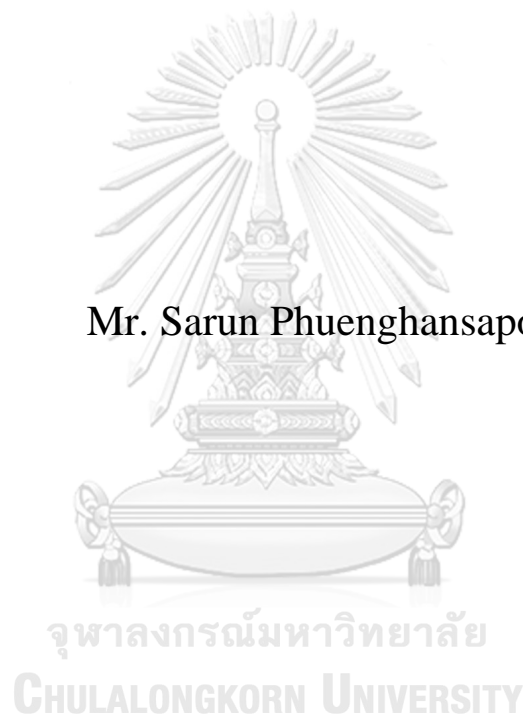# Effect of Salinity Contrast between Formation Water and Injected Low Salinity Water on Low Salinity Waterflooding in Shaly-sandstone Formation

Mr. Sarun Phuenghansaporn

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Georesources and Petroleum
Engineering
Department of Mining and Petroleum Engineering
FACULTY OF ENGINEERING
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ผลกระทบของความแตกต่างของความเค็มระหว่างน้ำในแหล่งกักเก็บและน้ำความเค็มต่ำที่ใช้ใน
การฉีดอัดที่มีต่อกระบวนการผลิตน้ำมันดิบด้วยการฉีดอัดน้ำความเค็มต่ำในชั้นหินทรายผสม
หินดินดาน

นายศรัณย์ พึ่งหรรษพร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมทรัพยากรธรณีและปิโตรเลียม ภาควิชาวิศวกรรมเหมืองแร่และปิโตรเลียม
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
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Thesis Title	Effect of Salinity Contrast between Formation Water and Injected Low Salinity Water on Low Salinity Waterflooding in Shaly-sandstone Formation
By	Mr. Sarun Phuenghansaporn
Field of Study	Georesources and Petroleum Engineering
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CHULALONGKORN UNIVERSITY

ศรัณย์ พึ่งหรรษพร : ผลกระทบของความแตกต่างของความเค็มระหว่างน้ำในแหล่งกักเก็บและน้ำความเค็มต่ำที่ใช้ในการฉีดอัดที่มีต่อ
กระบวนการผลิตน้ำมันดิบด้วยการฉีดอัดน้ำความเค็มต่ำในชั้นหินทรายผสมหินดินดาน. (Effect of Salinity Contrast
between Formation Water and Injected Low Salinity Water on Low Salinity
Waterflooding in Shaly-sandstone Formation) อ.ที่ปรึกษาหลัก : ผศ. ดร.ฟ้าลั่น ศรีสุริยชัย

      การฉีดอัดน้ำเกลือความเค็มต่ำเป็นหนึ่งในวิธีการเพิ่มการผลิตน้ำมันที่ได้รับการกล่าวถึงเป็นอย่างมากในปัจจุบัน เนื่องด้วยเป็นวิธีที่
ประหยัดและยังคำนึงถึงสิ่งแวดล้อม เทคนิคดังกล่าวสามารถทำได้ด้วยการฉีดอัดน้ำเกลือที่มีความเค็มต่ำกว่าความเค็มของน้ำเกลือในชั้นหินเพื่อเปลี่ยน
สมดุลของพื้นผิวหิน นำไปสู่การหลุดออกของหยดน้ำมัน อย่างไรก็ดีความสำเร็จของกระบวนการขึ้นอยู่กับหลายปัจจัย เช่นการปรากฏอยู่ของแร่ดิน ซึ่งแร่
ดินแต่ละชนิดที่พบในชั้นหินแหล่งกักเก็บน้ำมันต่างกันก็ทำปฏิกิริยากับไอออนบวกในน้ำเกลือความเค็มต่ำแตกต่างกันออกไป เป็นผลให้ผลลัพธ์จาก
กระบวนการแตกต่างกัน นอกจากนี้ ความแตกต่างของความเค็มระหว่างน้ำในชั้นหินและน้ำเกลือความเค็มต่ำยังเป็นอีกหนึ่งปัจจัยที่สำคัญเนื่องจากปัจจัย
ดังกล่าวก่อให้เกิดการละลายของไอออนจากเนื้อหินซึ่งนำไปสู่ผลลัพธ์ที่แตกต่างกันออกไป

      วิทยานิพนธ์ฉบับนี้ทำการศึกษาความสามารถการละลายของไอออนจากแร่ดินโดยใช้สูตรน้ำที่องค์ประกอบและความเค็มที่แตกต่างกัน
ตลอดจนทำการศึกษาผลของความแตกต่างระหว่างความเค็มของน้ำในชั้นหินและน้ำเกลือความเค็มต่ำที่ใช้ในการฉีดอัด การศึกษาแรกเริ่มจากการทำการ
ทดสอบด้วยวิธีการกรองและการไตรเตรต เพื่อให้ได้ชนิดของไอออนที่สำคัญรวมถึงช่วงของความเค็มที่เหมาะสมเพื่อการทดลองในลำดับถัดไป จากนั้น
สูตรน้ำเกลือที่เลือกมาจะถูกนำไปทดสอบกับตัวอย่างหินที่มีความเค็มของน้ำในชั้นหินที่แตกต่างกันด้วยชุดอุปกรณ์การแทนที่ของไหล

      จากการศึกษาพบว่าช่วงความเค็มที่ดีที่สุดต่อการละลายของไอออนอยู่ 1,000 ถึง 5,000 ส่วนในล้าน โดยไอออนที่มีส่วนสำคัญได้แก่
โพแทสเซียมไอออนและ ไอออนประจุสองบวกซึ่งสามารถเป็นได้ทั้งแคลเซียมไอออนหรือแมกนีเซียมไอออน เพื่อช่วยในการเกิดกลไกการแทนที่ของ
ไอออนหลายประจุ จากผลการศึกษาด้วยชุดอุปกรณ์การแทนที่ด้วยของไหล สามารถสรุปได้ว่าสารละลายผสมโพแทสเซียมและแคลเซียม ซึ่งมีแคลเซียม
ไอออนที่สามารถแทนที่แมกนีเซียมไอออนสามารถทำงานได้ดีที่ความแตกต่างของความเค็มสูง ซึ่งสามารถอธิบายได้ว่า การละลายของแมกนีเซียมที่มี
ขนาดไอออนเล็กเกิดขึ้นได้ค่อนข้างยาก จึงต้องใช้การมีอยู่ของแคลเซียมที่ความแตกต่างของความเค็มที่เฉพาะเจาะจงเพื่อส่งเสริมให้เกิดกลไกโดยรวม
ประกอบไปด้วย 1) มีความแตกต่างของความเค็มเพื่อเอื้อการละลายของแมกนีเซียมไอออน 2) มีแคลเซียมไอออนเพียงพอเพื่อเหนี่ยวนำให้เกิดปฏิกิริยา
กับกรดอินทรีย์ในน้ำมัน และ 3) มีไอออนบวกหนึ่งประจุเพื่อแทนที่แมกนีเซียมไอออนที่หลุดออกไป ค่าความแตกต่างความเค็มที่สารละลาย
โพแทสเซียมและแคลเซียมทำงานได้ดีที่สุดโดยอัตราส่วนของค่าความแตกต่างความเค็มอยู่ที่ 14 ซึ่งเพิ่มปัจจัยการผลิตน้ำมันเพิ่มเติมได้ถึง 0.1
เปอร์เซ็นต์ขณะที่ค่าความแตกต่างความเค็มที่มากหรือน้อยกว่านี้ก่อให้เกิดการลดลงของประสิทธิภาพการผลิต การแทนที่ของแมกนีเซียมไอออนบน
แคลเซียมไอออนสามารถเกิดขึ้นได้ง่าย เนื่องจากแคลเซียมไอออนมีขนาดใหญ่ ดังนั้นที่ความแตกต่างความเค็มต่ำสารละลายโพแทสเซียมแมกนีเซียมจึง
ทำงานได้ดี โดยอัตราส่วนของค่าความแตกต่างความเค็มอยู่ที่ 2.8 และสามารถเพิ่มปัจจัยการผลิตเพิ่มเติมได้ถึง 4.6 เปอร์เซ็นต์

      การเข้าใจถึงผลกระทบของความแตกต่างความเค็มและองค์ประกอบทางเคมีของน้ำที่ใช้ในการฉีดอัดจะช่วยนำไปสู่การเลือกสูตรน้ำที่ดี
ที่สุดได้อย่างถูกต้อง โดยเฉพาะอย่างยิ่งในแหล่งกักเก็บน้ำมันที่มีความยากลำบากในการเจือจางน้ำเค็มเพื่อใช้ในการฉีดอัด หรือ การหาแหล่งน้ำจืดเพื่อใช้
ในการเจือจางน้ำเค็ม

สาขาวิชา	วิศวกรรมทรัพยากรธรณีและปิโตรเลียม	ลายมือชื่อนิสิต ....
ปีการศึกษา	2565	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

6372810321 : MAJOR GEORESOURCES AND PETROLEUM ENGINEERING
KEYWORD: Enhanced Oil Recovery, Salinity Contrast, Multi-component Ion Exchange (MIE), Cation Exchange Capacity (CEC), Low-Salinity Waterflooding, Dissolution of Clay

Sarun Phuenghansaporn : Effect of Salinity Contrast between Formation Water and Injected Low Salinity Water on Low Salinity Waterflooding in Shaly-sandstone Formation. Advisor: Asst. Prof. FALAN SRISURIYACHAI, Ph.D.

Low salinity waterflooding is an improving oil recovery technique that is highly mentioned nowadays as it is cost-efficient and environmentally friendly. The technique involves injecting water with lower salinity compared to formation salinity to shift the surface equilibrium toward the liberation of oil from the rock surface. Nevertheless, successful of this technique depends on many parameters especially the presence of clays. Several types of clays can be found in oil reservoirs, and they may react to different cations in inject low salinity in different ways, resulting in different magnitudes of oil recovery. Moreover, the contrast of salinity between formation water and injected low salinity is also another important parameter as the contrast can result in different degrees of the dissolution of ions, leading to oil recovery mechanisms.

This study is therefore performed to investigate the dissolution of clays from different water formulations and the effect of the salinity contrast between formation water and injected low-salinity water. The first study was performed by filtration method combined with color titration to obtain important ions for different clays to identify water formulation and range of salinity of injected low salinity water in the following steps. After that, selected water formulations were tested in a core flooding test using shaly-sandstone core samples with different salinities of formation water to obtain various salinity contrasts.

From the study, the best concentration of injected low-salinity water is in the range of 1,000 to 5,000 ppm which is favorable for the dissolution of essential ions. Potassium ion is required to be mixed with calcium ion or magnesium ion to enhance oil recovery mechanism by Multi-component Ion Exchange. Based on the core flooding experiment, it can be concluded that K-Cl solution with calcium ions that replaces magnesium ion works well at higher salinity contrast. This can be explained that the dissolution of magnesium ions which is smaller in diameter must have the presence of calcium ions in specific contrast to allow three components to trigger the overall process including 1) high salinity contrast to allow the dissolution of magnesium ion; 2) adequate amount of calcium ions to induce reaction with an organic acid in oil and 3) presence of monovalent ion to substitute leaving magnesium ion. The K-Ca solution has the best salinity contrast ratio range of around 14, yielding additional oil recovery of around 0.1 percent, whereas too low or too high salinity contrasts would decrease its effectiveness. Magnesium ion replacing calcium ion occurs easily due to the larger size of calcium ion and hence, low salinity contrast allows magnesium ion to well. The salinity contrast ratio of 2.8 is found to be the best for K-Mg solution with an additional oil recovery of 4.6 percent.

Understanding the effects of both salinity contrast and chemical composition of injected water would lead to selecting the best water formulation, especially for fields having difficulties in the technique to dilute salinity water for injection or finding sources of fresh water to dilute salinity water.

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

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Waterflooding has been widely used for decades as a secondary oil recovery method with no regard for the effect of low salinity water injection. In the recent years, more researches have been conducted on the effects of low salinity water injection to improve reservoir performance. Waterflooding has been one of the most successful oil recovery methods due to the its high efficiency for displacing light to medium oil, ease of injecting into the formation, availability of water and cost effectiveness, less environmental impact, and lower operating costs compared to other EOR methods. The purpose of waterflooding methods is the same as other EOR methods, is to maximize oil recovery. In the past, the attention has been given to improve the efficiency of the volumetric sweep through practices eg, improved reservoir characterization, multilateral wells, in-fill drilling, and etc. After such execution, then EOR can be applied. Injection of chemistry-customized salinity water together with ionic composition into reservoir instead of any available water source may have several advantages over conventional EOR including the economic perspective as it can provide substantial oil recovery while maintaining the investment to minimal assuming waterflood facilities are already available. It also can be applied at the early stages of production not only during the late cycle of the reservoir.

Conventional waterflooding process associates with injecting water into reservoir formation by considering economic factors and compatibility between injected water and formation water in order to avoid formation damage. In 1990s, many researchers started to investigate on the effect of water composition and discovered that it could play a significant role for enhancing oil recovery. They found that there was a potential of low salinity waterflooding (LSWF) in EOR applications.

Extensive researches have been conducted based on LSWF with coreflooding experiments to improve oil recovery. Most of the experiments showed that when low salinity water was injected, up to 40% oil recovery can be recovered for both secondary and tertiary modes. Low salinity waterflooding has received substantial attention in recent years due to its low-cost EOR potential. In tertiary flooding, the results indicated that changing salinity of injected water by decreasing or increasing can slightly improve oil recovery.

However, many researches have shown that there is an optimum composition and salinity for waterflooding and applying the optimum salinity for the secondary recovery mode is more effective than applying the optimum salinity for tertiary recovery mode. Experiments have shown various results and potential improvement

of oil recovery. Many researches have shown that injection of brine with the salinity of approximately 1,000 – 2,000 ppm could have an effect on oil-brine-rock interactions in order to reduce oil saturation. Nevertheless, there are more than just total salinity of injected water controlling the success of LSWF project such as original salinity of formation water and composition of both formation water and injected water.

Oil recovery mechanisms of LSWF were mainly described for sandstone reservoirs especially those containing clay or so-called shaly-sandstone. Presence of shale in sandstone formation creates more complex situation where all possible oil recovery mechanisms can be reasonable. These oil recovery mechanisms include 1) fine migration together with oil droplets; 2) increasing of pH value resulting in in-situ saponification; 3) Multi-component Ion Exchange (MIE) with a consequence of wettability alteration; 4) Double Layered Expansion (DLE) occurring in parallel with MIE. Many studies in shaly-sandstone reservoir suggest performing low salinity waterflooding using injected water at specific salinity. However, difficulty in reducing or adjusting salinity of injected water can be crucial in specific locations and hence, understanding the effect of salinity contrast between formation water and injected water would help identifying the threshold of salinity of injected water when source of fresh water or low salinity must be considered.

