates a newly developed wettability testing technique by analysing the effect of particular SACs on oil adhesion to carbonate and sandstone minerals.

2.1.1 Forces that influence Oil-Formation interactions

Van der Waals: The van der Waals force, which frequently results from molecular-scale polarization between particles, is attractive and acts between two materials. Despite being weaker than electrostatic or hydrogen bonding interactions, this force is always present.

As the oil and mineral double layers approach one another, electrostatic forces will interact. Coulomb's law controls the interaction between two charged substances when they come near together in a vacuum. The Debye length, which is inversely related to the square root of the electrolyte concentration, is the distance at which the electrical field near a charged surface decays practically exponentially.

While van der Waals and electrostatic forces are long-range interactions, structural forces occur at a distance of less than 5 nm. These forces are generated when two surfaces meet at a distance of a few orders of molecular diameter. Surface interactions cannot be described by continuum theories of attractive van der Waal and repulsive double layer forces (Israelachivili, 2011).

2.2 Influence of Environment on Oil-Formation Interaction.

2.2.1 Effects of Minerology, Chemistry and Salinity:

All reservoir rocks are originally moist with water. Water-rich sandstone and carbonate reservoirs are buried. The nature of rock also impacts how the various polar compounds can change rock wettability. Despite reservoir solution chemistry, sandstone surfaces are anionic while limestone surfaces are cationic (Brady et al., 2012). Sandstone reservoirs include quartz, feldspar, oxides, carbonates, and clays. The smaller particle size, plate-like structure, and much higher surface areas of clay minerals cause them to commonly predominate the reactive surface area observed by oil. They have positively charged edges and negatively charged faces when wet. Oil adherence is likely mediated by electrostatic interaction between positively charged oil surface groups and negatively charged clay basal planes in sandstones containing clays such as illite or smectite (Brady et al., 2013). (Brady et al., 2013). The quantity of charged oil surface groups is based on the history of the oil and the chemistry of the oil and the connate fluid, whereas the amount of negatively charged basal plane clay groups is set by lattice composition (e.g. pH, brine salinity, brine composition) (e.g. pH, brine salinity, brine composition). The production of electrostatic "bridges" and oil adhesion, which raises the degree of oil wetting, should be supported by the presence of high numbers of nitrogen bases and calcium-terminated carboxyl groups (Alotaibi et al., 2011). (Alotaibi et al., 2011). Reducing calcium-terminated carboxyl groups and nitrogen bases makes the formation more water-wet, improving oil mobility and recovery. Carbonates have more sophisticated surface chemistry than sandstones. Anhydrite, clays, pyrite, Mg-rich calcites, and dolomite induce this (Ferno et al., 2011). Precipitation and dissolution alter carbonate rock surface chemistry (Hiorth et al., 2010). Brady et al. (2012) found that calcium and carbonate ions governed the surface potential of calcite, not hydrogen and hydroxide ions. Calcium ions boost calcite's surface charge, unlike carbonate and sulfate.

The aqueous chemistry however with the pH, ion concentration, and salinity of the pore water impact the oil and mineral surface charge and, subsequently, the system wettability. Temperature also impacts how wettable a material is in relation to water chemistry. Several organizations have achieved enhanced oil recovery from sandstone and carbonates by modifying the chemistry of floods (e.g. Lager et al., 2006; Zhang et al., 2006; Rezaei Doust & Puntervold, 2009). (e.g. Lager et al., 2006; Zhang et al., 2006; Rezaei

Doust & Puntervold, 2009). The surface charge of crude oil and reservoir rock is regulated by brine composition and salinity, which in turn determines the system's subsequent wettability (Brady et al. 2012). (Brady et al. 2012). Ions like sulfate, calcium, and magnesium can attach to mineral surfaces, changing the surface charge and perhaps affecting polar oil adsorption. Brine salinity and composition affect charged oil component concentration at the oil-water contact. This affects oil surface charge. Ions can also form complexes with polar oil components, changing their solubility in the oil phase.

Additionally, some companies have undertaken in-depth studies on the influence of brine salinity on wettability (Tang & Morrow, 1999; Lager et al., 2006; Zhang et al., 2006). (Tang & Morrow, 1999; Lager et al., 2006; Zhang et al., 2006). The University of Wyoming's Morrow group started this research on low-salinity brines' effects on wettability and oil recovery. These research have made oil and gas companies aware of how injected water chemistry may affect oil recovery. Most researchers believe low salinity brines improve wettability and oil output. However, a substantial number of study teams have revealed that low salinity water injection has no appreciable influence on oil recovery (Al-Shalabi et al., 2014). (Al-Shalabi et al., 2014). Low salinity waterflooding in Wyoming's Powder River Basin fields was evaluated (Thyne and Gamage et al., 2010). They found no difference in recovery between the 24 fields that received low salinity water and the 22 that received mixed or formation water. In 32 of these 46 fields, injected water salinity was considerably decreased, whereas in the remaining 10 fields it was only marginally reduced. Salinity decrease and oil recovery were unrelated. Boussour et al. (2009) tested a reservoir core sample with low salinity waterflooding but found no increased oil recovery. In this study, it is suggested that the inconsistent results are generated by the use of difficult materials (such as crude oil and reservoir rock) in experiments with a wide range of unknowns.

2.2.2 Influence of Oil chemistry and Temperature

Oil chemistry has a major impact on the wettability of a system. The base number (BN), which is frequently much higher than the acid number (AN), is a measurement of the crude oil's basic composition. Acid number (AN) is a measure of crude oil's acidic content (Punternold et al., 2007). Since naphthenic acids in crude oil possess the highest surface adsorptive capabilities, they may function as "anchor" molecules for other surface-active components also present in crude oil (Standnes & Austad, 2003). Due to the negative disjoining pressure, the thin water layer that forms between the negatively charged oil-water interface and the positively charged chalk surface becomes unstable, and the oil may make contact with the chalk surface. Carboxylates from the oil may stick to the chalk's surface and diminish its wetting ability (Thomas 1993). Thus, (AN) could determine the water's moisture content. Increasing AN increases the possibility of carboxylates clinging to the chalk surface and decreases the rock's capacity to absorb water. Additionally, steric acid was shown to promote oil-wetting (Thomas et al., 1993; Karoussi and Hamouda, 2007). As the AN increases, water humidity decreases. (Punternold et al., 2006) examined the influence of basic components on the wetting properties of chalk using oil with a constant AN of 0.5mg KOH/g oil and varying AN/BN ratios between 0.24 and 4.6. They used the basic chemical benzyl amine and discovered that when the base content increased to approximately four times the acid concentration, the water wetness decreased.

Nonetheless, it has been demonstrated that temperature has a significant effect on wettability. (Rao, 1999) revealed that when the temperature rises, sandstone reservoirs become normally more oil-wet and carbonate reservoirs become typically more water-wet. According to (Schembre et al., 2006), when water is pumped into a reservoir, the temperature changes, causing oil-wet surface particles to separate and leaving a water-wet surface. One result is that wettability changes during oil displacement by water and that oil displacement by water may vary with respect to its wettability. Schembre's results may explain the wettability behavior in sandstones, where systems grow more water-wet as temperature decreases, utilizing Rao's arguments and other comparable conclusions, but they do not account for the observed behavior in carbonates. In addition, research has demonstrated that decarboxylation of carboxylic substances happens at elevated temperatures and that carbonate may accelerate this process (Shimoyama & Johns 1972). Due to the decrease in AN, this action decreases the acid number (AN) to base number (BN) ratio and increases the oil-wetness of the system.

2.3 Measurement Methods

Amott and USBM tests are the most prominent quantitative methods for assessing wettability status (Amott, 1959; Donaldson et al., 1969; Sharma & Wunderlich, 1987). Both methods yield an estimate of the macroscopic average wettability of the rock-oil-brine system. Some of the methods used to measure wettability include the US Bureau Method (USBM), permeability/saturation relations, wire-line logs, imbibition rates, production performance, capillary pressure curves, relative permeability curves, microscope examination, flotation, nuclear magnetic resonance (NMR), displacement capillary pressure, dye adsorption, and capillary metric methods (Amott, 1959; Donaldson et al., 1969; Sharma & Wunderlich, 1987).

Contact angle is frequently used as an indication of wettability, and it is most accurate when applied to pure fluids and synthetic cores. This approach is recommended because it is more efficient than flow measuring methods. The ability to directly test wettability in reservoir conditions is an added advantage. This technology's downside is the hysteresis induced between the water-advancing and water-retreating angles. On a macromolecular scale, surface roughness, surface heterogeneity, and surface immobility may all contribute to contact angle hysteresis, as demonstrated by Anderson (1986). In addition, polishing the coarse mineral sample is required prior to cleaning it with various leaches and solvents. Any of the aforementioned mineral sample pretreatments may have an effect on the surface roughness and surface composition of the sample (Somasundaran, 1970; Kulkarni & Somasundaran, 1973, 1977).

Changes in the equilibrium contact angle and the kind of hysteresis, both of which are essential for determining the oil saturation, can be caused by changes in surface variations of comparable magnitude. In 1956, Brown and Fatt advocated discarding the concept of a reservoir rock contact angle. Due to the heterogeneous mineral composition of the bulk of reservoir rocks, each has a distinct surface chemistry and the ability to adsorb surface active components from reservoir fluids. Because of this, they offered this idea. Given the extraordinarily complex geometry of a pore, it is difficult to envision how a contact angle determines the structure of a fluid-fluid interface, according to the researchers. Some measurement methods used are shown in Figure (1).

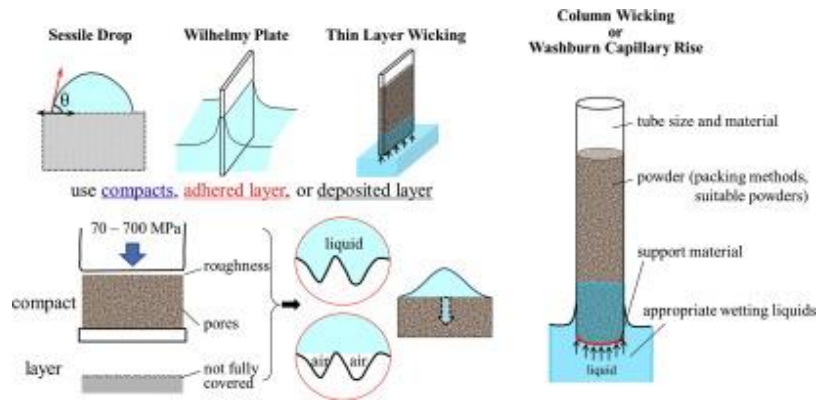


Figure (1): Measurement techniques used.

Over a century of extensive utilization of flotation techniques in the mining industry (Nguyen, 2004). A physicochemical process known as flotation is utilized to separate finely crushed particles based on their wettability. This wettability testing method has long been considered as a qualitative method for assessing wettability in the oil and gas industry (Anderson, 1986). Celik and Somasundaran (1980) examined the wettability of reservoir minerals using flotation and compared the results to data on adsorption and zeta potential. Both surfactant adsorption and mineral flotation exhibited a maximum micelle concentration very close to the critical value, as demonstrated by their research. Dubey and Doe (1993) used flotation to examine how crude oil's acid and base numbers affected its wetting properties. Using model compounds, Wu et al. (2008) investigated the wetting behavior and surfactant EOR of carbonates via flotation. Using MFT, the potential for alternative injection water compositions to increase wettability was evaluated. They discovered that a combination of flotation tests and geochemical simulations can be used to evaluate the potential for available injection water compositions to increase wettability. According to their findings, this combination has the potential to determine whether cation bridging or direct adsorption is the predominant wetting process.

