Effects of Clay Minerals on Oil Recovery Mechanism in Low Salinity Waterflooding in Shaly-sandstone Formation

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จุฬาลงกรณ์มหาวิทยาลัย
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ผลกระทบของแร่ดินต่อกลไกการผลิตน้ำมันด้วยวิธีการอัดฉีดน้ำเกลือความเค็มต่ำในแหล่งกักเก็บน้ำมันแบบหินทรายปนหินดินดาน

นายตรี ยุดดา ปุตรา

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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การฉีดอัดน้ำเกลือความเค็มต่ำเป็นหนึ่งในวิธีเพิ่มผลผลิตน้ำมันแบบตติยภูมิที่ได้รับความแพร่หลายในปัจจุบัน จากการศึกษาก่อนหน้าพบว่าการฉีดอัดน้ำเกลือความเค็มต่ำนำไปสู่กระบวนการและเปลี่ยนไอออนหลายประจุในหินกักเก็บน้ำมัน ซึ่งกระบวนการดังกล่าวเป็นหนึ่งในกลไลที่ก่อให้เกิดการผลิตน้ำมันโดยการฉีดอัดน้ำเกลือความเค็มต่ำ วิทยานิพนธ์นี้ได้จัดทำขึ้นเพื่อศึกษาผลกระทบจากชนิดของแร่ดินเหนียวในหินกักเก็บและไอออนในน้ำที่ใช้ในการฉีดอัดต่อกระบวนการโดยรวม

ในขั้นตอนแรก แร่ดินเหนียวแต่ละชนิดจะถูกทดสอบเพื่อยืนยันองค์ประกอบของแร่ชนิดนั้น ๆ และ แร่ที่ถูกเลือกจะถูกนำไปทดสอบด้วยวิธีการกรองไหลผ่านด้วยน้ำเกลือความเค็มต่ำที่มีสูตรน้ำแตกต่างกันเพื่อค้นหาความสามารถในการแลกเปลี่ยนไอออนหลายประจุของไอออนต่าง ๆ ในแร่ดินเหนียวแต่ละชนิด ผลการทดลองข้างต้นจะถูกนำมาใช้ประกอบกับปริมาณแร่ดินเหนียวในตัวอย่างหินแหล่งกักเก็บเพื่อระบุสูตรน้ำเกลือความเค็มต่ำสำหรับการทดลองในขั้นตอนที่สองโดยการทดสอบด้วยการแทนที่ของไหล ในระหว่างการทดสอบด้วยการแทนที่ของไหล ปัจจัยการผลิตน้ำมันและความแตกต่างความดันจะถูกบันทึกเพื่อการวิเคราะห์ผล และ ตัวอย่างน้ำจากการผลิตจะถูกเก็บเพื่อนำมาหาไอออนคงเหลือและนำไปใช้ประกอบคำอธิบาย

จากการทดลองพบว่าแคลเซียมไอออนเป็นไอออนที่ส่งผลกระทบสูงสุดต่อกระบวนการแลกเปลี่ยนไอออนหลายประจุโดยทำการแทนที่แมกนีเซียมไอออนได้เป็นจำนวนมาก โพแทสเซียมไอออนมีคุณสมบัติรองลงมาโดยทำหน้าที่แทนที่แคลเซียมไอออน ความเข้มข้นของน้ำเกลือสูง (5000 ส่วนในล้าน) ส่งเสริมให้เกิดการแลกเปลี่ยนไอออนในแร่ดินเหนียวที่มีความสามารถในการแลกเปลี่ยนไอออนประจุบวกต่ำ ได้แก่ อิลไลต์ และ เคาลิไนต์ แคลเซียมไอออนและโพแทซเซียมไอออนจึงถูกเลือกเพื่อการเตรียมสูตรน้ำสำหรับการทดลองถัดไป จากการทดสอบด้วยการแทนที่ของไหลพบว่า น้ำเกลือที่มีความเข้มข้นต่ำ (1000 ส่วนในล้าน) ให้ผลการทดลองที่ดีกว่าน้ำเกลือความเค็มสูงเนื่องจากความแตกต่างของความเค็มช่วยส่งผลให้พันธะของแมกนีเซียมที่ตรึงน้ำมันไว้บนพื้นผิวหินแตกออก ส่งผลให้หยดน้ำมันเป็นอิสระและถูกผลิต และยังก่อให้เกิดการเพิ่มขึ้นของความดันที่แตกต่างตลอดชิ้นตัวอย่างหินอย่างชัดเจน อิลไลต์ส่งผลดีต่อการผลิตมากกว่าเคาลิไนต์ซึ่งสามารถอธิบายได้ด้วยความสามารถในการแลกเปลี่ยนไอออนประจุบวกที่สูงกว่า จากการทดลองที่ให้ผลบวกต่อสูตรน้ำที่เลือกมาพบว่า การเพิ่มขึ้นของปัจจัยการผลิตอยู่ระหว่าง 0.07 ถึง 0.14 ภายหลังจากการฉีดอัดน้ำแบบปกติ

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Tri Yudha Putra : Effects of Clay Minerals on Oil Recovery Mechanism in Low Salinity Waterflooding in Shaly-sandstone Formation. Advisor: Asst. Prof. FALAN SRISURIYACHAI, Ph.D.

Low Salinity Waterflooding (LSWF) is one of Enhanced Oil Recovery (EOR) techniques that are often mentioned nowadays. Several studies showed that injecting low salinity water leads to Multi-component Ion Exchange (MIE) which is one of oil recovery mechanisms provided by this technique. This study was performed to investigate the effects of specific clay mineral in rock and ion in injected water.

First, representative clays were analytically tested to ensure their mineral compositions and the selected representative clays were tested by filtration with different water formulations to identify ionic capacities in MIE for each clay. Results obtained from filtration test and clay content of core were gathered to identify low salinity water formulations to use in second part performed by coreflooding test. During the coreflooding, oil recovery factor and pressure difference were detected and effluent from coreflood test was collected for ion analysis to accompany the explanation.

From the study, calcium ion was found to be the most powerful ion in MIE for all clays as it can replace magnesium ion at high magnitude. Potassium ion was the second powerful ion and it can replace calcium ion. High concentration of low salinity water (5,000 ppm) had more effect on clays with lower Cation Exchange Capacity (CEC) which are illite and kaolinite. Calcium ion and potassium ion were chosen to generate low salinity water formulation. From coreflood test, 1,000-ppm low salinity water was more favorable than 5,000 ppm. At lower concentration, magnesium ion bridging between oil and rock surface was broken from high salnity contrast, resulting in liberation of oil drops and pressure difference increases strikingly. Illite clay was favorable for MIE than kaolinite, which is lower in CEC. For cases that positively response to selected water formulations, and increment of oil recovery was in the range of 0.07 to 0.14 after conventional waterflooding.

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LIST OF ABBREVIATIONS

LSWF	Low Salinity Waterflooding
MIE	Multi-component Ion Exchange
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
CEC	Cation Exchange Capacity
wt%	Weight Total Percent
ppm	Part Per Million
pH	Potential Hydrogen
LSB	Low Saline Brine
EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
DLE	Double Layer Expansion
PZC	Point of Zero Charge
EBT	Eriochrome Black T
EDTA	Ethylene Diamine Tetraacetic Acid
STB	Sodium Tetraphenyl Borate
TDS	Total Disolve Solid
mD	Milidarcy

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LIST OF NOMENCLATURES

Φ	Porosity, fraction
q	Injection Rate, cm^3/sec
A	Cross-sectional Area, cm^2
V_p	Pore Volume, cm^3
W_{sat}	Saturated Weight, gr
W_{dry}	Dry Weight, gr
ρ_f	Fluid Density, g/cm^3
μ	Viscosity, cP
L	Length of Core, cm
ΔP	pressure differential, atm
S_{oi}	Initial Oil Saturation, fraction
V_w	Volume of Water Production, cm^3
V_D	Dead Pore Volume of Equipment, cm^3
K_a	Absolute Permeability, mD

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Oil wells may experience three different oil production stages: primary, secondary, and tertiary. Primary recovery allows oil to be produced by naturally stored energy presented in the reservoir, forcing oil to move toward the wellbore. Secondary recovery is an additional production phase performed to increase reservoir pressure that is important for prolonging the production period. This technique can be either the injection of water (waterflooding) or gas (gas flooding). The last phase of production is tertiary recovery or so called “Enhanced Oil Recovery (EOR)”. This production stage is performed by injected substances to enhance oil recovery beyond physical displacement mechanisms. EOR techniques can be classified into several groups: miscible gas injection, chemical injection, thermal recovery, and microbial enhanced oil recovery [1].

Low Salinity waterflooding (LSWF) is a technique that is often mentioned nowadays. Even though the name is related to waterflooding, LSWF involves the chemical reaction between rock and injected fluid and hence, it is considered as EOR instead of secondary recovery. The implementation of LSWF is quite simple: injected water must be lower in terms of total salinity. Several studies show that this condition leads to oil recovery mechanisms. Recently, it is found that the oil recovery mechanisms of LSWF are also triggered by many other additional factors. Srisuriyachai et al. [2] performed a series of studies and they discovered that not only total salinity of injected water plays important role in initiating oil recovery mechanisms, but the types of presented ions in injected water also play an even more important role. Another condition required for the oil recovery mechanism by LSWF is the presence of clay minerals. In shaly-sandstone, clays are bounded with pore surfaces as they are formed after the lithification process of sandstone (Neo-form clay). Due to the abundance of negative charges, clays tend to hold plenty of positive charges. These positive charges especially divalent ions or ions with two positive charges can link rock surface together with oil drop through binding with a carboxylic acid in the oil. The presence of this ion binding is therefore an important key to success for LSWF.

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Clay minerals found in reservoir rock can be varied in terms of structure and chemical composition. Hence, different types of clay minerals would cause different binding strengths between rock and oil, and on the other hand, they could result in different effectiveness when a certain type of water formulation is injected. According to this, different types of clay are tested in this study with different low salinity water to investigate the effects of different clays in oil recovery mechanisms.

The study is divided into two major parts. First, pure clay minerals (or representative clays) are tested with different water formulations to identify their capacities in Multi-component Ion Exchange (MIE). At this step, effluents obtained from flowing through the clay pack are detected for chemical composition changes. The second part is performed onto shaly-sandstone core samples. A small part of the core sample is taken for compositional analysis using X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) to identify types and amounts of clay.

Results from the first part are then used to select the appropriate water formulation for the core flood experiment. The chemical composition of effluent from the core flood is collected for analysis and the oil recovery factor is detected. Comparison between results from representative clays and combined clays in nature is performed for new findings.

This study would provide additional explanation for LSWF not only on the side of water formulation. Knowing the types and composition of clay minerals in rock samples would lead to the best water formulation for LSWF in the specific shaly-sandstone reservoir.

1.2 Objectives

1.2.1 To investigate effects of types of clay mineral on oil recovery mechanism in low salinity waterflooding in shaly-sandstone.

1.2.2 To identify appropriate low salinity water formulations for formation containing different types of clay in shaly sandstone.

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CHAPTER 2

LITERATURE REVIEWS

Austad et.al conducted experiments regarding chemical mechanisms of Low Salinity Waterflooding (LSWF) in sandstone and used the obtained results to compare with previous studies. From this study, it was found that the original wettability of rock plays an important role in LSWF. The candidate reservoir must be sandstone containing clays that can absorb acidic or basic compounds in the oil phase together with calcium ions in the aqueous phase. This initial condition was preferably occurred at a lower pH value around 5 to favor the adsorption pattern. The authors also proposed oil recovery mechanisms specifically for this type of reservoir. Once low salinity water lacking calcium ions was injected, the equilibrium was shifted. Calcium ion tended to desorb from clay surface to bulk water and hydrogen ion was required to balance the vacant charged site. This led to the generation of hydroxide ions from water molecules and consequently, the pH value adjacent to the clay surface was raised up. The generated hydroxide ion is then combined with protonated hydrogen in an adsorbed base compound or non-dissociated hydrogen ion from the acid compound to liberate water and base/acid molecules. Clay surface was free from adsorbed materials and tends to be more water wet. The authors also provided favorability of clay types which were mainly based on Cation Exchange Capacity (CEC) as Kaolinite < Illite < Montmorillonite. These clays did not only affect LSWF in different degrees, but they also had different pH windows in the adsorption/desorption process. From this study, oil recovery of about 75% (compared to that of conventional waterflooding) was obtained by using LSWF under the optimal conditions. Additionally, the authors explained the change of magnesium ion due to LSWF that was previously mentioned by other studies. The explanation may be due to the precipitation of magnesium ions into magnesium hydroxide at an elevated pH value which is a consequence of mechanisms created by low salinity water as mentioned before. [3]

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Ivuawuogu et.al performed three different experiments including the zeta potential test, clay swelling test, and core flood test to observe oil recovery mechanisms during low salinity waterflooding. The study emphasized four different rock components which were sand, montmorillonite, illite, and kaolinite. From the zeta potential test, it was observed that low salinity water resulted in more negative zeta potential for all components compared to high salinity. This could be inferred that low salinity can change rock wettability to a more water-wet condition which is a more favorable condition. In the clay swelling test, it was found that montmorillonite can swell by both high salinity and low salinity water. As montmorillonite was originally associated with a sodium ion, the first swelling can be explained by replacing sodium ion with calcium and magnesium ion (together with hydrated water) in high salinity water and the second swelling by low salinity water can happen by replacing calcium and magnesium ion by sodium ion (together with hydrated water) in low salinity water. Illite showed a little expansion due to high salinity water but did not show further swelling by low salinity water. Kaolinite with very low Cation Exchange Capacity (CEC) did not show any swelling effect by both high and low salinity water.

In the last experiment, core flooding revealed that three sand packs containing montmorillonite yielded outstanding higher oil recovery by low salinity water compared to those containing other clays. Among these three sand packs, a common thing to be observed was an increment of different pressure across the core sample during switching the injection from high salinity to low salinity water

From this study, it can be confirmed that the oil recovery mechanism by low salinity water was a combined effect from changing of wettability toward favorable conditions and from clay swelling that could block the high permeability path, resulting in a local increase of different pressure and oil mobilization. Therefore, the presence of montmorillonite which is clay with the highest swelling effect could yield benefits to low salinity waterflooding [4].

Wei et. al performed three experiments to determine the effects of clay types on low salinity waterflooding. This study mainly emphasized the effects of the double electron layer on a clay surface. The study was performed in three steps including zeta potential measurement, contact angle measurement, and displacement mechanism test in the micro model. From the first and the second experiments, it was observed that different clays showed a tendency to become more oil-wet at higher water salinity. Lower salinity caused the surface to be more negatively charged and therefore, polar interaction between oil and rock surface was inhibited. Calcium ions tended to reduce the double electron layer size and therefore oil could be easily adsorbed onto rock or clay surfaces. Sodium-ion was observed to have a better impact on low salinity waterflooding since the double electron layer was thicker and weaker. Among all clay types, montmorillonite and kaolinite showed the best results on both tests and therefore they were chosen for the micro-model test.

From the micro-model test, it was observed that both clays showed potential in improving oil recovery by low salinity waterflooding. However, for the case of kaolinite, the surface condition was observed to be more oil-wet with high salinity water, and oil recovery was much improved by the presence of low salinity water. However, in the case of montmorillonite, the improvement was also noticed but the initial condition was found to be already water-wet and the improvement in terms of water-wetness changed the displacement from snap-off into a piston-like pattern [5].

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Chaturvedi et al. performed sets of tests to determine which salt additives resulted in swelling of clays. The tests were not performed only with salt additives, freshwater was also used to observe the difference. The salt additives that the authors used were KCl and $CaCl_2$ and the concentration range of these additives was between 0 - 4 wt%. Nevertheless, the authors discovered the most suitable concentration was at 2 wt%. After that, clay content was investigated to find out the effects of swelling of clay content on the oil recovery mechanism. X-ray Diffraction (XRD) were utilized to indicate the compositional properties of samples. The authors measured the porosity of 12 samples in 3 scenarios using water, calcium salt, and potassium salt at concentrations of 2 wt%. Last, the comparison between conventional waterflooding and low salinity waterflooding was accomplished by using core flooding to assess pressure drop during displacement mechanism and oil recovery from their samples.

