

Interference of Potential Determining Ions in Low Salinity Waterflooding in Dolomite
Reservoirs

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ขณะพล เจริญธนาวารกุล : การรบกวนของไอออนที่สามารถส่งอิทธิพลต่อกระบวนการฉีดอัดน้ำเกลือที่มีความเข้มข้นต่ำในแหล่งกักเก็บโดโลไมต์ (Interference of Potential Determining Ions in Low Salinity Waterflooding in Dolomite Reservoirs) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.ฟ้าลั่น ศรีสุริยชัย, 93 หน้า.

ในปัจจุบันการฉีดอัดน้ำเกลือความเข้มข้นต่ำเป็นหนึ่งในวิธีการเพิ่มผลผลิตน้ำมันที่มีการศึกษาอย่างแพร่หลาย งานวิจัยหลายฉบับค้นพบว่าความสามารถในการเพิ่มผลผลิตน้ำมันนั้นขึ้นอยู่กับหลายปัจจัย เช่น ความเค็มของน้ำเกลือที่ใช้ฉีดอัด ความเข้มข้นของไอออนที่สามารถส่งอิทธิพลต่อกระบวนการฉีดอัดน้ำเกลือ อัตราการฉีดอัดและอุณหภูมิ เป็นต้น ในการศึกษาี้ ประสิทธิภาพของการฉีดอัดน้ำเกลือความเข้มข้นต่ำรวมถึงสภาวะในการอัดฉีดที่แตกต่างกันได้ถูกทำการศึกษา ขั้นตอนแรกเป็นการระบุความเค็มรวมของน้ำเกลือที่ใช้ฉีดอัดที่ให้ผลผลิตที่ดีที่สุดเพื่อใช้ในการตัดแปลงอัตราส่วนไอออนที่สำคัญในลำดับถัดไป หลังจากนั้นการปรับเปลี่ยนอัตราส่วนระหว่างไอออนที่สามารถส่งอิทธิพลต่อกระบวนการฉีดอัดน้ำเกลือรวมทั้งอุณหภูมิในการทดลองถูกศึกษาเพื่อสังเกตถึงการส่งอิทธิพลที่มีต่อกระบวนการฉีดอัดน้ำเกลือ ลำดับสุดท้ายเป็นการศึกษาผลจากการปรับเปลี่ยนอัตราการผลิตอัดเพื่อให้ได้ผลสัมฤทธิ์สูงสุดในการเพิ่มผลผลิตน้ำมันจากกระบวนการฉีดอัดน้ำเกลือ

จากผลการศึกษาแสดงให้เห็นว่าการฉีดอัดน้ำเกลือที่มีความเค็มรวม 80,000 ส่วนในล้านส่วนจะทำให้ได้ผลผลิตน้ำมันมากที่สุดซึ่งเป็นผลมาจากการลดลงของแคลเซียมไอออนและแมกนีเซียมไอออนส่งผลให้เกิดการละลายของไอออนจากหินซึ่งช่วยให้น้ำมันที่ถูกดูดซับหลุดออกมาจากพื้นผิวได้ อย่างไรก็ตาม ผลผลิตอื่นๆจากกระบวนการละลายของไอออนจากหินที่อุณหภูมิสูงสามารถยับยั้งปฏิกิริยาไม่ให้ดำเนินต่อไปได้เมื่อปฏิกิริยาถึงจุดสมดุล ในหัวข้อถัดไปซึ่งเป็นการศึกษาผลของการปรับเปลี่ยนอัตราส่วนของไอออนที่มีประจุสองบวก พบว่าการฉีดอัดน้ำเกลือที่มีอัตราส่วนระหว่างแคลเซียมไอออนกับแมกนีเซียมไอออนเท่ากับ 1 ต่อ 1 ได้ผลผลิตน้ำมันน้อยที่สุด เพราะว่าเมื่อปริมาณของทั้งสองไอออนใกล้เคียงกัน จะทำให้กระบวนการละลายของไอออนจากหินถูกยับยั้งและไม่สามารถดำเนินต่อไปได้ สำหรับผลของการปรับเปลี่ยนซัลเฟตไอออน พบว่าการฉีดอัดน้ำเกลือที่มีความเข้มข้นของซัลเฟตไอออน 2 เท่าของความเข้มข้นเดิมส่งผลดีที่สุดเนื่องจากแคลเซียมไอออนสามารถเข้าไปใกล้พื้นผิวหินได้มากที่สุดส่งผลให้เกิดการก่อตัวของสารประกอบเชิงซ้อนได้ดีและเกิดการตกตะกอนของแคลเซียมไอออนน้อยที่สุด ในหัวข้อสุดท้ายซึ่งเป็นผลของการปรับเปลี่ยนอัตราการผลิตอัดน้ำเกลือ พบว่าอัตราการผลิตอัดที่ช้าที่สุดจะทำให้ได้รับผลผลิตน้ำมันมากที่สุดเนื่องจากทำให้อัตราการแพร่ของไอออนจากสารละลายน้ำเกลือไปยังพื้นผิวของหินเกิดขึ้นได้มากที่สุด อย่างไรก็ตามอัตราการผลิตอัดในทางปฏิบัติไม่ควรจะต่ำจนเกินไปเนื่องจากน้ำเกลือสามารถไหลลงไปยังที่ต่ำในแหล่งกักเก็บ ซึ่งจะทำให้ประสิทธิภาพในการกวาดน้ำมันในเชิงปริมาตรลดลง จากผลการทดลองที่กล่าวมาข้างต้น สามารถกล่าวได้ว่าอัตราส่วนระหว่างไอออนที่สามารถส่งอิทธิพลต่อกระบวนการฉีดอัดน้ำเกลือมีความสำคัญอย่างมากต่อประสิทธิภาพในการเพิ่มผลผลิตน้ำมัน จึงเป็นตัวแปรหนึ่งที่ต้องคำนึงถึงในกระบวนการฉีดอัดน้ำเกลือความเข้มข้นต่ำในแหล่งกักเก็บหินโดโลไมต์

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Low salinity waterflooding is one of the most concerned improved oil recovery methods nowadays. Many studies indicated that its effect on increment of oil recovery is depended on various parameters such as total salinity of injected brine, concentration of potential determining ions, injection rate and also temperature. This study emphasizes on performance comparison of low salinity waterflooding in dolomite reservoirs with different brine formulations as well as injecting conditions by the use of coreflooding experiment. First, optimum total salinity of injected brine is determined and used in further modification. After that, the ratio between potential determining ions together testing temperature is adjusted in order to observe interference. Finally, the effect of injection rate is also studied in order to obtain the highest benefits from low salinity waterflooding.

The results show that the highest oil recovery is obtained when injecting with optimum total salinity of 80,000 ppm because decreasing of Calcium and Magnesium ions results in dissolution mechanism of rock matrix that helps to liberate adsorbed oil at the rock surface. However, products from dissolution mechanism at higher temperature may act as inhibitor of the process and could terminate the dissolution mechanism once the equilibrium is attained. For the study of effects of divalent ions, oil recovery factor is at the lowest when the ratio of Calcium ion to Magnesium ion is 1:1 because when both ions in injected brine are comparatively equal, this might inhibit dissolution of both Calcium and Magnesium from rock matrix. The highest value of oil recovery factor is obtained from the case that Sulfate ion concentration is twice compared to the original concentration because Calcium ions can approach closer to surface, resulting in an ease to form more Calcium Carboxylate complex with the least amount of inactive Calcium ion. Last, the highest value of oil recovery factor is obtained from the smallest brine injection rate because the diffusion rate of ions from the brine solution to rock surface is greater. Nevertheless, injection rate should not be too low in real implementation as water can underrun to bottom zone of reservoir, decreasing volumetric sweep efficiency. According to the results, the ratio of potential determining ions in injected brine is sensitive to effectiveness of the process and it should be principally considered in low salinity waterflooding process performed in dolomite reservoir.

Department: Mining and Petroleum Engineering Student's Signature

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Abbreviation

3D	Three Dimensions
%mol or %mole	Percentage by mole
%wt	Percentage by weight
AN	Acid Number
Ba ²⁺	Barium ion
BO ₃ ³⁻	Borate ion
Br ⁻	Bromide ion
C or °C	Degree Celsius
Ca ²⁺	Calcium ion
CaCl ₂	Calcium Chloride
CaCO ₃	Calcium Carbonate
CaMg(CO ₃) ₂	Calcium Magnesium Carbonate
c.c.	Cubic centimeter
c.c./min or cm ³ /min	Cubic centimetres per minute
Cl ⁻	Chloride ion
cm.	Centimeter
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
-CO ₃	Carbonate group
-COOH	Carboxylic group
cP	Centipoise
cSt/s	Centistokes per second
EOR	Enhanced Oil Recovery
Fe ²⁺	Ferrous ion
Fe ³⁺	Ferric ion

FW	Formation Water
g	Grams
g/cm^3 or gram/cm^3	Grams per cubic centimeter
g/L	Grams per liter
HCO_3^-	Hydrogen Carbonate ion
H_2O	Water
H_2S	Hydrogen Sulfide
K^+	Potassium ion
KCl	Potassium Chloride
KOH	Potassium Hydroxide
LSW	Low Salinity Waterflooding
Mg^{2+}	Magnesium ion
MgCl_2	Magnesium Chloride
Mn^{2+}	Manganese ion
MW	Molecular Weight
N_2	Nitrogen
Na^+	Sodium ion
NaCl	Sodium Chloride
NaHCO_3	Sodium Hydrogen Carbonate
Na_2SO_4	Sodium Sulfate
OH^-	Hydroxide ion
OOIP	Original Oil In Place
pH	Potential Hydrogen
PO_4^{3-}	Phosphate ion
ppm	Part per million
psia	Pound per square inch absolute
PV	Pore Volume

PZC	Point of Zero Charge
RF	Recovery Factor
SiO ₂	Silicon Dioxide
SO ₄ ²⁻	Sulfate ion
Sr ²⁺	Strontium ion



Nomenclature

ρ	Density
μ	Viscosity
E_D	Displacement efficiency
k_a	Absolute permeability
k_{ro}	Relative permeability to oil
k_{rw}	Relative permeability to water
S_{or}	Residual oil saturation
S_w	Water saturation
S_{wi}	Irreducible water saturation
t	Time

CHAPTER 1

INTRODUCTION

1.1 Background

Low Salinity Waterflooding (LSW) is considered to be one of the most concerned improved oil recovery methods nowadays. Over past decade, there have been a number of researches performed experiments on low salinity waterflooding in both sandstone and carbonate rock samples. Many studies indicated that its effect on increment of oil recovery is dependent on various parameters such as total salinity of injected brine, concentration of potential determining ions, injection rate and also temperature.

However, there is not clear evidence explaining how low salinity waterflooding can improve oil recovery in carbonate reservoir due to absence of clay and also its difference in wetting condition compared to sandstone surface. One of the mechanisms which are usually mentioned among the most recent researches is wettability alteration. This mechanism occurs when there is ion interaction among potential determining ions, i.e. Calcium ion (Ca^{2+}), Magnesium ion (Mg^{2+}), Sulfate ion (SO_4^{2-}), polar compounds in oil, i.e. carboxylic group, and positive charges on carbonate surface.

Recently, several investigators suggest that ion exchange will occur when sulfate ion can be adsorbed onto positively charged surface of carbonate rock, lowering positive charge density. As a result, attraction force occurs on the surface, making Calcium ions to come closer to surface and to react with negatively charged polar compound in oil to form Calcium Carboxylate complex which can be easily desorbed. However, Calcium ion may be displaced by Magnesium ion in Carboxylate complex at elevated temperature. In addition, adsorption of Sulfate ion onto surface will increase as higher temperature due to increase in diffusion rate of Sulfate ion. That means efficiency of Sulfate ion as wettability modifier is improved and thereby carbonate becomes more water-wet, which yields higher oil recovery. This

explanation is mainly applied for Carbonate formation which is in general referred to limestone. As another important carbonate reservoir is dolostone, this study is therefore emphasized on this rock type due to more complexity in elements. Dolomite which is Calcium-Magnesium Carbonate would obtain more effects from Magnesium ion during the displacement mechanism.

Another important mechanism that is also mentioned in the research is the dissolution mechanism which Calcium ions and Magnesium ions in the structure of calcium magnesium carbonate from the rock are dissolved and establish equilibrium with brine. When calcium carbonate dissolves, adsorbed oil components are removed and rock surface is shifted towards a more water-wet state.

To study impacts of low salinity waterflooding in dolostone, coreflood machine is utilized. First, optimum total salinity of injected brine is determined. After that, it is the step to study effects of concentration of potential determining ions by adjusting the ratio between potential determining ions in order to observe interference among each other. Moreover, the impact of injecting conditions, which are injection rate and temperature, are also observed in this study. This study would provide more visions and understanding on potential of low salinity waterflooding to enhance the oil recovery in dolomite reservoir which in real it is quite difficult to implement with other chemicals.

1.2 Objective

1. To study impacts of physical and chemical factors affecting oil recovery enhancement of low salinity waterflooding in dolomite reservoirs, including total salinity of injected brine, concentration of potential determining ions, injection rate and temperature.
2. To determine optimum total salinity and concentration of potential determining ions yielding the highest effectiveness improvement of oil recovery.

1.3 Outline of Methodology

1. Gather chemical analysis of formation brine in carbonate reservoirs from published literature.
2. Screen formation water data and identify tendency, average amount of each ion using basis of mole fraction according to chemicals available in laboratory including Sodium Chloride (NaCl), Sodium Sulfate (Na₂SO₄), Sodium Hydrogen Carbonate (NaHCO₃), Calcium Chloride (CaCl₂), Magnesium Chloride (MgCl₂) and Potassium Chloride (KCl) in order to obtain base formation brine composition for the entire experiment.
3. Perform core analysis to determine basic rock properties and prepare base formation brine as well as different diluted proportions of injected brines for displacement mechanism.
4. Imitate oil migration by saturating core samples with base formation brine followed by injection oil containing organic acid to replace brine. Saturation of sample requires aging time up to several weeks. In this study, a period of one week is spent to ensure completion of wettability alteration mechanism.
5. A coreflood test is firstly performed by using base formation brine with total salinity of 160,000 ppm which is the average value from the screening process as injected fluid although salinity of injected brine is equal to salinity of formation brine in this test. This experiment is performed to simulate conventional waterflooding mechanism by using produced water without any dilution or modification of salinity. Because porosity and initial fluid saturation is known, oil recovery factor can be calculated. Oil recovery factor will be detected after 1, 2, 5 and 10 pore volume of this brine is injected into core samples at a constant injection rate of 2 cm³/min.
6. Perform low salinity waterflooding by reducing total salinity of injected brine to 80,000, 40,000 and 20,000 ppm while maintaining proportion of

chemical composition same as base formation brine composition in order to observe effect of dilution total salinity of injected brine. Oil recovery factor for each experiment run is detected as similar as in step (5).

7. Brine which possesses total salinity yielding maximum oil recovery (the judgment may take recovery rate also) from step (6) is selected for further modification. Diluted brine from step (6) is modified for the ion ratio of divalent cations. To study effects of varying these ions concentration, ion ratio of Ca^{2+} to Mg^{2+} in injected brine are varied in five different ratios which are 1:0 , 4:1 , 1:1 , 1:4 and 0:1 while total salinity is kept constant. Preparation method is shown in following section. The temperature during the experiment is set and kept constant at 50 °C. Again, Oil recovery factor for each case is detected as similar as in step (5).
8. Repeat step (7) but the temperature is varied to other 2 values which are 30 and 70 °C to observe the effect of temperature on the interaction of divalent ions.
9. Select the case that yields the highest oil recovery to adjust ion mass of sulfate ion to be 0.5, 2, 5, and 10 times compared to brine in step (7).
10. Use the brine that yields the highest recovery in step (7). Then, vary flow rate in other 3 values which are 0.5, 1 and 4 cm^3/min to observe the effect of injection rate.
11. Oil recovery factors are also plotted with pore volume of injected brine in all cases. Results from different injected brine systems are compared to determine the optimum injected brine formulation for carbonate reservoirs. Data analysis and discussion are provided to point out new finding from this study.

1.4 Outline of Thesis

This thesis is divided into six chapters which are

Chapter I, this chapter introduces background of low salinity waterflooding in carbonate reservoirs and indicates the objectives and methodology of this study.

Chapter II, this chapter summarizes the previous studies related to low salinity waterflooding in carbonate reservoirs including effects of related parameters and evidences of oil recovery improvement from low salinity waterflooding.

Chapter III, this chapter reviews the chemical structure and wettability of carbonate surface, mechanisms of low salinity water injection in carbonates, difference between limestone and dolostone and composition of formation water in carbonate reservoirs.

Chapter IV, this chapter describes the details of methodology and steps in experiment. The first topic is an overall scope of work. And, the following topics are formation brine preparation, injected brine preparation, core samples preparation, acid oil preparation and experimental setup.

Chapter V, this chapter presents the results and discussion for each series of laboratory experiment. The results are mainly investigated on recovery factor as a function of injected pore volume of brine.

Chapter VI provides new findings and conclusions and recommendations for further study.

CHAPTER 2

LITERATURE REVIEW

This chapter summarizes previous studies related to low salinity waterflooding in carbonate reservoirs for both limestone and dolostone during the past decades including effects of related parameters and evidences of oil recovery improvement from low salinity waterflooding.

Study of Low Salinity Waterflooding in Carbonate Reservoirs

Although the study of low salinity waterflooding was proposed since last century, however most of them were performed in sandstone reservoirs, therefore the study of low salinity waterflooding in both limestone and dolostone reservoirs was quite new and some topics have not been clearly explained. Nevertheless, five recent researches on low salinity waterflooding in carbonate reservoirs are selected to use as the guide for further study which will fulfill missing data from previous studies for better understanding of oil recovery mechanism by low salinity waterflooding especially in dolomite reservoirs.

In 2012, Austad et al. [1] studied the Amott spontaneous imbibition test on oil bearing limestones and dolostone, together with Stevns Klint outcrop chalk and Silurian outcrop dolostone. After the core was imbibed until reaching capillary equilibrium, the formation brine was replaced by low salinity brine to observe incremental oil recovery. They observed that there was a significant distribution in the value of additional oil production due to difference in condition, i.e. temperature and also natural variation such as pore texture and permeability. Moreover, they concluded that increase in additional oil recovery was mostly from lowering the ionic strength or diluting the injected brine. Therefore, they indicated that lowering the ionic strength could shift the wettability of rocks towards a more water-wet state.

Zahid et al. [2] performed coreflood experiment by using Lower Cretaceous age carbonates and Aalborg outcrop chalk from Maastrichtian age in 2012. They

initially flooded cores with seawater. Later on, they injected various proportions of diluted seawater to observe the incremental oil recovery as a result from low salinity waterflooding. They found that there was no significantly additional oil recovery at 40 °C for carbonate cores but it was occurred at 90 °C. However, benefit was not observed at both 40 and 90 °C for outcrop chalk cores. Therefore, they indicated that there are two possible mechanisms that are related to incremental oil recovery in carbonates at 90 °C. The first one is migration of fines due to a significant increment in pressure drop across the core. Another one is rock dissolution because there is constant production of Calcium ion in the effluent during low salinity injection.

In 2012, Al-Harrasi et al. [3] investigated the potential and control factors of low salinity waterflooding in tertiary mode of oil recovery. In this study, both spontaneous imbibition and coreflood were performed by using carbonate cores from Oman with four different diluting ratios of injected water. They discovered that higher oil recovery could be obtained from decreasing total salinity of diluted brine in both spontaneous imbibition and coreflood experiments especially the incremental oil recovery was obviously observed in spontaneous imbibition.

In 2013, Sharifi and Shaikh [4] also performed the coreflood test on Indian outcrop limestones. Firstly, they measured contact angles of injected water with different ratios of Sodium ion, Chloride ion, Calcium ion, Magnesium ion and Sulfate ion and also different total salinities. Then, they flooded cores with brine which yielded the highest contact angle value followed by brines yielding lower contact angles respectively. They concluded that injecting brines with lower value of contact angle could yield additional oil recovery even though it had higher value of total salinity compared to brine which yielded higher value of contact angle. It means that factor affecting oil recovery is not only total salinity of injected water but it also includes the concentration of ions in brine.

Al-Attar et al. [5] also performed coreflood test on carbonates from Bu Hasa field, in Abu Dhabi by using seawater and injected water from the same field in 2013. They observed that low salinity waterflooding could increase oil recovery in

secondary mode. However, the optimum salinity, or salinity providing the highest oil recovery in this case, is not always the lowest value of salinity or the most diluted in that system. They observed that increasing Sulfate ion concentration could increase oil production until reaching critical value while increasing Calcium ion concentration would decrease oil recovery in clay-free cores.



CHAPTER 3

THEORY

This chapter reviews the chemical structure and wettability of carbonate surface. Alteration of limestone to dolostone is also explained. At the end, mechanisms of low salinity water injection in carbonate formations and composition of formation water in carbonate reservoirs are revealed.

3.1 Carbonate Surface

Carbonate is a potential reservoir rock composed of Calcium Carbonate in case of limestone and Calcium Magnesium Carbonate in case of dolostone. To describe surface structure and charge of properties of carbonate surface, the Hartree-Fock model is used to describe in which oxygen atoms can be categorized into two types. The first type is bridging oxygen atom which is bonding with two calcium atoms and another one is non-bridging oxygen atom which is bonding with one calcium atom [6]. These two types of oxygen atoms are shown in Figure 3.1.

