**School of Minerals, Energy and Chemical Engineering**

**Department of Petroleum Engineering**

# Wettability Alteration During Low Salinity Water Flooding in Carbonate Reservoirs: An Experimental and Theoretical Study

**Ahmad Sari**

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# Dedication

I dedicate this work to my wife Monica, and my children Zainab, Abbas, and Zahra who give me a reason to live and dream.

To my parents for their continuous love, support, and endless prayers.

To my beloved sisters Fatima and Narjes for showing courage and resolve in the face of adversities.

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# Abstract

Low salinity water flooding is emerging as a viable and greener Enhanced Oil Recovery (EOR) alternative, generating enormous interest in the past twenty years. Yet despite encouraging laboratory results, the application of low salinity water flooding has been limited to a few small scale field trials. This is in part due to lack of understanding about the influence of key parameters such as brine pH, oil composition and rock surface chemistry on wettability. The aim of this research is to examine the underlying mechanisms of low salinity effect in carbonate through systematic analysis of physical, chemical, and geochemical factors that influence oil-brine-carbonate interactions during low salinity water flooding.

To access the suitability of anhydrite-free carbonate for low salinity EOR, the dependence of low salinity effect on anhydrite dissolution process is studied. It is shown that anhydrite and sulfate ions are not pre-requisite elements for low salinity EOR in carbonate rocks, where wettability is primarily controlled by the electrostatic forces at the interfaces of oil-brine-rock as confirmed by zeta potential tests. Rock surface analysis has also shown that contact angle measurements overestimates low salinity induced wettability alteration when measurements are being conducted on smooth substrates. This suggests, due to natural pore surface roughness > 100 nm, wettability alteration by low salinity water flooding is more subtle than observed in contact angle measurements.

From brine chemistry perspective, experimental and geochemical modelling proved pH is a dominant parameter regulating the wettability of oil-brine-carbonate system. At high brine pH, contact angle measurements show salinity and ion type significantly impact wettability of carbonate, while at low pH carbonate becomes strongly water-wet and insensitive to variation in salinity and ion type. Surface complexation modelling revealed pH (5.6 – 7.5) triggers an oil-wet system, a favourable condition for low salinity water flooding, while pH < 5 exhibits a water-wet system. Yet, low pH carbonated water flooding demonstrated calcite dissolution deteriorates heterogeneity of reservoirs particularly near the wellbore, which significantly undermines the contribution of oil-swelling, viscosity reduction, IFT reduction and wettability alteration on incremental oil recovery and compromises wellbore stability. Nevertheless, the adverse impact of calcite dissolution may not prevail at in-depth of reservoirs as calcite dissolution reaches equilibrium at a certain distance depending on the injection rate.

Meanwhile, -COOH and -NH$^+$ functional groups in crude oil were found to play an important role in oil-brine-carbonate interaction thus wettability. A geochemical modelling demonstrates that breakage of electrostatic bridges between oil and calcite increases linearly with acid number/base number ratio, implying a higher potential of low salinity effect in high acidic oil-bearing carbonate reservoirs.

# Publications by the Author

Publications forming part of this thesis as standalone chapters

1. Sari, A., Q. Xie, Y, Chen., Saeedi, A., Pooryousefy, E., 2017. "Drivers of Low Salinity Effect in Carbonate Reservoirs." Energy & Fuels 31 (9): 8951-8958

2. Xie, Q., Sari, A., Pu, W., Chen, Y., Brady, P. V., Al Maskari, N.S., Saeedi, A., 2018. "pH effect on wettability of oil/brine/carbonate system: Implications for low salinity water flooding." Journal of Petroleum Science and Engineering 168: 419-425

3. Sari, A., Chen, Y., Xie, Q., Saeedi. A., 2019. "Low salinity water flooding in high acidic oil reservoirs: Impact of pH on wettability of carbonate reservoirs." Journal of Molecular Liquids 281: 444-450

4. Sari, A., Al Maskari, N. S., Saeedi, A., Xie, Q., 2019. "Impact of surface roughness on wettability of oil-brine-calcite system at sub-pore scale." Journal of Molecular Liquids 10.1016/j.molliq.2019.112107

5. Sari, A., Chen, Y., Myers, M., Seyyedi, M., Ghasemi, M., Saeedi, A., Xie. Q., 2020. "Carbonated Waterflooding in Carbonate Reservoirs: Experimental Evaluation and Geochemical Interpretation." Journal of Molecular Liquid 10.1016/j.molliq.2020.113055

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# Chapter 1 Introduction

## 1.1 Background

Waterflooding remains to be a preferred secondary recovery method and has been practiced world-widely for nearly a century to improve oil recovery [1]. Conventionally, waterflooding is performed to maintain reservoir pressure and to make use of viscous forces for oil displacement [2]. Consequently, water chemistry did not receive any attention. Given wettability is a key parameter that controls fluid flow in hydrocarbon reservoirs, the efficiency of conventional water flooding could be significantly improved by harnessing its potential to shift reservoir wettability towards a more favourable state for oil production.

In the past decades, substantial volume of studies investigated the EOR potential of low salinity water flooding in carbonate reservoirs, where results overwhelmingly show wettability alteration is one of the main driving forces for improved oil recovery by low salinity water. Nevertheless, the underlying physics of wettability alteration and its controlling factors remain controversial.

One of the hypotheses that is widely discussed in low salinity water flooding literature is ionic substitution theory, which postulates that certain active ions such as $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$, also known as potential determining ions (PDI), are essential for triggering low salinity effect [3]. Some studies suggested anhydrite dissolution is key to wettability alteration [4, 5], while other results showed no correlation between improved oil recovery and anhydrite dissolution [6, 7], raising further questions about the validity of ionic substitution theory.

In contrast, the electrical double layer theory explains wettability alteration phenomena by identifying the conditions that impact the electrostatic interactions in oil-brine-calcite system. Zeta potential measurements support this hypothesis, showing changes in the electrostatic forces at oil-brine-rock interfaces drive wettability alteration [8-11]. Surface complexation modelling were also performed to capture the geochemical interactions in oil-brine-rock system to explain low salinity effect in carbonate reservoirs [12]. There were also attempts to relate surface complexation modelling to zeta potential, although the new model was restricted to brine-rock interactions [13] and did not capture the oil-brine interactions. In general, despite the effect of parameters such as salinity [14, 15], ionic strength [16-18], oil compositions [19-21] and rock

mineralogy [13, 22] on wettability have been extensively investigated, a systematic analysis on the effect of pH on oil-brine-calcite interactions is still lacking.

The difference in opinions and lack of consensus about the underlying causes of low salinity effect are largely fuelled by contradictory research findings which exposes several key knowledge gaps that hamper our understanding of low salinity effect phenomena. Several key questions related to various aspects of low salinity topic remained unanswered. For example, can low salinity EOR-Effect take place in anhydrite-free carbonate reservoirs? If yes, what alternative mechanism(s) is behind to control wettability? Moreover, how does pH affect the oil and rock surface chemistry and thus the adhesion of oil and calcite? Furthermore, can wettability alteration process taking place at molecular-level (e.g., through contact angle measurements) remain to occur at pore-level?

While oil-brine-rock interactions have been examined at molecular level through thermodynamics and surface complexation modelling, how the surface roughness at pore surface affects the oil-brine-rock interaction thereby wettability has not been investigated. However, physical characteristics such as rock heterogeneity and surface roughness may play a certain role in system wettability. For example, experimental investigations pertaining to various gas-brine-rock system show contact angle increases with increasing surface roughness. This phenomenon is attributed to increase in surface energy of solid as surface roughness increases (Wenzel 1936). Nevertheless, it is not clear if surface roughness would have a similar effect on wettability of oil-brine-carbonate system, particularly in low salinity water, given wettability is controlled by other factors than surface energy. Therefore, to upscale the wettability alteration as a result of oil-brine-calcite interactions to pore-level, it is of vital importance to examine the how surface roughness affects the local wettability alteration.

## 1.2 Research Objectives

The aim of this research is to develop our understanding of wettability alteration by low salinity water flooding in carbonate reservoirs. We attempted to achieve this goal by implementing a series of experimental and geochemical modelling techniques.

The objectives of this research can be summarized as the following:

1.  Delineate the likely mechanisms of low salinity effect in carbonate reservoirs in absence of $SO_4^{2-}$ and anhydrite dissolution.
2.  Identify what factors control wettability of oil-brine-rock system, in particular, the effect of brine pH on charged surface species at oil-brine and brine-carbonate system thereby the wettability.
3.  Provide a framework which helps to screen the potential reservoirs with respect to the oil composition (i.e., acid number and base number) for low salinity waterflooding.
4.  Reveal the impact of surface roughness on wettability of oil-brine-carbonate system and upscale the mechanism of wettability alteration from molecular level to pore/sub-pore scale.
5.  Explore the potential of carbonated waterflooding in carbonate reservoirs and minimize the uncertainties associated with this technique using a combination of Coreflooding and one-dimensional reactive transport modelling.

## 1.3 Thesis Organization

The structure of this thesis includes eight chapters in total. Chapter 1 includes the introduction to this thesis. Chapter 2 covers the literature review relevant to the scope of this research. Chapters 3-7 form the main body of this research. Chapter 3 challenges the view that the presence of anhydrite is a prerequisite for low salinity effect in carbonate reservoirs. We also explored the likely wettability alteration mechanism in absence of sulfate and anhydrite dissolution. Chapter 4 focuses on the effect of brine pH on the physiochemical interactions of oil-brine-carbonate system and presents a surface complexation model that predicts surface speciation at oil-brine and brine-rock interfaces. In Chapter 5, low salinity water flooding in high acidic oil reservoirs and effect of pH on wettability is explored. Furthermore, the question on what type of crude oil would favour low salinity water flooding was addressed. Chapter 6 examines that how well wettability alteration in sub-pore scale represents that in pore-scale due to surface roughness contrast. Finally, Chapter 7 explores the EOR potential of carbonated water using Coreflooding experiments in carbonate rocks. Chapter 8 concludes this thesis by presenting its conclusions and providing recommendations and outlook for future work.

# Chapter 2 Literature review

## 2.1 Introduction

Review of existing literature on the topic of low salinity water flooding shows conflicting views which reflects the lack of consensus among research community on the underlying causes of low salinity effect in carbonate reservoirs. Several mechanisms have been proposed for low salinity effect in the literature, each attempting to explain this phenomenon differently, some of which have gained more acceptance by the wider scientific community, while other mechanisms received less attention. In general, these mechanisms are not correlated as they are governed by different physical, chemical and/or geochemical factors, although attempts have been made to correlate some mechanisms. This makes the task of presenting a seamless review of low salinity mechanisms rather laborious. Nevertheless, we have categorised these seemingly different mechanisms into three distinct classes based on different types of interactions in which they are involved which make the review more coherent. These classes are: 1) fluid-rock interaction, 2) fluid-fluid interaction, and 3) fluid-fluid-rock interaction. In the following sections, we present these distinct classes of interactions and provide a comprehensive review of different mechanisms that fall in that category.

## 2.2 Proposed Mechanisms of Low Salinity in Carbonate Rocks

### 2.2.1 Fluid-rock interaction

The mechanisms that fall in this category explain low salinity effect by only considering the interactions between the aqueous phase and the rock surface, while ignoring the relative impact of crude oil.

#### 2.2.1.1 Mineral dissolution

One of the mechanisms that have been proposed for low salinity effect in carbonate rocks is mineral dissolution which is believed to generate *in-situ* ions thereby acting as wettability modifying agents. Hiorth et al. [23] investigated the effect of water chemistry on surface charges and rock dissolution in carbonate rocks. They constructed a geochemical model to predict surface potential and sulfate adsorption on calcite at different temperatures. They concluded that mineral dissolution is a controlling factor in wettability alteration of calcite which causes pore collapse that could expel oil.

Moreover, Evje et al. [24] studied the role of water-rock chemistry on the wettability of porous media. They proposed a mathematical model that explains the dependence of oil recovery and brine composition that is reported in literature. The mathematical model showed that wettability alteration of calcite is directly related to change in brine composition due to calcite dissolution/precipitation. Additionally, the dissolution of anhydrite ($CaSO_4$) was hypothesised to be a contributing factor to low salinity effect [4, 5, 25]. For instance, Pu et al. [25] suggested that the improvement in oil recovery by low salinity water is related to a shift in wettability from weakly water-wet to water-wet. This involves dissolution of anhydrite, and associated release of dolomite crystals and fine materials from pore surfaces. Yousef et al. [26] also suggested that rock dissolution due to injection of brines with contrasting salinity can enhance connectivity in pore network, supported by their NMR results. The authors proposed that wettability alteration is caused by alteration of surface charges, leading to dissolution process. The process of anhydrite dissolution was a centre of focus in works of Austad et al. [4] and Austad et al. [5]. They argued that anhydrite-free sample may not lead to the incremental oil recovery in carbonate rocks during low salinity waterflooding.

Meanwhile, some experimental studies failed to observe tertiary low salinity effect despite anhydrite dissolution, while others showed lack of correlation between presence of anhydrite and EOR. For instance, Jiang et al. [6] reported no additional oil recovery in tertiary mode although anhydrite dissolution was detected. Similarly, Gandomkar et al. [27] did not observe tertiary low salinity recovery in their core flooding experiments although their limestone samples contained 10% anhydrite. Moreover, spontaneous imbibition results reported by Uetani et al. [7] showed improved oil recovery in carbonate cores regardless of their anhydrite content, prompting the authors to rule out anhydrite dissolution as a key low salinity EOR mechanism in carbonate reservoirs.

Given contradictory reports on the contribution of fluid-rock interaction to low salinity effect, particularly the role of anhydrite dissolution, we have conducted further investigation on this issue and present our findings in Chapter 3.

## 2.2.2 Fluid-fluid Interaction

The mechanisms proposed and discussed in this section attempt to explain low salinity phenomenon in carbonate by only considering the interaction between oil and

brine, while ignoring the relative impact of brine-rock interaction on wettability. Although experimental evidence in low salinity EOR literature overwhelmingly suggest these proposed mechanisms could not cause low salinity effect, to achieve a more comprehensive understanding of low salinity phenomenon, it is crucial to discuss these mechanisms.

### 2.2.2.1 Interfacial Tension (IFT) Reduction

The fluid flow in porous media is mainly controlled by different forces such as viscous and capillary forces. The capillary forces can act as a dragging force to trap oil clusters during waterflooding, namely residual oil saturation (Sor). To decrease the residual oil saturation, decreasing interfacial tension (IFT) thus capillary pressure can further decrease the residual oil saturation such as surfactant flooding. However, to achieve a pronounced residual oils reduction, the interfacial tension of oil-brine must decrease to $10^{-2}$ dyn/cm [28]. Published work show that low salinity water likely varies oil-brine interfacial tension largely due to the variation of the chemical species at oil-brine interfaces whilst contacting with low salinity water. A few researchers attributed low salinity effect to reduction in IFT [29, 30]. However, the reported IFT reduction was not significant enough to mobilize residual oil saturation. For example, Al Harrasi et al. [31] reported only 1.0 dyn/cm reduction when formation brine was diluted 100 times, while Al-Attar et al. [32] reported a reduction in IFT with decreasing salinity in the range of 14-30 dyn/cm for two different reservoir brines. Thus, the authors conclude that IFT is not responsible for increase oil recovery because of no clear trend between IFT and oil recovery. Furthermore, Yousef et al. [26] investigated the effect of fluid-fluid interaction on improved oil recovery by conducting series of IFT measurements and core flooding experiments. The author reported IFT reduction <10 dyn/cm and concluded that low salinity water flooding has a negligible impact on IFT, thus not responsible for low salinity effect.

### 2.2.2.2 Micro-Dispersion Formation

Apart from the reduction in the IFT between oil and brine, formation of micro-dispersions during low salinity water injection is considered by some researchers as a contributing mechanism to wettability alteration and improved oil recovery [33]. Emadi et al. [34] was the first to present a visual evidence of water micro-emulsions formation at oil-brine interface upon contact with low salinity brine. They hypothesized that in low salinity condition, the surface-active agents in crude oil encapsulate water micro-

emulsions. The progressive development of water micro-emulsions results in the depletion of surface-active components in oil-water interface and alteration of surface charges at fluids-rock interfaces which lead to wettability alteration. Mahzari et al. [35] further investigated the interactions between crude oil and brine by performing series of fluid characterization tests. The authors reported spontaneous formation of water-in-oil dispersion with salinity decrease, in line with previously published reports. Sarvestani et al. [36] investigated the impact of brine salinity on the stability of micro-emulsions droplets as one of the main mechanisms for enhanced oil recovery. The authors reported that emulsion droplets became more stable with decreasing brine salinity which may explain the increase in pressure drop that they observed during low salinity water flooding. Strictly speaking, formation of micro-emulsion, IFT reduction or any other fluid-fluid based mechanism is not unique to a particular rock formation given they do not consider fluids-rock interactions.

## 2.2.3 fluid-fluid-rock Interaction

The common feature of the mechanisms discussed in this section is that the wetting characteristics in oil-brine-rock system are determined through the symbiotic interactions between oil-brine and brine-rock.

### 2.2.3.1 Adsorption of Potential Determining Ions (PDI)

It has been proposed the desorption of carboxylic materials from carbonate rock surface can be achieved in presence of key divalent cations such as $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ which have been referred to as potential determining ions (PDIs). The effect of PDI on oil-brine-rock interactions has been extensively investigated through various techniques such as contact angle measurement, spontaneous imbibition, and core flooding experiments. The results overwhelmingly show that variation in concentration of PDI in brine result in wettability alteration. This finding prompted many researchers to attribute low salinity effect to potential determining ions adsorption process. Austad et al. [37] was able to demonstrate that the presence of $SO_4^{2-}$ in seawater improves the efficiency of spontaneous imbibition in chalk. They suggested that sulfate is a potential determining ion which will adsorb onto the chalk surface and lower the positive charge density to facilitate the release of polar components. In a similar study, Zhang et al. [38] showed that sulfate in the imbibing fluid can improve oil recovery in chalk, further confirming its wettability modifying effect. In a later work, Strand et al. [39] examined the effect of $Ca^{2+}$ and $SO_4^{2+}$ on wettability alteration in carbonate rocks.

The author used chromatographic technique to show that the adsorption of $SO_4^{2-}$ onto chalk increases with increasing $Ca^{2+}$ concentration. They proposed a mechanism in which adsorption of $SO_4^{2-}$ with contribution from $Ca^{2+}$ ions change the surface charge of calcite, leading to improved oil recovery. In addition to $Ca^{2+}$ and $SO_4^{2-}$ ions, it was also verified that $Mg^{2+}$ is another strong potential determining ion which at high temperatures can substitute $Ca^{2+}$ from chalk surface and increases its positive surface charge density [3]. The chemical mechanism which was proposed for this process is almost identical to that proposed by Strand et al. [39], with the addition of a process involving the co-adsorption of $Mg^{2+}$ ions at higher temperatures (Figure 2-1). subsequently, a few works have been conducted to show the effectiveness of potential determining ions in improving oil recovery by wettability alteration towards more water-wet [3, 4, 40, 41].
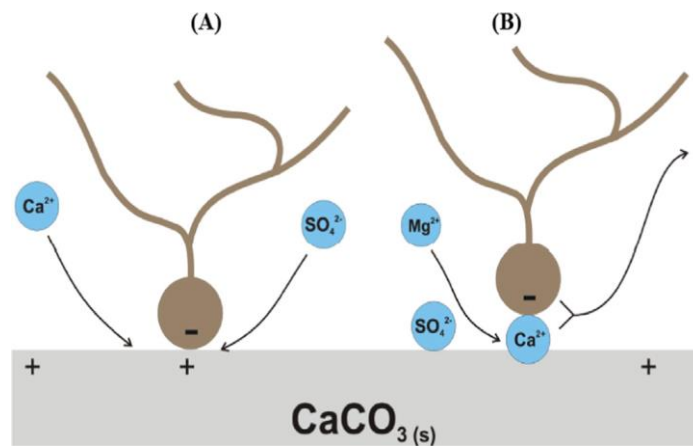


Figure 2-1. The schematic of wettability alteration mechanismthat was proposed by Zhang et al. showing the interaction between $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$ which result in desorption of carboxylic materials from chalk surface (Zhang et al., 2006).

Apart from brine chemistry, the presence of anhydrite ($CaSO_4$) in rock was also suggested as prerequisite for triggering low salinity effect in carbonate reservoirs. In the fluid-rock interaction part of this work we presented a detail discussion on the conflicting scientific views regarding the role of anhydrite dissolution on wettability alteration. Therefore, we will not discuss the role of anhydrite dissolution in this section further. However, it should be noted that anhydrite dissolution is thought to be a method of generating *in-situ* $SO_4^{2-}$ which is believed to act as a catalyst in wettability alteration process.

As we mentioned earlier, due to conflicting reports it is uncertain if anhydrite dissolution is prerequisite for wettability alteration by low salinity water. However, what is certain is that the presence of sulfate in injection brine poses series of major operational challenges. For example, sulfate has been identified as the main culprit in formation of various types of scales - calcium sulfate, barium sulfate, and/or strontium sulfate - which cause serious oil field problems [42-45]. In addition, reservoir souring has also been observed following injection of low salinity water with high sulfate content [46], posing yet another challenge. Therefore, it is imperative to understand if low salinity water flooding can achieve its full potential without the added $SO_4^{2-}$ in injection brine which would not only benefit oil recovery but may also minimize the operational challenges associated with sulfate. To answer this question, this research presents an experimental study consists of coreflooding experiment, contact angle measurements and zeta potential measurements in absence of sulfate ions. The result of this investigation is expected to provide further guidance about the mechanisms of low salinity effect.

2.2.3.2 Electric Double Layer Expansion (EDL)

An electrically charged surface such as calcite when in contact with aqueous solution, generate electrical field which result in unequal distribution of ions in the vicinity of the surface. Oppositely charged ions in the aqueous solution (counter-ions) are attracted to the surface to form a diffuse layer of charge outside the charged surface, while the ions with similar charge to the surface (Co-ions) are repelled from the surface [47]. The diffuse layer and the surface charge together form what is known as *electrical double layer*. The counter-ions within the double layer are not distributed equally, therefore a potential across the interface is developed. Some counterions are strongly adsorbed onto the surface forming a fixed layer known as Stern layer. The stern layer which is adjacent to the mineral surface may be further divided into inner and outer Stern layer or planes [11]. The electric potential of the surface at the location of shear or slip plane is called zeta potential which is commonly measured using electrophoresis method.

It has been proposed that surface of reservoir rocks is covered with thin water film in order of 10 nm which connects the bulk aqueous phase [48]. Hirasaki [49] used Laplace-Young and DLVO theory equation to describe how intermolecular surface forces affect wettability of oil-brine-rock system by affecting the thickness and the stability of water film. In a three-phase oil-brine-rock system, the distance between the

two interacting interfaces affects the energy of the system. System energy is a function of the distance between oil-brine and brine-rock interfaces and represented by disjoining pressure $\prod$, which is comprised of three components: van der Waals, electrical, and structural forces:

$$\prod_{total} = \prod_{van\text{-}der\text{-}Waal} + \prod_{electrical\ double\ layer} + \prod_{structural}$$

In the above equation, the electrical double layer force is estimated using zeta potentials, where negative disjoining pressure, Figure 2-2a, indicates an attractive electrostatic force between oil-brine-rock interfaces, thus compressed EDL, while positive disjoining pressure, Figure 2-2b, signifies a repulsive electrostatic force between the two interfaces and expanded EDL [50, 51].
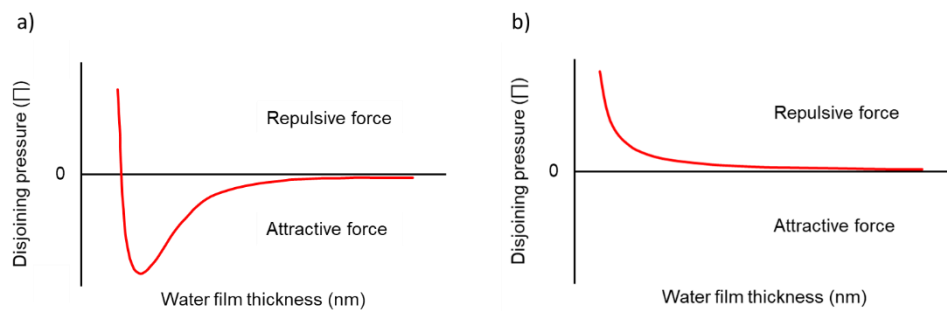


Figure 2-2. Illustration of disjoining pressure for oil-brine-rock systemat a) compressed electric double layer in high salinity water and b) expanded electric double layer in low salinity water.

Brine chemistry has been identified as a major factor influencing the thickness of electric double layer. Therefore, low salinity studies commonly rely on zeta potential measurements to characterize wettability or to demonstrate wettability alteration. For example, in a study by Alotaibi et al. [52], low salinity water was shown to create more negative charges on limestone and dolomite particles by expanding the thickness of electric double layer, thus altering the wettability of carbonate rock from oil-wet to water-wet. In a follow up study, Alotaibi et al. [8] measured the zeta potential of crude oil and limestone particles in various brines which showed that zeta potential is affected by salinity and ion type. They concluded that wettability of rock and oil recovery are affected directly by the zeta potential of oil droplet and mineral particles. Mahani et al. [10] presented an experimental study in which the effect of brine chemistry on wettability of carbonate was investigated through zeta potential and contact angle

measurements. The authors established a link between change in surface charges at oil-brine and brine-rock interfaces and contact angles where wettability alteration toward more water-wet occurs with decreasing brine salinity. Moreover, several other studies also concluded change in the zeta potential at the interfaces of oil-brine and brine-rock due to salinity reduction account for wettability alteration and improved oil recovery [9, 53, 54].

In general, although factors such as salinity, ionic strength, oil compositions and rock minerology have been extensively investigated leaving little doubt about their impact on wettability, the effect of brine pH on the electrostatic interactions between oil-brine and brine-rocks remain poorly understood. Therefore, for more reliable prediction of wettability alteration in carbonate reservoirs, it is important to understand the contribution of pH to electrical double layer expansion. To address this challenge, we performed a geochemical modelling study in light of diffused double layer to understand how pH controls wettability in oil-brine-calcite system.

### 2.2.3.3 Surface Complexation

The interaction at oil-brine and brine-rock interfaces is influenced by the geochemical reactions between the functional groups in crude oil and the surface groups in calcite. The extent and nature of these surface reactions determine the wetting characteristic of reservoir rocks. The concentration of these charged surface species depends on the chemical composition of brine, oil, and mineral surface and can be calculated using PHREEQC software [12]. Van Cappellen et al. [55] presented a surface complexation model (SCM) for brine-carbonate interface which postulate the formation of two hydrated species $>CO_3H$ and $>CaOH$ at calcite surface upon exposure to aqueous solution. The protonation/deprotonation of these primary exchange sites facilitate the adsorption of multivalent cations/anions (i.e. $Ca^{2+}$, $CO_3^{2-}$, and $SO_4^{2-}$) causing carbonate to develop surface charge [12]. The overall concentration of different charged species determines the overall charge of carbonate surface. Similarly, crude oil contains charged carboxylic acid ($-COOCa^{2+}$, and $-COO^-$) and nitrogen base ($-NH^+$) surface groups, whose concentrations can be quantified by measuring oil acid number (AN) and base number (BN). The oppositely charged surface species from oil and calcite are attracted to one another to form electrostatic bridges, instigating local oil adhesion. The magnitude of electrostatic attraction depends on the number of electrostatic bridges at oil-brine-calcite interfaces - bond product sum [12] - which is controlled by factors such as salinity [14, 15], ionic strength [16, 17], oil composition [19-

21] and rock mineralogy [56], thus impacting the oil adhesion. However, few studies have been conducted to exclusively focus on the effect of pH on oil-brine-rock interactions, thus wettability. For example, Mahani et al. [57] proposed a SCM to capture the behaviour of zeta potential with pH. The model showed the increase in zeta potential with pH is caused by the formation of surface species. Nevertheless, the model only considered speciation at brine-calcite interface, while the effect of pH on surface species at oil-brine interface was not included. Furthermore, Song et al. [58] measured the zeta potential of synthetic calcite in mixed brines containing potential determining ions - $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$ and $CO_3^{2-}$ - and developed a generalized double layer SCM to model the zeta potential results and predict wettability alteration. Although the model was able to accurately predict calcite zeta potential in various ionic solutions, the scope of the study was limited to brine-calcite interactions, while the contribution of charged surface species at oil-brine interface and the effect of pH on wettability alteration were overlooked.

Given wettability of oil-brine-carbonate system is governed by the symbiotic interactions between the surface species at both oil-brine and brine-rock interfaces which appears to be sensitive to brine pH, it is imperative to understand how pH affects surface speciation at oil-brine and brine-calcite interfaces, thus regulating wettability. Therefore, to answer the above question, we conducted an experimental study in which we demonstrated the correlation between contact angles and pH. A SCM was also developed to explain how brine pH controls the number of surface species at interfaces of oil-brine and brine-carbonate, thus explaining experimental results.

## 2.3 Wettability alteration at different length scales

In the above sections, we discussed several possible mechanisms that explained wettability alteration by low salinity water in carbonate rocks. Most researchers conduct experiments to support of their hypothesis and demonstrate wettability alteration by low salinity brine; contact angle measurements being a common method. For example, Al-Attar et al. [32] conducted a number of contact angle measurements to show that wettability alteration is likely the main physiochemical process during low salinity water flooding. Yousef et al. [26] also conducted a series of contact angle measurements on carbonate rocks in the presence of connate water and seawater with different dilutions, showing a shift of wettability towards the water-wet characteristics. Similarly, Alotaibi et al. [59] presented over 38 contact angle measurements to reveal the wettability alteration process for oil-brine-carbonate system in the presence of various

brines. Also, Alameri et al. [60] performed contact angle measurements to further confirm wettability alteration process from oil-wet to intermediate-wet in oil-brine-carbonate systems.