Results showed that potassium salt was more favorable in controlling the swelling of clay than calcium ion salt. In terms of the effectiveness of Low Salinity Water in shaly sandstone, the authors discovered that rock samples that obtained the highest improvement in oil recovery (compared to conventional mode) were rock containing shale from 20-25 percent. However, the higher percentage of clay content also came with difficulty for the oil recovery process due to the reduction of permeability and porosity from clay swelling even with the best low salinity water (KCl 2%wt). Nevertheless, the major oil recovery mechanism was not specified in this study [6].

Abdelmoneim and Nasr-El-Din performed a test to see assess the effect of low salinity waterflooding in a multilayered clay-rich reservoir. They investigated the effects called water blockage that can enhance sweep efficiency, especially in a reservoir containing multilayered permeability. LSWF was tested with secondary mode (injected water tended to by-pass low permeability zone) and tertiary mode (addition to secondary to improve more oil recovery in the unswept zone) by using core flooding in a parallel core system.

The authors revealed that most reservoirs are heterogeneous, and they may contain different permeability. Oil production from the multilayered reservoir was very complex and this could result in low oil production due to oil trapping and un-swept layers. From this study, it was found that LSWF can create formation damage from fines migration. This damage in high permeability forced injected water to flow into the lower permeability zone, resulting in the total core system having a more homogenous waterfront improvement. The flooded zone lost part of permeability, making the unflooded zone have a lower resistance path (lowering of permeability contrast) [7].

Kai He et.al performed a laboratory test with low saline brine with concentrations ranging from 1 – 12% in combination with surfactant (3,000 ppm) in core samples from Muskwa field which was a shale-rich formation in Canada. They believed that LSB combined with surfactant would be responding to each other and could be used as a hydraulic fracturing fluid. The authors found that the salinity of injected water that yielded the lowest interfacial tension was dependent also on temperature, pH value, and properties of crude oil. Oil recovery was higher when the salinity of KCl was lower than 4% while surfactant concentration was kept constant at 3,000 ppm. The oil recovery mechanism was explained by the authors that surfactant helped prevent the re-trapping of liberated oil due to destabilization. Injecting only low salinity water could result in the liberation of oil droplets but they could be re-trapped in flow paths again and hence, oil recovery was low. Low salinity brine was capable to recover oil from shaly formation areas as it can also produce oil from small pores as the capillary number can be substantially reduced by the presence of surfactant hence this combination was concluded to be a potential technique for shaly formation [8].

Chavan et.al did literature reviews from specific publications on LSW (Low Salinity Water) and LSWF (Low Salinity Waterflooding), implemented on a field scale. The authors summarized screening criteria for LSW injection regarding the presence of clay, initial wettability of rock, and chemistry of water. Regarding the presence of clay, the authors revealed that most investigators performed a study on kaolinite as it was the least favorable clay. However, Cation Exchange Capacity (CEC) was the most concerned parameter for low salinity waterflooding. The higher the CEC the better the effect on the oil recovery mechanism and hence montmorillonite > illite/mica

> kaolinite. The authors found that LSWF did not have a direct relationship with porosity, pore size, and permeability, but for wettability, they played an important role in controlling the effectiveness of LSWF. From all the research studies, most of them were conducted a study to illustrate favorable results on oil-wet conditions that changed into more water-wet conditions after LSWF. As rock surface changed to a more water-wet condition, residual oil saturation decreased and thus, higher recovery was achieved.

The last parameter to provoke the effects of LSWF was water chemistry. The authors discovered the best range of salinity of injected water for performing LSW injection with Total Dissolved Solid (TDS) ranging from 2,000 to 5,000 ppm. Moreover, for the optimum result of LSWF, the composition of the formation water must be known. Several investigators suggested that formation water favoring LSWF must contain divalent cation at low pH (e.g., Ca^{2+}). Encountering LSW with formation water results in desorption of organic material from clay surface. Therefore, the rock becomes more water-wet and oil recovery is increased [9].

Safari et.al performed a study of low salinity water injection in shale using water containing NaCl and $MgCl_2$ salts. The concentration of salt used that was ranging from 1,000 to 10,000 ppm. The authors discovered that the favorable salinity to change the wettability of shale was below 10,000 ppm. In this range of salinity, organic compounds adsorbed onto rock surfaces tended to migrate into the aqueous phase. To obtain the optimal results in terms of lowering interfacial tension, the authors used $MgCl_2$ as a polar component including the surface-active agent, in the oil phase tended to migrate in the aqueous phase, resulting in a high amount of surface-active agent at the boundary at inter-phase. Using high salinity water required only ionic activity from the aqueous phase, not from the oil phase. The result also showed that NaCl in low concentration decreased the contact angle of water on the shale surface. Nevertheless, when $MgCl_2$, the contact angle decreased at the same degree at a lower concentration, changing rock wettability from oil-wet to neutral-wet. As salinity was decreased, the solubility of the organic component was found to increase in the aqueous phase [10].

Gomari and Joseph performed laboratory studies on low salinity waterflooding in sandstone reservoirs by evaluating contact angle to assess wettability alteration of rock samples, investigating various parameters including temperature, clay particle, and salinity of injected water. The authors believed that during wettability alteration from oil-wet to water-wet, oil could be liberated from the rock surface when rock contained different types of clay such as kaolinite and montmorillonite. They conducted a group of tests using different water salinities of 500 ppm, 1,000 ppm, and 2,000 ppm which were labeled as B1, B2, and B3, respectively. Each water salinity was tested on 8 different rock samples. From the experiments, 6 samples yielded the highest change in contact angle when using solution B2 (1,000 ppm), whereas the other 2 samples showed the maximum wettability alternation when exposed to solution B3 (2,000 ppm). Therefore, the favorable salinity in this study was in the range of 1,000 to 2,000 ppm. Decreasing contact of angle was more obvious in rock containing kaolinite clay compared to montmorillonite clay. The amount of clay did not have many contributions to their study, but the temperature caused wettability alterations [11].

Regarding the literature reviews, the study of combining the effects of clay and the chemical composition of injected low salinity water is not fully implemented and hence, this study is performed to fill this gap to better understand the interaction of clays and injected water during the low salinity water flooding process, leading to capability to select appropriate water formulation for specific reservoir with a certain combination of clays.

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CHAPTER 3

THEORIES

3.1 Low Salinity Waterflooding (LSWF) and Oil Recovery Mechanisms

Low-salinity waterflooding (LSWF) is one of the Enhanced Oil Recovery (EOR) methods that could yield an improvement in oil recovery by approximately 5-40% beyond that of high-salinity conventional waterflooding. One of the works from Bernard explained that the water-sensitive core produced more oil when fresh water was injected compared to the case where high salinity water was injected. Not just freshwater flood, the core needed to have a decreased permeability and developed a high-pressure drop along with the core sample [12].

LSWF yields oil recovery through multiple mechanisms. Based on the study of Tang and Morrow Dislodging of clays is one of the impacts that has an effect to increase oil recovery, and so does the reduction of Interfacial Tension (IFT), liberating oil in small droplets or as emulsions. However, Multi-Component Ionic Exchange (MIE) is documented most of the time to be a dominant process, resulting in changing to wettability toward water wetness. Not only MIE, but Double Layer Expansion (DLE) of water layered covering rock surface is also observed to favor the MIE [13].

MIE based on Lager et.al was responsible for the increase in oil recovery in the injection of LSW by removing organic polar compound and organic-metallic complexes from the clay surface and replacing them with non-complexed cation. It can be simplified as clay surface tends to have a water-wet condition. As sandstone and clay surfaces can be oil-wet by having adsorbed layer of oil through divalent ion binding (Ca^{2+} and Mg^{2+}), once LSW which is lower in terms of concentration of all ions, these ions at the bridge tend to leave their position. The mechanism is favored by forming of calcium carboxylate complex between oil and calcium ion in water, reducing adsorption strength between oil and rock surface. At the same time, presenting monovalent ion replaces the site of the bridging divalent ion, and oil is then liberated [14]. LSWF can be performed in a carbonate reservoir as well with a wide range of Potential Determining Ions (PDI) including Ca^{2+}, $Mg^{2+,}$ and SO_4^{2-}. Presenting of sulfate ions results in the neutralization of positive charge on the rock surface and hence, calcium ions can approach the oil layer to form a calcium carboxylate complex. Reducing salinity of injected water induces the dissolution of calcium carbonate, resulting in increment of Hydroxide ion and once the pH value is above 9 which is the Point of Zero Charge (PZC) of carbonate rock, adsorbed material through negative charge is repulsed from the surface. The overall mechanisms trigger the liberation of oil [15]. Multi-component Ion Exchange in sandstone and clay surface and symbiotic actions of potential determining ions in carbonate surface are depicted in Figure 1a and 1b, respectively.

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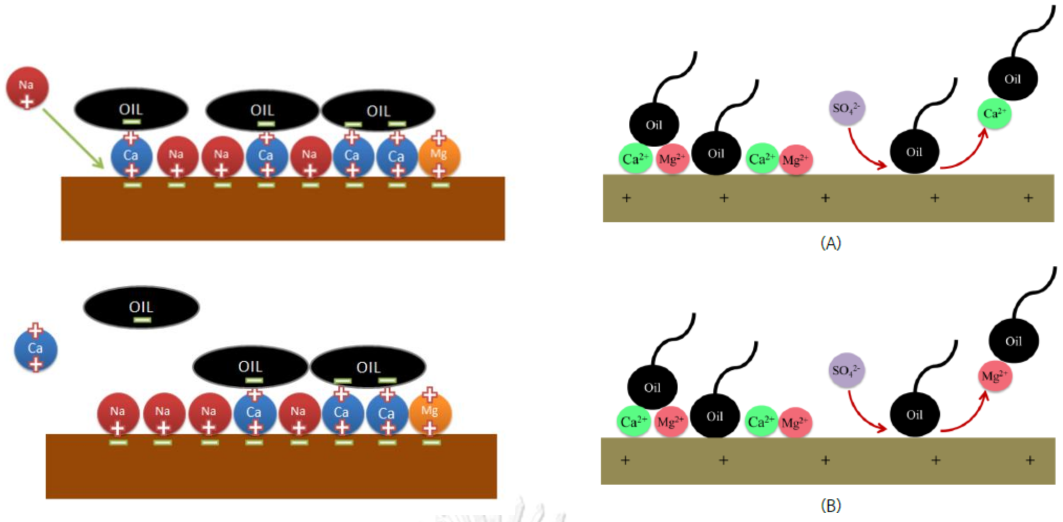


(a) (b)

Figure 1 a) Multi-component Ion exchange in Sandstone surface and b) Symbiotic actions of PDI in Carbonate surface [2]

Besides MIE, Double Layer Expansion (DLE) is another important mechanism that occurred during LSWF, favoring the overall oil recovery mechanism. During the injection of low salinity water, the water layer covering sandstone or clay surface is enlarged to balance the salt concentration in bulk water and adsorbed water layer. This results in the weakening of adsorption of oil through carboxylic acid – divalent ion – rock surface. Together with MIE, DLE facilitates the liberation of adsorbed oil. The mechanism of double-layer expansion is shown in Figure 2.

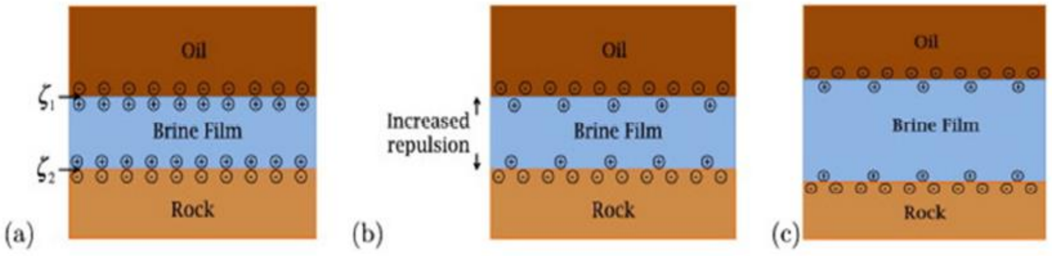


Figure 2 Schematic of Double Layered Expansion (DLE) weakening oil-wet surface [16]

3.2 Effect of Clay on Low Salinity Waterflooding

Clay can play an important role in LSWF, not just the quantity of clay in the rock matrix, the distribution of clay minerals also affects the LSWF performance. A large amount of clay surface area can affect oil recovery of the reservoir and due to this property. Clay can be divided into two major groups which are swelling and migrating clays. Both groups of clays can be distinguished from one important property which is Cation Exchange Capacity (CEC). A number of investigators performed experiment studies on clay swelling and the effect of clay swelling on LSWF performance [5]. Clay swelling can be considered as formation damage that has an adverse effect on reservoir conductivity, and so does on the LSWF. The clay structure layer is varied according to the positive charge due to cation exchange, and each layer needs to be balanced with negative charges. Clay detachment can cause pore blocking. This is caused by a different type of clay called migrating clay. Both types of clay are represented by Montmorillonite (swelling clay) and Kaolinite (Migrating clay) resulting in pore plugging in high permeability channels, giving benefit to the EOR [8].

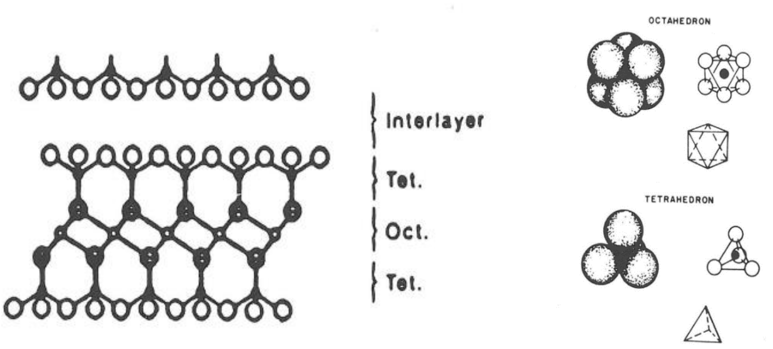
Gomari and Joseph performed a laboratory study on the effect of LSWF in sandstone reservoirs by evaluating the contact angle for assessing wettability alteration on the samples with various parameters including temperature, clay particle size, and salinity of injected brine. They believed that wettability alteration (from oil-wet to water-wet) would increase the recovery factor, with a different type of clay (kaolinite and montmorillonite), and with different brine salinity. From the experiments, 6 samples yielded the highest change in contact angle when using solution B2 (1,000 ppm), whereas the other 2 samples showed the maximum in wettability alternation when exposed to solution B3 (2,000 ppm). Therefore, the favorable salinity in this study was in the range of 1,000 to 2,000 ppm. Decreasing contact of angle was more obvious in rock containing Kaolinite clay after comparing it to Montmorillonite clay. The amount of clay did not have many contributions to their studies, but the temperature was causing wettability alterations [11].

3.2.1 Properties of Clays

In nature, clay is composed primarily of fine-grained minerals. Most clays are plastic at appropriate water contents and form a solid state when dried. Clay is generally silicate with the size of the minerals less than 2 microns. Clays are abundant at the earth's surface; they form rocks known as shales and are a major component in most sedimentary rocks. The small size of the particles and their unique crystal structures give clay materials special properties, including Cation Exchange Capability (CEC), plastic behavior when wet, catalytic abilities, swelling behavior, and low permeabilities [16].

Clay minerals consist of layers of silicates. There are two basic components to the structure: a sheet of corner-linked Tetrahedra and a sheet of edge-sharing Octahedra. Figure 3a illustrates the linkage of atoms to form the tetrahedra-octahedra-tetrahedra sequence, forming a clay structure as a layer. **Tetrahedral sheets** contain a dominant atom in the middle tetrahedron as Silicon cation (Si^{4+}). However, replacement of Aluminum cation (Al^{3+}) can occur. **Octahedral sheets** compose of edge-sharing octahedra. Different phyllosilicates have different cations in the octahedra. In the octahedra, it is required that for every two octahedra containing Al^{3+}, there is an empty octahedron.

