5-2019

Optimization of Low Salinity Water Flooding in Low Permeability Oil Reservoir Yang Li

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OPTIMIZATION OF LOW SALINITY WATER FLOODING IN LOW PERMEABILITY OIL RESERVOIR

Yang Li

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering

Under the Supervision of Professor Abdulrazag Y. Zekri

May 2019

Declaration of Original Work

I, Yang Li, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Optimization of Low Salinity Water Flooding in Low Permeability Oil Reservoir*", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Abdulrazag Y. Zekri, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

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Abstract

In recent decades, the demand of energy is growing sharply. Oil plays a very important role among all of the energy resources. Low permeability oil reservoirs classified as nonconventional oil reservoirs and needs special techniques for oil recovery. The primary aim of this study is to select a proper technique for oil recovery of low permeability carbonate oil reservoir. Different carbonated and non-carbonated brines were employed in this project. Formation brine (17500 ppm), carbonate formation brine, sea water, low salinity water, carbonated sea water (50000 ppm), and carbonated low salinity brine (5000 ppm) were used in this work. Core samples were grouped as composite cores with overall average permeability similar to the reservoir permeability. Four sequential low salinity water flooding systems were studied in this project. The following four different sequential water flooding systems were tested: (1) FW-SW-LSW-car LSW, (2) car SW-SW-LSW, (3) car FW-FW-SW-LSW, (4) car LSW-LSW-SW. In general the results of the experimental work indicated that Carbonated Water performs better than non-carbonated water. Carbonated Low Salinity water is the optimum brine among all tested brines in terms of oil recovery. A sequential composite core water flooding consists of car LSW- LSW-SW is the optimum sequential flooding system among the studied systems. The interfacial tensions, contact angle, and end point relative permeability results indicated that wettability is the dominant oil recovery mechanism of the studied systems.

Keywords: Low permeability reservoir, core flooding, LSWF, CWF, carbonated LSW, IFT, contact angle, EOR.

Title and Abstract (in Arabic)

اختيار الطريقة المثلى لاستخدام فيضان المياه المنخفضة الملوحة في خزان النفط منخفض النفاذية

الملخص

في العقود الأخيرة، ازداد الطلب على الطاقة بشكل حاد. يلعب النفط دوراً هاماً للغاية بين موارد الطاقة الآخرى. تصنف خزانات النفط منخفضة النفاذية على أنها خزانات نفط غير تقليدية و هي تحتاج إلى تقنيات خاصة لاستخراج النفط منها.الهدف الرئيسي من هذه الدراسة هو اختيار تقنية مناسبة لاستخراج النفط من خزان نفط غازي منخفض النفاذية. في هذا المشروع، تم استخدام محاليل ملحية مكربنة و غير مكربنة. تم استخدام محلول ملحي من الخزان (17500 جزء في المليون)، محلول ملحي مكربن من الخزان، مياه البحر، مياه منخفضة الملوحة، مياه بحر مكربنة (50000 جزء في المليون) ، ومياه منخفضة الملوحة مكربنة (5000 جزء في المليون) في هذا البحث. عينات اللب جمعت باعتبارها لب مركب ذو متوسط نفاذية إجمالية مماثلة لنفاذية الخزان. تم دراسة أربعة تسلسلات مختلفة من المياه منخفضة الملوحة. الأربع تسلسلات المختلفة التالية تم اختبارها: (1) مياه الخزان- مياه البحر- مياه منخفضة الملوحة- مياه مكربنة منخفضة الملوحة، (2) مياه بحر مكربنة- مياه بحر- مياه منخفضة الملوحة، (3) مياه خزان مكربنة- مياه خزان- مياه بحر- مياه منخفضة الملوحة، (4) مياه مكربنة منخفضة الملوحة- مياه منخفضة الملوحة- مياه بحرز بشكل عام أشارت نتائج التجارب إلى أن المياه المكربنة تؤدي بشكل أفضل من المياه غير المكربنة. محلول المياه المكربنة منخفضة الملوحة هو المحلول الملحي الأمثل بين جميع المحاليل الملحية المختبرة من حيث استخراج النفط. تسلسل غمر العينات المكون من المياه الكربونية منخفضة الملوحة، ثم المياه منخفضة الملوحة، ثم مياه البحر هو التسلسل الأمثل بين الأنظمة المدروسة. أشارت نتائج التوترات السطحية، وزاوية التلامس، والنفاذية النسبية لنقطة النهاية إلى أن قابلية التبليل هي آلية استخراج النفط المهيمنة في الأنظمة المدروسة.

مفاهيم البحث الرئيسية: خزان منخفض النفاذية، غمر عينات الصخور، غمر المياه منخفضة الملوحة، غمر المياه المكربنة، المياه المكربنة منخفضة الملوحة، التوتر السطحي، زاوية التلامس، تعزيز استرداد النفط.

Acknowledgements

It has been my honor to study at the United Arab Emirates University. I feel that I have achieved great things here and I want to thank the university, for the opportunity that it gave me to enjoy the experience I have had.

In terms of my research, I first have to thank my supervisor Abdurazak Zekri. He offered me an opportunity to work as a research assistant on this project for one and half years, and it became my research topic when I wrote my own thesis. He always helped me with the research. When I did not know what to do, or where to turn, he always taught and guided me patiently. I believe that without his help, I could not have finished this research. Therefore, I wish to thank him for everything he has done for me.

I also have to thank Professor Gamal Alusta, Coordinator of the Petroleum Engineering Department. He always helped me. If I was confused about any procedures, or anything else, he helped me to understand and to know what to do. I really appreciate his help during the last two years.

Furthermore, I have to thank the department chair, Sulaiman Al-Zuhair and the former chair Abdulrahman Y Alraeesi for their help in finishing my studies.

Finally, I have to thank Engineer Essa’s for his help. He taught me how to use the equipment and how to conduct experiments. He taught me a lot, not just about these experiments, but about petroleum, life and philosophy. It was very nice to spend time with him and I thank him for his help.

I also want to thank all the people who helped me both recently and before. Without your help, I would not have been able to achieve anything. However, we have become friends, got to know each other and helped each other. We have discussed our

subject area as well as life in general. We have studied together and grown together, I know all my friendships here will be lifelong.

During my time here I have learned to solve a lot of problems by myself. As a result I have grown as a person and become stronger. I am not the same person that I was two years ago and fully intend to keep on growing as a person.

Dedication

I dedicate this to my beloved parents and friends

who were always with me

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List of Abbreviations

Car FW	Carbonated Formation Water
Car LSW	Carbonated Low Salinity Water
Car SW	Carbonated Sea Water
CWF	Carbonated Water Flooding
EOR	Enhance Oil Recovery
EWI	Engineered Water Injection
FW	Formation Water
IFT	Interfacial Tension
LSWF	Low Salinity Water Flooding
LSWI	Low Salinity Water Injection
OOIP	Original Oil in Place
PV	Pore Volume
RF	Recovery Factor
SW	Sea Water
TDS	Total Dissolved Solid
UAEU	United Arab Emirates University

Chapter 1: Introduction

1.1 Overview

Current studies suggest that carbonate reservoirs is the most common oil reservoirs around the world, possibly accounting for up to 60% of the oil reservoirs are located in carbonate oi reservoirs (Klemme and Ulmishek, 1991). Carbonate rock is mainly composed of dolomite and impure mineral calcites. Additionally, we can find quartz, clay minerals, organic matter, apatite and other more minor components in carbonate rock (Reeder, 1983). Nevertheless, the recovery factor from carbonate rock reservoirs is usually quite low, often standing at less than 40%. Therefore, more economic, and also environmentally friendly, methods are required to increase oil recovery from carbonate oil reservoirs (Jackson et al., 2016). As the demand for energy increases, the technology designed to improve the oil recovery has become increasingly important. Therefore, this study takes a critical look at Enhanced Oil Recovery (EOR) techniques, which promises to produce significant amount of oil recovery after both primary and secondary recovery stages. Of course, reservoirs are different from each other, therefore a special EOR recovery technique should be determine for each reservoir. The development of these extraction techniques has to be viewed on a case-by-case basis, as certain reservoirs will require more specific methods in order to achieve optimal oil recovery. One effective EOR technique is Low Salinity Water Flooding. This is an effective method that changes the wettability of the reservoir. Reservoirs are normally considered as oil-wet and this retards the recovery of oil. However, after the injection of water, the reservoir changes from oil-wet to water-wet, or intermediate-wet, which vastly improves the recoverability of oil from the reservoir.

The first attempt to inject water into an oil reservoir was conducted in 1907 at the Bradford Field. However after that, many reservoirs carried out this operation to successfully expand the recovery potential of any given reservoir. This water injection technique resulted in adding 11% to the 6.6 million barrels extracted in the U.S.A. in 1955 (Preston et al., 2005). Today offshore reservoirs belonging to Brazil produce 74% of their oil using this method (Alvarado and Manrique, 2010). When they use this method, engineers also search for new brine deposits so that they can recover more oil than they can expect simply using normal water. This is referred to as a Smart Water Flooding Study. After engineers understood more about the chemical properties of smart water, the technique was refined into the Low Salinity Water Flooding method. Studies of this kind have proliferated in the past 20 years because of economic and operational reasons. Engineers can easily get hold of sea water and inject that to improve recovery rates after inducing flooding. The details of this method with be discussed below, as will the contents of the smart water. This smart water will be referred to as Low Salinity Water (LSW) due to the difference in the amount of salt in the water. Researchers show that alterations in the wettability is one major mechanism caused by LSW techniques in carbonate rock reservoirs. However, the exact factors affecting this alteration have yet to be clearly illustrated (Al Shalabi and Sepehrnoori, 2016). For example, most studies have found that LSW changes the wettability of reservoir rock from oil-wet to water-wet. Al Attar et al. (2013), also discovered that Low Salinity Water Injection (LSWI) changed the consistency from water-wet to intermediate-wet and that this also aided oil recovery more than with normal water. Although the exact mechanism of how LSWI works is still not clear, it is obvious that sulphate plays the role of catalyst in the adsorption process. It is also stronger than other carboxylate groups found in the oil. Therefore, it changes the surface charge of the rock from positive to negative and repulses oil and other carboxylate groups from the rock's surface (Austad et al., 2012). Finally, the consistency of the rock is altered from being oil-wet to water-wet, so that recovery is increased and more oil is produced from the reservoir. Nevertheless, the reasons behind this still require further research. Some studies have suggested that a double layer expansion is the main reason for these changes (Mahani et al., 2016). It is also thought that mineral dissolution may account for these changes (Hiorth et al., 2010), while another study suggests that surface complex excitation leads to changes in wettability (Mahani et al., 2016).

Moreover, with the LSWI technique, the pH value effects the interaction between the oil, brine and rock as well. For instance, Austad et al. (2012) assumed that LSWI triggers the substitution of Ca^{2+} by H^+ and compensates for the desorption found in the clay surfaces. This assumption is illustrated by the fact that LSWI always results in a pH increase. Furthermore, LSWI promotes ion exchange between the embedded Na^+ and H^+ in the system (Brady and Krumhansl, 2012), and results in an increase in the local pH value. Nevertheless, there remains plenty of work to be done in order to understand more about the effect of pH on the interaction between oil, brine and the rock itself.

The non-hydrocarbon gas, CO_2 is a suitable substance for bubbling into and through the smart water. The properties created when water has been treated with CO_2 will be discussed below. That said, the main point is that the water injection is significantly affected by the mobility ratio between the water and the oil. The mobility ratio can be defined as:

$$\lambda = \frac{K_{rw} * \mu_o}{K_{ro} * \mu_w} \tag{1.1}$$

As the relative permeability of the oil and water in the reservoir is not so very different, the viscosity ratio of the injected water and the oil becomes very important (Hickok et al., 1960). It was shown that if the mobility ratio reaches one (1), then the highest rate of oil recovery will be achieved (Paul W.G., 2004). Thus, carbonated water injections have huge potential to increase that mobility ratio further towards a rating of one (1). Khaksar et al. (2016) used different combinations of carbonated water in order to study this method. In this experiment, engineers added eleven different kinds of salt and different concentrations of both FW and distilled water to study the mechanisms of oil recovery. They followed this by bubbling various concentrations of brine with CO_2 to see if this further enhanced oil recovery.

1.2 Statement of the problem

Nowadays, primary and secondary oil recovery is conducted in large oil reservoirs all over the world, and in most of them they are attempting to enhance their oil recovery methods. As energy consumption requirements increase, EOR methods have become increasingly important to us. There is a lot of research on the LSW technique in both medium and high permeability reservoirs (Dong et al., 2011) and (Al Attar et al., 2013). However, there have still been very few studies that illustrate the effects of Low Salinity Water Flooding in low permeability reservoirs with composite cores. A study of a single core sample is not enough to illustrate real life reservoir conditions, therefore, more studies are needed on how brine can affect the composite core after flooding in a certain sequence. Furthermore, the results from such a study should allow for the construction of a simulation database where the study of smart water flooding in composite cores can be explored in much more depth.

1.3 Relevant literature

Primary recovery is seen as the most natural method for generating energy as the pressure applied pushes oil out of the reservoir. However, primary recovery only produces less than 20% of the OOIP. Secondary recovery always makes use of a water, or gas, injection. After such an injection, around 30% OOIP can be realized. Therefore, EOR methods are critical as there remains around 70% of the OOIP in the reservoir. The main EOR techniques can be classified into four categories as follows:

1. Miscible Drive: normally uses lean gas or a CO_2 injection.
2. Immiscible Drive: normally uses a CO_2 injection.
3. Chemical Drive: polymer, surfactant or LSW injection.
4. Thermal Drive: steam, in-situ combustion.

In terms of this study, the method being explored is the third technique: a form of LSW injection referred to as a chemical drive. The following section will explain this method in more detail.

1.3.1 Introduction to LSWI

Low Salinity Water Injection (LSWI) is one of the major EOR methods. It can alter the wettability in order to change the properties of the carbonate rock to obtain greater oil yields. This method is very efficient when dealing with both the light and medium components of crude oil formation (Brady and Krumhansl, 2012). On the other hand, because brine and water can be obtained both easily and economically, and are easily injected into the reservoir, LSWI has become the most popular EOR method in the oil industry today (Callegaro et al., 2014).

A lot of research has been conducted on this method in the laboratory and also in the field. LSWI has been seen to be effective, particularly in secondary and Enhanced Oil Recovery (EOR). This mechanism allows for incremental oil recovery whilst it is being carried out. Additionally, LSWI also works alongside methods such as fine migration or rock dissolution (Kozaki, 2012). Currently, only a few researchers are interested in LSWI applied to carbonate rocks because there are already many studies dealing with LSWI and sandstone. However, carbonate rock is the same, or at least similar to, sandstone rock. Therefore, if we accept that it is the presence of clay that is the major reason for alterations in wettability then this technique should aid oil recovery in carbonate rocks also (Awolayo et al., 2014). Furthermore, the complicated chemical interactions between the oil, water and rock, allied to the differences in specific carbonate rocks makes it is hard to predict the full range of incremental oil recovery that is due to LSWI. Another reason why LSWI is being considered for incremental oil recovery is due to its chemical properties and mechanisms.

