EFFECTS OF FORMATION BRINE COMPOSITIONS ON EFFECTIVENESS OF LOW SALINITY BRINE INJECTION IN CARBONATE RESERVOIR

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ผลกระทบขององค์ประกอบของน้ำในแหล่งกักเก็บต่อประสิทธิภาพของกระบวนการฉีดอัดน้ำเกลือที่มีความเค็มต่ำในแหล่งกักเก็บคาร์บอเนต

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กระบวนการฉีดอัดน้ำเกลือที่ความเค็มต่ำสามารถทำได้โดยการฉีดอัดน้ำที่เกลือที่มีความเค็มต่ำกว่าความเค็มของน้ำในแหล่งกักเก็บเพื่อเหนี่ยวนำให้เกิดการเปลี่ยนแปลงของสภาพความเปียกผ่านกระบวนการแลกเปลี่ยนไอออนหลายชนิด โดยในงานวิจัยนี้ทำการศึกษาองค์ประกอบของน้ำในแหล่งกักเก็บคาร์บอเนต เนื่องจากในงานวิจัยที่ศึกษาผ่านมาส่วนใหญ่จะมุ่งเน้นศึกษาเฉพาะผลกระทบขององค์ประกอบของน้ำที่ใช้ในการฉีดอัดน้ำเกลือที่มีความเค็มต่ำในแหล่งกักเก็บหินทราย โดยการทดลองในครั้งนี้จะใช้หินโดโลไมต์ซึ่งมีส่วนประกอบของแคลเซียมและแมกนีเซียม ซึ่งไอออนดังกล่าวนี้จะเป็นหนึ่งในตัวชี้วัดที่จะทำการศึกษา กระบวนการวิจัยนี้ประกอบไปด้วยการแทนที่ของเหลวด้วยแรงตามธรรมชาติ การฉีดอัดด้วยอุปกรณ์จำลองการไหลในแหล่งกักเก็บและการไทเทรตสารประกอบเชิงซ้อน โดยการทดลองทั้งหมดถูกนำมาใช้ในการศึกษาผลกระทบขององค์ประกอบของน้ำในแหล่งกักเก็บที่มีต่อประสิทธิภาพของการฉีดอัดน้ำเกลือที่มีความเค็มต่ำในแหล่งกักเก็บคาร์บอเนต

จากผลการทดลองแสดงให้เห็นว่าการฉีดอัดน้ำเกลือที่มีความเค็มต่ำจะมีประสิทธิภาพสูงเมื่อน้ำในแหล่งกักเก็บมีปริมาณแคลเซียมต่อแมกนีเซียมเป็น 1:1 ซึ่งเป็นน้ำเกลือที่มีปริมาณแคลเซียมน้อยที่สุดในการทดลองนี้ เนื่องจากปริมาณแคลเซียมที่ต่ำในน้ำในแหล่งกักเก็บจะทำให้แคลเซียมสามารถแพร่ออกมาในน้ำที่ฉีดอัดเพื่อให้มีปริมาณแคลเซียมเพียงพอในการสร้างสารประกอบเชิงซ้อนแคลเซียมคาร์บอกซิเลท และในขณะเดียวกันแคลเซียมซึ่งเป็นองค์ประกอบของหินยังมีความสามารถเพียงพอในการแพร่ออกจากหิน ซึ่งทั้งสองกระบวนการนี้ส่งผลให้น้ำมันสามารถหลุดออกจากพื้นผิวของหินได้โดยง่าย นอกจากนี้ยังพบว่าสัดส่วนองค์ประกอบของไอออนประจุคู่ต่อไอออนประจุเดี่ยวเท่ากับ 1:3 จะส่งผลให้การฉีดอัดน้ำเกลือที่มีความเค็มต่ำมีประสิทธิภาพสูงเช่นกัน เนื่องจากขนาดของโมเลกุลที่ล้อมรอบด้วยน้ำของไอออนประจุเดี่ยวนั้นเล็กกว่าของไอออนประจุคู่จึงยึดติดกับพื้นผิวของหินได้ง่าย ส่งผลให้หินมีสภาพความเปียกด้วยน้ำมันมากยิ่งขึ้น น้ำมันจึงยากต่อการหลุดออกจากหิน ความเร็วในการอัดฉีดต่ำเท่ากับ 0.2 ลูกบาศก์เซนติเมตร/นาทีซึ่งเป็นอัตราการฉีดอัดต่ำสุดในการฉีดอัดน้ำเกลือที่มีความเค็มต่ำส่งผลให้ประสิทธิภาพของการฉีดอัดน้ำเกลือนั้นเกิดขึ้นได้อย่างดีเนื่องจากไอออนจะมีเวลามากพอในการเกิดกระบวนการแลกเปลี่ยนระหว่างไอออนหลายชนิดบนพื้นผิวของหิน อีกทั้งผลการทดลองยังชี้ให้เห็นว่าเมื่อใช้อุณหภูมิที่สูงในกระบวนการฉีดอัดน้ำเกลือนั้นจะทำให้ได้ปริมาณน้ำมันในการผลิตเพิ่มมากขึ้น โดยผลการทดลองนี้ยังสามารถยืนยันได้จากการไทเทรตสารประกอบเชิงซ้อน ซึ่งแสดงให้เห็นปริมาณที่ลดลงของแมกนีเซียมไอออนในน้ำขาออกของอุปกรณ์จำลองการไหลในแหล่งกักเก็บเนื่องจากมีการสร้างสารประกอบคาร์บอกซิเลทของแมกนีเซียมเกิดขึ้น

ภาควิชา วิศวกรรมเหมืองแร่และปิโตรเลียม ลายมือชื่อนิสิต ....

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SUTHIDA MEEKANGWAL: EFFECTS OF FORMATION BRINE COMPOSITIONS ON EFFECTIVENESS OF LOWSALINITY BRINE INJECTION IN CARBONATE RESERVOIR. ADVISOR: FALAN SRISURIYACHAI, Ph.D., 71 pp.

Low Salinity WaterFlooding (LSWF) has been intensively studied in worldwide. The method is simply performed by injecting water with much lower salinity compared to formation brine in the reservoir to induce wettability alteration through multi-component ion exchange mechanism. In this study, ionic ratios of formation water in carbonate reservoir is investigated as most study only emphasize on effects of ion composition in injected water and most explanations are already available for sandstone reservoir. Experiments are performed with dolomite rock as it contains both calcium and magnesium ions and ratio of both ions in formation water is one of study parameters. Spontaneous imbibition test, coreflood test and complexometric titration are performed to investigate effects of ion composition in formation brine on effectiveness of LSWF.

The results show that LSWF is effective when formation brine contains calcium ion to magnesium ion ratio of 1:1 which is the least portion of calcium ion in this study. This ratio allows calcium ion to diffuse to injected low salinity water and adequate amount of calcium ion can still form calcium carboxylate complex and at same time, dissolution of calcium from rock surface is facilitated. Hence, oil is easily liberated from both mechanisms. The ratio of divalent ion to monovalent ion of 1:3, which is the smallest amount of monovalent ion is the most effective formation brine for LSWF. As hydrated size of monovalent, which is much smaller than that of divalent ions, surface is easily adhered by oil, leading to a more oil-wet condition and hence oil can be difficultly liberated. Small injection rate is an appropriate condition for LSWF. In this study, injection rate of 0.2 cm^3/min, which is the smallest value, yields the best benefit of LSWF as potential determining ions have more time to complete multi-component ions exchange mechanism onto rock surface. In addition, the highest oil recovery is obtained at high temperature. A confirmation of complexometric titration showing disappearance of magnesium ion in effluent explains the oil recovery mechanism by means of forming magnesium carboxylate complex at high temperature.

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LIST OF ABBREVIATIONS

AN	Acid Number
M^{2+}	Divalent ion
EBT	Eriochrome Black T
EDTA	Ethylenediaminetetraacetic acid
HSLF	High Salinity Waterflooding
HNB	Hydroxynaphthol Blue
LSWF	Low Salinity Waterflooding
OOIP	Original Oil in Place
PV	Pore Volume
pH	Potential of Hydrogen
WOR	Water Oil Ratio

LIST OF NOMENCLATURES

μ	Viscosity
ΔP	Pressure difference
ϕ	Porosity
K	Absolute permeability in Darcy's equation
A	Area
x	Distance
Q	Flow rate
f_w	Fractional flow of water
S_{wi}	Irreducible water saturation
L	Length
S_{or}	Residual oil saturation
t	Time
q_t	Total flow rate
S_w	Water saturation

CHAPTER 1

INTRODUCTION

1.1 Background

Oil productions are generally achieved by means of three recovery methods including primary, secondary, and tertiary recoveries. During the phase of primary recovery, oil is produced by natural forces stored inside the reservoir, whereas in secondary recovery, additional processes are performed to maintain reservoir pressure in order to prolong the production time. The secondary recovery techniques include conventional waterflooding and immiscible gas injection. Most reservoirs foreseen to encounter difficulties of recovering oil by means of previously mentioned techniques are usually aim to perform the tertiary recovery. This recovery technique is implemented by injecting absent materials into the reservoir to create oil recovery mechanisms beyond pressure maintenance or physical displacement process.

From literatures, waterflooding has been considered as one of the most effective methods for improving oil recovery based on availability of water as well as low investment cost. Moreover, reservoirs with moderate to light oil also exhibit good results due to favorability of mobility ratio when performing waterflooding. However, complexity of water, oil, and rock system sometimes causes waterflooding unable to exhibit the maximum capacity of producing oil to reach residual oil saturation. This indicates that the extension of waterflooding is necessary. In recent years, one of the most attractive modified techniques for waterflooding is Low Salinity Waterflooding (LSWF). The technique has been proven to recover more oil compared to conventional high salinity waterflooding. Principally, LSWF is performed by injecting water containing low ionic strength compared to that of formation water to create interaction at the rock surface. The new surface equilibrium is attained and wetting condition is shifted toward a more favorable condition for oil production.

In the past decade, LSWF is numerously studied in sandstone reservoirs and many studies have shown satisfactory. Several oil recovery mechanisms for sandstone reservoir were suggested including fine migration, increase in pH and in-situ saponification, Multi-component Ions Exchange (MIE), mineral dissolution, and Double Layer Expansion (DLE) [1]. Nevertheless, carbonate reservoirs which contribute more than half of the world's oil reserves, have been rarely investigated for application of LSWF. From current study, wettability alteration is a significant mechanism in LSWF. Wettability can be changed due to the presence of potential wettability modifiers comprising SO_4^{2-}, Ca^{2+}, K^+, Na^+, and Mg^{2+}. Multi-component Ion Exchange (MIE) at carbonate rock surface occurs from presence of SO_4^{2-} in the injected water, competing with adsorbed acid groups in the oil molecules. At the same time, adequate amount of divalent cations which are Ca^{2+} and Mg^{2+} will attract polar compounds in oil released from rock surface to form calcium or magnesium carboxylate complexes and eventually the whole compound is released from rock surface, resulting in more water-wet surface which is a more favorable condition [2, 3]. Most studies of LSWF in carbonate reservoir only focus on compositions of injected brine as a major cause of wettability alteration. As part of surface system, formation water should be thoroughly investigated since it could control several mechanisms and it could be essential factor affecting the efficiency of LSWF.

In this study, the different compositions of synthetic formation brine are studied in carbonate rocks by means of coreflood tests to assess the impact of ion compositions and concentration of formation water on wettability and effectiveness of LSWF technique in dolomitic formation.

1.2 Objectives

To assess effects of formation brine compositions including calcium ion and magnesium ion on effectiveness of low salinity brine injection in carbonate reservoir.

To evaluate suitable conditions of low salinity waterflooding in dolomite reservoir.

CHAPTER 2
LITERATURE REVIEWS

The overview of interaction between seawater and rock surface was studied by Austad et al. [2]. Based on spontaneous imbibition tests, seawater can recover more oil since the ions in brine modified the wettability of rock toward water-wet condition. The potential determining ions including calcium ion (Ca^{2+}.), magnesium ion (Mg^{2+}.), and sulfate ion (SO_4^{2-}) in seawater play important roles in wettability alteration on rock surface, especially on carbonate rock. The mechanism starts when Sulfate ion is adsorbed onto carbonate surface, leading to excess calcium ions near the rock surface. This calcium ion bonds with the negative charge which is carboxylic group (-COO-) in oil. Thus, oil is removed from the surface. At higher temperature, magnesium ion is also able to displace calcium ion and bonds with carboxylic group.

After assessing the impact of calcium ion and sulfate ion on the wettability alteration, Zhang et al.[3] continued their work by focusing on magnesium ion, one of the potential determining ions which is believed to have ability in modifying wettability of rock. The experiment was performed by coreflooding method and spontaneous imbibition technique. For coreflooding test, the cores were slowly saturated with brines which have varied of the concentration of potential determining ions. Then, the amounts of calcium ion and magnesium ion at the rock surface were determined by using chromatography and the effluent was collected by a fractional collector for further chemical analyzing. For imbibition tests, the cores were saturated with initial water. Then, cores were flooded with oil by using Hassler core holders and aged at different temperatures. The experiments demonstrated that magnesium ion is also a potential determining ion for chalk by replacing calcium ion on the rock surface at high temperatures. In conclusion, seawater which consists of calcium ion, magnesium ion and sulfate ion is able to improve oil recovery from carbonate reservoir.

Romanuka et al.[4] worked on enhance oil recovery process with low salinity brine by using Amott spontaneous imbibition test. The dolomite and limestone cores were saturated with formation water to restore initial water saturation. Then, cores are displaced by oil to simulate initial oil saturation. In a spontaneous imbibition process, the cores were placed in Amott cell to start the imbibition test with various synthetic brine formulas at different temperatures. The results of this experiment demonstrated that the wettability alteration of carbonate rock related with ionic composition and ionic strength of the brine. The lower ionic strength of brines induced the higher oil recovery so, the laboratory evidence can be used to confirm that low salinity brine is effective for enhance oil recovery process.

