EFFECT OF BRINE COMPOSITION ON WETTABILITY ALTERATION OF CARBONATE ROCKS IN THE PRESENCE OF POLAR COMPOUNDS

BY

MUHAMMAD YOUSUF JABBAR

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

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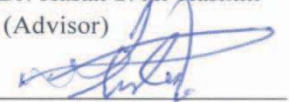## DHAHRAN 31261, SAUDI ARABIA

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This thesis, written by MUHAMMAD YOUSUF JABBAR under the direction of his thesis adviser and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN PETROLEUM ENGINEERING.
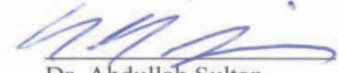
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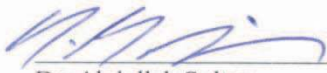(Advisor)

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ii

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ii

Dedication

To Mom and Dad

I owe this accomplishment to my beloved parents for teaching me the value of education.

Dad's unconditional support and Mom's immense sacrifices make me who I am today.

Every bit of me is a little bit of you.

So thank you for being you.

ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT (ENGLISH)

NAME: Muhammad Yousuf Jabbar

TITLE OF STUDY: Effect of brine composition on wettability alteration of carbonate rocks in the presence of polar compounds

MAJOR FIELD: Petroleum Engineering

DATE OF DEGREE: September-2012

The impact of brine salinity and ion composition on oil recovery for carbonate reservoirs has been an area of research in recent years. This was motivated by the additional oil recovery that was recovered by low salinity and ionic modifications in sandstone and chalk reservoirs and to some extent in carbonate reservoirs. Wettability alteration to more water-wet conditions has been proposed as the mechanism leading to the additional oil recovery.

This study presents a fundamental experimental study to confirm wettability alteration and identify the potential determining ions in the injected brines leading to the alteration of wettability of calcite and carbonate rocks and to understand rock/fluids interactions in the presence of polar compounds in the oil.

In this study, a systematic investigation was carried out by first establishing a well defined initial wettability conditions using short and long chain carboxylic acids dissolved in toluene with a total acid number (TAN) of 2. This was followed by subjecting the calcite and carbonates rock samples to Arabian Gulf Seawater and diluted Arabian Gulf seawater having different ion compositions to identify their impacts on wettability alteration to more water-wet conditions. This study focuses on identifying the roles of

SO_4^{2-}, Ca^{2+} and Mg^{2+} in the injected brines with different ratios on wettability alteration. The contact angle method was used to evaluate the wettability.

The results of this study showed that the long chain fatty acid (Stearic Acid) strongly adsorbs onto the calcite surface from the oil phase compared to the short chain (Heptanoic Acid) as confirmed by the measured contact angles. Twice dilution of Arabian Gulf seawater has been found to be a less effecient EOR fluid for wettability alteration as compared to Arabian Gulf seawater. This was confirmed by the changes in the measured contact angles toward more water-wet for Heptanoic Acid /Calcite, Stearic Acid/Calcite and Stearic Acid/Carbonate systems treated with seawater and twice diluted Arabian Gulf seawater with different concentrations of SO_4^{2-}, Ca^{2+} and Mg^{2+} in it. Significant wettability alteration was observed for the twice diluted Arabian Gulf seawater with higher concentrations of SO_4^{2-} and Mg^{2+}. The results are supported by ionic analysis of the brines and mineralogical rock analysis using XRD and rock surface characterizations using SEM after treatment with the different brines used.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS,
DHAHRAN
SEPTEMBER 2012

ABSTRACT (ARABIC)

الإسم: محمد يوسف جبار

عنوان الرسالة: تأثير تركيب المحلول المائى على تغيير خاصية التبلل للصخور الجيرية فى وجود مركبات قطبية

الدرجة العلمية: ماجستير العلوم الهندسية

التخصص: هندسة البترول

تاريخ التخرج: سبتمبر, 2012 م

الملخص

لقد كان تأثير درجة ملوحة المياه الجوفية وتركيبها الأيونى على إستخراج الزيت الخام من الصخور الجيرية مساحة للبحث العلمى فى السنوات الأخيرة. وكان الدافع وراء ذلك هو زيادة أستخراج الزيت الخام من الصخور الرملية والطباشيرية وإلى حد ما الصخور الجيرية باستخدام مياه أقل ملوحة وتعديل التركيب الأيونى لها. ويعتبر تغير قابلية الصخر للتبلل لأن يكون صخر محبب للمياه بدرجة أكبر من وسائل زيادة إنتاجية الزيت الخام. هذه الدراسة تقدم تجارب أساسية لتأكيد تغيير قابلية التبلل وتحديد أيونات المحاليل المائية التى تؤدى إلى تغيير قابلية الصخور الكربونية للتبلل ولفهم التفاعل بين الصخور والموائع فى حالة وجود مركبات قطبية فى الزيت الخام. تم إجراء التجارب عن طريق تعريف قابلية الصخر للتبلل مبدأيا باستخدام أحماض كربوكسيلية طويلة السلسلة وأخرى قصيرة السلسلة مذابه فى التولوين وذات رقم حمضى 2 للمحلول. وأعقب ذلك غمر الصخور الجيرية بماء الخليج العربى وأخر مخفف ذات تركيب أيونى مختلف لتحديد تأثيرهما على قابلية الصخرليتغير الى تبلل مائي. وتركز هذه الدراسة على تحديد تأثير أيونات الماغنسيون والكالسيوم والكبريتات فى المحلول المائى الذى تم حقنه بنسب مختلفة على تغيير قابلية التبلل للصخر.

وقد أظهرت نتائج هذه الدراسة أن الأحماض الدهنية طويلة السلسلة يتم إمتصاصها بقوة من الزيت الخام إلى سطح الصخر مقارنة بالأحماض الدهنية قصيرة السلسلة كما ظهر ذلك أيضا عن طريق قياس الزاوية الحرجة . ووجد أن ماء الخليج المخفف مرتين كان أقل تأثيرآ فى تغيير خاصية التبلل خلال عملية الإنتاج الحفزى للزيت الخام. وقد تأكد ذلك بقياس الزاوية الحرجة التى وجد أنها تتغير فى إتجاه صخر أكثر قابلية للتبلل بالماء فى حالة حمض الهبتان مع الحجر الجيرى و الحمض الدهنى مع الصخر الجيرى وكذلك الحمض الدهنى مع الصخر الجيرى عند معالجته بماء البحر وماء الخليج مضاعف التخفيف وتركيزات مختلفة من أيونات الماغنسيون والكالسيوم والكبريتات. وقد لوحظ تغيير واضح فى خاصية التبلل فى حالة ماء الخليج مع مضاعف التخفيف فى حالة وجود تركيز أعلى للماغنسيون والكبريتات. وقد تم تدعيم هذه النتائج بإستخدام التحليل الأيونى لمحاليل المياه والتحليل المعدنى للصخر بإستخدام XRD وكذلك التوصيف السطى للصخر باستخدام SEM بعد المعالجة بالمحاليل المائية التى تم إستخدامها.

CHAPTER 1

INTRODUCTION

Enhanced oil recovery (EOR), also referred to tertiary oil recovery, is becoming more critical in the industry as oil production from natural reservoirs is declining and its consumption is increasing. Conventional methods of oil production recover less than 30% of initial oil in place; therefore, EOR techniques are becoming more attractive to recover additional oil from the reservoirs.

EOR is generally achieved by injecting either miscible or immiscible fluids into the reservoir for pressure maintenance, viscosity reduction and increasing capillary number, which all contribute to enhance the amount of recoverable oil.

Some of the most common EOR methods include CO_2 injection, thermal treatment (e.g. steam assisted gravity drainage (SAGD)), chemical/surfactant injection, ASP (alkaline-surfactant-polymer) injection and low salinity water injection. It is expected that EOR will continue to perform extremely well in the world market place; nonetheless, technological challenges, hazy regulations, and costly implementation have in the past often kept oil companies from using EOR. However with the continuous increase of oil prices and world demand for oil, EOR is quickly becoming more feasible. It is also of interest because of current rising government interest and investment, new innovative technologies, and the availability of required materials such as CO_2 and sea water. The

market will continue to grow as more countries begin to see EOR results and as it becomes more feasible and common to oil producers.

In most observed cases, carbonate oil reservoirs have neutral to oil-wet character. The evaluation of the wetting state for 161 carbonate reservoirs indicated that 15% were strongly oil-wet, 65% were oil-wet, 12% were in the intermediate class and 8% were water-wet [1]. It is documented that close to 50% of the world proven petroleum reserves are located in carbonates, which usually show a rather low oil recovery factor (less than 30%), mainly due to wettability and the fractured nature of these reservoirs. The EOR potential for carbonates is high due to unfavorable wetting conditions, presence of fractures and low displacement efficiency [2]. The wetting state and the fact that carbonates are usually fractured, makes water flooding a challenging task due to possible bypassing of the oil in the matrix blocks.

The strategy for understanding the effects of interfacial active components in crude oil on the interactions between oil, water and solid, is often to separate the oils into various fractions. Since the surface of carbonate rocks are positively charged, acidic components (negatively charged) like carboxylic acids, $R\text{-}COO^{-}$, are much more important than basic components (positively charged). The presence of acid components in petroleum termed naphthenic acids was first reported in 1874 [4]. Historically, the slightly polar heavy components asphaltenes and resins are known to alter the wettability towards oil wet, but during the last two decades, the importance of acidic components in the crude oil have been emphasized [5]. The contents of these acids are not directly related to the asphaltene contents [7], but they are present in all crude oils [5].

The attractive electrostatic force between acidic components and carbonate rock surface is the key parameter in crude oil/carbonate rock surface interaction. Thus, due to opposite

surface charges, the organic acids of crude oil have the largest potential effect on carbonates wettability [6, 8].

Several researchers have reported the ability of acids to adsorb onto mineral surfaces and thereby alter the wetting properties of the surface [6, 7]. It is generally accepted that adsorption of polar compounds onto the rock surface has a significant effect on the wettability of reservoirs [6, 8-12, 20]. In other words, the wettability of hydrocarbon reservoirs depends on the specific interactions in the oil/rock/brine systems. However, there is only limited knowledge of the influence of organic acids on the three-phase system of oil/brine/rock.

Hence, the wettability of a reservoir is an important parameter affecting fluid distribution, location and flow of oil and water in the reservoir [8]. Therefore, the wetness of the reservoir has to be modified towards more water-wet in order to improve carbonate oil recovery.

A lot of studies have been made on carbonates, focusing on improved oil recovery. A new EOR method for chalk and possibly an applicable method for all carbonates is wettability alteration by seawater. Austad and co-workers have shown that seawater can act as a "Smart Water" to improve the water-wetness of chalk at high temperatures causing further oil production [2, 14, 15].

Water injection for both pressure maintenance and oil displacement is the most important secondary recovery method in sandstones but has also been implemented with some success in carbonate reservoirs [17]. Alteration of the injected water composition can presumably impact rock wettability and eventually provide additional oil recovery. This effect is attributed to the ion exchange between the key ions such as (SO_4^{2-}, Ca^{2+}, Mg^{2+}) present in seawater and the minerals of the rock resulting in altering rock surface charges

and releasing adsorbed carboxylic oil components from the rock surface, and consequently altering rock wettability to a more water-wet condition [2,18,14,15].

Figure 1 demonstrates the proposed mechanism by Austad (Strand et al. 2006). They proposed that calcium is substituted by magnesium in the presence of sulphate at high temperature.
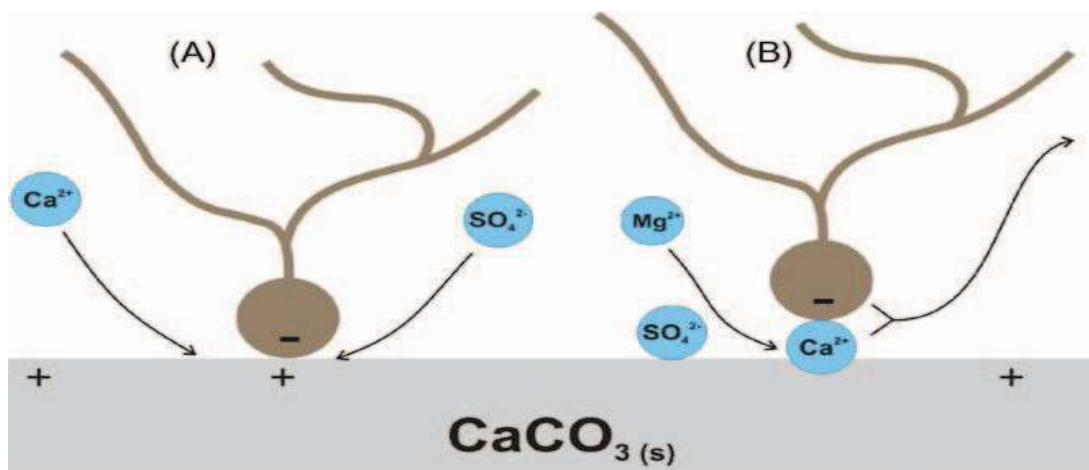
Figure 1 Wettability alteration induced by seawater [17]

Besides the positive effect on oil recovery, sea water appeared to enhance water weakening of the high porosity chalk causing increased compaction in the water-flooded area [21-24]. This is due to a chemically induced fluid–rock interaction, which also appeared to involve the same potential determining ions that are present in sea water [24]. The potential use of low salinity water as EOR technique has been found to be feasible as shown by different studies because it is cost effective compared to chemical/surfactant EOR, more appealing in terms of infra structure investments and environmental friendly approach. The great success in oil recovery by injection of seawater into mixed-wet Ekofisk chalk field is an example of successful low salinity seawater flooding [25]. Primary recovery factor of the Ekofisk field was estimated as 17% by pressure depletion; however, by the initiation of sea water injection in 1984, the recovery factor from the field is now close to 50% [25, 26].

The lifetime expectancy of the mature fields may be extended by enhanced oil recovery in addition the profitability of the small fields may increase. The main goal of EOR processes is the reduction of reservoir residual oil saturation by enhancement of its sweeping efficiency. To accomplish such objective and better designing it, it is necessary to have a full understanding of the reservoir rock, reservoir fluids, their interaction and how it affects wettability of the rock in the reservoir. The great success of sea water injection in Ekofisk field gave impetus to many research programs to evaluate the interaction between the carbonate rock and the injected seawater.

The aim of this study is to investigate the wettability alteration mechanisms in carbonates due to injection of different saline water on pre-treated carbonates with different carboxylic acids using contact angle and spectroscopic surface characterization techniques.

Thesis Organization

A comprehensive literature review is provided in chapter 2. It encompasses, about carbonates wettability, role of carboxylic acids in crude oils and the possibility of using sea water as an EOR method.

Chapter 3 involves the materials and method used in this study. Procedures for model oil and brine and rock sample preparation are presented. The contact angles method was adopted to study the wettability effect of the brines and the standard protocol for all the systems considered in this study are discussed. The pH measurements, brine analysis and surface characterization methods are also presented in this section.

Chapter 4 presents the results and discussion for the contact angle measurement for MO(HA)/Calcite, MO(SA)/Calcite, and MO(SA)/Carbonate. The contact angle measurement will be presented along with the change in the pH of the brines and the change in the ion concentrations of SO_4^{2-}, Ca^{2+} and Mg^{2+}. Surface characterization using SEM- EDX analysis is also presented.

Chapter 5 presents the conclusions and recommendations for further investigations.

Thesis Objectives

The overall objective of this study is to investigate the impact of brines having different ionic composition on alteration of wettability of carbonate rocks in the presence of adsorb carboxylic acids. The main objectives of the study are as follows:

- Identify the potential determining ions in the brine that can alter the wettability of carbonate rock surfaces to a more water-wet condition.

- Understand rock/fluids interactions responsible for the wettability alteration of carbonate rocks.

The polar compounds used in this study are two carboxylic acids of short and long chain length. The rocks were treated with brines to study treatment effect on the wettability from neutral-wet to water-wet. The effect of brine salinity and concentration of sulphate, calcium and magnesium in the brines on the wettability alteration was evaluated using contact angle measurement. To understand the subject of rock/fluid interactions pH analysis of the brines, analysis of the concentration of the potential ions in the brine (after treatment) and the surface characterization of the rock was carried out in order to understand the mechanism behind wettability alteration to more water-wet conditions.

CHAPTER 2

LITERATURE REVIEW

Carbonate reservoirs have for many years contributed significantly to the production of oil and gas worldwide. The importance of carbonate is due to their rich organic content and good reservoir properties. It is estimated that 40-60% of world's total hydrocarbon production is from carbonate rocks [27]. A survey covering hundreds of the largest hydrocarbon fields all over the world was reviewed in 1985, with the result that approximately 60% of all recoverable oil was held in carbonate reservoirs [28]. Another analysis performed by Schlumberger in 2007 also proposes that more than 60% of the world`s oil and 40% of the world`s gas reserves are held in carbonate reservoirs [29]. Many of the biggest carbonate reservoirs occur in the Middle East. Ghawar Field, Saudi Arabia, and South Pars/North Dome field, Iran and Qatar are the world's largest oil and gas fields respectively which are some examples of carbonate rocks [30, 31]. Other areas in which the reservoirs delivers large quantity of oil and gas are ; West Canada, Mexico, Texas (USA), Norway (Central North Sea), Poland, Kazakhstan, Western and Southern China, Iran and Libya [32].

2.1 Carbonate Rock Wettability

Wettability is defined by Anderson [8] as "the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids". The reservoir rock may be water-wet, oil-wet, or neutral-wet if both fluids have equal affinity for the rock surface.

At the triple point, where solid, oil and water are in contact, a contact angle between oil and water towards the solid can be determined. The contact angle is measured through the denser phase, and it is in the range of 0-180°. Anderson [34] graded the wetting state as preferentially water-wet when the contact angle is between 0 and 60 – 75°, oil-wet when the contact angle is between 105 – 120° and 180°, and intermediate or neutrally wet in between these two ranges. Other researchers use other cutoff values for the contact angle [1, 33].

The degree to which a reservoir rock is either water-wet or oil-wet or any other wetting conditions are strongly affected by the [35]

- Rock mineralogy,

- Constituents and conditions of the pore surfaces,

- The presence of polar components in the reservoir oil,

- Brine composition and

- Reservoir conditions.

Wettability is an important parameter in oil recovery processes, because it has strong impact on the distribution, location and flow of oil and water in the reservoir during production [3, 34, 36, 37, 39].

It was generally believed that all reservoir rocks were strongly water-wet (Morrow, 1990) [39]. However, in most observed cases, carbonate oil reservoirs have neutral to oil-wet character [40]. It is generally accepted that adsorption of polar compounds onto rock surface has a significant effect on the wettability of reservoirs [6, 8, 10-12, 20, 39, 41]. Specifically the neutral to oil-wet character of carbonate reservoirs may be related to the adsorption of carboxylate molecules diffusing from crude oil to positive sites of the calcite surface [41]. In other words, the wettability of hydrocarbon reservoirs depends on the specific interactions in the oil/rock/brine systems. Apparently, the original wetting-state of carbonate rocks has been changed to oil-wet when exposed to crude oil.

2.2   Role of Carboxylic Acids

Several authors have reported the ability of acids to adsorb onto mineral surfaces and thereby alter the wetting properties of the surface [6, 7, 43]. Acid/base interactions affect surface charge at both oil/water and solid/water interfaces [44]. Ionized acidic or basic sites at the interfaces will influence the adsorption behavior by which polar crude oil components may alter wettability. However, there is only limited knowledge of the influence of organic acids on the three-phase system of oil/brine/rock.

During the last two decades the importance of acidic components in the crude oil has been emphasized [5].This study applies carboxylic acids dissolved in toluene to alter the wettability of carbonate rock towards oil-wet.

Carboxylic acid consists of one or more carboxyl groups attached to a hydrocarbon chain of various length. The carboxyl group is polar, negatively charged, while the hydrocarbon chain is neutral. The surface of carbonates is positively charged below pH 8 to 9 [45]. The carboxylic material, quantified as acid number (AN), present in the crude oil absorbs

very strongly onto the positive sites of a carbonate surface [6]. It is therefore the most important wetting parameter for carbonates. Within the carboxylic group there are some water-soluble components. These components are believed to play an important role in the initial wetting state because the water-soluble acids may contribute in destabilization of the water film [49].

To illustrate the importance of carboxylic acids, Milter [46] showed that, by measuring the contact angle, a calcite crystal aged in the carboxylic acid stearic acid dissolved in dodecane became oil-wet. Hansen [9] suggested that strong adsorption of stearic acid on the calcite surface converts the calcite surface to strongly oil-wet. Legens [41] investigated the adsorption difference of benzoic and lauric acids on calcite surface from toluene and water.

The acid number (AN) (measured in mg KOH/gm oil; the mass of potassium hydroxide required to neutralize 1 g of oil.) is a measurement of the contents of acidic components in crude oil [50]. Wolcott [47] concluded that acid number and base number appeared to have some influence on wettability. To further illustrate the importance of acidic components, Standnes and Austad [48] performed Spontaneous Imbibition measurements of brine into cores saturated with various oils with various acid numbers (AN), and showed that the rate of SI decreased with increased AN. In other words, the water-wetness decreases with increasing acid number. A recent study has shown that the chemical properties of the acids present in the crude oil have also impact on the wetting properties of chalk. It was confirmed that cores saturated with oil depleted in water-soluble acids were somewhat more water-wet, indicating that water-soluble acids may affect the stability of the initial water film between the rock and the oil [49]. Also there is experimental evidence that the carboxylic material present in crude oil is the

most strongly adsorbed polar organic components onto the carbonate surface [6]. Hence this is regarded as the main cause of oil-wetness of most carbonate reservoirs.

It is unknown if the length of the hydrocarbon chain of the carboxylic acids is important for the initial wettability alteration from water-wet to oil-wet.

Zhang and Austad [20], confirm the importance of AN, and state that temperature had little effect on the oil-wetting process. The temperature and the acid number (AN) are not independent wetting parameters for carbonates, as decarboxylation and other types of decompositions of carboxylic acids take place as the temperature increases [20]. The catalytic effect of $CaCO_3$ speeds up a very slow reaction so that it becomes significant during the geological time but not during the aging period of the cores in the experiment [20].They found that the wetting state was mainly dictated by acid number and that aging temperature had a minor effect on the wetting state.

According to Buckley and Liu [42] there are two different mechanisms in the wettability alteration by crude oil adsorption. With initial water saturation they adsorb by acid-base interactions, while with no initial water they adsorb by polar binding. Usually they would adsorb stronger with initial water saturation [51].

To alter the oil-wet carbonates back to water-wet, the carboxylic acids and other polar components must be desorbed from the rock surface, and transported away.

2.3 EOR from carbonates reservoir

Oil recovery is traditionally subdivided into three stages: primary, secondary, and tertiary. Approximately 30-70 % of OOIP in the reservoir is left after the conventional secondary oil recovery processes [52, 53].After the secondary recovery stage became uneconomical, tertiary recovery processes was the final stage in the production process. Very often

reservoir production operations are not conducted in the specified order that tertiary process may be applied at secondary stage. Hence the term enhanced oil recovery" (EOR) became more accepted. Another term "improve oil recovery" (IOR), which includes EOR but also a broader range of activities, like reservoir characterization, improved reservoir management, and infill drilling [54].

One of the most common EOR techniques for this type of reservoirs is waterflooding in terms of accessibility and costs. However, water flooding in a fractured, oil-wet reservoir is not effective. If the rock were water-wet, water would imbibe spontaneously and displace oil from the matrix block to the fracture network. Unfortunately, approximately 90% of the carbonate reservoirs are neutral to oil-wet, which implies that spontaneous imbibition of water will not occur since most carbonate reservoir is on the oil-wet side. An example is Ghaba North field in Oman which is a highly fractured, oil-wet carbonate reached a recovery of 2% after more than 20 years of production [55].

The EOR potential of these oil-wet, fractured carbonate reservoirs is high. One of the tertiary methods includes Chemical EOR methods to increase recovery. The Chemical EOR processes involve injection of specific liquid chemicals such as surfactants and alkaline agents. The chemical methods are aimed to either increase the areal sweep efficiency at the macroscopic scale by changing the mobility ratio, or increase the displacement efficiency at the microscopic scale by reducing the interfacial tension, or altering the rock wettability [56].The surfactants are used to lower the IFT and has the potential to increase both microscopic and macroscopic displacement efficiency. However, the greatest set back to application of the surface active additives like cationic surfactants in the carbonate reservoirs is of economic consideration. Thus, seawater flooding became an attractive alternative because it is cheap and readily available. This

thesis uses modified seawater to alter the wettability and will be discussed in the following sections.

2.3.1 Sea Water as an EOR Fluid

Low salinity seawater flooding has been proposed as a secondary recovery method rather than an EOR method. However, it has been reported that in carbonate reservoirs certain parameters such as wettability, capillary pressures, etc. can be altered in favor of oil recovery by the help of potential determining ions present in sea water [18, 57, 58]. Thus, since the chemical and physical properties of a chalk reservoir can be altered, low salinity sea water flooding has been proposed as a new EOR method for chalk and possibly an applicable method for other carbonate reservoirs. It has been reported that up to 40% improvement in oil recovery could be reached by using sea water as imbibing fluid [59]. One of the fields where extensive challenges have been experienced is the Ekofisk field (1971); an over pressured, mixed-wet and naturally fractured high porosity chalk reservoir [60] with an initial temperature of 130°C and an initial estimated recovery of 17%. Today oil recovery from Ekofisk field is increased to 50-55%, which is well above most carbonate reservoirs characterized by a recovery factor below 30%. This great success gave impetus to many research programs to evaluate the interaction between the carbonate rock and the injected seawater.

Austad and co-workers have shown that seawater can act as a "Smart Water" to improve the water-wetness of chalk at high temperatures causing enhanced oil recovery by spontaneous imbibition [2, 14, 15]. Recent laboratory studies [15, 38, 61] had demonstrated that seawater contained potential determining ions (SO_4^{2-}, Ca^{2+} and Mg^{2+}). The mechanism for seawater induced wettability alteration in chalk has been suggested

14

by Zhang [16], and is shown in Figure 1. The process is a classic example of surface chemistry. It is experimentally verified that the interactions between the active components, Ca^{2+}, Mg^{2+}, and SO_4^{2-}, in seawater and the rock surface are responsible for the improvement in water wetness of chalk. The original formation water differs from the injected North Seawater in composition. The formation water usually has a high concentration of Ca^{2+} and a negligible SO_4^{2-} concentration, while in North seawater the concentration of SO_4^{2-} is about double the Ca^{2+} concentration. The potential determining ion SO_4^{2-} adsorbs on the chalk surface and lowering the positive charge density. Due to less electrostatic repulsion, more Ca^{2+} can attach to the rock surface and displace some of the carboxylic material (see Fig. 1A). The North seawater also contains a lot of Mg^{2+} ions. At temperature higher than 90-100°C Mg^{2+} ions are able to substitute the Ca^{2+} ions from the chalk surface. Thus, Mg^{2+} should be able to displace the Ca^{2+} linked to the carboxylic material, making the rock surface more water-wet (see Fig. 1B). North Seawater can change the wettability in chalk towards more water-wet. To alter it, the potential determining ion SO_4^{2-} must interact with Ca^{2+} or Mg^{2+}. Both the imbibition rate and oil recovery increases with increasing reservoir temperature due to stronger adsorption of sulfate and calcium ion onto the chalk surface.