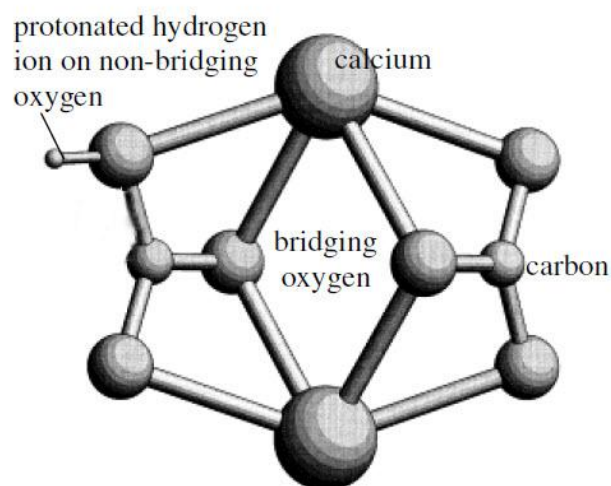


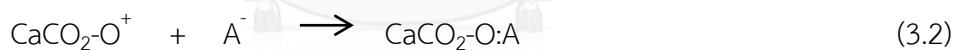
Figure 3.1 Surface structure of calcium carbonate [6]

According to the stabilized structure, the non-bridging oxygen atoms are located at the edge of the surface structure. The protonation of hydrogen ion occurs at the non-bridging oxygen atoms, resulting in the positive charge at carbonate surface. Therefore, surface of carbonate rocks are usually basic in the environment with pH value lower than 9 which is the Point of Zero Charge (PZC) for carbonate surface. When carbonate surface is positively charged, acidic compounds in crude oils can be adsorbed onto surface by their negative site such as OH^- . Lowe et al. showed that acid compounds in crude oils become attached to the basic surfaces of carbonates, forming chemisorbed films [7]. The basic characteristics of carbonates may be due to Arrhenius-Oswalt Calcium Hydroxide-type bases or due to Lewis bases because of the electron pairs available in the exposed oxygens of the $-\text{CO}_3$ carbonate groups.

If the characteristics are due to Calcium Hydroxide-type bases, the reaction is:



If the basic characteristics of the carbonates are due to Lewis-type bases, then the reaction is:



As carbonate surfaces consequently behave like weak bases, which react readily with acidic components in crude oils i.e. carboxylic acids, phenolic compounds and ring structures containing sulfur and oxygen, this results in the orientation of carboxylic molecule exposing the non-polar part outward from rock surface, yielding a range of wettability from neutral to strongly oil-wet.

3.2 Waterflooding in Carbonate Formations

Waterflooding involves the use of injected water to displace oil in a reservoir. This process is a method called secondary recovery. In waterflooding, water displaces oil from the pore spaces but displacement efficiency (E_D) depends on many factors, including mobility ratio and rock characteristics. Because carbonate surfaces

are mostly oil-wet, injected water has to be adjusted, generally by changing total salinity, which will affect concentration of potential determining ions i.e. sulfate ions (SO_4^{2-}), calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}).

Several studies have found that lowering total salinity of injection water can alter rock wettability and consecutively can improve oil recovery. But it still not very clear why lowering total salinity water results in this effect. However, according to Gupta et al. [8], three main theories are proposed including:

- Rock dissolution: This theory explains the low salinity effect by hypothesizing that the lower calcium concentration in low salinity brine causes calcium carbonate from rock to dissolve and establish equilibrium with brine. When calcium carbonate dissolves, adsorbed oil components are removed and rock surface is shifted towards a more water-wet state.
- In-situ surfactant formation: The potential of in-situ surfactant generation requires a high pH value. However, it is determined to be a rare mechanism in waterflooding.
- Surface ion exchange: For typical carbonate reservoir conditions, rock surfaces are positively charged, whereas acidic components in oil phase are negatively charge, causing adsorption onto carbonate surface and resulting in oil-wet condition. If the determining anions in the water (e.g. SO_4^{2-}) have higher attraction to the rock surface more than acidic components in oil, anions will be adsorbed and thereby oil will be replaced and desorbed. Moreover, if positive charges on rock surface are reduced (e.g. due to lowering of salinity), desorption of negatively charged material will occur easier. This mechanism can be illustrated as shown in Figure 3.2.

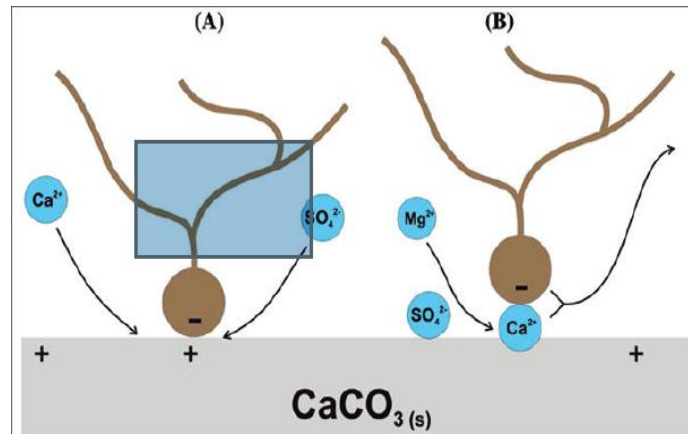


Figure 3.2 Illustration of surface ion exchange induced by brine. (A) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active. (B) Proposed mechanism when Mg^{2+} and SO_4^{2-} are active [9]

Waterflooding is the most commonly used method for recovering producible oil from reservoirs, mainly because: 1) water is efficient in displacing light to medium gravity oil; 2) water is fairly easy to inject into oil-bearing formations; 3) water is abundant in most places and readily available; 4) waterflooding requires lower capital investment and operating cost, which makes the technique more economical than other EOR methods. However, because approximately 80% of carbonate formations are oil-wet, carbonate reservoirs therefore establish a problem in oil recovery. The negatively-charged carboxylic acid anions in oil are attracted to positively-charged carbonate surfaces, generating oil-wet surface. Moreover, waterflooding can be ineffective in oil recovery from carbonate reservoirs because capillary pressure curve is predominantly negative, therefore chemical flooding is considered to be a more valuable option.

3.3 Dolomitization and Dolomite

Dolomitization is a process which limestone is transformed into dolomite by replacement of Magnesium ions onto Calcium ions in Calcite structure. If circulating pore water contains significant amounts of magnesium ion, Calcium ion can be exchanged for the Magnesium in the solution which must contain Carbonate ion

(CO_3^{2-}) or Hydrogen Carbonate ion (HCO_3^-). It is common for this mineral alteration into dolomite to take place due to evaporation of water. This process is described by this stoichiometric equation:



However, the reaction is thermodynamically favored in solutions of low Calcium ion to Magnesium ion ratio, low Calcium ion to Carbonate ion ratio or Calcium ion to Hydrogen Carbonate ion ratio and high temperatures. Moreover, kinetic considerations favor dolomitization under the same conditions and additionally at low or high salinities. For combination of thermodynamic and kinetic considerations, the following conditions and environments are considered to be favorable for dolomitization. One is environments of any salinity above thermodynamic and kinetic saturation respected to dolomite. The remaining ones are alkaline environments and environments with temperature greater than 50°C . Typically generate dolomite contains higher porosity compared to the previous limestone. Since atomic size of Magnesium is smaller than Calcium, replacement of Magnesium results in voids. Replacement of Magnesium might not occur fully and this could turn limestone into dolomitic limestone where it represents physical characteristics between limestone and dolomite. A complete replacement of Magnesium could increase porosity up to 13 percent and the matrix density becomes 2.87 gram/cm^3 , increasing from 2.71 gram/cm^3 from density of limestone. Structure of dolomite in 3D is illustrated in Figure 3.3.

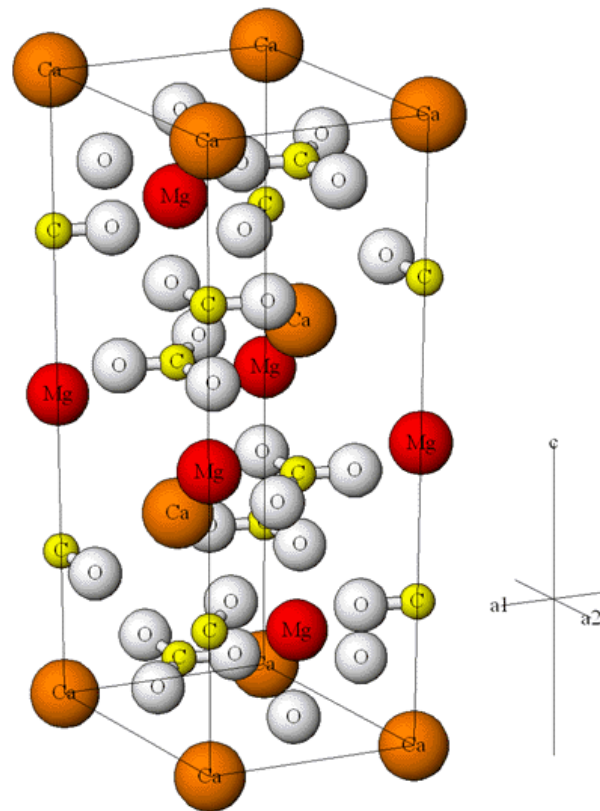


Figure 3.3 Structure of dolomite in 3D [10]

3.4 Formation Water

Most reservoir rocks are formed in aqueous environment by depositing of rock grains or biological detritus. Water that remains trapped in pores as sediments are more compressed is called connate water, whereas water in reservoir at the time it is penetrated by a drill bit is called formation water. Connate water reacts with rock to an extent. Chemical and biological reactions may begin as soon as sediments are deposited. Reactions can continue and accelerate as formation is subjected to greater pressure and greater temperature during burial.

Abdou et al. [11] suggested that properties of formation water vary from one reservoir to another as well as within reservoir. Water composition depends on a number of parameters, including depositional environment, mineralogy of the formation, pressure and temperature history and influx or migration of fluids.

Consequently, water properties can change over time as water and rock interact to each other, and as reservoir fluids are produced and replaced by water from other formations, injected water or other injected fluids.

Connate water mainly contains ionic components, including cations such as Sodium (Na^+), Magnesium (Mg^{2+}), Calcium (Ca^{2+}), Potassium (K^+), Manganese (Mn^{2+}), Strontium (Sr^{2+}), Barium (Ba^{2+}) and Iron (Fe^{2+} and Fe^{3+}); anions such as Chloride (Cl^-), Sulfate (SO_4^{2-}), Bicarbonate (HCO_3^-), Carbonate (CO_3^{2-}), Hydroxide (OH^-), Borate (BO_3^{3-}), Bromide (Br^-), Phosphate (PO_4^{3-}), and non-volatile weak acids. Water may also contain dissolved gases, such as Carbon Dioxide (CO_2), Hydrogen Sulfide (H_2S), Nitrogen (N_2), Organic acids, sulfur reducing bacteria, dissolved and suspended solids and traces of hydrocarbon compounds.

Concentrations of these components may vary as water is expelled by compaction and as it reacts with formation minerals. If connate water is undersaturated in the components of clay, it will interact with mineral grain by ion exchange, leaching ions into aqueous solution. Other minerals, such as quartz (SiO_2), have higher resistance to dissolution and hence they remain as grain matrix. If water is saturated with ions, minerals can precipitate and form new grains or grow on existing grains. Water properties such as pH and ion concentration are some of the factors that control water-rock interactions. Table 3.1 represents composition of each ion in formation water gathered from related literatures.

Table 3.1 Ionic composition in formation water from selected literatures

Component (g/L)	Austad (FW 1)	Austad (FW 2)	Austad (FW 3)	Austad (FW 4)	Zahid (FW)
Na ⁺	33.08	64.90	49.93	80.63	59.49
K ⁺	0.23	0.51	0.00	0.00	0.00
Mg ²⁺	1.17	2.24	3.26	3.23	2.44
Ca ²⁺	7.74	16.59	14.51	4.69	19.04
Cl ⁻	68.03	136.42	111.82	141.21	132.06
SO ₄ ²⁻	0.19	0.19	0.19	1.06	0.35
HCO ₃ ⁻	0.12	0.06	0.18	0.00	0.35
Sr ²⁺	0.00	1.31	0.00	0.00	0.00

Table 3.1 Ionic composition in formation water from selected literatures (continued)

Component (g/L)	Al-Harrasi (OD)	Al-Attar (SIM)	Al-Attar (UER)	Al-Attar (Seawater)
Na ⁺	59.97	68.21	57.61	13.90
K ⁺	0.00	0.00	0.00	0.00
Mg ²⁺	2.15	3.05	3.02	1.56
Ca ²⁺	11.62	20.81	14.03	0.60
Cl ⁻	118.79	150.62	122.02	24.30
SO ₄ ²⁻	0.69	0.35	0.42	0.42
HCO ₃ ⁻	0.01	0.12	0.24	0.20
Sr ²⁺	0.00	0.00	0.00	0.00

CHAPTER 4

METHODOLOGY AND EXPERIMENT

The details of methodology and steps in experiment of this study are described in this chapter. The first topic is methodology of this study followed by formation brine preparation, injected brine preparation, core samples preparation, acid oil preparation and experimental setup.

4.1 Methodology

1. Gather chemical analysis of formation brine in carbonate reservoirs from published literature.
2. Screen formation water data and identify tendency, average amount of each ion using basis of mole fraction according to chemicals available in laboratory including Sodium Chloride (NaCl), Sodium Sulfate (Na₂SO₄), Sodium Hydrogen Carbonate (NaHCO₃), Calcium Chloride (CaCl₂), Magnesium Chloride (MgCl₂) and Potassium Chloride (KCl) in order to obtain base formation brine composition for the entire study.
3. Perform basic core analysis to determine basic rock properties of dolostone and prepare base formation brine as well as different diluted proportions of injected brines for displacement mechanism tests. The preparation method of brine and description of basic rock properties are described in the following section.
4. Imitate oil migration by saturating core samples with base formation brine followed by injection oil to replace brine. Saturation of sample requires aging time up to several weeks. In this study, a period of one week is spent to ensure completion of wettability alteration. Core preparation process is summarized in Figure 4.1.

5. A coreflood test is firstly performed by using base formation brine as an injectant and from the literature survey chosen total salinity is 160,000 ppm. This experiment is performed to simulate conventional waterflooding mechanism by using produced water without dilution or modification of salinity. Because porosity and initial fluid saturation are known, oil recovery factor can be calculated. Oil recovery factors are detected continuously until 10 pore volume of displacing brine is injected into core samples at a constant injection rate of $2.0 \text{ cm}^3/\text{min}$.
6. Perform low salinity waterflooding by reducing total salinity of injected brine to 80,000, 40,000 and 20,000 ppm while maintaining proportion of chemical composition as same as base formation brine composition in order to observe effect of diluting total salinity of injected brine. The preparation of injected brine is summarized in the following section. Oil recovery factor for each experiment run is detected as similar as in step (5). The flow chart of this section is summarized in Figure 4.2.
7. Injected brine that yields maximum oil recovery (the judgment may include rate of oil recovery) from step (6) is selected for further modification. Diluted brine from step (6) is modified for the ion ratio of divalent cations. To study effects of varying these ions concentration, ion ratio of Calcium ion to Magnesium ion in injected brine are varied in five different ratios which are 1:0, 4:1, 1:1, 1:4 and 0:1 while total salinity is kept constant. Brine modification method is shown in following section. The temperature during the experiment is set and kept constant at $50 \text{ }^\circ\text{C}$. Again, Oil recovery factor for each case is detected as similar as in step (5).
8. Repeat step (7) but the temperature is varied to other two values which are 30 and $70 \text{ }^\circ\text{C}$ to observe effects of temperature on the interaction of divalent ions. The overall process to study effects of divalent cations is summarized in Figure 4.3.

9. From step (7), select the case that yields the highest oil recovery to adjust ion mass of Sulfate ion to be 0.5, 2, 5, and 10 times. The overall process of this section is summarized in Figure 4.4.
10. Use the brine that yields the highest recovery in step (9). Then, vary flow rate in other three values which are 0.5, 1.0 and 4.0 cm³/min to observe the effect of injection rate as illustrated in Figure 4.5.
11. Oil recovery factors are also plotted with pore volume of injected brine in all cases. Results from different injected brine systems are compared to determine the optimum injected brine formulation for dolomite reservoir. Data analysis and discussion are provided to point out new finding from this study.

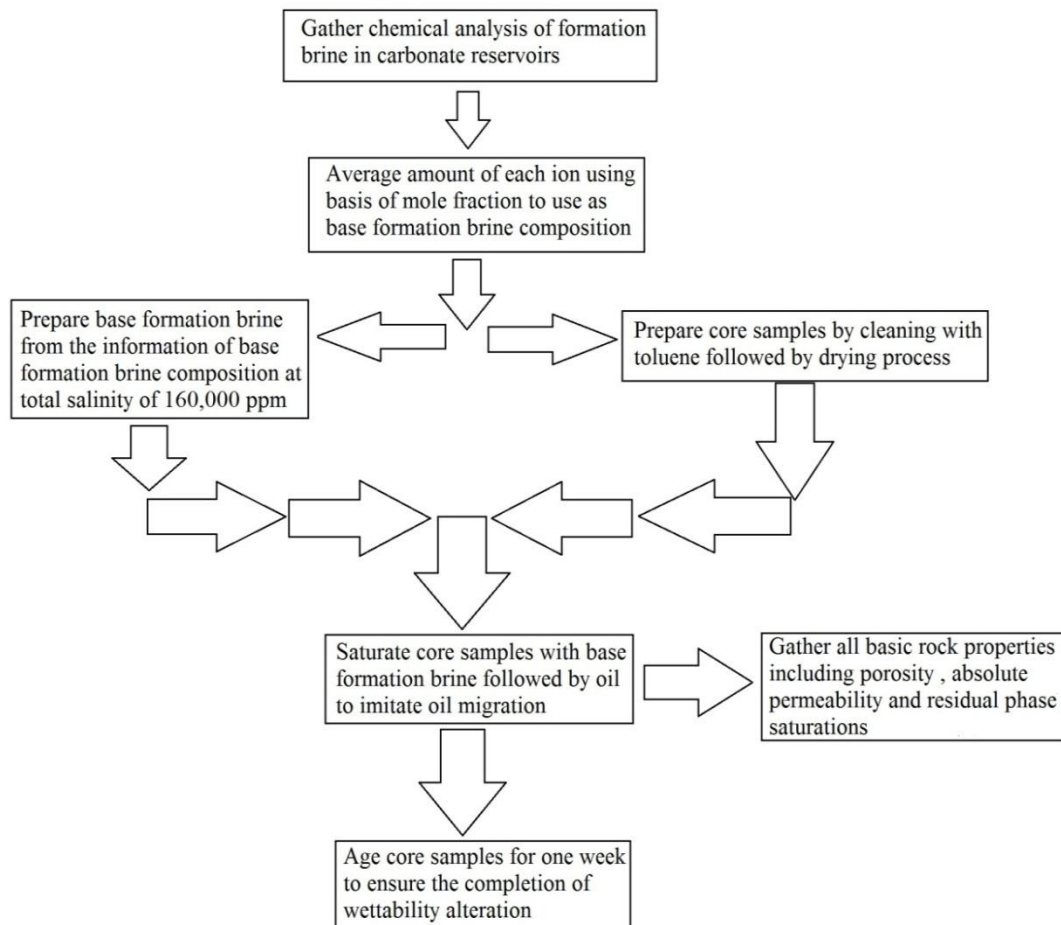


Figure 4.1 Overall process of core sample aging

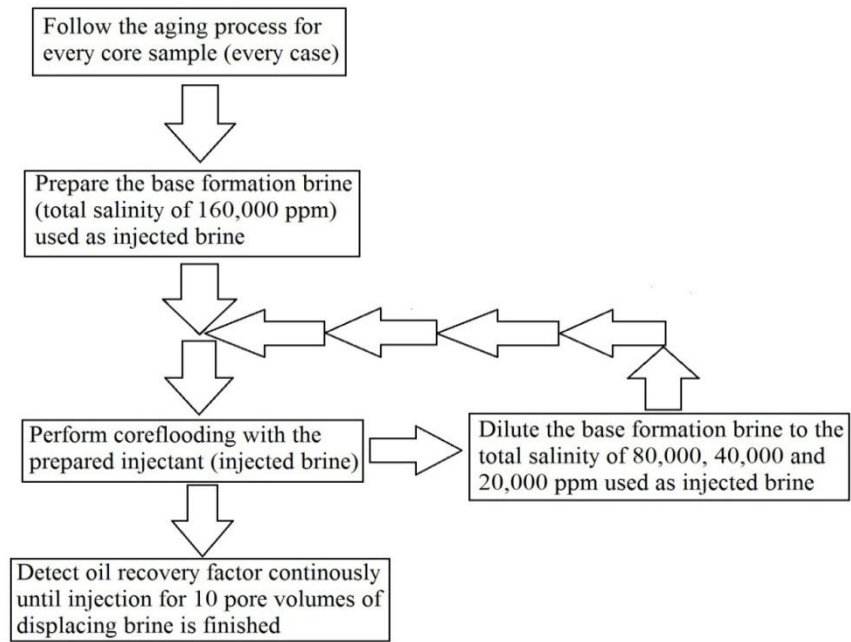


Figure 4.2 Overall process of a study for effect of total salinity in injected brine