Mohanty and Chandrasekha [1] investigated the impact of brine compositions on wettability alteration by means of contact angle method, imbibition test, coreflood test and ion analysis at high temperature. The experiments which were performed at 120°C demonstrated that synthetic seawater containing magnesium ion and sulfate ion is able to change wettability on the carbonate surface from oil-wet to a more water-wet condition. In contrast, seawater containing calcium ion alone without magnesium ion and Sulfate ion could not cause the change in wettability so, the multi-component ion exchange was the main concept of wettability alteration in carbonate reservoir. According to the laboratory results, injecting the modified seawater with high Sulfate ion and diluted seawater induced the improvement of oil recovery from 40% to 80% OOIP.

In the study of Alotaibi et al.[5], wettability of carbonate (dolomite and calcite) rocks was determined by using contact angle and Amott imbibition methods. Moreover, by using coreflooding, the optimum brine salinity for enhancing oil recovery could be obtained. The brines using in this study were formation brine, seawater, aquifer water, and de-ionized water. Based on contact angle test, aquifer water, seawater, and de-ionized water changed the wettability of carbonate rock from oil-wet to water-wet condition while formation brine provided only intermediate wet. In the part of spontaneous imbibition method, the various brines were filled to the Amott cell at 194°F. Formation brine produced 19.5% oil, whereas seawater gave 23.8% of oil production. At ambient temperature, formation brine recovered 27.85% of oil after five days. According to coreflood experiments, injecting aquifer water after formation brine increased higher oil recovery than seawater following by aquifer. In summary, carbonate rocks were oil-wet when seawater or formation brine were applied and became more water-wet when aquifer or deionized water was applied. Moreover, the results demonstrated that seawater can recovered more oil from carbonate reservoir.

From the chosen literatures it can be seen that injected water plays important role in controlling effectiveness of low salinity waterflooding in carbonate reservoir. However, none of these literatures has investigated impact of formation water. Therefore, this study aims to fulfill this missing gap in order to complete the understanding of ion behaviors from both formation and injected brines in carbonate reservoir. Moreover, understanding effects from formation brine which is uncontrollable parameter would also provide a guideline for choosing candidate fields to implement the low salinity waterflooding technique.

CHAPTER 3
THEORY

3.1. Waterflooding and Effects of Rock Wettability on Waterflood Behavior

Waterflooding, which is one of the most well-known secondary recovery processes, is performed by injecting water into the reservoir to maintain reservoir pressure. Thus, longer period of oil production is obtained without interference of liberated solution gas due to pressure difference between reservoir and production well is prolonged. The behaviors of waterflooding process are mainly controlled by wettability of rock. It is commonly known that waterflooding process is more effective in a water-wet reservoir than oil-wet reservoir as oil recovery factor is independent from number of water injected. Nevertheless, water/oil viscosity ratio must be considered since this ratio demonstrates effects on fractional flow in porous media containing oil and water.

Reservoir rock surface is originally water-wet condition as it is deposited in aqueous environment (e.g. sea, marine, and lake). However, wettability can be altered by inducing material during oil migration process. When rock surface becomes more oil-wet, surface tends to be adhered by oil, resulting in increment of relative permeability to water. Water will flow more rapidly compared to oil so, the earlier breakthrough usually occurs in oil-wet, causing less oil recovery. Hence, wettability is a significant factor that controls location, flow, and spatial distribution of fluids in the reservoir and therefore, it strongly affects behavior of displacement mechanisms by water.

In a water-wet reservoir, water will occupy small pores and forms a thin film on the rock surfaces, whereas oil will occupy centers of the larger pores. During a waterflooding process in water-wet system with moderate oil-water viscosity ratio, water moves through porous media in a uniform front. The injected water tends to imbibe into small or medium pore sizes, pushing oil forward to the larger pores where it is easily displaced. Thus, oil is moving ahead of water front until the breakthrough. Then, there is only little or no oil production after water breakthrough. The existing of disconnected residual oil can be divided into two forms which are small spherical globules in the center of the large pores and the larger patches of oil extending over many pores that are completely surrounded by water.

In oil-wet systems, rock surface prefers to contact with oil so, the position of oil and water are opposite from the water-wet systems. Oil is normally located in the smaller pores or formed as thin film covering rock surfaces, while water is located in the centers of the large pores. A waterflooding process in strongly oil-wet reservoirs is usually less efficient than in the water-wet systems. When water enters oil-wet porous medium, water will form continuous channels through the centers of larger pores, pushing oil out in front of it. As water is continuously injected, water will invades the smaller pores, leading to an increment of Water-Oil Ratio (WOR) and then, oil will flow at very small rate.

Factors controlling waterflooding process can be categorized as; (1) oil-in-place at the start of waterflooding process (2) areal sweep efficiency (3) vertical sweep efficiency and (4) displacement Sweep Efficiency

Buckley and Leverett [6] expressed the theory which is widely and simply used to describe the fluid displacement in an immiscible displacement process. The displacing fluids are usually gas and water. In most fields, oil is trapped in the reservoir and is displaced by the injected water. Thus, a basic understanding of an immiscible displacement of injected water in porous media was contributed as the fractional flow theory which based on the following assumptions: 1) flow is linear and horizontal; 2) water is injected into an oil reservoir; 3) oil and water are both incompressible; 4) oil and water are immiscible to each other; and 5) effects from gravity and capillary pressure are negligible.

According to the mentioned assumption, the Buckley-Leverett frontal advance equation is derived as:

$$\left(\frac{dx}{dt}\right)\left(S_W\right) = -\frac{q_t}{A\varphi}\left(\frac{df_W}{dS_W}\right)\left(S_W\right) \qquad (3.1)$$

This equation can be used to estimate the rate at which injected water moves through a porous media.

3.2. Characteristics of Carbonate Rock

Carbonate rock are mainly formed by chemical and biochemical precipitations in specific environment. Carbonates are anionic complexes of carbonate (CO_3^{2-}) and divalent metallic cations such as calcium (Ca), magnesium (Mg), Iron (Fe), manganese (Mn), zinc (Zn), barium (Ba), strontium (Sr), and copper (Cu). The breakdown chemical reaction normally takes place by acid on limestones which fizzes rapidly than on dolomites. Carbonates are founded naturally as sediments and reefs in oceans. Grains of carbonate can be divided into skeletal and non-skeletal. Skeletal grains compose of calcareous plants and animals such as mollusks, corals, calcified algae, brachiopods, arthropods, and echinoderms. Non-skeletal grains include ooids, pisoids, peloids, and clasts. Porosity of carbonate rock is usually about 5-15% but can be up to 40-70% in carbonate sediment. Carbonate reservoirs have a high value of separate vuggy porosity and have more secondary porosity than primary porosity. The major sources of secondary porosity are fracturing, solution, and chemical replacement [7]. The most abundant carbonate minerals are calcite ($CaCO_3$) and dolomite ($Ca,Mg(CO_3)$) which are in the hexagonal form. The secondary minerals in carbonate rocks include anhydrite, chert, and quartz. Calcite is polymorphs of calcium carbonate. Dolomite is different form calcite since it has magnesium ions in the structure. The two main rock types of carbonate reservoirs in the world are composed of calcite and dolomite called limestones and dolomites, respectively. Limestones composed of more than 50% carbonates, of which more than half is calcite while dolomites composed of 50% carbonates, of which more than half is dolomite. Dolomite can be precipitated directly from a solution containing magnesium, calcium, and carbonate ions. This type of rock can also be altered from limestone or calcareous mud and can perform better reservoirs than calcite because it can form large crystals structures. Dolomitization is an important geochemical process, where magnesium ions replace calcium ions and form dolomite as illustrated in an equation:

$$2CaCO_3 + Mg^{2+} \longrightarrow CaMg(CO_3) + Ca^{2+} \tag{3.2}$$

The porosity of dolomite is increased because of replacement of calcium ion by magnesium ion (magnesium ion is smaller than calcium ion). On the contrary, porosity decreases as the clay content of limestone increases [8].

3.3. Wettability Alteration in Carbonate Formation

Wetting conditions of carbonates are dependent on the pH of the equilibrium brine, temperature of the reservoir, crude oil properties (e.g. acid-base number or AN and BN), and composition of the equilibrium brine (e.g. potential determining ions (Ca^{2+}, CO_3^{2-}, and SO_4^{2-}) which are not independent on each other).

3.3.1. pH of the equilibrium brine

Calcium carbonate, in the carbonate formation, has the great buffer capacity so that the pH in reservoirs is quiet constant between 7 and 8. The great changes in pH are not provided that the system (oil/brine/formation) is in chemical equilibrium. Wettability alterations, which occurred through change of pH, are not permanent. Calcite surface has normally positive charge below pH 9.5 while oil-water film has negative charge because of carboxylic acids in the crude oil. Then, the water-film between rock and oil is instable, leading to the contact of oil and surface. Thus, the acid number, AN, of the crude oil is considered to be important factor for wetting state of carbonate reservoir as water wetness decreases when acid number increases.

3.3.2. Temperature and crude oil.

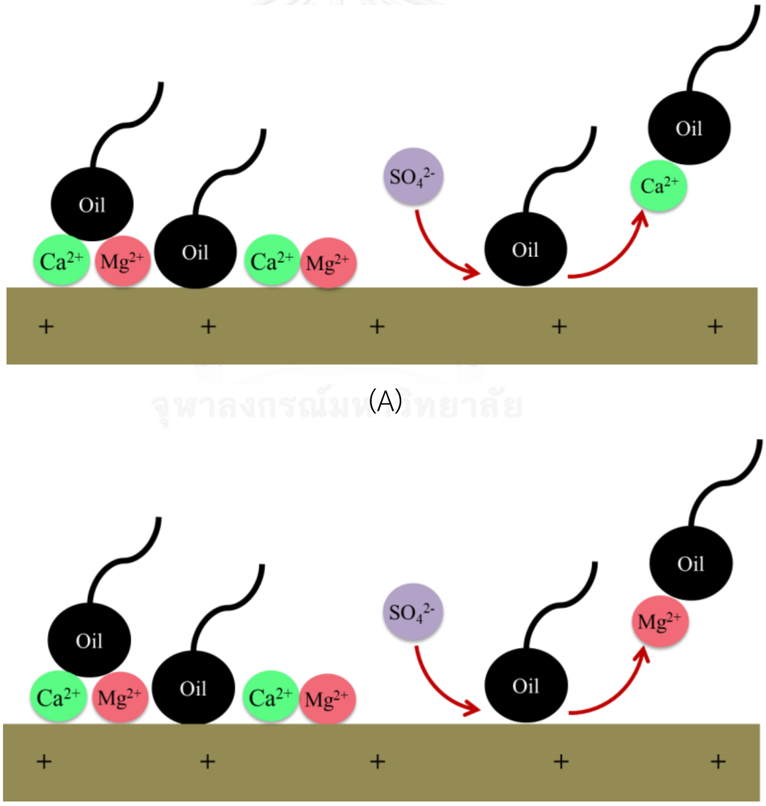
The water-wetting increases as temperature increases but the carboxylic group decomposes and so, the acid number decreases. Therefore, temperature and acid number are not independent on wetting parameters. Moreover, many types of clay minerals obviously act as catalyst in the decarboxylation process, especially, $CaCO_3$.

3.3.3. Potential determining ions

Potential determining ions affect the charge type and charge density on the rock surfaces due to adsorption process. Initially, reservoir rock is saturated with water. Then, oil moves into reservoir rock, displacing water. In the pH range about 3-9, oil-water interface will be negatively charged while the carbonate water interface will be positively charged. The water film will become instable, leading to absorption of crude oil onto rock surface so water-wetness will reduced. If the concentration of sulfate ion in water is much higher than calcium, the stability of water film will be increased from the electrostatic point of view due to adsorption of sulfate onto carbonate surface.

The most important wetting parameter for carbonates is the acid number (AN) which quantifies amounts of carboxylic acids in crude oil. Acid number normally decreases as reservoir temperature decreases. At natural pH, initial interface between carbonate surface and water is positively charged due to the high concentration of calcium ions in the formation brine while the interface between oil and water is negatively charged due to the carboxylic in the crude oil. Thus, the disjoining pressure in the water film becomes negative, and oil will contact the carbonate surface where strong bonds are formed.

Many researches on carbonate reservoirs demonstrated that composition of injected brine affects rock wettability and provides more oil recovery. The divalent ions in brine including calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}) and sulfate ion (SO_4^{2-}) were considered as potential determining ions since they are competing with the acid group in the crude oil to attach onto surface of carbonate rocks. Then, the wettability starts to change from oil-wet to water-wet condition. Moreover, high temperature accelerates mechanism and increases activity of Mg^{2+} because of the displacement of Mg^{2+} to Ca^{2+} as demonstrated in Figure 3.1 [1].



(A)

(B)

Figure 3.1 Schematic model of the suggested mechanism for the wettability alteration induced by seawater. (A) Proposed mechanism when Ca^{2+} and SO_4^{2-} temperature are active at lower temperature. (B) Proposed mechanism when Mg^{2+} and SO_4^{2-} are active at higher temperature.

3.4. Brine Composition of Carbonate Formation

In recent years, brine composition of carbonate formation has been considered as a significant factor that can affect wettability modification of rock surface which could lead to more oil recovered from reservoir. Thus, various compositions of brine have been modified and applied in order to study enhanced oil recovery process. According to several researches, both formation brine and injected brine (seawater) can cause carbonate dissolution and mineralogical changes over a certain range of temperature. Normally, ions that exist in aquifer, seawater, or formation brines are hydrogen ion (H^+), calcium ion (Ca^{2+}), hydrogen carbonate ion (HCO_3^-), sodium ion (Na^+), magnesium ion (Mg^{2+}), chloride ion (Cl^-), and sulfate ion (SO_4^{2-}). Example of the formulation of aquifer water, seawater, and formation brine are in the table 1.

Table 1: Compositions for formation brine and seawater used in experiments [1, 9, 10]

Ionic species (ppm)	Fathi et al.[9]		Gupta et al.[10]		Mohanty, Chandrasekhar[1]	
	FB	SW	FW	SW	FW	SW
Na^+	10,350	23,000	51,820	10,345	49,933	13,700
Ca^{2+}	1,160	520	15,992	521	14,501	521
Mg^{2+}	192	1,080	1,282	1,094	3,248	1,620
K^+	195	390	0	392	0	0
Cl^-	18,637.5	37,985	111,717	18,719	111,810	24,468
SO_4^{2-}	0	2,304	0	2,305	234	3,310
HCO_3^-	567	126	391	0	0	0
TDS	62,800	33,390	181,202	33,375	179,730	43,619

From the table, it can be observed that concentration of calcium ion is much higher than magnesium ion in formation brine because calcium carbonate can be dissolved faster than the magnesium carbonate. Moreover, since carbonate rock has less amounts of clays which are source of potassium ions so concentration of potassium ion, sulfate ion and hydrogen carbonate ion can also be present in trace amount or can be absent in formation brine. Nevertheless, majority of ions in formation water are chloride ion and sodium ion for anion and cation, respectively. According to the formation brine information, many researchers focused on injecting low salinity brine to carbonate reservoirs to improve oil recovery by using various methods to confirm the results such as coreflooding, contact angle and interfacial tension measurements. All of the results from the laboratory demonstrated that low salinity brine can increase oil recovery in the carbonate reservoirs by means of altering wettability from oil-wet to water-wet condition.