The surfaces on which these and other contact angle measurements are performed are either naturally smooth minerals, (i.e. mica, calcite crystals), or reservoir rocks that have undergone significant treatments (i.e. polishing) to minimize the effect of physical heterogeneity on contact angle results. Evidently, these surfaces do not correctly represent the *in-situ* pore networks with typical roughness > 100 nm. Given wettability is a multi-scale petrophysical property which is defined by interactions between molecules in fluid-fluid-rock system and the in-situ pore surface roughness [61-63], it is imperative to understand how surface roughness correlate with wettability in oil-brine-carbonate system. Also, it is crucial to realize if the mechanisms leading to wettability alteration on the sub-pore scale can also prevail at pore-scale. This is particularly important for upscaling the wettability alteration results from sub-pore scale to reservoir scale. To address this knowledge gap, an experimental and analytical study which consists of systematic contact angle measurements at different surface roughness and salinity conditions is conducted in this research.

# Chapter 3 Drivers of Low Salinity Effect in Carbonate Reservoirs

## 3.1 Abstract

Wettability alternation appears to be the main mechanism of low salinity water flooding in carbonate reservoirs. However, what factor(s) controls the wettability alteration is not clearly defined. We hypothesized that zeta potential at interfaces of oil/brine and brine/rock, controls the wettability alternation in carbonate reservoirs. To test our hypothesis, we removed $SO_4^{2-}$ ions from the aqueous ionic solutions because $SO_4^{2-}$ ions likely adsorb at the pore surface, triggering desorption of carboxylic materials. We examined the zeta potential of interfaces of crude oil/brines and brines/rock. We also measured the contact angle and conducted two core-flooding experiments. Moreover, we performed a geochemical study to examine the potential of calcite dissolution by low salinity water using PHREEQC software.

Our work demonstrates that contact angle strongly correlates with polarity of the zeta potential of interfaces of oil/brine and brine/rock, showing that same polarity of zeta potential for oil/brine and brine/rock, triggered strongly water-wet carbonate surface in the presence of formation brine. The opposite polarity of zeta potential of oil/brine and brine/rock on the other hand, yielded intermediate or slightly oil-wet surface in the presence of 10 times diluted formation brine. However, incremental recovery of 5.8-18.1% was observed under tertiary mode, implying that low salinity water likely shifts the reservoir wettability from strongly water-wet to intermediate-wet. In addition, geochemical modelling revealed negligible amount of calcite was dissolved in the presence of low salinity water, confirming that calcite dissolution is not a contributing factor to low salinity effect. Moreover, we demonstrate that contact angle on the carbonate substrate decreases linearly with increasing Z parameter, $Z_p = \left(\left|Zeta_{oil/brine} + Zeta_{birne/rock}\right|\right)$. We therefore argue that manipulating Z parameter (polarity of zeta potential of brine/rock and oil/brine) is of vital importance to shift the reservoir wettability and improving oil recovery. We suggest that the Z parameter may be used as an interpolant to model the low salinity effect, rather than using salinity level or individual ion in the solution.

## 3.2 Introduction

Carbonates rock host most of the world's oil reserves (>60 %) [64], which are composed primarily of the minerals calcite and dolomite together with impurities, e.g., quartz, anhydrite, clay minerals, organic matter and apatite [65]. However, the average recovery typically is lower than 40%. The cost-effective and environmentally friendly techniques to enhance the oil recovery are therefore of broad scientific interest [53]. One such technique that has gained interest within industry is low salinity water flooding (LSW), involving injection of low salinity brine into the reservoir under secondary and tertiary conditions [66].

Several mechanisms have been proposed to describe how the low salinity water (LSW) improves oil recovery in sandstone: fines mobilization [67], limited release of mixed-wet particles [67], increased pH and reduced IFT similar to the alkaline flooding [68], multi-component ion exchange (MIE) [69-72], electrical double layer expansion [51, 73, 74], salt-in effect [75], salting-out effect [76] and osmotic pressure [77].

However, deeper understandings of low salinity effect in carbonate reservoirs is yet to be reached, which places limitation on the application of low salinity water in carbonated reservoirs [66]. Previous studies suggest that wettability alternation is the main and most acceptable mechanism for the low salinity effect in carbonated reservoirs, despite of the fact that what factors controlling the wettability have not been completely elucidated. For example, most reports suggest that low salinity water shifts reservoir wettability from oil-wet towards water-wet, lifting oil film off the pore surface, whereas Al-Attar et al. [32] found the opposite, arguing that low salinity water shifted reservoir wettability from water-wet to intermediate condition, thus exhibiting measurable additional oil recovery. Existing theories suggest that sulphate acts as a catalyst to adsorb at the pore surface due to strong affinity compared to carboxylic group, thereby changing the rock charge locally from positive to negative, and generating repulsion force between carboxylic group and pore surface [4]. Consequently, the reservoir rock wettability is shifted from oil-wet to water-wet, thus exhibiting measurable increase in incremental oil recovery. However, there is still uncertainty about the nature of wettability change, with some reports suggesting it is double layer expansion, while others suggesting it is mineral dissolution [78].

It has been shown that zeta potential at the interfaces of oil/brine and brine/rock in carbonate reservoirs, depends on water chemistries and crude oil compositions, rather than salinity level itself [50]. In this context, we aimed to test the hypothesis that zeta potential at interfaces of oil/brine and brine/rock, governs the wettability alternation in carbonate reservoirs. To test our hypothesis, we removed $SO_4^{2-}$ ions from the aqueous ionic solutions because $SO_4^{2-}$ ions likely facilitate the wettability alteration due to adsorption at the pore surface, triggering desorption of carboxylic materials [79].

We examined the effect of salinity level (formation brine: 252,244 ppm, 10 times diluted), on zeta potential at interfaces of oil/brine, and brine/rock. We also measured the contact angles on aged and un-aged carbonated rocks, using crude oil and aqueous ionic solutions. Moreover, to validate our hypothesis, two core flooding experiments were conducted to access the effect of LS on incremental oil recovery. Furthermore, a geochemical study was conducted using PHREEQC software, to evaluate the effect of mineral dissolution on low salinity EOR process.

## 3.3 Experimental Methodology

### 3.3.1 Materials

#### 3.3.1.1 Rock Mineralogy

Given that the rock mineralogy is essential to unveil the mechanism(s) of low salinity water in carbonated reservoirs, we examined the mineralogy of the core plugs prior to wettability tests and core-flooding experiments. X-ray diffraction (XRD) results showed 98.1 % of calcite, 0.7% quartz and 1.2% Ankerite but without anhydrite ($CaSO_4$).

#### 4.3.2 Brine Properties

To test our hypothesis, we removed the $SO_4^{2-}$ from all of the experimental brines. Formation brine (FB) was synthesized based on the composition of produced water from North Rumaila field with salinity of 286,677 ppm [80]. Formation brine was then diluted 10 times (10dFB) using deionized water, to obtain low salinity brine required for this study (Table 3-1).

Table 3-1. Specification of the brines used in core flooding experiments.

| Brine | mg/L | | | | | | TDS (ppm) | pH |
|---|---|---|---|---|---|---|---|---|
| | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Fe^{2+}$ | $Cl^-$ | | |
| Formation brine | 74638 | 15200 | 4526 | 2013 | 303 | 155564 | 252244 | 2.55 |
| 10dFB | 7463.8 | 1520 | 452.6 | 201.3 | 30.3 | 15556.4 | 25224.4 | 4.42 |

Note that the brines used in this study had low pH value (Table 1) due to the reaction of iron (II) chloride ($FeCl_2$) in water, which resulted in formation of ferrous, and chloride ions. This process resulted in the removal of hydroxyl ions from the solution, leaving hydrogen ions in excess, which makes the solution acidic, hence having low pH value.

3.3.3 Crude Oil

The experimental crude oil was extracted from Stag field located in Commonwealth waters on the North West shelf of Western Australia. To avoid the precipitation and plugging of partials in the crude oil during injection of crude oil, the crude oil was filtered using 12-micron paper filter. Physical properties of crude oil are presented in (Table 3-2). Note: the experimental oil had a higher base number (1.02 mg KOH/g) than acid number (0.50 mg KOH/g), suggesting that concentration of $-NH2+$ at oil surface may be two times greater than $-COO-$ [12]. This implies that the zeta potential at the interface of oil/brine may be positive at low pH condition.

Table 3-2. Physical properties of crude oil.

| Property | Unit | Result |
|---|---|---|
| density | g/cm$^3$ | 0.94 |
| API gravity | °API | 18.50 |
| Specific Gravity 260/60°F | - | 0.94 |
| Acid number | mg KOH/g | 0.50 |
| Base number | mg KOH/g | 1.02 |
| Kinematic viscosity @ 20°C | cSt | 122.50 |
| Kinematic viscosity @ 40°C | cSt | 37.26 |
| Asphaltene content | % mass | 0.14 |
| Water content | % volume | 0.15 |
| Wax content | % mass | <5 |

### 3.3.2 Experimental Setup and Procedure

#### 3.3.2.1 Zeta Potential Measurements

It has been reported that the surface charges would be generated at the interfaces of fluid-fluid, and fluid-rock due to the ionization of the chemical group in the presence of aqueous ionic solutions [81]. The magnitude of electrical charges at the interfaces of fluid-fluid, and fluid-rock, can be determined by measuring zeta potential, which may control the rock wettability. We thus measured the zeta potential at interfaces of oil/brine, and brine/rock with various salinity level using Malvern Zetasizer ZS Nano series. Given that measured zeta potentials are much more stable at 25°C than at high temperatures due the evaporation of brine at high temperatures, all zeta potential measurement were conducted at 25°C, knowing that zeta potentials tend to decrease uniformly with an increase in temperature [82]. The detail experimental procedures for zeta potential measurements is described by Xie et al. [51].

#### 3.3.2.2 Contact Angle Measurements

To investigate the effect of water chemistries on wettability of carbonated rock, we tested the contact angle on the rock with crude oil and aqueous ionic solutions using Vinci IFT-700 (Figure 3-1). The experimental temperature and pressure were 60 °C

and 2000 psi respectively. Contact angle tests were conducted on various aged, and un-aged substrates using sessile droplet method.
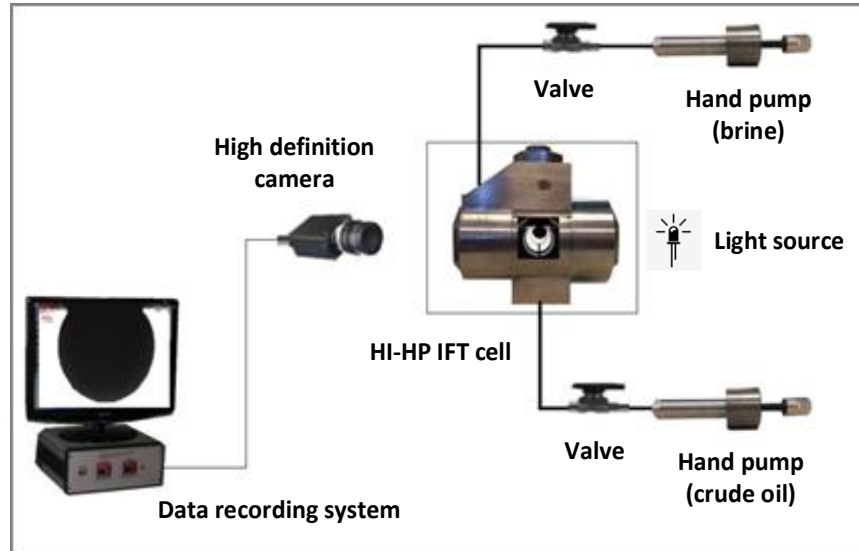


Figure 3-1. Schematic diagram of contact angle and interfacial tension apparatus.

3.3.2.3 Core Flooding Experiments

Core-flooding experiment is an integral part of our investigation to test our hypothesis, showing directly the effect of water chemistries on additional oil recovery during low salinity water injection. We tested low salinity effect under tertiary mode using two core plugs from North Rumaila oil field, Iraq. Samples C3, and C5 were extracted from North Rumaila oil field with permeability of 2.6 mD and 6.0 mD, respectively (Table 3-3).

Table 3-3. The petrophysical properties of core plugs.

| Core samples | Porosity (%) | Pore volume (ml) | Permeability (mD) | Flooding sequence |
| --- | --- | --- | --- | --- |
| C3 | 18.5 | 9.2 | 2.6 | FB+10dFB |
| C5 | 23.0 | 13.0 | 6.0 | FB+10dFB |

The core flooding experimental setup was shown in (Figure 3-2). The core holder used in this experiment was capable of withstanding pressure up to 10,000 psi. The outlet of the core holder was connected to a spring-loaded type back pressure regulator, providing required pore pressure for core flooding experiments. The system was heated using heating jackets encasing both the core holder and the accumulator and was maintained by two temperature controllers. Pressure transducers were installed at both the inlet and outlet of the core holder, to monitor the differential pressure. The crude oil was delivered through an accumulator connected to a syringe pump. 5.0-micron line filter was also placed in crude oil injection line to remove any suspended particles.
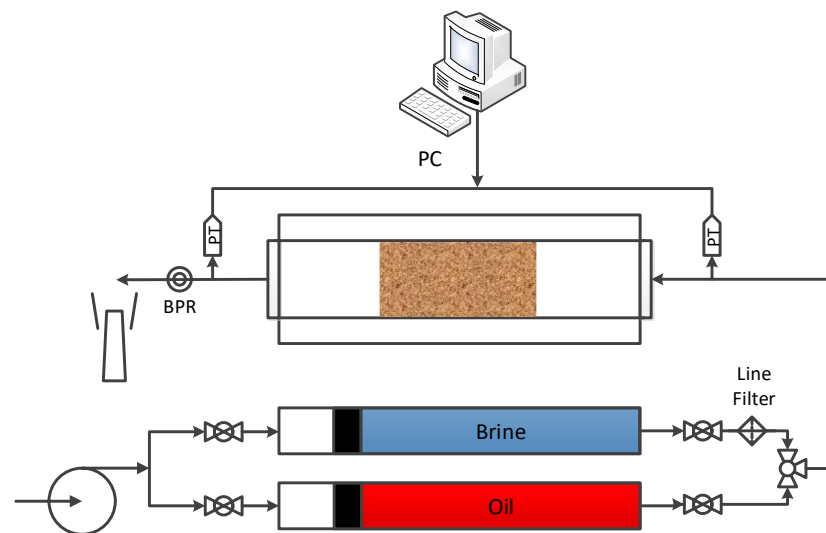


Figure 3-2. Schematic diagram of experimental setup used for core flooding experiment.

To avoid the effect of remaining oil attached at the pore surface on low salinity effect, all core plugs were cleaned with toluene followed by methanol using Dean-Stark method to remove any organic and inorganic substances. This process was repeated multiple times until solvent in Dean-Stark apparatus remained clean. The core plugs were then placed in an oven and subjected to moderate temperature of 60 °C until fully dry. Core samples were placed into the core holder and subjected to overburden pressure. The system was then vacuumed using a vacuum pump for 24 hours to remove any trapped air inside of the system. After the vacuuming process, samples were injected with formation brine at a rate of 0.2 ml/min for a total of 5 PV to stablish

the initial water saturation. The samples were then kept under 1000 psi pressure for 24 hours to enhance saturation process. To stablish initial water saturation ($S_{wi}$), crude oil was injected into the samples at multi-flow rate of 0.2-1.0 ml/min, until no more water was observed in the effluent. The injection continued for a further 2 PV to ensure the initial water saturation was reached and in an equilibrium state. The initial water saturation of the core plugs is given in Table 3-3. The core samples were then left inside of the system to age for the period of four weeks at 60 °C.

After the aging process, samples were flooded with various brines under tertiary mode at a rate of 0.5 ml/min to investigate the response to variation in salinity in different injection modes. Given that the impact of end effect is negligible in low permeability rock, multi-flow rate was not applied during the water flooding [83].

## 3.4 Results and Discussions

### 3.4.1 Effect of Water Chemistry on Zeta Potential

Zeta potential at the interface of oil/brine were positive in the presence of FB and 10dFB and decreased with the decline in the salinity level. For example, the zeta potential at oil/brine interface decreased from 6.07 mV in FB, to 3.97 mV in presence of 10dFB. This can be interpreted by the surface complexation modelling, which show that the concentration of $-NH^+$ at the oil surfaces increases with the decrease of the pH, whereas the concentration of $-COO^-$ decreases slightly with decrease of the pH, particularly for crude oil with high base number [12]. Note: the high concentration of $-NH^+$ at the oil surfaces triggers positive zeta potential, and the high concentration of $-COO^-$ leads to negative zeta potential. This is consistent with the available data reported by Mahani et al. [15] and Hirasaki et al. [84], suggesting that the zeta potential of oil/brines is negatively charged at pH>4.5, but can become positive at lower pH. Note: the pH of the solution in this study was 3.08, 4.36 in the presence of the FB, 10dFB, respectively. However, existing data also show that zeta potential of crude oil/brine becomes strongly negative with the decrease in salinity [15, 85]. For example, Mahani et al. [15] measured the zeta potential of oil emulsion in FW, SW, and 25dSW where the surface charge at oil/brine interface was found to decrease from -2.5 mV for oil/FW, to -10 mV for oil/SW and -25 mV for oil/25dSW at pH level of 6.5. This is also consistent with the surface complexation modelling, which showed that at pH=6.5, the concentration of $-NH^+$ decreased sharply compared to low pH (<6). Yet, the concentration of $-COO^-$ slightly increased with the decrease of the salinity level

and the concentration of –COOCa$^+$ decreased with the decrease of the salinity level. Together, lowering salinity level triggers negative surface charges, mainly –COO$^-$ at the surface of oil/brine as the pH level greater than 6 (see Figure 5 [12]).

The zeta potential of rock/brine decreased from 5.91 mV to -1.46 mV as the salinity level declined from FB to 100dFB (Table 3-4), consistent with Mahani et al. [15] who showed that surface charge of limestone decreased from 5 mV in FW, to -5 mV in SW and -15 mV in 25dSW. We believe that this phenomenon can also be interpreted by surface complexation modelling. For example, the surface charge at the surface of calcite shifts from positive to negative with the increase of the pH due to the increase of the >CO$_3^-$ at the calcite surface [12]. This implies that with increase in the pH level, the zeta potential at the interface of brine/carbonate shifts toward negative from positive, in line with our data and existing results [15]. Note that in our experiment, as salinity decreased from FB to 10dFB ppm, pH of the solution increased from 4.87 to 6.43 for brine/rock. Together, our zeta potential results and those reported in the literature suggest, a strong correlation between the zeta potential and surface complexation. This is because the physics behind the zeta potential and surface complexation are similar in nature. Note: the physics here means that the interaction of Crude Oil/Brine/Rock is controlled by both electrostatic and non-electrostatic physisorption together with competitive ion chemisorption (ion exchange and surface complexation).

Table 3-4. Zeta potential, and pH results for fluid-fluid and fluid-rock.

| | Zeta potential (mV) | | pH | |
|---|---|---|---|---|
| Samples | Rock/Brine | Oil/Brine | Oil/brine | Brine/rock |
| FB | 5.91 | 6.07 | 3.08 | 4.87 |
| 10dFB | -1.48 | 3.97 | 4.36 | 6.43 |

## 3.4.2 Effect of Water Chemistry on Contact Angle

The contact angle on the carbonate substrate increased with the decrease of salinity level. For example, the contact angle on un-aged carbonate substrate increased from 30 to 50$^o$ with decrease in the salinity from FB, to 10dFB (Figure 3-3). This indicates wettability alteration in carbonate from strongly water-wet, to less water-wet condition.

Our contact angle results were consistent with the zeta potential measurements. For instance, zeta potential at the interface of oil/brine and brine/rock had the same polarity, both positive (Table 3-4), suggesting a repulsive electrical double layer force. Yet, the opposite polarity of zeta potential at the interface of oil/brine and brine/rock was observed in the presence of 10dFB, implying the attractive electrical double layer force. Note: the polarity of the zeta potential is an electric property [86] which should be positive or negative. Same polarity of the zeta potential means that both zeta potential of oil/brine and brine/rock should be positive or negative. Otherwise, we consider them as different polarity.

Given that the interfaces of crude oil/brine/rock in reservoir conditions are in thermodynamic and electrostatic equilibrium, we also measured the contact angle between oil and various salinity brines on crude oil-aged carbonate rock samples. Our results show that contact angle shifted from 35 to 105°, as the salinity level decreased from FB to 10dFB (Figure 3-4). This indicates that 10dFB rendered an intermediate or slightly oil-wet surface. This is also consistent with our zeta potential test. We therefore believe that there is a strong correlation between wettability and zeta potential, whereby same polarity of zeta potential likely triggers water-wet surface, and the opposite polarity of the zeta potential likely renders intermediate or oil-wet surface.

Although we observed a similar trend in contact angle alteration for both aged and un-aged rock samples, the effect of reduction in salinity on wettability was much more profound on aged substrate compared to un-aged substrate. This implies that aged substrates should be applied to examine the effect of water chemistry on contact angle. Our results are in line with Al-Attar et al. [32] who reported that the contact angle increased with the decrease in the salinity level. For example, they observed the contact angle increased from 45° in the presence of FB (197,000 ppm), to 70° when salinity was reduced to 1,000 ppm. They argue that a shift in carbonate wettability from water wet to intermediate condition triggered incremental oil recovery.

Furthermore, similar results were reported by Mohsenzadeh et al. [30] who found that successive dilution of FB increased the contact angle from 63° in FB (203,000 ppm), to 130° in 20dFB, triggering wettability alteration from water-wet to oil-wet condition. However, opposite results have also been reported in some literatures, suggesting that low salinity brine shifts the wettability of carbonate rocks from oil-wet to preferentially water-wet condition [15, 59, 87, 88]. For example, Mahani et al. [15] reported that the contact angle was decreased by 5-17° as the high salinity fromation brine was

switched over to sea water after 40 hours. Note: the pH for the fluids before and after the contact angle test did not change (pH for FW=6.9, and pH for SW=8.0). The contact angle shifting towards more water-wet can be interpreted by surface complexation modelling. For example, at pH above 6, the –COO⁻ dominated the surface charge of the interface of oil/brine, although –COOCa⁺ incrases slightly with the increase of pH. This probably shifts the zeta potential towards more negative from positive, triggering repulsive electrical double layer force as the zeta potential of the brine/rock becomes strongly negative as the salinity decreases. This may be the reason why the low salinity water shifted the wettability towards more water-wet from oil-wet or slightly oil-wet. However, although the both pH and salinity level affected the contact angle, zeta potential at the interfaces of fluid-fluid and fluid-rock strongly correlate to the rock wettability. This is because that zeta potential is closely related to surface complexation, chemisorpion and physisorption [89].



Figure 3-3. Contact angle of various brine and oil on the carbonate (un-aged) sample.
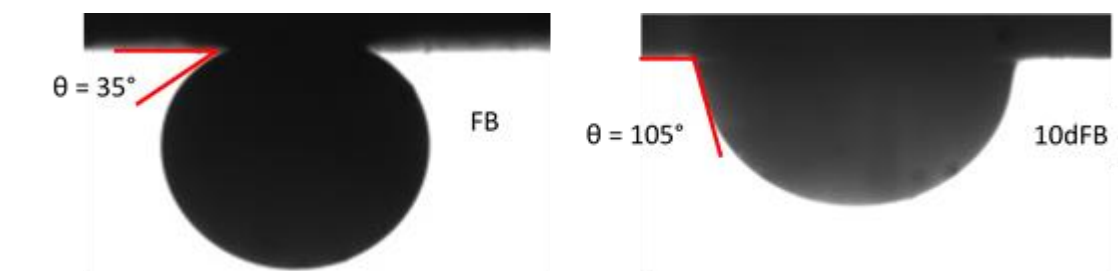


Figure 3-4. Contact angle of various brine and oil on the carbonate (aged) sample.

### 3.4.3 Low Salinity Effect Under Tertiary Mode

To further test our hypothesis, two core plugs were used to test the low salinity EOR-effect under tertiary mode. Our results showed that injecting 5 PV of formation brine into sample C3 in secondary mode yielded total recovery of 41.6 % of OOIP (Figure 3-5). 10dFB was then injected under tertiary mode, exhibiting 18.1 % of OOIP additional oil recovery. Similarly, sample C5 was flooded with high salinity formation brine in secondary mode until maximum oil recovery of 57.7 % was achieved after injecting 3.7 PV. Subsequently, 10dFB was injected under tertiary mode, and incremental oil recovery increased to 63.5% of OOIP, showing 5.8% of additional oil recovery (Figure 3-5). Compared to sample C3, formation brine flooding exhibited higher ultimate oil recovery. This could be attributed to the fact that initial water saturation of sample C3 was much lower than that of sample C5, suggesting that crude oil locked in relatively small pores may not be removed.

Together, our core-flooding experiments show that 10dFB gave 5.8-18.1% of OOIP incremental oil recovery under tertiary mode, consistent with Nasralla et al. [90], who reported that diluted formation brine (1,750 ppm) yielded an incremental 5% of OOIP in tertiary mode. Yousef et al. [26] also reported that approximately 10% of OOIP additional oil recovery was achieved in tertiary mode with 10dSW. However, literature data also showed that low salinity effect was not observed under tertiary mode [91], albeit low salinity water was effective under secondary mode. This discrepancy may largely be attributed to the pore-structure distribution of the reservoir rock, which controls the initial oil and remaining oil saturation distribution [92], although the effect of pore structure on low salinity effect is still open for discussion [93].

In addition to the effect of pore structure on low salinity effect in secondary and tertiary mode, it is worth noting that the low salinity effect was observed only after 1.5-2.5 PV of diluted brine was injected (Figure 3-5). The same phenomenon was also observed in previous study by Yousef et al. [26], showing that low salinity effect was observed after injection of approximately 0.5 to 0.7 PV of low salinity brine. The delay in observation of low salinity effect suggests that this phenomenon is not instantaneous, rather is time dependant. We thus argue that time-dependent geochemical reactions need to be considered in predicting low salinity effect in reservoir scale.

The adsorption of potential determining ions (PDI) such as sulfate onto the surface of the rock, together with contribution of $Ca^{2+}$ and $Mg^{2+}$ have been suggested to facilitate

the desorption of carboxylic groups by changing the surface charge, hence improving oil recovery [39]. Low salinity effect was not observed when the anhydrite free chalk core plugs were flooded with sulfate free diluted FW by Austad et al. [4], and Fathi et al. [40]. They argued that dissolution of anhydrite ($CaSO_4$) present in the matrix, into $Ca^{2+}$ (aq), and $SO_4^{2-}$ (aq), would create catalytic agent sulphate required to release the carboxylic groups from the surface of reservoir rock. However, we observed the low salinity effect in the absence of anhydrite and sulphate ions from the core plugs and injection brines respectively. We believe that the EOR observed in our core flooding experiment is attributed to the shift in wettability from strongly water-wet, to intermediate-wet in the presence of the 10dFB.

While how wettability regime governs ultimate oil recovery has been widely debated, previous studies show that intermediate-wet system triggers the highest ultimate oil recovery. For example, Anderson [94] reported that intermediate-wet systems results in lower capillary forces, minimizing the trapping forces, thus unlocking oils trapped in small pores. However, a strongly water-wet system leads to a relatively high residual oil saturation, $S_{ro}$, due to a strong snap-off effect, which isolates oils in larger pores. The shift from intermediate wet to oil wet system also increases $S_{ro}$ because oil would be trapped in smaller pores due to capillary forces, and water does not have sufficient driving force to displace the oil from the pores. On the contrary, the smaller pores in the intermediate wet system, do not contain oil that can be trapped during the process of water flooding, hence resulting in optimum oil recovery. Also, Hadia et al. [95] observed that neutral wet condition ($I_{AH}$ = 0.12) gave the highest ultimate oil recovery among all the wettability conditions. Furthermore, Gandomkar et al. [27] reported the relationship between the Amott wettability index and total oil recovery for various salinity brines in secondary mode. They showed that neutral-wet system resulted in a maximum oil recovery and increasing water-wetness decreases oil recovery. Similar results was reported by Hendraningrat et al. [96], showing that intermediate-wet system gave greater oil recovery than water-wet system.

Wettability alteration towards intermediate condition observed in our work is also consistent with the results of zeta potential, which showed that 10dFB drove the zeta potential of brine/oil from positive (5.91 mV), to negative (-1.48 mV), triggering opposite polarity in oil/brine and brine/rock interfaces. We believe that the opposite electrostatic potential in oil/brine and rock/brine interfaces shifted the wettability of the reservoir from strongly water-wet to intermediate wet, which is supported by the contact angle results. Note that wettability shift from water-wet to intermediate wet in

Berea sandstone with decrease in salinity level during water flooding process, was also reported by Sharma et al. [97]. They reported that 20 wt% NaCl brine injection gave 57% of OOIP recovery, yet injection of 0.3% NaCl yielded 70% of OOIP recovery. They attributed this dependence of oil recovery to alteration of the wettability to mixed-wet condistions from water-wet cnodistions. Moreover, the results from Atomic Force Microscopy experiments (AFM) have shown that the critical disjoining pressures (the disjoining pressure at film rupture) increased with increasing brine salinity [98]. Consequently, more stable brine films which are bound by the two inter-faces of oil/brine and solid/brine would be generated, promoting more water wetness. They therefore suggest that low salinity brine probably causes the wettability of the rock to shift towards more oil-wet condition.
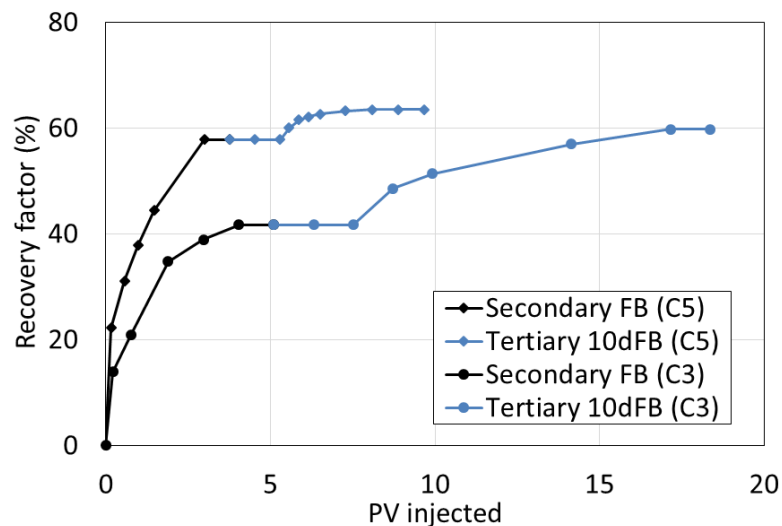


Figure 3-5. Oil recovery vs. injected PV under secondary and tertiary mode (sample C3 and C5).