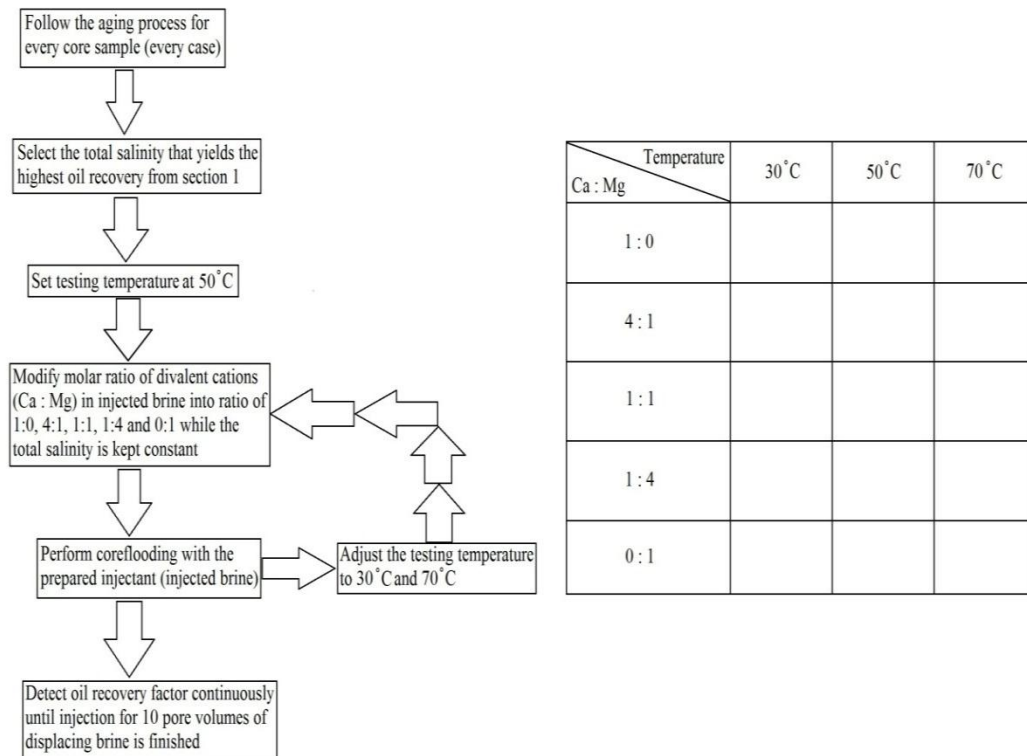
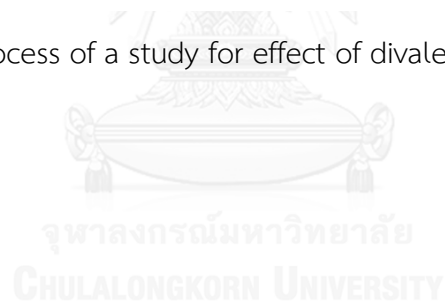


Figure 4.3 Overall process of a study for effect of divalent cations ratio in injected brine



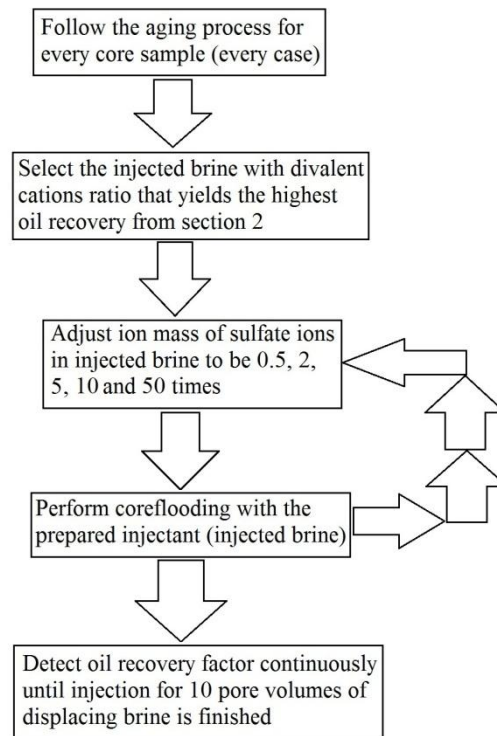


Figure 4.4 Overall process of a study for effect of anions in injected brine



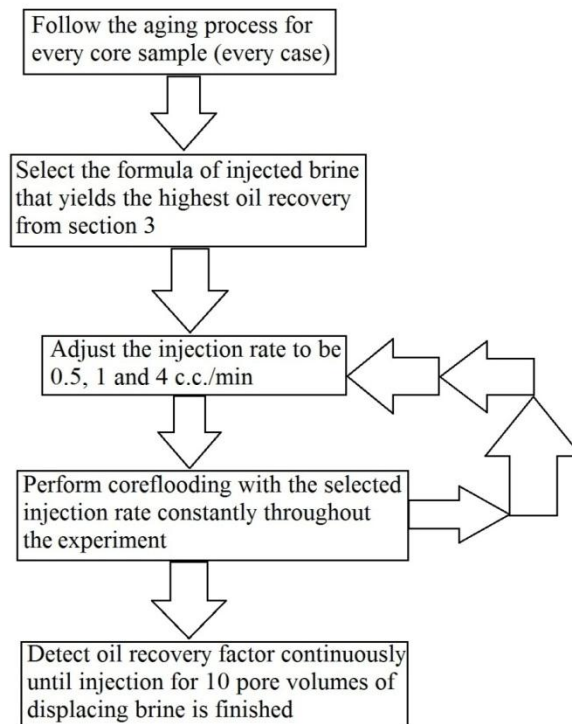


Figure 4.5 Overall process of a study for effect of injection rate

4.2 Preparation of Formation Brine

4.2.1 Screening of Formation Water Data

The criteria used for screening data from related literatures are that the amount of each ion (in unit of mole fraction) should be closed to each other and Strontium ion (Sr^{2+}) is assumed to behave like Calcium ion due to similar cations with positive charge of 2. Therefore, six different formation brine used in experiments all around the globe are selected to synthesize the base formation brine as shown in Table 4.1.

Table 4.1 Selected formation water composition from related literatures

Component (% Mole)	Austad (FW 1)	Austad (FW 2)	Austad (FW 3)	Zahid (FW)	Al-Attar (SIM)	Al-Attar (UER)
Na ⁺	39.87	39.16	37.27	37.52	37.72	38.97
K ⁺	0.17	0.18	0.00	0.00	0.00	0.00
Mg ²⁺	1.33	1.28	2.30	1.45	1.59	1.93
Ca ²⁺	5.35	5.95	6.21	6.89	6.60	5.44
Cl ⁻	53.17	53.39	54.13	54.00	54.01	53.52
SO ₄ ²⁻	0.06	0.03	0.03	0.05	0.05	0.07
HCO ₃ ⁻	0.06	0.01	0.05	0.08	0.02	0.06

4.2.2 Averaging Component from Selected Formation Water

After formation water formulations from different studies are selected, each ion is averaged among selected brine by using the basis of mole fraction as shown in Table 4.2.

Table 4.2 Average ion composition from selected formation water data

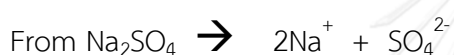
Component	Average % Mole (Used as base formation brine)
Na ⁺	38.48
Mg ²⁺	1.65
Ca ²⁺	6.07
Cl ⁻	53.70
SO ₄ ²⁻	0.05
HCO ₃ ⁻	0.05
Total	100.00

4.2.3 Preparation of Base Formation Brine Solution

Next step is to determine quantity of chemicals which are available in the laboratory including Sodium Chloride (NaCl), Sodium Sulfate (Na_2SO_4), Sodium Hydrogen Carbonate (NaHCO_3), Calcium Chloride (CaCl_2), and Magnesium Chloride (MgCl_2) based on specified total salinity in order to prepare the base formation brine solution. Since Potassium ion is absent in average percent mole as shown in Table 4.2, Potassium Chloride (KCl) is not required in this study.

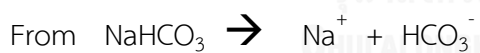
Firstly, in this obligate to calculate the amount of chemicals required using basis of 1 molar of ions in formation water whose composition is averaged.

Consider SO_4^{2-} which is from Na_2SO_4



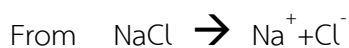
Therefore, if 0.0005 mol of SO_4^{2-} is required, **0.0005 mol** of Na_2SO_4 should be prepared and 0.0010 mol of Na^+ will also be obtained from this chemical.

Consider HCO_3^- which is from NaHCO_3



Therefore, if 0.0005 mol of HCO_3^- is required, **0.0005 mol** of NaHCO_3 should be prepared and 0.0005 mol of Na^+ will also be obtained from this chemical.

Consider remaining Na^+ which is from NaCl



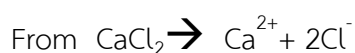
Therefore, if $(0.3848 - 0.0010 - 0.0005) = 0.3833$ mol of Na^+ is required, **0.3833 mol** of NaCl should be prepared and 0.3833 mol of Cl^- will also be obtained from this chemical.

Consider Mg^{2+} which is from $MgCl_2$



Therefore, if 0.0165 mol of Mg^{2+} is required, **0.0165 mol** of $MgCl_2$ should be prepared and 0.0330 mol of Cl^- will also be obtained from this chemical.

Consider Ca^{2+} which is from $CaCl_2$



Therefore, if 0.0607 mol of Ca^{2+} is required, **0.0607 mol** of $CaCl_2$ should be prepared and 0.1214 mol of Cl^- will also be obtained from this chemical.

So, the total amount of $Cl^- = 0.3833 + 0.0330 + 0.1214 = 0.5377$ mol

Then, mole fraction and mass fraction of base formation brine can be calculated. The data are summarized in Table 4.3.

Table 4.3 Composition of base formation brine

Chemical	Mole	% Mole	MW	Mass (Gram)	Mass Fraction (%wt)
NaCl	0.3833	83.06	58.44	22.40	72.69
$MgCl_2$	0.0165	3.57	95.21	1.57	5.09
$CaCl_2$	0.0607	13.16	110.98	6.74	21.87
$NaHCO_3$	0.0005	0.11	84.01	0.04	0.13
Na_2SO_4	0.0005	0.10	142.04	0.07	0.22
Total	0.4615	100.00		30.82	100.00

If 1 liter of brine solution is prepared, total mass of chemicals in brine is equal to 160.00 g for total salinity of 160,000 ppm. Hence, mass of each chemical

can be calculated by multiplying mass fraction with total mass as shown in Table 4.4.

Table 4.4 Amount of chemicals in base formation brine with total salinity of 160,000 ppm

Chemical	Mass (Gram)	Molecular Weight	Mole	% Mole
NaCl	116.30	58.44	1.9899	83.06
MgCl ₂	8.15	95.21	0.0856	3.57
CaCl ₂	34.99	110.98	0.3153	13.16
NaHCO ₃	0.21	84.01	0.0025	0.11
Na ₂ SO ₄	0.35	142.04	0.0025	0.10
Total	160.00		2.3958	100.00

4.2.4 Preparation of Injected Brine

The preparation method of injected brine is similar to preparation of formation brine but just change the value of total salinity or total mass of chemicals in the brine while fixing proportion or mass fraction of all chemicals. For example, if total salinity is reduced to 80,000 ppm, total mass of chemicals in brine is going to be 80.00 grams and amount of each chemical in this brine can be shown as Table 4.5.

Table 4.5 Amount of chemicals in injected brine with total salinity of 80,000 ppm

Chemical	Mass (Gram)	Molecular Weight	Mole	% Mole
NaCl	58.15	58.44	0.9950	83.06
MgCl ₂	4.07	95.21	0.0428	3.57
CaCl ₂	17.50	110.98	0.1577	13.16
NaHCO ₃	0.11	84.01	0.0013	0.11
Na ₂ SO ₄	0.17	142.04	0.0012	0.10
Total	80.00		1.1979	100.00

4.2.5 Modification of Ions Concentration in Injected Brine

1. Modification of Calcium Ion and Magnesium Ion Ratio

In this study, Magnesium ion behaves as same as Calcium ion due to similar cations with positive charge of 2. Therefore, other ion compositions are kept constant as much as possible. However, since total salinity is preferentially fixed, Sodium Chloride is then adjusted to make up specified total salinity due to abundance of Sodium ion and Chloride in the brine solution.

An example of modification of Calcium ion and Magnesium ion ratio into a ratio of Calcium ion to Magnesium ion of 1:4 is explained in this section.

Based on 1 liter of brine solution and total salinity of 160,000 ppm, from Table 4.4, amount of each ion in unit of mole can be calculated and shown in Table 4.6.

Table 4.6 Amount of each ion of base formation brine with total salinity of 160,000 ppm

Component	Mole
Na^+	1.997
Mg^{2+}	0.086
Ca^{2+}	0.315
Cl^-	2.792
SO_4^{2-}	0.002
HCO_3^-	0.003

From Table 4.6, total amount of Magnesium ion and Calcium ion is equal to 0.315 plus 0.086 which is 0.401 mole, so that if the ratio of Calcium ion to Magnesium ion is changed to 1:4, the amount of CaCl_2 is equal to $1/5 \times 0.401$ which is 0.080 mole and the amount of MgCl_2 is equal to $4/5 \times 0.401$ which is 0.321 mole. Then, if adjusting only amount of CaCl_2 , MgCl_2 and NaCl amount of each chemical and each ion can be shown in Tables 4.7 and 4.8, respectively.

Table 4.7 Amount of each chemical at molar ratio of Calcium ion to Magnesium ion adjusted to be 1:4 with total salinity of 160,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	2.053	58.44	120.01
MgCl_2	0.321	95.21	30.53
CaCl_2	0.080	110.98	8.90
NaHCO_3	0.003	84.01	0.21
Na_2SO_4	0.002	142.04	0.35
Total	2.459		160.00

Table 4.8 Amount of each ion at ratio of Calcium ion to Magnesium ion adjusted to be 1:4 with total salinity of 160,000 ppm

Component	Mole
Na ⁺	2.061
Mg ²⁺	0.321
Ca ²⁺	0.080
Cl ⁻	2.855
SO ₄ ²⁻	0.002
HCO ₃ ⁻	0.003

2. Modification of Sulfate Ion

As previously mentioned that ions that are not studied are kept as constant as possible among cases together with the fixed of total salinity, NaCl which is the most abundant is therefore adjusted to achieve specified total salinity.

Example of modification of Sulfate ion by doubling mole of sulfate ion compared to base formation brine (total salinity of 160,000 ppm). Therefore, amount of Na₂SO₄ is increased to 0.005 mole. If adjusting only amount of Na₂SO₄ and NaCl, amount of each chemical and each ion can be summarized in Tables 4.9 and 4.10, respectively.

Table 4.9 Amount of each chemical required for brine with double amount of Sulfate ion compared to base formation brine with total salinity of 160,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	1.984	58.44	115.95
MgCl ₂	0.086	95.21	8.15
CaCl ₂	0.315	110.98	34.99
NaHCO ₃	0.003	84.01	0.21
Na ₂ SO ₄	0.005	142.04	0.70
Total	2.392		160.00

Table 4.10 Amount of each ion required for brine with double amount of Sulfate ion compared to base formation brine with total salinity of 160,000 ppm

Component	Mole
Na ⁺	1.996
Mg ²⁺	0.086
Ca ²⁺	0.315
Cl ⁻	2.786
SO ₄ ²⁻	0.005
HCO ₃ ⁻	0.003

4.3 Acid Oil Preparation

In this study, acid oil is used in both aging and flooding process in order to alter the original wettability of carbonates from water-wet to oil-wet by adsorption of polar compounds in acid oil onto carbonate surface which is positively charged by their negative site i.e. carboxylic group (-COOH).

In addition, in order to indicate the acidity of acid oil, the value of acid number (AN) is introduced. Acid number is the amount of Potassium hydroxide (KOH) in unit of milligram required for neutralizing 1 gram of acid oil. Therefore, when acid oil contains high value of acid number, it means that there is large amount of acidic compound in the oil.

For the experiment, acid oil with acid number (AN) of 5.0 is prepared by mixing Dodecane with Oleic acid. The reason of using this high value of acid number is achieve the maximum adsorption of acidic group onto dolomite surfaces which ensures wettability alteration of rock from water-wet to oil-wet. However, the period of one week has to be taken for aging in order to ensure the wettability alteration. After aging process is finished, acid oil with acid number of 1.0 is injected into the core samples in order to remove excess oleic acid and also to attain new surface equilibrium at testing temperature. The amount of Oleic acid in acid oil used in the experiment is shown in Table 4.11 and calculation methodology for the amount of Oleic acid is described in appendix B.

Table 4.11 The amount of Oleic acid in acid oil used in the experiment

Formula	n-Dodecane (g)	Oleic acid(g)
Acid number = 1	1,000	5.03
Acid number = 5	1,000	25.17

4.4 Liquid Density and Viscosity Measurement

In this study, liquid density is measured by using equipment called pycnometer which is a glass flask with a close-fitting ground glass stopper that has a capillary hole through it for releasing gas bubble and excess liquid after closing as shown in Figure 4.6. Because the volume of measured liquid is known, therefore the density, which is the ratio of mass to volume, can be determined by measuring the

mass of fully filled pycnometer subtracted by the weight of dry flask together with glass stopper.

Meanwhile, the liquid viscosity, which is used in calculation for absolute and effective permeability to both oil and brine, is measured by using Cannon-Fenske viscometer. The measurement is performed by recording the time that liquid travels from the above red line to the below red line in Figure 4.7. However, in order to obtain the value of liquid viscosity via this equipment, the value of density is also used in calculation by the following equation:

$$\mu = k\rho t \quad (4.1)$$

where μ is the dynamic viscosity in unit of centipoise, k is the constant of the equipment which is equal to 0.01509 cSt/s at 40 °C or 0.01502 cSt/s at 100 °C, ρ is the density of liquid in unit of g/cm³ (obtained from pycnometer) and t is the measured time in second.

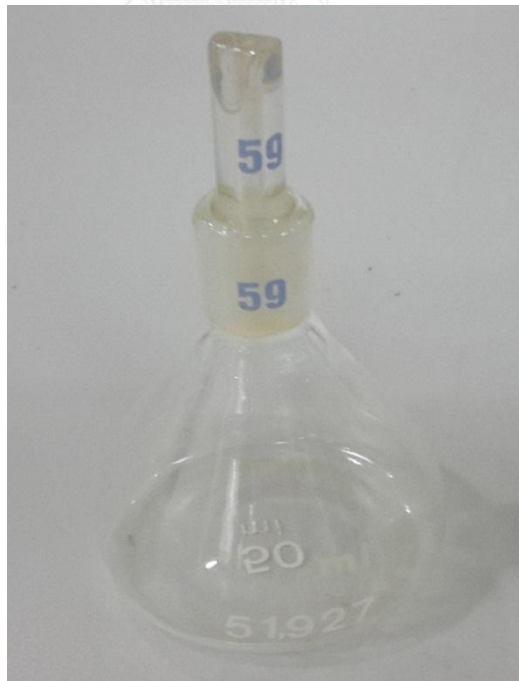


Figure 4.6 Pycnometer

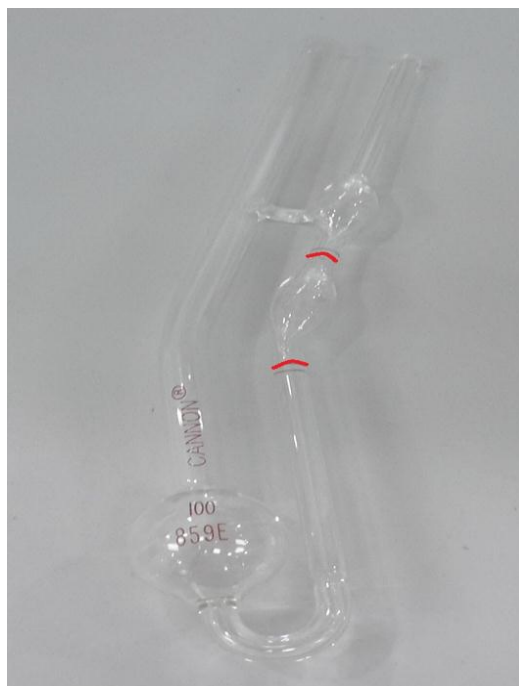


Figure 4.7 Cannon-Fenske viscometer

The density and viscosity of acid oil with different values of acid number at each testing temperature can be shown in Table 4.12.

