EFFECT OF SALINITY CONTRAST BETWEEN FORMATION WATER AND INJECTED LOW SALINITY WATER ON LOW SALINTY WATER FLOODING IN DOLOSTONE FORMATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Georesources and Petroleum Engineering
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ผลกระทบของความแตกต่างของความเค็มระหว่างน้ำในแหล่งกักเก็บและน้ำความเค็มต่ำที่ใช้ในการฉีดอัดที่มีต่อกระบวนการผลิตน้ำมันดิบด้วยการฉีดอัดน้ำความเค็มต่ำในชั้นหินโดโลสโตน

นายณัฏฐพล จันทร์พุฒ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ณัฏฐพล จันทร์พุฒ : ผลกระทบของความแตกต่างของความเค็มระหว่างน้ำในแหล่งกักเก็บและน้ำความเค็มต่ำที่ใช้ในการฉีดอัดที่มีต่อกระบวนการผลิตน้ำมันดิบด้วยการฉีดอัดน้ำความเค็มต่ำในชั้นหินโดโลสโตน. (EFFECT OF SALINITY CONTRAST BETWEEN FORMATION WATER AND INJECTED LOW SALINITY WATER ON LOW SALINTY WATER FLOODING IN DOLOSTONE FORMATION) อ.ที่ปรึกษาหลัก : ผศ. ดร.ฟ้าลั่น ศรีสุริยชัย

การฉีดอัดน้ำเกลือความเค็มต่ำได้รับความนิยมเป็นอย่างมากในปัจจุบัน ถือเป็นหนึ่งในวิธีการทางวิทยาศาสตร์ในปัจจุบันสำหรับการเพิ่มผลผลิตน้ำมันแบบตติยภูมิเนื่องจากความเรียบง่าย ความคุ้มค่า และเป็นมิตรต่อสิ่งแวดล้อม การศึกษาต่างๆก่อนหน้านี้ได้เน้นย้ำถึงบทบาทสำคัญของความเค็มของน้ำเกลือที่ใช้สำหรับฉีดอัดเข้าไปในแหล่งกักเก็บและความเข้มข้นของไอออนที่มีผลต่อการกระตุ้นกลไกในการผลิตน้ำมันดิบ อย่างไรก็ตามการศึกษาส่วนใหญ่มุ่งเน้นที่แหล่งกักเก็บชนิดหินทรายเป็นส่วนใหญ่ จากข้อเท็จจริงที่ว่าปริมาณสำรองไฮโดรคาร์บอนมากกว่า 50 เปอร์เซ็นต์ อยู่ในแหล่งกักเก็บชนิดหินคาร์บอเนต งานวิจัยนี้จึงเน้นศึกษาเฉพาะที่แหล่งกักเก็บชนิดหินโดโลไมต์เพื่อตรวจสอบและประเมินความเป็นไปได้ของการนำเทคนิคการฉีดอัดน้ำเกลือความเค็มต่ำไปใช้ในแหล่งกักเก็บชนิดหินดังกล่าว

ในขั้นตอนแรกผงโดโลไมต์จะถูกเคลือบด้วยน้ำมันดิบเพื่อจำลองสภาพความสามารถในการเปียกแบบน้ำมันและทดสอบตัวอย่างนี้ผ่านการกรองไหลผ่านด้วยน้ำเกลือความเค็มต่ำที่มีสูตรน้ำแตกต่างกันเพื่อระบุความสามารถในการแลกเปลี่ยนไอออนหลายประจุของไอออนต่างๆ ส่วนที่สองดำเนินการกับตัวอย่างหินไซลูเรียนโดโลสโตน ผลการทดลองในขั้นตอนแรกจะถูกนำไปใช้เพื่อเลือกสูตรน้ำที่เหมาะสมสำหรับทำการทดสอบด้วยการแทนที่ของไหล โดยการทดสอบด้วยการแทนที่ของไหลจะทำเพื่อประเมินผลกระทบของความแตกต่างของความเค็มระหว่างน้ำในชั้นหินและน้ำที่ใช้ในการฉีดอัดในกลไกการเพิ่มผลผลิตน้ำมันดิบด้วยการฉีดอัดน้ำความเค็มต่ำในชั้นหินโดโลไมต์

จากการศึกษาพบว่าผลของการผสมกันระหว่างแคลเซียมไอออนและซัลเฟตไอออนจะช่วยให้การฉีดอัดน้ำความเค็มต่ำในชั้นหินโดโลสโตนมีประสิทธิภาพ องค์ประกอบของแคลเซียมไอออนและซัลเฟตไอออนจะนำไปสู่การสลายตัวของแมกนีเซียมไอออนในขณะที่แคลเซียมไอออนจะไม่ถูกใช้ไปมากเนื่องจากการทำให้ประจุบวกของพื้นผิวโดโลสโตนเป็นกลางโดยซัลเฟตไอออน อย่างไรก็ตามการเติมแมกนีเซียมไอออนลงในสารละลายจะช่วยเพิ่มประสิทธิภาพของสารละลายเนื่องจากแมกนีเซียมไอออนสามารถแทนที่แคลเซียมไอออนในแคลเซียมคาร์บอกซิลิกคอมเพล็กซ์ในหยดน้ำมันและส่งผลให้แคลเซียมไอออนในระบบทำงานได้ดีมากยิ่งขึ้น จากการทดสอบด้วยการแทนที่ของไหลสรุปได้ว่าการมีอยู่ของแคลเซียม แมกนีเซียม และซัลเฟตไอออนในน้ำเกลือความเค็มต่ำที่ใช้ในการฉีดอัดมีผลร่วมกันที่จะช่วยเพิ่มกลไกการเพิ่มผลผลิตน้ำมันดิบผ่านการแลกเปลี่ยนไอออนหลายประจุของไอออนต่างๆ การทดสอบด้วยการแทนที่ของไหลแสดงให้เห็นว่ากระบวนการโดยรวมต้องการแคลเซียมไอออนและซัลเฟตไอออนในปริมาณที่เพียงพอเพื่อลดความแข็งแรงระหว่างชั้นน้ำมันที่ถูกดูดซับกับพื้นผิวภายนอกของโดโลสโตน อัตราส่วนของความแตกต่างของความเค็มที่เหมาะสมที่สุดสำหรับการฉีดอัดน้ำความเค็มต่ำเข้าไปในชั้นหินในการศึกษานี้อยู่ในช่วงตั้งแต่ 5.64 ถึง 14.10 เมื่อความเค็มของน้ำในชั้นหินมีค่า 28,196 ส่วนในล้านส่วน อัตราส่วนของความแตกต่างของความเค็มนี้นำไปสู่ปัจจัยการเพิ่มผลผลิตน้ำมันที่เพิ่มขึ้นมากกว่า 25 เปอร์เซ็นต์ หลังจากการฉีดอัดด้วยน้ำที่ผลิตได้จากแหล่งกักเก็บ สำหรับค่าความเค็มของน้ำในชั้นหินที่มีค่าความเค็ม 56,392 ส่วนในล้านส่วน อัตราส่วนของความแตกต่างของความเค็มในอุดมคติคือประมาณ 11.28 ส่งผลให้ปัจจัยการเพิ่มผลผลิตน้ำมันดิบเพิ่มขึ้นประมาณ 8.6 เปอร์เซ็นต์ การแลกเปลี่ยนไอออนหลายประจุของไอออนต่างๆ ไม่สามารถเกิดขึ้นได้อย่างมีประสิทธิภาพที่อัตราส่วนของความแตกต่างของความเค็มต่ำมากหรือสูงมากส่งผลให้การผลิตน้ำมันดิบลดลงเมื่อเทียบกับช่วงอัตราส่วนของความแตกต่างของความเค็มที่เหมาะสมที่สุด ประสิทธิภาพของการฉีดอัดน้ำเกลือความเค็มต่ำมีประสิทธิภาพน้อยกว่าที่ความเค็มของน้ำในชั้นหินมีค่าความเค็มที่สูงมาก (56,392 ส่วนในล้านส่วน) เมื่อเทียบกับชั้นหินที่มีความเค็มของน้ำในชั้นหินที่มีความเค็มต่ำ (28,196 ส่วนในล้านส่วน) ที่ในชั้นหินที่มีค่าความเค็มของน้ำในชั้นหินที่สูงมากการเพิ่มขึ้นของปัจจัยการเพิ่มผลผลิตน้ำมันจะน้อยกว่าในชั้นหินที่มีค่าความเค็มของน้ำในชั้นหินที่ต่ำในทุกกรณี นอกจากอัตราส่วนของความแตกต่างของความเค็มระหว่างน้ำในชั้นหินและน้ำที่ใช้สำหรับฉีดอัดเข้าไปแล้วระดับความเค็มของน้ำในชั้นหินเป็นอีกปัจจัยหนึ่งที่ควบคุมกระบวนการเพิ่มผลผลิตน้ำมันด้วยวิธีการนี้ อัตราส่วนของแมกนีเซียมไอออนที่ละลายต่อแคลเซียมไอออนที่ใช้แสดงผลลัพธ์ที่คล้ายคลึงกันทั้งในแหล่งกักเก็บที่มีความเค็มของน้ำในชั้นหินที่มีความเค็มสูงและต่ำ อัตราส่วนรับดับปานกลางของการแทนที่ไอออน (ในการศึกษานี้ที่ 1.49 และ 2.37 สำหรับความเค็มของน้ำในชั้นหินที่ 28,196 และ 56,392 ส่วนในล้านส่วนตามลำดับ) เกิดขึ้นที่ความเค็มที่เหมาะสมส่งผลให้การเพิ่มขึ้นของผลผลิตน้ำมันดิบเพิ่มขึ้นอย่างเห็นได้ชัด

สาขาวิชา วิศวกรรมทรัพยากรธรณีและปิโตรเลียม ลายมือชื่อนิสิต ....
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Nuttapol Junput : EFFECT OF SALINITY CONTRAST BETWEEN FORMATION WATER AND INJECTED LOW SALINITY WATER ON LOW SALINTY WATER FLOODING IN DOLOSTONE FORMATION. Advisor: Asst. Prof. FALAN SRISURIYACHAI, Ph.D.

Low Salinity Waterflooding (LSWF) has gained substantial prominence in current scientific method for oil recovery improvement, owing to its simplicity, cost-effectiveness, and environmental friendliness as an Enhanced Oil Recovery (EOR) technique. Various studies have highlighted the crucial role of injected brine salinity and the concentration of Potential Determining Ions (PDI) in stimulate oil recovery mechanisms. However, the majority of these studies have predominantly concentrated on sandstone reservoirs. In light of the fact that over 50% of hydrocarbon reserves are situated in carbonate reservoirs, this research focuses specifically on dolomite reservoirs to examine the applicability and feasibility of implementing LSWF in such contexts.

First, Dolomite powder was treated with crude oil to simulate oil-wet condition and treated samples were tested with different water formulations to identify their capacities in Multi-component Ion Exchange (MIE). The second part was performed onto Silurian dolostone core samples. Results from the first part were then used to select the appropriate water formulation for the core flood experiment. Core flooding experiment was performed to assess the impact of salinity contrast between formation water and injected water on the oil recovery mechanism during low salinity waterflooding in dolomite formations.

From this study, the combination effect between calcium ion and sulfate ion yielded benefits in low salinity waterflooding in dolostone formation. This led to the dissolution of magnesium ion while calcium ion was not largely consumed due to the neutralization of positive charges of dolostone surface. Nevertheless, the addition of magnesium ion into the solution enhanced the effectiveness of the solution as magnesium ion could replace calcium ion in calcium carboxylic complex in oil droplets, resulting in more active calcium ion in the system. Based on the core flooding experiment, it was concluded that the presence of calcium, magnesium, and sulfate ions had a combined effect that enhanced the oil recovery mechanism through Multi-component Ion Exchange (MIE). The core flooding experiment demonstrated that the overall process required an adequate amount of calcium ion and sulfate ion to decrease the strength between the adsorbed oil layer and external dolostone surface. The optimal salinity contrast ratio for the injection of low-salinity water into the formation water in this study ranged from 5.64 to 14.10 when the salinity of formation water was 28,196 ppm. This salinity contrast ratio led to an incremental recovery factor (RF) of more than 25% after conventional waterflooding. For a formation water salinity of 56,392 ppm, the ideal salinity contrast ratio was approximately 11.28, resulting in an incremental RF of about 8.6%. Multi-component Ion Exchange (MIE) cannot occur effectively at extremely low or high salinity contrasts, resulting in lower oil production compared to the optimal salinity contrast range. The performance of LSWF was less effective at very high formation water salinity (56,392 ppm) compared to low formation water salinity (28,196 ppm). At very high formation water salinity, the magnitude of improvement or incremental oil recovery was much smaller in all cases. Besides the salinity contrast between formation water and injected water, the magnitude of formation water can be another controlling factor of the process. The ratio of dissolved magnesium ion to consumed calcium ion showed similar results in both high and low salinity of formation water. A moderate ratio of ion replacement (in this study 1.49 and 2.37 for the formation water salinity of 28,196 and 56,392 ppm respectively) occurred at the optimum salinity, resulting in an obvious increment of oil recovery.

Field of Study:	Georesources and Petroleum Engineering	Student's Signature ....
Academic Year:	2022	Advisor's Signature ....

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Primary, secondary, and tertiary oil production stages are possible in oil wells during the life of the oil production well. Oil can be produced through primary recovery, which uses the reservoir's naturally occurring energy to push oil into the wellbore. An additional production phase known as secondary recovery is carried out to raise reservoir pressure, which is crucial for extending the production duration. Gas or water can be injected as part of this approach (waterflooding or gas flooding). Tertiary recovery, often known as "Enhanced Oil Recovery (EOR)", is the final stage of production. In this step of production, chemicals are introduced to improve oil recovery beyond mechanical displacement methods.

Since many years ago, low salinity water injection has been employed extensively in waterflooding as a secondary oil recovery technique. More studies on the impacts of low salinity water injection to enhance reservoir performance have been undertaken recently. Due to its high efficacy for displacing light to medium oil, simplicity of injection into the formation, availability of water, cost-effectiveness, less negative effects on the environment, and lower operating costs when compared to other EOR methods, waterflooding has been one of the most successful oil recovery techniques.

Low Salinity Waterflooding (LSWF) has gained substantial prominence in current scientific methods for oil recovery improvement, owing to its simplicity, cost-effectiveness, and environmental friendliness as an Enhanced Oil Recovery (EOR) technique. LSWF is relatively easy to implement: the water that is injected must have a lower total salinity. This situation triggers oil recovery mechanisms, according to numerous research. It has now been discovered that numerous other additional variables also activate the oil recovery mechanisms of LSWF. According to a series of studies, Srisuriyachai et al. [1] discovered that the types of presented ions in the injected water, in addition to total salinity, have a significant influence on the beginning of the oil recovery process.

Low salinity waterflooding has been shown in several experimental investigations to increase oil recovery in sandstone reservoirs. According to the general consensus on LSWF in sandstone, injecting low brine salinity, preferably less than 5000 ppm, would cause wettability to change in favor of becoming more water-wet, improving oil recovery. Additionally, the greater the predicted reaction of LSWF is, the lower the divalent cations (Ca^{2+} and Mg^{2+}) in the injected brine. According to Tang and Morrow [2], the presence of clays in sandstone reservoirs and formation brine with a high concentration of divalent cations (Ca^{2+} and Mg^{2+}) are inextricably related to the favorable LSWF response.

In contrast to sandstone, carbonate reservoirs have a distinct geological composition and may include little to no clay. In addition, there are other kinds of carbonate rocks, including limestone, dolomite, and chalk, each of which has distinct properties. LSWF may not behave exactly the same in carbonates as it does in sandstones as a result. Due to the complexity of carbonate and the diagenetic variation of carbonate rock, LSWF in carbonate is not as mature as in sandstone, and research in this area is still underway to improve the fundamental knowledge. Research conducted in laboratories by Lager et al. [3] revealed that injecting water with low salinity can boost oil recovery by up to 25%. These studies, however, tended to concentrate on sandstone reservoirs. In this work, we concentrated on dolomite reservoirs to examine the viability of using this technology because more than 50% of hydrocarbon reserves are in carbonate reservoirs. In this study, Silurian dolostone cores were used as potential determining ions (PDI) and core flooding experiments, and the impact of low salinity water flooding on this type of reservoir was examined.

The study is divided into two major parts. First, Silurian dolomite samples are tested with different water formulations to identify their capacities in Multi-component Ion Exchange (MIE). At this stage, dolomite sample dissolving tests were carried out using Potential Determining Ions (PDI), which include Ca^{2+}, Mg^{2+}, and SO_4^{2-} for carbonate rocks. To replicate an oil-wet environment, dolomite samples were treated with crude oil, and then their abilities to dissolve in multi-component ion exchange (MIE) were examined using various water formulations. Since Ca^{2+} and Mg^{2+} are the ions that link the dolomite surface to the oil drop, they were measured in the supernatants obtained from the dissolving test. The findings of this study can be utilized to assist in choosing the right water formulation for LSWF in particular dolomite reservoirs. On samples from Silurian dolostone cores, the second section is done. After then, the right water formulation for the core flood experiment is chosen based on the previous part's findings. The reservoir conditions used for the core flooding experiment are higher in pressure and temperature than those found in a typical room. To simulate conventional waterflooding, formation water is injected initially. Once oil recovery is constant, a chosen low salinity water formulation is injected. Pressure differential and the volume of oil produced over time are both measured. In order to determine the amount of Ca^{2+} and Mg^{2+} in the effluent from the core flood and to determine the oil recovery factor, the chemical composition of the effluent is collected for analysis by color titration. Comparison between results from each salinity contrast is performed for new findings.

This study aims to determine the impact of salinity contrast on the oil recovery process during low salinity waterflooding. It seeks to provide a better understanding of the effects of different types of ions on oil recovery mechanisms in dolomite formations. By doing so, it aims to develop an optimal water formulation for low salinity waterflooding in carbonate reservoirs, specifically in dolomite formations.

1.2 Objectives

1.2.1 To evaluate the effects of salinity contrast between formation water and injected water on oil recovery mechanism in low salinity waterflooding in dolomite formation.