Some of the previous work that investigated the spontaneous imbibition mechanism in chalk was performed with surfactants. Strand [13] discovered that sulfate ions present in the imbibing fluid catalyzed the wettability alteration process. The result initiated another work [2] to explore the potential of sulphate as a wettability alteration agent, using seawater as the imbibing fluid.

It was also experimentally documented that sulfate can act as a wettability modifier alone, without any expensive surfactant present [18, 62]. Sulfate is, in fact, a very strong

potential determining ion towards $CaCO_3(s)$ [45], and knowing that the concentration of sulfate is about twice the concentration of Ca^{2+} in seawater, it may change the zeta potential of the carbonate surface.

Spontaneous imbibition even increased with increased concentration of sulfate. Furthermore, Høgnesen [38] pointed out that the oil recovery by spontaneous imbibition of water into neutral to preferential oil-wet carbonate (reservoir limestone, outcrop chalk cores) increased as the concentration of sulfate and temperature increased. They also determined the affinity of sulfate towards the chalk surface at different temperatures using the chromatographic separation between a tracer, SCN^- , and sulfate. The area between the effluent curve of the tracer and sulfate is a measure of the affinity of the sulfate towards the chalk sulfate [2]. Yu [63] validated using contact angle measurements the importance of sulphate and high temperature towards more water-wet surfaces on calcite crystal and chalk slices. Zhang and Austad [14, 15] showed that the imbibition rate and oil recovery increase as the temperature increases due to a stronger adsorption of sulphate and calcium onto the chalk surface.

Strand et. al [2, 64] and Austad et. al [65] confirmed through imbibtion tests using seawater that the SO_4^{2-} and Ca^{2+} ions concentration and temperature appeared to be crucial in wettability modification. They further observed increased adsorption of sulphate as the concentration of calcium in seawater increased due to co-adsorption of calcium on the carbonate surface. They supported that adsorption of sulphate onto carbonate decreased the positive charge on rock surface, which increased the excess of calcium at the surface because of reduced electrostatic repulsion.

Rezaei Gomari [66] showed the influence of sulfate and magnesium ions on the adsorption of fatty acids onto calcite surfaces towards more water-wet surface. The

degree of wetting is dependent on the pH. At pH greater than 7 in stearic acid dissolved in an n-decane, water, and calcite system, both ions reduce the contact angle.

In summary, the alteration of the wettability of modified calcite surface in presence of SO_4^{2-} is not only due to possible reduction of the available active sites on the calcite surfaces but could also be due to a displacement process of various preadsorbed carboxylate ions of the tested fatty acids [66].

In addition to SO_4^{2-} and Ca^{2+}, Mg^{2+} is also an important potential determining ion. When the concentration of ions in sea water is examined, it can be seen that Mg^{2+} has the highest concentration among divalent ions (Ca^{2+} and SO_4^{2-}). The Mg^{2+} ion is small with a high charge density, and it is therefore strongly solvated in water [67]. As the temperature increases, Mg^{2+} becomes more reactive due to partial dehydration of the ion [64].

Karoussi and Hamouda [68] have shown that initial presence of sulfate and magnesium ions makes the carbonate rock surfaces more water-wet. The presence of magnesium ions indicates a more stable water film (compare to DIW and SO_4^{2-}) and requires an increase in the capillary pressure to rupture the water film as the temperature increases. Also the potential interaction between the calcite surface and modified calcite by fatty acid in presence of Mg^{2+} are always repulsive and for sulfate and distilled water, the interaction potentials are slightly more attractive and become less attractive with the temperature, T, reaching a repulsive status a T >70 °C. Lahann and Campbell [69] also observed that the presence of Mg^{2+} ions reduced the adsorption of fatty acids.

Korsnes and Zhang [15,24] have experimentally shown substitution of Ca^{2+} by Mg^{2+} at the chalk surface at temperatures greater than 90-100°C, when flooding seawater slowly through an outcrop chalk core. They explained that the substitution mechanism at higher temperatures releases the Ca^{2+} and R-COO- compound from the surface. Hence the

17

wetting state of the core becomes more water-wet and at the same time oil recovery increases. Petrovich and Hamouda [70] also observed an increase of calcium ion and a decrease in the magnesium ion concentrations in produced water as a result of seawater injected into Ekofisk field samples (chalk reservoir). They concluded the possible adsorption/exchange process increases between Mg^{2+} in seawater with Ca^{2+} in calcite with the increase of temperature.

From the above discussion it is confirmed that the presence of calcium, magnesium, and sulphate ions is necessary to increase the spontaneous imbibition of water and changes the rock wettability.

In a recent study, the effect of salinity of smart water on oil recovery at different temperatures was studied [71]. They carried out spontaneous imbibition and flooding tests with low salinity brine solutions using Stevens Klint outcrop chalk core plugs at 110 and 120°C. A negative impact of diluting the seawater to low salinity was reported which significantly decreased the change in oil saturation by spontaneous imbibition. It was confirmed that not only is the concentration of the active ions Ca^{2+}, Mg^{2+} and SO_4^{2-} important for wettability alteration to take place, but also the amount of non-active salt, such as NaCl, has an impact on the wettability alteration process, which is discussed as a double-layer effect at the chalk surface. Seawater depleted in NaCl appeared to have the greatest effect on the wetting properties by increasing the water-wet area by 29% compared to the effect of ordinary seawater. Also, Fjelde [72] carried out spontaneous imbibtion with formation water and low salinity water using limestone. The low salinity water increased oil recovery in limestone and showed similar oil recovery results to seawater experiments. Doust et. al [73] reported different chemical mechanism may also be responsible for difference in the low salinity effect.

18

The increase recovery with low salinity brine was supported by the decrease in the concentration of the active ions (SO_4^{2-}, Ca^{2+} and Mg^{2+}) for drastic decrease in change of oil saturation. However, the results only reflect effect on spontaneous imbibition and may not be relevant for waterflood oil recovery.

Unlike the others Yousef et. al [74] reported 16-18% OOIP increase in oil recovery by low salinity waterflooding in composite rock samples from Saudi Arabian carbonate reservoirs. Experiments were carried out using live oil and at a reservoir temperature of 212°F. Wettability alteration was reported as a key mechanism for the increment in oil recovery.

In addition to wettability alteration, the compaction of the rock caused by seawater is also an important drive mechanism for oil recovery. Due to the high porosity of chalk, compaction takes place during the primary production phase. In Ekofisk, the contribution in the drive mechanism due to compaction was estimated to be in the order of about 40% [15].

Korsens [24] suggested a mechanism for the enhanced-chemically induced weakening of chalk. Substitution of Ca^{2+} by Mg^{2+} at the inter-granular contacts reduces the mechanical strength of chalk. Due to this chemical substitution, the mechanical strength of the chalk decreased by a factor of 2.7 when the cores were flooded with seawater compared to the distilled water or other aqueous solutions free from Mg^{2+} and SO_4^{2-} ions [21,22].

Smart water flooding has several advantages compared to other EOR methods [75]: It can achieve higher ultimate oil recovery with minimal investment in current operations, can be applied during the early life cycle of the reservoir and is economical.

In summary, seawater has been found to be able to act as a wettability modifier to improve spontaneous imbibition of water into oil-wet chalk and also as a pore compaction

agent. The key parameters are high temperature and the potential determining ions in seawater: Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Thus, seawater can be modified to contain these ions in proper concentration to improve oil recovery for carbonate reservoirs.

CHAPTER 3

MATERIALS AND METHOD

3.1   Materials and Chemicals

Calcite crystals (Iceland Spar) purchased from Ward's Natural Science and carbonate rocks from Saudi Arab-D outcrop are used in this study for contact angle measurements. Rocks were cut within 15 x 6 x 2 mm and polished to certain roughness before measurements. The mineralogy of both surfaces was examined by X-ray diffraction technique (XRD). As shown in Figures 2 and 3, both samples are made up of calcite $(CaCO_3)$.
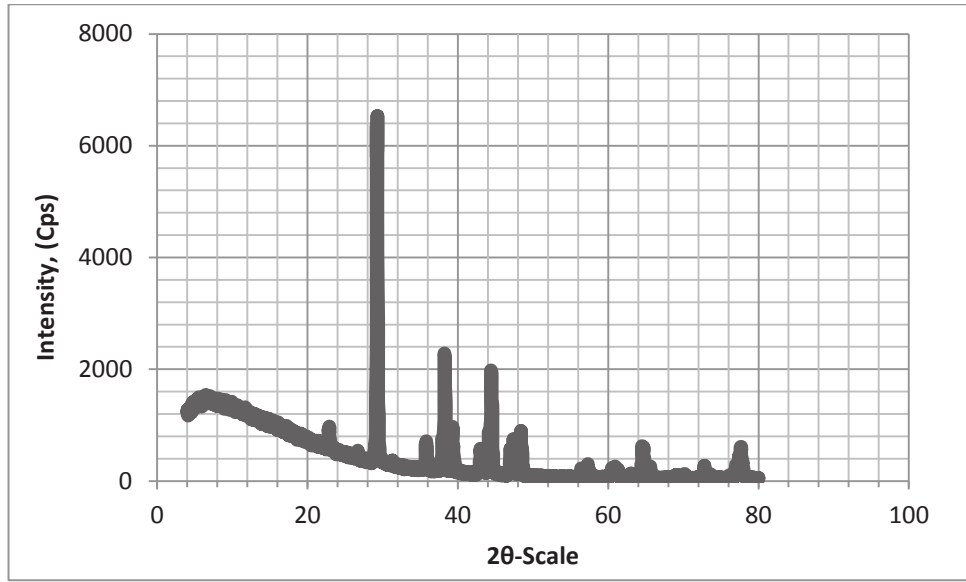
Figure 2 XRD of Calcite crystal
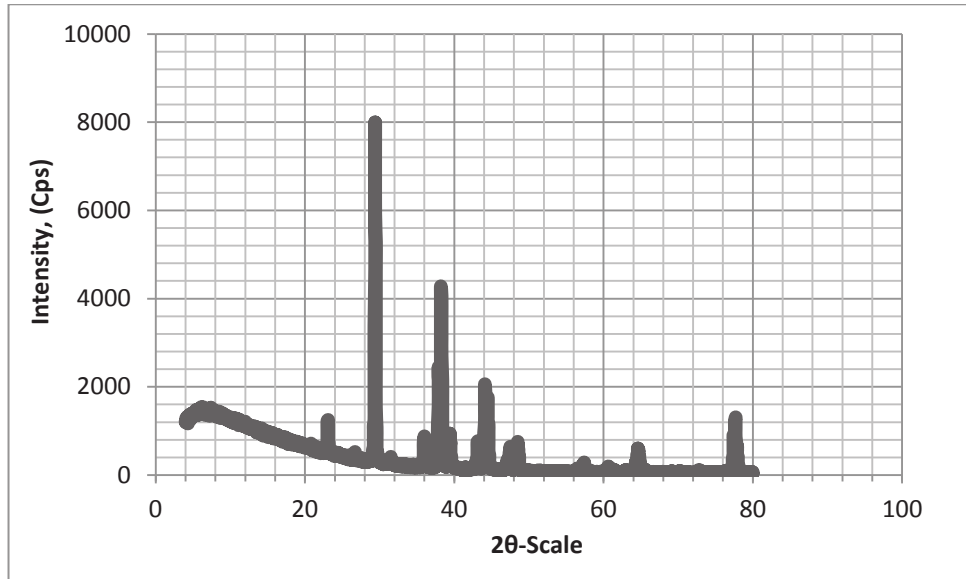
Figure 3 XRD of Outcrop Carbonate sample

The fluids used in the experiments include different chemicals and brines. Two different carboxylic acids are used in this study to represent the polar species of the reservoir crude oil. Heptanoic acid ($CH_3(CH_2)_5COOH$) and stearic acid ($CH_3(CH_2)_{16}COOH$) are both supplied by Sigma Aldrich with purity high than 99%, their chemical number is 100992537 and 100978191 respectively. A model oil is prepared by dissolving either acid in toluene (Lot S87624-279) which is supplied by Sigma Aldrich in HPLC grade (purity >99.8%).

3.1.1 Model Oil Preparation

Model oil was prepared with the carboxylic acid dissolved in toluene in the given ratios presented in Table 1 and Table 2 for the respective heptanoic and stearic acid. The toluene used to prepare model oil was first equilibrated with deionized water for 24 hours. The equilibrated toluene and the required amount of carboxylic acid were then measured by weight. The model oil prepared with heptanoic/toluene and stearic acid/toluene were both for a total acid number (TAN) of 2.

Table 1 Model oil (heptanoic acid) of TAN=2

Components	Mass (gms)
Toluene	348.36
Heptanoic Acid	1.63
model oil	**349.99**

Table 2 Model oil (stearic acid) of TAN=2

Components	Mass (gms)
Toluene	120.1
Stearic Acid	1.247
model oil	**121.347**

3.1.2 Brines

The electrolyte concentrations of the formation Water (FW) and all used brines are listed in Tables 3 to 6. The brine termed SWME is a synthetic Arabian Gulf Seawater, and SWME* is Arabian Gulf Seawater twice diluted. The synthetic Arabian Gulf Seawater (SWME) and the modified versions of the synthetic Arabian Gulf Seawater (SWME*, SWME*0S, SWME*2S, SWME*4S, SWME*0Ca, SWME*2Ca, SWME*4Ca, SWME*0Mg, SWME*2Mg and SWME*4Mg) were used in the contact angle measurements in this study.

In this study each brine was prepared by adding specific weight of the desired salts to deionized water. NaCl was supplied by LOBA CHEMIE (batch # A681209), Na_2SO_4, $CaCl_2.2H_2O$ and $MgCl_2.6H_2O$ were used to vary divalent ion concentration in brine. Na_2SO_4 was supplied by TECHNO PHARMCHEM. (lot # 261394) and $CaCl_2.2H_2O$ and $MgCl_2.6H_2O$ was supplied by LOBA CHEMIE (batch # SL106010 and batch # SL020310).

Table 3 Composition of brines used for salinity effect

Ions	FW (ppm)	SWME (ppm)	SWME* (ppm)
Na^+	62000	18043	9021.5
Ca^{2+}	23314	652	326
Mg^{2+}	1268	2159	1079.5
Cl^-	120000	31808	15904
SO_4^{2-}	250	4450	2225
HCO_3^-	79	173	86.5
TDS	206911	57285	28642.5
Ionic Strength	4.31	1.15	0.57

Table 4 Composition of brines used for sulphate effect

Ions	SWME*0S (ppm)	SWME*2S (ppm)	SWME*4S (ppm)
Na^+	9021.5	9021.5	9021.5
Ca^{2+}	326	326	326
Mg^{2+}	1079.5	1079.5	1079.5
Cl^-	15904	15904	15904
SO_4^{2-}	0	4450	8900
HCO_3^-	86.5	86.5	86.5
TDS	26417.5	30867.5	35317.5
Ionic Strength	0.53	0.62	0.71

Table 5 Composition of brines used for calcium effect

Ions	SWME*0Ca (ppm)	SWME*2Ca (ppm)	SWME*4Ca (ppm)
Na^+	9021.5	9021.5	9021.5
Ca^{2+}	0	652	1304
Mg^{2+}	1079.5	1079.5	1079.5
Cl^-	15904	15904	15904
SO_4^{2-}	2225	2225	2225
HCO_3^-	86.5	86.5	86.5
TDS	28316.5	28968.5	29620.5
Ionic Strength	0.56	0.59	0.62

Table 6 Composition of brines used for magnesium effect

Ions	SWME*0Mg (ppm)	SWME*2Mg (ppm)	SWME*4Mg (ppm)
Na^+	9021.5	9021.5	9021.5
Ca^{2+}	326	326	326
Mg^{2+}	0	2159	4318
Cl^-	15904	15904	15904
SO_4^{2-}	2225	2225	2225
HCO_3^-	86.5	86.5	86.5
TDS	27563	29722	31881
Ionic Strength	0.48	0.66	0.84

3.2 Contact angle measurements

The contact angle measurements were performed by the sessile drop technique using an NRL contact angle Goniometer from Kruss (model DSA-100). The sample is placed inside a designed high temperature/high-pressure cell. A 500-µml Gilmont micrometer inverted syringe was used for deposition of the model oil droplets on rock samples. Droplets of the equilibrated oil phase were deposited on rock samples surrounded by the equilibrated aqueous phase. Electronic data processing was used to solve the theoretical equation of a drop profile. Drop Shape Analysis System (DSA) is used to determine the contact angles from the shape of sessile drops. The angle between the baseline and the tangent at the drop boundary is measured. The oil droplet displaces water at the polished surface, giving a dynamic water receding condition. After a static condition is obtained, the contact angle is measured, and the observed angle represents a static contact angle initiated by a water receding angle. Approximately two replicates were performed for each combination of oil and water phase.

In this work the contact angle was also measured at the air interface. This was done in cases where the formed oil droplets were not stable on the calcite surface at the water interface (water-wet surface).

Initially three approaches have been followed in this work for the MO(SA)/Calcite system as shown in Figure 4.

All the samples were wet-polished and were immersed for one day each in toluene and methanol. The purpose of toluene was to remove any traces of oil on the surface and methanol to remove the salts deposited on the surface.
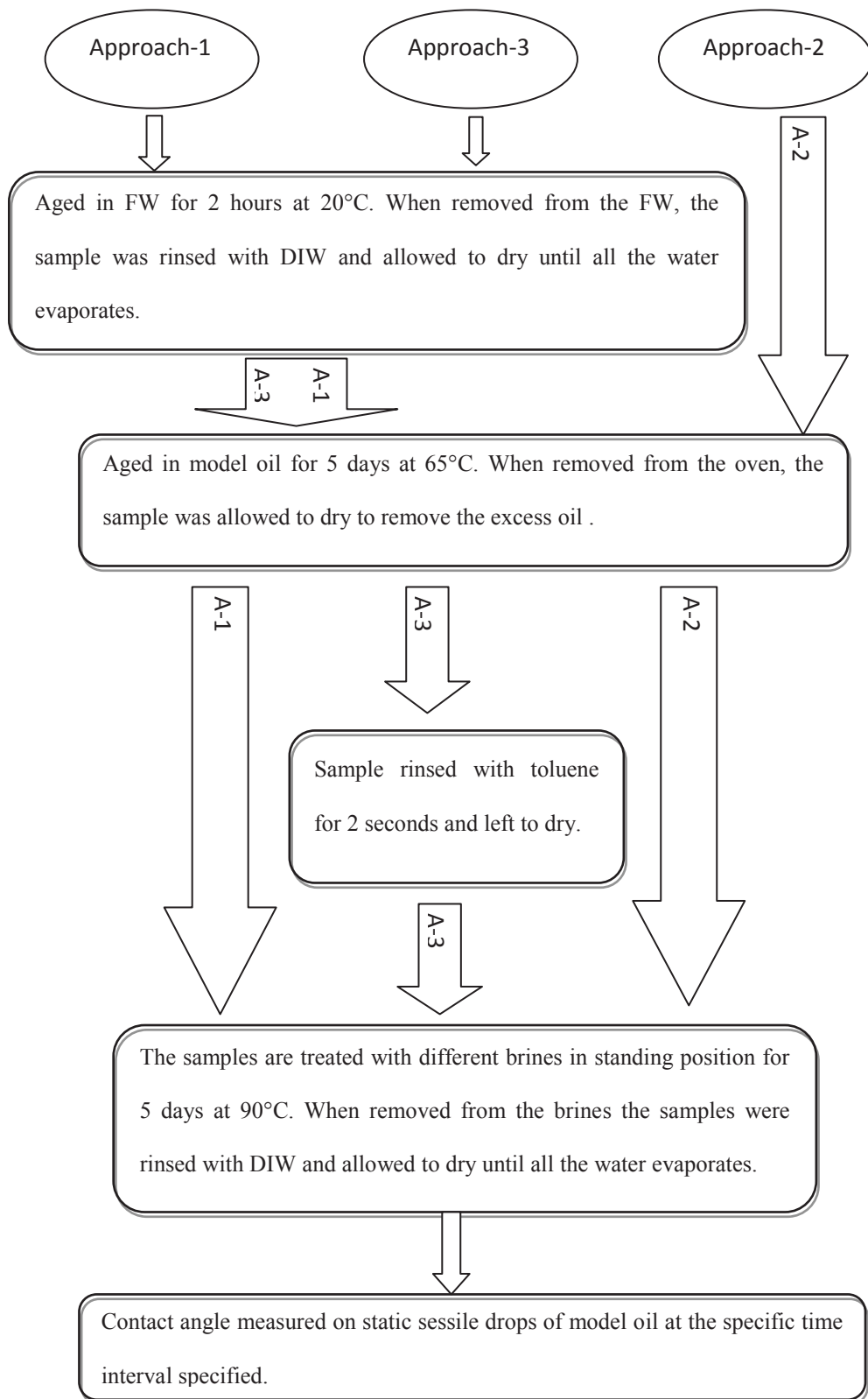
Figure 4 Flow Chart of the three approaches followed in the sample preparation

Right, and left contact angles, aging time, as well as fitting errors are recorded with time for all experiments. The contact angle for each drop is presented as the mean value of those two angles. The contact angles were measured using the software included with the goniometer whenever possible. By visual inspection, the uncertainty in any single measurement seemed very small under optimal lighting, less than $\pm 1°$. In the cases where it was possible to observe that the calculations were a little off, the contact angles were more often overestimated. When measuring several drops deposited on one crystal, the lighting occasionally had to be alternated from drop to drop to result in a satisfactory measurement. As such the uncertainty increases to perhaps $\pm 1°–2°$ because the contact angles of a specific drop are not measured under identical conditions in each measurement.

In some cases contact angles had to be measured manually using a semi-circle, because the software could not produce a curve fit for a particular drop. The uncertainty was in the range of $\pm 2°–3°$ especially if computer measurements and manual measurements are combined in any given data set, mixing two sets of interpretations. This rarely happened, but there were a few times when the contact angles during the course of the experiment decreased below the optimal range for the software to calculate.

Crystals which were reused were re-polished on all surfaces to remove surface-active materials. To an extent, the quality of the measurements relies very much on the skill of the experimentalist and the heterogeneity of the rock substrates. In this study, only advanced contact angle is reported.

A very important step before any experiment is a thorough cleaning of the apparatus, because the presence of any trace amounts of contamination can alter the results. Flow line was cleaned first with toluene several times. Acetone was then used to flush the lines.

The line was dried by flowing dry air and was flushed with copious amounts of deionized water.

All measurements in this work are performed at room temperature, 20°C and atmospheric pressure.

3.2.1 MO(HA) system

Figures 5 to 7 present the mean value of the left and right contact angles, for one drop over a period of 50 minutes. Two drops were deposited on each crystal surface.

During the first few seconds, a decrease was observed in the contact angle for the Calcite/MO(HA). The contact angles recorded at t=0 for this system is not the contact angles upon immediate contact with the crystals surface as it would be difficult to measure when drop is just released, but measured when the decrease is no longer easily visible on the monitor, typically after 1 minute when the drop was released. Therefore initial measurements should not be paid much attention. After this, a more gradual decrease occurred until the contact angles entered apparent equilibrium. The final contact angle for a given system was reported as the equilibrium left and right contact angle measurements value at t=50 mins rounded to the nearest first decimal place.

It may be argued that, as the apparent equilibrium region is not completely stable and the duration for each run could be more than 50 minutes. However, comparing with the long-term results, the contact angle was decreasing by approximately 0.63°/hour in this region, an accuracy which is far below the expected measurement accuracy. The contact angles experiments were run for 50 mins for this system and this time was found to be reasonable enough for the drop to reach equilibrium. The system was assumed to be in equilibrium when the change in the contact angle is less than 0.2°/hour .For the same system, the equilibrium time and the change between the initial value and final value at t=

50 minutes varies. Still to be consistent for the comparison purpose, all the experiments in this system were run for the same period of time.

Long-term experiments revealed that this apparent equilibrium is not entirely stable. We have conducted experiments for 13 hours for SWME*2S. The drops for MO(HA) in bulk of SWME*2S resulted in contact angles reduction by 10.4° .This was calculated as the difference between the value obtained at the start of the apparent equilibrium and the end of the run. The results in this study were calculated from the apparent equilibrium time between 5 and 50 minutes.