This study is performed to investigate effects of salinity contrast on oil recovery mechanism in low salinity waterflooding in shaly-sandstone formation and to investigate the combined effects of chemical composition and salinity of the injected water. Clay samples representing clays in shaly-sandstone formation are tested with different low salinity water formulations using filtration test where filtrate solution is taken to detect for dissolution of important ions. In this study, divalent ions included Calcium ion and Magnesium ions are detected by color titration with color indicator, using Ethylene Diaminetetraacetic Acid as titrant. Calcium and Magnesium ions in clays are associated on clay surface and can interact with organic acid in oil, causing oil-wet surface through ion binding. Dissolution of these two ions implies the breaking of oil attached on rock surface and as a consequence oil is more recovered. Several water formulations with specific composition and salinity are selected for coreflooding test. The experiment is performed at reservoir conditions (high pressure and temperature compared to room conditions). Formation water is injected first to imitate conventional waterflooding and once oil recovery is constant, selected low salinity water formulation is injected. Volume of produced oil as a function of time is detected together with pressure difference. To confirm the effect from low salinity water, effluents from water injection are collected and are tested by color titration as in the previous step to identify amount of Calcium and Magnesium ions.

From this study, the effects of salinity contrast on oil recovery mechanism of low salinity waterflooding would be obtained. By knowing this, preparation of low salinity water would be more efficient especially for those reservoir having difficulties in finding source of fresh water. Combination effects of salinity and

chemical composition of injected water would help understanding the compensation of lowering salinity of injected water.

1.2 Objectives

1.2.1   To investigate effects of salinity contrast on oil recovery mechanism in low salinity waterflooding in shaly sandstone formation.

1.2.2   To investigate combined effects of chemical composition together with concentration of the injected water

CHAPTER 2

LITERATURE REVIEWS

The mechanism for low salinity oil recovery has been studied by Kakati et al [1]. They conducted a study on the effect of low salinity sea water through coreflooding experiments. Interfacial tension and wettability were measured to determine the low salinity effect on crude oil, brine, and rock properties. Effluent brine produced during the coreflooding experiment was also investigated in order to obtain more insight on low salinity EOR mechanism. The result of waterflooding showed that injecting low salinity seawater can significantly improve the waterflooding process when comparing to high salinity injection of seawater. The result for the interfacial tension and contact angle experiments showed that there is an optimum dilution level where the wettability and interfacial tension for the most effective enhanced oil recovery including the case of light paraffinic crude oil. The results are in line with those results from the coreflooding experiment.

The result of oil recovery by varying salinity level from 10%, 25% and 50%, the highest additional oil recovery based on the experiment is the case of 25% seawater injection. The effect of 50% seawater injection was trivial, and the impact of 10% seawater injection was significant but not as significant as 25% water injection case. A higher-pressure drop was detected when injecting with low salinity water when compared to high salinity water injection. The recovery mechanism shows that diluted water injection has major impact on oil-water interfacial tension and reservoir rock wettability. At optimum dilution condition, a minimum interfacial tension and a strong water-wet condition can be achieved, which leads to additional oil recovery. Preferential movement of cations to the oil-water interface in a low acid number crude oil is associated with the primary mechanism of interfacial tension reduction and wettability alteration.

The effect of low salinity water injection has also been studied by Snosy et al. [2]. The paper aims to study the effect of low salinity water with various concentrations of water based on more than 500 core flood experiments. Several parameters such as clay type, clay content and temperature are also investigated in this paper. Clay swelling which is controlled by exchangeable Sodium percentage (ESP) and Sodium absorption ratio (SAR) is also studied in this paper. The results are concluded as follows:

1. There is an optimum level of salinity and injected water composition as well as pH value for each reservoir rock. A well-designed water injection will enhance the displacement efficiency, thus increasing oil recovery.
2. Good permeability and clean sand reservoirs (without clay content) are expected to have lesser oil recovery when applied with high salinity waterflooding.
3. In tertiary stage EOR, adjusting the water salinity can give additional oil recovery.

4. A good case for the low salinity waterflooding effect on the second stage EOR can be achieved when there are the presence of kaolinite, albite, and calcite. Permeability should be at least 2 md. In the injected water, divalent cations should be less than monovalent cations. The reservoir temperature should be at least 140 °F.

5. The ratio of Calcium ions to Sodium ions should be less than 0.04 for the tertiary stage EOR. The suitable condition of the tertiary stage EOR when: kaolinite, albite and calcite are presence, permeability should be at least 2 md, divalent cations should be less than monovalent cations for the injected water, the reservoir temperature should be between 140 – 212 °F

AlQuraishi, et al. [3] conducted the experiment regarding low salinity water flooding in sandstone and carbonate reservoirs. The 20% brine (synthetic formation) salinity and Saudi medium crude oil were used in the experiment as formation fluids. The experiment investigated in both secondary and tertiary flooding modes where potential of low salinity waterflooding was found for both carbonate and sandstone reservoirs. Interfacial tension and contact angle were measured to investigate the recovery mechanisms. Zeta potential and contact angle measurements verified that the alteration of wettability has positive effect on improving the oil recovery. The wettability for both rock types was shifted from intermediate wetting condition to water-wet condition. The results obtained were used to analyze the effects of brine and ionic composition to study oil recovery mechanisms.

The results showed a good potential for low salinity water injection for both sandstone and carbonate reservoirs in both tertiary and secondary waterflooding modes. The improvement oil recovery for carbonate experiment may be explained by the ions exchange and sulfate presence in water injection in addition to anhydrite dissolution. Carbonate samples also have severe damage with significant decrease in absolute permeability post tertiary flooding. This phenomenon can be resulted from the dispersion of dolomite induced by the double layer expansion. Fines migration and the detachment of mixed-wet kaolinite clay particles are the mechanisms that explain the sandstone sample recovery mechanism. In addition, the initial rock wetting condition at the start of the brine injection play a major role in determining the effectiveness of low salinity water injection. Finally, Interfacial tension reduction due to salinity reduction had minimal effect in oil recovery.

Chavan et al. [4] conducted comprehensive literature review regarding low salinity enhanced oil recovery and related screening criteria. The review primarily focuses on various relationships of the following screening criteria:

1. Classification of clays that have proven to be beneficial with low salinity waterflooding;
2. Clay types versus variety of residual oil saturations;
3. API gravity and the range of down-hole oil viscosity that is compliant with low salinity;
4. Salinity range for EOR benefits;
5. Wettability range, pore sizes, permeability and porosity for low-salinity EOR;
6. Possible low-salinity mechanisms;
7. Relationship between field evidence and laboratory experiments;

8. Variations in tested low salinity water.

There has not been a universal primary mechanism that can entirely explain low-salinity waterflooding yet. However, many theories that are most related to low salinity waterflooding such as electric double-layer expansion, MIE, and wettability alteration due to pH alteration are widely discussed. Important parameters namely presence of clay, water chemistry, wettability and reservoir conditions are often related to the low-salinity waterflooding. Optimum level of salinity injection also depends on the reservoir brine composition. The optimum range of water salinity injection can be ranging from 2,000 ppm to 5,000 ppm. In addition, slug-wise low salinity injection can be used to improve the project economics.

Clay type has been discussed in numerous researches. For example, kaolinite, this type of clay would be the least favorable. Unlike sandstone reservoir, in carbonate reservoir, clay do not play a major role in the low salinity waterflooding as it is mainly tied to diluted seawater. Table 1 illustrates favorable and unfavorable conditions for low salinity waterflooding.

Table 1. Reservoir and EOR conditions affecting in favorable and unfavorable results on low salinity waterflooding

Variable	Favorable	Unfavorable
Clay present	Yes	No
Clay content	High	Low
Salinity of brine	2,000 – 5,000 ppm	> 7,000 ppm
pH of the medium	> 7	< 7
Oil composition	Polar components	Non-polar components
Wettability	Strongly oil-wet	Strongly water-wet
Formation type	Sandstone	Carbonate
EOR mode	Secondary	Tertiary

A critical review of low salinity water flooding from multiple papers regarding the its mechanism, laboratory and field application was carried out by Katede and Sagala [5]. They covered the studies of core flooding, tertiary low salinity waterflooding (well-to-well pilots) and (SWCITs) single well reactive chemical tracer tests. The conclusions were stated as follows:

1. Low salinity waterflooding is still immature with potential to further increase oil recovery as verified by many studies. The range of oil recovery was reported from 0 – 15% OOIIP depending on the rock types, fluid properties and reservoir conditions.
2. There are many mechanisms proposed by researchers, but there is no unanimity stating which mechanisms are dominant in enhancing oil recovery with low salinity water injection.

3. The application of low salinity water can be used together with other EOR techniques such as surfactant, alkaline, and polymer flooding to further increase the oil recovery. In addition, injecting low salinity water also helps reducing conventional problems such as scaling and souring.

Another experiment done by Al-Saedi and Flori [6]. In this experiment, sandstone core flooding was performed to determine EOR mechanisms and the effect of clay on the recovery factor. A high salinity brine (100,000 mg/L) was injected to stimulate formation water. After that, low salinity water (1,000 mg/L) was injected at various temperature. pH level and concentration of Ca^{2+} and CH_3COO^- were recorded.

At first a chromatography column was prepared with minerals to imitate sandstone cores. The sandstone core was made up of pure quartz, and the sandstone core with clay are composed of 5% kaolinite, 5% illite, and 90% quartz. The cores are 6.3 cm long with 1.5 cm in diameter. The column was packed by using wet packing method. Fine filter was used to prevent mineral grains from moving out of the column ports. High salinity brine was prepared by dissolving $CaCl_2$ and $NaCl$ in deionized water. Low salinity water was prepared by dissolving reagent $NaCl$ in deionized water. The brine composition can be found in Table 2.

Table 2. Chemical composition of high salinity water and low salinity water in mg/l from the study of Al-Saedi and Flori

Element	HS	LS
Na^+	35 000	350
Cl^-	60 000	600
Ca^{2+}	4 500	0
Acetate (aging)	820	0
TDS	98.32	1.182
Salinity	~100 000	~1 000

The column was flushed with high salinity brine and then aged for 7 days at 70 °C. This process was done to maximize the absorption of carboxylic material to be bonded with the reservoir rock. The sample was then flushed with high salinity brine until the pH become stable. Water sample was collected to analyze the concentration of ions.

In can be concluded that in the case of core flooding with no clay flushed with low salinity water, the amount of Ca^{2+} and CH_3COO^- were significant. This indicates that the ion exchange on the quartz's surface is facilitated by low salinity water by detaching the carboxylate from the core thus, enhancing oil recovery. Clay has insignificant effect on oil recovery for low salinity waterflooding.

This study provides the isolation between pH, carboxylate release, and ion exchange in which this allows to better decode the mechanisms that regulate low salinity water and enhanced oil recovery in sandstones. This study stated in the conclusion that clays are not necessary for sandstone formation during low salinity

water flooding. Oil recovery and be increased with low salinity waterflooding without clay in the porous media. When the clay is presence, the ion exchange and carboxylic detachment (Ca^{2+} absorption and acetate released) occurred on the quartz surface.

Yousef et al. [7] conducted the research on low salinity injection and ionic content on the carbonate reservoirs. They found that injecting low salinity water with various concentrations into composite rock sampled from carbonate reservoir results in improving the oil recovery up to approximately 14% OOIC in both secondary and tertiary recovery modes. The study shows that varying the salinity and ionic content of seawater has an impact on IFT and on the carbonate rock wettability towards a more water-wet state. The oil recovery potential also depends on each carbonate reservoir condition, primarily on the reservoir temperature, oil properties, chemistry of the formation water, and the reservoir heterogeneity.

Another study of low salinity waterflooding in carbonate reservoirs was done by Tetteh and Barrati [8]. In seawater waterflooding, based on the measurement of contact angle, the wettability of IL (uniform limestone mineralogy with no clay content) is shown to be altered towards mixed wet whereas in the case of low salinity waterflooding is shown to be towards water-wet state. Improvement of oil recovery can be found on both aged cores and non-aged cores. This indicates that wettability alteration might not be the only mechanism involved in oil recovery since, the contact angle measurement on the non-aged cores indicated a water-wet sate.

Dynamic IFT measurement indicated the reduction in IFT values for seawater when comparing to low salinity brine. As a result, surface elasticity becomes higher, the effect of snap-off in core flooding becomes lower, thus improving oil recovery in tertiary mode. Water-in-oil micro-dispersion formation occurs at the salinity of less than 8,200 ppm. This caused the improvement of oil recovery in both aged and non-aged cores during low salinity injection. The most appropriate brine for EOR depending on the core flooding data is low salinity brine. Significant improvement was also observed with seawater. Using seawater could be considered as an economically viable option for EOR where such water is abundant and more cost effective to operate.

Table 3 shows the summary of the research on low-salinity waterflooding on the sandstone reservoir on various proposed mechanism of oil recovery [5]. With many conducted researches, there was no salinity contrast effect being specifically studied to assess for the optimum salinity contrast for the shaly-sandstone reservoirs. Also, the combined effect of chemical composition with salinity contrast has never been studied before. Therefore, this study is conducted to determine the correlation between them.

Table 3. Summary of LSWF research with different salinity contrast

Reference	Pressure and Temperature	Injected water salinity (ppm)	Reservoir Formation Salinity (ppm)	Proposed mechanism	Remarks
Bernard [9]	Ambient condition	100 – 15,000	15,000	Wettability alteration	• There will be no additional oil being produced if the fresh waterflooding does not develop a high pressure drop. • In water-sensitive core, when hydratable clays are present, a higher oil recovery can be achieved with fresh waterflooding than with brine. • Oil recovery increases when water salinity decreases.
Jadhunaiidan [10]	Ambient condition at 26, 50, and 80 °C	200 – 18,000	18,814	Wettability alteration	• Intermediate to wet systems provide the best amount oil recovery, leaving the lowest residual oil saturation. • Dominant parameters affecting wettability are temperature and initial water saturation.
Yildiz and Morrow [11]	Ambient conditions at	6,370	63,700	Wettability alteration	• Interactions between rock and brine are responsible for the alteration of wettability. • Oil recovery mainly depends on initial salinity

Reference	Conditions			Mechanism	Description
	110 °C				and composition of the brine.
Tang and Morrow [12]	Ambient pressure at 75 °C	<8,000	24,168	Wettability alteration	• When the temperature increases during the course of dispersion, wettability changes towards a more water-wet condition.
Tang and Morrow [13]	2,000 psi and 55 °C	36,960	15,150	Fines mobilization (limited released of mixed wet particles)	• Injected brine composition could affect the oil recovery at a high water cut. • Changes in oil recovery with salinity could be partially caused by the effect of brine composition. Such effect is caused by the forces needed to strip particles from the pores during waterflooding.
McGuire et al. [14]	Ambient conditions at 40 °C	1,500	15,000	Saponification	• The effective range of waterflooding appears to be approximately 5,000 ppm or less. • The EOR mechanism involved in the low-salinity waterflooding appears to be the changes in wettability, generation of surfactants, reduction of interfacial tension, and detachment of clay particles.
Lager et al. [15]	Ambient and Reservoir Conditions	1,550	20,000	Cation exchange	• Cation-exchange verifies the reason why low salinity waterflooding is not effective. When a core is acidized, capacity of the clay minerals is destroyed. Also, this theory explains why the low salinity waterflooding has no effect on mineral oil as non-polar elements strongly interact with clay minerals.