### 3.4.4 Geochemical Modelling

Given that the injected water with different water chemistry compared to formation brine likely triggers geochemical reactions with the rock, e.g., calcite dissolution and precipitation, depending on the water chemistries of injected and connate water. For example, the calcite dissolution generates an increased $Ca^{2+}$ concentration in the in-jected brine (low salinity water), triggering the variation of the surface complexation at the interface of oil/brine and brine/rock. In addition, the calcite dissolution might cause

reservoir subsidence during the low salinity water injection. Therefore, there is a pressing need to understand the geochemical reactions during the low salinity water injection, de-risking the implementation of the low salinity water flooding project.

We used PHREEQC software [99] to perform a geochemical study, examining the effect of water chemistry (FB and 10dFB) on the mineral dissolution and precipitation. The equilibrium condition for the bulk (or batch) was calculated as the rock is brought in contact with brine. The rock was assumed to be 100% calcite in the geochemical model because the experimental rock samples were mainly calcite based on the X-ray diffraction (XRD) results (98.1 % of calcite). To calculate how much calcite dissolved in the brines (FB, 10dFB, and 100dFB) to generate the $Ca^{2+}$, which might affect the low salinity effect, we assumed that the interaction of brines with the calcite reached an equilibrium with saturation index equivalent to 0. Our results showed that formation brine, 10dFB dissolved $3.966 \times 10^{-3}$, $4.091 \times 10^{-3}$ moles/mole of calcite. However, the increase in $Ca^{2+}$ in the brines was limited, giving an increase by 0.7 %, 8% compared with the original concentration of $Ca^{2+}$ in the FB and 10dFB, respectively. This proves that the calcite dissolution triggered by low salinity water is negligible to trigger low salinity effect. The similar results were also reported by Nasralla et al. [100], who showed that sea water (SW) caused calcite dissolution of $2.13 \times 10^{-4}$ moles/moles of calcite, and 100dSW (sea water was diluted by 100 times using deionized water) led to dissolution of $2.10 \times 10^{-4}$ moles/mole. However, the increase in $Ca^{2+}$ in the brines was 3% and 6% compared with the original concentration of 25dSW (sea water was diluted by 25 times using deionized water) and 100dSW. Together, we argue that in this context, the incremental oil recovery observed by 10dFB flooding under tertiary mode is attributed to wettability alteration rather than dissolution of calcite.

## 3.5. Implications

Understanding the dominant factor(s) and mechanism(s) controlling the low salinity effect in carbonate rocks is of fundamental importance in constraining the intrinsic uncertainty in implementation of low salinity water flooding technique. This study has provided insights into the interaction of interfaces (fluid-fluid, and fluid-rock), and provided evidence relating the zeta potential of interface of oil/brine and brine/rock to the contact angle, and incremental oil recovery observed in core-flooding experiments. The experimental data essentially contributes to a deeper understanding of the factors controlling low salinity effect in carbonate reservoirs at the interfacial scale (Nano),

hence constraining the intrinsic uncertainty of the low salinity water flooding in field application.

To validate the hypothesis that low salinity effect in carbonate reservoirs is governed by electrostatic potential at the interfaces of fluid-fluid and rock-fluid rather than salinity level, we compared our results with data available in literatures. Although numerous studies have been conducted to investigate the effect of water chemistries on zeta potential and contact angle using various rock samples (limestone and dolomite), fewer studies have been carried out to relate the zeta potential to the contact angle directly. Therefore, we only reported data published by Mahani et al. [15] and Alshakhs et al. [9] who reported the zeta potential at interfaces of oil/brine and brine/rock, along with contact angle measurements, using the same type of rock and oil.

Given that the contact angle is a function of disjoining pressure which consists of double layer expansion force, Van-der-Waal attractive force, and structural force [101], brine chemistry, e.g., salinity and ions strength, dominates the Debye-length and zeta potential. Decreasing the salinity and ions strength causes the zeta potential of fluid-fluid and fluid-rock to become strongly negative [85], thus resulting in a larger double layer expansion force, which compensates the Van-der-Waal attractive force, thereby causing the reservoir to become more water wet [50]. We therefore particularly focused on the electrical double layer force, assuming that the geometry of oil and rock surfaces is simplified as flat-charged surfaces with different potentials separated by a thin film of electrolyte [15]. Considering that the same polarity of the zeta potential of oil/brine and brine/rock triggers repulsive electrical double layer force, and the opposite polarity of the zeta potential of oil/brine and brine/rock generates the attractive electrical double layer force [102], we introduce a Z parameter that is the absolute value of zeta potential of oil/brine and  brine/rock (Eq.1), which can be applied with both opposite, and same polarity of zeta potential. A plot of Z parameter versus contact angle for various references was then constructed (Figure 3-6).

$$Z_p = \left| Zeta_{oil/brine} + Zeta_{brine/rock} \right| \qquad \text{(Eq. 1)}$$
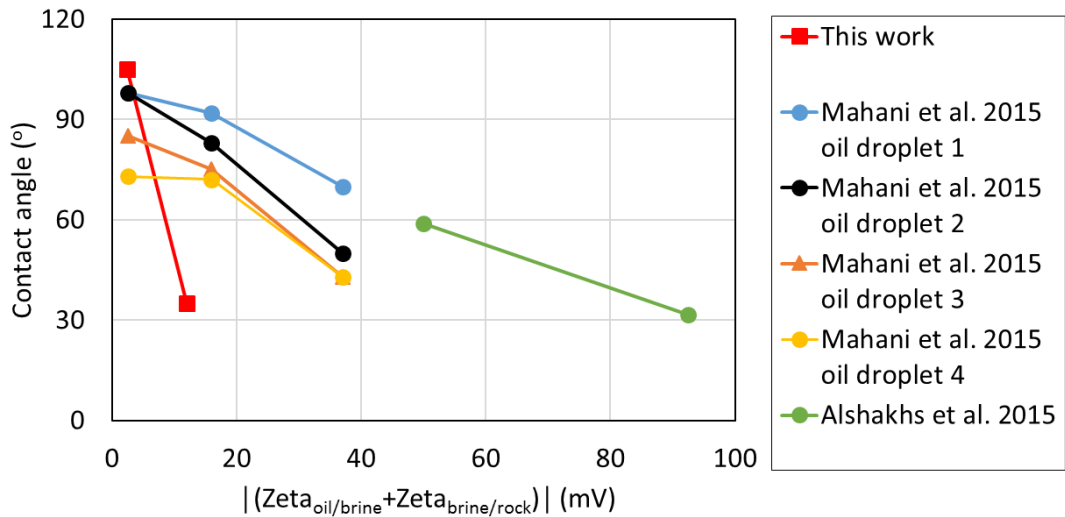
Figure 3-6. Contact angles and their corresponding zeta potential values found in various studies.

We found a strong correlation between the zeta potential of brine/oil and rock /brine and contact angle. For example, the contact angle on the carbonate decreases linearly with the increase of Z parameter. This might imply a higher oil recovery with the increase of the Z parameter, however, this needs to be confirmed by core-flooding experiments, as low salinity water can also increase oil recovery by shifting the wettability from water-wet to intermediate-wet [97]. We therefore argue that the same polarity of the zeta potential at both interfaces of oil/brine, and brine/rock, will likely result is water-wet surface. However, the opposite polarity of the zeta potential triggers attractive force, rendering oil-wet surface. We also overserved variation the slop of contact angle vs. Z parameter of the system of oil/brine/rock. The variation in the slop could be attributed to factors such as the composition of crude oil, water chemistries, and mineralogy of the reservoir rock, which requires further investigation. However, the linear relationship between contact angle and the Z parameter is obvious. We therefore argue that manipulating Z parameter (polarity of zeta potential of brine/rock and oil/brine) is of vital importance to shift the reservoir wettability and improving oil recovery. We suggest that the Z parameter may be used as an interpolant to model the low salinity effect, rather than using salinity or individual ion in the solution. We also believe that double layer and surface complexation modelling likely predict the same wettability trend because of the same physical and chemical nature, although more quantitative work remains to be made to integrate the two mechanisms.

## 3.6. Conclusions

Our study demonstrates that low salinity effect in carbonate reservoirs is governed by zeta potential at the interfaces of fluid-fluid and fluid-rock rather than salinity level. We used a crude oil with base number (BN=1.02 mg KOH/g) and acid number (AN=0.5 mg KOH/g). We examined the zeta potential of fluid-fluid, fluid-rock and tested the contact angle on aged and un-aged carbonate rocks, with crude oil and aqueous ionic solutions under pressure of 2,000 psi and temperature of 60oC. Further, to validate our hypothesis, we conducted two low salinity core-flooding experiments under tertiary modes.

Our work demonstrates that zeta potential at interface of oil/brine can be positive, and zeta potential decreases with decreasing salinity. Our experimental results showed that contact angle (CA) of un-aged rock increased from 30o to 50o as salinity decreased from formation brine (252,244 ppm) to 10dFB, suggesting that low salinity water shifted carbonate wettability from strongly water-wet to less water-wet. Moreover, aged rock exhibited the same trend of wettability alteration, but low salinity water drove the rock to be oil-wet. Contact angle tests were consistent with the zeta potential results, showing that zeta potential at the interface of fluid-fluid became positive at low pH level (<6), particularly for crude oil with high base number. On the other hand, the polarity of zeta potential at the interface of fluid-rock was shifted from positive to negative with decreasing salinity, thus the wettability shifted from strongly water-wet to intermediate-wet or slightly oil-wet. In addition, core flooding experimental results showed that 10dFB in tertiary mode improved the incremental oil recovery in the range of 5.8-18.1% of OOIP, suggesting that low salinity water may improve oil recovery by shifting wettability from strongly water-wet to intermediate-wet. Together, these results support our hypothesis that low salinity effect in carbonate reservoirs is governed by zeta potential at the interfaces of fluid-fluid and fluid-rock. Moreover, we demonstrate that contact angle on the carbonate substrate decreases linearly with the increasing Z parameter. We therefore argue that manipulating Z parameter (polarity of zeta potential of brine/rock and oil/brine) results in alteration of reservoir wettability, thus improving oil recovery. Moreover, the Z parameter likely can be used as an interpolant to model the low salinity effect rather than using salinity level or individual ion in the solution.

# Chapter 4 pH Effect on Wettability of Oil-Brine-Carbonate System: Implications for Low Salinity Water Flooding

## 4.1 Abstract

Wettability of oil/brine/carbonate system is a critical parameter to govern subsurface multi-phase flow behaviour, thus remaining oil saturation and ultimate oil recovery in carbonate reservoirs. Despite the fact that salinity level, ionic strength, oil composition and rock chemistry (e.g., limestone and dolomite) have been extensively investigated, few works has been done regarding the effect of pH on oil/brine/rock interaction, thus wettability.

We thereby measured contact angles at two different pH (pH=3 and 8) in the presence of either 1mol $Na_2SO_4$ or 1mol $CaCl_2$ using a crude oil with acid number of 1.7 and base number of 1.2 mg KOH/g. Moreover, we performed a geochemical modelling study in light of the diffuse double layer to understand how pH controls the number of surface species at interfaces of oil/brine and brine/carbonate. Our results show that pH scales with oil/brine/carbonate wettability, demonstrating that pH is one of the controlling factors to govern the system wettability. Further, our results suggest that pH (6.5-7.5) likely triggers an oil-wet system, which is favourable for low salinity water flooding, but pH<5 usually exhibits a water-wet system, which explains why low salinity effect is not always observed in carbonate reservoirs. This also confirms that $CO_2$ flooding, carbonated water flooding, and $CO_2$ huff-and-puff EOR very likely renders a strongly water-wet system due to $H^+$ adsorption on the interface of oil/brine and brine/carbonate as a result of $CO_2$ dissolution.

## 4.2 Introduction

Carbonates rock host most of the world's oil reserves (> 60 %) [64], which are composed primarily of the minerals calcite and dolomite together with impurities, e.g., quartz, anhydrite, clay minerals, organic matter, and apatite [65]. However, average recovery typically is lower than 40%. Cost-effective and environmentally friendly techniques to enhance oil recovery from carbonates are therefore of broad scientific interest [53]. One such technique that has gained interest is to manipulate the injected water chemistry, thus shifting reservoir wettability from oil-wet to water-wet in a process termed low salinity water flooding, which is also called *LoSal* flooding by BP [70,

103], *Smart Water* flooding by its originators, Austad and co-workers, at the University of Stavanger, Saudi Aramco [104], and *Designer Water flooding* by Shell [105, 106].

While a number of mechanisms [66, 107, 108] have been proposed in attempts to decipher the controlling factor(s) of low salinity water flooding in sandstone reservoirs, the low salinity effect in carbonate reservoirs is less clear, which limits the application of low salinity water in carbonate reservoirs [66]. While previous studies [12, 109-111] suggest that wettability alteration is the main mechanism for the low salinity water effect in carbonate reservoirs, understanding factors which drive this process (wettability alteration) have yet to be clearly defined [66].

To understand the controlling factor(s) of the low salinity effect in carbonate reservoirs, electrokinetic/double layer expansion theory was proposed to examine the interaction of oil/brine and brine/rock interfaces, which governs the wettability of the oil/brine/carbonate system. For example, zeta potential of oil/brine and brine/limestone were measure, and the results show that who showed that the charges at the limestone/brine and oil/brine interfaces became more negative with decreasing salinity [15], implying a weaker electrostatic adhesion between oil/brine and brine/rock interfaces, thus recession of the three-phase contact line. Further, a new parameter, $Z_f = \left( \left| Zeta_{oil/brine} + Zeta_{birne/rock} \right| \right)$, is proposed to relate the contact angle data remarkably well [112], showing that the oil contact angle on the carbonate substrate in the presence of various brines decreases linearly with increasing $Z_f$. They further argued that manipulating the $Z_f$ is of vital importance to shift the reservoir wettability, thus decreasing residual oil saturation.

Apart from the electrokinetic theory, multi-component ion exchange theory was also proposed to decipher the low salinity effect in carbonate reservoirs. For example, sulfate ions in brines would adsorb at the carbonate surface, thus triggering the adsorption of $Ca^{2+}$, which in return releasing carboxylic materials from carbonate surface [79]. Note: in this mechanism, $SO_4^{2-}$ acts as a catalyst to promote the adsorption of $Ca^{2+}$ to the surface of mineral. Literature data also show that the retention of $SO_4^{2-}$ increases with increasing temperature [39]. This implies that adding $SO_4^{2-}$ in the injected brine yields more incremental oil recovery in high temperature reservoirs. Moreover, Sari et al. [112] showed that with an absence of $SO_4^{2-}$, the wettability of oil/brine/carbonate system shifted from water-wet to oil-wet with decreasing salinity at various pH. They conclude that the wettability alteration can probably be explained by electrical double layer theory.

Furthermore, surface complexation modelling were also performed to interpret the low salinity effect in carbonate reservoirs. For example, an independently derived diffuse layer geochemical model [12] was developed which quantitatively interprets the pH shift, plateau of incremental oil recovery, and the oxyanion role in increased oil recovery observed from core-flooding experiments. To relate the surface complexation modelling to zeta potential, Mahani et al. [113] proposed a new geochemical model which demonstrates that the increase of zeta potential with pH is triggered by surface species at interfaces of brine/carbonate. In particular, $>CaSO_4^-$ is substituted by the neutral $>CaOH$ moiety and $>CaCO_3^-$, reducing the negative charge at the surfaces. They also concluded that the number of surface species of $>CO_3Ca^+$ and $>CO_3Mg^+$ are relatively insensitive to pH change. However, the effect of pH on the number of surface species of oil/brine interfaces was not included in their surface complexation modelling.

In general, despite the fact that based on the theories outlined above , salinity level [14, 15], ionic strength [16, 114, 115], oil composition [19-21] and rock mineralogy (e.g., limestone and dolomite  [113, 116]) have been extensively investigated, few studies have been conducted to exclusively focus on the effect of pH on oil/brine/rock interaction, thus wettability.

In this study, we hypothesize that apart from salinity level, ionic strength, oil composition and rock mineralogy, pH of brines controls the number of surface species at interfaces of oil/brine and brine/rock, governing the interaction of oil/brine/rock system, hence wettability. To test our hypothesis, we measured contact angles at two different pH (pH=3 and 8) in the presence of either 1 mol $Na_2SO_4$ or 1 mol $CaCl_2$. Moreover, we performed a geochemical modelling study in light of diffuse double layer to understand how pH controls the number of surface species at interfaces of oil/brine and brine/carbonate. Note that while we did not explicitly investigate the relative contribution of the mechanisms, e.g., electrical double layer, multi-component ion exchange, and surface complexation, our new findings may allow us to put boundaries on designing injected water chemistries. Furthermore, these findings may also explain why low salinity effect is not always observed in carbonate reservoirs.

## 4.3 Materials and Methods

### 4.3.1 Calcite Substrates

Rock mineralogy is essential to wettability alteration in carbonate reservoirs. In this work, we used crystal calcite (Iceland Spar from Ward's Science) to run contact angle tests. To ensure the integrity of contact angle measurements, the rock substrates were cleaned with methanol to remove any trace of inorganic contaminants, then rinsed with equilibrated deionised water. Then, clean and dry substrates were exposed to air plasma for 10 min to remove organic surface contamination [117].

To avoid the surface roughness on contact angle tests, we imaged the cleaved calcite substrate using atomic force microscopy (AFM) (WITec, ALPHA 300 RA for combined Raman-AFM imaging). Results show that the surface roughness was in a range of 0 to 4.8 nm (Figure 4-1), implying that the surface roughness effect on contact angle should be negligible [118, 119]. It is worth noting that advancing contact angle of brine on calcite surface in the presence of $CO_2$ decreases from 85 to 75$^\circ$ with increasing surface roughness from 7.5 to 140 nm [118].
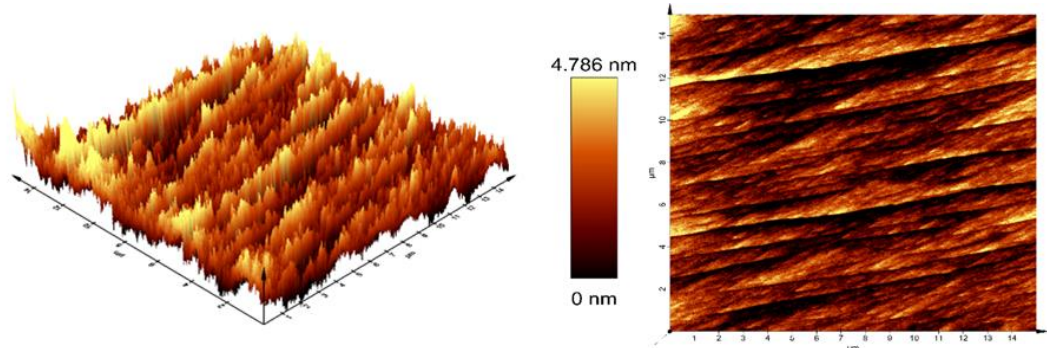


Figure 4-1. AFM topographic images of the cleaved carbonate substrate used for contact angle measurements.

### 4.3.2 Experimental brines

Two different ionic solutions were used to test the effect of brine pH on system wettability. We measured contact angles at two different pH (pH=3 and 8) in the presence of 1 mol $Na_2SO_4$ and 1 mol $CaCl_2$ solutions. We did not manipulate and monitor the pH change during the contact angle tests because of the current capability of the experimental system. We assumed that the pH increase due to the calcite dissolution

should not be significant because the specific reactive surface area for the brine/cubic calcite (experimental substrate, 0.000025 $m^2/g$) is much lower than brine/calcite powers (0.11 $m^2/g$ ) [113, 120].

### 4.3.3 Experimental Oil

An oil was used to test the pH effect on the system wettability with acid number of 1.7, and base number 1.2 mg KOH/g. Gas chromatograph mass spectrometer (GC-MS) was used to examine the oil properties, showing that the oil was comprised of asphaltenes (37.1 wt %), naphthenes (26.3 wt %), wax (3.8 wt %) and sulphur (3.9 wt %) with density of 0.89 $g/cm^3$ at 20 °C.

### 4.3.4 Experimental Set-up

In this study, contact angles for oil/brine/rock system were performed using Vinci IFT-700 (Figure 1 in reference [121]). The experimental temperatures were 25, 60 and 100 °C which cover the temperature range for typical oil reservoirs. Pressure was kept constant at 100 bar for all experiments. Contact angle tests were performed using the sessile droplet method. Substrates were placed inside the HT-HP cell and vacuumed before filling with the relevant brine. Subsequently, pressure and temperature were applied. Once the state of temperature and pressure equilibrium was achieved, a droplet of crude oil (0.04 – 0.06 ml) was released through a small needle (D = 0.6 mm) onto the substrate surface. A high definition video camera continuously recorded the experiment where contact angles were measured over the period of 48 hours using the built-in software. Once the state of equilibrium was achieved and no more change in contact angle was detected, result was reported as the final contact angle for the system. It it worth noting that while factors such as the substrate roughness, contact angle hysteriss, and preparation procedure all may affect the the macroscopoic contact angle [15], the philosophy of the contact angle tests in this study was to highlight the actual trend of the contact angle with pH, rather than the exact initial value of the contact angle. Also, in this study, we did not age the substrates before testing contact angles. This is because aging process tends to make the rock more oil-wet by re-establishing adsorption equilibrium between the rock surface and the crude oil [122]. This study aims to investigate the pH effect on the wettability. Using carbonate rocks with a strongly oil-wet surface in our experiments would mean that possible change in the wetting preference from water-wet to oil-wet due to change in pH could not be observed.

## 4.3.5 Surface Complexation Modelling

Given that directly sorbed oil probably doesn't respond to low salinity waterflooding, and that only oil-rock with an intervening water layer will respond [12]. Our analysis focusses solely on the water-present situation which can be modelled using surface complexation theory [12, 123]. Surface complexation model input parameters were provided in (Table 4-1) to calculate the number of charged species that are thought to cause local adhesion of the oil/brine interface to the brine/calcite interface, hence wetting. The bond product sum is a measure of the amount of electrostatic attraction between the two interfaces. Surface complexation modelling (and DLVO theory) presumes an electric double layer at each interface and the existence of charged surface species whose concentrations depend upon the chemical makeup of water, oil and mineral surface [121]. In the surface complexation model, the calcite surface area was assumed to be 0.11 $m^2$/g with site density of 5 sites/$nm^2$ [113]. Geochemical reactions in (Table 4-1) because water chemistry dominates the surface complexation of the oil/brine/rock system and temperature plays a secondary role [121]. The surface species concentrations were calculated using PHREEQC version 3.3.9 and a diffuse layer surface model. It is worth noting that NaOH was used to adjust the pH for calculating the site density of surface species, and we assumed that the number of acid (summation of -COOH, -COO$^-$, and –COOCa$^+$) and base (summation of –NH$^+$ and –N) functional group did not change with pH.

Table 4-1. Surface complexation model input parameters [12, 55, 78, 124].

| Interface | Reaction | Log $K_{25oC}$ | Reaction |
|---|---|---|---|
| oil/brine | $-NH^+ = -N + H^+$ | -6.0 | 1 |
| | $-COOH = -COO^- + H^+$ | -5.0 | 2 |
| | $-COOH + Ca^{2+} = -COOCa^+ + H^+$ | -3.8 | 3 |
| calcite/brine | $>CaOH + H^+ = >CaOH_2^+$ | 11.85 | 4 |
| | $>CaOH + HCO_3^- = >CaCO_3^- + H_2O$ | 5.8 | 5 |
| | $>CaOH_2^+ + SO_4^{2-} = >CaSO_4^- + H_2O$ | 2.1 | 6 |
| | $>CO_3H = >CO_3^- + H^+$ | -5.1 | 7 |
| | $>CO_3H + Ca^{2+} = >CO_3Ca^+ + H^+$ | -2.6 | 8 |

Where ">" denotes a site on the carbonate surface while "-" denotes a site on the oil surface.

## 4.4 Results

### 4.4.1 Effect of pH on Contact Angle

pH appeared to strongly affect the contact angle in oil/brine/carbonate system (Figure 4-2), indicating that pH is very likely to be one of the controlling factors that govern the wettability in oil/brine/rock system. To be more specific, low pH (pH=3), in the presence of $Na_2SO_4$, rendered a slightly water-wet oil/brine/carbonate system. Rather, high pH (pH=8) led to a strongly oil-wet system. For example, at 60 °C, contact angle was measured to be 53° at low pH (pH=3), whereas at high pH (pH=8) contact angle increased to 175°. While similar trend was observed in the presence of $CaCl_2$, the contact angle difference in the presence of pH=3 and 8 was less pronounced compared to $Na_2SO_4$ solution. For example, at 60 °C, low pH (pH=3) yielded a contact angle of 44°. Yet, high pH (pH=8) gave a contact angle of 54°. Both pHs exhibited a water-wet system (see Figure 4-3).
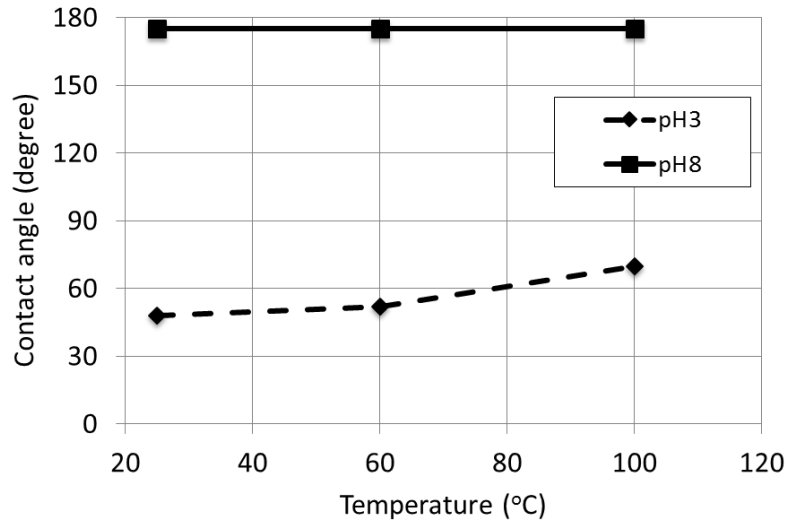
Figure 4-2. Contact angle vs. temperature in the presence of Na$_2$SO$_4$ at pH=3 and 8.
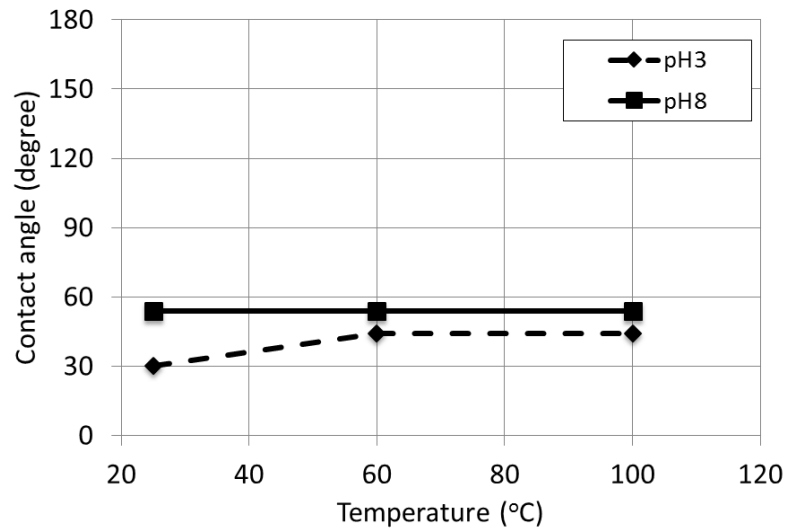


Figure 4-3. Contact angle vs. temperature in the presence of CaCl$_2$ at pH=3 and 8.

## 4.4.2 Effect of Ion Type on Contact Angle

Ion type had a little effect on contact angle at low pH (pH=3). In other words, low pH dominated the interaction of oil/brine/rock system, thus wettability. For example, at pH=3 (60 °C), the contact angle in the presence of Na$_2$SO$_4$ and CaCl$_2$ were 44 and 52°, respectively, showing a water-wet system.

However, at high pH, ion type strongly affected the contact angle (pH=8), suggesting that ion type plays a vital role in dominating the interaction of oil/brine/rock system,

thus wettability. To be more specific, at pH=8, $Na_2SO_4$ gave a strongly oil-wet system with a contact angle of 175°. Rather, $CaCl_2$ exhibited a water-wet system with a contact angle of 54°.

In general, our results suggest that at low pH, ion type does not govern the wettability of oil/brine/carbonate system. This is not because ion type, salinity and ionic strength are not important, rather this is because low pH has much greater influence on governing the number of surface species at oil/brine and brine/carbonate surfaces, thereby wettability. This was quantitatively demonstrated using surface complexation modelling in the Discussion section.

### 4.4.3 Effect of Temperature on Contact Angle

Temperature had a little effect on contact angle. At high pH=8, contact angle did not change with increasing temperature for both $Na_2SO_4$ and $CaCl_2$ although contact angles increased slightly with increasing temperature at pH=3. For example, at pH=8, $Na_2SO_4$ gave contact angle of 175°, and $CaCl_2$ gave contact angle of 54°C as temperature increasing from 20 to 100°C. At pH=3, contact angle increased from 48 to 70°, and 30 to 44° in the presence of $Na_2SO_4$ and $CaCl_2$. The variation in contact angles in the presence of different pH was physiochemically described in the Discussion section.