2.4 Sandstone formation-wettability dynamic

Forty to fifty percent of the world's oil reserves are located in reservoirs composed of sandstone. Sandstone reservoirs are composed of negatively charged quartz and clays. Due to their significant negative charge and large surface area, clays have a tendency to absorb cationic SAC components from crude oil. In the past decade, low salinity waterflooding in sandstone reservoirs has gained considerable attention (e.g. Tang and Morrow, 1999; Morrow & Buckley, 2011; Winoto et al., 2012). Multiple laboratory and field investigations have demonstrated that altering the composition of the brine may greatly boost oil recovery (10–30% of OOIP).

This technique is extensively utilized because it is cost-efficient, water is easily accessible, it is straightforward to implement on-site, and it is excellent in replacing light to medium gravity crude oils. In the laboratory and in the field, injecting low-salinity brine into carbonate and sandstone reservoirs has been shown to boost waterflood efficiency (Robertson, 2010; Hadia et al., 2013; Aladasani et al., 2014; Myint & Firoozabadi, 2015). When conducting coreflooding investigations on sandstone cores, (Gamage & Thynn, 2011) proved the advantages of adopting low salinity water injection in secondary mode rather than tertiary mode by producing 6 to 20% more oil.

The low salinity effect is believed to be caused by a variety of factors. In all theorized low salinity waterflooding processes, the adhesion of oil SACs to the rock surface is stated. In order to establish forecasts for low salinity waterflooding, the role of SAC adhesion must be quantitatively evaluated and comprehended.

According to (Tang and Morrow, 1999), the mobility of tiny particles, notably kaolinite, can greatly affect the sensitivity of oil recovery to salt. They concluded that the idea that heavy polar components of crude oil adsorb onto particles and pore walls to create mixed wetness might explain a range of facts about oil recovery and wettability. Clay fines are aged when in contact with and exposed to crude oil, resulting in the formation of mixed-wet particles. Since the fines movement revealed the underlying surfaces, increasing the water-wetting of the system, the development of oil droplets on these clays would contribute to the system's transformation into a more water-wetting system. In the presence of high salinity brine, clays stay undisturbed and maintain their oil-wet condition, resulting in decreased displacement efficiency (Lager et al., 2006). In the presence of low salinity water, clay particles will detach from the surface of the

pores. Unfortunately, clay migration can plug pore throats and reduce permeability while fluid is moving (Lever and Dawe, 1984).

2.4.1 Salinity and Migration in Sandstone formations

(Tang & Morrow, 1999) and (McGuire et al., 2005) reported a pH increase with low salinity injection in Sandstone and North Slope field samples. According to (McGuire et al., 2005), low-salinity processes resembling alkaline floods may be caused by an increase in pH and a drop in IFT. It has been proposed that this increase in pH is the result of hydrogen ions in the water exchanging with sodium ions that have been adsorbed (Mohan et al., 1993). A moderate variation in the bulk pH of the rock can have a considerable effect on its zeta potential. When the pH rises, organic molecules may be absorbed from clay surfaces (Austad, 2013).

According to Austad et al. (2010), the following elements are critical for low salinity effects in sandstones: (1) rock mineralogy (such as clay properties, kind, and quantity); (2) crude oil chemistry (such as SACs); and (3) aqueous chemistry (e.g. brine composition and pH). According to the suggested method, polar components and active cations must be adsorbed onto clay first (Austad et al., 2010). The adsorption and desorption windows of clays vary. Clay minerals having a high cation exchange capacity are often helpful for researching the influence of low salinity. At a pH of around 5 in the reservoir, organic material, active cations, and protons initially balance-adsorb onto the clay minerals. A typical acid-base interaction occurs between OH⁻ and the adsorbed acid and protonated base, which promotes the desorption of organic molecules. The oil recovery rate increases as the water's moisture content increases. Due to calcium ions being replaced by hydrogen ions on the surface of the clay, injection of low salinity brine would result in the desorption of adsorbed cations, elevating the pH along the water-clay interface. Due to the fact that the rock is already saturated with water, the low salinity EOR impact will be negligible if there is little organic material adsorption and an abundance of active ion adsorption. As long as the concentration of active ions is low enough to promote considerable desorption from the clay surface, the composition of the injected low-saline water may not be critical.

2.5 Carbonate formation-wettability dynamic

According to (Chilingar and Yen, 1983), 15% of the 161 carbonate rocks investigated were highly oil-wet, 65% were oil-wet, 12% were intermediate-wet, and 8% were water-wet. In fractured and low-permeability carbonate reservoirs, oil displacement from matrix blocks by spontaneous imbibition of the injection fluid is the major driving factor for achieving high oil recovery. The adverse wetting state of carbonates limits the spontaneous absorption of water (and ejection of oil) into the matrix due to negative capillary pressure. The spontaneous imbibition of wettability-altering water into fractured reservoirs of chalk, limestone, and dolomite is a key secondary oil recovery technology (carbonate reservoirs). Under water-wet to mixed-wet conditions, the strategy appears to be rather effective (Thomas et al., 1987). By modifying the wettability of the rock surface to a more favorable water-wet state, the capillary pressure can be increased to promote spontaneous imbibition into oil-wet carbonate matrices and improve oil recoveries. To do this, one must first know the relationship between wettability and SACs.

Carbonates in brines with pH values near to neutral have positively charged and weakly basic surfaces (Anderson, 1986). Due to the carboxylic acids in the oil, the contact between rock and brine is positively charged, whereas the interaction between oil and brine is negatively charged. Due to the electrostatic attraction caused by opposing charges on the oil/brine and mineral/brine surfaces, the brine coating tends to weaken and the oil may come into direct contact with the mineral surface (Hiraski et al. 2004).

Low salinity waterflooding is a newly discovered EOR technology for modifying the wettability of carbonate reservoirs. The influence of low salinity water injection in carbonate reservoirs has not been examined as thoroughly as in sandstone reservoirs. Low salinity waterflooding of sandstone reservoirs modifies their wettability due to the presence of clay (Lager et al., 2006; Doust et al., 2009). Only a few field-scale low-salinity waterflood projects have been reported, including those at the Ekofisks and Valhall oil fields (Sylte et al., 1988; Hallenbeck et al., 1991). The discovery of an abnormally significant oil recovery by injecting saltwater into the fractured Ekofisk chalk reservoir of the North Sea aroused interest in modifying the water chemistry in the injected water (Sylte et al., 1988; Hallenbeck et al., 1991).

2.5.1 Effects of Rock Dissolution and Salinity

Increased oil recovery due to changing brine chemistry of injection water has been connected to increased wettability of carbonates. Fundamental findings from laboratory tests and real-world settings reveal that altering the water's chemistry improves oil mobility underflow and imbibition, indicating that the water's wettability has altered. The bulk of observed data attributed increased oil recovery to wettability shifting to a more water-wet or mixed-wet state (Yousef et al., 2010, 2011; Fathi et al., 2006; Zhang et al., 2006, 2007; Strand et al., 2006). (Sharma et al., 2000; Agbalaka et al., 2008; Hazim et al., 2013). As wettability modification options, decreasing the total salinity of the injected water and adding potential determining ions are proposed. However, there is limited consensus on a single basic mechanism behind the impact of low salinity. This is due to the complex interaction between crude oil, brine, and rock, as well as a number of contradicting experimental findings. Therefore, either there are many mechanisms in play or the optimal method for enhancing oil recovery using chemically modified water has not yet been identified (Suijkerbuijk et al., 2012).

Calcium carbonate from the rock dissolves and reaches equilibrium with the low-salinity brine as a result of the brine's lower calcium concentration (Hiorth et al., 2010). As the calcium carbonate dissolves, the components of the adsorbed oil are liberated, leaving the rock surface moist. During carbonate dissolution, an excessive quantity of OH⁻ will increase the pH. In Middle Eastern reservoir limestone coreflooding tests, Gupta et al. (2011) observed that soft water dissolved a small amount of rock, desorbing a portion of the oil, and changing the wettability towards a more water-wet state. In carbonate coreflooding investigations conducted under reservoir conditions, (Yousef et al., 2012) investigated pore coupling and revealed that microscopic anhydrite dissolution was responsible for the link between micro and macro pores. Utilizing geochemical modeling to evaluate the concept of rock dissolution, (Hiorth et al., 2010) concluded that chemical dissolution of calcite appears to be the primary factor.

CHAPTER III

3. Methodology

3.1 Research Questions

How do surface active compounds affect wettability?

How do surface-active compounds interact with Oil, Brine and Formation dynamic?

How can surface-active compounds be used to enhance recovery rate?

Can surface active compounds be used in EOR?

3.2 Research Design

This section describes the components and methods used to explore how surface active compounds alter wettability in relation to rock mineralogy, brine chemistry, and temperature.

3.2.1 Rock Samples

Sandstone, shale, and carbonate were the three reservoir materials taken into consideration. In experiments, the impact of brine composition on sandstone, shale, and carbonate rocks was investigated. All of the rocks originated in various regions of Czechia. As seen in Figure 2, the four rock samples were pulverized and sieved into five sizes: 50 m, 50-100 m, 100-150 m, and >200 m. Grain size distribution of 50–200 m was employed in this project. The mortar, pestle, and sieves were thoroughly cleaned in order to prevent contamination. To do this, the following steps were taken: blast the equipment with 110 psi air inside a fume hood until all loose powder is removed; rinse with DI water; dry with air; then crush a small quantity of the target rock into a fine powder; use the powder to scrub the equipment's surface in an effort to remove any contamination that may have become stuck to the surface. The equipment is then ready for use after the possibly contaminated powder has been decanted.



Figure (2): Grinding process of rocks.

3.2.2 Oil & Brine Samples

This experiment employed model oils mixes of pure decane and surface-active compounds to replicate the oleic phase in order to separate the impacts of specific SACs. A model oil can only loosely match natural petroleum since it is a complicated brew of organic components. Model oils, however, are a helpful tool for separating the impacts of various SACs on wettability. Aromatic, oxygen-bearing, sulfur-bearing, nitrogen-bearing, and a natural condensate sample are the four types of SAC that were examined. The SACs used in this investigation are listed in Table (1).

Table (1): Oil sample contents

Surface-active compounds	Chemical compound	Chemical formula	Molecular weight (g/mol)
Oxygen	Acetic Acid	CH_3COOH	60
	Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	227
	Naphthenic acids	$\text{C}_7\text{H}_{10}\text{O}_2$	125
Nitrogen	Carbazole	$\text{C}_{12}\text{H}_9\text{N}$	165
	Quinoline	$\text{C}_9\text{H}_7\text{N}$	130

	Pyridine	C ₅ H ₅ N	80
Sulfur	Dibenzothiophene	C ₁₂ H ₈ S	185
	Di-n-Butyl Sulfide	C ₈ H ₁₈ S	147
	1-Tetradecanethiol	CH ₃ (CH ₂) ₁₃ SH	231

The condensate was provided by a significant oil corporation. This fluid is transparent, and its specific gravity, density, and viscosity at 20 degrees Celsius are 60°API, 0.8 g/cm³, and 1.03 cp, respectively. The condensate's constituents are listed in Table 2.

