Effects of Formation Brine Compositions on Low Salinity Waterflooding Using Seawater

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ผลกระทบขององค์ประกอบของน้ำในแหล่งกักเก็บที่มีต่อกระบวนการฉีดอัดน้ำเกลือที่มีความเค็มต่ำโดยใช้น้ำทะเล

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ภายหลังจากกระบวนการผลิตในขั้นปฐมภูมิสิ้นสุดลง จะทำกระบวนการฉีดอัดน้ำเพื่อรักษาความดันของแหล่งกักเก็บและในเวลาเดียวกันไฮโดรคาร์บอนที่หลงเหลืออยู่จะถูกผลิตออกมา จากการศึกษาที่ผ่านมาพบว่า การฉีดอัดน้ำเกลือที่มีความเค็มต่ำสามารถเพิ่มผลผลิตน้ำมันได้ การศึกษานี้เป็นการศึกษาผลขององค์ประกอบของน้ำในแหล่งกักเก็บที่มีต่อกระบวนการฉีดอัดน้ำเกลือที่มีความเค็มต่ำซึ่งในที่นี้คือน้ำทะเล แต่ละองค์ประกอบของน้ำในแหล่งกักเก็บถูกปรับเปลี่ยนตามสัดส่วนต่างๆ โดยมีความเค็มรวม 100,000 ส่วนในล้าน ตัวอย่างหินทรายถูกนำไปวิเคราะห์คุณสมบัติทางกายภาพก่อนทำให้อิ่มตัวด้วยน้ำในแหล่งกักเก็บ เพื่อเปลี่ยนสภาพความเปียกให้เป็นสภาพความเปียกด้วยน้ำมัน หินตัวอย่างที่อิ่มตัวด้วยน้ำจะถูกแทนที่ด้วยน้ำมันที่มีกรดอินทรีย์เป็นส่วนผสม จากนั้นหินตัวอย่างถูกแทนที่ด้วยน้ำทะเลสังเคราะห์ที่มีความเค็ม 35,000 ส่วนในล้าน

จากผลการศึกษาแสดงให้เห็นว่า หากอัตราส่วนของแคลเซียมไอออนต่อแมกนีเซียมไอออนของน้ำในแหล่งกักเก็บเพิ่มขึ้น อัตราการผลิตน้ำมันจะมีค่าเพิ่มขึ้น ทั้งนี้เนื่องจากขนาดของแคลเซียมไอออนที่ใหญ่กว่าแมกนีเซียมไอออน จึงทำให้แรงดึงดูดระหว่างแคลเซียมไอออนกับน้ำมันมีค่าน้อยกว่าเมื่อเทียบกับแรงดึงดูดระหว่างแมกนีเซียมไอออนกับน้ำมัน แต่เมื่อปริมาณแคลเซียมไอออนมีมากเกินไป จะทำให้ปริมาณแคลเซียมไอออนที่หลุดออกจากผิวหินตัวอย่างมีปริมาณมากขึ้นเช่นกัน ส่งผลให้แคลเซียมไอออนดังกล่าวกีดกันการแทนที่ของไอออนประจุเดี่ยวที่เข้าแทนที่ไอออนประจุคู่ที่ตรึงน้ำมันอยู่ ทำให้อัตราการผลิตน้ำมันลดลง เมื่อพิจารณาอัตราส่วนระหว่างโซเดียมไอออนต่อโพแทสเซียมไอออนของน้ำในแหล่งกักเก็บ หากปริมาณโพแทสเซียมไอออนในแหล่งกักเก็บน้อยลง อัตราการแพร่ของโพแทสเซียมไอออนจากน้ำทะเลที่ถูกฉีดอัดจะแพร่ไปยังน้ำในแหล่งกักเก็บและจะเข้าแทนที่ไอออนประจุคู่ที่ตรึงน้ำมันอยู่ ส่งผลให้อัตราการผลิตน้ำมันเพิ่มขึ้น ต่อมาผลของความเค็มของน้ำในแหล่งกักเก็บได้ถูกศึกษาโดยทำการลดความเค็มของน้ำในแหล่งกักเก็บลงให้เหลือ 75,000 และ 50,000 ส่วนในล้านตามลำดับ จากผลการศึกษาพบว่า ยิ่งความแตกต่างระหว่างความเค็มของน้ำในแหล่งกักเก็บกับความเค็มของน้ำทะเลที่ถูกฉีดอัดมีค่ามากขึ้น จะยิ่งส่งผลให้อัตราการผลิตน้ำมันเพิ่มขึ้น ทั้งนี้เนื่องจากผลของความต่างระหว่างความเค็มจะช่วยส่งเสริมให้ไอออนบวกประจุคู่ที่ตรึงน้ำมันอยู่หลุดจากผิวของหินผ่านกระบวนการแพร่และกระบวนการแทนที่ด้วยไอออนบวกประจุเดี่ยวได้ง่ายยิ่งขึ้น ในการทดลองขั้นสุดท้าย ชนิดของน้ำที่ใช้ในการฉีดอัดได้ถูกทำการศึกษา โดยใช้น้ำจากแหล่งกักเก็บลดความเค็มให้เหลือ 50,000 และ 35,000 ส่วนในล้านตามลำดับ จากการศึกษาพบว่า น้ำจากแหล่งกักเก็บที่ความเค็ม 35,000 ส่วนในล้านให้อัตราการผลิตน้ำมันที่สูงกว่า แต่อย่างไรก็ตาม อัตราการผลิตดังกล่าวยังคงน้อยกว่าเมื่อเทียบกับการฉีดอัดด้วยน้ำทะเลที่ความเค็มเดียวกัน ทั้งนี้เนื่องจากในน้ำทะเลมีปริมาณแคลเซียมไอออนที่น้อยกว่า ทำให้ความแตกต่างระหว่าง แคลเซียมไอออนของน้ำในแหล่งกักเก็บและน้ำที่ถูกฉีดอัดมีค่ามาก อีกทั้งในน้ำทะเลมีปริมาณโพแทสเซียมไอออนที่มากกว่า ทำให้การแพร่ของโพแทสเซียมไอออนจากน้ำที่ถูกฉีดอัดไปยังน้ำในแหล่งกักเก็บเกิดขึ้นได้ง่ายกว่า ด้วยเหตุนี้จึงทำให้อัตราการผลิตน้ำมันสูงกว่าเมื่อใช้น้ำทะเลในการฉีดอัด จากที่กล่าวมาข้างต้น ปริมาณแคลเซียมไอออนของน้ำในแหล่งกักเก็บควรมีค่ามาก ในขณะที่ปริมาณโพแทสเซียมไอออนของน้ำในแหล่งกักเก็บควรมีค่าน้อย ซึ่งถือเป็นเงื่อนไขที่เหมาะสมในการเพิ่มผลผลิตน้ำมันโดยวิธีการฉีดอัดด้วยน้ำทะเล

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Water injection is a process to maintain reservoir pressure and at the same time to sweep remaining hydrocarbon in reservoir when forces provided by primary recovery is not adequate. Recent studies concluded that injecting Low Salinity Brine (LSB) could yield additional oil recovery. In this study, effects of ion compositions in formation brine on low salinity seawater injection are emphasized. The composition of formation brine with total salinity of 100,000 ppm is modified in various formulations. First, physical properties of sandstone core samples are measured prior to core saturation process with different formation brines. After that, core samples are altered to oil-wet condition by flushing with organic-acid oil. Sandstone core samples are then displaced by synthetic seawater.