## 4.5 Discussion

To gain a deeper understanding of the pH effect on the interaction of oil/brine/rock system and its impact on wettability, we conducted a surface complexation modelling, quantitatively describing how pH, affects the bond product sum which is an indicator of wettability [12]. Note: bond product sum means a measure of the amount of oil-mineral electrostatic attraction, which is given by the summed products of the oppositely charged surface species on the interface of oil/brine and brine/mineral [125].

### 4.5.1 pH Effect on Number of Surface Species at Oil/Brine Surfaces

pH strongly affected the number of surface species at interfaces of oil/brine at the presence of $Na_2SO_4$, implying a wettability alteration in line with contact angle results. For example, the number of -COO- increased from 16 to 22 µmol/m$^2$ with increasing pH from 2 to 9 due to the Reaction 2 shifting towards right-hand side (Figure 4-4). However, the number of –NH$^+$ decreased from 19 to 16 µmol/m$^2$ with increasing pH

due to the Reaction 1 shifting towards right-hand side (Figure 4-4). Our results are in line with Brady et al. [81] who showed that $-NH^+$ decreases with increasing pH. Moreover, $-COO^-$ increases with increasing pH although salinity level also affects the variation trend of the number of surface species at interfaces of oil/brine.

pH also strongly affected the number of surface species at interfaces of oil/brine at the presence of $CaCl_2$ (Figure 4-5). However, the number of $-COO^-$ did not increase monotonically, but increased up to pH 5.2, then decreased with increasing pH. This is because the presence of $Ca^{2+}$ enabled Reaction 3 shifting towards left-hand side, thus decreasing $-COO^-$ in line with Brady, et al. who showed that $-COO^-$ increases slightly as pH increasing from 4 to 5.8, then decreases slowly at the presence of 0.02 M NaCl+10 mM $CaCl_2$ [81]. Figure 4-5 also shows that $-COOCa^+$ increased until pH increased to 4 due to the Reaction 3 shifting towards right-hand side. Moreover, $-NH^+$ decreased with increasing pH due to the Reaction 1 shifting towards right-hand side. The variation of the $-COOCa^+$ and $-NH^+$ are in line with previous studies [12, 121], confirming that pH controls the number of surface species at interfaces of oil/brine and brine/rock, thus wettability.
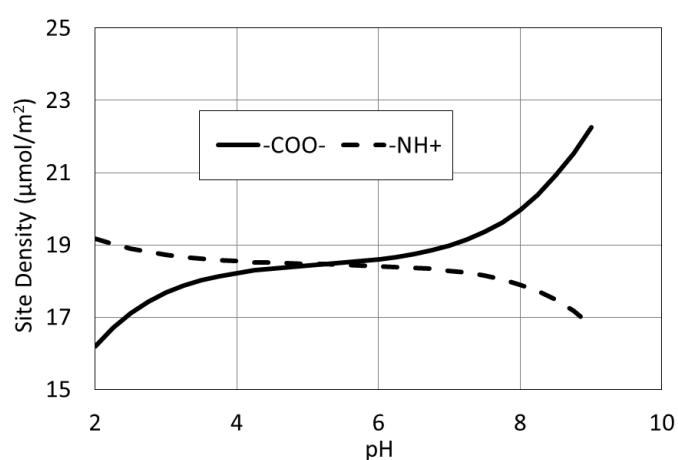


Figure 4-4. Site density of surface species at oil/brine interface as a function of pH in the presence of 1 mole $Na_2SO_4$.
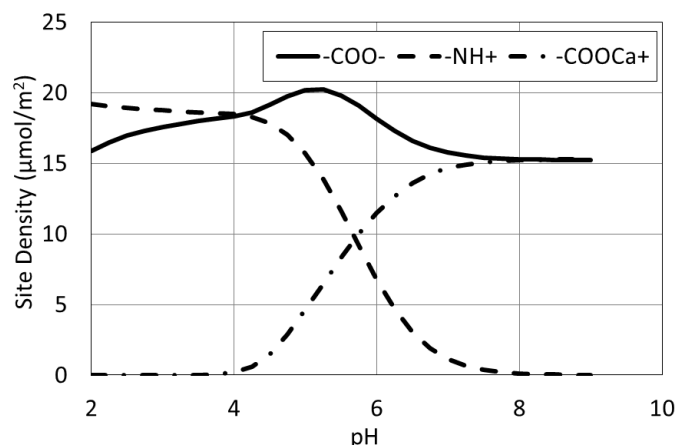
Figure 4-5. Site density of surface species at oil/brine interface as a function of pH in the presence of 1 mol $CaCl_2$. Although the pH strongly affects the number of surface species at oil/brine for both $Na_2SO_4$ and $CaCl_2$, in order to directly relate pH to contact angle, hence wettability, the number of surface species at brine/carbonate surface need to be calculated, details of which were presented in the section below.

## 4.5.2 pH effect on number of surface species at brine/calcite surfaces

pH strongly affected number of surface species at brine/carbonate interface in the presence of $Na_2SO_4$ (Figure 4-6). For example, when pH increased from 2 to 9, $>CaSO_4^-$ decreased from 2.7 to 0.9 $\mu mol/m^2$, $>CO_3^-$ increased from 0.001 to 4.5 $\mu mol/m^2$, and $>CaOH_2^+$ increased from 1.8 to 3.6 $\mu mol/m^2$.

pH also strongly affected the number of surface species at brine/carbonate in the presence of $CaCl_2$ (Figure 4-7). For example, apart from $>CaOH_2^+$, which was almost constant with increasing pH, the number of surface species, $>CO_3^-$, increased from 0.01 to 2.82 $\mu mol/m^2$ as pH increased from 2 to 5.5. However, further pH increase had little effect on the number of surface species. Similarly, $>CO_3Ca^+$ increased from 0.01 to 1.64 $\mu mol/m^2$ as pH increased from 2 to 5.5, whereas further pH increase had negligible effect on the density of surface species. This is because in the presence of $CaCl_2$, Reaction 7 and 8 shift towards right-hand side with increasing pH as pH is lower than 5.5. Our results are also in line with Brady et al. who show that in the presence of 0.1 M NaCl at 100°C, $>CO_3^-$ and $>CO_3Ca^+$ increase with increasing pH till pH reaches at 7 [12].
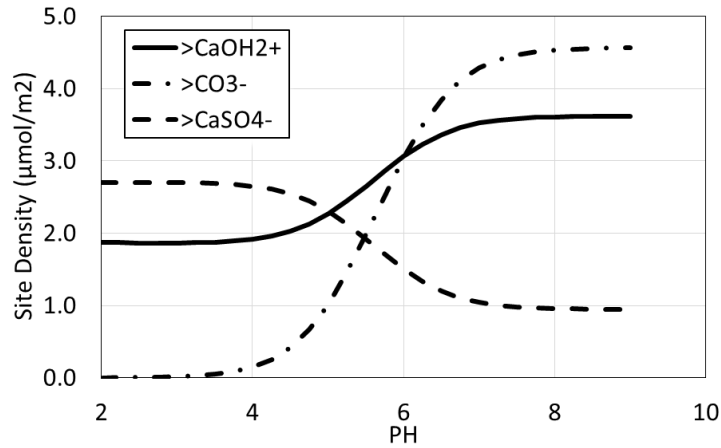
Figure 4-6. Site density of surface species at brine/carbonate interface as a function of pH in the presence of 1 mol $Na_2SO_4$.
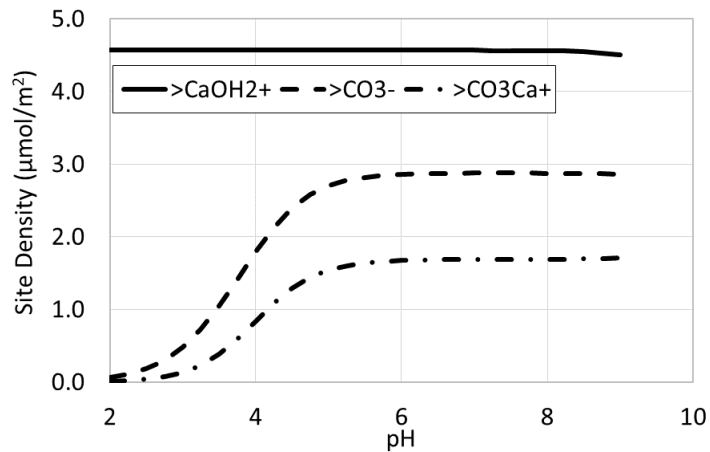


Figure 4-7. Site density of surface species at brine/carbonate interface as a function of pH in the presence of 1 mol $CaCl_2$.

### 4.5.3 pH effect on electrostatic bridges between oil and rock

pH strongly affected the bond product sum in the presence of either $Na_2SO_4$ or $CaCl_2$, suggesting that pH is a critical parameter that governs the oil/brine/carbonate system wettability. Note that bond product sum of oppositely charged species at oil/brine/carbonate system [81] is $[>CaOH_2^+][-COO^-]+[>CO_3^-][-NH^+]+[>CaSO_4^-][-NH^+]$ at presence of $Na_2SO_4$, and $[>CaOH_2^+][-COO.]+[>CO_3^-][-NH^+]+[>CO_3^-][-COOCa^+]$ $+[>Ca_3Ca^+][-COO^-]$ at presence of $CaCl_2$. To be more specific, in the presence of $Na_2SO_4$, bond product sum increased from 84 to 172 $(\mu mol/m^2)^2$ as pH increased from 2 to 9 in line with contact angle results. For example, at low pH=3, contact angle was 48° with bond

product sum 84 (µmol/m$^2$)$^2$, whereas at pH=8, contact angle was 175° with bond product sum 172(µmol/m$^2$)$^2$. Note: a greater bond product sum means more electrostatic bridges, thus more oil-wet system [126].

In the presence of CaCl$_2$, bond product sum increased with increasing pH up to pH=5.2, then decreased with further increasing pH. This is largely because –NH$^+$ decreases with increasing pH due to the Reaction 1 shifting towards right-hand side, thus decreasing the bond of [>CO$_3^-$][-NH$^+$]. Moreover, [>CO$_3^-$][-COOCa$^+$] decreased with increasing pH after pH reaches at 5.2 (Figure 4-5). Surface complexation modelling results are also in line with contact angle results in the presence of CaCl$_2$. For example, at pH=3, the contact angle was 30$^°$ with bond product sum of 91 (µmol/m$^2$)$^2$; whereas at pH=8, the contact angle was 54° with bond product sum of 139 (µmol/m$^2$)$^2$. Together, surface complexation modelling show that low pH triggers water-wet system, and high pH triggers oil-wet or slightly water-wet system as a result of a greater bond product sum. This result further implies that manipulating water chemistry to disturb the in-situ oil/brine/rock physiochemical equilibrium may lift off the oil film adsorbed at the rock surface, altering wettability towards more water-wet, thus maximizing oil recovery. However, the potential of low salinity effect likely decreases at low pH because of the strong water-wet system. This may explain why low salinity effect was not always observed in carbonate reservoirs. This is also in line with Sari et al. [127] who reported that pH=2.55 results in a strong water-wet oil/brine/carbonate system (contact angel=35$^o$) although in the presence of formation brine (high salinity=252,244 ppm). In contrast, contact angle increases with increasing pH while at a lower salinity (10 times diluted formation brine). Surface complexation modelling was also applied to interpret the contact angle results, showing a lower bonds between oil-calcite in formation brine compared to 10 times diluted formation brine [128]. Similar results were also observed by Jackson et al. [53] who found that positively charged oil-water interface likely fails low salinity effect in carbonate. Interestingly, low pH likely triggers positive charged oil-water interface [15] because –NH$^+$ dominates the surface charges at low pH [12, 81] thus a strong water-wet system. However, it is worth noting that pH effect is likely more pronounced on aged samples. For example, our previous results show that contact angle increased from 30° (in formation brine, FB, with salinity of 252,244 ppm) to 81° (100 times diluted FB) as pH increased from 2.55 to 5.68 in un-aged samples [127]. However, for aged samples, contact angle increased from 35° to 175° with the same pH increase. Together, the experimental results show that

pH effect on age samples becomes more obvious although more quantitative work remains to be made to characterize and model this physical process.
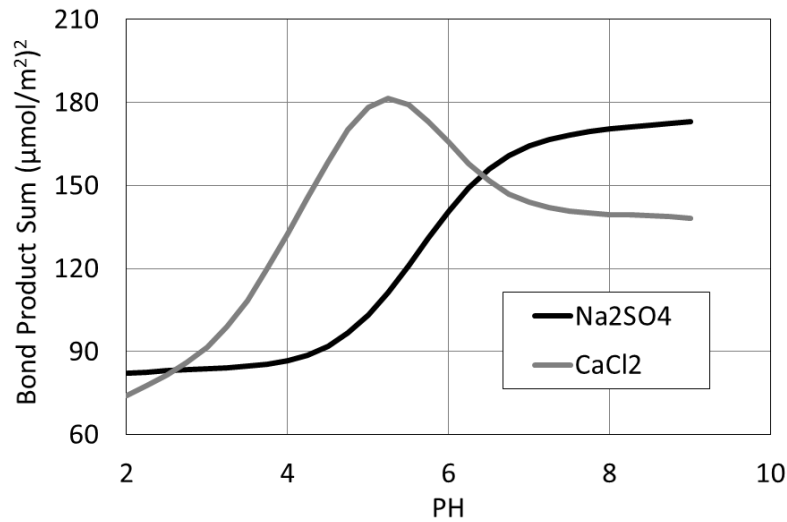


Figure 4-8. Bond product vs. pH in the presence of $Na_2SO_4$ and $CaCl_2$, respectively.

## 4.6 Implications

In this study, we combined contact angle with geochemical modelling, particularly focusing on the effect of pH on system wettability (see Figure 4-8). Our results provide insights to demonstrate that pH significantly controls the surface chemistries in the oil/brine and brine/rock interfaces, consistent with previous studies [12, 129, 130]. In particular, surface complexation modelling results show that contact angle increases with increasing bond product sum, correlating well with contact angle (Figure 4-9). This implies that bond product sum can likely be used as a guideline to manipulate injection water chemistry for a given reservoir. Note that bond product sum can also be related to zeta potential [112, 113], which is another parameter that indicates the wettability.

pH scales with contact angle, thus oil/brine/rock wettability as pH is lower than 6 (Figure 4-10). In other words, oil composition, salinity, ionic strength, ion type may play a secondary role in the interaction of oil/brine/rock system at low pH, thus wettability. This also implies that $CO_2$ flooding and $CO_2$ huff-and-puff EOR very likely renders a strongly water-wet system due to the pH decrease as a result of $CO_2$ dissolution into connate water, although a more quantitative work remains to be conducted. However, the significance of these parameter (e.g., oil composition, salinity, ionic strength, ion

type) increases with increasing pH although a quantitative work remains to be made. For example, at pH=8, 1 M $Na_2SO_4$ rendered a strongly oil-wet system (contact angle=175°), whereas 1 M $CaCl_2$ gave a water-wet system (contact angle=54°).
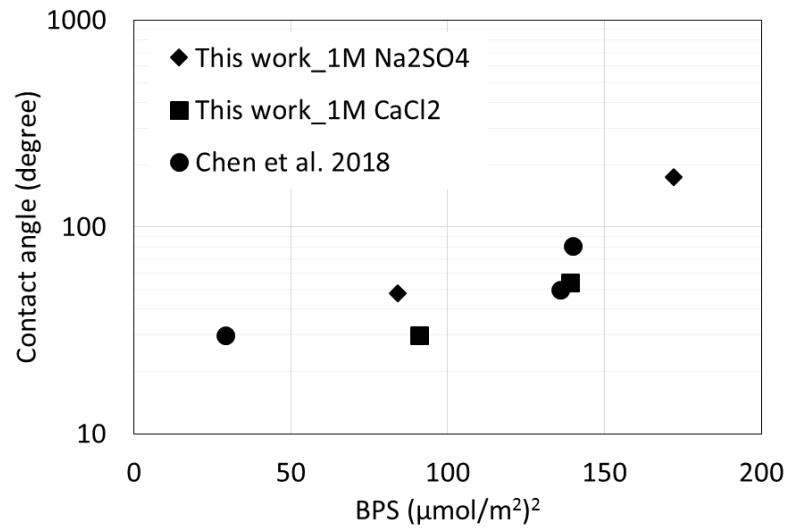


Figure 4-9. Contact angle vs. bond product sum in this work and previous work.
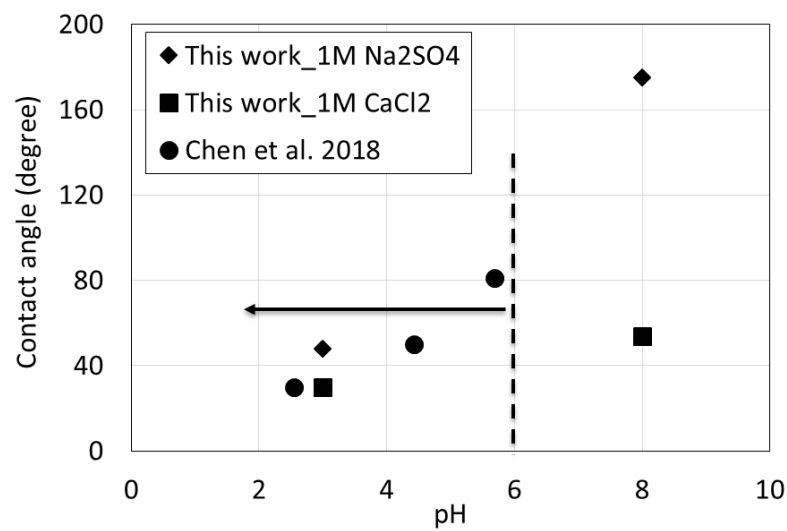


Figure 4-10. Contact angle vs. pH in this work and previous work.

## 4.7 Conclusions

Low salinity water flooding has been in the centre of attention in industry as a cost-effective and environmentally friendly technique [50]. This is particularly true in the period of low oil prices [66]. Despite the fact that salinity level [14, 15], ionic strength [16, 114, 115], oil composition [19-21] and rock mineralogy (e.g., limestone and dolomite [113]) on low salinity effect in carbonate reservoirs have been extensively investigated, few studies have been conducted regarding the effect of pH on oil/brine/rock interaction, thus wettability.

To test the pH effect on oil/brine/carbonate system wettability, we measured oil contact angles in the presence of either $Na_2SO_4$ or $CaCl_2$ at pH of 3 and 8. To gain a deeper understanding of the physiochemical interaction of the oil/brine/carbonate system, we performed a geochemical study to demonstrate that contact angle increases with increasing bond product sum, implying that bond product sum can likely be used as a guideline to manipulate injection water chemistry for a given reservoir [12]. Further, we conclude that pH scales with contact angle, thus oil/brine/rock system wettability. In particular, low pH (pH<5) likely triggers a strongly water-wet system due to $H^+$ adsorption on the interface of oil/brine and brine/carbonate [131], and the salinity, ionic strength, and ion type paly a minor role in wettability alternation at low pH. This also confirms that $CO_2$ flooding, carbonated water flooding, and $CO_2$ huff-and-puff EOR very likely renders a strongly water-wet system as a result of $CO_2$ dissolution.

# Chapter 5 Low Salinity Water Flooding in High Acidic Oil Reservoirs: Impact of pH on Wettability of Carbonate Reservoirs

## 5.1 ABSTRACT

Wettability alteration has been identified as an important mechanism during low salinity water flooding in carbonate reservoirs. Oil composition, particularly, acidic and basic functional groups, plays an important role in regulating wettability. In this paper, we explored the potential of low salinity effect in reservoirs with high acidic components (acid number = 4.0 mg KOH/g and base number = 1.3 mg KOH/g) with a combination of approaches (e.g., contact angle and zeta potential measurements, and surface complexation modelling). We measured the contact angles of oil on calcite surfaces in presence of aqueous ionic solutions at different pH (3 and 8), salinity (0.01 and 1 mol/L), ion type ($CaCl_2$ and $Na_2SO_4$) and temperatures (25-100 °C).

Our results show that both salinity and ion type significantly affect contact angle at pH=8. However, at low pH (pH 3), the oil-brine-calcite system becomes strongly water-wet with minor effect from salinity, ion type, and temperature. Lowing salinity drives the zeta potential of both oil-brine and brine-calcite to be strongly negative, particularly in the presence of $Na_2SO_4$ at pH 8, confirming the contribution of the electrical double layer to low salinity effect. Geochemical modelling reveals that breakage of electrostatic bridges between oil and calcite increases linearly with acid number, implying a higher potential of low salinity effect in high acidic oil-bearing carbonate reservoirs.

This study provides an insight into how acid number parameter influences the wettability of oil-brine-carbonate system and underscores the significance of acid components in wettability alteration of carbonate reservoirs, assisting in a better prediction and screening of low salinity EOR in carbonate reservoirs.

## 5.2 INTRODUCTION

Oil will be an important energy source for the rest of the 21st century [132] and carbonate reservoirs host most of the world's oil (> 60 %) [64]. However, oil recovery in carbonate reservoirs is low (<40%) [133], prompting enormous motivation to improve oil recovery in a cost-effective manner, with as little ecological footprint as possible.

Low salinity water flooding appears to be a viable option that boosts oil recovery while fulfilling the above-mentioned criteria. However, the full benefit of low salinity water flooding is prevented at least in part by poor understanding of how low salinity water, affects *in situ* oil-brine-calcite wetting [12], thus subsurface multiphase flow and residual oil saturation [27, 93].

While wettability alteration has been identified as an important effect during low salinity water flooding, and core-scale numerical simulation has been applied to derive relative permeability of oil and brine through history matching in both sandstone [83, 134-137] and carbonate [138], the nature of the wettability alteration remains controversial due to the complex chemiophysical interaction of oil/brine/calcite system. To better understand the controlling factor(s) behind wettability alteration in oil-brine-carbonate system, how brine chemistry regulates system interaction [12, 113, 139-141], hence wettability, has been extensively investigated. For example, Austad et al. [4], Hadia et al. [19], Hopkins et al. [21], Hadia et al. [95], Hadia et al. [142] along with other researchers [32, 113, 128, 143, 144] have conducted extensive experimental tests, e.g., contact angle measurements, spontaneous imbibition tests and core flooding experiments to substantiate that modifying the ionic composition of injected brine indeed shifts wettability of oil-brine-carbonate system, hence decreasing residual oil saturation. In particular, potential determining ions (e.g., Ca, Mg and $SO_4^{2-}$) have been proved to be key components that facilitate the wettability alteration [79, 145-147].

Apart from the brine chemistry effect on wettability, oil composition also significantly affects the interaction of oil-brine-rock. Dubey et al. [148] showed that wetting behaviour of crude oil is correlated with its acid and base number which is well demonstrated by surface complexation modelling [12, 58, 113]. The effect of oil compositions (e.g., $-CH_3$, -COOH and $-NH^+$) on the adhesion force at a molecular level using AFM has also been examined [20, 149, 150]. Although few AFM tests have been performed on calcite surfaces to examine how adhesion forces are influenced by polar functional groups, the effect of polar functional groups on adhesion forces on mica, quartz, and kaolinite minerals has been investigated extensively. For example, Hassenkam et al. [151] show that low salinity water leads to 20 – 30% decrease in adhesion force between carboxylate functional group and clean muscovite surfaces, whereas $CH_3$ causes only 10 – 20% decrease in adhesion force on the same substrate.

Wu et al. [152] also performed AFM experiments using polar ($-NH_2$ and $-COOH$) and non-polar ($CH_3$ and $-C_6H_5$) functional groups, confirming that low salinity decreases adhesion force. Moreover, the study shows that the decrease in adhesion force of polar functional groups is 5 times higher than non-polar functional groups.

Coreflooding experiments also indicate that oil properties, particularly the polar groups, have a significant influence on low salinity effect. Analysing the results from numerous core flooding experiments involving a variety of crude oils indicate higher oil recovery for low acid number crude oil compared to high acid number crude oil, hence greater low salinity EOR-Effect [4, 153]. While it appears that there is a likelihood of correlation between acid number and oil-brine-carbonate system wettability, hence oil recovery and low salinity EOR potential, few studies have been done to identify this correlation and fewer have looked beyond how low salinity water shifts wettability with increasing carboxylic components in carbonate reservoirs.

To investigate the likelihood of this correlation and evaluate low salinity EOR potential in high acid number oils similar to that from the West of China, we conducted contact angle measurements at different pH (3 and 8), salinity (0.01 and 1 mol/L), ion type ($CaCl_2$ and $Na_2SO_4$) and temperatures (25, 60, 100 °C) using high acidic crude oil with acid number of 4.0 mg KOH/g and basic number of 1.3 mg KOH/g. Moreover, we tested zeta potential for oil/brine and brine/calcite to verify the contribution of electrical double layer to wettability alteration in high acidic oil-bearing carbonate reservoirs. Furthermore, we computed electrostatic bridges as a function of acid number ranging from 0 to 4 mg KOH/g at a fixed base number (1.0 mg KOH/g) in seawater against existing literature data using PHREEQC.

## 5.3 EXPERIMENTAL METHODOLOGY

### 5.3.1 Materials

#### 5.3.1.1 Rock Mineralogy

Specimens used in this study were Calcite (Iceland Spar). X-ray diffraction showed samples were 100% calcite and no other major minerals were present within the detectable range. Calcite surface roughness was imaged using atomic force microscopy (WITec, ALPHA 300 RA for combined Raman-AFM imaging), with surface roughness ranging from 0 to 4.8 nm (see Figure 1 in Xie et al. [154]).

### 5.3.1.2 Brine Properties

Given that $Ca^{2+}$ and $SO_4^{2-}$ are two key potential determining ions necessary for low salinity effect in carbonate reservoirs, two different ionic aqueous solutions ($CaCl_2$ and $Na_2SO_4$) with different concentrations (0.01 and 1.0M) were prepared using deionized water (DI) and reagent grade salts in this work. Given that pH strongly affects the surface chemistry of oil/brine and brine/rock interfaces [155, 156], hence wettability, solutions were adjusted to two different pH (3 and 8) to examine the pH effect on contact angle. To gain a better understanding of contact angle, we measured zeta potential of oil-brine and brine-calcite at pH 8. We did not measure zeta potential of brine-calcite at pH 3 due to calcite dissolution at low pH. Hydrochloric acid (HCl) and/or sodium hydroxide (NaOH) buffer solutions were used to adjust the pH.

### 5.3.1.3 Crude Oil

In this study, we used high acidic crude oil with acid and base number of 4.0 and 1.3 mg KOH/g, respectively. Note: this step was necessary to quantify the concentration of amine group ($-NH_2^+$) and carboxylic group ($-COO^-$) at oil surfaces which affects the adhesion between oil and calcite surfaces [12, 128].

### 5.3.2 Experimental Procedure

### 5.3.2.1 Contact Angle Measurements

Sessile drop method was used to conduct contact angle tests using Vinci IFT 700 (see the schematic in Figure 1 in Xie et al. [121]). Contact angle tests were performed at a constant pressure of 2000 psi and variable temperatures of 25-100 °C. Calcite mineral substrates were cleaned with methanol and rinsed with deionized water to remove contaminants from the surface. It is worth noting that to avoid calcite dissolution, the deionized water used for rinsing was previously equilibrated by aging a few calcite pieces in it. The pH level was continuously monitored (using Orion Star A211 pH meter with Orion ROSS Ultra triode pH electrode) until no more change in pH was detected. Cleaned substrates were placed in an oven to dry at a temperature of 60 °C. Substrates were then placed in a high pressure-temperature cell and vacuumed before being exposed to experimental brines. Subsequently, brine was introduced into the cell at the starting temperature of 25 °C. An oil droplet was then released onto the substrate surface, and the contact angle between the substrate and the line tangent

to the oil droplet was recorded until equilibrium was reached (Figure 5-1). Subsequently, the temperature was incrementally increased to 100 °C and corresponding contact angles were recorded. The system was allowed to reach equilibrium (up to 24 hours) at each temperature interval before the final contact angle was reported. The above procedure was repeated until every brine was tested.
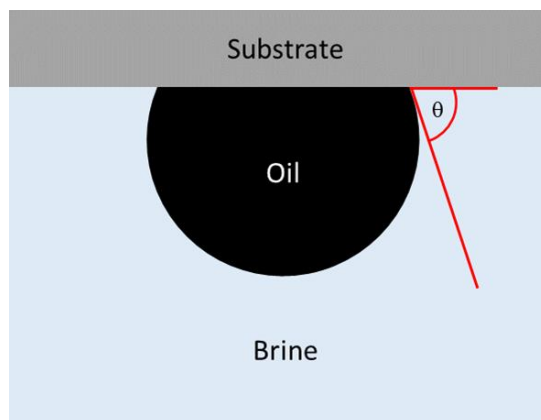


Figure 5-1. Schematic of contact angle measurement for oil/brine/rock system.

5.3.2.2 Zeta Potential Measurements

Electrophoretic mobility (EPM) measurement technique was utilized to measure zeta potentials in all measurements using Malvern Zetasizer ZS Nano series. Rock samples were first cleaned and dried in an oven at 60° temperature before being crushed to fine powder ranging in diameter from 10-100 μm. Then, 1% wt of various aqueous solutions were prepared by adding 1 gram of crushed powder to 10 ml of ionic solution to create suspensions. Due to rapid dissolution of calcite particle, zeta potential measurement below pH 5-6 was not practical [10, 15], thus, we only conducted brine/rock zeta measurements at pH 8. Aqueous solutions were left to reach equilibrium until the measured change in pH reached zero. Supernatant parts of suspensions containing the finest suspended particles (1 – 20 μm) were transferred to a cuvette using a syringe to carry out zeta potential measurements. Also, various emulsions of brine-oil with a volume ratio 1:9 were prepared and zeta potential at brine-oil interface was measured at pH 3 and 8 [51]. Prior to zeta potential tests, the crude oil was filtered through a 5-μm filter to remove particles from the oil. Because zeta potentials are much more stable at 25 °C than high temperatures, we performed all zeta potential measurements at 25 °C to evaluate the surface potential dependencies of oil, and rock surface reactivity. The experimental procedures to test zeta potential follow the

procedures proposed by Xie et al. [51]. The standard deviation for zeta potential measurements was +/-2%.