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Reference	Conditions			Mechanism	Observations
Zhang et al. [16]	Ambient conditions at 60 °C	1,479	29,690	Wettability alteration and Cation exchange	• Low salinity waterflooding for carbonate reservoirs is not effective as explained by cation exchange theory. • The effluent pH is dependent on the crude oil and its role in the oil-brine-rock interactions but no obvious relationship between oil recovery and effluent pH was found. • Additional oil recovery obtained when divalent ions were added to the injected brine. • When injecting low salinity brine for the mixed wet cores, there was no oil recovery found.
Loahardjo et al. [17]	Ambient conditions at 60 °C	<5,000	35,000	Wettability alteration and Cation exchange	• Core properties was changed during low salinity waterflooding for several cycles.
Austad et al. [18]	Ambient conditions at 40 °C	-	-	Wettability alteration (Toward increased water Wetness) and Cation Exchange	• Low salinity waterflooding for water-wet condition, there was a significant increase in oil recovery of 75%. • Cation exchange is considered as an important parameter for low salinity effects.
Suijkerbuijk	Ambient	1,681	237,858	Wettability	• The crude-oil-brine-rock system becomes more

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Reference	Conditions			Mechanism	Key findings
et al. [12]	conditions at 60 °C			alteration	• oil-wet when the concentration of divalent cations in the formation brine increases. • There was an increase in oil recovery in the imbibition phase when the salinity was either lower or higher than the brine formation.
Salehi et al. [19]	1700 psi and 80 °C	up to 200,000	200,000	Wettability alteration	• Interfacial tension decreases when salinity decreases • Oil recovery increases when injected with low salinity water.
Suijkerbuijk et al. [20]	Ambient Conditions	-	-	Wettability alteration and Expansion of the double layer	• Low salinity waterflooding leads to more water-wet system, but it requires a long-time scale. • MIE is not an economically feasible mechanism behind low salinity waterflooding since it occurs at the retardation front.
Xie et al. [21]	Ambient Conditions	2,000	174,000	Cation (Expansion of the double Layer)	• Double-layer expansion is caused by the positive disjoining pressure in a system of crude oil, brine and rock that are triggered by low salinity water. • The cation type has dominant effect on disjoining pressure of the brine, oil and rock rather than the effect of salinity. • If low salinity effect was to be observed, the divalent cations are to be removed. • DLVO theory can be applied to screen for low salinity water flooding.

Pooryousef et al. [21]	200 bar at 50 °C and 100°C	2,000	50,000	Wettability alteration and Influence of temperature	• Wettability changes from oil-wet to more water-wet when temperature increases. • When the concentration of Ca^{2+} is low, it produces an oil-wet condition. When the concentration of Ca^{2+} is high, it produces a water-wet system. • Contact angle with the presence of softened brine varies with the change in temperature. • Zeta potential of brine increases when salinity increases • Wettability alteration and MIE does not support each other.

CHAPTER 3

THEORY

3.1 Low Salinity Waterflooding and Oil Recovery Mechanisms

The overview oil recovery mechanisms from low salinity waterflooding can be illustrated as in Figure 1 composing of 1) Physical displacement by waterflooding; 2) Fine migration; 3) Increased pH value; 4) Multi-component Ion Exchange (MIE); 5) Double-Layer Expansion (DLE); and 6) Osmosis. Nevertheless, only some of the mechanisms relating to shaly-sandstone formation are described in this study.
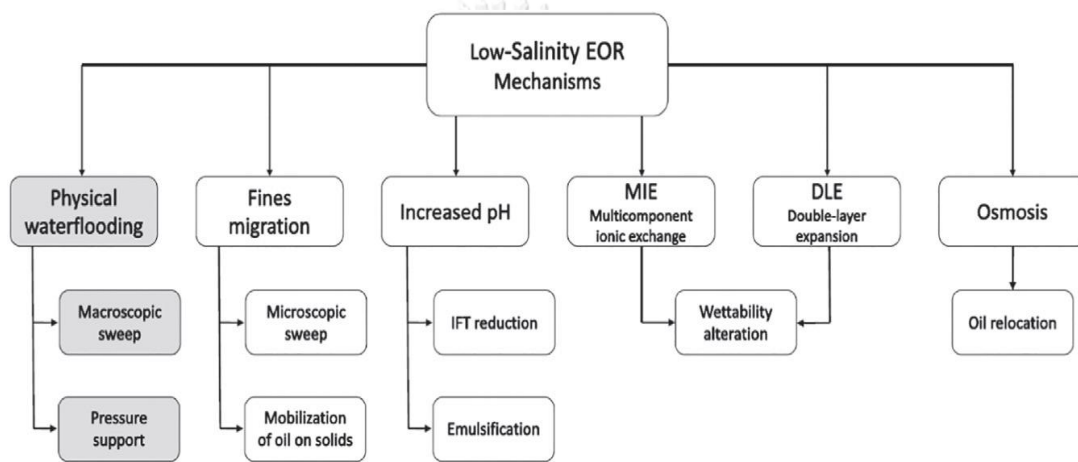
Figure 1. Overview of oil recovery mechanism from low salinity waterflooding

3.1.1. Fines Migration

Fines migration occurs when clay or fines that are adhered onto the rock surface by electrostatic forces start to mobilize by the drag forces. By decreasing of salinity or increasing of flow rate, the equilibrium of electrostatic forces and drag torques are disturbed. Decreasing water salinity weaken the electrostatic forces resulting in detachment of clay particles and promotion of flux diversion at the micro-scale. The movement of the fluid helps mobilizing the fines and result in the generation of drag force. This causes the displacement of the trapped oil, which results in enhanced oil recovery. In addition, the relative permeability decreases since some pore throats will be plugged by these fine particles.

The clay content concentration is inversely proportional to the residual oil saturation; the higher the movable clay content, the more oil can be produced. The effect has been proven by the injection of low salinity water into low-clay cores and the result showed no enhanced oil recovery. Figures 2 and 3 depict how the fine particles migrate to the thin pores, causing flux diversion to release oil.
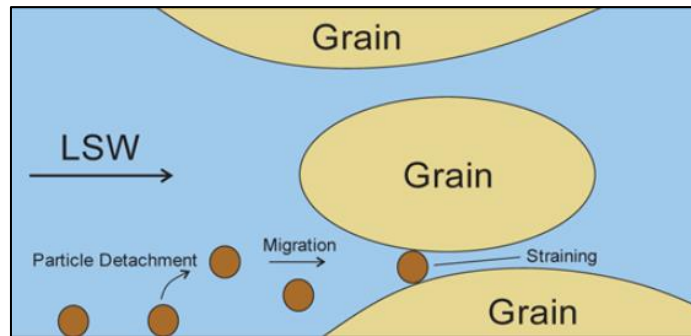
Figure 2. Fine particles detachment, migration and straining in thin pores [22]
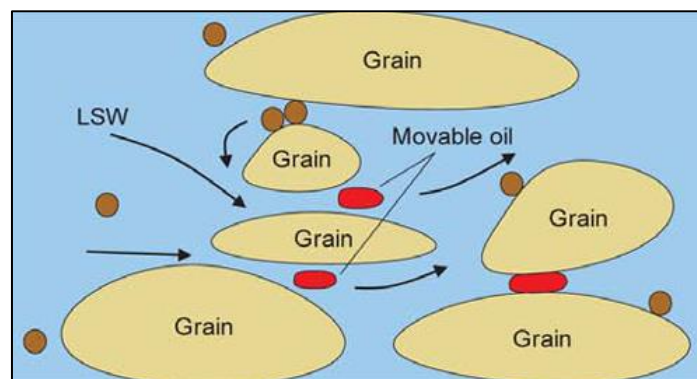
Figure 3. LSW Microscopic Flux diversion due to particles detachment [22]

Katede and Sagala [5] concluded that the following are the keys to decipher the mystify condition of oil recovery with a decrease in salinity; presence of potentially mobile fines (clay minerals), initial water saturation, absorption from crude oil. A reduction in brine permeability caused by fines migration and confirmed that the presence of potentially mobile fines, such as kaolinite, played a key role in increased oil recovery.

However, contradictory results have also been reported and become more numerous. Several studies showed no evidence of fine migration or clay content during their experiments and have proposed that the fine migration assumption is not the major point of advancing the oil recovery from low salinity waterflooding [23]. In addition, kaolinite-free core was indicated as a substantial incremental LSW recovery which supports this dispute [24].

3.1.2. MIE and Wettability Alteration

An experiment done by Lager et al. [15] concluded that the mechanism based on various interactions, including anion exchange, cation exchange, ligand exchange, cation bridging, hydrogen bonding, or van der Waals interaction that could happen between various organic functional groups and the rock mineral. When LSW is injected, rich in multi-valent ions, stronger ligand bonding between the metal cation in the brine and the carboxylic material overcomes the weaker cation bridging

associations between the carboxylic material and the rock surface. Wettability alteration that is caused by Multi-component Ion Exchange (MIE) is believed to be a major mechanism, leading to the enhanced oil recovery. Normally, sandstone formation contains less amount of Potassium ion and Magnesium ion to favor oil recovery mechanism. By injecting low salinity water with reduced amount of Calcium and Potassium ion, this would be favorable in enhance oil recovery. Figure 4 depicts oil recovery mechanism by Potassium and Calcium ions in sandstone formation.
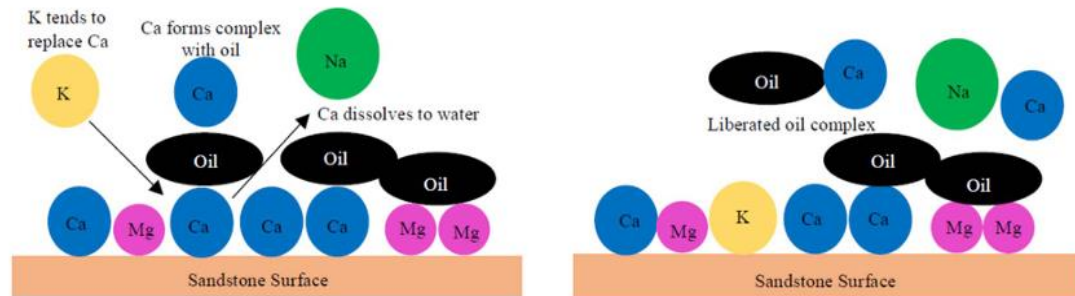
Figure 4. Replacement of Potassium ion onto the site of Calcium ion (left) and liberation of oil in a form of Calcium carboxylate complex (right) [25]

In sandstone reservoir, oil containing organic acid may be attached onto rock surface through divalent ion binding. liberation of oil can occur by the substitution of monovalent ion onto the linking divalent ion site. Minimum quantity of divalent ion such as Magnesium and Calcium ion with the presence of monovalent ion in injected brine could allow the favorable conditions for the MIE mechanism. Once the mechanism is achieved, oil is then released and the surface becomes more water-wet condition.

After coreflooding experiment, it is found that the cores are more water-wet as the low salinity water wash up wet clay particles. Oil production can be increased by a water-wet condition, resulting in an increase in tertiary oil recovery and faster oil production rate in secondary flooding. A mechanism behind the effect of salinity on wettability can be explained based on the disjoining pressure. The salinity affects the electrostatic forces in which some crude oils have large surface density where electrostatic force dominates, resulting in a thicker film and thus, increasing the water wetness. In coreflooding experiments with water-wet, oil-wet, and neutral-wet conditions, it was observed that after ageing and flooding with high salinity, the water-wet core had the strongest effect.

Katede and Sagala [5] reviewed that the wettability of any rock can be back and forth between soaked in water-wet condition to increase the water absorption or being oily soaked to release capillary trapping, and oil counter-current production. It is stated that the water film which segregates the crude oil from the mineral surface can rupture if the disjoining pressure is perturbed diminish the stability by altering the wettability.

3.1.3. DLE and Wettability Alteration

Double Layer Expansion (DLE) is proposed as one of the mechanisms that are responsible for enhancing oil recovery during low salinity waterflooding. The expansion is caused by the overlap between the diffuse double layers. DLE can be explained by the concept of disjoining pressure. Disjoining pressure is derived from the sum of van der Waals forces, consisting of structural force and electrical double layer force. Figure 6 illustrates the Gouy-Chapman-Stern model showing different layers and the location of positive and negative ions.
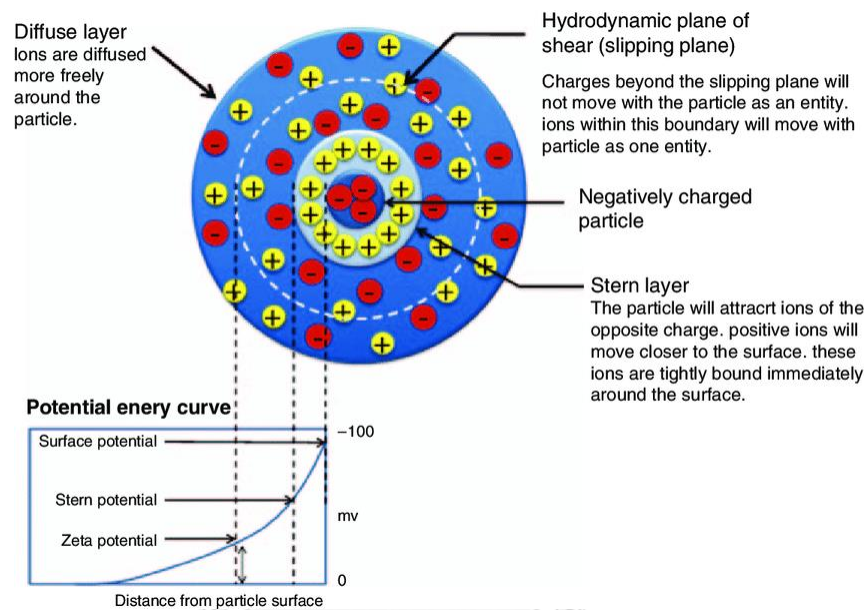
Figure 5. The electrical double layer on the surface of a nanoparticle is based on the Gouy-Chapman-Stern model [26]

The Electrical Double Layer (EDL) is the force that is derived from Coulombic interactions between a polar particle and charged ions. The counter-ions from the solution help balancing the excess surface charge, forming a layer called "stern layer". The energy potential curve in the Figure 6 shows the location of surface potential surrounding a particle while the stern layer is the electrical potential. Electrical double layer comes from the combination of diffuse layer and stern layer. The zeta potential is the electrical potential in the plane where the counter-ions concentration begins at the hydrodynamic plane of shear (slipping plane).

Adsorption can occur through chemical bonds or physical adsorption for example, hydrogen bonds and van der Waals forces. The inner layer will be formed by such absorption, and the counter-ions will be accumulated on top to form the second layer. When the salinity changes, the surface charges will change while the surface potential will remain unchanged. When the low salinity water is injected, the surface potential becomes smaller while the surface charges remain unchanged. This triggers the wettability alteration. Wettability alteration depends on chemical properties and electrical properties of the brine, rock and oil. In conclusion, by

changing water salinity from high salinity to lower salinity by injecting low salinity water with the DLE can induce the wettability alteration.

3.1.4. pH Effect

The main function in the low-salinity-enhanced oil recovery process is the desorption of organic material from the surface of clays by a local increase in pH at the clay-water interface. It is also provided that the following are the experimental observations of the chemical mechanism foundation recommended for the enhancement of oil recovery using the LSW method, the following condition has to be fulfilled:

1. Clay must be present in the sandstone core,
2. The polar components (acidic and/or basic material) must be found in the crude oil,
3. The formation water must contain active ions such as Ca^{2+}.