The results show that rate of oil recovery is improved when the ratio of Calcium ion to Magnesium ion is increased. Due to the larger ionic size of Calcium ion compared to Magnesium ion, the ionic strength between oil and Calcium ion is weaker than of with Magnesium ion. However, if Calcium ion is excessive in formation brine, the abundance of Calcium ion will result in high rate of mineral dissolution and this will obstruct the substitution of monovalent ions from injected seawater to divalent ions on sandstone surface, resulting in decreasing of rate of oil recovery. Low Potassium ion concentration in formation brine causes diffusion of Potassium ion from injected seawater back to formation brine, substituting divalent ions between oil and surface and this increases rate of oil recovery. In addition, formation bine concentration is diluted to 75,000 and 50,000 ppm to study effects of total salinity in formation brine. The highest salinity contrast between formation and injected brines favors dissolution of bridging divalent ion through MIE mechanism and this yields the highest oil recovery factor. Lastly, when comparing seawater and diluted formation brine, the result shows that seawater yields more benefits in terms of higher oil recovery factor and rate of oil recovery than using diluted formation brine. This can be concluded that impoverishment in Calcium ion and enrichment in Potassium ion in seawater is recommended condition for injected fluid. Consequently, high amount of Calcium ion and low amount of Potassium ion in formation brine are considered as favorable conditions for seawater injection.

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Abbreviation

bbl/day	Barrel per day
C or ^{o}C	Degree Celsius
Ca^{2+}	Calcium ion
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CEC	Cation Exchange Capacity
Cl^{-}	Chloride ion
cP	Centipoise
cSt	Centistroke
DLE	Double Layer Expansion
EOR	Enhanced Oil Recovery
F or ^{o}F	Degree Fahrenheit
ft^3/bbl	Cubic feet per barrel
g	Gram
gmol	Gram mole
GOR	Gas-Oil Ratio
H^{+}	Hydrogen ion
HCO_3^{-}	Hydrogen carbonate ion
IWS	Irreducible Water Saturation
K^{+}	Potassium ion
KCl	Potassium chloride
LSW	Low Salinity Waterflooding
mD	Millidarcy
Mg^{2+}	Magnesium ion
$MgCl_2$	Magnesium chloride

MIE	Multi-Component Ionic Exchange
MW	Molecular Weight
Na^+	Sodium ion
NaCl	Sodium chloride
$NaHCO_3$	Sodium hydrogencarbonate
Na_2SO_4	Sodium sulphate
OH^-	Hydroxide ion
OOIP	Original Oil In Place
pH	Potential hydrogen
psia	Pound per square inch absolute
ppm	Part per million
PV	Pore Volume
RF	Recovery Factor
ROS	Residual Oil Saturation
TDS	Total Dissolved Solid

Nomenclature

μ_0	Oil viscosity
μ_w	Water viscosity
ρ	Density
ϕ	Porosity
θ	Contact angle
γ_{so}	Interfacial tension term for surface-oil
γ_{sw}	Interfacial tension term for surface-water
γ_{ow}	Interfacial tension term for oil-water
k_a	Absolute permeability
k_{ro}	Relative permeability to oil
k_{rw}	Relative permeability to water
S_w	Water saturation
S_{wi}	Initial water saturation
S_{oi}	Initial oil saturation
S_{or}	Residual oil saturation
V	Volume

CHAPTER I

INTRODUCTION

1.1 Background

The recovery of oil by natural drive mechanisms so-called primary recovery is generally declined with time due to depletion of natural reservoir energy. It is therefore necessary to provide additional energy to reservoir system to boost up or maintain production level through the application of secondary oil recovery methods. Waterflooding has been known as the most widely used secondary oil recovery method. This technique is implemented by injecting adequate amount of water into injection well to displace movable or displaceable oil toward production well. However, not all the reservoirs can obtain benefit from waterflooding. In general, waterflooding would yield benefit to those reservoirs containing light to medium oils which are displaceable by water. Availability and inexpensiveness of water are considered as major benefits of this technique. Moreover, waterflooding involves relatively lower capital investment as well as operating costs compared to other techniques. Nevertheless, under favorable rock and fluid properties, current technology, and economics, only 20 - 40 percent of Original Oil in Place (OOIP) is typically produced by means of waterflooding.

In recent years, researchers concern more on effects obtained from controlling salinity and composition of injected water. This technique is widely known as Low Salinity Waterflooding (LSW). Modification of the water composition has shown to be an excellent way to increase oil recovery in both sandstone and carbonate reservoirs. The mechanisms associated to this process are still indistinct. Several investigators have proposed oil recovery mechanisms with reliable evidences such as fine migration that alters displacement flow path, reduction of Interfacial Tension from in-situ saponification of acid compounds as a result from increment of pH value, and wettability alteration in sandstone when salinity or Total Solid

Dissolved (TSD) in injected water is reduced. However, recent literatures believe that wettability alteration is the most reliable reason among all mechanisms.

In sandstone reservoir, rock surface is first in contact with formation brine, resulting in water-wet condition after oil migration process. Due to presence of divalent cations in formation brine, sandstone surface can be altered to a more oil-wet condition from ion binding between negative charge of sandstone surface and positive charge of carboxylic acid group in oil. Many LSW studies are concluded that when low salinity brine is injected into formation, Multi-component Ion Exchanged (MIE) occurs. During the MIE mechanism, monovalent cations in injected brine tend to substitute divalent cations forming bridging between sandstone surface and oil layer. Oil which is absorbed onto rock surface through bridging ions is therefore liberated after this substitution and surface returns to a more water-wet condition, leading to improving of oil [2].

Moreover, wettability alteration may be favored by Double-Layer Expansion (DLE). In the DLE, injection of low salinity brine increases electrostatic repulsion between film of formation brine/oil and formation brine/rock interfaces, resulting in expansion of two electrical double layers. Consequently, this film becomes thicker and more stable, resulting in weakening interaction between adsorbed materials and sandstone surface. Eventually, this leads to rupture of adsorbed layer, yielding surface a more water-wet condition [3].

From several previous LSW studies, one of the most dominant factors controlling the effectiveness of LSW is formation brine. Formation brine properties and composition depend on a number of parameters, including depositional environment, mineralogy of the formation, its pressure and temperature history and the influx or migration of fluids. Consequently, all of reservoirs in sub-surface have different properties and composition in formation brine.

In this study, modification of composition of formation brine is performed and sandstone samples saturated with different formation brines are experimented in coreflooding apparatus. This study emphasizes on effect of ion concentration in formation brine on changing of petrophysical properties that eventually affect ultimate oil recovery. Results from this study will be useful as a guideline for implementation of LSW especially in selecting candidate field that would yield great benefit from LSW when injected brines are limitation of the process.

1.2 Objective

1. To study the effects of ion compositions in formation brine on effectiveness of low salinity waterflooding for different available injected brines.
2. To provide initial guideline for selecting candidate field for low salinity waterflooding based on formation brine of the field when different injected waters are available.

1.3 Outline of Methodology

1. Gather chemical analysis of formation brine from candidate sandstone reservoirs located in offshore around the globe.
2. Prepare formation brine solution at concentration of 100,000 ppm in various ratios of divalent ions which are Calcium ion (Ca^{2+}) and Magnesium ion (Mg^{2+}) and monovalent ions including Sodium ion (Na^{+}) and Potassium ion (K^{+}).
3. Prepare injected brine to simulate composition of seawater with total salinity 35,000 ppm.
4. Determine basic rock properties including effective porosity and absolute permeability and petrophysical properties including irreducible water saturation and residual oil saturation of core samples.
5. Perform high salinity waterflooding by using formation brine as injected brine (equal salinity of 100,000 ppm)
6. Perform low salinity waterflooding to study the following effects;
    - Effect of cation type in formation brine by using seawater as injected brine.
    - Effect of total salinity of formation brine by using seawater as injected brine.
    - Effects from using diluted formation brine as injected brine.
7. Results from different formation brine compositions and injected brine systems are discussed to express suitable conditions for low salinity water injection in different cases with different injected brine.