Layers of tetrahedral and octahedral sheets can be modular components of a phyllosilicate. It is necessary to join the two sheets. The lateral dimensions of the two sheets are approximately equal so it is possible to join them together. In the case of montmorillonite, there are two tetrahedral sheets, inverted relative to each other, and with an octahedral sheet in between the tetrahedral sheets. Thus, some of the oxygens that belonged to tetrahedral sheets also belonged to the octahedral sheet. Only the hydroxyl ions do not link directly to the tetrahedra.



(a) (b)

Figure 3 a) Unit of clay sheet containing tetrahedra-octahedra-tetrahedra sequence and b) Three-dimensional structure of octahedra and tetrahedra [17]

3.2.1 Illite

Illite is a clay mineral that its structure is a 2:1 layer (2 tetrahedral sheets and 1 octahedral sheet) and in the between units, there are potassium cations to balance negative charge as shown in Figure 4.

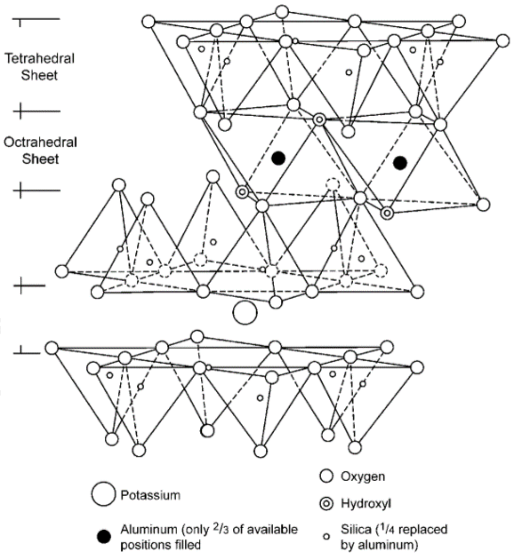


Figure 4 Three-dimensional structure of Illite clay composed of two tetrahedral sheets and one octahedral sheet in the middle [16]

As potassium ions can fit perfectly with the hexagonal ring of silica tetrahedral sheets, the structure of illite interlocks potassium ions with high strength, preventing water molecules to occupy this inter-layered gap. In nature, aluminum ions in octahedral layers can be replaced by Mg^{2+} and Fe^{2+}. The replaced Al^{3+} can also replace Si^{4+} in the tetrahedral layer. Illite is commonly found together with Kaolinite and Montmorillonite. Mixed-layered or interstratified clay is one example that is a combination of illite and montmorillonite.

3.2.2 Kaolinite

One Kaolinite clay unit consists of a single tetrahedral sheet and a single octahedral sheet with the thickness of the layer being 7.13 Å. The structure of kaolinite is $Al_4Si_4O_{10}(OH)_8$ and the theoretical chemical composition is SiO_2, 46.54%; Al_2O_3, 39.50%; and H_2O, 13.96%. The charge of kaolinite structure is balanced, so it is called a 1:1 layer that combines octahedral and tetrahedral sheets. However, only two-thirds of the octahedral positions are filled with Aluminum atoms. Kaolin is another term to represent rock or mineral that is enriched in Kaolinite. For the Kaolin mineral, other clays can also be found in small quantities such as Dickrite, Nacrite, and Halloysite. Cations in tetrahedral and octahedral sheets of Kaolinite are rarely replaced. Ferric ion with an ionic radius of 0.67 Å can replace Aluminum ion with the ionic radius of 0.57 Å but only in a limited number. The replaced Aluminum ion then can continuously replace the Silicon ion in a tetrahedral sheet. As the replacement of ions is quite limited, the CEC of Kaolinite is much smaller compared to swelling clay such as Montmorillonite. In the normal range of reservoir pH value, Kaolinite is quite inert and has low conductivity for both heat and electricity. This can result in difficulty in shaly-sand interpretation since Kaolinite does not affect the correction of water saturation, but it could result in overestimation of porosity when using neutron log. Figure 5 illustrates a unit of Kaolinite composed of one tetrahedral and one octahedral structure.

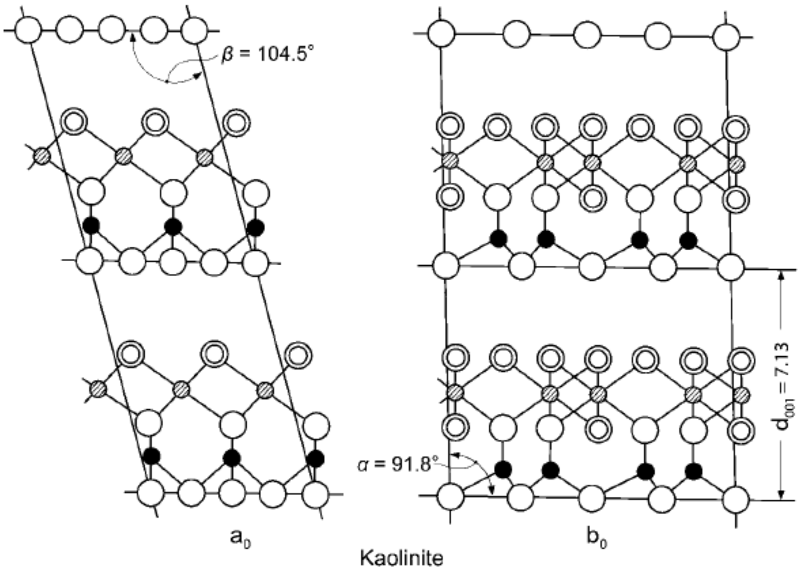


Figure 5 Three-dimensional structure of Kaolinite clay composed of two tetrahedral sheets and one octahedral sheet in the middle [16]

3.2.3 Montmorillonite

Montmorillonite is a clay formed from two silica tetrahedral sheets with a central octahedral sheet and has a layer as a 2:1 layer mineral, as shown in Figure 6.

The formula for montmorillonite is $(OH)_4Si_8Al_4O_{20}\cdot NH_2O$ and the theoretical chemical composition is SiO_2, 66.7%; Al_2O_3, 28.3%; and H_2O, 5%. Montmorillonite can be combined with other cations and the most common Montmorillonites are sodium montmorillonite and calcium montmorillonite, which means the negative charge is balanced by sodium ions and calcium ions, respectively. The term Smectite is used for hydrated minerals with montmorillonite that are accompanied by sodium, calcium, and other cations such as magnesium, iron, and lithium. The term Bentonite is mainly used for smectite from any origin and the most used Bentonite in the industry mainly has sodium and calcium montmorillonite clays. The octahedral of montmorillonite clay is often replaced by a divalent cation such as Fe^{2+} and Mg^{2+} and there can be a replacement of Al^{3+} on Si^{4+} in a tetrahedral layer. Approximately 80% of the cation exchange capacity is responsible by charges in the gaps between clay units. Sodium montmorillonite is higher in terms of CEC and can result in swelling of its original volume about 10-15 times when in contact with water. Calcium montmorillonite instead is smaller in terms of CEC. Calcium montmorillonite can swell around 2-3 times but this can be increased when it is in contact with sodium ions as sodium can replace calcium ions.

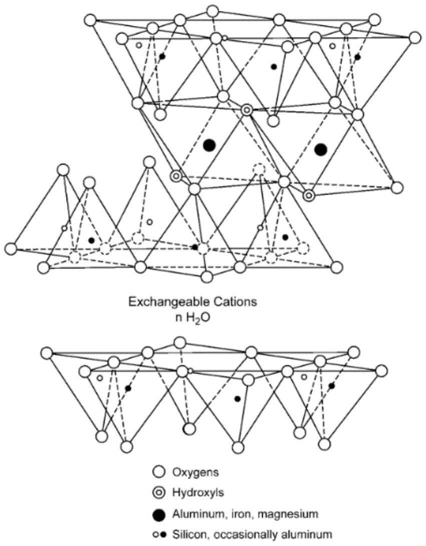


Figure 6 Three-dimensional structure of Montmorillonite clay composed of two tetrahedral sheets and one octahedral sheet in the middle [16]

CHAPTER 4

METHODOLOGY

In this study, the methodology is subdivided into 5 sections including 1) rock mineralogy assessment; 2) filtration and titration test; 3) selection of low salinity water formulation; 4) preparation of core samples and properties of fluids; and 5) Coreflooding test. At the end of this chapter, an overall flow chart of the study is provided.

4.1 Rock Mineralogy Assessment

Clay and shaly-sandstone samples were assessed for mineralogy by using X-ray Fluorescence (XRF), and X-ray Diffraction (XRD). XRF was utilized to find the elements contained in samples. XRF was useful in determining minerals contained in samples by comparing them with atomic elements. The obtained data was also applied to the data XRD to summarize the representing minerals of the samples. The function of XRD is based on the diffraction of X-ray radiation from the crystal of minerals into the detector. Reading of detector is shown as peaks for specific minerals based on counts and angles of the measurement compared with the database of the equipment. Figure 7 illustrates two important instruments for mineralogy assessment in this study

The assessment of clay minerals was conducted to confirm the representing clay in this study including Montmorillonite, Kaolinite, and Illite. Once the type of clay was confirmed, specific clay was used in the filtration test which is explained in section 4.2. Three examples of clay, their physical appearance, and commercial names are summarized in Table 1.

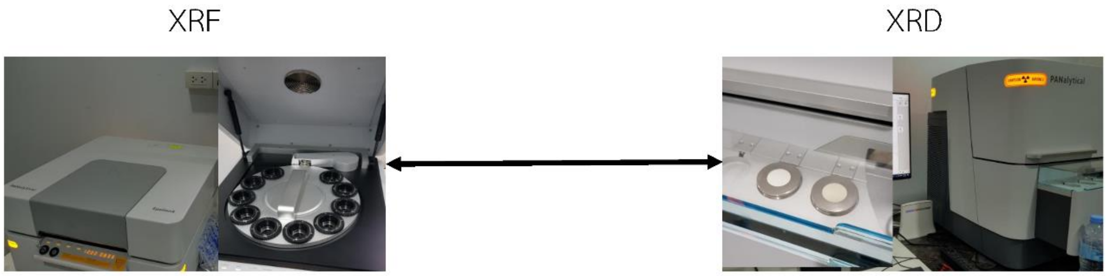


Figure 7 Instruments used for Assessment of Rock Mineralogy

Mineralogy of shaly-sand core sample was also performed similarly to representing clay. The core sample was slightly cut for one end and was grinded and sieved to obtain homogeneity of the sample. Constituent of clays in each core sample was used together with results obtained from filtration and titration (section 4.2.1 and 4.2.2) in the process to select low salinity water formulation (section 4.3).

Table 1 Summary of Clays representing Montmorillonite, Kaolinite, and Illite

Representing Clay	Colors	Commercial Name
Montmorillonite	Reddish Brown	Bentonite
Kaolinite	Light Brown	Ball Clay
Illite	Light Green	French Green Clay

4.2 Filtration and Titration Test

4.2.1 Filtration Test

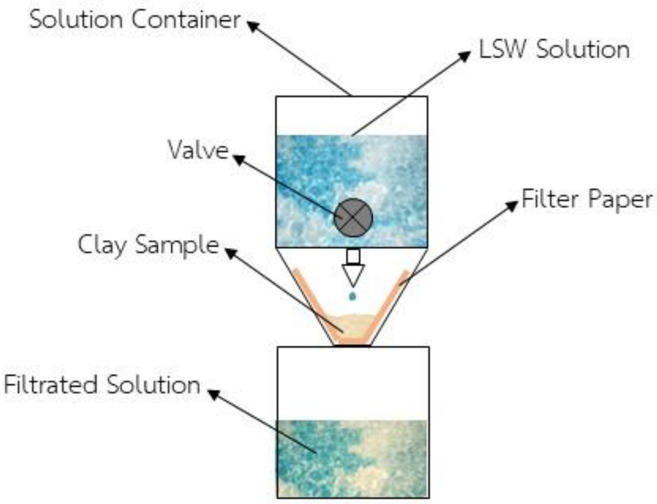


Figure 8 Setup of Clay Filtration Test

A filtration test was performed to study the dissolution of specific ions from clays when they are in contact with low salinity water containing different ions. Clay samples were firstly sieved at the mesh size number 30 with an aperture of 600 microns in order to have homogeneous grain. In each experiment, 20 grams of clay were packed into filter paper grade 5 with a pore size of filter paper of 2.5 μm and 100 cm^3 of low salinity water the clay sample was flowed through the packed paper and placed in a funnel, and the filtrate was collected at the interior part of the equipment. The equipment for the filtration test is illustrated in Figure 8.

In this study, different low salinity water formulations were studied. Both concentration and ion of water formulation are summarized in Table 2.

Table 2 Summary of Water Formulations for Each Clay

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Representing clay	Water Formulation	
	1,000 ppm	5,000 ppm
Montmorillonite	$CaCl_2$	$CaCl_2$
	$MgCl_2$	$MgCl_2$
	NaCl	NaCl
	KCl	KCl
Kaolinite	$CaCl_2$	$CaCl_2$
	$MgCl_2$	$MgCl_2$
	NaCl	NaCl
	KCl	KCl
Illite	$CaCl_2$	$CaCl_2$
	$MgCl_2$	$MgCl_2$
	NaCl	NaCl
	KCl	KCl

4.2.2 Titration Test

To observe the dissolution of ions from clays when they are in contact with low salinity water, the filtrates obtained from 4.2.1 were titrated to identified interest ions including calcium ion (Ca^{2+}), magnesium ion (Mg^{2+}), and potassium ion (K^{+}).

To titrate for calcium and magnesium ions (total divalent ions or total hardness), 5 cm^3 of the filtrate was pipetted into a flask and three drops of ammonium solution were added as a buffer solution. Then, a pinch of Eriochrome Black T (EBT) was added as the color indicator and the mixture was titrated with Ethylene Diamine Tetraacetic Acid EDTA with a concentration of 0.01M. In several cases where the concentration of Calcium and Magnesium ions was high from the low salinity water, the amount of sample was reduced to 1 $cm^{3,}$ and the concentration of EDTA was increased to 0.05M to ease the titration process. The end point of titration was detected when the color of the solution changes from wine red to sky blue.

The second titration test was the determination of solely calcium ions. Similar to the first test, 5 cm^3 of the filtrate was pipetted into a flask and a few drops of Sodium Hydroxide solution was added to precipitate the magnesium ion. A pinch of Hydroxy Naphthol Blue (HNB) was added to the solution, and the mixture was then titrated using EDTA. The end point of titration was detected when the color of the solution changes from wine red to sky blue. The concentration of magnesium was obtained from the difference in total hardness and concentration of calcium ion.

The last titration was for potassium ions where the technique called back titration technique was utilized. The filtrate was pipetted for 5 cm^3 and placed into the flask. After that, 5 cm^3 of Sodium Tetraphenyl Borate (STB) with an exact concentration of 0.02M was added to the flask to precipitate potassium ion and a pinch of Titan Yellow was added into the mixture as a color indicator. The mixture was then titrated with Zephiramine also known as Benzyldimethyltetradecylammonium Chloride Dihydrate with a concentration of 0.01M. The endpoint was detected by changing color from yellow to orange and the concentration of potassium ion was calculated from the remaining STB compared to the initial concentration. The equipment used for titration is depicted in Figure 9.

As mentioned in section 4.1, results obtained in this section were used together in the determination of low salinity water formulation in section 4.3. As divalent ions are important ions linking between a rock and clay surfaces with hydrocarbon. Releasing these divalent ions is evidence of the breaking of the linkage between rock and oil, resulting in the liberation of oil. The net amount of divalent ions is then considered as important criteria in selecting the best water formulation for specific clay.