Table 4.12 Properties of acid oil with different value of acid number at each testing temperature

Acid number	Temperature (°C)	Viscosity (cP)	Density (g/cm ³)
1.0	30	1.15	0.723
1.0	50	0.90	0.694
1.0	70	0.67	0.668
5.0	30	1.23	0.736

4.5 Core Samples Preparation

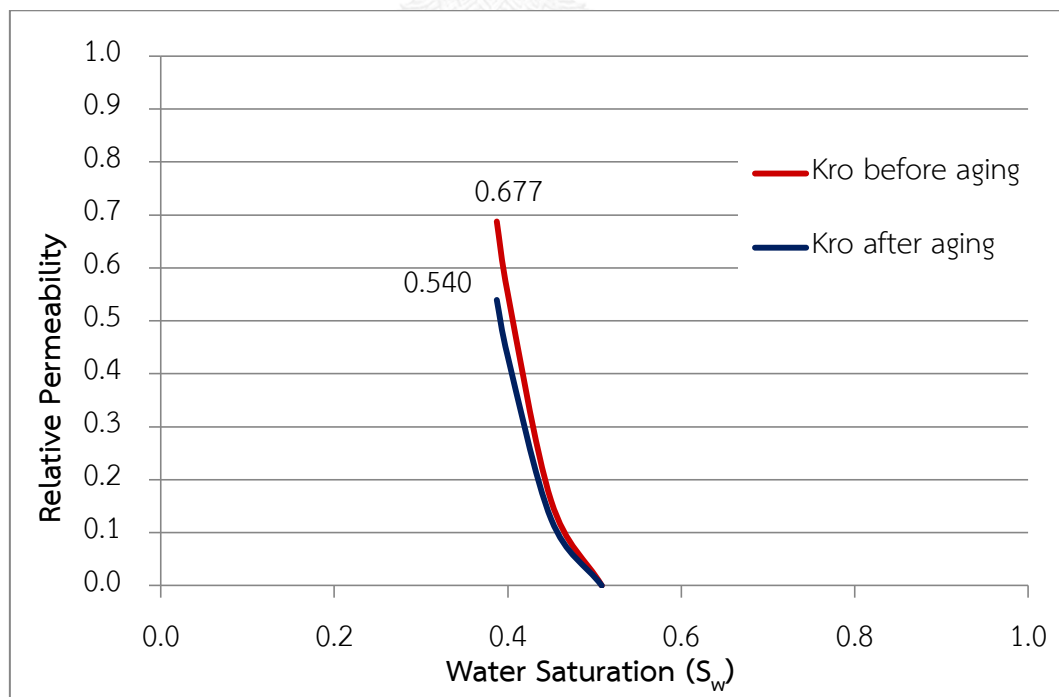
In this study, three Silurian dolomite outcrop cores are used for the experiments. From core preparation processes, physical properties of core samples are summarized in Table 4.13. The steps to prepare these cores for the experiments including measure their properties are as follows:

1. Cores are cleaned by toluene extraction (Soxhlet) and dried in oven at 70 Celsius and are measured for dimensions and dry weights to calculate the bulk volume as well as porosity.
2. Core samples are then fully saturated in coreflooding apparatus by injecting base formation brine in ambient environment at four different flow rates (2.5, 5, 7.5 and 10 cm³/min) until no detection of gas bubble at the outlet and also no fluctuation of pressure drop across the core sample. The pressure drop across the core sample is collected and used in calculation for absolute permeability (k_a).
3. As oil-wet condition is usually formed in carbonate sample and it is the major cause of low oil recovery factor, core samples are prepared to possess strongly oil-wet condition. Oleic acid which represents carboxylic acid in this study is mixed with n-Dodecane representing hydrocarbon phase in this study. Acid oil with acid number of 5.0 is injected to saturate a core at four different flow rates (2.5, 5, 7.5 and 10 cm³/min) until no detection of water flow at the outlet and also no fluctuation of pressure drop across the core sample. The pressure drop across the core sample is collected and used in calculation for relative permeability to oil (k_{r_o}) at irreducible water saturation (S_{wi}).
4. Volume of displaced water is measured and used in calculation for S_{wi} .
5. Saturated core samples are aged in oil for a week to ensure completion of wettability alteration.

Table 4.13 Physical properties of Silurian outcrop dolomite core samples

Core ID	Length (cm.)	Diameter (cm.)	Dry wt. (g)	PV (c.c.)	Porosity (%)
1	12.68	3.77	336.80	23.78	16.80
2	12.69	3.77	342.58	21.87	15.44
3	12.69	3.77	340.57	22.58	15.94

During the step of core sample preparation when core samples are saturated with base formation brine followed by injection of oil for aging process, pressure drop across the core is detected for relative permeability to oil calculation. After core samples are aged for one week, acid oil with acid number of 1.0 is injected into the core samples in order to remove excess oleic acid before the start of waterflooding. Again pressure drop across the core sample is also detected in this step. Therefore, the comparison between relative permeability to oil before and after aging of core number 1 can be shown in Figure 4.8.

**Figure 4.8** Comparison of relative permeability to oil before and after aging of core number 1

From the figure, the value of relative permeability to oil after the period of aging is lower than that value before core aging. This is a confirmation that oleic acid is already adsorbed onto dolomite surface by the negative site, altering the wettability to oil-wet because the flow ability of oil after aging is reduced due to attraction force from positive charges on dolomite surface.

4.6 Coreflooding Apparatus

The coreflooding equipment consists of several systems. The first one is injection system which consists of pumps that are used to inject the fluid into the core at a specified rate and chambers containing fluids that are desired to displace fluids in core sample. The next unit is core holder which possesses confining system to prevent bypassing of fluid over core. Confining system is functioned by injecting distilled water to the space between a core holder and a core rubber that covers. In this study, the confining pressure is set at 1,500 psia. This pressure is related to pressure drop across the cores which is already calculated at the designed flow rate in the experiment. Next unit is the fluid separator that can record fluid volume together with time. Therefore, a plot between oil recovery factor and pore volume injected can be accomplished. The last one is the gas chamber that creates the back pressure to increase pressure at core exit for better accuracy of measuring pressure drop across the core. The schematic of coreflooding equipment is shown in Figure 4.9.

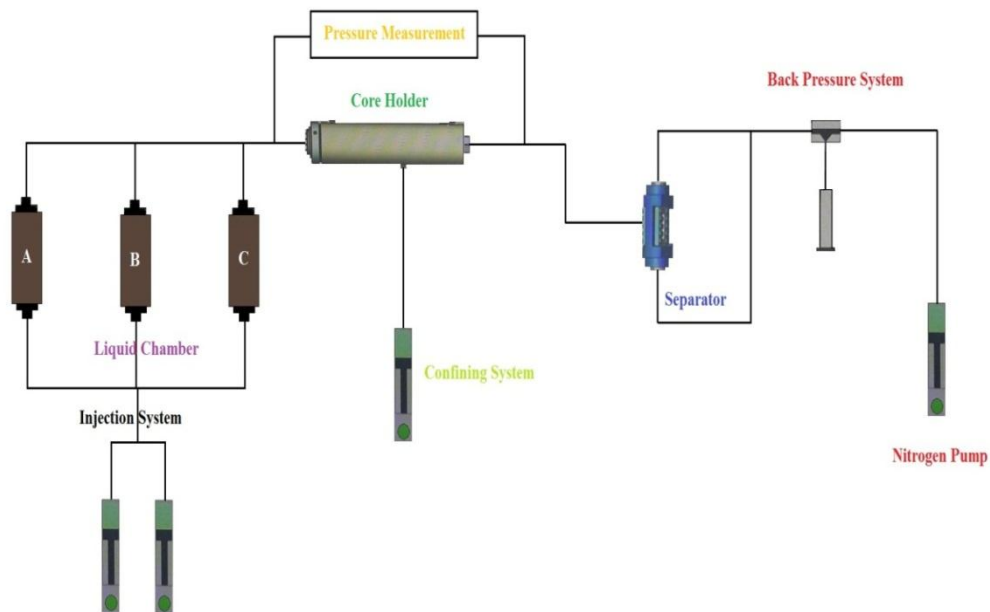


Figure 4.9 Schematic of Coreflooding equipment

4.7 Measurement of Displaced Oil Volume

The volume of produced oil is detected together with time for calculation of oil recovery factor by the liquid separator in coreflooding apparatus. In order to detect the liquid interface level, two different liquids have to be already inside the separator and the movement of interface level depends on type of liquid entering and also the position of outlet valves opening (top or bottom valves). In this study, the bottom valve is opened while top valve remains closed during the brine injection process for volume detection of displaced oil. When the displaced oil comes in the separator, the liquid interface becomes lower due to lower density of oil compared to water and increment of oil volume in the separator as shown in Figure 4.10. After the water breakthrough occurs, liquid interface is slightly moved because little more amount of oil recovery can be recovered. Then, the change of liquid interface level can be converted to the volume of displaced oil by the size of separator (volume per height).

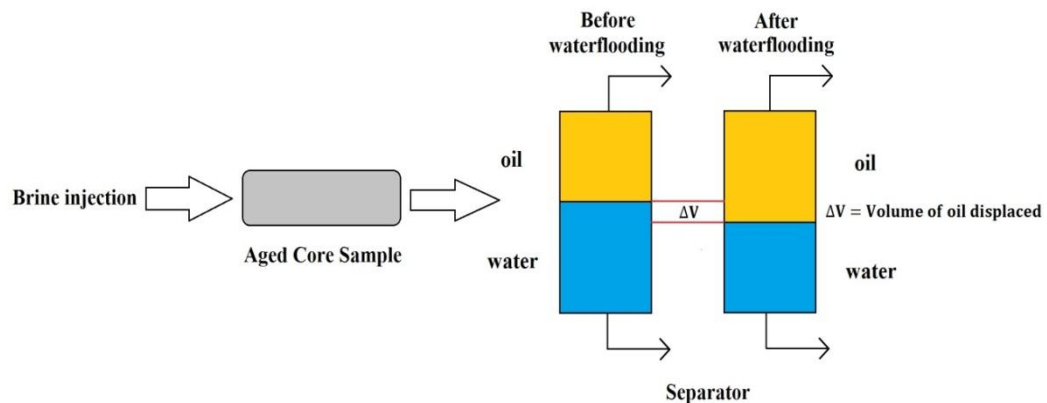


Figure 4.10 Change of liquid level in the fluid separator after waterflooding

From Figure 4.11, before starting water injection, there is still oil remained in tube between core holder and separator because acid oil with acid number of 1 has to be pre-injected in order to remove excess oleic acid and this volume of oil is called as “dead pore volume” which has to be taken out from the value of detected oil volume before oil recovery factor calculation. By the way, the dead pore volume can be determined by using test core plug together with fixed length outlet tube which are shown in Figure 4.12 and 4.13 respectively. In this process, two types of liquid are alternately injected to identify dead pore volume of the system. For this study, oil is firstly injected to fill in the whole coreflooding system, consisting of three different parts which are 1) inside the test core plug whose the volume is 0.1 c.c., 2) inside the fixed length outlet tube whose the volume is 0.37 c.c., and 3) inside the unknown dead pore volume or volume of tube between core holder outlet and separator. Then, water is injected and total oil volume inside all three parts can be determined by the change of interface level as same as displaced oil volume measurement. Therefore, the dead pore volume can be determined from equation 4.2. And for this coreflooding apparatus, dead pore volume is equal to 2.03 c.c.

$$\text{Dead Pore Volume} = V_{\text{displaced oil}} - V_{\text{test core plug}} - V_{\text{fixed length tube}} \quad (4.2)$$

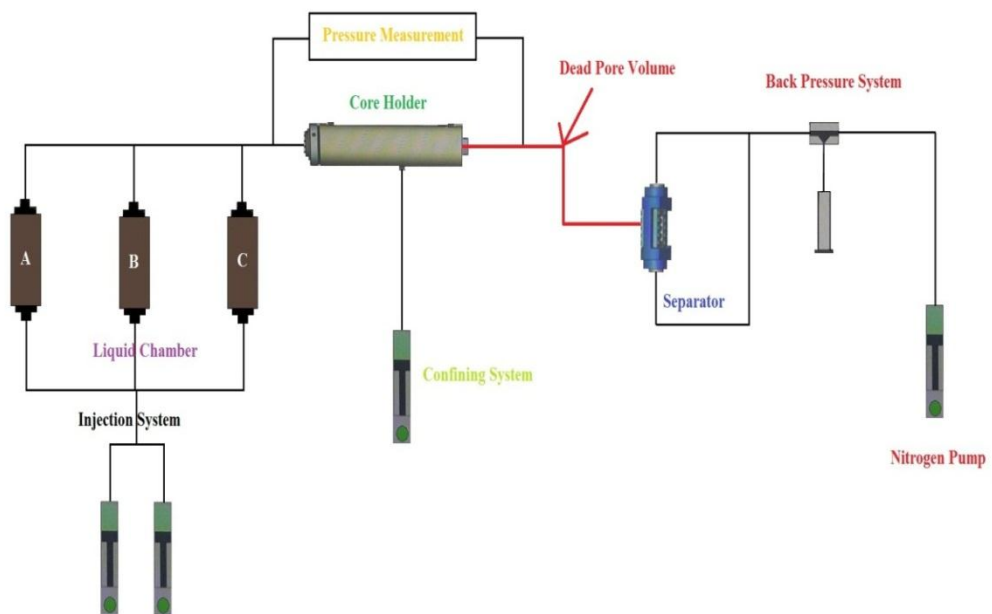


Figure 4.11 Dead pore volume in the coreflooding system

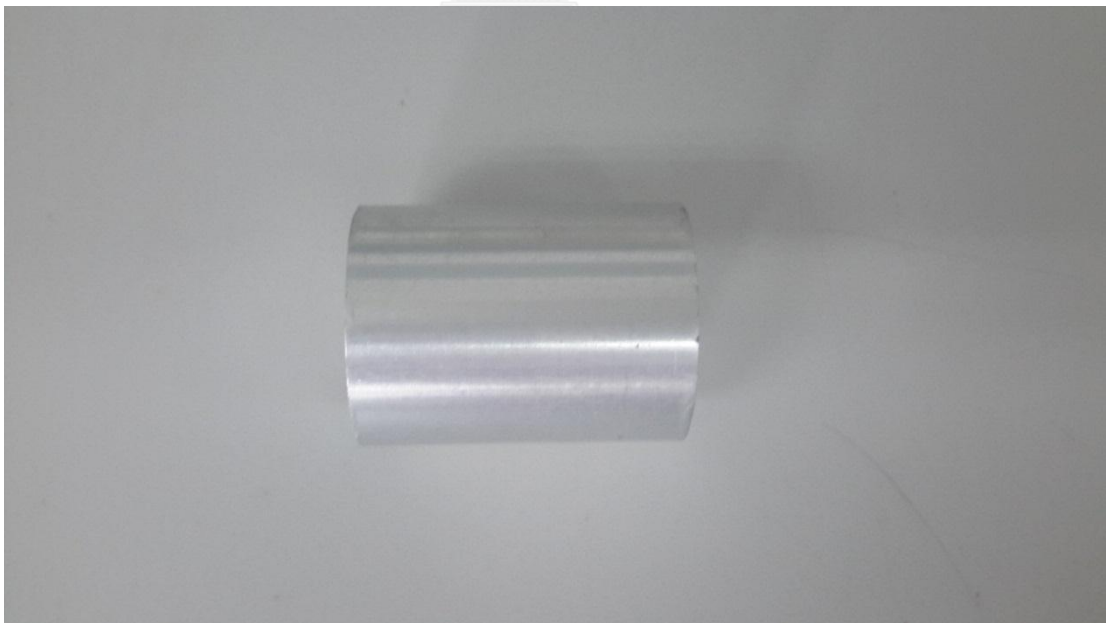


Figure 4.12 Test core plug



Figure 4.13 Fixed length outlet tube at the outlet of core holder



CHAPTER 5

RESULTS AND DISCUSSION

This chapter presents the results and together with discussions on each study parameter for laboratory experiment. The parameters in this study include total salinity, concentration of potential determining ions together, temperature and also injection rate. Results are mainly investigated on oil recovery factor and rate of oil recovery. End point relative permeability curves are utilized to assist discussion.

5.1 Effects of Total Salinity of Injected Brine

In this section, total salinity is varied from the highest total salinity which is the same value as formation brine of 160,000 ppm. This experiment is performed to simulate the conventional waterflooding and is labeled as high salinity waterflooding case for comparison with other low salinity cases. Then, total salinity of injected brine is diluted to the values of 80,000 ppm, 40,000 ppm and 20,000 ppm, while formation brine is kept constant at 160,000 ppm. In diluting process, formation brine is mixed with distilled water to maintain proportion of ions. The amount of additional oil recovery compared to high salinity waterflooding case is the effect of mechanism obtained by low salinity waterflooding that is already mentioned from previous chapter. Ion compositions of formation brine and injected low salinity brine are summarized in Table 5.1.

Table 5.1 Ion compositions of formation brine and diluted injected brine

Composition	Formation brine 160,000 ppm	Low Salinity injected brine		
		80,000	40,000	20,000
Na ⁺	45,920	22,960	11,480	5,740
Ca ²⁺	12,637	6,319	3,159	1,580
Mg ²⁺	2,080	1,040	520	260
SO ₄ ²⁻	237	118	59	30
HCO ₃ ⁻	154	77	39	19
Cl ⁻	98,973	49,487	24,743	12,372

Relationship between oil recovery factor and injected pore volume is illustrated in Figure 5.1 and the ultimate oil recovery from each case is taken and plotted over bar chart in Figure 5.2. Pressure difference, fluid viscosity, fluid rate and core dimensions are used for calculation of effective permeability of each flowing fluid and these are presented as end point relative permeability curve as a function of water saturation. Relative permeability curves are constructed by adding curvaceous between two end points (relative permeability values at irreducible water saturation and residual oil saturation) using Corey's correlation with an exponent value of 2 which is recommended for carbonate reservoirs as shown in the following equations:

$$k_{ro} = k_{ro@S_{wi}} \cdot \left(1 - \frac{S_w - S_{wi}}{1 - S_{or} - S_{wi}}\right)^2 \quad (5.1)$$

$$k_{rw} = k_{rw@1-S_{or}} \cdot \left(\frac{S_w - S_{wi}}{1 - S_{or} - S_{wi}}\right)^2 \quad (5.2)$$

Relative permeability curves obtained from all different cases are depicted in Figure 5.3 and the summary of end point saturation and end point relative permeability are shown in Table 5.2.

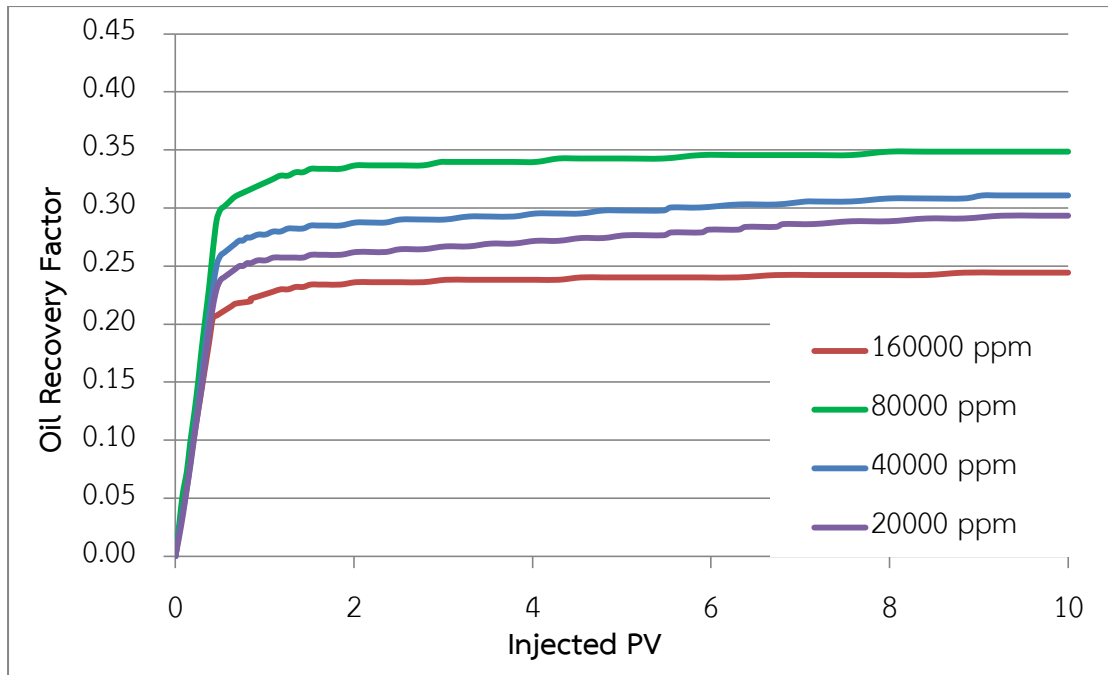


Figure 5.1 Oil Recovery factors obtained from different injected brines with different total salinities as a function of injected pore volume

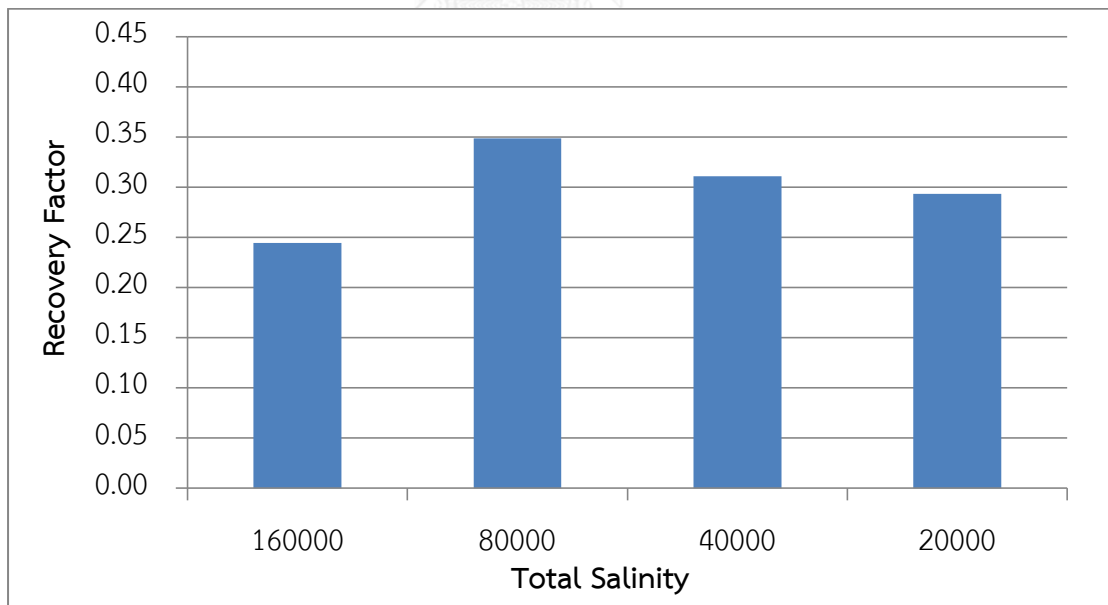


Figure 5.2 Oil recovery factors at the end of experiment obtained from different injected brines with different total salinities