1.4 Outline of Thesis

This thesis is divided into six chapters as shown in outline following

Chapter I, this chapter introduces the background of low salinity waterflooding process and indicates the objectives and outline methodology of this study.

Chapter II, this chapter, various literatures related to the study of low salinity waterflooding are compiled in this chapter including proposed low salinity mechanism and evidences of ion exchange affecting effectiveness of low salinity waterflooding.

Chapter III reviews the concept of conventional waterflooding, low salinity water injection, wettability, and also effects affecting the performance of low salinity water injection.

Chapter IV provides the details of methodology and experiment. This chapter starts with the detailed methodology. Then, details of formation brine preparation, injected brine preparation, core samples preparation and their petrophysical properties, oil preparation, experiment setup, and experimental study are revealed.

Chapter V presents results and discussions from laboratory experiments for each study. The results are mainly investigated on rate of oil recovery and oil recovery factor.

Chapter VI provides conclusions and recommendations.

CHAPTER II

LITERATURE REVIEW

This chapter summarizes previous studies related to low salinity waterflooding in the past decades. These include the proposed low salinity mechanisms and evidences of ion exchange that affects effectiveness of low salinity waterflooding.

2.1 Study of Low Salinity Waterflooding

During the past decade, low salinity brine injection has been given a great attention as a new tertiary oil recovery method. The first observation of effects from injecting low salinity water on oil recovery was published in early 1976.

Bernard [4] observed an increase of oil recovery when lowering concentration of Sodium Chloride (NaCl) content in the injection brine in 1967. The outcrop sandstone cores were flooded with fresh water and brine solutions with different concentrations of NaCl, and with a reduction of concentration of NaCl from 1 to 0.1%. Increase of oil recovery was observed. It was discovered that increment of oil recovery was dependent from salinity ranging from zero to 0.1% of NaCl.

In 2007, Zhang et al. [5] studied performance of brine injection with different water salinities and oil properties. Two consolidated reservoir cores and two synthetic brines with salinity of 29,690 and 1,480 ppm respectively were used in this study. Investigators observed that oil recoveries were increased approximately 3.8-16.5% of OOIP after injection of low salinity brine in tertiary mode. In addition, injection of low salinity brine also increased recovery of 29.2% of OOIP compared to high salinity brine.

In 2009, Boussour et al. [6] proposed unsuitable condition for low salinity waterflooding. In their work, waterflood experiments were performed on cores from unconsolidated formation. The results showed that there was no additional production after injection low salinity brines. Therefore, they concluded that the negative result of low salinity waterflooding was obtained from unconsolidated formation.

2.2 Proposed Oil Recovery Mechanism by Low Salinity Water

In most laboratory experiments, low salinity water injection leads to an increase of oil recovery. There are several promising data from the field that indicate positive effects. Several oil recovery mechanisms have been proposed over years based on observations from experiments. However, oil recovery mechanisms of low salinity brine injection are still uncertain. The most mentioned oil recovery mechanisms by means of low salinity water are summarized below.

2.2.1 Fines Migration

Tang and Morrow [2] proposed oil recovery mechanism from low salinity brine based on migration of clay fragments or fines in 1999. The experiments were performed on outcrop cores which are Berea with high clay content and Bentheimer with low clay content. Their results showed that there was a relationship between amount of clay present in the cores, fines migration and amount of oil recovered by means of low salinity water injection. Almost clay-free sandstone cores showed smaller increment in oil recovery with decreasing of salinity than sandstone core samples containing high clay content. They explained that when the salinity of the brine is reduced, the double layer between the individual clay particles expand, and the initial stabilized flocculated state of the clay particles in presence of high salinity is disturbed, and as a result fines migration takes place.

But more important is the suggested case two, where release of clay particles can block pore throats and divert the flow of water into new un-swept regions, and thereby improve the sweep efficiency. Increased oil recovery due to this technique was proposed by Martin in 1959 [7] and Bernard in 1967 [4]. They also explained log-jamming or bridging process which is the blocking process of pore throat entry by colloids in solution to be an important EOR contribution, by giving both microscopic diversion flow and sweep improvement.

They explained the increased recovery related to acceleration of particles which will be slower than water due to differences in their mass, thereby when the particles reach the pore throat water has already swept the pore throat the particles will start blocking. Figure 2.1 illustrates the log-jamming process at pore throat entry.

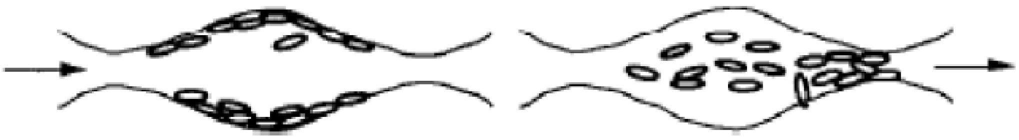


Figure 2.1 Reduction of salinity in injected brine causes release of clays from pore walls, resulting in blocking of pore throat entry, a process is so-called log-jamming [8]

However, in 2011 Soraya et al. [6] performed low salinity waterflooding on a sandstone cores and their results showed that there was no increment in production of oil, despite a significant amount of fines production. Thus, these observations questioned relationship between oil recovery and fines migration.

In 2010, Austad [11] proposed oil recovery mechanisms on clay surface by means of low salinity waterflodding. In this study, investigators explained that clay surface acts as a cation exchanger. Initially, both basic and acidic organic materials are adsorbed onto clay surface together with inorganic cations, especially Calcium ions from formation brine. Chemical equilibrium is then established at actual reservoir conditions regarding pH, temperature, and pressure. When low salinity water is injected into reservoir with much lower ion concentration than that of initial formation brine, the equilibrium associated with brine–rock interaction is disturbed. To compensate loss of cations, protons (H^+) from water adjacent to clay surface is instead adsorbed and substitution of Ca^{2+} by H^+ takes place. This creates local increment of pH value close to clay surface as illustrated by following equation using Ca^{2+} as an example:

$$\text{Clay-Ca}^{2+} + H_2O \rightarrow \text{Clay-H}^{+} + Ca^{2+} + OH^{-} \qquad (2.1)$$

Local increase of pH value close to clay surface causes reactions between adsorbed basic and acidic materials as in an ordinary acid-base proton transferring reaction, as shown by equations 2 and 3.

$$\text{Clay-NHR}_3^{+} + OH^{-} \rightarrow \text{Clay} + R_3N + H_2O \qquad (2.2)$$

$$\text{Clay-RCOOH} + OH^{-} \rightarrow \text{Clay} + RCOO^{-} + H_2O \qquad (2.3)$$

After these above mentioned chemical equations occurred, oil is liberated from rock surface and wettability of rock surface is altered toward water-wet condition and oil recovery is therefore increased. This mechanism is schematically illustrated in Figure 2.2 for adsorbed basic and acidic materials.