CHAPTER 4

METHODOLOGY

In this study, the experiment is divided into four parts which are determination of basic parameters, imbibition test, coreflooding test, and complexometric titration. The compositions of formation brines, which are investigated parameter, are varied during imbibition and some formulations are selected for coreflooding tests. In addition, injection rate and temperature are also studied for low salinity waterflooding in carbonate reservoir performed by coreflooding test.

4.1. Determination of basic parameters

4.1.1. Petrophysics parameters

In this study, outcrop Silurian dolomite is selected to represent carbonate reservoir. Petrophysics parameters of core samples including absolute permeability, porosity, pore volume, irreducible water saturation, and residual oil saturation are determined by means of coreflooding apparatus. Figure 4.1 illustrates physical appearance of Silurian dolomite core samples.

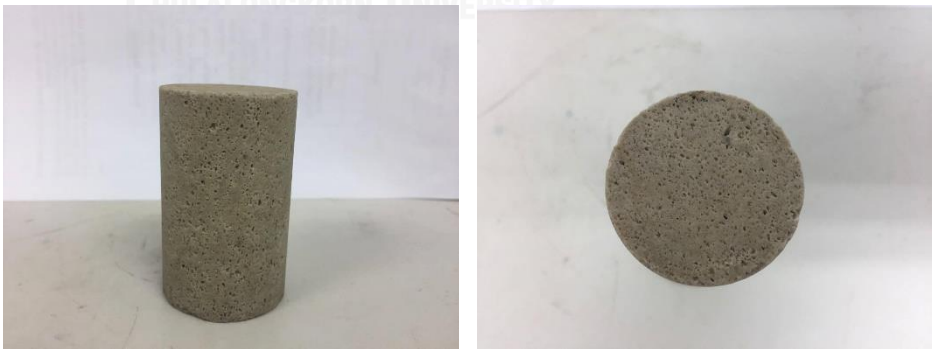


Figure 4.1 Outcrop Silurian dolomite core sample

4.1.1.1. Absolute permeability

Absolute permeability can be evaluated by using coreflooding equipment. First, core sample is placed into core holder at temperature of 30 degree Celsius and confining pressure of 2,500 psi. Second, formation brine with salinity of 160,000 ppm is injected into core sample until difference of pressure inlet and pressure outlet (***ΔP***) is stable. After ***ΔP*** of first injection rate is stable, injection rate is raised to other rates varying from 2 to 8 cm^3/min until ***ΔP*** is stable in each rate in order to assure that core is fully saturated. Once core sample is fully saturated, ***ΔP*** data can be used to calculate for absolute permeability using Darcy's equation:

$$k = \frac{q\mu L}{A\Delta P} \quad (4.1),$$

where *k* is absolute permeability in Darcy, *q* is flow rate in cm^3/sec, μ is viscosity in centipoise, *L* is length of core sample in cm, *A* is cross-sectional area of core sample in cm^2 and ***ΔP*** is pressure difference in atm.

4.1.1.2. Porosity of rock

Porosity is a value of void in rock sample which can be successfully obtained from dividing the difference from weight of dry and fully saturated core sample by density of saturating fluid

4.1.1.3. Pore volume

The value of pore volume is obtained from multiplying bulk volume by porosity in fraction. Bulk volume is simply calculated from volume of cylindrical shape where length and diameter of core sample are directly measured by Vernier caliper and porosity is obtained from 4.1.1.2.

4.1.1.4. Irreducible water saturation

After the core sample is placed into core holder and fully saturated by formation brine until it is fully saturated, dodecane with acid number (AN) of 5 is followed immediately. Again, oil injection rate is varied in several steps from 2 to 8 cm^3/min and changing of injection rate is performed when ΔP obtained from each rate is stable. Then, the recoverable volume of formation brine collected from oil injection is equivalent to initial oil in place. Therefore, irreducible water saturation is calculated from the equation below;

$$Swi = \frac{PV - re\cos erablewater}{PV} \qquad (4.2),$$

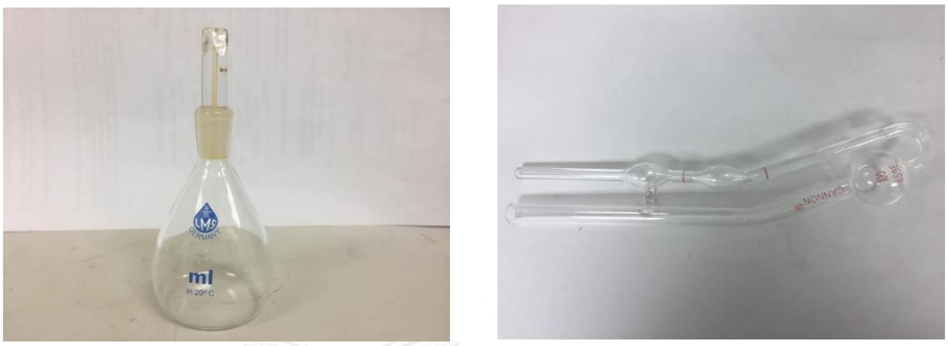
where S_{wi} is irreducible water saturation and PV is pore volume in cm^3.

4.1.1.5. Residual oil saturation

Residual oil saturation can be determined after waterflooding phase. Thus, after sample is fully saturated with brine follow by dodecane, core is aged for one whole week prior to waterflooding phase to ensure completion of wettability alteration. Brine injection rate is varied in steps until ultimate oil recovery is attained. Therefore, oil that is left in core sample after waterflooding process is acted as residual oil saturation (S_{or}).

4.1.2. Basic properties of brines

Properties of brines including density and viscosity can be determined by means of pycnometer (figure 4.2a) and Cannon-Fenske viscometer tube (figure 4.2b), respectively.



(a) (b)

Figure 4.2 Equipment for measuring density and viscosity (a) Pycnometer (b) Cannon-Fenske viscometer

4.2. Imbibition test

4.2.1. Preparation of formation brine

Formation brine is prepared from the selected formation brine of carbonate reservoirs around the world with average concentration of 160,000 ppm. For various types of brine, amount of divalent ions and monovalent ion are adjusted. The study can be divided as:

4.2.1.1. Effects of the ratio between calcium ion and magnesium ion, mass ratios of divalent Ca^{2+} to Mg^{2+} are varied into four different ratios (1:1, 1:3, 1:10 and 1:15).

4.2.1.2. Effects of portion of divalent ions to monovalent ions, mass ratios of divalent ions (Ca^{2+} and Mg^{2+}) to monovalent ions (Na^{+}) are varied into four different ratios (1:1, 3:1, 10:1, and 15:1)

Table 4.1 Ratio of calcium ion to magnesium ion (Ca^{2+}: Mg^{2+}) and Divalent ions to monovalent ions (Ca^{2+} and Mg^{2+}: Na^{+})

Brines	calcium ion to magnesium ion ratio (Ca^{2+} : Mg^{2+})	Divalent ions to monovalent ions ratio (Ca^{2+} and Mg^{2+} : Na^{+})
Formation brine	1:1	1:1
	3:1	1:3
	10:1	1:10
	15:1	1:15
Injection brine	seawater (35,000 ppm) As low salinity brine	

4.2.2. Preparation of injection brine

In this experiment, seawater with total salinity of 35,000 ppm is used as injection brine in low salinity waterflooding process. Seawater is prepared from combining water with formulation as summarized in table 4.2 which is obtained from average ions in seawater.

Table 4.2 Formulation of seawater preparation for 1 liter

	MW	Mass(g)
$MgCl_2$	95	4.5805
$CaCl_2$	111	1.0231
KCl	74.6	0.5802
NaCl	58.5	21.4758
Na_2SO_4	142	7.165
$NaHCO_3$	84	0.1754
Total		35

4.2.3. Preparation of hydrocarbon

Dodecane is served as synthetic oil which is used for saturating and aging cores. Dodecane with acid number of 5.0 is used for saturating cores in order to ensure total acid adsorption onto rock surface, whereas Dodecane with acid number equal to 1.0 is used for flowing through aged core samples to eliminate remaining acid. Synthetic oils with acid number of 1.0 and 5.0 are obtained by by adding 5.03 and 25.17 g of oleic acid into 1 liter of Dodecane, respectively.

4.2.4. Water saturation stage

After a core sample is cleaned by toluene followed by methanol, the sample is dried in oven at temperature of 70 degree Celsius. Then, core is weighted to measure dry weight and formation brine is injected through core sample by means of coreflooding apparatus with injection rate varied from 2 to 8 cm^3/min until sample is fully saturated. After that, core sample is removed from coreflooding apparatus for weighting brine saturation weight.

4.2.5. Drainage stage

In this stage, fully saturated core with brine is assembled in coreflooding apparatus again and synthetic oil with acid number of 5.0 is injected through core sample to imitate oil migration process with oil injection rate varied from 2 to 8 cm^3/min until no more water comes out from coreflooding process. Maximum volume of water collected from outlet of coreflooding is volume of water displaced by oil and this amount of oil is equivalent to original oil in place. Next, core sample fully saturated with brine and synthetic oil is aged in synthetic oil with acid number of 5.0 for 1 week to complete wettability alteration during drainage process.

4.2.6. Imbibition stage

After 1 week of aging stage, core is soaked in injection water which is seawater until weight of core is stable. As water spontaneously imbibes into core sample to replace synthetic oil, weight of sample is continuously increased. Sample is weighed every 24 hours and sample weight is calculated into fluid saturations.

4.2.7. Calculation

Oil and water saturations of core samples soaked in various formation brines are calculated. Then, results are discussed to select suitable brine formulations for low salinity injection by means of coreflooding apparatus.

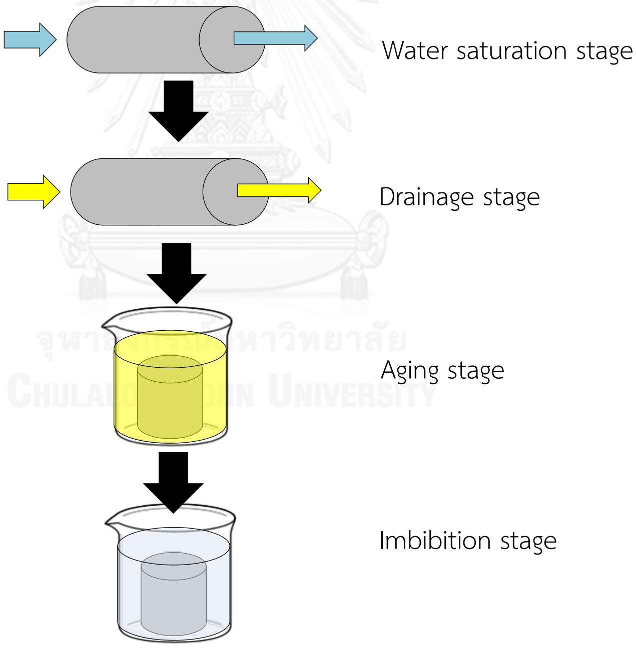


Figure 4.3 Summarizes core preparation process prior to imbibition process

4.3. Coreflooding test

4.3.1. Preparation of formation brine

Formation brine used in coreflooding test is prepared by methodology described in 4.2.1. Only formation brine formulation that yields the highest oil recovery from imbibition process is chosen for coreflooding experiment.

4.3.2. Preparation of injection brine

Injection brine used in coreflooding test is prepared by methodology described in 4.2.2.

4.3.3. Preparation of hydrocarbon

Synthetic oil used in coreflooding test is prepared by methodology described in 4.2.3.

4.3.4. Restoration reservoir condition

Cleaned core sample is initially prepared by injecting chosen formation brine obtained from imbibition process until core is fully saturated; followed by synthetic oil with acid number of 5.0 to restore original oil in place stage. After that, core is aged in oil with acid number of 5.0 for 1 week to complete wettability alteration.

4.3.5. Coreflooding experiment

Coreflooding experiment phase is divided into two parts which are high salinity waterflooding (conventional waterflooding) and low salinity waterflooding. During high salinity waterflooding, formation brine is used as high salinity brine. This process is performed to imitate the idea of reinjection of produced water that has the same salinity of formation brine. After the difference between pressure inlet and pressure outlet attains the constant value and no more oil is recovered, injection brine is switched from high salinity brine to seawater to perform low salinity waterflooding. Figure 4. 4 illustrates essential components of coreflooding apparatus. In low salinity waterflooding phase, other two parameters considerably influenced wettability alterations are also investigated which are:

Injection flow rate: 0.2, 0.4, 0.6 cm^3/min,

Temperature: 30, 50, 70 °C.

4.3.6. Calculation

Oil recovery can be calculated from the imbibition tests and coreflooding experiments. Then, the results are discussed to represent suitable conditions together with appropriate formation brine for low salinity injection.