Dang et al. (2013) have reviewed the extant literature on LSWI, modeling, numerical simulations, LSWI pilot tests, and Hybrid LSWI projects with a focus on sandstone rocks. Furthermore, Sheng et al. (2014) have discoursed on LSWI in regard to sandstone and offered their observations of laboratory and reservoir conditions, mechanisms and simulations.

Lee et al. (2010) conducted an overall summary of the performance of LSWI, its applications and effect on both carbonated rock and sandstone reservoirs, finding that injecting diluted water with brine gave the best LSW configuration. Additionally, the softening and hardening of the water to be injected is referred to as Engineered Water Injection. This is a suitable EOR technique as well. LSWI has been used with both carbonated rock and sandstone reservoirs, but most commonly with sandstone.

Meanwhile, EWI has mostly been used in carbonated rock reservoirs. Lee et al. (2010) also discussed the various ways of using LSWI and EWI in their paper. This included issues such as correspondence control and the combination of LSWI/ EWI with other components such as polymers, CO_2 and surfactant. Their study gave a detailed explanation of the following aspects: The effects of LSWI/ EWI on carbonated rock and sandstone reservoirs, modeling LSWI/ EWI, LSWI/ EWI desalination, other applications of LSWI/ EWI, proposed chemical mechanisms for use with carbonated rocks and sandstone, and a comparison between carbonated and sandstone rock samples. Bagci et al. (2001) looked at LSWI and its effect on carbonated rock cores (limestone) after they had finished researching the effect of LSWI on sandstone. They found that it was appropriate to reduce the salinity of the water injection for enhanced recovery in a carbonated rock reservoir.

Al Harrasi et al. (2012) carried out Low Salinity Water Flooding experiments using different carbonated rock core samples. The brine injections were mixed with four different distilled water concentrations. The brine was mixed with distilled water and diluted twice, 5 times, 10 times and 100 times respectively. Also, spontaneously imbibed and core flooding experiments have been conducted and have resulted in a 16-21% increase in oil recovery.

1.3.2 Mechanisms for LSWI

1.3.2.1 IFT reduction

Several studies have discussed surface tension, because of its importance in the EOR process. Changes in pressure or temperature affect this property regardless of the addition of water additives. Because of the pressure and temperature changes, the IFT behavior of the water and oil cannot be illustrated very clearly. Wang and Gupta (1995) produced complete IFT data on two distinct brine and crude oil samples with pressure ranging from an ambient pressure to 10,000 psi, and a temperature range of 70°F to 200°F. They also recorded data for distilled water and oil at the same pressure and temperature ranges as for the former data. When they plotted the IFT versus the temperature and kept the pressure constant for crude oil and brine, they found that when the temperature decreased, the IFT decreased as well. However, with another system, the phenomena reported were opposite, when the temperature decreased, the IFT increased. They used this information to suggest a direct relationship between IFT and temperature. The trend suggested that an increase in pressure leads to an increase in IFT, but there still remained some cases of dispersion that went against the trend. Jennings and Newman (1971) compared the IFT data on oil and water within a pressure range from ambient to 12,000 psi, and a greater temperature range of 74°F to 350°F. From their data no specific trend emerged when they considered IFT versus pressure at different temperatures. The IFT data reported by Hjelmeland and Larrondo (1986) showed that in two different laboratories, the respective IFTs were totally different from each other when the temperature was increased. A similar phenomenon could be seen operating between oil, brine and fresh water systems (Mulyadi and Amin, 2010). These studies on the effects of pressure and temperature on IFT show that the relationship between IFT, pressure and temperature depend on the system. Figure 1 shows the contact angle in the oil-water system.

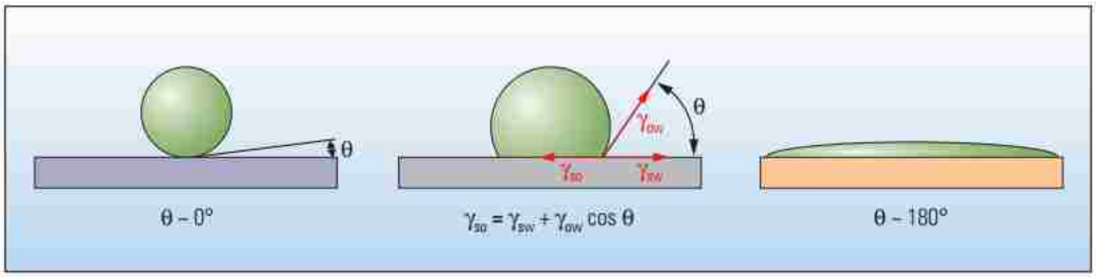

Figure 1: Contact angle example

The contact angle is determined by the IFT. Therefore, in order to reduce the IFT, the contact angle should be reduced.

This mechanism still requires further research and there is no real theoretical definition to support this study yet. However, IFT data and the oil-brine system can, indeed, be studied. Significant outcomes can be found in the literature. Despite a huge range of temperature and pressure, the IFT data was mostly found to have an average value of around 25 mN/ m. Thus, the literature suggests that the IFT varies according to different pressures and temperatures. However, 25 mN/ m cannot be considered as the mean value of the oil-brine system as reservoirs are different from each other.

1.3.2.2 Wettability alteration

A change in the wettability is an important technique to increase oil recovery when using the LSWI technique. There are several mechanisms that have been put forward, such as an IFT reduction due to an increase in pH value, double layer expansion and multi-ion exchange. However, an alteration of the wettability has always been considered as the main mechanism making LSWI effective. Tang and Morrow (1999a) found that in a sandstone reservoir, because of clay minerals, the FW with had a high concentration of Ca^{2+} and Mg^{2+} in the composition of the oil. Therefore, the consistency is altered due to a reaction between the rock and the LSWI.

Many studies have investigated the effect of LSWI on the consistency of sandstone. Tang and Morrow (1999b) conducted an investigation into the necessary conditions for LSWI. They found that the type of clay in the sandstone plays an important role. Another condition is that the water injected should have elements such as Mg^{2+} and Ca^{2+}, while the oil should have their polar components. The salinity concentration of the water injected should be around 1,000 to 2,000 ppm. However, they also found that even if the salinity of the water was as high as 5,000 ppm, the effect was still significant. They also discovered that there was a small increase in pH values in the effluent and that the ratio of Ca^{2+} to Na^{+} had some effect. When the pressure in the core increased, they found fine migration phenomena and that there was no limit for the temperature. That said, normally such experiments are conducted below 100°C. Figures 2 and 3 show the mechanism.

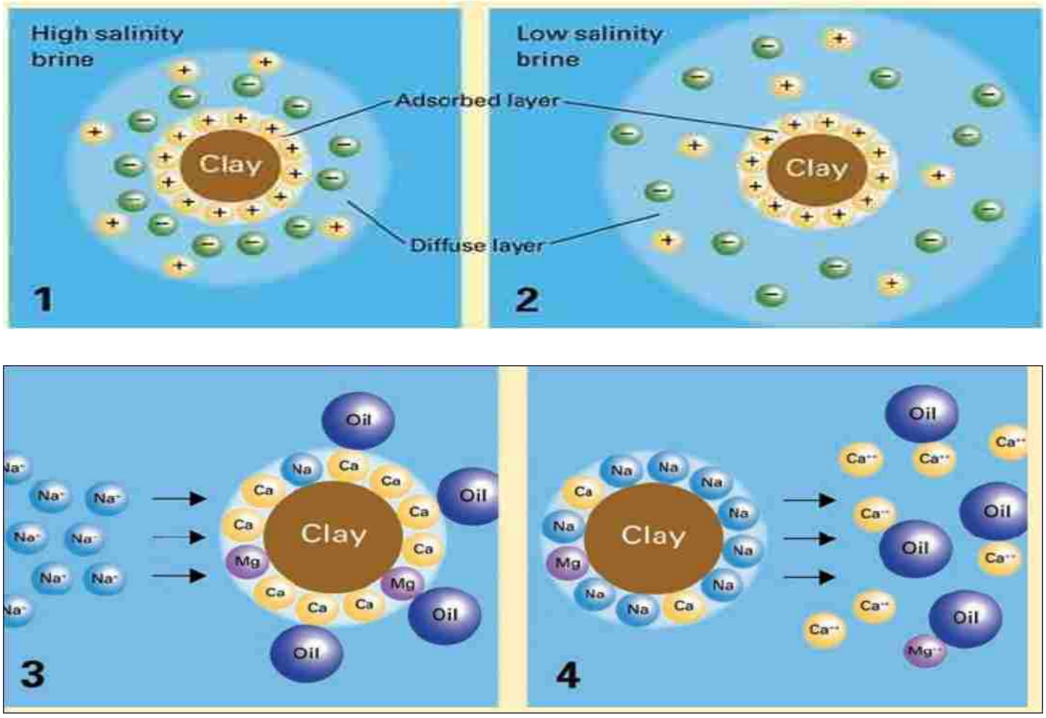

Figure 2: Microscopic mechanism of the chemical reaction

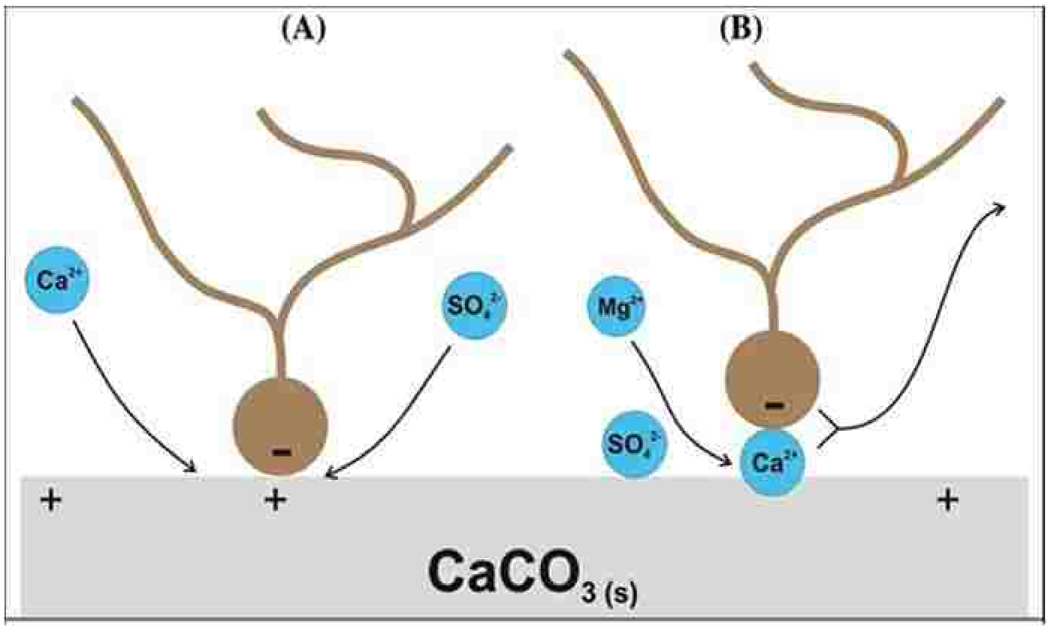

Figure 3: Microscopic mechanism of the wettability alteration

When low salinity brine comes to the rock surface, the diffuse layer changes the divalent cation is by a univalent cation such as Na^+ (replacing Ca^{2+} or Mg^{2+}). Then, the oil on the diffuse goes with the newly replaced cation in order to increase oil recovery.

The phenomenon where spontaneously imbibed water enters the matrix happens when the rock is water-wet or intermediate-wet. Toraseter (1998) found that on the other hand, if the rock is oil-wet, the spontaneously imbibed reaction does not happen because of negative capillary pressure. However, if the oil-wet reservoir is fractured, the water which has been injected will move easily through the fractured pores and an early breakthrough will be achieved.

Once the highly fractured reservoir in the Ekofisk Field in the North Sea was successfully injected with water, this technique became very popular (Zhang et al., 2006). The resulting compositions of calcium and sulphate showed enormous potential to have an effect of the calcite surface (Pierre, 1990). Meanwhile, LSWI experiments also displayed positive results in carbonate rock reservoirs (Al Attar et al., 2013). Unfortunately, there are few studies around that suggest that an increase in the concentration of sulphate in sea water will benefit the situation. Therefore, Zahid et al. (2012) did extensive experiments to measure key properties at 90°C and at ambient temperatures to see if they had a significant effect on the wettability alteration of oil, brine and rock system.

According to these experiments, the adsorption of sulphate increases as the concentration of calcium increases. This is because calcium ions are co-adsorbed by the carbonate rock surface. When sulphate adsorption takes place on the carbonate rock, the positive charge on the rock surface decreases. Then, the calcium ions on the rock surface decrease too due to reduced electrostatic repulsion (Austad et al., 2007). The adsorption of calcium and sulphate is stronger on the rock’s surface when the temperature increases. This changes the consistency of the rock and, as a result, increases oil recovery (Strand et al., 2017). When the temperature is low, the adsorption of calcium ions is better than that of magnesium ions on the rock surface

(Zhang et al., 2006). Therefore, if the temperature increases, calcium ions will be replaced by magnesium ions. It is desirable for magnesium ions to replace the calcium ions on the rock surface because they are more reactive than calcium ions, due to greater dehydration. With oil, brine and rock the composition of sulphate, magnesium and calcium is significant in terms of altering the wettability consistency. Furthermore, limestone displays a similar interaction with sea water (Al Otaibi et al., 2010).

1.3.2.3 Rock dissolution

There are other reactions that happen in reservoir rock when it is injected with water as part of the oil production process. When CO_2 is used to bubble through the injected fluid during the EOR process (or bubble to the aquifer), the interaction between the water and the rock is highly significant, especially in carbonated reservoirs. When CO_2 is bubbled through the water, carbonic acid is formed. After that, the carbonic acid reacts with the salts in the rock, such as magnesium carbonate or calcium carbonate, and they dissolve. When the rock has dissolved, a lot of its properties are changed, such as permeability and how porous it is (Luquot and Gouze, 2009). Furthermore, the dissolved salt may cause formation damage because it accumulates as very small particles in the low permeability carbonate reservoir. In this method, the main way that permeability decreases is through precipitation (Bacci et al, 2011). An injection of carbon dioxide and brine may cause either effect. Due to dissolution it will either increase the porosity and permeability of the rock, or it could decreases it due to precipitation (Grigg et al., 2003). Sayegh et al. (1990) found that carbonated minerals in the rock such as magnesium carbonate or calcium carbonate react very quickly with carbonated water once they meet. The equations to describe this mechanism are as follow (Sayegh et al., 1990):

$$H_2O + CO_2 \Leftrightarrow H_2CO_3 \quad (1.2)$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (1.3)$$

The presence of magnesium carbonate and calcium carbonate explain the mechanism of the reaction:

$$H_2O + CO_2 + CaCO_3 \Leftrightarrow Ca^{2+} + HCO_3^- \quad (1.4)$$

$$H_2O + CO_2 + MgCO_3 \Leftrightarrow Mg^{2+} + HCO_3^- \quad (1.5)$$

These reactions release grains from the dissolution through the flow path, which causes the grains to accumulate near to the throat of the pores and thus reduce permeability. On the other hand, if the size of the grains is smaller than the bottleneck of the pores, there will be no precipitation and the resultant reaction will increase permeability. Ross et al. (1982) found that to increase the temperature of carbon dioxide at a constant pressure, more bubbling of CO_2 into the water was required and that it also increased the permeability of calcite rock (Ross et al., 1982). When pressure decreases, precipitation occurs. For the equations that explain this mechanism see below (Sayegh et al., 1990):

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3 \quad (1.6)$$

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + H_2O + CO_2 \quad (1.7)$$

The effect of mineral dissolution because of LSWI can be measured using PHREEQC software. The result showed that Ca dissolution could be ignored in calcite rock due to LSWI. Therefore, if there is any anhydrite ($CaSO_4$), it will trigger SO_4^{2-} ions in the water. Also, because of the dissolution of Ca^{2+} in formation brine is limited, it is believed that mineral dissolution must have a relationship with LSWI (Mayers et al., 1988).

