Effects of Monovalent Ions on Low Salinity Waterflooding in Shaly-sandstone Reservoir

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ผลของไอออนประจุเดี่ยวในกระบวนการฉีดอัดน้ำความเค็มต่ำในแหล่งกักเก็บหินทรายปนหินดินดาน

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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อติวิชญ์ ยมจันทร์ : ผลของไอออนประจุเดี่ยวในกระบวนการฉีดอัดน้ำความเค็มต่ำในแหล่งกักเก็บหินทรายปนหินดินดาน. (Effects of Monovalent Ions on Low Salinity Waterflooding in Shaly-sandstone Reservoir) อ.ที่ปรึกษาหลัก : อ. ดร.ฟ้าลั่น ศรีสุริยชัย

กระบวนการแลกเปลี่ยนไอออนหลายชนิดได้รับการพิสูจน์แล้วว่าเป็นกระบวนการสำคัญที่เกิดขึ้นในระหว่างการฉีดอัดน้ำความเค็มต่ำ การลดค่าความเค็มของน้ำและลดความเข้มข้นของไอออนประจุคู่ในน้ำ ร่วมกับการผสมไอออนประจุเดี่ยวลงในน้ำ จะทำให้ไอออนประจุคู่ที่สร้างพันธะเชื่อมหินและน้ำมันเข้าด้วยกันหลุดออก เป็นผลให้น้ำมันถูกผลิตออกจากแหล่งกักเก็บได้

วิทยานิพนธ์นี้ได้ศึกษาผลกระทบของไอออนประจุเดี่ยวในกระบวนการแลกเปลี่ยนไอออนหลายชนิด การทดลองด้วยการกวน (stirring test) พบว่า ไอออนประจุเดี่ยวที่มีน้ำล้อมรอบโมเลกุลน้อยมีแนวโน้มที่จะทำปฏิกิริยาได้รวดเร็วกว่าในระหว่างกระบวนการแลกเปลี่ยนไอออนหลายชนิด และเมื่อเปรียบเทียบไอออนประจุเดี่ยวในหมู่ 1 พบว่า โพแทสเซียมและซีเซียมมีศักยภาพในกระบวนการเพิ่มผลผลิตน้ำมันดิบ จากนั้น น้ำที่มีเพียงซีเซียมไอออน น้ำที่มีเพียงโพแทสเซียมไอออน และน้ำที่ผสมระหว่างซีเซียมไอออน-โซเดียมไอออน-แคลเซียมไอออน ในอัตราส่วน 20-40-40 ถูกใช้ในการทดลองฉีดอัดน้ำในอุปกรณ์แทนที่ของไหล พบว่า น้ำที่มีเพียงซีเซียมไอออนและน้ำที่มีเพียงโพแทสเซียมไอออนมีประสิทธิภาพในการเพิ่มผลผลิตน้ำมันดิบได้เป็นอย่างดี ขณะที่ซีเซียมไอออนจะมีความว่องไวในการแทนที่น้ำมันดิบบนหินมากกว่า ส่วนน้ำที่ผสมระหว่างซีเซียมไอออน-โซเดียมไอออน-แคลเซียมไอออน ในอัตราส่วน 20-40-40 มีประสิทธิภาพใกล้เคียงกับน้ำที่มีเพียงโพแทสเซียมไอออน โดยน้ำที่มีเพียงซีเซียมไอออนเป็นน้ำที่มีประสิทธิภาพสูงสุดและสามารถเพิ่มผลผลิตน้ำมันดิบได้มากถึง 26% อย่างไรก็ตาม ผลการไตเตรทน้ำที่ผ่านหินมาแล้วในขั้นตอนการทดลองฉีดอัดน้ำในอุปกรณ์แทนที่ของไหล พบว่า แตกต่างจากผลการทดลองด้วยการกวน เนื่องจากผลการไตเตรทแสดงให้เห็นว่า ซีเซียมไอออนและโพแทสเซียมไอออนมีแนวโน้มเข้าแทนที่แมกนีเซียมไอออนบนหินมากกว่าแคลเซียมไอออนบนหิน จากการศึกษาในครั้งนี้สามารถพิสูจน์ทฤษฎีการถูกล้อมรอบของไอออนประจุเดี่ยวด้วยน้ำได้

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Multi-component Ion Exchange (MIE) was proved to be a major mechanism occurred during Low Salinity Waterflooding (LSWF). Reduction of both total salinity and concentration of divalent ions of injected water together with a presence of monovalent ion results in dissolution of divalent ions linking between rock surface and oil. As a consequence, oil is liberated from rock surface.

This study aims to study effects of monovalent ions in MIE mechanism. Stirring test is performed and results show that ion with less hydration radius tends to be more active in MIE; hence, potassium ion and cesium ion illustrate potential in oil recovery mechanism. Then, the best three water formulations can be selected to perform imbibition and coreflood tests and both tests show results in the same direction. Pure cesium ion is very fast in MIE mechanism while pure potassium ion with a few water molecules can also function well in oil recovery. However, its mobility is less than cesium ion. The combination of cesium-sodium-calcium at 20-40-40 tends to be similar results of pure potassium ion. In comparision, Pure cesium ion is the best water formulation enhacing recovery factor up to 0.26. However, complexometric titration result shows remarkable contrast to the stirring test that both cesium ion and potassium ion tend to displace magnesium ion better than calcium ion. In conslusion, this study has already proved the theory regarding the hydrate of monovalent ion.

Field of Study:	Georesources and Petroleum Engineering	Student's Signature ....
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Ativish Yomchan

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List of Abbreviations

1-D	One Dimension
CEC	Cation Exchange Capacity
cm	Centimeter
cP	Centipoise
DLE	Double-Layers Expansion
EBT	Eriochrome Black T
EDTA	Ethylenediaminetetraacetic acid
FW	Formation Water
g	Gram
g/l	Gram per Litre
HNB	Hydroxynapthol Blue
IOR	Improved Oil Recovery
LS EOR	Low Salinity Water Enhanced Oil Recovery
LSWF	Low Salinity Waterflooding
M^+	Monovalent ion
mD	Milidarcy
MIE	Multi-component Ion Exchange
mol/L	Molar concentration
^oC	Degree Celsius
OOIP	Original Oil In Place
pH	potential of Hydrogen
ppm	part per million
psi	Pound per square inch
PV	Pore volume
T	Temperature

List of Nomenclatures

ρ_f	Fluid density
ρ_o	Oil density
ρ_w	Water density
ΔP	pressure difference across core sample
μ_o	Viscosity of oil
μ_w	Viscosity of water
A	Cross-sectional area
f_w	Fractional flow of water
k_a	Absolute permeability
k_{ro}	Relative permeability to oil
k_{rw}	Relative permeability to water
L	Core length
M	Mobility ratio
q	Injection rate
S_w	Water saturation
S_{wi}	Initial water saturation
V_b	Bulk volume
V_p	Pore volume
V_r	Recoverable of formation water
V_w	Volume of water
W_{dry}	Dry weight
W_f	Weight of fluid
W_{sat}	Saturated weight
φ	porosity

CHAPTER I

INTRODUCTION

1.1 Overviews

In 2014, the oil price was dramatically dropped more than 50% and this created serious problems to oil companies. Hence, in order to get through this problem, oil companies have to maximize the efficiency of oil production as much as possible. Typically, extraction of oil and gas from reservoirs often comes together with produced water especially those reservoirs supported by strong water aquifer beneath. Hence, the higher the oil production, the higher the amount of produced water. In most production sites, the idea of conventional waterflooding takes place to dispose this produced water and at the same time, to maintain reservoir pressure, pushing oil ahead to adjacent production well. Due to its simplicity and cost-effectiveness, waterflooding is usually implemented in most of the oil-producing fields. However, conventional waterflooding has also several disadvantages. One occurs when water is reinjected to the heterogeneous reservoirs; for example, reservoir containing layers with different values of permeability. Injected water will tend to flow through a layer with the highest permeability first, leaving oil in other layers with lower permeability un-swept. Moreover, conventional waterflooding is ineffective especially when reservoir rock is strongly oil-wet. Injected water will flow through the middle space of large pores, leaving most of oil attached on rock surface as well as in smaller pores.

Low Salinity Waterflooding (LSWF) has become one of the methods to solve these problems, especially in one with unfavorable wetting condition. In details, LSWF is performed to increase oil recovery by injecting water with lower salinity compared to that of formation water to displace oil more efficiently by both physical displacement and chemical displacement mechanisms. Obtained oil recovery factor from LSWF is generally higher than conventional technique; however, the magnitude of the increment still depends on many factors. Naturally, sandstone reservoir is mostly discovered as water-wet surface but in certain conditions, it can be found as oil-wet. As divalent ions and carboxylic acid are presented in reservoir fluids, oil-wet condition can be formed through ion-binding using divalent ion as a bridge between sand and clay surfaces and organic acid dissolved in oil (Buckley et. al 1998). By this mechanism, sandstone surface can be adhered to oil and eventually becomes oil-wet condition. Reduction of total salinity as well as concentration of divalent ions of injected low salinity water results in dissolution of divalent ions linking between oil layer and rock surface. In addition, presence of monovalent ions in injected water helps replacing divalent ions. At the same time, presented divalent ions in injected water will form carboxylate complex with carboxylic acid in crude oil (Lager et. al 2008). From these three mechanisms, oil can be liberated from rock surface and these explain why oil recovery factor is generally higher than the case of conventional waterflooding. The overall mechanism is so-called Multi-component Ion Exchange (MIE). As the role of monovalent ions mentioned during the MIE mechanism is also important, the study nowadays aims to pay attention on monovalent ions in completion of the whole MIE mechanism to enhance oil recovery. Several monovalent ions including both species found in formation water and foreign species added by additional chemicals are therefore chosen for this study to understand their effects on MIE. Lithium ion (Li^+), sodium ion (Na^+), potassium ion (K^+), and cesium ion (Cs^+) are chosen as monovalent ions in these studies. These elements are different in terms of atomic number but they all have only one valent electron. However, higher atomic number comes with more numbers of electron orbits as well as atomic size. This eventually causes each ion to have different capacities to attract different numbers of water molecule and ionic mobility.

In this study, effect of monovalent ions on LSWF in sandstone is performed. Shaly-sandstone sample from S1 oilfield located in the north of Thailand is used to represent reservoir rock. The study begins with stirring and titration tests. Grinded rock sample is stirred with low salinity water formulations containing different monovalent ions in order to determine capability of each ion in MIE mechanisms. Determining of capability in MIE is measured from dissolution of calcium and magnesium ions from rock surface as well as disappearance of monovalent ion from the solution. Complexometric titrations are used for determining divalent ion in the solution, whereas back titration is the technique chosen for measurement of disappearance of monovalent ions. Selected two monovalent ions are then mixed with calcium ion in various ratios at suitable total concentration obtained from previous step in order to assess the collaboration of monovalent and divalent ions in MIE. In the last step of stirring test, sodium ion which is abundant formation water is added into two-component solution to represent the most realistic case when formation water is considered to be a major source of making up of low salinity water. After that, four water formulations are selected for the imbibition and coreflooding tests. Finally, effectiveness of each solution can be concluded and the best LSW formulation can be identified.

1.2 Objectives

- To evaluate the effectiveness of monovalent ions in low salinity water during low salinity waterflooding in shaly-sandstone formation.
- To compare the effectiveness of selected monovalent ions as three-component low salinity water related to their ionic properties.

CHAPTER II

LITERATURE REVIEW

In recent years, number of researches and studies related to LSWF has been noticeably increased. As the core explanation is still under investigation, many branches of study are created. The selected literature reviews for this study are separated into two groups which are the studies that show evidences of oil recovery by LSWF in sandstone and shaly-sandstone formations and the studies that document effects of ion composition on effectiveness of LSWF.

2.1 Evidences of Oil Recovery by Low Salinity Waterflooding in Sandstone Formation and Shaly-sandstone Formation

In 2010, there were only a few papers studying on experiments in order to proof LSWF concepts in a reservoir scale. The first literature review is one of the studies performed by Vledder et al. (2010). They conducted spontaneous imbibition experiments on core samples and a single well log-inject-log test in an analogue field in order to proof the wettability alteration by injecting low salinity water in a field implementation over a period of about 10 years. The field observations in this study were divided into three conditions: (1) initial condition where reservoir should be mixed- to oil-wet (2) final condition where the wettability of reservoir should be more water-wet comparing to the initial condition and (3) intermediate condition which was the condition in between the initial and final conditions. Laboratory experiments were also used in order to compare the results obtained from field scale experiments. According to both scales of experiment, the results showed that, based on the observed water-cut development and 1-D fractional flow calculations, increased recovery factor can be estimated between 9 to 23% from laboratory experiments and 5 to 15% from field scale experiments. Therefore, the results can be summarized from mostly overlap of such results that the increased recovery factor due to low salinity injection in Omar Field was about 10 to 15% of the stock tank oil initial in place. In conclusion, this study illustrated that the wettability can be changed at a reservoir scale similar to laboratory experiments by LSWF.

Austad et al. (2010) performed waterflooding experiments, adsorption measurements, and chemical model simulations in order to observe chemical mechanism of LSWF in sandstone reservoir. After completion of experiments, results showed that adsorption of basic compounds onto clay minerals was significantly depending on the pH value which yielded the maximum adsorption at pH value of about 4. Changing of temperature decreased the adsorption onto clay minerals only small amount. The adsorption of acidic compounds onto clay minerals was dependent on pH value. Higher acid adsorption was observed in a lower pH environment. Furthermore, this study also observed the suitable conditions for LSWF effect by performing experiments and the results showed that the favorable type of clay minerals for observation were montmorillonite > illite/mica > kaolinite based on Cation Exchange Capacity (CEC). Type of polar components in oil did not significantly affect LSWF. In addition, compositions of formation water including active cations, protons, and organic material was also important as well as composition of the injection fluid as low salinity water has to have action ions low enough to drive desorption mechanism.

Cissokho et al. (2010) did several experiments dealing with tertiary and secondary recovery tests performed on an outcrop sandstone containing 9.2% of clays without kaolinite. Secondary recovery mode was performed by injecting low salinity water directly into aged core, whereas tertiary mode experiment referred to a technique performed by injecting high salinity water followed by low salinity water. The results showed that low salinity water injection can lead to additional oil recovery in both secondary and tertiary modes. In details, relating to effect of brine concentration and composition, additional oil recovery of about 9% was obtained from tertiary recovery experiments at moderate temperature (T = 35 ^{o}C) when salt concentration was reducing from 50 g/l to 1 g/l (from 50,000 ppm to 1,000 ppm). Moreover, oil recovery was increased with increasing displacement temperature. No significant additional oil recovery was obtained when LSWF was performed at 60 and

90 °C. However, in the first three pore volumes, the results showed that the benefit of low salinity water injection might be temperature dependent.