The contact angle experiments were repeated a number of times to make sure that we have control on the variables which could affect the reading .It is also worth noting that the drops did not approach a common contact angle and will be addressed in the discussion section. The drop volume of MO(HA) deposited on the crystal was kept consistent to be around 10-15 μL.
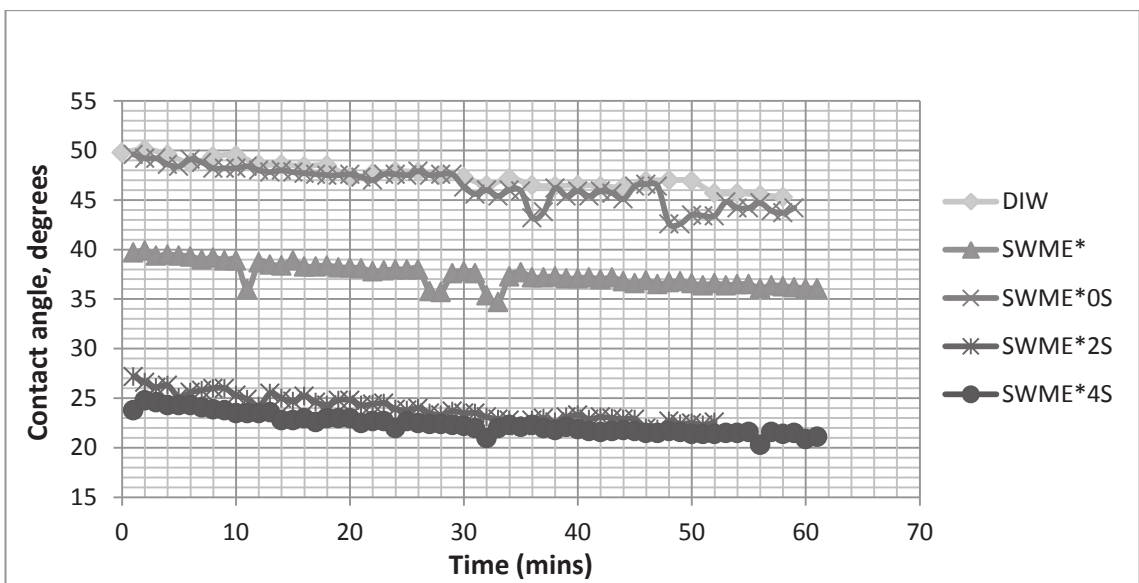
Figure 5 Effect of sulphate on the stability of contact angle for Calcite/MO(HA) and various brine systems
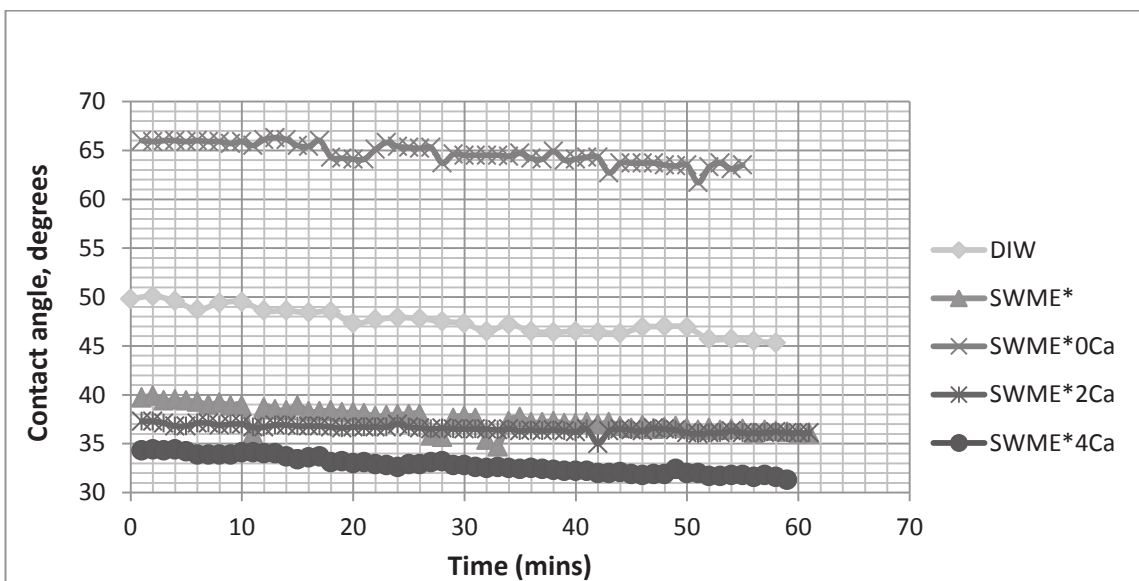
Figure 6 Effect of calcium on the stability of contact angle for Calcite/MO(HA) and various brine systems
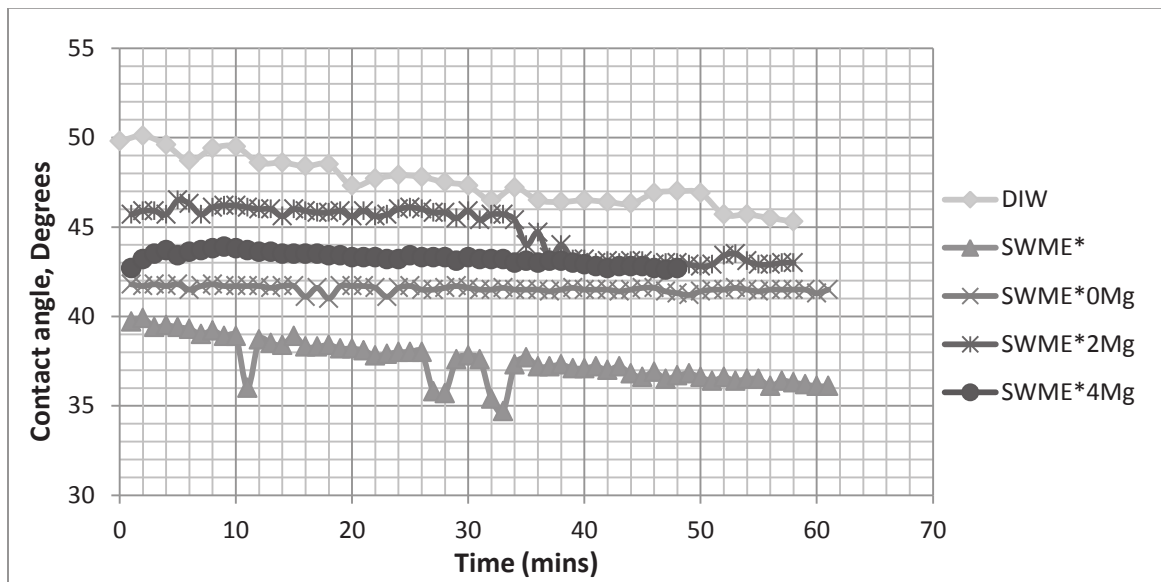
Figure 7 Effect of magnesium on the stability of contact angle for Calcite/MO(HA) and various brine systems

3.2.2 MO(SA) systems

For MO(SA) system, the effect of aging time (1 to 2 days) and TAN of model oil (TAN=2 and TAN=3) on the initial wettability of the calcite crystals (Figure 8) was studied first. It can be seen from Figure 8 that for aging time of 2 days, the difference in the contact angle is 0.7° for sample aged in MO(SA) of TAN of 2 and 3 respectively. The contact angles were measured with a droplet of DIW at air interface.

A TAN=2 was considered for this study for two reasons. Firstly a TAN=2 is considered a higher number of TAN and most of the oils found in Saudi Arabian have TAN of around 0.1. Secondly, MO(HA) being used in our earlier study was also of TAN=2.

For samples aged in MO(SA) system three different approaches were followed in the preparation of the calcite crystals for the contact angle measurements. The details of the three approaches are described in Figure 4. After inspecting the observed trends and the stability of the drop deposited on the calcite crystal for the three approaches, the first approach was adapted for the study of the samples aged in MO(SA). Likewise the effect of the sulphate, calcium and magnesium ions on the wettability of the calcite crystal and carbonate surface was studied. The contact angle measured at brine interface with captive bubble technique with a drop of MO(SA) was run over a period of 20 minutes and 10 minutes on the calcite crystal and carbonate surface. Two drops were released on each crystal surface. Initially when the drop was just released an increase was observed in the contact angle on the calcite crystal and carbonate surface. However the increase was reasonable enough for DSA (Drop Shape Analysis) software to capture the image and calculate the appropriate contact angle. After the observed time for the contact angle measurement of each surface as mentioned above, a more gradual increase occurred and the drop started spreading unequally from the left and right. For this system, the

equilibrium time and the change between the initial value and final value at the end of the experiment varies depending on the ion composition of the brines. Still to be consistent for a comparison purpose, all the experiments in this system for the two surfaces were run for the same period of time.

Again the contact angle experiments were repeated a number of times to make sure to have full control on the variables which could affect the reading. It is also worth noting that the drops did not approach a common contact angle and will be discussed later in the discussion part. The drop volume of MO(SA) deposited on the calcite crystal and carbonate rock sample was kept consistent to be around 15 and 10 µL. The contact angle for a given system was reported as the initial mean value of left and right contact angle measurements rounded to the nearest first decimal place.
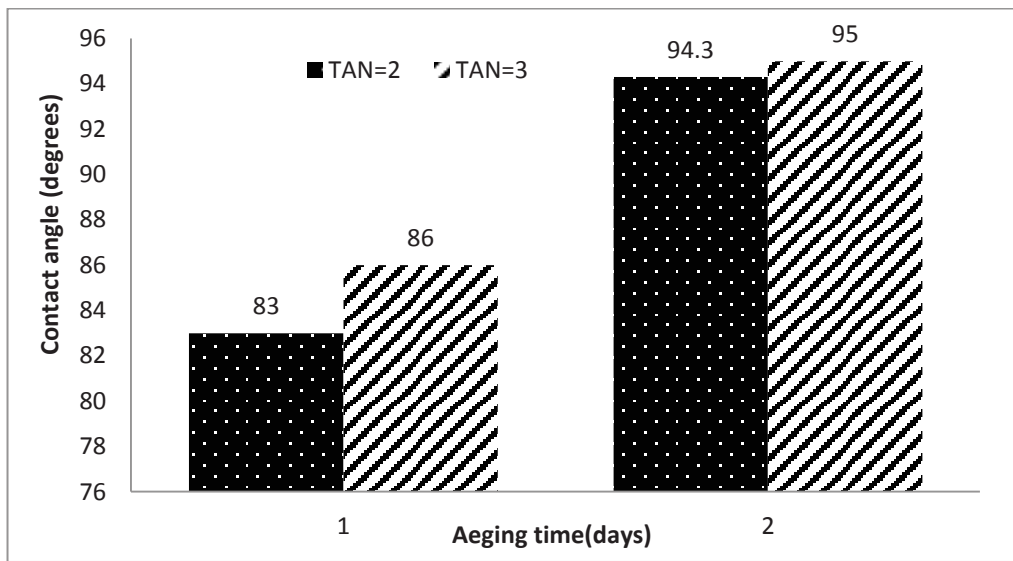
Figure 8 Effect of aging time and TAN for Calcite /MO(SA)

3.3 TAN measurement of model oil

A TAN=2 mg KOH/gm of model oil is used in this study for both short chain (HA) and long chain (SA) carboxylic acid.

After aging the sample, the TAN of the model oil (HA) was calculated using the following equation:

$$TAN = \frac{V \times N \times 56.1}{P}$$

Where

N=0.03664 mol/dm3 of KOH,

V= Volume of KOH used, and

P= density of model oil (0.86716 gms/ml).

The volume of KOH used to neutralize the acid is determined from an acid-base titration.

The following equipments were used in the titration:

- Burette (50 ml),

- Pipette (5 ml),

- pH indicator (phenolphthalein),

- Conical flask (25 ml),

- Titrant (a standard solution (KOH) of 0.03664mol/dm^3 concentration), and

- Titrand (solution of unknown concentration).

Before the start of each titration, the burette was rinsed with the standard solution. The pipette with the unknown solution, and the conical flask were rinsed with DIW. A known volume of the titrand was taken with the pipette and placed into the conical flask, along with a small amount of the indicator (phenolphthalein).The standard solution (KOH) was

then drained out of the burette, into the conical flask. The solution was let out of the burette until the indicator changes color and the initial and final value on the burette were recorded. The equivalence point of the reaction at which the indicator changes color is called the end point. Subtracting the initial volume from the final volume will yield the amount of titrant used to reach the endpoint. The experiment was repeated in order to minimize the experimental error.

3.4   pH measurement

The pH-measurements were performed by a ROSS combination pH electrode (0–14 pH, glass body, model no. 8102) connected to an OAKTON ACORN pH-meter (s. #:1292107). Sodium hydroxide and hydrochloric acid were used for adjusting to the desired pH value. The accuracy of the measured pH is reported to be about $\pm$ 0.05.

The initial pH of the brines before aging of the sample was recorded for our reference. The pH of the brines after aging the sample in brine for 5 days at 90°C was also measured. All the pH measurements were performed at room temperature.

3.5   Brine Analysis

3.5.1   Calcium and magnesium analysis

An Atomic Absorption Spectroscopy (AAS), ICE-3000 Reagent-free produced by Thermo Scientific, USA was used to analyze the ionic concentrations of Ca^{2+} and Mg^{2+}. In order to stay in the linear region (Figure 9 for Ca^{2+} and Figure 10 for Mg^{2+}), the effluent samples were diluted 1:200 (for Ca^{2+}) or 1:2000 (for Mg^{2+}) by DIW prior to the analysis, and the ion concentrations were calculated based on an external standards.
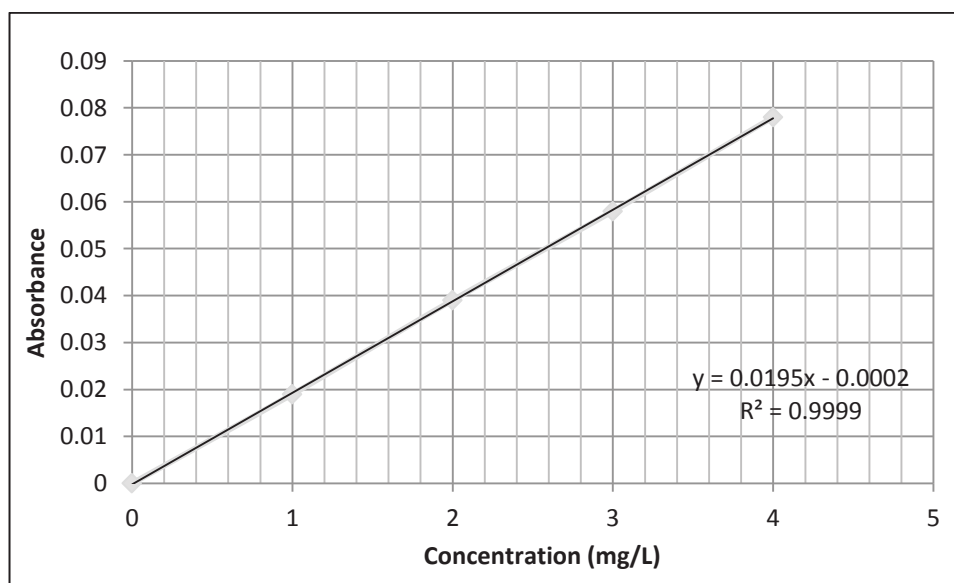
Figure 9 Calibration for Ca^{2+} ion
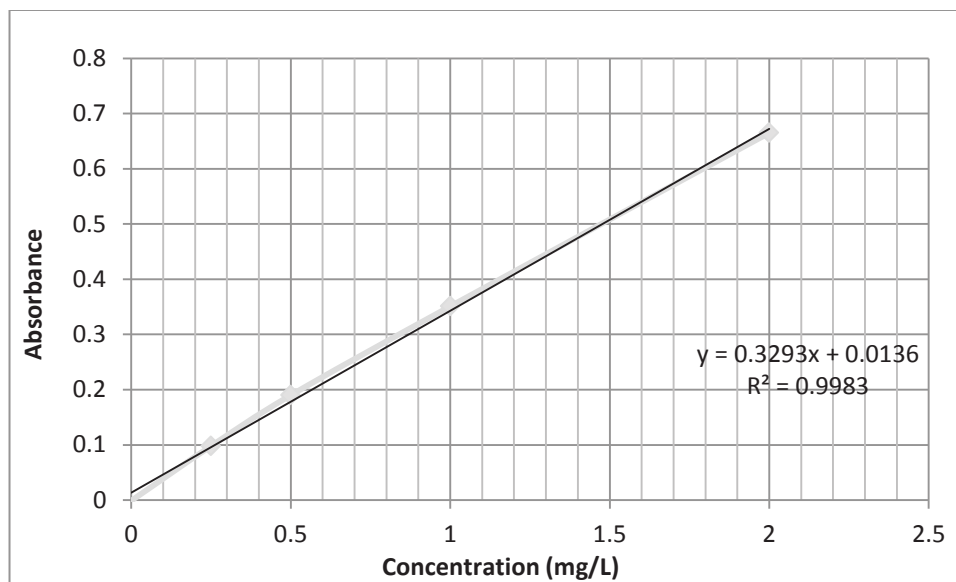
Figure 10 Calibration for Mg^{2+} ion

3.5.2 Sulphate Analysis

The sulfate concentration was determined by adding the exact sample volume to a Sulfate Cell Test Kit delivered by Merck. The sulfate ions in the sample were precipitated with barium ions:

$$Ba^{2+}{}_{(aq.)} + SO_4{}^{2-} \rightarrow BaSO_{4(s)}$$
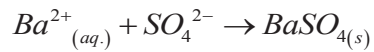
The resulting turbidity was measured at wavelength of 525nm by the Spectroquant NOVA60 photometer. The standard deviation of the procedure is $\pm$ 3.0 ppm $SO_4{}^{2-}$. The sulfate concentration was calculated using the external standard method.

3.6   Surface Characterization

3.6.1 SEM

Elemental composition of the calcite and carbonate samples was obtained by Energy Dispersive X-ray (EDX) carried out on a Tescan LYRA3 scanning electron microscope assembled in Czech Republic. An area of the rock sample with a typical grain size distribution was selected and the EDX analysis was applied at a low magnification, normally 400 times. The sample was analyzed for the elements C, O, Ca, Mg, S, Cl, Si and Na and the atomic% was calculated. EDX analyses were also performed on single rock grains of interest at a high magnification.

CHAPTER 4

Results and Discussion

4.1 Contact angles

The contact angle measurements were performed on two specific samples, referred to as calcite crystals and outcrop carbonate. In order to make the surface less water-wet or neutral wet, two model oils (polar components dissolved in a solvent) were used. The polar components used were mentioned in the materials section. In this section the effect of the chain length of the carboxylic acid is discussed.

4.1.1 Effect of short and long chain fatty acid

During the last two decades the importance of acidic components in the crude oil have been emphasized on the wettability modification towards oil-wet [5]. The contents of these acids are present in all crude oils [5]. In this study carboxylic acids are dissolved in toluene to establish neutral wet and to define the initial wettability of the calcite crystal and carbonate rocks.

Carboxylic acids consist of one or more carboxyl groups attached to a hydrocarbon chain of various length. The carboxyl group is polar, negatively charged, while the hydrocarbon chain is neutral. The acidic and basic characters of the mineral surfaces are indicated by the value of zero point of potential charge (pHzpc). The zpc for calcite is between pH 8 and 10, above this value the calcite surface is negatively charged and below that is

positively charged [76]. The surface of carbonates is positively charged below pH 8 to 9 [77]. Therefore carbonate surface is more likely to be basic, hence has affinity for acidic species. The negatively charged carboxyl groups adsorb onto the positively charged carbonate rock surface when the water-wetting film is displaced.

In order to study the effect of acid chain length on the surface wettability, contact angle through a droplet of water on calcite crystal surrounded by air were measured. This was done on the calcite crystal surface pretreated with two different carboxylic acids having different chain length and the results are presented in Figure 11. The measured contact angles of droplet of water on the calcite surface treated with the selected carboxylic acids shows that stearic acid is more-oil wet than heptanoic acid as compared to fresh calcite surface. The emerged trend sets well with the "Traube's rule" which states that the long chain fatty acid (stearic acid), strongly adsorbs onto the calcite surface as compared to the short chain fatty acid (heptanoic acid) which adsorbs on the calcite surface to a lesser extent, as indicated by contact angle measurements presented in Figure 11.
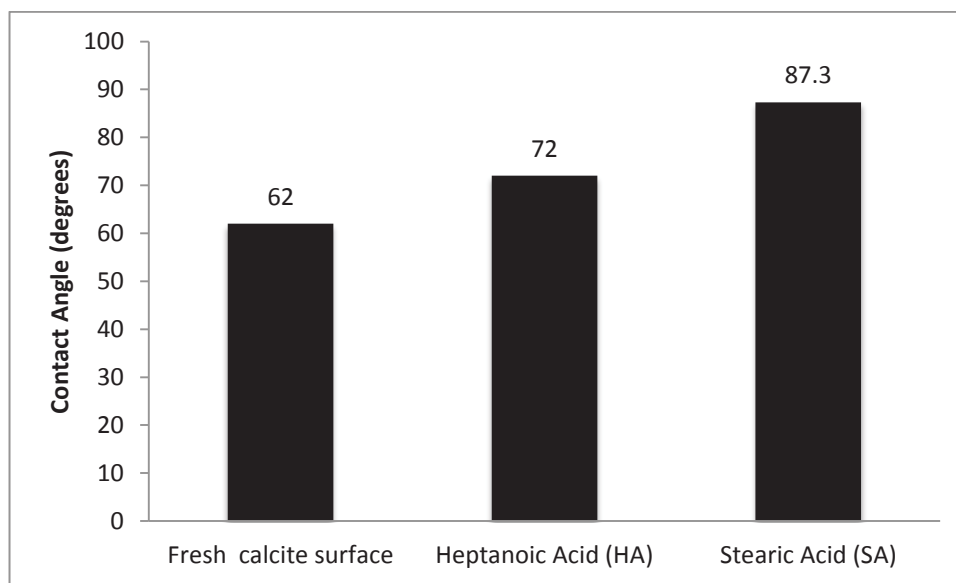
Figure 11 Effect of chain length of carboxylic acid on wettability of calcite measured by water at air interface T=23°C

The untreated calcite surface has the smallest contact angle for water, which is 62°. The contact angle decreases with time for the both heptanoic and stearic acid model oils. This may be because of trace amounts of the adsorbed carboxylic acid layer on the calcite being transferred from the treated surface to the water phase due to solubility effect. As this occurs, there is less carboxylic acid on the surface and so the contact angle gradually decreases until no more phase transfer occurs. This explanation is supported by the fact that the contact angle changes very little for the fresh calcite crystal.

Furthermore, these results indicate, as expected, that the degree of induced decrease in water-wetting increases as the carboxylic acid is more hydrophobic. For example, stearic acid (alkyl chain with 18 carbons) increases water contact angle more than the heptanoic acid (alkyl chain with only 7 carbons). It is recognized that such increase of water contact angle is caused by decrease of surface energy of calcite surface. Milter [46] illustrated the importance of carboxylic acids, by measuring the contact angle; a calcite crystal aged in the stearic acid dissolved in dodecane became oil-wet, while pure dodecane showed less alteration of wettability of the calcite surface towards oil-wet.

Rezaei Gomari [78] reported adsorption of acidic components onto calcite is higher for stearic acid as compared to oleic acid. Also by Anders study it's been shown clearly the importance of the chain length where stearic acid resulted in the highest contact angles (concentration was several orders of magnitude lower) than lauric acid [79].

As demonstrated in Fig. 11, an increase in contact angle on pure calcite was observed when heptanoic acid and stearic acid were used due to adsorption of polar components. Again, this suggests that polar components alter rock wettability to less water-wet and it is in agreement with capillary pressure, spontaneous imbibition and relative permeability work by Chukwudeme et. al [80].

Based on the results obtained from this study, we may conclude that the long chain fatty acids are the main reasons for wettability alteration of carbonate rocks toward oil-wet condition. To alter the oil-wet carbonates back to water-wet, the carboxylic acids must be desorbed from the rock surface.

4.1.2 Fluid–rock interaction

The calcite and carbonate samples modified with MO(HA) and MO(SA) was treated with brines. This was done in order to see the effect of the potential determining ions on desorbing the carboxylic group being adsorbed on the surface. The modified samples with model oil were treated with brines at 90°C. The ionic exchange is expected to take place in the form of dissolution, substitution, and precipitation. The following equation helps to understand the chemical reaction [81]:

Dissolution Reactions:

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{1}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \tag{2}$$

$$\tag{3}$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$

$$\tag{4}$$

$$H_2CO_3 \rightleftharpoons CO_{2(aq.)} + H_2O$$

$$\tag{5}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Substitution reactions: $\tag{6}$

$$CaCO_3(s) + Mg^{2+} \rightleftharpoons MgCO_3(s) + Ca^{2+}$$

Precipitation reactions

$$\tag{7}$$

$$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(s)$$

Ion pair formation

$$Ca^{2+} + SO_4^{2-} \xrightleftharpoons{} [Ca^{2+}...SO_4^{2-}]_{(aq.)} \tag{8}$$

$$Mg^{2+} + SO_4^{2-} \xrightleftharpoons{} [Mg^{2+}...SO_4^{2-}]_{(aq.)} \tag{9}$$
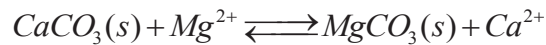
4.1.3 Effect of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions on the wettability alteration of the calcite surface to a more water-wet

Wettability alteration of a carbonate can depend on parameters like brine salinity and concentration of the potential ions in the brine.

One factor that could be important to the wettability reversal and imbibition performance of modified sea water is its ability to release the polar compounds from the carbonate surface. Presumably if these components are stripped away from the surface, then the carbonate would have the desired water-wet condition. This section discusses the effect of the potential ions concentration present in the brines on the wettability alteration of the calcite crystal modified with heptanoic acid and calcite crystal, carbonate surface modified with stearic acid.

4.1.4 MO(HA) system

This subsection presents a discussion of the effect of the salinity and SO_4^{2-}, Ca^{2+} and Mg^{2+} ions concentration present in brines on the wettability of the modified calcite crystals. The wettability measurement will be presented along with the change in the pH of the brines and the change in the ion concentrations of SO_4^{2-}, Ca^{2+} and Mg^{2+} ions.

The modified calcite crystal being treated with DIW for five days at 90°C will be used as a reference for comparison purpose. The contact angle measured at DIW interface for DIW/ MO(HA)/Calcite at equilibrium time is 45.3° (Figure 12).

The effect of the salinity on the wettability is studied by treating the modified calcite crystal with SWME and SWME*. The salinity of SWME is approximately 57000 ppm and SWME* (twice diluted) is roughly 28000 ppm. Hence the concentration of the ions in SWME* is half of that present in SWME. During the contact angle experiment, the MO(HA) droplet doesn't stick to the surface being treated with SWME and the surface is completely non-wetting (completely water-wet). The contact angle measured at brine interface for SWME*/MO(HA)/Calcite at equilibrium time is 36.1° (Figure 12). Hence as obvious, the decrease in the concentration of the potential ions increases the contact angle from completely water-wet surface to 36.1°. However when compared to DIW, SWME and SWME* have changed the calcite crystal towards more water-wet.

The effect of SO_4^{2-}, Ca^{2+} and Mg^{2+} ions present in the brines is also studied and the brines used are presented in Table 4, 5 and 6. The lowest selected concentrations for the three ions in SWME*2S, SWME*2Ca and SWME*2Mg represent their corresponding concentrations in seawater, while the higher concentrations in SWME*4S, SWME*4Ca and SWME*4Mg is twice the concentration of the three ions present in sea water for comparison purposes.

The equilibrium value for the effect of sulphate brines is shown in Figure 12. It can be seen from this figure the importance of SO_4^{2-} ions on the wettability of the calcite crystal. The first observation is that the lowest contact angle is obtained when brine SWME*2S is used. When the concentration of SO_4^{2-} was doubled there was no further change in the measured contact angle. For brines SWME*2S and SWME*4S the contact angle measured were 22.6° and 21.1° respectively. The second observation is that removing sulphate from the brine SWME*0S resulted in a contact angle of 44.2° which is close to the DIW (45.3°).

The first observation for the effect of sulphate brines is perhaps related to the affinity of SO_4^{2-} brines to adsorb onto the calcite surface which was shown to alter the calcite surface [66]. Rezaei Gomari [66] showed that alteration of the wettability is not only due to possible reduction of the available active sites on the calcite surfaces but could also be due to a displacement process of various preadsorbed carboxylate ions of the tested fatty acids including heptanoic acid, which is in agreement with the obtained results in this study.