Table (2): Oil sample datasheet

Components	Carbon No.	% Mole	% Weight
Methane	C1	0.002	0.003
Ethane	C2	0.05	0.010
Propane	C3	0.891	0.4
i-Butane	iC4	1.16	0.7
n-Butane	nC4	3.6	2
i-Pentane	iC5	4.35	3.5
n-Pentane	nC5	5.6	3.8
Hexane	C6	12.6	10
Heptane and above	C7	71.5	80
Total	100.00	100.000	100.00

Deionized water was used for baseline experiments, and then various salts were added to create chemically distinct brines in order to separate the specific impacts of brine composition on wettability.

Table(3): Brine sample datasheet

Brine	NaCl	Na ₂ CO ₃	NaSO ₄	NaHCO ₃	CaCl ₂	AlCl ₃	MgCl ₂	FeCl ₃	Salinity (ppm)
1	Water (Deionized)								0
2	900	-	30	10	30	-	30	-	1,000
3	9000	-	300	100	300	-	300	-	10,000
4	90,000	-	3,000	1,000	3,000	-	3,000	-	100,000

3.3 Sample Preparation

All of the rock samples that were used to assess the wettability were pulverized and sieved into a fine powder. Dolomite rocks were cut and polished into thin wafers for use in the contact angle investigations. The wafers were cleaned before the contact angle tests using a combination of 20% methanol and 80% chloroform.

Two thousand ppm of surface-active compounds were added to pure decane to produce ten model oils. Decane is not polar, is not surface reactive, and does not include SACs. Therefore, the additional SAC is responsible for any observed change in wettability from that of the baseline decane. I examined the wettability of the condensation.

3.4 Measurement methods

3.4.1 Contact angle

When using pure fluids and artificial cores, the contact angle is the most precise method for measuring wettability. This is the preferred method for testing wettability since it is quicker than the methods for measuring flow. In addition, it provides the added benefit of assessing the reservoir's wettability immediately. As seen in Figure (3), a surface is deemed water-wet when the contact angle is less than 75 degrees, neutral-wet between 75 and 105 degrees, and oil-wet above 105 degrees.

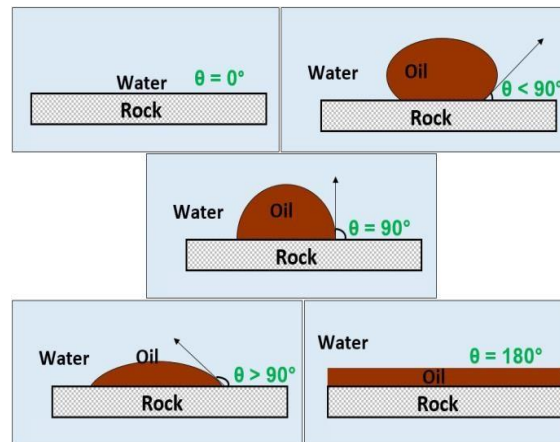


Figure (3) Contact angle demonstration.

This approach is affected by the hysteresis produced by the water-advancing and water-retreating angles. Anderson (1986) demonstrated that on a macromolecular scale, surface roughness, surface heterogeneity, and surface immobility can generate contact angle hysteresis. In addition, this method necessitates the preparation of the coarse mineral sample by polishing, followed by cleaning with a variety of solvents and leachants. All of the aforementioned mineral sample pretreatments are likely to impact the surface roughness and surface composition of the sample (Somasundaran, 1970; Kulkarni & Somasundaran, 1973, 1977). During polishing, contamination of the mineral surface might also have a substantial impact (Bangs, 1962). According to Wagner and Leach's (1959) study, the removal of bituminous or organic coatings, which play a controlling role in imparting oil-wettability to rock surfaces, while polishing can also result in inaccurate findings that are not reflective of the original samples. Changes in the equilibrium contact

angle and the form of hysteresis, which are crucial in determining the oil saturation, can be caused by changes in surface variations of equal importance. In 1956, Brown and Fatt proposed abandoning the idea of a contact angle as it pertained to reservoir rock. Due to the diverse mineral composition of most reservoir rocks, each having a varied surface chemistry and adsorption capability for surface active elements from reservoir fluids, they issued this recommendation. In addition, they noted that it is difficult to visualize the function of a contact angle in defining the shape of a fluid-fluid interface in the extremely complicated geometry of a pore.

3.4.2 DDDC method.

The dual drop dual crystal technique was developed by (Rao and Girard, 1996). Two droplets of crude oil (A) are put on parallel, polished rock surfaces that are supported by the horizontal and vertical arms of an optical cell. Before measuring the advancing and retreating contact angles in relation to aging time, the water film between the crude oil sessile droplets and mineral crystal surfaces is drained with the aid of buoyancy forces to achieve adhesion equilibrium. By inverting the bottom crystal (A B), there are three different behaviors for the oil drop. In example B1, the oil drop remains adhered to the bottom crystal owing to adhesion. In case B2, a portion of the oil drop floats away due to buoyancy. In cases B1 and B2, the higher crystal is lowered such that the two oil droplets can combine (C). In example B3, the upper crystal is lowered to contact with the surface where the oil drop from the lower crystal was located. The advancing and retreating contact angles are determined by laterally moving the bottom crystal (D). The water advancing contact angle explains the wettability and rock/oil adhesion, whereas the water receding contact angle governs the spreading behavior of reservoir fluids. Depicted in Figure (4).

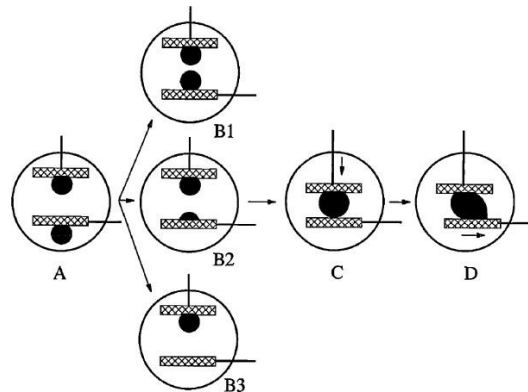


Figure (4): DDDC method depiction (Rao and Girard, 1996).

CHAPTER IV

4.1 Findings

In this chapter results and findings are presented and discussed with all the data record and/or collected. Once the results are presented with the data, this chapter will discuss and explain the meaning of these findings.

4.1.1 Baseline conditions of rock samples

As indicated in Figure (5), baseline conditions were determined by measuring the wettability of each rock in the presence of decane and deionized water. Decane is a hydrocarbon alkane with the formula ($C_{10}H_{22}$) with 75 structural isomers. Between the carbon and hydrogen atoms of decane, a dipole moment provides a mild polar charge. This charge is strong enough to interact with the opposing charge on the rock surface in the presence of DI water. Since 92% of the rock component is water-wet (quartz and feldspar) and 8% is clay, sandstone is called water-wet. The 8% of Sandstone that floats is caused by the interaction between the weak polar charge in decane and the charge on the clay particles.

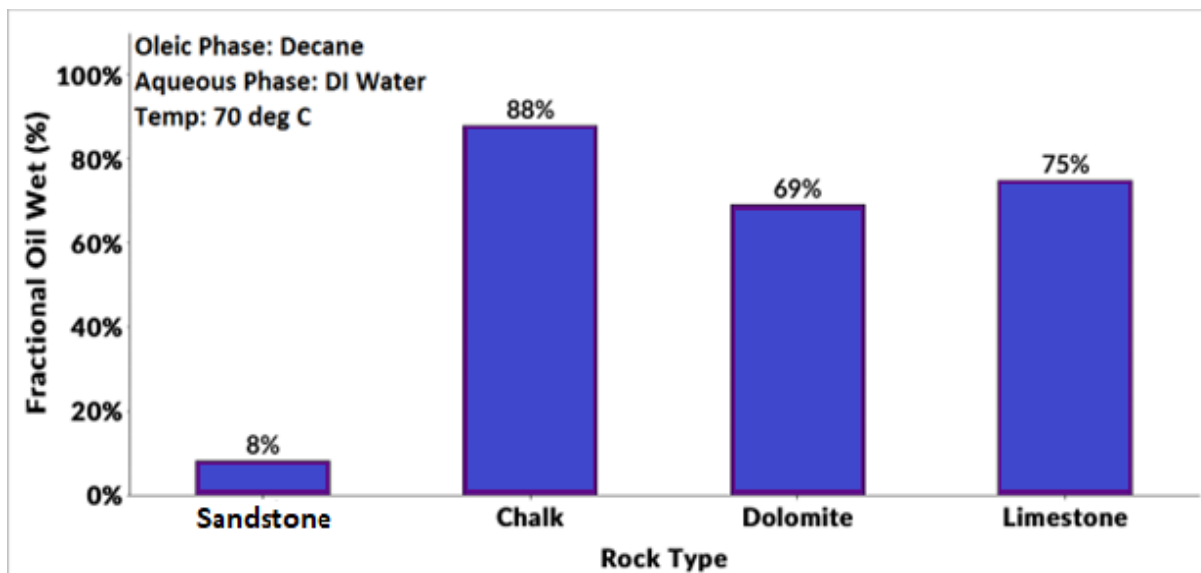


Figure (5): Rock samples baseline conditions.

The majority of the carbonate rocks are oil-wet, before transferring the rock to the oleic phase. Consequently, the initial wettability is often water-wet, and the presence of the oleic phase may or may not encourage contact with the rock surface. As seen in Figure 26, decane binds to a significant proportion of carbonate rocks, namely 88% of chalk ($\text{Ca}_{0.845}\text{Mg}_{0.155}\text{CO}_3$), 75% of dolomite ($\text{CaMg}(\text{CO}_2)$), and 69% of limestone (CaCO_3). The observed binding of decane to carbonate rocks is due to the interaction between the dipole moment of decane and the positively charged carbonate rock surfaces. These interactions are mild, but as salinity increases, electrostatic forces become more widespread and powerful.

4.1.2 Effects of Surface-active compounds on Sandstone wettability.

At 72°C, three SAC concentrations (1000, 2000, and 4000 parts per million) were evaluated. The aqueous phase consisted of DI water. The findings of these studies are categorized by rock type, with each graph displaying the percentage of wettability change for each of the nine SACs, Tetralin, and condensate. The percentage change in wettability is computed by adjusting each SAC and condensate's wettability result to that of decane. A positive change in wettability indicates an increase in the percentage of oil-wet rock. A negative change indicates an increase in the proportion of wet rock. Results within a range of 10% are considered an indicator of analytical uncertainty and are thus normalized to zero.

4.1.2.1 Impact of SACs on sandstone wettability

Figure (6) depicts the impact of SAC concentration on the wettability of Sandstone in DI water at 72°C. Only condensate and the long-chained oxygen SAC influence wettability, pushing it toward oil-wettability. As the percentage of myristic acid (O₂) rises, a greater proportion of the Sandstone becomes oilier. In contrast, condensate and naphthenic acid similarly move the wettability of Sandstone toward oil-wettability; nevertheless, the wettability shift was same across all concentrations.