Morrow and Buckley (2011) summarized the effects of LSWF in several tests. For the first test, LSWF at initial water saturation as a secondary-mode clearly increased oil recovery factor. In addition, in case that connate water was low in salinity, either low or high salinity of injected water, the oil recovery factor was maximized. For the second test, LSWF was performed at residual oil saturation (from high salinity waterflooding) as tertiary-mode, requiring many pore volumes of injected water. The results showed that LSWF can increase oil recovery factor up to 25% with the average oil recovery factor increment of 14%. Moreover, the authors also explained about wettability alteration mechanisms by changing rock surface to be more water-wet during LSWF. This mechanism enhanced liberation oil from rock surfaces and raised oil recovery factor.

Pinerez et al. (2016) conducted corefloods in order to investigate effects of changing of pH value on oil recovery factor of core samples from six different locations in USA including Briar Hill, Idaho Gray, Leopard, Cedar Creek, Boise, and Sister Gray. Core samples were flooded by four different types of injected water. Formation water was prepared with salinity of 35,604 ppm (FW1) and it was diluted 20 times to 1,780 ppm (d20FW1) and was used as low salinity water. In addition, formation water with high salinity of 100,000 ppm (FW2) and low salinity water of 1,000 ppm (LS) were also used in this study. After performing pH screening test and oil recovery test, results were discussed. Cores with high content of feldspars as Idaho Gray and Boise were changed for pH values only 0.5 and 1.0 respectively, resulting in the low tertiary LS EOR effects 3.27% and 1.09% of original oil in place for Idaho Gray and Boise respectively. This can be explained by small displacement of H^+ onto the rock surface that is in line with small value increment of pH value. In addition, the core with the highest clay content as Cedar Creek and the core with the lowest clay content as Leopard were changed for pH values only 0.5 and 0.4 respectively and recovery factors were increased only 0.74% and 1.05% respectively, showing a very small LS EOR effects. However, there were two cores which yielded different results. The core from Sister Gray did not show LS EOR effects as pH was not changed and it was observed that there was no tertiary LS EOR effect. In addition, for Briar Hill, the pH was not changed significantly but recovery factor was increased by 3.65% of OOIP, showing the largest increment in tertiary LS EOR effects. In conclusion, it was difficult to prove any correlation between change in pH value and observed LS EOR effect. It is definitely not only the change of pH value which is important for observing LS EOR effect, but there are also other factors relating to LS EOR effect to consider such as mineralogy and initial pH of injected water.

2.2 Effects of Ion Compositions in Injected Water on Low Salinity Waterflooding

Ramez et al. (2011) conducted coreflood experiment using Berea sandstone core samples and two different types of crude oils. Solutions of NaCl, $CaCl_2$, and $MgCl_2$ at different salinities including 1 wt% and 5 wt% (10,000 ppm and 50,000 ppm) for each salt were artificially prepared as used as injected water. The objective of this study was to understand how type of cation in injected water affects oil recovery mechanism. Moreover, this study also investigated the effect of cation concentration on magnitude of oil recovery. The results showed that since NaCl and $MgCl_2$ brines allowed leaching or dissolution of Ca^{2+} from the rock surface which is the major cause of oil recovery enhancement. Therefore, injection of NaCl and $MgCl_2$ brines helped increase oil recovery remarkably compared to $CaCl_2$ injection at the same concentration where Ca^{2+} in injected water prohibited dissolution mechanism of Ca^{2+} from sandstone surface. Moreover, NaCl have stronger negative charge compared to $CaCl_2$. Hence, it can alter the charge of the rock to be more negative and generate repulsion forces between oil and rock, causing oil to be liberated from rock surface. Decreasing cation concentration in single-cation brines did not improve oil recovery significantly. In summary, the effect of cation type was observed to be more important on oil recovery than total salinity of injected water.

RezaeiDoust et al. (2011) performed dynamic coreflood in order to observe oil recovery factor. Moreover, pH value and density of effluent water were also detected. Results showed that, according to pH gradient in LSWF along core sample, increasing of pH due to injecting NaCl brine was the highest compared to $CaCl_2$, KCl, and $MgCl_2$ brines since Na^+ has the lowest affinity toward the clay surface. Hence, H^+

can substitute the Ca^{2+} on the clay surface causing the reduction of H^+ in formation water as well as increasing of the pH. Moreover, initial pH value of formation water also had an effect on oil recovery factor. The core containing dissolved CO_2 which had lower pH value comparing to the core without yielded higher oil recovery factor about 5% of original oil in place for secondary LSWF and 8% of oil in place for enhancing oil recovery factor from tertiary LSWF. This can be explained by increasing of viscosity of oil due to CO_2 in such core. Different crude oils with different acid and base numbers were also tested in order to determine effects of crude oil properties on LSWF. Results showed that both basic and acidic crude oils showed quite similar low salinity effects in core sample containing clay minerals. This study also performed a coreflood test to determine possible end-effects which is the oil recovery factor that cannot be increased even injection rate is higher. It was interesting that oil recovery factor did not increase until injection rate of LSWF was raised up to 16 pore volume/day. Furthermore, this study also performed static adsorption/desorption of polar components which were quinoline representing base component and 4-tert-butyl benzoic acid representing acid component. For basic component, the adsorption of quinoline onto all the studied clays which were kaolinite, illite, and montmorillonite at pH of 5 was significantly higher than adsorption at pH around 8 to 9. For acidic component, the adsorption of 4-tert-butyl benzoic acid onto kaolinite showed that great hysteresis was happened for the low salinity brine in the concentration where precipitation took place at concentration of acid higher than 0.004 mol/L in the pH range 5.5 – 6.0, whereas no hysteresis occurred for high salinity brine.

Awolayo et al. (2014) performed experimental studies on carbonate core samples, consisting of zeta potential measurement, contact angle measurement and coreflooding experiment in order to determine the impacts of formation water and various five different sulfate concentrations of seawater (smart brine) as injected water on oil recovery factor, wettability and surface modification. The results demonstrated that increasing sulfate concentration in smart brine plays important role on oil liberation. In addition, monitoring of wettability through contact angle, sulfate ion can alter wetting state of the rock to be more water-wet. The higher the sulfate ion concentration resulted in higher degree of water-wetness of rock surface. However, the optimum sulfate concentration in smart brine yielding the highest oil recovery was four times compared to concentration in formation brine. In addition, this could be explained with zeta potential measurement that beyond four times of sulfate concentration, there was no further surface charge alteration.

Srisuriyachai et al. (2017) conducted experiment mainly emphasizing on imbibition test dictating how fast each ion can replace the divalent ion in water film between sandstone surface and crude oil. The experiments were divided into two parts. First experiment was imbibition test with five different injected water including KCl 5,000 ppm, NaCl 35,000 ppm, KCl 35,000 ppm, Seawater 35,000 ppm, and seawater without KCl 35,000 ppm. The results of this experiment showed that experiment performed by using KCl yielded higher oil recovery factor compared to NaCl at the same salinity. This can be explained by the hydrated size of potassium ion which is smaller than that of sodium ion and as a result, potassium ion was better in terms of ionic mobility. Moreover, higher salinity of potassium ion provided higher oil recovery factor compared to the lower concentration since there were more available potassium ions to displace divalent ion linking between adsorbed oil layer and sandstone surface. Furthermore, seawater with much lower amount of potassium ion (369 ppm) can liberate more oil than solution of KCl at 35,000 ppm. This could be explained that collaboration of several ions took place to release oil form rock surface. Without potassium ion in injected water, oil factor recovery was substantially low. This confirmed that potassium ion played an important role oil recovery mechanism. Second experiment was imbibition test in large core samples with KCl 5,000 ppm compared to NaCl 5,000 ppm. As multi-component ion exchange occurred, calcium ion from bridging layer was released in effluent and it can be detected by complexometric titration to identify replacing amount. The results showed that potassium ion which is more reactive than sodium ion can displace higher amount of calcium, supporting the results from the first section.

Srisuriyachai and Peerakham (2017) used coreflooding test to study effects of potassium ion in formation water. The samples of formation water were prepared to have different ratios of sodium to potassium including 150:1 (low potassium amount) and 50:1 (high potassium amount). Then, ratio of calcium ion to magnesium ion was varied to 3:1, 5:1, 7:1, 9:1, and 11:1. Samples were prepared using formation water with total salinity of 100,000 ppm referring to information of formation water in sandstone reservoirs with high salinity around the world. From this study, the results showed that, in case of low K^+, oil recovery factor was the highest when ratio of Ca^{2+}:Mg^{2+} was 11:1. This can be explained by the ionic radius of Ca^{2+} which is larger than that of Mg^{2+}, causing oil to be loosely absorbed onto sandstone surface and as a consequence, oil liberation occurred easily. Furthermore, oil recovery from the case with low K^+ was higher than the case of high K^+. As hydrated radius of Na^+ is bigger than that of K^+, the water film covering sandstone surface was thicker and oil was loosely adsorbed. Moreover, this paper also studied effects of formation water with extremely high content of potassium ion by injecting formation water with 48,000 ppm of K^+ from the total salinity of 134,000 ppm, corresponding to Na^+ to K^+ ratio of about 1:3. The results showed that oil recovery factor was low since K^+ is smaller in hydrated radius compared to Na^+ and hence, the water film was thinner and oil was adhered onto rock surface with higher strength. On the other hand, if mixing seawater with smaller portion of formation water, it created low ionic strength with adequate amount of ions to initiate multi-component ion exchange mechanism.

From literature reviews, only a few paper mentioned the mechanisms where monovalent ion replaces the site of divalent ion which is in between clay surface and oil drop. In order to enhance this mechanism, the best monovalent ion should be selected and hence, this study is performed to assess the capability of different monovalent ions in different modes including as single-component, two-component and also three-component. The results obtained from this study confirms the properties of monovalent ion required for LSWF.

CHAPTER III

Relevant Theory

3.1 Conventional Waterflooding and Low Salinity Waterflooding

Typically, oil production from petroleum reservoir is started with natural drive mechanisms so-called primary recovery, lifting hydrocarbons from the reservoir to the surface by natural stored force. Usually, there are five common drive mechanisms including water drive, gas expansion, solution gas, rock or compaction drive, and gravity drainage (Hartmann and Beaumont 1999) . As production continues, the primary recovery reaches its limitation and reservoir pressure is not adequate to lift hydrocarbon up to the surface. At this point, oil production rate reduces while water production rate often rises up. In some countries, produced water is disposed to nearby streams or rivers in case of onshore or water reservoir under subsea in case of offshore. However, in order to utilize the produced water, conventional waterflooding is applied by reinjecting produced water. Reservoir pressure is increased by this water to its initial level, prolonging the production. The injected water displaces oil from pore spaces as voidage replacement. The efficiency of oil displacing (waterflooding efficiency) can be explained by mobility ratio (M) as the mobility of the displacing phase (water) divided by the mobility of the displaced phase (oil) illustrating in Equation 1:

$$M = (k_{rw}/\mu_w)(\mu_o/k_{ro}) \qquad \text{(Equation 1)},$$

where μ_w = viscosity of water (cP), μ_o = viscosity of oil (cP), k_{rw} = relative permeability to water, and k_{ro} = relative permeability to oil.

According to Equation 1, in case that mobility ratio is lower than unity, this means that oil, which is displaced phase, can move faster than water, which is displacing phase, and this is considered to be favorable mobility ratio. On the other hand, when mobility ratio is higher than unity, this indicates that oil moves slower than water, leading to an “unfavorable mobility ratio”. In conclusion for mobility ratio, if the value can be lower, oil production tends to be more favorable.

The efficiency of waterflooding process can be determined by fractional flow theory which is based on the study of Buckley and Leverett (1942). The fractional flow equation can be derived from;

$$\frac{\partial S_w}{\partial t} + \frac{q}{A\varphi}\frac{df_w}{dS_w}\frac{\partial S_w}{\partial x} = 0 \qquad \text{(Equation 2)}$$

where q = the injection rate, A = the cross-sectional area, $\boldsymbol{\varphi}$ = porosity, and Sw = water saturation; and the fractional flow of water (f_w) is expressed as;

$$f_w = \frac{k_{rw}/\mu_w}{k_{rw}/\mu_w + k_{ro}/\mu_o} \qquad \text{(Equation 3)}$$

where k_{rw} and k_{ro} are relative permeabilities to water and to oil, respectively, and μ_w and μ_o are water and oil viscosities.

Although Buckley-Leverett analysis uses simple mathematical models, this theory provides prompt and decent estimations of water breakthrough and oil bank height and duration in both experiments as well as in the fields (Luo et al 2017).

However, conventional waterflooding can increase recovery factor at only certain amount as there are many reasons causing an adverse situation for waterflooding such as existing of permeability contrast in several layers, reservoir heterogeneity, unfavorable mobility ratio due to inappropriate fluid viscosities and oil-wet condition. These cause oil to remain upswept and due to these reasons, LSWF has been studied to increase recovery from this remaining portion of oil.

LSWF is one of Improved Oil Recovery (IOR) methods, performed by using water containing salinity lower than that of formation water as an injected water. Injecting low salinity water will cause a shift of rock-oil-water equilibrium, resulting in liberation of oil. In sandstone reservoir where oil-wet condition can occur through several mechanisms, LSWF can alter the wettability of rock to a more water-wet condition. Even though sandstone is mostly found water-wet in nature, some of sandstone reservoirs can be altered to oil and can possess oil-wet condition. Figure

3.1 illustrates ion-binding mechanism which is one that usually causes sandstone surface to become more oil-wet. In details, divalent ions in formation water such as calcium ion and magnesium ion act as the linking bridge between the negative charges of sandstone surface and the negative charges from carboxylic acid in oil. By this mechanism, oil can be adsorbed onto sandstone surface in a presence of divalent ions. A presence of high shale content also facilitates higher degree of oil-wet condition. As shale possesses large surface area, shale can also be bound with large amount of divalent ions to balance surface charges. It is therefore usually found that shaly-sand reservoir shows greater benefit by LSWF compared to clean-sand.