## 5.4 RESULTS AND DISCUSSION

### 5.4.1 Effect of pH on Contact Angle

The contact angle of the high acidic oil on calcite increased with increasing pH for both $Na_2SO_4$ and $CaCl_2$ at a given concentration (Figure 5-2 and Figure 5-3). For example, at 100 °C, in the presence of 1.0 M $CaCl_2$, pH 3 yielded a contact angle of 29°. Rather, pH 8 gave a contact angle of 92°, suggesting a wettability shift from strongly water-wet to intermediate-wet with increasing pH. Similarly, for 0.01 M $CaCl_2$ at 100 °C, contact angle increased from 24° to 37° with increasing pH from 3 to 8. Likewise, for 1.0 M $Na_2SO_4$ solution at 100°C, pH 3 gave a contact angle of 25°, while pH 8 showed a contact angle of 115°, implying that increasing pH triggers an oil-wet system. Furthermore, for 0.01M $Na_2SO_4$ solution at 100 °C, contact angle behaviour followed a similar trend, showing a slight increase from 23° to 27° with increasing pH from 3 to 8. Similar behaviour of increasing contact angle with increasing pH is also observed in Mahani et al. [15] work. At pH 7.5 they observed contact angles ranging from 40°-70° using 25dSW (25 times diluted sea water), whereas at pH 9.2, in 25dSWEQ (25 times diluted seawater equilibrated), contact angles of 120°-130° was reported. Their results indicate that a wettability shift from water-wet to oil-wet can be achieved with increasing brine pH.

Our previous results show that pH strongly influences the surface chemistry of oil/brine and brine/carbonate [155], hence the polarity and magnitude of electrostatic forces at oil/brine and brine/rock [148]. This very likely explains why we observed an increase in contact angles with increasing pH regardless of ion type and concentration (Figure 5-2 and Figure 5-3). The crude oil with high acid (4.0 mg KOH/g) and base (1.3 mg KOH/g) number, contains surface active acid (-COOH) and base compounds (-NH$^+$) [81] which can be present at the interface simultaneously. Also, these polarized ends can be ionized depending on pH. Lower pH means more amount of –NH$^+$ at oil surface, and more >CaOH$^+$ at calcite surface [12, 128]. At higher pH, -COO$^-$ group will dominate surface charges [157]. Similarly, for oil with a high base number, low pH likely triggers a strongly water-wet system. This is also experimentally demonstrated in our previous work showing contact angle of 30° in high salinity formation brine (FB = 252.244 g/l) at low pH (2.55), meaning a strongly water-wet system. In contrast,

higher pH (5.68) gave contact angle of 81° in low salinity water (100 times diluted FB). It is worth noting that our previous experiments were conducted using $SO_4^{2-}$-free solutions on calcite mineral at a temperature of 60 °C and a pressure of 2000 psi without aging [128].
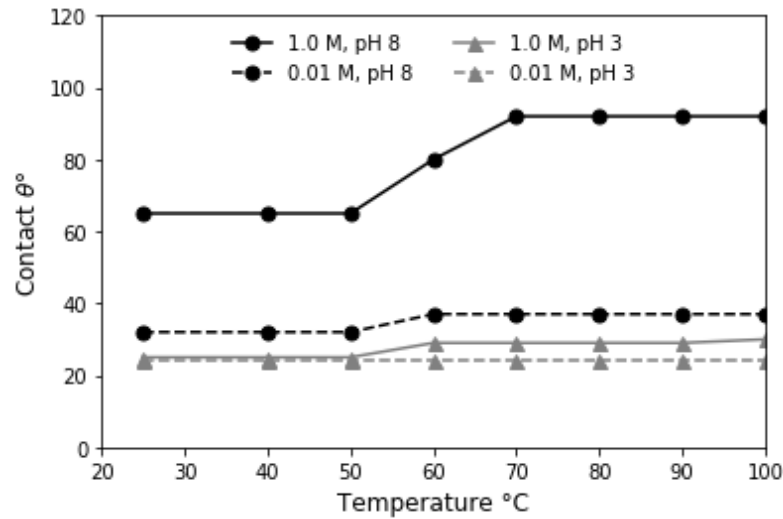


Figure 5-2. Contact angle variation at different temperature (25 - 100 °C) in the presence of $CaCl_2$ at different concentrations (0.01 and 1.0 M) and pH (3 and 8).
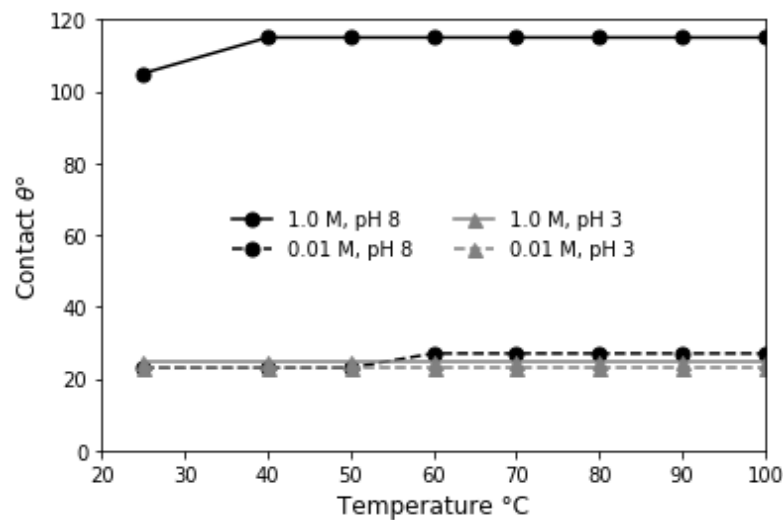


Figure 5-3. Contact angle variation at different temperature (25 – 100 °C) in the presence of $Na_2SO_4$ at different concentrations (0.01 and 1.0 M) and pH (3 and 8).

## 5.4.2 Effect of Ion Type and Concentration on Contact Angle

Although both $CaCl_2$ and $Na_2SO_4$ gave strong water-wet systems at low pH 3 regardless of concentration, the contact angles were over all affected by ion type. In general, $CaCl_2$ gave slightly higher contact angles compared to $N_2SO_4$ at both concentrations (with the exception of $Na_2SO_4$ at pH 8) (Figure 5-2 and Figure 5-3). For example, at pH 3, $CaCl_2$ gave contact angles of 24° and 29° at 0.01 and 1.0M, while in $Na_2SO_4$ solution, contact angles were 23° and 25° at 0.01 and 1.0M. Similarly, at pH 8, contact angles for $CaCl_2$ and $Na_2SO_4$ were found to be 37° and 27° respectively at 0.01M. However, at high concentration, $CaCl_2$ showed lower contact angle (92°) compare to $Na_2SO_4$ (115°).

Salinity reduction led to contact angle decrease in both $CaCl_2$ and $Na_2SO_4$ (Figure 5-2and Figure 5-3), suggesting a more water-wet system. For example, at pH 8, $CaCl_2$ gave contact angles of 92° and 37° in high (1.0M) and low (0.01M) concentration respectively. A similar trend, although less substantial was also observed at pH 3, where contact angles decreased from29° to 24° decreasing concentration. Likewise, for $Na_2SO_4$ solution, contact angle also decreased from 115° to 27° when the concentration was reduced. It is worth noting that all contact angles reported above were final contact angles at 100 °C. Al-Attar et al., [32] investigated the effect of varying ion types and concentration on the wettability of carbonate rocks. They found that decreasing $SO_4^{2-}$ concentration has a greater impact on wettability alteration from weakly water-wet to strongly water-wet compared to decreasing $Ca^{2+}$ concentration. For instance, brine with $SO_4^{2-}$ concentration of 47.66 ppm gave contact angle of 80°, whereas decreasing $SO_4^{2-}$ concentration to 23.7 ppm decreased the contact angle to 60°. In comparison, reducing the concentration of $Ca^{2+}$ in brine from 1992 ppm to 664 ppm, decreased the contact angle from 70° to 60°. Furthermore, at high concentration, $SO_4^{2-}$ based aqueous solution showed higher contact angle (less water wet) than $Ca^{2+}$ based solution, indicating a more water-wet condition in the presence of $Ca^{2+}$ solution in line with our observation. It is worth noting that both high and low concentration brines showed a strongly water-wet system at pH 3, and decreasing concentration had little impact on contact angles. For example, reducing $CaCl_2$ concentration from 1.0M to 0.01M decreased the contact angle by 6°, whereas contact angle decreased by only 2° with decreasing $Na_2SO_4$ concentration from 1.0M to 0.01M.

Two possible explanations are proposed for this observation:

1. Low pH 3, rather than concentration, dominates electrostatic charges at oil/brine and brine/carbonate [154]. In other words, the effect of concentration on contact angle is likely to be constrained at low pH, which can be interpreted by surface complexation modelling [12, 154].

2. Low pH 3 offers excess $H^+$ which can adsorb at the interface of oil/brine and brine/carbonate to generate massive $-COOCa^+$ and $-NH^+$ on oil surface, and $>CaOH_2^+$ at calcite surface [12], hence creating a more hydrophilic system because of surface complexation [155].

### 5.4.3 Effect of Temperature on Contact Angle

The temperature had a negligible effect on contact angle at pH 3 regardless of ion type and concentration. In 0.01 M $CaCl_2$ solution, contact angle did not change with increasing temperature, although contact angle slightly increased from 25° to 30° with increasing temperature in 1.0 M $CaCl_2$. Similarly, for $Na_2SO_4$, contact angles remained almost unchanged with the temperature variation at both concentrations. In contrast, at pH 8, systems showed more sensitivity to temperature variation. For example, in 1.0 M $CaCl_2$ brine, contact angle significantly increased from 65° to 92° with increasing temperature from 25 to 70 °C, while further increasing the temperature up to 100 °C had no effect on contact angle. For 1.0 M $Na_2SO_4$ brine, a noticeable increase in contact angle was observed albeit at a lower temperature, as contact angle increased from 105° to 115° with increasing temperature from 25 to 40 °C, above which contact angle remained constant.

Alotaibi et al. [59] studied the effect of temperature change on wettability of oil/brine/carbonate system by measuring contact angles at various temperatures using brines with various composition and salinity. They have found that in the presence of $Na_2SO_4$ solutions, contact angle increases with increasing temperature, implying less water-wet preference at high temperatures. For example, at 60 °C, $Na_2SO_4$ solution (3,560 ppm) gave contact angles 57.3-57.6°, whereas at 90 °C, contact angles 62.1-70.7° were reported, in line with our observation. A similar trend was also observed for lower salinity $Na_2SO_4$ solution (1,780 ppm), where contact angles increased from 39.9-38.4° at 60 °C, to 49.9-44.8° at 90 °C.

In our previous work [155], we reported contact angle increased from 29 to 70° with increasing temperature from 25 to 60° for 1 M $Na_2SO_4$ solution on carbonate rocks. Although the contact angle behaviour with temperature in both works is comparable,

we believe the discrepancy in the results is due to the use of different surfaces. In this work, we used pure calcite mineral, whereas our previous work was conducted on reservoir rock with different mineral composition, which may influence the geochemical interactions due to the presence of other surface species. In addition, we believe physical variations such as surface roughness may also contribute to this discrepancy.

## 5.4.4 Effect of Ion Type and Concentration on Zeta Potential of Oil-Brine and Brine-Calcite

Zeta potential was significantly affected by both ion type and concentration. (Figure 5-4 and Figure 5-5) shows zeta potential of oil-brine and brine-calcite in the presence of ionic aqueous solutions at various pH. For oil-brine interfaces, decreasing salinity increased the magnitude of zeta potential in a negative direction regardless of ion type in line with existing literature data [158-160]. For brine-calcite surfaces, calcium chloride ($CaCl_2$) gave positive zeta potential on brine-calcite surfaces for both salinities due to the formation of $>CO_3Ca^+$ surface species at calcite surfaces [123, 128]. However, zeta potential decreased with decreasing salinity because of less $>CO_3Ca^+$ surface species. Sodium sulfate ($Na_2SO_4$) showed negative zeta potential at brine calcite interface for both salinities due to the generation of $>CaSO_4^-$, and became increasingly more negative with decreasing ($Na_2SO_4$) salinity. Together, zeta potential results show that for $Na_2SO_4$, lowering salinity triggers a strong negative zeta potential for both oil-brine and brine-calcite, indicating an increase of electrical double layer repulsion, thus more water-wet condition in line with contact angle measurements.
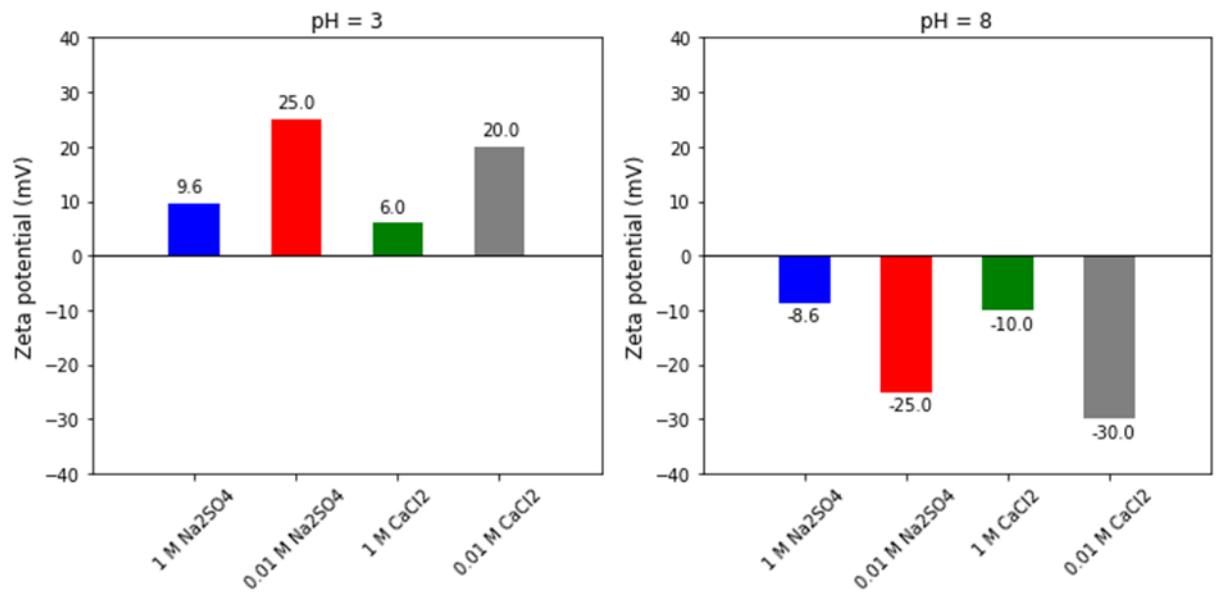
Figure 5-4. Zeta potential results for crude oil-brines emulsion at various ionic concentrations at pH 3 and 8, T = 25 °C.
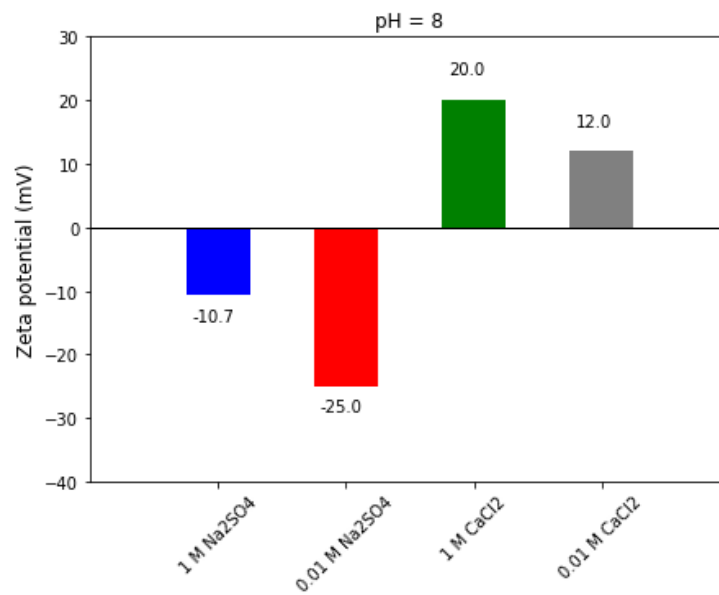


Figure 5-5. Zeta potential results for calcite suspension in experimental brines with various concentrations at pH 8, T = 25 °C.

## 5.5 IMPLICATIONS

We hypothesise that high acidic oil would be more sensitive to low salinity effect than low acidic oil because $-COO^-$ from oil surface and $>CO_3^-$ from rock surface increase with decreasing salinity, which generates repulsive force, thus more hydrophilicity. To further test our hypothesis, we collected literature data where authors reported oil and brine properties, along with incremental oil recovery from either coreflooding experiments or spontaneous imbibition tests in tertiary mode (Table 5-1). We plotted incremental oil recovery versus crude oil acid number in (Figure 5-6), demonstrating that incremental oil recovery increases with increasing acid number, although questions remain regarding the existence of spread in Y-axis (incremental oil recovery). We believe that the following two reasons likely account for the spread in Y-axis:

1. Rock type significantly influences rock surface chemistry thus affecting oil-brine-calcite interaction. For example, Mahani et al. [113] showed that rock type affects both zeta potential and isoelectric point even between samples composed of almost entirely calcite.

2. Pore surface roughness of porous media likely affects system wettability thus incremental oil recovery. For example, AlRatrout et al. [161] characterized the impact of surface roughness (limestone) on wettability using micrometre-resolution X-ray tomography combined with automated methods. Their results show that the variation of both contact angle and interfacial curvature increases with the local degree of roughness.

Besides the above two reasons, the base number of oils may also play a role in oil-brine-carbonate system wettability, but we can reasonably assume that acidic components govern the wettability at *in-situ* reservoir pH range during low salinity water flooding. This is because $-NH$ decreases sharply with increasing pH particularly when pH is greater than 8. Also, $-NH$ is less sensitive to salinity compared to $-COO^-$ and $-COOCa^+$ in light of previous surface complexation modelling at pH greater than 8 [12, 81, 128].

To further confirm that high acidic oil would be more sensitive to low salinity effect, we conducted a geochemical study using PHREEQC with geochemical reactions and thermodynamic parameters listed in Brady et al., [12]. Seawater used by Nasralla et al. [90] (Table 5-1) was applied to calculate surface species on both oil and carbonate surfaces. Surface properties (e.g., site density and surface area) for calcite and oil are

listed in Chen et al. [162]. Given that the concentration of surface species at oil and calcite surface is a function of pH, to calculate surface species, we first computed pH of seawater (7.3) and 100 times diluted seawater (9.7) with consideration of calcite dissolution using PHREEQC. Then, we computed oil and calcite surface species concentration at a given pH. To examine the effect of acidic component on wettability, the concentration of surface species was computed as a function of acid number ranging from 0 to 4 mg KOH/g at a fixed base number (1.0 mg KOH/g) in seawater. This range of AN/BN ratio is sufficiently broad to cover the majority of reservoir oil properties in terms of polarized functional groups (see Figure 4 in [12]).

To characterize the adhesion force, a parameter namely bond product sum [12, 163], BPS, which is equal to $[-NH^+]$ $[>CO_3^-]$ + $[-NH^+]$ $[>CaCO_3^-]$ + $[-COOCa^+]$ $[>CO_3^-]$ + $[-COOCa^+]$ $[>CaCO_3^-]$ + $[-COO^-]$ $[>CaOH_2^+]$ + $[-COO^-]$ $[>CO_3Ca^+]$ was calculated, where bracketed terms are calculated concentrations of surface species ($\mu mol/m^2$). Figure 5-7 shows that BPS increases linearly with acid number in both seawater and 100 times diluted seawater, implying that carbonate reservoirs likely become more oil-wet with increasing acidic components. This likely explains why Strand et al. [164] observed a low secondary oil recovery (8.5% OOIP) for spontaneous imbibition tests with a high acidic oil (AN = 1.9 mg KOH/g), whereas low acidic oil (AN = 0.7 mg KOH/g) yielded 30.7% of OOIP using the same formation water. Austad et al. [4], also reported higher secondary oil recovery (≈ 42%) for low acid number oil (AN = 0.08 mg KOH/g). In contrast, oil with a high acid number (AN = 0.7 mg KOH/g) gave ≈ 13% oil recovery using same formation brine, further confirming that water wetness increases with decreasing oil acid number as previously suggested [4, 153].

Together, given that low salinity water flooding is mainly deployed in tertiary mode, the EOR potential should be greater in reservoirs containing oils with high AN and increase further with increasing AN, mainly due to their higher residual oil saturation. (Figure 5-7) also shows that the difference of BPS between seawater and 100 times diluted seawater increases with acid number. This explicitly shows that high acidic oils become more sensitive to low salinity effect due to a decrease in electrostatic bridges caused by salinity reduction. Surface complexation modelling in combination with existing literature data confirm that the potential for low salinity EOR increases with increasing crude oil acid number.

Table 5-1. Core flooding results for tertiary low salinity water flooding using crude oils with wide range of acid number reported in the literature. (CF-coreflooding; SW-seawater, dil-SW- diluted seawater; IOR- incremental oil recovery in tertiary mode).

| Authors | AN | BN | IOR (%) | Method | Brines | Rock type | T (°C) | Aging (weeks) |
|---------|------|------|---------|--------|---------------|-------------|-----|-----|
| [26] | 0.25 | - | 18 | CF | dil-SW | carbonate | 100 | 2 |
| | 0.25 | - | 19.5 | CF | dil-SW | carbonate | 100 | 2 |
| [165] | 0.11 | - | 6 | CF | Modified brine | dolomite | 70 | 6 |
| | 0.11 | - | 9 | CF | Modified brine | dolomite | 70 | 6 |
| | 0.11 | - | 5.1 | CF | Modified brine | limestone | 121 | 6 |
| | 0.11 | - | 7.1 | CF | dil-SW | limestone | 121 | 6 |
| | 0.11 | - | 9 | CF | dil-SW | limestone | 121 | 6 |
| [166] | 0.96 | 0.15 | 19 | CF | dil-SW | carbonate | 90 | 4 |
| | 0.96 | 0.15 | 10.7 | CF | dil-SW | carbonate | 90 | 4 |
| | 0.96 | 0.15 | 1.9 | CF | dil-SW | carbonate | 22 | 4 |
| [167] | 2.45 | - | 32 | CF | dil-SW | limestone | 120 | 4 |
| [90] | 0.1 | 0.32 | 7.5 | CF | dil-SW | limestone | 120 | - |
| | 0.1 | 0.32 | 4 | CF | dil-SW | limestone | 120 | - |
| | 0.38 | 1.14 | 5 | CF | dil-FW | limestone | 70 | - |
| | 0.38 | 1.14 | 4 | CF | dil-SW | limestone | 70 | - |
| [4] | 0.08 | 0.34 | 1 | CF | dil-SW | limestone | 110 | 2 |
| | 0.34 | 0.45 | 2 | CF | dil-SW | limestone | 110 | 2 |
| | 0.7 | 0.42 | 5 | CF | dil-FW | limestone | 90 | 2 |
| | 0.7 | 0.42 | 4 | CF | dil-SW | limestone | 110 | 2 |
| [9] | 1.15 | 1.25 | 5.3 | CF | dil-SW | carbonate | 80 | 2 |
| | 1.15 | 1.25 | 6.4 | CF | dil-SW | carbonate | 80 | 2 |
| | 1.76 | 1.77 | 9.7 | CF | dil-SW | limestone | 24 | 2 |
| [40] | 1.9 | - | 22.5 | CF | dil-SW | Klint chalk | 120 | 4 |
| | 1.9 | - | 7 | CF | SW | Klint chalk | 120 | 4 |
| [164] | 0.7 | - | 6 | CF | SW | Klint chalk | 90 | 4 |
| | 1.9 | - | 18 | CF | SW | Klint chalk | 110 | 4 |
| | 1.9 | - | 18.8 | CF | SW | Klint chalk | 110 | 4 |
| | 1.9 | - | 23.4 | CF | SW | Klint chalk | 120 | 4 |
| | 1.9 | - | 20 | CF | SW | Klint chalk | 120 | 4 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| [168] | 0.18 | 0.01 | 3.7 | CF | Dil-SW | limestone | 90 | 3 |
| | 0.18 | 0.01 | 5.4 | CF | Modified brine | limestone | 90 | 3 |
| | 0.18 | 0.01 | 2.5 | CF | Dil-SW | limestone | 90 | 3 |
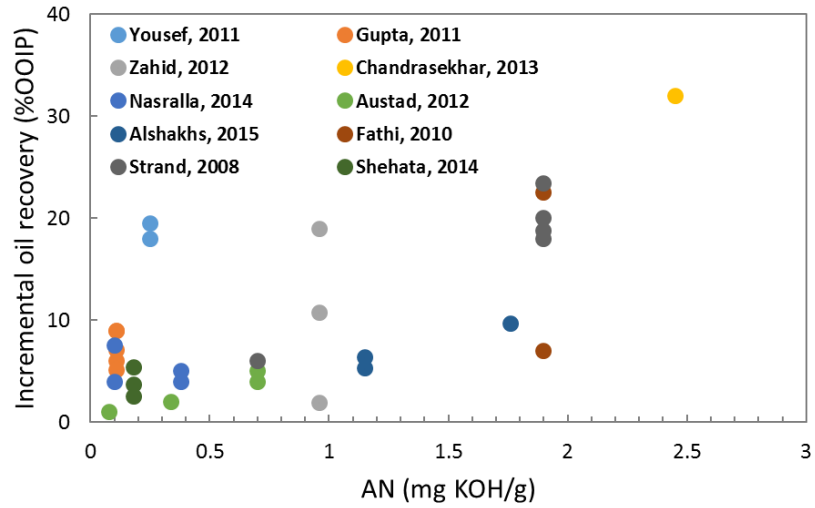
Figure 5-6. Incremental oil recovery versus oil acid number in spontaneous imbibition and coreflooding experiments.
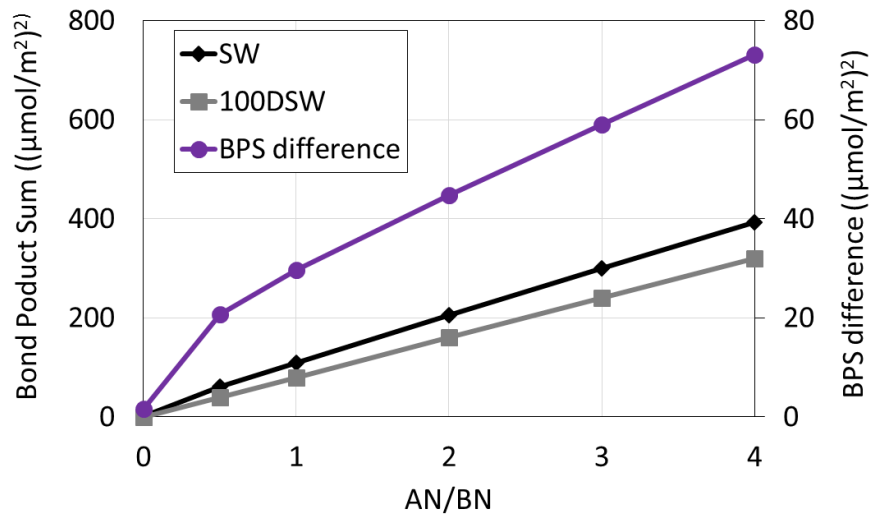


Figure 5-7. Effect of AN/BN on bond product sum (BPS) in presence of seawater (SW) and 100 times diluted seawater (100DSW). (BPS difference between SW and 100DSW means the breakage of oil-calcite bonding.)

## 5.6 CONCLUSIONS

Wettability alterations appears to be an important physicochemical process during low salinity water flooding in carbonate reservoirs. Oil composition, particularly specific functional groups (e.g., -COOH, -NH$^+$) plays an important role in oil-brine-calcite interactions, thus wettability. In this paper, we explored the potential of low salinity effect in reservoirs with high acidic components (acid number = 4.0 mg KOH/g and base number = 1.3 mg KOH/g) with a combination of approaches (e.g., contact angle and zeta potential measurements, surface complexation modelling). Our contact angle results show at pH=8, salinity and ion type play a significant role in shifting wettability from slightly oil-wet to strongly water-wet. However, low pH (pH 3) triggers a strongly water-wet system with minor effect from salinity, ion type, and temperature. Zeta potential experiments show that the electrostatic charges at oil-brine and brine-calcite interfaces became strongly negative with decreasing brine salinity, particularly for $Na_2SO_4$ at pH 8, further confirming the role of electrical double layer in wettability alteration of carbonate rocks. Geochemical modelling suggests that the difference between electrostatic bridges, i.e., breakage of oil-calcite bonding that stems from lowering salinity, increases with acid number, implying a better potential of low salinity effect in high acidic oil-bearing carbonate reservoirs.

# Chapter 6 Impact of Surface Roughness on Wettability of Oil-Brine-Calcite System at Sub-Pore Scale

## 6.1 ABSTRACT

Wettability alternation appears to be an important physicochemical process in carbonate reservoirs during low salinity water flooding. Contact angle measurement is widely used as a simple and direct method to demonstrate wettability alteration by low salinity water. The effect of various parameters, e.g., brine salinity, oil composition, and rock mineralogy on contact angle have been well documented. However, uncertainty over effect of rock surface roughness on contact angle of oil-brine-calcite is a major impediment to upscaling laboratory results and predicting wettability at field scale, knowing oil-brine-rock interaction is governed by electrostatic forces. We thus measured contact angle of oil on calcite substrates with different surface roughness (17 nm, 366 nm, and 943 nm), in high and low salinity brines. Moreover, we compared our experimental results with contact angles predicted by Wenzel's equation.