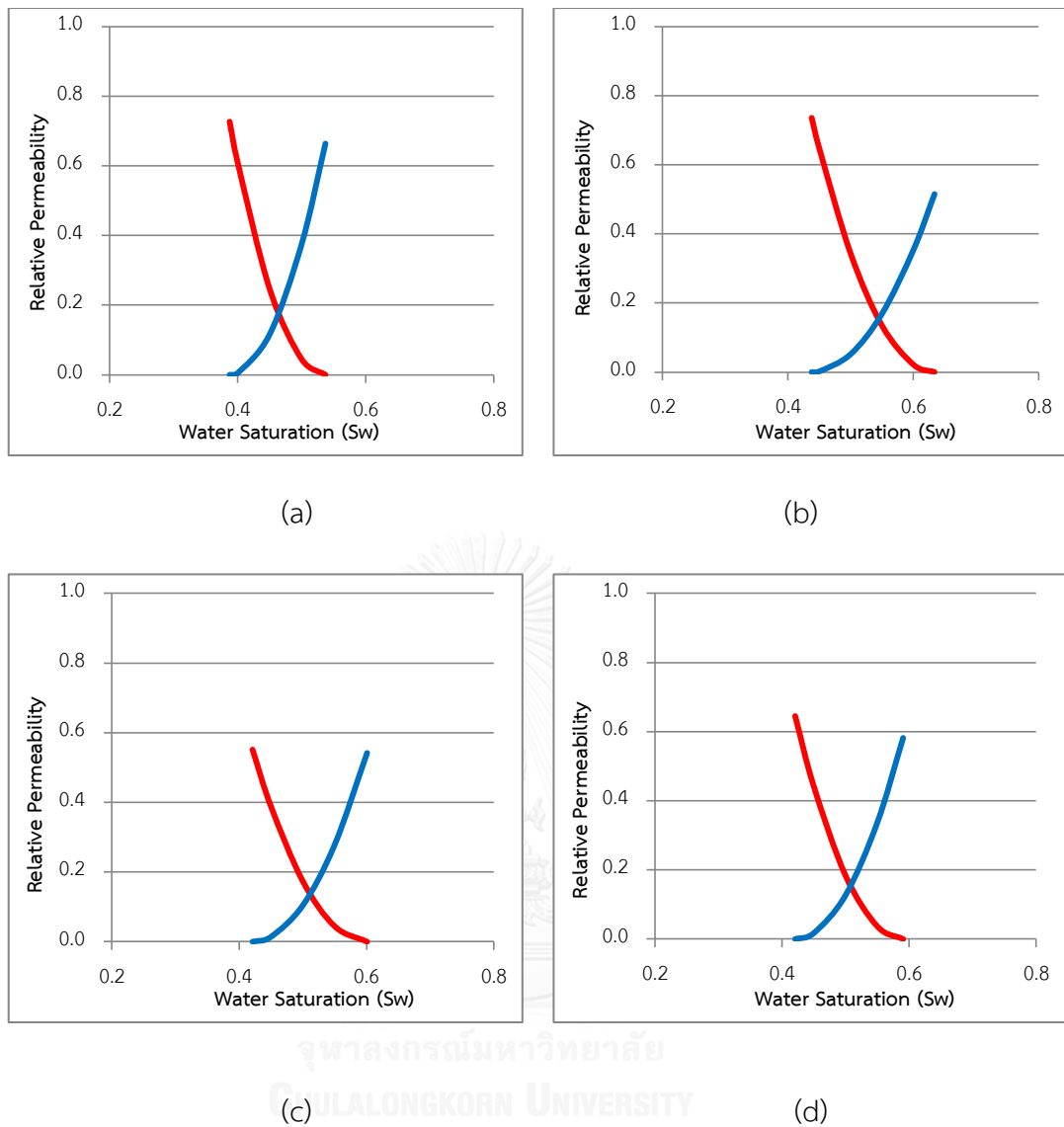
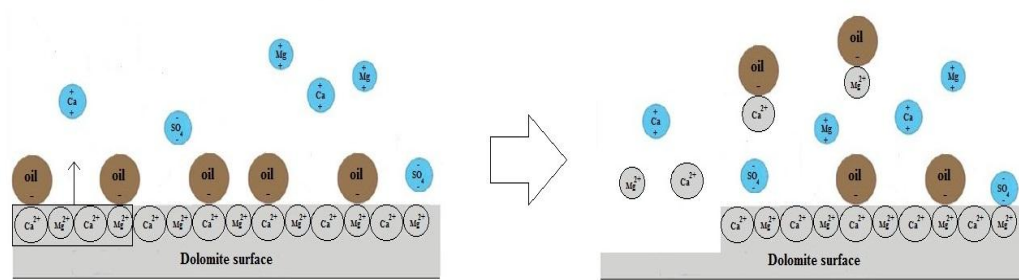


Figure 5.3 Relative permeability curves as a function of water saturation for different injected brines with different total salinities a) 160,000 ppm; b) 80,000 ppm; c) 40,000 ppm; and d) 20,000 ppm

Table 5.2 End point relative permeability and saturations obtained from cases with different salinities

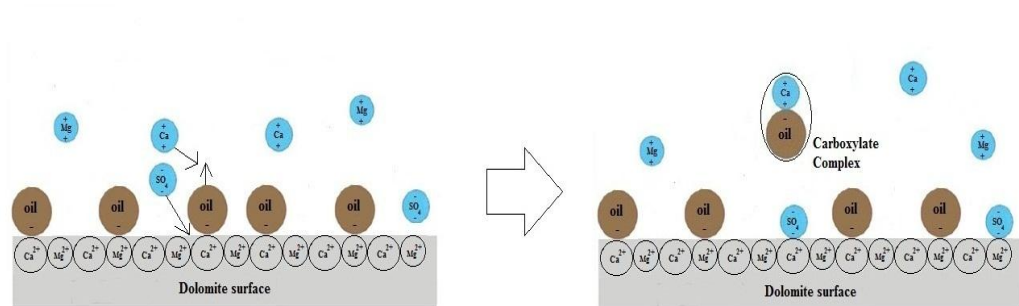
Salinity (ppm)	Irreducible water saturation (S_{wi})	1-Residual oil saturation ($1-S_{or}$)	Recovery factor (RF)	End point k_{ro}	End point k_{rw}
160,000	0.3873	0.5370	0.2443	0.728	0.664
80,000	0.4378	0.6337	0.3485	0.736	0.516
40,000	0.4209	0.6009	0.3108	0.551	0.542
20,000	0.4209	0.5908	0.2934	0.645	0.582

From Figure 5.1, it is shown that the period of oil recovery can be divided into two periods. The first period is the period before water breakthrough where the slope is the steepest one. In this period, the oil is displaced mainly from physical displacement which comes from the mass of injected brine. However, chemical mechanisms take place at the same time. These mechanisms include rock dissolution and ion interaction between positive charges on rock surface and potential determining ions in injected brine, which are Calcium ion, Magnesium ion and Sulfate ion. After water breakthrough, oil patches in pore space are in contact more with injected brine and this leads to second period of oil recovery mechanism which chemical process dominates. In order to better explain chemical mechanisms taken place during the displacement mechanism by means of low salinity waterflooding in dolostone, Figure 5.4 and Figure 5.5 are illustrated for two different mechanisms which are dissolution mechanisms and ion exchange mechanism respectively.



Dissolution Mechanism

Figure 5.4 Illustration of dissolution mechanism induced by brine injection



Ion Exchange Mechanism

Figure 5.5 Illustration of ion interaction mechanism induced by brine injection

When injected brine, with different salinity compared to formation water, comes in contact with rock surface, the system tends to attain new equilibrium by dissolution reaction. From Figure 5.4, Calcium ion and Magnesium ion in the structure of dolomite or Calcium Magnesium Carbonate from the rock matrix tend to dissolve in order to raise the amount of Calcium ion and Magnesium ion in the solution phase for establishing the equilibrium. When these minerals are dissolved, adsorbed components including oil are also removed and this causes the rock surface shifting towards a more water-wet state. Another mechanism is the ion exchange mechanism which is related to Calcium ion, Magnesium ion and Sulfate ion. From Figure 5.5, Sulfate ion tends to be adsorbed onto positively charged surface of carbonate rock, lowering positive charge density. As a result, attraction force occurs on the surface, making Calcium ions be able to come closer to surface, reacting with negatively

charged polar compound in oil to form Calcium Carboxylate complex which can be easily desorbed. However, Calcium ion can be displaced by Magnesium ion in Carboxylate complex at the suitable condition.

From Figure 5.1 and Figure 5.2 it can be obviously seen that the case of injection by low salinity brine of 80,000 ppm yields the highest oil recovery factor with ultimate oil recovery of about 34.85% while cases of injection by low salinity brine of 40,000 ppm and 20,000 ppm yield oil recovery factor of 31.08% and 29.34% respectively. However, oil recovery when injecting low salinity brine is still greater than the use of high salinity brine of 160,000 ppm which yields only 24.43% OOIP. As dolostone which is considered as a derivation from limestone generally possesses positively charge at normal reservoir pH condition (6-8), a presence of carboxylic acid in oil phase results in acid interaction and eventually this could turn into direct adsorption of acid. This results in strongly oil-wet condition as can be observed from relative permeability curves in Figure 5.3a where magnitude of both relative permeability to oil and relative permeability to water are mostly equal at their end point saturations.

When making comparison between results from conventional waterflooding at the highest salinity of 160,000 ppm and low salinity water at 80,000 ppm it can be observed that oil recovery is much improved by reduction of total salinity of 50 percent. In order to explain the difference between these two cases, Figure 5.6 is used to illustrate mechanisms occurred during the displacement mechanism. From the figure, it can be explained that even though low salinity waterflooding causes the oil recovery from ion exchange mechanism to be lower due to less amount of potential determining ions, resulting in less formation of carboxylate complex with oil, it increases dissolution mechanism by the driving force from salinity difference between formation brine and injected brine. Because the oil recovery obtained from injected brine of 80,000 ppm is higher than the case of 160,000 ppm, therefore it can be concluded that dissolution mechanism is dominant than ion exchange mechanism between these two cases.

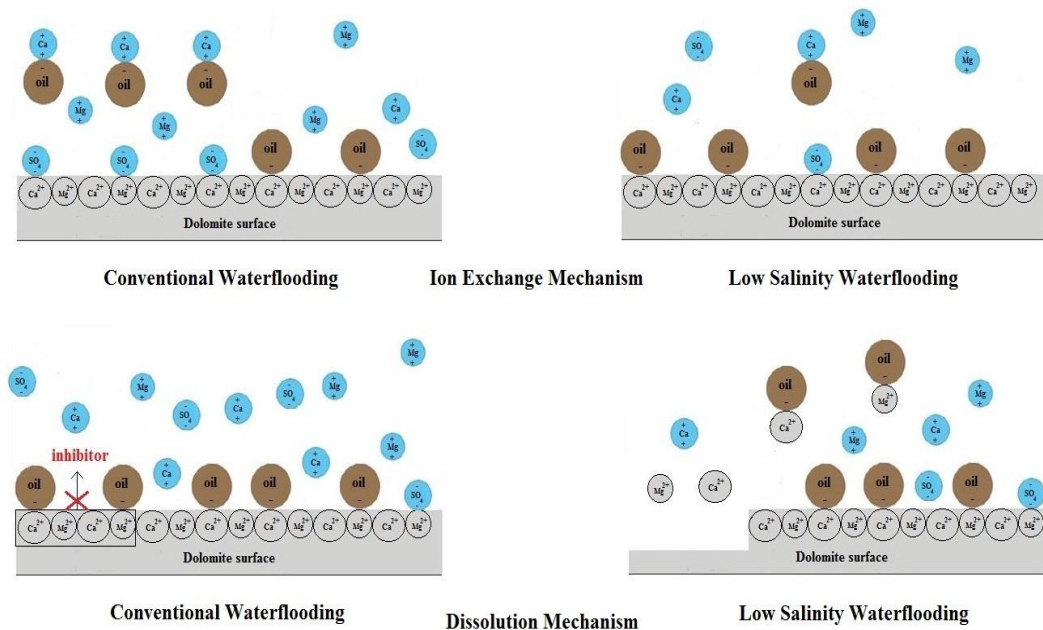


Figure 5.6 Illustration of oil recovery mechanism compared between conventional and low salinity waterflooding

However, when diluting the brine up to 40,000 and 20,000 ppm, less amount of additional oil recovery in the second period can be recovered. It could be explained that dissolution mechanism is limited and becomes less dominant compared to ion interaction mechanism because rapid dissolution of Calcium ion and Magnesium ion starts to cause dissolved ions as an inhibitor of dissolution process itself and this will decelerate the dissolution reaction. Owing to the limitation of dissolution reaction together with fewer occurrences of ion interactions which is due to the decreased amount of potential determining ions, the ultimate oil recovery is therefore less when diluting injected brine more than the optimum value. Another supported possible reason is that the sweep efficiency may be reduced when the injected brine is more diluted due to less density as well as viscosity which means even oil recovery mechanism can be occurred continuously but the portion of pores that can be in contact with injected brine is smaller. Comparison between chemical mechanisms during displacement mechanism using optimal total salinity

and too low total salinity is illustrated in Figure 5.7 while the values of brine viscosity for different total salinity are shown in Table 5.3.

Table 5.3 Brine viscosity for different total salinity

Total Salinity (ppm)	Brine viscosity (cp)
160,000	0.874
80,000	0.740
40,000	0.673
20,000	0.640

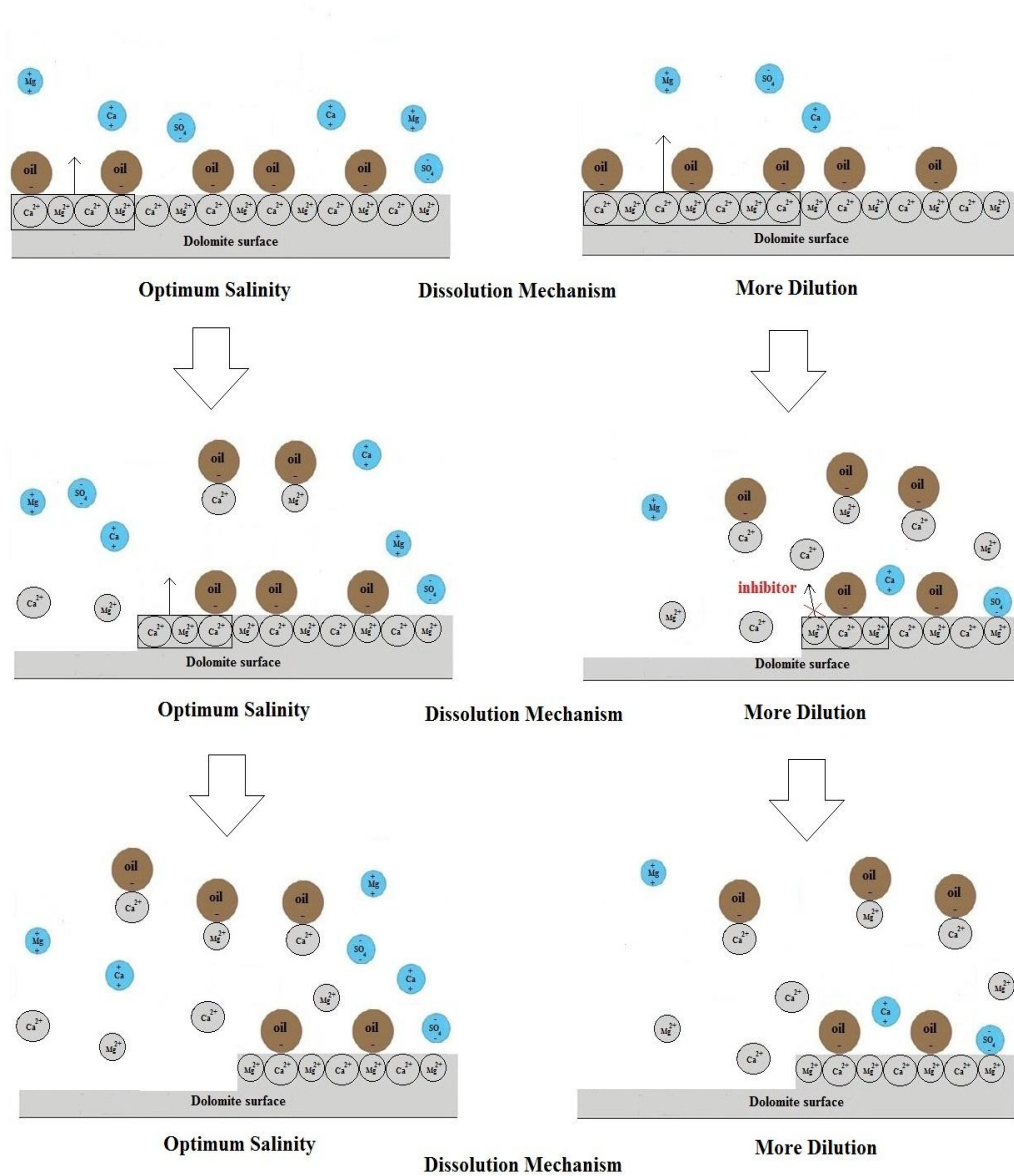


Figure 5.7 Illustration of dissolution mechanism compared between optimum total salinity case and more dilution case

From the figure, it can be seen that even though brine injection with very low total salinity can induce more dissolution reaction in the first period, the dissolution reaction is inhibited in the latter period because divalent ions from the rock that is rapidly dissolved especially Calcium ion will become an inhibitor that will limit the continuity of the reaction. On the other hands, even brine injection with optimum

total salinity can induce less dissolution reaction in the first period, divalent ions from the rock does not dissolve much, dissolution can occur continuously which means benefits from this mechanism is not much different between these two cases.

In order to confirm results from chemical process, wettability alteration is evidence used for this explanation. From Figure 5.3, it can be seen that the case provides the best oil recovery factor also provides relative permeability curves with a tendency toward a more water-wet condition. This can be observed from comparison between end point relative permeability to water and end point relative permeability to oil. Moreover, as summarized in Table 5.2 the value of $1-S_{or}$ is also the highest in the case of using total salinity of 80,000 ppm which infers to the least residual oil saturation.

From this section, it can be concluded that diluted formation brine can be used as an injectant to increase oil recovery in dolostone formation. Decreasing of Calcium and Magnesium ions results in dissolution mechanism of rock matrix that in turn helping to liberate adsorbed oil at the rock surface and hence, improving oil recovery. However, products from dissolution mechanism may act as inhibitor of the process and could terminate the dissolution mechanism once the equilibrium is attained. Therefore, optimum total salinity exists and in this study, the total salinity of 80,000 ppm is found as an optimal salinity and this value is utilized for further study in next sections.

5.2 Effects of Divalent Cation of Injected Brine

According to Chapter 3 describing that surface ion exchange is one of the mechanisms that help recovering oil by means of low salinity waterflooding from carbonate surface and ions that are related to this mechanism include Calcium ion, Magnesium ion and Sulfate ion. These ions are generally called as potential determining ions. Therefore, the effects of these potential determining ions concentration are observed in this section in order to identify an appropriate formulation of injected brine for oil recovery enhancement.

In this section, effects of divalent cations which are Calcium ion and Magnesium ion are considered. First, the value of total salinity that yields the highest oil recovery factor is chosen based on the experiment in section 5.1. Then, ratio between Calcium ion and Magnesium ion is modified into various ratios which are 1:0, 4:1, 1:1, 1:4 and 0:1 in order to observe interference among each other while total salinity of injected brine is kept constant by adjusting the amount of Sodium Chloride due to abundance of Sodium ion and Chloride ion in the solution. The ion composition including amount of Sodium ion, Calcium ion, Magnesium ion and Chloride ion of different injected brines is shown in Table 5.4.

Table 5.4 Ion compositions of different injected brines with different ratio of Calcium ion and Magnesium ion

Composition	Ca ²⁺ : Mg ²⁺ ratio				
	1 : 0	4 : 1	1 : 1	1 : 4	0 : 1
Na ⁺	22,694	22,943	23,316	23,689	23,938
Ca ²⁺	8,033	6,426	4,016	1,607	0
Mg ²⁺	0	974	2,436	3,897	4,872
Cl ⁻	49,077	49,461	50,036	50,611	50,995

However, because both ion exchange and dissolution mechanism are dependent on the temperature, testing temperature is therefore varied into other three values which are 70, 50 and 30°C together with the ratio of Calcium ion to Magnesium ion in order to observe effects of temperature on the interference of divalent ions. The plots between oil recovery factor and injected pore volume at different temperatures are shown in Figures 5.8 to 5.10 for different testing temperatures of 70, 50 and 30°C, respectively. Figure 5.11 compares ultimate oil recovery factor of all cases at different ratios of Calcium ion to Magnesium ions as well as different temperatures. End point relative permeability values as well as end

point saturations obtained from all different cases at different temperatures are also summarized in Tables 5.5 to 5.7 for different three testing temperatures.