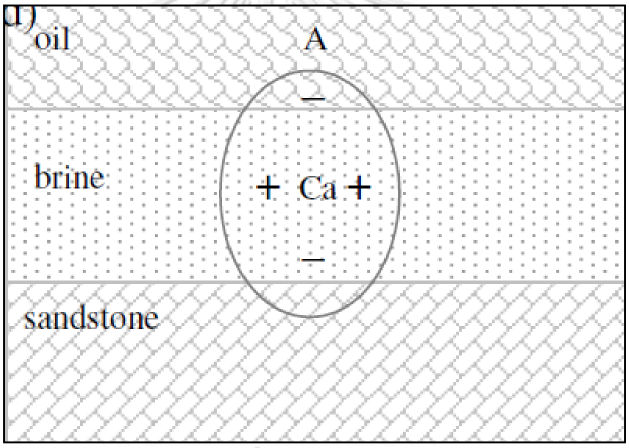


Figure 1 *Ion-binding interaction between sandstone surface and oil, creating oil-wet condition (Buckley and Liu 1998)*

Nowadays, oil recovery mechanisms by LSWF are revealed in different ways. A very first oil recovery mechanism was proposed by Tang and Morrow (1999) that, in a presence of high salinity brine, clay particles are undisturbed and the surface is oil-wet condition, causing low oil production. However, once low salinity water is injected into formation, clay particles on rock surface undergo the salinity shock, resulting dislodging of these clays that can accompany oil in droplet form. However, this explanation was not observed in every case and therefore, additional explanation was researched. The second explanation aimed for the rising up of pH value by dissolution of calcium carbonate that can be found in sandstone as a cementing material. The dissolution mechanism of calcium carbonate is shown in Equation 4 as chemical reaction below, causing an excess of OH^- which is responsible for rising up of pH value.

$$CaCO_3 \longleftrightarrow Ca^{2+} + CO_3^{2-}$$
$$CO_3^{2+} + H_2O \longleftrightarrow HCO_3^- + OH^- \qquad \text{(Equation 4)}$$

These chemical reactions are relatively slow and depending on amount of carbonate compounds in the rock. While cation exchange occurs on clay minerals faster, the clay mineral surface will exchange H^+ presenting in liquid phase with cations previously adsorbed, leading to a reduction of H^+ concentration, resulting in rising up of pH value. Increasing pH value during LSWF may provoke situation as in alkali flooding. Higher pH value favors the generation of natural surfactant that can further reduce interfacial tension between oil and aqueous phase. Residual oil saturation can be therefore, produced in a form of emulsion. Nevertheless, it is observed that not every case that the effluent from LSWF shows high pH value. The only oil recovery mechanism that has been proved to fit in most cases is so called Multi-component Ion Exchange (MIE). This mechanism however, is still complicated as there are several theories that are not totally coincident.

3.2 Multi-component Ion Exchange

Explanation of Multi-component Ion Exchange (MIE) is graphically illustrated in figure 3.2. A MIE mechanism occurs at sandstone surface in collaboration with different ions due to different affinities of various cations toward the sandstone surface. Typically, sandstone surface can turn to an oil-wet condition as previously explained and crude oil/brine/sandstone surface system is intrinsically in a thermodynamic equilibrium. Injection of water that is low in both total salinity and divalent ions concentration into sandstone reservoir results in disturbing of the equilibrium system. This consecutively causes dissolution of divalent ions that link as bridges between sandstone surface and oil. At the same time, presence of monovalent ions helps completing of MIE mechanism. Negative charges from monovalent ions therefore, neutralize sandstone surface. Oil droplet is liberated together with calcium ion from sandstone surface in a form of calcium carboxylate complex with carboxylic acid in crude oil. Similar to calcium ion, magnesium ion in injected water can also form magnesium carboxylate complex but this only occurs at elevated temperature.

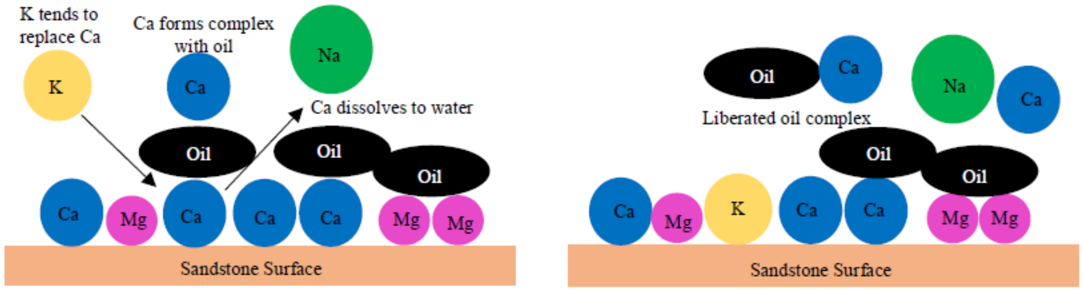


Figure 2 *Illustration of Multi-component Ion Exchange mechanism in sandstone surface (Srisuriyachai et al. 2017)*

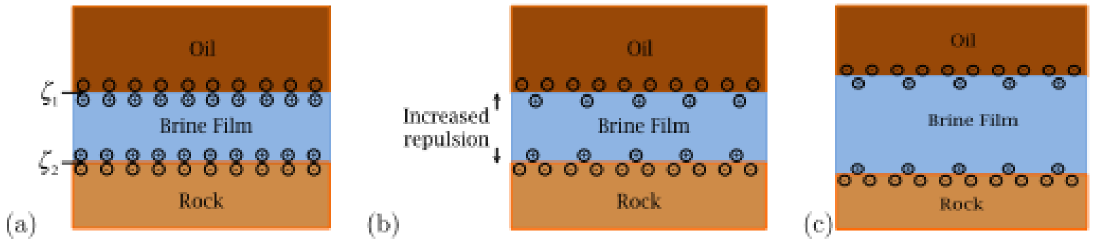


Figure 3 *Double Layered Expansion (DLE) phenomenon*
(a) Counter ions in the thin brine film adsorb to the negative charges of rock and oil forming an electrical double layer at each interface, (b) Reduction of salinity causing more repulsion between two interfaces and (c) Thicker brine film as result of DLE showing rock is becoming more water-wet (Myint and Firoozabadi 2015)

Together with MIE, additional mechanism may occur during LSWF and this can favor the oil recovery mechanism in the same direction. Myint and Firoozabadi (2015) have explained the phenomenon called Double Layered Expansion (DLE). Ions expand electrical diffuse double layers surrounding the negatively charged clay and adsorbed oil particle. The expansion leads to weakening of the adhesion between oil and rock surface. So, oil can be easily liberated as shown in figure 3.3. Nevertheless, several documents confirm that DLE only occurs when salinity of injected water goes below 500 ppm.

3.3 Brine Chemistry

Brine is a high-concentrated solution of salt (usually sodium chloride) in water. Percentage of salt content in brine can range from about 3.5%, which is typical concentration of seawater, up to about 26%. Water formulations with lower concentrations of salt are called by different names such as fresh water, brackish water, and saline water.

Naturally, brine occurs on Earth's surface (salt lakes), crust, and within brine pools on ocean bottom. Typically, high-concentrated brine lakes is emerged due to evaporation of ground saline water on high ambient temperatures, releasing water content out of ground saline water and, increasing salt concentration. Brine is used for food processing and cooking (pickling and brining), for de-icing of roads and other structures, and in a number of technological processes. It is also a by-product of many industrial processes, such as desalination, and may cause environmental impacts due to its corrosive and toxic effects if it is not treated properly by wastewater treatment system.

Chemically, compositions of brine are related to seawater as well as lithology where sediments are deposited during sedimentation processes. Commonly, compositions of brine mainly consist of chloride, sodium, sulfate, magnesium, calcium, and potassium ions varying from area to area. Figure 3.4 shows the example of brine compositions compared to seawater. By the way, salinity of brine is related to these elements which can be classified as slightly saline water at 1,000 – 3,000 ppm, moderately saline water at 3,000 – 10,000 ppm, and highly saline water at

10,000 – 35,000 ppm. In petroleum industry, chemistry of brine as formation water is essential for the design of drilling and completion fluids, corrosion damage to equipment, fines mobilization, clay swelling and scale precipitation, and design of surface fluid handling facilities (Thyne and Brady 2016).

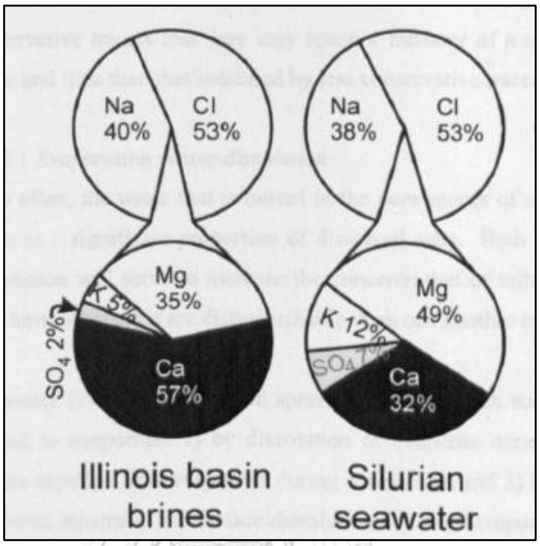


Figure 4 *Chemical compositions of typical Illinois basin brine (Walter et al. 1990) and Silurian seawater (Lowenstein et al. 2011)*

3.4 Ionic Properties and Fundamental of Hydration

The properties of ionic compounds play an important role in LSWF which relate to how strongly the positive and negative ions attract each other in an ionic bond. When an ionic bond is formed, there is a large electronegativity difference between the elements participating in the bond. The greater the difference of electronegativity between ions causes stronger attraction between positive ion (cation) and negative ion (anion). Ionic bonded compounds exhibit five main properties as follow;

- Crystal lattices are formed in three-dimensional structure based largely on the smaller ion which results in better filling in the gaps.

- Ionic compounds have high melting points and high boiling points, meaning that requirement of energy for melting and boiling ionic compounds is high.
- Ionic compounds have higher enthalpies of fusion and vaporization than molecular compounds, meaning that, in case of fusion, more heat is required for melt a single mole of a solid under constant pressure and, in case of vaporization, more heat is also required for vaporize a single mole of a liquid compound under constant pressure.
- Ionic compounds are hard due to strongly attachment between positive and negative ions. However, when ions or charges are forced to be closer, electrostatic repulsion can split ionic compounds meaning that it is hard but it can also be brittle.
- Ionic compounds can conduct electricity when they are dissolved in water because dissociated ions are free, resulting in conduction of electricity. However, Ionic compounds cannot conduct electricity very well due to tightly bonding of ions.

In addition, when ionic compounds are dissolved in water, the ions in the compound will react with molecules of water. The water then cluster and attract around positive ions. This process is called "hydration". The attraction between water molecules and ions can be strengthened when ions are smaller and charges of ions are higher. For the alkali metal ions, the degree of hydration is different due to the size of ion. In detail, as shown in Table 1, hydrated radius decreases down the alkali group meaning that $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

<u>Table 1</u> *Ionic radius and hydrated radius of alkali metals (Shrestha 2016) and divalent ions (Shannon 1976)*

Ions	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}
Ionic radius (pm)	76	102	138	152	167	86	114
Hydrated radius (pm)	340	276	232	228	226	800	600

From Table 1, it can be observed that ionic radius increases with atomic weight among alkali metals. However, the hydrate radius shows the opposite trend. As atomic number increases, number of orbital where electrons are filled are also increased, resulting in large volume of atom. However, proton which is located at the center of nucleus has also an effect to molecule of water surrounding. The attraction force of proton to water molecule is therefore the highest for lithium, resulting in many layers of water molecule surrounding around one lithium ion and consecutively causes the largest size of hydrated radius. Cesium ion instead, the orbital system contains many orbits and hence, the ionic radius is large. However, the attraction force from proton in the center of to water molecule cannot reach the area outside and hence, cesium does not cause hydration with water molecule and its hydrate size is the smallest one.

Number of water molecule surrounding monovalent ion does not determine only the size of hydrate but also the mobility in ionic activity. From Table 1, cesium ion, which is the smallest in terms of hydrate size, therefore is very fast in terms of ionic activity. Multi-component ion exchange is one of the activities where monovalent ion must participate and hence, a presence of ion such as cesium should accelerate a completion of MIE as well as oil recovery mechanism.

CHAPTER IV

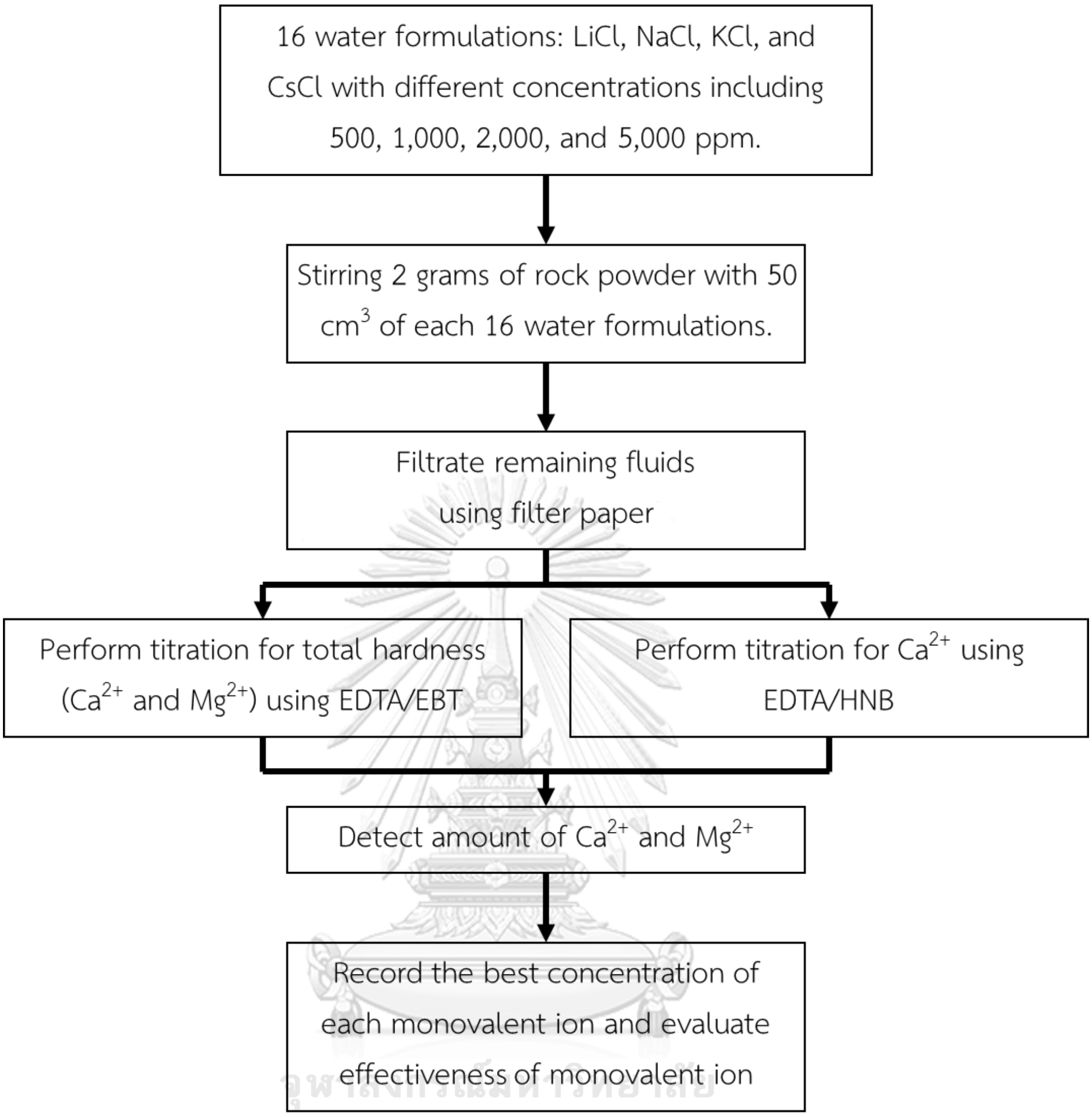
Methodology

The steps to determine effectiveness of monovalent ions in LSWF in shaly-sandstone reservoir are divided into four parts which are: 1) screening for appropriate concentration and compositions of injected water by stirring test together with color titrations; 2) determination of rock, fluid and petrophysical properties; 3) imbibition test to select water formulations; and 4) coreflooding test of selected water formulations. After the screening step, several water formulations expressing good MIE mechanisms are chosen for imbibition and coreflooding tests.