1.2.2 To identify the appropriate water formulation concerning potential determining ion together with salinity contrast between formation water and injected water in low salinity waterflooding in dolomite formation.

CHAPTER 2
LITERATURE REVIEWS

General mechanisms of low salinity waterflooding were performed by Lager et al. [3]. The authors performed core flood tests to investigate fine migration and pH increase mechanism during ambient and reservoir condition low salinity flooding including the new mechanism based on the extended DLVO theory and cation exchange of low salinity waterflooding in sandstone reservoir. From this study, it can be concluded that during low salinity waterflooding, pH-induced IFT reduction or emulsification, as well as fines migration, were not prominent. They were an effect rather than the cause. The primary mechanism underlying the increased waterflood recovery observed with low salinity waterflood has been established to be cation exchange between the mineral surface and the invading brine. Multi-component Ion Exchange (MIE) took place during the injection of low salinity brine, removing organic polar compounds and organometallic complexes from the surface and replacing them with un-complexed cations, leading to a more water-wet surface and resulting in an increase in oil recovery.

Besides the main mechanism occurred during low salinity waterflooding, Tang and Morrow [2] performed a laboratory study of the effect of cation valence and salinity on wetting and oil recovery of Berea sandstone. The results revealed that brine composition has a significant impact on oil recovery efficiency by waterflooding and spontaneous imbibition at the microscopic level. From this study, it was found that the valence of cations is particularly important in crude oil/brine/rock interactions. When the salinity was high, increasing the cation valence tends to decrease water-wetness while increasing the oil recovery by waterflooding. When the salinity was low, the effect of cation valence on wetting and oil recovery was substantially smaller. They also observed that decreasing in NaCl and $CaCl_2$ brine concentrations can cause wettability transitions, leading to increased water-wetness and waterflooding recovery. In the case of $AlCl_3$ brine, however, a decrease in salinity might lead to increased water-wetness and decrease oil recovery which is ascribed to the effect of pH value.

Oil recovery mechanism and effects of ions were clearly explained in the cases of sandstone reservoir. However, oil recovery mechanisms as well as effects from salinity and chemical constituent were also studied by several investigators as follows. Yousef et al. [4] performed a laboratory study targeting different carbonate reservoirs, to investigate the impact of altering the salinity and ionic content of the injection water on oil/brine/rock interactions and performed new reservoir condition laboratory core flooding studies. To test the effect of ionic content on oil recovery in secondary and tertiary recovery modes, tests were carried out utilizing composite rock samples from various carbonate sources.

The experimental results demonstrated that modifying the ionic concentration of field injection water can result in significant tertiary oil recovery beyond conventional waterflooding where similar potential has been confirmed also in the secondary recovery mode. From this study, it can be concluded that altering the salinity and ionic content of seawater also had a significant impact on carbonate rock wettability or fluid-rock interactions. In terms of recovery mechanisms, the author revealed that wettability changes were the primary source of the significant increase in oil recovery. The differences in oil recovery between two carbonate reservoirs can be related to differences in reservoir temperature as well as the chemistry of the original formation water.

Romanuka et al. [5] performed a core flooding test to investigate the larger-scale screening study into the possibility of modifying the wettability of carbonate rock samples by the altering ionic composition and the ionic strength of the brine. The findings of this study showed that by reducing the ionic strength of the brine, oil recovery from several carbonate rock samples might be enhanced, possibly because of the wettability shifting towards a more water-wet state. This strategy had certain practical advantages over the injection of brines with high concentrations of surface-interacting ions (i.e., sulphate ion, borate ion, phosphate ion) for increased oil recovery. However, the possibility for scale formation in the production tubing and/or reservoir rock plugging around the production well was increased by adding high sulfate seawater to reservoirs that have formation water that contains barium and strontium. From this study, it can be concluded that the injection of low salinity brine into carbonate reservoirs has potential as an EOR technology.

Yi Zhang and Hemanta Sarma [6] performed comprehensive core flooding test and wettability monitoring tests on carbonate rock conducted at temperature ranging from 70°C to 120°C to experimentally investigate the potential of oil recovery enhancement and wettability alteration by manipulating the salinity and/or ionic composition of injected brines, and to unveil the recovery mechanism/mechanisms for “smart waterflood” in carbonates. According to the results of this study, extra oil recovery might be mobilized by lowering the salinity of the water and increasing the sulfate concentration of the injection brine, in addition to the typical seawater and formation water injection at 70°C and 120°C. The procedure was impacted by temperature. Due to the lower water salinity and higher sulfate concentration of the injection water, the incremental oil recovery was much higher at 120°C than it was at 70°C. The results of this study also showed that, at 70°C, lowering the salinity of the water was more effective than increasing the sulfate concentration in the injection water in terms of incremental oil recovery following a secondary conventional waterflood, and low salinity water could change the wettability toward less oil-wetness. And at 90°C, the water-wetness of carbonates can be increased by either reducing the salinity of the surrounding water or increasing the concentration of sulfate in it. On the other hand, the wettability of the rocks was only moderately impacted by the divalent cations in the water. The positive performance of "smart waterflood" in carbonates was thought to be due to wettability alteration and fines migration, according to all the derived data.

Nasralla et al. [7] carried up a core flooding experiment utilizing carbonate core plugs from two Middle Eastern carbonate reservoirs to qualitatively assess the potential of low salinity waterflooding to enhance oil recovery and change the wettability of rock. The experimental findings supported the hypothesis that reducing water salinity can change rock wettability in favor of becoming more water-wet, improving oil recovery in tertiary waterflood in plugs from the two reservoirs. Furthermore, seawater yielded more oil in the tertiary mode after formation brine injection, making it more favorable to oil recovery than formation brine. This showed that in addition to brine salinity, brine composition also plays a significant effect during waterflooding in carbonate reservoirs. Additionally, low salinity brines have the potential to significantly increase oil recovery compared to seawater injection since they change the rock's wettability toward decreased oil-wetness. They also observed that some of the injected brines that cannot dissolve calcite improved oil recovery whereas other injected brines that could dissolve calcite did not produce any additional oil. Therefore, it could not be concluded that calcite dissolution is the primary mechanism of improved oil recovery by low salinity waterflooding. Although low salinity water can cause dissolution of calcite, it had little to no effect on raising the salinity of low salinity brine during core flood.

Mahani et al. [8] performed an experiment study using limestone and dolomite to demonstrate the wettability alteration caused by low-salinity water on carbonate surfaces and to determine whether the wettability may be connected to the change in carbonate surface charge caused by low salinity waterflooding. Based on this study, they also evaluated whether the low salinity waterflooding-induced wettability change was usually associated with calcite dissolution. The results of the study revealed that limestone surface became less oil-wet as a result of switching from formation water to seawater, diluted seawater, and diluted seawater equilibrated with calcite. This change was represented in a decrease in contact angle. The 3-phase contact line receded in seawater as well as diluted seawater equilibrated with calcite, indicating that low salinity waterflooding can still occur in the absence of mineral dissolution. The surface-charge-change mechanism for limestone was amply confirmed by the trends in the zeta-potential data on brine composition, wherein at lower salinities the charges at the limestone-brine interface were more negative, resulting in lower adhesion or even repulsion between oil and rock. Dolomite, on the other hand, had a different behavior because it responded with a significantly reduced change in contact angle. Additionally, when compared to limestone, dolomite's zeta-potential generally shows more positive charges at higher salinities and less decrease at lower salinities, where the electrostatic interaction either remained attractive or very slightly altered into a repulsive force. From this study, it can be inferred that low salinity waterflooding had a beneficial effect on carbonate rock without causing any dissolution, and that this effect was caused by electrostatic interactions between crude oil and rock that depended on the composition of the brine. However, the mineralogy of the carbonate material affected the strength of the favorable outcomes.

Abdulrahman et al. [9] conducted a laboratory investigation using a core flooding test to determine the impacts of brine salinity and ionic composition on potential interactions of the rock, brine, and oil systems and to pinpoint potential oil recovery mechanisms in carbonate and sandstone samples corresponding to Saudi reserves. The findings showed that low salinity waterflooding in secondary and tertiary flooding modes could improve both sandstone and carbonate reservoirs. Oleic and various salinity water solutions' interfacial tension (IFT) exhibited a little decrease with falling salinity. Zeta potential and contact angle measurements revealed that wettability modification was primarily responsible for the improved oil recovery in both carbonate and sandstone samples.

Based on the results of this investigation, it can be said that the alteration in wettability was what led to better oil recovery in carbonate and sandstone samples. Contact angle and zeta potential studies show that the wettability changes from an intermediate-wet state with high salinity formation brine to a primarily water-wet state with ten times diluted seawater. Moreover, Improved recovery of the tested carbonate sample may be attributed to multi-component ions exchange and the presence of sulfate in both the water that was injected and the water that was generated naturally during the anhydrite dissolving process. They also discovered throughout the experiment that after tertiary flooding, the carbonate sample experiences substantial degradation with a drastic drop in absolute permeability. This can be related to the dolomite dispersion induced by the double-layer expansion.

Ahmed et al. [10] carried out extensive experimental work to investigate the rock-fluid and fluid-fluid interactions at rock-water and oil-water interfaces as well as to investigate the effects of the modified-salinity brine on the zeta potential measurement when the rock is saturated with various fluids. They did this using IFT, zeta potential, and wettability alteration experiments. From this study, IFT measurements showed a trend toward increase as the salinity decreased. The IFT values, however, had increased as the sulfate ion concentration in the smart water increased. This implies that the effects of rock-water interactions are more significant than those of oil-water interactions. This demonstrates that employing diluted brine results in increased oil recovery. From the zeta potential measurements, due to the growth of the electrical double layer, zeta potential tests clearly demonstrated a trend toward producing more negative values as seawater was diluted down to 1% diluted seawater. Additional dilution did not show an increase in the negative zeta potential values. Even greater negative zeta potential values compared to 1% diluted seawater might be obtained by increasing the sulphate ion concentration in the smart brine. Therefore, a better performance of the smart brine in terms of the wettability alteration might be attained by achieving more negative zeta potential values. This should result in a higher oil recovery. In comparison to the experiments utilizing seawater, the wettability alteration experiments showed that both diluted and composition-modified brine produced a higher imbibition rate, which led to a higher total oil production. Additionally, as shown by the contact angle measurements, the rock surface's wettability changed, leaning more toward conditions of water-wetness.

Yousef et al. [11] conducted a wide range of laboratory experiments, such as wettability, surface chemistry, and zeta potential studies, to clarify the role of water ions in the induced wettability alteration and to confirm potential mechanisms for a new recovery technique or process dubbed "SmartWater Flood" that focuses on carbonate reservoirs. The findings are summarized as follows:

1. The recovery mechanism study confirmed that SmartWater Flood can alter the wettability of rocks in order to make them more water-wet. When seawater was diluted twice and then ten times, the significant change was observed, and these two slugs significantly increased the amount of oil recovered.
2. Investigations of the rock surface chemistry utilizing core flooding and NMR tools showed that the surface charges of the rock were significantly altered after the injection of various salinity slugs of saltwater into carbonate core samples, enhancing interaction with water molecules. This was one of the mechanisms behind the change in wettability seen during SmartWater Flood.
3. According to zeta potential studies, a decrease in the ionic strength of seawater in a field was sufficient to modify the surface charge of carbonate rock toward a more negative state, resulting in more interactions with water molecules and ultimately changing the wettability of the rock. These findings confirmed the study's hypothesis that injecting diluted seawater could shift the surface charge of carbonate rock toward a more negative state.
4. Contact angle measurements proved that the effect of wettability alteration required a large decrease in the ionic strength of field seawater. The contact angle results also demonstrated that multivalent ions in the injected water enhanced wettability alteration of SmartWater Flood. As a result, it could be concluded that SmartWater Flood was more complicated than simple low salinity waterflooding and that the interaction of ions with carbonate rock surfaces was crucial to the current process.

Mohammad and Murtdha [12] carried out a core flooding study based on the wettability study's contact angle measurement findings to look into how the salinity level affects oil recovery in a limestone reservoir. For the wettability study, they used calcite plates to represent carbonate rocks, and for the core flooding study, they used a core plug from an Indian limestone outcrop. The experimental results demonstrated that all of the recoveries results were consistent and showed that lower wettability angle correspond to higher oil recovery. The experiments revealed an incremental of oil recovery ranging from 12 to 18%, demonstrating the significant potential of flooding carbonate reservoirs with low salinity water. From this study, the result showed a direct correlation between core flooding recovery and the calcite plate contact angle measurement. They demonstrated that contact angle values were more accurate predictors of the optimum injected water composition than salinity level. The maximum recovery was achieved by sequentially injecting water with lower measured contact angles. Because their wettability investigations demonstrated that there was no direct correlation between the measured contact angle and the salinity level of water, this relationship was not always true for salinity levels.

From the literature reviews, none of them mentioned about the effects of salinity contrast between formation water and injected water together with the effects of ions presented in the injected water. Several studies tried to perform on diluting of formation water or sea water, but none mentioned about injected water with selected ion. This study is therefore performed to fulfill this gap. Knowing of effects from salinity contrast would yield an extreme benefit especially in case that diluting of injected water has some difficulties such as finding sources of fresh water for dilution or high cost for de-ionization system of the produced water.

CHAPTER 3

THEORY

3.1 Low Salinity Waterflooding (LSWF) and Oil Recovery Mechanism in Carbonate

Low salinity waterflooding (LSWF) has been identified as a technology with promise for enhancing oil recovery but the principal mechanism underpinning this recovery method is not fully understood especially in carbonate reservoir. Several mechanisms have been proposed to be the primary mechanism of low salinity waterflood including 1.) Multi-ion exchange (MIE), 2.) Rock dissolution, 3.) Fines migration, 4.) Reduction of Interfacial Tension, and 5.) Expansion of Electric Double Layer.

Although wettability alteration toward a more desired condition for oil recovery may be the primary reason of LSWF, how this alteration occurs is still up for question. In general, it is thought that more than one process is involved in LSWF of carbonates. However, there are inconsistencies regarding the fundamental mechanisms of wettability alteration in carbonates, and the following section outlines the principles of each mechanism.

3.1.1 Multi-component Ion Exchange (MIE)

The MIE theory in carbonates was suggested and supported by Austad and his co-workers [13], [14], [15], [16], [17], [18]. They suggested that the fundamental mechanism of enhanced oil recovery during LSWF is a reduction in the ionic contact between oil molecules and rock surface, which is caused by the presence of MIE between the injected brine and the rock surface. The exchange of anions, which includes the adsorption of potential determining anions (SO_4^{2-}) and co-adsorption of divalent cations (Ca^{2+} and Mg^{2+}) onto the rock surface, is thought to be the mechanism of MIE in carbonates (Figure 1). Desorption then causes the release of negatively charged fatty acid components of crude oil from the rock surface. This theory states that SO_4^{2-} ions function as a catalytic agent and adsorb onto the surface of carbonate rocks, reducing the density of positive surface charges. This reduces electrostatic repulsive forces and causes Ca^{2+} and cations to co-adsorb on the surface of the rock. The attractive connections between the oil and rock interface can then be broken by the Ca^{2+} ions reacting with carboxylic acid groups that are attached to the rock surface. As a result, the rock surface's carboxylic acid components are released, changing its water-wettability to a more favorable state. Additionally, at high temperature (above 90°C), Mg^{2+} can displace the Ca^{2+} ion bonded to carboxylic group. In this way, the organo-metallic complex could also be detached from the rock surface [19]. Due to this, the capacity of anions (SO_4^{2-}) to adsorb on carbonate surfaces can be impacted by the presence of divalent cations (Ca^{2+} and Mg^{2+}) in brine. According to this theory, the preconditions for this theory are: (1) the presence of SO_4^{2-} in addition to Ca^{2+} and/or Mg^{2+} in the invading water; and (2) a high temperature (often above 90°C). Furthermore, it was clarified that the MIE mechanism might also operate at high brine salinities since the injected brine has a different relative concentration of active ions than the formation water does [20].

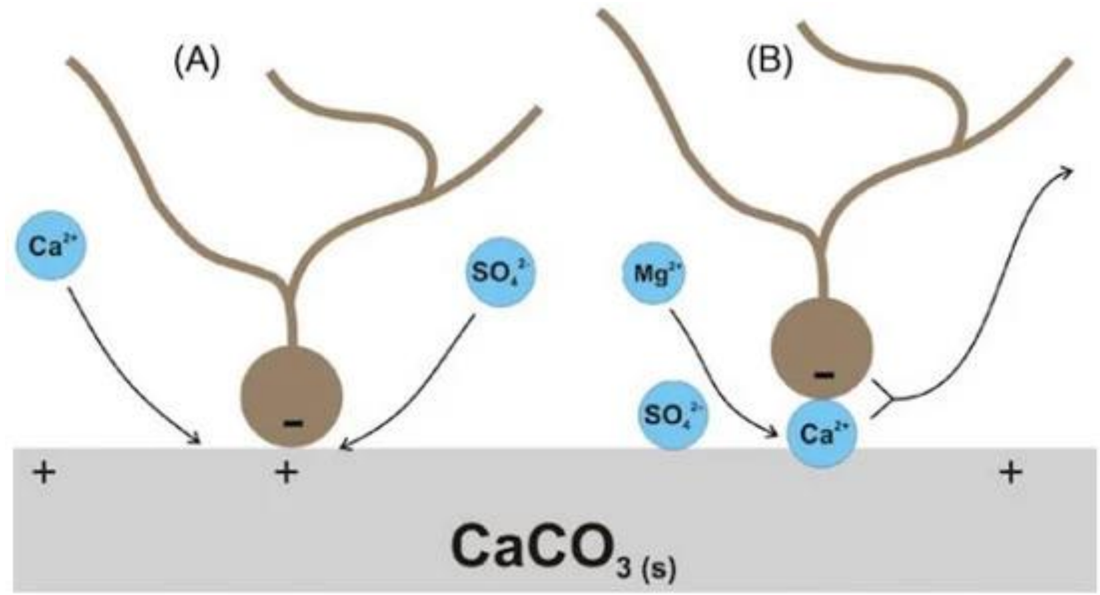

Figure 1. Schematic for proposed wettability alteration mechanism by LSWF from Zhang et al. [16]

3.1.2 Rock dissolution

This theory was proposed by Hiorth et al. [21], [22], using a geochemical thermodynamic model, based on experimental spontaneous imbibition tests conducted by Austad and co-workers [15], [23], [24], [25]. The simulation results indicated that the improvement in oil recovery with changes in pore water chemistry or temperature, according to Hiorth et al., it cannot be explained by changes in surface potential. Instead, they argued that lowering the Ca^{2+} ion concentration might cause calcium carbonates to dissolve, allowing the brine and calcium carbonates to rebalance each other. Such chemical dissolution of calcite will release the adsorbed polar components of crude oil from the rock surface, consequently improving water-wetness. In contrast to the mechanism of calcite dissolution proposed by Hiorth et al. based on published experimental results, Austad et al. questioned the applicability of the geochemical model to calculate the chemical equilibrium between calcite and seawater during few days of spontaneous imbibition at high temperature (70-130°C). Despite the fact that some researchers have suggested that one of the potential processes for LSW in carbonates may be rock dissolution. One school of thought contends that a chemical equilibrium at rock-brine interfaces cannot be accurately calculated to define mineral dissolution by their geochemical model because in such a situation a sizeable portion of the minerals will be supersaturated, causing the precipitation of minerals in the solution. In the absence of mineral dissolution, Mahani et al. [26] showed improved oil recovery and asserted that surface charge alteration is most likely the primary mechanism causing LSWF. Therefore, despite the fact that rock dissolving has been proposed by certain writers and is supported by thermodynamic geochemical modeling, there is currently no experimental evidence to support this mechanism.