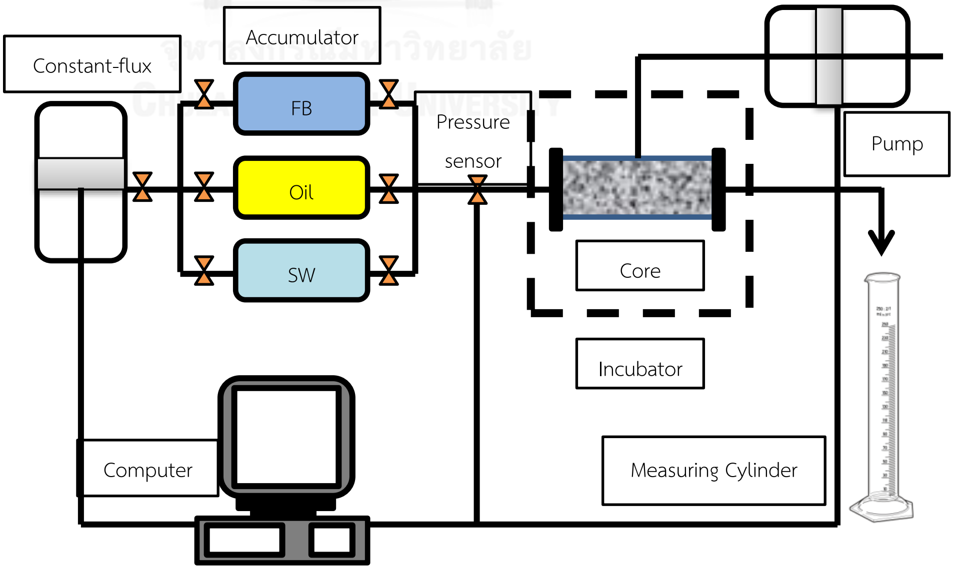


Figure 4.4 Coreflooding apparatus

4.4. Complexometric Titration

Confirmation of the oil recovery mechanisms from coreflooding experiment is performed by using complexometric titration with ethylene diamine tetraacetic (EDTA) to identify the amount of calcium and magnesium in brine before and after low salinity water injection.

4.4.1. Determination of total hardness

10 cm^3 of water sample is taken by pipette into a flask. Then, 2 cm^3 of ammonium chloride-ammonium hydroxide buffer solution and a pinch of Eriochrome Black T (EBT) indicator are added into water sample. After preparation of water sample, the solution is titrated with 0.01 molar EDTA until color changes from red to blue.

4.4.2. Determination of concentration of calcium and magnesium ions

10 cm^3 of water sample is taken by pipette into a flask. After that, 30% w/v of sodiumhydroxide solution (NaOH) is dropped until pH of the solution reaches value of 11. The flask is swirled and stood for 5 minutes to perfectly precipitate magnesium ions. A pinch of hydroxynaphthol blue (HNB) is added into solution as an indicator. Then, the solution is titrated with 0.01 molar EDTA until the color changes from red to blue. Figure 4.5 illustrates chemical equation and changing of color from red to blue color.

4.4.3. Calculation

Concentration of calcium and magnesium ions can be calculated from the result of 4.4.1 and 4.4.2 by the below equations,

- Determining of the concentration of total hardness (Calcium ion and magnesium ion or M^{2+})

$$M^{2+} + \underset{\text{Blue}}{\text{Eriochrome Black T (EBT)}} \xrightarrow{\text{pH 10}} \underset{\text{Red}}{[\text{M-EBT}]} + 2H^{+}$$

$$\underset{\text{Red}}{[\text{M-EBT}]} + \text{EDTA} \xrightarrow{\text{pH 10}} [\text{M-EDTA}] + \underset{\text{Blue}}{\text{EBT}}$$

- Determining of the concentration of calcium ion

$$M^{2+} + \text{NaOH} \xrightarrow{\text{pH 11}} Mg(OH)_{2\,(s)} + Ca^{2+}_{(aq)}$$

$$Ca^{2+} + \underset{\text{Blue}}{\text{Hydroxynaphthol Blue}} \xrightarrow{\text{pH 11}} \underset{\text{Red}}{[\text{Ca-HNB}]} + 2H^{+}$$

$$\underset{\text{Red}}{[\text{Ca-HNB}]} + \text{EDTA} \xrightarrow{\text{pH 11}} [\text{Ca-EDTA}] + \underset{\text{Blue}}{\text{Hydroxynaphthol Blue}}$$

Figure 4.5 A change of color of solution from red to blue

Therefore, the concentration of magnesium ion can be founded by subtract amount of calcium ion from amount of the total hardness.

4.5. Summary of methodology

In this thesis, experiments mainly consist of spontaneous imbibition test and coreflood test. Outcrop Silurian dolomite sample is used for both tests. First, petrophysics properties of rocks are determined. Then, samples are restored reservoir condition by means of coreflood apparatus and soaked in various formulation of formation brine until weight of samples maintain constant. After that, cores are switched to soak in seawater as LSWF until the weighs are stable again. The selected formulations are chosen to perform coreflood test. In the part of coreflood experiment, formulation of brines, injection rates, and temperatures are varied. In addition, complexometric titration is applied for confirm the presence of multi-ions exchange mechanism. In the end, the most effective of brine formula, injection rate, and temperature in order to operate LSWF in dolomite reservoir are identified from the experiments. A summary of overall methodology is demonstrated in figure 4.6.

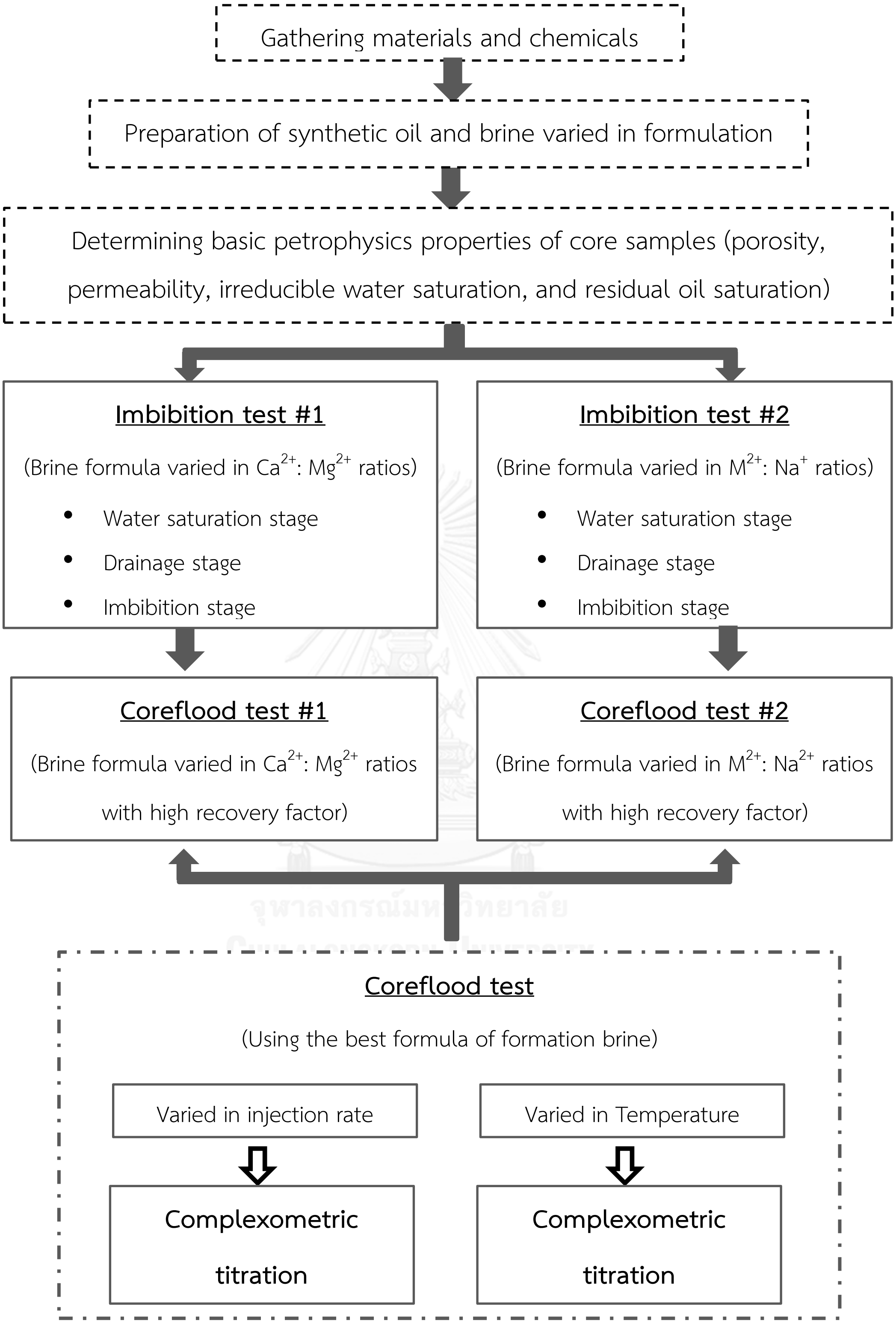


Figure 4.6. Summary of overall process

CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, results from experiments are investigated and discussed. Results are divided into four parts. First, petrophysical properties of core samples are measured and revealed. In this section, properties of fluids used are also included. Second, effect of monovalent ions to divalent ions ratio are investigated. Next, effects of ratio of calcium ion to magnesium ions are studied since these ions which are potential determining ions directly influence multi-ions exchange mechanism in wettability alteration process. Last, results from complexometric titration during coreflood experiment are discussed in order to better understand the oil recovery mechanism during LSWF.

5.1. Rock, Fluids and Petrophysical Properties

Determining petrophysics properties and basic parameters of rock samples as well as fluid samples are particularly important to obtain precise results in the following experiments. Important rock and petrophysical properties in this section compose of absolute permeability, porosity, pore volume, irreducible water saturation, and residual oil saturation. Furthermore, density and viscosity of brine are also identified for the calculation section.

First, Silurian dolomite samples representing reservoir rock which are in cylindrical shape are measured for their length and diameter. Bulk volume is then calculated from the simple calculation since rock sample is perfectly cut. As explained in Chapter 4, cores are cleaned, dried and measured for theirs dry weight prior to the measurement of absolute permeability and porosity. Table 5.1 summarized physical rock data of samples used in this study.

Table 5.1 Rock properties of samples

#core	length (cm)	Diameter (cm)	Bulk volume (cm^3)	Dry weight (g)	permeability (mD)	porosity	Pore volume (cm^3)
3.1	6.25	3.76	69.40	165.17	43.60	0.15	10.20
3.2	6.32	3.76	70.18	174.75	6.16	0.15	10.53
4.1	6.02	3.77	67.20	159.49	28.48	0.17	11.42
4.2	6.54	3.77	73.00	171.95	16.42	0.17	12.41
5.1	6.53	3.77	72.89	170.21	247.96	0.18	13.12
5.2	6.06	3.77	67.65	157.42	435.04	0.18	12.18

According to table 5.1, core samples using in this experiment are various in porosity in a small range between 15-17%. However, absolute permeability is varied in larger range of 6-400 mD. The wide range of absolute permeability depends on the connectivity of pores inside rock matrix and localization of rock particles as well as presences of vugs and fractures which are quite common for carbonate rocks. Therefore, core samples with exceptionally high permeability are used less often to avoid error biased from high permeability value. However, since all the samples are cored from the same location and the major part of the experiment should be mainly affected from chemical composition of rock (imbibition test), effects from difference in permeability may be diminished.

In this experiment, brines are prepared in various formulations so it is important to define density and viscosity of brines in every formulation. As mentioned in Chapter 4, density is measured through the use of pycnometer whereas viscometer measurement is performed by the used of Cannon-Fensk viscometer. Densities of brine and oil are important for calculation of fluid saturations whereas viscosity is important for calculation of absolute permeability. Table 5.2 summarizes fluid density and viscosity for brine with different formulations and oil at various temperatures. From table 5.2, even though salinity of each brine formulation is equal (160,000 ppm) density of brines is slightly different due affinity of each ion with water molecule and this may include slight error in each measurement.

Table 5. 2 Density and viscosity of fluids used in the experiment at various temperatures

Fluids	Ratio	Temperature (^{0}C)	density (g/cm^3)	viscosity (cP)
Calcium ion to Magnesium ion ratio (Ca^{2+}: Mg^{2+})	1:1	30	1.105	1.020
	3:1	30	1.112	1.026
	10:1	30	1.104	1.020
	15:1	30	1.103	1.012
Divalent ions to monovalent ions ratio (Ca^{2+} and Mg^{2+} : Na^{+})	1:1	30	1.108	1.042
	1:3	30	1.093	1.023
	1:10	30	1.104	1.045
	1:15	30	1.106	1.036
Selected formula	Selected	30	1.106	1.149
	Selected	50	1.103	1.141
	Selected	70	1.097	1.126
Dodecane (Acid Number = 5)	-	30	0.745	1.290
	-	50	0.745	1.205
	-	70	0.744	1.104

After knowing rock and fluid properties, petrophysical properties of rocks can be identified. In this study, important petrophysical properties include irreducible water saturation (S_{wi}) and residual oil saturation (S_{or}) which are important to determine Recovery Factor (RF). Table 5.3 summarized irreducible water saturation and residual oil saturation of each core samples. From the table, it can be seen that data are not scattered from each other since the rock compositions and fluids are the same. However, these properties maybe change every time samples are cleaned and therefore, these data will be illustrated again in the following section.

Table 5.3 Irreducible water saturation and residual oil saturation of specific core samples together with information of imbibition test of each core

Test	#Core	S_{wi} (%)	1-S_{or} (%)
Imbibition test of Effect of Calcium ion to Magnesium ion ratio (Ca^{2+}: Mg^{2+})	4.1	37.38	62.62
	4.2	36.65	63.35
	5.1	32.56	67.44
	5.2	30.64	69.36
Imbibition test of Effect of divalent ions to monovalent ion ratio (Ca^{2+}: Mg^{2+})	5.1	51.02	48.98
	5.2	40.59	59.41
	4.2	38.28	61.72
	3.2	33.43	66.57

5.2. Spontaneous Imbibition experiments

The imbibition test is performed to study wettability alteration which is taken place by means of Multi-component Ions Exchange (MIE) mechanism during LSWF. As carbonate reservoirs are mostly oil-wet rock, spontaneous imbibition process cannot be easily occurred. Once rock sample is in contact with water again, different water will show different ability in imbibition. If formation water is used for imbibition process, salinity and chemical composition which are as same as water in rock sample and this results in difficulty in shifting of equilibrium. Hence, imbibition process will occur at very slow rate. But if total salinity and composition are modified to favor oil recovery mechanism by low salinity water, this water will be spontaneously imbibe into rock sample and at the same time, wettability of rock will be altered to a more water-wet condition and imbibition can also be speeded up. As a consequence, more oil production can be achieved. As this study will emphasize more on formation brine and seawater is used to represent low salinity water, formulation of formation brine are varied in 1) ratios of divalent ion and monovalent ion and 2) ratio of calcium ion to magnesium ion to investigate the suitable composition of formation brine that could yield the largest improvement of wettability alteration and gain the highest oil recovery factor by using seawater.