Initially, the cation exchange on the clay surfaces both basic and acidic materials including inorganic cations, especially Ca^{2+}, are adsorbed from the formation water. The chemical equilibrium then takes place at the actual reservoir state concerning pH, temperature, pressure, and other related factors while the low brine salinity infiltrates through the porous medium with an ion concentration much lower than that in the formation of connate water.

The net desorption of cations, especially Ca^{2+}, then occurs when the brine-rock equilibrium is perturbed. In the frame of cation loss, the protons (H^+) from the formation water distributed over the clay surface are adsorbed onto the clay, leading to a substitution of Ca^{2+} by H^+ occurs. This process creates an incretion of pH close to the clay surface which can be described by the following Eq (1) using Ca^{2+} as the active cation:

$$Clay - Ca^{2+} + H_2O \leftrightarrow Clay + H^+ + Ca^{2+} + OH^- \tag{1}$$
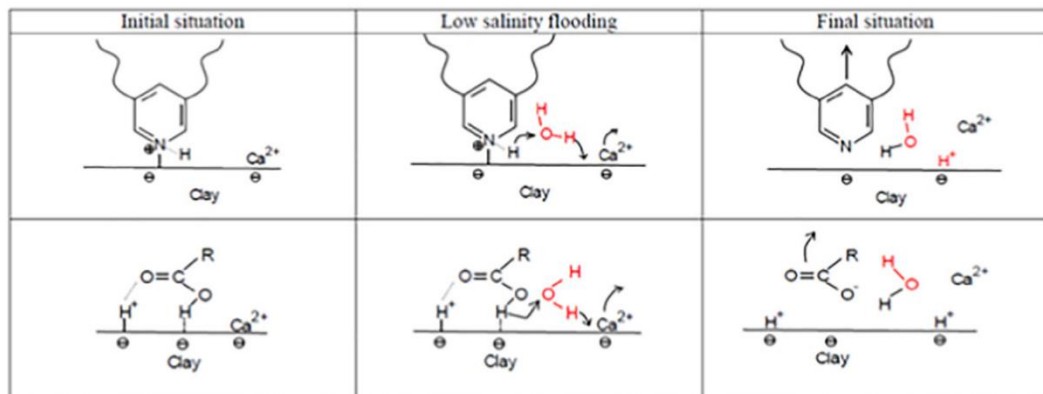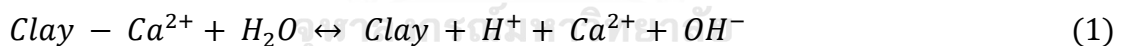
Figure 6. Upper: desorption of basic material lower. Lower: desorption of acidic material [27]

The local increase in pH, close to the clay surface, causes reactions between adsorbed basic and acidic material as in an ordinary acid and base proton transfer

reaction, as shown by Eqs (2), (3), and Figure 7, both acidic and basic crude oil components are partly desorbed from the surface, changing the wettability toward a more water-wet condition after flooding with LSW [27].

$$Clay - NHR_3^+ + OH^- \leftrightarrow Clay + R_3N + H_2O \qquad (2)$$

$$Clay - RCOOH + OH^- \leftrightarrow Clay + RCOO^- + H_2O \qquad (3)$$
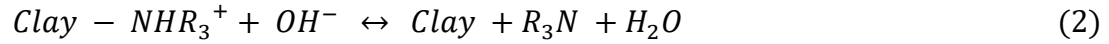
3.1.5. Osmosis

Recent research presents that considering the osmosis mechanism in the low salinity waterflooding method may advance the enhancement of oil recovery. It is promising that with the low-high brine salinities separated with clay creates a pressure osmosis driving the water transport. The experiments were performed later on with the supportive finding of water and oil transport under various wettability conditions stated in Yousef and Ayirala [28].
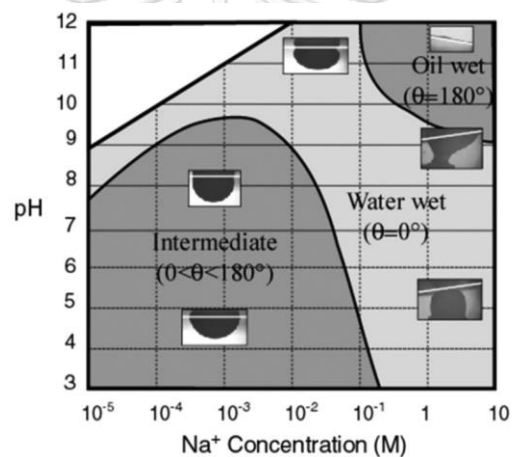
Figure 7. Diagram showing the relationship among pH, salinity and wettability [29]

Sandengen and Arntzen [29] demonstrated this scenario using experiments that oil droplets acted as semi-permeable membranes found in Figure 7. Osmotic pressure gradient could drive the droplets by expanding an inaccessible aqueous phase in a porous rock medium. They suspected that low salinity water allows oil to be relocated and open new pathways via a microscopic diversion mechanism since the water flows from the main paths into a less conductive network by diffusing through oil. They also believed that the oil-wet condition with high temperature, high saturation, and a large pore size distribution could represent the ideal condition for the osmosis to show the effect

3.2 Parameters Affecting Low Salinity Waterflooding

Many parameters can affect the low salinity waterflooding conditions including salinity contrast, chemical composition, pH value, initial wettability, rock composition, temperature, oil, and brine.

3.2.1. pH value

The exchange of absorbed Na^+ with H^+ in water causes the pH to elevate. Experiments indicated that an increase of pH value of approximately 2-4 when injected with low salinity brine, in-situ surfactant that reduces oil and water interfacial tension (IFT) is produced when the reaction of the organic acids in the crude oil occur in high-pH conditions. The formation of surfactants and IFT reduction forms either water in oil or oil in water emulsion, resulting in an increase of water sweep efficiency.

Austad [30] proposed a chemical mechanism that emphasize the role of the clay at low pH values. At reservoir condition, thermodynamic chemical equilibrium exists. Anions and cations get absorbed onto the clay surface, causing the pH value to increase. The injection of low salinity water disturbs the chemical equilibrium and results in the reaction between brine and rock to occur especially with the presence of Calcium ions. To compensate for the loss of cation, H^+ ions reaction occurs and pH increases near the clay surface. The increase of pH is introduced by the low salinity water in alteration of the chemical structure that is initially present.

3.2.2. Initial wettability

Al-Nofli [31] performed experiments on low salinity and high salinity brine on five different initial wettability condition namely, strongly water-wet, water-wet, neutral wet, oil-wet, and strongly oil-wet. The result showed that low salinity water is more effective for wettability alteration of calcite surfaces in neutral wet and oil-wet conditions. As for high salinity brine is suitable for reservoir rock with initial wettability of strongly water-wet and neutral-wet conditions.

3.2.3. Rock Composition (clay content)

Clay composition cay play a major role in low salinity waterflooding as well as the distribution of clay mineral can affect the performance. Clay can be categorized in two main groups; swelling (Montmorillonite) and migrating (Kaolinite and Illite) clays. Cation Exchange Capacity (CEC) is an important property that distinguishes these two types of clay. Clay swelling can be regarded as formation damage that affects reservoir conductivity and low salinity waterflooding. The clay structures layer varies based on the positive charges that are due to cation exchange and negative charges in order to balance the charge. Pores can be blocked when the clay detaches and this is caused by various types of clay called migrating clay.

Safari et al. [32] conducted research on the low salinity waterflooding on sandstone reservoirs by determining the contact angle for analyzing wettability alteration on samples with different parameters such as clay particle size, various

salinity of injected brine and temperature. They believed that wettability alteration from oil-wet to water-wet kaolinite and montmorillonite could increase the recovery factor. Based on the experiments, six samples yielded the highest contact angle using the solution B2 (1,000 ppm) while 2 samples resulted in the highest wettability alteration when subjected to solution B3 (2,000 ppm). The result showed that the favorable salinity was in the range between 1,000 to 2,000 ppm. Reducing in the contact angle was more visible in the rock containing Kaolinite when comparing to the Montmorillonite. The amount of clay does not affect the wettability alteration as much as the temperature.

3.2.4. Brine and Oil

Many studies revealed that a lower salinity threshold is favored in order to increase the oil recovery provided that other conditions are fulfilled [14], [15], [18]. The research shows that reducing the water salinity to approximately 1,000-2,000 ppm has a strong effect of increasing oil recovery in almost all instances. An upper threshold of 5,000 ppm is well-known to increase in the oil recover [33]. Some researcher observed that in order for low-salinity brine to successfully work, the brine has to contain some forms of divalent cations and other multi-valent cations [34], [15], [35]. Another research concluded that injection of high concentration of divalent cations prohibit oil recovery [13]. Even by removing the divalent cations, the injected brine was still not sufficient. Some researchers suggested that there should be optimum level of the brine composition in accordance with their proposed mechanism for the low salinity effect.

For the case of refined oil, no extra recovery found when adjusting the salinity of the injected brine while all other parameters are remained constant [13], [36]. This scenario can be described by polar component. Polar components in oil are necessary for the oil recovery and the refined oil has no polar component, therefore, no response found when injecting with low salinity water. Similarly, Morrow et al. [37] found similar results when oil with different acid numbers was used. The authors concluded that the high acidic and basic condition of oil gave out effective oil recovery due to their polar components. Therefore, polar components are essential for low salinity effect in oil.

3.2.5. Temperature

Flooding temperature can influence the low salinity water effect. The oil recovery was found to be higher when using higher flooding temperature with a high salinity secondary waterflooding. Morrow et al. [37] and Cissoko et al. [24] conducted low salinity core waterflooding with varying flooding temperature and aging. Cores aged at 60 °C exhibits no response to low salinity waterflooding at 60 and 130°C, while aging at 90 °C shows some responses to the low salinity waterflooding at 60°C, 90°C and 130°C. Skrettingland et al. [38] conducted core aging at 60°C and followed by flooding with high salinity and low salinity tertiary at 35°C and 60°C in which low salinity effect was found only in coreflooding experiment at 35°C.

The experiment of xie et al.[39] showed that when the temperature increases from 59°C to 63°C, oil-rock contact angle in the formation slight increased with no effect for pressure change depicted in Figure 8. This is due to the pressure contribute less in double layer expansion and pore surface chemistry at which they control the interfaces of oil-brine and brine-rock. This means the temperature causes the rock formation to be more water-wet. Therefore, the oil recovery increases.
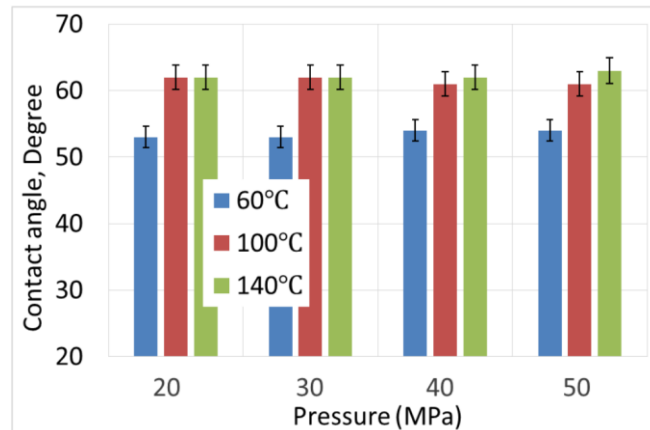
Figure 8. Formation brine contact angles as a function of pressure and temperature [39]

CHAPTER 4

METHODOLOGY

The methodology of this study can be divided into two parts. The first part is to determine the best low salinity water in terms of the concentration and chemical composition. After obtaining the suitable low salinity water concentration and chemical composition, the second set of experiment then conducted using the low salinity water solution obtained from the first part of experiment. Then, coreflooding experiment was performed on three different core samples (core A, core B, core C) to learn the effect of the low salinity water on two different cases of formation water. Figure 9 provides summary of this study in the form of flow chart.
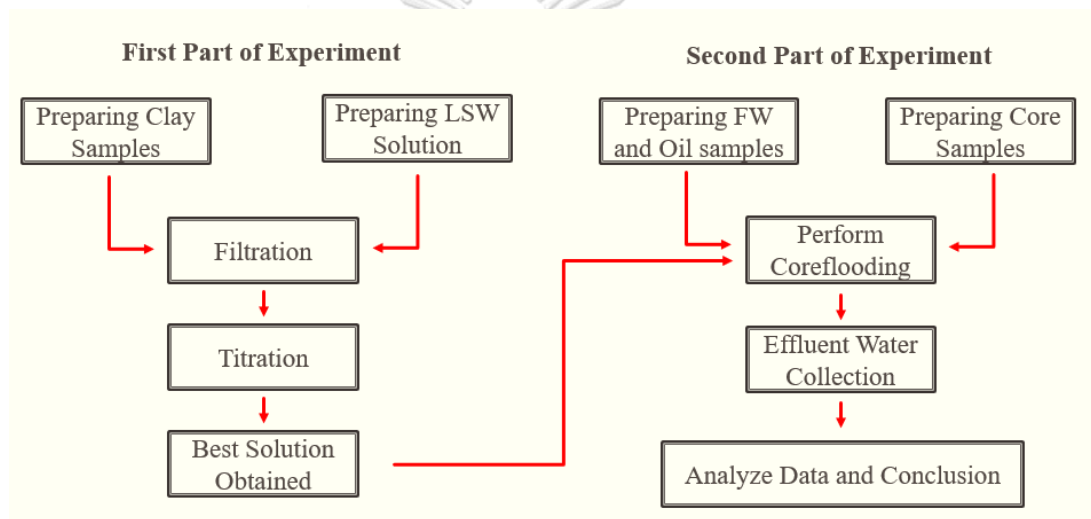
Figure 9. Summary of Flow Chart in this study

4.1 First Part of Experiment

4.1.1. Preparing of solutions

For preparation of low salinity water formulation, Table 4 summarizes the overall water formulations for the filtration test, using single cation solution. The test is performed on two types of clay: Illite and Kaolinite which are clays that are found in core sample. Both clays undergo the filtration process at which it has been filtrated by different low salinity waters at different concentration.

Table 4. Summary of water formulations for filtration test

Representing Clay	Low Salinity Water Formulation	Concentration (ppm)
Illite	$CaCl_2$	500 ppm, 1,000 ppm, 2,000 ppm, 5,000 ppm,
	$MgCl_2$	
	$NaCl$	

	KCl	10,000 ppm, 20,000 ppm
Kaolinite	$CaCl_2$	
	$MgCl_2$	
	NaCl	
	KCl	

4.1.2. Filtration Test

Regarding results of clay analysis from this step, representing clays (Kaolinite and Il-lite) are dried and sieved to obtain similar grain size. 20 g of Clay was packed over filter paper in the funnel for filtration test. 100 ml of low salinity water solution was poured into funnel and the filtrate was collected for titration test. This filtration test was performed to allow clay and low salinity water formulation to be in contact, resulting in dissolution of specific ions. In this study, dissolution of Calcium and Magnesium ions are expected as they are key ions bridging oil and clay surface together. Figure 10 illustrates the schematic diagram of filtration test of this study.
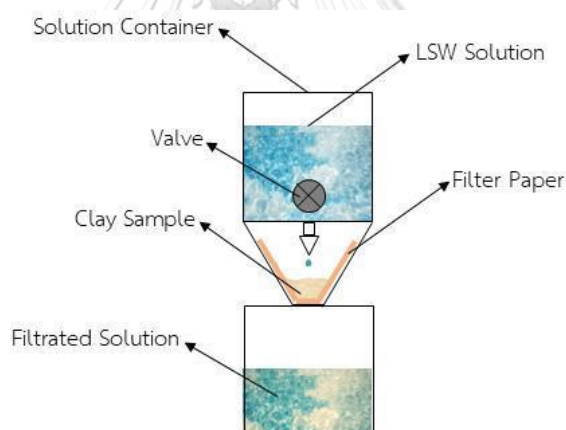
Figure 10. Set up of Clay for Filtration Test [40]

4.1.3. Titration

Titration was used to determine the ions dissolution from the low salinity water that has been soaked with the clays and filtrated. Ions of interest are Calcium ion (Ca^{2+}), Magnesium ion (Mg^{2+}), and Potassium ion (K^+).