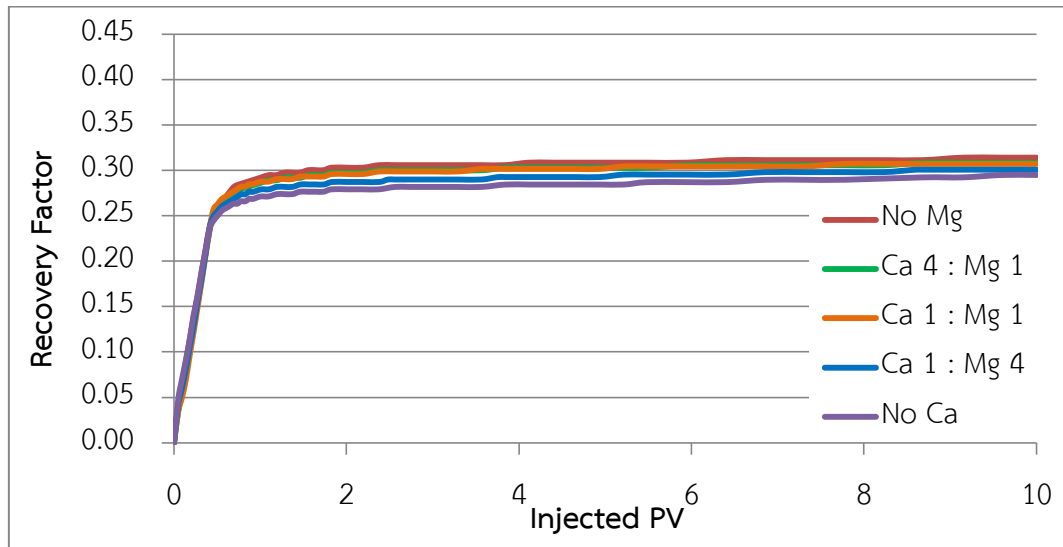


Figure 5.8 Oil Recovery factors obtained from different brines with different ratios of Calcium ion to Magnesium ion as a function of injected pore volume at testing temperature of 70 °C

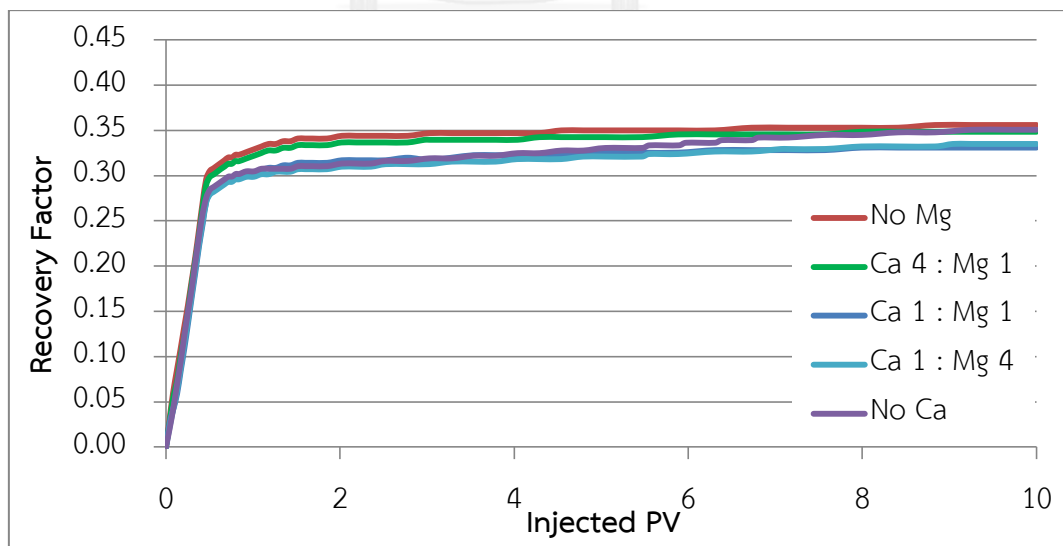


Figure 5.9 Oil Recovery factors obtained from different brines with different ratios of Calcium ion to Magnesium ion as a function of injected pore volume at testing temperature of 50 °C

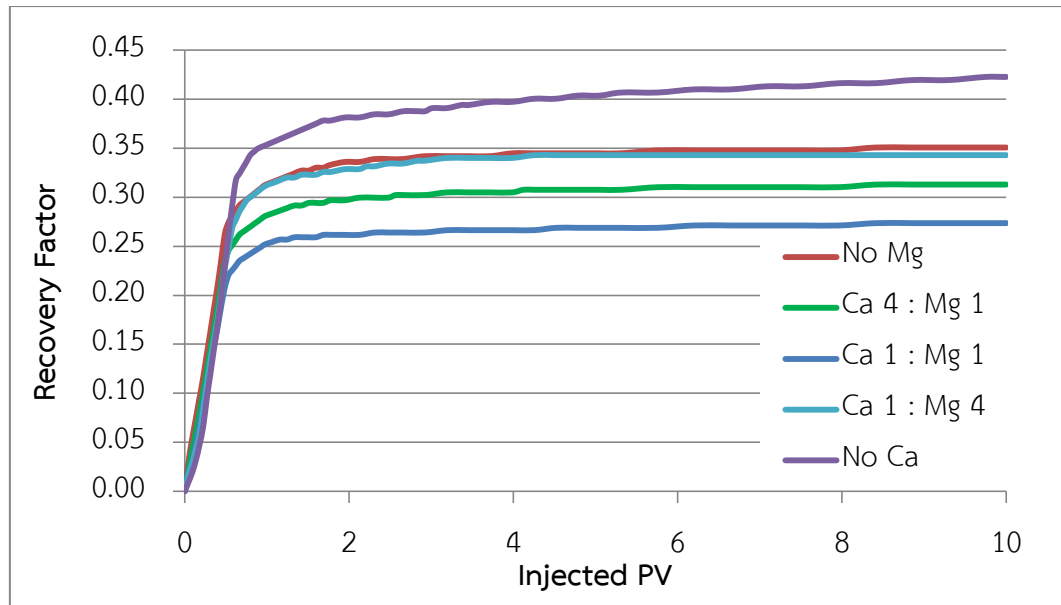


Figure 5.10 Recovery factors obtained from different brines with different ratios of Calcium ion to Magnesium ion as a function of injected pore volume at testing temperature of 30 °C

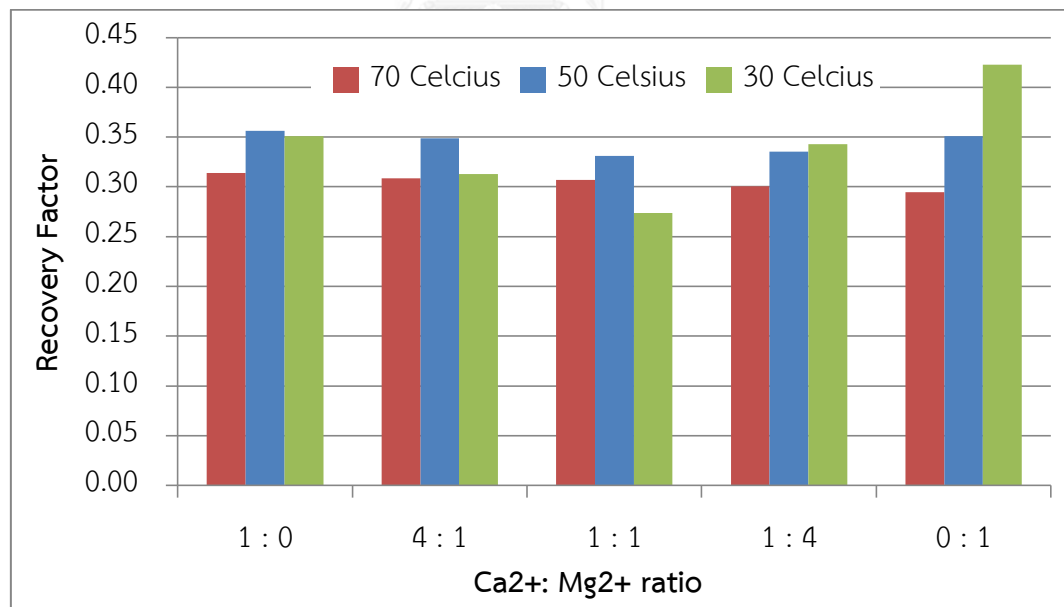


Figure 5.11 Oil recovery factors at the end of experiment obtained from different injected brines with different ratios of Calcium ion to Magnesium ion and different testing temperatures

Table 5.5 Summary of end point saturations and end point relative permeability values at end point saturations together with oil recovery factors obtained different injection brines with different ratios of Calcium ion to Magnesium ion at testing temperature of 70 °C

$\text{Ca}^{2+}:\text{Mg}^{2+}$ ratio	Irreducible water saturation (S_{wi})	1-Residual oil saturation ($1-S_{or}$)	Recovery factor (RF)	End point k_{ro}	End point k_{rw}
1 : 0	0.3795	0.5743	0.3139	0.354	0.161
4 : 1	0.3978	0.5834	0.3083	0.540	0.254
1 : 1	0.4252	0.6017	0.3071	0.402	0.351
1 : 4	0.3978	0.5789	0.3007	0.323	0.432
0 : 1	0.3704	0.5560	0.2948	0.550	0.518

Table 5.6 Summary of end point saturations and end point relative permeability values at end point saturations together with oil recovery factors obtained different injection brines with different ratios of Calcium ion to Magnesium ion at testing temperature of 50 °C

$\text{Ca}^{2+}:\text{Mg}^{2+}$ ratio	Irreducible water saturation (S_{wi})	1-Residual oil saturation ($1-S_{or}$)	Recovery factor (RF)	End point k_{ro}	End point k_{rw}
1 : 0	0.4378	0.6379	0.3560	0.217	0.112
4 : 1	0.4378	0.6337	0.3485	0.459	0.252
1 : 1	0.4462	0.6295	0.3311	0.329	0.360
1 : 4	0.4378	0.6262	0.3351	0.433	0.335
0 : 1	0.4294	0.6295	0.3508	0.402	0.145

Table 5.7 Summary of end point saturations and end point relative permeability values at end point saturations together with oil recovery factors obtained different injection brines with different ratios of Calcium ion to Magnesium ion at testing temperature of 30 °C

Ca ²⁺ :Mg ²⁺ ratio	Irreducible water saturation (S _{wi})	1-Residual oil saturation (1-S _{or})	Recovery factor (RF)	End point k _{ro}	End point k _{rw}
1 : 0	0.3990	0.6098	0.3508	0.342	0.285
4 : 1	0.3547	0.5567	0.3130	0.493	0.370
1 : 1	0.3105	0.4991	0.2736	0.362	0.455
1 : 4	0.3725	0.5877	0.3430	0.363	0.355
0 : 1	0.3547	0.6275	0.4228	0.391	0.213

From Figure 5.11, at the highest testing temperature of 70 °C, the values of oil recovery factor are very near to each other even the ratio of Calcium ion to Magnesium ion in injected brine is varied. Then, when the testing temperature is reduced to 50 °C, oil recovery factors start to deviate from each other with various ratios of Calcium ion to Magnesium ion. The trend of oil recovery factor at this temperature is that the values are descending when the ratio of Calcium ion to Magnesium ion is altered from 1:0 to 1:1 and becomes ascending when the Ca²⁺:Mg²⁺ ratio is altered from 1:1 to 0:1. The case of injection by brine with the ratio of Calcium ion to Magnesium ion 1:0 yields the highest oil recovery factor. When the temperature is further reduced to 30 °C, the trend of oil recovery factor as a function of ratio of Calcium ion to Magnesium ion is still as same as in case of 50 °C but the case of injection by brine with ratio of Calcium ion to Magnesium ion 0:1 yields the highest oil recovery factor instead although the recovery rate in the first period is small.

From the result, it can be explained that at certain temperature, when the ratio of Calcium ion to Magnesium ion is increased which means the amount of

Calcium ion is increased while the amount of Magnesium ion is decreased, ion interaction mechanism can occur better due to increased formation of Carboxylate complex by Calcium ion. Although Magnesium ion can still form the Carboxylate complex with acidic compound in oil but the testing temperature may be not high enough for formation in the same amount as Calcium ion can do. However, when the ratio of Calcium ion to Magnesium ion is increased, oil recovery from dissolution mechanism will be slightly lower because dissolved Calcium ion is a strong inhibitor that decelerates the dissolution reaction as illustrated in Figure 5.12. However, dissolution of Magnesium may still occur as dolostone composes of both Calcium and Magnesium in the matrix. When both ions in injected brine are comparatively equal, this might inhibit dissolution of both Calcium and Magnesium from rock matrix, resulting in the least dissolution mechanism as well as the least ultimate oil recovery factor. At the temperature of 70°C dissolution of both Calcium and Magnesium from rock mineral could occur quickly, resulting in equilibrium of divalent ions in the system and these ions turn into inhibitors of dissolution process. Hence, changing ratio of Calcium ion to Magnesium ion in injected brine does not affect much on oil recovery mechanism and hence oil recovery factors from all cases remain the same.

However, at lower temperature especially at 30°C, it can be seen that the highest value of ultimate oil recovery factor is obtained from low salinity brine injection with the ratio of Calcium ion to Magnesium ion of 0:1 even though the oil recovery rate in the first period is low. The reason why high oil recovery factor is obtained at lower temperature is that the rate of dissolution at this temperature is at the optimal value where reaction can continuously occur without deceleration of dissolution mechanism. If the rate of dissolution is too fast in the early period, the reaction may be terminated earlier because dissolved Calcium ion and Magnesium ion from rock dissolution will be an inhibitor that decelerates the dissolution reaction as shown in Figure 5.13. The phenomenon that the dissolution mechanism is in the best condition at optimum temperature was also observed by Ronghua et al. [12]. They found that the average dissolution rate increases until it reaches the optimum

temperature and then the rate decreases as shown in Figure 5.14. Again, From Table 5.5 to Table 5.7, it can be seen that the case provides the best oil recovery factor also provides relative permeability curves with a tendency toward a more water-wet condition.

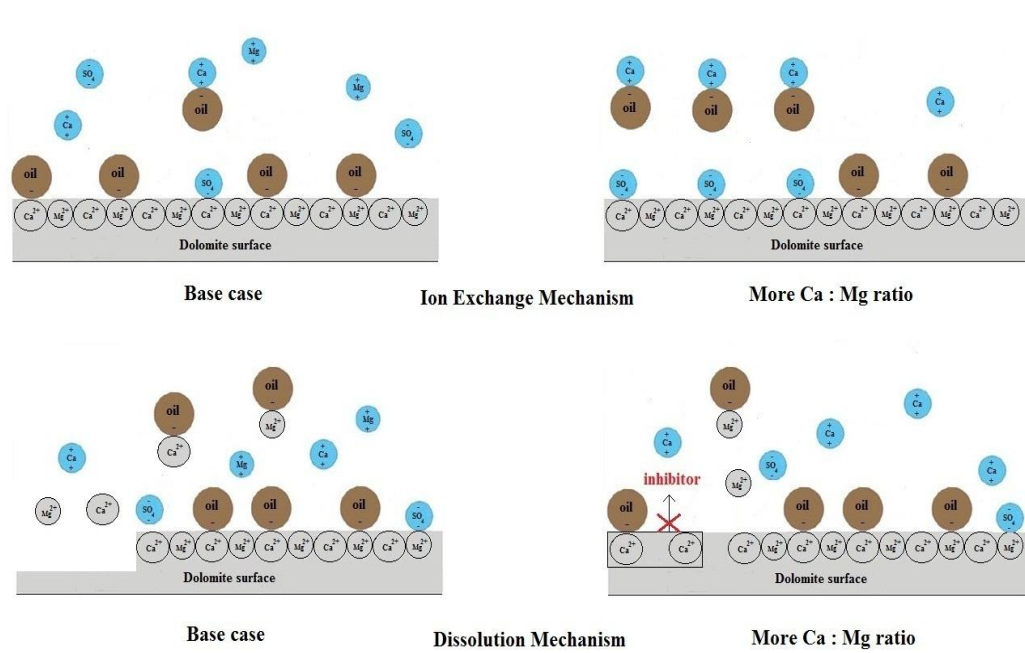


Figure 5.12 Illustration of oil recovery mechanism comparing between different ratios of Calcium ion to Magnesium ion

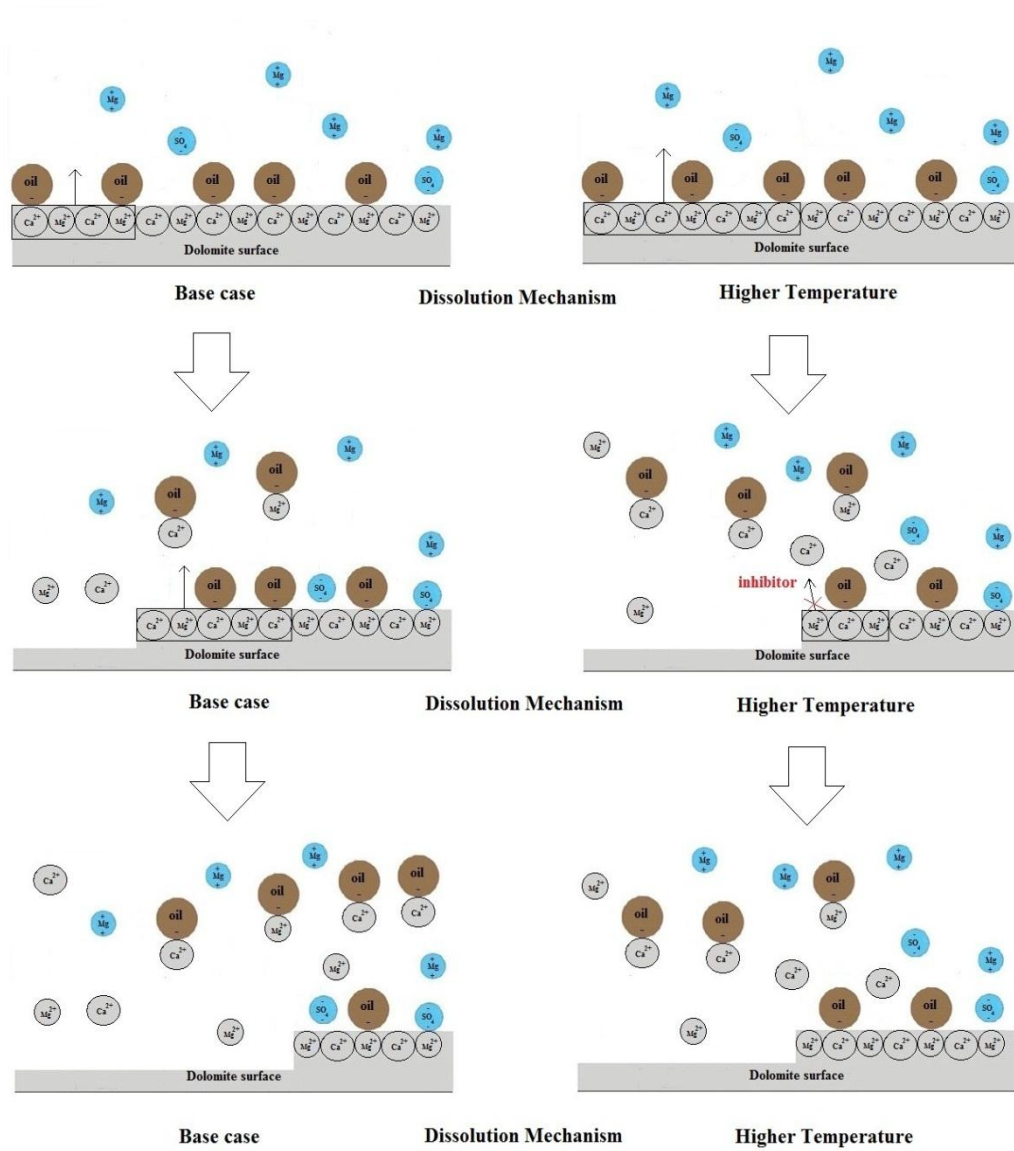


Figure 5.13 Illustration of dissolution mechanism comparing between different testing temperatures

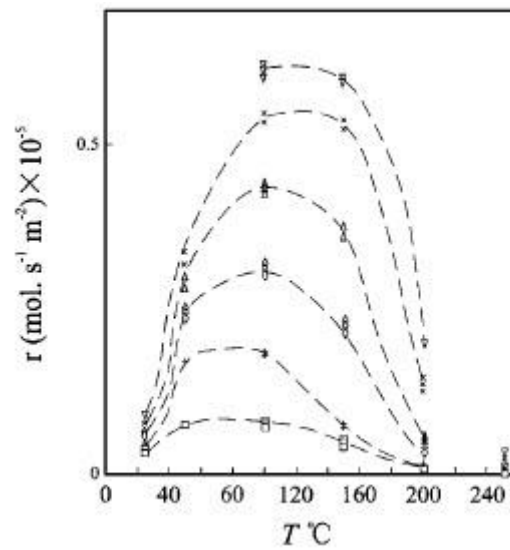


Figure 5.14 Plot of dissolution rate as a function of temperature [12]

From this section, it can be observed that divalent ions play important role in controlling effectiveness of low salinity waterflooding in dolostone. High reservoir temperature would accelerate dissolution mechanism of both Calcium and Magnesium in rock matrix, resulting in attaining ion equilibrium that at the same time, dissolution mechanism is inhibited. At lower temperature, dissolution mechanism of rock is slower and this causes the continuity of chemical process. When Calcium ion in brine is high and Magnesium ion in brine is low, Calcium Carboxylate complex is generated and dissolution mechanism may occur through that of Magnesium ion. At the same amount of both Calcium ion and Magnesium ion in brine, dissolution mechanism of dolostone is the lowest, resulting in the lowest ultimate oil recovery factor. At 30°C with the lowest amount of Calcium ion in brine, these conditions allow dissolution mechanism and forming of Carboxylic complex to occur simultaneously. Deceleration of mineral dissolution is therefore avoided and the highest ultimate oil recovery factor is obtained from this condition.