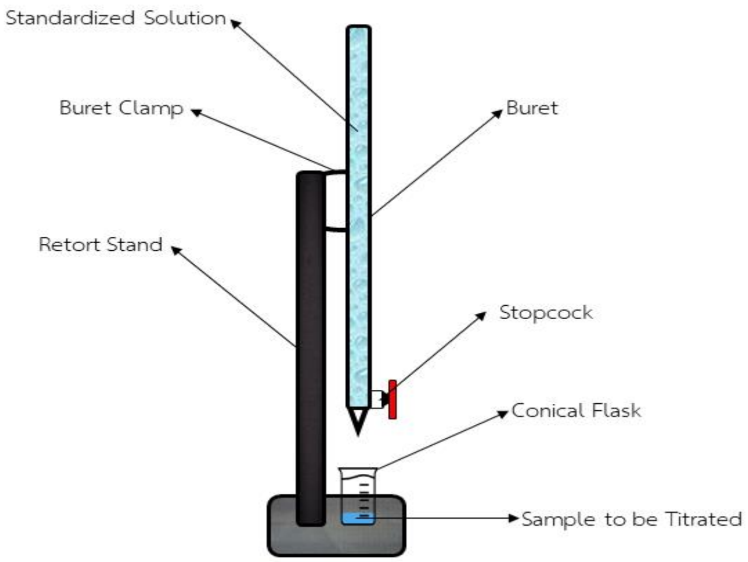

Figure 9 Equipment used in Color Titration

4.3 Selection of Low Salinity Water Formulation

Determination of water formulation for this study was based on results from both 1) assessment of clay content in a rock sample and 2) dissolution of ions from each clay. As mentioned in section 4.2.2, calcium and magnesium ions in filtrates are major criteria for the selection of key ions in water formulation. Up to two ions from 4 (calcium ion, magnesium ion, potassium ion, and sodium ion) resulting in the highest dissolution of calcium ion and magnesium ion will be picked. The portion of key ions in water formulation was weighed based on clay content in each core. Approximately 4 water formulations were chosen to cover the interesting aspects of this study. An additional explanation for each selected water formulation is described in section 5.3.

4.4 Preparation of Core Samples and Properties of Fluids

4.4.1 Preparation of Core Samples

In this study, four core samples labeled as D, F, G, and J were utilized to represent the shaly-sandstone reservoir. All cores are from the Sirikit oilfield located in the north of Thailand. Screening of the core was made by the measurement of permeability. Even though core samples are taken from the same field, different taking depth results in changing of clay contents and could result in different heterogeneity. Core treatment is described as follows

After a piece of core was cut for the assessment of mineralogy, the core was cleaned to restore natural wettability by using Soxhlet extraction. Each core sample was cleaned with Toluene for 8 hours to remove heavy hydrocarbon and followed by Methanol for another 8 hours to remove light hydrocarbon and remaining Toluene from the previous step. Figure 10 illustrates the Soxhlet apparatus used in cleaning core samples in this study

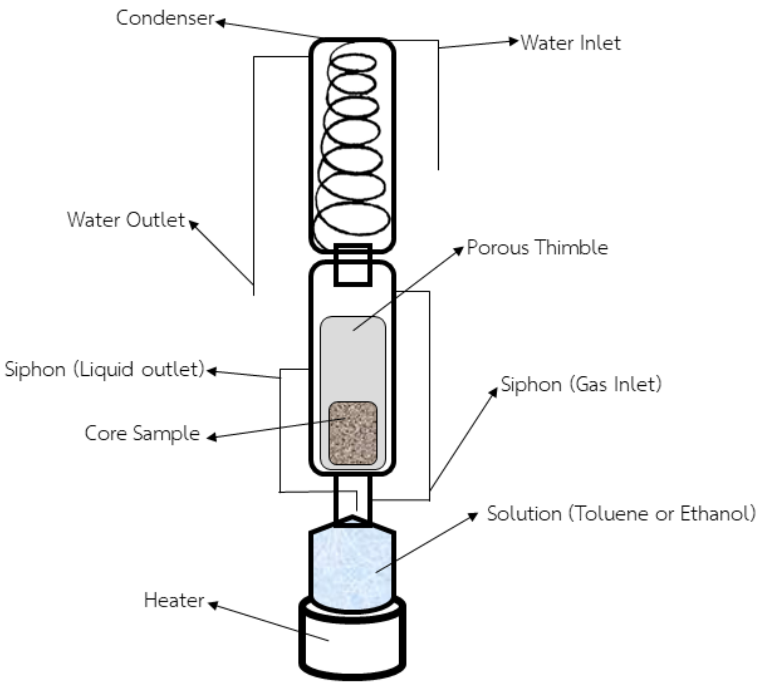

Figure 10 Soxhlet Extraction for Core Cleaning Process

Rock and petrophysical properties required in this study included pore volume, absolute permeability, and initial oil and water saturation (irreducible water saturation). Determining these properties was performed by using a core flooding machine. Synthetic formation water was prepared and using data obtained from the Sirikit oilfield and crude oil from the same oilfield was used to represent the hydrocarbon phase. However, as crude oil from the Sirikit oilfield showed wax properties, mixing crude oil with n-Dodecane was performed to prevent internal wax in the core sample. Fluid preparation is explained in section 4.4.2.

The pore volume of the core sample was obtained from the difference between the dry weight and saturated weight of core samples. The difference weight was then changed to volume by using a fluid density. In this section, the core sample was fully saturated using a core flooding machine. Equation 4.1 explains how pore volume is obtained:

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

where V_p is pore volume, W_{sat} is saturated weight, W_{dry} is dry weight, and ρ_f is fluid density in g/cm^3.

During the saturation process, absolute permeability (K_a), was obtained by using Darcy's equation as shown in equation 4.2:

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

where q is injection rate (cm^3/sec), μ is the viscosity of saturated fluid (cP), L is the length of the core sample (cm), A is the crossectional area of the core sample (cm^2), and ΔP is pressure differential across the core sample (atm).

Once pore volume and absolute permeability were obtained, the core was then flushed by crude oil to represent oil migration. In this study, the temperature of 50°C was chosen to observe the effects of low salinity as at higher temperatures, this effect might be obscured by changing of wettability toward water wetness. Crude oil was injected into each core until there was no water exiting and the pressure difference was constant. Initial oil saturation was calculated using Equation 4.3:

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

where S_{oi} is initial oil saturation (fraction), V_w is the volume of water production (cm^3), V_D is the dead pore volume of equipment (cm^3). By knowing initial oil saturation, irreducible water saturation was obtained by subtracting from 1. After initial oil saturation was obtained core samples were aged in crude oil for two weeks to allow rock samples to attain wettability equilibrium.

4.4.2 Properties of Fluids

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

Formation water was prepared using the ionic analysis of formation water obtained from the Sirikit oilfield. The Total Dissolved Solid (TDS) of formation water is 14,098 ppm and it was prepared from Sodium Chloride (NaCl), Potassium Chloride (KCl), Magnesium Chloride ($MgCl_2$), Calcium chloride ($CaCl_2$), and Sodium Hydrogen Carbonate ($NaHCO_3$), Table 3 summarizes chemical required to make up formation water in this study.

Table 3 Chemical composition of formation water

Chemicals	Molecular Weight	Weight (gram)
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	0.719
Total		14.098
Total Dissolved Solid (TDS) = 14,098 ppm		

The fluid properties of formation water required in this study were density and viscosity. Fluid density was determined using a Pycnometer and the obtained value was used in 1) determination of pore volume (as mentioned in equation 4.1) and 2) determination of fluid viscosity. Fluid viscosity was measured by the use of a Cannon-Fenske viscosimeter. As the testing temperature of this study was set at 50°C, fluid viscosity was conducted at the same temperature. The obtaining fluid viscosity in centipoise (cP) was used in the calculation of absolute permeability (as mentioned in equation 4.2).

Low salinity water formulations that were selected from section 4.3 were prepared using different chemicals (depending on key ions). Details of each selected formulation are summarized in section 5.3. For the preparation of the oil phase, as crude oil from Sirikit contains a high portion of wax, this could lead to internal wax inside crude oil that can be problems in many steps of study such as saturation process and high-pressure difference during fluid displacement mechanism. To solve this problem, Dodecane was added at an appropriate position to dissolve wax, making oil mobilize at room temperature as well as the testing temperature of 50°C. The

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best mass ratio of Dodecane to crude oil observed was 70:30 and therefore preparation of 1,000 g of crude oil fluid required 300 g of crude oil and 700 g of Dodecane.

4.5 Core Flooding Test

A core flooding test was performed to find out the effectiveness of low salinity water formulation. The tests were performed at the temperature of 50°C and confining pressure of 1,500 psi. Aged core was placed in the apparatus and conventional waterflooding using formation water was firstly performed at injection rate of 0.5 cm^3/min. Produced crude oil together with pressure difference was detected with times. Once there was no-more oil produced and the pressure difference was constant, a selected low salinity water formulation was injected, and produced oil and pressure difference were detected continuously until there was no more oil produced. Exiting effluents were collected for ionic titrations using the color titration technique as in section 4.2.2. A schematic diagram of the core flooding machine is shown in Figure 11.

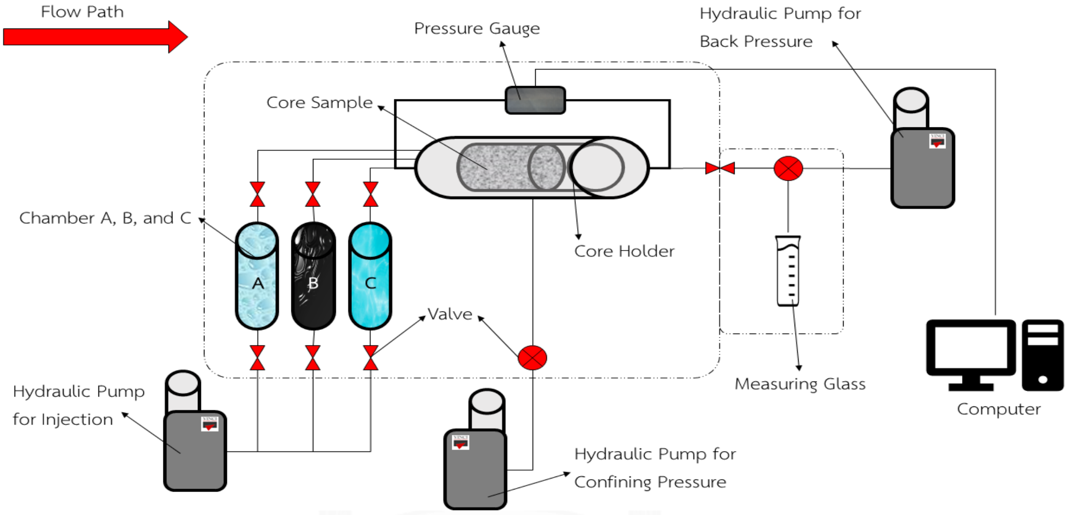

Figure 11 Schematic Diagram of Coreflooding Machine

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The overall methodology can be illustrated as a flow chart shown in Figure 12.

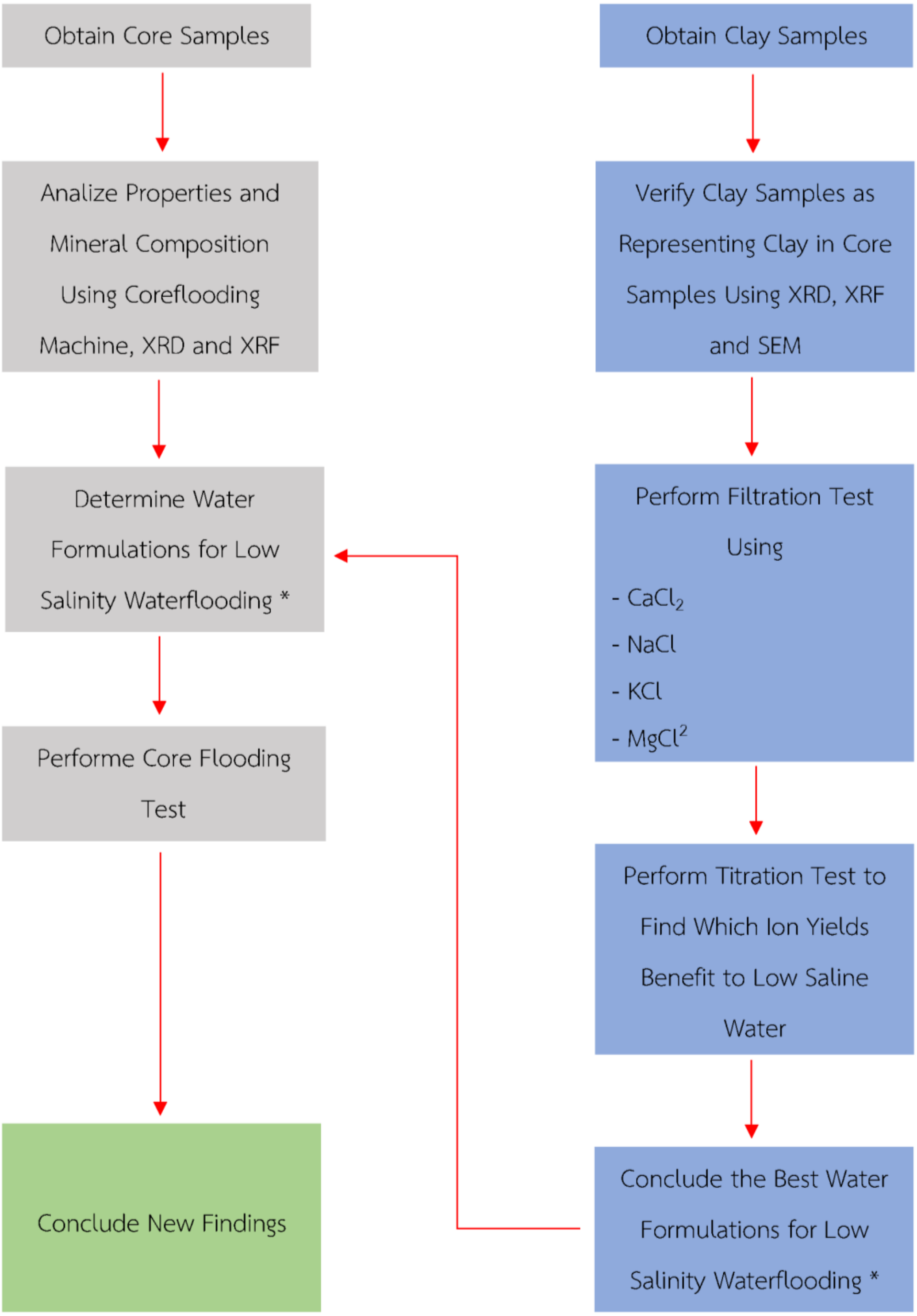

Figure 12 Summary of methodology in Flow Chart

CHAPTER 5

RESULT AND DISCUSSION

5.1 Rock Mineralogy Assessment

5.1.1 Clay Samples

As mentioned in chapter 4.1, XRD was utilized to determine the mineral composition of representative clay in terms of quantity and quality, and XRF was accompanied to confirm the results obtained from XRD by providing the majority of elements. The importance of this step of work was to confirm the representability of chosen clays as this consequently affects the selection of low salinity formulation.

For the montmorillonite clay sample, minerals found in samples from XRD and major elements of clay from XRF are summarized in Table 4.

Table 4 Results Obtained from XRD and XRF for Montmorillonite Clay Sample

XRD		XRF	
Mineral	Percentage	Elements	Percentage
Montmorillonite (I)	69.6	Si	38.812
Calcite	23.3	Fe	28.121
Benitoite	4.7	Al	14.644
Montmorillonite (II)	2.3	K	13.423
		Ca	7.852

Montmorillonite clay in this study was from bentonite clay that is commercial grade used for drilling purposes. From the table, the summation of montmorillonite clays which may have different substituting divalent elements was about 71.9% and Calcite was detected as it is additive for specific purposes of this clay in drilling activity. XRF results showed the highest five elements in weight percent, the appearance of both silicon and aluminum indicates the existence of clay minerals. However, the enriching of iron elements reveals a high replacement of iron ions in alumina octahedral structure, which is common for montmorillonite clay with high CEC. Potassium ion is commonly found in most clay to associate with abundant of negatively charge and presence of calcium ion is responsible by calcite mineral and possibly by calcium montmorillonite.