Another modeling calculation contains FW and FW diluted 100 times and injected into limestone core samples. There is also anhydrite in the brine used for the secondary and later injections (Grigg et al., 2003). Simulations showed that as the core is plugged with anhydrite, the recovery factor is increased after being injected with the FW and the diluted FW. However, when the anhydrite was removed in another simulation (simulation B), there was no increase in oil recovery. This illustrates that diluted brine alone cannot increase oil recovery. Therefore, it was suggested that there should be SO_4^{2-} in the LSW when the rock is depleted by anhydrites (Grigg et al., 2003).

In terms of sandstone, the dissolution of silicate minerals is so slow that it can be ignored. Meanwhile, because of the accumulation of negative charges on the silica surface due to the salinity of the brine, there is also electrostatic repulsion between the silica surface and the negatively charged fines. This means that oil on the silica surface will be released. Sometimes, a pressure drop will occur because the core throat has been plugged by fines migrating (Bacci et al, 2011).

To dilute the salinity of brine injected into the carbonated reservoir rock, the balance of the brines in the reservoir can be broken down but may cause calcium carbonate to dissolve or fines to migrate. Figure 4 shows this phenomenon. As such, on the rock’s surface, the oil can be removed. Figure 5 shows this phenomenon. The alteration of the rock from oil-wet to water-wet can occurs. Furthermore, because of the dissolution of the rock, the minerals that have been dissolved in the LSW may flow through the reservoir rock and then stop, precipitate, and possibly block the pores.

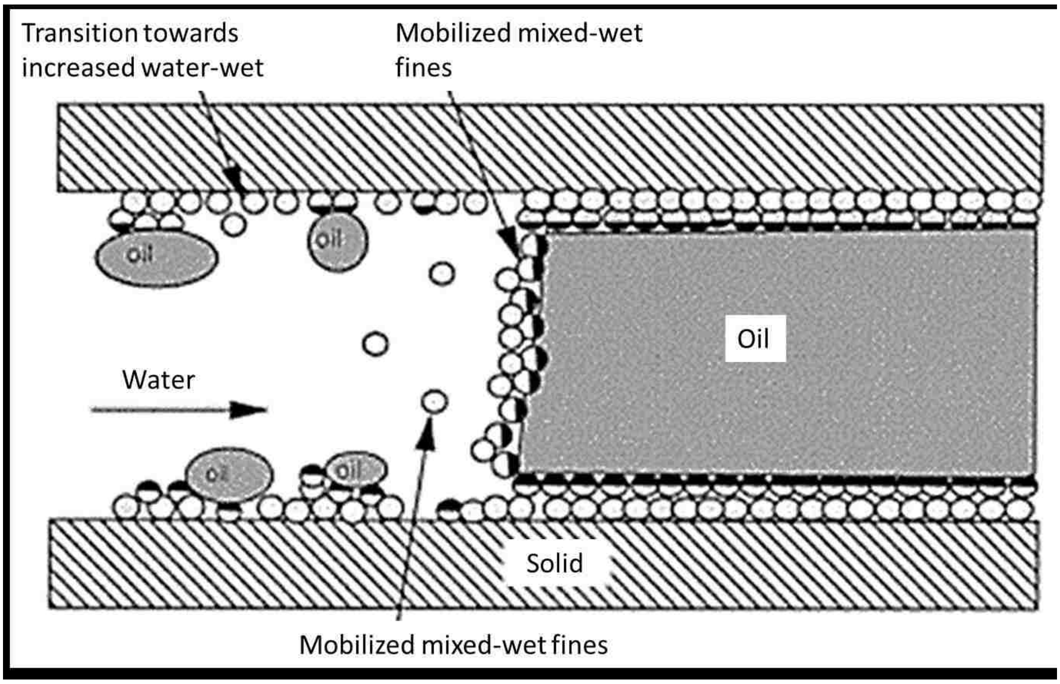

Figure 4: Low saline water dissolve fine carbonate particles

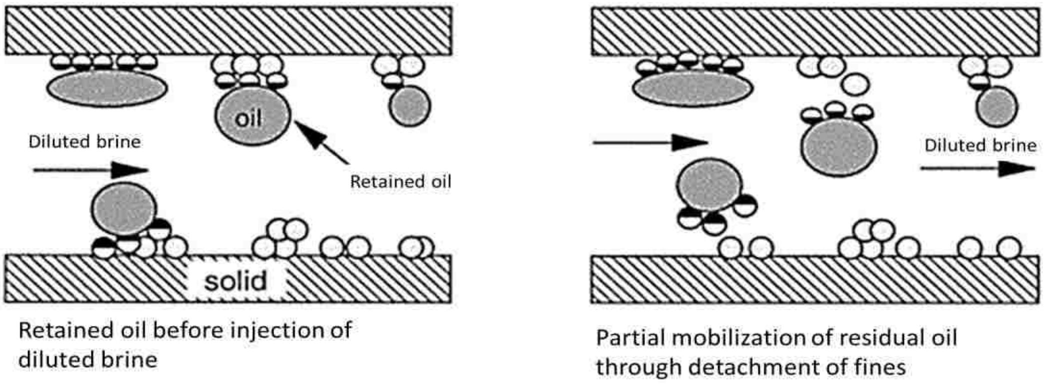

Figure 5: Trapped Oil Mobilization during LSWF (Tang and Morrow, 1999b)

When the throats of the pore are blocked, the flow path is changed to another, which is oriented to the sun's sweep zone and so increases microscopic sweep efficiency (Austad et al., 2007). This kind of behavior is the main LSW behavior that can effect incremental oil recovery (Tang and Morrow, 1999a).

1.4 Introduction of carbonated water flooding

Carbonated Water Flooding (CWF) is an EOR process which had been used, and subsequently improved, in oil fields for a long time (Christensen et al., 2013). The earliest CWF process was in the 1950s. Experimental research on CWF was widespread during the 1960s and 1980s. However, in the last thirty years, very few studies have been carried out in this area. Some of the experimental data in this area fails to show any obvious effect of CWF, such as a big difference in incremental oil recovery, yet the same experimental conditions can have very different and much more positive results (Hickok et al., 1960).

Numerous studies have shown that WF can be improved by changing chemical composition. To change the chemical composition of brine, there are many compounds that can be used (Hickok et al., 1962). CO_2 is one of the best compounds for this purpose. Bubbling CO_2 through brine changes the process to Carbonated Water Flooding (CWF). The CWF process is similar to the WF process as it injects CO_2 saturated water into the reservoir to displace any other water.

In the reservoir, we first have the water phase. Once the water is in contact with the oil, CO_2 will help us move to the oil phase without issues as both phases are in a liquid state. This occurs when the CO_2 moves from the water to the oil they are at the same temperature and pressure, but CO_2 dissolves more easily oil than in water. So, once the CO_2 moves to the oil, the viscosity of the oil will decrease, while the density of the also decreases. This means that the mobility ratio between the water and the oil has gone down (Martin, 1951). Meanwhile, the permeability of the oil has increased as the viscosity declined. This process shows that CWF can improve oil recovery more than the conventional WF. Because miscibility is not necessary during the CWF process, the oil type required for the CWF process has CO_2 injected than in the WAG process (Scott and Forrester, 1965). Furthermore, since the water and CO_2 mixture is easy to separate at the production well, CWF is easy to implement in reservoirs using WF process equipment. Moreover, when the CWF process has finished, the reservoir can still perform other EOR methods that do not cause any conflict. Figure 6 shows the process.

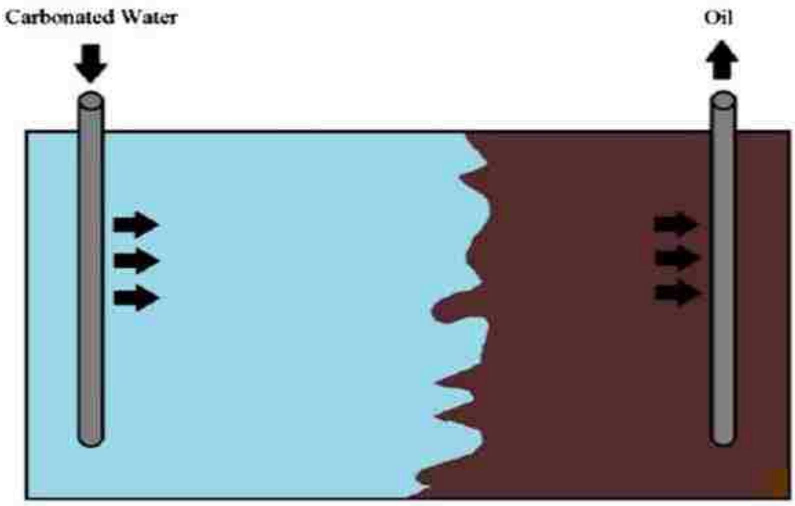

Figure 6: Example of the CWF Process (Cleverson et al., 2015)

As we can see from Figure 6, CW comes from the injection well and displaces the oil due to its immiscible properties. When the water contacts the oil, the oil will be pushed (by water and CO_2) into the oil phase and so reduce the viscosity of the oil and mobility ratio between the oil and the water (Ahmad et al., 2016).

Engineers bubble CO_2 into water to create the water flooding process as the CO_2 is readily dissolved into the water more easily than oil dissolves into water. Figure 7 shows the solubility of different gases.

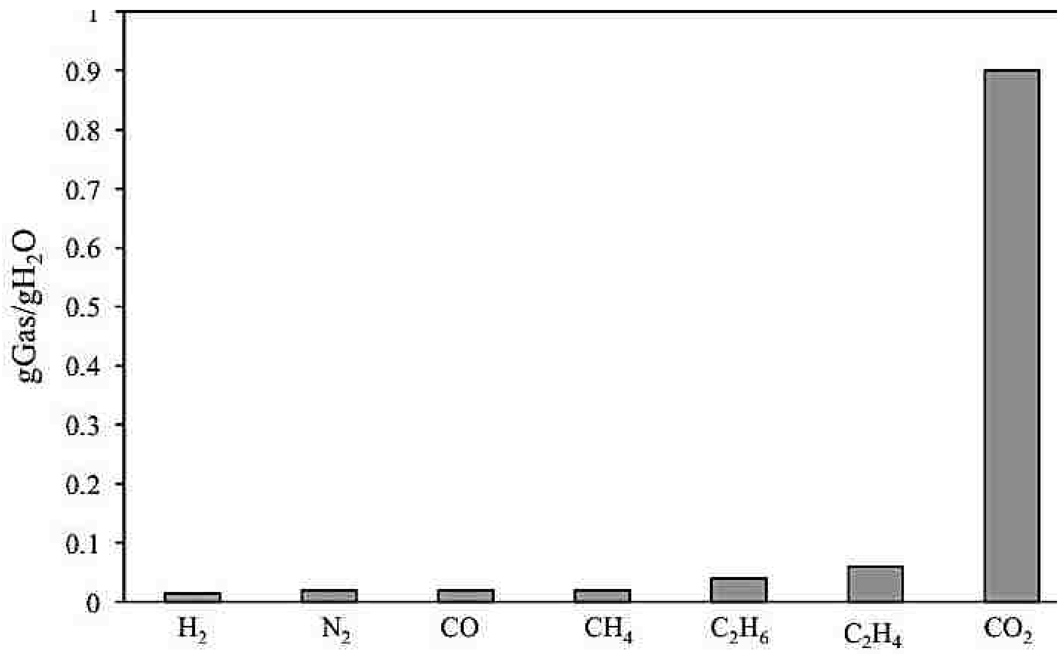

Figure 7: Solubility of Different Gases (Cleverson et al., 2015)

Figure 7 illustrates that CO_2 is significantly more soluble than other gases. It is almost ten times more soluble than the other gases depicted here. Therefore, bubbling CO_2 into water is easy, and CO_2 is also easy to get from industry waste gases (Sheng et al., 2014).

The CWF process is similar to the more common LSWI process as it changes the constitution of the rock, and reduces the IFT of the fluid and rock dissolution that also occurs. Therefore, these mechanisms will not be addressed in great detail here. Instead, the pore scale mechanism for this process will be highlighted. Figure 8 shows the pore scale example for the CWF process.

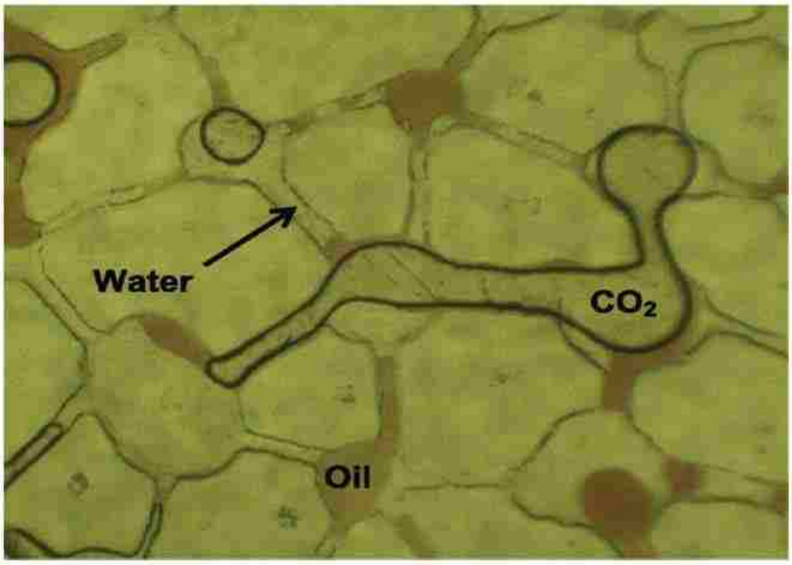

Figure 8: Pore Scale Mechanism for the CWF Process (Alizadeh et al., 2014)

In Figure 8, the brown color is oil, while the white color is fluid in the pores which is water, inside the water is the CO_2. Thus, the water contains CO_2 which will go through the pores and once it meets the oil the water will push the oil out of the pores. The oil will occupy the cores, while CO_2 will leave the water, join with the oil and then expand the volume of oil from pore to pore.