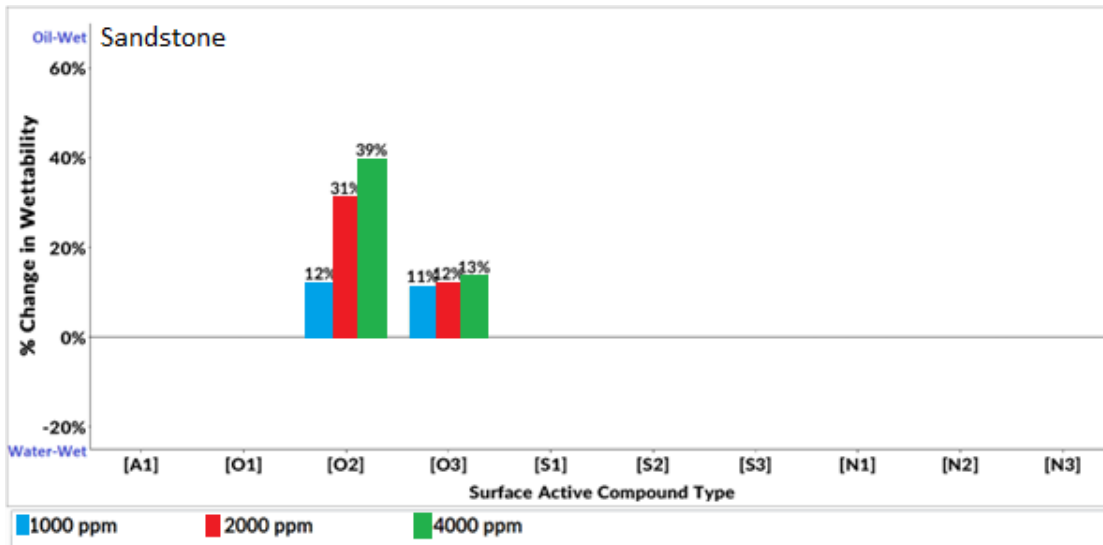


Figure (6): Impact of SACs on sandstone wettability.

4.1.2.2 Impact of SACs on Chalk wettability

Figure 7 demonstrates the influence of SAC concentration on the wettability of chalk. Myristic acid (O₂) and naphthenic acid (O₃), two long-chained oxygen SACs, increase the oil-wetness of chalk. Conversely, the short-chained oxygen SAC increases the water-wetness of chalk. As the quantity of sulfur SAC dibenzothiophene (S₁) grew, chalk became more water-wet. At 4000 ppm, di-n-butyl sulfide (S₂) marginally moved the wettability toward water-wet, however at lower concentrations, the wettability was unaffected. As the concentration of 1-tetradecanolthiol (S₃) rose, its wettability moved slightly toward oil-wet. All nitrogen SACs altered wettability towards water-wet particularly at 2000 ppm and 4000 ppm. Carbazole (N₁) considerably altered the baseline oil-wet system to highly water-wet.

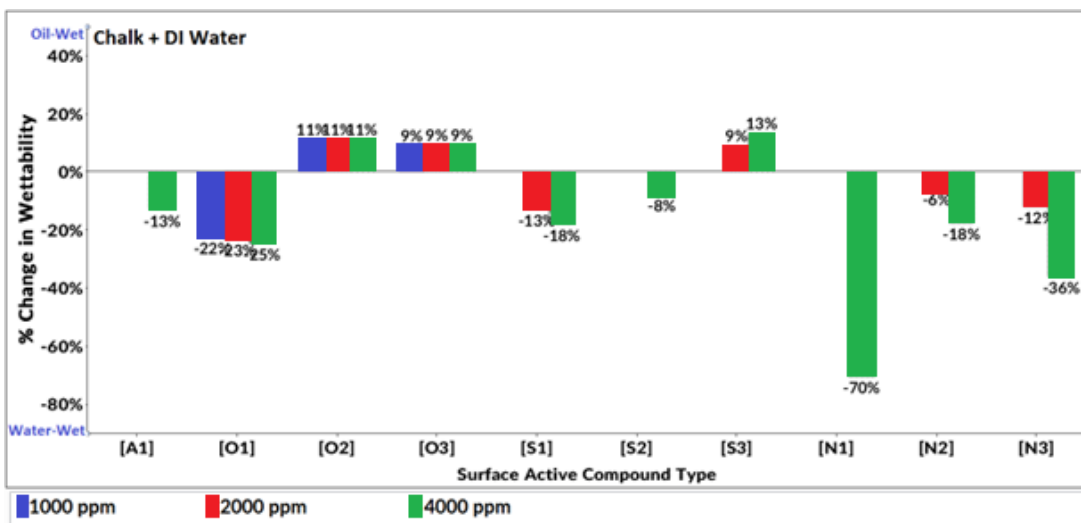


Figure (7): Impact of SACs on Chalk wettability.

4.1.2.3 Impact of SACs on dolomite wettability.

The impact of SAC concentration on the wettability of dolomite is seen in Figure (8). Similar to chalk, long-chained oxygen SAC compounds enhanced the oil-wetness of dolomite; however short-chained oxygen SAC increased the water-wetness of the rock. At greater concentrations, the sulfur SACs dibenzothiophene (S₁) and Di-n-butyl sulfide (S₂) altered the wettability of dolomite towards water-wet. At 2000 ppm and 4000 ppm, 1-Tetradecanethiol (S₃) had the reverse effect, causing the system to become more oily. At 2000 ppm and 4000 ppm, all nitrogen SACs alter the wettability of dolomite towards water-wet. At 2000 ppm and 4000 ppm, carbazole (N₁) changed the wettability of dolomite from oil-wet to highly water-wet. The two higher concentrations of Quinoline (N₂) altered the water-wettability of dolomite somewhat. All three amounts of Pyridine (N₃) significantly altered the water-wettability of dolomite.

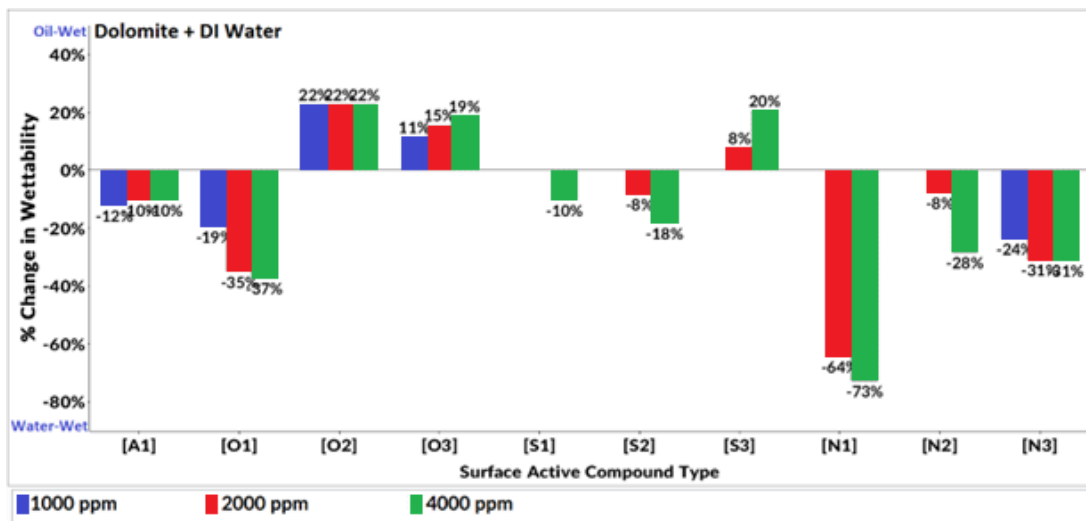


Figure (8): Impact of SACs on dolomite wettability.

4.1.2.4 Impact of SACs on Limestone wettability.

The impact of SAC concentration on the wettability of limestone is seen in Figure (9). Similar to dolomite and chalk, long-chained oxygen SAC changed the wettability of limestone from oil-wet to water-wet, but short-chained oxygen SAC had the opposite effect. At 4000 ppm, sulfur SACs, dibenzothiophene (S₁) and Di-n-butyl sulfide (S₂), shifted dolomite's wettability towards water-wet. At 2000 ppm and 4000 ppm, 1-tetradecanethiol (S₃) had the reverse effect; the system became more oily. At 2000 ppm and 4000 ppm, all

nitrogen SACs moved limestone wettability towards water-wet. At all concentrations, carbazole (N₁) altered the wettability of limestone from oil-wet to water-wet. The presence of quinoline (N₂) and pyridine (N₃) caused a substantial increase in the wettability of limestone.

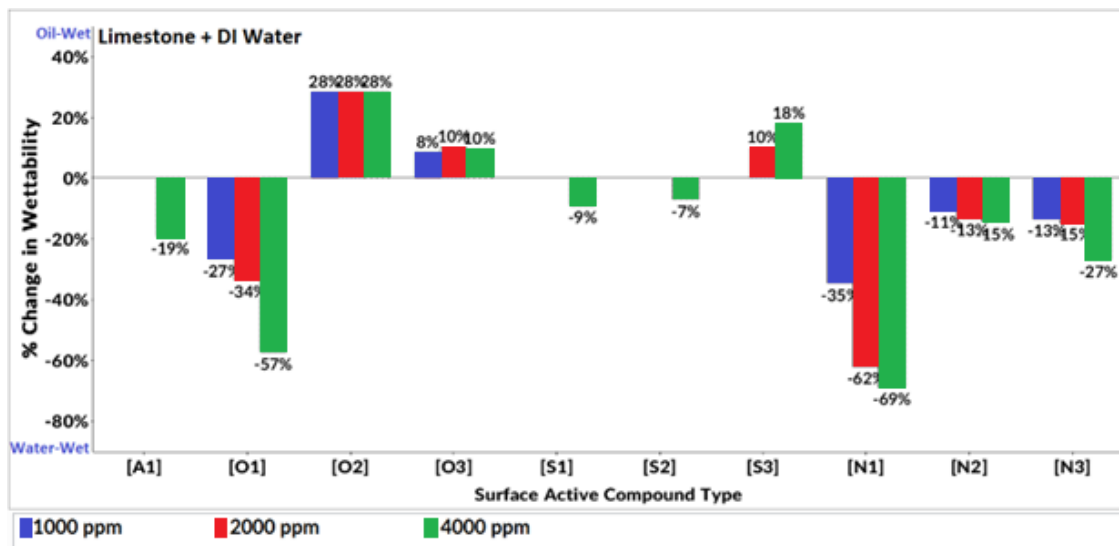


Figure (9): Impact of SACs on Limestone wettability.

4.1.2 Summary

In conclusion, long-chained organic acids change the oil-wettability of all four rock types. The short-chained organic acids had no influence on the wettability of Sandstone, but they pushed the wettability of the three carbonate rocks toward water-wettability. Sulfur SACs had no influence on the wettability of sandstone. When present in large quantities, Dibenzothiophene (S₁) and Di-n-butyl sulfide (S₂) alter the wettability of carbonate rocks towards water-wet. 1- Tetradecanethiol (S₃) has the opposite impact on the wettability of 1- tetradecanethiol. The tested nitrogen SACs had no influence on the wettability of Sandstone, however they changed the wettability of carbonate rocks towards water-wet. These studies also demonstrate that the sensitivity of SAC to concentration depends on the mineralogy of the rock. In the case of Sandstone, for instance, all SAC except for the long-chained acids had no influence on wettability regardless of the SAC content. The only SAC with concentration sensitivity was naphthenic acid. At the lowest concentration (1000 ppm), myristic acid moved the wettability of 100 percent of the rock towards

oil-wettability; consequently, the sensitivity to concentration could not be identified. However, these findings also demonstrate the dynamic character of carbonate rock-oil-water systems. All SACs altered the wettability of carbonate rocks to some degree, particularly at 4000 ppm. For instance, as the quantity of acetic acid (O_1), non-acidic sulfur compounds (S_1 & S_2), and nitrogen SACs rose, the water content of carbonate rocks increased. For carbonate rocks, it is difficult to determine the concentration sensitivity of the long-chained acids since, at the lowest concentration, these acids completely oil-wet the rock.