For the kaolinite clay sample, minerals found in samples from XRD and major elements of clay from XRF are summarized in Table 5.

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Table 5 Results obtained from XRD and XRF for kaolinite clay sample

XRD		XRF	
Mineral	Percentage	Elements	Percentage
Dickite	51.9	Si	58.606
Quartz	24.9	Al	25.301
Kaolinite	21.7	K	6.482
Muscovite	0.9	Fe	4.515
Montmorillonite	0.6		

Regarding the fact that ball clay can contain kaolinite from 20 to 80 percent, ball clay was preliminarily selected for this study. The ball clay used in this study was from Saraburi province and from the table, the summation of dickite which is the mineral that has a similar chemical formula as kaolinite ($Al_2Si_2O_5(OH)_4$) was the highest in terms of mass. Dickite is slightly different from Kaolinite by its morphology but as its chemical formula is as same as Kaolinite, they are both combined to represent the Kaolinite group in this study. The total mass percentage of dickite and kaolinite was 73.6. From the XRF results, the presence of silicon and aluminum indicates the existence of clay minerals. However, as kaolinite is very low in CEC, the replacement of other divalent ions in alumina octahedral is more difficult, and therefore, the portion of iron (as well as other divalent ions) is quite small compared to montmorillonite. A potassium ion in a clay structure is considered an associated ion to balance the excessive negative charge.

For the illite clay sample, minerals found in samples from XRD and major elements of clay from XRF are summarized in Table 6.

Table 6 Results obtained from XRD and XRF for illite clay sample

XRD		XRF	
Mineral	Percentage	Elements	Percentage
Illite	44.5	Si	37.500
Biotite	43	Al	16.656
Calcite	8.2	Fe	15.782
Quartz	4.2	K	13.423
		Ca	10.626

From the table, the portion of illite was 44.5%; however, the portion of biotite was about 43%. According to the study by Fordham in 1990, illite can be derived from biotite. First, iron ions in biotite were oxidized while a number of potassium ions remained. Biotite then started to be cracked and solution can enter into the structure, creating chemical weathering which resulted in a thinner and shorter structure, and eventually, this turned into a clay-size particle of illite [18]. Therefore, biotite and illite were combined together in this study, as they are chemically related (iron-riched) and the summation of both was about 87.5%. From the XRF results, the presence of silicon and aluminum shows that an aluminosilicate compound exists. Enriching in iron ions is evidence of the presence of biotite and the transformation of biotite to enriched-iron life. Potassium ion is also another ion found in association with a large negatively-charged surface. Calcium ion is mainly responsible for calcite and part could be found as calcium-illite.

A summary of the representative clays is shown in Table 7 with the portion of the percentage of representative clays and a list of minerals.

Table 7 Summary of representative clays, percentage of representative clays, and list of minerals

Representative Clay	Percentage of Clay	Mineral
Montmorillonite	71.9	Montmorillonite
Kaolinite	73.6	Kaolinite and Dickite
Illite	87.5	Illite and Biotite

5.1.2 Core Samples

Prior to the core flooding test, the core must be checked for mineralogy using XRD and XRF. However, the portion of clays was mainly considered from XRD. In this study, core samples were taken from the Sirikit oilfield and even though the cores were taken from the same well, clay content can be different due to different depths (different time of deposition, different environmental energy, and hence, different clays). There were four core samples used in this study, including core D, core F, core G, and core J. Based on the XRD results, major clays were biotite, kaolinite, and muscovite. Results obtained from XRF showed that four major elements found in these core samples were Si, Al, Fe and K. Silicon was found in almost 70 percent which represents quartz in sandstone. The appearance of aluminum and iron supported a majority of illite group clay and potassium ion as associated ions. Nevertheless, montmorillonite was absent and therefore, a clay swelling problem was not expected. The portion of clays for each core sample is summarized in Table 8.

Portions of clays (illite and kaolinite) were used in the calculation of the ionic portion of low salinity water formulation (section 5.3), using results from the filtration test in section 5.2.

Table 8 Clay content and a portion of clays in core samples

Core Sample	Clay Content	Illite Group	Kaolinite Group
D	30.8%	84.4%	15.6%
F	42.2%	57.8%	42.2%
G	34.9%	98.2%	1.8%
J	40.2%	87.1%	12.9%

5.2 Filtration and Titration Test

A filtration test was performed to study the Multi-ionic Exchange Capacity (MIE) that occurred during the contact between clay and low salinity water. As mentioned in section 4.2, dissolution of calcium and magnesium ions was expected as it explained the MIE mechanism by replacing divalent ions bridging between sand/clay surface and hydrocarbon. The breaking of divalent ions, therefore, can be expected to intimately relate to high oil recovery. Potassium ion was another important ion in this study as it proved to be able to replace divalent ion due to its high mobility from small size and low water hydration. Consumption of potassium ion was therefore additionally performed. Table 9 is the summary of the base case of this study using distilled water, and Table 10 summarizes concentrations of calcium ion, magnesium ion, and potassium ion in filtrates of different tests. From Table 10, it shows that there are negative (-) as well positive values (+) for concentrations of cation. In this study, negative value refers to the situation where cations are consumed by clay samples and positive value indicates ion dissolution from clay that is greater than consumption by clay. Discussion in this section is divided into distilled water, low salinity water of 1,000 ppm, and low salinity water of 5,000 ppm in sections 5.2.1, 5.2.2, and 5.2.3, respectively.

Table 9 Concentration of Calcium Ion, Magnesium Ion, and Potassium Ion From Filtrates Using Distilled Water as Base Case

Clay	Ionic concentration (ppm)		
	Ca^{2+}	Mg^{2+}	K^{+}
Montmorillonite	4.007	12.152	48.872
Kaolinite	4.007	3.645	50.827
Illite	8.015	2.430	62.557

Table 10 Concentration of Calcium Ion, Magnesium Ion, and Potassium Ion From Filtrates

Clay	Water Formulation	Ionic concentration (ppm)					
		1,000 ppm			5,000 ppm		
		Ca^{2+}	Mg^{2+}	K^{+}	Ca^{2+}	Mg^{2+}	K^{+}
Montmorillonite	KCl	18.035	2.430	-59.178	14.828	4.374	-2039.6
	NaCl	8.015	4.861	152.483	12.023	4.861	97.745
	$MgCl_2$	26.050	14.510	371.433	100.195	-121.888	80.542
	$CaCl_2$	-240.88	139.753	43.008	-503.04	91.143	66.467
Kaolinite	KCl	8.817	1.944	-0.531	18.035	4.861	-2051.4
	NaCl	4.007	3.645	78.196	16.031	7.291	125.114
	$MgCl_2$	20.039	-12.225	50.827	100.195	-0.363	74.286
	$CaCl_2$	-280.95	121.525	76.241	-633.29	291.66	31.278
Illite	KCl	28.054	7.291	-4.440	23.245	15.555	-2070.9
	NaCl	18.035	2.430	117.294	24.046	17.0135	86.0162
	$MgCl_2$	30.058	2.357	62.557	100.195	-30.744	62.557
	$CaCl_2$	-280.95	145.83	70.376	-703.43	352.422	54.737

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5.2.1 Distilled Water

When using distilled water in the filtration test, all clays show similar results of high dissolution of potassium ions compared to calcium and magnesium ions as can be seen in Figure 13. This can be explained that calcium and magnesium ions are bounded with alumina octahedral and hence, their solubility is low whereas potassium ions which are just loosely associated with clay structure can form hydrate molecules easily. Nevertheless, the dissolution of divalent ions is different among each clay but not an insignificant amount.

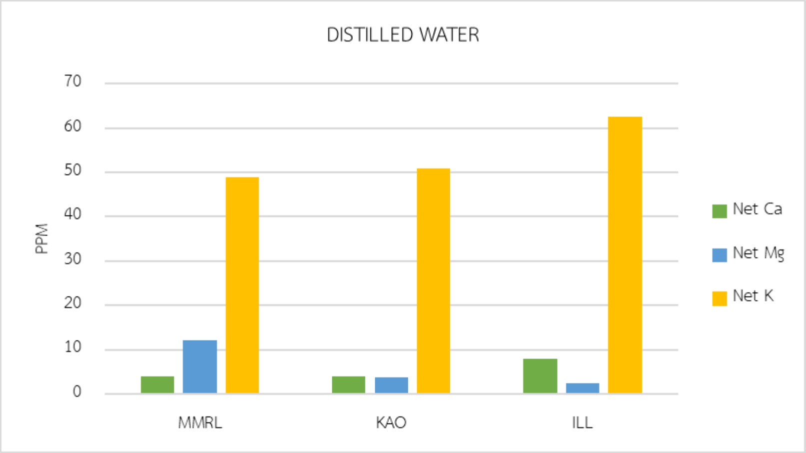

Figure 13 Concentration of Ions in Fitrates from Different Clays Using Distilled Water

5.2.2 Low Salinity Water at 1,000 ppm

When different ions were added into low salinity water, results deviated from using distilled water. Using sodium ions tends to displace potassium ions from clay structures especially in montmorillonite with a high CEC as can be seen in Figure 14. The MIE in the presence of sodium ions is obvious on potassium ions but not for divalent ions. Compared to Table 4, the dissolution of potassium is nearly double. Sodium ion, therefore, tends to replace the associate potassium ion in clays.

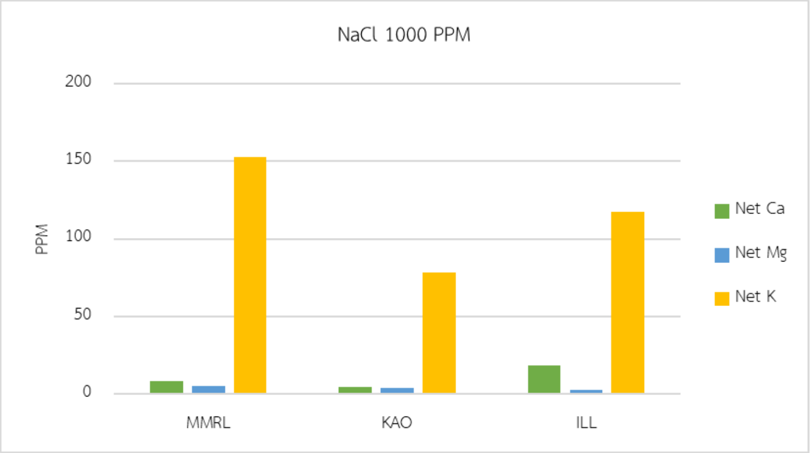

Figure 14 Concentration of Ions in Fitrates from Different Clays Using NaCl 1,000 ppm

For potassium ion, it can be seen from Figure 15 that potassium ion is highly consumed depending on the CEC of clay which is montmorillonite>illite>kaolinite. By using potassium ion, calcium ion is highly expulsed, especially for illite. Kaolinite which is extremely low in CEC showed a slight improvement in calcium ion dissolution. From this section, it can be observed that potassium ion potentially replaces calcium ion.

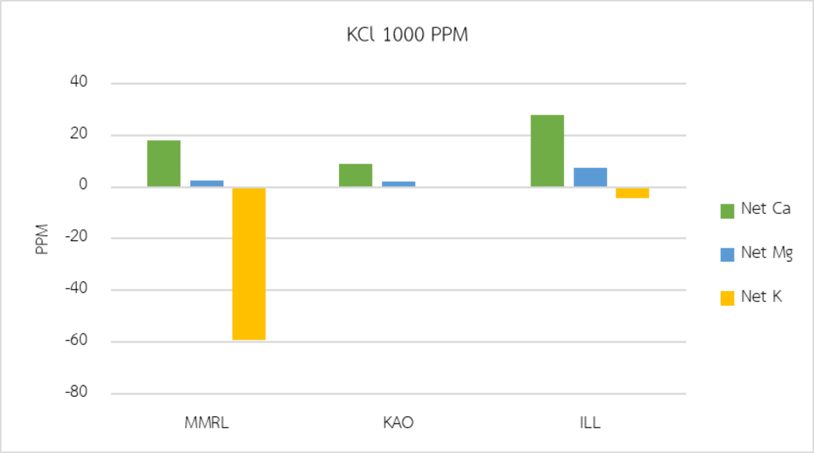

Figure 15 Concentration of Ions in Fitrates from Different Clays Using KCl 1,000 ppm

From Figure 16, a solution of calcium chloride was used and the consumption was obvious in all three clays. However, magnesium ion was mainly observed in filtrate even in the case of kaolinite which is clay with low CEC. Hence, calcium ion tends to create MIE, displacing magnesium ion in all clays and clays that are enriched in magnesium ion, presenting calcium ion in water might yield benefit in the oil recovery mechanism.

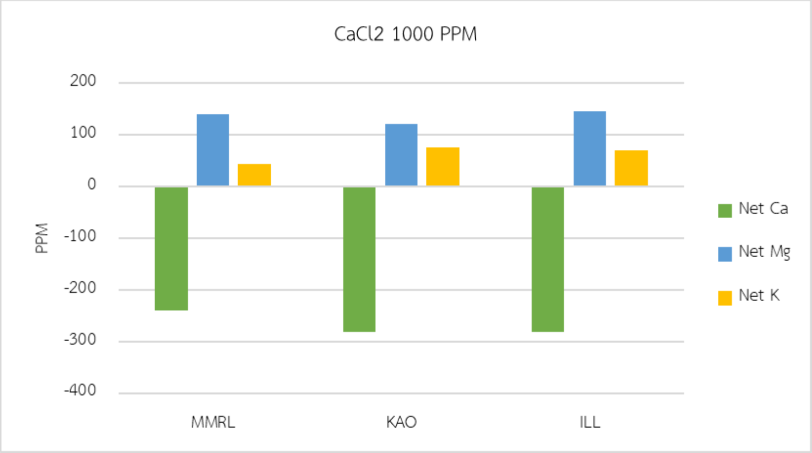

Figure 16 Concentration of Ions in Filtrates from Different Clays Using $CaCl_2$ 1,000 ppm

The effects of magnesium ions on MIE of different clays are illustrated in Figure 17. Magnesium ions tended to be consumed in all clays but not as much as in the case of calcium. Only in case of montmorillonite shows the effect of potassium ion dissolution. The amount of calcium dissolved is improved compared to distilled water but not as good as what occurred when calcium ion replaced magnesium ion.

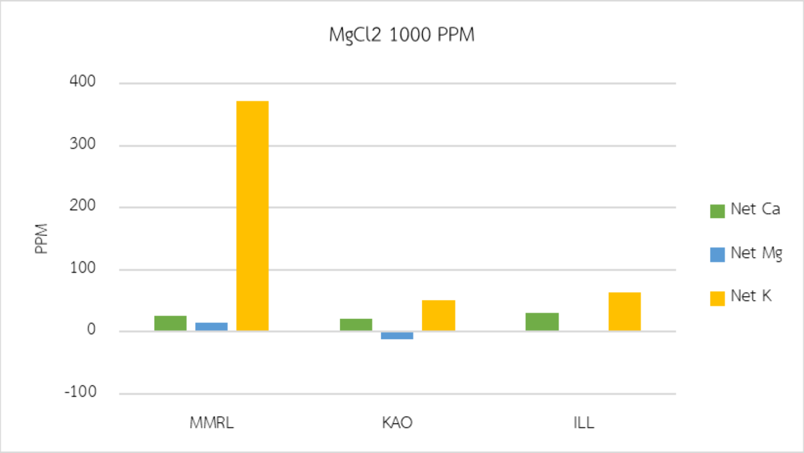

Figure 17 Concentration of Ions in Filtrates from Different Clays Using $MgCl_2$ 1,000 ppm

From this section of 1,000 ppm concentration, it can be concluded that calcium ion is the most important ion in low salinity water as it can replace magnesium ion in high magnitude. The second important ion in injected water is the potassium ion as it can replace the calcium ion which is also another divalent ion that is important to building up oil-wet conditions. However, the MIE mechanism that happened by potassium ions was not important as calcium ions, and it does not show any significant effect on the kaolinite sample.