The studies reviewed here give an overall understanding of the CWF process and other pre-identified factors such as salinity, TDS, flow rate and so on. The major contributions gleaned from these studies are:

1. The final oil recovery after the CWF process is better than a conventional WF of 3-35%, when using light oil with a low viscosity.
2. To get an optimal flow rate, the other conditions during the CWF process must match reservoir conditions.
3. From previous studies, there is a plethora of experimental data that can be drawn on and that is of great value.

The benefits and convenience of choosing CO_2 to saturate the water are due to:

1. CWF can be carried out with minimal modification to the WF equipment. This makes the process economical.
2. Using CO_2 as a saturated gas may decrease the emissions of such a potentially harmful gas into the environment. Meanwhile, collecting this waste gas can be a source of profit for many industries.

Figure 9 shows the solubility of CO_2 in oil and the different conditions.

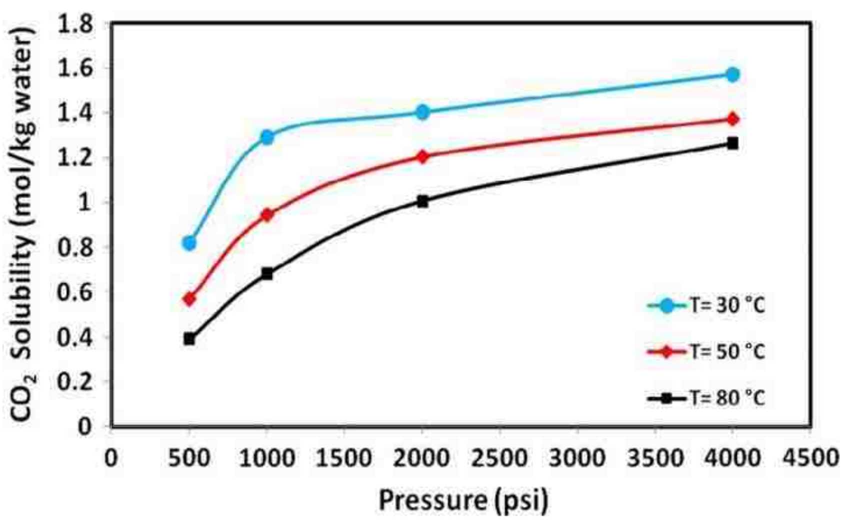

Figure 9: Solubility of CO_2 in different conditions (Yannong et al., 2011)

1.5 Research purpose

In this research, the effect of different brines on the recovery of oil will be studied. Then the reasons why certain brines or brine sequences are best for oil recovery will be discussed. Finally, according to the experimental results gleaned and an analysis of the results, better brines or brine sequences will be recommended to enhance the oil recovery through both LSWI and CWF.

Chapter 2: Experimental Work

2.1 Experiment equipment

All equipment used in this study are available in the core analysis lab, chemical and petroleum engineering department, UAE University.

2.1.1 Core holder

The core holder used in this study was purchased from “Core laboratories” company. It is used to hold the core during injection experiments after loading the samples.

2.1.2 Injection pump

The injection pump, from “Teledyne ISCO” company, was utilized in this study. The pump can be filled with any kind of brine that can be injected through the injection line brine of the pump. The pump can be used as constant pressure or constant flow rate. In this project a number of experiments were conducted at constant injection rate and others were performed at injection pressure depending on the overall permeability of the system.

2.1.3 Saturation instrument

The saturation instruments employed in this work was purchased from “VINCI” company. The instrument was used to saturate the samples with a certain brine. The description of the system is presented in section 3.

2.1.4 Core sample cleaning system

Soxhlet system was used for cleaning the core samples. Toluene was used in removing the oil from the cores and methanol was used in removing toluene and water. The description of the system is presented in section 3.

2.1.5 IFT measurement system

The IFT measurement system used in this study was obtained from “Teclis” company. The system is utilizing a microscopic camera to determine precisely the contact angel which then was used to measure the IFT. The description of the system is presented in section 3.

2.1.6 Core cutting machine

A core cutting machine obtained from “Wiltion” company was used in this work. It can cut the rock to core samples of desirable size, and these core samples were used later to perform analysis. The description of the system is presented in section 3.

2.1.7 Porosity and permeability measurement system

The porosity and permeability measurements system from “VINCI” company was used to measure the porosity and permeability of the core samples. The description of the system is presented in section 3.

2.2 Experiment material

Crude oil, formation brine, and core samples were collected from Asab field in UAE. Other brine types were made in the lab. Asab field is one of the major fields in UAE. Large area of the field has low permeability and never tabbed before and requires to find a new technique to recover the oil. The field contains around 3.6 billion bbls of oil in place. Therefore a minimal increase in the oil recovery will lead to production of large amount of oil, and subsequently that will lead to a huge financial benefit.

2.2.1 Core samples

Seventeen core samples obtained from Asab field were employed in this study. After saturating the samples with Asab oil, they were divided into 4 groups. The water flooding tests were conducted on all of these different groups to examine the oil recovery. The properties of the samples and water were measured. All the cores had permeability less than 1 md, and the samples were grouped into 4 composite cores with an average permeability between 0.43 to 0.7 md. Figure 10 shows the cleaned core samples. Detail data of all the samples are presented in Table 1, and details of the composite cores used in this study are presented in Table 2.

Figure 10: Cleaned core samples

Table 1: Detail data of all the samples

Samlpe id	Dry wt	Sat. wt.	Length	Diameter	Pore vol.		Bulk vol.	Grain vol.		Garin den.	Porosity		Permeability
	(gm)	(gm)	(cm)	(cm)	air (cc)	water (cc)	(cc)	air (cc)	water (cc)	(gm/cc)	air (%)	water (%)	Liquid (md)
2	171.35	185.20	6.884	3.801	14.57	12.67	78.15	63.57	65.47	2.70	19	16.2	0.29
3	173.44	188.04	6.929	3.806	14.75	13.36	78.86	64.11	65.51	2.71	19	16.9	0.40
4	175.12	190.55	7.091	3.797	15.08	14.12	80.33	65.25	66.21	2.68	19	17.6	0.55
5	169.02	185.52	6.986	3.798	16.47	15.10	79.18	62.71	64.08	2.70	21	19.1	2.01
7	169.89	181.15	6.507	3.805	10.86	10.30	74.02	63.16	63.72	2.69	15	13.9	0.15
10	94.98	108.15	4.262	3.792	13.01	12.05	48.15	35.15	36.10	2.70	27	25.0	3.77
13	140.50	158.94	6.186	3.797	18.02	16.87	70.07	52.06	53.20	2.70	26	24.1	1.03
14	105.73	118.63	4.633	3.797	13.24	11.80	52.48	39.24	40.68	2.69	25	22.5	1.45
17	132.48	148.51	5.716	3.807	16.00	14.67	65.09	49.10	50.43	2.70	25	22.5	1.43
18	164.65	177.28	6.609	3.800	12.97	11.55	74.98	62.01	63.43	2.66	17	15.4	0.16
19	130.14	145.39	5.649	3.798	15.66	13.95	64.02	48.36	50.07	2.69	24	21.8	0.75
21	102.23	113.85	4.407	3.799	12.09	10.63	49.97	37.88	39.34	2.70	24	21.3	1.41
23	106.69	118.46	4.538	3.798	12.17	10.77	51.43	39.27	40.66	2.72	24	20.9	1.45
24	138.20	154.48	5.988	3.799	16.68	14.89	67.90	51.22	53.01	2.70	25	21.9	1.04
25	142.78	159.34	6.157	3.793	16.73	15.15	69.60	52.87	54.45	2.70	24	21.8	1.60
26	145.89	163.86	6.401	3.814	19.26	16.44	73.16	53.90	56.72	2.71	26	22.5	1.44
28	107.96	120.01	4.692	3.825	13.49	11.02	53.94	40.45	42.91	2.67	25	20.4	1.28

The cores have diameter around 3 cm and length in the range of 3-7 cm. In most of single core flooding experiments, the permeability of the cores used was less than

1 md, representing the permeability of tight oil reservoir. Darcy's law was used to calculate the permeability from the collected data.

$$K = \frac{1000q\mu L}{A\Delta P} \tag{2.1}$$

Where q is the flow rate: cm^3/s

K is the permeability: md

A is the cross section: cm^2

ΔP is the pressure change: atm

μ is the viscosity: cp

L is the length: cm

Table 2: Group status of cores

Kw	Sample ID:	Flooding sequence	
Group #1		1.FW→2.SW→3.Low Sal→4.Carbonate Water	kavg
0.16	18		0.43
1.25	28		
1.55	25		
3.73	10		
Group #2		1.SW Car →SW→ 2.Low Sal	kavg
0.15	7		0.44
1.03	13		
1.93	5		
1.38	21		
Group #3		1. fw car →FW → SW →Low Sal	kavg
0.40	3		0.70
1.02	24		
1.45	17		
0.73	19		
Group #4		1. Low Sal Car →2.Low Sal→SW	kavg
1.38	23		0.62
0.29	2		
1.51	26		
1.45	14		
0.55	4		

2.2.2 Crude oil

In this research, crude oil from Asab oil reservoir was used. The physical properties of the Asab crude oil are presented in Table 3. All the properties were measured at ambient environment (Temp=25°C, Pressure=14.73 pisa). Figure 11 shows a sample of Asab crude oil.

Figure 11: Asab crude oil

Asab oil reservoir produces light oil with a gravity equal to 38.52°API. The viscosity of the Asab crude equal to 3.96 cp and density of 0.8322 g/cc. The overall quality of Asab's oil is excellent. Table 3 presented the physical properties of Asab oil.

Table 3: Asab crude oil properties

Asab crude oil properties at ambient environment	
Property	Value
Viscosity (μ)	3.96 cp
Density （ρ）	0.8322 g/cc
Specific Gravity （γ）	38.52°API

2.2.3 Brines

Six different brines were used. Tables 4, 5, and 6 present the composition of Asab formation brine, sea water, and low salinity water respectively.

Table 4: Composition of FW

CHEMICALS	1 LITRE
	mg
NaHCO3 (Anhy)	457.10
Na2SO4 (Anhy)	1308.65
NaCl	111120.96
CaCl2 (Anhydrous)	38324.34
CaCl2 2 H2O	50766.50
MgCl2.6H2O	13416.82
CaCl2 6 H2O	75649.44

Table 5: Composition of SW

CHEMICALS	1 LITRE
	mg
NaHCO3 (Anhy)	169.35
Na2SO4 (Anhy)	5831.99
NaCl	37706.28
CaCl2 (Anhydrous)	1910.68
CaCl2 2 H2O	2530.99
MgCl2.6H2O	17833.33
KCL	1281.30
CaCl2 6 H2O	3771.54

Table 6: Composition of LSW

CHEMICALS	1 LITRE
	mg
NaHCO3 (Anhy)	16.93
Na2SO4 (Anhy)	583.20
NaCl	3770.63
CaCl2 (Anhydrous)	191.07
CaCl2 2 H2O	253.10
MgCl2.6H2O	1783.33
KCL	128.13
CaCl2 6 H2O	377.15

Carbon dioxide was passed through formation brine, sea water, and low salinity water to form carbonated formation brine (car FW), carbonated sea water (car SW), and carbonated low salinity water (car LSW).

The procedures used in order to prepare the brines will be illustrated with full details in Appendix A.

2.3 Experimental content

Figure 12 shows flow chart of different stages of the experimental work performed in this project.

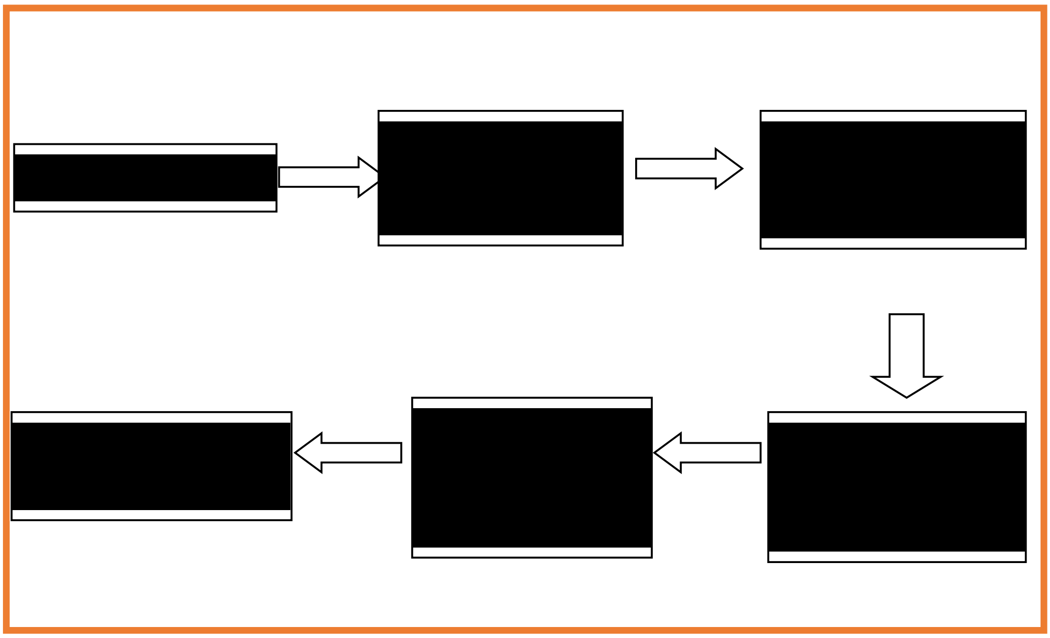

Figure 12: Flow chart of experiment

2.3.1 Samples preparation

In order to prepare the samples, cutting machine was used to cut the cores to the required sample size. All of the core samples were prepared to similar dimensions after cutting (length ≈7 cm, diameter ≈3.8 cm). The cutting of the core samples were done with extreme care to avoid fracturing the core samples. Fractured cores were excluded and only non-fractured cores were selected. Figure 13 shows the Wilton core cutting machine employed in this project.

Figure 13: Wilton sample cut machine.

After that, samples were cleaned using soxhlet extraction system. The first step was extraction of hydrocarbon components from the samples using toluene. Then, methanol was used to clean toluene in order to ensure that all samples were fully clean removing all of the water and oil from them. Figure 14 shows the soxhlet extraction system.

Figure 14: Soxhlet extraction system

After that, samples were dried in an oven for one day to get rid of all wettability. After this drying period, if any of the core samples were still not fully dry indicating that it still contains moisture, extra drying time was given to these cores. Figure 15 shows the oven used to dry the samples.

Figure 15: Oven

After fully drying the samples inside the oven, samples were weighed to measure their dry weight.

2.3.2 Sample saturation

VINCI saturator system was used to saturate the core samples with Asab reservoir formation water. Figure 16 shows the saturation system employed in this project.