First, ratio of calcium ion and magnesium ion is studied. Since calcium ion is more abundant in formation brine especially in dolomite reservoir, the ratio is varied as 1:1, 3:1, 10:1 and 15:1. Synthetic formation brines are prepared by adding chemicals into distilled water. Initially, average formation brine is generated based on formation brines obtained from carbonate oilfield around the globe. As low salinity waterflooding should be performed when injected water and formation water have difference in salinity, an average total salinity of 160,000 ppm is selected to make such difference from injected water which is seawater. Table 5.3 summarizes composition of formation water used in this study that is averaged from carbonate oilfields. In addition, seawater with average salinity of 35,000 is served as low salinity water in the experiment. The ion compositions of seawater are demonstrated in table 5.4

Table 5.4 Ions compositions of formation brines with various ratios of calcium ion and magnesium ion

Ratios of calcium ion to magnesium ion	**Ions**	**mol/L**	**g/L**	**ppm**
1:1	Na^+	2.0284	46.65	46,653
	Ca^{2+}	0.2004	8.02	8,017
	Mg^{2+}	0.2004	4.87	4,871
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.8227	100.20	100,205

Table 5.4 Ions compositions of formation brines with various ratios of calcium ion and magnesium ion (Continued)

Ratios of calcium ion to magnesium ion	**Ions**	**mol/L**	**g/L**	**ppm**
3:1	Na^+	2.0013	46.03	46,031
	Ca^{2+}	0.3007	12.03	12,026
	Mg^{2+}	0.1002	2.44	2,435
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7956	99.24	99,245
10:1	Na^+	1.9841	45.63	45,635
	Ca^{2+}	0.3644	14.58	14,577
	Mg^{2+}	0.0364	0.89	886
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7784	98.63	98,634
15:1	Na^+	1.9810	45.56	45,564
	Ca^{2+}	0.3758	15.03	15,033
	Mg^{2+}	0.0251	0.61	609
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7753	98.52	98,525

Table 5.5 Ions compositions in seawater

Ions	**mol**	**g/L**	**ppm**
Na^+	0.4701	10.81	10,813
Ca^{2+}	0.0092	0.37	369
Mg^{2+}	0.0482	1.17	1,172
K^+	0.0078	0.30	303
Cl^-	0.4897	17.39	17,386
SO_4^{2-}	0.0505	4.84	4,844
HCO^{3-}	0.0021	0.13	127

Results from spontaneous imbibition test are obtained from soaking core sample saturated in synthetic formation brine and oil in formation brine to imbibe by conventional waterflooding until weight of the samples is stable. This step is performed to remove oil that is mobile by ability of formation brine and moreover, to obtain the baseline prior to imbibition by low salinity water. Then, core samples are continuously switched to soak in seawater as low salinity water and measure weight of core samples until it attains constant value. From weight data, amount of oil displaced by imbibition of brine in core samples can be calculated in a form of oil recovery factor from mass balance of total fluid weight, using different values of fluid density and fixed pore volume. Relationship between oil recovery factor from imbibition by both formation water and seawater showing additional oil recovery factor, as a function of soaking time is illustrated in figure 5.1.

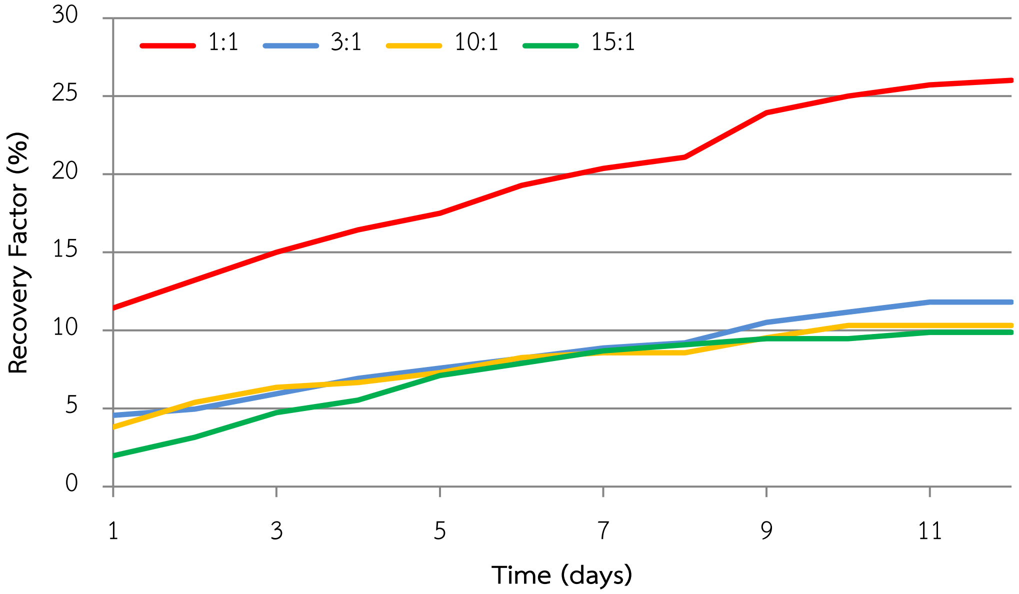


Figure 5.1 Oil recovery factors from imbibition tests for different formation brines with various ratios of calcium ion to magnesium ion as a function of soaking time

According to figure 5.1, weight of core samples is significantly increased as brine imbibes into core sample, expelling oil out. It can be also noticed that oil recovery factor gained from most cases are quite small during imbibition with formation brine as conventional waterflooding except one imbibed with formation brine with formulation of calcium ion to magnesium ion ratio of 1:1. At the end of the conventional waterflooding phase, 21.08% oil recovery is obtained from this case, whereas 9-11% oil recovery factor are obtained from the ratios of 1:1. In addition, after weights of all samples in this part stay constant at the 8th day, it can be obviously observed that the highest improvement of 26.02% oil recovery factor is obtained from the case with calcium ion to magnesium ion ratio of 1:1. The additional oil recovery from low salinity water in this case is 4.93%.

Moreover, it can also be noticed from the figure that the formation brine with the highest amount of calcium ion, oil recovery factor and additional oil recovery is the least since oil is difficultly displaced by both formation brine and seawater. The results from imbibition experiment can explain activity of calcium ion and magnesium ion during LSWF.

Calcium and magnesium ions are considered as important compositions in crystalline structure of carbonate rocks especially for dolomite which represents rock formation in this study. Therefore, dissolution mechanism of both ions depends on quantity of ions in rock matrix itself and also brines. Considering first calcium ion, calcium is considered as one of potential determining ions in wettability alteration mechanism by means of LSWF. The mechanism is started when sulfate ion in injected brine is adsorbed onto rock surface, neutralizing carbonate surface. Then, calcium ion in injected brine starts to bond with carboxylic acid in oil to from calcium carboxylate complex, changing interaction between oil to rock surface into oil-brine. Therefore, attraction between oil and rock surface is lessened and oil can be easily liberated. At the same time, dissolution of calcium ion at rock surface is required in order to liberate adsorbed oil out from surface. The dissolution mechanism can rapidly take place when amount of calcium ion in injected brine is relatively smaller compared to formation brine since this mechanism is attempt to balance the equilibrium of ions between carbonate rock and brines.

In case of high concentration of calcium ion of formation water, these ions will rapidly diffuse to injected water thus total amount of calcium ions in the environment can be rapidly increased. Then, dissolution of calcium ion is obstructed and calcium carboxylate complex cannot be formed as carboxylic acid still form a strong bond with calcium at rock surface. Hence, oil cannot be easily liberated in this case.

Magnesium ion is one of potential determining ions for wettability alteration mechanism in carbonate rock as same as calcium ion but its potential is smaller. Nevertheless, magnesium ion is found to be able to form magnesium carboxylate complex only in high temperature (higher than 70 degree Celsius). Therefore, presence of magnesium ion will not much affect oil recovery mechanism during imbibition test since the test is performed at 30 degree Celsius. However, the case with formation brine containing high portion of magnesium ion equal to calcium ion, dissolution mechanism is still favored to occur as long as amount of calcium ion in both rock surface and injected brine are adequate to form calcium carboxylate complex. Even though dolomite also contains magnesium ion and dissolution of magnesium ion at rock surface may be the least favorable in these all the cases, maximum portion of magnesium in dolomite is 0.5. That means, with formation brine containing calcium ion to magnesium ion ratio of 1:1, both ion still can perform dissolution. However, only calcium ion that is still active in forming of calcium carboxylate complex and this ratio is adequate to induce the mechanism.

Next, effect of monovalent ion is investigated. Formation brine formulation is varied in ratios of divalent ion to monovalent ion of 1:1, 1:3, 1:10 and 1:15. In this part, divalent ions refer to combination of calcium ion and magnesium ion and the ratio of divalent ion to monovalent ion is applied throughout this section. Synthetic formation brines and seawater are prepared and their compositions are summarized in table 5.6.

Table 5.6 Ions compositions of formation brines with various ratios of divalent ion and monovalent ion

Ratios of divalent ions and monovalent ion	Ions	mol/L	g/L	ppm
1:1	Na^{+}	0.9615	22.11	22,115
	Ca^{2+}	0.7692	30.77	30,768
	Mg^{2+}	0.1923	4.67	4,673
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^{-}	2.8771	102.14	102,137
1:3	Na^{+}	1.6938	38.96	38,958
	Ca^{2+}	0.452	18.07	18,067
	Mg^{2+}	0.1129	2.74	2,744
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^{-}	2.8156	99.95	99,953

Table 5.6 Ions compositions of formation brines with various ratios of divalent ion and monovalent ion (Continued)

Ratios of divalent ions and monovalent ion	Ions	mol/L	g/L	ppm
1:10	Na^+	2.3094	53.12	53,117
	Ca^{2+}	0.1848	7.39	7,390
	Mg^{2+}	0.0462	1.12	1,122
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7639	98.12	98,118
1:15	Na^+	2.4359	56.03	56,026
	Ca^{2+}	0.1299	5.20	5,197
	Mg^{2+}	0.0325	0.79	789
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7533	97.74	97,741

Results obtained from imbibition test in this section are illustrated as relationship between oil recovery factor and soaking time in Figure 5.2.

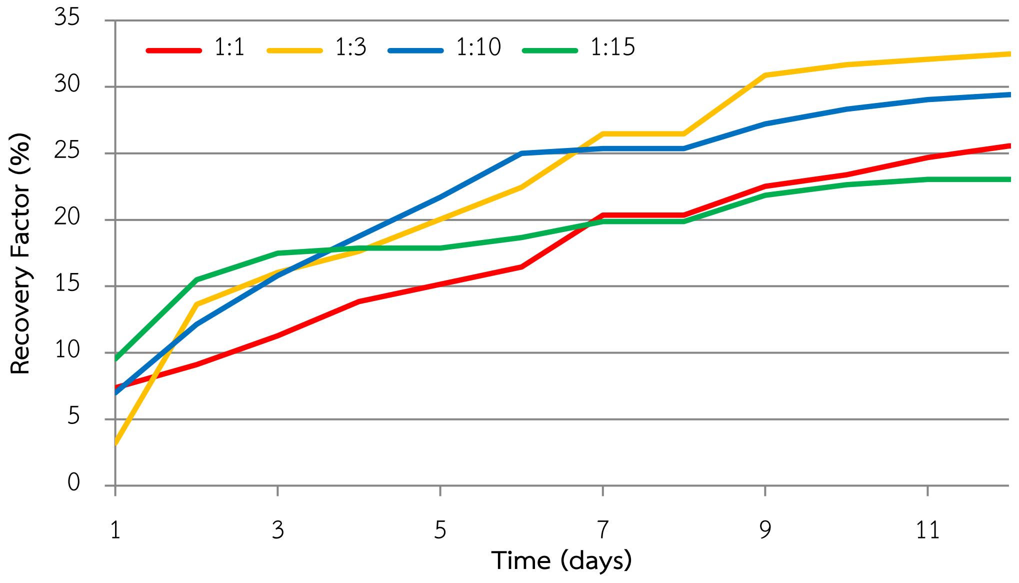


Figure 5.2 Oil recovery factors from imbibition tests for different formation brines with various ratios of divalent ion to monovalent ion as a function of soaking time

According to the figure 5.2, it can be noticed that the weight of core samples saturated with formation brine in the first 7 days are fast increased in a large amount especially in cases of formation brines containing divalent ion to monovalent ion ratio of 1:3 and 1:10 with corresponding oil recovery factor are 26.46% and 25.37%, respectively. After sample weights remain constant, samples are switched to soak in seawater representing low salinity water in this study. In this phase, sample with formation brine with a ratio of 1:3 yields the highest oil recovery factor which is 32.48% with additional oil recovery factor by means of LSWF of 6.01%.

From the results, it can be explained that multi-component ion exchange mechanism can be occurred rapidly and high oil recovery factor can be obtained in case of using formation brine containing large amount of divalent ions which are calcium ion and magnesium ion compared to monovalent ion since formation of calcium carboxylate complexes can be favored. Moreover, size of hydrated ions may interfere stabilization of adsorbed oil. In case of formation brine with appropriate amount of divalent ions, with less monovalent ion, calcium and magnesium ion which have larger hydrated sizes compared to monovalent ions would cause water film covering rock surface to be thicker. Oil-wet condition is therefore no very strong in this case and effect of LSWF is more obvious. Nevertheless, when excessive amount of divalent ions are presented, these ions may even though the water film is thick enough to favor LSWF. For the case with the highest portion of monovalent ion, as size of hydrated monovalent ions are much smaller than those of divalent ion as shown in table 5.7, water film covering rock surface is thin and chance that acid oil is in direct contact is higher. Hence, adsorption of oil onto rock surface can be occurred at very high strength. As a consequence, oil-wet condition is strong in this case and LSWF is the least effective. Moreover, due to small number of divalent ion, carboxylate complex is less generated and oil is hardly induced to be liberated from rock surface.