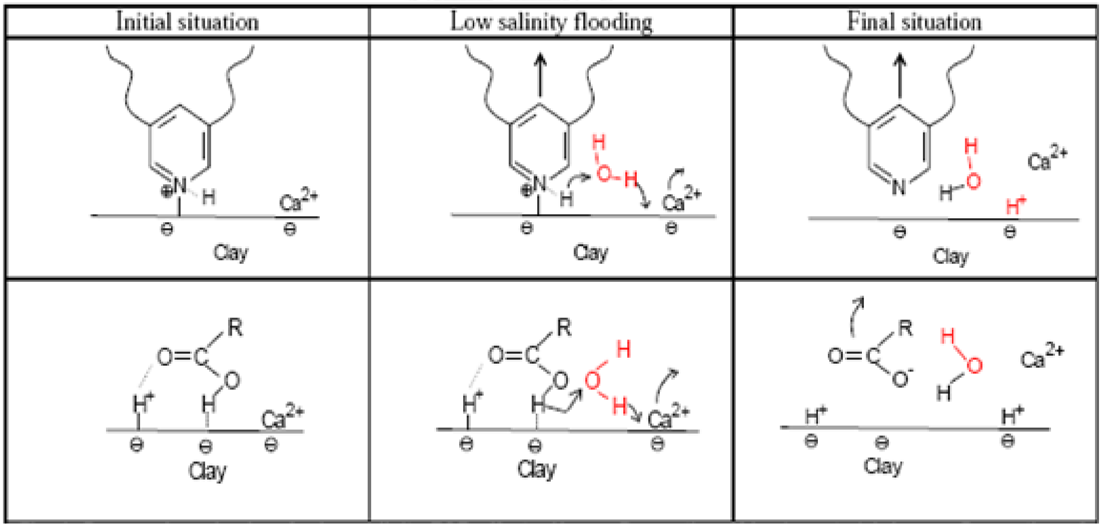


Figure 2.2 Proposed oil mechanism from low salinity water. Upper: Desorption of basic material. Lower: Desorption of acidic material [11]

2.2.2 Multi-component Ion Exchange (MIE)

In 2008, Lager et al. [12] proposed that cation exchange between rock surface and low salinity brine was a primary mechanism in increasing of oil recovery when using low salinity water. Reduction of ion concentration in brine phase changes equilibrium of rock surface and fluid. When monovalent ions from injected low saline brine substitute divalent ions linking between rock surface and organic material, adsorbed organic material is liberated and then, rock surface is altered to a more water-wet condition. This mechanism was termed later as Multi-component Ion Exchange (MIE). Figure 2.3 illustrates stages prior and after the occurrence of multi-component ion exchange.

Figure 2.3 Illustration of multi-component ion exchange of sandstone surface covered by adsorbed oil through cation binding layer [13]

2.2.3 Double Layer Expansion (DLE)

In 2015, Myint and Firoozabadi [3] reviewed recent studies on wettability alteration mechanisms that affect interactions between brine-oil and brine-rock interfaces of thin brine films wetting surface of reservoir rocks. Investigators concluded that effects of low salinity waterflooding are resulted from combination of more than one mechanism. From this study, they focused on mechanisms which change stability of thin brine films wetting surface of oil reservoir rocks and they called this mechanism as "Double-Layer Expansion" (DLE). In DLE, injecting low salinity brine causes an increase in electrostatic repulsion between brine-oil film and brine-rock film, resulting in an expansion of two electrical double layers.

Consequently, the film becomes thicker and more stable, resulting in a more water-wet condition. Steps occurred during the DLE are summarized in Figure 2.4.

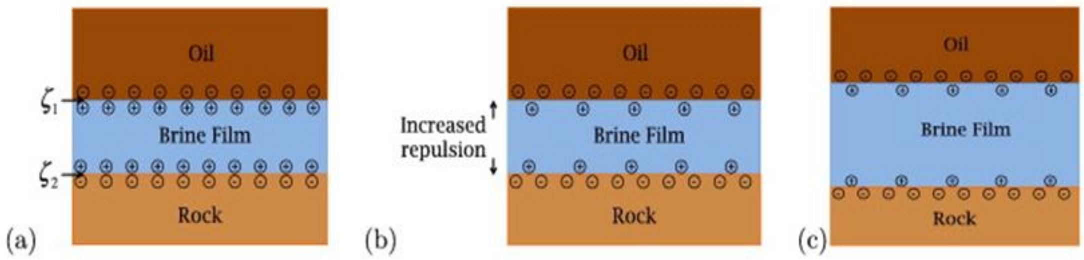


Figure 2.4 Effect of low salinity water injection on thin brine film (a) before injection of low salinity, (b) when salinity is decreased, screening from counter ions becomes weaker, (c) DLE appears as a thicker brine film, indicating a more water-wet condition [3]

Nowadays, there is still no definite agreement on which mechanism is dominant in improving oil recovery by means of low salinity waterflooding. However, effects of both double-layer expansion together with multi-component ionic exchange are the most mentioned and accepted hypothetical mechanisms for wettability alteration towards a more water-wet condition [14].

2.3 Evidences of Ion Exchange Affecting Effectiveness of Low Salinity Waterflooding

2.3.1 Effect of Ion Exchange through MIE Mechanism

In 2013, Srisuriyachai and Muchalintamolee [13] performed an experiment to study effects of cation interference in low salinity water injection in sandstone formation. Sandstone core samples were prepared and displaced by injected brines with different formulations. They observed that lowering salinity of injected brine resulted in higher values of displacement by water ratio. This result could be explained that higher difference between formation brine and injected brined helps promoting dissolution mechanism of bridging divalent ion through MIE. Moreover, concentration of calcium ion in injected brine should be kept at low value and ratio of calcium ion and magnesium ion has to be adequate for uninhibited dissolution mechanism by magnesium ion. In contrast, higher amount of sodium ion in injected brine can promote MIE mechanism as sodium ion is a monovalent ion that can substitute divalent ions once MIE occurs.

2.3.2 Effect of Cation type on Effectiveness of Low Salinity Brine Injection

In 2011, Nasralla [15] studied effect of cation type and cation concentration in injected water to identify optimum salinity in 2011. Berea sandstone cores were used to perform waterflooding and cation exchange experiments. Three concentrations of Sodium Chloride (NaCl), Calcium Chloride ($CaCl_2$), and Magnesium Chloride ($MgCl_2$) were tested with two crude oil properties. Zeta potential data showed that NaCl changes electrical charge at both oil-brine and rock-brine interface to highly negative value, resulting in repulsion forces between two interfaces. This eventually resulted in the highest degree of wettability alteration. Coreflood experiment showed that injecting NaCl brine yields the highest oil recovery, followed by $MgCl_2$ and $CaCl_2$ brines respectively. Moreover, decreasing concentration of single cation did not affect oil recovery. Therefore, cation seems to be a more dominant effect than total salinity.

CHAPTER III

THEORY

This chapter reviews the concept of conventional waterflooding, low salinity waterflooding, fundamentals of wettability, and also factors affecting performance of low salinity waterflooding.

3.1 Conventional Waterflooding

Waterflooding has been the most widely used secondary oil recovery technique. By using waterflooding, reservoir pressure is maintained and oil production is re-accelerated when water physically displaces oil from reservoir [16]. Performance of a waterflooding process is typically affected from the following parameters:

- Reservoir geology and geometry,
- Physical properties: porosity, permeability, heterogeneity,
- Fluid properties: viscosity, mobility ratio,
- Mineralogical properties: Clay type and amount,
- Presence of various chemicals.

However, potential of waterflooding in oil recovery is limited in certain cases such as formation with oil-wet surface. It is common that amount of oil recovered in oil-wet reservoir is a direct function of amount of injected water. Therefore, high amount of water is produced to recovery more oil. Several Enhanced Oil Recovery (EOR) techniques are then developed to alter rock and fluid interactions. However, EOR is also known as a very sensitive technique especially for reservoir containing high salinity of divalent ions that could precipitate injected chemical (surfactant and polymer). Moreover, EOR is also one of the most expensive techniques. A technique involving changing of surface chemistry without additional chemical is therefore investigated. Low salinity waterflooding is therefore emphasized since this technique exploits the difference of salinity of formation and injected brines to create new surface equilibrium that eventually results in additional recovery of oil.