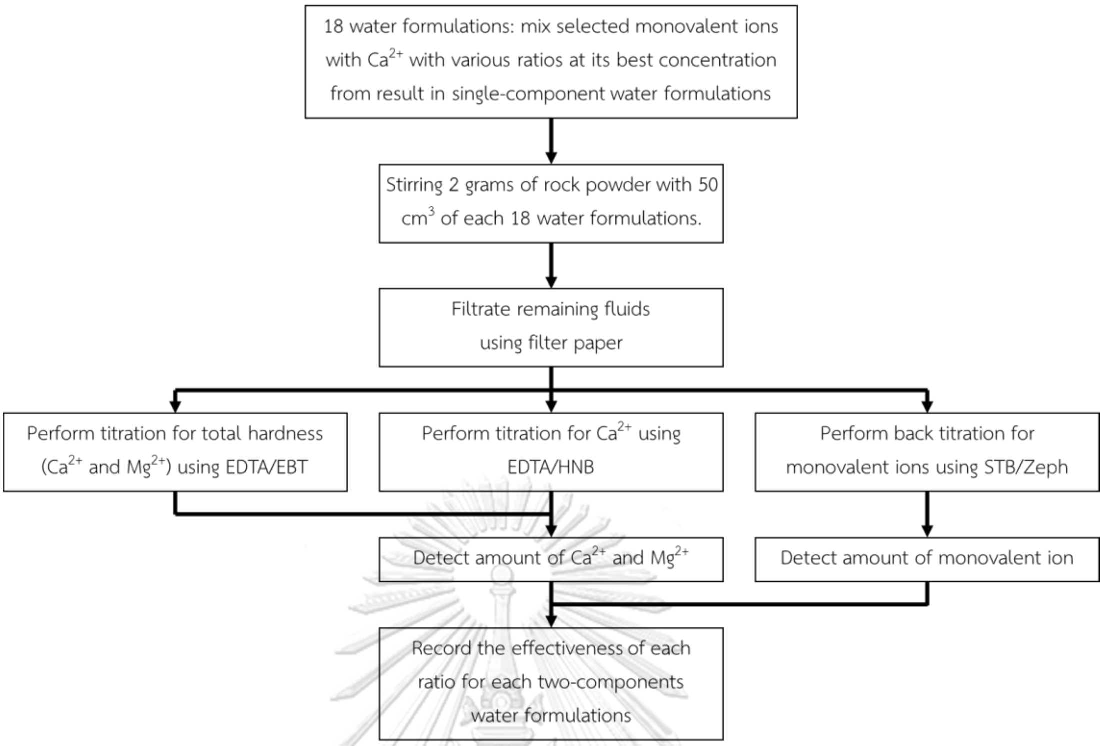
4.1 Screening for Appropriate Concentration and Compositions of Injected Water by Stirring Test together with Color Titrations

Overall of this study can be divided into three sections illustrated in figures 5 – 7 summarized the overall work plans for the studies of single component, two-component and three-component water formulations.

In this study, shaly-sandstone sample from S1 oilfield is prepared by grinding cores and cuttings into fine powder to express the highest surface conditions. The sample will not be cleaned by toluene and methanol to preserve linking bond between clay surface and hydrocarbon.



<u>Figure 5</u> *Screening for appropriate concentration of single-component water formulation and best monovalent ions by using stirring test and titrations*



<u>Figure 6</u> *Determination of the effectiveness of two-component water formulation using stirring test and titrations*

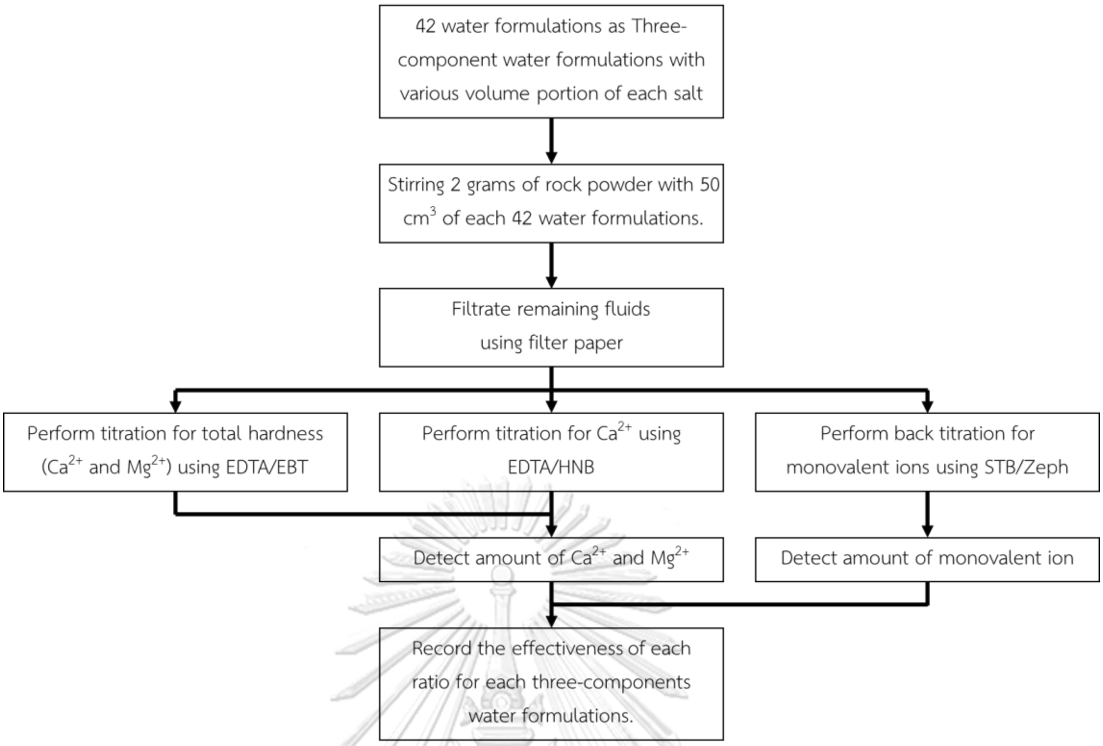


__Figure 7__ Determination for effectiveness of three-component water formulations using stirring test and titrations

4.1.1 Preparation of Water formulation

For the first step, chloride salts containing alkali including lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), and cesium chloride (CsCl) are prepared in solution at different salinity including 500 ppm, 1,000 ppm, 2,000 ppm, and 5,000 ppm. From this step, the best salinity is picked together with two monovalent ions representing the best performance in MIE mechanisms.

After that two-component water formulation is studied. As calcium ion is observed to be one of the potential determining ions, two monovalent ions from the previous step are then selected to mixed with calcium ion at various mass ratio including 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9.

As produced water is abundant and it can be one of the sources to make up injected water, sodium ion which is the most abundant ions in most fields is therefore, selected to add into a system as third component. The selected two monovalent ions from single-component water formulation are mixed in different portions with calcium ion and sodium ion to create three-component water formulations, covering area of ternary diagram. Table 2 shows the overall cases for one set to construct ternary diagram.

<u>Table 2</u> *Overall cases in mass portion of each ion to cover the whole area of ternary phase diagrams*

Volume portion							
Selected monovalent ion no.1				Selected monovalent ion no.2			
Case	$M1^+$	Na^+	Ca^{2+}	Case	$M2^+$	Na^+	Ca^{2+}
1	0	0	100	**1**	0	0	100
2	0	20	80	**2**	0	20	80
3	0	40	60	**3**	0	40	60
4	0	60	40	**4**	0	60	40
5	0	80	20	**5**	0	80	20
6	0	100	0	**6**	0	100	0
7	20	0	80	**7**	20	0	80
8	20	20	60	**8**	20	20	60
9	20	40	40	**9**	20	40	40
10	20	60	20	**10**	20	60	20
11	20	80	0	**11**	20	80	0
12	40	0	60	**12**	40	0	60
13	40	20	40	**13**	40	20	40
14	40	40	20	**14**	40	40	20
15	40	60	0	**15**	40	60	0
16	60	0	40	**16**	60	0	40
17	60	20	20	**17**	60	20	20
18	60	40	0	**18**	60	40	0
19	80	0	20	**19**	80	0	20
20	80	20	0	**20**	80	20	0
21	100	0	0	**21**	100	0	0

4.1.2 Stirring Test and Titrations

Shaly-sandstone powder weighed 2 grams (prepared in 4.1.1) is stirred with 50 cm^3 of each water formulation listed in 4.1.1 (and also Table 2). The most effective formulation will result in the maximum replacement of divalent ions (calcium and magnesium ions) on clays surface and hence, the highest amount of total hardness should detected in remaining liquid. Nevertheless, the optimum stirring time should be identified first from the salt with the lowest salinity. Remaining fluid must be filtrated to remove rock powder using filter paper. Filtrate is then used for titration of total hardness, calcium ion, and monovalent ion detection.

Complexometric titration using Ethylenediaminetetraacetic acid (EDTA) as a titrant and Eriochrome Black T (EBT) as an indicator is performed to determine total hardness which is the summation of calcium ion (Ca^{2+}) and magnesium ion (Mg^{2+}) dissolved filtrate. Titration is performed by pipetting 10 cm^3 of the filtrate into a conical flask and then, adding 3 – 4 drops of NH_3/NH_4Cl buffer solution and a little pinch of EBT indicator. After that, the mixture is titrated with 0.01 molar of EDTA from burette until color of the solution turns from wine red to sky blue with no hint of red. The amount of EDTA consumed to reach endpoint is detected for further calculation process.

Next, concentration of only calcium ion is determined. Again, 10 cm^3 of filtrated is pipetted into conical flask and a few drops of 50% w/v NaOH solution are added. Mixture is swirled vigorously to precipitate magnesium ion into magnesium hydroxide [$Mg(OH)_2$] insoluble compound. Then, pH of the solution is checked and the value should be at least 10 to ensure that there is no magnesium ion remained. A pinch of Hydroxynaphthol blue (HNB) is added and mixture is titrated with 0.01 molar EDTA until the color of solution turns to be sky blue. Volume of EDTA is detected to calculate calcium ion concentration in ppm. The different amount of EDTA in previous step and this step determines amount of magnesium ion in ppm. From the amount of calcium ion and magnesium ion, relationship of ionic properties and effectiveness in MIE mechanism are determined. Equation 5 and 6 illustrate how indicators change the color of solution for the total hardness and calcium ion titrations.

For determining of the concentration of total hardness (calcium ion and magnesium ion);

$$M^{2+} + \text{EBT}_{\text{(sky blue)}} \longrightarrow [\text{M-EBT}]_{\text{(wine red)}} + 2H^{+}$$

$$[\text{M-EBT}]_{\text{(wine red)}} + \text{EDTA} \longrightarrow [\text{M-EDTA}] + \text{EBT}_{\text{(sky blue)}} \qquad \text{(Equation 5),}$$

Note: EBT = Eriochrome Black T indicator (sky blue)

For determining of the concentration of calcium ion;

$$M^{2+} + \text{NaOH} \longrightarrow \text{Mg(OH)}_{2(s)} + \text{Ca}^{2+}{}_{(aq)}$$

$$\text{Ca}^{2+} + \text{HNB}_{\text{(sky blue)}} \longrightarrow [\text{Ca-HNB}]_{\text{(wine red)}} + 2H^{+}$$

$$[\text{Ca-HNB}]_{\text{(wine red)}} + \text{EDTA} \longrightarrow [\text{Ca-EDTA}] + \text{HNB}_{\text{(sky blue)}} \qquad \text{(Equation 6),}$$

Note: HNB = Hydroxynaphthol blue indicator (wine red)

For determining monovalent ion in water formulations, it is mainly performed to identify disappearance of cesium ion as it may function to replace calcium and magnesium ions. However, this technique will also include potassium ion as well as and hence, the amount of monovalent ion will represent mainly cesium ion from water formulation and potassium ion dissolved from clay surface. The titrimetry technique (Iwachido 1966) is performed by mixing certain volume of filtrate with known concentration of Sodium Tetraphenylborate (STB) to precipitate potassium ion and cesium ion (sodium ion will not be precipitated) and the remaining solution is titrated with known concentration of Zhephiramine (Zhep) also known as Benzyldimethyltetradecylammonium Chloride Dihydrate using Titan yellow as an indicator. The endpoint is detected when color of solution is changed from yellow to red.

4.2 Determination of Petrophysical and Fluid Properties

After best water formulations have been selected, the next step of experiments involve with interaction with rock and fluids and hence, it is compulsory to identify basic properties of all the materials as they are important for analyzing results in next steps.