Figure 13 shows the effect of calcium ions in the presence of SO_4^{2-} and Mg^{2+} ions on wettability of calcite. The first observation is that the lowest contact angle is obtained for calcium brines when SWME*4Ca is used and it is a function of Ca^{2+} ions concentrations (tested here are two concentrations for each ion: SWME*2Ca and SWME*4Ca). For brine SWME*2Ca and SWME*4Ca the contact angles measured are 36.1° and 31.3° respectively. Hence the brine SWME*4Ca resulted in a more water-wet surface. The second observation is that with no calcium in brine (SWME*0Ca), contact angle increases to 63.5°. The contact angle measured for brine without calcium (SWME*0Ca) is even higher than the reference DIW (45.3°).
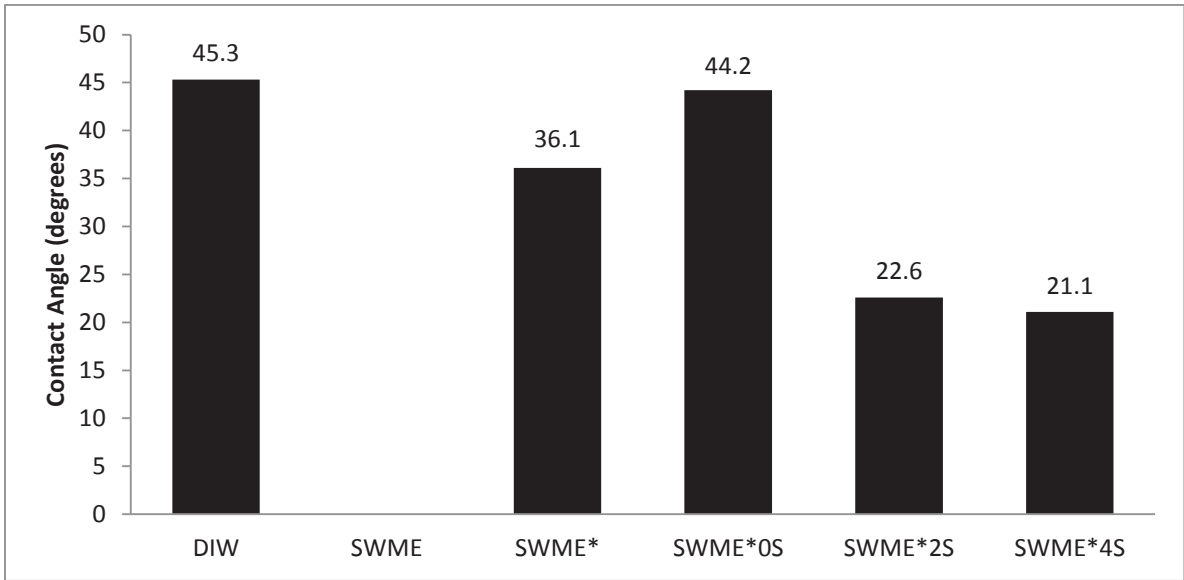
Figure 12 Effect of sulphate on contact angle for Calcite/ MO(HA) and various brines systems
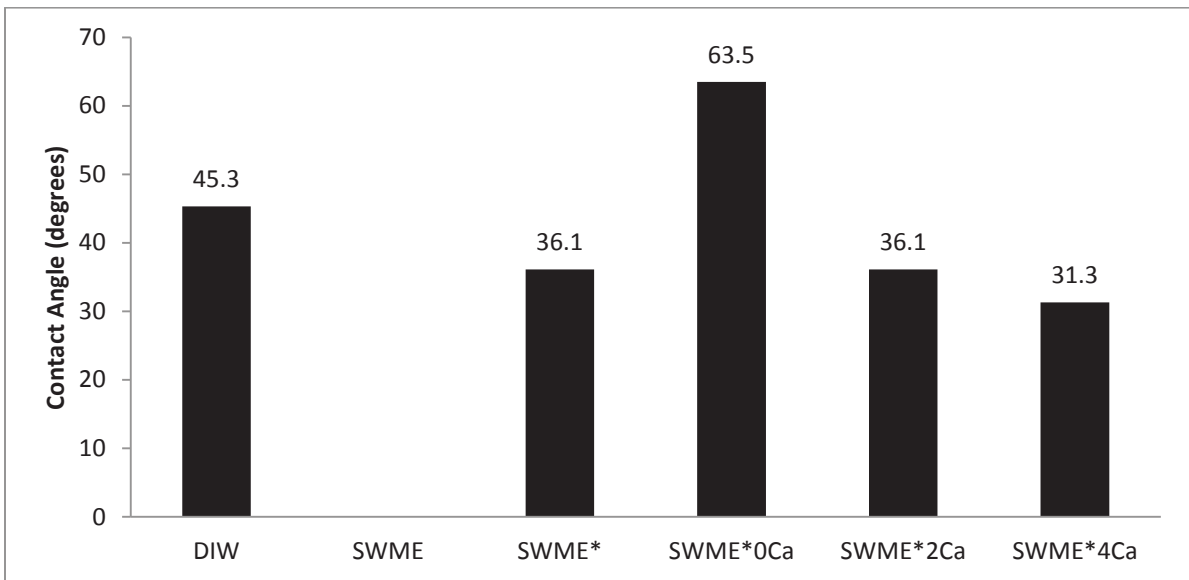

Figure 13 Effect of calcium on contact angle for Calcite/ MO(HA) and various brines systems

Figure 14 shows the effect of Mg^{2+} in the presence of SO_4^{2-} and Ca^{2+}. It can be seen from this figure that the effect of magnesium ions is insignificant and has no effect on the wettability of the calcite crystal for this system. In the absence of the magnesium ions for SWME*0Mg and with high concentration of magnesium ions in SWME*4Mg, the contact angles measured were 41.5° and 42.7° respectively.

Table 7 presents a summary of all contact angles measured for the MO(HA)/Calcite with the different brines at T=23°C. Table 7 shows that the calcite samples treated with Arabian Gulf sea water (SWME) possess the lowest measured contact angles (completely water-wet) followed by the sulphate brine SWME*4S (21.1°), calcium brine SWME*4Ca (31.3°) and DIW (45.3°) .The result for the Arabian Gulf sea water is in line with the recently emerged research trend on chalk reservoir that injecting seawater rather than any other type of water will improve oil recovery [14,15,18, 19].

Our results are also in line with the observations being made by Gupta [82]. The sulfate ions and calcium ions are found to change the contact angle to water-wet conditions. Higher sulfate concentration with constant Ca^{2+} and Mg^{2+} concentration causes the highest degree of wettability alteration. From our study, SWME*4S gives the lowest contact angle (21.1°) as compared to the magnesium and calcium brines.

For the effect of calcium ions, Tweheyo [58] made similar observations on chalk surface. He showed that calcium ions can alter the wettability in the presence of sulfate ions at T=130°C. From our study, the contact angle measured for SWME*4Ca is 31.3° as compared to SWME*0Ca (63.5°) at T=23°C.

Figure 15 shows images for wettability measurements using DIW, Arabian Gulf seawater, and modified forms of Arabian Gulf seawater with varying concentrations of the potential ions. All contact angles were monitored over a period of approximately 1 hour to make

51

sure that the system is in static equilibrium. The contact angle images for the SWME cannot be seen in Figure 15 since the treated surface was completely non-wetting. This confirmed and validated that the ions concentration and salinity of injected Arabian Gulf seawater has a significant impact on rock wettability, and ultimately has the potential to provide additional oil recovery.
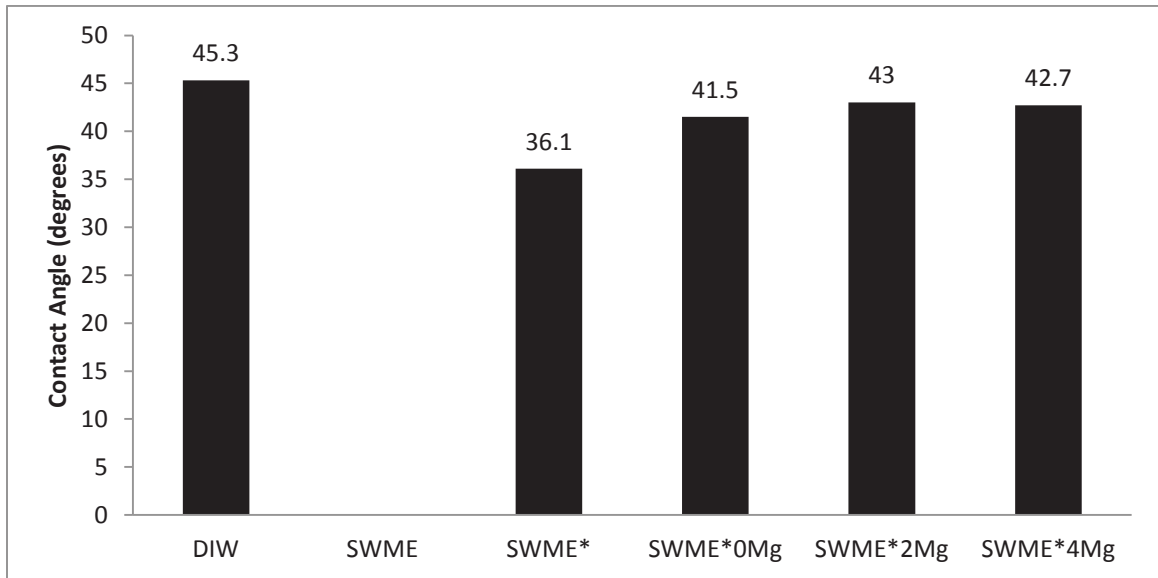
Figure 14 Effect of magnesium on contact angle for Calcite/ MO(HA) and various brines systems

Table 7 Summary of contact angles of Brine/MO(HA)/Calcite

	MO(HA)-Drop 1		MO(HA)-Drop 2	
	initial	after 50 mins	initial	after 50 mins
DIW	49.8	45.3	48.5	45.1
SWME	Completely water-wet			
SWME*	39.7	36.1	18.8	16.8
SWME*0S	49.6	44.2	51	48.7
SWME*2S	27.2	22.6	32.8	30.1
SWME*4S	23.8	21.1	28.2	27.1
SWME*0Ca	66	63.5	72.6	68.6
SWME*2Ca	37.3	36.1	38	38.1
SWME*4Ca	34.3	31.3	35.5	32.7
SWME*0Mg	41.8	41.5	42.8	43.5
SWME*2Mg	45.7	43	46.4	46.6
SWME*4Mg	42.7	42.7	42	40.5

| At t=0 | At t=60 mins |
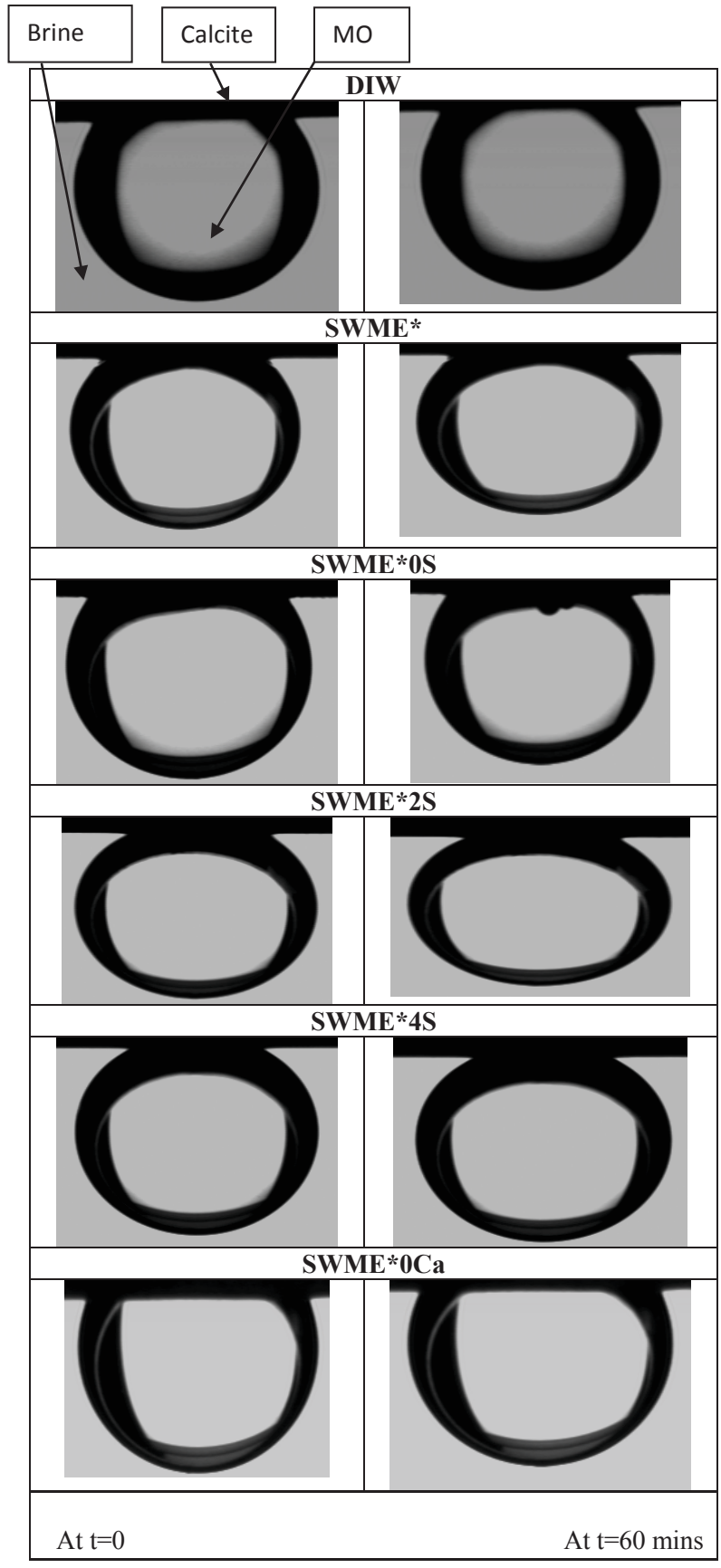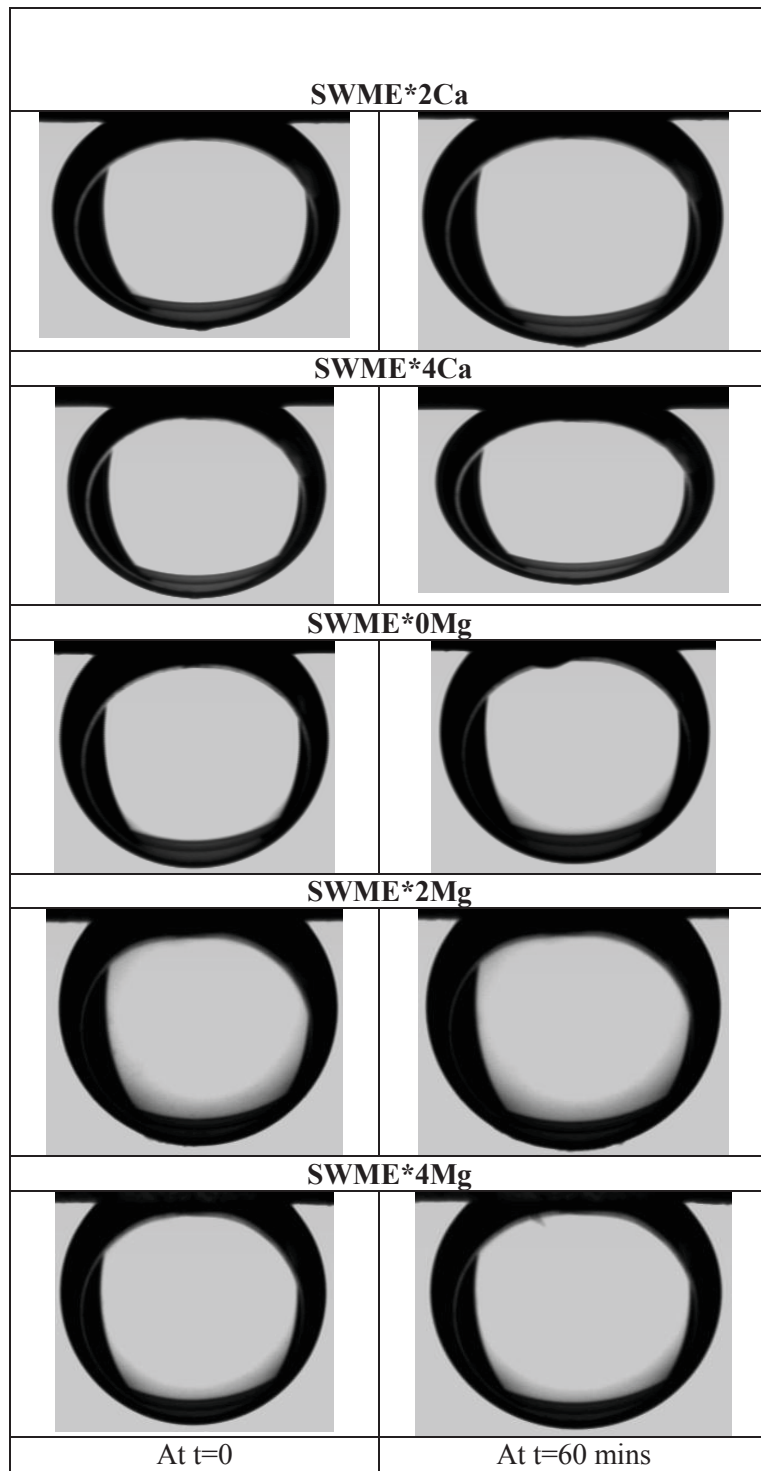
Figure 15 Contact angle images for Brines/MO(HA)/Calcite at T=23°C.

4.1.5 MO(SA)/Calcite and Carbonate system

During the recent last years, many researchers have focused on the wettability alteration of carbonate rock towards more water-wet using different techniques [9, 61, 70]. Among these different techniques, sea water injection has shown very promising results with a slight modification of the sea water composition. Arabian Gulf seawater discussed in the previous sections for MO(HA)/Calcite with different brine systems altered rock wettability towards more water-wet.

In this subsection the effect of the salinity, sulphate, calcium and magnesium ions concentration in brines on the wettability of the modified calcite crystals and outcrop carbonate rocks aged in long chain acid (stearic acid) will be presented and discussed. The adsorption of dissociated acid species onto the surface results in wetting alteration of the calcite surface and the change in wettability is indicated by the change in contact angle. The lowest selected concentrations for the three ions in SWME* represent their corresponding concentrations in Arabian Gulf seawater with twice diluted, while the high ions concentrations in SWME*4S, SWME*4Ca and SWME*4Mg are twice the concentrations of the three ions present in Arabian Gulf seawater for comparison reasons. For the MO(SA) system, three approaches have been followed for sample preparation of calcite crystal as illustrated in Figure 4. The three approaches differ from each other at the sample preparation level. For the first approach, initially the samples were saturated in highly saline brine (FW) for 2 hours. In the second approach, there was no initial saturation in FW. In Approach 3, the prewetted samples in FW and aged in MO(SA) were rinsed with toluene for 2 seconds. The wettability of the calcite crystals was checked before and after the treatment with brine at air interface with a drop of DIW and second

56

drop of brine. The drop of DIW and the different brine were blown off with air and the samples were dried with air. The contact angle was then measured with a captive bubble technique with a drop of MO(SA) and bulk of brine.

The contact angles measured at air interface with a droplet of DIW for Approach 1 are shown in figure 16, for Approach 2 in figure 17 and for Approach 3 in figure 18 respectively. The average contact angles for the sample aged in MO(SA) only (before treatement) is 91.4° (Figure 16) , 92.2° (Figure 17) and 51.5° (Figure 18). Hence the surface is changed from less water wet to neutral wet for the first and second approach. In Approach 3, the effect of rinsing with toluene is quite evident from the average value of the contact angle as it washed away the carboxylic acid being adsorbed on the surface. The contact angles after the treatment of the samples with the respective brines are also shown in the same figures. From Figure 16 and 17, it can be seen that the effect of ions is obvious as they alter the surface to more water-wet as compared to the reference DIW (52.8°) for Approach 1 and DIW (84.2°) for Approach 2. However no obvious trend was seen at air interface with a droplet of DIW for both Approach 1 and Approach 2.

In Figure 19, the contact angles measured with a drop of brine at air interface for calcite crystals are shown. The contact angles before treatment with brine and after treatment are both shown in the same figure. It is evident that the surface changed towards more water-wet after treatment. For the samples aged in MO(SA) only the contact angle measured with the brine SWME* is almost the same compared to SWME. After the treatment the contact angles with brine SWME is observed to be greater than SWME*. Hence the trend emerged before treatment is not the same after treatment at the air interface.

For Approach 1, the same calcite crystals used for wettability measurement at air interface were dried and contact angle was measured with a drop of MO(SA) and bulk of

brine. The results will be discussed later in this subsection with the effect of SO_4^{2-} and Ca^{2+} ions.

For Approach 2, the contact angles were not measured at brine interface with a drop of MO(SA) due to the instability of the drop at the calcite surface.

The results (Figure 16 and 17) are shifted with no overlap in results from Approach 1 (FW) and Approach 2 (no-FW) experiments. Aging the crystals in FW clearly had a small effect in reducing the contact angle significantly. The layer of deposited salts from FW may reduce the ability of the carboxylic acids to adsorb onto the calcite surface.

Figure 16 Effect of magnesium on contact angle for modified Calcite/MO(SA) –drop of DIW at air interface (Approach 1)

Figure 17 Effect of magnesium on contact angle for modified Calcite/MO(SA) –drop of DIW at air interface (Approach 2)

Figure 18 Effect of magnesium on contact angle for modified Calcite/MO(SA) –drop of DIW at air interface (Approach 3)

Figure 19 Effect of magnesium on contact angle for modified Calcite/MO(SA) –drop of brine at air interface (Approach 1)

The results for Approach 3 at air interface with a droplet of DIW are shown in Figure 18 and with a drop of brine are shown in Figure 20. For both the drop of DIW and brine at air interface for Approach 3, it became difficult to measure the contact angle for the treated calcite when it reached below 12° and hence the error in the measurement was recorded to be higher. Therefore only two concentrations of magnesium brines were used in the third approach were SWME* and SWME*2Mg. The same calcite crystals were used to measure the contact angle in a bulk of brine with a drop of MO(SA). In Figure 21, the trend obtained for the third approach is unlike what we have seen in our previous study. The lowest contact angle was measured with the calcite crystal aged in DIW and highest for the brine SWME*. The emerged trend obtained in Figure 21 for Approach 3 was ignored in this study. The effect of rinsing with toluene has greatly reduced the effect of polar compounds in the third approach. Also brines are generally believed to be a better wettability modifier than DIW. However in Approach 3, DIW appeared to be a better wettability modifier compared to SWME* as can be seen from the contact angle measurement (Figure 20).

The first approach (FW saturation) was adapted for the rest of the study carried out for MO(SA) system. The decision was based on the trends observed, stability of the drop on the surface and consistency of the results obtained from the three approaches for the effect of the magnesium ions concentration on the wettability alteration of modified calcite crystals.
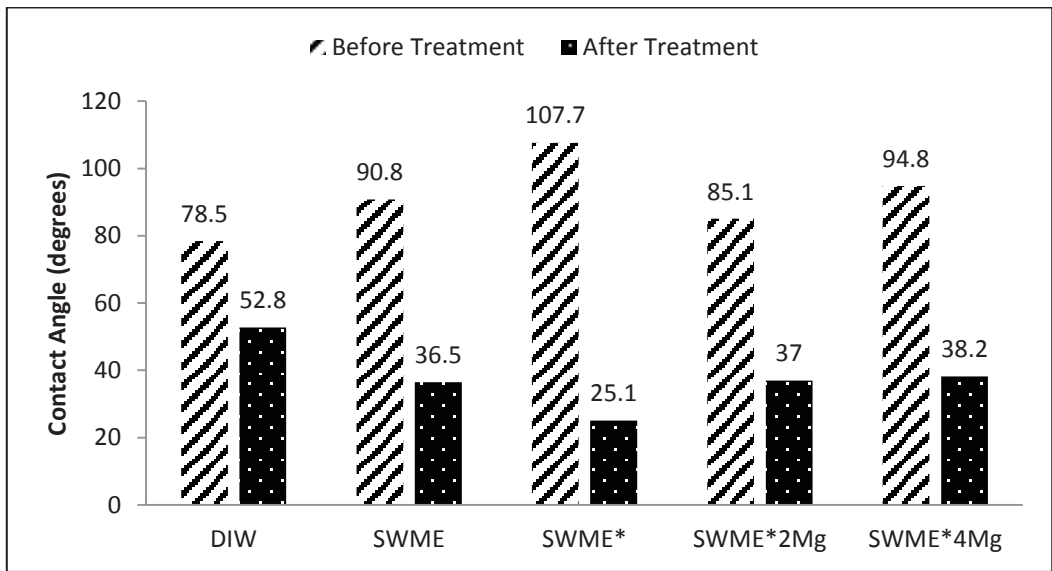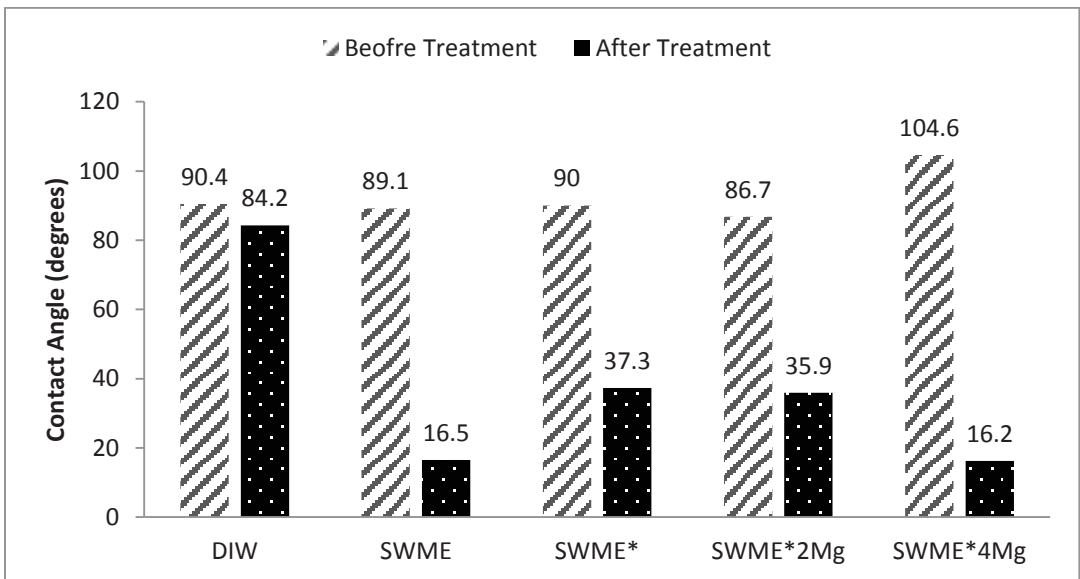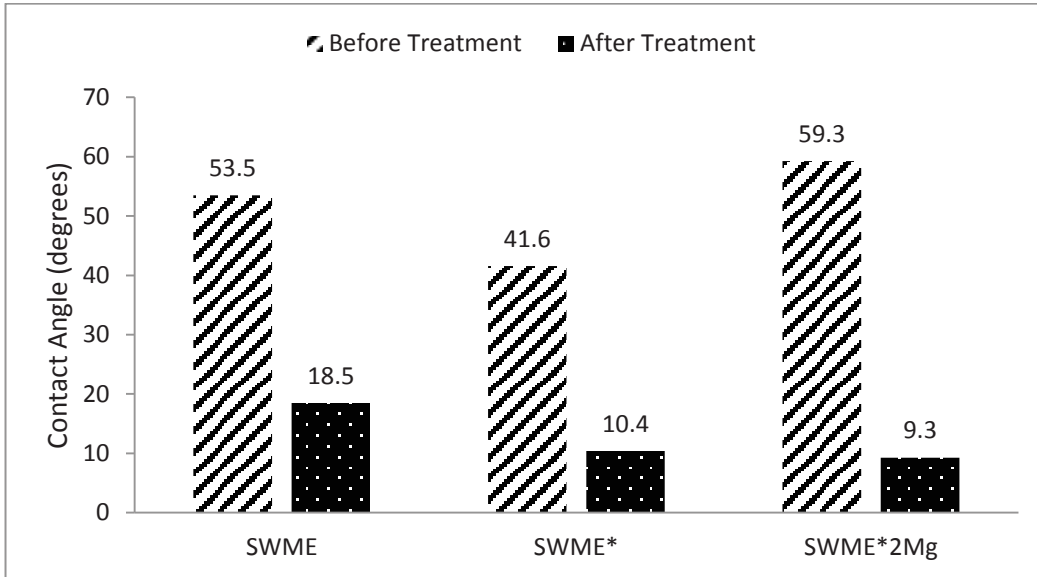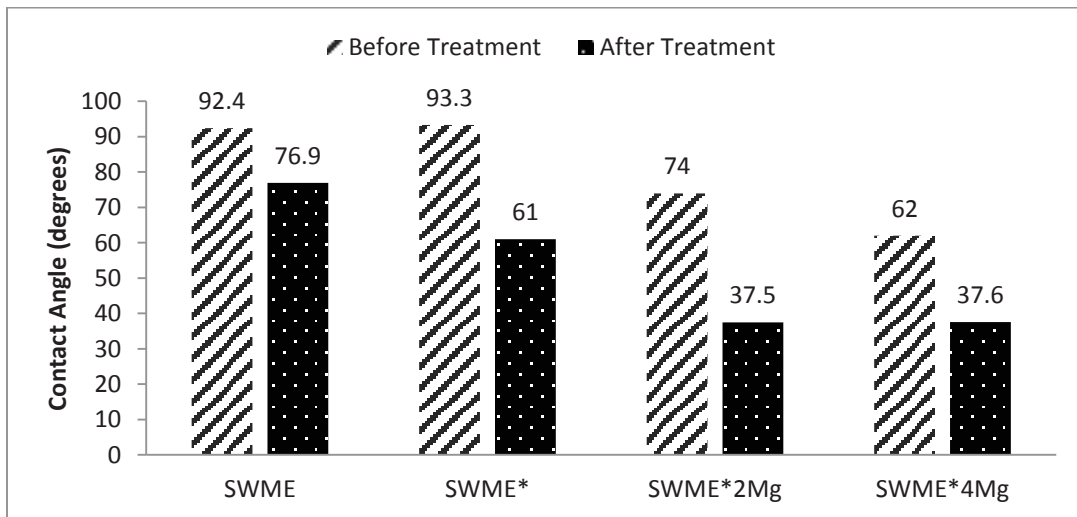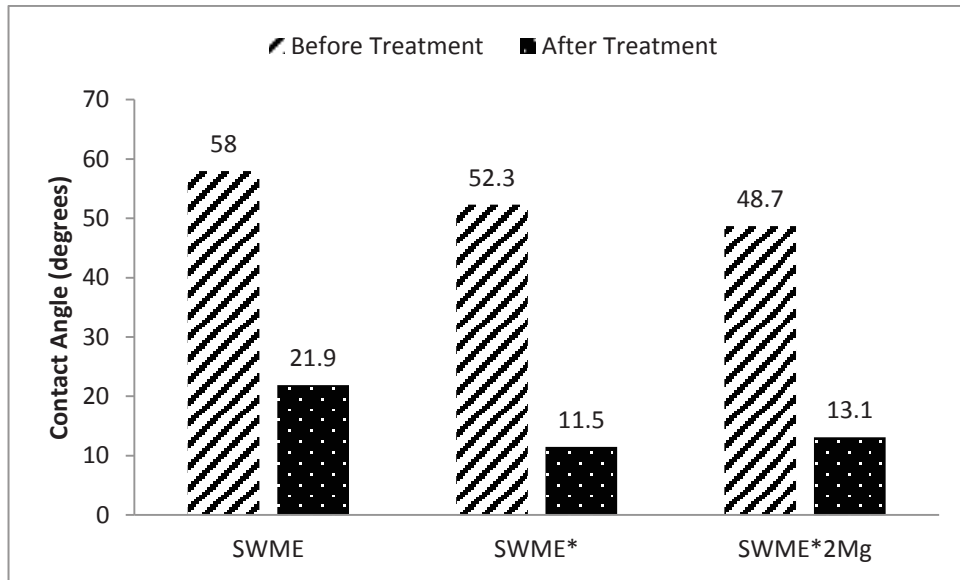
Figure 20 Effect of magnesium on contact angle for modified Calcite/MO(SA) –drop of brine at air interface (Approach 3)
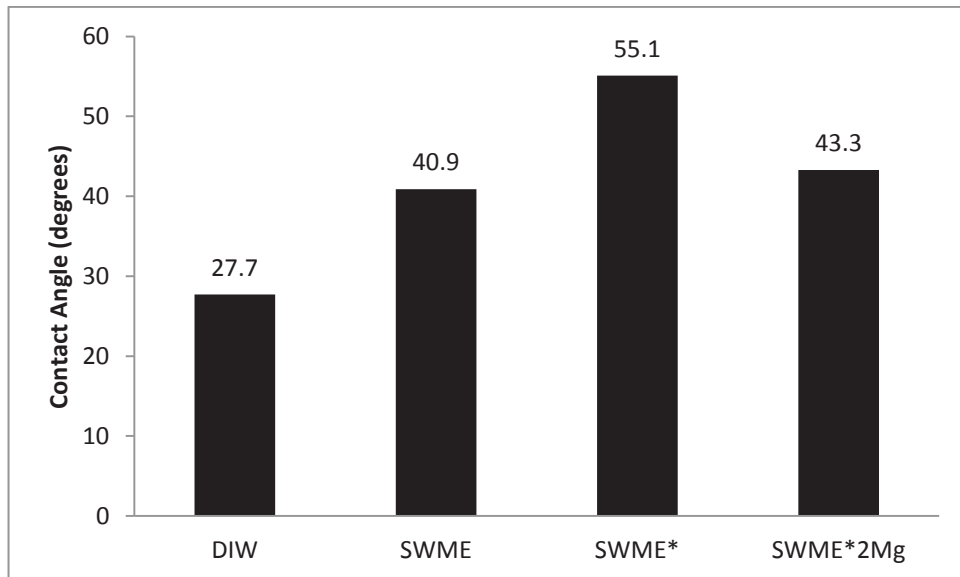