Contact angle results show that in high salinity brine, contact angles decreased from $170°$ to $134°$ ($36°$ decrease) with increasing surface roughness from 17 to 943 nm, suggesting a less hydrophobic system. Similar correlation between contact angles and surface roughness was observed in low salinity brine. Nevertheless, contact angles only slightly decreased from $117°$ to $101°$ ($16°$ decrease) in low salinity brine, suggesting the effect of surface roughness on contact angle is more subtle in low salinity condition. We also found that for oil-brine-calcite system, the correlation between contact angle and surface roughness contradicts the trend predicted by Wenzel's equation. This is largely because the surface forces that govern oil-brine-calcite interactions are not captured by Wenzel's equation. Therefore, we hypothesize that at pore-scale level, wettability alteration by low salinity brine will likely be more subtle than that shown by contact angles when performed on smooth substrates (at sub-pore scale). To predict contact angle at pore-scale, surface roughness and surface forces governing oil-brine-calcite interactions need to be considered. The findings of this research will provide further insight into water-assisted EOR in carbonate reservoirs.

## 6.2 INTRODUCTION

Enhanced Oil Recovery (EOR) in carbonate reservoirs will remain important for the remainder of the 21$^{st}$ century for achieving hydrocarbon reservoirs' potential and securing increased global energy demand [169]. Low salinity water flooding appears to be a cost-effective and environmentally friendly means towards achieving the above objectives [113, 128, 154, 170-172]. One of the main petrophysical parameters targeted by low salinity water flooding is wettability alteration from oil-wet to intermediate-wet or weakly water-wet [12, 14, 155, 173, 174] which in return drives relative permeabilities towards a lower residual oil saturation [138, 175]. Contact angle measurements are widely used as a direct evidence for wettability alteration and evaluating the potential of low salinity water flooding in a given carbonate reservoir [10, 32, 88, 127, 128, 155, 176, 177]. For example, Al-Attar et al. [32] conducted series of contact angle measurements that showed wettability alteration is likely the main physiochemical process during low salinity water flooding. Yousef et al. [26] also conducted several contact angle measurements on carbonate rocks in the presence of connate water and seawater with different dilutions and reported a shift in wettability towards water-wet with decreasing brine salinity. Similarly, Alotaibi et al. [59] performed over 38 contact angle measurements to demonstrate wettability alteration process by low salinity water in oil-brine-carbonate system, while Alameri et al. [60] further confirmed wettability alteration in carbonate using contact angle measurements.

Several mechanisms (e.g., electrical double layer theory [51, 127, 178], surface complexation modelling [12, 15, 113, 128, 141, 171, 179]) have been proposed to decipher the factors that control wettability of oil-brine-carbonate system. Moreover, zeta potential measurements and surface complexation modelling (SCM) including bond product sum (BPS) calculations have been used to explain contact angle behaviour in various brines [127, 128]. For instance, AlQuraishi et al. [88] performed a series of zeta potential measurements and demonstrated that ionic composition of aqueous phase can impact the electrical charges at rock-brine interface, resulting in alteration of rock wettability. Likewise, Mahani et al. [10] showed that brine chemistry significantly affects the zeta potential at oil-brine-rock interface, leading to electrical double layer expansion, thus alteration of rock wettability. Xie et al. [154] presented contact angle results in conjunction with geochemical modelling to show that pH controls the wettability of oil-brine-carbonate system.

Wettability of oil reservoirs is a multi-scale petrophysical property which is defined by interactions between molecules in fluid-fluid-rock system and *in-situ* pore surface roughness [61-63]. While extensive investigations have been carried out to understand the wettability alteration process at interfacial scale (nano-scale) with respect to oil-brine-rock interactions, how surface roughness at pore surfaces together with oil-brine-rock interactions at sub-pore scale (from 10 to 1000 nm) affects wettability has not been examined. Therefore, to better understand fluids flow in pore network during low salinity water flooding, thus predicting the relative permeabilities and capillary pressure and upscaling to reservoir scale, surface roughness in conjunction with fluid-fluid-rock interactions needs to be investigated. Our previous research showed that alteration of surface roughness due to calcite dissolution during contact angle measurements have a negligible impact on contact angle results [180]. This finding suggested that contact angle measurement remains a valid approach to directly examine the wettability alteration process during low salinity water flooding. Nevertheless, the effect of *in-situ* pore surface roughness on contact angle measurement at different brine salinity conditions remains unknown. The key question addressed in this work is how *in-situ* surface roughness affects fluid-fluid-rock interactions which impact contact angle and wettability. Therefore, we measured contact angles of oil on calcite substrates ranging in surface roughness at different brine salinities. Moreover, we compared our experimental results with contact angles predicted by Wenzel's equation to demonstrate its limitation for oil-brine-rock system. The outcome of this study provides deeper insights into how the wettability obtained at different lengthscales impacts flow properties, e.g., relative permeabilities and capillary pressure.

## 6.3 MATERIALS AND PROCEDURES

### 6.3.1 Fluids

#### 6.3.1.1 Oil

The crude oil used in this study was sourced from the US, and its acid and base numbers were measured to be 1.7 and 1.2 mg KOH/g, respectively. Gas chromatography analysis found the crude oil was comprised of asphaltene (37.1 wt %), naphthene (26.4 wt %), wax (3.8 wt %) and sulphur (3.09 wt %), while its density was measured to be 0.89 g/cm$^3$ at 20° C.

### 6.3.1.2 Brine

Two multi-component brines with contrasting salinities were formulated for this study. We used reagent grade salts - NaCl and $CaCl_2$, from Scharlau - and ultra-pure deionised water to prepare high and low salinity ionic solutions. The high salinity brine is comprised of 1.0 mol/L NaCl + 0.01 M $CaCl_2$. The high salinity brine was diluted 100 times to make the low salinity brine. The rationale for using $Ca^{2+}$ over other ions such as $Mg^{2+}$ are:

1. $Ca^{2+}$ is more abundant in formation brine than $Mg^{2+}$,

2. Surface complexation modelling indicates replacing $Ca^{2+}$ with $Mg^{2+}$ has little effect on the predicted results due to the similarity in $Ca^{2+}$ and $Mg^{2+}$ equilibria [181].

We also omitted $SO_4^{2-}$ because we previously demonstrated that $SO_4^{2-}$ is not a necessary element for triggering low salinity effect in carbonate rocks [127]. Given wettability of oil-brine-rock system is significantly affected by brine pH [154] and susceptibility of calcite to dissolution, we used PHREEQC software to quantify calcite dissolution by high and low salinity brines at their natural pH level. The results showed that calcite dissolution increases the concentration of $Ca^{2+}$ in high salinity brine by 6.0 x $10^{-5}$ mole (a 0.56% increase) and in low salinity brine by 1.16 x $10^{-4}$ (a 9% increase). This level of calcite dissolution may inadvertently alter surface roughness and causes pH rise during contact angle tests. We also noticed that when calcite was exposed to experimental brines, the pH reached approximately 10. Therefore, to preserve the integrity of calcite specimens and eliminate pH influence on contact angles, the pH of brines was set to 10 with a buffer solution. It worth noting that although the *in-situ* brine pH in the reservoir ranges from 5 to 6.5 [12], a higher pH value of 10 has been observed following low salinity water flooding [27].

### 6.3.2 Rocks

Three calcite substrates were used in this study. X-ray diffraction analysis showed samples were composed of 100% calcite, while no traceable impurities were found in the specimens. We aimed to produce samples having high, intermediate and low surface roughness. Therefore, we modified the surface roughness of two substrates using abrasive papers with different grit size (P120 for high, and P360 for intermediate roughness). The sanding process was performed from various directions to ensure

the entire surface of substrate was equally treated. Note that the letter P is the standard for grit size as designated by Federation of European Producers of Abrasives (FEPA). The third substrate (i.e. low surface roughness) did not undergo treatment with abrasive paper. This sample was simply split along the plane of cleavage to expose a fresh surface with low roughness. Samples were cleaned with methanol to remove inorganic contamination, then rinsed with equilibrated de-ionised water. It is worth noting that minerals such as calcite and quartz/mica are widely used in wettability studies as they are the main constituents of carbonate and sandstone rocks respectively [182]. It has also been recommended that contact angle measurements be conducted on minerals rather than rocks, as the heterogeneity of rock substrates may significantly compromise the experimental result [183]. Moreover, since surface roughness was the subject of our investigation, calcite mineral enables better control over surface roughness modification.

### 6.3.3 Surface Roughness Measurement using Atomic Force Microscope

The surface roughness of all three substrates were measured using Atomic Force Microscope (WITec alpha 300 SAR) at ambient conditions and found to be 17 nm, 336 nm, and 943 nm (Table 6-1). WITec Project FOUR software was used for AFM topography data collection, background correction, and calculation of the average roughness parameter [184]. The AFM tips were (NPG-10), supplied by Bruker Corporation. The roughness factor (r) which is defined as the ratio of actual surface area to geometric surface area was also calculated. The actual surface area refers to the total area of a rough surface including its peaks and valleys, while geometric surface area is surface area measured in the plane of the interface [185-189], both of which were collected from AFM data.

Table 6-1. Topographical data pertaining to the calcite samples used in this study. Surface roughness, actual surface area, and geometric surface area were acquired by Atomic Force Microscope (AFM), while roughness factor (r) was calculated.

| Roughness (nm) | Actual surface area ($\mu m^2$) | Geometric surface area ($\mu m^2$) | Roughness factor (r) |
|---|---|---|---|
| 17 | 897 | 893 | 1.004 |
| 336 | 1340 | 893 | 1.501 |
| 943 | 1630 | 893 | 1.825 |
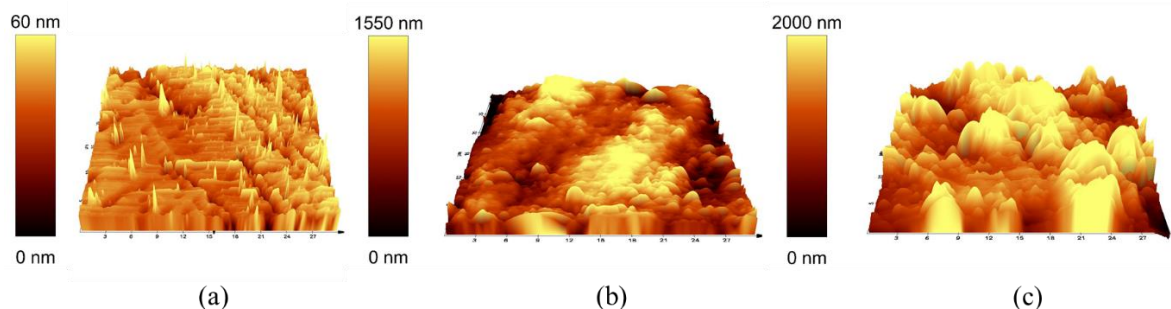
Figure 6-1. Atomic Force Microscopy (AFM) images of calcite substrates used in this study. (a): the topography of the highly rough substrate (943 nm), (b): the substrate with intermediate roughness (336 nm), and (c): corresponding to the smooth substrate (17 nm).Height on the images is colour coded where the darkest shade (black) indicates 0 nm elevation. Yellow shows the highest elevation ranging from 60 nm to 2000 nm.

## 6.3.4 Contact Angle Measurement

Given that we aimed to examine the effect of surface roughness on contact angle in the presence of low and high salinity brines, the effect of temperature on oil-brine-rock interactions was minimized by conducting sessile drop contact angle measurements under ambient conditions (T = 20 °C, P = 1.0 bar) [154, 190]. The schematic of the contact angle measurement setup is shown in (Figure 6-2). Samples were rinsed with methanol followed by equilibrated de-ionised water. To remove organic contamination, substrates were exposed to air plasma for 15 minutes. A substrate was placed inside the glass cell and immersed in each experimental brine. An oil droplet was then dispensed onto the calcite surface through a small needle (D = 0.64 mm). High resolution recording of the droplet evolution was captured and the contact angle between the substrate and the oil droplet through the aqueous phase was recorded until the contact angle reached equilibrium. This process was repeated for all substrate-brine combinations. To ensure the repeatability of our contact angle results, each experiment was repeated three times. Contact angle results had a standard deviation 3.5°.
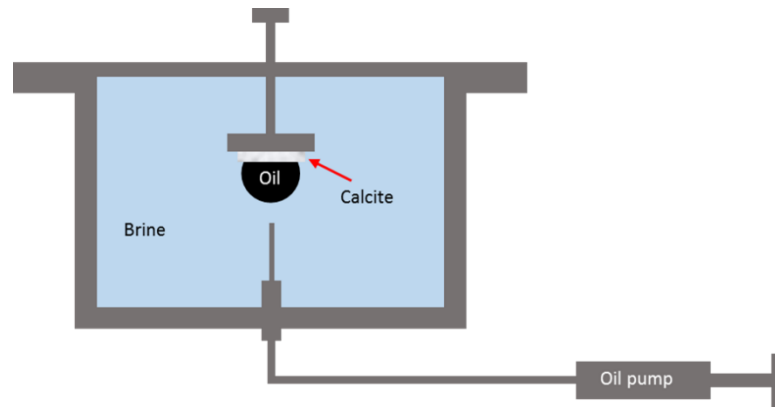
Figure 6-2. Schematic diagram of contact angle measurement setup.


## 6.4 RESULTS AND DISCUSSION

### 6.4.1 Effect of Surface Roughness on Contact Angle

Figure 6-3 shows that contact angle consistently decreases (becomes less oil-wet) with increasing surface roughness regardless of the salinity level. For example, in high salinity brine, contact angle decreased from 170° to 134° (36° decrease) with increasing surface roughness from 17 to 943 nm. We also found a similar trend for low salinity brine where the contact angle decreased from 117° to 101° (16° decrease) with increasing surface roughness.  These results are consistent with literature [62, 191]. For instance, Vijapurapu et al. [191] reported a decrease in the contact angle from 165° to 155° with increasing surface roughness from 1.17 to 5.46 μm for calcite surfaces. Moreover, using micrometre resolution X-ray imaging technique, AlRatrout et al. [62] measured contact angles at pore-scale for oil-brine-limestone system. Their results showed that contact angles decrease with increasing surface roughness implying a less hydrophobic system in line with our observation. Figure 6-3 also shows the effect of surface roughness on contact angle becoming more subtle in low salinity brine which indicates in low salinity condition, the electrostatic forces have greater impact on contact angle of oil-brine-calcite than surface roughness.
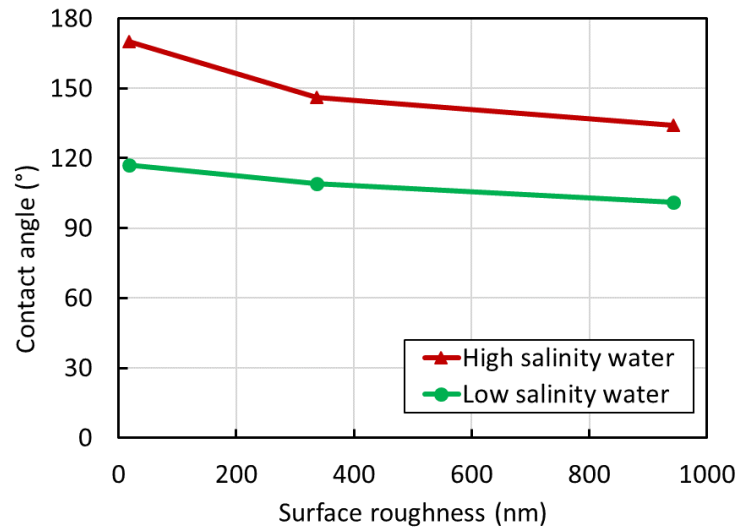
Figure 6-3. Effect of surface roughness on contact angles in calcite surfaces.

## 6.4.2 Effect of Salinity on Contact Angle at Different Surface Roughness

Figure 6-3 shows that contact angle decreases with decreasing salinity at a given surface roughness. For instance, at surface roughness of 17 nm contact angle decreased from 170° to 117°, while at surface roughness of 943 nm contact angle decreased from 134° to 101 which was expected as low salinity brine shifts wettability towards more water-wet. Figure 6-3 also shows that contact angle difference between low salinity and high salinity brine decreases with increasing surface roughness. At 17 nm surface roughness, the difference between contact angle at low salinity and high salinity brine (i.e. wettability alteration) was 53°, whereas at 943 nm surface roughness, the difference in contact angle was 33°. Our results imply that contact angle measurements made on smooth substrates likely overestimates the degree of wettability alteration in a reservoir due to pore-scale surface roughness which is mostly above 0.1 µm [192].

We also observed slight decrease in IFT from 8.3 to 3.8 mN/m with increasing salinity from 0.01M to 1.0 M. Nevertheless, it is unlikely that this negligible reduction in IFT triggers wettability alteration [10, 26], and many studies ruled out IFT reduction as a key factor in improved oil recovery [19, 26, 193]. Despite many studies reported IFT at different salinities, no clear correlation between IFT and salinity has yet been found, and both IFT increase [194] and decrease [29, 195] with decreasing brine salinity are reported in the literature.
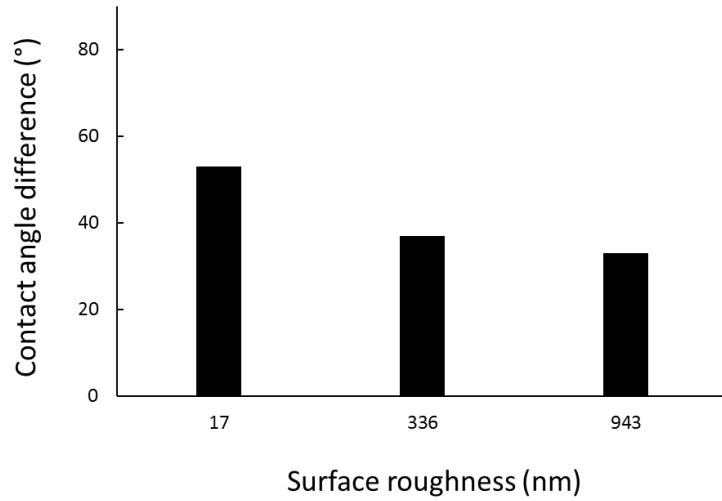
Figure 6-4. Contact angle difference between low salinity and high salinity brines decreases with surface roughness.

To understand why low salinity effect (the observable change in contact angle) decreases with increasing surface roughness, we revisited the oil-brine-rock interactions which is governed by disjoining pressure isotherm. We also propose a possible mechanism behind our experimental observation. It is widely accepted that the wettability of oil-brine-rock system is governed by the thermodynamics of thin water film [50, 196, 197], and disturbing the thermodynamic equilibrium may directly affect the system wettability. The thermodynamics of thin water film has been explained in details by Hirasaki [49] using the DLVO theory and Laplace-Young equation (Eq.1).

$$P_c = \Pi_{total} + \frac{2\sigma_{ow}cos\theta}{r} \qquad \text{(Eq.1)}$$

The disjoining pressure ($\Pi_{total}$) is comprised of three intermolecular forces: Van der Waals ($\Pi_{van\,der\,waals}$), electrical double layer ($\Pi_{electrical}$), and structural forces ($\Pi_{structural}$) (Eq.2).

$$\Pi_{total} = \Pi_{van\,der\,waal} + \Pi_{electrical} + \Pi_{structural} \qquad \text{(Eq.2)}$$

It is well documented that water chemistry, oil composition and rock surface chemistry influence the disjoining pressure which affects the wettability characteristics of rocks [48, 50, 158, 198]. In carbonate rocks, low salinity water causes the expansion of the electric double layer and results in establishment of a thicker and more stable water film which drives wettability alteration [148, 158, 193, 199]. We believe that surface roughness very likely instigates the formation of water film with irregular thickness

which accounts for the variation in contact angle with surface roughness (Figure 6-3). On rough surfaces, the water film is thicker due to a greater pore rugosity compared to smooth surfaces where the water film is relatively thin [200] (Figure 6-5.a). Consequently, on rough surfaces, the impact of electric double layer expansion on contact angle would diminish (Figure 6-5.b). In contrast, on a smooth surface where the water film is generally thin (Figure 6-5.c), the electrical double layer expansion under low salinity conditions plays a significant role in wettability alteration (Figure 6-5.d).
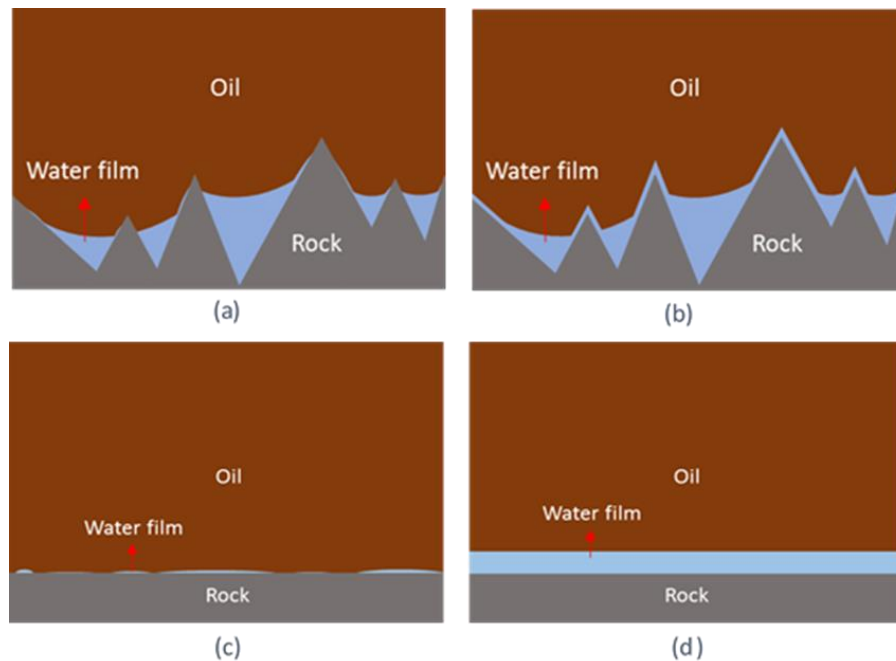


Figure 6-5. Impact of low salinity on electrical double layer expansion and wettability alteration in rough and smooth surfaces.The water film would be thicker on a rough surface due to a significant number of asperities where majority of oil/mineral interactions take place due to retention of smaller number of water layers. Consequently, the impact of the double layer expansion on wettability alteration due to lowering salinity from high (a) to low (b) may be subtle. Conversely, water film is thinner in general on a smooth surface, thus the impact of double layer expansion on wettability alteration due to lowering salinity from high (c) to low (d), may be more significant.

Our experimental data implies that using smooth or highly polished surfaces for contact angle measurements likely overestimates wettability alteration at in-situ pore surfaces in the presence of low salinity brine. Therefore, we argue that, to achieve a representative wettability at pore-scale in high salinity brine, surface roughness needs to be considered. However, low salinity brine significantly compromises the surface roughness effect due to a thicker water film caused by the increase of electrical double layer forces [50, 113]. Our argument is also supported by the contact angle measurements reported by Vijapurapu et al. [191] who showed that the impact of surface roughness on contact angle variation at low salinity brine (9200 ppm) becomes minor on calcite substrates. The authors reported that the contact angle decreases by only $10°$ despite considerable increase in surface roughness from 1.17 to 5.46 µm.

### 6.4.3 Comparison with Wenzel's Equation

To better understand the relative impact of surface roughness on contact angle, thus wettability in oil-brine-rock system, we calculated contact angles as predicted by Wenzel's equation for a range of roughness factors (r). Figure 6-6 shows that the correlation between surface roughness and contact angles in our oil-brine-rock system contradicts the prediction made by Wenzel's equation [187]. Published works also show this contradiction, although no interpretation is provided to explain this observation [185, 189, 201]. To understand the cause of this contradiction which will likely provide new insights into wettability alteration in oil-brine-rock system, we further examined the Wenzel's equation considering fluid-fluid-rock interactions.
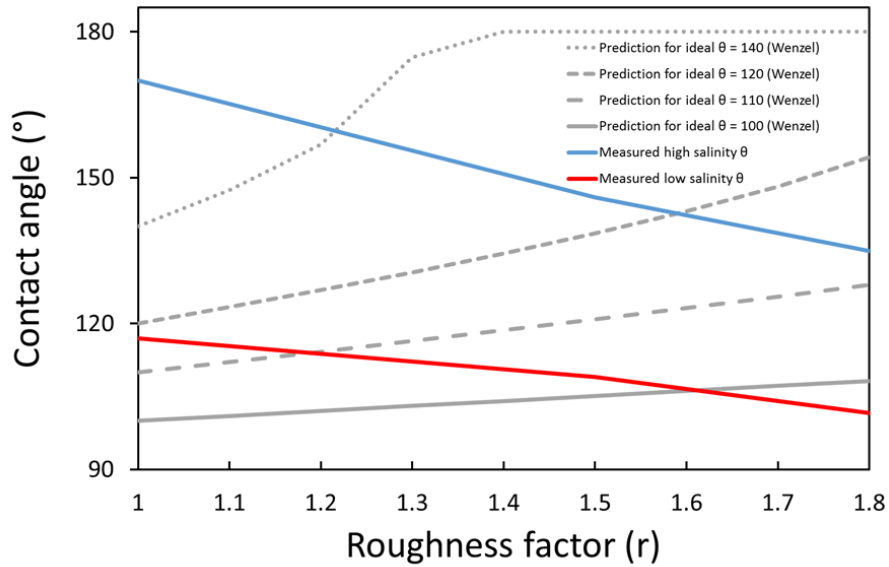
Figure 6-6. A comparison between the experimental contact angles measured in our work and the predicted contact angles calculated using Wenzel's equation over the same range of roughness factors.The predicted contact angles based on Wenzel's equation clearly show an opposite trend to that seen in our measured contact angles. This may suggest that the correlation between surface roughness and wettability in an oil-brine-rock system is different to that in gas-brine-rock system, meaning that Wenzel's equation does not hold for oil-brine-rock system.

On the basis of Wenzel's equation, the hydrophobicity of hydrophobic surfaces and the hydrophilicity of hydrophilic surfaces will increase with surface roughness [188, 189]. Theoretically, Wenzel's theory describes the wetting principle for air-water-solid system where interfacial boundaries are solid-liquid, solid-air and liquid-air. Also, the liquid phase (droplet) is in direct contact with the solid phase (i.e. rock). In such a system, changes in the specific surface energy content of each interface yields a change in the system wettability. Therefore, the wetting process involves the replacement of an area of solid-gas interface by solid-liquid interface of an equal area, while de-wetting is the reverse process. In a gas-brine-solid system where the surface is rough, there is a greater net energy loss (a larger surface area constitutes more energy) to induce spreading of the liquid phase. Thus, the rough surface is wetted more rapidly than a smooth surface [188].

However, the fundamental difference between the gas-brine-solid system described by Wenzel and oil-water-rock system is the presence of a thin water film (1-100 nm)

that exists between the crude oil and the reservoir rock surface [48, 49, 198, 202-206], which as mentioned before is thicker on rough surfaces due to pore rugosity [200]. SEM imaging show that pore surfaces of reservoir rocks are rough and densely populated with surface asperities [151, 157, 207-209]. Although the interactions between pore surfaces and the polar compounds in crude oil govern wettability characteristics, nevertheless, these interactions do not occur uniformly across the entire rock surface. In fact, a majority of oil/mineral interactions take place at the tips of these asperities where a smaller number of water layers are retained [157]. In principle, the limitation on oil/rock interaction sites imposed by water film may impede oil adsorption and reduce the contact angle on rough surfaces, (Figure 6-7.b). In contrast, smooth surfaces have more regular geometry and contain significantly less asperities [189] as illustrated in Figure 6-7.a. Thus, less water is retained on the surface which facilitate more sites for adsorption of oil's polar species on the surface.
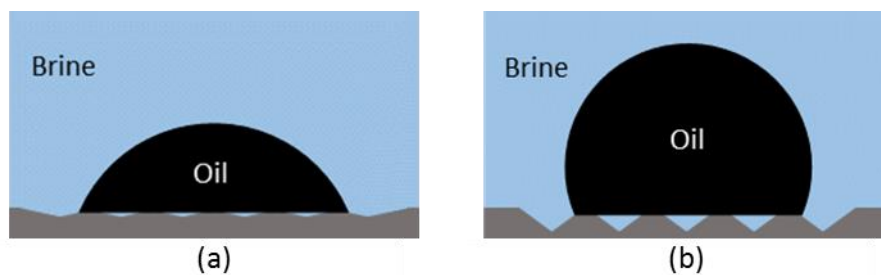


Figure 6-7. Illustration of variation in the thickness of water film on different surfaces. Smooth surface (a) has substantially less asperities which results in an overall thinner water film.Consequently, more contact area is involved in oil/rock interaction, thus, larger contact angle is observed (hydrophobicity enhancement). Conversely, on a rough surface (b) where water film is generally thicker, oil/rock interactions mostly occur at the tips of asperities which limits the available sites for oil/brine interactions, resulting in a smaller contact angle.

Our experimental results in combination with studies made by AlRatrout et al. [62] and Vijapurapu et al. [191] provide evidence against the assumption drawn from Wenzel's equation that in oil-brine-rock system, the hydrophobicity of hydrophobic surfaces is enhanced with increasing surface roughness. Moreover, the contact angle results presented by Vijapurapu et al. [191] also demonstrate that hydrophilicity in oil-brine-rock system increases with increasing surface roughness regardless of the wettability preference of a surface. Moreover, the surface roughness also gives rise to local surface

curvature, inducing capillaries, which may be absent on a smooth surface [206, 210]. Such capillaries may trigger capillary effect when two immiscible fluids are involved, thus affecting contact angles in oil-brine-rock system which may require further investigation.