The first titration was to determine both Calcium and Magnesium ions (total divalent ions). The sample of 5 cm^3 was pipetted into a flask, three drops of ammonium buffer solution were added and Eriochrome Black T (EBT) was used as the color indicator. The solution was then titrated with Ethylene Diaminetetraacetic acid (EDTA) with a concentration of 0.01M. In the case that the low salinity water

solution contains high amount of Calcium and Magnesium, the sampled amount is reduced to 1 cm^3. The end point was detected when color changes from red wine color to sky blue.

The second test was performed to identify only the amount of Calcium ions. A filtrated sample of 5 cm^3 of solution was added with three drops of Sodium Hydroxide (NaOH) ion to precipitate Magnesium ion. Hydroxy Naphthol Blue (HNB) was used as the color indicator in this case. the mixture was titrated with EDTA until end point. The end point was detected when color changes from red wine color to sky blue. Similar to the first step, Concentrations of total divalent ions and Calcium ion can be calculated and amount of Magnesium ion obtained from the difference of these two values.

The third test called back titration, was used to perform to identify the Potassium ions. A filtrated sample of 5 cm^3 of solution was added with 5 cm^3 of Sodium Tetraphenyl Borate (STB) of a concentration of 0.02M to precipitate Potassium ions. Titan Yellow was then added to as the color indicator in this case. The solution was then titrated with 0.01M of Benzyldimethyltetradecylammonium Chloride Dihydrate, also known as Zephiramine. The end point was detected when the color changes from yellow to pink. The amount of Potassium ions was then calculated by subtracting the remaining STB with the initial concentration. Figure 11 shows the illustration for titration test.
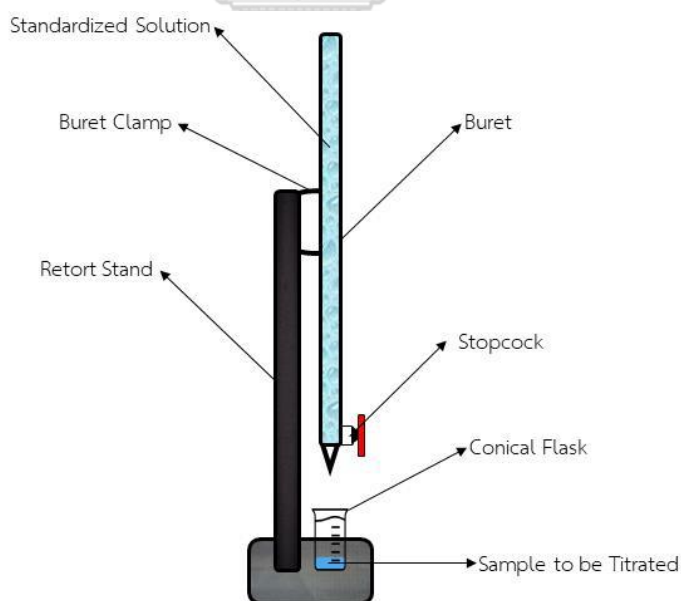
Figure 11. Equipment used for Color Titration [40]

4.1.4. Low Salinity Water Solution Selection

   The results obtained from titration test where the most ions dissolution occur on each clay together with amount of clay content in each core sample from XRD and XRF. This result would yield the most suitable low salinity water solution has been interpret for the next coreflooding experiment.

4.2 Second Part of Experiment

4.2.1. Formation Water Preparation

   The formation water and low salinity water were prepared in this step. For base formation water, chemical composition for making one liter of water is shown in Table 5. In coreflooding test, concentration of formation water is double. However, portions of each ion are maintained as this formulation. Constituent of formation water with total salinity of 14,098 ppm is shown in Table 5.

Table 5. Composition of Formation water of Sirikit oilfield at 14,098 ppm

Chemical Compositions	Molecular Weight (g/mol)	Weight (g)
$NaCl$	58.5	12.403
KCl	74.6	0.160
$MgCl_2$	95.0	0.110
$CaCl_2$	111.0	0.706
$NaHCO_3$	84	0.719
Total		14.098
Total Dissolved Solid (TDS) = 14,098 ppm		

   For formation water at higher concentration (double concentration), the solution is prepared in the same proportion as in the Table 5 with total concentration of 28,196 ppm.

4.2.2. Core Sample Preparation

   For this experiment, core sample A, B, and C were used to perform in coreflooding experiment. These cores represented the shaly-sandstone reservoir collected in Sirikit Oilfield in the northern Thailand. Although all the cores were sampled in the same oilfield, each core was collected at different depth. This could result in different core properties such as permeability, porosity and clay content.

   After the cores were cut and their minerology were assessed, they were cleaned by using Soxhlet extraction to restore their original wettability. The cleaning process involved with removing heavy hydrocarbon using Toluene for 8 hours and then soaked in Methanol for another 8 hours to remove light hydrocarbon and the remaining Toluene from the previous step. The Figure 12 depicts the Soxhlet extractor for the core cleaning process.
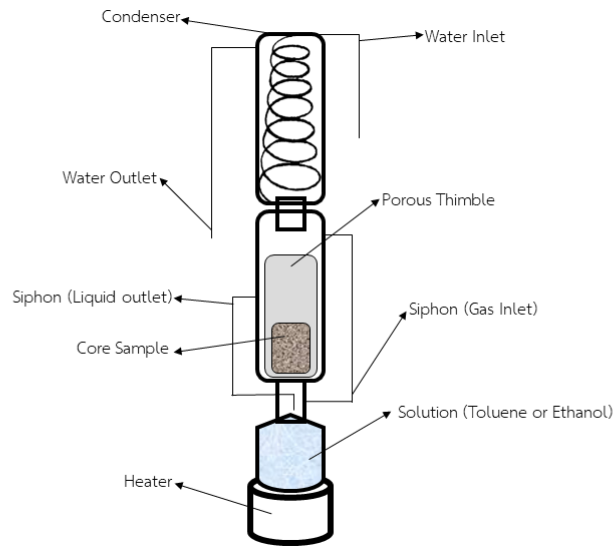
Figure 12. Soxhlet Extractor for Core Cleaning [40]

After the cleaning has finished, the cores were then dried in an oven and stored in a desiccator.

4.2.3. Core Sample Saturation and Properties Determination

Before coreflooding test can be started, properties such as absolute permeability, pore volume, initial oil and water saturation have to be determined. This procedure was performed using the coreflooding machine. The formation water of 14,098 ppm and 28,196 ppm from Sirikit Oilfield were used in this part of experiment depending on experiment cases. The crude oil was prepared from Sirikit Oilfield in which it showed some wax properties. Therefore, to avoid internal wax problem, n-Dodecane was added to the crude oil.

The cores' pore volume can be obtained by measuring the cores' diameter and length using a vernier caliper. Then, the dry weight of the cores was measured. Then, they were placed into the coreflooding machine to initiate the saturation test. Each core was then flushed with formation water at a rate of 0.5 cc/min until the core becomes saturated. Next, each core was taken out from the machine to measure wet weight. The pore volume then can be found using Equation 4.2.3.1.

$$V_p = \frac{W_{sat} - W_{dry}}{\rho_f} \qquad \text{(Equation 4.2.3.1)}$$

Where, V_p - Pore volume (cm^3)

W_{sat} - Saturated weight (g)

W_{dry} - Dry weight (g)

ρ_f – Fluid density (g/ cm^3)

Then, each core was reinserted into the machine and injected with formation water to saturated the core once again. The temperature was raised to 50 $C°$ to imitate the reservoir condition. Darcy's equation was used to determine the absolute permeability during the saturation process.

$$K_a = \frac{q\mu L}{A\Delta P}$$
(Equation 4.2.3.2)

Where, q – injection rate (cm³/sec)

μ – Fluid viscosity (cp)

L – Core sample length (cm)

A – Core cross-sectional area (cm²)

ΔP – Differential pressure across the sample (atm)

Once the absolute permeability and pore volume were obtained, the core was then being saturated with formation water, the was then flushed with the crude oil to allow oil migration to occur. The crude oil was injected at a rate of 0.5 cc/min until there was no water being produced. The initial oil saturation thus calculated as the equation below:

$$S_{oi} = \frac{V_w - V_D}{V_P}$$
(Equation 4.2.3.3)

Where, S_{oi} – Initial oil saturation

V_w – Water production volume (cm³)

V_D – Dead pore volume (cm³)

By obtaining initial oil saturation, the initial water saturation also can be determined by subtracting it with 1. After that, each core was taken out and aged for one week before the coreflooding experiment begins to allow the cores to attain their wettability equilibrium.

4.2.4. Coreflooding Test

Coreflooding test is performed using coreflooding machine, the purpose of this experiment was to determine the effect of the low salinity water formula. The test was carried out at 50 $°C$ with the confining pressure of 1,500 psi and the back pressure of 500 psi. The core was placed in the machine and firstly flushed with oil until saturation. Then, formation water was injected to perform conventional water flooding until there was no oil being recovered. Then, the injected fluid was changed to the selected low salinity water until no oil being produced. The injection rate was 0.5 cc/min for all cases. During the entire experiment, the pressure difference across the core, amount of oil, water and time were being recorded. A schematic below shows the coreflooding diagram.
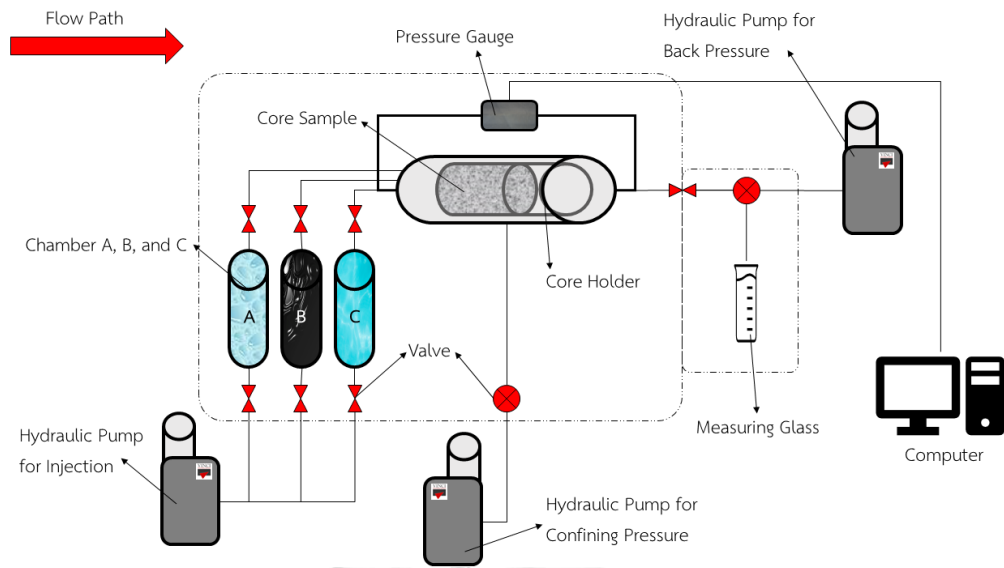
Figure 13. Schematic of Coreflooding Machine [40]

4.2.5. Effluent Collection and Detection of Ion Dissolution

Effluents from coreflooding test are collected both from conventional waterflooding and low salinity waterflooding to study the effect of low salinity water on the core samples by analyzing from the ion dissolution of the effluent brine. Amounts of Calcium ion and Magnesium ion are identified by color titration as explained in step 4.1.3.

4.2.6. Evaluation and Result interpretation

Results were interpreted and discussed and new findings were concluded in chapter 5.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Rock Mineralogy and Fluid Assessment

5.1.1. Clay Samples

XRD was used to determine the mineralogy of the representative clays regarding quality and quantity. From clay analysis using XRD machine, it can be observed from the Figure 14 that representative clays which contain 90.3% Illite and 9.7% Calcite. In Figure 15, the XRD result showed that the clay contains 81.8% Kaolinite, 11.2% Illite, and 7.1% Muscovite. This step is essential to confirm the representability of the clays.
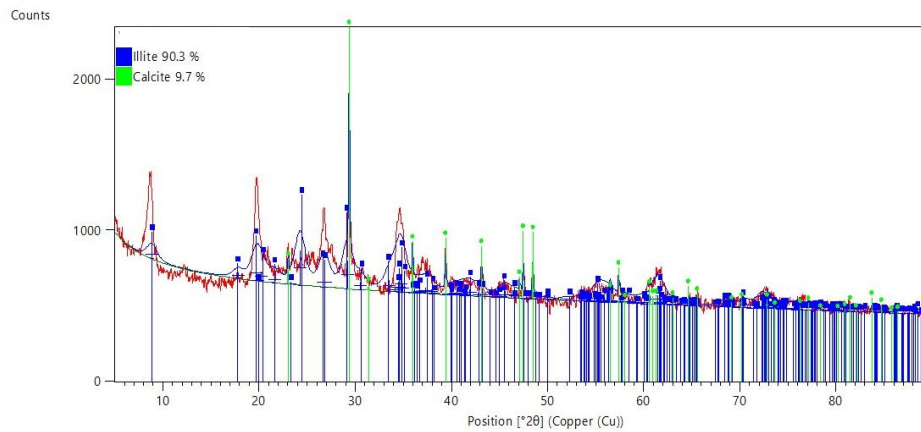
Figure 14. XRD result of representative Illite, showing the purity of 90.3%
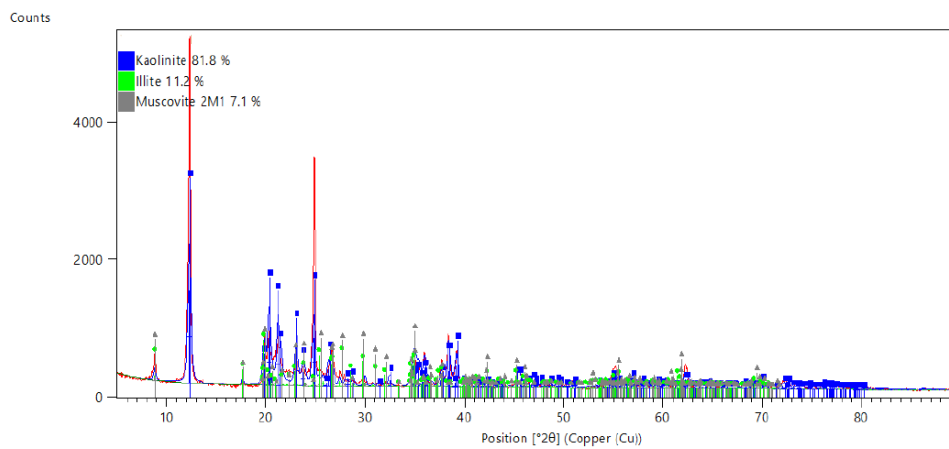
Figure 15. XRD result of representative Kaolinite, showing the purity of 81.8%

5.1.2. Core Samples

Before coreflooding experiment can be conducted, all the cores must be assessed for their mineralogy using XRD and XRF. Although the cores were sample in the same oilfield (Sirikit Oilfield), the sampled depth was different. Therefore, the properties would likely to be different. There are three core samples in this experiment (core A, core B, and core C). The XRF result showed four major elements inside these cores, mainly were Al, Fe, Si, and K. Silicon (total of almost 70 percent) in which represented quartz in sandstone. Due to the absent of Montmorillonite, therefore a clay swelling issue was not expected. The percentage of the clay content and its type was listed in Table 6.