3.1.3 Fines migration

As part of the LSWF process, Tang and Morrow [27] proposed fines migration and the removal of oil-bearing rock particles from rock surfaces in sandstone. The dispersion of these particles would increase the water-wetness, and their movement would block some pore-throats, diverting fluid flow and enhancing sweep efficiency. According to Doust et al. [20], the wettability modification caused by fines release would not be as significant as the diverting of the initial flow path, and these particles would behave like polymers in this case. Additionally, according to the research, pressure drop increases during LSWF processes in carbonates. However, based on core flooding experiments performed under reservoir conditions, where improved oil recovery was observed without fines migration or permeability reduction, Lager et al. [28] hypothesized that fines migration is not a mechanism of improved low salinity oil recovery but rather a phenomenon of MIE. Although the mechanism of fines migration in LSW was initially described for sandstone reservoirs, some researchers who carried out actual core flooding tests have since hypothesized that it may also apply to carbonates. Additionally, it is believed that LSW may cause anhydrite and dolomite to dissolve, which will lead to the migration of particles.

3.1.4 Interfacial Tension (IFT) Reduction

A probable mechanism during LSWF is an increase in pH and a decrease in interfacial tension (IFT) [29], which can lead to a reduction in the residual oil saturation. A decrease in IFT is believed to increase capillary number, which lowers residual oil saturation and improves oil recovery. The ratio of viscous force to capillary force (capillary number) at the conclusion of the waterflooding operation determines the residual oil saturation. After LSWF treatment, reduced salinity and modifications to the ionic composition have little impact on viscosity; as a result, modifications to capillary force will predominantly influence the remaining oil saturation. Capillary force is the main mechanism that makes the injected brine ingest into the matrix micropores where oil is held. As the wettability of the rock is transformed to a more water-wet condition, this mechanism becomes stronger. To lessen residual oil saturation, fluid-fluid and fluid-rock interactions, which produce capillary force, must be greatly diminished. However, it is unclear from the research whether applying LSWF alters contact angle (fluid-rock interactions), IFT (fluid-fluid interactions), or both.

Meng and colleagues [30] came to the conclusion that the two main processes for LSWF in carbonates could be wettability change and reduction of IFT. In contrast to contact angle data, Yousef et al. [11] asserted that brine salinity had little effect on the IFT of crude oil and seawater. As a result, it is likely that LSW has a greater impact on rock-brine interactions (contact angle) than on interactions between oil and brine (IFT). A few experimental experiments also revealed no connection between LSW and a rise in pH. Therefore, despite the fact that some authors identified a mechanism for IFT reduction in carbonates, others claimed that pH value change and IFT reduction are not the main factors behind the improvement in LSW oil recovery.

3.1.5 Electric Double Layer (ELD) Effect

Ligthelm et al. [31] hypothesized this mechanism. As seen by the thicker EDL surrounding the oil droplets and rock particles, they proposed that the low salinity oil recovery is caused by a change in wettability toward increasing water-wetness. Expansion of the EDL raises the electrostatic repulsive forces at the interfaces between the oil-brine and rock-brine layers, which leads to the formation of a thicker and more stable water film on the rock surface and alters the wettability by increasing the water-wet condition. The decrease in electrolyte content in brine lowers the screening potential from ions, which leads to the expansion of electrical diffuse double layers around the mineral particles and oil droplets. Then, when the attraction between these particles and droplets increased, it might encourage the liberation of oil droplets and/or mineral particles, which would finally cause fines migration and/or wettability alterations. This was further supported by Fathi and coworkers [19], who explained that because seawater includes significantly more NaCl than PDIs (Ca^{2+}, Mg^{2+}, and SO_4^{2-}), the EDL surrounding charged rock surfaces has a lot of ions that are not involved in the inner Stern layer and are not active in the wettability alteration process. This inhibits active ions from reaching the rock surface. So, EDL expansion and wettability change when saltwater with low levels of NaCl is present. The mechanism of EDL expansion has been suggested by Sohal and coworker [32] for wettability alteration and LSW oil recovery improvement in carbonates (Figure 2).

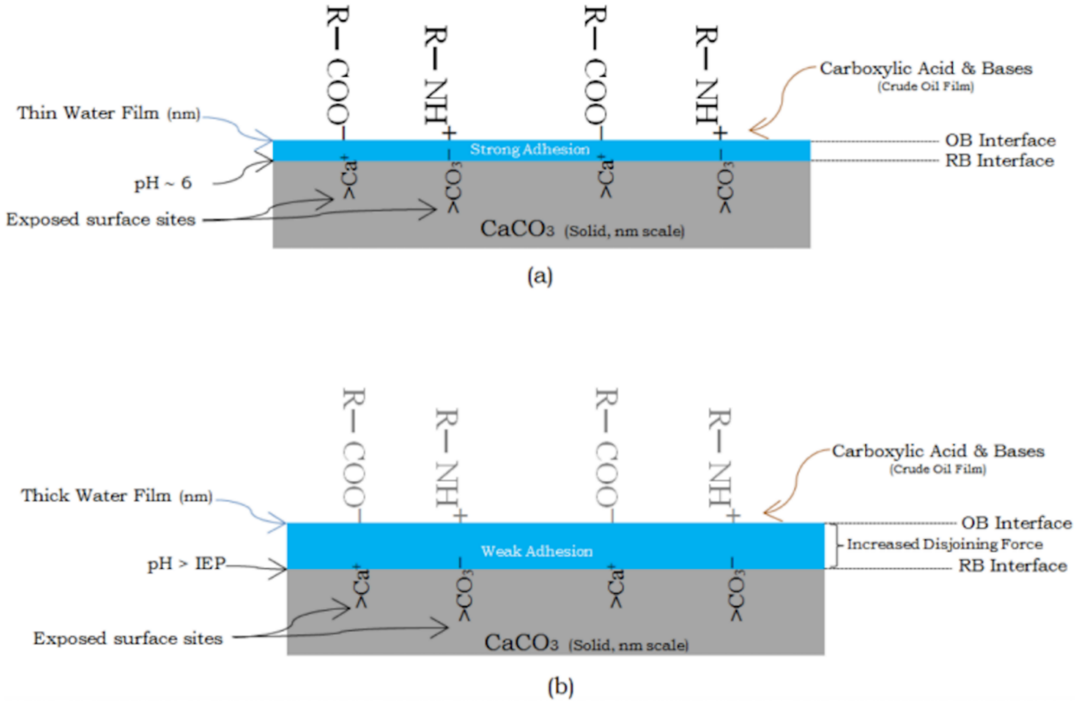

Figure 2. Schematic of suggested mechanism for wettability alteration by EDL effect: (a) original wetting condition; and (b) low salinity brine condition from Sohal et al. [32]

3.2 Effect of brine salinity and composition on oil recovery

The results of numerous laboratory investigations suggested that reducing the brine salinity could improve oil recovery in carbonate rock. According to Alotaibi et al. [33], when low-salinity aquifer water was injected after the injection of formation water, incremental oil recovery increased by 8.6%. Yousef et al. [4] performed a core flood test on a limestone reservoir core where various dilutions of seawater were consecutively injected. By a dilution factor of ten times, the incremental oil recovery following seawater injection was around 19%. From spontaneous imbibition studies on limestone and dolomite core plugs, Romanuka et al. [5] demonstrated that reducing the ionic strength of brines led to increased oil production. Numerous research has shown that the potential determining ions (PDIs), such as Ca^{2+}, Mg^{2+} and SO_4^{2-}, have a significant impact on oil recovery in carbonates in addition to the effect of lowering brine salinity. According to Zhang and Austad [34], the wettability shifted in favor of a more water-wet condition when the concentration of sulfate ions (SO_4^{2-}) in saltwater increased. Additionally, when the amount of Ca^{2+} in seawater was raised after 30 days of imbibition, 32% more oil was collected. Romanuka et al. [5] reported the same sulfate effect in spontaneous imbibition studies on chalk, limestone, and dolomite core plugs using sulfate-modified-low-salinity brine as the imbibing brine. Seawater typically contains high concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} and that can likely explain why seawater often resulted in increased oil recovery in several studies. Contact angle measurements have been used to analyze the effects of PDIs. An oil-aged calcite surface and a limestone surface were used by Chandrasekhar and Mohanty [35] to measure the contact angle. The findings demonstrated that increasing SO_4^{2-} levels were effective in shifting wettability from oil-wet to water-wet, and Mg^{2+} and SO_4^{2-} were identified as the primary potential-determining ions having a beneficial impact. According to Ferno et al. [36], various carbonate rocks may respond differently to the same brine composition. In several outcrop chalks, the authors investigated the impact of sulfate concentration on oil recovery during spontaneous imbibition (Stevns Klint, Rordal and Niobrara). Only the Stevns Klint chalk was affected by sulfate's ability to increase oil recovery; the other rock types were not affected. Comparatively, Romanuka et al. [5] demonstrated that limestone and dolomite samples responded to a lowering in brine salinity but not in the chalk core plugs. Additionally, Gomari et al. [37] discovered that contact angle measurements on a calcite surface modified with oil and long-chain fatty acids revealed that PDIs become more efficient as temperature increases.

The injected brine parameters are outlined in this section based on past research that suggests they may influence oil recovery enhancement during LSWF in carbonate deposits.

3.2.1 Ionic Composition

The three main PDIs Ca^{2+}, Mg^{2+}, and SO_4^{2-} have all been widely researched for their impact on carbonate surfaces. According to Zhang and Austad [34], the wettability shifted in favor of a more water-wet condition when the concentration of sulfate ions (SO_4^{2-}) in saltwater increased. Additionally, when the amount of Ca^{2+} in seawater was raised after 30 days of imbibition, 32% more oil was collected. They also suggested that by adjusting the concentration of Ca^{2+} and SO_4^{2-} ions in seawater and the initial brine, it would be possible to improve oil recovery while also changing the wettability of chalk surfaces. The co-adsorption of Ca^{2+} and SO_4^{2-} ions onto chalk surfaces with rising temperatures was found to potentially increase water-wetness conditions for oil recovery. It was investigated how the ions Ca^{2+} and SO_4^{2-} affected the change of chalk surfaces' wettability. Furthermore, Chandrasekhar and Mohanty [35] suggested that Mg^{2+} and SO_4^{2-} ions are superior to Ca^{2+} ions in their ability to modify the wettability and improve oil recovery of reservoir limestone.

Yi Zhang and Hemanta Sarma [6] performed comprehensive core flooding using limestone conducted at temperature ranging from 70°C to 120°C to investigate the effect of reducing ionic strength and increasing concentration of SO_4^{2-} ions on wettability alteration and oil recovery. They argued that lowering the salinity of the water and raising the sulfate concentration of the injection brine could mobilize a significant amount of additional oil recovery. Temperature had an impact on the process. The incremental oil recovery was significantly higher at 120°C than it was at 70°C due to the lower water salinity and increased sulfate concentration of the injection water.

Polyatomic anions, such as borate (BO_3^{3-}) and phosphate (PO_4^{3-}) have been found to have a positive impact on the wettability alteration and enhanced oil recovery of limestone and dolomite cores free of anhydrite, allowing for an additional 15-20% OOIP oil recovery [38]. When soft water (formation water low in Ca^{2+} and Mg^{2+}) was utilized, it is expected that significant amounts of oil can be recovered when SO_4^{2-} ions are replaced with BO_3^{3-} and PO_4^{3-} ions in the injected brine.

Injection brine for LSWF in carbonates should be deficient in NaCl, contain PDIs (Ca^{2+} and/or Ca^{2+}, SO_4^{2-}), and operate at high temperatures (over 70°C), according to earlier research, which has led to this result. There is a limit to how much SO_4^{2-} concentration can rise with temperature, though, as high SO_4^{2-} concentrations at high temperatures cause $CaSO_4^{2-}$ to precipitate and impede oil recovery.

3.2.2 Ionic Concentration

With the use of both diluted brine (formation water or seawater) and tuned brine, the impact of salinity on the wettability alteration of carbonate rocks was investigated. Diluted seawater (up to 20 times) has a greater potential to boost oil recovery from carbonate reservoirs than formation water and seawater, according to a number of experimental observations that have been documented in the literature. For instance, Yousef and colleagues' [39] use of synthetic saltwater (57,600 ppm) and up to 100 times diluted seawater increased oil recovery from a carbonate reservoir (composite limestone cores). The highest levels of oil recovery were obtained with twice diluted seawater (28,800 ppm at 7-8.5% of OOIP) and ten times diluted seawater (5,760 ppm at 9-10% of OOIP). However, oil recovery did not rise at all when seawater was 100 times diluted, and it only slightly increased (1–1.6% of OOIP) when seawater was 20 times diluted (2880 ppm). As a result, utilizing diluted seawater led to an overall additional oil recovery of around 18% when compared to conventional waterflooding. Al-Harrasi et al. [40] used formation water that was diluted 2, 5, 10, and 100 times at 70 °C to make the case for the likelihood of improved oil recovery in carbonate cores at concentrations that are substantially greater than those noted in the literature. While the high salinity, twice-diluted formation brine (9225 ppm) demonstrated better oil recovery even at 10% of OOIP, the 100 times-diluted formation brine (1944 ppm) delivered the highest oil output and the fastest oil production rate (up to 21% of OOIP). Additionally, Romanuka et al. [5] discovered that increasing the salinity of saltwater in limestone and dolomite core plugs led to an increase in oil recovery of between 4% and 20% of OOIP.

It has been suggested that diluted brine with low concentrations of PDIs can improve oil recovery from carbonates at high temperatures, despite the fact that low salinity brine has typically been reported to boost oil recovery [41]. Reducing ionic concentration is said to not necessarily boost oil recovery and that the concentration of PDIs may play a more significant role [20].

3.3 Dolostone (Dolomite)

The Dolostone, also referred to as dolomite (not to be confused with the mineral dolomite), is a carbonate sedimentary rock primarily composed of dolomite [$CaMg(CO_3)_2$], with lesser amounts of other carbonates such as calcite and aragonite. The name "dolomite" originates from the French mineralogist Déodat Gratet de Dolomieu, who also lends his name to the Dolomites in Italy, where the rock was initially discovered. Similar to limestone, the formation of dolostone occurs through the precipitation of carbonates, particularly dolomite, resulting from the following reaction in water:

$$Ca^{2+} + Mg^{2+} + 2(CO_3)^{2-} \rightleftharpoons CaMg(CO_3)_2$$

The precipitation of dolomite from aqueous solutions is governed by factors such as temperature, pressure, and the solubility of CO_2. In contrast to limestone, which can form through a wide range of organic and inorganic processes under ambient conditions, the direct precipitation of primary dolomite from the water column is exceedingly rare and does not appear to occur in the present-day ocean, despite the saturation of seawater with respect to dolomite. Instead, most dolomitic rocks originate from the chemical replacement and cementation of original calcite and aragonite carbonate sediments by secondary dolomite.

The process of dolomitization often yields rhombohedral crystals of dolomite, altering the texture of the original limestone to varying degrees. Some dolostones still retain fossils or other allochems, while others exhibit a crystalline texture consisting of recrystallized rhombohedrons of dolomite. These textures may indicate either the presence of primary dolomite or complete dolomitization of the limestone. The dolomitization of carbonate sediments appears to occur primarily through two mechanisms: the evaporation of seawater, resulting in the formation of gypsum-rich brines that migrate into the underlying carbonate sediment and react with calcite to produce dolomite (known as evaporative reflux), or the interaction between meteoric and marine groundwater involving the mixing of seawater and meteoric water [42].

Figure 3. Sample of dolostone from the Silurian of Ohio. Pike County, Ohio, USA. Photo from James St. John. [42]

CHAPTER 4

METHODOLOGY

The methodology of this study is divided into two major parts. First, Silurian dolomite samples are tested with different water formulations to identify their capacities in Multi-component Ion Exchange (MIE). At this stage, dolomite sample dissolving tests were carried out using Potential Determining Ions (PDI), which include Ca^{2+}, Mg^{2+}, and SO_4^{2-} for carbonate rocks. To replicate an oil-wet environment, dolomite samples were treated with crude oil, and then their abilities to dissolve in multi-component ion exchange (MIE) were examined using various water formulations. Since Ca^{2+} and Mg^{2+} are the ions that link the dolomite surface to the oil drop, they were measured in the supernatants obtained from the dissolving test. The findings of this study can be utilized to assist in choosing the right water formulation for LSWF in particular dolomite reservoirs.