4.2 Discussion

One of the reasons for conducting this research is to give knowledge that may be utilized to assist unravel the mechanisms of wettability modification. Using chemically well-understood materials (model oils and deionized water) and well-characterized rocks ought to enable the identification of potential wettability controls. The following overview on wettability controls is grouped by oleic phase chemistry.

4.2.1 Impact of Aromatics on wettability

Aromatic compounds are naturally present in crude oil and are composed of from one to four fused rings, and very rarely more. They are virtually never seen as peri-condensed or linear fused rings, shown in figure (10).

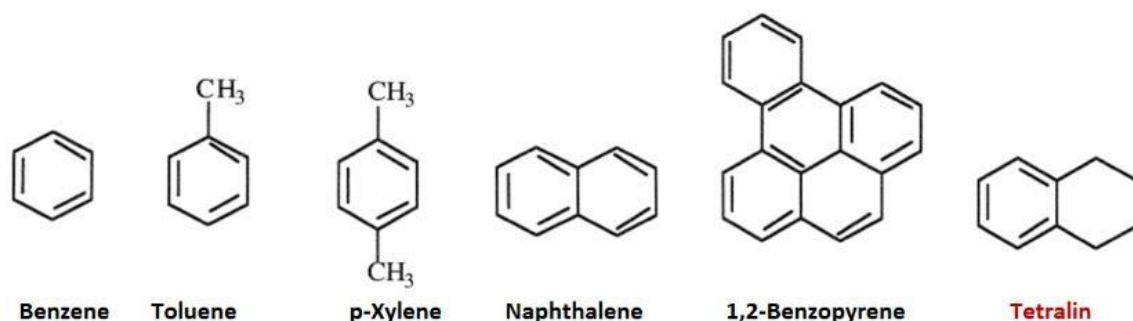


Figure (10): Aromatics present in crude oil.

Remember that Sandstone is water-wet when DI water and decane are present. Tetralin's addition to decane had no effect on Sandstone's wettability, indicating the absence of surface interactions between Tetralin and Sandstone. This might be because Tetralin has the same dipole moment as decane. Tetralin, on the other hand, appears to have marginally changed the wettability of the three carbonate rocks towards water-wettability, particularly at 4000 ppm. Remember that the wettability baseline for carbonates is oil-wet shown in figure (11). The presence of Tetralin in decane, particularly at higher concentrations, appears to disturb the weak connections between decane and the three carbonate rocks, hence changing water-wettability. The wettability of dolomite is somewhat altered by tetralin at all three concentrations, but concentration has little effect.

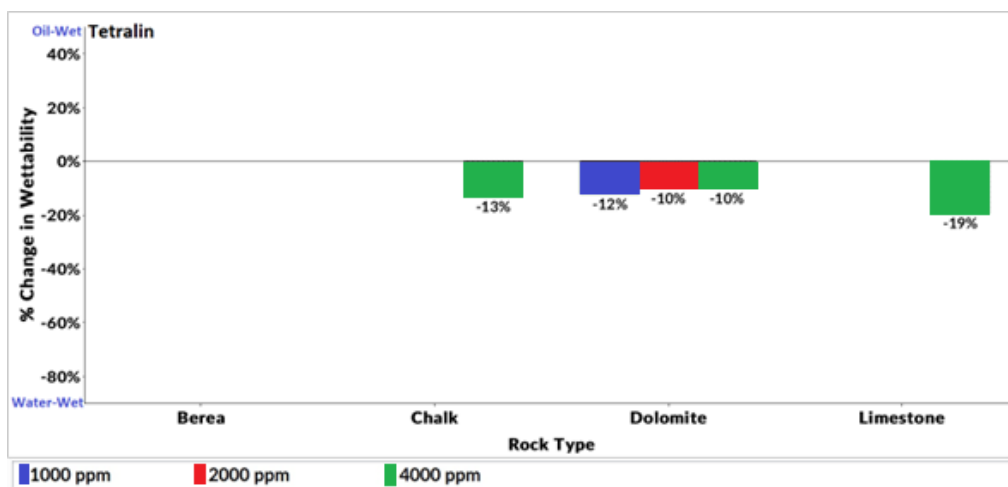


Figure (11): Impact of Tetralin on wettability.

4.2.2 Impact of Sulfuric SACs on Wettability.

The predominant form of sulfur in crude oils is organosulfur compounds. The only significant inorganic sulfur component present in crude oil is hydrogen sulfide. Organosulfur compounds may be categorized as either acidic or non-acidic. Figure (12) illustrates examples of acidic and neutral SAC. The structure of the three sulfur SACs chosen for this experiment is depicted in Figure (13); two were non-acidic and one was acidic.

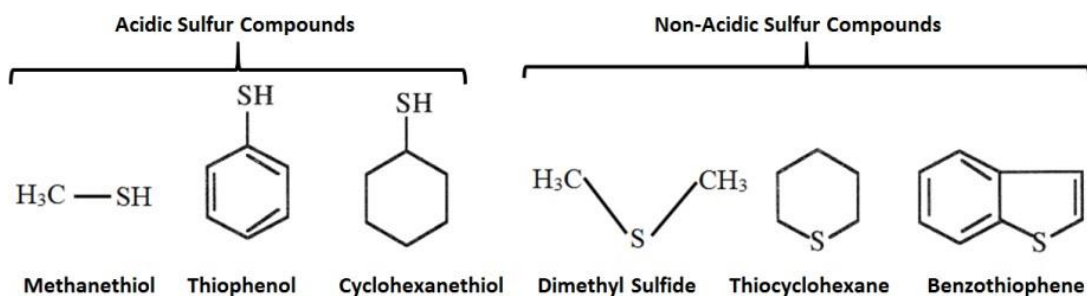


Figure (12): Sulfuric Acidic & non-acidic compounds present.

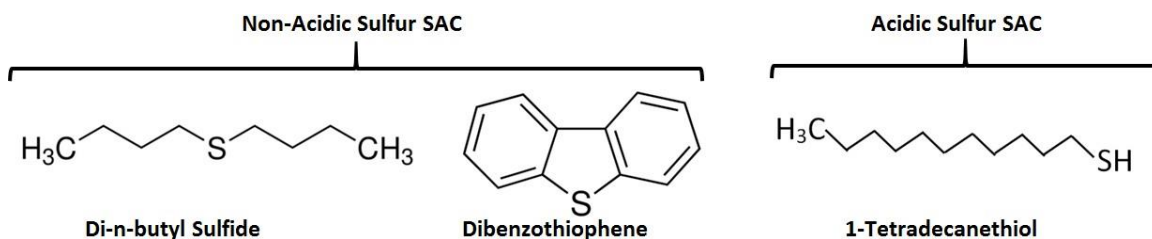


Figure (13): Structure of sulfuric compounds.

Sulfur SACs had no effect on Sandstone's wettability. Especially at higher concentrations, the non-acidic sulfur SACs altered the wettability of chalk, dolomite, and limestone toward water-wet. When Tetralin (aromatic chemical) was analyzed, a similar pattern was also seen. Carbon-sulfur bonds in the case of non-acidic SACs and carbon-carbon bonds in the case of Tetralin contribute to the dipole moments of both non-acidic SACs and Tetralin. Even though these dipole moments are small, I think that at larger concentrations of SAC, their polarity is sufficient to disrupt the weak polar connections between decane and carbonate rock.

In contrast, the acidic sulfur compound SAC 1-tetradecanethiol marginally changed the wettability of carbonate rocks towards oil-wetting. This trend is comparable to what was seen for the oxygen SAC with long chains shown in figure (14). By the processes described below, it is predicted that deprotonated thiol groups interact with positively charged carbonate surface groups to improve oil wetting. Due to the fact that thiols are just weak acids, they are not completely deprotonated in the test fluids, hence the change in oil-wetness is minimal.

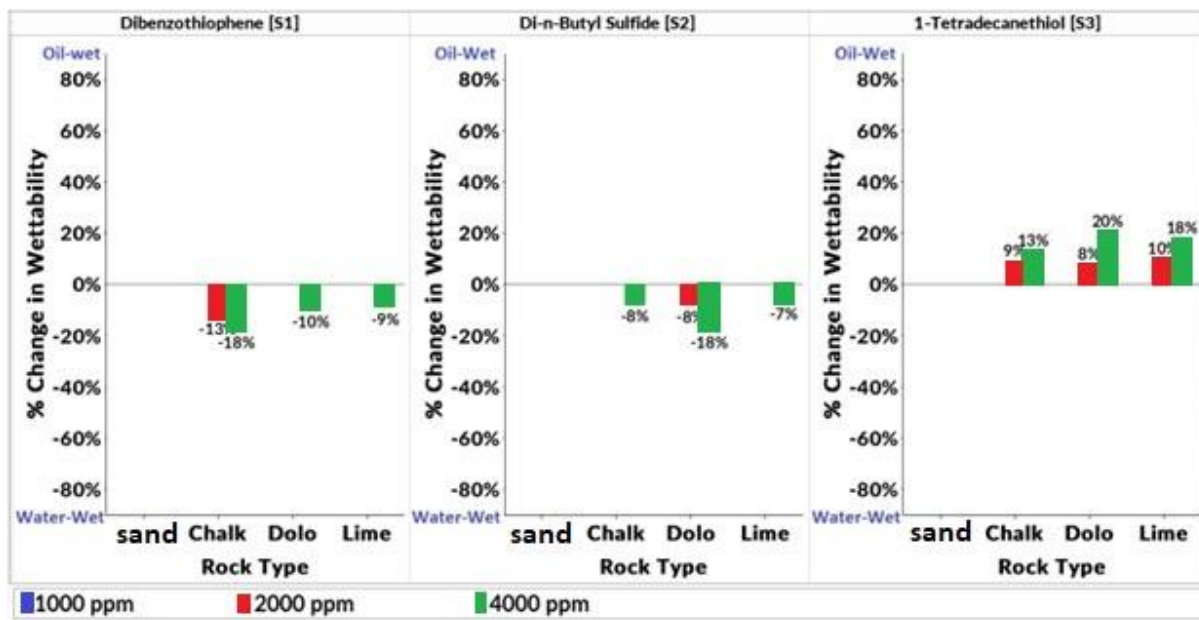


Figure (14): Impact of Sulfuric SACs on Wettability

4.2.3 Impact of Oxygen SACs on Wettability.

The majority of oxygen compounds present in crude oils, such as carboxylic acids, cresylic acid, phenol, and naphthenic acid, are moderately acidic. Figure (15) and Figure (16) illustrate acidic and non-acidic oxygen SAC, respectively. Naphthenic acids are mostly carboxyalkyl-terminated cyclopentane and cyclohexane derivatives. Since acidic oxygen compounds have long been recognized as wettability-altering chemicals, the structures of three of them are shown in Figure (17).