5.2.3 Low Salinity Water at 5,000 ppm

In this section, all solutions were prepared at a higher concentration of 5,000 ppm. The first solution in this section was sodium chloride. At a higher concentration of sodium ion, potassium ion was replaced and this could force the replacing of a calcium ion by a potassium ion. Illite with a high associated portion of potassium ion tended to obtain benefit from sodium ion compared to the same solution at 1,000 ppm. Figure 18 depicts results obtained from using sodium chloride solution at 5,000 ppm.

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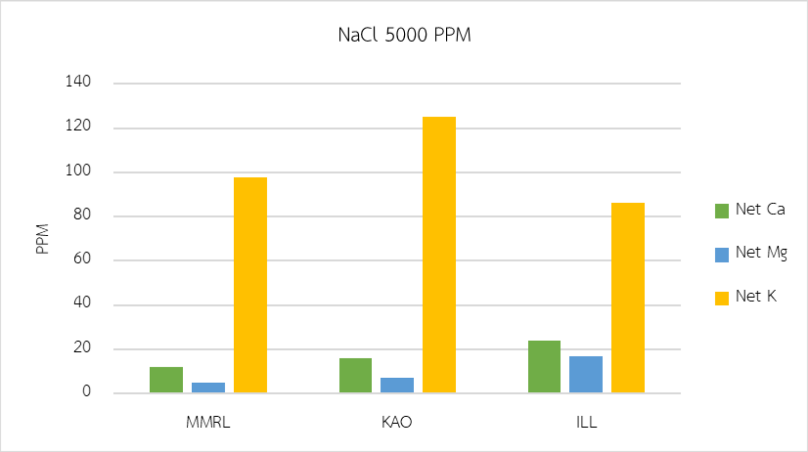

Figure 18 Concentration of Ions in Filtrates from Different Clays Using NaCl 5,000 ppm

For potassium ion solution, it can be seen that potassium ion was highly consumed at high concentrations in all clays. Different from Figure 19, the presence of a large amount of potassium ion creates a positively-changed driving force toward the clay surface. However, the benefit in return for the dissolution of calcium ions is not proportional. Effects of potassium ions are therefore favorable only at lower salinity concentrations.

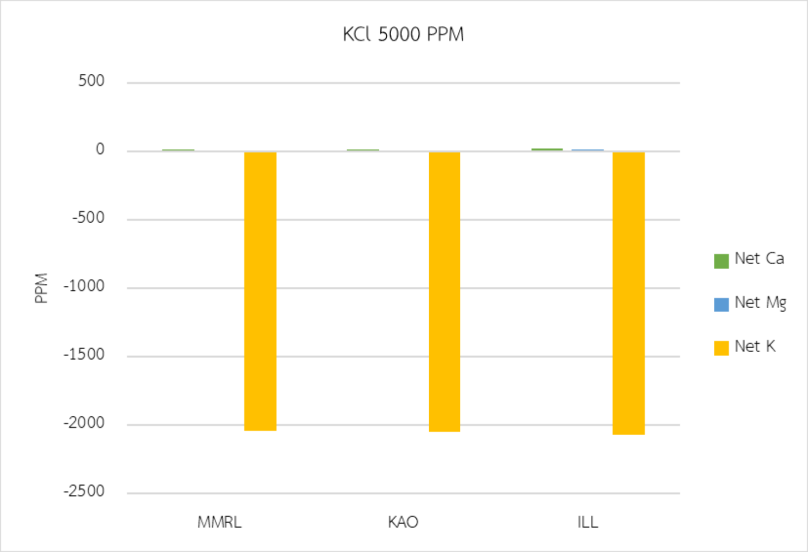

Figure 19 Concentration of Ions in Filtrates from Different Clays Using NaCl 5,000 ppm

Figure 20 depicts MIE effects from calcium ions at a concentration of 5,000 ppm in different clays. The figure showed that calcium ions can replace magnesium ions at a high magnitude. However, the replacement in montmorillonite did not show much improvement compared to kaolinite and illite. This can be explained that montmorillonite is extremely high in CEC and the replacement of calcium ion on magnesium ion reaches its saturation quickly. Dissolution of magnesium ion, in this case, is therefore does not show the difference from the case of lower concentration at 1,000 ppm.

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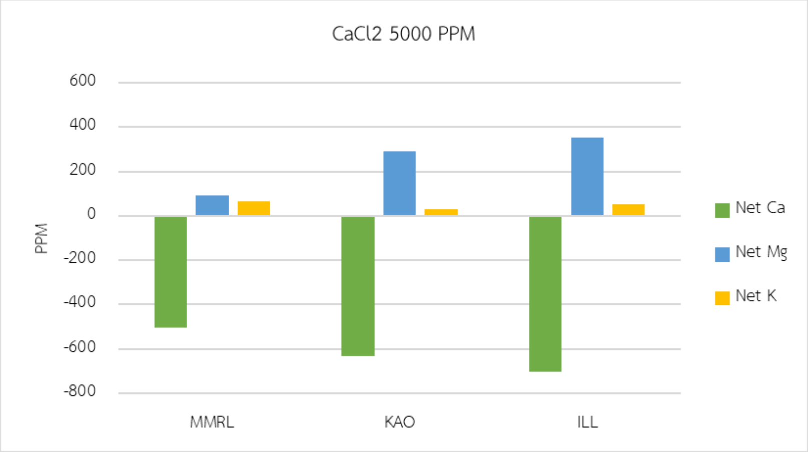

Figure 20 Concentration of Ions in Filtrates from Different Clays Using $CaCl_2$ 5,000 ppm

The effect of magnesium ions at higher concentrations is shown in Figure 21. From the figure, a magnesium ion is consumed mostly by clays with high CEC. However, dissolution of calcium ion is not as high in the opposite direction of calcium ion replacing magnesium ion. The result from this section is similar to that of low concentration (Figure 17).

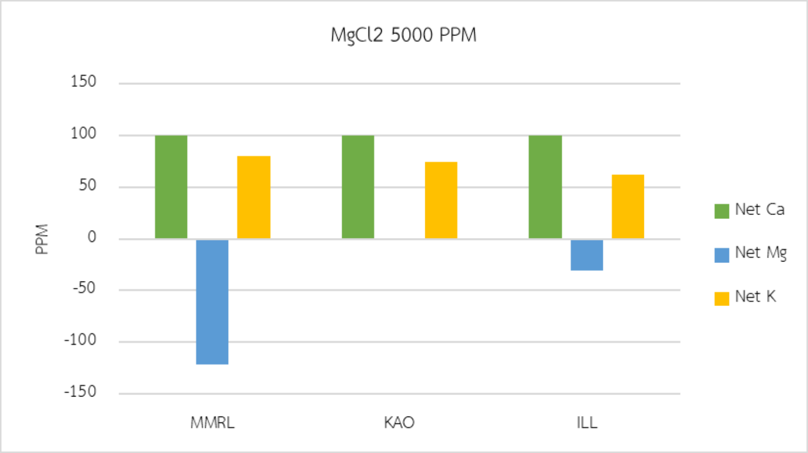

Figure 21 Concentration of Ions in Filtrates from Different Clays Using $MgCl_2$ 5,000 ppm

From this section, it can be concluded that the calcium ion plays important role in replacing the divalent ion which is a magnesium ion. Potassium ion at high concentration is strikingly adsorbed but replacing of calcium ion is not proportional. The effects of magnesium ions are remarkable but not as obvious as calcium ions. A higher concentration of low salinity water shows great benefit to clays that are low in CEC such as kaolinite.

5.3 Selection of Water Formulation

As mentioned in sections 5.1 and 5.2 results from those sections were combined to choose the appropriate water formulation. From the filtration test, it can be observed that calcium ion was the most powerful in replacing magnesium and potassium ion can replace calcium ion, especially in low salinity conditions (1,000 ppm). Calcium ion and potassium ion were then chosen to mix to represent a low salinity water formulation. Results from Table 5 were used in the calculation of the concentration of calcium ions and potassium ions.

The calculation was based on the portion of illite and kaolinite portions and each clay had a different response to potassium ion and calcium ion. The concentration of calcium ion replaced by potassium ion and magnesium ion replaced by calcium ion were summed and ratios of dissolution of both ions were created for each clay. The ratios were then weighed by portions of illite and kaolinite to have total salinity as desired. Table 11 summarizes water formulations for each core sample. For test no.1, water formulation was related to the formation of water and therefore, the portion of calcium ion and potassium ion was very low and the majority of ions was sodium ion. For test no.7, the replacement of calcium ion by potassium ion was multiplied by 4 to compare the potential of replacement of calcium ion and magnesium ion.

Table 11 Summary of Water Formulation

Case no.	Core Sample	Type of LSW	$CaCl_2$ (%)	KCl (%)
1	F	Diluted Formation Water 1,000 ppm		
2	G	Calculated LSW 1,000 ppm	84.04	15.96
3	D	Calculated LSW 1,000 ppm	85.33	14.67
4	J	Calculated LSW 5,000 ppm	85.07	14.93
5	F	Calculated LSW 1,000 ppm	65.37	34.63
6	D	Calculated LSW 5,000 ppm	85.33	14.67
7	D	Adjusted Ratio LSW 1,000 ppm	59.79	40.21

5.4 Properties of Core Samples and Properties of Fluid

5.4.1 Properties of Core Samples

The key properties of the core as mentioned in section 4.4.1 were absolute permeability, pore-volume, porosity, initial oil saturation, and irreducible water saturation. All properties were determined by using a core flood machine. Table 12 summarizes of properties of core samples used in this study.

Table 12 Summary of Properties of Core Samples

Core sample	Permeability (mD)	Porosity/ Pore volume (cm^3)	Initial Oil Saturation (%)	Irreducible Water Saturation (%)
D	131.07	19.48/17.03	67.34	32.66
F	160.56	20.38/18.46	66.44	33.56
G	176.48	19.90/18.11	64.96	35.04
J	48.55	14.73/13.66	64.00	36.00

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From Table 12, it can be observed that cores D, F, and G had absolute permeability in the same range. These values were also in the same direction with porosity and pore volume (core dimensions were nearly the same). For core J, permeability and porosity were both lower than in other cores which could be due to different grain size distribution. However, the initial oil saturation and irreducible water saturation of all core samples were in the same range. These parameters implicitly explained the similarity of the wetting condition of the rock and this was important for the core selection process as the wetting condition of the core affects the effectiveness of low salinity waterflooding.

5.4.2 Properties of Fluids

Formation water was used for the measurement of permeability and pore volume at room temperature (25°C). Therefore, viscosity and density of formation water were required. For hydrocarbon, crude oil from the Sirikit oilfield was mixed with Dodecane at the ratio of 30:70 to prevent the formation of wax and its viscosity was measured to approximate pressure difference during the core flood experiment and hence, viscosity and density at testing temperature (50°C) were measured. Table 13 summarizes fluid properties in this study.

Table 13 Summary of Properties of Fluid Samples

Fluid	Temperature (°C)	Density (g/cm^3)	Viscosity (cP)
Formation Water	25	1.0027	0.946
Oil	50	0.769	1.574

5.5 Core Flooding Test and Titration

5.5.1 Core Flooding Test

Core flooding tests were performed to assess effectiveness of different water formulations and major data used in analysis were oil recovery factor and pressure difference across the core sample. Appearance of fluid turbidity was also detected to confirm the occurrence of the MIE mechanism. This turbidity can be explained by migration of clay and fine particles usually occurred during reduction of salinity and this migration occurs together with liberation of oil drops from MIE mechanism. Hence, color of water will be changed to light brown and the transparent of water will be changed to turbidity as shown in Figure 22

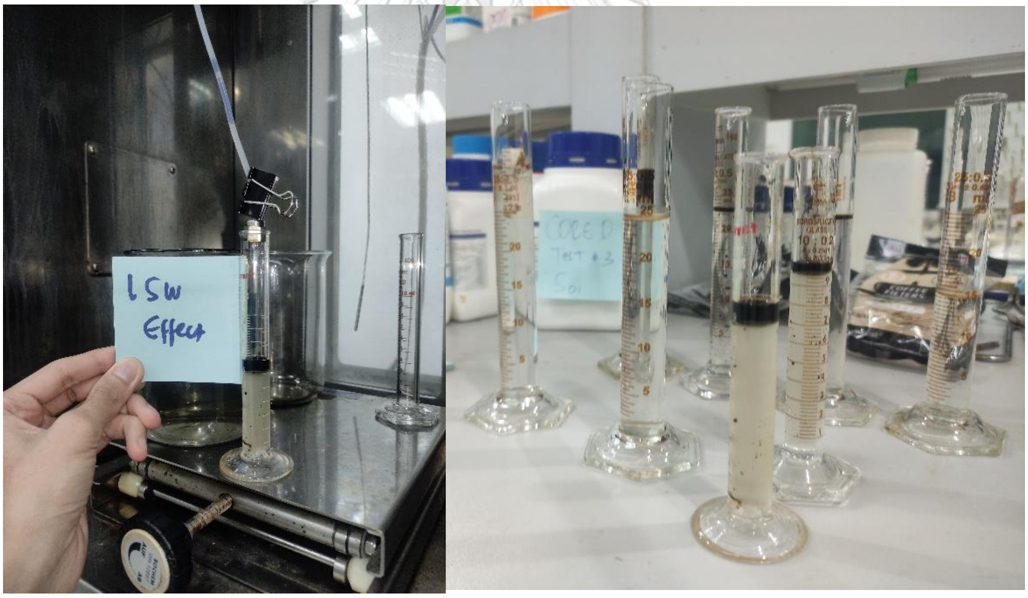

Figure 22 Evidence of Effect of Low Salinity Water Creating Turbidity of Effluent

Case 1 Core F and diluted formation water

Figure 23 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of diluted formation water using core F. From the figure, the oil recovery factor obtained from conventional waterflooding was slightly above 0.5, and once injected water was switched to low salinity water, the oil recovery factor gradually increased. Evidence of MIE was shown by a sudden increment of pressure difference and turbidity of effluent was also detected. In summary, the oil recovery factor was increased from 0.51 to 0.53 by switching from formation water to diluted formation water and the pressure difference was increased from 70 to 100 psi. A sudden increment of pressure difference can be explained by the effect of low salinity water as oil is being liberated together with the MIE mechanism (liberation of divalent ion located between rock surface and oil), small oil drops then block the flow path inside the core and co-evidence of this explanation can be observed from turbidity of solution as previously mentioned. Regarding clay content of core F which was around 57% of illite and 43% of kaolinite, the major ion in low salinity water was sodium ion and a small amount of important ions (calcium ion and potassium ion) might be the reason for the slight improvement in oil recovery.