The second part was performed onto Silurian dolostone core samples. The proper water formulation for the core flood experiment was then chosen based on the first part's findings. The reservoir conditions used for the core flooding experiment were higher in pressure and temperature than those found in a typical room. To simulate conventional waterflooding, formation water was injected first. Once oil recovery was steady, a chosen low salinity water formulation was injected. Along with pressure differential, the volume of generated oil as a function of injected water pore volume was measured. The chemical composition of effluent from the core flood was collected for analysis by color titration to identify amount of Ca^{2+} and Mg^{2+} and the oil recovery factor was detected. Figure 4 provides summary of this study in the form of flow chart.

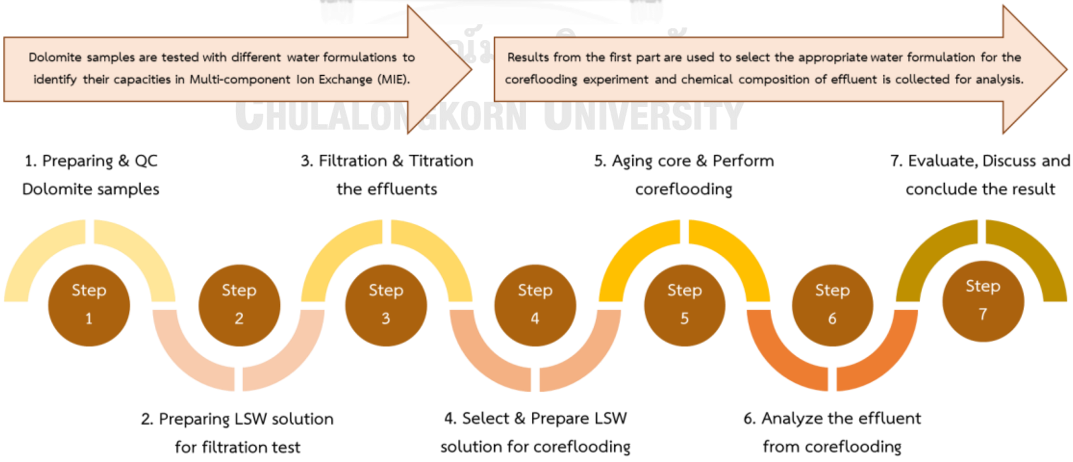

Figure 4. Summary of Flow Chart in this study

4.1 First Part of Experiment

4.1.1 Preparing of Dolomite samples

Dolomite samples are first checked for their purity by using X-ray Fluorescence (XRF), and X-ray Diffraction (XRD). The elements presented in the samples were identified using XRF. By comparing the samples' minerals to atomic elements, XRF was helpful in identifying the minerals they contained. To summarize the representing minerals in the samples, the acquired data was also applied to the results from an XRD analysis. The basis for XRD's operation is the diffraction of X-ray radiation entering the detector through the crystal of a mineral. Based on counts and measurement angles compared to the detector's database, the reading is shown as peaks for particular minerals. Two important instruments for evaluating the mineralogy in this investigation are shown in Figure 5. After its quality is proved, the dolomite powder is directly mixed with crude oil to simulate oil-wet surface condition then crushed into the oil-covered dolomite powder form. The oil-covered dolomite powder is used for the filtration test with various low salinity water formulations.

Figure 5. Instruments used for Assessment of Rock Mineralogy [43]

4.1.2 Preparing of solutions

For low salinity water formulations, this study emphasizes on three potential determining ions which are sulphate ion, calcium ion and magnesium ion. Total salinities of injected water are 1,000 ppm, 2,000 ppm, 5,000 ppm, 10,000 ppm. In each salinity, 10 compositions are chosen as shown in Table 1.

Calcium salt in the study is represented by Calcium Chloride, Sulphate salt is represented by Sodium Sulfate Anhydrous, and Magnesium salt is represented by Magnesium Chloride.

Table 1. Chemical constituent of each water formulation

Formulation no.	**Calcium salt (%)**	**Sulphate salt (%)**	**Magnesium salt (%)**	**Composition Ratio**
1	100	0	0	1:0:0
2	67	33	0	2:1:0
3	67	0	33	2:0:1
4	33	67	0	1:2:0
5	33.33	33.33	33.33	1:1:1
6	33	0	67	1:0:2
7	0	100	0	0:1:0
8	0	67	33	0:2:1
9	0	33	67	0:1:2
10	0	0	100	0:0:1

4.1.3 Filtration Test

The dissolution of particular ions from dolomite samples in the presence of other ions in low salinity water was investigated using a filter test. The 20 grams of oil-covered dolomite powder was mixed with 100 cm^3 of selected solution and stirred for 1 hour to simulate the flow of low salinity water in dolostone formation. Then, the mixture was filtered through filter paper and filtrates obtained from the test were collected and analyzed for concentrations of calcium ion and magnesium ion as they represent ions linking between dolomite surface and oil drop. Figure 6 illustrates the schematic diagram of filtration test of this study.

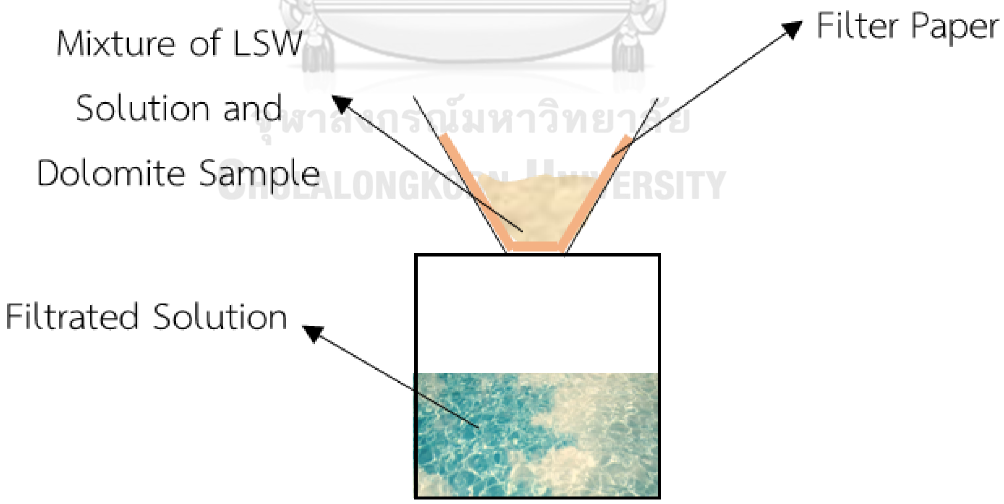

Figure 6. Set up of Filtration of Dolomite Powders [43]

4.1.4 Titration Test

Using a color titration approach with EDTA, the dissolution of calcium ions and magnesium ions from dolomite powder is found in the filtrates. In the titration test, a volumetric flask containing 5 cm^3 of sample was pipetted into it. Three drops of ammonium solution were used as a buffer solution, and Eriochrome Black T (EBT) was employed as a color indicator. To reduce the amount of EDTA solution needed, the sample volume was decreased to 1 cm^3 in some instances where the generated low salinity water had high calcium and magnesium ion concentrations. Total divalent ions (calcium and magnesium ions) were discovered in the initial step. When the color was altered, the end point was discovered.

The purpose of the second test was to just measure the quantity of calcium ions. To precipitate magnesium ion from a sample, a few drops of sodium hydroxide ion were applied. In this instance, hydroxy naphthol blue (HNB) was utilized as the color indication. The mixture was titrated with EDTA till the end point, just like in the first step. When the color was changed from red wine to sky blue, like in the prior instance, the end point was detected. The amount of magnesium ion was determined from the difference between the concentrations of calcium ions and total divalent ions. The equipment used for titration is depicted in Figure 7.

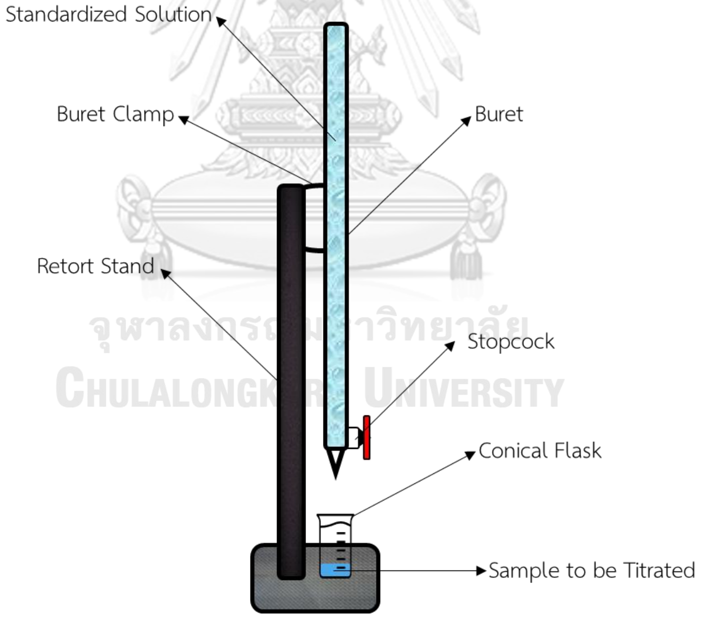

Figure 7. Equipment used for Color Titration [43]

4.2 Second Part of Experiment

4.2.1 Preparing of Testing Fluid

Three fluids were used in this study including 1) formation water; 2) low salinity water and 3) crude oil.

Formation water was prepared using the ionic analysis of formation water obtained from Charoenworakul and Srisuriyachai [44] where the average value of each chemical composition was obtained from averaging dolostone fields around the globe. The selected Total Dissolved Solid (TDS) of formation water were 28,196 ppm and 56,392 ppm. The selected TDS values in this study were chosen from previous studies of Phuenghansaporn and Srisuriyachai [45] where total salinity of formation water was investigated in case of shaly-sandstone formation. Formation water formulations were prepared from Sodium Chloride (NaCl), Calcium chloride ($CaCl_2$), Magnesium Chloride ($MgCl_2$), Sodium Hydrogen Carbonate ($NaHCO_3$), and Sodium Sulfate (Na_2SO_4). Table 2 summarizes chemical required to make up formation water formulations in this study.

Table 2. Chemical composition required to make up formation water of 28,196 and 56,392 ppm

Chemical Composition	Mass Percent	Weight for 28,196 ppm (g)	Weight for 56,392 ppm (g)
$NaCl$	72.69	20.495	40.990
$CaCl_2$	21.87	6.166	12.332
$MgCl_2$	5.09	1.435	2.870
$NaHCO_3$	0.13	0.037	0.074
Na_2SO_4	0.22	0.063	0.126
Total	100.00	28.196	56.392

For this study, the fluid parameters of formation water were density and viscosity. A Pycnometer was used to measure the fluid density, and the results were utilized to calculate the pore volume and fluid viscosity. A Cannon-Fenske viscosimeter was used to gauge the viscosity of the fluid. Fluid viscosity testing was done at the same 50°C testing temperature that was chosen for this study. The absolute permeability was calculated using the centipoise (cP) measurement of fluid viscosity.

Low salinity water formulations that were selected for core flooding experiment were prepared using same chemical composition but were varied in term of total salinity.

For the preparation of the oil phase, due to the high wax content of the crude oil from Sirikit used in the oil phase preparation, internal wax within the crude oil may result, which may cause issues during various study processes like the saturation process and high-pressure difference during fluid displacement mechanism. Dodecane was added in the right amount to boost wax's solubility and make oil more mobile at both room temperature and the testing temperature of 50°C. This solved the issue. Given that the ideal mass ratio of dodecane to crude oil was 70:30, 300 g of crude oil and 700 g of dodecane were needed to prepare 1,000 g of crude oil fluid.

4.2.2 Preparing of Core Sample

For the purposes of this investigation, the dolomite reservoir was represented by two core samples designated C and D. All cores are Silurian Dolostone. By measuring permeability, the core's screening was accomplished. Although core samples are taken from the same location, rock heterogeneity could result in different core properties such as permeability and porosity.

Soxhlet extraction was used to purify the core to its original stage wettability. Every core sample was cleaned for 24 hours with toluene to remove heavy hydrocarbons, then for another 24 hours with methanol to remove light hydrocarbons and any remaining toluene from the earlier process. The Soxhlet apparatus used to clean core samples for this study is shown in Figure 8.

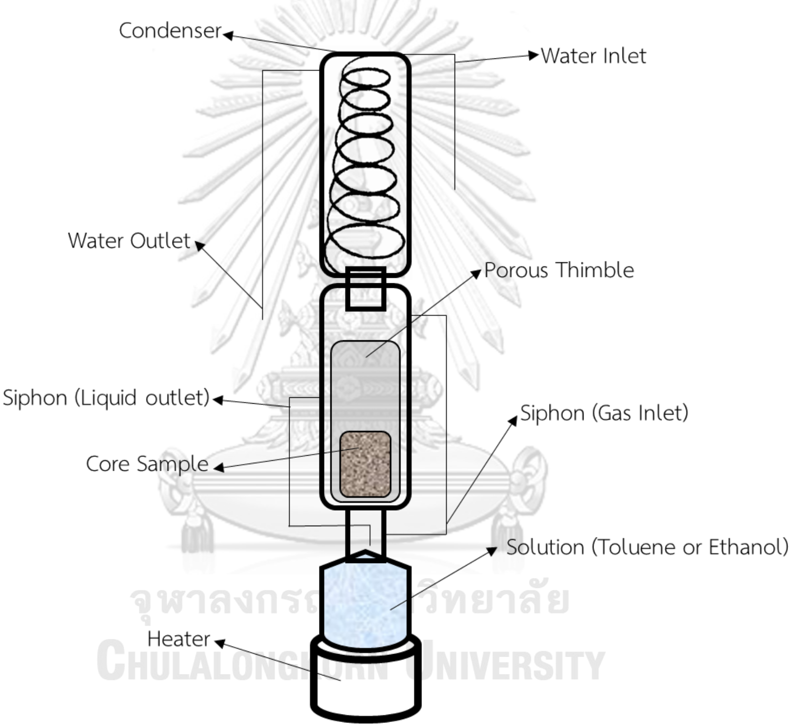

Figure 8. Soxhlet Extractor for Core Cleaning [43]

After the core cleaning step was completed, cores were dried in an oven and stored in a desiccator prior to the following steps.

4.2.3 Core Sample Saturation and Determination of Petrophysical Properties

Pore volume, absolute permeability, and initial oil and water saturation (irreducible water saturation) were petrophysical criteria that had to be met before the core flooding test could begin. Using a core flooding machine, these properties were determined. To mimic the hydrocarbon phase, synthetic formation water was created using the data from Table 2 and Sirikit oilfield crude oil blended with dodecane.

The difference between the dry weight and saturated weight of core samples was used to calculate the pore volume of the sample. Using a fluid density, the difference in weight was then converted to volume. In this stage, formation water was introduced into each core at a rate of 0.5 cm^3/min until the core was completely saturated. Each core was then removed from the machine to have its saturated weight measured. After that, Equation 4.1 can be used to get the pore volume.

$$V_p = \frac{W_{sat} - W_{dry}}{\rho_f} \qquad \textit{(Equation 4.1)}$$

where V_p is pore volume

W_{sat} is saturated weight

W_{dry} is dry weight

ρ_f is fluid density in g/cm^3

Each core was put inside the apparatus and given an additional saturating of formation water. To replicate the reservoir environment, the temperature was increased to 50°C. The absolute permeability during the saturation phase was determined using Darcy's equation, which is depicted in Equation 4.2.

$$K_a = \frac{q\,\mu\,L}{A\Delta P} \qquad \textit{(Equation 4.2)}$$

where q is injection rate (cm^3/sec),

μ is the viscosity of saturated fluid (cP)

L is the length of the core sample (cm)

A is the cross-section area of the core sample (cm^2)

ΔP is pressure differential across the core sample (atm)

The core was then flushed by crude oil to simulate the next step in oil migration after pore volume and absolute permeability had been determined. Until there was no longer any water being created and the pressure differential remained constant, crude oil was injected at a rate of 0.5 cm^3/min. Equation 4.3 was used to compute the initial oil saturation.

$$S_{oi} = \frac{V_w - V_D}{V_p} \qquad \textit{(Equation 4.3)}$$

where S_{oi} is initial oil saturation (fraction)

V_w is the volume of water production (cm^3)

V_D is the dead pore volume of equipment (cm^3)

Once the first oil saturation has been obtained, the initial water saturation can be calculated by deducting it from 1. Then, before starting the core flooding experiment, each core was removed and aged for one week to allow the cores to reach their wettability equilibrium.

4.2.4 Core Flooding Test

To determine the efficiency of low salinity water formulation, a core flooding test was conducted. The experiments were conducted at a temperature of 50°C and a confining pressure of 1,500 psi. The aged core was placed inside the machine, and conventional waterflooding was started with formation water injections at a rate of 0.5 cm3/min. Pressure differences and produced crude oil were periodically detected. A chosen low salinity water formulation was injected, and the amount of oil generated and the pressure difference were continuously monitored until no more oil was formed, and the pressure difference remained constant. At that point, a low salinity water formulation was added. Utilizing the color titration technique, exiting effluents were collected for ionic titrations. Figure 9 depicts a schematic of the core flooding mechanism.