4.2.1 Basic Properties of Fluids

Densities of formation water, low salinity water and crude oil must be measured. Fluid density is measured by using pycnometer with a known volume. After filling in pycnometer with any fluid, the weight is detected and density is obtained from fluid weight divided by volume of pycnometer.

Density is important for identifying the pore volume of core sample and since the core sample is saturated at room temperature by using formation water, the density of formation water at room temperature (approximately at 30°C).

In the imbibition test in section 4.3, density is also important for calculation of fluid saturations. Therefore, densities of formation water, low salinity water and crude oil at testing temperature (60°C) must also be determined.

As absolute permeability of core sample is one of the properties required in this study, fluid viscosity is also required for this calculation. The measurement of absolute permeability is performed at room temperature and hence, viscosity of formation water which is the flowing fluid, is measured at room temperature which is around 30°C. In this study, the fluid viscosity is measured by utilizing Cannon-Fensk viscometer. The viscometer is soaked in water to control surrounding temperature and then, exact amount of formation water is added into this glass. Formation water is pulled up by pipetting on the testing side and fluid is allowed to flow naturally. Time required for fluid to flow from upper fixed level to lower fixed level, passing through narrow spot is recorded viscosity is obtained by multiplying flowing time by fluid density and temperature dependent constant of the equipment. Figures 4.5a and 4.5b depict pycnometer for determination of fluid density and Cannon-Fensk viscometer of determination of fluid viscosity.

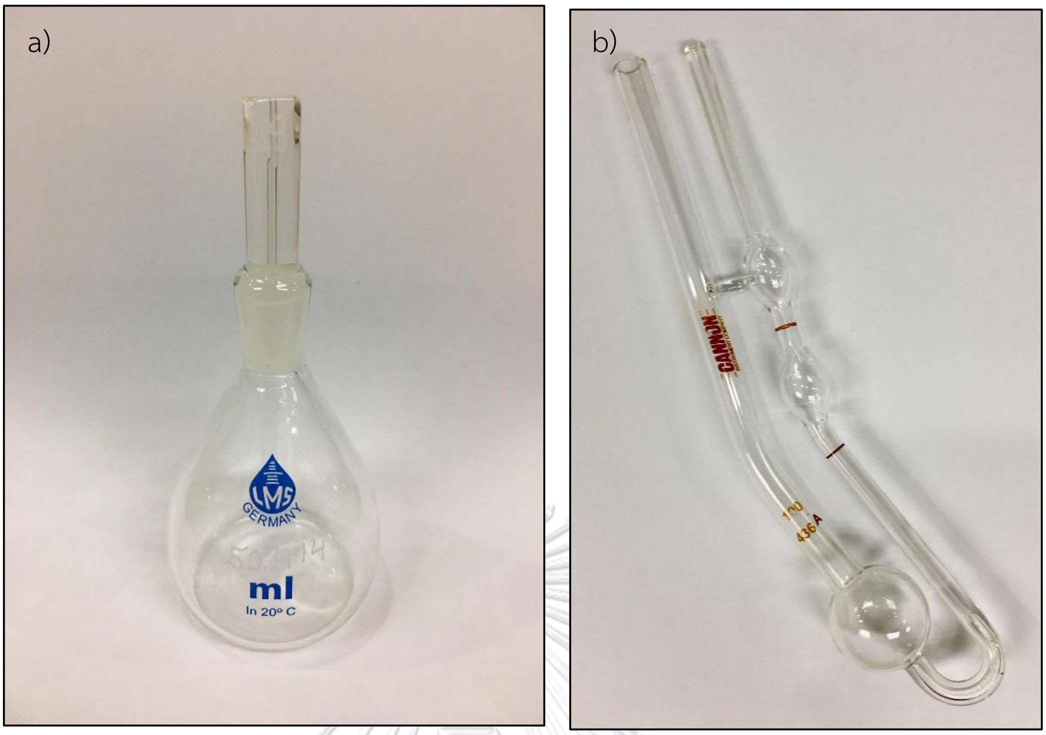


Figure 8 a) Pycnometer for determination of fluid density and b) Cannon-Fensk viscometer of determination of fluid viscosity

In this section, formation water is used during the porosity and permeability measurements. Formulation of formation water from S1 oilfield and is prepared by using deionized water and chemicals as listed in Table 3.

Table 3 *Chemicals required for preparing formation water of S1 oilfield at 14,098 ppm*

Chemicals		Molecular Weight	Weight (g)
NaCl		58.5	12.403
KCl		74.6	0.160
$MgCl_2$		95.0	0.110
$CaCl_2$		111.0	0.706
$NaHCO_3$		84.0	0.719
Total volume	**gram**	-	14.098
	ppm	-	14,098

4.2.2 Petrophysic Properties

One of the most important properties in this study is porosity. This property identifies the total volume that rock can store the fluid inside. The term Pore Volume (PV) may appear more often this term represents a countable amount. Prior to measurement of porosity, core samples must be cleaned by the Soxhlet Extraction (Luque de Castro and GarceHa Ayuso 2000).

Core sample is placed in paper container or extraction thimble and placed inside the body of extraction column. The column is then connected with heating mantle in the bottom, containing toluene which possesses boiling point around 110 °C. The top part of extraction column is connected with condenser tower to condense toluene vapor back to saturated liquid into the column. The hot toluene liquid removes hydrocarbon from rock sample and once the mixture level inside the extraction column is above the reflux tube, mixture of fluid flows back to the heating mantle. As the boiling point of crude oil is much higher than the boiling point of toluene, crude oil will not vaporize and will remain inside the heating mantle, leaving toluene to continue extracting crude oil from rock sample. Figure 4.4 illustrates the schematic diagram of Soxhlet apparatus.

A major function of toluene is to remove moderate to heavy hydrocarbon from core samples. However, to eliminate remaining toluene as well as light hydrocarbon, core samples must be cleaned by Soxhlet again using methanol as a solvent. The samples are cleaned for each solvent approximately 24 hours for each solvent in this study. Once samples are cleaned by methanol, samples are left to dry in oven at 70°C for 24 hours and then, store in desiccator prior to the measurements.

Measurement of Porosity (φ) and Pore Volume (PV) of core samples is started with weighing the dry weight of samples. After that, each sample is displaced by formation water with known density (see 4.2.1), by using coreflood apparatus. The injection rate is adjusted from 1 cm^3/min until 8 cm^3/min and once the pressure difference and injection rate increases or decrease proportionally, sample is fully saturated and the saturated weight is measured. Prior to obtain porosity value, bulk volume of sample is determined. Bulk volume is calculated from dimensions of core samples by measuring core diameter and core length using Vernier caliper. After that porosity is calculated by:

$$\varphi = {\left[\frac{W_{sat}-W_{dry}}{\rho_f}\right]}\Big/{V_b} \qquad \text{(Equation 7),}$$

where W_{sat} is saturated weight in gram, W_{dry} is dry weight in gram, ρ_f is fluid density in g/cm^3, and V_b is bulk volume in cm^3. And pore volume is simply obtained from:

$$V_p = V_b \times \varphi \qquad \text{(Equation 8),}$$

where V_p is pore volume in cm^3.

$$k_a = \frac{q \times \mu \times L}{A\,\Delta P} \qquad \text{(Equation 9),}$$

where k_a is absolute permeability in Darcy, q is liquid flow rate in cm^3/min, L is core length in cm, A is cross-sectional area in cm, and ΔP is pressure difference across core sample (atm).

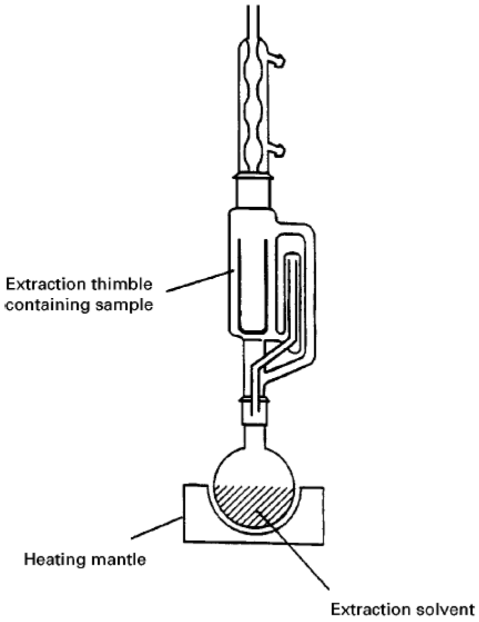


Figure 9 Illustration of Soxhlet extraction apparatus (Luque de Castro and GarceHa Ayuso 2000)

After core samples are fully saturated by formation water. Each sample is injected by crude oil at various injection rates using coreflood apparatus. Recoverable volume of formation water is collected to calculate the irreducible water saturation (S_{wi}). As recovery volume of formation water includes the dead pore volume of the coreflood system, the dead pore volume must be subtracted from this recoverable volume to represent the volume of replacing crude oil. Irreducible water saturation can be calculated as:

$$S_{wi} = \frac{V_p - V_r}{V_p} \qquad \text{(Equation 10)},$$

where S_{wi} is irreducible water saturation in fraction and V_r is recoverable volume of formation water subtracted by dead pore volume of coreflood system in cm^3.

By knowing irreducible water saturation and pore volume of core sample, the initial oil saturation is known and hence, during waterflooding and LSWF, recovery factor can be calculated.

4.3 Imbibition Test

4.3.1 Selection and Preparation of Water Formulations

Regarding results obtained from stirring tests, three water formulations are selected based on the performance in MIE mechanisms. The best water formulation should be able to cause dissolution of divalent ions and therefore, appearances of calcium ion and magnesium ion are major criteria in consideration. Together with appearances of divalent ions, disappearance of monovalent ion could also prove the MIE. However, in case of cesium ion where potassium ion from clays can dissolve back to solution, consideration of disappearance of monovalent ions will be less due to complexity of ionic system. Selected water formulations are prepared using deionized water and reagent-graded chemicals. In order to compare results obtained from low salinity waterflooding with conventional waterflooding, a blank case which is formation water at 14,098 ppm is also performed and hence, 4 imbibition cases are conducted in this stage.

4.3.2 Imbibition Process and Detection of Water Saturations

Core samples prepared from step 4.2.1 are aged for 2 weeks under crude oil to allow the cores to restore original wettability. The weight of core sample prior to imbibition test is also detected to cross-check the initial water saturation obtained during the preparation step. Cores are then soaked in different water formulations and the temperature of water is kept constant at 60°C. During the imbibition process, water imbibes into core sample, displacing oil out and therefore, weight of sample is increased during this period. The best water formulation is expected to cause high increment rate of sample weight as water is heavier than crude oil. To quantify the increment of water saturation, weight of sample is detected every 24 hour and it converted to water saturation using the equations:

$$V_w = \frac{W_f - [V_p \times \rho_o]}{\rho_w - \rho_o} \qquad \text{(Equation 11),}$$

$$S_w = \frac{V_w}{V_p} \qquad \text{(Equation 12),}$$

Where V_w is volume of water in core sample in cm^3,W_f is weight of fluid in core sample in grams, ρ_o is oil density in g/cm^3, , ρ_w is water density in g/cm^3, and S_w is water saturation of core sample in fraction.

The weight measurement is ceased after the weight of core sample is constant, implying that no more water imbibes into core sample. After that the plot of increment of water saturation against time can be prepared for further discussion.

4.4 Coreflooding Test

Coreflooding test is a final step to assess the flooding characteristic at reservoir conditions. Besides recovery factors, the physico-chemical changes during displacement mechanism are also detected.

4.4.1 Coreflood Setting

Coreflood is an apparatus to measure displacement behavior at reservoir conditions. The equipment composes of several sections including: 1) core holder and confining system; 2) injection pumps; 3) fluid accumulators; 4) back pressure regulator; 5) temperature control system; and 6) fluid separator. Figure 10 depicts the schematic diagram of coreflood apparatus.

After prepared core from 4.2.1 has been aged for 2 weeks, core is placed in core holder. Water is used as a medium to build up pressure surrounding core sample to confine the lateral flow. In general confining pressure must be higher than injection pressure at least 300 psi to avoid fluid by-passing. Selected formulation, oil and formation water are filled in accumulators which are linked to injection pumps. Back pressure regulator controls the exit pressure at 500 psi and temperature controller are set at 60°C. It this study, fluid volume is directly detected at the exit after back pressure regulator; hence, fluids are bypass the separator. Oil is first injected into system to fill the dead pore volume with oil. This technique facilitates detection of exact recoverable oil if dead pore volume of the system is known.

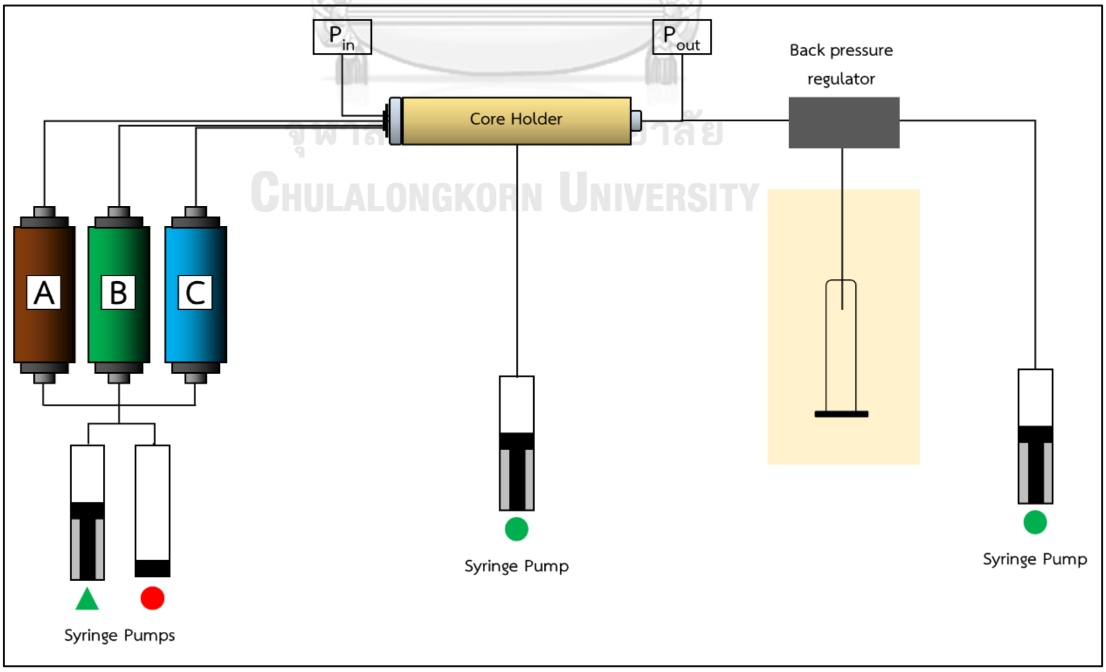


Figure 10 Schematic diagram of coreflood apparatus

After that, formation water is injected to core sample at the rate of 0.5 cm^3/min to imitate conventional waterflooding where salinity of water is as same as that in core sample. Once no more oil is recovered or oil drop is seldom collected, injection process is switched to low salinity water. Volume of oil recovered and pressure different across core sample are detected as a function of time.