Figure 16: VINCI saturator system

First of all, the samples were loaded into the cylinder and closed tightly. Secondly, all injection lines were connected and the valve opened to start the vacuum pump in order to remove all the air from the brine and the core. After ensuring all the trapped air is removed, the valve was switched to “inject” mode. The pressure then increased to 1000 psia by pressing the handle. After that, the samples were kept for one day inside the cylinder at this high pressure to ensure that all samples are fully saturated by formation water. Then, the cylinder was opened and the samples were removed form the core holder. Finally, the weight of the samples after saturation with formation water was measured.

2.3.3 Water permeability measurement

Figure 17 shows the core lab water permeability measurements system. The procedure of the water permeability measurements followed in this project consist of the following steps: samples were loaded in the core holder, and then the cylinder was closed tightly as it will serve under high pressure. Then, the pump was used to raise the pressure up to 800 psia. After that, the injection line was connected and the valve was opened. The fluid was removed out of the core by using a tube. Then, the injection pump was filled with formation water. Figure 18 shows the pump operation system and Figure 19 shows the injection line of the pump. After filling the pump with formation water, refill valve was closed, and the injection valve was opened in order to start the injection process. The pump ran initially at constant flow rate of 1 cc/min because the permeability of the cores was unknown. Then, once a sudden sharp increase in the pressure was noticed, injection was changed from constant flow rate of 1 cc/min to constant pressure of 600 psia, and the pressure of the core holder was raised to 1000 psia. The values of the pressure and flow rate were recorded 5 minutes after the pressure becomes stable, in order to calculate the Kw after flooding. The values of pressure and flow rate were recorded again every 10 minutes. The flooding stopped when the pressure and flow rate values become stable.

Figure 17: Core lab core holder and hydraulic pump

Figure 18: Teledyne ISCO D-series pump controller

Figure 19: Teledyne pump injection line

2.3.4 Oil permeability measurement

Figure 20 shows the core lab oil permeability measurements system. The procedure of the oil permeability measurements followed in this project consist of the following steps: samples were loaded in the core holder, and then the cylinder was closed tightly as it will serve under high pressure. Then, the pump was switched on to raise overburden pressure to 800 psia. After that, all injection lines were connected to the cylinder, and the injection line of the oil cylinder was opened. Figure 21 shows the oil cylinder that to inject oil to the core samples. Following that, the injection pump was filled with distilled water, and the injection line was connected to the bottom of the oil cylinder. Then, the injection valve of the injection pump was opened to start injecting. Figure 22 shows pump controller system employed in this project.

Figure 20: Core lab system

Figure 21: Oil cylinder

Figure 22: Pump controller

The pump can be set either for constant flow rate or constant pressure as desired. The pump was running at constant flow rate until the pressure increase up to 600 psia, then it was changed to constant pressure, and the pressure of the core holder was raised as well to 1000 psia. The constant pressure and flow rate were recorded. The injection water was continued until there is no water coming out from the core which indicated that irreducible water saturation was reached. The volume of the produced water was recorded, and the oil permeability was calculated using Darcy’s Law. The oil saturated core was placed in a container full of Asab oil for aging to restore the core condition to the initial reservoir condition. The aging process takes around one month.

2.3.5 Water flooding experiments

A number of different brines flooding experiments were conducted using composite cores. Composite cores were arranged in ascending, descending, and random with similar average permeability to simulate reservoir conditions. Figure 23 shows different composite core arrangements. The physical properties of the core samples are presented in Table 2. Figure 24 shows the “Liner X-Ray System” from “Core Lab” company used to conduct different composite cores water flooding experiments.

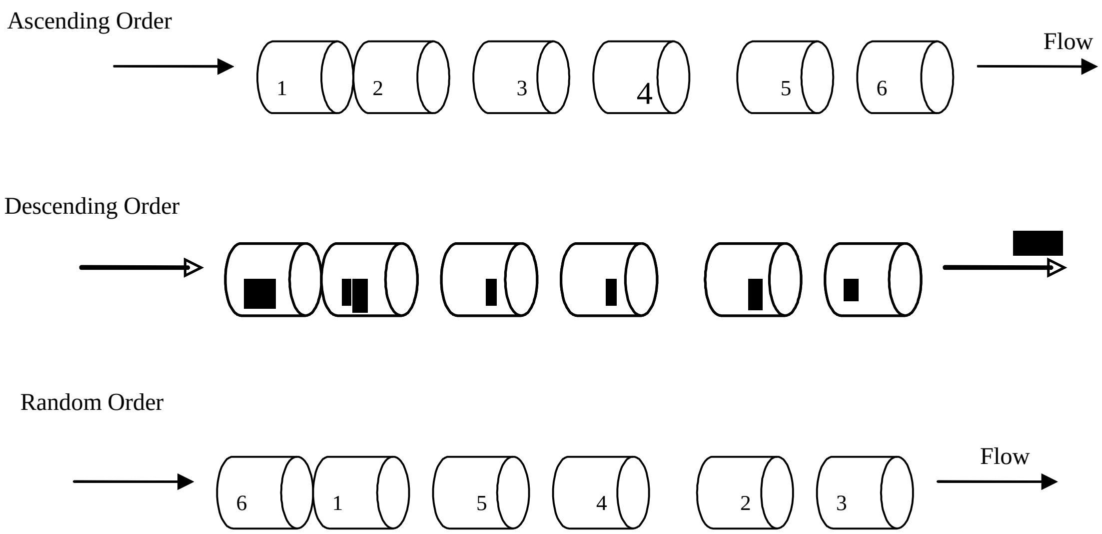

Figure 23: Water flooding sequence of composite core

Figure 24: Liner X-ray System

Unsteady state constant flow rates water flooding runs were conducted. Produced fluids and pressures were measured as function of time. Experiments were terminated at the point of reaching 100% water cut, i.e. no more oil production.

2.3.6 pH measurement

The pH of the injected and produced brines of all of the runs were conducted using Oakton pH meter, see Figure 25. The following steps were followed in the measurements of the pH: buffer solution was used to calibrate the meter, and the measuring pen was cleaned using brine solution. Then, the measuring pen was inserted in a container full of brine to measure the pH value.

Figure 25: pH meter

Chapter 3: Experimental Results and Data Analysis

Oil-brine Interfacial tension, brines pH, viscosity and total dissolved solids TDS, and brines-oil contact angles were measured and the detailed data are presented in this chapter. The results of different brines flooding experiments are also presented in this chapter. In addition to that a complete discussion of the flooding results are also covered in this chapter.

3.1 Water properties

The salinity of different waters employed in this work were measured pre and post flooding at ambient temperature. Tables 7 and 8 show TDS of each brine before and after flooding. Meanwhile, Figure 26 is a plot for these two sets of data. In general the salinity of produced low salinity and sea waters are higher than injection water which implies the possibility of dissolution. On the other hand a reduction of water salinity after flooding for formation brine is observed. This reduction can be attributed to the possibility of either precipitation or adsorption on the rock surface of different ions. The pH of injected and produced waters were measured. Figure 27 shows the pH data for each brine solution before and after flooding. A reduction of the produced water pH is reported in the case of sea water and low salinity water. On the other hand an increase of the pH of the produced water is reported in all of carbonated water flooding in addition to the formation brine flooding. The previously mentioned results indicates that the ionic composition of the produced water is slightly changed. The brines viscosity was measured using rolling ball viscometer at 20°C. As presented in Table 9 the viscosity of different brines are very close to 1 cp which implies that the viscosity will not play significant role in the oil recovery mechanism. However, Asab field oil viscosity before flooding is 3.96 cp; which is higher than that of brine solutions. The viscosity of oil after flooding will be discussed later in detail, as the carbonated brine is known to decrease the oil viscosity during the flooding procedure.

Table 7: TDS of all brines before flooding

TDS Summarize of different brine								
Chemical	Na+	Ca++	Mg++	K+	Cl -	SO4 -	HCO3 -	TDS
FW	40,454	12,687	1,518	0	88,190	862	361	144,072
SW	16,767	690	2,132	672	30,924	3,944	123	55,252
LSW	1676.7	69	213.2	67.2	3092.4	394.4	12.3	5,525
Car FW	40,454	12,687	1,518	0	88,190	862	361	144,072
Car SW	16,767	690	2,132	672	30,924	3,944	123	55,252
Car LSW	1676.7	69	213.2	67.2	3092.4	394.4	12.3	5,525

Table 8: TDS of all brines after flooding

TDS Summarize of different brine								
Chemical	Na+	Ca++	Mg++	K+	Cl -	SO4 -	HCO3 -	TDS
FW	31,918	10,010	1,198	0	69,582	680	285	113,673
SW	22,669	933	2,882	909	41,809	5,332	166	74,701
LSW	6,641	273	844	266	12,249	1,562	49	21,885
Car FW	32,849	10,302	1,233	0	71,610	700	293	116,987
Car SW	23,004	947	2,925	922	42,428	5,411	169	75,806
Car LSW	6,913	284	879	277	12,750	1,626	51	22,780

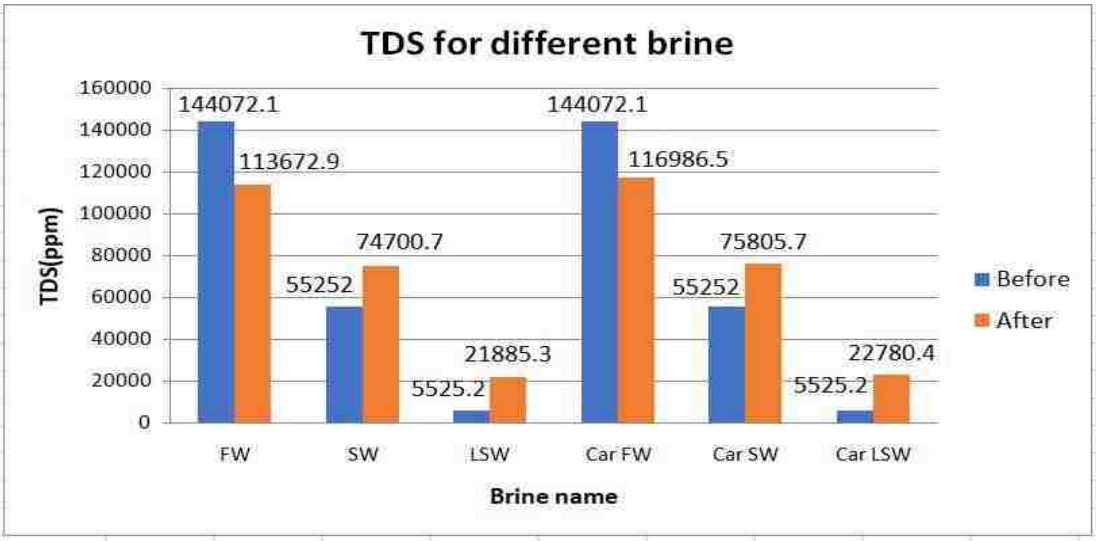

Figure 26: The salinity of different brines

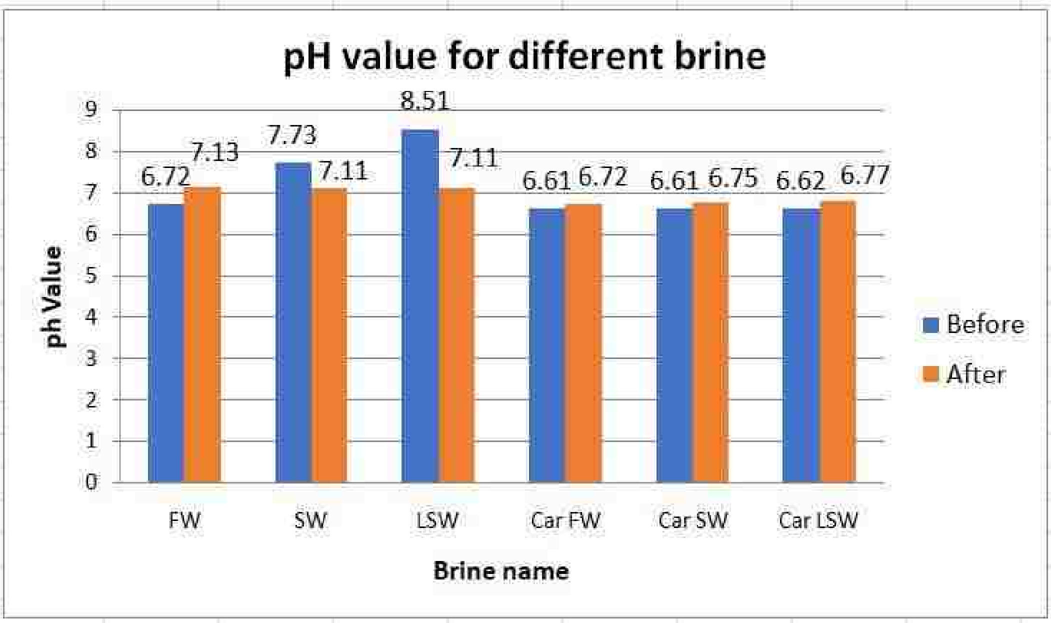

Figure 27: pH value plot

Table 9: Viscosity of brines at 20°C

Viscosity of each brine at 20°C		
No.	Brine's name	Viscosity(cp)
1	FW	1.04
2	SW	1.02
3	LSW	1
4	Car FW	1.04
5	Car SW	1.02
6	Car LSW	1

3.2 Interfacial tension measurements

The interfacial tension between oil and different brines used in this project were measured at 90°C. Figure 28 presnts the results of the interfacial tension measurments of different brines. As shown in Figure 28, Car LSW was found produce the lowest IFT of 9.032 mN/m. Meanwhile, the highest value for IFT was observed formation brine and Asb oil of 13.037. Interfacial tension reduction will result in lowering of the capillary forces and that will lead to better oil recovery. Capillary forces is one of the main forces responsible of oil trapping after water flooding.