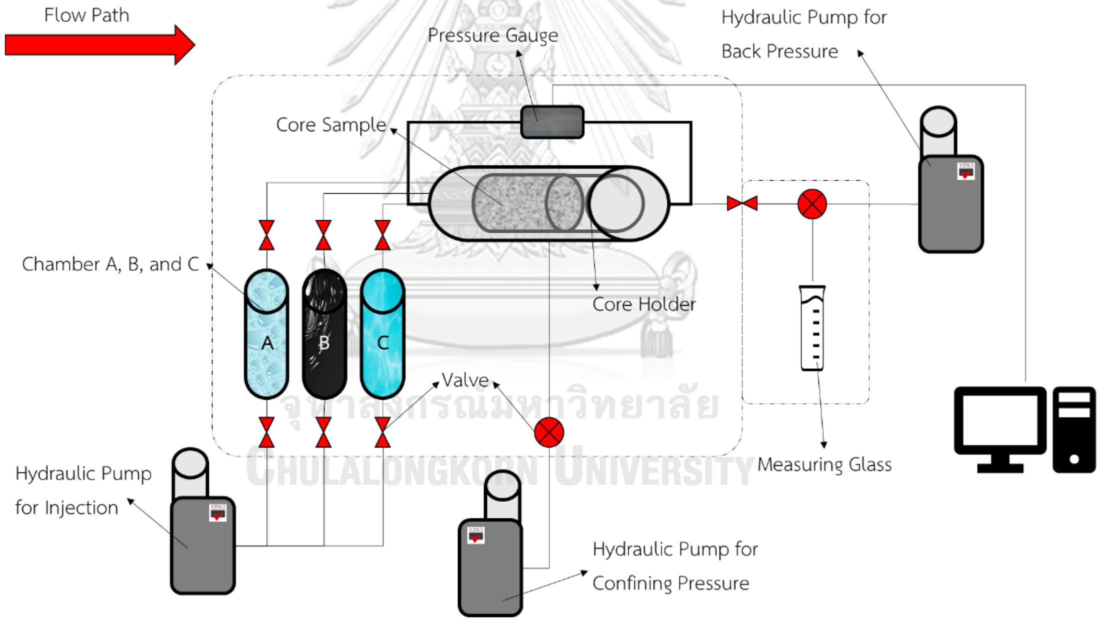

Figure 9. Schematic of Core flooding Machine [43]

4.2.5 Effluent Collection and Detection of Ion Dissolution

Both conventional and low salinity core flooding effluents were collected in order to examine the impact of low salinity water on the core samples by evaluating the ion dissolution of the effluent brine. Color titration was used to determine the concentrations of calcium and magnesium ions.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Rock Mineralogy and Fluid Assessment

5.1.1 Dolomite Samples

XRD was utilized to determine the mineralogy of the representative dolomite sample regarding the quality. From dolomite composition analysis using XRD machine, it can be observed from the Figure 10 that representative dolomite contains 94.4% Dolomite and 5.6% Calcite. This step is essential to confirm the representability of the dolomite sample.

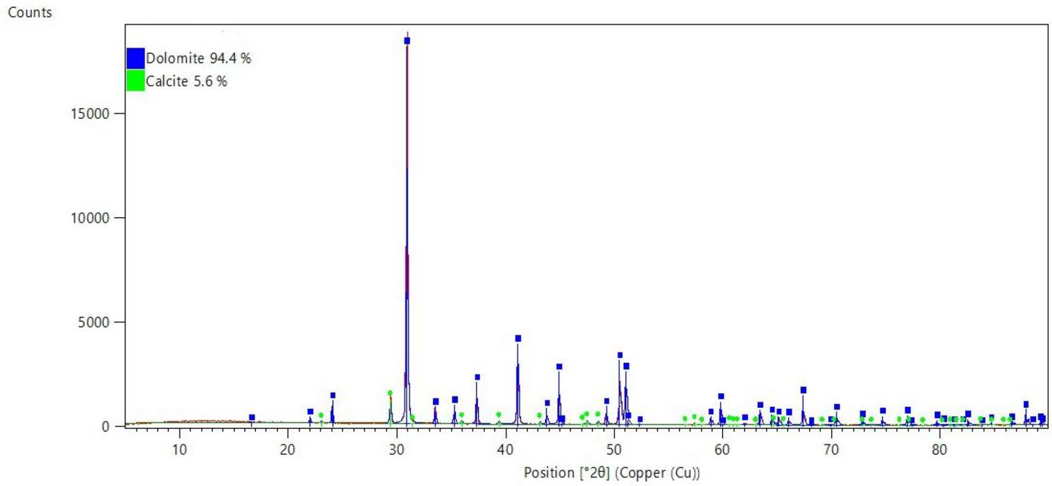

Figure 10. XRD result of representative dolomite samples.

XRF was accompanied to confirm the results obtained from XRD by providing the majority of elements. For the dolomite sample, major elements found in sample from XRF are summarized in Table 3.

Table 3. Results obtained from XRF for dolomite sample.

Elements	Mass Percent
Ca	76.071
Mg	21.972
Si	0.866
Al	0.394
Ag	0.298
Fe	0.260

5.1.2 Core Samples

Two core samples were used in this study which were core C and core D. The properties of each core sample were determined using the core flooding machine. The important properties including porosity, absolute permeability, initial oil saturation, and irreducible water solution are summarized in Table 4.

Table 4. Summary of Core Samples Properties.

Core Sample	Porosity	Permeability (md)	Initial Oil Saturation (%)	Irreducible Water Saturation (%)
C	0.0945	198.27	83.03	16.97
D	0.1026	487.02	85.53	14.47

Based on the core samples result, it can be noticed that core D possesses higher absolute permeability value compared to core C. As cores have been re-used from previous studies. Small particles might block some of the flow paths resulting in difference in permeability value. Nevertheless, both permeability values are in good permeability range and values of initial oil saturation and irreducible water saturation revealed that both cores have similar wettability conditions. Both core samples were used in the core flooding step with chosen low salinity water formulations.

5.1.3 Fluid Properties

For this study, the fluid parameters of formation water were density and viscosity. A Pycnometer was used to measure the fluid density, and the results were utilized to calculate the pore volume and fluid viscosity. A Cannon-Fenske viscosimeter was used to gauge the viscosity of the fluid. Fluid viscosity testing was done at the same 50°C testing temperature that was chosen for this study. The absolute permeability was calculated using the centipoise (cP) measurement of fluid viscosity. The fluid characteristics of this investigation are shown in Table 5.

Table 5. Summary of Fluid Density and Viscosity.

Fluid	Density (g/cm3)	Viscosity (cP)
Formation Water (28,196 ppm)	1.0150	0.613
Formation Water (56,392 ppm)	1.0335	0.940
Mixed Crude (Crude oil with Dodecane)	0.7725	1.672

5.2 Filtration and Titration Results

In this section, the outcomes of each water formulation from the lab experiment were discussed, along with their implications. A titration test was performed to evaluate the outcomes of the dolomite surface's dissolving when it was combined with various water formulations. Concentrations of ions were produced when low salinity water formulation and rock power came into contact. In the plot, a positive concentration value indicates that the ion is dissolved, whereas a negative value indicates that the ion is devoured or absorbed by the dolomite during the process. Table 6 summarizes results obtained from filtration and titration tests. The amount of EDTA required for obtaining end point was then converted to concentration of divalent ions. The concentrations of Calcium and Magnesium ions in the table are the net concentration (concentration obtained from titration subtracted by initial concentration in the water formulation). The negative value refers to the situation where ions were consumed. Positive values can be interpreted as dissolution of ion (in case that more concentration of ion was observed compared to ion concentration in low the water formulation) or ions were slightly consumed. Net divalent ion is the summation of calcium ion and magnesium ion concentration. Negative value of divalent ion is not expected as it means divalent ion is highly consumed and smaller amount of divalent ion is returned from dissolution mechanism. Results from Table 6 were then plotted for each low salinity water formulation as shown in Figures 11 to 20.

Table 6. Summary of Calcium ion and Magnesium ion from dissolution of dolomite from different water formulations with different ions and concentrations.

LSW Formulation No.	Concentration (ppm)	Calcium ions (ppm)	Magnesium ions (ppm)	Net Divalent ions (ppm)
1	1,000	-240.88	170.14	-70.75
	2,000	-642.07	571.17	-70.91
	5,000	-903.82	607.63	-296.20
	10,000	-2709.40	1579.83	-1129.57
2	1,000	-121.71	97.22	-24.49
	2,000	-243.43	206.59	-36.83
	5,000	-408.18	243.05	-165.13
	10,000	-1116.94	729.15	-387.79
3	1,000	-121.71	110.20	-11.51
	2,000	-363.66	317.62	-46.04
	5,000	-608.57	733.28	124.72
	10,000	-1818.30	1891.90	73.60
4	1,000	21.11	85.07	106.17
	2,000	-57.98	170.14	112.15
	5,000	105.53	-121.53	-16.00
	10,000	-289.92	607.63	317.70
5	1,000	-18.97	98.05	79.07
	2,000	-158.18	269.01	110.83
	5,000	-195.06	429.47	234.41
	10,000	-590.51	1101.99	511.48
6	1,000	41.14	23.41	64.55
	2,000	-57.98	168.34	110.35
	5,000	105.53	663.89	769.42
	10,000	-891.09	1084.73	193.64
7	1,000	60.12	24.31	84.42
	2,000	40.08	97.22	137.30
	5,000	300.59	546.86	847.45
	10,000	200.39	0.00	200.39
8	1,000	120.23	12.98	133.21
	2,000	160.31	1.65	161.97
	5,000	200.39	307.95	508.34
	10,000	400.78	69.03	469.81
9	1,000	120.23	-25.20	95.03
	2,000	240.47	34.66	275.13
	5,000	300.59	117.03	417.61
	10,000	300.59	659.39	959.98
10	1,000	200.39	-154.52	45.87
	2,000	140.27	-138.91	1.36
	5,000	300.59	-225.75	74.83
	10,000	400.78	95.36	496.14

Figure 11 shows the ionic concentrations from the filtrates of water formulation No.1. Presence of Ca^{2+} without other ions in low salinity water led to the replacement of Mg^{2+} by Ca^{2+}. However, it was observed that this replacement was not propositional replacement when the concertation of low salinity water was higher than 5,000 ppm.

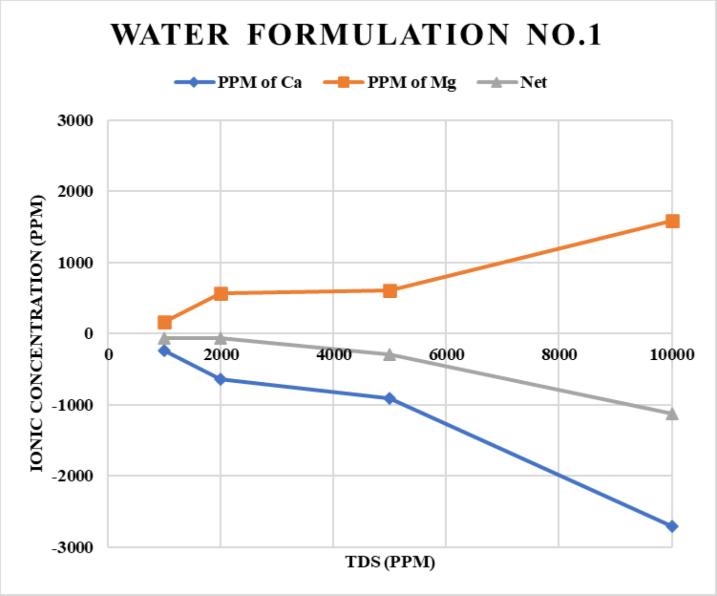

Figure 11. Ionic concentration from the filtrates with different TDS of water formulation No.1.

Figure 12 presents the ionic concentrations from the filtrates of water formulation No.2. Adding of SO_4^{2-} into Ca^{2+} solution provided similar result as in formulation No.1 but smaller dissolved ions.

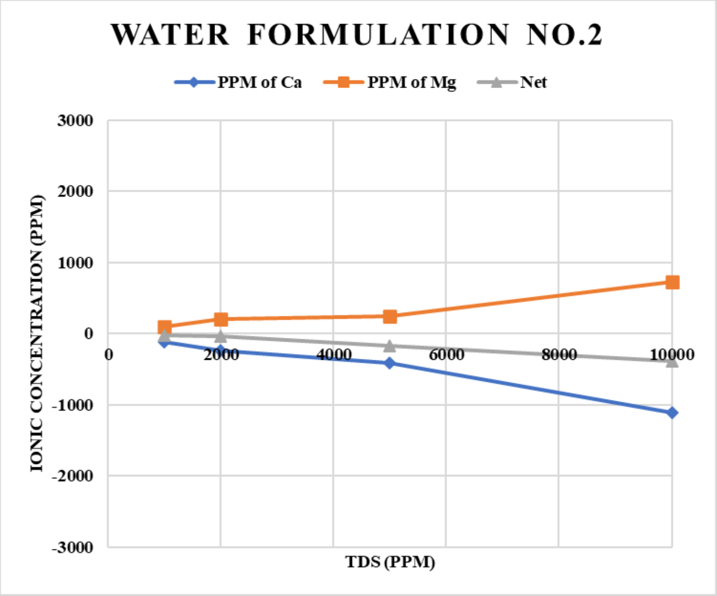

Figure 12. Ionic concentration from the effluents with different TDS of water formulation No.2.

Figure 13 depicts the ionic concentrations from the filtrates of water formulation No.3. Presence of Mg^{2+} together with Ca^{2+} led to constant ratio of ion exchange as Mg^{2+} can replace also Ca^{2+} and hence, net amount of Ca^{2+} consumed was decreased. At concentration higher than 5,000 ppm, the dissolution of Mg^{2+} increased strikingly as same as in solution No.1.

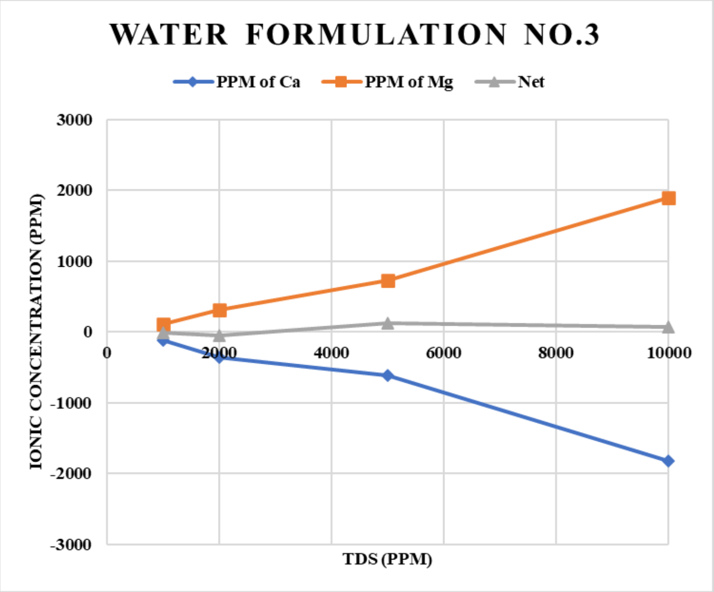

Figure 13. Ionic concentration from the filtrates with different TDS of water formulation No.3.

Figure 14 illustrates the ionic concentrations from the filtrates of water formulation No.4. Increasing of SO_4^{2-} concentration led to the difficulty of Mg^{2+} dissolution but this effect was compensated when the low salinity water concentration was as high as 10,000 ppm with adequate amount of Ca^{2+}.

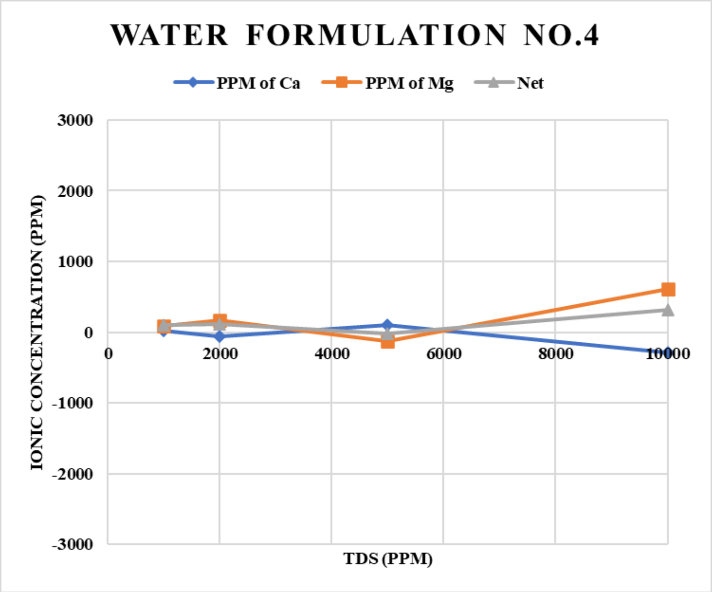

Figure 14. Ionic concentration from the filtrates with different TDS of water formulation No.4.

Figure 15 presents the ionic concentrations from the filtrates of water formulation No.5. Combination of three ions (Ca^{2+}, Mg^{2+} and SO_4^{2-}) at the same portion provided good results in term of net ion dissolution. Ca^{2+} was consumed by dolomite to replace Mg^{2+} at 5,000 ppm and better result was observed at 10,000 ppm.

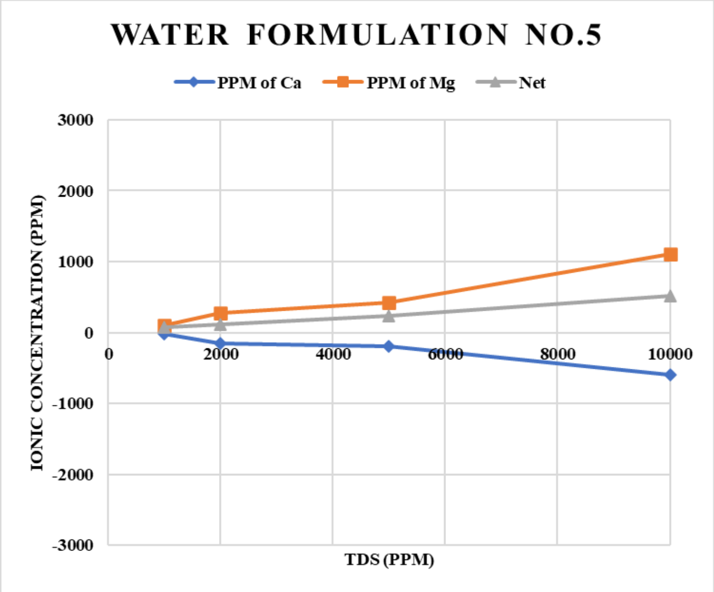

Figure 15. Ionic concentration from the filtrates with different TDS of water formulation No.5.

Figure 16 shows the ionic concentrations from the filtrates of water formulation No.6. Presence of higher Mg^{2+} concentration together with lesser amount of Ca^{2+} led to dissolution of both Mg^{2+} and Ca^{2+}. It can be observed that Ca^{2+} was able to displace Mg^{2+} more than Mg^{2+} displaces Ca^{2+} and Ca^{2+} was consumed more than Mg^{2+} ion at high concentration (10,000 ppm).