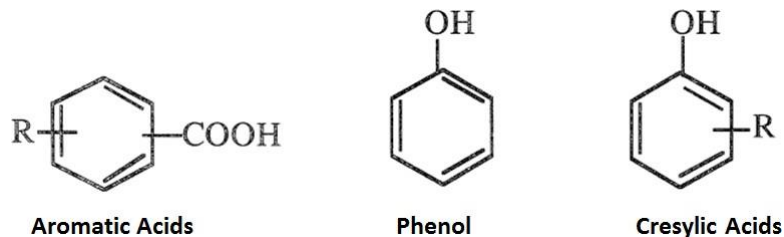


Figure (15): Structure of Oxygen compounds(Acidic).

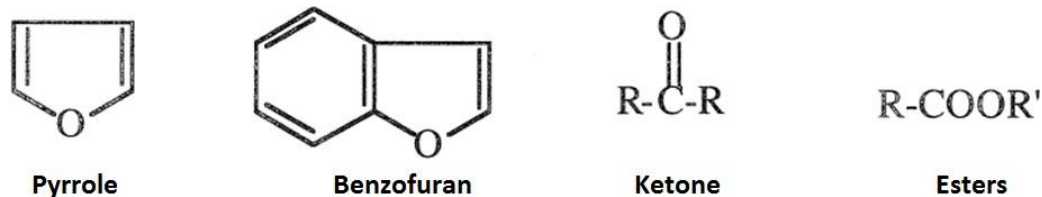


Figure (16): Structure of Oxygen compounds(Non-Acidic).

The studied oxygen SACs had varying effects on wettability. The long-chained oxygen SAC significantly moved both Sandstone and carbonate rocks into oil-wet conditions. Similarly, (Benner and Bartell, 1941) found that naphthenic acid displaced water to generate a contact angle of 106° on calcite when measured via the water phase. (Morrow et al., 1973) discovered that octanoic acid (0.1 molar in decane) had a maximum contact angle of 145° on dolomite. The suggested electrostatic interaction responsible for the oil-wet shift of carbonates, where myristic and naphthenic acids are represented by $RCOOH$, is shown in the table below. Organic acids are thought to provide a higher oil-wet shift than acidic sulfur SAC because they are stronger acids ergo are more deprotonated under the testing circumstances.

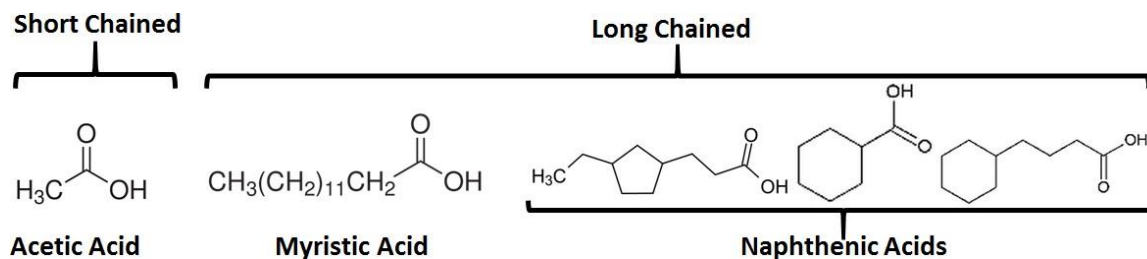


Figure (17): Structures of selected compounds.

It is unclear why long-chained SACs caused Sandstone to become more oily. Sandstone clays should be negatively charged comparable to the deprotonated organic acids, so unlikely to interact electrostatically. Possibly the organic acids absorbed to positively charged clay edge sites or were connected to anionic clay basal planes through Ca^{++} bridges. Notably, despite the relative magnitude of the organic acid-driven

change in Sandstone wettability towards oil-wettness, the total degree of oil-wettness obtained is limited since Sandstone wettability is mostly water-wet to begin with.

Acetic acid, a short-chained acid, altered the wettability of carbonate towards water-wet, but had no effect on the wettability of sandstone. Figure (18) demonstrates that acetic acid is more soluble in water than in oil. The impact of acetic acid on carbonate wettability may be explained by the fact that acetic acid partitioned into the aqueous phase and then connected to cationic calcite surface sites, preventing them from coordinating with decane.

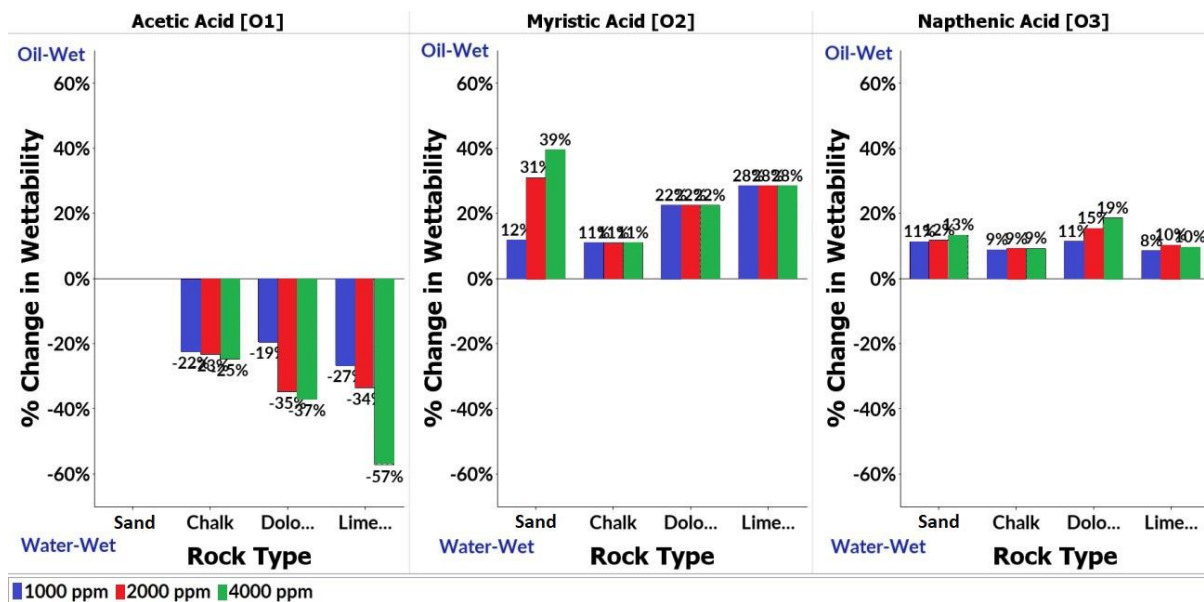


Figure (18): Impact of Oxygen SACs on Wettability.

4.2.4 Impact of Nitrogenous SACs on Wettability.

There are two categories of nitrogen compounds: (1) pyridinic forms, which are considered basic nitrogen compounds, and (2) pyrrolic forms, which are neutral or non-basic nitrogen compounds. The nitrogen content of the majority of crude oils does not exceed 0.1% by weight. In certain heavy crudes, the nitrogen content can reach up to 0.9% by weight. Since nitrogen compounds are more thermally stable than sulfur compounds, they are concentrated in heavier fractions and residuals of petroleum shown in Figure (19) and (20) respectively.

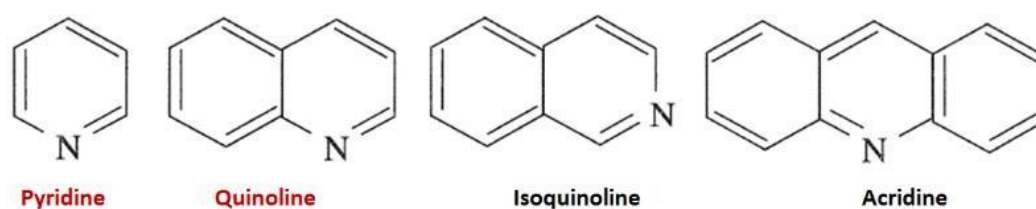


Figure (19): Nitrogenous SACs present in crude oil (Basic).

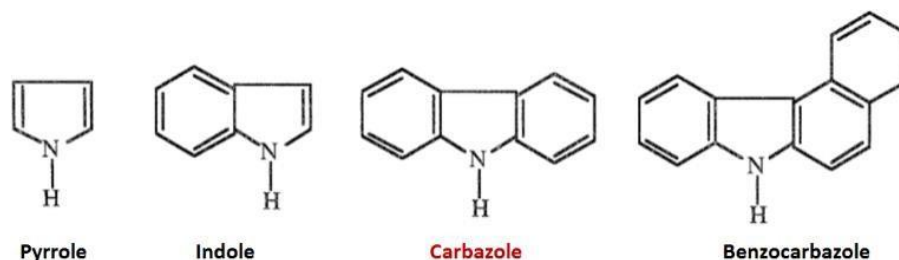


Figure (20): Nitrogenous SACs present in crude oil (Non-Basic).

The three nitrogen SACs examined had no effect on the wettability of Sandstone, but they pushed carbonate wettability toward water-wetness. The non-basic nitrogen SAC carbazole had the greatest impact on wettability. At the pH of the Sandstone tests (pH 7), quinoline and pyridine will be mostly uncharged and unlikely to interact electrostatically with charged Sandstone clay surfaces, as quinoline and pyridine have pKa values of and, respectively. The calcite trials probably had an even higher pH (pH 8) where even fewer cationic nitrogen bases are exposed at the surface of the model oil shown in Figure (21). The change in the

water-wetness of nitrogen bases may be a result of the dipole effect. Note that carbazole, which lacks a positive charge, has the greatest effect on the wetting of water.

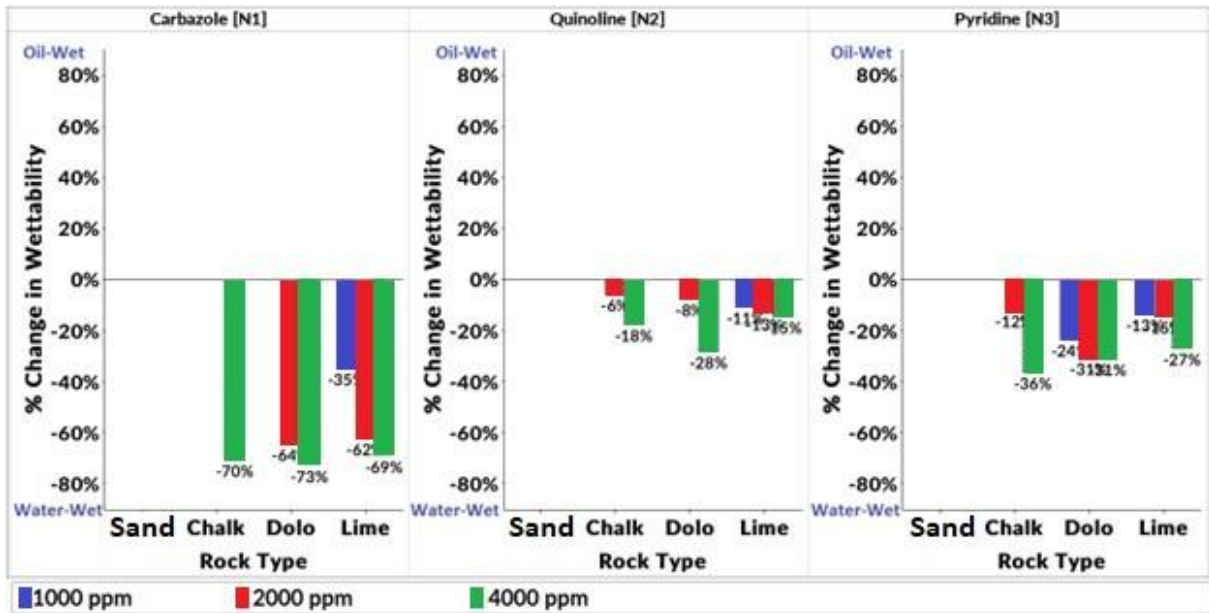


Figure (21): Impact of Nitrogenous SACs on Wettability.