Table 5.7 Hydrated radius of divalent and monovalent ion [11]

Ion	Hydrated radius of ions (pm)
Na^+	450
K^+	300
Mg^{2+}	800
Ca^{2+}	600

From the experiment, it can be observed that ion composition in formation brine plays important role in controlling effectiveness of LSWF. Effect of calcium ion is the most pronounced at testing temperature. Presence of calcium ion in formation water could provide amount of calcium ion for injected water through diffusion and this amount of calcium ion is important to generate calcium carboxylate complex which is part of the important mechanism to liberate oil from rock surface. Too many calcium ions in formation brine may result in abundant of calcium ion in injected water which consecutively obstructs dissolution mechanism of rock mineral which is another part of overall mechanisms favoring oil recovery mechanism by LSWF. From this study, the ratio of calcium ion to magnesium ion of 1:1 in formation brine shows the best performance for LSWF by seawater injection. Even though magnesium ion is the highest in this case, dissolution mechanism may still occur as portion of magnesium in dolomite formation and in formation brine is balanced with portion of calcium in dolomite formation and in formation brine.

Higher amount of monovalent ion results in very thin layer of water film and hence adsorption of oil onto rock surface can tightly occurred and hence, LSFW is less effective due to stronger oil-wet condition. Too high amount of divalent ion compared to monovalent ion results in weak adsorbed layer but higher amount of divalent ion causes rapid diffusion once seawater is injected, obstructing dissolution mechanism of rock minerals.

From the experiment it is noticed that best formation brine contains ratio of calcium ion to magnesium ion of 1:1 whereas, ratio of divalent ion to monovalent of 1:3 shows the best response by LSWF.

5.3. Coreflood experiments

5.3.1. Coreflood experiment with various formulations of formation brine

From spontaneous imbibition test, the highest oil recovery factors are obtained from the tests performed by formation brines with ratios of calcium ion to magnesium ion of 1: 1 and 3: 1 and the cases with ratios of divalent ions to monovalent ions of 1:3 and 1:10. These cases are chosen to perform in coreflood test to confirm result and the occurrence of wettability alteration by multi-ions exchange mechanism. Coreflood apparatus is an equipment that can imitate reservoir conditions including pressure, temperature, and flow rate via computer system. Therefore, conventional waterflooding and low salinity waterflooding can be effectively studied at reservoir condition in order to obtain precise data of oil recovery factor prior to real implementation.

In this study, coreflood experiments are mainly performed at 30 degree Celsius with confining pressure of 2,500 psi. Brines are injected into core samples with a fixed flow rate of 0.5 cm^3/min for both conventional waterflooding and low salinity waterflooding phases in order to study only effects of ratios of ion composition. However, the effects of flow rate and temperature are investigated in further experiment.

Due to the fact that significant petrophysical properties consist of irreducible water saturation (S_{wi}) and residual oil saturation (S_{or}) are slightly different in each test therefore, these properties must be re-measured prior to performing coreflood tests. The data in table 5.8 demonstrates value of S_{wi} and S_{or} of each core samples be used in coreflood experiments.

Table 5.8 Irreducible water saturation and residual oil saturation of specific core samples together with information of coreflood test of each core

Test	#Core	S_{wi} (%)	$1-S_{or}$ (%)
Coreflood test varied in ratios of calcium and magnesium ions	4.1	50.66	61.03
	5.1	47.94	57.70

Table 5.8 Irreducible water saturation and residual oil saturation of specific core samples together with information of coreflood test of each core (Continued)

Test	#Core	S_{wi} (%)	$1\text{-}S_{or}$ (%)
Coreflood test varied in ratios of divalent ion to monovalent ion	5.1	51.78	60.01
	5.2	40.59	55.25
Coreflood test varied in injection rate	4.1	48.89	62.80
	5.1	54.09	64.63
	5.2	38.93	51.94
Coreflood test varied in Temperature	4.1	48.89	62.80
	5.1	54.09	68.47
	5.2	35.62	56.91

In the study of ratio of calcium ion to magnesium ion in formation brine, the ratio of 1: 1 and 3: 1 are chosen to conduct by coreflood experiment. Ions compositions of brines are calculated and illustrated in table 5.9.

Table 5.9 Ion composition of formation brines in the study of ratio of calcium ion and magnesium ion in coreflood test

Ratios of calcium and magnesium ions	Ions	mol/L	g/L	ppm
1:1	Na^+	2.0284	46.65	46,653
	Ca^{2+}	0.2004	8.02	8,017
	Mg^{2+}	0.2004	4.87	4,871
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.8227	100.20	100,205
3:1	Na^+	2.0013	46.03	46,031
	Ca^{2+}	0.3007	12.03	12,026
	Mg^{2+}	0.1002	2.44	2,435
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7956	99.24	99,245

After coreflood tests, results in terms of oil recovery factor in percent are demonstrated as a function of injected pore volume as shown in figure 5.3.

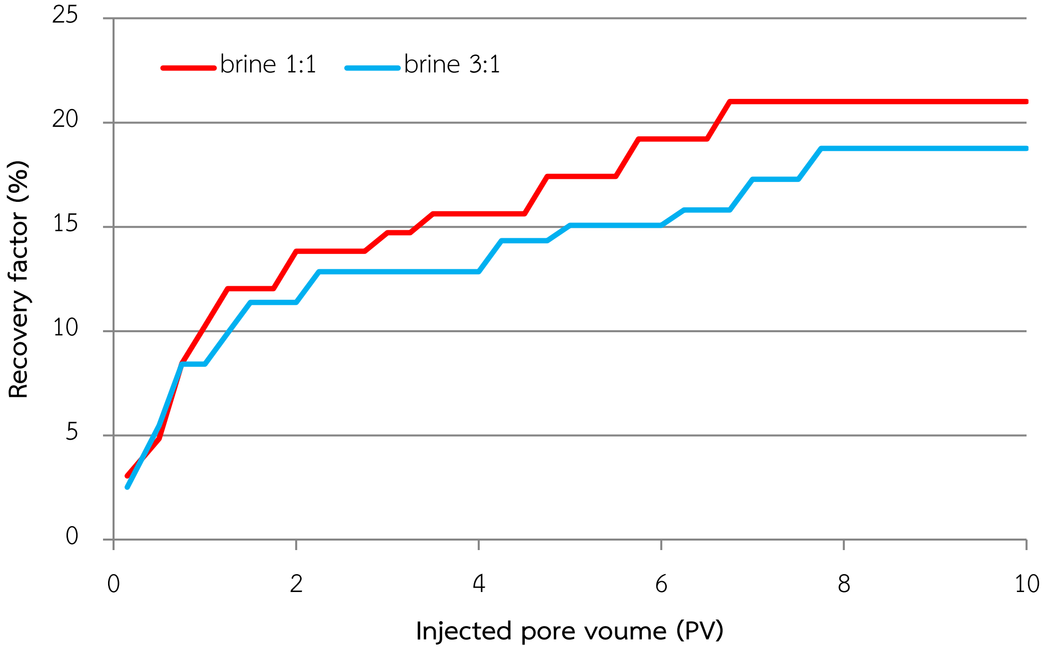


Figure 5.3 Oil recovery factors from coreflood tests obtained from formation brines with different ratios of calcium ion to magnesium ion as a function of injected pore volume

From figure 5.3, the trend of oil recovery factor obtained from coreflood test is remarkably similar to the trend of imbibition test. Formation brine with calcium ion to magnesium ion ratio of 1:1 yields the highest oil recovery factor of 12.03% by conventional waterflooding and up to 21.01% from low salinity water flooding or 8.97% additional oil recovery factor whereas, formation brine with calcium ion to magnesium ion ratio of 1:3 can yield approximately 5.91% additional oil recovery factor. The results can confirm that presence of explanation in imbibition test. The least amount of calcium ion in formation brine compared to magnesium ion shows better results in terms of improvement by mean of LSWF compared with case at higher ratio of calcium ion to magnesium ion. Calcium ion is important in forming calcium carboxylate complex which is part of total mechanisms to liberate oil from carbonate surface. Nevertheless, excess amount of calcium ion from formation brine would result in rapid increment of calcium ion in environment when low salinity water is injected and this can inhibit oil recovery mechanism since high amount of calcium ion itself can obstruct dissolution of calcium ion at rock surface which is another part of oil recovery mechanisms. Therefore, oil cannot be easily liberated due to incomplete of the total oil recovery mechanism cycle.

Considering ratios of divalent ion to monovalent ion in formation brine, the highest oil recovery factor are obtained from formation brines with ratios of 1:3 and 1:10 and thus, these two cases are selected to perform coreflood experiment and ion compositions of these two brines are summarized in table 5.10.

Table 5.10 Ion composition of formation brines in the study of ratio of divalent ion and monovalent ion in coreflood test

Ratios of divalent ions and monovalent ion	**Ions**	**mol/L**	**g/L**	**ppm**
1:3	Na^+	1.6938	38.96	38,958
	Ca^{2+}	0.452	18.07	18,067
	Mg^{2+}	0.1129	2.74	2,744
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.8156	99.95	99,953
1:10	Na^+	2.3094	53.12	53,117
	Ca^{2+}	0.1848	7.39	7,390
	Mg^{2+}	0.0462	1.12	1,122
	SO_4^{2-}	0.0025	0.24	236
	HCO^{3-}	0.0025	0.15	154
	Cl^-	2.7639	98.12	98,118

Results obtained coreflood tests are demonstrated in term of oil recovery factor as a function of injected pore volume as shown in Figure 5.4.

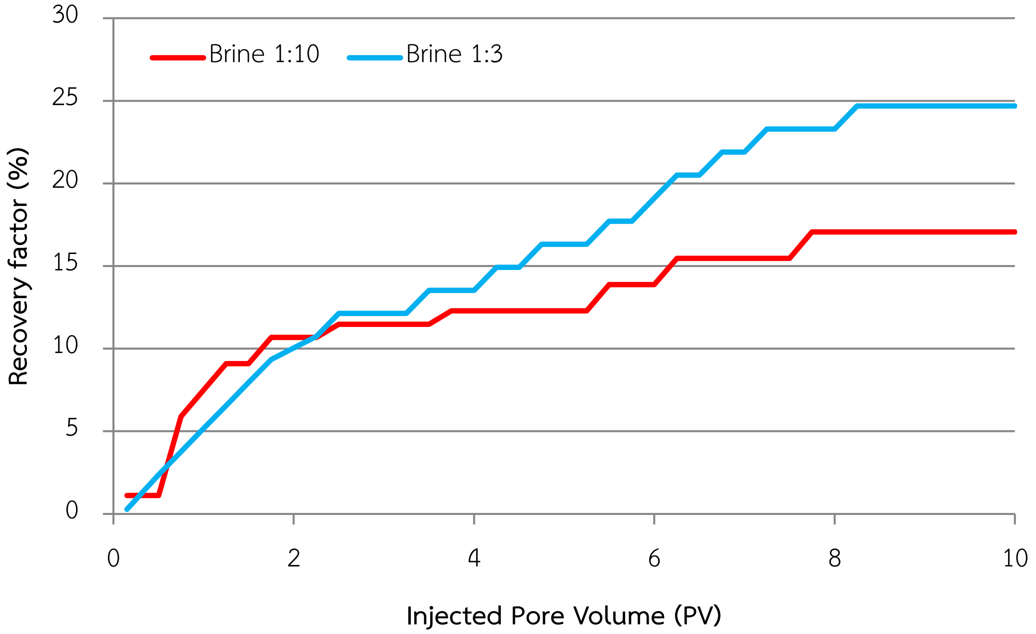


Figure 5.4 Oil recovery factors from coreflood tests obtained from formation brines with different ratios of divalent ion to monovalent ion as a function of injected pore volume

The result in figure 5.4 can be clearly interpreted that carbonate sample saturated with formation brine containing of divalent ion to monovalent ion ratio of 1:3 can recover higher amount of oil. In this experiment, oil recovery factor obtained from conventional waterflooding is 13.53% and by means of LSWF oil recovery factor reaches 24.69% and additional oil recovery from LSWF is 11.16%. On the contrary, the core samples saturated with divalent ion to monovalent ion ratio of 1:10, oil recovery is only 10.68% by means of conventional waterflooding and can reach up to 17.06% during LSWF. According to laboratory results, higher oil recovery factor is obtained from the case with formation brine with higher amount of divalent ions which are calcium and magnesium ions. As calcium and magnesium ions are considered as potential determining ions in multi-component ion exchange mechanism, these ions can diffuse to injected low salinity water and calcium and magnesium carboxylate complexes can be formed. Thus, oil can be liberated from rock surface.

Moreover, as explained in previous section, formation brine containing higher portion of monovalent ion can result in stronger bond between adsorbed oil layer onto carbonate surface as can be explained by smaller hydrated size of monovalent ion resulting in an ease of oil to be closer to rock surface. Moreover, comparing between effects from divalent ions and monovalent ions (comparison between figure 5.3 and figure 5.4) it is obvious that variation of monovalent ion in formation water is more sensitive to effectiveness of LSWF compared to variation of portion between calcium and magnesium ions.

From these two studied parameters, the best formulation of formation brine is synthesized with the best ratios of calcium ion to magnesium ion and divalent ion to monovalent ion ratio to confirm the previous explanation as well as best suited formation brine for LSWF. Formulation of synthetic formation brine is demonstrated in table 5.11.

Table 5.11 Ions composition of the best formation brine

Ions	mol/L	g/L	ppm
Na^+	1.7226	39.62	39,620
Ca^{2+}	0.2871	11.48	11,484
Mg^{2+}	0.2871	6.98	6,977
SO_4^{2-}	0.0025	0.24	236
HCO^{3-}	0.0025	0.15	154
Cl^-	2.8635	101.66	101,657

Ion composition of the chosen formation brine formulation has portion of calcium ion equal to portion of magnesium ion while total monovalent ion is three times of summation of divalent ions. Total salinity of formation brine is maintained at 160,000 ppm same as salinity obtained from average formation brine of carbonate rock in the world. This formation is used in further experiments.

5.3.2. Coreflood experiment varied with various injection rates

Besides chemical compositions of formation brine, injection rate is also considered as one of important parameters for completion of multi-ions exchange and wettability alteration mechanisms in LSWF in carbonate rock. Experiments are performed with injection rate of 0.2, 0.4, and 0.6 cm^3/ min during low salinity waterflooding phase, whereas conventional waterflooding is performed at the same injection rate in previous section. The best formulation of formation brine with total salinity of 160,000 ppm obtained from previous section is used for all the tests and seawater with total salinity of 35,000 ppm is still served as low salinity water. In this section, temperature is still controlled at 30 degree Celsius with confining pressure of 2,500 psi and back pressure of 500 psi. The experiments start with injecting formation brine as conventional waterflooding stage into saturated core samples. After that, seawater is continuously injected to perform LSWF with various injection rates for each sample. Results are illustrated in figure 5.5 as a relationship between oil recovery factor and injected pore volume.