3.2 Low Salinity Waterflooding

In recent year, modification of injected water composition has shown to be an excellent method to increase oil recovery in both sandstone and carbonate formations. Comparing to other tertiary recovery methods available for sandstone reservoirs, low salinity waterflooding is considered as one of the cheapest technique and it is also environmentally friendly approach as there is no foreign chemical added into the injected water. Low salinity waterflooding was first discovered in the late 1950’s when fresh water was injected to increase oil recovery and displace viscous oil [7]. After that, Bernard [4] continued the investigation of low salinity brine in 1967.

Salinity is defined as a content of Total Dissolved Solids (TDS) suspended in water which are usually mineral salts. It is usually expressed in the unit of part per million (ppm) or mg/L. According to the US Geological Survey, saline water can be categorized into three types which are slightly saline water (1,000-3,000 ppm), moderately saline water (3,000-10,000 ppm), and highly saline water (10,000 – 35,000 ppm). Normally, the average salinity of seawater is around 35,000 ppm. Since benefit of low salinity brine has been observed, dilution and/or modification of seawater or produced water which are major sources of injected water is considered to be used in this oil recovery technique.

3.3 Wettability

3.3.1 General Aspects

Wettability is defined as the tendency of a fluid to adhere to, or spread onto, a rock surface. Forces of wetting influence hydrocarbon reservoir behavior in many ways, including saturation, multiphase flow and certain log interpretation parameters. When two fluids are present near a surface at the same time, the preferentially wetting fluid will displace the other fluid at the surface, and in the most extreme case, spread over it entirely. When it comes to hydrocarbon reservoirs, one often talks about reservoirs as being either water-wet or oil-wet. If the wetting conditions are neither strongly oil-wet nor strongly water-wet, the balance of forces in the system will result in a contact angle, θ, between the fluids and the solid surface as shown in Figure 3.1. On the left, an oil drop on a strongly water-wet surface will form a bead and the contact angle is approximately zero. An intermediate-wet surface, depicted in the center, also forms a bead, but the contact angle comes from the force balance between the interfacial tension terms, which are γ_{so} and γ_{sw} for the surface-oil and surface-water terms, respectively, and γ_{ow} for the oil-water term. On the right, the same oil drop will spread on a strongly oil-wet surface and the contact angle becomes close to 180° [17].

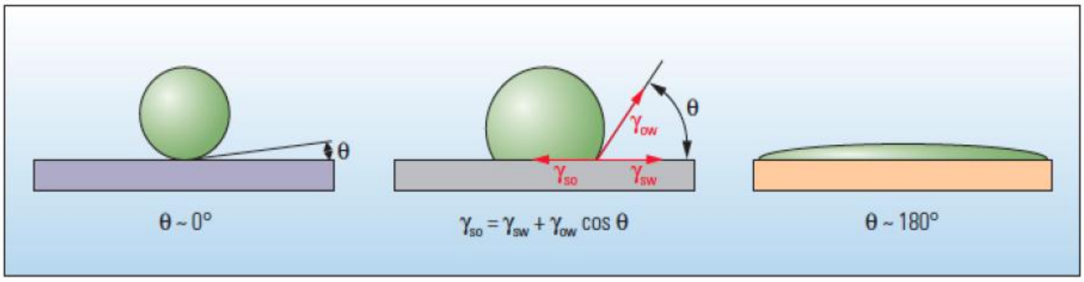


Figure 3.1 Contact angle for an oil drop on a different wettability surface [17]

It is common to confuse the terms intermediate wettability and mixed wettability, and to think that they are the same. An intermediate-wet rock does not have a strong preference for one or another fluid, while mixed wettability means that the rock has a variety of preferences, which may also include intermediate wetting. In a mixed-wet rock, the preference for either oil or water (or gas) can be varied from pore to pore, depending on saturation history. Understanding the complexity of the wettability term and how it plays a role in oil recovery, is important in order to maximize recovery. Figure 3.2 shows how the different wetting state distributes the fluids in the pore system.

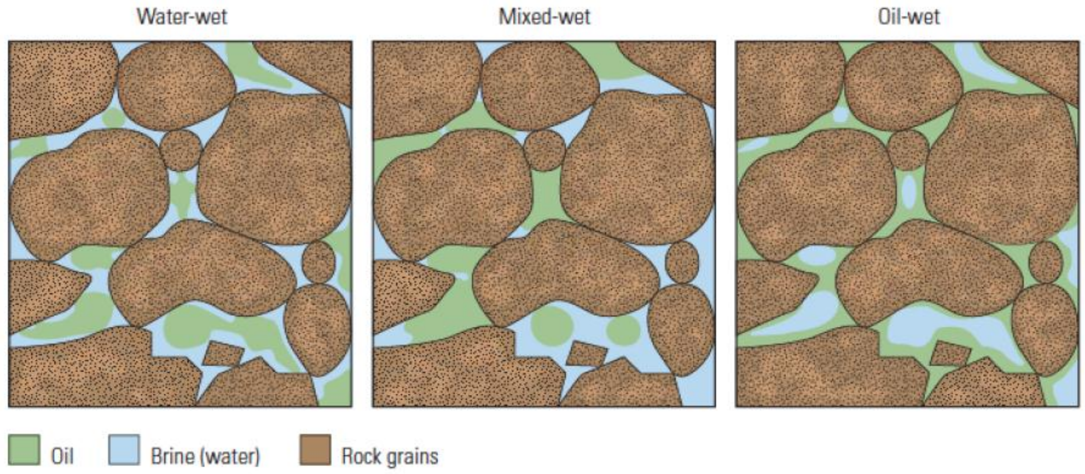


Figure 3.2 Different wetting conditions and their fluid distributions [17]

The wettability state of a reservoir can have a great impact on both oil recovery and field economics, especially in sandstone reservoirs under waterflooding. The wettability dictates how the fluids are distributed throughout the pore system. In a water-wet reservoir, pore walls are coated by water, and capillary forces between the oil and water prevents the oil from entering the smaller pores. The oil is therefore usually contained in larger pores. Initially, both oil and water phases are continuous along the flow paths, but after the start of production, the oil may eventually snap off and become trapped inside the pores. This can lead to high residual oil saturation. However, when implementing waterflooding to maintain reservoir pressure, water breakthrough occurs late and most of the oil is produced before the breakthrough, which has its economical advantages. Factors associated with oil-wet reservoirs are early water breakthrough accompanied by high water cuts and a long tail production, which is not desirable. Even though the residual oil saturation is usually lower in oil wet reservoirs due to the oil film on the surface creating a continuous oil phase, more money is made by producing the oil at an earlier time.

3.3.2 Wettability Alteration

Historically, porous media of reservoirs have been considered of being originally water-wet. The most common minerals present in reservoirs - quartz, calcite and dolomite - are originally covered by water prior to oil migration and it has tendency to become more water-wet. When oil migrates into a fully water saturated formation, the saturation history changes. Surface wetting condition is influenced by saturation history, system temperature and pressure, which leads to an equilibrium condition between the three substances: solid, brine and oil. Oil composition is a major cause of changing original water-wet surface towards more oil-wet. Polar components in crude oil, especially in the heavy asphaltene and resin fractions, can be adsorbed onto mineral surfaces and consecutively alter wetting properties. Bukley et al. [19] studied the mechanisms of wetting alteration by crude oils through experimental observations of contact angles between pure fluids on surfaces after exposure to crude oil. The main categories of crude oil-brine-rock interactions identified in that study were:

- Polar interactions that predominate in the absence of a water film between oil and solid,
- Surface precipitation, mainly dependent on crude oil solvent properties with respect to asphaltenes,
- Acid/base interactions that control surface charge at oil-water and solid-water interfaces, and
- Ion binding or specific interactions between charged sites and higher valence ions.