CHAPTER V

5.1 Conclusion.

This project's objective was to determine how oil surface active chemicals (SACs) affect wettability in carbonate and sandstone reservoirs. The relationship between subsurface chemistry, wettability, and oil recovery allows us to address one of the most fundamental challenges in petroleum engineering. This is a significant advancement that has the potential to significantly develop the field and enable us to accurately modify waterflood chemistry for maximum oil recovery.

By examining the influence of rock mineralogy (chalk, limestone, dolomite, and sandstone), surface active compounds (SACs), and temperature. To isolate the effects of particular SACs, the oleic phase of this experiment was represented by mixes of pure decane and a single SAC. The principal findings of this investigation were:

1. In the case of Sandstone, only the long-chained oxygen acids altered wettability by causing an increase in oil-rock adhesion as salinity declined. Therefore, among the studied SACs, long-chained oxygen SACs had the greatest effect on the wettability of Sandstone.
2. As their concentration grew, short-chained oxygen SACs, non-acidic sulfur SACs, and nitrogen SACs encouraged water-wet conditions in carbonate rocks. On the other hand, long-chained oxygen SACs and sulfur SACs with an acidic pH increased oil-rock adhesion. Organic acids exhibited a greater oil-wet shift than acidic sulfur SACs due to the fact that they are more acidic and, thus, more deprotonated under the experimental circumstances. Nitrogen and oxygen SACs must have had the biggest effect on the wettability of carbonates.
3. It was discovered that carbonates are more vulnerable to salt than sandstone. As brine salinity fell in the case of carbonate rocks, nitrogen SACs and short-chained oxygen SACs altered the wettability of the carbonate rocks towards water-wet conditions. In contrast, long-chained acid

SACs, sulfuric acid SACs, and aromatics changed the wettability of carbonates towards oil-wet conditions. This disparity in SAC response to salinity has been suggested as one of the reasons why low salinity waterflooding is successful in certain reservoirs but not others. This study argues that the absence of a low salinity impact may also be attributable to a crude oil containing high levels of oil-wet promoting SACs with minimal sensitivity to salinity variation and/or low amounts of water-wet promoting SACs. In order for IOR operations relying on wettability modification to be effective, it is crucial to have a comprehensive understanding of the crude oil, brine, and rock mineralogy. This study suggests a further definition of crude oils in which SACs may be discovered and measured according to their potential to promote oil-wetness or water-wetness

4. Temperature was discovered to influence the wettability of carbonate rocks. Low temperatures (25 °C) and higher temperatures (70 °C and 110 °C) resulted in considerable differences in the wettability of the rocks. The majority of the wettability change occurred at higher temperatures, and the difference between the two highest temperatures was little to nonexistent.

This study identified two fundamental features of wettability: microscale vs macroscale wettability and intrinsic versus situational wettability. Traditionally, wettability categories are often determined by the standard procedures for measuring wettability. Typically, these approaches test wettability at various scales. This has led to a great deal of uncertainty in the literature, particularly in the definition of heterogeneous wettability. I have discovered that scale must be taken into account while considering wettability. On a microscopic size (grain scale), wettability is uniform. On a large scale, wettability is heterogeneous because it represents the average wettability of all grains. Lastly, it is not an intrinsic quality of the rock surface to be water- or oil-wettable. Rather, it depends on the oil, water, rock, and temperature. These four criteria establish a distinct geochemical situation that results in a particular wettability state. Consequently, the wettability of a rock might range from water-wet to oil-wet depending on the existing geochemical situation. This makes a rock's wettability situational rather than an inherent property.

CHAPTER VI

6.1 Recommendations

The experimental study upon which this thesis is based has yielded several intriguing results that merit further examination. Listed below are some suggestions on future work proposals:

1. I advise the development of an analytical method for identifying and quantifying surface-active chemicals in crude oils. Subsequently, these surface-active chemicals will be analyzed under various geochemical settings in order to compile a database relating their capacity to increase, decrease, or have no effect on the wettability of various rock types. This work aims to better define crude oils and give relevant and reliable information that can be utilized to construct accurate models for predicting wettability.
2. I discovered that both long-chained oxygen SACs and nitrogen SACs play a significant influence in carbonate rock wettability. To identify which of the two SAC groups has the greater influence on wettability, it is necessary to conduct a systematic research of the effects of mixing long-chained oxygen SAC (acids) that enhance oil-rock adhesion with nitrogen SAC (bases) that improve water-wettability. This proposed study would emphasize the synergistic effects of the two groups, but more critically, it would identify the SACs that promote or inhibit oil-rock adhesion.
3. The effects of SACs on the wettability of sandstone and carbonate rocks in the presence of different brine salinities and temperatures were investigated. I suggest further this research by evaluating the impact of SACs in the presence of identified possible deciding ions, varying pH levels, and diverse sandstone and shale rock types. Additionally, I suggest researching more than three SACs per chemical group.

4. To gain a better understanding of how these SACs might alter wettability in a real reservoir, I suggest repeating these tests at pH settings typical of the reservoir and analyzing the influence of the basic SACs.

5. Finally, I suggest incorporating the data collected by this experiment in a model of surface complexation. A surface complexation model is a chemical model that mimics the chemical equilibrium and depicts the processes occurring at the interface of mineral and solution. The reactions result in the creation of surface complexes, which are ultimately responsible for the charges at the mineral surface and have particular equilibrium (stability) constants comparable to bulk solution reactions.

CHAPTER VII

7.1 References

1. Abdallah, W., J.S. Buckley, A. Carnegie, J. Edwards, B. Herold, E. Fordham, A. Graue, T. Habashy, N. Zeleznev, C. Signer, H. Hussien, B. Montaron, and M. Ziauddin, 2007, Fundamentals of wettability: Oilfield Review, v. 19/2, p. 44-61.
2. Agbalaka C, Abhijit Y. Dandekar, Shirish L. Patil, Khataniar S, Hemsath JR. (2008) “The effect of wettability on oil recovery: a review”, paper SPE 114496 presented at SPE Asia Pacific oil and gas conference and exhibition, Perth, Australia, 20–22 October 2008.
3. Al-Adasani Ahmad, Bai, B., & Wu, Y.-S. (2012) “Investigating Low-Salinity Waterflooding Recovery Mechanisms in Sandstone Reservoirs”. SPE 152997, 18th SPE Improved Oil Recovery Symposium.
4. Al-Attar, H. H., Mahmoud, M. Y., Zekri, A. Y., Almehaideb, R. A., and Ghannam, M. T., (2013) “Low salinity flooding in a selected carbonate reservoir: experimental approach,” in Proceedings of the EAGE Annual Conference & Exhibition incorporating SPE Europec, London, UK, June 2013.
5. Al Harrasi, A., Al-Maamari, R. S., and Masalmeh, S. K., (2012) “Laboratory investigation of smart waterflooding for carbonate reservoirs,” in Proceedings of the Abu Dhabi International Petroleum Conference and Exhibition, SPE-161468-MS, Abu Dhabi, UAE.
6. Al-Shalabi, E.W., Sepehrnoori, K., and Delshad, M. 2014 “Mechanisms behind low salinity water injection in carbonate reservoirs” Fuel, vol. 121, pp. 11–19

7. Al Quraishi, A. A., Al Hussinan, S. N., and Al Yami, H. Q. (2015) “Efficiency and recovery mechanisms of low salinity waterflooding in sandstone and carbonate reservoir,” in Proceedings of the Offshore Mediterranean Conference and Exhibition, OMC-2015-223, Ravenna, Italy.
8. Alotaibi, M.B., Nasralla, R.A., and Nasr-El-Din, H.A. (2011) “Wettability Studies Using Low-Salinity Water in Sandstone Reservoirs.” SPE Reservoir Evaluation & Engineering, 14, pp. 713–725. SPE-149942-PA
9. Anderson, William G., 1986. “Wettability Literature Survey-Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability”, SPE 13932, Pages 1125 – 1127
10. Austad, T., Shariatpanahi, S.F., Strand, S., Black, C.J.J. and Webb, K.J., 2011. Condition for low salinity EOR-effect in carbonate oil reservoirs. 32nd Annual IEA EOR Symposium and Workshop, 17-19 October.
11. Austad, T., RezaeiDoust, A. and Puntervold, T., 2010. Chemical mechanism of low salinity water flooding in sandstone reservoirs. Paper SPE 129767 prepared for presentation at the 2010 SPE Improved Oil Recovery Symposium, 24-28 April.

12. Austad, T., Strand, S., Madland, M.V., Puntervold, T. and Korsnes, R.I., 2008a. Seawater in chalk: An EOR and compaction fluid. *SPE Reservoir Evaluation & Engineering*, 11(4): 648- 654.
13. Austad, T., Strand, S., Puntervold, T. and Ravari, R.R., 2008b. New method to clean carbonate reservoir cores by seawater. Paper SCA2008-15 presented at the International Symposium of the Society of Core Analysts, 29 Oct - 2 Nov.
14. Austad, T., (2012) "Enhanced Oil Recovery Field Case Studies: Chapter 13. Water-Based EOR in carbonates and sandstones. New Chemical Understanding of the EOR potential using "Smart Water".
15. Ayello, F., Robbins, W.K., Richter, S., & Nestic, S. (2008a). Crude oil chemistry effects on inhibition of corrosion and phase wetting. 17th International Corrosion Congress, paper no. 3149
16. Bangs. L.B. (1962) "Hysteresis of Contact Angles in the System Benzene-Water-Quartz." M.S. thesis. M.I.T. Cambridge, Mass. (1962).
17. Benner, F.C., and Bartell, F.E. (1942) "The effect of polar impurities upon capillary and surface phenomena in petroleum production." *Drill. and Prod. Prac.*, API, New York City, pp. 341-348.
18. Bergeron, V., Radke, C.J., (1995) "Disjoining pressure and stratification in asymmetric thin- liquid films." *Colloid Polymer Science*, 273, pp. 165–174.
19. Binks, B.P., and Horozov, T.S., (2007) "Colloidal particles at liquid interfaces: An Introduction." Cambridge University Press, pp. 1-10.

20. Blake, T. D., Kitchener, J. A., (1972) *J. Chem. Soc. Faraday Trans 1*, 68, pp. 1435.
21. Bloom, F., and Heindel, T.J., (1997) “A Theoretical Model of Flotation Deinking Efficiency,” *Journal of Colloid and Interface Science*, 190, pp.182-197.
22. Boussour, S., Cissokho, M., Cordier, P., Bertin, H., Hamon, G., (2009) “Oil Recovery by Low-Salinity Brine Injection: Laboratory Results on Outcrop and Reservoir Cores.” SPE 124277 presented at the SPE Annual Technical Conference and Exhibition. New Orleans, Louisiana, 4–7 October.
23. Boutin, P. and Wheeler, D. A. (1967), “Column Flotation Development Using an 18 Inch Pilot Unit”, *Canadian Mining Journal*, March 1967, Vol. 88, pp. 94-101.
24. Brady, P., Krumhansl, J. and Mariner, P. (2012) “Surface Complexation Modeling for Improved Oil Recovery.” Paper SPE 153744 presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, USA, 14–18.
25. Brady, P., Krumhansl, J. and Sandia National Laboratories, (2013) “Surface Complexation Modeling for Waterflooding of Sandstones.” SPE 163053.