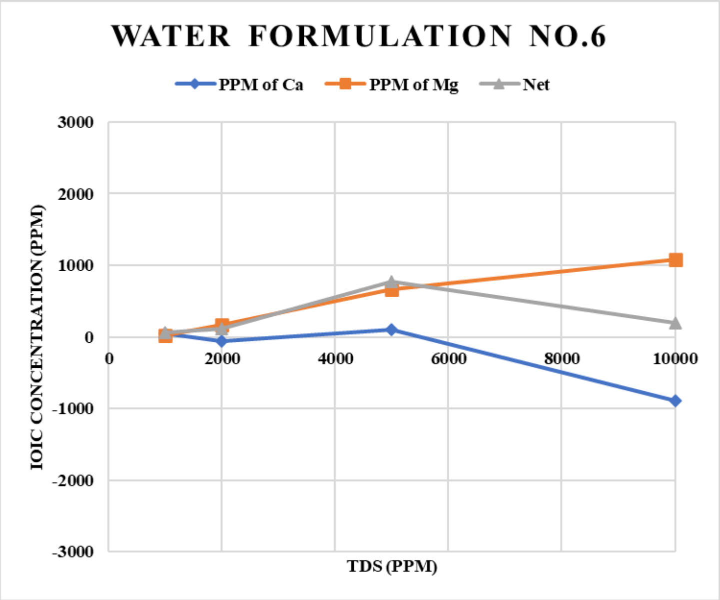

Figure 16. Ionic concentration from the filtrates with different TDS of water formulation No.6.

Figure 17 illustrates the ionic concentrations from the filtrates of water formulation No.7. Presence of only SO_4^{2-} ion without other ions resulted in poor dissolution of both Mg^{2+} and Ca^{2+}. At 5,000 ppm, dissolutions of Mg^{2+} and Ca^{2+} were slightly increased. At higher concentration of SO_4^{2-}, Mg^{2+} disappeared and this could be explained by dolomitization process where Mg^{2+} was consumed and stored back to dolomite by an aid of SO_4^{2-}.

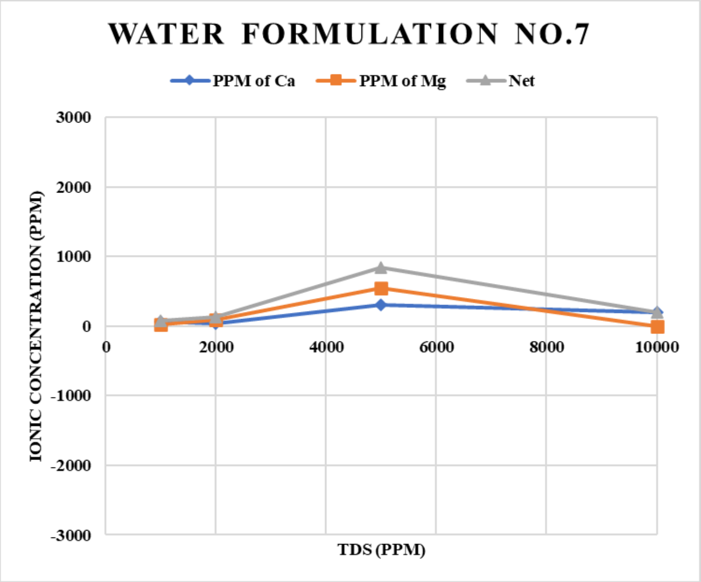

Figure 17. Ionic concentration from the filtrates with different TDS of water formulation No.7.

Figure 18 reveals the ionic concentrations from the filtrates of water formulation No.8. The result was similar to that of water formulation No.7. Present of SO_4^{2-} together with Mg^{2+} led to an occurrence of the dolomitization process at high concentration of SO_4^{2-}.

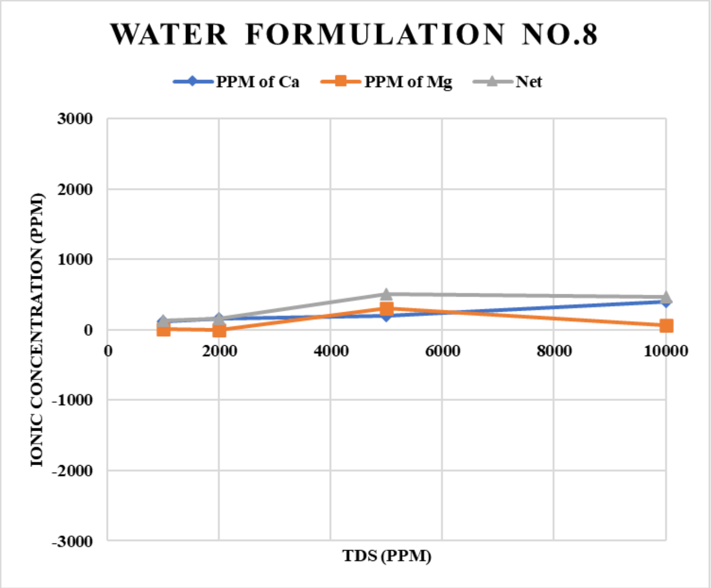

Figure 18. Ionic concentration from the filtrates with different TDS of water formulation No.8.

Figure 19 depicts the ionic concentrations from the s of water formulations No.9. Mg^{2+} worked together with SO_4^{2-} better at high concentration of Mg^{2+} ion especially at the highest concentration (10,000 ppm).

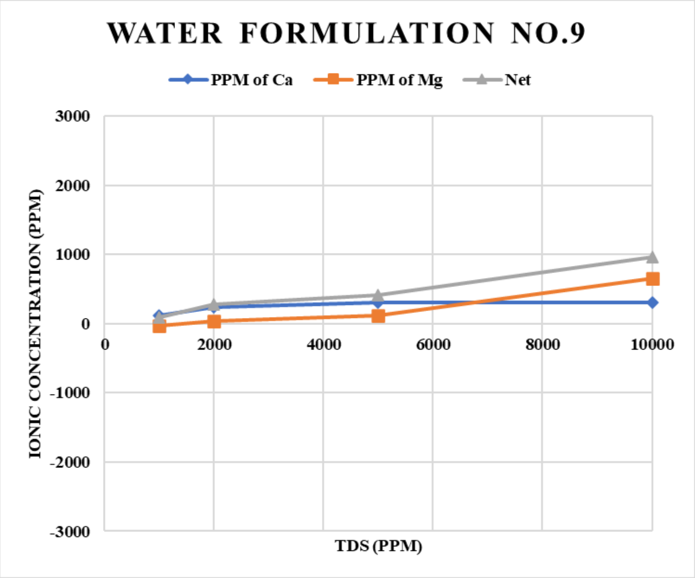

Figure 19. Ionic concentration from the filtrates with different TDS of water formulation No.9.

Figure 20 illustrates the ionic concentrations from the filtrates of water formulation No.10. Presence of only Mg^{2+} without other ions in low salinity water formulation provided better result compared to presence of only Ca^{2+} ion in terms of the ratio of replacement. However, the magnitude of replacement was not as good as in water formulation No.1. This could be explained by the complexity of hydrate form of Magnesium, resulting in smaller reactivity of Mg^{2+}. However, result was slightly improved at higher concentration (10,000 ppm).

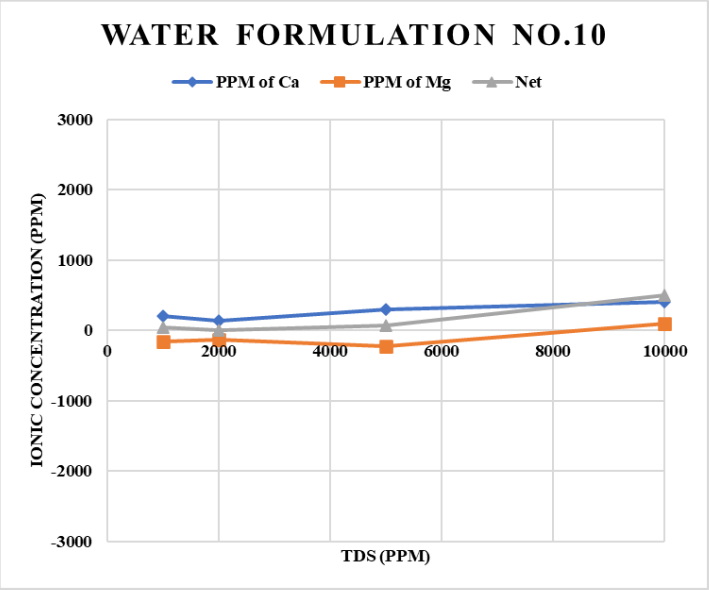

Figure 20. Ionic concentration from the filtrates with different TDS of water formulation No.10.

From all the filtration and titration tests obtained from different low salinity water formulations, the results can be characterized based on ion domination into four different zones as follow:

1. Calcium domination: Ca^{2+} was mainly consumed to replace Mg^{2+}. Within this zone, presence of SO_4^{2-} reduced dissolution of Mg^{2+} whereas, the presence of Mg^{2+} increased the net divalent ion in the system. This zone included water formulation No.1, 2, and 3.
2. Combined effect: Ca^{2+} was consumed to replace Mg^{2+} but consumption was smaller than that of Calcium domination zone due to negatively charged effects from SO_4^{2-}. However, the magnitude of dissolution was also smaller compared to the Calcium domination zone. This zone included water formulation No.4 and 5.
3. Sulfate domination: Mg^{2+} was consumed due to dolomitization effects. This happened at very high total concentration. This effect included water formulation No.7 and 8.
4. Magnesium domination: Mg^{2+} was consumed to replace Ca^{2+}. Nevertheless, due to hydrate structure of Mg^{2+}, the magnitude of dissolution of Ca^{2+} was not as high as Ca^{2+} replacing Mg^{2+}. This zone included water formulation No.6, 9, and 10.

Comparing these four different zones of different low salinity water formulation, the combination effect between Ca^{2+} and SO_4^{2-} seems to be the best water formulation. Presence of SO_4^{2-} reduces positive charges of dolostone, resulting less consumption of Ca^{2+} during the dissolution mechanism.

5.3 Selection of Low Salinity Water Formulations

In this section, the results from previous sections were combined to select the appropriate low salinity water formulation. There were three selection criteria for this section including; 1) the amount of liberated magnesium ion should be as high as possible as magnesium ion from dolostone structure forms very tight interaction with oil due to smaller size of ionic radius compared to calcium ion; 2) Net divalent ion must be positive and the higher the value is favorable as this refers to the situation where less divalent ion is consumed but more divalent ion dissolves to liberate oil; 3) tendency of Net divalent ion must be observed throughout the range of TDS. From the filtration test, there are only two water formulations that fit the criteria which are water formulations number 5 and 9. For water formation number 9, presence of sulfate ion reduces positive charges of dolostone, resulting in less consumption of calcium ion during the dissolution mechanism. For water formulation number 9, due to higher amount of added magnesium ion in water formulation, the consumed amount is small as can be observed by the remaining of calcium ion. Even though the net divalent ion is high in the whole range of TDS, magnesium ion is not as described in criterion no.1 together with explanation of Magnesium domination zone in the previous section. Water formulation number 5 which comprise of magnesium ion, calcium ion, and sulfate ion with ratio 1:1:1 is then selected for the core flooding test. It can be observed that presence of magnesium ion, calcium ion, and sulfate ion together can create dissolution of magnesium ion with less consumption of the calcium ion with positive net divalent ions. Presence of magnesium ion in the system may result in more active calcium ion as magnesium ion can replace calcium in calcium carboxylic compound inside the oil drops. Table 7 summarizes water formulations for each core sample. The contrast ratio which is a ratio of formation water concentration divided by injected water concentration, is also presented in the table, accompanying each test number.

Table 7. Summary of water formulations for core flooding tests.

Test No.	Core	Formation Water (ppm)	Injected Water (ppm)	Contrast Ratio
1	C	28,196	10,000	2.82
2	D	28,196	5,000	5.64
3	C	28,196	2,000	14.10
4	D	28,196	1,000	28.20
5	C	56,392	10,000	5.64
6	D	56,392	5,000	11.28
7	D	56,392	2,000	28.20
8	C	56,392	1,000	56.40

5.4 Core Flood Results from Selection of Water Formulations

Based on the results of the core flooding, the injected pore volume of water was computed at each detected time step using the injection rate (0.5 cm^3 per minute) and time divided by the pore volume of each core sample. Oil recovery factor was shown on the y-axis. Volume of oil produced at each time step divided by initial oil saturation was used to establish the oil recovery factor. Conventional waterflooding was first carried out using formation water until no more oil was produced. Selected low salinity water was then switched until the end of the process.

Figure 21 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 28,196 ppm formation water and 10,000 ppm injection water using core C (Case 1). From the figure, the oil recovery factor obtained from conventional waterflooding was about 65.4%, and once injected water was changed to low salinity water, the oil recovery factor suddenly increased. In summary, the oil recovery factor was increased from 65.4% to 81.9% (16.5% incremental of oil recovery) by switching from formation water to low salinity water.

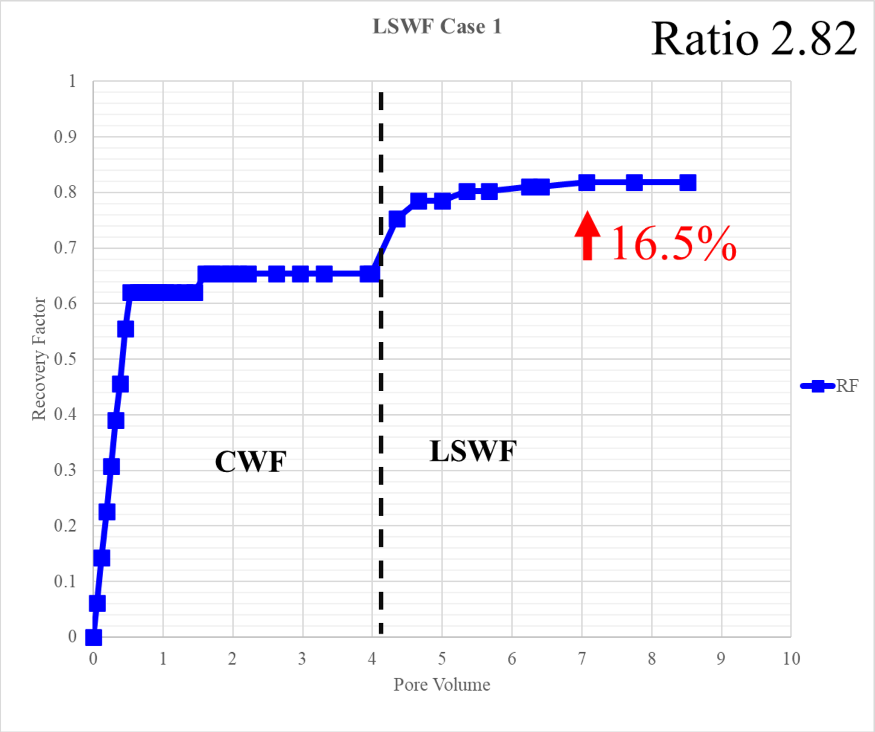

Figure 21. Oil recovery factor as a function of injected pore volume obtained from the case of 28,196 ppm formation water and 10,000 ppm injection water using core C (case1).

Figure 22 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 28,196 ppm formation water and 5,000 ppm injection water using core D (Case 2). From the figure, the oil recovery factor obtained from conventional waterflooding was about 56.0%, and once injected water was changed to low salinity water, the oil recovery factor suddenly increased. In summary, the oil recovery factor was increased from 56.0% to 85.2% (29.2% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is higher than the incremental of oil recovery in case 1 more than 10%.

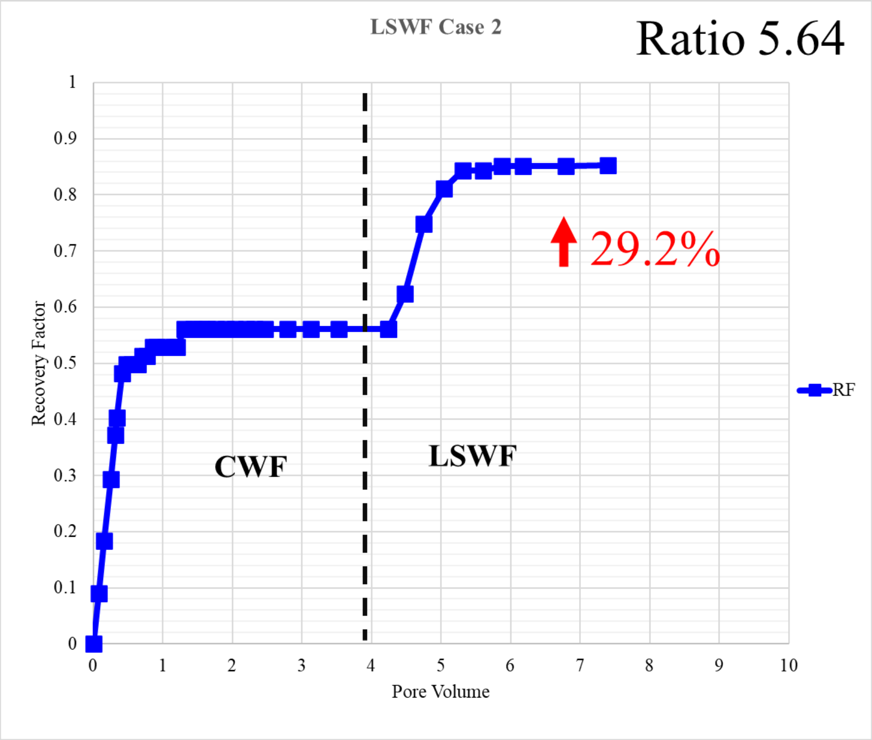

Figure 22. Oil recovery factor as a function of injected pore volume obtained from the case of 28,196 ppm formation water and 5,000 ppm injection water using core D (case2).

Figure 23 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 28,196 ppm formation water and 2,000 ppm injection water using core C (Case 3). From the figure, the oil recovery factor obtained from conventional waterflooding was about 57.2%, and once injected water was changed to low salinity water, the oil recovery factor suddenly increased. In summary, the oil recovery factor was increased from 57.2% to 84.4% (27.2% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is similar to case 2 and the incremental oil is higher than that of case 1 more than 10% same as observed in case 2.