Figure 21 Effect of magnesium on contact angle for Calcite/MO(SA) and various brines systems (Approach 3)

Unlike calcite crystal, the wettability of the carbonate rock was checked before and after the treatment with brine at air interface with a second drop of FW. The rest of the measurements followed the same procedure as on calcite crystal.

The average contact angle at air interface for the sample aged in MO(SA) only is 88.7° with a drop of DIW and 94.8° with a drop of FW. Hence the surface is changed from less water wet to neutral-wet as can be seen from the contact angles measurement presented in Figure 22, 24 and 26 with a droplet of DIW and Figure 23, 25 and 27 with a droplet of FW.

The contact angles measured for the effect of sulphate and calcium brines at air interface with a drop of DIW are shown in Figure 22 and 24 and with a drop of FW in Figure 23 and 25 respectively. The contact angles measured with a drop of FW to study the effect of sulphate and calcium ion observed to have almost no change in the wettability of the carbonate surface treated with SWME*2S (Figure 23) and the surface turned towards oil-wet after the treatment with SWME*2Ca (Figure 25). Also, there is no consistent trend seen for the effect of sulphate and calcium ions concentration on the wettability of the carbonate surface measured at air interface.

The contact angles measured for the effect of brines containing magnesium at air interface with a drop of DIW are shown in Figure 26 and with a drop of FW in Figure 27. From Figure 26, it is seen that surface turned towards more water-wet with increasing the concentration of the magnesium ion which indicates that magnesium is a potential ion for this system. The contact angles measured for the brine SWME*2Mg and SWME*4Mg is 71.2° and 27.9° respectively. Hence twice the concentration of magnesium ion concentration in the Arabian Gulf Seawater in SWME*4Mg brings a greater change in

the wettability (Figure 26).However with a drop of FW at air interface, the same trend is not observed (Figure 27).

It was observed that a droplet of FW resulted in higher contact angles at air interface as compared with a droplet of DIW presented in Figs. 22 to 27. Brines are generally better wettability modifiers than DIW, particularly dependent on concentration of SO_4^{2-} ions together with Ca^{2+} or Mg^{2+}ions, but the effect decreases with decreasing temperature [38,65]. The low concentration of SO_4^{2-} in the FW (250 ppm) can be one of the reasons for the FW to give higher contact angles as compared to DIW.

Figure 22 Effect of sulphate on contact angle for modified Carbonate/MO(SA) –drop of DIW at air interface

Figure 23 Effect of sulphate on contact angle for modified Carbonate/MO(SA) –drop of FW at air interface

Figure 24 Effect of calcium on contact angle for modified Carbonate/MO(SA) –drop of DIW at air interface

Figure 25 Effect of calcium on contact angle for modified Carbonate/MO(SA) –drop of FW at air interface
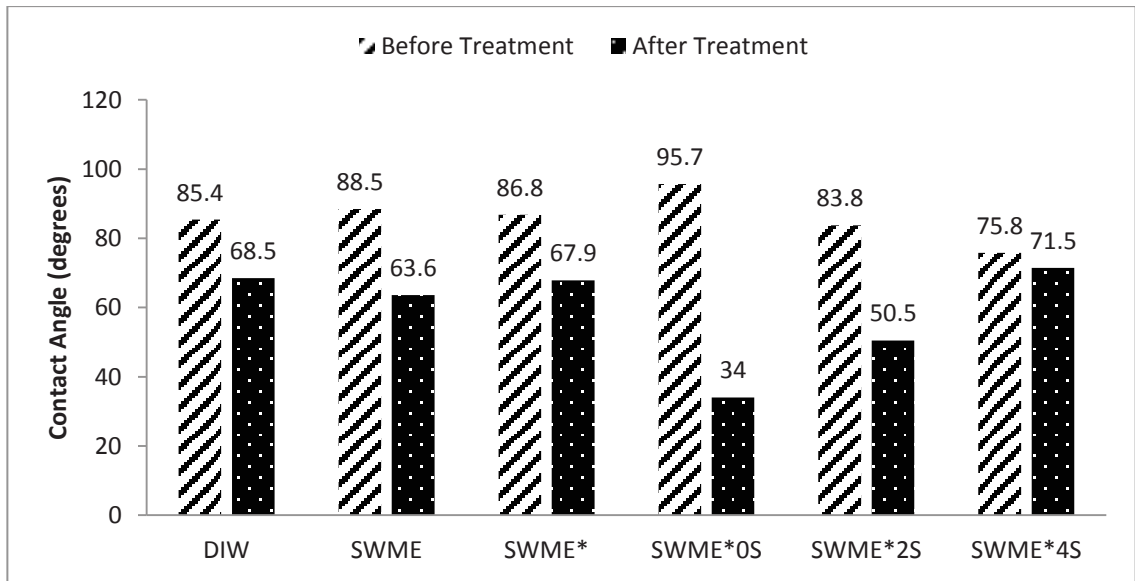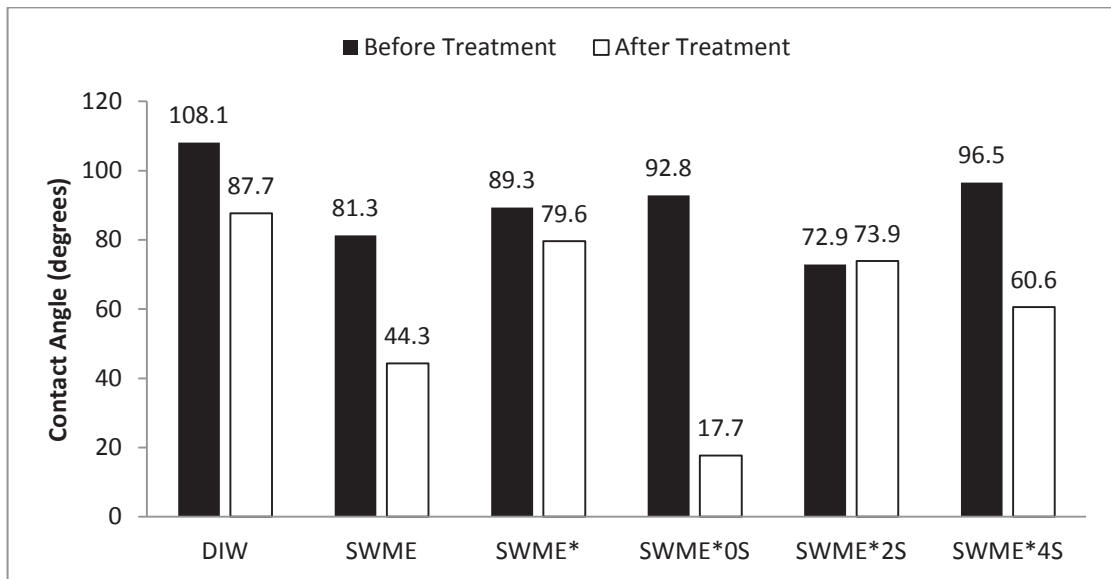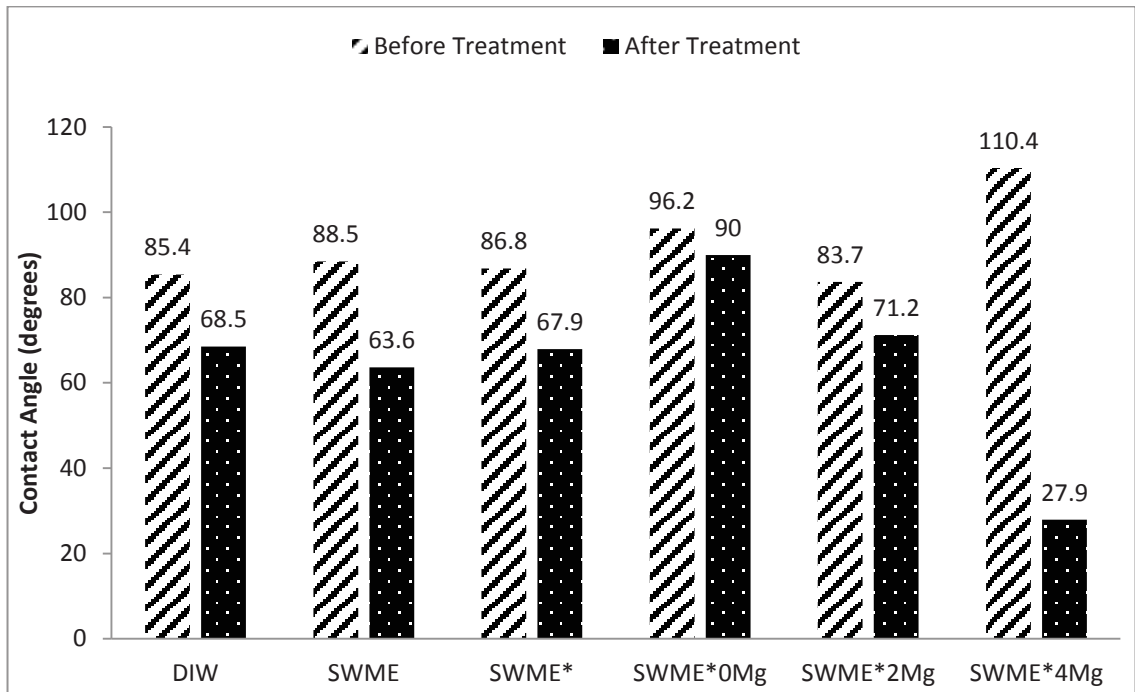
Figure 26 Effect of magnesium on contact angle for modified Carbonate/MO(SA) –drop of DIW at air interface
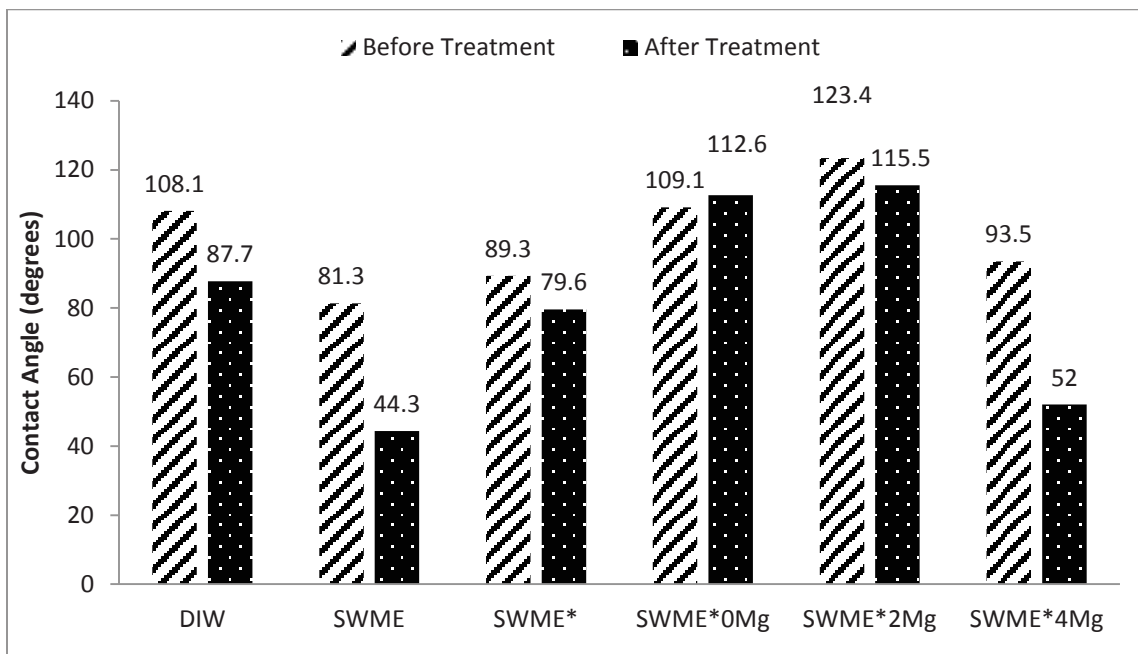
Figure 27 Effect of magnesium on contact angle for modified Carbonate/MO(SA) –drop of FW at air interface
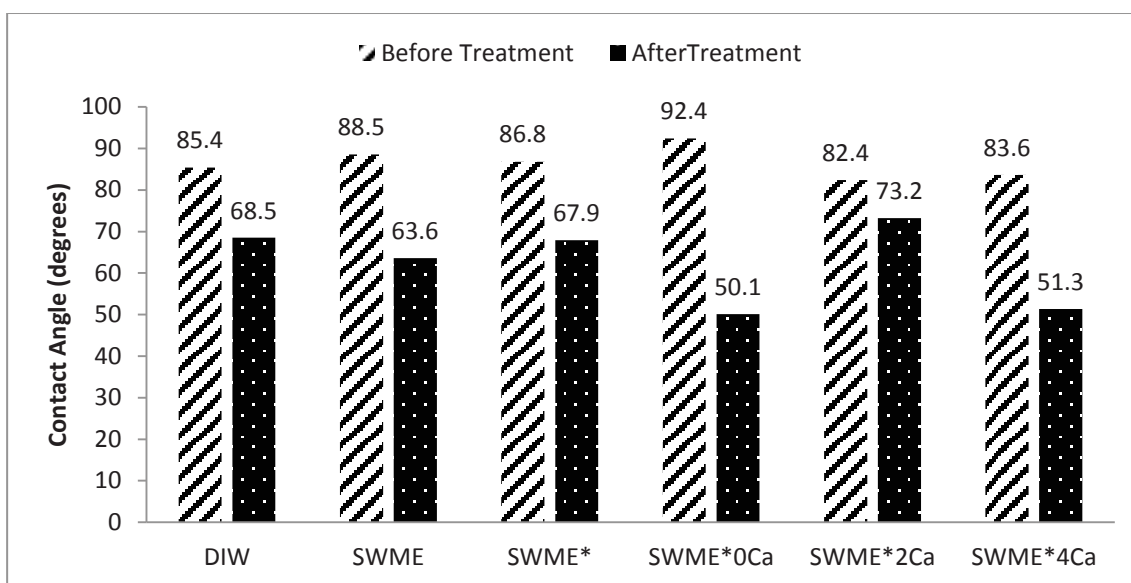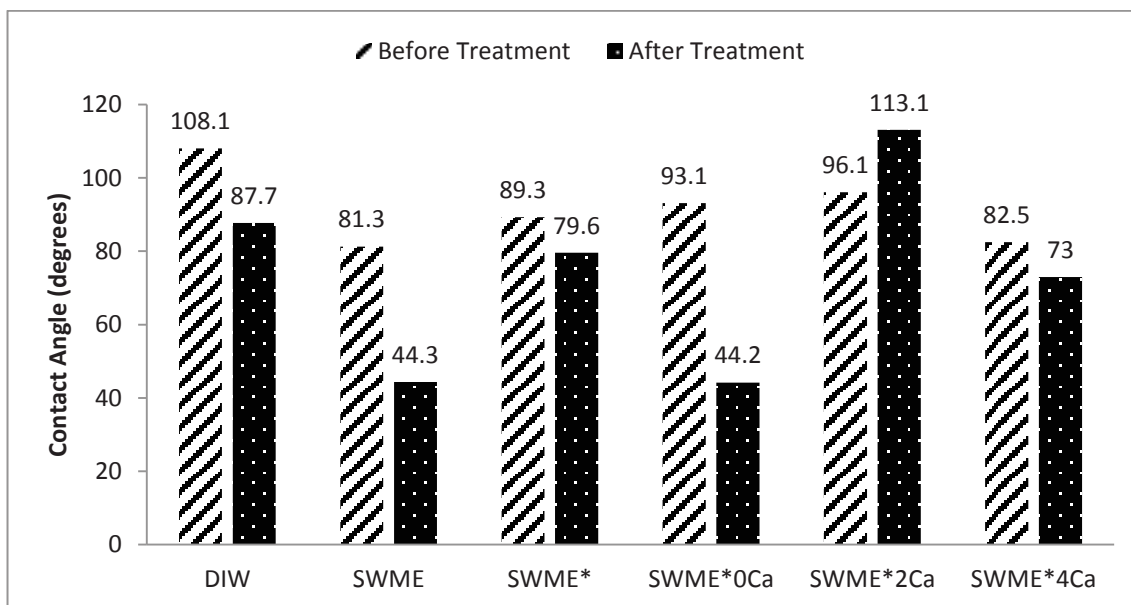
For each sample in MO(SA) system the contact angle was also measured with a drop of MO(SA) in bulk of brine. This last set of measurement of contact angle for MO(SA) on calcite crystal and carbonate rock will be discussed in light of the change in the pH and the change in the ion concentrations for SO_4^{2-}, Ca^{2+} and Mg^{2+} in brine.

In all our comparisons the reference measurement is the modified sample being treated with DIW. The contact angle measured at DIW interface for DIW/MO(SA)/Calcite and DIW/MO(SA)/Carbonate at equilibrium time is 46.2° and 35° (Figure 28).

For the salinity effect, the sample was treated with SWME and SWME*. The salinity of SWME is approximately 57000 ppm and SWME* is twice diluted with roughly 28000 ppm. Hence the concentration of the ions in SWME* is half of that present in SWME. Unlike for carbonate reservoirs, the effect of low-salinity for sandstone reservoirs has been associated with wettability alteration due to the presence of clay minerals towards water-wet [83,84]. Therefore, reported studies have excluded the potential of diluting seawater for carbonate reservoirs due to lack of clay minerals [73, 84]. From Figure 28, the effect of dilution is evident. The contact angles measured for treated calcite and carbonate rock with SWME and SWME* at brine interface with a drop of MO(SA) are 25°,47.9° and 21° and 36.9° respectively. An increase in the contact angle was observed with twice diluted sea water brine SWME* due to the decrease in the concentration of the ions. In short dilution of Arabian Gulf sea water makes the surface less water-wet.

Our results for dilution effect of Arabian Gulf sea water are in line with the emerged research trend stating that injecting North seawater rather than any other type of water will improve oil recovery from chalk reservoirs [2,14,15,18,19]. This effect is attributed to the reactivity of key seawater ions (SO_4^{2-}, Ca^{2+} and Mg^{2+}) that has the capability to

change rock surface charges, release adsorbed carboxylic oil component from the rock surface, alter rock wettability, and eventually improve oil recovery.

Fathi et. al [71] demonstrated through spontaneous-imbibition tests using crude oil with AN=1.90, sulfate-free formation water, and chalk core samples characterized by very low permeability of 1 to 3 md and high porosity of 40 to 45% that diluting seawater will decrease oil recovery.

Although the past work has been done on chalk samples and unlike our study which is being carried on calcite crystal and carbonate rock, the same trend is observed for the effect of dilution on both of the lithologies.

From the Figure 28, the importance of SO_4^{2-} ions concentration in brines on the wettability alteration of the calcite crystal and carbonate rock can be observed. The first observation is that the lowest contact angle is obtained with brine SWME*2S on calcite crystal and SWME*4S on carbonate rock. However for calcite crystal, the wettability is not a linear function of SO_4^{2-} ions concentrations (tested here are two concentrations for each ion: SWME*2S and SWME*4S). The contact angles measured on calcite crystal are 26.2° and 36.2° and 34.7° and 20.8° on carbonate rocks for the brines SWME*2S and SWME*4S respectively. Therefore for the calcite crystal only the change in the contact angle is towards less water-wet when the concentration of the sulphate is increased from 4450 ppm to 8900 ppm. The second observation is that removing sulphate from the brine SWME*0S resulted in contact angle of 32.3° and 42.7° for calcite crystal and carbonate rock respectively.

The presence of sulfate not only can decrease the amount of fatty acid but also makes the treated calcite more hydrophilic. In contrast to SO_4^{2-}, which shows a significant effect on desorption of SA, hence on wettability of calcite, DIW has minor effect.

AlOtaibi et. al [85] demonstrated the effect of sulphate ion on the wettability with three sulphate ion concentration (3560 ppm (equivalent concentration in Arabian Gulf seawater), 1780 ppm and 890 ppm) in Brine/West Texas Crude Oil/Calcite system. They observed the lowest contact angle at the 1780 ppm concentration of the sulphate ion carried out at 194°F and 2000 psi.

As compared to AlOtaibi study, the difference in the experimental conditions (room temperature and atmospheric pressure) and the different system (model oil) gives us a higher concentration of SO_4^{2-} ions to make the surface more water-wet.
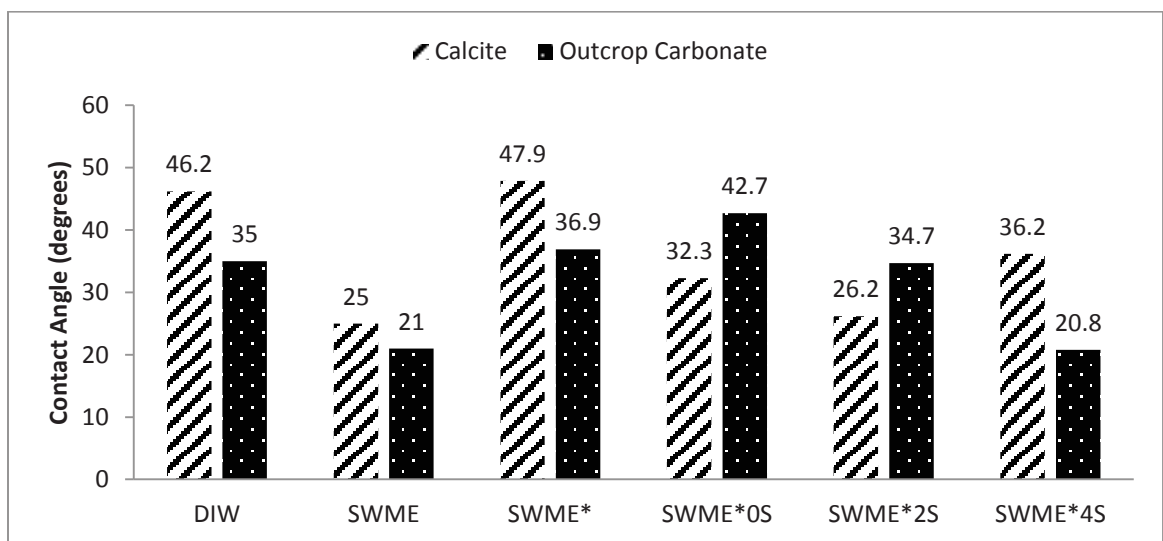
Figure 28 Effect of sulphate on contact angle of MO(SA) and various brines systems for calcite and carbonate

The effect of calcium ions in the presence of SO_4^{2-} and Mg^{2+} ions on wettability of calcite crystal and carbonate rock is shown in Figure 29. The first observation is that the lowest contact angle (36.8°) is obtained with brine SWME*4Ca on calcite crystal and SWME*0Ca on carbonate rock (21.3°). The wettability is dependant on Ca^{2+} ions concentrations (tested here two concentrations: SWME*2Ca and SWME*4Ca) for calcite crystal. The contact angles measured on calcite crystal are 39.9° and 36.8° , and 25.7° and 31.9° on carbonate rocks for brine SWME*2Ca and SWME*4Ca respectively. The second observation is that with no calcium ion (SWME*0Ca) the contact angle was 54.4° and it is even higher than the reference DIW (46.2°) for calcite crystal. However for the carbonate surface increasing calcium ion concentration turns the surface towards less water-wet.