For a given oil or solid surface, surface charge depends on the extent of acid/base dissociation reactions which in turn depends on the pH at the surface [20].

A variety of forces, including van der Waals, electrostatic, and structural or solvation interactions, are acting on the solid-brine and oil-brine interfaces. The net force is often expressed as a force per unit area, termed the disjoining pressure [15]. A positive disjoining pressure will keep the interfaces apart, while a negative disjoining pressure will attract the interfaces. When the charges at the two interfaces are the same, repulsive forces will stabilize the water film and crude oil components are not able to adsorb at the solid surface. The presence of dissolved divalent cations, such as Ca^{2+} and Mg^{2+}, may also contribute to destabilization of the water film through ion binding as shown in Figure 3.3.

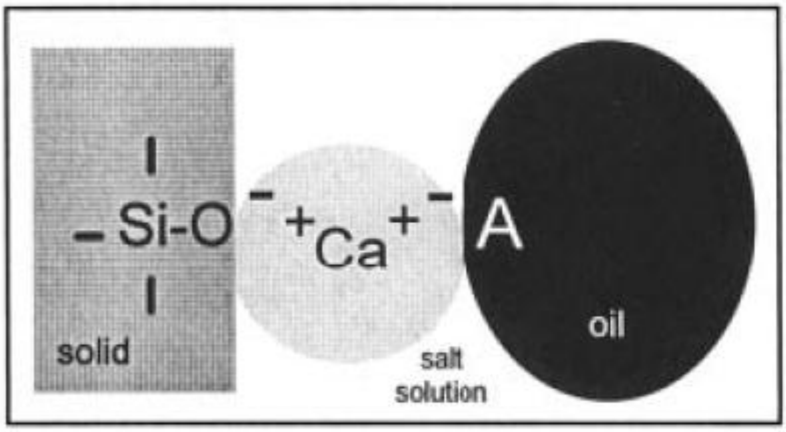


Figure 3.3 Ion-binding interactions between crude oil components and solid surface [19]

3.4 Factors Affecting Low Salinity Waterflooding

3.4.1 Mineral Surface

Several researchers have reported that types of clay mineral affect effectiveness of low salinity waterflooding in sandstone cores. Experiments performed on clay-free cores, which were fired at 800 °C and acidized to remove clay mineral, did not show any response to low salinity water [2]. Researchers have observed an increase of oil recovery from low salinity waterflooding on cores containing different clays, such as kaolinite, illite, muscovite and chlorite [21]. He presence of chlorite has been related to poor results of low salinity waterflooding by researching on Berea sandstone cores [5]. Austad et.al. [11] also stated that because of its low Cation Exchange Capacity (CEC), kaolinite may be one of the least advantageous clay types. In addition, sandstone cores without clay, but with a content of dolomite crystals have shown positive results from injection of low salinity water. Behind these observations, surface charge is one reason responsible for all the explanation. Positive results from injecting low salinity water would come from situation where oil recovery mechanism can be completed. In case of sandstone formation, the point of zero charge of silica is around 2.5. That means, at the reservoir conditions where pH value ranges around 6-8, the surface will possess negative charges. The sandstone surface therefore can simply turn to oil-wet condition through ion binding with Calcium and Magnesium ions in brine and carboxylic acid in oil. This condition creates oil-wet sandstone surface that can be affected from low salinity waterflooding as breaking of bridging ion due to changing of surface equilibrium would results in liberation of oil as well as increase of oil recovery.

For carbonate surface, point of zero charge is much higher and this causes surface to become positively charge at normal reservoir condition. Hence, adsorption of carboxylic acid does not occur through ion binding but it is a direct interaction of polar compound. This causes oil recovery mechanism by means of low salinity waterflooding to be different from sandstone formation.

3.4.2 Component in Oil

From experiments with refined oil, no extra oil recovery was observed by adjusting salinity of the injection brine. In 1999, Tang et.al. [2] reported that polar components in oil are necessary requirement for improved oil recovery by means of low salinity waterflooding as the use of refined oil without polar components did not show any response to low salinity water injection. As explained in previous section, a proper sandstone surface would be affected from low salinity waterflooding. Without polar compounds such as carboxylic acid, sandstone surface will not change its wetting condition toward oil-wet and complex surface structure will not be formed. Nevertheless, basic compounds in oil will adsorption directly on sandstone surface and this result in very strong interaction. Certain studies have concluded that presence of organic base compounds in oil phase causes ineffectiveness of low salinity waterflooding due to lacking of complex surface structure that favors oil recovery mechanisms.

3.4.3 Injected Water

Injected water is considered to be one of the most important factors in low salinity waterflooding. As this parameter is controllable, effectiveness of the process can be controlled. Usually, seawater is a typical source of water in conventional waterflooding project in offshore field. If formation water contains much higher salinity than that of seawater, high effectiveness of low salinity waterflooding would be obtained. Several studies suggested that reducing water salinity in injected brine has been demonstrated to be a very effective way to recover more oil. Successful corefelooding experiments showed an increase in oil recovery of 5-20% when water salinity is lower than 5,000 ppm. Nevertheless, highly reduction of salinity in injected brine could also provoke clay problems since certain clays associated in pore space can be very sensitive to changing of water salinity. Clay control program should be concerned.

Not only total salinity of injected brine plays an important role in controlling effectiveness of low salinity waterflooding process, ion composition of injected brine might be as important as total salinity. In certain conditions, total salinity of injected brined cannot be further reduced. Modification of potential determining ions would turn the process positive results without great reduction of total salinity of injected brine. Evidence of importance of ion composition is reported in the study of Srisuriyachai and Muchalintamolee [13]. From their work, it is concluded that concentration of Calcium ion injected brine should be kept as low as possible while total salinity can still be maintained constant.

3.4.4 Formation Water

Formation water is water that firstly occupies pore space of sedimentary rock and is free to move under appropriate hydrodynamic conditions [22]. If the formation water is the same water that was included in pore spaces at the time of deposition, it is known as connate water [23]. All formation waters generally contain soluble salts at certain degree but variation of salt concentration and nature of these dissolved salts is considerable. The word "brine" is commonly used to describe any water containing dissolved salts, however Carpenter [23] set out a classification scheme which easily applied to formation waters. It is required that a brine must contain over 100,000 mg/L total dissolved salts, water containing between 10,000 and 100,000 mg/L dissolved salts is termed saline water, and any water containing less than 10,000 mg/L of dissolved salts is fresh water or brackish. By these definitions, seawater with average salinity of 35,000 mg/L is saline water, but not brine.

Properties of formation water and composition depend on a number of parameters, including depositional environment, mineralogy of formation, pressure and temperature history and influx or migration of fluids. Consequently, all of reservoirs in sub-surface conditions possess different properties and composition in formation brine.

Although there is significant variation in nature of formation waters globally, there is a tendency of property that fits for all formation waters. For example, formation waters are commonly enriched in Calcium ion (Ca^{2+}) and Chloride ion (Cl^-) and impoverished in Sodium ion (Na^+), Sulfate ion (SO_4^{2-}) and Potassium ion (K^+) related to seawater [22]. The overall concentration of the major ions which are Na^+, Ca^{2+}, Cl^- etc. in brine tends to increase with [22]. The following sections describe properties of typical formation waters.