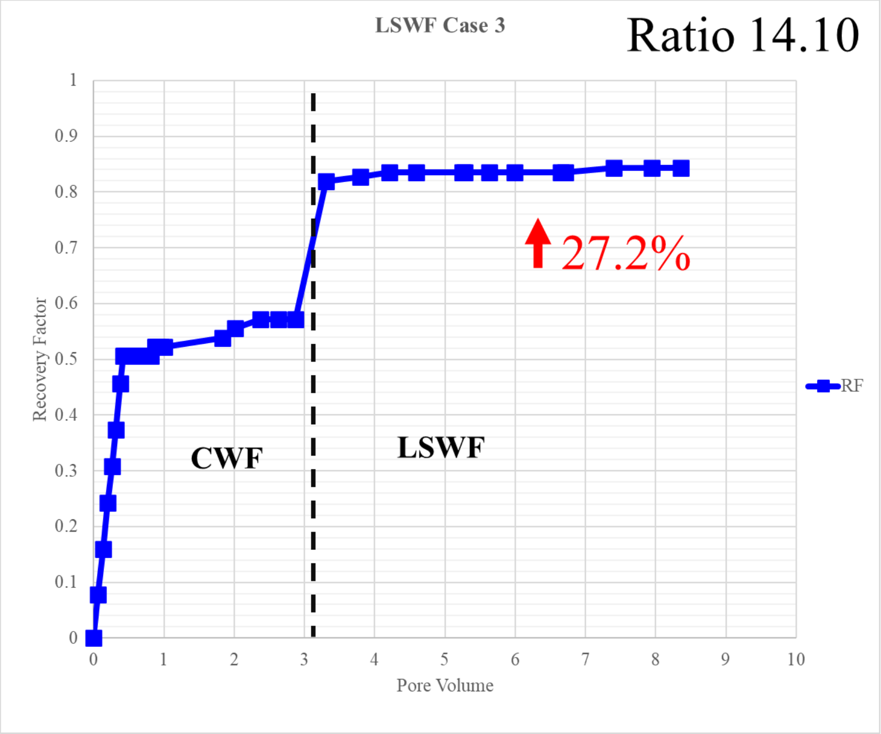

Figure 23. Oil recovery factor as a function of injected pore volume obtained from the case of 28,196 ppm formation water and 2,000 ppm injection water using core C (case3).

Figure 24 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 28,196 ppm formation water and 1,000 ppm injection water using core D (Case 4). From the figure, the oil recovery factor obtained from conventional waterflooding was about 59.2%, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. In summary, the oil recovery factor was increased from 59.2% to 70.2% (11.0% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is similar to case 1 but less than the incremental of oil recovery in case 1 by about 5%.

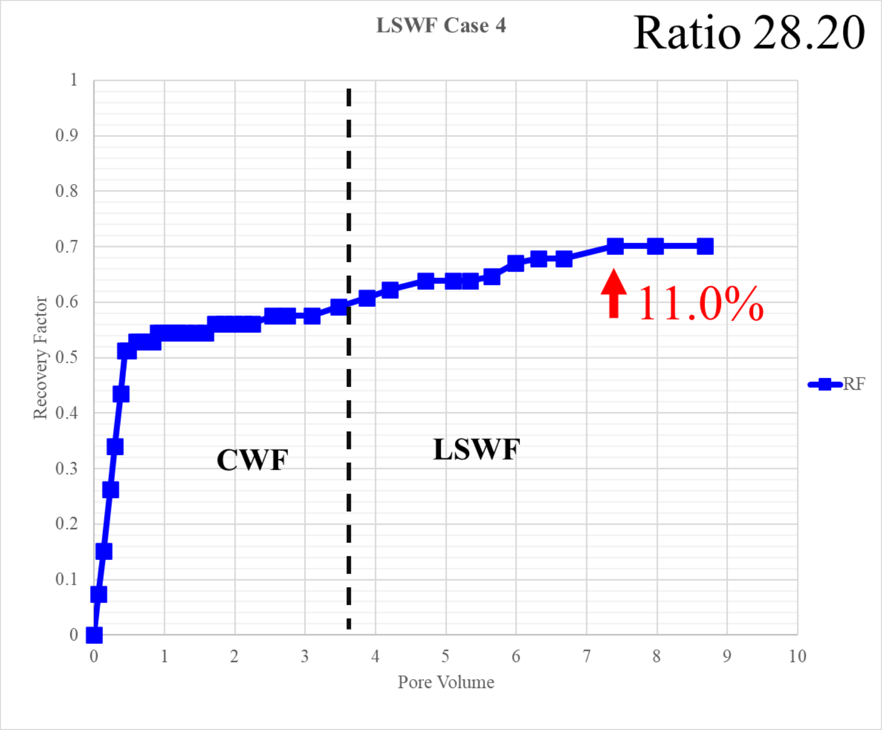

Figure 24. Oil recovery factor as a function of injected pore volume obtained from the case of 28,196 ppm formation water and 1,000 ppm injection water using core D (case4).

From Figures 21 to 24, considering case 1 to case 4 which using formation water at 28,196 ppm concentration, it can be observed that the best increment of oil recovery was obtained from low salinity water with concentration at 5,000 ppm followed by low salinity water at 2,000 ppm. Additional oil recovery as a function of salinity contrast is illustrated in Figure 25.

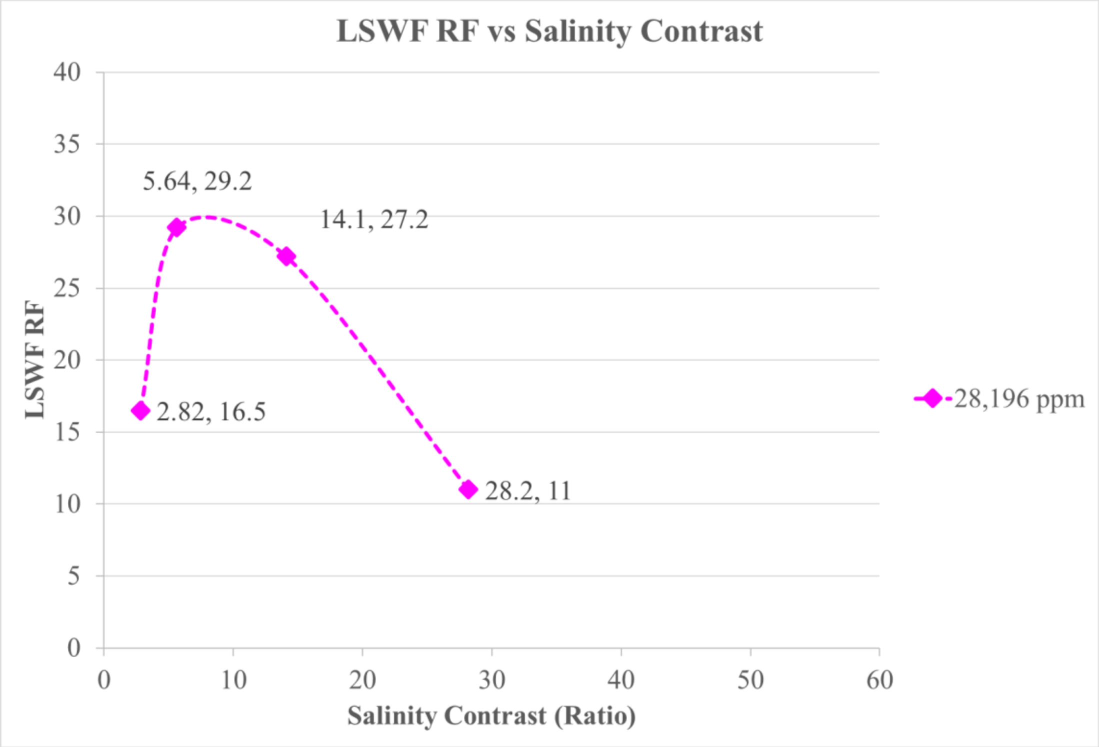

Figure 25. Increment of oil recovery factor from low salinity water as a function of salinity contrast for formation water of 28,196 ppm.

From Figure 25 it can be observed that lowering salinity of injected water does not always yield the benefit to the LSFW. Decreasing of ion concentration in injected low salinity water would favor dissolution mechanism, resulting in liberation of oil but presence of adequate concentration of potential determining ions is important to initiate the whole process. Therefore, this can be concluded that the overall process required adequate amount of calcium ion and sulfate ion to decrease the strength between adsorbed oil layer and external dolostone surface. From this study, the range of salinity contrast between 5.64 to 14.10 was found to be favorable range. Another interesting observation in this case is that, when using 1,000 ppm solution, the increment of oil recovery during low salinity waterflood gradually occurred. This supports the previous explanation regarding the lacking of important ion to initiate the mechanism.

When performing LSFW at small ratio or injecting low salinity water at higher concentration of 10,000 ppm, it can be observed that the recovery was sudden but the magnitude of recovery was smaller than other lower contrast ratio. This can be explained that there were adequate amounts of potential determining ion in this case and the dissolution mechanism can be initiated. Nevertheless, due to small contrast between formation water and injected water, the external layer of dolostone cannot be dissolved as in other cases with higher salinity contrast, resulting limitation in liberation of oil.

The results from different set of experiments using formation water of 56,392 ppm and various 4 different salinities are revealed in Figures 26 to 29.

Figure 26 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 56,392 ppm formation water and 10,000 ppm injection water using core C (Case 5). From the figure, the oil recovery factor obtained from conventional waterflooding was about 58.0%, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. In summary, the oil recovery factor was increased from 58.0% to 60.5% (2.5% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is the lowest compared to other cases.

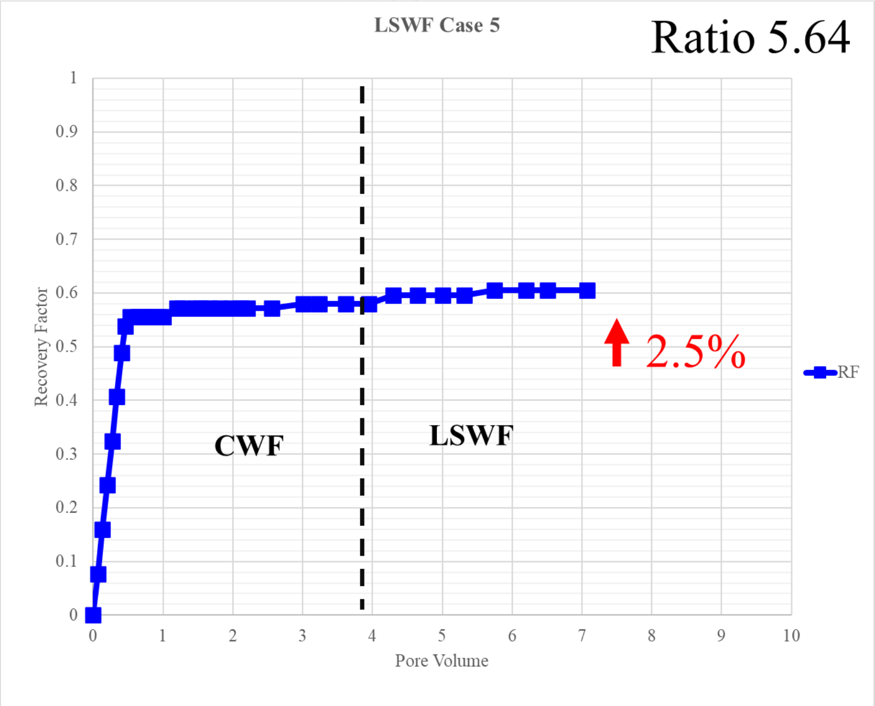

Figure 26. Oil recovery factor as a function of injected pore volume obtained from the case of 56,392 ppm formation water and 10,000 ppm injection water using core C (case5).

Figure 27 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 56,392 ppm formation water and 5,000 ppm injection water using core D (Case 6). From the figure, the oil recovery factor obtained from conventional waterflooding was about 60.8%, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. In summary, the oil recovery factor was increased from 60.8% to 69.4% (8.6% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is higher than case 5 but still smaller when compared to the case of 28,196 ppm formation water (in case 1 to case 4).

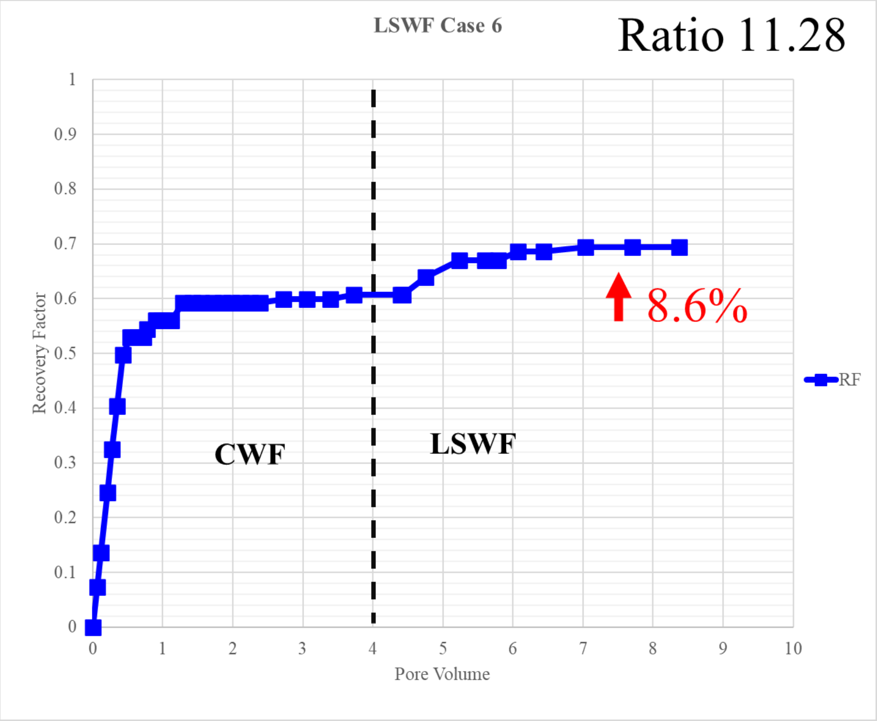

Figure 27. Oil recovery factor as a function of injected pore volume obtained from the case of 56,392 ppm formation water and 5,000 ppm injection water using core D (case6).

Figure 28 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 56,392 ppm formation water and 2,000 ppm injection water using core D (Case 7). From the figure, the oil recovery factor obtained from conventional waterflooding was about 73.3%, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. In summary, the oil recovery factor was increased from 73.3% to 76.5% (3.1% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is lower compared to the case of 28,196 ppm formation water (in case 1 to case 4) but quite the same response with case 5.

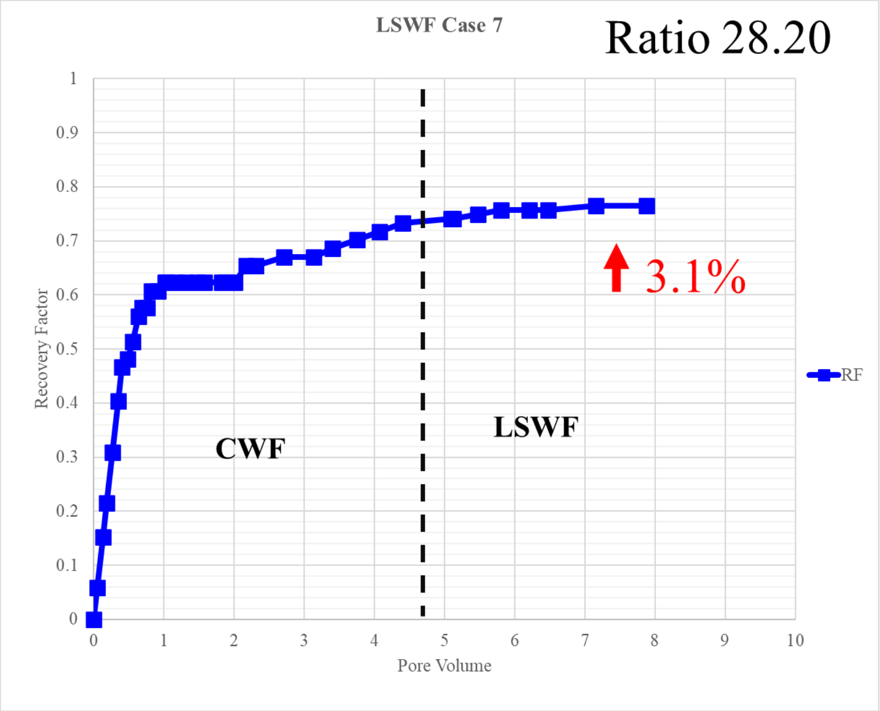

Figure 28. Oil recovery factor as a function of injected pore volume obtained from the case of 56,392 ppm formation water and 2,000 ppm injection water using core D (case7).

Figure 29 illustrates the oil recovery factor as a function of the injected pore volume of water for the case of 56,392 ppm formation water and 1,000 ppm injection water using core C (Case 8). From the figure, the oil recovery factor obtained from conventional waterflooding was about 63.8%, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. In summary, the oil recovery factor was increased from 63.8% to 67.1% (3.3% incremental of oil recovery) by switching from formation water to low salinity water. From this case, it can be observed that the incremental of oil recovery in this case is quite same response with case 7 and quite low compared to the case of 28,196 ppm formation water (in case 1 to case 4).