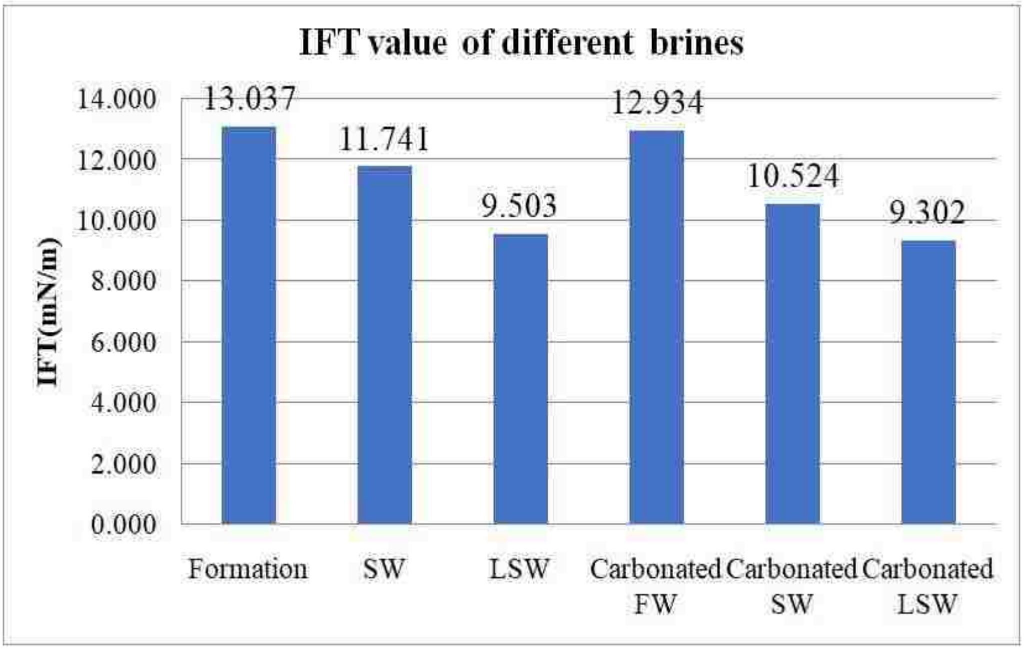

Figure 28: Interfacial tension data for different brines

3.3 Contact angle measurements

The contact angle between Asab oil and different waters employed in this project were measured at 20°C. Table 10 presents the results of the contact angle measurements for the six brined used in this work. Meanwhile, Figure 29 is the plot of the contact angel of each brine. As presented in Table 10 and displayed in Figure 29 the contact angle of all the brines were found to be around 110-140, which indicate that in general the rock system exhibits intermediate wettability behavior. The lowest contact angle was obtained using LSW and Car LSW with a value of 110. Reduction of contact angle indicates that the tested system is moving toward water wetness and that will improve the oil recovery as the water spreads on the rock surface and oil moves to the larger pores.

Table 10: Contact angle of different brines

Contact Angle of different brines		
No.	Brine name	Contact angle
1	FW	122
2	SW	133
3	LSW	110
4	Car FW	122
5	Car SW	133
6	Car LSW	110

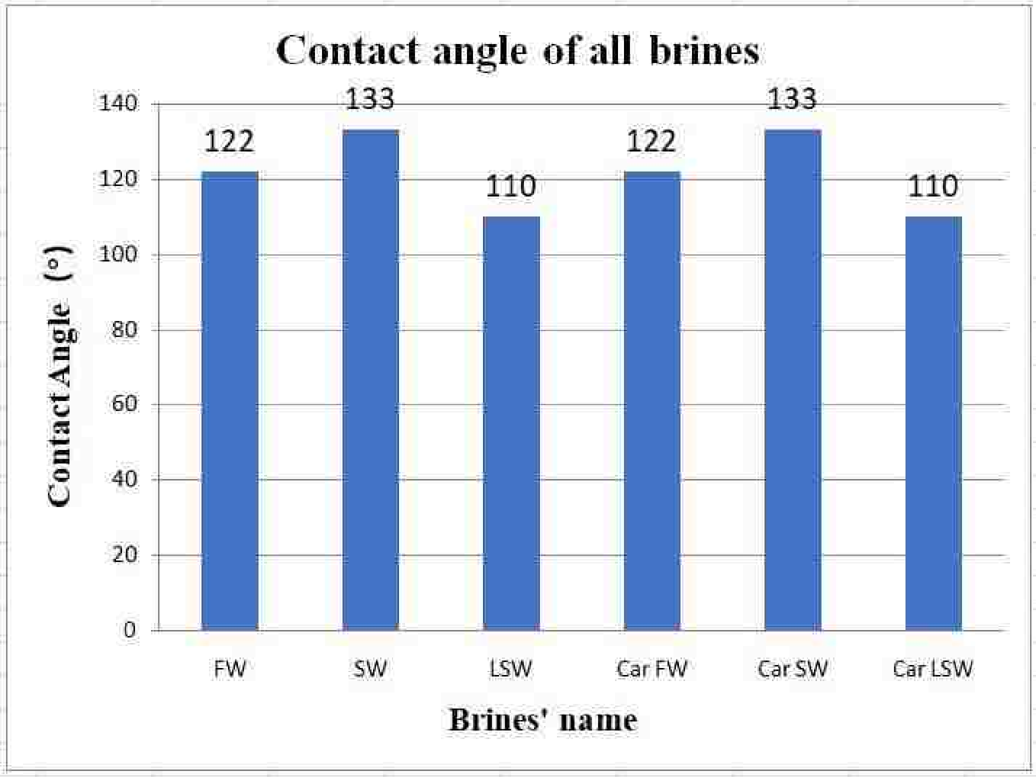

Figure 29: The plot of contact angle

3.4 Sequential water flooding of composite cores

Three different composite core sets were employed in preforming four different sequential high and low salinity carbonated water flooding. The following four different sequential water flooding systems were tested: (1) FW-SW-LSW-car LSW, (2) car SW-SW-LSW, (3) car FW-FW-SW-LSW, (4) car LSW-LSW-SW. Table 11 presents oil recovery data as function of pore volume injected for sequential no.1 water flooding. Results indicated that the overall recovery of the tested system is 67.26% of original oil in place and the contribution of carbonated low salinity water flooding around 1.5% of original oil in place. Figure 30 shows the oil recovery during different flooding stages of sequential no.1. Sequential water flooding no.1 improves the oil recovery over formation water flooding by 20% which is quite significant improvement.

Table 11: Oil recovery versus pore volume injected-Sequential No.1

Samlpe id	Pore vol.	OOIP(CC)	Injected Brine	Water injected	Water Injected	Oil produced	RF	Incremental RF	Residual oil	Sor
	(cc)			(cc)	PV	(cc)	%	%	(cc)	(%)
10	12.05	39.25	FW	500.00	10.05	22.00	56.05	56.05	17.25	43.95
18	11.55		SW	500.00	10.05	2.10	61.40	5.35	15.15	38.60
25	15.15		LSW	500.00	10.05	1.70	65.73	4.33	13.45	34.30
28	11.02		Car LSW	500.00	10.05	0.60	67.26	1.53	12.85	32.70
total	49.77		Total voluеme	2000.00	40.18	26.40	67.26	67.26	12.85	32.70

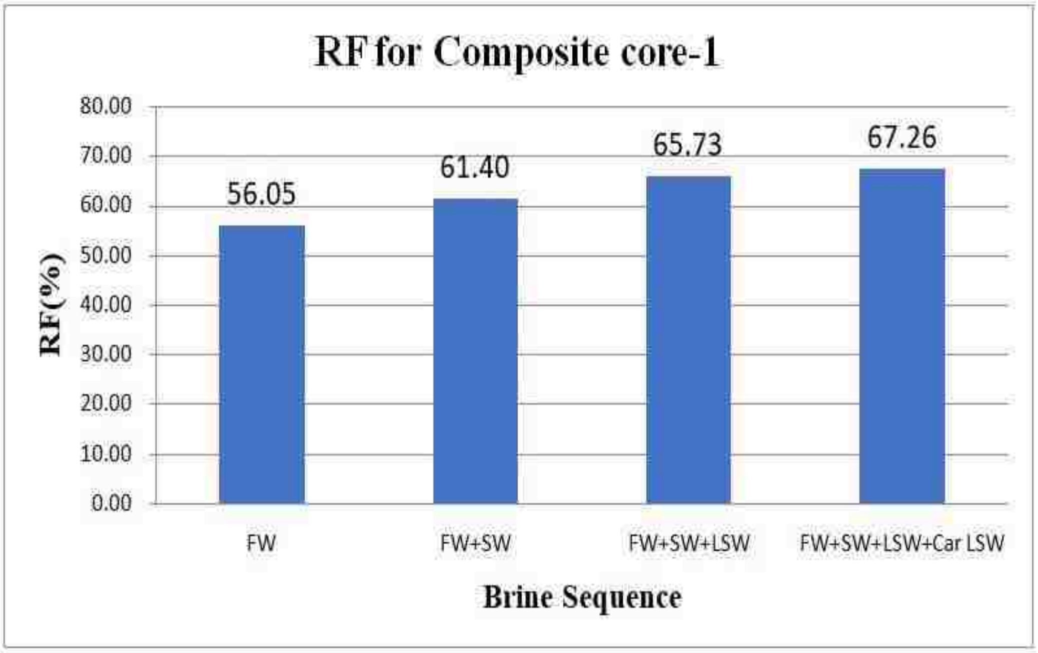

Figure 30: Oil recovery during different stages of water injection-Sequential No.1

Table 12 presented oil recovery data as function of pore volume injected for water flooding sequential no.2. Results indicated that the overall recovery of the tested system is 68.04% of original oil in place and the contribution of sea water flooding around 7.75% of original oil in place. Figure 31 shows the oil recovery during different flooding stages of sequential no.2. Sequential water flooding no.2 improved the oil recovery over formation water flooding by 21% which is quite significant improvement.

.

Table 12: Oil recovery versus pore volume injected-Sequential No.2

Samlpe id	Pore vol. (cc)	OOIP(CC)	Injected Brine	Water injected (cc)	Water Injected PV	Oil produced (cc)	Total oil produced (cc)	RF %	Incremental RF %	Residual oil (cc)	Sor (%)
5	15.10	41.30	Car SW	500.00	9.45	24.50	24.50	59.32	59.22	16.87	40.80
7	10.30		SW	500.00	9.45	3.20	27.70	67.07	7.75	13.67	33.00
13	16.87		LSW	500.00	9.45	0.40	28.10	68.04	0.97	13.27	32.10
21	10.63		Total volume	1500.00	28.36	28.10	28.10	67.92	67.94	13.27	32.10
total	52.90										

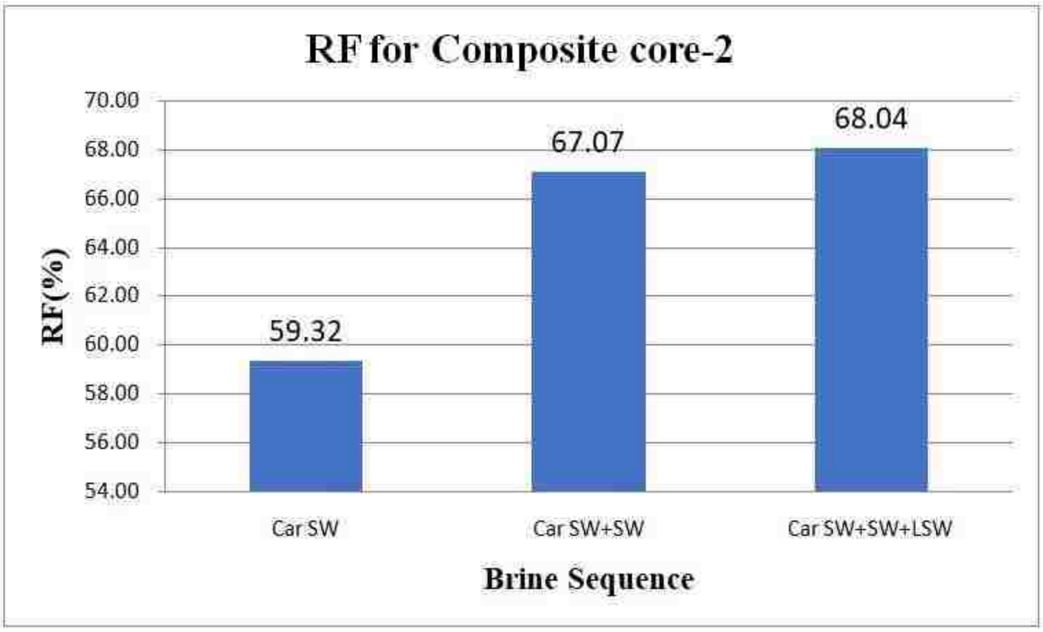

Figure 31: Oil recovery during different stages of water injection-Sequential No.2

Table 13 presented oil recovery data as function of pore volume injected for water flooding sequential no.3. Results indicated that the overall recovery of the tested system is 67.36% of original oil in place and the contribution of sea water flooding around 4.46 % of original oil in place. Figure 32 shows the oil recovery during different flooding stages of sequential no.3. Water flooding Sequential flooding no.3 improved the oil recovery over formation water flooding by 20% which is quite significant improvement.

Table 13: Oil recovery versus pore volume injected-Sequential No.3

Samlpe id	Pore vol. (cc)	OOIP(CC)	Injected Brine	Water injected (cc)	Water Injected PV	Oil produced (cc)	Total oil produced (cc)	RF %	Incremental RF %	Residual oil (cc)	Sor (%)
3	13.36	47.40	Car FW	500.00	8.79	26.13	26.13	55.13	55.13	21.27	44.90
17	14.67		FW	500.00	8.79	2.30	28.43	59.98	4.85	18.97	40.00
19	13.95		SW	500.00	8.79	2.20	30.63	64.62	4.64	16.77	35.40
24	14.89		LSW	500.00	8.79	1.30	31.93	67.36	2.74	15.47	32.60
total	56.87		Total volume	2000.00	35.17	31.93	31.93	67.36	67.37	15.47	32.60

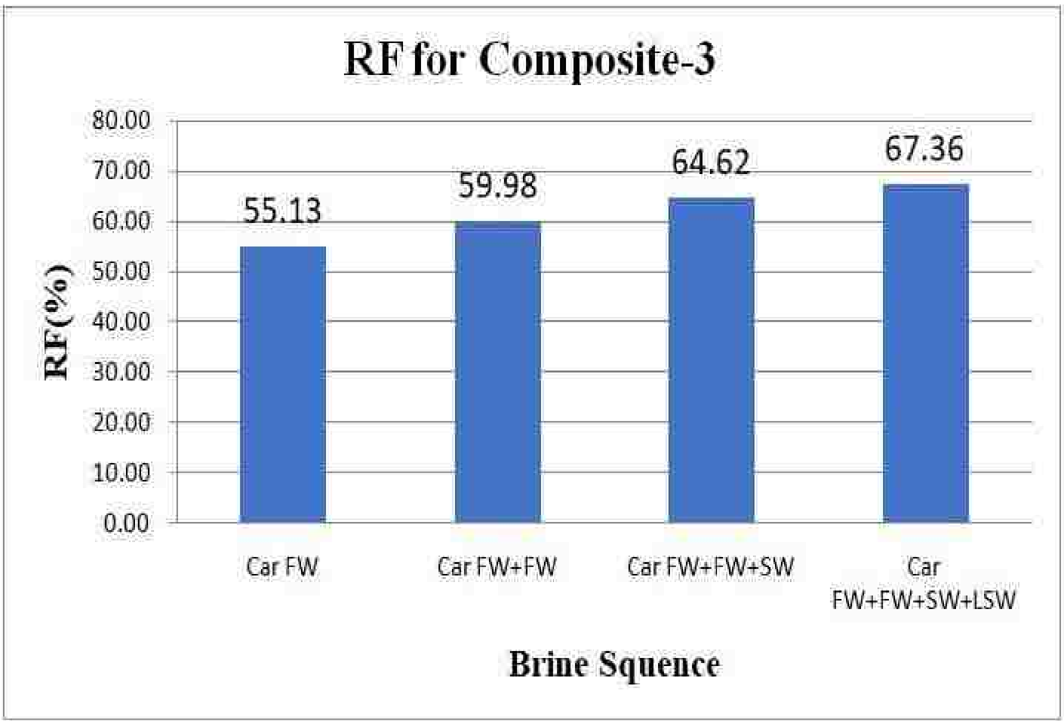

Figure 32: Oil recovery during different stages of water injection-Sequential No.3

Table 14 presents oil recovery data as function of pore volume injected for water flooding sequential no.4. Results indicated that the overall recovery of the tested system is 69.04% of original oil in place and the contribution of low salinity water flooding is around 3.87% of original oil in place. Figure 33 shows the oil recovery during different flooding stages of sequential no.4. Water flooding Sequential flooding no. 4 improved the oil recovery over formation water flooding by 23.2% which is quite significant improvement. Experimental results indicated that water flooding sequential no.4 is the optimum system among the studied sequential systems for the candidate low permeability oil reservoir. Results also show that slightly carbonated low salinity produced around 64.19% of original oil in place compared to 56.05% of OOIP for formation brine. In water flooding sequential no.3 three different brine solutions were used and hence, the total amount of water injected was low around 22.18 PV which is the lowest amount of water employed comparing to other sequential used in this study.