5.3 Effects of Sulfate Ions in Injected Brine

From previous section, effects of Calcium ion and Magnesium ions on oil recovery mechanism in dolostone formation are already mentioned. In this section, effects of the last potential determining ion, which is Sulfate ion, is considered. The ratio between Calcium and Magnesium ions yielding the highest oil recovery factor from previous section is chosen for the experiment in this section. Ion mass of sulfate ion is adjusted to be 0.5, 2, 5, 10 and 50 times of the initial mass while total salinity of injected brine is also kept constant by adjusting the amount of Sodium Chloride as similar as in the previous section and the testing temperature is fixed at 50 °C.

According to the results from section 5.2, the highest oil recovery factor is obtained when injection brine possesses the ratio of Calcium ion to Magnesium ion at 1:0. Therefore, this brine formula is selected to modify Sulfate ion concentration and the ion composition including amount of Sodium ion, Calcium ion, Sulfate ion and Chloride ion of different injected brines is summarized in Table 5.8.

Table 5.8 Ion compositions of different injected brines with different concentrations of Sulfate ion

Composition	Sulfate ion mass (times of original value)					
	0.5x	1x	2x	5x	10x	50x
Na ⁺	22,701	22,694	22,682	22,646	22,585	22,097
Ca ²⁺	8,033	8,033	8,033	8,033	8,033	8,033
SO ₄ ²⁻	59	118	237	591	1,183	5,914
Cl ⁻	49,130	49,077	48,971	48,653	48,122	43,879

The plot between oil recovery factor and injected pore volume of brines with different concentrations of Sulfate ion is shown in Figure 5.15. Comparison of

ultimate oil recovery factors obtained from all cases is depicted in Figure 5.16. Summary of end point relative permeability values as well as end point saturations obtained from all different cases are also gathered in Tables 5.9.

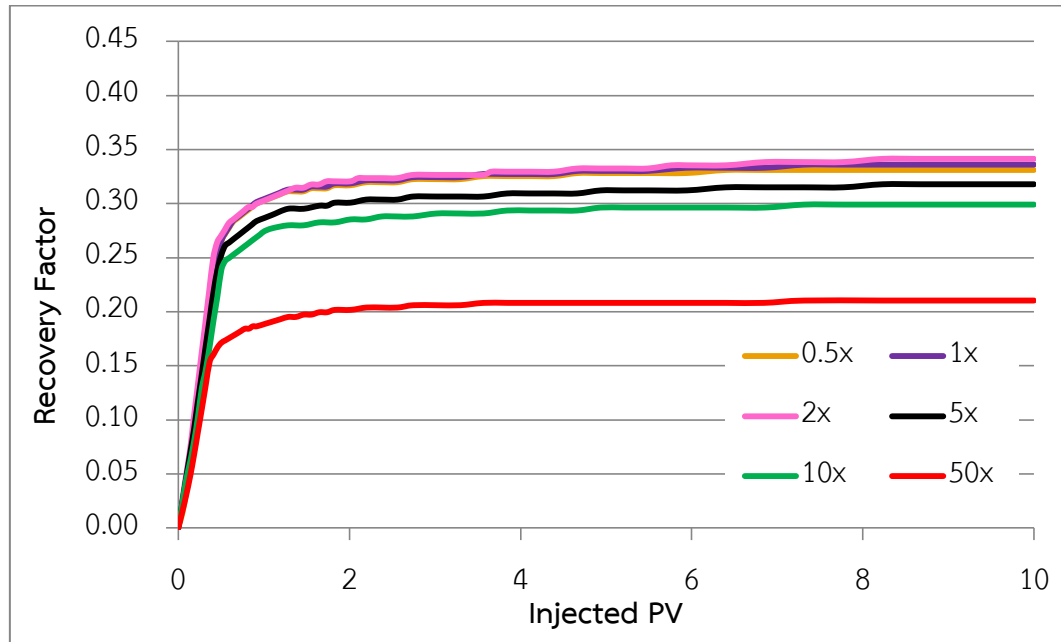


Figure 5.15 Oil Recovery factors obtained from different brines with different concentrations of Sulfate ion as a function of injected pore volume at testing temperature of 50 °C

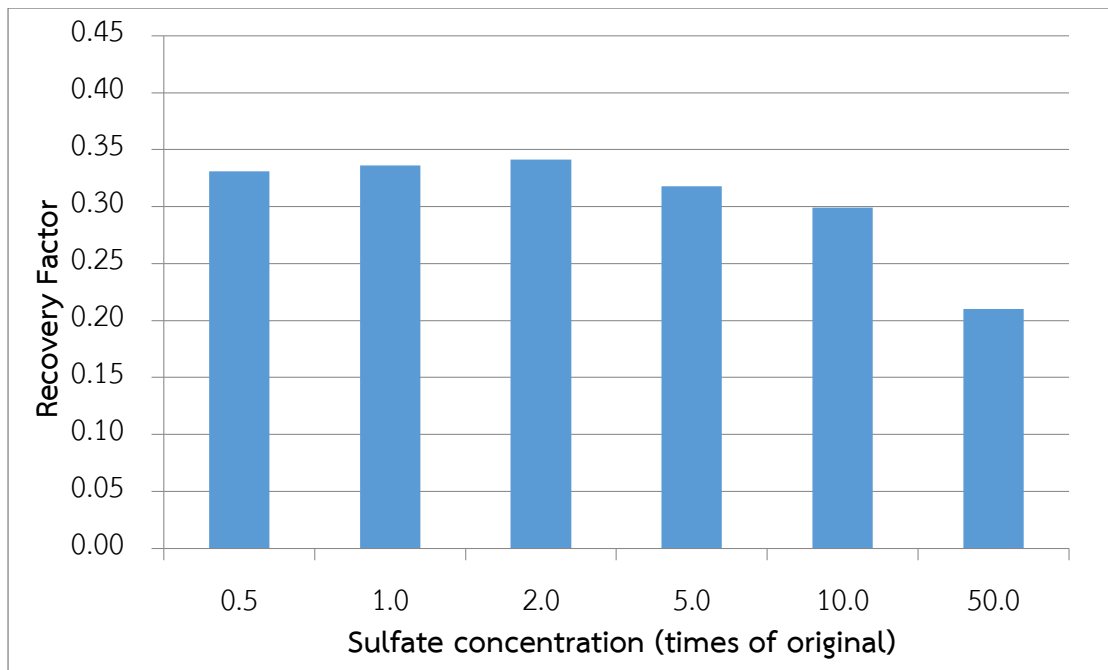


Figure 5.16 Oil recovery factors at the end of experiment obtained from different brines with different concentrations of Sulfate ion

Table 5.9 Summary of end point saturations and end point relative permeability values at end point saturations together with oil recovery factors obtained different injection brines with different concentrations of Sulfate ion at testing temperature of 50 °C

Sulfate ion	Irreducible water saturation (S_{wi})	1-Residual oil saturation ($1-S_{or}$)	Recovery factor (RF)	End point k_{ro}	End point k_{rw}
0.5x	0.3704	0.5789	0.3312	0.370	0.326
1x	0.3932	0.5972	0.3361	0.272	0.263
2x	0.4161	0.6155	0.3414	0.217	0.227
5x	0.4161	0.6017	0.3179	0.354	0.328
10x	0.4252	0.5972	0.2991	0.303	0.352
50x	0.4435	0.5606	0.2104	0.277	0.363

From Figures 5.15 and 5.16, the highest value of oil recovery factor is obtained from the case that Sulfate ion concentration in injected brine is twice compared to the original concentration. The increment of ultimate oil recovery factor is quite small when changing Sulfate ion concentration from 0.5 to 2 times. However, the decrease of ultimate oil recovery factor is very obvious when changing concentration of Sulfate ion from 2 to 50 times.

For the trend that oil recovery factor increases when concentration of Sulfate ion is raised from 0.5 to 2 times, it can be explained that when the amount of Sulfate ion is increased, ion interaction mechanism can occur better. When the positive charge density of the dolomite surface is lowered due to larger amount of anions which are Sulfate ions attracted to the positive-charged surface, Calcium ions can approach closer to surface, resulting in an ease to form Calcium Carboxylate complex which yields more oil recovery as illustrated in Figure 5.17.

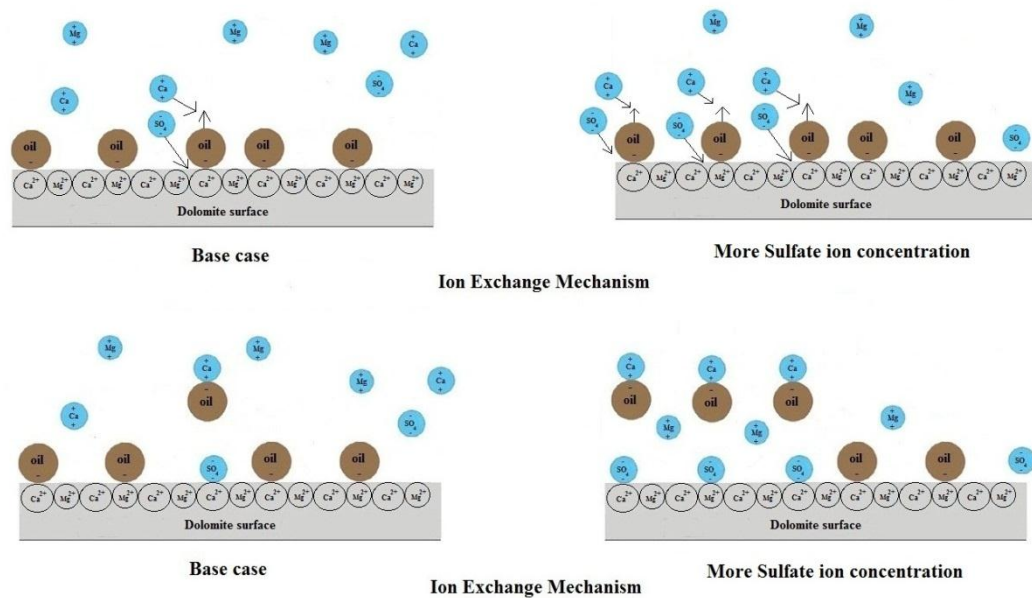


Figure 5.17 Illustration of ion exchange mechanism comparing between different concentrations of Sulfate ion

However, when increasing the concentration of sulfate ion exceeding the optimum value which is twice of original concentration, it can be seen that the ultimate oil recovery factor is in the decreasing trend. This can be explained that there are large amounts of Sulfate ion together with Calcium ion. Calcium ion tends to precipitate together with Sulfate ion, converting back into the crystalline solid form of either Calcium Sulfate which is owing to the solubility limit of Calcium Sulfate compound in the solution phase or Calcium Carbonate which is the product from surface reaction called as dedolomitization process. The dedolomitization process is the process that dolomite ($\text{CaMg}(\text{CO}_3)_2$) tends to convert into calcite (CaCO_3) if the environment contains a lot of Calcium ion and Sulfate ion as shown in equation 5.3 [13].



The parameter that is used to indicate the precipitation of Calcium ion in this experiment is the increment of pressure drop across the core during the waterflooding experiment. This increment of pressure drop is a result of reduction of relative permeability to water during the experiment. The comparison of relative permeability to water at different periods of experiment between two different cases is shown in Table 5.10 to confirm an occurrence of precipitation of Calcium ion that consecutively reduces the flow path of water.

Table 5.10 Comparison of relative permeability to water at different periods of experiment between two different cases

Sulfate ion	k_w at 0.1PV (mD)	End point k_w (mD)
2x	2.496	2.603
50x	3.803	3.734

From the above phenomenon, when Sulfate ion concentration exceeds the optimum value, more Calcium ions are therefore inactive for ion exchange mechanism due to Calcium precipitation which results in the less formation of Carboxylate complex and also less oil recovery as shown in Figure 5.18.

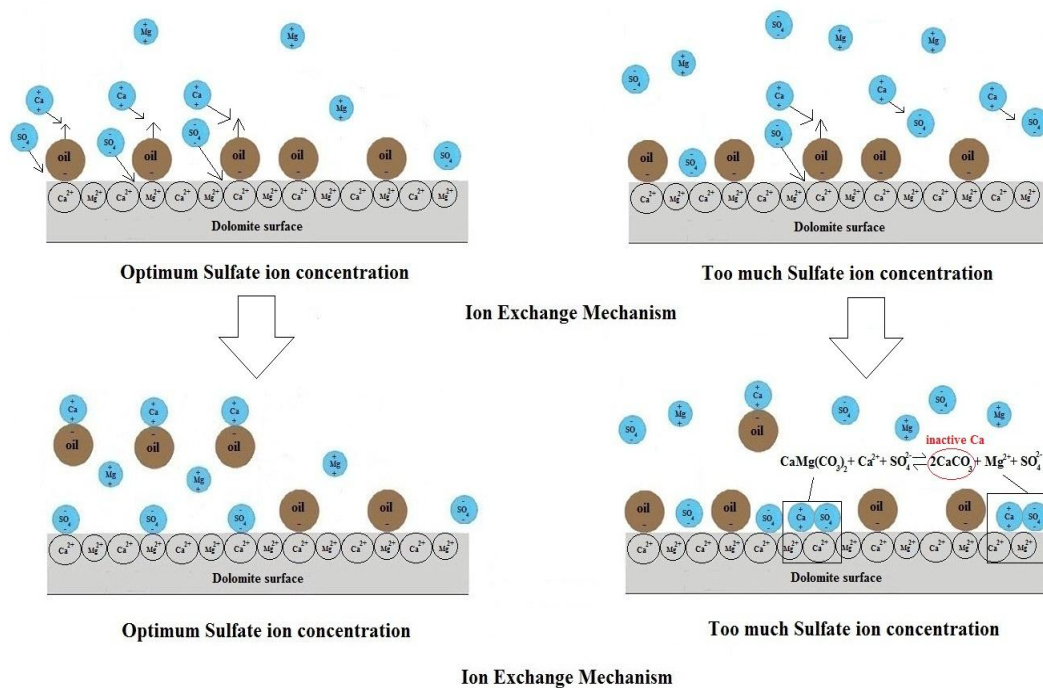


Figure 5.18 Illustration of ion exchange mechanism comparing between optimum and too much sulfate ion concentration

In this section, it can be seen that changing concentration of Sulfate ion can slightly increase oil recovery by favoring ion exchange mechanism. As Sulfate ion possesses negative charge, surface interaction of Sulfate ion onto dolomite surface results in less positively charged condition and hence, forming of Calcium Carboxylate complex can occur easier. Nevertheless, higher concentration of Sulfate ion beyond the optimal value causes deactivation of Calcium ion by precipitation of Calcium ion together with Sulfate ion as well as dedolomitization process. Modification of injected brine by adding Sulfate ion should never go exceeding the

optimal value that must be identified by laboratory experiment for different surface and brine system.

5.4 Effects of Injection Rate

In the last section, brine with optimum concentration of potential determining ions at testing temperature of 50°C from the previous section is selected to use in waterflooding while the ion composition of this brine formula, which is the amount of Sodium ion, Calcium ion, Magnesium ion, Sulfate ion and Chloride ion, is summarized in Table 5.11.

Table 5.11 Ion composition of injected brines used in this study section

Composition	Ion concentration (ppm)
Na ⁺	22,682
Ca ²⁺	8,033
Mg ²⁺	0
SO ₄ ²⁻	237
Cl ⁻	48,971

By using the brine with this formula as an injectant, the injection rates for this study section are varied into other 3 values, which are 0.5, 1.0 and 4.0 cm³/min while the testing temperature is fixed at 50 °C. The plot between oil recovery factor and injected pore volume of brines with different injection rates is shown in Figure 5.19. Comparison of ultimate oil recovery factors obtained from all cases is depicted in Figure 5.20. Summary of end point relative permeability values as well as end point saturations obtained from all different cases are also gathered in Tables 5.12.

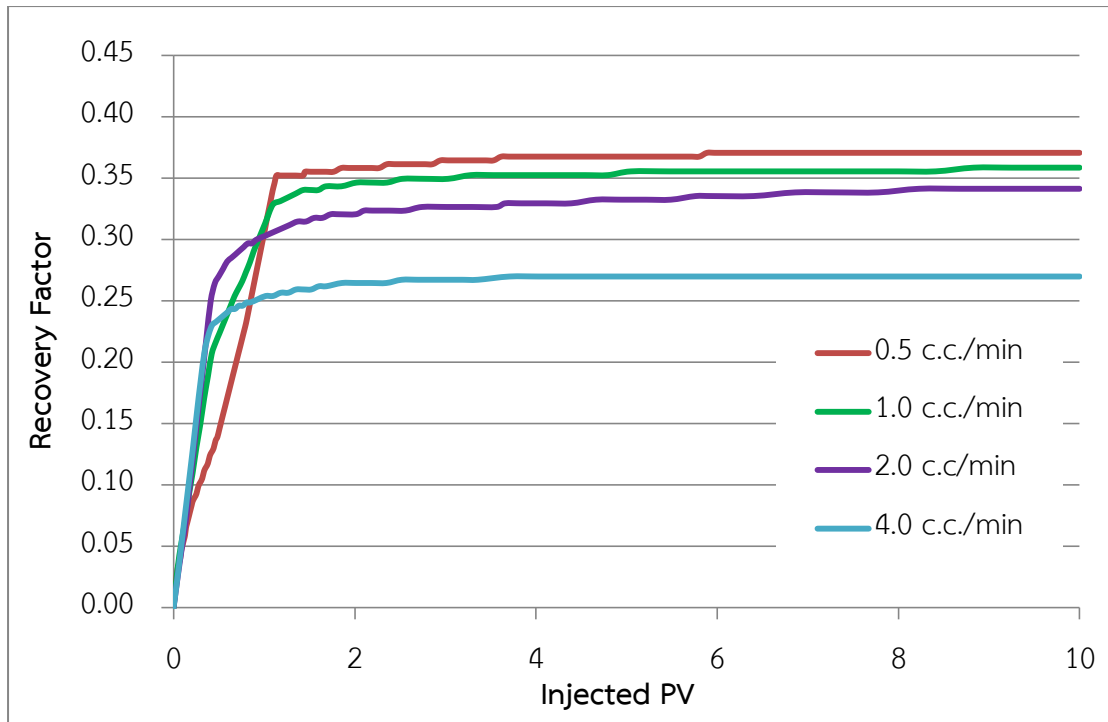


Figure 5.19 Oil Recovery factors obtained from different injection rates as a function of injected pore volume at testing temperature of 50 °C

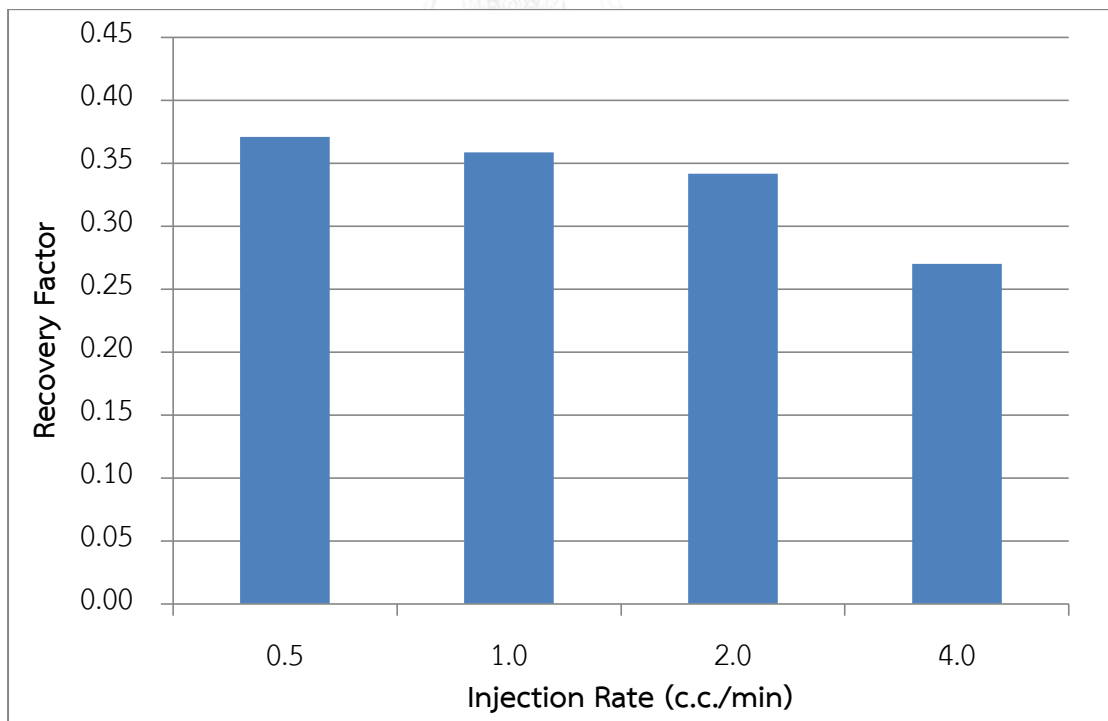


Figure 5.20 Oil recovery factors at the end of experiment obtained from different injection rates

Table 5.12 Summary of end point saturations and end point relative permeability values at end point saturations together with oil recovery factors obtained from different injection rates at testing temperature of 50 °C

Injection rate (c.c./min)	Irreducible water saturation (S_{wi})	1-Residual oil saturation ($1-S_{or}$)	Recovery factor (RF)	End point k_{ro}	End point k_{rw}
0.5	0.4294	0.6409	0.3707	0.203	0.138
1.0	0.4336	0.6367	0.3586	0.215	0.201
2.0	0.4161	0.6155	0.3414	0.217	0.227
4.0	0.4546	0.6018	0.2699	0.182	0.254

From Figures 5.19 and 5.20, the highest value of oil recovery factor is obtained from brine injection with the smallest injection rate and when the injection rate is increased, the total amount of oil that can be recovered is reduced even though the rate of oil recovery in the first period for low injection rate is lower than that of higher injection rate.