The effect of magnesium ions on calcite surface is shown in Figure 30 in the presence of Ca^{2+} and SO_4^{2-}. The first observation is that the wettability of the calcite crystal is independent of the magnesium ion concentration in the brines. This can be seen from three different sets of measurement carried out in Approach 1. For treated calcite with SWME*2Mg and SWME*4Mg, the contact angles measured with a drop of DIW at air interface are 37° and 38.2° respectively (Figure 16); the contact angles measured with a drop of brine at air interface are 37.5° and 37.6° respectively (Figure 19); the contact angles measured with a drop of MO(SA) at brine interface are 42.8° and 39.7° respectively (Figure 30). Hence 2159 ppm of Mg^{2+} ions in SWME*2Mg and 4318 ppm of Mg^{2+} ions in SWME*4Mg doesn't make any significant effect on altering the wettability of the calcite crystal.
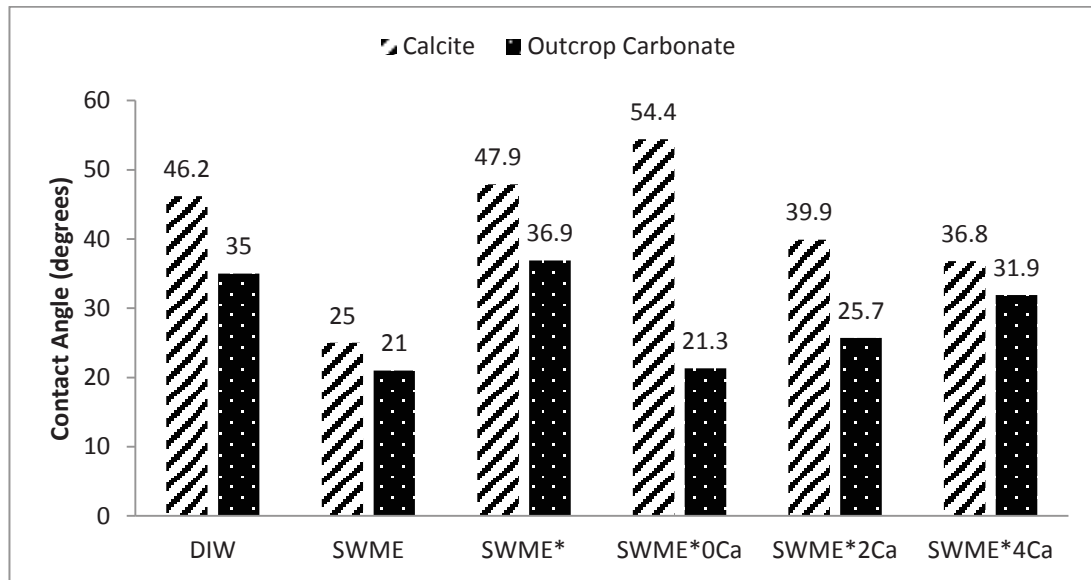
Figure 29 Effect of calcium on contact angle of MO(SA) and various brines systems for calcite and carbonate
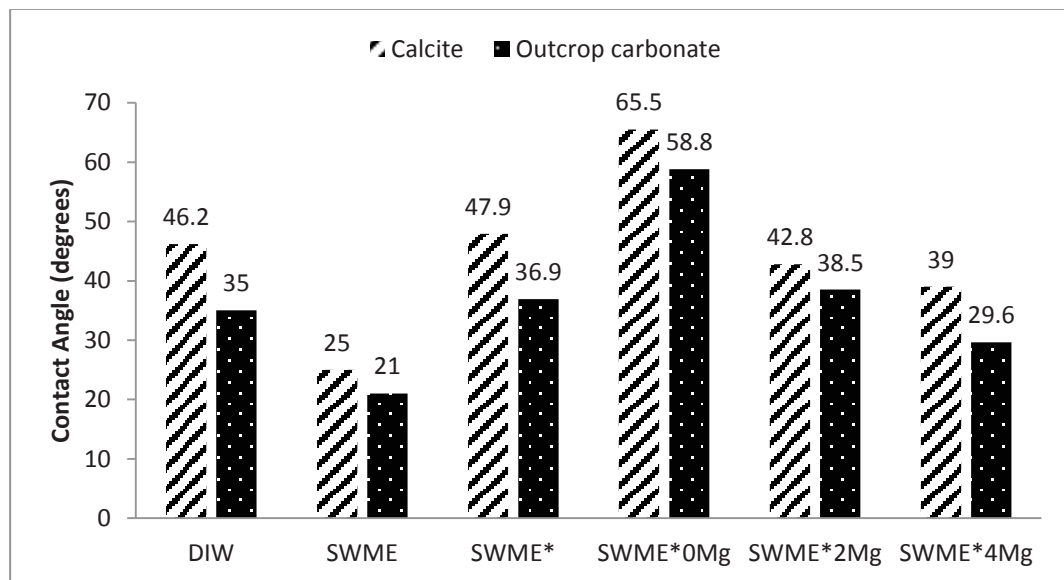
Figure 30 Effect of magnesium on contact angle of MO(SA) and various brines systems for calcite and carbonate

However a different relation is being observed on the carbonate surface as can be seen from Figure 30. The emerged trend for the dependence of the wettability of the carbonate rock on the magnesium ion concentration is in line with the one obtained at air interface with a drop of DIW (Figure 26). This can be seen from figure 30 , the increase in the concentration of Mg^{2+} decreases the contact angle from 38.5° to 29.6° for SWME*2Mg and SWME*4Mg respectively. This indicates that the carbonate rock wettability is dependent on the magnesium ion concentration in the brine.

The second observation is that removing magnesium from the brines gives a contact angle of 65.5° and 58.8° for calcite and carbonate surfaces respectively. The contact angle measured for the surfaces treated with brine without magnesium SWME*0Mg is higher than the reference measured DIW (46.2° for calcite and 35° for carbonate).

The contact angle images at the equilibrium condition for all the cases presented on Figures 28-30 are being displayed in Figure 31 and 32 for each experiment on calcite crystal and carbonate rock.

Zhang studied the effect of divalent cations (Ca^{2+} and Mg^{2+}) in the presence of SO_4^{2-} on wettability alteration towards water-wet conditions on chalk. They concluded that sulphate must be present together with either Ca^{2+} or Mg^{2+} in order to improve oil recovery [86]. These results are consistent with earlier published data on chalk cores treated with stearic acid.

The effect of ions on the wettability for calcite crystal and carbonate rocks has been discussed above. All the experimental measurements have been summarized in Table 8 and 9. For MO(SA)/Calcite system, Table 8 displays some of the brines measurement were repeated for more than once. Especially the effect of dilution was repeated a number of times in order to be more confident on the trend obtained. In table 8 the values

of the contact angle for this system show good repeatability keeping in mind the experimental error and the homogeneity of the polished surfaces. The values for the contact angle for MO(SA)/Carbonate system are displayed in Table 9. The repeatability for this system is fair in comparison to the calcite surface. This could be due to the inhomogeneous nature of the outcrop carbonate surface.

Extensive work has been done on calcite by the Norwegian group [66, 68, 70] and demonstrated the possible exchange between Mg^{2+} and Ca^{2+}. Introduction of Mg^{2+} ions disturbs the existing equilibrium at the calcite solid surface with possible exchange/precipitation modifying the calcite surface, hence reducing the interaction/adsorption of stearic acid on the calcite surface. In other words, less adsorbed stearic acid remained on the calcite surface in the presence of magnesium ions compared to that for sulfate ions.

In this study for MO(SA) and different brine system, the ability of Mg^{2+} ions to remove the preadsorbed organic groups is less pronounced compared to sulphate ion. However, it may cover the negative sites of calcite crystal due to cation exchange capacity and improving the wettability of modified minerals.

The little discrepancies between our research findings are attributed to the differences in rock types and the characteristics of the rock surfaces as well as the experimental procedures, followed and experimental conditions.

The results reported in this study clearly indicate a significant potential method in carbonate reservoirs. The evidence gathered during this research work is in line with the injection of seawater in chalk reservoirs. The recovery-mechanism studied confirmed that altering injection-water salinity and ionic content is able to alter the rock wettability toward a more water-wet state.

Table 8 Summary of contact angles of Brine/MO(SA)/Calcite

	MO(SA)-Drop 1		MO(SA)-Drop 2		MO(SA)-Drop 3		MO(SA)-Drop 4		MO(SA)-Drop 5	
	initial	after 20 mins	initial	after 20 mins	initial	after 20 mins	initial	after 20 mins	initial	after 20 mins
DIW	46.2	96.2								
SWME	25	49.8	28.3	98.7	28.6	46.5	26.1	28.6	25.9	27.1
SWME*	47.9	94.4	47.1	67.9	40.8	78.4	52.9	79.7	49.1	91.4
SWME*0S	32.3	34	31.7	32.3						
SWME*2S	26.2	30.1								
SWME*4S	36.2	53.8	39.3	59.6	37.9	72.6	36.4	69.4		
SWME*0Ca	54.4	98								
SWME*2Ca	39.9	46.3								
SWME*4Ca	36.8	62.9								
SWME*0Mg	65.5	92								
SWME*2Mg	42.8	74.7	43.6	93.5	15	17.8				
SWME*4Mg	39	44.3	31.6	66.8	15.4	30.9				

Table 9 Summary of contact angles of Carbonate /MO(SA)/ Brine systems

	MO(SA)-Drop 1		MO(SA)-Drop 2	
	initial	after 10 mins	initial	after 10 mins
DIW	35	44.3	35.2	49
SWME	21	64.4		
SWME*	36.9	52.4	62.9	87.3
SWME*0S	42.7	45	32.5	37.6
SWME*2S	34.7	66.7	64.3	93.8
SWME*4S	20.8	30.4	20.7	60.4
SWME*0Ca	21.3	36.8	28.9	
SWME*2Ca	25.7	52.6	24.6	
SWME*4Ca	31.9	59	59	87.2
SWME*0Mg	58.8	100.9	43.6	116.9
SWME*2Mg	38.5	41.1	44.8	95.4
SWME*4Mg	29.6	27.6	36.9	35.4

DIW	SWME	SWME*
SWME*0S	SWME*2S	SWME*4S
SWME*0Ca	SWME*2Ca	SWME*4Ca
SWME*0Mg	SWME*2Mg	SWME*4Mg
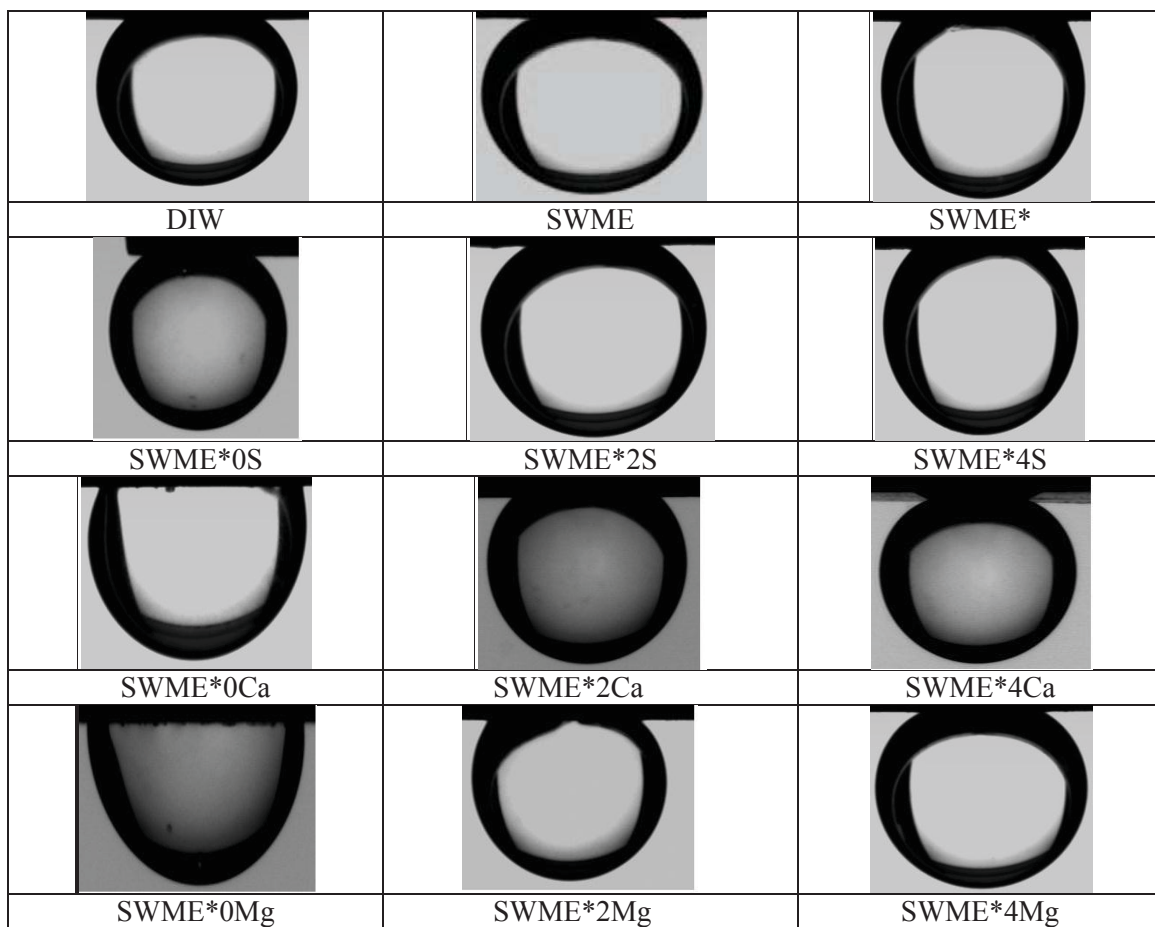
Figure 31 Contact angle images of Calcite /MO(SA)/Brine systems at T=23°C

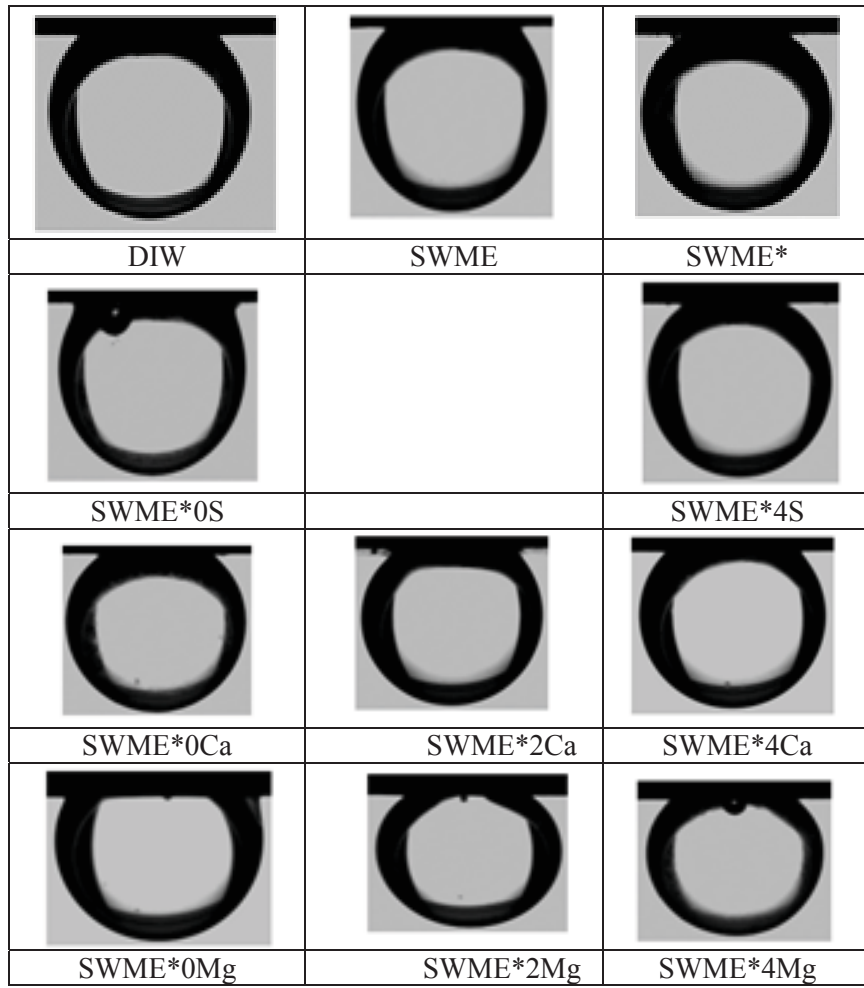|		
DIW	SWME	SWME*
SWME*0S		SWME*4S
SWME*0Ca	SWME*2Ca	SWME*4Ca
SWME*0Mg	SWME*2Mg	SWME*4Mg

Figure 32 Contact angle images of Carbonates /MO(SA)/Brine systems at T=23°C

4.2 pH- Results

The pH measured for the brines for the system MO(HA)/Calcite is shown in Table 10. The change in the pH is also shown. For some of the brines, the change in the pH is one unit. This section presents a discussion of the effect of dilution and the effect of the three potential ions concentration on the change in the pH of brines.

The calcite and carbonate samples aged in MO(HA) and MO(SA) were treated with brines. The contact angles increased for the samples (calcite and outcrop carbonate) after the aeging process. This is due to the adsorption of the carboxylic group from the model oil to the rock surface.

From Tables 10, 11 and 12 it is evident that the change in the pH for the Arabian Gulf sea water (SWME) is more than SWME*(twice diluted Arabian Gulf seawater). This indicates that brine SWME can removed more of the adsorbed carboxylic acid from the surface as compared to the SWME*. This is supported by the contact angle measurement as SWME showed to be a better wettability modifier than SWME* for the three systems considered in this study.

For MO(HA)/Calcite and MO(SA)/Calcite (Table 10 and 11), the effect of increasing sulphate, calcium and magnesium ions concentration in the brines and the change in the pH is discussed below. It can be seen that increasing the sulphate and calcium ion concentration decreases the change in the pH of the brines. However this does not agree with the contact angle measurement. At higher temperature, sulphate is highly unstable in the aqueous phase because of the weak hydrogen bonding. This could be due to adsorption of sulphate on the carbonate surface and precipitation of calcium sulphate at higher temperature with the later one being more dominant. The change in the pH

increases with increasing magnesium ion concentration in the brine. From the contact angle measurement, there is almost no effect for the magnesium ion concentration on the wettability of the calcite surface for both the MO(HA) and MO(SA) system.

For MO(SA)/Carbonate system (Table 12), the ion concentration and the pH change are not showing a systematic trend.

There was no specific trend seen for sulphate ion concentration in the brine and the change in the pH. However the highest change of pH is for brine with no calcium ion concentration. This is in agreement with the contact angle measurement. The surface treated with SWME*0Ca gives a lower contact angle as compared to SWME*4Ca.

On the other hand, the change in the pH increases with the increasing magnesium ion concentration in the brine. This is in agreement with the contact angle measurement. The carbonate surface changed towards more water-wet with increasing the magnesium ion concentration for the MO(SA) system.

Table 10 pH measurements-Calcite/MO(HA)

Brines	pH (initial)	pH (after treatment of sample for 5 days)	Difference in pH
SWME	8.2	7.13	1.07
SWME*	8.12	7.68	0.44
SWME*OS	8.13	7.94	0.19
SWME*2S	8.12	7.98	0.14
SWME*4S	8.05	7.98	0.07
SWME*0Ca	9.11	7.6	1.51
SWME*2Ca	8.27	7.16	1.11
SWME*4Ca	8.2	7.45	0.75
SWME*0Mg	8.4	8.07	0.33
SWME*2Mg	8.25	7.32	0.93
SWME*4Mg	8.23	7.11	1.12

Table 11 pH measurements-Calcite/MO(SA)

Brines	pH (initial)	pH (after treatment of sample for 5 days)	Difference in pH
SWME	8.1	7.32	0.78
SWME*	8.12	7.5	0.62
SWME*OS	8.13	7.73	0.4
SWME*2S	8.12	7.64	0.48
SWME*4S	8.05	7.88	0.17
SWME*0Ca	9.01	7.7	1.31
SWME*2Ca	8.21	7.75	0.46
SWME*4Ca	8.19	7.66	0.53
SWME*0Mg	8.43	8.34	0.09
SWME*2Mg	8.11	7.68	0.43
SWME*4Mg	8.23	7.56	0.67

Table 12 pH measurements-Carbonate/MO(SA)

Brines	pH (initial)	pH (after treatment of sample for 5 days)	Difference in pH
SWME	8.1	7.61	0.49
SWME*	8.12	8.09	0.03
SWME*OS	8.13	8.02	0.11
SWME*2S	8.12	7.69	0.43
SWME*4S	8.05	8.16	0.11
SWME*0Ca	9.01	8.07	0.94
SWME*2Ca	8.21	8.14	0.07
SWME*4Ca	8.19	7.86	0.33
SWME*0Mg	8.43	8.4	0.03
SWME*2Mg	8.11	8.25	0.14
SWME*4Mg	8.23	7.81	0.42

4.3 TAN measurement of model oil

The TAN of the oil is considered as the key parameter dictating the wetting conditions of carbonate reservoirs [87]. In this study, a TAN=2 mg KOH/gm of oil was used for both short chain (HA) and long chain (SA). The TAN of the MO(HA) after aging the sample was calculated using the potentiometric titration.

From Table 13, the average TAN≃2.65 is calculated after aging the calcite crystal for five days in MO(HA). Taking into account the experimental error, there was not much difference in the TAN from the initial value. This was also observed by Standnes and Austad since decarboxylation is a slow process. (No significant change in the TAN was observed during the aging period of 30 days at 120°C) [87].

Table 13 TAN measured for MO(HA) (after aging)

MO(HA)	TAN (mg KOH/gm of MO(HA))
CA0,CA6 and CA7	2.6
CA8,CA9 and CA10	2.48
CA11,CA12 and CA13	2.48
CA1,CA2 and CA3	2.96
CA4 and CA5	2.73

4.4 Brine Analysis

The brine analysis was done in order to understand the mechanism leading to the change in the wettability of the calcite and carbonate rock surfaces. The concentrations of sulfate, calcium and magnesium in the brines were determined before and after the treatment of the samples to quantify the adsorption/desorption of the potential determining ions.

4.5 Calcium, Magnesium and Sulphate Analysis

The previously presented results in this study showed some trend in the change of Ca^{2+} and Mg^{2+} ion concentration for the surfaces treated with MO(HA) and MO(SA) carboxylic acid.

Figures 33-35 present the analysis of Ca^{2+} and Mg^{2+} for the various brines/calcite/model oil and brines/carbonate/model oil systems.

For the brine SWME and SWME* (Figure 33-35), it can be seen that there is an increase in the concentration for Ca^{2+} and Mg^{2+}. However the increase in the ions concentration for the brine SWME* is greater than SWME for all the three systems. The increase in the calcium and magnesium ion concentration is due to the desorption of calcium and magnesium from the rock. Therefore due to desorption mechanism, the content of the calcium and magnesium ions is reduced on the surface. The measured contact angles reveal the role of the calcium and magnesium ions in altering the wettability of the surface towards more water-wet. Hence the lower calcium and magnesium ion on the surface treated with SWME* resulted in higher contact angle as compared to Arabian Gulf seawater SWME. However in Figure 35 a much higher increase of magnesium ion concentration (134%) is observed. From the XRD of the outcrop carbonate rock, traces of

dolomite were seen in the carbonate rock. Dolomited dissolution could be the source of the increase in the Mg^{2+} concentration for the brine SWME*.

For the brine SWME*2Ca there is an increase in the calcium ion and a decrease in the magnesium ion concentration for the MO(HA)/Calcite and MO(SA)/Calcite system. The consistent trend seen on the calcite crystals for the two systems confirms that the change in the wettability is due to the substitution mechanism of Ca^{2+} with Mg^{2+}. However for MO(SA)/Carbonate, there is an increase for both Ca^{2+} and Mg^{2+} ions. The increase in the calcium and magnesium ion concentration for the MO(SA)/Carbonate system is due to desorption mechanism which reduces the calcium and magnesium ion content on the carbonate surface. The calcium and magnesium ions are shown to be a potential ions towards wettability alteration towards more water-wet and hence desorption of the two ions from the carbonate surface results in a higher contact angle as compared to SWME*0Ca for the carbonate surface.

For the brine SWME*4Mg, a decrease in the calcium and magnesium ion concentration is observed for MO(HA)/Calcite, MO(SA)/Calcite and MO(SA)/Carbonate systems. The decrease in the calcium and magnesium ion concentrations is due to the possible adsorption mechanism. The decrease in the calcium and magnesium ion concentrations for the MO(HA)/Calcite and MO(SA)/Calcite is approximately 2:1. However the decrease for MO(SA)/Carbonate systems is 6:1 for calcium and magnesium ion respectively. This indicates that higher adsorption of Ca^{2+} as compared to Mg^{2+} on the surface makes the surface more water-wet. This is also in agreement with the contact angle measurement as the lowest contact angle (29.6°) is measured on the carbonate surface treated with SWME*4Mg as compared to the calcite surface for MO(HA) (42.7°) and MO(SA) (39°) system.

However, there is no particular trend seen with brine SWME*4S for all the three systems considered in this study.