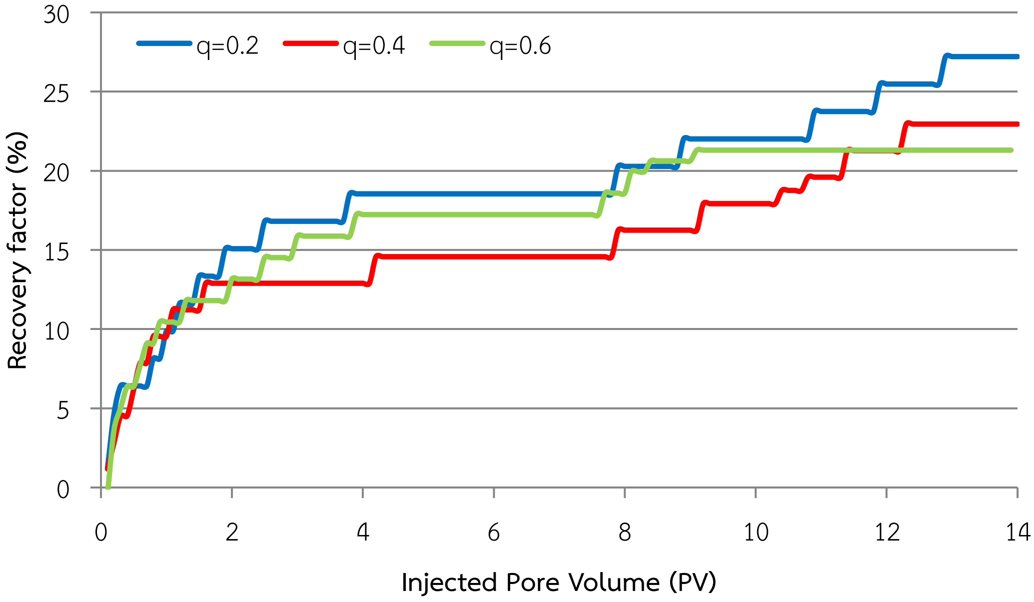


Figure 5.5 Oil recovery factors from coreflood experiments with various injection rates as a function of injected pore volume

According to results shown in figure 5.5, final oil recovery factor from an experiment using injection rate of 0.2 cm^3/min, is 27.21% with additional oil recovery of 8.67% oil recovery factor from LSWF while additional oil recovery factor of 8.37% and 4.07% are obtained from the cases with injection rate of 0.4 and 0.6 cm^3/min. It can be noticed that the highest additional oil recovery factor is obtained from the test with lowest injection rate as wettability alteration is a time-consuming process and the mechanism is not immediately occurred. As each ion would take time to complete the mechanism, slow injection rate provides more retention time where ion can be attracted by rock surface. It can be obviously seen that using small injection rates of 0.2 and 0.4 cm^3/min, period of incrementing of oil production last longer than the use of higher injection rate. Therefore, injection rate of 0.2 cm^3/min is chosen to be operated in next session.

5.3.3. Coreflood experiment varied in temperature

Temperature, one of the key factors for success of enhancing oil recovery process, is also chosen to study. From the limitation of coreflood apparatus together with current configuration of the apparatus, temperatures can be varied from 30 to 70 degree Celsius. At higher temperature than 70 degree Celsius, the value of inlet pressure and outlet pressure of coreflood apparatus are not stable due to vaporization of working fluid, leading to inaccurate results. Injection rate with highest oil recovery factor from previous experiment is used while formation brine and seawater are still kept the same. The results are collected in term of oil recovery factor as a function of time both steps, conventional waterflooding and LSWF and eventually interpreted as a function of injected pore volume as shown in Figure 5.6.

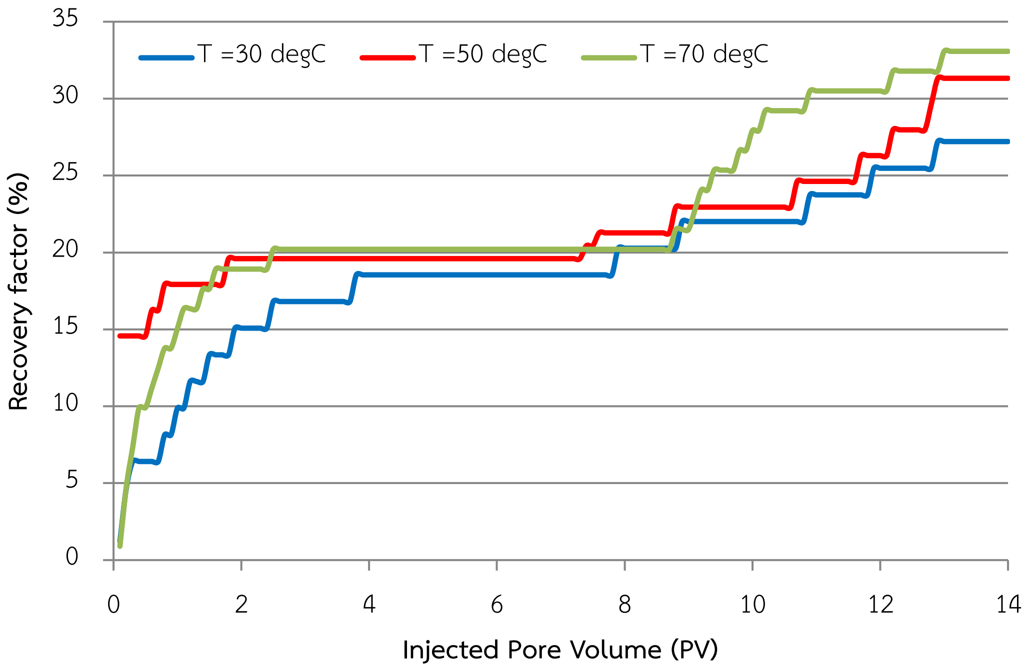


Figure 5.6 Oil recovery factors from coreflood experiments with various temperatures as a function of injected pore volume

It can be observed from the figure 5.6 that the highest additional oil recovery factor of 12.87% in LSWF phase is obtained from the test with temperature of 70 degree Celsius, whereas 8.67% and 11.82% additional oil recovery are recovered from the experiments performed at temperatures of 30 and 50 degrees Celsius, respectively. At higher temperature, ion activity is also higher especially in aqueous phase and fluid viscosity is decrease so fluid has better ability to flow. This also results in difficulty for rock to form a firm bond with adsorbed layer of oil. Therefore, wettability has a higher tendency for water-wet and as a consequence, this oil can be easily liberated. Moreover, at higher temperature, chemical reaction is faster hence, both carboxylate complex formation as well as mineral dissolution are favored. Some literature reviews also explain that at lower temperature, magnesium carboxylate complex is hardly occurred and this tends to happen at higher temperature by replacing calcium in calcium carboxylate complex, resulting adequate amount of calcium and magnesium ion to remove oil in a form of carboxylate complex.

In summary, formation brine with small portion of calcium ion compared to magnesium ion is desirable as usually calcium is much more abundant compared to magnesium ion. Nevertheless, smaller portion of monovalent ion should be presented in formation brine as monovalent ions are smaller than divalent ions in terms of hydrated size and this could cause a stronger in terms of direct contact between rock surface and adsorbed oil layer. In addition, appropriate injection rate LSWF are also determined. The smallest injection rate in this study which is 0.2 cm^3/ min yields the best benefit from LSWF as retention time between potential determining ions and rock surfactant is extended. High reservoir temperature is recommended for LSWF for several reasons. First, potential determining ions are more active at higher temperature and second, the oil-wet condition of carbonate surface maybe not as strong as in low reservoir temperature.

Complexometric Titration

The titration section is implemented to confirm an occurrence of multi-ions exchange mechanism as well as wettability alteration mechanism during LSWF in carbonate reservoir. As potential determining ions for this mechanism in carbonate rocks consist of calcium, magnesium, and sulfate ions, only calcium and magnesium ions are chosen to be identifying ions since they can be easily measured in the injected and effluent fluids by means of Complexometric titration. The titration experiment is divided into two parts, at the beginning, total hardness or total divalent ions composing of calcium ion and magnesium ion are measured using Ethylenediaminetetraacetic acid (EDTA) as titrant and Eriochrome Black T as an indicator at pH value of 10. In the next step, only portion of calcium ion in water is identified by EDTA titrant and hydroxynaphthol blue indicator at pH value 11. Then, amount of magnesium ion can be determined from the difference of these two experiments. Complexometric titration is particularly performed for the case of coreflood experiments using the selected formulation with various injection rates and temperatures by collecting effluents from coreflood apparatus for titration.

In the first stage, total hardness is determined; effluents from coreflood tests are gathered both from conventional waterflooding as well as LSWF for 10 cm^3. Then, buffer solution and Eriochrome Black T are added. Initially, solution color is wine red with pH 10 as shown in figure 5.7 (left). After titration with EDTA until the end point, the effluent color is turned to sky blue as illustrated in figure 5.7 (right). The volume of EDTA for titration until the end point is converted to total amount of divalent ions in solution.

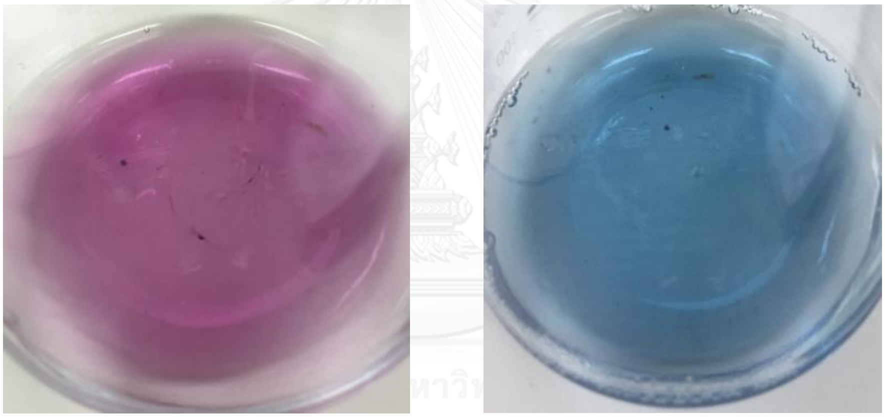


Figure 5.7 Colors of solution during Complexometric titration of total divalent ions (left) before titration and (right) at the end point of titration

Next, NaOH 50% w/v is added into the effluent in order to precipitate magnesium ion out from the solution in a form of magnesium hydroxide ($Mg(OH)_2$) and the color is shown in figure 5.8 (left). Again, the solution is titrated with EDTA but using hydroxynaphthol blue as an indicator until color of solution is changed from red wine to sky blue as shown in figure 5.8 (right). Volume of EDTA to titrate solution until end point in this session is converted to quantity of total calcium ion in the effluents.

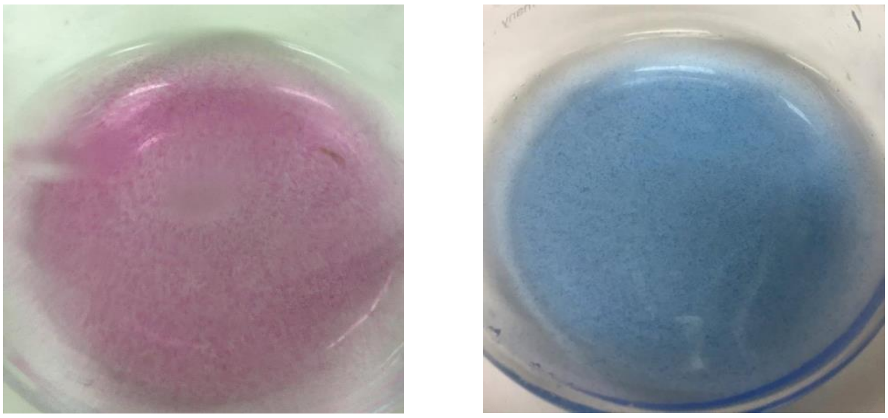


Figure 5.8 Colors of solution during Complexometric titration of calcium ion (left) before titration and (right) at the end point of titration

At the beginning, formation brine and seawater are titrated in order to determine the amount of total divalent ions, calcium ion, and magnesium ion prior to the start of multi-component ion exchange mechanism. Since the ion compositions in these synthetic brines are known from calculation data therefore, percentage error can be evaluated as illustrated in table 5.12.

Table 5.12 The amount of total divalent ions, calcium ion, and magnesium ion from calculation by preparation and titration

Brine	Ion	Calculation data (ppm)	Titrated data (ppm)	%Error
Selected brine	Total divalent ions	18,460.65	17,364	5.94
	Calcium	11,484.07	10,940	4.74
	Magnesium	6,976.57	6,424	7.92
Seawater	Total divalent ions	1,461	1,399	4.24
	Calcium	304	283	6.91
	Magnesium	1,157	1,116	3.54

From the amount of total divalent ions, calcium ion, and magnesium ion obtained from calculation from brine preparation process and from titration in table 5.12, percent differences are about 3 – 8% which may be due to the weighting technique, purity of chemicals and also from limitation of titration equipment. Nevertheless, the numbers are all in similar range and therefore, are acceptable for this study.

5.3.4. Complexometric titration test for the coreflood test with various injection rates

The effluents for titration analysis are collected from both conventional waterflooding and LSWF phases during coreflood test. In the conventional waterflooding, formation brine is injected with injection rate of 0.5 cm^3/min whereas injection rate of 0.2, 0.4, and 0.6 cm^3/min are applied during LSWF stage at temperature of 30 degree Celsius. The amounts of total divalent ions, calcium ion, and magnesium ion from titration are summarized in table 5.13 and table 5.14 for conventional waterflooding and LSWF, respectively.