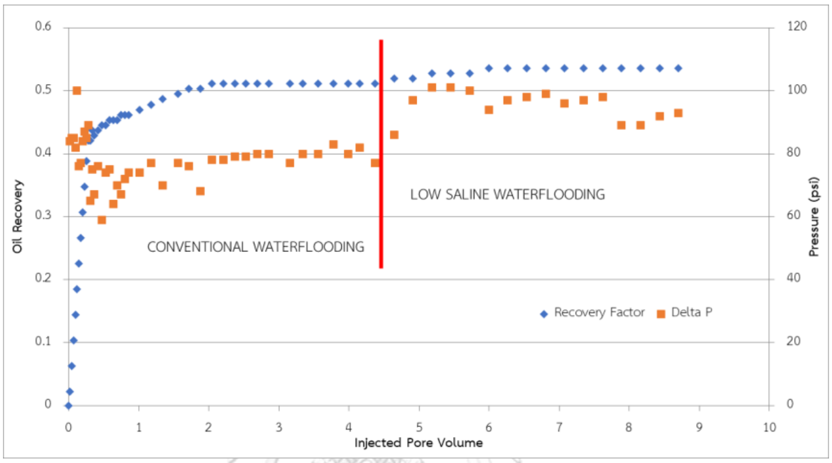

Figure 23 Oil Recovery Factor and Pressure Difference Obtained from Diluted Formation Water on Core F as a Function of Injected Pore Volume

Case 2 Core G and calculated low salinity water at 1,000 ppm

Figure 24 illustrates oil recovery factor and pressure difference as a function of injected pore volume of water for the case of calculated low salinity water at 1,000 using core G. Based on calculation of water formulation, majority of ion in low salinity water was calcium ion in this case. From the figure, oil recovery factor obtained form conventional waterflooding was slightly under 0.5 but once injected water was switched to low salinity water, oil recovery factor strikingly increased to 0.62. This increment can be explained by the effect of MIE as mentioned in case 1 but due to the presence of calcium ion, oil recovery improvement was very obvious compared to the result obtained from case 1. Regarding pressure difference, the value was increased from 18 to 27 psi and the turbidity of effluent was also detected. These results confirm that the preparation of water formulation using data from filtration tests and clay analysis would yield benefits in maximizing oil recovery.

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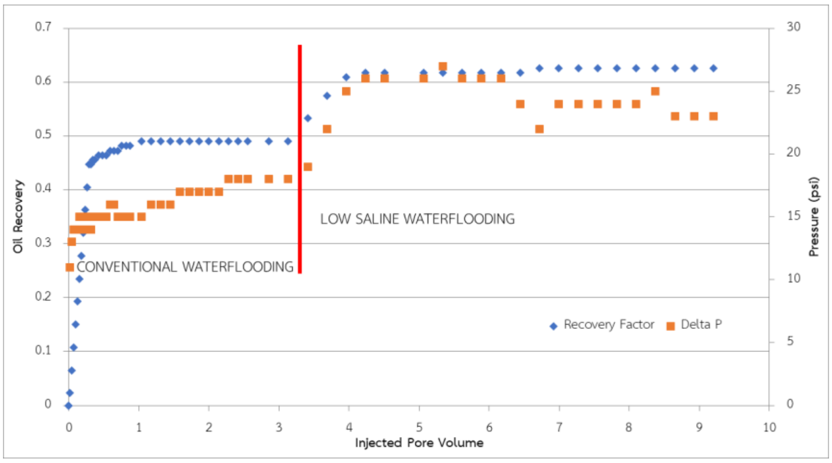

Figure 24 Oil Recovery Factor and Pressure Difference Obtained from Calculated LSW at 1,000 ppm on Core G as a Function of Injected Pore Volume

Case 3 Core D and calculated low salinity water at 1,000 ppm

Figure 25 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of calculated low salinity water at 1,000 using core D. Similar to core G, abundant of illite clay results in the majority of calcium ions in low salinity water. From the figure, the oil recovery factor obtained from conventional waterflooding was around 0.72 but once injected water was switched to low salinity water, the oil recovery factor was increased to 0.86. The positive response of calculated low salinity water confirms a similar conclusion as mentioned for case 2. In this case, the pressure difference was increased from 55 to 68 psi.

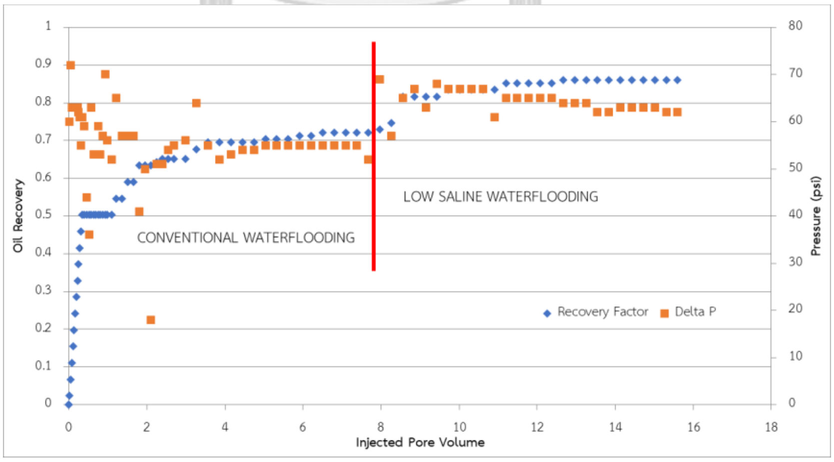

Figure 25 Oil Recovery Factor and Pressure Difference Obtained from Calculated LSW at 1,000 ppm on Core D as a Function of Injected Pore Volume

Case 4 Core J and calculated low salinity water at 5,000 ppm

Figure 26 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of calculated low salinity water at 5,000 using core J. As mentioned in section 5.4.1 core J is the only core that possesses the smallest absolute permeability and porosity. Due to these properties, oil recovery during conventional waterflooding takes a longer time to reach a constant value. From the figure, the oil recovery factor obtained from conventional waterflooding was around 0.75 but once injected water was switched to low salinity water, the oil recovery factor was slightly increased to 0.80. Slight improvement by low salinity water can be explained by two reasons. First, the petrophysical properties of the rock sample resulted in the favorability of conventional waterflooding and hence, the amount of oil to be recovered by low salinity water was smaller. Nevertheless, the second reason for this improvement might be due to the effectiveness of low salinity water at 5,000 ppm. As the salinity of injected water is higher, the salinity contrast between formation water and injected salinity water is becoming less, and hence, the driving force for the MIE mechanism is lessened. However, the increment of pressure difference from 108 to 140 and the appearance of turbidity confirmed the occurrence of effects of low salinity water.

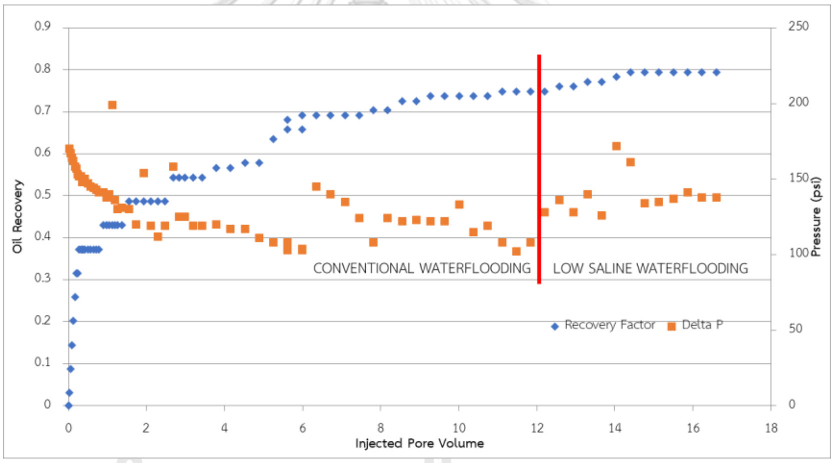

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Figure 26 Oil Recovery Factor and Pressure Difference Obtained from Calculated LSW at 5,000 ppm on Core J as a Function of Injected Pore Volume

Case 5 Core F and calculated low salinity water at 1,000 ppm

Figure 27 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of calculated low salinity water at 1,000 using core F. To ensure that effects from core properties were not the reason for small improvement by diluted formation water, core F was cleaned and restored and performed using calculated low salinity water at 1,000 ppm. From the figure, it can be seen that response to low salinity water was quite slow from core F but the improvement in oil recovery factor was still observed. Oil recovery obtained from conventional waterflooding was around 0.52 but once injected water was switched to low salinity water, the oil recovery factor was gradually increased to 0.58. Comparing case 5 and case 1, it can confirm that calculated brine using selected ion yields better results compared to diluted brine at the same concentration. Evidence of MIE by low salinity water was observed from the increment of pressure difference from 50 to 63 psi and turbidity of affluence was also observed.

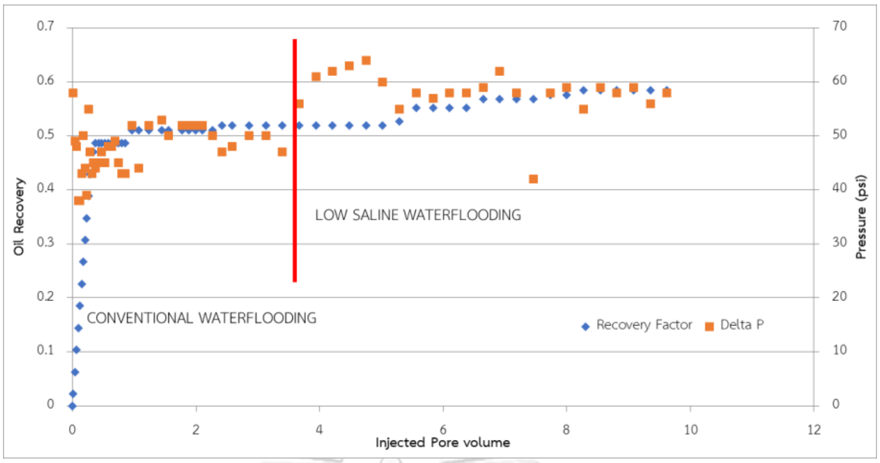

Figure 27 Oil Recovery Factor and Pressure Difference Obtained from Calculated LSW at 1,000 ppm on Core F as a Function of Injected Pore Volume

Case 6 Core D and calculated low salinity water at 5,000 ppm

Figure 28 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of calculated low salinity water at 5,000 using core D. Comparing this case and case 3 where the same core D was utilized, it can be observed that using low salinity water at higher concentration of 5,000 ppm did not yield many benefits. Oil recovery was increased from around 0.51 to 0.53 and pressure difference showed an increasing trend from 76 to 78 psi for short time. Together with case 4, using low salinity water at 5,000 ppm yields a small increment of oil recovery and the explanation can be due to the effect of salinity contrast. However, this result must be confirmed by the dissolution of ions in effluents detected by titration in section 5.5.2.

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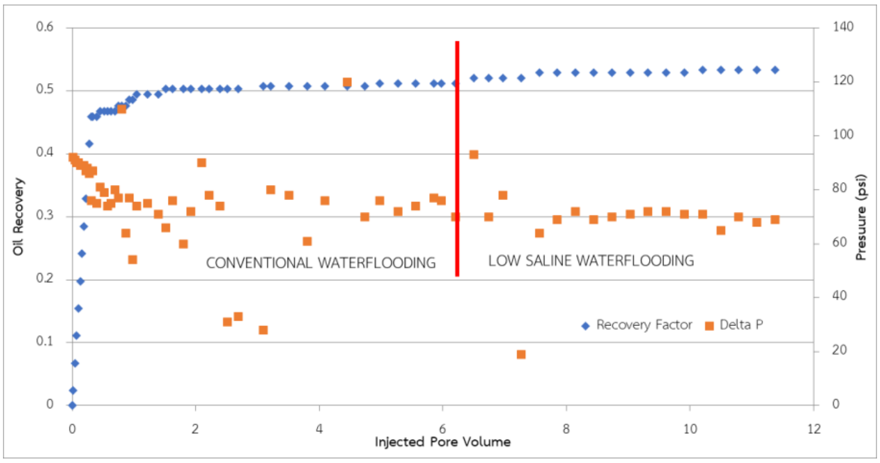

Figure 28 Oil Recovery Factor and Pressure Difference Obtained from Calculated LSW at 5,000 ppm on Core D as a Function of Injected Pore Volume

Case 7 Core D and adjusted ratio low salinity water at 1,000 ppm

Figure 29 illustrates the oil recovery factor and pressure difference as a function of the injected pore volume of water for the case of adjusted ratio low salinity water at 1,000 using core D. Adjusted ratio for low salinity water was performed to assess the effect of replacement of potassium ion on calcium ion and calcium ion on magnesium ion. As the majority of ion in the most calculated water was calcium ion, this test was performed by increasing the effect of the replacement of potassium ion on calcium ion by 4 times. The final ratio of calcium ion to potassium was shown in Table 10. From the figure, it can be observed that the oil recovery factor was improved from conventional waterflooding of 0.56 to 0.63. However, compared to case 3 where core D was used in both cases, it can be found that incremental of oil recovery is smaller in this case. As core D was re-used for case 6 and case 7, it can be seen that the effects of low salinity water take a longer time compared to case 3 and this could be the effects from the core cleaning process and could reduce the reactivity of clays. When a portion of potassium ion was increased, MIE may shift to replacing of calcium ion. However, as calcium ion is larger in ionic size compared to magnesium ion, oil drops that are attached to sand and clay surface though bridging with calcium ion may be recovered during the conventional waterflooding, leaving oil that is bridged with magnesium ion with smaller ionic size. Therefore, low salinity water with a higher amount of calcium ions is more favorable. Evidence of MIE from low salinity waterflooding was observed from incremental of pressure difference from 45 to 69 psi and effluent during low salinity water injection was also turbid.

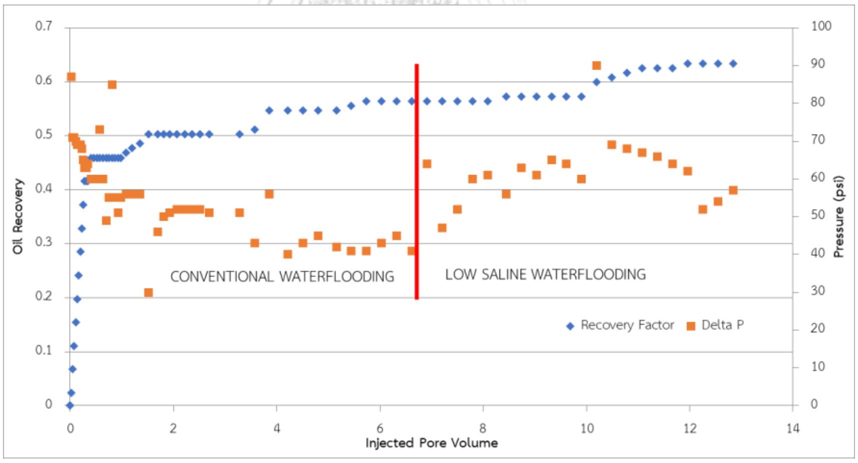

Figure 29 Oil Recovery Factor and Pressure Difference Obtained from Adjusted Ratio LSW at 1,000 ppm on Core D as a Function of Injected Pore Volume

Summary of recovery factor and ratio of pressure difference before and after injection of low salinity waterflooding is shown in Table 14

Table 14 Summary of Oil Recovery Factor and Ratio of Pressure Differences for All Tests

Core	Water formulation	RF from WF	RF from LSWF	Improvement RF	Ratio of ΔP
F	Diluted Formation Water 1,000 ppm	0.511	0.535	0.024	1.43
G	Calculated LSW 1,000 ppm	0.490	0.626	0.135	1.50
D	Calculated LSW 1,000 ppm	0.721	0.860	0.139	1.24
J	Calculated LSW 5,000 ppm	0.749	0.794	0.045	1.09
F	Calculated LSW 1,000 ppm	0.519	0.584	0.065	1.26
D	Calculated LSW 5,000 ppm	0.511	0.533	0.021	1.03
D	Adjusted Ratio LSW 1,000 ppm	0.564	0.633	0.069	1.53

The pressure difference or ΔP ratio was obtained from the pressure after injection of low salinity water which is the highest pressure suddenly occurred after injection of low salinity water caused by liberation of oil droplets and fine migration divided by the pressure before injection of low salinity water which has the constant trend. From Table 14, besides improvement of oil recovery factor there was explained for each case previously, the ratio of pressure difference after to before injection of low salinity water shows that, the use of low salinity water at 5,000 ppm did not create much the increment of pressure difference (for both case 4 and case 6) and this can be explained by the salinity contrast that could be one of the crucial parameters in low salinity waterflooding.