Figures 33 to 35 show one common observation is that there is slight increase in the sulphate ion concentration for all the systems. The increase for all the three systems is within 10% and could be due to experimental error.
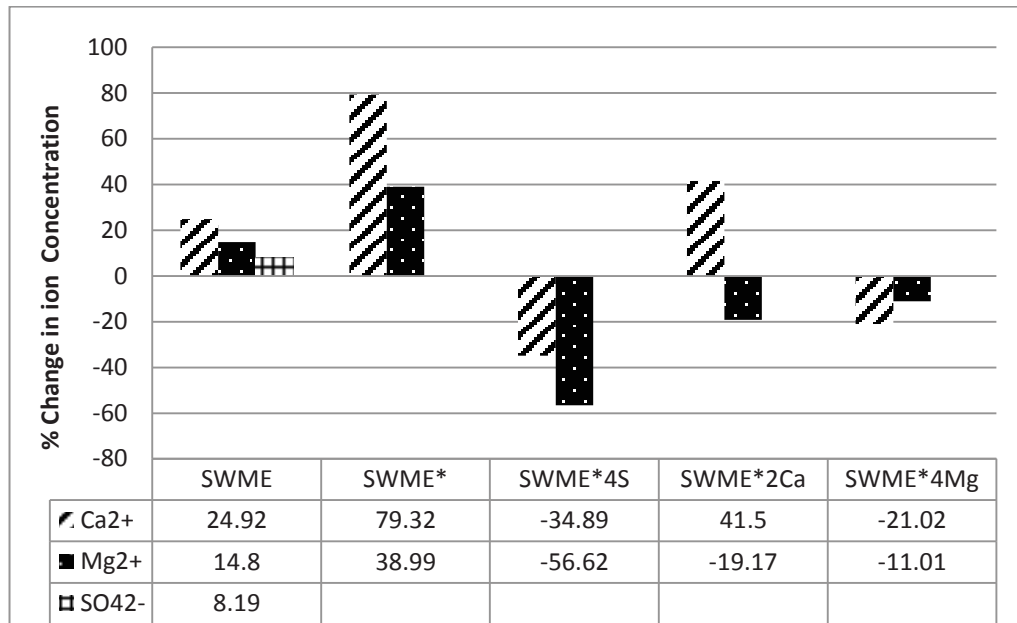
	SWME	SWME*	SWME*4S	SWME*2Ca	SWME*4Mg
Ca2+	24.92	79.32	-34.89	41.5	-21.02
Mg2+	14.8	38.99	-56.62	-19.17	-11.01
SO42-	8.19				

Figure 33 Change in ions concentration for Calcite/MO(HA) and various brine systems

	SWME	SWME*	SWME*4S	SWME*2Ca	SWME*4Mg
Ca2+	16.91	28.91	12.58	42.11	-34.42
Mg2+	16.72	46.95	-28.06	-30.22	-15.65
SO42-	10.29				
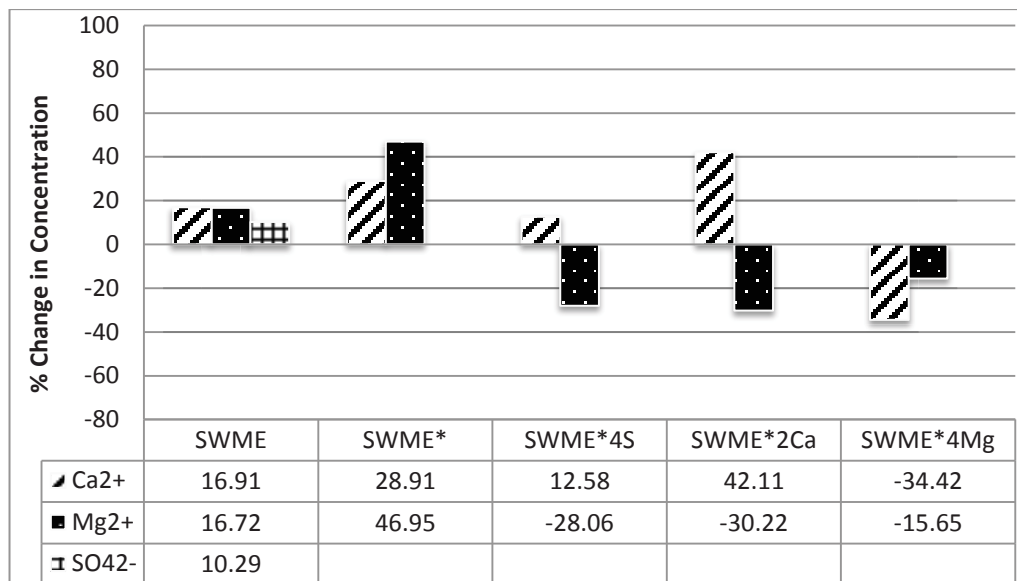
Figure 34 Change in ions concentration for Calcite/MO(SA) and various brines system

	SWME	SWME*	SWME*4S	SWME*2Ca	SWME*4Mg
Ca2+	6.81	14.94	-1.19	15.53	-18.8
Mg2+	27.16	134.51	27.41	71.07	-3.63
SO42-	5.04				

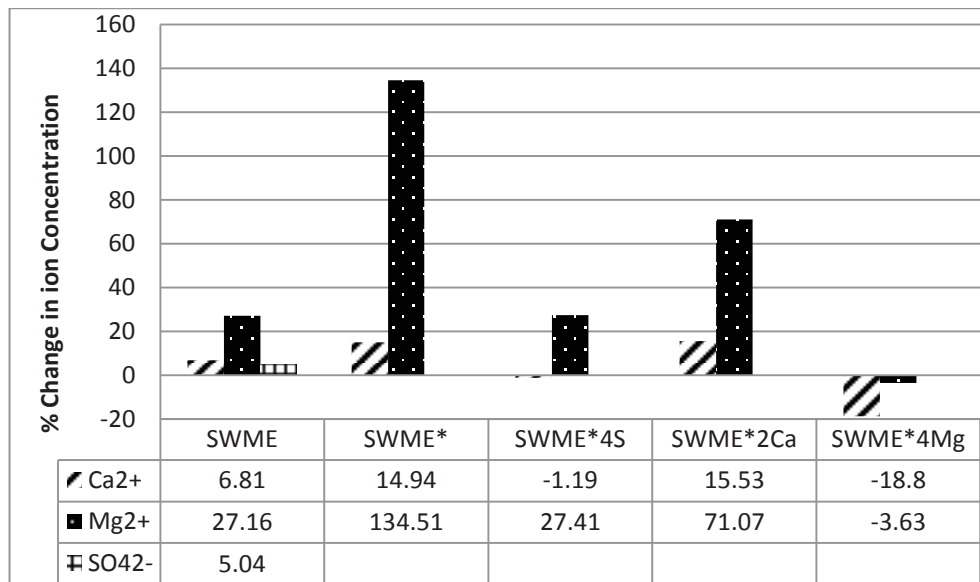Figure 35 Change in ions concentration for Carbonate/MO(SA) and various brines system

Surface Characterization

4.6 SEM

This section discusses the surface characterization for the treated samples for Calcite/MO(SA) and Carbonate/MO(SA) systems.

The section is divided into two sub sections. First the SEM images were done for four samples each treated with different brine. A sample treated with DIW was characterized for comparison with the ones treated with brine. A sample saturated in FW only was taken as a reference. Second the EDX analysis was done for the same surfaces for specific areas with high resolution. The purpose of the EDX was to have a quantitative analysis of the elements on the surface in order to understand the rock/fluid interaction and the possible mechanism for the wettability alteration.

4.6.1 MO(SA)-Calcite and Carbonate

The SEM images for the calcite and carbonate are shown in Figures 36 and 37 respectively. Comparison of Figure 36 (a) and (b) (calcite saturated in FW only) and Figure 37 (a) and (b) (carbonate saturated in FW only) with the rest of the images in Figures 36 and 37, the following observations can be made. The first observation is that the surfaces have been modified. The second observation is that the surface modification is heterogeneous. This can also be supported by the contact angle measurement for not approaching similar value for the MO(SA)/Calcite and MO(SA)/Carbonate systems (Table 8 and 9) and also by the EDX analysis where different areas taken into consideration shows differences in the elemental composition deposited on the surface.

The observations made at the SEM analysis for the surfaces were further studied quantitatively by looking at the EDX for the surfaces (Tables 14 and 15).The values for

each element in Table 14 and Table 15 are the average values of the elements for all the spectrum considered for the particular treated sample. For both surfaces (calcite and carbonate) we can say that there is not much difference in the elemental composition on the surface for the sample treated with DIW and the reference sample (FW only). The differences are seen on the surfaces in the SEM images in Figures 38 and 39 (a) and (b) can be accounted for the carboxylic group adsorbed on the surface which the DIW is unable to remove it. This was also observed during the EDX analysis for the surface treated with DIW. The organic component on the surface was seen vibrating when heated with the electron beam unlike the elemental components on the surface. However treatment with sea water and modified versions of seawater have a significant impact on the wettability as seen from the contact angle measurement and the EDX analysis ((c), (d), (e) and (f) in Figures 38 and 39).

Some trends observed from the EDX analysis of the four samples for each lithology treated with brines are discussed. From Tables 14 and 15, the first trend observed is that the amount of magnesium on the surface increases for all the samples treated with SWME, SWME*4S, SWME*4Ca and SWME*4Mg as compared to the reference sample (FW only).However it is observed that the quantity of magnesium on the calcite surface is different for SWME*4Ca and SWME*4Mg as compared to the SWME and SWME*4S.The lower amount of magnesium for calcite crystal treated with SWME*4Ca (Table 14) can be due to two possible mechanism. In the presence of higher concentration of calcium in SWME*4Ca, there is more adsorption of positive calcium on the calcite surface with the negative carboxylic group. Also the precipitation of $CaSO_4$ increases which can be further supported by the lowest concentration of sulphur (for SWME*4Ca) as compared to the rest of the four brines. Hence the above mentioned two possible

mechanisms may be responsible for less available calcium on the calcite surface for substitution reaction with magnesium. For SWME*4Mg, the substitution reaction predominates due to higher concentration of magnesium present in the brines. Hence the amount of magnesium present on the calcite surface for SWME*4Mg is the highest among the other brine.

The second trend observed is that sulphur deposition is seen on the calcite and carbonate surfaces for the samples treated with the all the brines. In the initial saturation of the calcite sample with the FW, no sulphate deposition is seen on the surface and therefore sulphate is coming after the treatment with the brines. This is in line with the literature as well that the sulphate is a potential wettability modifier at higher temperature [14,15]. The sulphate content is the lowest for the calcite treated with SWME*4Ca due to higher precipitation reaction of the $CaSO_4$ (Table 14).

The observations for carbonate as mentioned above for the calcite surface cannot be supported by any potential mechanism responsible for the wettability alteration and the exact mechanism is still unclear for carbonate surfaces.
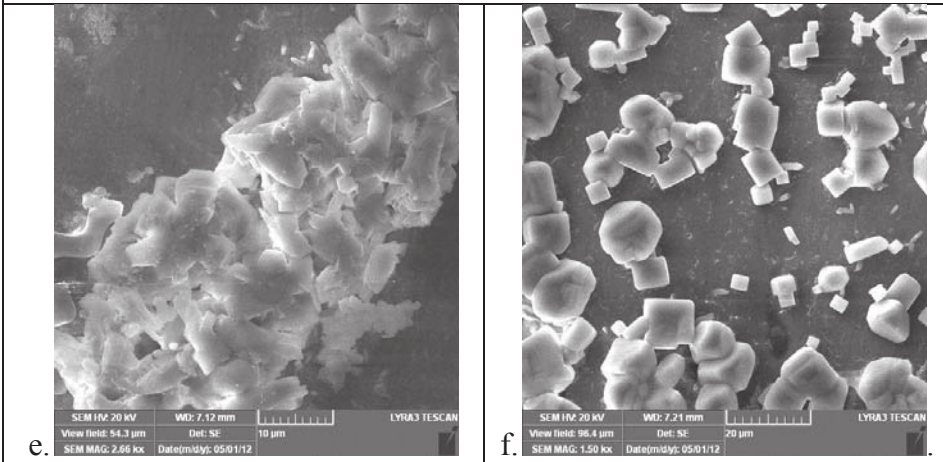
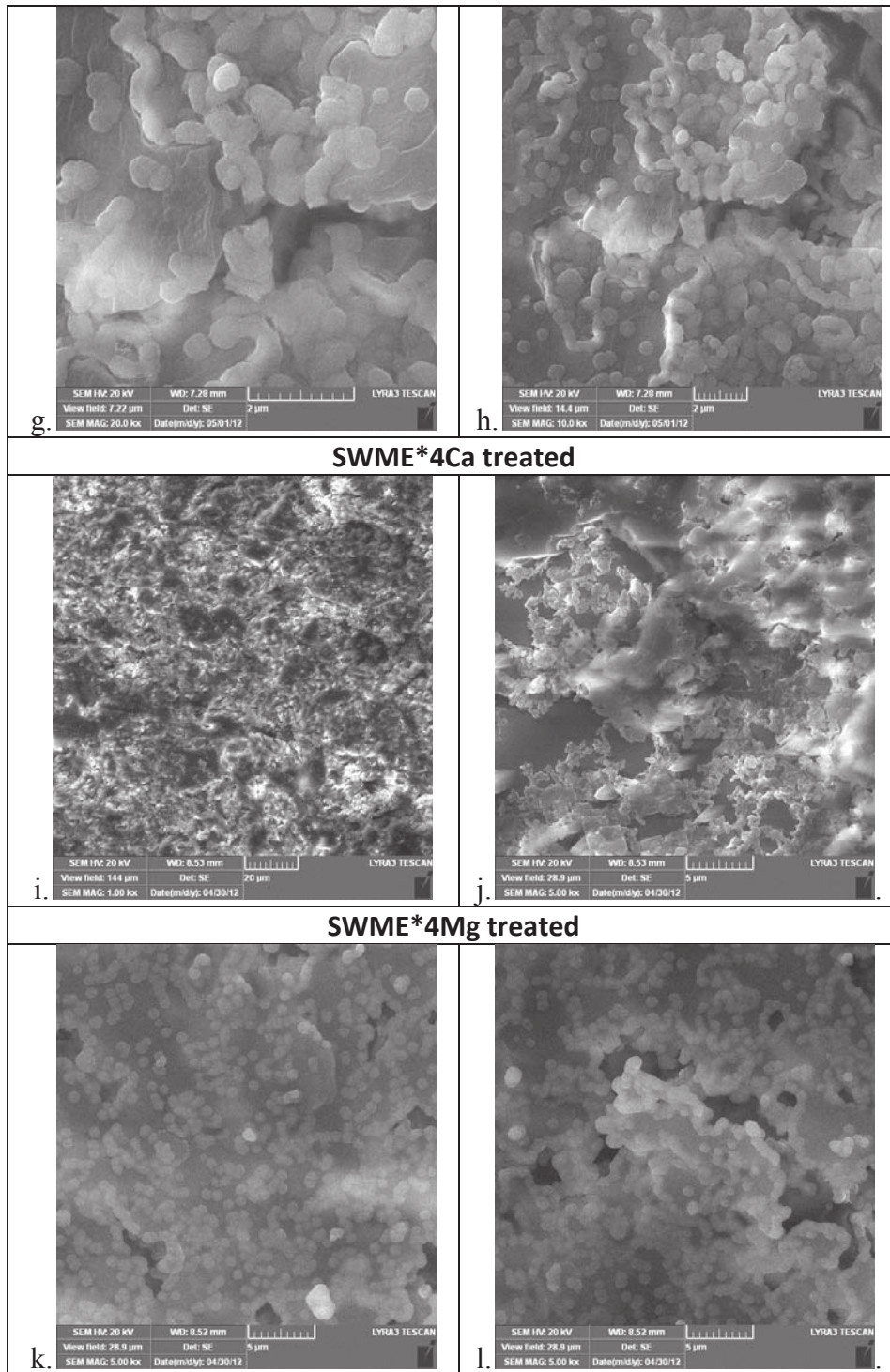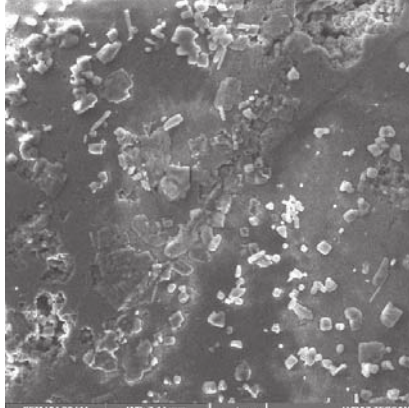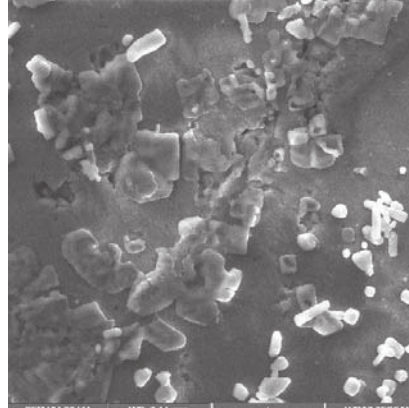**FW**

DIW treated

SWME treated

SWME*4S treated

g.	h.
SWME*4Ca treated	
i.	j.
SWME*4Mg treated	
k.	l.
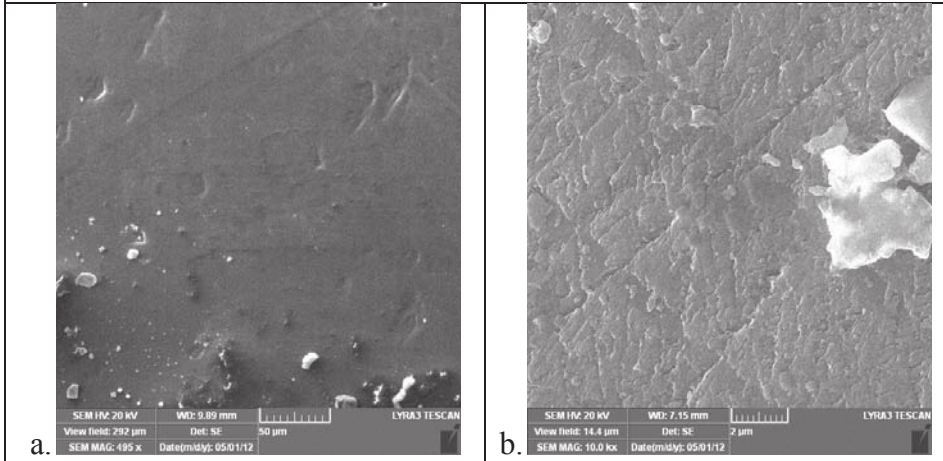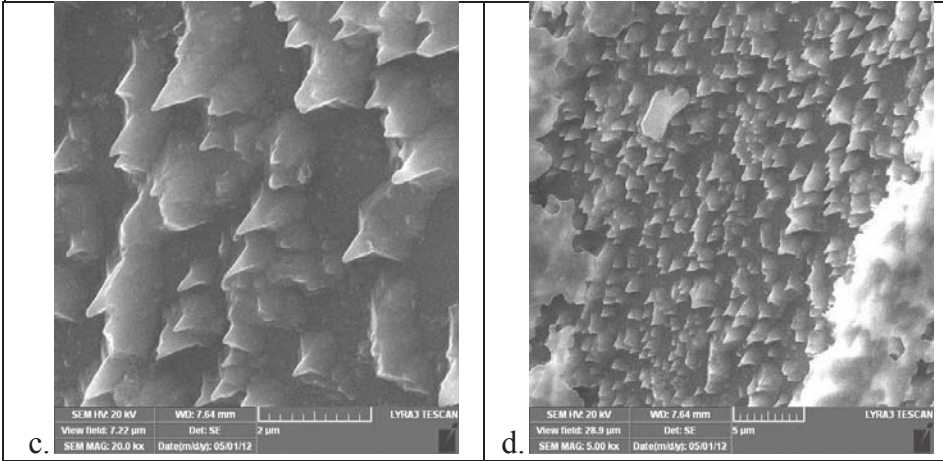
Figure 36 Images of calcite, taken by a scanning electron microscope (SEM).