Table 5.13 The amount of total divalent ions, calcium ion, and magnesium ion from conventional waterflooding with various injection rates

		Rate (cm^3/min)		
		0.2	0.4	0.6
Ion (ppm)	FB	HSWF	HSWF	HSWF
Total divalent ions	18,164	28,898	30,962	28,691
Calcium	10,940	12,178	13,830	13,210
Magnesium	7,224	16,720	17,132	15,481

Table 5.14 The amount of total divalent ions, calcium ion, and magnesium ion from LSWF with various injection rates

		Rate (cm^3/min)		
		0.2	0.4	0.6
Ion (ppm)	SW	LSWF	LSWF	LSWF
Total divalent ions	1,399	10,321	11,146	10,527
Calcium	283	4,335	4,747	4,541
Magnesium	1,116	5,986	6,399	5,986

According to results in table 5.13, it can be observed that amounts of both calcium ion and magnesium ion are obviously increased from the initial values. This can be explained by dissolution mechanisms of both calcium and magnesium ions from dolomite itself. However, the increment of magnesium ion is more obvious in all cases. Even though dolomite composes of both calcium ion and magnesium ion in similar ratio, dissolution of both ions may be different. Another reason can be provided here is that part of calcium ion is consumed for creating calcium carboxylate complex whereas magnesium ion cannot induce oil to produce magnesium carboxylate complex at this temperature.

From table 5.14, when water is switched into seawater, the increasing trends of both ions are slightly changed. The increment of both calcium and magnesium ion is in the same level. Calcium ion is increased around 4,000 ppm whereas magnesium ion is increased 5,000 ppm. This increment of ion ratio is more reasonable to the fact that dolomite composes of both calcium and magnesium ions in similar proportion. And since most oil is already produced, only small fraction of calcium ion maybe used to produce calcium carboxylate in this case. Nevertheless, there is no relationship between amounts of divalent ions and injection rate in this case. Only tendency of amount of divalent ions during conventional waterflooding and during LSWF can be made.

5.3.5. Complexometric titration test for the coreflood test with various temperatures

In this session, effluents are collected from coreflood experiments from two tests with three different temperatures which are from 30, 50 and 70 degree Celsius. Injection rate of 0.5 cm^3/min is utilized in conventional waterflooding while 0.2 cm^3/min which is the selected rate from the previous part is operated during the phase of LSWF. The number of total divalent ions, calcium ion, and magnesium ion from complexometric titration are shown in table 5.15 and table 5.16 for conventional waterflooding and LSWF, respectively.

Table 5.15 The amount of total divalent ions, calcium ion, and magnesium ion from conventional waterflooding with various temperatures

		Temperature (°C)		
		30	50	70
Ion (ppm)	FB	HSWF	HSWF	HSWF
Total divalent ions	18,164	28,898	25,595	24,150
Calcium	10,940	12,178	12,178	12,385
Magnesium	7,224	16,720	13,417	11,765

Table 5.16 The amount of total divalent ions, calcium ion, and magnesium ion from LSWF with various temperatures

		Temperature (°C)		
		30	50	70
Ion (ppm)	SW	LSWF	LSWF	LSWF
Total divalent ions	1,399	10,321	7,844	4,335
Calcium	283	4,335	4,747	3,096
Magnesium	1,116	5,986	3,097	1,239

The results shown in table 5.15 demonstrate that comparing with table 5.13, multi-component ion exchange is obviously a function of temperature. Even when conventional waterflooding is performed, the amount of magnesium ion is remarkably decreased whereas amount of calcium ion tends to be constant. At higher temperature, both calcium and magnesium can start to form calcium carboxylate complex as well as magnesium carboxylate complex. More interesting results are observed when LSWF is performed. From table 5. 16, amount of magnesium ion starts to decrease and reaches the minimum at 70 degree Celsius. Not only magnesium ion, calcium ion is also decreased compared together two temperature. When LSWF is performed in higher temperature, dolomite would yield this benefit over limestone as released magnesium can assist calcium ion in form in carboxylate complex. This reducing trend of both ion concentrations compared to performing at lower temperature shows together with greater improvement oil recovery may conclude the effects of both ions in forming carboxylate complex at high temperature.

The results from complexometric titration experiment show that changes of proportion of divalent ions would come together with multi-component ion exchange mechanism. During conventional waterflooding, this mechanism may occur but due to equality of salinity between formation water and injected water, part of mechanisms is inhibited. When LSWF is performed, changing in proportion of both divalent ions compared to initial concentration and compared to conventional waterflooding would confirm the occurrence of multi-component ion exchange mechanism. Dramatically decrease of magnesium ion as well as calcium ion which comes together with high amount of recovered oil is also another evidence of multi-component ion exchange that occurs in dolomite at higher temperature.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions from the overall experiments are summarized in this section. Recommendations for further study are also provided.

1.1. Conclusions

1. Calcium ion is considered as one of important factors in multi-component ion exchange mechanism in carbonate reservoir which is a major process for wettability alteration. However, the amount of calcium ion in the system is also required for investigation. Amount of calcium should be adequate to generate calcium carboxylate complex to induce adsorbed oil out from carbonate surface. Formation water with high amount of calcium ion can lead to excessive calcium ion in environment. Instead of facilitating calcium carboxylate complex, high amount of calcium ion will inhibit dissolution mechanism of calcium in carbonate rock which is another side of oil recovery mechanism. From this study, the least portion of calcium ion in formation brine which is the calcium ion to magnesium ion ratio of 1:1 is the best to yield effectiveness by LSWF which is confirmed by both imbibition and coreflood tests.

2. High portion of monovalent ion in formation brine results in ineffectiveness of LSWF in carbonate reservoir. Smaller amount of divalent ions diffusing to injected brine causes formation of carboxylate complex to be less. Moreover, monovalent ions which are smaller in hydrated size compared to divalent ion causes strong interaction between rock surface and adsorbed oil, resulting in more oil-wet condition and so, oil can be difficulty liberated. From this study, the ratio of divalent ion to monovalent ion in formation brine that yields the best effectiveness of LSWF is 1:3 which is confirmed by both imbibition and coreflood tests.

3. For the study of injection rate, the highest amount of oil is obtained by LSFW when small injection rate is applied. This is due to the longer retention time providing potential determining ion to complete multi-component ion exchange mechanism. From this study, the injection rate of 0.2 cm^3/ min shows the most effectiveness by LSWF in carbonate surface when best formation brine is used for sample preparation.

4. Both calcium ion and magnesium ion are increased in injected water in both conventional waterflooding and LSWF as these ions are enriched in formation brine as well as they are the main compositions in carbonate rock and can naturally dissolve to water. Nevertheless, presence of calcium ion is less compared to magnesium ion which can be described by favorability of carboxylate complex of calcium and magnesium at different temperatures. Changing injected water also changes the ratio of both ions. From the study, when LSWF is injected portion of calcium ion is increased from the period of conventional waterflooding which can be explained by higher dissolution from rock and less quantity of calcium ion is consumed from calcium carboxylate complex once remaining oil is less.

5. For the effect of temperature on LSWF, high temperature results in higher amount of recoverable oil. This can be explained by faster chemical reaction. Ions can move faster and reaction is rapidly occurred so calcium carboxylate complex can be swiftly generated. Moreover, reduction of magnesium ion during LWSF which is tested by complexometric titration can also explain the favorability of generating of magnesium carboxylate complex at higher temperature.

1.2. Recommendations

In order to better understand oil recovery mechanisms of LSWF process in carbonate rock for the field implementation in the future, following recommendations are provided.

1. Only dolomite is studied in this thesis. So it would give be better conclusion by performing similar study with limestone to confirm effects of divalent ions in formation brine.

2. In this study, injection rates are chosen under limitation of time and coreflood apparatus performance. However, the range of injection rate should be comparable to the operational practice obtained from field.

3. Maximum temperature in the experiment is at 70 degree Celsius in order to maintain constant pressure of coreflood apparatus. Nevertheless, higher temperature should be operated for confirmation of relationship between temperature and oil recovery by LSWF.

4. Manual titration technique is applied in complexometric titration part of this experiment and this can still cause certain error mainly from resolution of equipment itself. Automated titration machine could provide better accuracy.

5. For complexometric titration, effluents are collected from coreflood instrument at the end of conventional waterflooding process and at the end of LSWF. The study would be more in details if more frequent water samples during displacement mechanism can be collected from coreflood system to observe trend of dissolution and spending of ions for forming carboxylate complex.

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APPENDIX A

Formation brine compositions

The formation brine in this thesis is averaged from ion compositions of formation brine of carbonate reservoir around the globe. In addition, the formation brine formulations are adjusted in order to study the effects of calcium ion to magnesium ion ratio and divalent ion to monovalent ion ratio. Therefore, the adapted ion compositions of each brine formulation are shown in this session and the portion of chemical for preparation the brines are also demonstrated.

Formation brine with ratio of calcium ion to magnesium ion = 1:1

Ion	MW	mol	ppm
Na^+	23	2.0284	46,653
Ca^{2+}	40	0.2004	8,017
Mg^{2+}	24	0.2004	4,810
Cl^-	35.5	2.8227	100,205
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
$NaCl$	58.5	2.0209	118,225
$MgCl_2$	95	0.2004	19,041
$CaCl_2$	111	0.2004	22,248
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of calcium ion to magnesium ion = 3:1

Ion	MW	mol	ppm
Na^+	23	2.0013	46,031
Ca^{2+}	40	0.3007	12,026
Mg^{2+}	24	0.1002	2,405
Cl^-	35.5	2.7956	99,245
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	1.9939	116,642
$MgCl_2$	95	0.1002	9,521
$CaCl_2$	111	0.3007	33,372
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of calcium ion to magnesium ion = 10:1

Ion	MW	mol	ppm
Na^+	23	1.9841	45,635
Ca^{2+}	40	0.3644	14,577
Mg^{2+}	24	0.0364	875
Cl^-	35.5	2.7784	98,634
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	1.9767	115,635
$MgCl_2$	95	0.0364	3,462
$CaCl_2$	111	0.3644	40,451
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of calcium ion to magnesium ion = 15:1

Ion	MW	mol	ppm
Na^+	23	1.9810	45,564
Ca^{2+}	40	0.3758	15,033
Mg^{2+}	24	0.0251	601
Cl^-	35.5	2.7753	98,525
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	1.9736	115,456
$MgCl_2$	95	0.0251	2,380
$CaCl_2$	111	0.3758	41,716
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of divalent ions to monovalent ion = 1:1

Ion	MW	mol	ppm
Na^+	23	0.9615	22,115
Ca^{2+}	40	0.7692	30,768
Mg^{2+}	24	0.1923	4,615
Cl^-	35.5	2.8771	102,137
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	0.9541	55,813
$MgCl_2$	95	0.1923	18,269
$CaCl_2$	111	0.7692	85,383
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of divalent ions to monovalent ion = 1:3

Ion	MW	mol	ppm
Na^+	23	1.6938	38,958
Ca^{2+}	40	0.4517	18,067
Mg^{2+}	24	0.1129	2,710
Cl^-	35.5	2.8156	99,953
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	0.9541	98,653
$MgCl_2$	95	0.1923	10,728
$CaCl_2$	111	0.7692	50,137
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of divalent ions to monovalent ion = 1:10

Ion	MW	mol	ppm
Na^+	23	2.3094	53,117
Ca^{2+}	40	0.1848	7,390
Mg^{2+}	24	0.0462	1,109
Cl^-	35.5	2.7639	98,118
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	2.3020	134,667
$MgCl_2$	95	0.0462	4,388
$CaCl_2$	111	0.1848	20,508
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

Formation brine with ratio of divalent ions to monovalent ion = 1:15

Ion	MW	mol	ppm
Na^+	23	2.4359	56,026
Ca^{2+}	40	0.1299	5,197
Mg^{2+}	24	0.0325	779
Cl^-	35.5	2.7533	97,741
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	2.4285	142,066
$MgCl_2$	95	0.0325	3,086
$CaCl_2$	111	0.1299	14,421
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

The best formula of formation brine with ratio of calcium ion to magnesium ion = 1:1 and ratio of divalent ions to monovalent ion = 1:3

Ion	MW	mol	ppm
Na^+	23	1.7226	39,620
Ca^{2+}	40	0.2871	11,484
Mg^{2+}	24	0.2871	6,890
Cl^-	35.5	2.8636	101,657
SO_4^{2-}	96	0.0025	236
HCO_3^-	61	0.0025	154
Total			160,000

Chemical	MW	mol	ppm
NaCl	58.5	2.3020	100,337
$MgCl_2$	95	0.0462	27,275
$CaCl_2$	111	0.1848	31,868
$NaHCO_3$	142	0.0025	359
Na_2SO_4	142	0.0025	350
Total			160,000

APPENDIX B

Modification of Oil

In the experiment, oil is used in both imbibition and coreflood tests in order to age and saturate core samples. In this thesis, dodecane with acid number of zero is served as crude oil. However, since modification of dodecane is important for wettability alteration in carbonate, oleic acid is added in oil for changing dodecane with acid number of zero to acid number more than 1.0. The calculation for determination of oleic acid adding in oil is studied in this section.

Acid number (AN) can be identified by the equation below:

$$AN = \frac{56.1xC_{KOH}\,xV_{KOH}}{m_{pureoil}} \qquad (1),$$

Where C_{KOH} is concentration of the potassium hydroxide solution in mole per litre, V_{KOH} is volume of potassium hydroxide solution required for titration with acid oil in millilitres and $m_{pureoil}$ is the mass of dodecane in gram.

Moreover, mass of oleic acid can be calculated from a chemical equation for titration and definition of solution concentration in the following equation

$$m_{oleicacid} = \frac{C_{KOH}\,xV_{KOH}}{1000}\,xMW_{oleicacid} \qquad (2),$$

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

In summary, from equation (1) and (2), the equation of mass of oleic acid ($\mathbf{m}_{\mathbf{oleic\ acid}}$) become;

$$m_{oleicacid} = \frac{\frac{ANxm_{pureoil}}{56.1}}{1000}\,x282.46 = 0.005035xANxm_{pureoil} \qquad (3).$$

In this thesis, only dodecane with acid number of 1.0 and 5.0 is used therefore, these fluids are prepared from dodecane and oleic acid. Dodecane with acid number of 5.0 can be prepared by adding 25.17 grams of oleic acid in 1,000 g of dodecane and for oil with acid number of 1.0, 5.03 grams of oleic acid is added in 1,000 g of dodecane.

VITA

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