From the study in this section, it can be concluded that calculating water formulation from information obtained from the titration test and clay content is effective for low salinity waterflooding especially for the salinity of 1,000 ppm. Comparing results obtained from several cores conducted using calculated water formulation at 1,000 ppm, results were still better than using diluted formulation water where sodium ion was the most abundant.

Comparing between using salinity of 1,000 and 5,000 ppm, the overall conclusion is that the lower salinity results in a better in oil recovery factor as can be explained by the salinity contrast that drives the MIE mechanism. Changing of pressure difference from conventional waterflooding to low salinity water flooding is greater in the case of lower salinity water.

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Replacing of calcium ions with magnesium ions might be a major reason for high oil recovery compared to replacing of potassium ions with calcium ions. As calcium ion is larger in ionic size (weak bonding between rock surface and oil), then replacing by potassium ion can occur easily during conventional waterflooding and remaining magnesium ion with smaller ionic size (strong bonding between rock surface and oil) can be replaced by calcium ion during low salinity waterflooding.

5.5.2 Titration Test of Effluents

During core flooding experiment, effluents were collected and titrated to identify remaining concentration. Table 15 summarizes net amount of calcium ion, magnesium ion and potassium ion from the coreflood experiments.

Table 15 Summary of the Remaining Amount of Calcium ion, Magnesium ion, and Potassium ion from the Core Flood Experiments

Core	Water Formulation	WF (ppm)			LSWF (ppm)		
		Ca^{2+}	Mg^{2+}	K^{+}	Ca^{2+}	Mg^{2+}	K^{+}
F	Diluted Formation Water 1,000 ppm	83.63	57.72	87.08	35.56	10.63	57.78
G	Calculated LSW 1,000 ppm	75.15	48.61	76.24	58.11	24.58	57.08
D	Calculated LSW 1,000 ppm	110.21	54.69	74.77	80.16	34.43	67.77
J	Calculated LSW 5,000 ppm	95.18	54.68	82.11	511.00	94.18	103.61
F	Calculated LSW 1,000 ppm	90.25	60.34	93.83	75.15	25.82	68.42
D	Calculated LSW 5,000 ppm	116.89	52.66	72.98	480.94	111.40	93.84
D	Adjusted Ratio LSW 1,000 ppm	107.69	45.57	80.27	78.56	36.42	118.55

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From Table 15, it can be observed that the dissolution response of each core to formation water was slightly different. Calcium ion was higher than magnesium ion in all cases and the ratio of around 1.4-2.0. Differences in the ratio of dissolution could be explained by differences in the portion of clays as well as the type of clay in each core. Moreover, as magnesium ion is smaller in ionic radius, it can link the rock surface and oil drop with higher strength compared to calcium ion and hence, its dissolution is more difficult. Potassium ion in clays is abundant; however, the amount of potassium ion tended to be in the same range for all clays. This can be explained that by using the same formation of water in all cases, clays tend to buffer the concentration of potassium ions in water.

Differentiation of ions can be observed in all cases during low salinity waterflooding. For case 1 with core F, the amount of all ions was reduced and the ratio of calcium to magnesium ions was around 3. For cases with higher oil recovery (case 2, case 3, and case 7) it can be observed that the ratio of calcium to magnesium ion was around 2.3. This can be concluded that the high oil recovery factor was related to the shifting of dissolution toward magnesium ion. For case 5 using core F, even calculated water formulation at total salinity of 1,000 was used, low oil recovery factor was obtained. As mentioned in Table 8, core F has a higher portion of kaolinite compared to other cores and due to its low CEC, a higher portion of Kaolinite may result in less MIE effect.

For cases with a high salinity of 5,000 ppm, it can be seen that dissolution of magnesium ions increases by 3-4 times compared to cases performed at 1,000 ppm. This can be explained by the replacement of calcium ions with magnesium ions may occur. But at a higher concentration of total salinity, a replacement can occur only in certain locations where oil was not present (the sites of magnesium ions that were not bridged with hydrocarbon), and in order to break the sites where hydrocarbon is attached, total salinity should be lower at 1,000 ppm.

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CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

The conclusions of this study can be divided into two major sections which are 1) the dissolution study of representative clays from filtration tests and 2) the dynamic dissolution of shaly-sandstone from core flooding tests.

From the first section, it can be concluded that

1. Calcium ion is the most powerful ion in Multi-component Ion Exchange (MIE) for all clays as it can replace magnesium ion at high magnitude. Magnesium ions can also replace calcium ions but the magnitude may not be as high as calcium ions. Potassium ion tends to replace only calcium ion but its potential is not as high as calcium ion and potassium ion does not have much effect on clay with low CEC clay (Kaolinite).
2. A higher concentration of low salinity water tends to have higher dissolution effects on low CEC clays where mechanisms may be difficult to conduct at lower ionic concentrations.

From the first section, it can be concluded that

3. Using information from ionic dissolution and clay content to create specific water formulation shows better results than using diluted formation water at the same concentration. By selecting appropriate key ions and total salinity, oil recovery can be maximized.
4. The benefit of low salinity waterflooding in shaly-sandstone is more obvious at lower salinity (1,000 ppm). At higher salinity (5,000 ppm) MIE mechanism still occurs but calcium ions can replace magnesium ions only at the sites where oil is not attached. Liberation of oil is favored at a lower concentration as the salinity contrast between formation water and low salinity water helps dissolution of magnesium ion bridging between rock surface and oil, liberating of oil drops from the rock surface. Moreover, high salinity contrast from using 1,000 ppm low salinity water causes liberation of oil drops and fine particles, resulting in higher ratio of pressure difference during in low salinity waterflooding to conventional waterflooding compared to the use of higher salinity water (5,000 ppm). From this study, the increment of oil recovery in favorable cases is from 0.07-0.14.
5. The positive effects of low salinity water have a relationship with the ratio of calcium ions to a magnesium ions. A portion of magnesium ion is increased in cases where oil recovery is high and this could be due to the breaking of magnesium ion bridging.
6. Illite clay is favorable for the MIE mechanism, whereas the higher portion of kaolinite which is clay with low CEC tends to lower the benefit of low salinity water. In this study, the effects of montmorillonite were not performed as the core sample did not contain this clay.

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6.2 Recommendations

1. Core samples with montmorillonite clay should be included in the future study as this clay is one of the most commonly found in reservoir rocks. However, treating cores with montmorillonite clay may be difficult and must be different from cores with illite and kaolinite clays as montmorillonite is swelling clay. Potassium ions may show more importance for cores with montmorillonite as it helps prevent clay swelling problems.

2. Heterogeneity of the core samples is another property that may cause additional effects on the core flooding process. Selecting core should be based on core homogeneity and therefore, core samples should be checked by CT Scan.

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APPENDIX

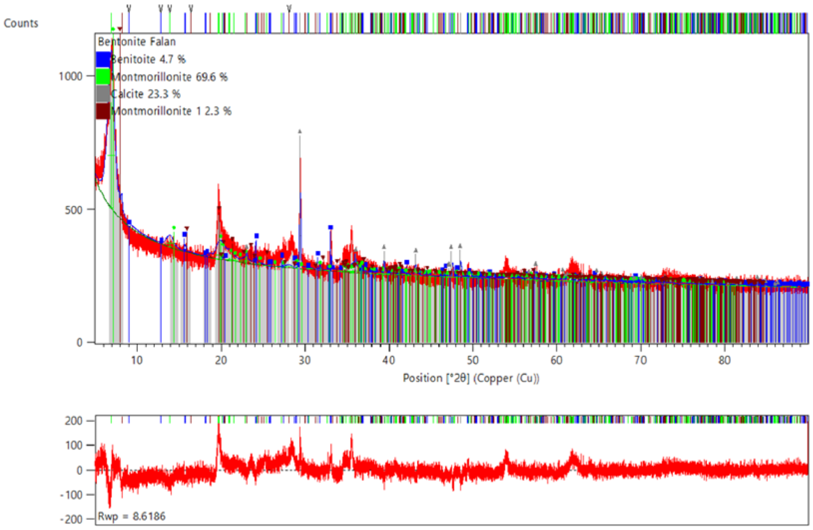


Figure 1 XRD Result of Montmorillonite

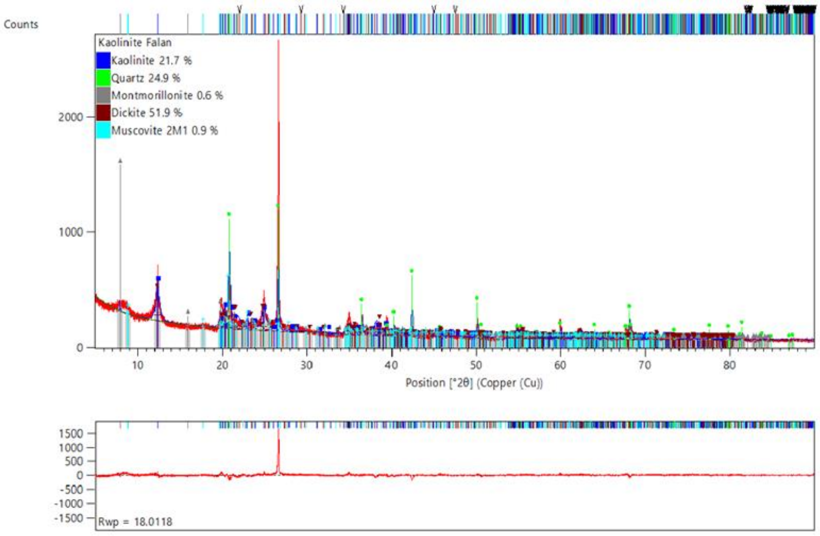


Figure 2 XRD Result of Kaolinite

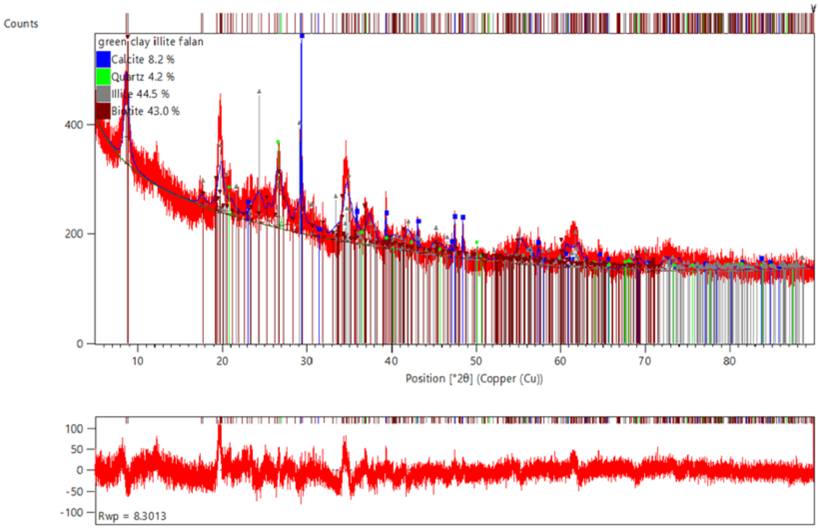
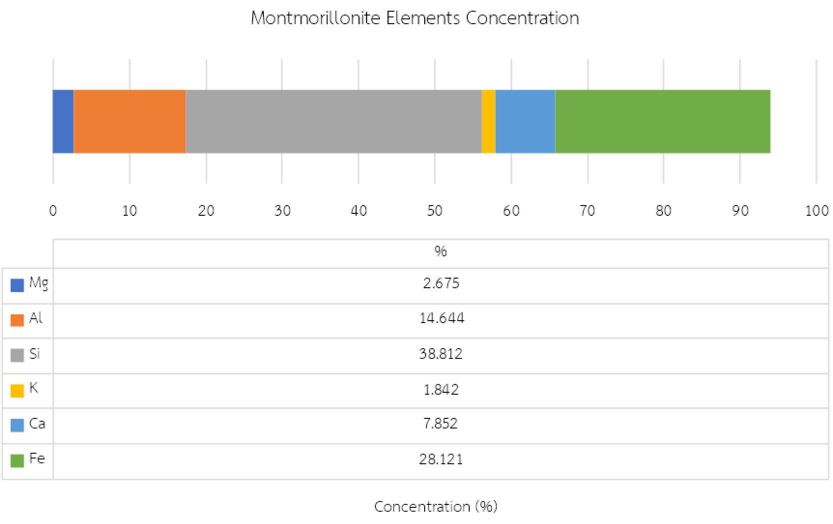
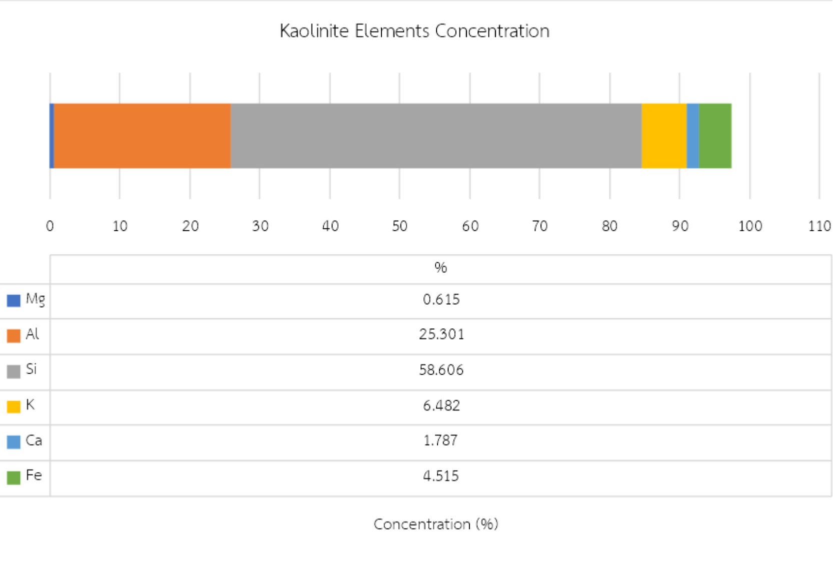


Figure 3 XRD Result of Illite



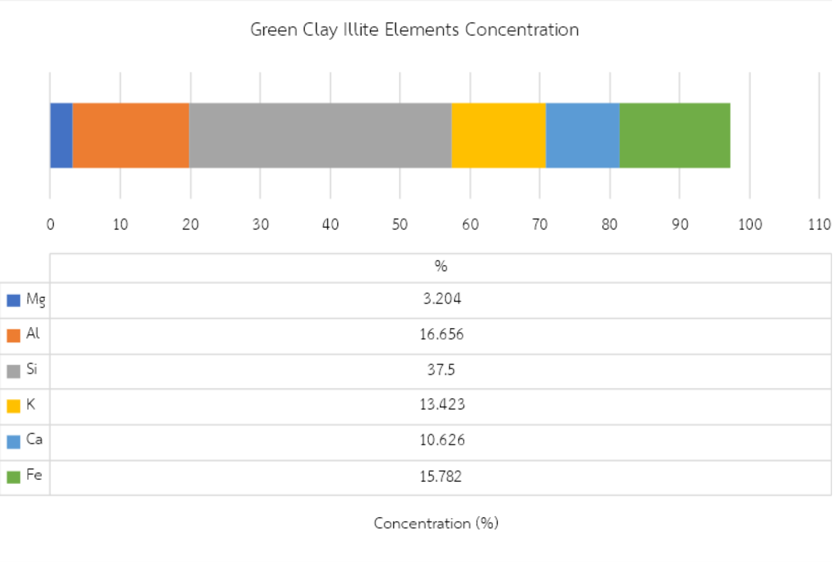
	%
🟦 Mg	2.675
🟧 Al	14.644
⬜ Si	38.812
🟨 K	1.842
🟦 Ca	7.852
🟩 Fe	28.121

Figure 4 XRF Result of Montmorillonite



	%
Mg	0.615
Al	25.301
Si	58.606
K	6.482
Ca	1.787
Fe	4.515

Figure 5 XRF Result of Kaolinite



	%
Mg	3.204
Al	16.656
Si	37.5
K	13.423
Ca	10.626
Fe	15.782

Figure 6 XRF Result of Illite

VITA

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