FW	
DIW treated	
SWME treated	

SWME*4S treated
g.   h.
SWME*4Ca treated
i.   j.
SWME*4Mg treated
k.   l.
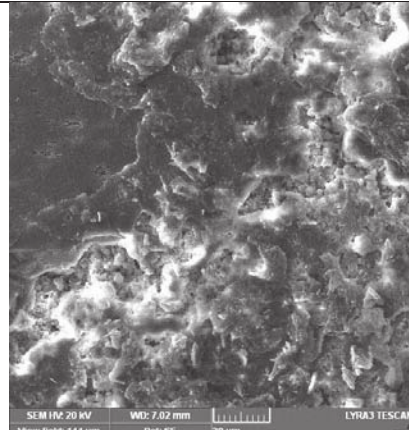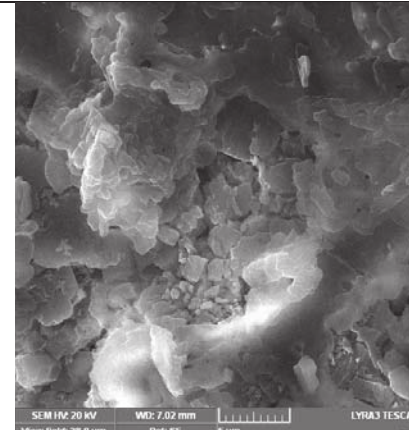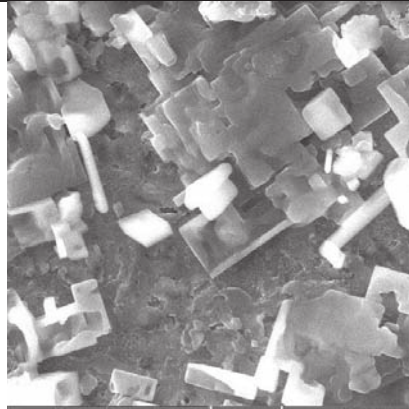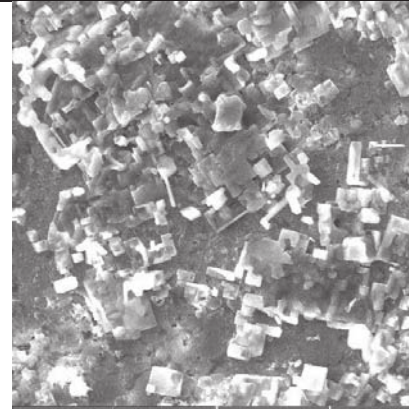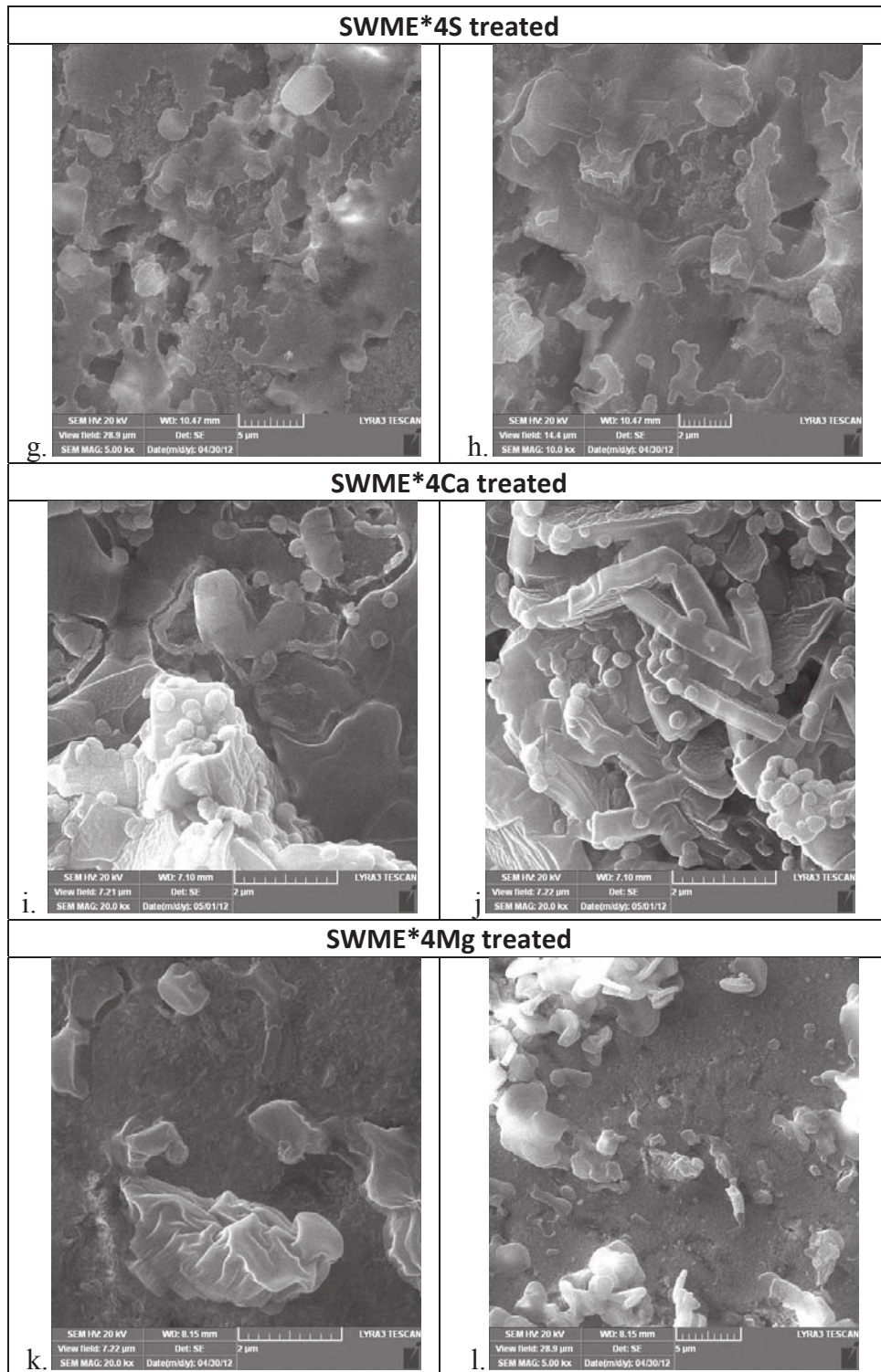
Figure 37 Images of carbonate, taken by a scanning electron microscope (SEM)
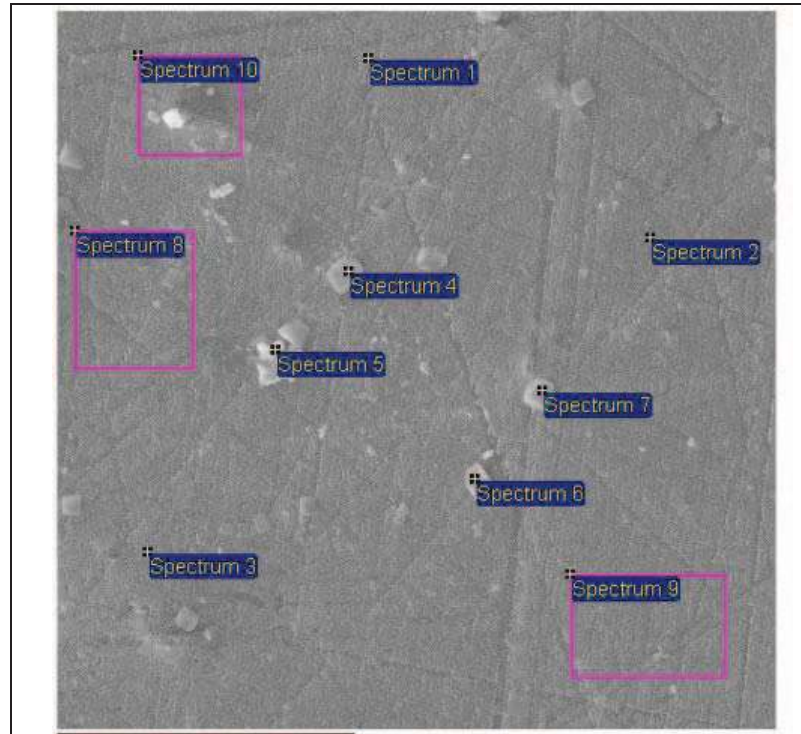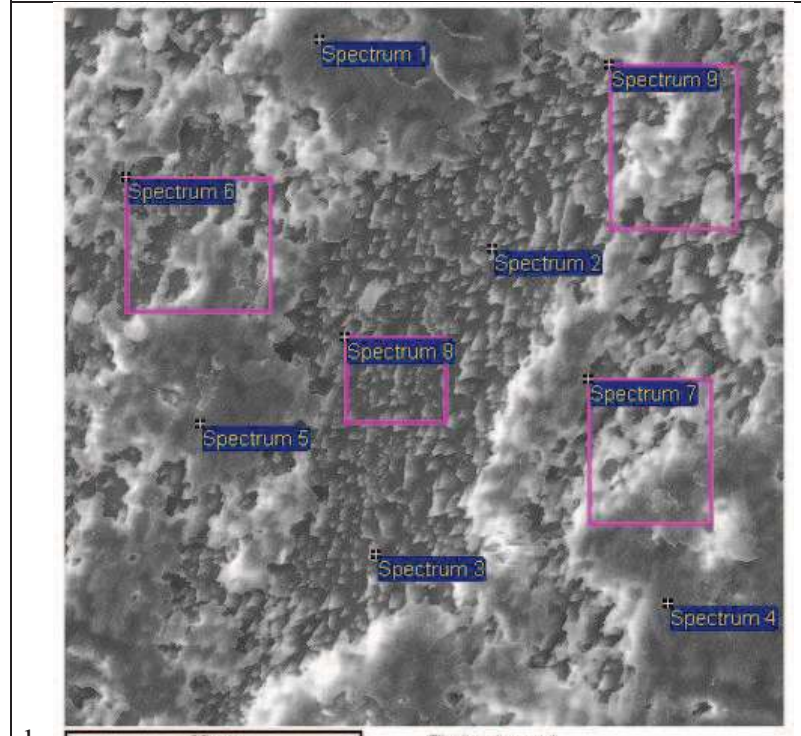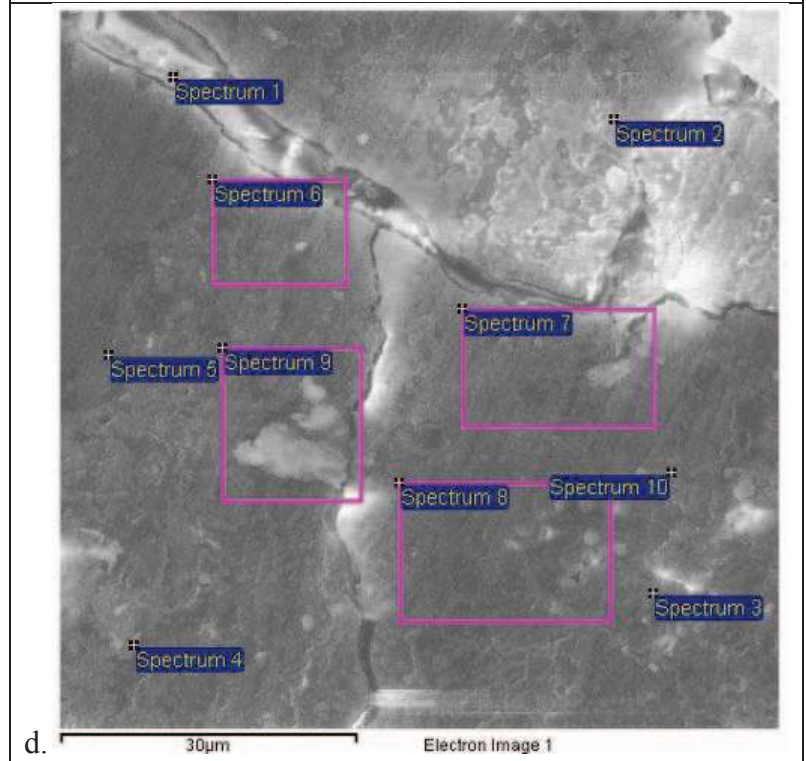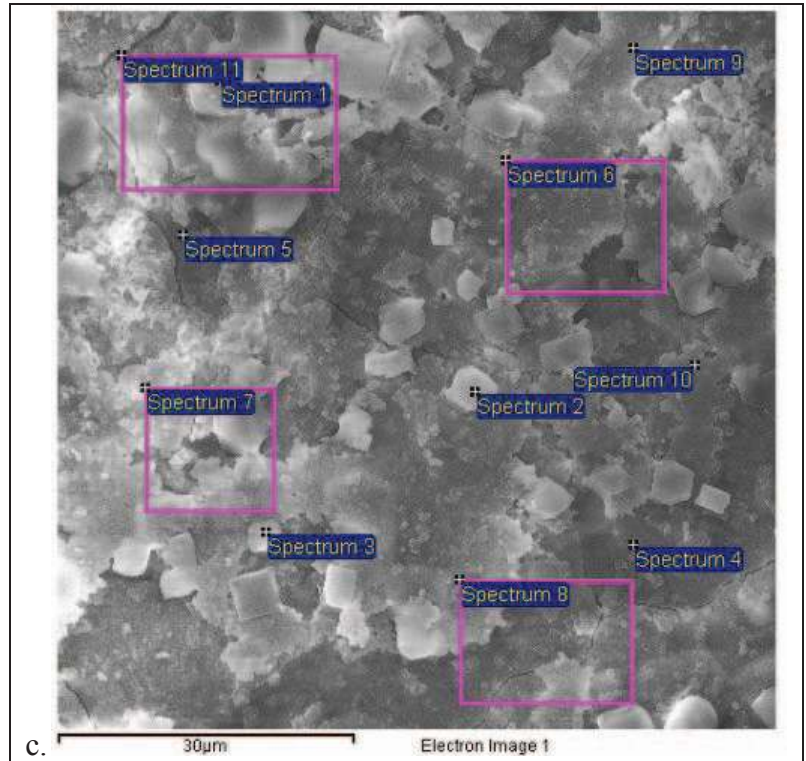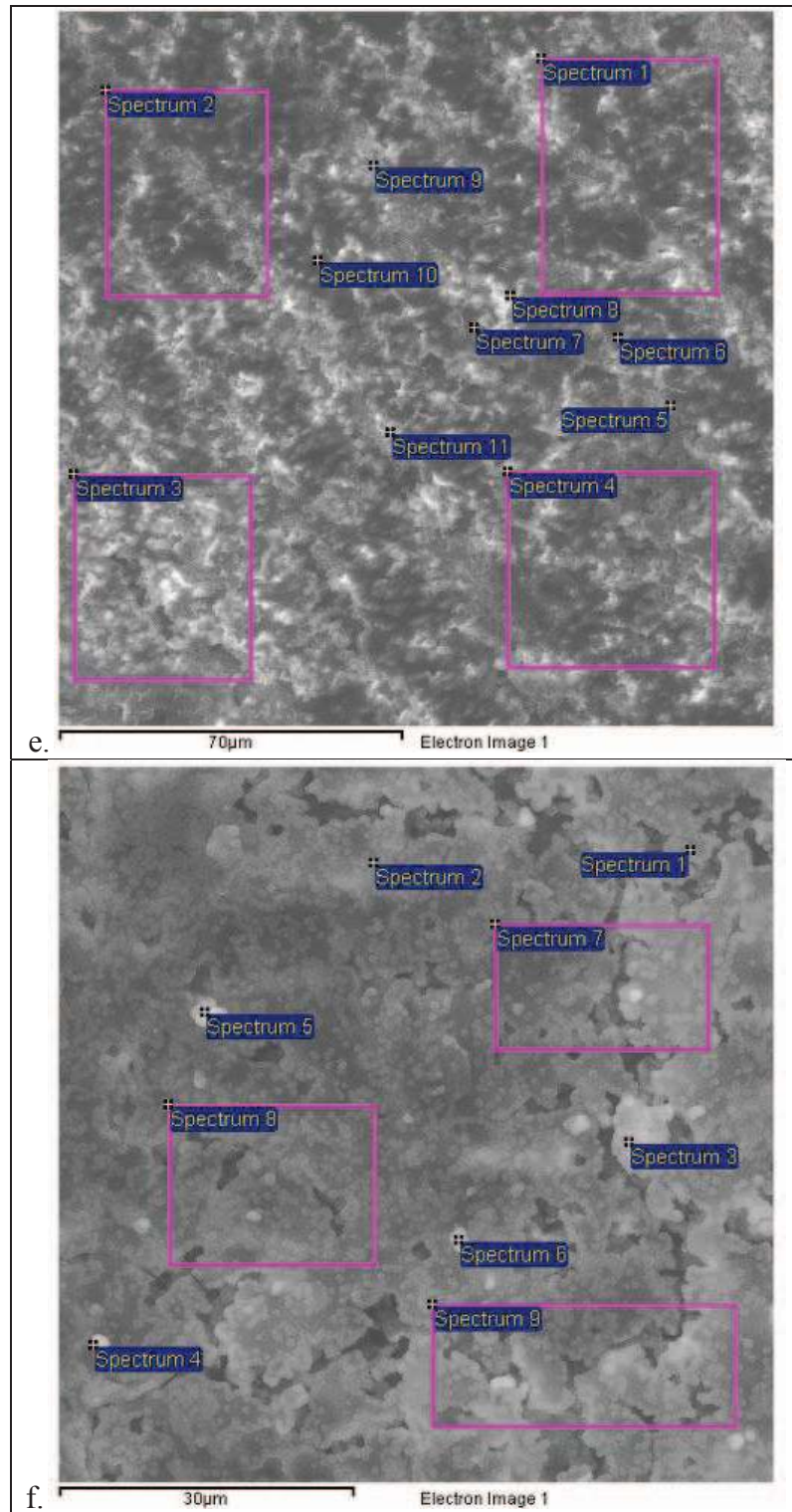
Figure 38 SEM images for EDX of calcite crystals

(a) Saturation of FW only (b) DIW treated (c) SWME treated
(d) SWME*4S treated   (e) SWME*4Ca treated and
(f) SWME*4Mg treated

Table 14 EDX for calcite crystals

Treated Calcite	C	O	Na	Mg	S	Cl	Ca	Contact angle	Change in pH
FW	22.735	36.168	6.384286	0.206667	0	3.656	32.755		
DIW	27.31	41.15111	0.545	0.157143	0	0.387778	30.44	46.2	
SWME	11.78545	42.30636	8.68	6.496364	0.15625	10.47455	15.33636	25	0.78
SWME*4S	20.375	48.976	0.985	6.506	0.236667	0.428889	17.007	36.2	0.17
SWME*4Ca	19.38182	46.32727	0.983	1.592727	0.035	1.003	29.80091	36.8	0.53
SWME*4Mg	17.25222	45.95333	1.24	10.36222	0.33625	6.446667	12.02222	39	0.67

a.

Electron Image 1

30μm

b.

Electron Image 1

30μm

c.

d.

e.

f.
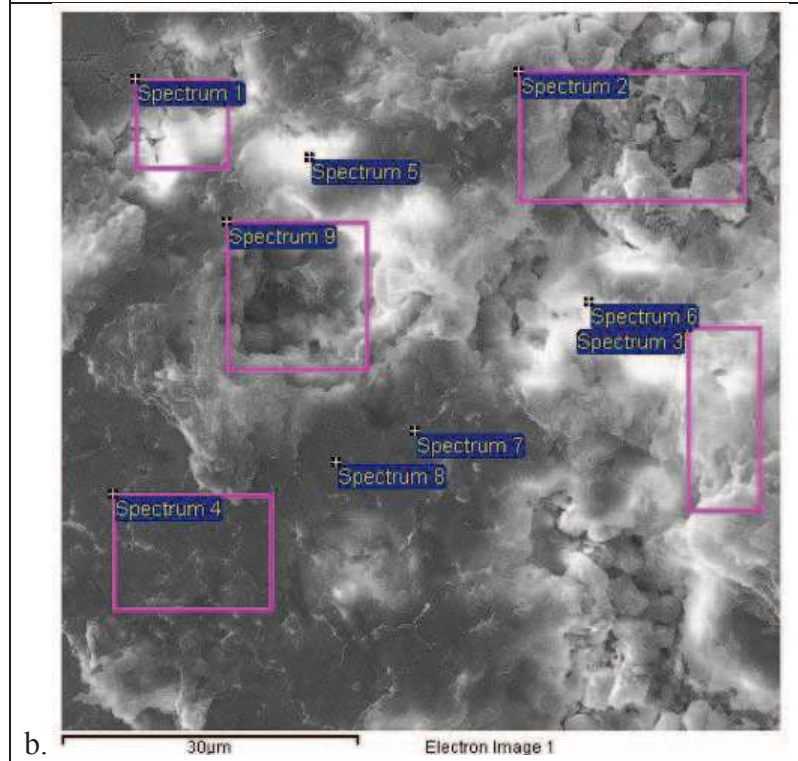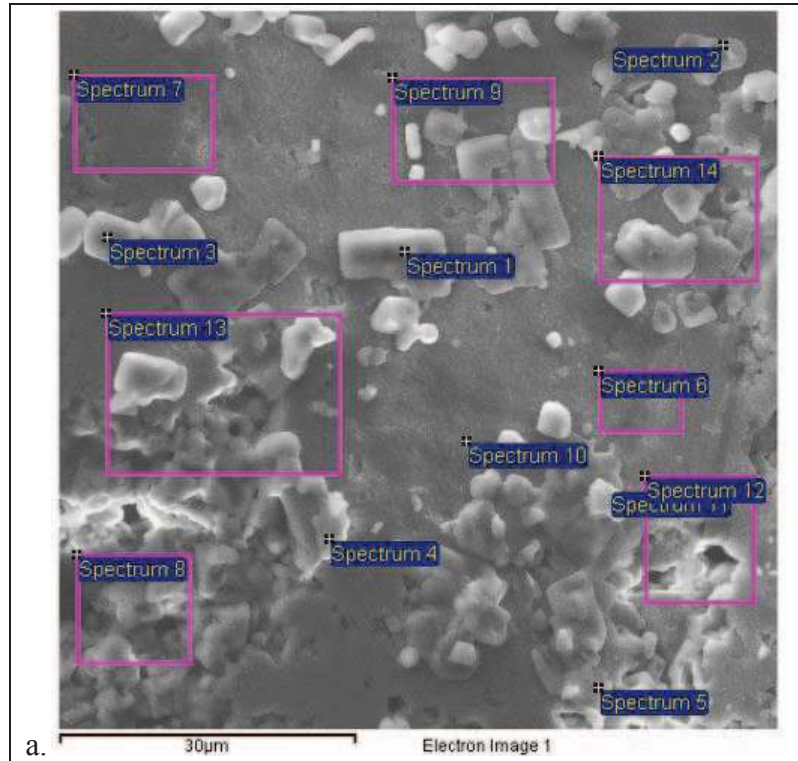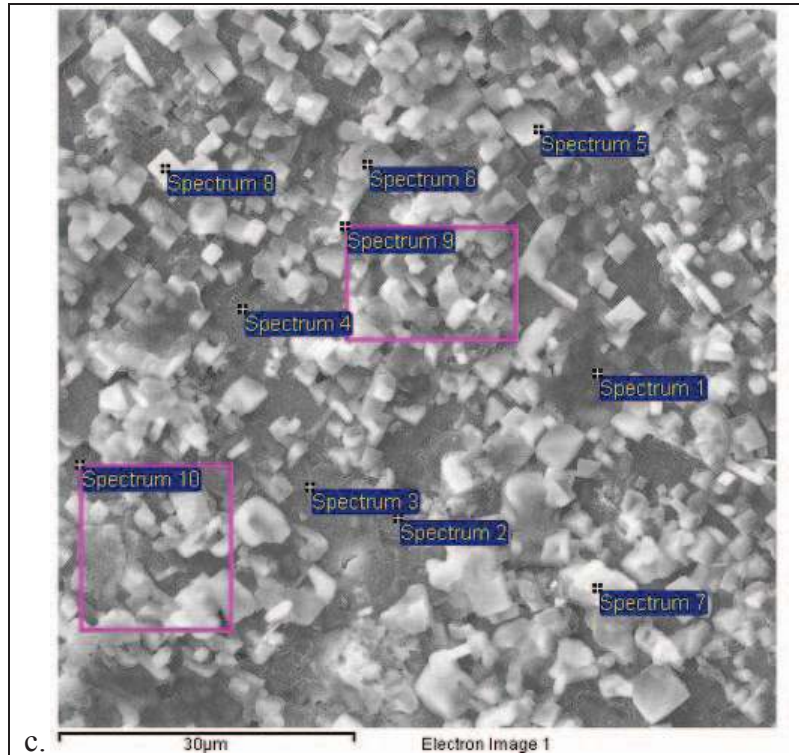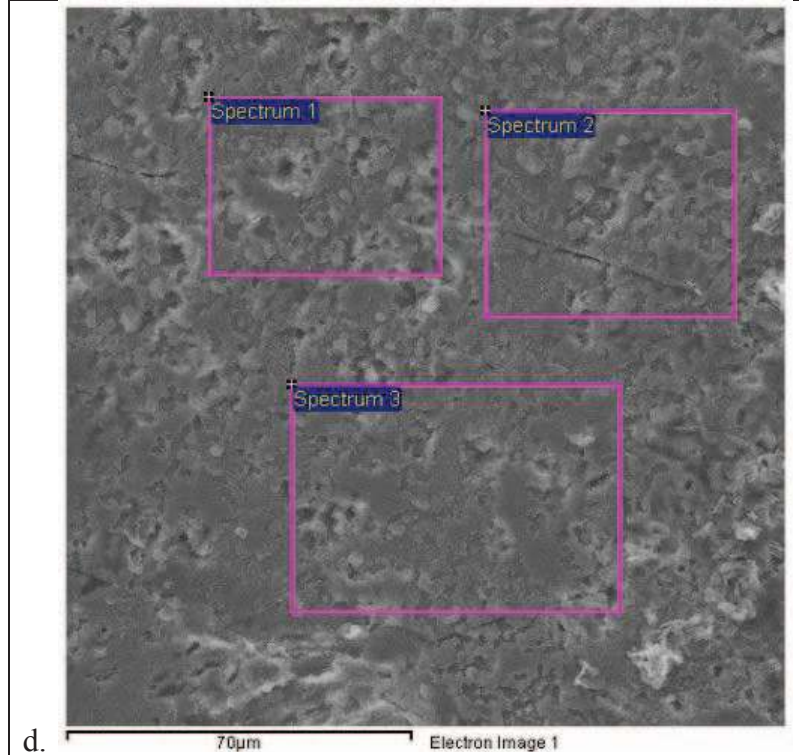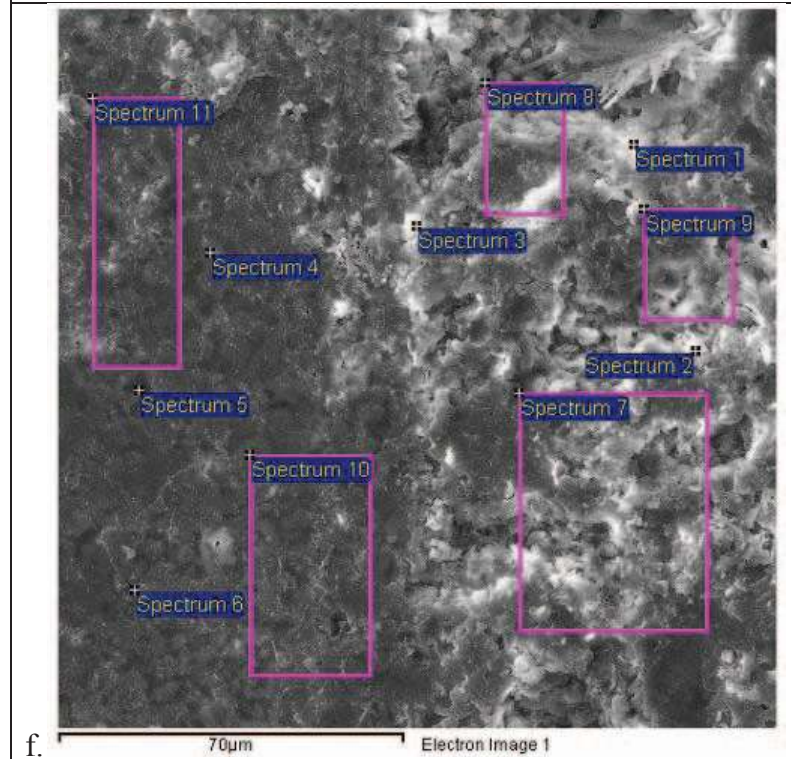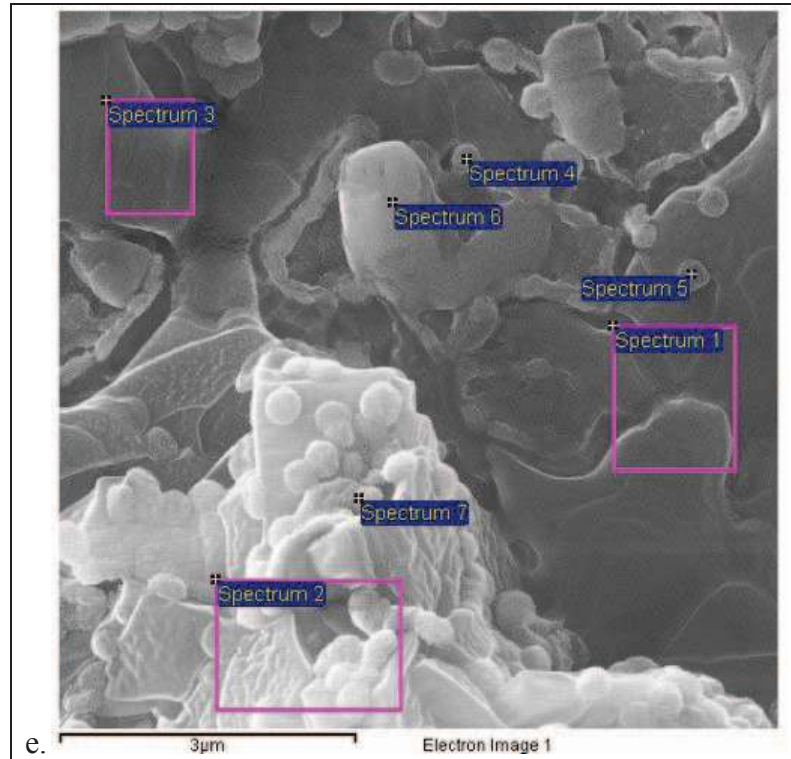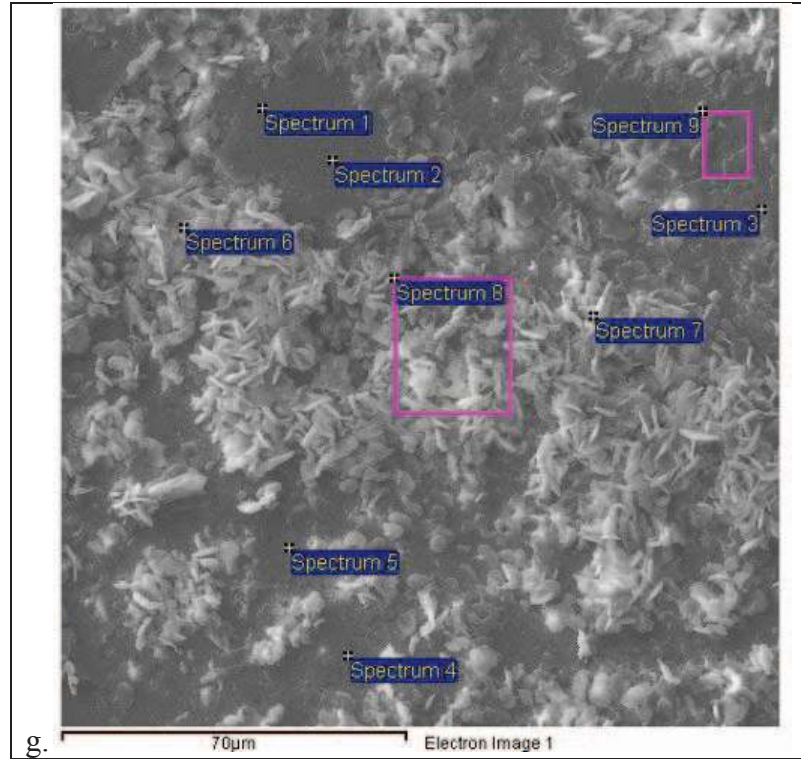
Figure 39 SEM images for EDX of carbonate

    a. FW only
    b. DIW treated
    c. SWME treated
    d. SWME*4S treated
    e. SWME*4Ca treated
    f. SWME*4Ca treated- EDX-2
    g. SWME*4Mg treated

Table 15 EDX for carbonate

	C	O	Na	Mg	S	Cl	Ca	Contact angle	Change in pH
FW	23.10571	32.757857	13.09143	0.171	0	13.83143	16.94071		
DIW	39.90444	34.311111	0.055	0.107143	0	0.075	25.51111	35	
SWME	28.236	19.025	16.47	0.766	0.318	18.013	16.648	21	0.49
SWME*4S	22.70333	44.583333	0.993333	0.403333	0.216667	0.25	30.73	20.8	0.11
SWME*4Ca	45.8675	30.641429	9.455714	2.455714	0.076667	13.27857	15.95	31.9	0.33
SWME*4Mg	34.70222	35.847778	2.12875	0.942222	0.286667	2.692222	16.81667	29.6	0.42

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The present study shows that tuning or modifying the chemistry of the injection water is very important as it has a significant impact on the wettability of calcite and carbonate rocks. The measured contact angles at brine/model oil (containing acidic components)/carbonate interface give valuable information for understanding the mechanisms leading to alteration of wettability of carbonate surfaces. Based on the experimental results obtained from this study, the following conclusions can be drawn:

1. Contact angle measurements have shown that oil soluble fatty acids play an important role in the wettability alteration of the calcite surfaces. Moreover, the chain length of the fatty acids greatly influences the wettability of calcite and carbonate rock samples. Increasing the acid chain length resulted in higher contact angles (more oil-wet). Long chain fatty acid (SA) alters the calcite wettability to neutral-wet as compared to short chain fatty acid (HA) to less water-wet.

2. The procedure to measure contact angles on treated calcite crystals for the MO(HA) and MO(SA) offers good repeatability. The crystals must appear identical to offer good repeatability and hence great care must be taken when polishing the crystals. The drop volume and deposition are also important and

results from the experiments with slight deviations in the procedure may not be comparable to each other.

3. Arabian Gulf seawater (SWME) was found to be more effective in changing the wettability of calcite and carbonate surface towards more water-wet as compared to twice diluted Arabian Gulf seawater (SWME*).

4. Sulfate ion had the largest effect on wettability in the presence of magnesium and calcium ions. Sulfate is a potential determining ion towards calcite and carbonate, which has impact on the wetting state towards more water-wet. However for calcite there exists an optimal concentration for SO_4^{2-} (same concentration of SO_4^{2-} in Arabian Gulf seawater) ions to give the most water-wet surface. It is confirmed that sulfate dictates the wettability and should be present in the injected seawater. The ratio between sulfate and calcium concentration should be as high as possible without causing precipitation of $CaSO_4(s)$.

5. The presence of Mg^{2+} ions has inconsiderable effect on wettability of calcite as compared to the reference measured DIW. However Mg^{2+} has shown as a potential ion towards the carbonate surface and the surface is altered towards more water-wet with increasing the concentration of Mg^{2+} ion.

Recommendations

The contact angle measurements for the MO(HA)/Calcite, MO(SA)/Calcite and MO(SA)/Carbonate should be performed at higher temperature and pressure in order to mimic reservoir conditions. The same set of experiments should be carried out for dolomite in order to be able to better understand the exact mechanisms for carbonate rocks.

The pH of the brines can be altered to study the effect of pH on the wettability modification of the carbonate rocks.

Also crude oil with some specific reservoir in mind should be used and contact angle measurements should be performed using the same protocol as for model oil.

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