Table 14: Oil recovery versus pore volume injected-Sequential No.4

Samlpe id	Pore vol.	OOIP(CC)	Injected Brine	Water injected	Water Injected	Oil produced	Total oil produced	RF	Incremental RF	Residual oil	Sor
	(cc)			(cc)	PV	(cc)	(cc)	%	%	(cc)	(%)
2	12.67	52.03	Car LSW	500.00	7.60	33.40	33.40	64.19	64.19	21.27	35.80
4	14.12		LSW	500.00	7.60	2.01	35.41	68.06	3.86	18.97	31.80
14	11.80		SW	500.00	7.60	0.70	36.11	69.40	1.35	16.77	30.40
23	10.77		Total volume	1500.00	22.80	36.11	36.11	69.40	69.40	15.47	30.40
26	16.44										
total	65.80										

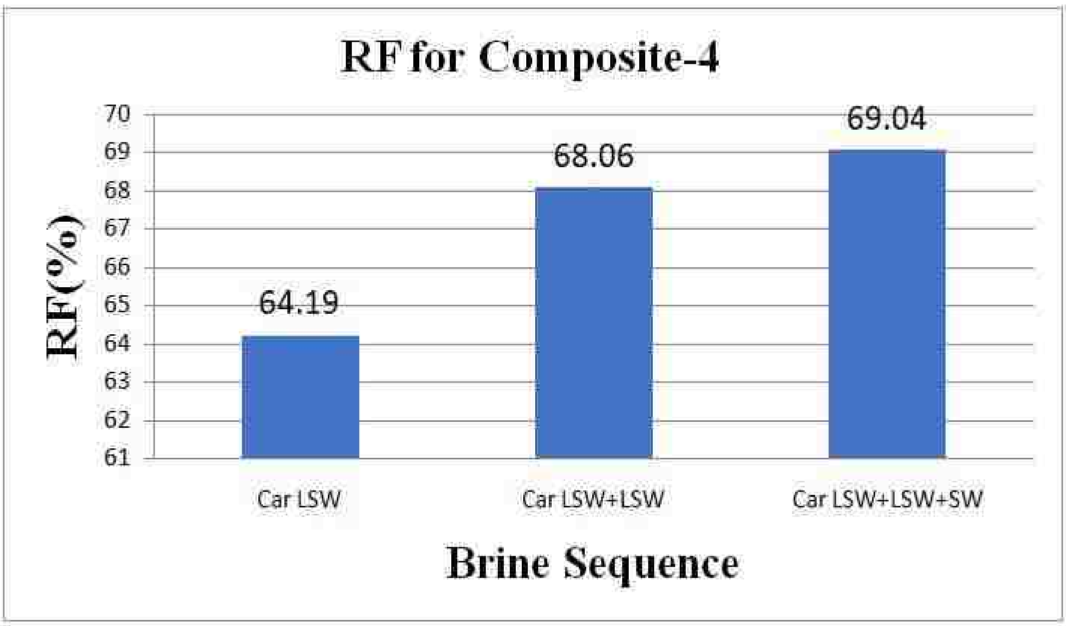

Figure 33: Oil recovery during different stages of water injection-Sequential No.4

3.5 Analysis and comparison

In this part, the effect of contact angle, IFT, and endpoint relative permeability on the performance of different water flooding sequential will be studied. Table 15 presents the average values of the properties of Asab crude oil after flooding water flooding.

Table 15: Asab crude oil properties after flooding

Asab crude oil properties at ambient environment	
Property	Value
Viscosity (μ)	3.31cp
Density （ρ）	0.80130g/cc
Specific Gravity （γ）	45.088°API

As presented in the Table 15, there are slight changes of both oil viscosity and oil density after flooding with the brine solutions. The oil viscosity drops from 3.96 to 3.31 cp after flooding with carbonated brines. This result can be attributed to the possibility of carbonated water slightly extract few of heavy oil components and that will lead to slightly lowering of oil viscosity, and oil density and increasing the oil API gravity as presented in Table 15. Other possibility to explain this phenomena is as follows: carbon dioxide transfers form the water phase into the oil phase and that will lead to the change of oil property. The previous theory is supported by results obtained from pH measurements as the pH of carbonated water is slightly increased after water flooding, i.e. the solution becoming slightly more basic solution.

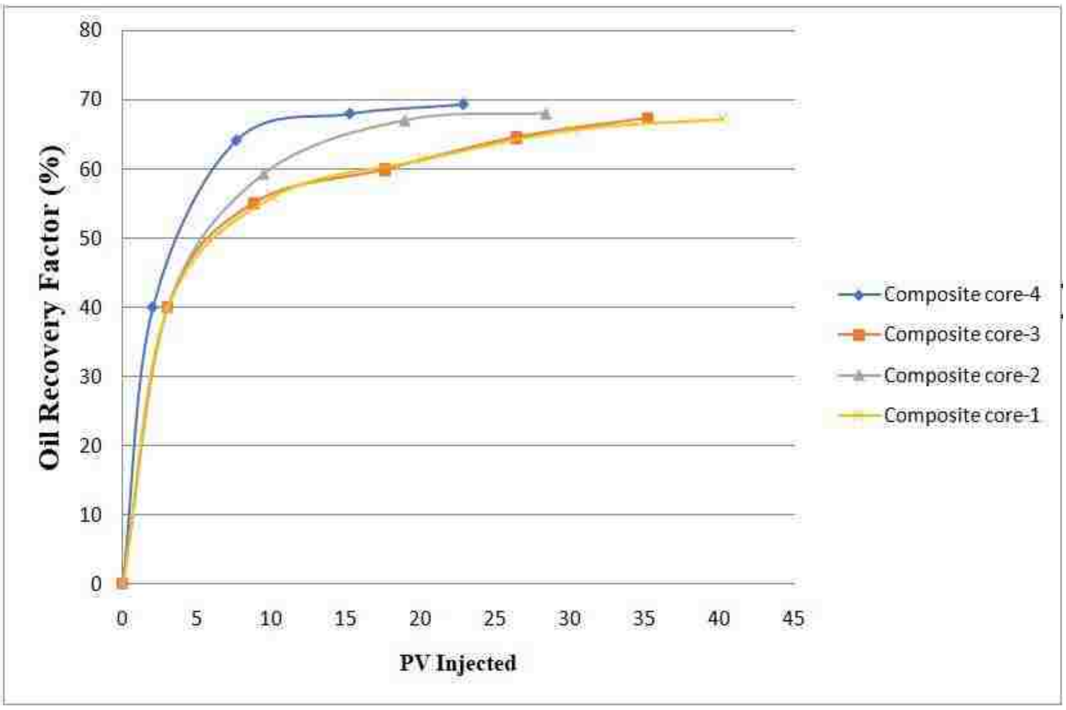

Figure 34: Oil recovery versus pore volume injected, sequential water flooding

Figure 34 shows the oil recovery vs pore volume injected for the four sequential water flooding systems. The experimental results of the four different sequential high and low salinity carbonated and non-carbonated composite core flooding indicate that water flooding sequential no.4 is the optimum system. It consist of the following sequence car LSW-LSW-SW. Results also indicate that starting the sequential flooding with car low salinity or car sea water improves the oil recovery as compared to high salinity or car high salinity flooding. Over all sequential water flooding no.4 increases the oil recovery by 2.6% as compared to sequential water flooding no.1. Keeping in mind that sequential no.4 requires less water to achieve the optimum oil recovery as compared to the other three sequential water flooding employed in this project.

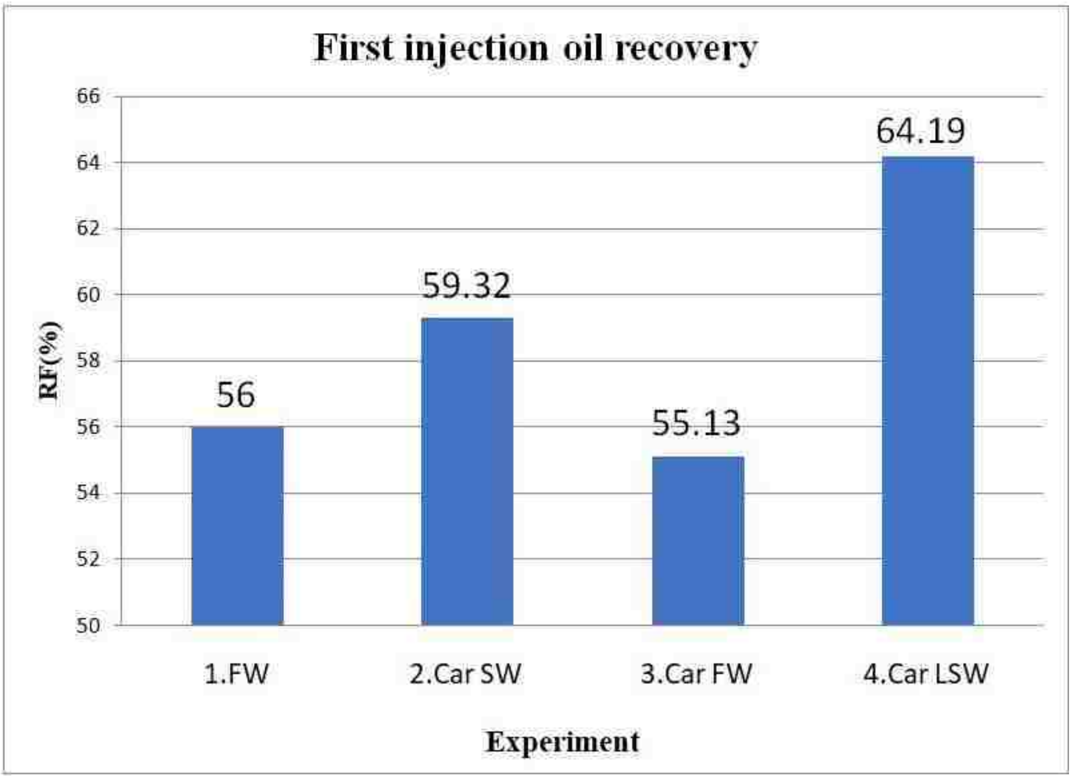

Figure 35: Oil recovery of different water flooding systems

Figure 35 shows the results of water flooding for the formation brine, car SW, Car FW, Car LSW. Results indicate that car low salinity water flooding is the optimum system. An improvement of oil recovery around 15% was obtained by car LSW flooding over formation brine flooding. Oil recovery obtained by LSWF is equal to 64.19% compared to oil recovery of 56% by formation brine. From the IFT and contact angle results of the two brines namely carbonated FW and carbonated LSW, carbonated LSW has the lowest IFT and contact angle values among the employed brines. However, both carbonated FW and FW produced the highest IFT and contact angle value among all brines. This result proves that both IFT and contact angle have a direct relation with oil recoverability of the brines. It also can be considered as an indicator of the wettability alteration toward water wetness. Reduction of the contact angle indicating that system wettability moves toward more water wetness and that will lead to higher oil recovery. The pH of formation brine is slightly higher than the other three brines used in this study. Higher pH value indicates that the system will behave like caustic flooding and that will improve the oil recovery of acidic oil by in-situ formation of surfactant. Since Asab oil is non-acidic, a conclusion can be drawn with great confidence that the pH did not play any significant role in the improvement of oil recovery.

The end point water relative permeability to water Krw was measured for the four different brines used in this study using Darcy's law. Darcy's law was applied using the following equation:

$$K = \frac{1000 q \mu L}{A \Delta P} \tag{3.2}$$

Where q is the flow rate: cm^3/s

K is the permeability: md

A is the cross section: cm^2

ΔP is the pressure change: atm

μ is the viscosity: cp

L is the length: cm

Table 16 presents the Krw data of the four brines and Figure 36 shows a plot of Krw for the employed brines.

Table 16: End point water relative permeability data for different brines

Krw after first injection brine		
No.	Brine name	Krw
1	FW	0.83
2	Car SW	0.72
3	Car FW	0.75
4	Car LSW	0.59

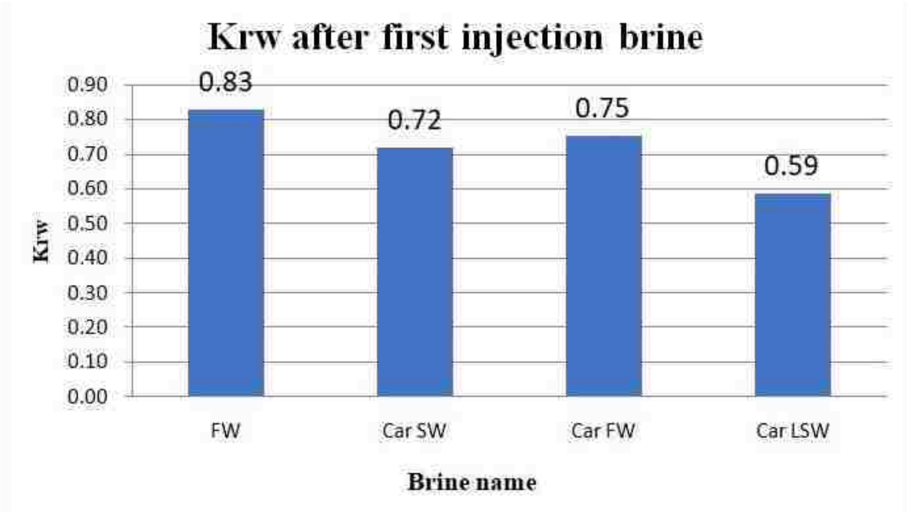

Figure 36: End point water relative permeability for different brines

End point water relative permeability results support the previous conclusion of the optimum water flooding system. Car low salinity water flooding system exhibited the lowest krw as compared with other brines employed in this project. Reduction of krw at the end point indicating that the system moves toward more intermediate wettability system and that will result in higher oil recovery. Relative permeabilities of 0.2 and lower are normally considered as water wet system while krw value of close to 0.5 can be classified as intermediate wettability system.

All the data of the composite cores of krw are presented in appendix B.