Table 6. Percentage of Clay Content and Clays types in Core samples

Core Sample	Clay Content (%)	Illite (%)	Kaolinite (%)
A	30.8	84.4	15.6
B	42.4	57.8	42.2
C	34.9	98.2	1.8

Next, the properties of each core sample were determined using the coreflooding machine. The important properties including porosity, permeability (absolute), initial oil saturation, and irreducible water solution were listed in Table 7.

Table 7. Summary of Core Samples Properties

Core Sample	Porosity	Permeability (md)	Initial Oil Saturation (%)	Irreducible Water Saturation (%)
A	0.169	106.5	72.4	27.6
B	0.184	109.9	62.1	37.9
C	0.191	109.2	62.4	37.6

Based on the core samples result, it can be noticed that all the cores had similar properties with core A being slightly different than core A and B. These parameters could imply that they had similar wettability condition of the rock. In this study, all cores were re-used and re-saturated. Values of petrophysical properties after re-using may be slightly changed.

5.1.3. Fluid Properties

As for the formation water and oil sample from Sirikit oilfield, their properties were measured at the reservoir temperature (50°C). The oil sample for Sirikit oilfield was mixed with Dodecane (30:70) to prevent wax formation, resulting in difficulty of coreflooding at 50°C. In the study of high salinity formation water, the original formation water was prepared at the concentration of 28,196 ppm by multiplying by two to all compositions. The viscosity was measured using a viscometer soaked in the water bath (50°C). Table 8 represents the fluid properties of this study.

Table 8. Summary of Fluid Density and Viscosity

Fluid	Density (g/cm^3)	Viscosity (cP)
Formation Water (14,098 ppm)	1.0015	0.588
Formation Water (28,196 ppm)	1.0015	0.613
Oil	0.7725	1.672

5.2 Filtration and Titration Results

Titration test was conducted to study the effect of Multi-component Ion Exchange (MIE) mechanism that occurred between the injected low salinity water and the clay inside the core samples. Dissolution of Magnesium and Calcium ions was expected to occur as described by the MIE mechanism by replacing divalent ions connecting hydrocarbon and the clay surface. Table 9 summarizes results obtained from filtration and titration. The amount of EDTA required for obtaining end point was then converted to concentration of divalent ions. The concentration of Magnesium ion was obtained from the difference between results obtained from total divalent ion concentration and concentration of Calcium ion. Net concentrations in the table refer to apparent concentration subtracted by the input concentration. Table 9 shows the amount of ion dissolution of Kaolinite and Illite clays at different concentration where net ion exchange was calculated. Positive values mean the ion concentration increases and negative values mean the ion concentration decreases.

Table 9. Summary of Calcium ion and Magnesium ion from dissolution of clays from different water formulations with different cations and concentrations.

Concentration (ppm)	Ion	Dissolution Kaolinite (ppm)				Dissolution Illite (ppm)			
		Ca^{2+}	Mg^{2+}	Net Ca^{2+}	Net Mg^{2+}	Ca^{2+}	Mg^{2+}	Net Ca^{2+}	Net Mg^{2+}
500	Na$^+$	6.0	4.9	6.0	4.9	6.0	0.1	6.0	0.1
	K$^+$	6.0	4.9	6.0	4.9	10.0	0.1	10.0	0.1
	Ca^{2+}	125.4	8.5	-55.2	8.5	156.3	1.9	-24.2	1.3
	Mg^{2+}	18.0	43.8	18.0	-83.9	15.6	5.5	15.6	-122.1
1,000	Na$^+$	6.0	1.2	6.0	1.2	14.0	0.4	14.0	0.4
	K$^+$	10.0	1.2	10.0	1.2	24.1	0.7	24.1	0.7
	Ca^{2+}	156.3	69.3	-204.8	69.3	270.8	7.0	-90.4	7.0
	Mg^{2+}	60.1	72.9	60.1	-182.4	32.1	12.3	32.1	-243.0
2,000	Na$^+$	8.0	3.7	8.0	3.7	20.1	1.0	20.1	1.0
	K$^+$	8.0	3.7	8.0	3.7	28.1	1.0	28.1	1.0
	Ca^{2+}	256.5	48.6	-465.7	48.6	405.6	23.3	-316.7	23.3
	Mg^{2+}	56.4	245.7	56.4	-264.9	82.2	31.9	82.2	-478.7
5,000	Na$^+$	8.0	6.1	8.0	6.1	28.1	1.8	28.1	1.8
	K$^+$	8.0	7.3	8.0	7.3	32.1	1.5	32.1	1.5
	Ca^{2+}	296.6	65.6	-1509.1	65.6	769.8	70.1	-1035.9	70.1
	Mg^{2+}	112.5	405.6	112.5	-870.8	188.4	50.0	188.4	-1226.5
10,000	Na$^+$	10.0	4.6	10.0	4.6	30.1	1.2	30.1	1.2
	K$^+$	8.0	6.7	8.0	6.7	32.1	1.1	32.1	1.1[
	Ca^{2+}	200.4	145.7	-3411.0	145.7	1603.1	86.8	-2008.2	86.8
	Mg^{2+}	175.7	1093.7	175.7	-1459.2	300.6	249.1	300.6	-2303.8
20,000	Na$^+$	10.0	3.0	10.0	3.0	36.1	1.0	36.1	1.0
	K$^+$	8.0	3.6	8.0	3.6	36.1	1.2	36.1	1.2
	Ca^{2+}	800.6	289.7	-6422.1	289.7	2204.3	247.4	-5018.4	247.4
	Mg^{2+}	450.3	699.9	450.3	-4405.9	400.8	297.7	400.8	-4808.1

From Table 9, comparing between dissolution of Calcium and Magnesium ions obtained from replacing by monovalent ions (Sodium and Potassium ions) it can be observed that dissolution of divalent ions by monovalent ion occurs between in Illite clay than in Kaolinite clay especially at higher salt concentration. This can be explained by the Cation Exchange Capacity (CEC) of Illite that is much higher than Kaolinite, resulting in different magnitude of replacing of divalent ions by monovalent ions. In both clays, Calcium ion is more displaced compared to Magnesium ion by monovalent ion. In Kaolinite clay, portion of displacement of Magnesium ion is higher than that of Illite clay and this can be explained by the composition of clay itself. As ionic radius on Magnesium ion is smaller than Calcium ion, Magnesium ion bounds with the main structure of clays with higher strength and hence, replacing of Magnesium ion by monovalent ion is more difficult than replacing Calcium ion.

For Kaolinite clay, the effect of type of monovalent ion cannot be significantly observed. However, for Illite clay, Potassium ion which is highly mobile shows better replacement ability especially in low-to-medium salinity. Potassium ion forms hydrate structure with only a few molecules of water, whereas Sodium ion may require 5-11 molecules of water when it turns into hydrate structure. The size of hydrated Sodium is then larger than hydrated Potassium and therefore, Potassium ion is more active in MIE mechanism. Nevertheless, both ions show almost the same magnitude in replacing divalent ion at total concentration from 5,000 ppm. As amount of ion increases, mobility of monovalent ion is compensated.

Regarding the best total salinity for dissolution by monovalent ion, Kaolinite clay is slightly improved its dissolution from concentration of salt in low salinity range (500 to 2,000 ppm) whereas for Illite clay which is high CEC clay, dissolution shows the best range from 2,000 to 5,000 ppm. Figures 16 and 17 summarize the dissolution of Calcium and Magnesium ions by Sodium and Potassium ions at different concentrations for Kaolinite clay and Illite clay, respectively.
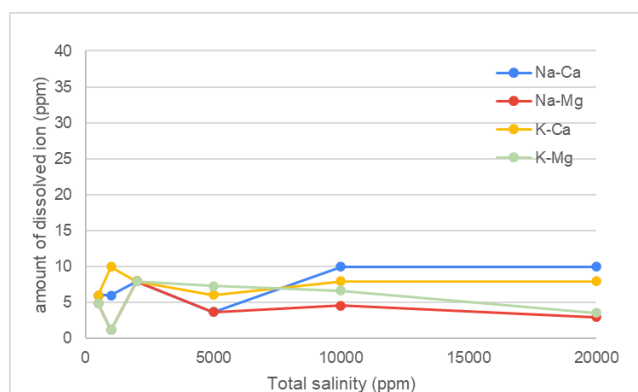

Figure 16. Dissolution of Calcium and Magnesium ions by Sodium and Potassium ion at different salt concentration of Kaolinite clay
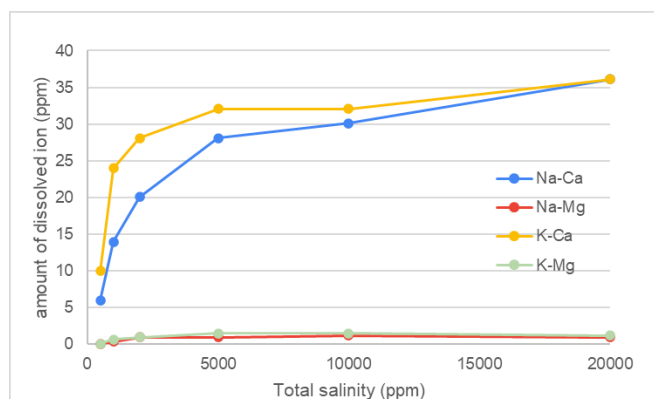
Figure 17. Dissolution of Calcium and Magnesium ions by Sodium and Potassium ion at different salt concentration of Illite clay

For dissolution of Calcium and Magnesium ions by themselves, the net values are calculated prior to discussion. The input ppm of Calcium and Magnesium ion is obtained from ratios of Calcium and Magnesium ions in their salt. Portion of Calcium ion is 0.361 and portion of Magnesium ion is 0.255 and these numbers are multiplied to total salinity in ppm. From Table 9, it can be observed that amounts of Calcium ion and Magnesium ion are negative. This means that instead of dissolution, Calcium ion and Magnesium ion are consumed. Moreover, when Calcium ion is consumed, dissolution of Magnesium ion can be obviously seen. When Magnesium ion disappeared from the input, Calcium ion is expelled into solution. Therefore, both Calcium ion and Magnesium ion are important in dissolution mechanisms. To discover best total salinity, the ratio of dissolution to amount of ion consumed is calculated for both Calcium ion replacing Magnesium ion and Magnesium ion replacing Calcium ion as shown in Table 10.

Table 10. Ratio of dissolution of ion to amount of ion consumed for both Calcium ion replacing Magnesium ion and Magnesium ion replacing Calcium ion

Clay	Ratio of Dissolution	Total Salinity (ppm)					
		500	1,000	2,000	5,000	10,000	20,000
Kaolinite	Ca replaces Mg	0.154	0.338	0.104	0.043	0.042	0.045
	Mg replaces Ca	0.215	0.330	0.213	0.129	0.120	0.102
Illite	Ca replaces Mg	0.052	0.077	0.074	0.068	0.043	0.049
	Mg replaces Ca	0.128	0.132	0.172	0.154	0.130	0.083

From Table 10, it can be observed that ratio of Calcium ion replacing Magnesium ion is smaller than ratio of Magnesium ion replacing Calcium ion in overall. This can be interpreted in two ways which are: 1) Magnesium ion is more potential in dissolution mechanism compared to Calcium ion and; 2) the MIE mechanism of Calcium ion to replace Magnesium ion can occur with more difficulty which can be due to the interaction of Magnesium ion in clay structure. Comparing between Kaolinite and Illite, the ratio does not show an absolute significance. However, at the best total salinity, the ratio is much higher in case of Kaolinite than

Illite. The best total salinity can be seen from this table. For most of the dissolution mechanisms, the total salinity of 1,000 ppm results in the highest dissolution ratio, whereas 2,000 ppm shows the best dissolution ratio of Magnesium ion replacing Calcium ion.

5.3 Selection of Water Formulations

In order to study the effect of salinity contrast, low and high concentrations were picked as 1,000 and 5,000 ppm. These numbers are the boundaries where effects of low salinity water formulations can be observed in dissolution mechanism. The concentration of 500 ppm which is the initial range for Kaolinite is neglected as dissolution effect is more expected from Illite clay which is higher in CEC.

Regarding the effect of monovalent ion, Potassium ion was selected over Sodium ion as can be observed in Figure 17 that its effect in dissolution of Calcium ion is much higher. For divalent ion, Magnesium ion tended to displace Calcium ion better than the opposite direction. However, clays may contain both Calcium and Magnesium ion and hence, both Calcium ion and Magnesium ion were selected in this study. In total, two system of water formulation were selected: 1) Potassium-Calcium (K-Ca) and 2) Potassium-Magnesium (K-Mg).

To confirm the combination effect, one Potassium-Calcium and Potassium-Magnesium solutions at the concentration of 1,000 and 5,000 was used to test with mixed clay (80% Illite and 20% Kaolinite) and the result is shown in Table 11. Weight of KCl, $CaCl_2$, and $MgCl_2$ were obtained from the ratio of divalent ion dissolution contribution. For example, from Table 9, at concentration of 1,000 ppm in Kaolinite:

1. Potassium solution displaced Calcium ion and Magnesium ion in total 11.2 ppm (10 and 1.2);
2. Calcium ion displaces Magnesium ion 69.3 ppm
3. The total dissolution of divalent ion is 80.5 ppm
4. The contribution of Potassium ion is 0.14 and contribution of Calcium ion is 0.86
5. Using similar technique for Illite clay, the contribution of Potassium ion is 0.78 and Calcium ion is 0.22
6. Apply these 4 numbers to weight with clay contents (80% Illite and 20% Kaolinite
7. The portion of KCl is 0.652 and $CaCl_2$ is 0.348
8. The ratio of contribution of divalent ion dissolution for Kaolinite and Illite clays at total concentration of 1,000 and 5,000 ppm are summarized in Table 11.

Table 11. Results from dissolution test of combined water formulations

Test	Formulation	TDS (ppm)	KCl (ppm)	CaCl₂ (ppm)	MgCl₂ (ppm)	Net Ca²⁺ (ppm)	Net Mg²⁺ (ppm)
1	K-Ca	1,000	652	348	-	-33.50	25.52
2	K-Mg	1,000	380	-	620	80.16	-118.18
3	K-Ca	5,000	1,485	3515	-	-267.44	486.10
4	K-Mg	5,000	725	-	4275	601.17	-362.22

Table 12. Summary of the ratio of contribution of divalent ion dissolution

Clay	Salinity (ppm)	Formulation	K⁺ ratio	Ca²⁺ ratio	Mg²⁺ ratio
Kaolinite	1,000	K-Ca	0.14	0.86	-
	1,000	K-Mg	0.16	-	0.84
	5,000	K-Ca	0.19	0.81	-
	5,000	K-Mg	0.12	-	0.88
Illite	1,000	K-Ca	0.78	0.22	-
	1,000	K-Mg	0.44	-	0.56
	5,000	K-Ca	0.32	0.68	-
	5,000	K-Mg	0.15	-	0.85

From Table 12, it can be observed that the net dissolution of both Calcium ion and Magnesium ion are greater than results obtained using just single salt. This ensures the symbiotic action of the system of two-ion in dissolution mechanism. Regarding clay contents mentioned in Table 6, summary of the selected formulation for coreflooding tests were made and summarized in Table 13.