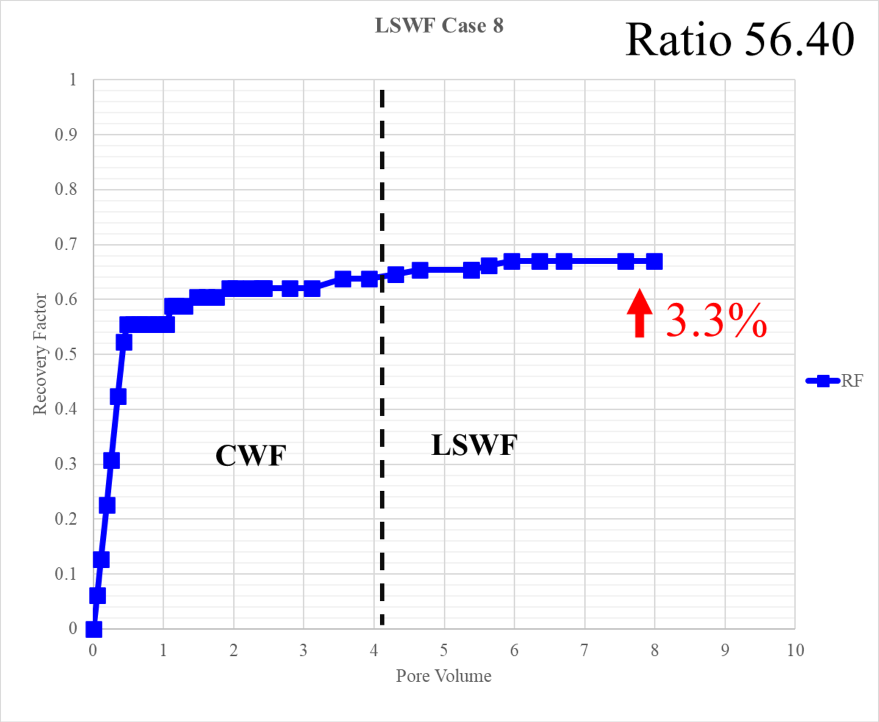

Figure 29. Oil recovery factor as a function of injected pore volume obtained from the case of 56,392 ppm formation water and 1,000 ppm injection water using core C (case8).

From Figures 26 to 29, considering case 5 to case 8 which using formation water at 56,392 ppm concentration, it can be observed that the best increment of oil recovery was obtained from low salinity water with concentration at 5,000 ppm. Other salinity contrasts show only small additional oil recovery as a function of salinity contrasts illustrated in Figure 30.

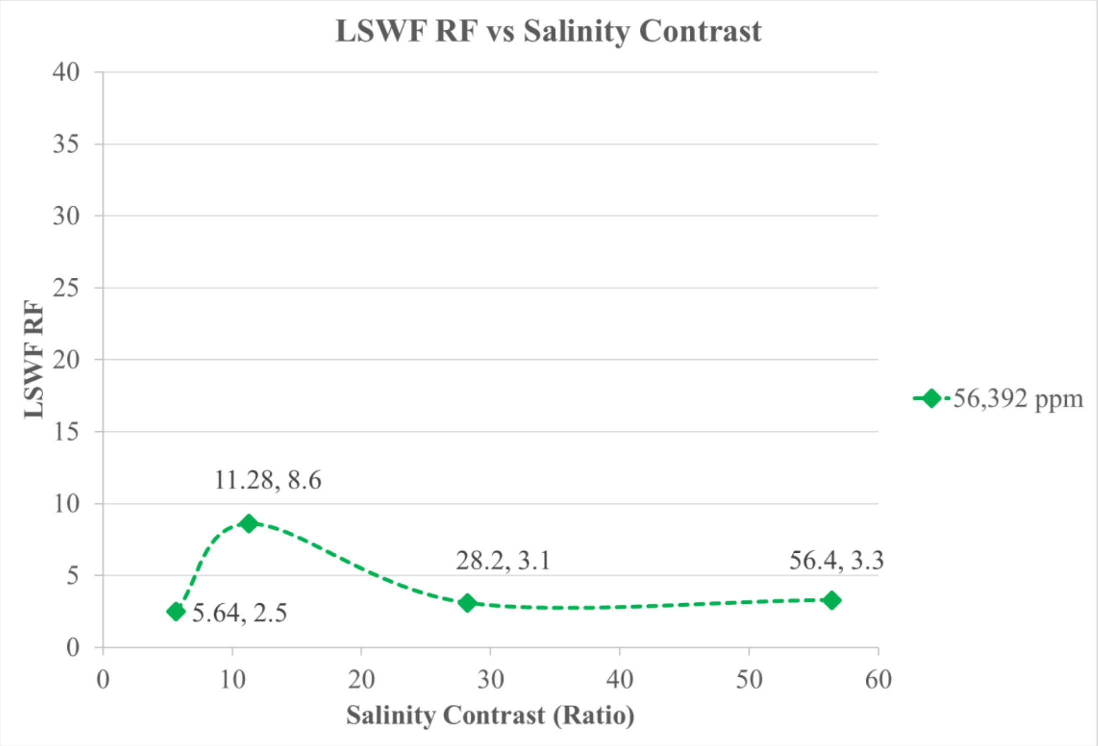

Figure 30. Increment of oil recovery factor from low salinity water as a function of salinity contrast for formation water of 56,392 ppm.

From Figure 30, it can be observed that the optimum salinity contrast appears for formation water of 56,392 ppm which is 11.28. Low salinity contrast of 5.64 and high salinity contrasts of 28.20 and 56.40 results in disadvantages as explained in the explanation of Figure 25. Nevertheless, it can be observed that the magnitude of improvement or incremental of oil is much smaller in all cases. Besides salinity contrast between formation water and injected water, the magnitude of formation water may be another controlling factor of the process. At higher salinity of formation water, number of ions is abundant, and this can drive the mixing process at higher diffusion rate based on Fick’s law of diffusion. According to Fick's law, molecules will move from the region of high concentration to the region of low concentration until equilibrium is reached. The rate of diffusion depends on the concentration gradient, surface area, and diffusion coefficient. So, the original salinity contrast changes to the average concentration quickly and hence, the dissolution mechanism could be limited.

Comparing between the case of formation water at salinities of 28,196 ppm and 56,392 at the same salinity contrast of injected water of 5.64 it can be observed that this contrast still shows good result in formation water at 28,196 ppm. However, at the higher formation water at 56,392 ppm, this same contrast would result in the faster mixing with low salinity water and this could result in the average lower salinity water where ion exchange effect cannot take place anymore.

From all figures, summaries of oil recovery from conventional waterflooding, low salinity waterflooding, and additional oil recovery from LSWF are gathered and reported in Table 8.

Table 8. Summary of oil recovery data from core flooding tests.

Test No. (Core)	Formation Water (ppm)	Injected Water (ppm)	Contrast Ratio	RF Conv. (%)	RF LSWF (%)	Incremental RF (%)
1 (C)	28,196	10,000	2.82	65.4	81.9	16.5
2 (D)	28,196	5,000	5.64	56.0	85.2	29.2
3 (C)	28,196	2,000	14.10	57.2	84.4	27.2
4 (D)	28,196	1,000	28.20	59.2	70.2	11.0
5 (C)	56,392	10,000	5.64	58.0	60.5	2.5
6 (D)	56,392	5,000	11.28	60.8	69.4	8.6
7 (D)	56,392	2,000	28.20	73.3	76.5	3.1
8 (C)	56,392	1,000	56.40	63.8	67.1	3.3

From the study in this section, it can be concluded that optimal salinity contrast exists in different formation water salinity. For the formation water of 28,196 ppm, best salinity contrast was found in the range of 5.64 to 14.10 whereas in case of formation water of 56,392 ppm, the best salinity contrast was discovered at 11.28. The appropriate range of salinity contrast is explained by the contrast that results in adequate number of potential determining ions (calcium ion and sulfate ion) to initiate the dissolution mechanism. And at the same time, the contrast should be high enough to result in the dissolution mechanism. To further support of the existence of MIE mechanism is the appearance of effluent. Not only the MIE, this turbidity of effluent can be explained by liberation of fine particles together with the release of oil drops from the MIE mechanism. Moreover, salinity of formation water is also another property to consider. Higher salinity of formation water results in faster mixing rate, causing injected low salinity to become higher quicky and hence, effects on ion exchange and oil recovery mechanism is limited.

5.5 Titration Test of Effluents

Summary of the titration results from all effluents in all tests are summarized in Table 9. From the table, the replacement ratio is a ratio of net dissolution of magnesium ion concentration divided by net consumption of calcium ion concentration.

Table 9. Summary of divalent ions from effluents in different tests.

Test No.	**Net Ca^{2+} (ppm)**	**Net Mg^{2+} (ppm)**	**Replacement Ratio**	**RF Conv. (%)**	**RF LSWF (%)**	**Incremental RF (%)**
1	-2613.17	1337.271	0.51	65.4	81.9	16.5
2	-1306.58	1944.648	1.49	56	85.2	29.2
3	-113.838	551.8228	4.85	57.2	84.4	27.2
4	524.212	1266.34	-	59.2	70.2	11
5	-2953.83	1701.846	2.37	58	60.5	2.5
6	-940.552	2228.289	0.58	60.8	69.4	8.6
7	-133.881	2945.865	22	73.3	76.5	3.1
8	765.746	2032.774	-	63.8	67.1	3.3

From the table, it can be observed that for formation water at 28,196 ppm the range of salinity contrast comes together with the replacement ratio of calcium ion to magnesium ion. For case 1, the replacement ratio is around 0.51 which means calcium ion was consumed more to produce less magnesium ion. For case 2 with lower salinity of injected water results in less consumption of calcium ion to produce more magnesium ion with the ratio of 1.49. For case 3 the ratio is very high as concentration injected salinity very low. This results in small number of adsorption and higher number of the dissolution of magnesium ion. The ratio in case 3 is found to be 4.85. Case 4 with very small input of injected salinity and hence, the adsorption of calcium ion does not occur. From this ratio, it can be observed that the ratio higher than zero results in good replacement of injected calcium ion to dissolution of magnesium ion. This result comes together with high incremental oil recovery in case 2 and 3.

For cases with formation water at 56,392 ppm, case no.5 with highest concentration of low salinity water, the replacement ratio is 0.58 which is below 1.0. For case no.6 with lower concentration of low salinity water, it shows similar result as cases of formation water at 28,196 ppm with the best incremental oil with the ratio of ion replacement of 2.37. For. For case no.7 where salinity of injected water is quite low, the adsorption of calcium ion occurs at smaller magnitude resulting in the ratio of 22. For case 8 with very small salinity, the total amount of calcium ion does not show adsorption and hence, the replacement ratio cannot be reported.

From this section, the ratio of dissolved magnesium ion to consumed calcium ion shows similar results in both high and low salinity of formation water. Lower ratio than 1 occurs at low salinity contrast, resulting in more consumption of calcium ion than dissolution of magnesium ion. Moderate ratio of ion replacement (in this study 1.49 and 2.37 for the formation water salinity of 28,196 and 56,392 ppm respectively) occurs at optimum salinity, resulting in obvious increment of oil recovery. Higher ratio of ion replacement occurs when salinity of injected water starts to lower and the benefit to oil recovery mechanism start to be from dissolution from high salinity contrast.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

From this study, the conclusions can be divided into two major sections which are 1) the dissolution study of dolomite sample from filtration tests and 2) the effectiveness of low salinity water flooding in dolostone formation from core flooding tests.

From the first section of this study, the result of a capacity in Multi-component Ion Exchange (MIE) of Potential Determining Ions (PDI) which were Calcium ion, Magnesium ion, and Sulfate ion on dolomite will be concluded. The following summarizes the key outcomes of the first section of this study:

1. Calcium ion is powerful in replacing magnesium ion. Even though magnesium ion is smaller in ionic size, its hydrate structure is more complex, resulting reactivity in MIE.

2. Adequate amount of Sulfate ion can facilitate the overall dissolution of divalent ions. However, the magnitude can reduce as positive charges of dolomite are neutralized by sulfate ion.

3. In Sulfate domination, magnesium ion tends to be consumed by dolomite especially at very high concentration which can be explained by dolomitization process to capture magnesium ion back into matrix as $CaMg(CO_3)_2$.

4. From this study, the combination effect between calcium ion and sulfate ion would yield benefit in low salinity waterflooding in dolostone formation. This would lead to dissolution of magnesium ion while calcium ion is not largely consumed due to neutralization of positive charges of dolostone surface. Nevertheless, adding of magnesium ion into the solution enhances the effectiveness of the solution as magnesium ion could replace calcium ion in calcium carboxylic complex in oil drop, resulting in more active calcium ion in the system.

According to the second section of this study, the following summarizes the key outcomes of the second section of this study:

5. The presence of Calcium, Magnesium, and Sulfate ions has a combined effect that enhances the oil recovery mechanism through Multi-component Ion Exchange (MIE). The core flooding experiment demonstrates that the overall process required adequate amount of calcium ion and sulfate ion to decrease the strength between adsorbed oil layer and external dolostone surface.

6. The optimal salinity contrast ratio for the injection of low-salinity water into the formation water in this study ranges from 5.64 to 14.10 when the salinity of formation water is 28,196 ppm. This salinity contrast ratio leads to an incremental recovery factor (RF) of more than 25% after conventional waterflooding. For a formation water salinity of 56,392 ppm, the ideal salinity contrast ratio is approximately 11.28, resulting in an incremental RF of about 8.6%.

7. Multi-component Ion Exchange (MIE) cannot occur effectively at extremely low or high salinity contrasts, resulting in lower oil production compared to the optimal salinity contrast range. Insufficient salinity contrast results in an external layer of dolostone cannot be dissolved as in other cases with higher salinity contrast resulting limitation in liberation of oil, whereas excessive salinity contrast can lead to an inadequate number of active ions to initiate the MIE process.

8. The performance of LSWF is less effective at very high formation water salinity (56,392 ppm) compared to low formation water salinity (28,196 ppm). At very high formation water salinity, the magnitude of improvement or incremental of oil is much smaller in all cases. Besides salinity contrast between formation water and injected water, the magnitude of formation water is considered as another controlling factor of the process. At higher salinity of formation water, number of ions is abundant, and this can drive the mixing process at higher diffusion rate based on Fick’s law of diffusion. Hence, the original salinity contrast changes to the average concentration quickly and hence, the dissolution mechanism could be limited.

9. The ratio of dissolved magnesium ion to consumed calcium ion shows similar results in both high and low salinity of formation water. Lower ratio than 1 occurs at low salinity contrast, resulting in more consumption of calcium ion than dissolution of magnesium ion. Moderate ratio of ion replacement (in this study 1.49 and 2.37 for the formation water salinity of 28,196 and 56,392 ppm respectively) occurs at optimum salinity, resulting in obvious increment of oil recovery. Higher ratio of ion replacement occurs when salinity of injected water starts to lower and the benefit to oil recovery mechanism start to be from dissolution from high salinity contrast.

From this study, knowing the effects of salinity contrast, the different behaviors of different combined ionic solutions and effects on oil recovery mechanism in LSWF in dolomite would lead to ability to select the best water formulation for LSWF in the carbonate reservoir especially in dolostone formation.

6.2 Recommendation

1. The detail range of salinity contrast ratio between formation water and injected low salinity water can be investigated in the future as this might need several more runs to find specific contrast ratio between 5 to 20. It is expected to obtain a specific contrast ratio of this injected water formulation that would cause the highest recovery factor.

2. The detail range of formation water salinity that suitable for LSWF method in dolostone formation can be investigated in the future since this study found that the different salinity of formation water result in different effectiveness of LSWF method.

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APPENDIX

Appendix 1. Summary of divalent ions from effluents in different tests.

Test No.	Collected Water	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Net Ca^{2+} (ppm)	Net Mg^{2+} (ppm)
1	CWF1	380.74	1276.01	380.74	1276.01
	CWF2	220.43	1361.08	220.43	1361.08
	LSWF1	160.31	1324.62	-1031.37	482.21
	LSWF2	541.05	1178.79	-650.63	336.38
	LSWF3	260.51	1361.08	-931.17	518.67
Total net ions from LSWF effluent				-2613.17	1337.27
2	CWF1	160.31	1470.45	160.31	1470.45
	CWF2	120.23	1348.93	120.23	1348.93
	LSWF1	140.27	1312.47	-455.57	891.27
	LSWF2	240.47	1154.49	-355.37	733.28
	LSWF3	100.20	741.30	-495.64	320.10
Total net ions from LSWF effluent				-1306.58	1944.65
3	CWF1	160.31	1239.56	160.31	1239.56
	CWF2	120.23	1336.78	-118.10	1168.29
	LSWF1	200.39	486.10	-37.95	317.62
	LSWF2	200.39	315.97	-37.95	147.48
	LSWF3	200.39	255.20	-37.95	86.72
Total net ions from LSWF effluent				-113.84	551.82
4	CWF1	240.47	1324.62	240.47	1324.62
	CWF2	160.31	1324.62	160.31	1324.62
	LSWF1	260.51	1215.25	141.34	1131.01
	LSWF2	420.82	170.14	301.65	85.89
	LSWF3	200.39	133.68	81.22	49.44
Total net ions from LSWF effluent				524.21	1266.34
5	CWF1	180.35	1348.93	180.35	1348.93
	CWF2	240.47	1543.37	240.47	1543.37
	LSWF1	160.31	1616.28	-1031.37	773.87
	LSWF2	220.43	1409.69	-971.25	567.28
	LSWF3	240.47	1203.10	-951.21	360.69
Total net ions from LSWF effluent				-2953.83	1701.85
6	CWF1	541.05	1385.39	541.05	1385.39
	CWF2	140.27	1470.45	140.27	1470.45
	LSWF1	400.78	1506.91	-195.06	1085.71
	LSWF2	160.31	1069.42	-435.53	648.22
	LSWF3	440.86	680.54	-154.98	259.34
	LSWF4	440.86	656.24	-154.98	235.03
Total net ions from LSWF effluent				-940.55	2228.29
7	CWF1	240.47	1494.76	240.47	1494.76
	CWF2	240.47	1920.10	240.47	1920.10
	LSWF1	180.35	1458.30	-57.98	1289.82
	LSWF2	200.39	1494.76	-37.95	1326.28
	LSWF3	200.39	498.25	-37.95	329.77
Total net ions from LSWF effluent				-133.88	2945.87
8	CWF1	220.43	1045.12	220.43	1045.12
	CWF2	260.51	1543.37	260.51	1543.37
	LSWF1	260.51	1008.66	141.34	924.42
	LSWF2	440.86	668.39	321.69	584.15
	LSWF3	300.59	352.42	181.42	268.18
	LSWF4	240.47	340.27	121.30	256.03
Total net ions from LSWF effluent				765.75	2032.77

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