## 6.5 IMPLICATIONS AND CONCLUSIONS

In this work, we measured contact angle of an oil on calcite substrates with a range of surface roughness (from 17 to 943 nm) in the presence of high and low salinity brines (1.0 and 0.01 mol/L) at pH = 10. We also compared our experimental contact angle results with contact angles predicted by Wenzel's equation. Our results show that contact angle consistently decreased (becomes less oil-wet) with increasing surface roughness regardless of the salinity level. However, the effect of surface roughness on contact angle becomes subtle with decreasing salinity. Our results suggest that while contact angles measured on smooth surfaces may indicate a significant wettability alteration in low salinity water, the actual extent of wettability alteration at pore-level would be subtle due to pore surface roughness which is mostly above 0.1 μm [192]. The variation in pore surface roughness depends on the type of minerals and shape of grains that form the surface of pores [211]. For example, the presence of clay as well as mineral overgrowth on rock's grains can cause sever roughness in pore and throat surface. This may explain the underwhelming incremental oil recovery from core flooding experiments during low salinity waterflooding despite contact angle results showing significant wettability alteration. For example, core flooding experiments on carbonate rocks reported by Alameri et al. [60] show an incremental oil recovery of only 5-7 %. However, the study reported contact angle decrease of up to 37°, suggesting a shift from strongly oil-wet to intermediate-wet condition which is considered to be the most favourable wetting condition for oil recovery [60, 127].

We compared our experimental results with contact angles predicted by Wenzel's equation and found that for oil-brine-rock system, the correlation between surface roughness and contact angle contradicts the prediction made by Wenzel's equation. We believe that this is largely due to the physiochemical reactions in oil-brine-rock systems which have been examined using disjoining pressure isotherm [180] and surface complexation modelling [12, 113, 128, 140, 141, 154, 179]. Therefore, we argue that to predict contact angle behaviour with surface roughness in oil-brine-rock system, surface forces governing oil-brine-rock interaction should be incorporated into

Wenzel's Equation. While smooth surfaces can be used for contact angle measurements to examine controlling factors which determines oil-brine-rock wetting characteristics, our work shows that we may overestimate the degree of wettability alteration at pore surfaces.

# Chapter 7 Carbonated Waterflooding in Carbonate Reservoirs: Experimental Evaluation and Geochemical Interpretation

## 7.1 Abstract

Carbonated water flooding (CWF) appears to be an important means in enhanced oil recovery (EOR) in carbonate reservoirs. While a few CWF coreflooding experiments have been done to reveal the controlling factor(s) behind incremental oil recovery, few has examined the impact of calcite dissolution on the contribution of the proposed mechanisms, and fewer have looked beyond the impact of calcite dissolution on different length scale (from core to reservoir). We thus conducted a series of core flooding experiments to investigate the residual oil saturation and recovery factor during waterflooding with and without carbonation. We also imaged the core plugs using a computed tomography scanner to examine the evolution of calcite dissolution along the core plug. Furthermore, we performed 1D reactive transport modelling at core- and reservoir-length-scale to delineate the impact of calcite dissolution process during carbonated waterflooding.

Coreflooding experiments confirm that lowering salinity increases oil recovery from 53% to 64.5% without carbonation. However, low salinity carbonated water at secondary mode yielded 47.6% and 52% oil recovery, between 1-5.4 % less recovery compared to formation brine flooding without carbonation, lower than the formation brine flooding without carbonation. Carbonated waterflooding also resulted in a significantly increases of permeability. CT images clearly show the generation of wormholes along the core, accounting for the low recovery and increased rock permeability. 1D reaction transport modelling at core-scale reveals the calcite dissolution taking place throughout the core plugs, supporting the wormholes evolution from CT images. One-dimensional reactive transport modelling at reservoir-scale shows the calcite dissolution distance from wellbore increases from 13 to 45m with increasing flow rate from 0.05 to 1m/day. Taken together, our results imply that calcite dissolution may deteriorate heterogeneity of reservoirs particularly near the wellbore. This may significantly undermine the contribution of oil-swelling, viscosity reduction, IFT reduction and wettability alteration on incremental oil recovery, as well as wellbore stability.

However, the negative impact of calcite dissolution may not prevail at in-depth of reservoirs because the calcite dissolution would reach equilibrium at a certain distance, which is also associated with injection rates.

## 7.2 Introduction

Carbonate reservoirs host most of the global oil reserve, yet they yield < 40% oil recovery Downs et al. [212] due to their strong oil-wet characteristics in nature [213, 214]. Wettability of oil-brine-carbonate systems is a key petrophysical parameter, which regulates the relative permeabilities, residual oil saturation thereby oil recovery. In this context, finding practical, yet feasible solutions to alter carbonate wettability towards more water-wet has been the perceived the centre point of shifting relative permeability whilst reducing the residual oil saturations.

Published works have demonstrated that lowering salinity or engineering injected water chemistry would disturb in-situ geochemical equilibrium between oil and carbonate pore surfaces. This physicochemical process would enable oil film lifting off from pore surfaces and thus yield incremental oil recovery. Although the mechanism(s) of wettability alteration remains incomplete, brine pH is shown to play a key role in regulating wettability of oil-brine-carbonate system particularly at low pH (pH < 7). For examples, surface complexation modelling supported by contact angle measurements confirm carbonate rocks become strongly hydrophilic in acidic brines regardless of brine salinity and ion types [190]. Similar results were also reported for carbonated brine, showing that $CO_2$ uptake by water (i.e., carbonation) increases hydrophilicity of oil-brine-carbonate system [215]. Chen et al. [216] reported that acidic and carbonated brines give a strongly water-wet system (oil-brine-carbonate) from contact angle measurements. Their surface complexation modelling shows that for both carbonated and acidic water, $>CaOH_2^+$ dominates surface charges at calcite surface, while $-NH^+$ governs surface charges on oil surfaces. The combination of these two processes increase the repulsive forces and thus increases the hydrophilicity of carbonate rocks. Xie et al. [154] also investigated the impact of pH on oil-brine-carbonate interactions using contact angle and surface complexation modelling. The results show that pH is one of the controlling factors to govern wettability, whereas salinity, ionic strength and ion type play a minor role in wettability alteration at low pH. This study suggests that $CO_2$-assisted Enhanced Oil Recovery, such as $CO_2$ flooding, carbonated water flooding and $CO_2$ huff-and-puff EOR likely render a strongly water-wet system due to $H^+$

adsorption on the interface of oil-brine and brine-carbonate as a result of $CO_2$ dissolution. The findings of these studies boast a promising outlook for the application of acidic and carbonated water flooding for oil recovery improvement in carbonate reservoirs.

Published works also show that carbonate waterflooding leads to wettability alteration (fluid-fluid-rock interactions) towards a lower residual oil saturation, which leads to an incremental oil recovery [217-221]. For example, spontaneous imbibition tests by Ruidiaz et al. [222] on limestone and dolomite rocks show significant improvement in oil recovery by carbonated water. Further quantitative assessment by the Amott-Harvey index indicates wettability alteration from oil-wet to neutral-wet due to carbonated water. It is worth noting that apart from the wettability alteration process, published works also reveal that carbonated waterflooding would trigger oil-swelling [221, 223-229], viscosity reduction [218, 221, 223-229] and interfacial reduction (fluid-fluid interactions), which play an important role in incremental oil recovery.

However, the EOR potential of carbonated water flooding in carbonate reservoirs remains in doubt. This is largely due to highly reactive nature of carbonate rocks which makes them susceptible to dissolution in acidic conditions. The calcite dissolution process during carbonated water flooding may result in an increase of heterogeneity and in extreme cases may compromise wellbore stability and reservoir integrity. For example, Khather et al. [230] studied the change in petrophysical properties of dolostone following the process of carbonated water flooding. Their results reveal that carbonated water significantly increases the permeability and creates wormholes in core samples. In a later study, Khather et al. [231] also showed significant dissolution and establishment of preferential flow paths through initially larger pores, eventually leading to formation of wormholes along the length of limestone core samples. Nevertheless, the effect of calcite dissolution on oil recovery was not examined in these two studies. Sanaei et al., [232] indeed examined potential of carbonated waterflooding by performing a mechanistic modelling coupled with UTCOMP and IPhreeqc. They conclude that calcite dissolution during carbonated waterflooding leads to wormholes generation rather than wettability alteration, although the effect of calcite dissolution on incremental oil recovery was not investigated.

Collectively, while published work show that wettability alteration (fluid-fluid-rock interactions) and fluid-fluid interactions [221, 223-229] contribute to incremental oil recovery during carbonated waterflooding in carbonate reservoirs, the effect of fluid-

rock interactions, which leads to calcite dissolution, on the contributing mechanisms has received little attention. The lack of research and understanding poses a serious challenge to managing the risks and predicting the outcome of carbonated waterflooding in carbonate reservoirs. Moreover, the existing accounts fail to resolve the contradiction between wettability alteration and calcite dissolution at different length scales (i.e., core and reservoir-scale). We thus hypothesized that calcite dissolution likely significantly undermines the impact of wettability alteration and other contributing mechanisms on oil recovery. To test this hypothesis, a combination of Coreflooding experiments, CT imaging and 1D reactive transport modellings at core and reservoir scale were performed.

## 7.3 Experimental Materials and Procedure

### 7.3.1 Oil

The oil used in this work was sourced from West Texas. The acid and base number of this oil was measured to be 1.7 and 1.2 mg KOH/g respectively. Gas chromatograph mass spectrometer (GC-MS) was used to examine the oil properties, showing that the oil was comprised of naphthenes (26.3 wt %), wax (3.8 wt %) and sulphur (3.9 wt %) with density of 0.89 g/cm$^3$ at 20 °C.

### 7.3.2 Rocks

To examine the effect of calcite dissolution and wettability alteration on carbonated waterflooding performance, we conducted three core flooding experiments on Indiana limestone core plugs. The X-ray diffraction test (XRD) shows that the rocks were primarily composed of 99.4% calcite, with minor traces of quartz (0.4%) and ankerite (0.2%), yet no detected anhydrite ($CaSO_4$) in rock samples. To minimize the effect of heterogeneity of rock samples on carbonated waterflooding performance, rock plugs with similar permeabilities and porosity were selected for the coreflooding experiments. The physical properties of rocks are listed in Table 7-1.

Table 7-1. Petrophysical properties of carbonate core samples used in this study.

| Sample ID | D (mm) | L (mm) | K (mD) | $\phi$ (%) | PV (mL) |
|-----------|--------|--------|--------|------------|---------|
| LS1 | 37.8 | 76 | 202 | 17.6 | 15.0 |
| LS2 | 37.8 | 76 | 243 | 17.6 | 15.0 |
| LS3 | 37.8 | 76 | 217 | 17.0 | 14.5 |

### 7.3.3 Preparation of Non-carbonated Brine

The non-carbonated brines used in this study ranged in salinity and pH. The high salinity formation brine (FB) is composed of (NaCl = 3.0 M, $CaCl_2$ = 0.03 M), with pH = 8. Given that the one of the aims of this study is to understand if the wettability alteration mechanism, which has been characterized using geochemical models [128, 141, 154], can be up-scaled to core-scale, accounting for oil detachment, coalescence and transport in porous media, we used low salinity brine to obtain the carbonated water. This is because low salinity carbonated brine favours hydrophilicity [139-141] due to a synergistic effect of low salinity water and higher dissolution of $CO_2$ [140, 141]. The low salinity brine was prepared by diluting the high salinity brine 100 times (100dFB) using de-ionized water, while maintaining the pH at 8, consistent with the pH of high salinity brine. To verify the impact of pH on wettability alteration and oil recovery, we also conducted acidic water flooding. The pH of low salinity brine was reduced to 3 using HCl and NaOH buffer solutions to be comparable with pH of carbonated brine.

### 7.3.4 Preparation of Carbonated Brine

The low salinity carbonated brine was prepared by saturating the low salinity brine with high purity $CO_2$ (99.99 wt%) using a high pressure-high temperature Parr reactor at ambient temperature. Since the saturation process was carried out at ambient temperature, we used the Chang's $CO_2$ solubility correlation [233] to calculate the required pressure that yields GWR - Gas/Water Ratio - identical to that encountered in experimental conditions of 2000 psi and 70 °C. Low salinity experimental brine was first transferred into a reactor using a syringe pump. The $CO_2$ gas was introduced into the reactor with the aid of a compressor to speed up the process. The mixing process commenced while $CO_2$ was continuously fed into the reactor. This process continued

until the equilibrium pressure was reached. The carbonated brine was then transferred into an accumulator and stored at a pressure above the saturation pressure (2500 psi) as a precautionary measure. The pH of carbonated brine in our experimental pressure and temperature condition was calculated to be 3.5 using PHREEQC geochemical software.

## 7.3.5 Core flooding experiments

The core flooding experiments were performed in line with the stablished core flooding protocol in the literature [234]. The schematic diagram of the Coreflooding system is given in work published by Saeedi et al. [235] ( *in Figure 1*). The Coreflooding system includes a high temperature/temperature core holder with internal heater, a pair of Keller transducers, a dome type back pressure regulator (BPR) with $N_2$ cylinder for pressure support, and two accumulators for oil and carbonated brine injection respectively. Firstly, the core samples were wrapped with a layer of Teflon tape followed by a layer of aluminium foil, then encased in a heat-shrink Viton® tube to prevent $CO_2$ percolation. Samples were then mounted into the core holder with a confining pressure (3000 psi). The system was then heated to 70 °C, whilst maintaining the confining pressure via a syringe pump. The samples were then vacuumed for 24 hours and flooded with the high salinity formation brine to measure the absolute permeability of rocks to brine at various flowrates (1.0-5.0 cc/min). To establish initial oil saturation, crude oil was injected at multi-flowrate steps (1.0-3.0 cc/min), and the produced brine was carefully collected to determine fluids saturation. The system was then closed and aged for 48 hours. The oil recovery stage began by injecting several pore volumes (5-10 PV) at a flowrate (1.0 cc/min) until negligible oil was recovered (i.e., water cut up to 99.9%). To overcome the end effect, the flowrate was increased to 3.0 and 5.0 cc/min from 1.0 cc/min (initial flow rate) for approximately 5-10 PV. To capture the evolution of calcite dissolution during carbonated waterflooding, core plugs were imaged using a medical CT scanner (Siemens SOMATOM Definition AS) before and after carbonated waterflooding. ImageJ software was used to process the CT images and construct 2D models to visualise the evolution of dissolution fronts over the course of the core flooding experiments.

## 7.3.6 One-Dimension Reactive Transport Modelling at Core and Reservoir Scale

To evaluate the calcite dissolution at different length scale, we did 1D reactive transport modelling using PHREEQC. To mimic the core flooding and waterflooding conditions, the input parameters were consistent with the physical Coreflooding experiment with respect to the length, connate brine and injected brine compositions. To be more specific, in the reactive transport model, the flooding domain is initially saturated with formation brine; then carbonated brine (the reactions can be referred to Chen et al. [236] *in Table 5* and literature therein) was injected to formation brine occupied domain. Moreover, in order to access the dissolution kinetics, the reactive transport modelling was coupled with calcite dissolution kinetics reported by Plummer et al. [237].

To simulate the physical Coreflooding experiments, we employed a column with 100 cells. Each of the cell is 7.6×10-4 m, sum of which is equal to the total length of the core (76 mm). The time step for each shift (time to flow in one cell) of TRANSPORT in PHREEQC is set to 1×10-4 day, which corresponds to injection velocity of 7.6 m/d (estimated by injection rate of 1 cc/min and porosity of 17%). For carbonated coreflooding, we injected carbonated water 100 shifts and plotted the pH and saturation index (SI, SI $= \frac{IAP}{K}$ , where IAP is ion activity product and K is equilibrium constant.) profile against flow distance.

To examine the calcite dissolution process at reservoir scale, the same method was applied, but the flow column was set to be 200m, which was divided into 100 cells with a length of 2m per cell. Furthermore, given that water injection rate likely affects the calcite dissolution process at a given location, three velocities were used (0.05, 0.27 and 1 m/day) which proximately simulates the flow rates near, and far from the wellbore. According to Pang et al. [238], we approximate the injection velocity to be 1 m/day at distance of 10 m, and 0.27 m/day at distance of 20m from the wellbore. Therefore, the shift time is set to 2 days and 3.7 days in PHREEQC to simulate the above two flow velocities. Moreover, to confirm calcite dissolution at extreme slow injection condition for example at a location far from wellbore (>100m), we calculated the calcite dissolution at injection velocity of 0.05 m/day.

## 7.4 Results and Discussion

### 7.4.1 Confirmation of Low Salinity Effect at Tertiary Mode

Lowering the brine salinity from FB to 100dFB increases oil recovery from 53% to 64.5% of OOIP at tertiary mode, confirming the low salinity effect in carbonate rocks, Figure 7-1. The incremental oil recovery was observed after 1.5 PV of low salinity brine injection, implying that wettability alteration in carbonate rocks is time-dependant as a result of geochemical reactions. During formation brine flooding, increasing flow rate increases oil recovery due to the capillary end effect at the high permeability rock (>200mD). Similar trend was also observed during the low salinity waterflooding at tertiary mode, implying the wettability alteration towards more water-wet. Moreover, the pressure drop was higher during high salinity water flooding and decreased considerably when flooding was switched to low salinity brine. This is due to i) $S_o$ was higher during high salinity water flooding, and ii) viscosity of high salinity brine is slightly higher compared to low salinity water. The pH of effluent low salinity brine was also higher compared to pH of effluent high salinity brine largely due to the calcite dissolution, Figure 7-2. This geochemical process (i.e., calcite dissolution and pH increase) would significantly decrease the concentration of $-NH^+$ at oil surface species, and thus decreases adhesion between $-NH^+$ and $>CO_3^-$ at calcite surfaces [12, 128, 141]. Consequently, a more water-wet system would be generated, accounting for the incremental oil recovery in line with literatures [9, 26, 31, 87, 88, 165]. It is worth noting that the results of acidic water flooding and carbonated water flooding would be discussed in the following sections.
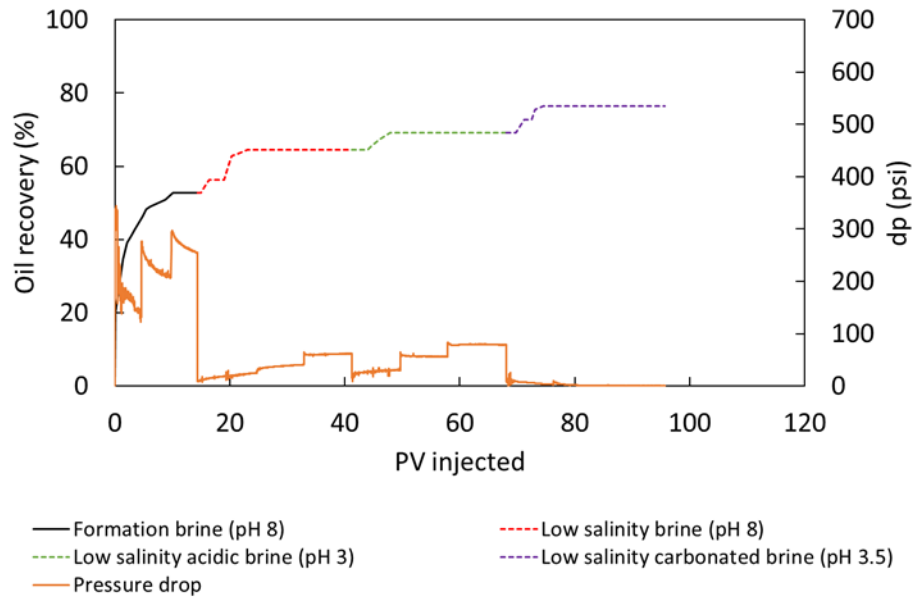
Figure 7-1. Oil recovery results from various brines for core LS1. Oil recovery increases with decreasing brine salinity and pH. For carbonated brine injection, oil recovery plateaus after approximately 5 PV of brine injection and corresponds to significant drop in differential pressure, which is likely caused by the development of wormholes in the core.
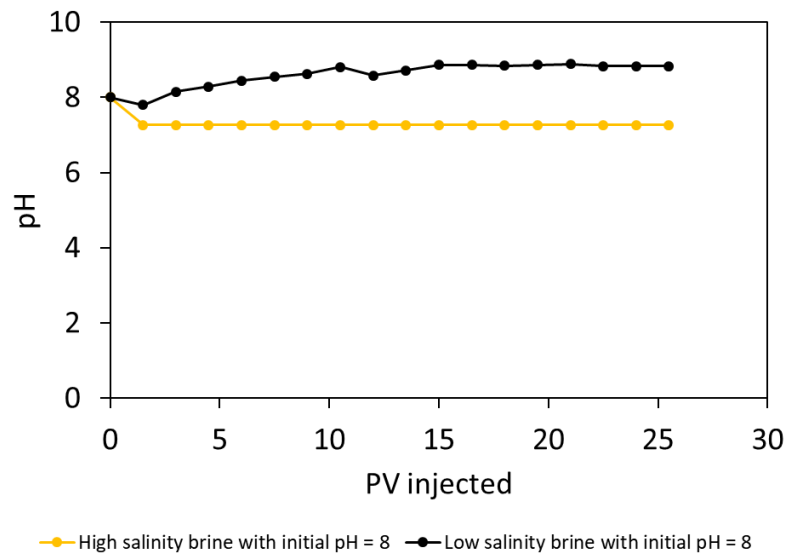


Figure 7-2. Variation in the pH of effluent high salinity brine and low salinity brine during water flooding process.

## 7.4.2 Acidic Waterflooding and carbonated waterflooding at Tertiary Mode

To test if the wettability alteration achieved by acidic water at sub-pore scale through contact angle measurements can be up-scaled at core scale, acidic water was injected into the core plug after low salinity waterflooding. Our results show that decreasing pH of injected brine increases oil recovery 5% of OOIP at tertiary mode, Figure 7-1. However, the pH increases sharply during the acidic waterflooding and reaches 8 after 1 PV injection mainly due to the calcite dissolution process, Figure 7-3. The coreflooding experiment also confirms that acidic water cannot maintain the pH at the low level as a result of calcite dissolution in carbonate, suggesting that acidic waterflooding in carbonate reservoir should not be practical although wettability alteration can take place at sub-pore scale as verified by contact angle measurements [128, 140, 154]. We tentatively believe that the incremental oil recovery is due to the increase of calcium as a result of calcite dissolution, which likely decreases adhesion between oil and calcite due to the repulsion between –COOCa+, and >CO3Ca+ [12, 128, 141, 154]. Nevertheless, the differential pressure across the sample did not decrease, suggesting the dissolution is likely limited to core inlet region.



Figure 7-3. Variation in the pH of effluent low salinity acidic brine and low salinity carbonated brine during water flooding process.

Low salinity carbonated water improved oil recovery by 7% when implemented in tertiary mode after acidic waterflooding as shown in Figure 7-1. However, the incremental oil recovery was observed after injecting 3.0 PV of carbonated brine, suggesting that EOR-effect offered by carbonated waterflooding is time-dependent. This is largely because that the mechanisms of carbonated water 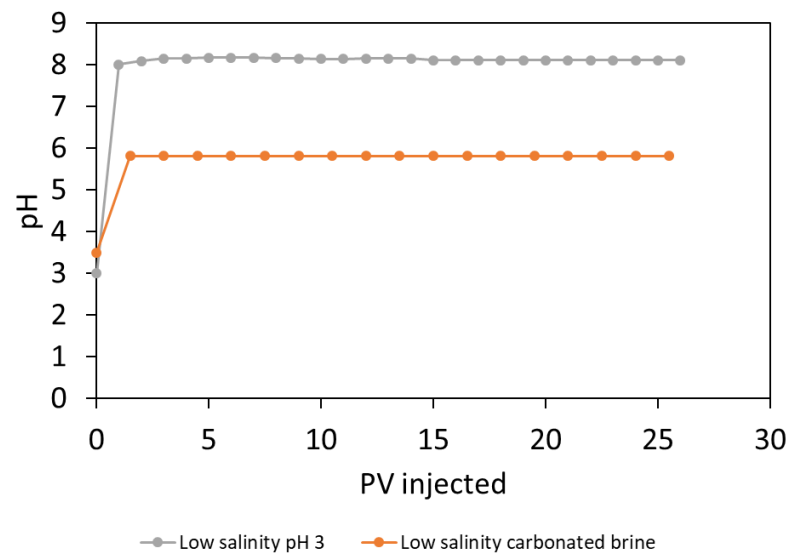flooding such as oil swelling [221, 223-229], coalescence of the trapped oil ganglia [223, 224], oil viscosity reduction [218, 221, 223-229] and wettability alteration [217-221] need time to process. Figure 7-1 also shows that carbonated waterflooding leads to a sharp decrease of pressure drop even before a noticeable recovery factor increase, implying a severe calcite dissolution throughout the core plug during carbonated water flooding. Comparing to acidic water flooding, carbonated water likely carries hydrogen along the core to allow calcite dissolution taking place far from the inlet. This is largely because the rate of dissolution of calcite in carbonated water is essentially governed by the kinetics of surface reaction [239], which is also supported by pH profile of carbonated water flooding, showing that pH reaches only 6 compared to 8 as was the case in acidic water flooding, Figure 7-3. It is worth noting that the pH during carbonated water flooding was measured at atmosphere condition, which gave less dissolved $CO_2$ in the effluent thereby a slightly higher pH. However, we have performed geochemical modelling to examine the in-situ pH level, which would be discussed later.

### 7.4.3 Carbonated Waterflooding at Secondary Mode

Carbonated waterflooding at secondary mode in samples LS2 yielded oil recovery of 47.6% which is 5.4% less than the secondary high salinity waterflooding without carbonation, Figure 7-4a. Also, carbonated water flooding led to a significant pressure drop, almost reaching 5 psi after 10 PV injection. Similarly, for sample LS3, carbonated water yielded 52% of OOIP oil recovery, 1% less than formation brine flooding with significant pressure drop even after water breakthrough, Figure 7-4b. We also report significant increase in rocks permeability following carbonated water injection, Table 7-2. Our results are inconsistent with other published works which show roughly 10 to 20% increase in oil recovery following carbonated waterflooding in secondary mode. For example, Bakhshi et al. [229] used 4 wt.% carbonated and non-carbonated brines in secondary mode floodings and reported 13.6% increase in oil recovery in favour of carbonated brine. Similarly, Shakiba et al. [240] also reported higher oil recovery for low salinity carbonated brine (57.2%) compared to low salinity non-carbonated brine (31.7%) at secondary mode. The followings are the possible reasons to account for the inconsistency.

90

1. Heterogeneity of carbonate rocks may favour the formation of wormholes during carbonated waterflooding. We suspect that the high permeability carbonate rocks selected for our Coreflooding experiments exhibit stronger heterogeneity compared to the low permeability rocks which were used in the other studies. In this context, calcite dissolution would be more severe in the high permeability zones of the rock and thus promotes wormholes formation. This is also supported by our CT imaging, which would be discussed in the following section.

2. Increasing injection rate promotes calcite dissolution process in porous media. The injection rate in our experiments was 1.0-5.0 cc/min, which was designed to overcome end effect in high permeability carbonate rocks. The high injection rate would increase the rate of calcite dissolution. This is also supported by 1D reactive transport modelling which will be discussed in the section. However, Bakhshi et al., [229] and Shakiba et al., [240] conducted coreflooding experiments at 0.2 cc/min using rock samples with permeabilities of 0.9 and 11 mD respectively. Moreover, carbonated water flooding in the aforementioned references continued for 5 < PV which may have been insufficient to trigger large scale dissolution in low permeability rocks.

Table 7-2. Comparison between the petrophysical properties of core samples before and after carbonated water flooding.

| Sample ID | Pre-carbonated water flooding | | | Post-carbonated water flooding | | |
| --- | --- | --- | --- | --- | --- | --- |
| | K (mD) | $\phi$ (%) | PV (mL) | K (mD) | $\phi$ (%) | PV (mL) |
| LS1 | 202 | 17.6 | 15 | 636 | 18.1 | 15.4 |
| LS2 | 243 | 17.6 | 15 | 484 | 17.2 | 14.6 |
| LS3 | 217 | 17 | 14.5 | 657 | 17.9 | 15.3 |

a)
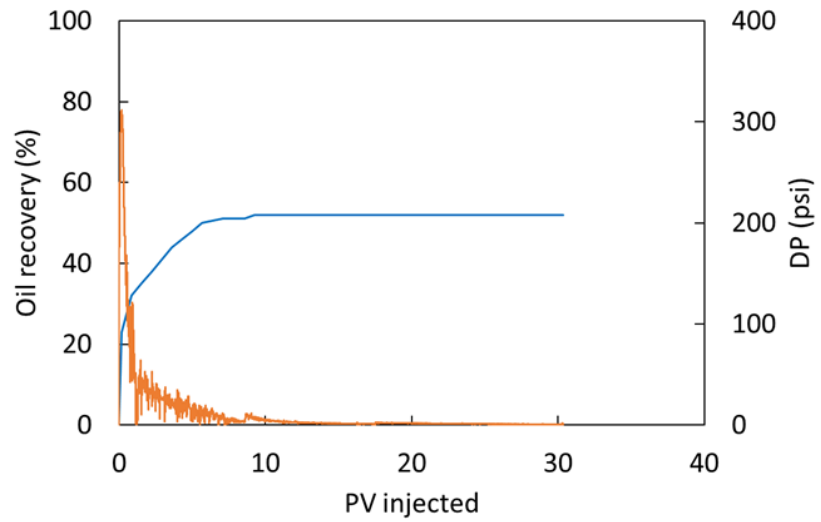
b)
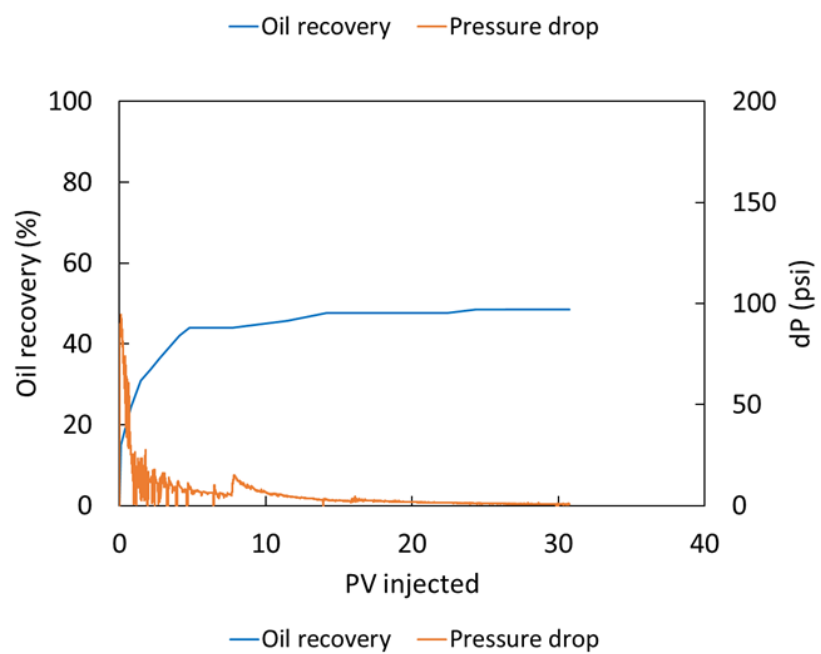
Figure 7-4. Oil recovery from low salinity carbonated brine vs differential pressure for samples a) LS2, and b) LS3 respectively. The differential pressure across both core plugs progressively decreases with the injection of carbonated brine.