Table 13. Summary of water formulations for coreflooding tests

Test No.	Core	Formation Water (ppm)	Injected Water (ppm)	KCl (ppm)	CaCl₂ (ppm)	MgCl₂ (ppm)
1	A	14,098	1,000	392	-	608
2	B	14,098	1,000	509	491	-
3	C	14,098	5,000	1,608	3,392	-
4	A	14,098	5,000	732	-	4,268
5	B	28,196	1,000	509	491	-
6	C	28,196	5,000	1,608	3,392	-
7	A	28,196	5,000	732	-	4,268

5.4 Coreflooding Results

From the coreflooding results, injected pore volume of water was calculated at each detected time steps from injection rate ($0.5cm^3$ per minute) and time divided by pore volume of each core sample. On y-axis, oil recovery factor and pressure drop across the core samples were plotted. Oil recovery factor was calculated from volume of oil produced at each time step divided by initial oil saturation. First, formation water was used to perform conventional waterflooding until there was no more oil recovered. Selected injected low salinity water was then switched until the end of the

process. Figures 18-22 illustrates results obtained from test no.1 to test no.7. The red line indicates the point where low-salinity water has been injected.
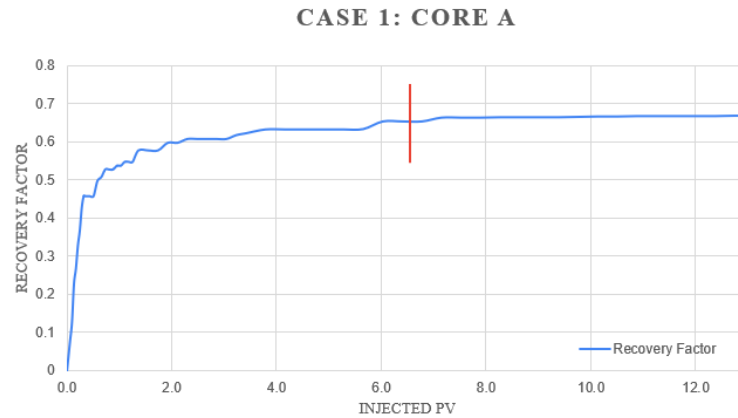
Figure 18. Case 1: Differential Pressure and Recovery Factor (Core A)

Figure 19. Case 2: Differential Pressure and Recovery Factor (Core B)

Figure 20. Case 3: Differential Pressure and Recovery Factor (Core C)

CASE 4: CORE A

Figure 21. Case 4: Differential Pressure and Recovery Factor (Core A)

CASE 5: CORE B

Figure 22. Case 5: Differential Pressure and Recovery Factor (Core B)
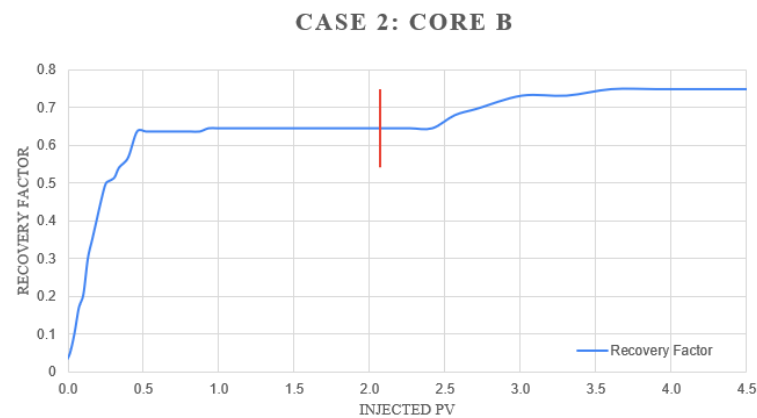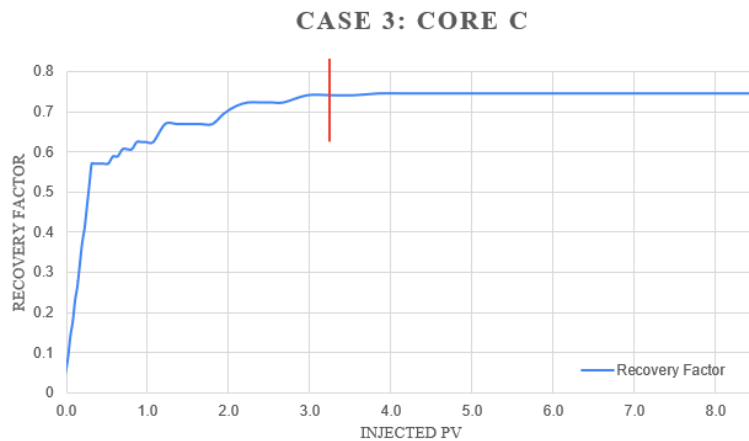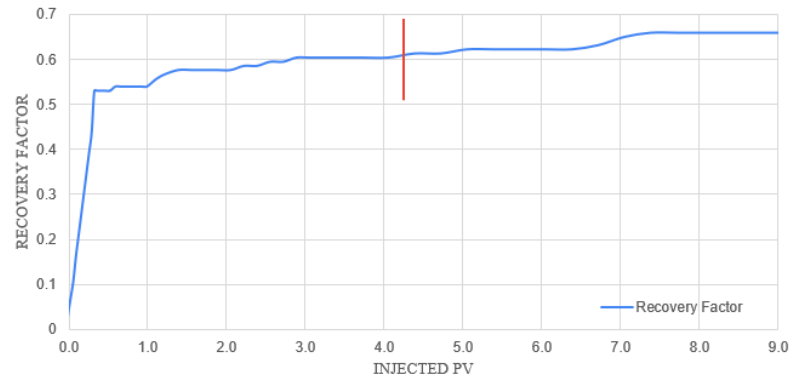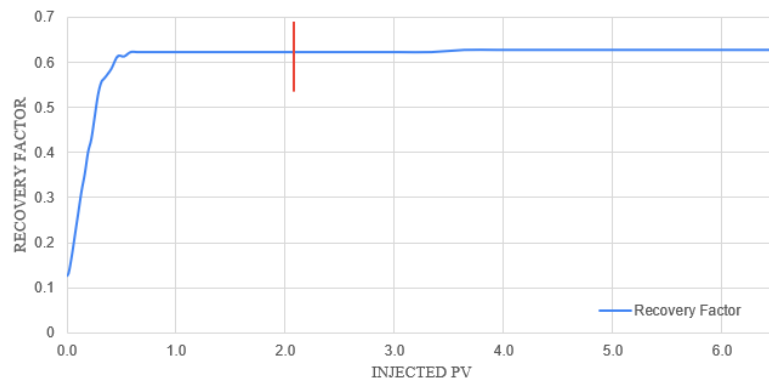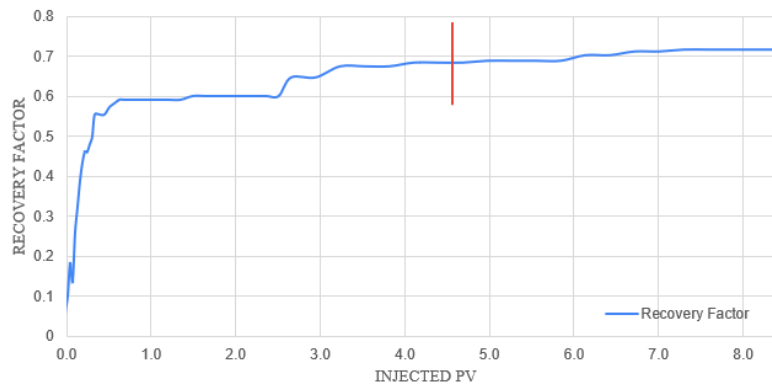
CASE 6: CORE C

Figure 23. Case 6: Differential Pressure and Recovery Factor (Core C)
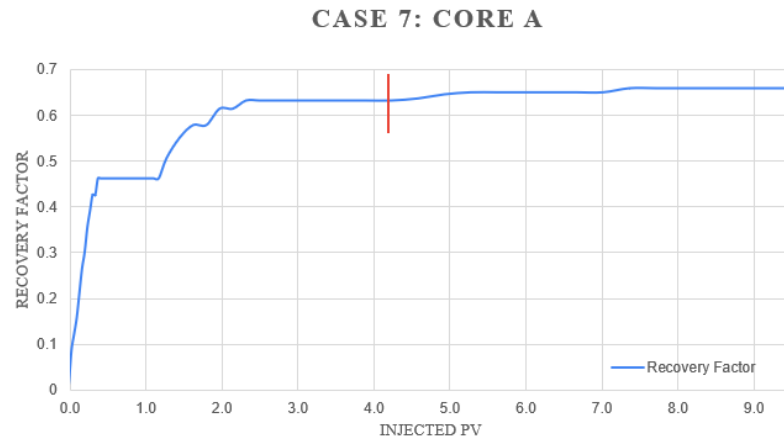
CASE 7: CORE A

Figure 24. Case 7: Differential Pressure and Recovery Factor (Core A)

From these figures, summaries of oil recovery from conventional waterflooding, low salinity waterflooding, additional oil recovery from LSWF, and pressure difference are gathered and reported in Table 14.

Table 14. Summary of oil recovery data and pressure difference from coreflooding tests

Test No. (Core)	Clay Content (%)	Clay (%)		Formation Water (ppm)	Injected Water (ppm)	Formulation	RF Conv. (%)	RF LSWF (%)	RF Increase (%)
		Kao.	Illite						
1(A)	30.8	15.6	84.4	14,098	1,000	K-Mg	66.5	67.0	0.5
2(B)	42.2	42.2	57.8	14,098	1,000	K-Ca	64.6	74.9	10.4
3(C)	34.9	98.2	1.8	14,098	5,000	K-Ca	74.0	74.5	0.4
4(A)	30.8	15.6	84.4	14,098	5,000	K-Mg	61.4	66	4.6
5(B)	42.2	42.2	57.8	28,196	1,000	K-Ca	62.4	62.9	0.5
6(C)	34.9	98.2	1.8	28,196	5,000	K-Ca	68.4	71.7	3.2
7(A)	30.8	15.6	84.4	28,196	5,000	K-Mg	63.3	66.0	2.7

From the table, considering test no.1 to test no.4, it can be observed that the best increment of oil recovery was obtained from the system of K-Ca at 1,000 ppm followed by K-Mg at 5,000 ppm. Using information in Table 10 it can be observed that at 1,000 ppm, dissolution by Magnesium ion by Calcium ion is the highest for both Kaolinite and Illite clays. Moreover, in core B, portion of kaolinite is very high and therefore, the benefit from appearance of Calcium ion to replace Magnesium ion was maximized.

However, in case of dissolution of Magnesium ion the optimum range for kaolinite is 1,000-2,000 ppm whereas for Illite the optimum range is 2,000-5,000 ppm. Therefore, case number 4 using core A, containing Illite of about 84.4 percent, obtained the benefit in dissolution of Calcium ion by Magnesium ion.

Comparing between high salinity contrast (14,098-1,000 ppm) and low-salinity contrast (14,098-5,000), it can be observed that best salinity contrasts depend

mainly on the major divalent ions; Calcium ion prefers higher salinity contrast whereas Magnesium ion tends to work well at lower salinity contrast.

Considering case no.5 to no. 7, it can be observed that total salinity of 1,000 ppm for K-Ca solution does not result in good additional oil recovery, this can also be explained by very big contrast, resulting adjustment of chemical concentration quickly, and hence, the concentration of injected K-Ca was raised over the optimal range. However, for both K-Ca and K-Mg at 5,000 ppm, both solutions yield good additional recovery of 3.2 and 2.7, respectively. This can be confirmed that low salinity waterflooding does not always require injected water to be extremely diluted. Appropriate range of concentration and ions are much more important.

In this section, the lower salinity contrast (28,196-5,000 ppm), both K-Ca and K-Mg solutions, yields better results compared to higher salinity contrast (28,196-1,000). Nevertheless, to compare results from low formation salinity and high formation salinity cases, additional oil recovery data were summarized in Table 15 and plotted in Figure 23. The salinity contrast ratio is defined by dividing formation water salinity with injected low-salinity water.

Table 15. Summary of additional oil recovery from different salinity contrast ratio

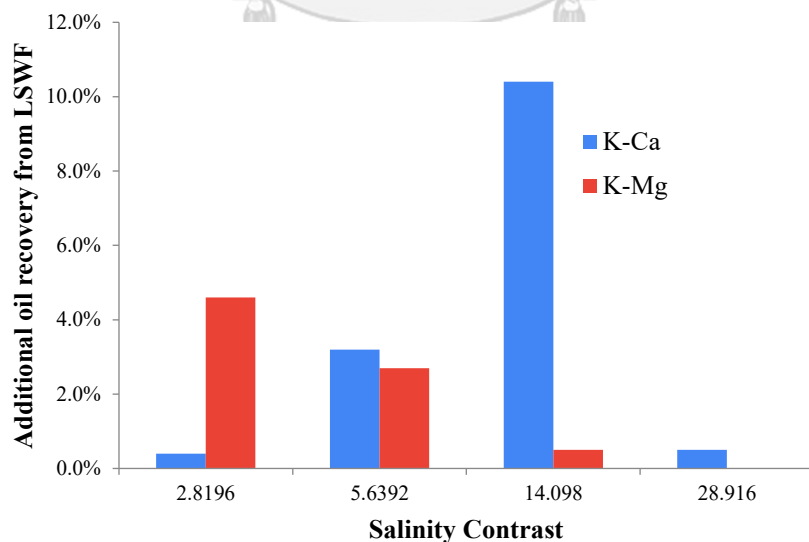| Salinity Contrast Ratio	K-Ca Recovery Factor (%)	K-Mg Recovery Factor (%)
2.8196	0.4	4.6
5.6392	3.2	2.7
14.098	10.4	0.5
28.916	0.5	-

Figure 25. Additional oil recovery from K-Ca and K-Mg solutions as a function of salinity contrast ratio

From the figure, it can be observed that K-Ca solution has the best salinity contrast ratio range around 14 whereas too low and too high salinity contrast ratio result in less benefit. This can be explained that combination of K-Ca tends to dissolve Magnesium ion which is firmly attached between clay surface and oil drop due to small ionic radius (72 picometer) and hence, appropriate contrast ratio of salinity in formation water and injected low salinity water would favor three important triggering mechanisms including 1) lowering concentration of salt concentration of injected water to induce dissolution of Magnesium ion; 2) providing Calcium ion to induce Calcium carboxylate complex, reducing strength between carboxylic acid in oil and rock surface; and 3) providing Potassium ion to substitute the leaving Magnesium ion after finishing the process. In case too low salinity contrast ratio, or high salt concentration in injected water, the mechanism no.1 is exhibited and hence, Magnesium ion cannot dissolve. In case of too high salinity contrast ratio, mechanisms no.2 and no.3 might not have enough active potential ions to trigger the overall mechanism.