26. Brady, P., Morrow, N., Fogden, A., Deniz, V., Loahardjo, N., and Winoto., (2015) Electrostatics and the low salinity effect in sandstone reservoirs. *Energy and Fuels*, 29, pp. 666-677.
27. Brown, R.J. and Fatt, I., (1956) "Measurements of fractional wettability of oilfield rocks by the nuclear magnetic relaxation method" *Trans., AIME*, 207, 262-264.
28. Buckley, J.S., Takamura, K., and Morrow, N.R. (1989) Influence of Electric Surface Charges on the Wetting Properties of Crude Oils. *SPE Reservoir Engineering*, 4 (3), pp. 332-340.
29. Buckley, J.S. (2001) "Effective wettability of minerals exposed to crude oil." *Curr. Opin. Colloid Interface Sci.* 6(3), pp. 191–196.
30. Busireddy, C., and Rao, D. N., (2004) "Application of DLVO Theory to characterize spreading in crude oil brine rock systems" *SPE* 8942.
31. Celik, M.S., and Somasundaran, P., (1980) "Wettability of Reservoir Minerals by Flotation and Correlation with Surfactant Adsorption," *SPE Paper* 9002.
32. Chilingar, G.V. and Yen, T.F., (1983) "Some notes on wettability and relative permeabilities of carbonate rocks, II." *Energy Sources*, 7, pp. 67-75.
33. Cueic, L., (1984) "Rock/crude-oil interactions and wettability: An attempt to understand their interrelation." Paper SPE 13211 presented at the 59th Annual Conference and Exhibition, Texas, pp. 16-19.

34. Cueic, L. E., (1991) "Evaluation of Reservoir Wettability and Its Effect on Oil Recovery," in Interfacial Phenomena in Petroleum Recovery, N. R. Morrow ed., Marcel Dekker Inc, New York Ch.9 319-373.
35. Danov, K.D., Kralchevsky, P.A. (2010) "Capillary forces between particles at a liquid interface: General theoretical approach and interactions between capillary multipoles" *Advances in colloid and interface science* 154 (1), pp. 91-103
36. Davis, J.A., James, R.O., and Leckie, J.O. (1978) "Surface ionization and complexation at the oxide/water interface: I. Computation of electrical double layer properties in simple electrolytes". *J. Colloid Interface Sci.*, 63: pp. 480-499.
37. de Gennes, P.G., (1985) "Wetting: statics and dynamics" *Rev. Mod. Phys.* 57, 827 (1985) – Published.
38. Denekas, M.O., Mattax, C.C. and Davis, G.T., (1959) "Effects of crude oil components on rock wettability." *Petroleum Transactions AIME*, 216, pp. 330-333.
39. Derjaguin, B. V., & Landau, L. (1941). *Acta Physicochim URSS*, 14, 633

40. Dixit, A.B., Buckley, J.S., McDougall, S.R., Sorbie, K.S., (2000) "Empirical measures of wettability in porous media and the relationship between them derived from porescale modeling." *Trans. Porous Media*, 40, pp. 27–54.
41. Donaldson, E.C., Thomas, R.D. and Lorenz, P.B., (1969) "Wettability determination and its effect on recovery efficiency." *Soc. Pet. Eng. J.*, pp. 13-20.
42. Drummond, C., Israelachvili, J., (2002) Surface forces and wettability, *Journal of Petroleum Science Engineering*, 33, pp. 123–133.
43. Dubey, S.T., Doe, P.H., (1993) "Base number and wetting properties of crude oils." *Soc. Pet. Eng. Res. Eng.* 8, 195.
44. Efird, K.D., & Jasinski, R.J., (1989). Effect of the crude oil on corrosion of steel in crude oil/brine production. *Corrosion Engineering*, 45(2), 165-171.
45. Emerson, ZI., (2007) "Particle and bubble interactions in flotation systems" PhD dissertation, Submitted to the Graduate Faculty of the Auburn University.
46. Fatt, I. And Klikoff, W.A., (1959) "Effect of fractional wettability on multiphase Flow through porous media" *Trans. AIEA*, pp. 426-432.
47. Fathi, S. J., Austad, T., and Strand, S. Smart Water as a Wettability Modifier in Chalk: The Effect of Salinity and Ionic Composition, *Energy & Fuels* 2010 24 (4), 2514-2519. (2010a)

48. Fathi, S.J., Austad, T., Strand, S., and Puntervold, T. Wettability Alteration in Carbonates: The Effect of Water-Soluble Carboxylic Acids in Crude Oil. *Energy & Fuels* 2010 24 (5), 2974- 2979.
49. Fathi, S. J., Austad, T., and Strand, S. Water-Based Enhanced Oil Recovery (EOR) by Smart Water: Optimal Ionic Composition for EOR in Carbonates, *Energy & Fuels* 2011 25 (11), 5173-5179.
50. Fathi, S. J., Austad, T., & Strand, S. (2012, January). Water-Based Enhanced Oil recovery (EOR) by " Smart Water" in Carbonate Reservoirs. In SPE EOR Conference at Oil and Gas West Asia. Society of Petroleum Engineers.
51. Fatt, I., Klikoff, W. (1959) "Effect of Fractional Wettability on Multiphase Flow Through Porous Media." SPE-1275-G, v. 11(10).
52. Ferno, M. A., Gronsdal, R., Aheim, J., et al. (2011) "Use of Sulfate for Water Based Enhanced Oil Recovery during Spontaneous Imbibition in Chalk." *Energy & Fuel*, 25, pp. 1697-1706.
53. Fjelde, I., Omekeh, A., Haugen, P., (2017) "Screening of the potential for different injection water compositions to alter wettability to more water-wet" SPE 184918.
54. *Frontiers*, BP Magazine, "Less Salt, More Oil," Issue 25, August 2009

55. Gamage, P., Thyne, G. (2011a), "Comparison of Oil Recovery by Low Salinity waterflooding in secondary and Tertiary Recovery Modes", SPE 147375. SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA
56. Gamage, P. and Thyne, G. D., (2011b), Systematic Investigation of the Effect of Temperature during Aging and Low-Salinity Flooding of Sandstones, 16th European Symposium on Improved Oil Recovery, Cambridge, UK, 12-14 April 2011.
57. Gregory, J., (1975) "Interaction of Unequal Double Layers at Constant Charge." *Journal of Colloid and Interface Science*. 51, pp. 44-51
58. Gregory, J., (1981) "Approximate Expressions for Retarded van der Waals Interaction." *Journal of Colloid and Interface Science*. 83, pp. 138-145
59. Gupta, R. Smith, G. G, Hu, L., (2011) "Enhanced waterflood for carbonate reservoirs—impact of injection water composition," in Proceedings of the SPE Middle East Oil and Gas Show and Conference, SPE-142668-MS, Manama, Bahrain.
60. Hadia, N. J.; Ashraf, A.; Tweheyo, M. T.; Torsæter, O., (2013) "Laboratory investigation on effects of initial wettabilities on performance of low salinity waterflooding". *Journal of Petroleum Science Engineering*, 105, pp. 18–25.
61. Hallenbeck, L., Sylte, J., Ebbs, D., Thomas, L. (1991) "Implementation of the Ekofisk field waterflood" *SPE Form. Eval.* 6, pp. 284–290.
62. Hamaker, H. C. (1937). *Physica*, 4, 1058–1072.

63. Haugen, P. E., (2016) “Characterization of wettability alteration by flotation” M.Sc. Thesis, Submitted to The Graduate School of Natural and Applied Sciences, University of Stavanger.
64. Hazim H. Al-Attar, Mohamed Y. Mahmoud, Abdulrazag Y. Zekri, Reyadh Almehaideb, Mamdouh Ghannam. (2013) “Low-salinity flooding in a selected carbonate reservoir: experimental approach” *J Petrol Explor Prod Technol*, 3, pp. 139–149.
65. Helgeson, H., Kirkham, D., (1974) “Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures; ii, debye-huckel parameters for activity coefficients and relative partial molal properties.” *Am J Sci*, 274, pp. 1089–1198
66. Hiorth, A. Cathles, L.M., and Madland, M.V., (2010) “The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability” *Transport Porous Media*, 85, pp. 1-21.
67. Hirasaki, G.J., (1991) “Wettability: Fundamentals and surface forces” *SPE Formation Evaluation*. 6, pp. 217-226
68. Hoiland S., Barth T., Blokhus A. M., Skauge A., (2001) “The effect of crude oil acid fractions on wettability as studies by interfacial tension and contact angles” *Journal of Petroleum Science and Engineering*, 30, pp. 91-103.

69. Hunter, R.J., (1981) "Zeta Potential in Colloid Science: Principles and Applications." 3rd Edn., Academic Press, New York, USA., ISBN-13: 9780123619600, pp. 386.
70. Israelachvili, J.N., (2011), Intermolecular and Surface Forces, Revised Third Edition, Academic Press, New York city
71. Jaafar, M.Z. and Pourbasirat, A., (2011) "Measurement of streaming potential coupling coefficient on carbonate rocks for downhole monitoring in smart wells". Journal Technology (Sains Kejuruteraan), 56: pp. 87-99.
72. Jaafar, M.Z., Mohd Nasir, A., and Hamid, M.F. (2014) "Measurement of Isoelectric Point of Sandstone and Carbonate Rock for Monitoring Water Encroachment". Journal of Applied Sciences, 14, pp. 3349-3353
73. Karoussi, O., Hamouda, A., (2007) "Imbibition of sulfate and magnesium ions into carbonate rocks at elevated temperatures and their influence on wettability alteration and oil recovery." Energy Fuels 21, pp. 2138–2146
74. Kasmaei, A.K., & Rao, D. (2014) "Is Wettability Alteration the Main Cause for Enhanced Recovery in Low Salinity Waterflooding?" SPE-169120-MS, 12.
75. Kelebek, S. (1984) "Surface properties and selective flotation of inherently hydrophobic minerals' M.Sc. Thesis, Submitted to the faculty of graduate studies and research, Department of Mining and Metallurgical Engineering, McGill University, Montreal, Quebec, Canada.

76. Kilybay, A., Ghosh, B., and Thomas, N., (2017) “A Review on the Progress of Ion-Engineered Water Flooding” *Journal of Petroleum Engineering*, Volume 2017 (2017), Article ID 7171957, 9 pages

77. Klassen, V. I., (1948a) Theoretical reasons for intensification of the flotation process - activation of floated minerals by air precipitating from solution” v 22(8), pp. 991-998.

78. Klassen, V. I., (1948b) Effect of gas adsorption on the floatability of minerals, *Gomyi Zhur.* 122(9), 32-34.

79. Koper, G. J. M., (2009) “An Introduction to Interfacial Engineering.” VSSD, Delft.

80. Kocurek Industries, Hard Rock Division, 8535 State Highway 36 S, Caldwell, TX 77836, (979) 596-3504,

81. Kavscek, A.R., Wong, H., Radke, C.J., (1993) “A pore-level scenario for the development of mixed wettability in oil-reservoirs.” *AICHE Journal*, 39 pp. 1072–1085

82. Kralchevsky, PA., Nagayama, K., (2000) “Capillary interactions between particles bound to interfaces, liquid films and biomembranes” *Advances in colloid and interface science*, 85(2), pp. 145-192.