Chloride is the predominant anion in oilfield brines [23], making up to 95% by mass of total anions in most sedimentary formation waters that have total salinities greater than 10,000mg/L. Water with salinity less than 10,000 mg/L may contain bicarbonate ion, sulfate ion or acetate ion as dominant anions. Most oilfield waters contain more sodium ion by weight than other cations. During evaporation, overall sodium content of brines increases together with total salinity until halite starts to precipitate at approximately 300,000 mg/L. Potassium exists as another major cation component in many reservoir fluids and though present only in very small quantities. It can be even said that potassium is a trace element. It forms only 160 ppm (0.16%) of the bulk Earth. However, it is an important constituent of K-feldspar and mica and these are among the main components of granite. Then, potassium is abundant in granite formation. Lithium is also a common constituent of formation water. In waters with salinities higher than 300,000 mg/L, removal of Sodium ion through halite precipitation results in enrichment of Calcium ion and this could turn Calcium ion to become dominant cation by mass. For example, in most formation brines from Gulf of Mexico are with this property. The highest relative concentration of Magnesium ion is found in seawater but, in unusual oxidizing conditions, Magnesium ion can be important in waters interacting with mafic rocks containing ferromagnesian minerals as well as marine mud. Strontium and Barium are also commonly found in formation waters, though generally subordinate to Calcium and Magnesium ions. Although only a trace component in seawater, silica can reach level of 10s to 100s ppm in formation waters. Moreover, formation waters typically also contain detectable amounts of transition metals, in particular lead, zinc iron and copper.

According to several compositions of formation brine, it is considered as one of the key factors which can significantly affect the effectiveness of low salinity waterflooding process. Composition of formation brine from oil field around the globe is summarized in Tables 3.1 and 3.2.

Table 3.1 Composition of formation water in milligrams per liter (mg/L) from oil fields around the globe compared to composition of seawater [22, 23]

Ion component (mg/L)	Seawater	Miller, North Sea	Statfjord, North Sea	Thames, North Sea	Mahakam Basin, Indonesia	Central Missisippi	Gulf of Mexico, Offshore Louisiana
Li^+	0.170	x	x	x	x	63	2.3
Na^+	10,760	28,800	8,165	70,360	2,328.9	66,700	29,600
K^+	399	1,820	121	9,020	43.1	7,860	144
Mg^{2+}	1,290	115	68	3,560	86	2,840	620
Ca^{2+}	411	1,060	1,050	10,860	131.5	47,200	2,080
Sr^{2+}	8.1	110	x	390	x	2,190	49
Ba^{2+}	0.021	1,030	41	x	x	80	33
Fe ion	0.034	10	x	160	x	414	8.6
Zn ion	0.005	x	x	x	x	19	0.06
Silica	3	32	x	x	0.058	45	51
Cl^-	19,350	47,680	14,286	145,630	2,816.8	207,400	48,250
SO_4^{2-}	2,700	7	29	1,500	190.3	36	21
HCO_3^-	142	2,070	360	70	2,934.7	x	226
pH	7.5	6.7	6.18	5.73	6.44	x	x
Major rock type		Sandstone	Sandstone and Carbonate	Sandstone and Carbonate	Channel sandstone	Sandstone	Sandstone and salt

x : Not analyze

Table 3.2 Composition of formation water in moles from oil fields around the globe [24]

Ion component (mole)	Alberta Younger, Canada	Alberta Older, Canada	Offshore Angola, North of Launda	Azerbaijan	Central Mississippi	Columbia	Mahakam Basin, Indonesia
Li^+	0.0032	0.0053	x	x	x	x	x
Na^+	1.4	1.6	2.1	2.9	2.6	0.087	0.22
K^+	0.026	0.049	0.0085	0.0023	0.23	0.00085	0.0014
Mg^{2+}	0.077	0.076	0.032	0.00029	0.16	0.00024	0.0025
Ca^{2+}	0.12	0.16	0.18	0.00084	0.99	0.01	0.0025
Sr^{2+}	0.0021	0.0024	0.0042	0.000041	0.019	0.00036	x
Ba^{2+}	0.00056	0.0000082	0.0000077	0.0000022	0.00063	0.00014	x
Fe ion	0.000005	0.0000048	0.00019	0.000091	0.0023	x	x
Mn ion	0.000002	0.0000035	x	x	0.00019	x	x
Zn ion	x	x	x	0.000031	0.0001	x	x
Cl^-	1.8	1.9	2.5	0.24	5.2	0.1	0.16
Br^-	0.0032	0.0044	x	0.00055	0.034	x	x
SO_4^{2-}	0.012	0.011	0.00013	0.000078	x	0.00014	0.00004
HCO_3^-	x	x	0.0057	0.049	x	0.0052	0.079
pH	7.7	6.1	6.1	7.8	x	8.3	7.0
Major rock type	Carbonate with some sandstone	Carbonate with some sandstone	Lacustrine, turbiditic sediments	Immature Sandstone	Sandstone	Sandstone	Sandstone

Table 3. 3 Composition of formation water in moles from oil fields around the globe (continued) [24]

Ion component (mole)	Offshore Gulf of Mexico Field 1	Offshore Gulf of Mexico Field 2	Offshore Gulf of Mexico Field 3	Offshore Gulf of Mexico-Louisiana	Offshore Gulf of Mexico-Texas	San Juan Basin , Colorado/ New Mexico
Li^+	0.00039	0.0026	x	0.0005	x	x
Na^+	5.3	3.1	0.59	1.3	1.4	0.11
K^+	0.017	0.031	0.0033	0.0047	0.016	0.0002
Mg^{2+}	0.11	0.036	0.0011	0.024	0.019	0.00063
Ca^{2+}	0.31	0.21	0.0045	0.051	0.1	0.0011
Sr^{2+}	0.0048	0.0023	0.00037	0.00077	0.0062	0.00018
Ba^{2+}	0.0015	0.00015	0.00012	0.00032	0.0044	0.00021
Fe ion	0.0027	0.0025	0.00085	0.00035	x	0.0000027
Mn ion	0.0004	x	x	0.000024	x	x
Zn ion	0.000083	x	x	0.0000008	x	x
Cl^-	6.1	3.6	0.59	1.4	1.6	0.083
Br^-	x	0.001	0.0011	0.0011	0.00084	x
SO_4^{2-}	0.0012	0.00058	0.00058	0.000032	0.00001	0.000016
HCO_3^-	0.013	0.0065	0.018	0.0034	0.003	0.0011
pH	5.0	5.2	7.6	x	5.9	x
Major rock type	Sands and salt	Sands and salt	Sands and salt	Sands and salt	Muddy Sandstone	Coal beds and muddy sandstone

CHAPTER IV

METHODOLOGY AND EXPERIMENT

The details of methodology and experiment in this study are described in this chapter. This chapter starts with the detailed methodology then followed by the details experiments including formation brine preparation, injected brine preparation, core samples preparation, measurements of petrophysical properties of core samples, oil preparation, coreflood apparatus, and experimental study.

4.1 Methodology

This study is performed starting from setting up phase. The details are as follow.