4.4.2 Detection of Ions in Effluent

During the displacement mechanisms by both formation water and low salinity water, effluent are collected to detect for total hardness and calcium ion concentration. As injection rate is very small, each interval of effluent collecting is approximately 12-15 cm^3, corresponding to 24-30 minutes. Effluent must be hydrocarbon-free and must be filtered prior to the titration process. Instead of using 10 cm3 per each titration, volume of sample is reduced to 4-5 cm^3 in order to have more points of fluid detections. The titration process for total hardness and calcium ion is explained in section 4.1.2.

Results from stirring test, imbibition test and coreflood test (together with ions detection) are then gather and new findings are discussed and concluded.

CHAPTER V

Results and Discussion

In this section, only three subsections are presented including stirring test, imbibition test and coreflood test. As the section 4.2 (determinations of petrophysical and fluid properties) is part of the other three subsections, this section is therefore reduced and results from this section is included in other three subsection based on type of experiment.

5.1 Stirring Test

5.1.1 Single-component Water Formulation

In this part, only one monovalent ion is appeared in low salinity water and its major function is to replace divalent ion on rock surface. Hence, the expected results should show higher concentration of divalent ion in low salinity water. Amount of calcium ion, magnesium ion and total hardness are summarized in Table 4.

From Table 4, it can be observed that higher concentration of single-component low salinity water yields higher number of divalent ions which can be related to high replacement of divalent ion on clay surface by monovalent ions. It can be observed that sodium chloride yields the least amount of divalent ions which can be explained by its orbital system and hydration properties. Potassium ion tends to replace divalent ion at low concentration as potassium ion is also presented ion in clays and extremely total salinity may provoke dissolution of potassium ion from clay as well as replacing divalent ions from clay surface. Considering cesium ion at 500 ppm, its replacing function is not as high as potassium ion. This can be explained that cesium is much larger than potassium in terms of atomic weight (132.9 and 39.1 for cesium and potassium respectively) number of ion of cesium ion is therefore much smaller than potassium ion. However, at higher concentration (from 1,000 ppm) it can be observed that properties of cesium ion regarding hydration properties result in higher replacement of divalent ions compared to potassium ion. One exception can be observed for lithium ion. As lithium is the smallest in terms of size and weight among all ions, number of ion is the highest at the same salinity. However, at the concentration of 500 ppm, effects of hydration results in low replacement of divalent ions. Once, the salinity is raised up to 2,000 ppm, number of lithium ion is abundant in aqueous solution that this could result in substantial reduction of hydration number that could consecutively results in improvement of ionic mobility.

Table 4 *Summary of appearance of calcium ion, magnesium ion, and total salinity from stirring test with single-component low salinity water*

Low salinity water	Concentration (ppm)	Appearance of Ca^{2+} ($\times 10^{-4}$ Molar)	Appearance of Mg^{2+} ($\times 10^{-4}$ Molar)
LiCl	500	3	1
	1,000	4	1
	2,000	8	2
	5,000	11	2
NaCl	500	2	2
	1,000	3	2
	2,000	4	2
	5,000	5	2
KCl	500	3	6
	1,000	6	4
	2,000	7	3
	5,000	8	5
CsCl	500	5	1
	1,000	6	5
	2,000	7	6
	5,000	9	8

From Table 4, it is very obvious that potassium ion and cesium ion greatly improves MIE mechanism by increasing replacement of magnesium ion compared to lithium ion and sodium ion. As magnesium is smaller in its atomic size, magnesium ion is firmly attached on rock surface and hence, the replacement of magnesium ion by monovalent ion is more difficult than replacing calcium ion. Criteria for selecting total salinity firstly emphasizes on dissolution of magnesium ion than dissolution of calcium ion. Secondly, both monovalent ions should be selected at the same concentration for an ease of interpretation. By these two criteria, the total salinity of 500 ppm is neglected since amount of cesium ion is not enough to cause dissolution of magnesium ion. The last criterion for selecting appropriate monovalent ion is an efficiency concern, as total salinity increases the dissolution of both calcium ion and magnesium ion only increases slightly. Therefore, the total salinity of 1,000 ppm meets all the criteria and is selected for the rest of the study.

5.1.2 Two-component Water Formulation

From results shown in Table 5, it can be observed that appearance of calcium ion is sometimes under negative value whereas, appearance of magnesium ion is always positive as it is not input into the system. As amount of calcium ion is increased, calcium ion starts to disappear from the solution through shifting of equilibrium. At the same time, it can be noticed that amount of magnesium ion starts to increase. Therefore, it can be concluded that presence of monovalent ion favors the replacing of calcium ion on clay surface and consecutively, the presence of calcium ion may favor the replacing of magnesium ion. However, disappearance of cesium ion also shows significance. At higher cesium ion concentration, disappearance of cesium ion is due to replacing of other divalent ions. As amount of calcium ion is higher, disappearance of cesium ion starts to become negative which is impossible that clays emits cesium ion. This can be explained by dissolution of potassium ion from clay and as the amount of potassium ion is enriched in aqueous solution, potassium ion may start to replace magnesium ion at very high calcium ion concentration.

Nevertheless, the presence of solely calcium ion results in less amount of magnesium ion produced. This can be explained that monovalent ion is probably part of important steps in MIE. Even though monovalent ion is absent from aqueous phase, the replacement of divalent ion can still happen but with less effective than the case with presence of cesium ion.

For the case of calcium-potassium solution, results are summarized in Table 6, illustrating appearance of calcium ion, appearance of magnesium ion and disappearance of potassium ion. Results show similar direction as explained for the calcium-cesium case. However, the magnitude of magnesium is smaller than the previous case. Even though potassium ions are enriched on clay surface, the MIE may requires an initiation of monovalent ion and since cesium ion possesses better hydration properties, this causes cesium ion solution to be better than potassium ion solution. Higher amount of potassium ion is obtained during the stirring process as number is obtained from dissolution of potassium ion from clay together with input potassium ion from the solution. Nevertheless, the case with calcium ion solution, appearance is magnesium ion is the highest and potassium ion is consumed from the system. This could be explained replacement of calcium ion on potassium following by replacing of magnesium ion.

Based on the stirring test of two-component low salinity water, it can be observed that, performance of cesium ion is slightly better than potassium ion in replacing divalent ions as cesium ion is not hydrated and hence, its mobility is higher than hydrated potassium ion. From these two sets of experiment, it can be observed that presence of high calcium ion in aqueous solution results in new equilibrium of clay surface. Dissolution of potassium ion is more obvious at the same time; replacement of magnesium ion starts to occur. For both potassium-calcium and cesium-calcium systems, higher portion of calcium tends to yield better amount of magnesium ion in the solution.

Table 5 *Appearance of calcium ion and magnesium ion and disappearance of cesium ion from stirring test with two-component low salinity water*

Volume portion (Ca:Cs)	Appearance of Ca^{2+} ($\times10^{-4}$ Molar)	Appearance of Mg^{2+} ($\times10^{-4}$ Molar)	Disappearance of Cs^{+} ($\times10^{-4}$ Molar)
100% Cesium	6	5	35
1:9	1	4	20
2:8	2	1	10
3:7	-3	1	-14
4:6	-8	2	-86
5:5	-6	4	-48
6:4	-7	3	-52
7:3	-13	12	-38
8:2	-36	30	-14
9:10	-40	47	-10
100% Calcium	-30	31	2

Table 6 *Appearance of calcium ion and magnesium ion and disappearance of potassium ion from stirring test with two-component low salinity water*

Volume portion (Ca:K)	Appearance of Ca^{2+} ($\times10^{-4}$ Molar)	Appearance of Mg^{2+} ($\times10^{-4}$ Molar)	Disappearance of K^{+} ($\times10^{-4}$ Molar)
100% Potassium	6	4	28
1:9	1	1	-49
2:8	-3	6	-57
3:7	-3	3	-56
4:6	-6	9	-68
5:5	-5	3	-75
6:4	-11	6	-82
7:3	-10	27	-84
8:2	-22	10	-95
9:1	-22	11	-95
100% Calcium	-30	31	2

5.1.3 Three-component Water Formulation

For this section, it can be divided into two types of three-component water formulation which are cesium-sodium-calcium and potassium-sodium-calcium in order to compare the effectiveness of cesium ion and potassium ion supported by sodium ion and calcium ion in liberation of oil from rock surface. Sodium ion which is the most abundant ion found in most formation water is inserted into majority of the total hardness. Total salinity for both water formulation are still kept at 1,000 ppm which is previously selected for two-component section.

For water formulation of cesium-sodium-calcium, the appearances of calcium ion and magnesium ion are illustrated in figures 11a and 11b respectively. From the figure 11a, it can be observed that dissolution of calcium ion occurs when calcium ion is not presented in low salinity water. Calcium ion starts to disappear when its concentration is higher. Nevertheless, the presence of sodium ion results in higher adsorption of calcium ion more than cesium ion as cesium is foreign ion and it may be adsorbed together with calcium ion. Appearance of magnesium ion in figure 11b shows that the highest dissolution of magnesium occurs in certain area where the composition consisted of calcium and sodium ions and only a few percent of cesium ion. As calcium ion may take responsibility in replacing magnesium ion, less amount of cesium ion is then favorable as cesium ion is not very competitive in adsorption. In order to understand the overall mechanism, disappearance of cesium ion is illustrated in figure 12a. In fact, back titration technique can detect both cesium ion and potassium ion in the system. Therefore, the zone with positive value can be interpreted as monovalent ion is consumed. Whereas the negative value of disappearance can be related to a summation of remaining cesium ion and repulsed potassium ion from clays. From figure 12a, the highest adsorption of cesium ion is observed when it is combined with calcium ion especially with higher concentration of cesium ion. This can be fit with the appearance of calcium ion in figure 11a. Nevertheless, it is interesting that when sodium ion is higher, amount of cesium ion is observed. This can be explained that since the detected value may include potassium ion, it is possible that presence of high amount of sodium ion results in dissolution of potassium ion. The vast blue area above cesium ion and calcium ion direct line is also observed to be negative disappearance of cesium ion. Using the same explanation, this zone might represents also potassium ion and it is caused from adsorption of both calcium and cesium ions. Another disappearance of cesium ion above the middle of the figure is then probably the point where adsorption is changing from cesium/calcium ions domination to domination of sodium ion.

Based on three diagrams consisting of figures 11a, 11b, and 12, A few areas may represent interesting water formulations to improve oil recovery by means of low salinity waterflooding. The first area is high cesium ion content. This water formulation results in high dissolution of calcium ion and detectable amount of dissolution of magnesium ion. Moreover, this area is also extended to adding of sodium ion in high portion to maintain dissolution of calcium ion. However, increasing sodium ion tends to yield an adverse effect on dissolution of magnesium ion. Another interesting area is obviously shown in figure 11b where dissolution of magnesium ion is detected in yellow color in the middle between sodium ion and calcium ion line. However, at this point the amount of cesium ion is only from zero to 20 percent and from figure 12 the amount of cesium ion is higher than it is injected that is impossible. This water formulation can be described by the high dissolution of potassium ion from clays. With abundance of potassium ion and calcium ion, the dissolution of magnesium ion can occur.

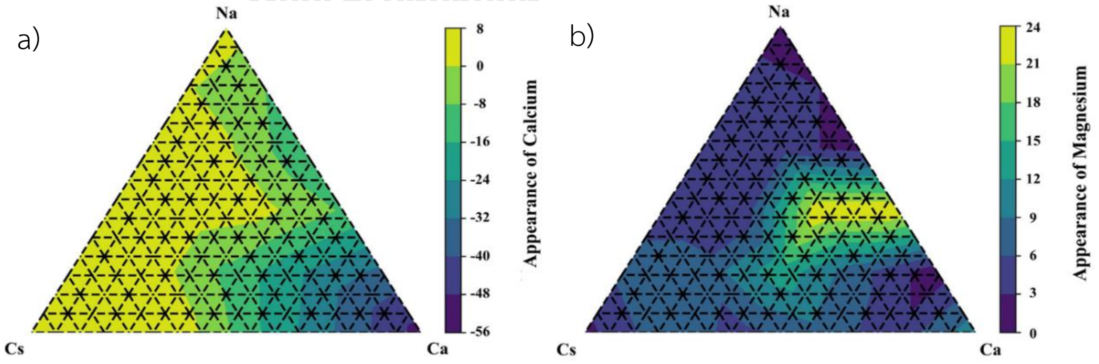


Figure 11 *a) appearance of calcium ion and b) appearance of magnesium ion as a function of concentration of cesium ion, sodium ion, and calcium ion*

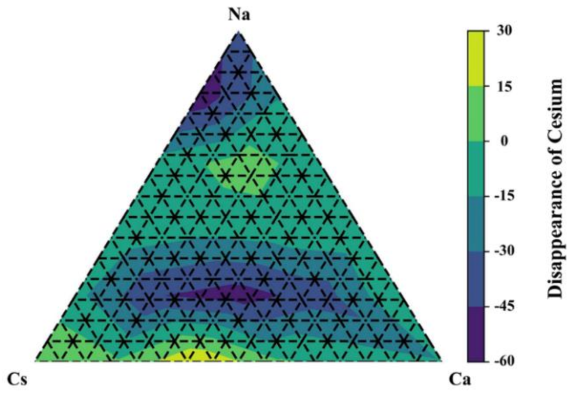
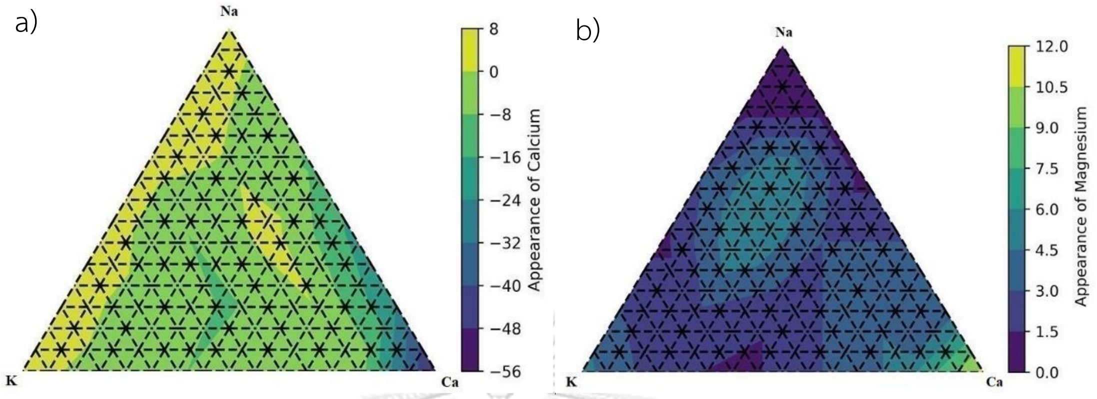