From the result, it can be seen that oil recovery factor is dependent from injection rate which is the consequence of two main effects. The first one is the effect from water underrunning which is owing to the injecting direction that is perpendicular to the gravity force. For this effect, when injecting brine with low rate, the brine tends to underrun, resulting in less sweep efficiency compared to the case of injection with high rate. In this case, the effect from water underrunning can be seen from less recovery rate in the first period when injecting with lower rate.

Another effect is from ion diffusion, in this case ions transport from the brine solution to the rock surface. This effect occurs because the reaction between oil attached to the rock surface and potential determining ions in brine is the diffusion-controlled reaction which means that the rate of ion diffusion is slower than the rate of chemical reaction, therefore the amount of carboxylate complex that can be

formed is mainly dependent on the amount of ions in the brine that can be diffused to the rock surface to interact with oil.

However, this effect gives the opposite consequence from water underrunning effect because the diffusion rate of ions from the brine solution to rock surface is greater when the injection rate is lower due to less force from injection. Since this force tends to push the dissolved ions towards the producer in the horizontal direction rather than allow these ions to diffuse to the rock surface, therefore injection with lower rate which means more contact time of brine on rock surface will yield more oil recovery as illustrated in Figure 5.21.



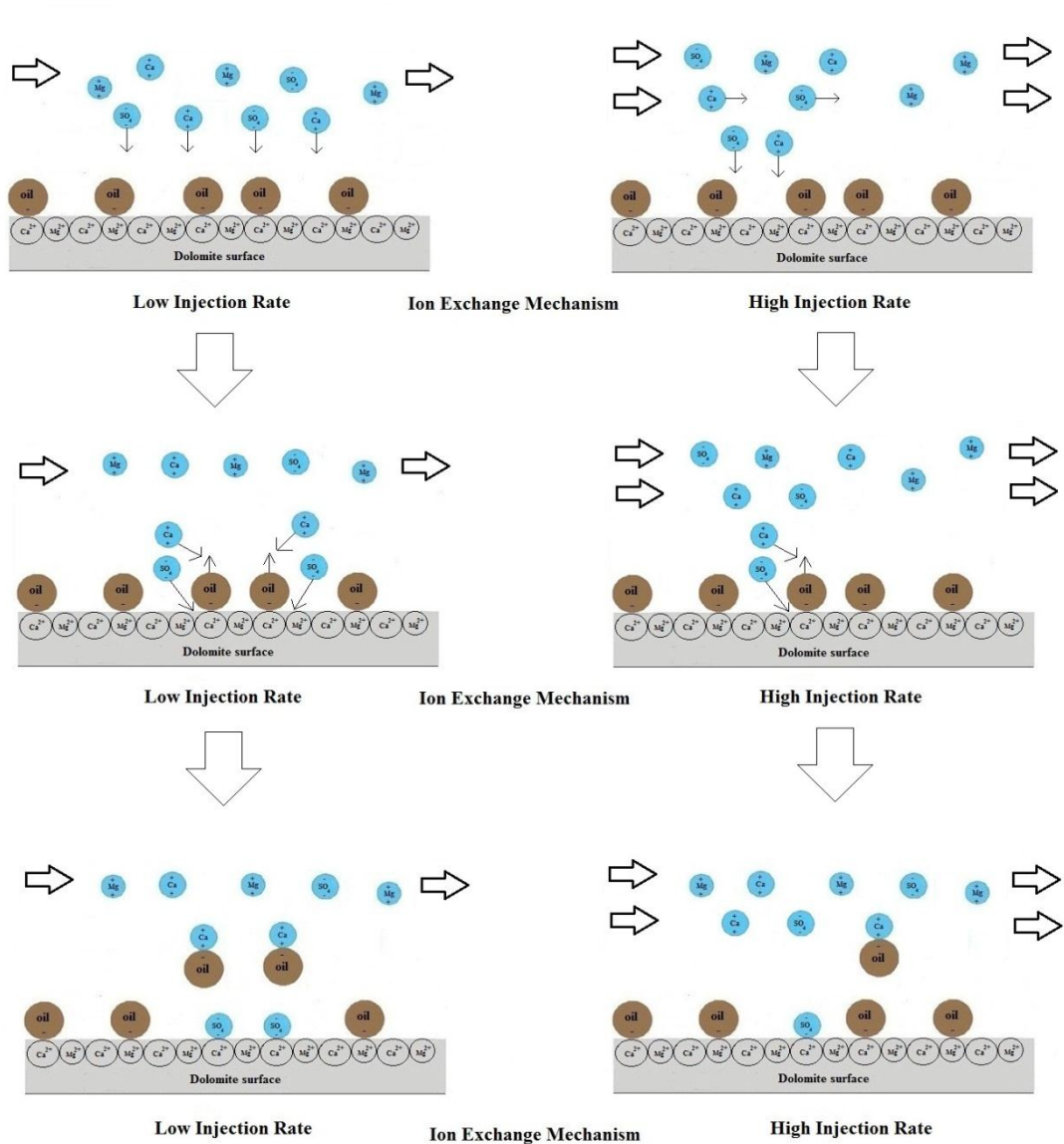


Figure 5.21 Illustration of ion exchange mechanism comparing between different injection rates

In this section, it can be observed that smaller injection rate allows potential determining ions to complete the oil recovery mechanism on rock surface. Nevertheless, the smaller injection rate would cause the underrunning of water that could result in less sweep efficiency. Therefore, optimal injection rate in field implementation would not be as same as one obtained from the laboratory scale

where effects of underrunning is diminished from small cross-section area of core samples.



CHAPTER 6

CONCLUSION AND RECOMMENDATION

In this chapter, conclusions from the experiment are made which can be divided into four sections. First, effects of total salinity of injected brine are concluded. Then, effects of potential determining ions of injected brine are made with two sub-sections consisting of effects of divalent cations i.e. Calcium ion and Sulfate ion, and effects of anions i.e. Sulfate ion. The final section is effects of injection rate. However, several recommendations are also prepared for the further study.

6.1 Effects of Total Salinity of Injected Brine

Oil recovery periods can be divided into two periods. The first period is the period before water breakthrough. In this period, the oil is displaced mainly from physical displacement which comes from the mass of injected brine. However, chemical mechanisms take place at the same time. These mechanisms include rock dissolution and ion interaction between positive charges on rock surface and potential determining ions in injected brine. After water breakthrough, oil patches in pore space are in contact more with injected brine and this leads to second period of oil recovery mechanism when chemical process dominates.

For the result, injection by low salinity brine with optimum total salinity, in this study 80,000 ppm, yields the highest oil recovery factor because decreasing of Calcium and Magnesium ions results in better dissolution mechanism due to the driving force from salinity difference between formation brine and injected brine. However, too much brine dilution is not helpful because the brine viscosity is also reduced resulting in less portion of pores that can be in contact with injected brine. Therefore, the optimum salinity should be studied case by case in order to yield the highest benefits from low salinity waterflooding.

6.2 Effects of Divalent Cation of Injected Brine

At low temperature, the oil recovery factor is the lowest when the amount of Calcium ion and Magnesium ion is equal and becomes increasing when the amount of either Calcium ion or Magnesium ion is more dominant than another ion. This is because when both ions in injected brine are comparatively equal, this might inhibit dissolution of both Calcium and Magnesium from rock matrix of dolomite that contains both Calcium and Magnesium, resulting in the least dissolution mechanism as well as the least ultimate oil recovery factor.

However, when considering the effect of temperature, oil recovery factors are more deviated from each other with various ratios of Calcium ion to Magnesium ion when the temperature is lower. This is because high reservoir temperature would accelerate dissolution mechanism, resulting in faster ion equilibrium attainment. However, this also causes the earlier deceleration of dissolution mechanism and finally the termination of chemical reaction. On the other hands, dissolution mechanism of rock is slower at lower temperature but this causes the continuity of chemical process which results in better performance of oil recovery from dissolution mechanism.

In conclusion, it can be observed that divalent ions play important role in controlling performance of low salinity waterflooding in dolostone. However, the optimum ratio of divalent ions is different from reservoir to reservoir due to the dependence on reservoir temperature.

6.3 Effects of Sulfate Ions in Injected Brine

The highest value of oil recovery factor is obtained from the case that Sulfate ion concentration in injected brine is twice compared to the original concentration. Oil recovery factor increases when concentration of Sulfate ion is raised to this value and becomes decreasing when adding more Sulfate ion than this optimum value because when the amount of Sulfate ion is increased, ion interaction mechanism can

occur better due to reduction of the positive charge density of dolomite surface, resulting in more formation of Calcium Carboxylate complex.

However, when increasing the concentration of Sulfate ion until it exceeds the optimum value, Calcium ion tends to precipitate together with Sulfate ion, converting back into the crystalline solid, resulting in more inactive Calcium ions for ion exchange mechanism that can be observed from reduction of relative permeability to water as the experiment continues.

In conclusion, it can be seen that changing concentration of Sulfate ion also affects the effectiveness of low salinity waterflooding by favoring ion exchange mechanism. However, modification of Sulfate ion should be identified by laboratory experiment for different system in order to prevent precipitation of Calcium ion.

6.4 Effects of Injection Rate

The highest value of oil recovery factor is obtained from brine injection with the smallest injection rate and when the injection rate is increased, the total amount of oil recovery is reduced. This can be explained that amount of Carboxylate complex that can be formed is mainly dependent on the amount of ions in the brine that can be diffused to the rock surface to interact with oil which is increased when the injection rate is lower. However, the injection rate should not be too low when injecting perpendicular to the gravity force because brine tends to underrun, resulting in less sweep efficiency.

6.5 Recommendations

These following topics are recommended for further study for better understanding in oil recovery mechanism of waterflooding in dolomite reservoir.

1. To prove that there is an occurrence of dissolution reaction, the amount of ions in the effluent should be detected for performing ion mass

balance in order to indicate whether there are additional ions besides dissolved ions in injected brine.

2. The effect of other potential determining ions, which are also mentioned in the research such as Borate ion (BO_3^{3-}) and Phosphate ion (PO_4^{3-}), may be included in the further study.

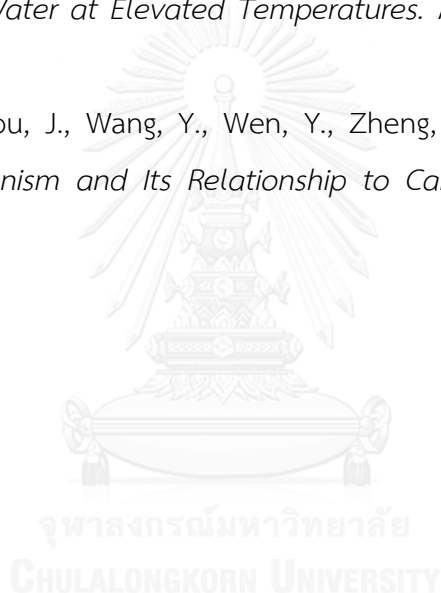
Moreover, because the brine formula used for further ion modification in this study is selected from the brine yielding the highest oil recovery from previous section, the optimum concentration of ions in injected brine may not be preferable for other reservoirs which have the different conditions. Therefore, the specific reservoir condition should be obtained from the real field in order to synthesize the optimum injected brine formula used in waterflooding for the real implementation.



REFERENCES

1. Austad, T., Romanuka, J., Hofman, J.P., Ligthelm, D.J., Suijkerbuijk, B.M.J.M., Marcelis, A.H.M., Oedai, S., Brussee, N.J., van der Linde, H.A., and Aksulu H., , *Low Salinity EOR in Carbonates*, in *Eighteenth SPE Improved Oil Recovery Symposium*. 2012, SPE: Tulsa, Oklahoma, U.S.A.
2. Zahid, A., Shapiro, A., and Skauge, A., *Experimental Studies of Low Salinity Water Flooding in Carbonate Reservoirs : A New Promising Approach*, in *SPE EOR Conference at Oil and Gas West Asia*. 2012, SPE: Muscat, Oman.
3. Al-Harassi, A.S., Al-Maamari, R.S., and Masalmeh, S., *Laboratory Investigation of Low Salinity Waterflooding for Carbonate Reservoirs*, in *Abu Dhabi International Petroleum Exhibition & Conference*. 2012, SPE: Abu Dhabi, UAE.
4. Sharifi, M., and Shaikh, M., *Investigation of Optimum Salinity of Injected Water in Carbonate Reservoirs Using Wettability Measurement and Core Flooding*, in *SPE Reservoir Characterisation and Simulation Conference and Exhibition*. 2013, SPE: Abu Dhabi, UAE.
5. Al-Attar, H.H., Mahmoud, M.Y., Zekri, A.Y., Almehaideb, R.A., and Ghannam, M.T., *Low Salinity Flooding in a Selected Carbonate Reservoir: Experimental Approach*, in *EAGE Annual Conference & Exhibition incorporating SPE Europec*. 2013, SPE: London, United Kingdom.
6. Srisuriyachai, F., *Evaluation of Alkali Flooding Combined with Intermittent Flow in Carbonate Reservoir*, in *Department of Chemical, Mining and Environmental Engineering*. 2008, University of Bologna , Bologna, Italy.
7. Tiab, D., and Donalson, E.C. , *Petrophysics :theory and practice of measuring reservoir rock and fluid transport properties*. Second ed. 2004, Burlington, Massachusetts, U.S.A: Gulf Professional Publishing.
8. Gupta, R., Smith, P.G.J., Hu, L., Willingham, T.W., Cascio, M.L., Shyeh, J.J., and Harris, C.R., *Enhanced Waterflood for Middle East Carbonate Cores – Impact of Injection Water Composition*, in *SPE Middle East Oil and Gas Show and Conference*. 2011, SPE: Manama, Bahrain.

9. Zahid, A., *Smart Waterflooding in Carbonate Reservoirs*, in *Department of Chemical and Biochemical Engineering*. 2012, Technical University of Denmark, Lyngby, Denmark.
10. *Dolomite Powder*. 2016 [cited 2016 18th June]; Available from: <http://www.reade.com/products/dolomite-powder>.
11. Abdou, M., Carnegie, A., Mathews, S.G., McCarthy, K., O'Keefe, M., Raghuraman, B., Wei, W., and Xian, C. . *Finding Value in Formation Water*. Schlumberger Oilfield Review 2011 [cited 2015 1 November].
12. Ronghua, Z., Shumin, X., Xuetong, Z., Wenbin, Y., *Dissolution Kinetics of Dolomite in Water at Elevated Temperatures*. *Aquat Geochem*, 2007. **13**: p. 309-338.
13. Zhang, J., Shou, J., Wang, Y., Wen, Y., Zheng, X., Hu, A. *Dedolomitization: Types, Mechanism and Its Relationship to Carbonate Reservoir Properties*. 2011.



APPENDIX A

Injected Brine Preparation

The summary of ion compositions for every various ratio between Calcium ion and Magnesium ion including the compositions at different concentration of Sulfate ion are presented in this section. Moreover, the amount of chemicals used for brine preparation, which are Sodium Chloride (NaCl), Magnesium Chloride (MgCl₂), Calcium Chloride (CaCl₂), Sodium Hydrogen Carbonate (NaHCO₃) and Sodium Sulphate (Na₂SO₄), are also shown in this section.

Table A.1 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9871	22.99	22,694
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.3843	35.45	49,077
SO ₄ ²⁻	0.0012	96.06	118
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.2 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9834	58.44	57.47
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0012	142.04	0.17
		Total	80.00

Table A.3 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 4:1 at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9980	22.99	22,943
Mg ²⁺	0.0401	24.30	974
Ca ²⁺	0.1603	40.08	6,426
Cl ⁻	1.3951	35.45	49,461
SO ₄ ²⁻	0.0012	96.06	118
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.4 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 4:1 at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9942	58.44	58.11
MgCl ₂	0.0401	95.21	3.82
CaCl ₂	0.1603	110.98	17.80
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0012	142.04	0.17
		Total	80.00

Table A.5 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:1 at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	1.0142	22.99	23,316
Mg ²⁺	0.1002	24.30	2,436
Ca ²⁺	0.1002	40.08	4,017
Cl ⁻	1.4113	35.45	50,036
SO ₄ ²⁻	0.0012	96.06	118
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.6 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:1 at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	1.0105	58.44	59.05
MgCl ₂	0.1002	95.21	9.54
CaCl ₂	0.1002	110.98	11.12
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0012	142.04	0.17
		Total	80.00

Table A.7 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:4 at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	1.0304	22.99	23,689
Mg ²⁺	0.1603	24.30	3,897
Ca ²⁺	0.0401	40.08	1,607
Cl ⁻	1.4276	35.45	50,611
SO ₄ ²⁻	0.0012	96.06	118
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.8 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:4 at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	1.0105	58.44	60.00
MgCl ₂	0.1603	95.21	15.27
CaCl ₂	0.0401	110.98	4.45
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0012	142.04	0.17
		Total	80.00

Table A.9 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 0:1 at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	1.0412	22.99	23,938
Mg ²⁺	0.2004	24.30	4,872
Ca ²⁺	0	40.08	0
Cl ⁻	1.4384	35.45	50,995
SO ₄ ²⁻	0.0012	96.06	118
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.10 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 0:1 at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	1.0375	58.44	60.64
MgCl ₂	0.2004	95.21	19.08
CaCl ₂	0	110.98	0
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0012	142.04	0.17
		Total	80.00

Table A.11 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 and half amount of Sulfate ion compared to original brine at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9874	22.99	22,701
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.3858	35.45	49,130
SO ₄ ²⁻	0.0006	96.06	59
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.12 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 and half amount of Sulfate ion compared to original brine at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9849	58.44	57.56
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0006	142.04	0.09
		Total	80.00

Table A.13 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 and double amount of Sulfate ion compared to original brine at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9866	22.99	22,682
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.3813	35.45	48,971
SO ₄ ²⁻	0.0025	96.06	237
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.14 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 and double amount of Sulfate ion compared to original brine at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9804	58.44	57.30
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0025	142.04	0.35
		Total	80.00

Table A.15 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 5 times compared to original brine at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9850	22.99	22,646
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.3723	35.45	48,653
SO ₄ ²⁻	0.0062	96.06	591
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.16 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 5 times compared to original brine at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9714	58.44	56.77
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0062	142.04	0.87
		Total	80.00

Table A.17 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 10 times compared to original brine at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9824	22.99	22,585
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.3574	35.45	48,122
SO ₄ ²⁻	0.0123	96.06	1,183
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.18 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 10 times compared to original brine at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.9565	58.44	55.90
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0123	142.04	1.75
		Total	80.00

Table A.19 Amount of each ion in brine with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 50 times compared to original brine at total salinity of 80,000 ppm

Component	Mole	Molecular Weight	Mass (ppm)
Na ⁺	0.9612	22.99	22,097
Mg ²⁺	0	24.30	0
Ca ²⁺	0.2004	40.08	8,033
Cl ⁻	1.2377	35.45	43,879
SO ₄ ²⁻	0.0616	96.06	5,914
HCO ₃ ⁻	0.0013	61.02	77
		Total	80,000

Table A.20 Amount of each chemical with ratio of Calcium ion to Magnesium ion = 1:0 and amount of Sulfate ion 50 times compared to original brine at total salinity of 80,000 ppm

Chemical	Mole	Molecular Weight	Mass (Gram)
NaCl	0.8368	58.44	48.90
MgCl ₂	0	95.21	0
CaCl ₂	0.2004	110.98	22.25
NaHCO ₃	0.0013	84.01	0.11
Na ₂ SO ₄	0.0616	142.04	8.74
		Total	80.00

APPENDIX B

Acid oil Preparation

In this study, acid oil is used in both aging and flooding process in order to alter the original wettability of carbonates and the value of acid number (AN) is used in order to indicate the acidity of acid oil. Therefore, the methodology for oleic acid quantity determination is described in this section in order to accurately prepare the acid oil with desirable acid number.

First, the definition of acid number (AN) is expressed in the following equation:

$$AN = \frac{56.1 \times c_{KOH} \times V_{KOH}}{m_{pure\ oil}} \quad (B.1),$$

where c_{KOH} is the concentration of the potassium hydroxide solution in unit of mole per litre, V_{KOH} is the volume of potassium hydroxide solution required for titration with acid oil in unit of millilitres and in this study $m_{pure\ oil}$ is the mass of Dodecane in unit of gram.

And, from chemical equation for titration and definition of solution concentration, the mass of oleic acid (m_{oleic}) can be expressed as

$$m_{oleic} = \frac{c_{KOH} \times V_{KOH}}{1000} \times MW_{oleic} \quad (B.2),$$

where MW_{oleic} is the molecular weight of oleic acid which is equal to 282.46 g/mol.

Therefore, from equation B.1 and B.2, the mass of oleic acid (m_{oleic}) can be rearranged as

$$m_{oleic} = \frac{\left(\frac{AN \times m_{pure\ oil}}{56.1}\right)}{1000} \times 282.46 = 0.005035 \times AN \times m_{pure\ oil} \quad (B.3).$$

For example, in order to prepare acid oil with acid number of 5.0, 25.17 grams of oleic acid has to mix with 1,000 g of Dodecane. Moreover, the mixture between 5.03 grams of oleic acid and 1,000 g of Dodecane will have acid number of 1.0.



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