Chapter 4: Conclusions and Recommendation

4.1 Conclusion

As all the experimental results of this project shown, the following conclusions are preferred:

1. Among all the brines, Car LSW is the best brine and it will give the best recovery factor. The IFT and contact angle of this brine is so low compared to other carbonated waters, therefore, its performance is better than other brines for Asab reservoir.

2. It seems that wettability alteration is the main mechanism behind the increase of oil recovery of the carbonated low salinity water flooding. The contact angle, IFT, and end point relative permeability indicate that the low salinity carbonated system is moving the rock toward intermediate wettability.

3. After the flooding, the weight of the core samples were almost the same as before flooding, therefore, rock dissolution phenomenon has no significant effect on the process.

4. A sequential composite core flooding consisting of Car LSW- LSW-.SW is the optimum flooding system among all the studied systems.

4.2 Recommendation

1. If more composite core samples are availabe, experiments by Car LSW are suggested and the Car LSW composition should be changed with more calcium or magnesium because literature review shows that these two compoents will have significant effect on the wettability of the rock system.

2. Carbonated water should be used in the heavy oil reservoir to see its effect, because carbonated water will reduce the oil viscosity and the main issue that heavy oil has is the high viscosity, which prevents the oil from moving. Therefore, if CWF is applied in this type of oil, it could be more useful than the case of light oil reservoir.

3. Another 20 samples could be prepared with similar properties. They should be separated into two groups; the first 10 samples should be used as composite cores, while the other 10 samples should be flooding as single cores. After the flooding the samples should be evaluated to study the difference between composite cores and single cores.

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Appendix A

For preparing of the brines the procedures are as follow:

1. Chemical preparation

Figure A-1: Different chemicals used in this project

2. Distilled water preparation

Figure A-2: 2 L container and funnel

3. Salt addition

4. Filtration

Figure A-3: Filter and 2 L container

5. Degassing for the brine

Figure A-4: Degassing process example

6. Storing the brine

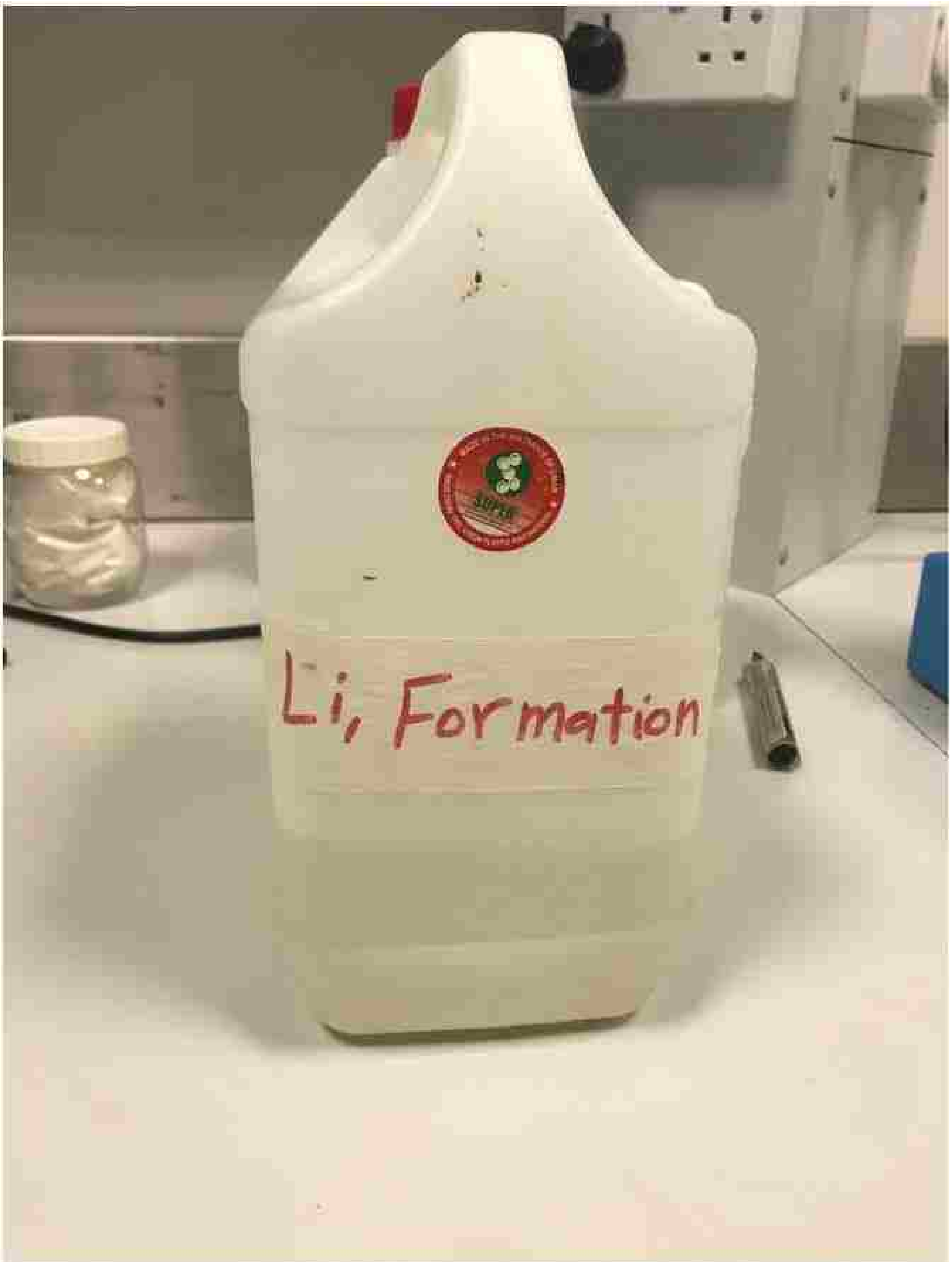

Figure A-5: The completed brine example

When preparing the carbonated water, CO_2 pump should be used so that the gas is bubbled to the brine.

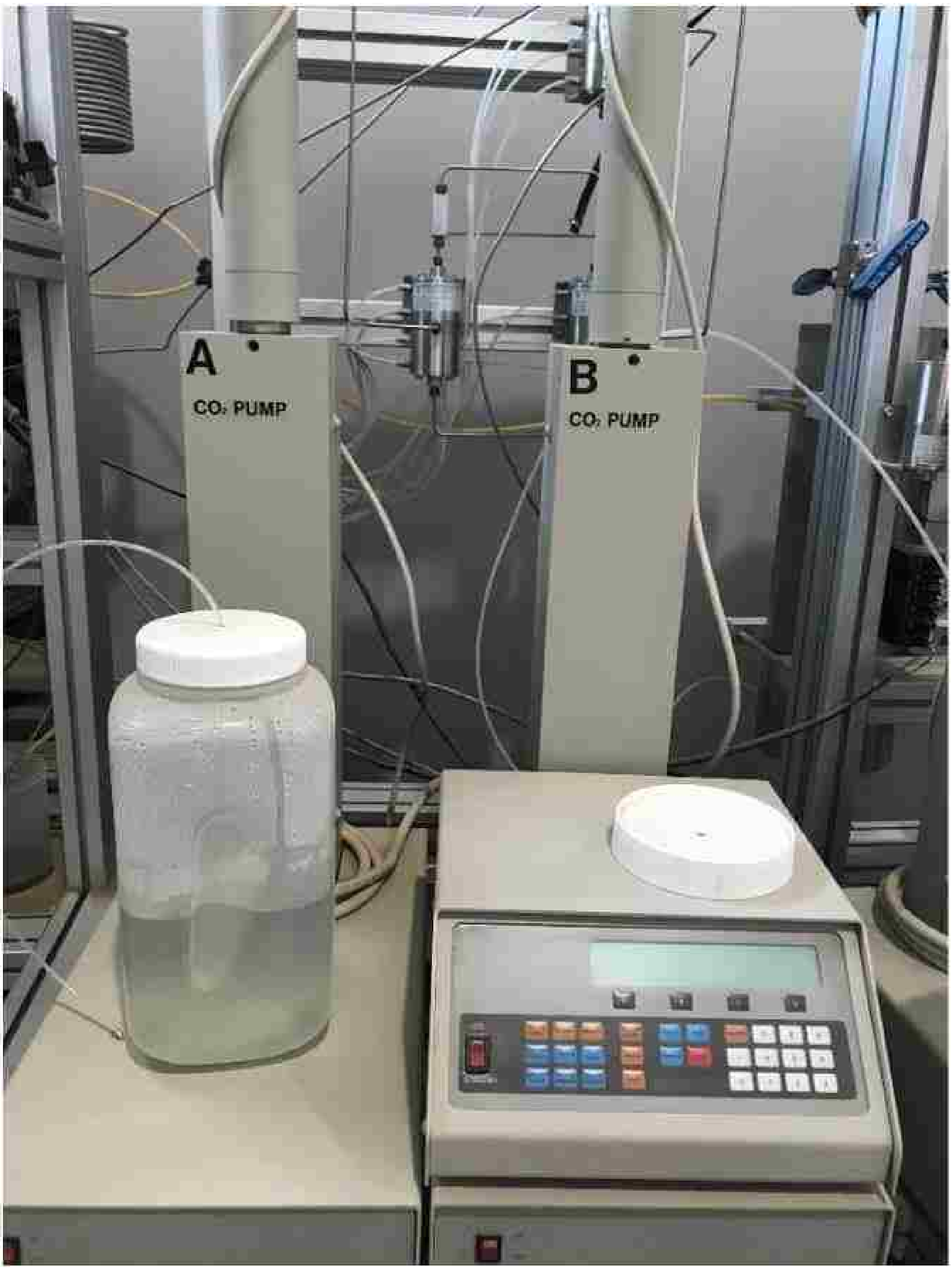

Figure A-6: CO_2 pump example

Appendix B

Table B-1: The needs data plot of composite core-1

Composite core-1 after first injection data							
Brine name: FW, μ=1.04cp, IFT=13.0.37mN/m q=0.013cc/s, ΔP=1100psia							
Samlpe id	Bulk Volume	Cross section areal	Pore vol.	Porosity	Length	Kw(avg)	Kw
	cc	(cm2)	(cc)	%	(cm)	(md)	
10	48.15	11.30	12.05	25.00	4.26		0.35
18	74.89	11.34	11.55	15.40	6.61	0.428	Krw
25	69.06	11.30	15.15	21.94	6.16		
28	53.94	11.49	11.02	20.40	4.69		0.83
Total/Average	246.04	11.36	49.78	20.23	21.72		

Table B-2: The needs data plot of composite core-2

Composite core-2 after first injection data							
Brine name: Car SW, μ=1.02cp, IFT=10.524mN/m, q=0.015cc/s, ΔP=1500psia							
Samlpe id	Bulk Volume	Cross section areal	Pore vol.	Porosity	Length	Kw(avg)	Kw
	cc	(cm2)	(cc)	%	(cm)	(md)	(md)
5	79.18	11.33	15.10	19.06	6.99		0.37
7	74.02	11.37	10.30	13.92	6.51	0.4406	Krw
13	70.07	11.33	16.87	24.08	6.19		
21	49.97	11.34	10.63	21.27	4.41		0.72
Total/Average	273.24	11.34	52.90	19.36	24.09		

Table B-3: The needs plot of composite core-3

Composite core-3 after first injection data							
Brine name: Car FW, μ=1.04cp, IFT=12.934mN/m, q=0.01933cc/s, ΔP=1200psia							
Samlpe id	Bulk Volume	Cross section areal	Pore vol.	Porosity	Length	Kw(avg)	Kw
	cc	(cm2)	(cc)	%	(cm)	(md)	(md)
3	78.86	11.38	13.36	16.94	6.93	0.700	0.53
17	65.09	11.38	14.67	22.53	5.72		
19	64.02	11.33	13.95	21.79	5.65		Krw
24	67.09	11.34	14.89	22.20	5.99		0.75
Total/Average	275.06	11.36	56.87	20.67	24.28		

Table B-4: The needs plot of composite core-4

Composite core-4 after first injection data							
Brine name: Car LSW, μ=1cp, IFT=9.302mN/m, q=0.0033cc/s, ΔP=300psia							
Samlpe id	Bulk Volume	Cross section areal	Pore vol.	Porosity	Length	Kw(avg)	Kw
	cc	(cm2)	(cc)	%	(cm)	(md)	(md)
							0.43
2	78.15	11.35	12.67	16.21	6.88		
4	80.33	11.33	14.12	17.57	7.09		
14	52.48	11.33	11.80	22.49	4.63	0.623	Krw
23	51.43	11.33	10.77	20.94	4.54		
26	73.16	11.43	16.44	22.47	6.40		0.58
Total/Average	335.55	11.33	65.80	19.61	29.55		

Table B-5: Saturate data of composite core-1

Composite core-1 saturated data						
Samlpe id	Dry wt	Sat. wt.	Pore volume (water)	Water produced after saturated with oil	Swi	Soi
	(gm)	(gm)	(cc)	(cc)	%	%
10	94.98	108.15	12.05	10.30	14.51	85.49
18	164.65	177.28	11.55	7.62	34.05	65.95
25	142.78	159.34	15.15	12.46	17.76	82.24
28	107.96	120.01	11.02	8.87	19.54	80.46
Total/Average	510.37	564.78	49.78	39.25	21.15	78.85

Table B-6: Saturate data of composite core-2

Composite core-2 saturated data						
Samlpe id	Dry wt	Sat. wt.	Pore valume (water)	Water produced after saturated with oil.	Swi	Soi
	(gm)	(gm)	(cc)	(cc)	(%)	(%)
5	169.02	185.52	15.10	12.00	20.50	79.50
13	140.50	158.94	16.87	13.45	20.27	79.73
7	169.89	181.15	10.30	7.2	30.11	69.89
21	102.23	113.85	10.63	8.72	17.97	82.03
Total/Average	581.64	639.46	52.90	41.37	21.79	78.21

Table B-7: Saturate data of composite core-3

Composite core-3 saturated data						
Samlpe id	Dry wt	Sat. wt.	Pore volume (water)	Water produced after saturated with oil.	Swi	Soi
	(gm)	(gm)	(cc)	(cc)	(%)	(%)
3	173.44	188.04	13.36	10.70	19.89	80.11
17	132.48	148.51	14.67	11.5	21.58	78.42
19	130.14	145.39	13.95	12.05	13.63	86.37
24	138.20	154.48	14.89	13.15	11.71	88.29
Total/Average	574.26	636.42	56.87	47.40	16.65	83.35

Table B-8: Saturate data of composite core-4

Composite core-4 saturated data						
Samlpe id	Dry wt	Sat. wt.	Pore volume (water)	Water produced after saturated with oil.	Swi	Soi
	(gm)	(gm)	(cc)	(cc)	(%)	%
2	171.35	185.20	12.67	9.30	26.6	73.40
4	175.12	190.55	14.12	10.57	25.1	74.88
14	105.73	118.63	11.80	9.36	20.7	79.31
23	106.69	118.46	10.77	9.25	14.1	85.90
26	145.89	163.86	16.44	13.55	17.6	82.42
Total/Average	704.78	776.70	65.80	52.03	20.9	79.08