Figure 12 *disappearance of cesium ion as a function of concentration of cesium ion, sodium ion, and calcium ion*

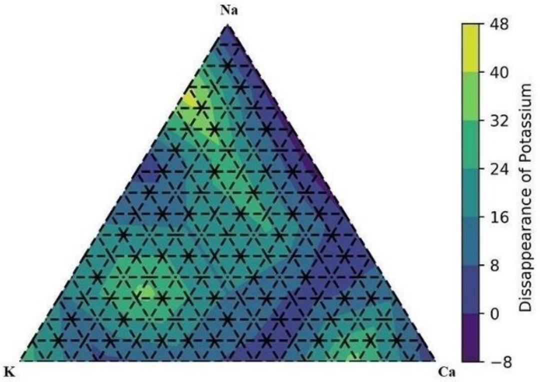
For water formulation of potassium-sodium-calcium system, the appearances of calcium ion and magnesium ion are illustrated in figures 13a and 13b, respectively. From figure 13a, it can be observed that dissolution of calcium ion from rock surface is obvious when the low salinity water contains high amount of sodium ion and potassium ion (absent of calcium ion). On the other hand, calcium ion in low tends to be consumed when its concentration is higher. However, there is a combination where calcium ion can be observed (potassium-sodium-calcium at the ratio 20-40-40). This only one data point may be occasionally happened due to the heterogeneity of rock that may contain excessively high clay portion. Comparing figures 13a and 12a it can be seen than system with cesium ion creates larger positive area of calcium ion concentration.

Overlaying figures 13a and 13b it can be seen that, disappearance of calcium ion results in appearance of magnesium ion at the combination around pure solution of calcium ion. This seems to happen without the collaboration of potassium ion which is monovalent ion. However, when considering figure 14 it can be found that potassium ion is still consumed around the corner and it is appeared at the pure calcium point that means, replacement of magnesium ion by calcium ion may still require potassium ion to collaborate. From figure 14, potassium ion is also highly consumed when calcium ion is absent in the system. When combining figures 14 and

13b together, it can be seen that disappearance of potassium ion could be responsible for appearance of magnesium ion.



*<u>**Figure 13**</u>* *a) appearance of calcium ion and b) appearance of magnesium ion as a function of concentration of potassium ion, sodium ion, and calcium ion*



*<u>**Figure 14**</u>* *disappearance of potassium ion as a function of concentration of potassium ion, sodium ion, and calcium ion*

Based on the three-component study it can be concluded that both cesium ion and potassium ion when it is pure solution, it has tendency to displace calcium ion first. This can be explained by the ionic radius of calcium ion which is larger than magnesium ion; hence, interaction of calcium ion is loosely formed on clay skin with compared with magnesium ion. Nevertheless, when sodium ion and calcium ion are presented in the system, cesium still show the tendency to replace calcium ion while potassium ion starts to replace magnesium ion. The high dissolution of magnesium ion in case of cesium-sodium-calcium system is also related to the presence of potassium ion.

5.1.4 Selection of Water Formulation

From the result in 5.1.3, three water formulations can be selected. Pure solution of cesium chloride and pure solution of potassium ion are selected as they show similar ability in replacing calcium ion. Then, the test by imbibition and coreflood tests help to clarity the characteristics when they are in core samples. Another case selected here is the water formulation consisting of cesium-sodium-calcium at the ratio 20-40-40. The reason behind is that this formulation can results in remarkable amount of magnesium ion that could be a great benefit in oil production. Moreover, with higher portion of sodium ion compared to other two formations, the making up of water formation is more practical since formation water can be used by mixing with fresh water resources as major ion found in formation water is sodium ion.

5.2 Imbibition Test

The imbibition test is performed by measuring the weight of samples for certain periods. Initially, samples illustrated core properties in Table 7 are at the stage of irreducible water saturation where water saturation is at the minimum value. Samples are soaked in four different water formulations (three formulation selected from section 5.1.4 and formation water a blank test). As water imbibes into core samples, weight of samples correspondingly increases as density of water is remarkably higher than oil. Sample weights are then converted to water saturation using equations 11 and 12 in chapter 4. Results are illustrated in terms of differential water saturation as a function of time and the results are shown in figure 15.

Table 7 *Irreducible water saturation and residual oil saturation of each core samples with information of water formulation soaking cores*

Core No.	Permeability (mD)	S_{wi}	Initial oil (cm^3)	Water formulation
15	10.20	0.384	10.27	Formation water at 14,098 ppm.
11	3.77	0.543	5.40	100% of CsCl at 1,000 ppm.
20	9.03	0.492	4.76	100% of KCl at 1,000 ppm.
32	2.54	0.371	8.80	Cs-Na-Ca: 20-40-40 at 1,000 ppm.

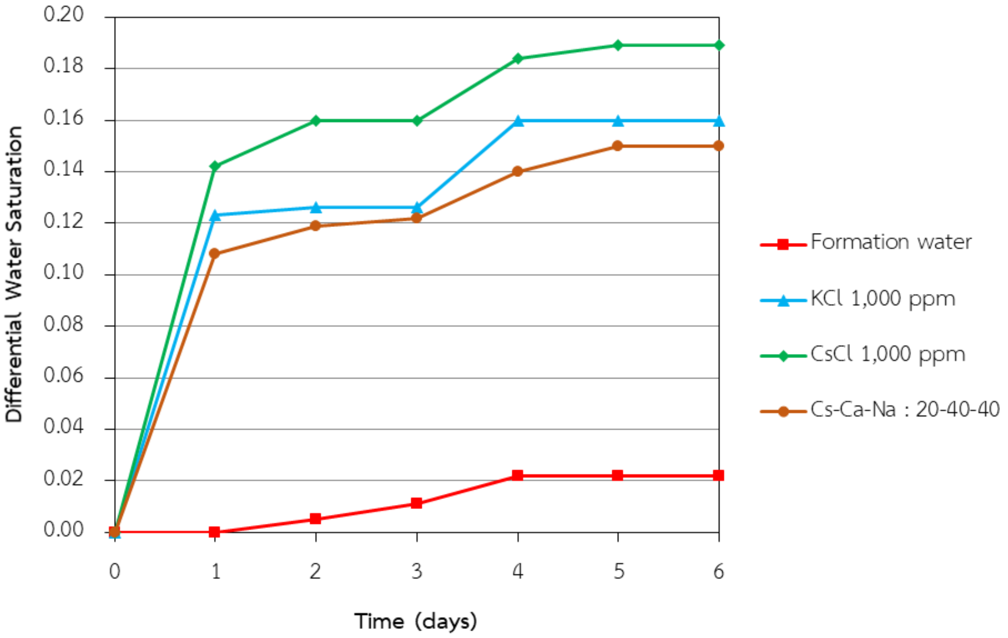


Figure 15 *Differential water saturation from imbibition tests for difference water formulations as a function of soaking time*

From figure 15, it can be seen that soaking core sample in formation water result in the least increment of water saturation of in another word, water hardly imbibes into core sample. Since the salt concentration and composition are the same, the movement of ion in both formation water and injected water hardly occurs. Besides, other three water formulations show strikingly increasing trend especially in first 24 hours. Since the water formulations are prepared at 1,000 ppm which is 14 times less than formation water, this results in movement of both water from outside the core to inside the core and also dissolution of highly concentrated ion such as sodium ion from core sample to the solution outside. For monovalent ion instead, it may tend to move inside the core sample since the concentration in the water formulation is higher than for formation water. In over all, water imbibes into core samples, bringing monovalent ions into core samples and spontaneous imbibition continues. In all three cores, sample weights are mostly constant after 4 days.

At the end of the test, water formulation consisting of 100% of cesium ion shows a total increment of water saturation of 0.189. Next, 100% of potassium ion can increase water saturation at nearly the same as pure cesium ion at about 0.160. Lastly, 0.150 of water saturation is increased by the solution of Cs-Ca-Na at 20-40-40. From the imbibition test, water formulation with Cs-Ca-Na in portion of 20-40-40 does not show the highest effectiveness as expecting from the results in stirring test section which can be a result from many reasons such as permeability of core sample, presence of fractures inside cores, difference in clay types and amount. Therefore, in order to overcome external factors, coreflooding test is conducted.

5.3 Coreflood Test

5.3.1 Oil Recovery Factors and Pressure Difference

To further study selected water formulation from 5.1.4, three selected water formulation are performed coreflood test to determine the effectiveness of each water formulation. Coreflood apparatus is used to simulate reservoir conditions including temperature, pressure, and flow rate controlling by computer system. Hence, conventional waterflooding and low salinity waterflooding are performed at reservoir conditions to precisely obtain recovery factor as well as pressure difference across core samples.

In this study, coreflooding test is performed at confining pressure of 1,500 psi and temperature of 60 degree Celsius. Water are injected at flow rate of 0.5 cm^3/min for both conventional waterflooding and low salinity waterflooding cases.

Table 8 summarizes core properties important for coreflooding including absolute permeability, irreducible water saturation and volume of initial oil.

Table 8 *Irreducible water saturation and residual oil saturation of each core samples with information of water formulation injected into the core*

Case No.	Core No.	Permeability (mD)	S_{wi}	Initial oil (cm^3)	Water formulation at 1,000 ppm
1	37	18.72	0.097	15.01	100% of CsCl
2	29	35.66	0.093	14.06	100% of KCl
3	43	55.13	0.314	11.87	Cs-Na-Ca: 20-40-40
4	34	22.64	0.277	9.71	Cs-Na-Ca: 20-40-40

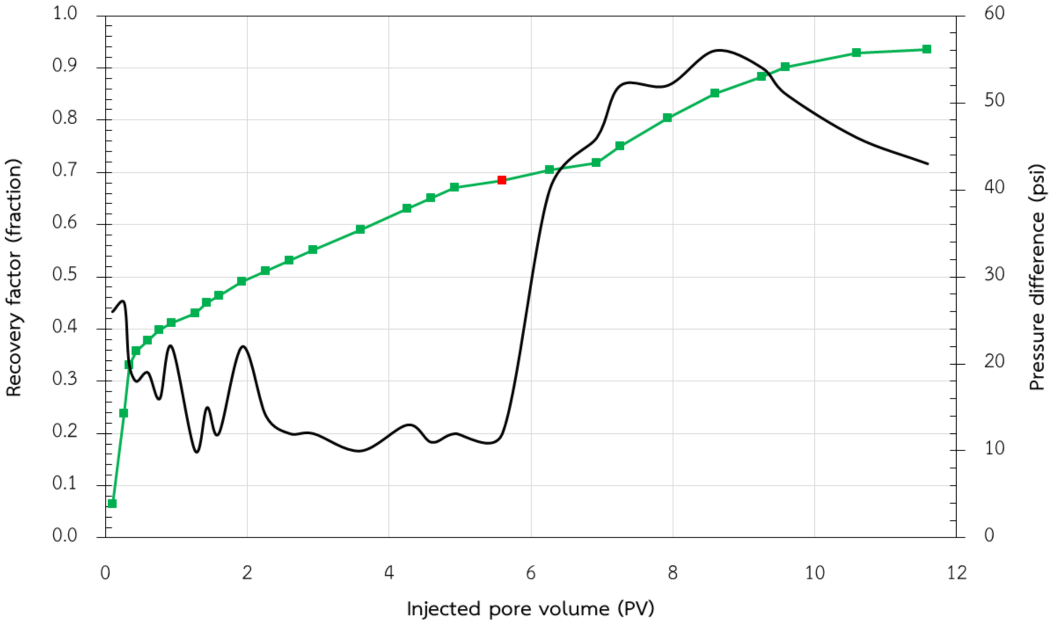


Figure 16 *Oil recovery factor (green line) and pressure difference (black line) from coreflooding test obtained from water formulation of 100% of CsCl at 1,000 ppm as a function of injected pore volume*

Figure 16 illustrates recovery factor and pressure difference from conventional waterflooding followed by pure cesium chloride solution. From the figure, conventional waterflooding by formation water can liberate oil at recovery factor of 0.71 (counted after 1.0 PV of low salinity water injection as remaining water in core sample is formation water) and by water formulation of 100% of CsCl at 1,000 ppm, recovery factor is increased up to 0.94, accounting for incremental of oil recovery of 0.23. It is interesting that suddenly after low salinity water is injected, pressure difference is increased from 12 to 50 psi which is nearly 4 times. The increment of pressure is expected to be due to rapid liberation of oil and since oil causes changes in relative permeability of the flow path, pressure increases rapidly. After less than 2 PV injecting low salinity water, oil recovery increases rapidly (right red point) due to arrival of the oil bank. Something interesting can be observed is that oil that is recovered due to low salinity water is produced together with muddy water. This can be explained that cesium ion results in MIE and some oil drops may be formed as small emulsion due to this liberation. However, at cooler temperature of the effluent, these oil drops return back to oil phase and can be easily removed by filtration.