For the solution of K-Mg, it can be observed that the optimal salinity contrast ratio is smaller than the case of K-Ca. As Magnesium can replace Calcium ion easily due the link between clay surface and carboxylic acid in oil through Calcium ion is weaker compared to the linkage by Magnesium ion as ionic radius of Calcium ion is larger (100 picometer). Hence, smaller contrast ratio of formation water and injected water with high concentration of Magnesium ion is favorable. However, this does not mean that K-Mg will not have minimum boundary. Lowering the contrast ratio might result in difficulty of dissolution of Calcium ion and hence, Magnesium ion cannot work efficiently.

Considering the result from test number 1, 4 and 7, for K-Mg water solution, it can be seen that as the salinity contrast ratio increases, the oil recovery decreases. This could be deducted that when the salinity contrast ratio reaches 28.916, there would be little to no oil being revered. As well as the time constraint on this project, thus, the test number 8 which involved with using K-Mg at 1,000 ppm of low-salinity water and 28,916 ppm of formation water was cancelled due to this reason.

5.5 Analysis of Effluent from Coreflooding

Effluents from coreflooding were collected in several portions in both conventional waterflooding and low salinity waterflooding. Average concentration of Calcium ion and Magnesium ion during conventional waterflooding and low salinity waterflooding are summarized in Table 16.

Table 16. Summary of Calcium and Magnesium concentration for both conventional and low-salinity water flooding on different water formulation

Test no.	Formation Water (ppm)	Injected Water (ppm)	Formulation	Conventional (ppm)		Low Salinity (ppm)	
				Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
1	14,098	1,000	K-Mg	25.05	21.27	7.01	3.04
2	14,098	1,000	K-Ca	27.05	10.33	9.02	3.65
3	14,098	5,000	K-Ca	24.05	7.29	96.19	14.58
4	14,098	5,000	K-Mg	27.39	16.20	27.39	53.07
5	28,196	1,000	K-Ca	48.09	25.52	14.70	10.13
6	28,196	5,000	K-Ca	39.58	20.96	90.18	25.11
7	28,196	5,000	K-Mg	48.09	32.81	28.72	51.85

From Table 16, it can be observed that portion of Calcium ion is higher than Magnesium ion during conventional waterflooding in both low and high formation water cases. However, during low salinity waterflooding, amount of them can be varied due to selected water formulations. In all cases, it can be observed that the opposite ions were always found such as, in the injection of K-Ca solution, Magnesium ion can be observed even though it is not injected. Similarly, when K-Mg was injected, Calcium ion is retrieved. This shows evidence of dissolution of the opposite divalent ions whereas the injected divalent ions are always less than the injected amount, meaning that they are consumed to dissolve the opposite ion. Nevertheless, it is difficult to conclude for relationship between effects from ions in effluents as a function of effectiveness of the process as ions that are liberated may not be ions linked with oil drops and some of the ions may exit together with oil as carboxylate complex.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

From this study, Calcium ion, Magnesium ion and Potassium ion were discovered to be potential determining ion in oil recovery mechanism by low salinity waterflooding in shaly-sandstone reservoir. Calcium ion tends to displace Magnesium ion whereas Magnesium ion tends to displace Calcium ion. However, both requires monovalent ion to complete the multi-component ion exchange mechanism. Moreover, different clays tend to have different effective concentrations. Illite with higher Cation Exchange Capacity prefers the concentration around 2,000 to 5,000 ppm whereas Kaolinite which is lower in CEC prefers the concentration around 500 to 2,000 ppm.

In the study of salinity contrast and chemical composition, it can be concluded that Calcium ion which is the ion to replace Magnesium ion works well at higher salinity contrast ratio. This can be explained that dissolution of Magnesium ion which is smaller in diameter, presence of Calcium must be at specific contrast ratio to allow three components to trigger. However, Magnesium ion which can replace Calcium ion prefers low salinity contrast ratio as higher concentration results in high displacement. In this study, the salinity contrast ratio for K-Ca is around 14 whereas salinity contrast ratio can be lower down to 2.5.

Effects of salinity contrast on oil recovery mechanism would be an important information for implementation of low salinity waterflooding in shaly-sandstone reservoir in the future. This would help to reduce investigation time for specific reservoir since the appropriate range of salinity of injected water will be obtained for specific range of salinity of formation water. More than that, not only total salinity, effects of chemical composition of injected water will be included.

6.2 Recommendation

1. Lower limit of salinity contrast ratio of K-Mg can be identified in the future as this might need several more runs to find specific contrast ratio between 1 and 2.58. It is expected to obtain a specific contrast ratio of K-Mg that would cause the highest recovery factor.
2. In this study core samples contain only Illite and Kaolinite which are not swelling clay. Studying of samples containing, for example, Montmorillonite, Smectite and bentonite which are swelling clays would lead to new additional findings.
3. Combination of both salinity and chemical composition would lead to the best water formulation especially for fields having difficulties in technique to dilute

salinity water for injection or fining sources of fresh water to dilute salinity water.

REFERENCES

[1]   A. Kakati, G. Kumar, and J. S. Sangwai, "Oil Recovery Efficiency and Mechanism of Low Salinity-Enhanced Oil Recovery for Light Crude Oil with a Low Acid Number," *ACS Omega*, vol. 5, no. 3, pp. 1506–1518, 2020, doi: 10.1021/acsomega.9b03229.

[2]   M. F. Snosy, M. Abu El Ela, A. El-Banbi, and H. Sayyouh, "Comprehensive investigation of low-salinity waterflooding in sandstone reservoirs," *J. Pet. Explor. Prod. Technol.*, vol. 10, no. 5, pp. 2019–2034, 2020, doi: 10.1007/s13202-020-00862-z.

[3]   A. A. AlQuraishi, S. N. AlHussinan, and H. Q. AlYami, "Efficiency and Recovery Mechanisms of Low Salinity Water Flooding in Sandstone and Carbonate Reservoirs," 2015, vol. All Days.

[4]   M. Chavan, A. Dandekar, S. Patil, and S. Khataniar, "Low-salinity-based enhanced oil recovery literature review and associated screening criteria," *Pet. Sci.*, vol. 16, 2019, doi: 10.1007/s12182-019-0325-7.

[5]   A. Katende and F. Sagala, "A critical review of low salinity water flooding: Mechanism, laboratory and field application," *J. Mol. Liq.*, vol. 278, pp. 627–649, 2019, doi: https://doi.org/10.1016/j.molliq.2019.01.037.

[6]   H. N. Al-SAEDI and R. E. FLORI, "Enhanced oil recovery of low salinity water flooding in sandstone and the role of clay," *Pet. Explor. Dev.*, vol. 45, no. 5, pp. 927–931, 2018, doi: https://doi.org/10.1016/S1876-3804(18)30096-X.

[7]   A. A. Yousef, S. Al-Saleh, and M. Al-Jawfi, "Improved/Enhanced Oil Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic Content," 2012, vol. All Days, doi: 10.2118/154076-MS.

[8]   J. T. Tetteh and R. Barati, "Crude-Oil/Brine Interaction as a Recovery Mechanism for Low-Salinity Waterflooding of Carbonate Reservoirs," *SPE Reserv. Eval. Eng.*, vol. 22, no. 03, pp. 877–896, 2018, doi: 10.2118/194006-PA.

[9]   G. G. Bernard, "Effect of floodwater salinity on recovery of oil from cores containing clays," [Online]. Available: https://www.osti.gov/biblio/6172628.

[10]   R. A. Nasralla and H. A. Nasr-El-Din, "Coreflood Study of Low Salinity Water Injection in Sandstone Reservoirs," 2011, vol. All Days, doi: 10.2118/149077-MS.

[11]   H. O. Yildiz and N. R. Morrow, "Effect of brine composition on recovery of Moutray crude oil by waterflooding," *J. Pet. Sci. Eng.*, vol. 14, no. 3, pp. 159–168, 1996, doi: https://doi.org/10.1016/0920-4105(95)00041-0.

[12] B. M. Suijkerbuijk *et al.*, "Fundamental investigations into wettability and low salinity flooding by parameter isolation," 2012, vol. All Days, doi: 10.2118/154204-MS.

[13] G.-Q. Tang and N. R. Morrow, "Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery," *J. Pet. Sci. Eng.*, vol. 24, no. 2, pp. 99–111, 1999, doi: https://doi.org/10.1016/S0920-4105(99)00034-0.

[14] P. Mcguire, J. R. Chatham, F. Paskvan, D. M. Sommer, and F. H. Carini, "Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope," 2005.

[15] A. Lager, K. J. Webb, C. J. J. Black, M. Singleton, and K. S. Sorbie, "Low Salinity Oil Recovery - An Experimental Investigation1," *Petrophysics - SPWLA J. Form. Eval. Reserv. Descr.*, vol. 49, no. 01, 2008.

[16] H. H. Al-Attar, M. Y. Mahmoud, A. Y. Zekri, R. Almehaideb, and M. Ghannam, "Low-salinity flooding in a selected carbonate reservoir: experimental approach," *J. Pet. Explor. Prod. Technol.*, vol. 3, no. 2, pp. 139–149, 2013, doi: 10.1007/s13202-013-0052-3.

[17] J. Batias, G. Hamon, B. Lalanne, and C. M. C. Romero, "FIELD AND LABORATORY OBSERVATIONS OF REMAINING OIL SATURATIONS IN A LIGHT OIL RESERVOIR FLOODED BY A LOW SALINITY AQUIFER," 2009.

[18] T. Austad, A. RezaeiDoust, and T. Puntervold, "Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs," 2010, vol. All Days, doi: 10.2118/129767-MS.

[19] M. Mohammad Salehi, P. Omidvar, and F. Naeimi, "Salinity of injection water and its impact on oil recovery absolute permeability, residual oil saturation, interfacial tension and capillary pressure," *Egypt. J. Pet.*, vol. 26, 2016, doi: 10.1016/j.ejpe.2016.05.003.

[20] B. M. J. M. Suijkerbuijk *et al.*, "The Development of a Workflow to Improve Predictive Capability of Low Salinity Response," 2013, vol. All Days, doi: 10.2523/IPTC-17157-MS.

[21] Q. Xie, A. Saeedi, E. Pooryousefy, and Y. Liu, "Sari, Drivers of low salinity effect in sandstone reservoirs, J. Mol.," *J. Mol. Liq.*, vol. 221, pp. 658–665, 2016, doi: https://doi.org/10.1016/j.molliq.2016.06.004.

[22] A. Al-Sarihi, A. Zeinijahromi, L. Genolet, A. Behr, P. Kowollik, and P.

Bedrikovetsky, "Fines Migration as an EOR Method During Low Salinity Waterflooding," 2018, vol. Day 2 Wed, doi: 10.2118/192070-MS.

[23] S. Berg, A. W. Cense, E. Jansen, and K. Bakker, "Direct Experimental Evidence of Wettability Modification By Low Salinity," *Petrophysics - SPWLA J. Form. Eval. Reserv. Descr.*, vol. 51, no. 05, 2010.

[24] M. Cissokho, H. Bertin, S. Boussour, P. Cordier, and G. Hamon, "Low Salinity Oil Recovery On Clayey Sandstone: Experimental Study," *Petrophysics - SPWLA J. Form. Eval. Reserv. Descr.*, vol. 51, no. 05, 2010.

[25] F. Srisuriyachai and S. Meekangwal, "Evidence of Multi-Component Ion Exchange in Dolomite Formation during Low Salinity Waterflooding," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 95, p. 32037, 2017, doi: 10.1088/1755-1315/95/3/032037.

[26] F. Mohd Omar, H. Aziz, and S. Stoll, "Nanoparticle Properties, Behavior, Fate in Aquatic Systems and Characterization Methods," *J. Colloid Sci. Biotechnol.*, vol. 3, pp. 1–30, 2014, doi: 10.1166/jcsb.2014.1090.

[27] P. Vledder, J. C. Fonseca, T. Wells, I. Gonzalez, and D. Ligthelm, "Low Salinity Water Flooding: Proof Of Wettability Alteration On A Field Wide Scale," 2010, vol. All Days, doi: 10.2118/129564-MS.

[28] A. A. Yousef and S. C. Ayirala, "A Novel Water Ionic Composition Optimization Technology for SmartWater Flooding Application in Carbonate Reservoirs," 2014, vol. All Days.

[29] K. Sandengen and O. J. Arntzen, "Osmosis During Low Salinity Water Flooding," 2013.

[30] T. Austad, "Water-Based EOR in Carbonates and Sandstones: New Chemical Understanding of the EOR Potential Using 'Smart Water,'" *Enhanc. Oil Recover. F. Case Stud.*, pp. 301–335, 2013, doi: 10.1016/B978-0-12-386545-8.00013-0.

[31] K. Al-Nofli, P. Pourafshary, N. Mosavat, and A. Shafiei, "Effect of Initial Wettability on Performance of Smart Water Flooding in Carbonate Reservoirs—An Experimental Investigation with IOR Implications," *Energies*, vol. 11, 2018, doi: 10.3390/en11061394.

[32] M. Safari, A. Rahimi, R. Gholami, A. Permana, and W. S. Khur, "Underlying mechanisms of shale wettability alteration by low salinity water injection (LSWI)," *J. Dispers. Sci. Technol.*, vol. 43, no. 1, pp. 33–41, 2022, doi: 10.1080/01932691.2020.1813156.

[33] K. J. Webb, C. J. J. Black, and H. Al-Ajeel, "Low Salinity Oil Recovery - Log-Inject-Log," 2003, vol. All Days, doi: 10.2118/81460-MS.

[34] M. M. Sharma and P. R. Filoco, "Effect of Brine Salinity and Crude-Oil Properties on Oil Recovery and Residual Saturations," *SPE J.*, vol. 5, no. 03, pp. 293–300, 2000, doi: 10.2118/65402-PA.

[35] B. W.B., "Fast X-Ray Micro-CT Study of the Impact of Brine Salinity on the Pore-Scale Fluid Distribution During Waterflooding," *Fast X-Ray Micro-Ct Study Impact Brine Salin. Pore-Scale Fluid Distrib. Dur. Waterflooding*, 2017, [Online]. Available: https://www.scopus.com/inward/record.uri?eid=2-s2.0-85060535957&partnerID=40&md5=bb942a942aa0bb29a20c052f1ba1a536.

[36] Y. Zhang, X. Xie, and N. R. Morrow, "Waterflood Performance By Injection Of Brine With Different Salinity For Reservoir Cores," 2007, vol. All Days, doi: 10.2118/109849-MS.

[37] N. R. Morrow, G. Tang, M. Valat, and X. Xie, "Prospects of improved oil recovery related to wettability and brine composition," *J. Pet. Sci. Eng.*, vol. 20, no. 3, pp. 267–276, 1998, doi: https://doi.org/10.1016/S0920-4105(98)00030-8.

[38] K. Skrettingland, T. Holt, M. T. T. Tweheyo, and I. Skjevrak, "Snorre Low-Salinity-Water Injection—Coreflooding Experiments and Single-Well Field Pilot," *SPE Reserv. Eval. Eng.*, vol. 14, no. 02, pp. 182–192, 2011, doi: 10.2118/129877-PA.

[39] Q. Xie, P. Brady, E. Pooryousefy, D. Zhou, Y. Liu, and A. Saeedi, "The low salinity effect at high temperatures," *Fuel*, vol. 200, pp. 419–426, 2017, doi: 10.1016/j.fuel.2017.03.088.

[40] F. Putra, T. Y., & Srisuriyachai, "Combined Effects of Water Formulation and Clay Type in Low Salinity Waterflooding," *Proceeding 1st Int. Conf. Earth Resour. Geo-Environment Technol. (EraGET), 1, 102–107.*, 2022.

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