### 7.4.4 Evolution of Calcite Dissolution at Core-Scale-Experimental from CT Images

To further interpret the results obtained from Coreflooding experiments, we scanned the core plugs before and after carbonated water flooding. Figure 7-5, Figure 7-7a and Figure 7-7c show that our carbonate core samples were heterogeneous and contained vugs which appear to be connected in some areas. Figure 7-6a and Figure 7-6b show sample LS1 after high salinity and low salinity water flooding respectively, neither of which caused visible petrophysical changes to the core sample confirming the negligible dissolution. Similarly, core sample remained unaltered after low salinity acidic brine flooding, Figure 7-6c. However, after carbonated water flooding, CT images indeed support the experimental observation, clearly showing the evolution of wormholes during carbonated waterflooding.

Figure 7-6d shows that several distinct dissolution layers or bands have been developed along the length of core sample LS1 following tertiary carbonated water flooding. Similar features are also observed in samples LS2 and LS3 following secondary carbonated water flooding, Figure 7-7. These so-called bands or wormholes appear to be more pronounced and localized close to the inlet and branch out into smaller fingers or channels further out. Calcite dissolution is slightly more pronounced closer to the injection point given fresh carbonated brine is under-saturated with $Ca^{2+}$ ions. As injection progresses, concentration of $Ca^{2+}$ ions in carbonated brine increases, diminishing the dissolution potential of carbonated brine.

Combination of several factors may contribute to the development of these features and the variation in the shape of the dissolution front: 1) permeability heterogeneity within the rock, 2) discrepancy in exposure level to reactive brine at different locations, 3) variation in the concentration of $Ca^{2+}$ ions in carbonated brine during the flooding process. For example, Ortoleva et al. [241] presented a numerical model which showed the instability of a planar dissolution front, and that the flow of reactive aqueous solution tend to spread through high permeability fingers through the rock. Moreover, experimental and simulation results also show that initial heterogeneity and porosity/permeability contrast play an important role in the development of dissolution fronts in rocks. A 3D continuum-scale reactive transport models using carbonated brines performed by Hao et al. [242] showed that wormholes tend to develop in areas of greater porosity and permeability contrast, and grow with increasing heterogeneity

in carbonate rocks. The band-like nature of dissolution observed in our work demonstrates the existence of several layers with contrasting permeabilities, and further support the notion that permeability heterogeneity is a key factor in the development of dissolution front, particularly in a reactive system such as carbonate. High permeability zones provide preferential flow paths for reactive brine which result an uneven distribution of flow, hence dissolution in the rock. Consequently, most of the injected carbonated brine is channelled into the high permeability flow paths, facilitating localized dissolution, while the low permeability zones are largely bypassed.
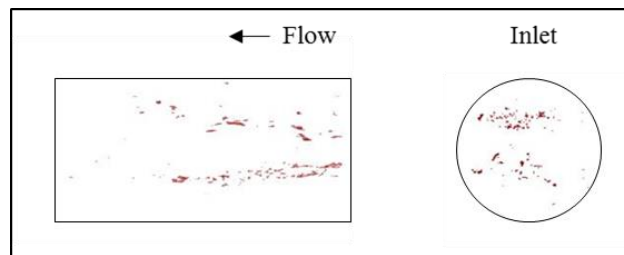


Figure 7-5. The processed CT image of sample LS1 before flooding process. The red colure represents macro-pore connectivity in the sample.
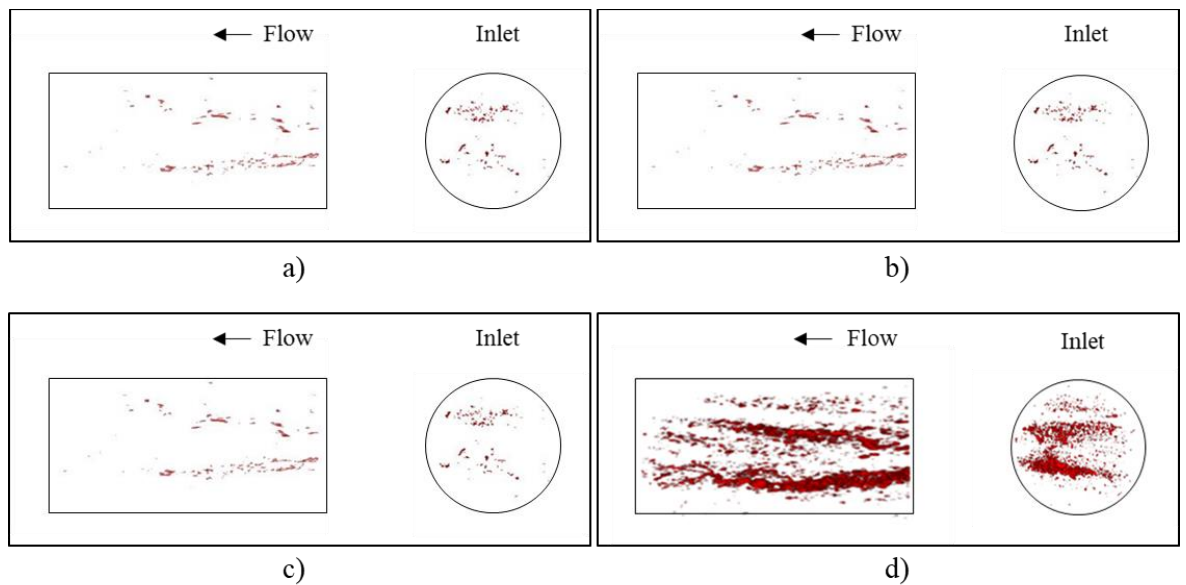


Figure 7-6. The evolution of dissolution fronts in sample LS1 after a) secondary high salinity water flooding, b) tertiary low salinity water flooding, c) tertiary low salinity acidic water flooding and d) tertiary carbonated water flooding.
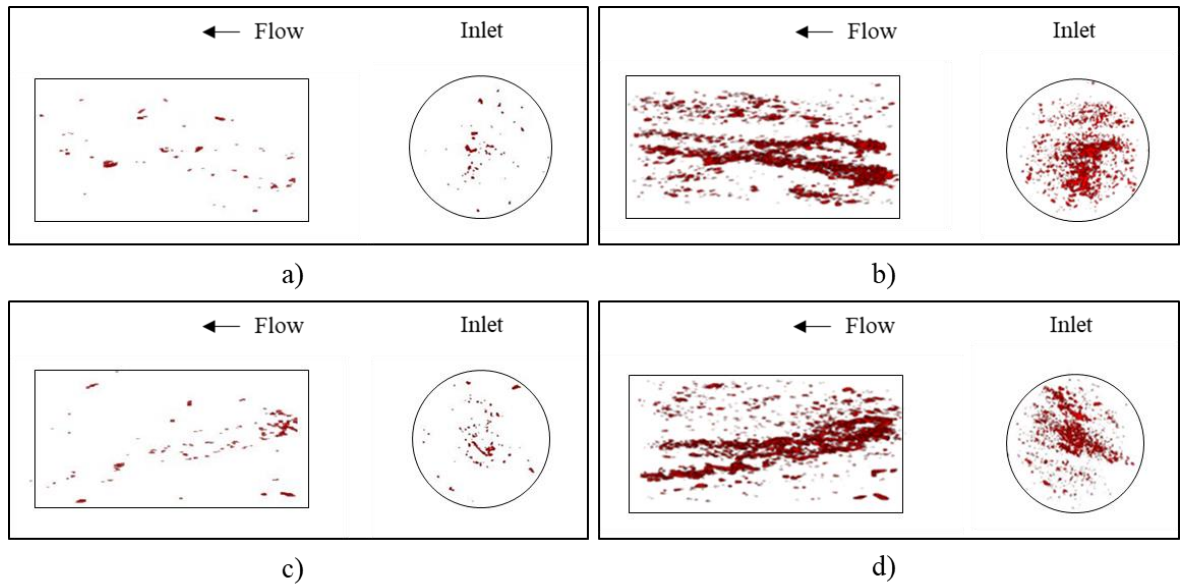
Figure 7-7. Image a) shows sample LS2 before and b) after carbonated water flooding. Image c) shows sample LS3 before and d) after carbonate water flooding.

### 7.4.5 One-Dimension Reactive Transport Modelling at Core Scale

Our 1D reactive transport simulation confirms that the calcite dissolution would take place throughout the core, which is supported by the low pH (from 2.94 to 2.96) and negative saturation index (from -3.86 to -3.83) as shown in Figure 7-8. The low pH and negative SI demonstrate that the calcite dissolution occur in the whole sample, supporting the coreflooding experiments and CT images (i.e., wormholes evolution). In addition, the negligible pH and SI increase can be explained by the high injection rate and a limited length of the core. The time to flow through the sample takes around 15 min at a flow rate of 1 cc/min. The limited contact time indicates the in-contact time would be not long enough to modify the brine composition. Moreover, we indeed modelled the pH and SI profile over the distance at low flow rate (0.05ml/min). Our results show an increase of pH and SI at the downstream of the core plug although negligible increase was observed at the inlet. Taken together, our results imply that high flow rate of carbonated water flooding likely promotes the calcite dissolution process, favouring wormholes evolution at core-scale. This also explains why we observed a severe evolution of wormholes during carbonated waterflooding, but the same experimental phenomenon was not observed by [229] and [240] because of the low flow rate (0.2/min) due to low permeability carbonate rocks (1 to 10 mD).
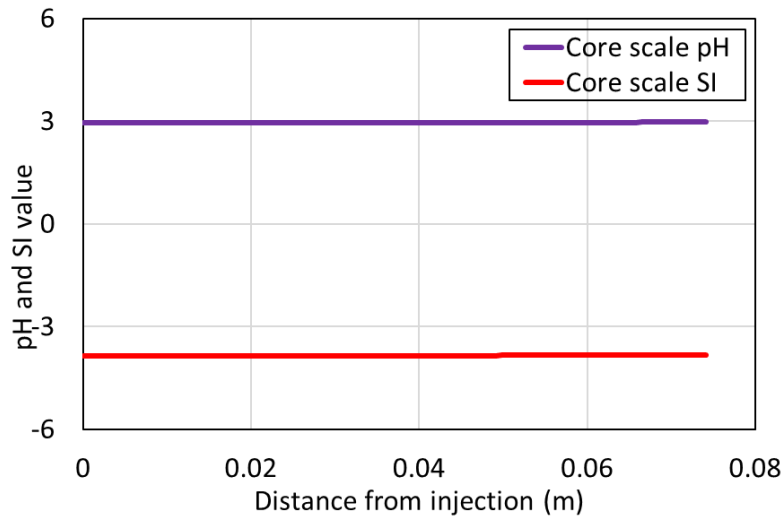
Figure 7-8. pH and SI profile for carbonated water flooding

### 7.4.6 One-Dimension Reactive Transport Modelling at Reservoir-Scale

Figure 7-9 shows pH and SI over the distance at reservoir scale during carbonated waterflooding as a function of injection rate. Results show that at high injection rate (1m/day), SI gradually increases with distance to almost 0 until reaching in 45 meters far from wellbore, implying that calcite dissolution process becomes negligible at 45 meters. This is also supported by the pH profile over distance, showing that pH-rise halts at 45 meters. However, decreasing flow rate indeed undermines the calcite dissolution process at reservoir scale. For example, decreasing flow rate from 1 to 0.27 m/day decreases the calcite dissolution distance from 45 to 20 meters, which is proved by the pH and SI profiles over the distance. Moreover, further decreasing the injection rate to 0.05m/day, the calcite dissolution process would cease at 13 meters from wellbore.

Our results reported here have important relevance to at least two classes of problems that are significant in carbonated waterflooding in carbonate reservoirs. (1) Carbonated waterflooding may play an adverse role in heterogeneity near the wellbore due to the generation of wormholes as a result of calcite dissolution. This may not only decrease the sweep efficiency near the wellbore, but also undermines the integrity of the wellbore, which depends on the degree of the calcite dissolution taking place at the wellbore. However, the calcites dissolution process would not prevail in-depth of the reservoir because the calcite dissolution equilibrium would be achieved along the injected water advancing front. We also believe that the calcite dissolution

process may significantly compromise the contribution of oil swelling, viscosity reduction and wettability alteration on incremental oil recovery during carbonated waterflooding near the wellbore. However, this negative impact due to the calcite dissolution would be minimized at in-depth of the reservoirs. (2) Calcite dissolution during carbonated waterflooding may become minor in low permeability carbonate reservoirs near the wellbore. This is because low injection rate may be applied in developing tight carbonate oil reservoirs. In this context, we expect less challenge in wormholes evolution and wellbore integrity near the wellbore in such reservoirs. Also, the negative impact of calcite dissolution on contributing mechanisms of incremental oil recovery (e.g., oil-swelling, viscosity reduction, wettability alteration, IFT reduction etc.) would be minimized.
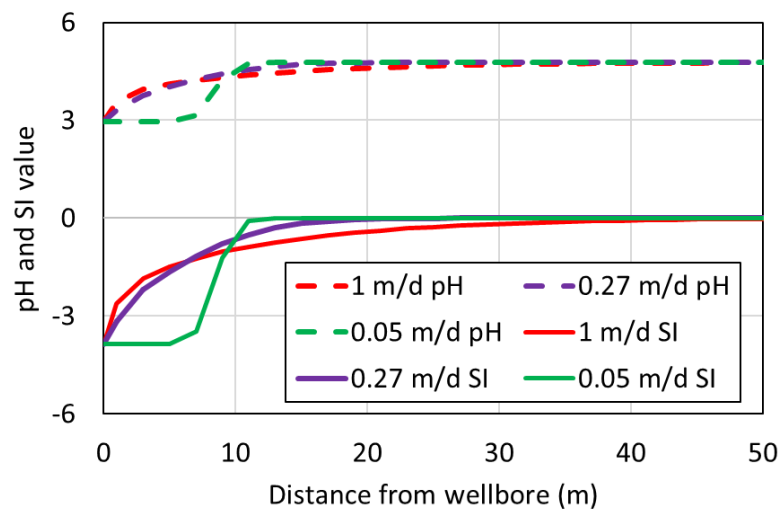


Figure 7-9. Calcite dissolution distance with different injection velocity.

## 7.5 Implications and Conclusions

Carbonated water flooding (CWF) has been perceived as an important means in enhanced oil recovery (EOR) in carbonate reservoirs. While a few mechanisms have been proposed to account for the incremental oil recovery, very few has examined the impact of calcite dissolution on the contribution of the proposed mechanisms (e.g., oil-swelling, viscosity reduction, wettability alteration, IFT reduction etc.), and fewer have looked beyond the calcite dissolution at different length scale, i.e., from core to reservoir scale. In this context, we conducted Coreflooding experiments, CT imaging and 1D reactive transport modelling using brines with and without carbonation. Our

results show that low salinity carbonated water at secondary mode gave only 47.6 and 52% oil recovery, between 1-5.4 % less recovery compare to formation brine flooding without carbonation, together with significant permeability increase. CT images clearly show the generation of wormholes which accounts for the low recovery and increased rock permeability. 1D reaction transport modelling at core scale reveals the calcite dissolution taking place throughout the core plugs, supporting the wormholes evolution from CT images. 1D reactive transporting at reservoir scale shows the distance of dissolve zone from wellbore increases from 13 to 45 meters with increasing flow rate from 0.05 to 1m/day. Taken together, our results imply that calcite dissolution may play an adverse role in heterogeneity of reservoirs, particularly near the wellbore. This may significantly undermine the contribution of oil-swelling, viscosity reduction, IFT reduction and wettability alteration on incremental oil recovery, and compromise wellbore stability. However, the negative impact of calcite dissolution may not prevail at in-depth of reservoirs because the calcite dissolution would reach in equilibrium at a certain place, which is also associated with injection rates.

# Chapter 8  Conclusions, Recommendations and Outlook for Future Work

## 8.1 Conclusions

Low salinity water flooding is emerging as an alternative EOR method due to its economic and environmental advantages compared to other techniques. While previous studies suggested wettability alteration is the main mechanism for low salinity effect in carbonate rocks, the underlying factors that control wettability alteration in carbonate reservoirs are poorly understood. The main objective of this research was to improve the existing understanding of low salinity phenomenon in carbonate reservoirs by investigating key areas that have been less explored. This research presents several key findings that impact our understanding of low salinity water flooding topic. The following points summarize the main conclusions of this work.

### 8.1.1 Drivers of Low Salinity Mechanism (Chapter 3)

- Presence of anhydrite proved to be unnecessary for triggering low salinity effect in carbonate rocks. Core flooding experiments conducted on anhydrite free carbonate samples using low salinity brine depleted in sulfate ions $SO_4^{2-}$, showed improvement in oil recovery between 5.8-18.1% OOIP. This indicates a lack of correlation between anhydrite dissolution and improved oil recovery.

- Low salinity effect in carbonate reservoirs is governed by zeta potential at the interfaces of oil-brine and brine-rock rather than the salinity level. Experimental results show that at low pH condition (6 <), the zeta potential at the interface of oil-brine is positive, particularly for basic crude oil, while the zeta potential at brine-rock becomes more negative with decreasing salinity. The zeta potential results were also consistent with contact angle measurements showing wettability alteration from strongly water-wet to intermediate-wet system with dilution of formation brine. Thus, it is concluded that electric double layer expansion is the likely mechanism of low salinity effect in carbonate reservoirs.

- A new parameter Zp which is the sum of the absolute value of zeta potential of oil-brine and brine-rock, Zp = │Zeta oil/brine + Zeta brine/rock│ is introduced. A strong correlation between Zp and contact angle is found in which

contact angle increases linearly with increase of Zp. it is suggested that Z parameter may be used as an interpolant to model the low salinity effect rather than using salinity level or ion types in the aqueous solution.

### 8.1.2 Effect of pH on Wettability (Chapter 4)

- Geochemical study demonstrate that pH is one of the controlling factors that govern the wettability of oil-brine-carbonate system. Low pH (pH < 5) usually exhibit a strongly water-wet system due to $H^+$ adsorption on the interface of oil-brine and brine-carbonate, while pH 6.5-7.5 likely triggers an oil-wet system which is favorable for low salinity water flooding.

- Contact angle measurements on calcite substrate with different aqueous solutions ($Na_2SO_4$ and $CaCl_2$) and pH (pH = 3 and 8) revealed calcite surface becomes more hydrophobic with increasing brine pH, in line with surface complexation modelling.

- Contact angle results show salinity, ionic strength, and ion type play a minor role in wettability alteration at low brine pH.

- Surface complexation modelling demonstrates contact angle increases with increasing bond product sum, implying that bond product sum can likely be used as a guideline to manipulate injection water chemistry for a given reservoir.

### 8.1.3 Low Salinity Effect in Acidic Reservoirs (Chapter 5)

- Contact angle measurements performed on calcite substrate at various salinities (1.0 and 0.01 M), ion types ($Na_2SO_4$ and $CaCl_2$), and pH (3 and 8) suggest at pH 8, salinity and ion type play significant role in shifting wettability from slightly oil-wet to strongly water-wet. In contrast, low salinity pH (pH 3) triggers a strongly water-wet system with minor effect from salinity, ion type, and temperature.

- Zeta potential experiments show that the electrostatic charges at oil-brine and brine-calcite interfaces becomes strongly negative with decreasing brine salinity, particularly for $Na_2SO_4$ at pH 8, further confirming the role of electrical double layer in wettability alteration of carbonate rocks.

- Surface complexation modelling suggests that the difference between electrostatic bridges – breakage of oil-calcite bonding that stems from lowering salinity – increases with acid number, implying a better potential of low salinity effect in high acidic oil-bearing carbonate reservoirs.

### 8.1.4 Effect of Surface Roughness on Wettability (Chapter 6)

- Contact angle measurements on carbonate show that in both high and low salinity brines, contact angles decrease with increasing surface roughness, suggesting a less hydrophobic system. Nevertheless, contact angle decreased slightly less in low salinity brine, suggesting that the effect of surface roughness on contact angle is more subtle under low salinity condition.

- The correlation between contact angle and surface roughness contradict the prediction by Wenzel's equation. This is largely because the surface forces that govern oil-brine-calcite interactions are not captured by Wenzel's equation.

- Smooth surfaces may be used to examine the controlling factors that determine oil-brine-rock characteristics. Nevertheless, in doing so, the degree of wettability alteration at pore surfaces may be overestimated due to pore surface roughness.

### 8.1.5 Carbonated Water Flooding (Chapter 7)

- Carbonated waterflooding may result in a significantly increases of permeability at high injection rate due to the generation of wormholes throughout core plugs.

- One-dimensional reactive transport modelling at reservoir-scale shows that calcite dissolution distance from wellbore increases from 13 to 45m with increasing flow rate from 0.05 to 1m/day.

- Calcite dissolution may deteriorate heterogeneity of reservoirs particularly near the wellbore. This may significantly undermine the contribution of oil-swelling, viscosity reduction, IFT reduction and wettability alteration on incremental oil recovery, as well as wellbore stability. However, the negative impact

of calcite dissolution may not prevail at in-depth of reservoirs because the calcite dissolution would reach equilibrium at a certain distance, which is also associated with injection rates.

## 8.2 Recommendation and outlook for future work

Wettability alteration triggered by low salinity water flooding appears to be driven by physiochemical variation occurring at the interfaces of oil-brine and brine-carbonate. Two major low salinity wettability alteration mechanisms were the focus of investigation in this thesis: 1. electric double layer expansion and 2. surface complexation at oil and calcite surfaces. Although the coupled experimental and surface complexation modelling works presented in this thesis suggest these two mechanisms drive wettability alteration at sub-pore scale, more work is required to verify if wettability alteration by the above-mentioned mechanisms can be replicated on pore-scale. It is recommended that future research take advantage of X-ray microtopography technique and the processing capability of various computer software to visualize the pore-scale arrangement of fluids and their evolution during various stages of low salinity water flooding process. This would help to upscale the understanding at molecular level to the pore- and core-scale thereby accounting for the oil detachment, coalescence, oil transport and banking at reservoir scale.

Another important aspect of low salinity EOR, which is not covered in this thesis, is to provide a quantitative procedure to minimize the uncertainty of low salinity waterflooding from lab-scale to reservoir-scale. To be more specific, low salinity waterflooding likely gives more additional oil recovery at secondary mode compared to the tertiary mode, although the key factor(s) behind this observation remains open for discussion. This observation imposes a significant stress on a quantitative procedure for the design of coreflooding experiments which is expected to minimize the intrinsic uncertainty of the timing for low salinity waterflooding.

Moreover, adequate and reliable low salinity EOR reservoir modelling studies with consideration of geochemical reactions at oil and calcite surfaces are currently lacking. This is another area of interest that is recommended to be the focus of future research. Overall, the work that was started in this thesis is far from complete and I strongly believe there is a tremendous potential for further research in low salinity EOR in carbonate reservoirs.

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# Appendices

The following page contains the tables of contribution illustrating the contribution of all co-authors, in addition to the copyright for all publications.

Paper title: "**Drivers of Low Salinity Effect in Carbonate Reservoirs**" Energy Fuels 2017, 31, 9, 8951-8958

Ahmad Sari [†‡*], Quan Xie [†‡*], Yongqiang Chen [†], A. Saeedi [†], Ehsan Pooryousefy [†]

[†] Department of Petroleum Engineering, Curtin University, GPO Box U1987, Australia, Perth, W.A. 6845

[‡]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

| Name | Conception & design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
|---|---|---|---|---|---|---|
| **Ahmad Sari** | X | X | X | X | X | |
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| **Yongqiang Chen** | | | | X | X | |
| Signature: | | | | | | |
| **Quan Xie** | | | X | X | X | X |
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| **Ali Saeedi** | | | | | | X |
| Signature: | | | | | | |
| **Ehsan Pooryousefy** | | | | | X | |
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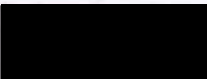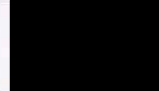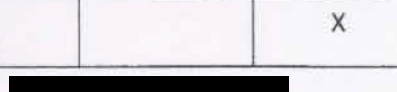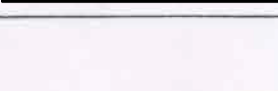
Quan Xie [a,*], Ahmad Sari [a], Wanfen Pu [b], Yongqiang Chen [a], Patrick V. Brady [c], Nasser Al Maskari [a], Ali Saeedi [a]

[a] Department of Petroleum Engineering, Curtin University, 26 Dick Perry Avenue, 6151, Kensington, Western Australia, Australia

[b] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan, 610500, China

[c] Sandia National Laboratories, Albuquerque, NM, 87185-0754, United States

| Name | Conception & design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
|---|---|---|---|---|---|---|
| **Ahmad Sari** | X | X | X | X | X | |
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| **Ali Saeedi** | | | | | | X |
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| **Wanfen Pu** | | | | | X | |
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| **Patrick V. Brady** | | | | X | X | |
| Signature: | | | | | | |
| **Nasser S. Al Maskari** | | X | X | | X | |
| Signature: | | | | | | |

Paper title: "**Low Salinity Water Flooding in High Acidic Oil Reservoirs: Impact of pH on Wettability of Carbonate Reservoirs**" Journal of Molecular Liquids 281 (2019) 444–450

Ahmad Sari, [†,*] Yongqiang Chen, [†] Quan Xie, [†,*] Ali Saeedi, [†]

[†] Department of Petroleum Engineering, Curtin University, GPO Box U1987, Australia, Perth, W.A. 6845

| Name | Conception & design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
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| **Ahmad Sari** | X | X | X | X | X | |
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| **Quan Xie** | | | X | X | X | X |
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| **Ali Saeedi** | | | | | | X |
| Signature: | | | | | | |

Paper title: "**Impact of Surface Roughness on Wettability of Oil-Brine-Calcite System at Sub-Pore Scale**". Journal of Molecular Liquids 2019.112107

Ahmad Sari *, Nasser S. Al Maskari, Ali Saeedi, Quan Xie*

Discipline of Petroleum Engineering, WA School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Western Australia, Australia

| Name | Conception & design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
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| **Nasser S. Al Maskari** | | X | X | | X | |
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| **Quan Xie** | | | X | X | X | X |
| Signature: | | | | | | |
| **Ali Saeedi** | | | | | | X |
| Signature: | | | | | | |

Paper title: **"Carbonated waterflooding in carbonate reservoirs: Experimental evaluation and geochemical interpretation"** Journal of Molecular Liquids. 2020.113055

Ahmad Sari [a,*], Yongqiang Chen [a], Matt B. Myers [b], Mojtaba Seyyedi [b], Mohsen Ghasemi [a], Ali Saeedi [a], Quan Xie [a,*]

[a] Department of Petroleum Engineering, Curtin University, 26 Dick Perry Avenue, 6151, Kensington, Western Australia, Australia.

[b] CSIRO - Energy, 26 Dick Perry Ave., Kensington, WA 6151, Australia.

| Name | Conception & design | Acquisition of data & method | Data conditioning & manipulation | Analysis & statistical method | Interpretation & discussion | Final approval |
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| **Ahmad Sari** | X | X | X | X | X | |
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| **Yongqiang Chen** | | | X | X | X | |
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| **Matt B.Myers** | | X | | | X | |
| Signature: | | | | | | |
| **Mojtaba Seyyedi** | | X | | | | |
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| **Mohsen Ghasemi** | | X | | | | |
| Signature: | | | | | | |
| **Ali Saeedi** | | | | | X | X |
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| **Quan Xie** | X | | X | X | X | X |
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## Drivers of Low Salinity Effect in Carbonate Reservoirs

**Author:** Ahmad Sari, Quan Xie, Yongqiang Chen, et al

**Publication:** Energy & Fuels

**Publisher:** American Chemical Society

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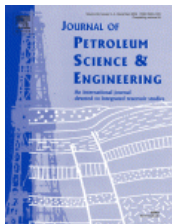
## pH effect on wettability of oil/brine/carbonate system: Implications for low salinity water flooding

**Author:**
Quan Xie,Ahmad Sari,Wanfen Pu,Yongqiang Chen,Patrick V. Brady,Nasser Al Maskari,Ali Saeedi

**Publication:** Journal of Petroleum Science and Engineering

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**Date:** September 2018

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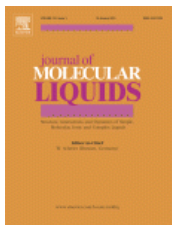
## Impact of surface roughness on wettability of oil-brine-calcite system at sub-pore scale

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