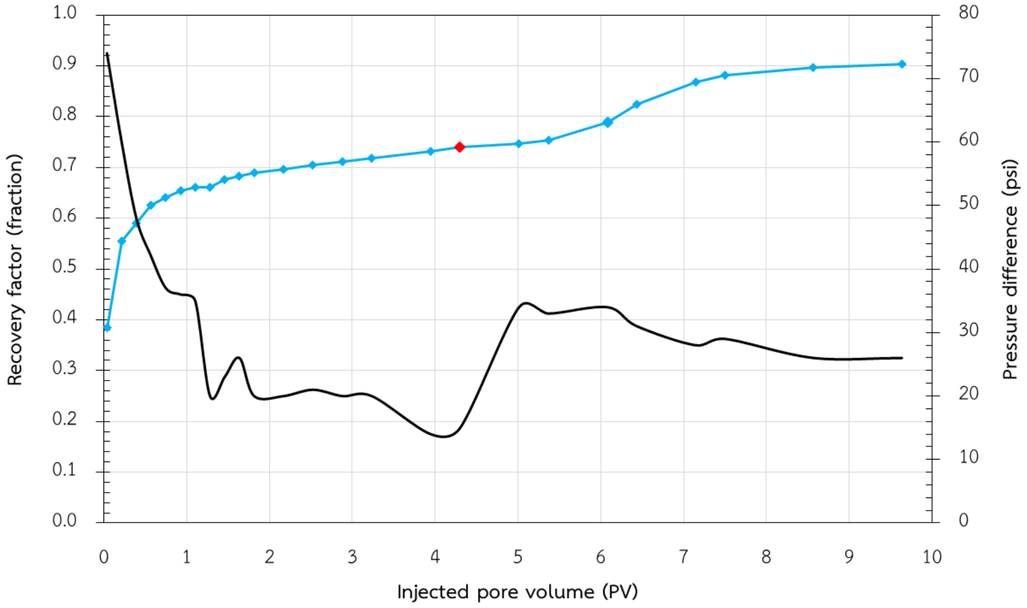


Figure 17 *Oil recovery factor (blue line) and pressure difference (black line) from coreflooding test obtained from water formulation of 100% of KCl at 1,000 ppm as a function of injected pore volume*

Figure 17 depicts coreflood results including oil recovery factor and pressure difference from using pure potassium chloride solution at 1,000 ppm during low salinity waterflooding phase. From the figure, it can be seen that conventional waterflooding liberates oil with recovery factor of 0.75 and then, it takes approximately 1.8 PV of injected PV to observe the result from low salinity water. However, the result is slightly different from the previous case. Oil starts to be produced slowly not as in the previous case. Moreover, the increment of pressure difference from about 15 to 35 psi also shows that, liberation of oil occurs slower than the previous case. As explained previously, cesium ion is the monovalent ion that does not form hydrate. Hence, it can create the MIE quickly when it is supported by the viscous force and this results in a rapid response in terms of oil recovery factor as well as increment of pressure difference. At the end of the test, recovery factor is raised up to 0.90 which accounts for the increment of oil recovery of 0.15 which is obviously smaller than the previous case.

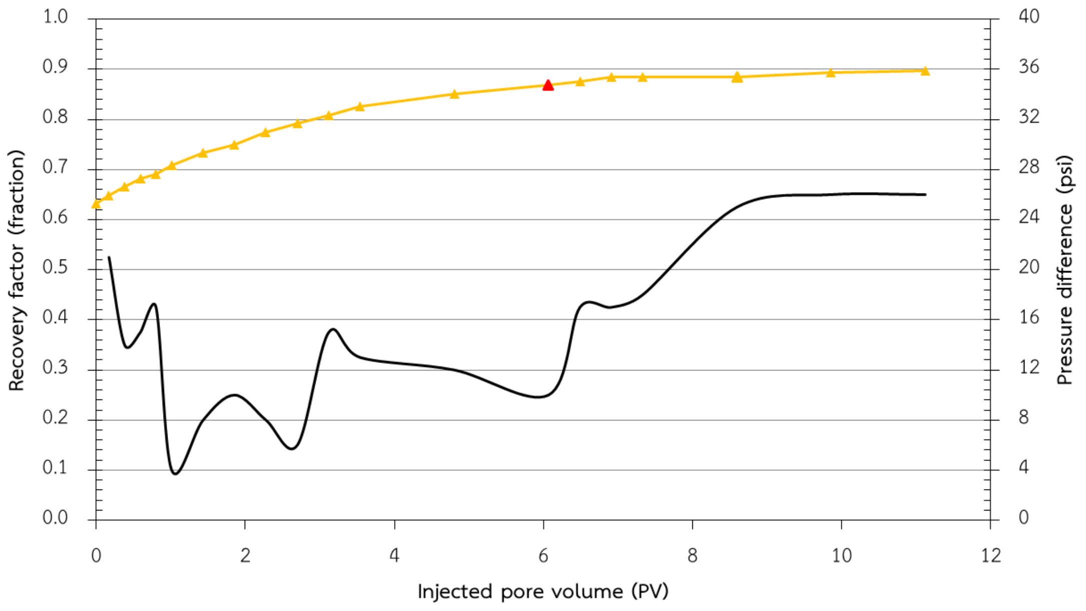


Figure 18 *Oil recovery factor (orange line) and pressure difference (black line) from coreflooding test obtained from water formulation of Cs-Na-Ca: 20-40-40 at 1,000 ppm as a function of injected pore volume (unsuccessful case)*

Figure 18 illustrates oil recovery factor together with pressure difference as a function of injected pore volume of water for the case of low salinity water formulation: Cs-Na-Ca: 20-40-40 at 1,000 ppm. This is the only case where effect from low salinity waterflooding deviates from other 2 previous cases. After injecting low salinity waterflooding in this observed that there is a rise up of difference pressure from 10 to 25 psi; however, there is only a small increment of oil recovery. Moreover, the muddy effluent cannot be observed from the test and that probably means the MIE does not take place. Further investigation for the reason of failure is explained in the next section. Therefore, the test is repeated by performing the same water formulation with different core sample.

The repeating case is performed with core sample no. 34 with absolute permeability of 22.64 mD, irreducible water saturation of 0.277 and initial oil volume of 9.71 cm^3. The results including oil recovery factor and pressure difference are shown in figure 19. From the figure, oil recovery factor obtained from conventional waterflooding is 0.67 and after injected water is switched to low salinity water (red point on the left), oil starts to liberate after about 1.6 PV of injected water (red point on the right). In this case, the muddy effluent can be obviously seen and at the end of the experiment, oil recovery raises up to 0.80, accounting for the increment of 0.13. In comparison between pressure difference at the end of conventional waterflooding and low salinity waterflooding, the incremental of pressure difference is from 60 to 90 psi. The reason is from magnitude of water saturation at the end of low salinity waterflooding is higher causing the lower of relative permeability.

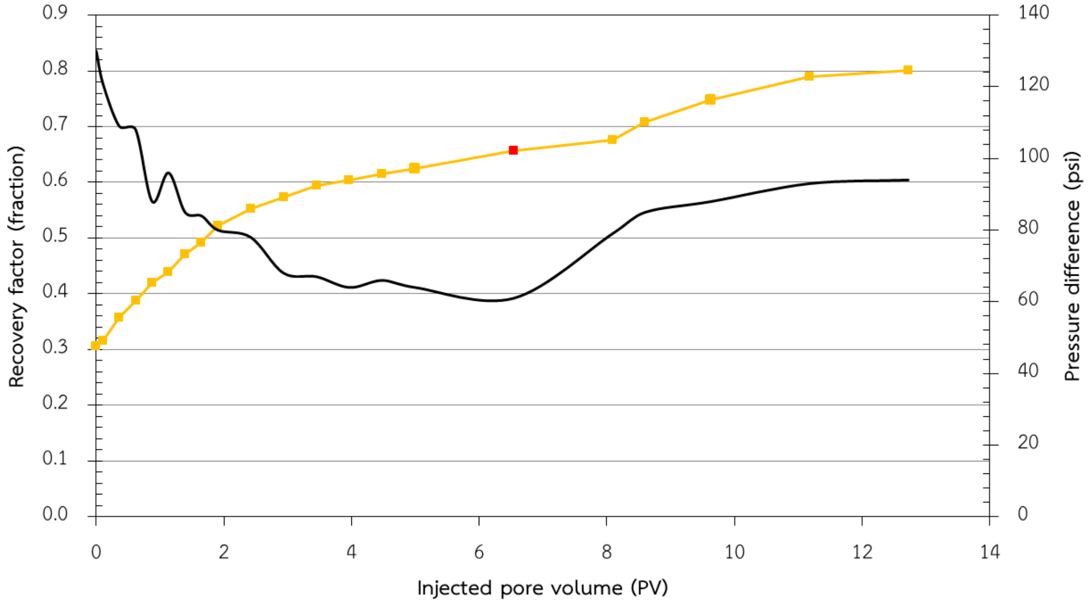


Figure 19 *Oil recovery factor (orange line) and pressure difference (black line) from coreflooding test obtained from water formulation of Cs-Na-Ca: 20-40-40 at 1,000 ppm as a function of injected pore volume*

From case no 1, 2 and 4 where the coreflood results are valid, it can be observed that incremental of oil recovery goes in the same direction with incremental of pressure difference. The pure solution of monovalent ion tends to yield higher relative pressure difference between injecting low salinity water is started and oil liberation from low salinity water is started. It can be explained that since the concentration of monovalent ion is high, MIE mechanism may occur quickly causing changes in relative permeability of the flow path. For the last formulation, the incremental of pressure starts slowly and that can be explained by minimal amount of cesium ion added the system might need dissolution of potassium ion prior to the start of MIE mechanism. Nevertheless, results from titration of effluent in next section may help to confirm these explanations.

5.3.2 Ion Detections

In this section, complexometric titration is performed in order to validate occurrence of MIE mechanism during both conventional waterflooding and low salinity waterflooding in coreflooding test. Verification of disappearance of monovalent ion is not performed in this section since the titration technique will determine both cesium ion and potassium ion at the same time and by removing this test, frequency of sample collecting can be increase. Effluents are collected approximately 10 cm^3 per one sample and 4 cm^3 of effluent is titrated for total hardness and calcium ion as per the step in 4.1.2 and results are shown in Table 9.

From the results, it can be observed that after injecting low salinity for a certain period (when oil from MIE starts being produced form core sample), dissolution of magnesium ion from rock surface can be obviously observed and there is no calcium ion presented in the effluents. This can be explained that even though cesium and potassium ion tends to displace more calcium ion in the stirring test, the mechanism from coreflood shows that the calcium ion from primary replacement together with calcium ion in formation water can drive the mechanism forward the replacing of magnesium ion. Moreover, the amount of magnesium ion also goes in the same direction of amount of oil recovery and this can be additionally explained collaboration of adequate cesium ion together with presence of calcium ion can replace magnesium ion which is smaller in terms of ionic size and consecutively forms very tight bond between oil and rock surface. The case of combination between Cs-Na-Ca maybe different as major monovalent ion in this case might be potassium ion from the dissolution and hence the result is quite similar to the case of pure potassium ion.

The failure for case no.3 can be noticed also from this Table. It can be observed that during conventional waterflooding, releasing of magnesium ion is quite obvious. That can be interpreted that oil that is captured by magnesium ion which creates strength bond is already produced, resulting in no more oil left for low salinity water. The reason for high oil recovery during conventional waterflooding can be that the core sample may contain very high portion of calcium ion that may lead to the replace of magnesium ion even during the low salinity waterflooding process

Table 9 *Summary of appearance of calcium ion and magnesium ion from titration with effluents collected in coreflooding test*

Water formulation at 1,000 ppm	Stage	No. of effluent	Appearance of Ca^{2+} ($\times 10^{-4}$ Molar)	Appearance of Mg^{2+} ($\times 10^{-4}$ Molar)
100% of CsCl	Conventional waterflooding	1	118	13
		2	80	48
		3	78	10
		4	60	28
		5	60	15
	Low salinity waterflooding	1	0	38
		2	0	70
		3	0	75
		4	0	125
		5	0	83
100% of KCl	Conventional waterflooding	1	85	35
		2	65	35
		3	58	35
		4	53	25
	Low salinity waterflooding	1	43	68
		2	0	93
		3	0	123
		4	0	90
		5	0	123
Cs-Na-Ca: 20-40-40	Conventional waterflooding	1	95	68
		2	80	105
		3	68	68
		4	75	85
		5	65	20
	Low salinity waterflooding	1	90	7
		2	18	68
		3	0	100
		4	0	85

Table 9 Summary of appearance of calcium ion and magnesium ion from titration with effluents collected in coreflooding test (continued)

Water formulation at 1,000 ppm	Stage	No. of effluent	Appearance of Ca^{2+} ($\times 10^{-4}$ Molar)	Appearance of Mg^{2+} ($\times 10^{-4}$ Molar)
Cs-Na-Ca: 20-40-40	Conventional waterflooding	1	53	25
		2	58	13
		3	43	23
		4	28	35
	Low salinity waterflooding	1	28	23
		2	0	10
		3	0	8
		4	0	5

CHAPTER VI

Conclusions

6.1 Conclusions

In this section, several conclusions can be made. First, it is obvious that hydrate size together with water of hydration of monovalent ion play very important role during the Multi-component Ion Exchange mechanism. Ion with less water of hydration tends to be more active in MIE and hence, potassium ion and cesium ion illustrate potential in oil recovery mechanism.

From the two-component study it can be concluded that increasing portion of calcium ion to both cesium and potassium ions, the dissolution shifts from calcium ion to magnesium ion. And however, without forming hydrate, cesium ion is slightly better than potassium ion.

For the system including sodium ion, system of cesium-sodium-calcium tends to create dissolution of calcium ion where the system of potassium-sodium-calcium shifts slightly toward the dissolution of magnesium ion. However, the dissolution of magnesium ion also occurs in case of the cesium-sodium-calcium system but it is linked with the dissolution of potassium ion from clay itself.

Selected water formulations which are pure cesium chloride, pure potassium chloride and the combination of cesium-sodium-calcium at 20-40-40 show great imbibition rate over formation water. Moreover, the coreflood test also goes in the same direction. Cesium ion is very fast in MIE mechanism and at the adequate quantity it can liberate oil though MIE quickly, resulting in building up of pressure in several magnitude. Potassium ion with a few water molecules can also function well in oil recovery however, its mobility is less than cesium ion. The selected combination tends to be similar to potassium ion solution as major monovalent ion to work on MIE may be potassium ion, not the cesium ion. With the selected reservoir conditions, oil recovery factor can be increased up to 0.26 by the best water formulation (Cesium 100%)

The complexometric titration shows remarkable contrast to the stirring test that both cesium ion and potassium ion tend to displace magnesium ion instead of calcium ion. This can be explained by the availability of calcium ion in the system from the formulation, driving mechanism toward replacing of magnesium ion.

6.2 Recommendations

Even though the price of cesium ion may be much higher than potassium ion, this study has already proved the theory regarding the hydrate of monovalent ion. The further study should emphasize of the feasibility on mixing cesium ion with other ions that can still maintain the mobility function of cesium ion when its concentration is very low to save the cost.

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