1. Gather chemical analysis of formation brine from candidate sandstone reservoirs located in offshore around the globe. Since seawater is used as injected brine, offshore oil is the only main target in this study.
2. Find the range of mass ratio between two dominant divalent ions which are Calcium ion and Magnesium ion and two dominant monovalent ions including Sodium ion and Potassium ion. As sandstone surface is negatively charged at reservoir condition only these cations will have direct interaction with sandstone surface. Anions are neglected in this study.
3. Prepare based formation brine solution at concentration of 100,000 ppm using deionized water and reagent grade chemicals including Sodium Chloride ($NaCl$), Sodium Sulfate (Na_2SO_4), Sodium Hydrogencarbonate ($NaHCO_3$), Magnesium Chloride ($MgCl_2$), Calcium Chloride ($CaCl_2$) and Potassium Chloride (KCl). The mass ratio of Calcium ion to Magnesium ion is kept at 7:1 whereas the mass ratio of Sodium ion to Potassium ion is kept at 120:1. These ratios are obtained from averaging ion data of candidate fields in step (1).

4. Prepare injected brine by simulating composition of seawater at 35,000 ppm. Preparation method is described in section 4.3. The composition of seawater and total salinity are the average values of seawater around the globe.
5. Determine basic rock properties as well as petrophysical properties including porosity (ϕ), absolute permeability (k_a) and irreducible water saturation (S_{wi}). Rock samples used in this study are Berea sandstone and details of measurement are described in section 4.4.
6. Restore wettability of core sample by saturating samples with base formation brine followed by displacing oil containing carboxylic acid to imitate oil migration process. Displacing by acid oil is performed until there is no additional water is expelled from core sample and this is represented by initial oil saturation (S_{oi}). The restoration of wettability requires aging period. In this study, a period of one week is applied to ensure completion of wettability alteration.
7. A blank coreflood test is performed to draw a base line of waterflooding process. This experiment represents conventional waterflooding where the salinity of injected water is equal to that of formation water. Hence, the base formation brine with salinity of 100,000 ppm is utilized as injected brine. Oil recovery factor is detected until 10 pore volume of injected brine is injected and the chosen injection rate in this study is fixed at 2 cm^3/min.
8. Modify mass ratio of Cation in base formation brine in order to study effects of these ions. Ion modification of formation brine starts with Calcium ion to Magnesium ion ratio. From the base ratio of 7:1, it is varied into other four different ratios which are 3:1, 5:1, 9:1 and 11:1. For monovalent ions, Sodium ion to Potassium ion ratio is varied from the original value of 150:1 to other 3 values including 50:1, 120:1 and 180:1. Nevertheless, in order to avoid the effects from total salinity, total mass of divalent ions and monovalent ions are kept constant. Details on preparation of formation water are described in section 4.2.

9. Perform seawater injection by using different modified formation brines in step (8) and simulated seawater from step (4). Again, oil recovery of each experiment is detected as similar as in step (7).
10. Select one case obtained from step (9) that yields the highest oil recovery factor for further studies. The selected formation brine compositions from this step will be used for next two sections:
    - 10.1 Formation brine is diluted from 100,000 to 75,000 and 50,000 ppm to study effects of total salinity of formation brine. Seawater injection is performed by using simulated seawater from step (4) with salinity of 35,000 ppm and oil recovery of each case is detected as similar as in step (7).
    - 10.2 Formation brine is diluted to 50,000 and 35,000 ppm and they are used as injected brine instead of seawater. Low salinity water injection is performed by maintaining formation brine salinity at 100,000 ppm to observe different effects when produced water is used as injected water instead of seawater. Again, oil recovery of each case is detected as similar as in step (7).

11 All of oil recovery factors is calculated and plotted as a function of pore volume of injected water.

12 Results from different formation brine compositions and injected brine systems are discussed to express suitable conditions for seawater injection and low salinity water injection.

Figure 4.1 shows the overall process of blank coreflood test and a study of effects of formation brine composition (step 1 to step 9), whereas a study of effects of total salinity in formation brine (step 10) and a study of effects of diluted formation brine injection (step 11) are illustrated in Figures 4.2 and 4.3 respectively.

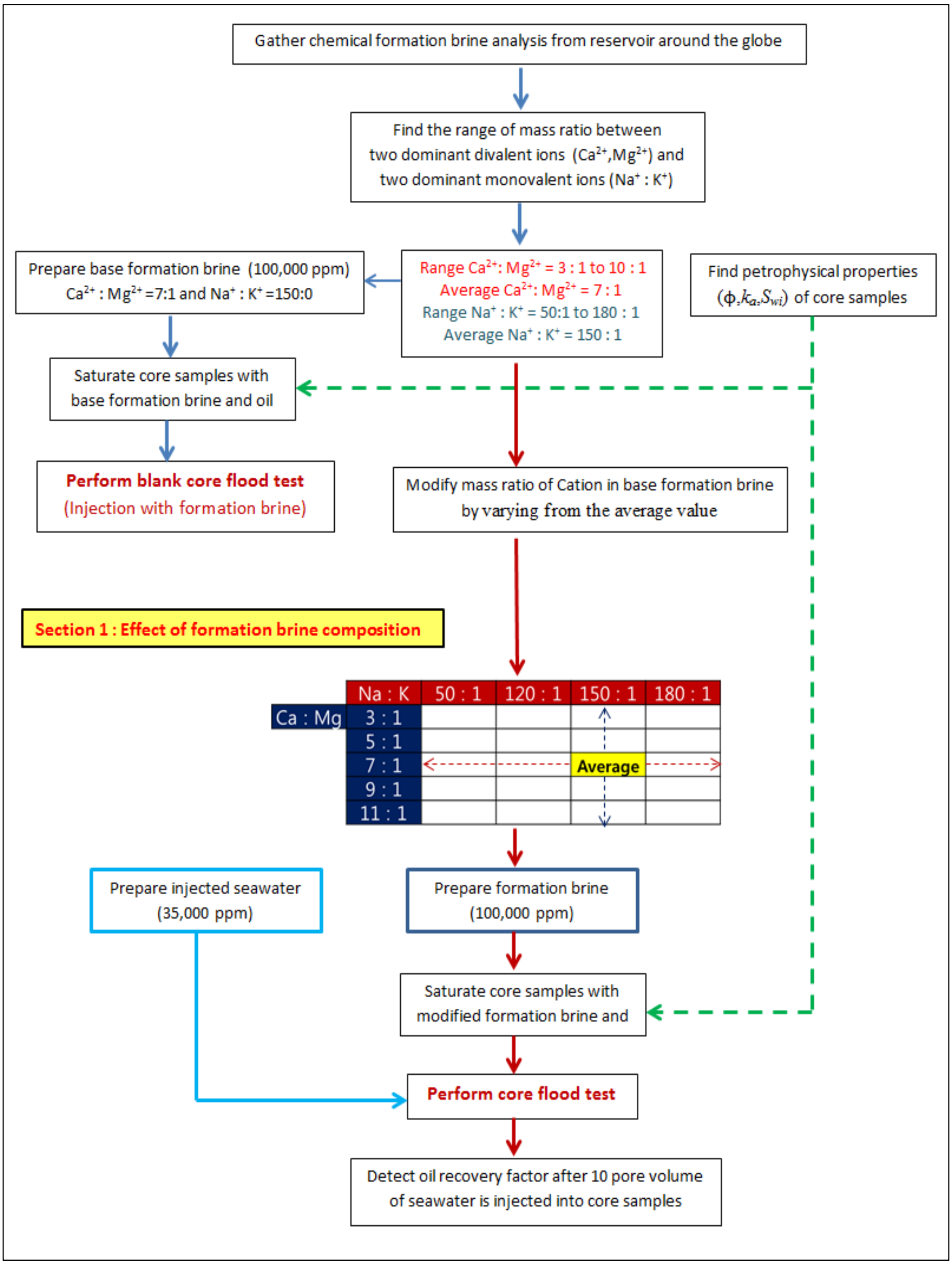


Figure 4.1 Overall process of blank coreflood test and a study of effects of formation brine composition

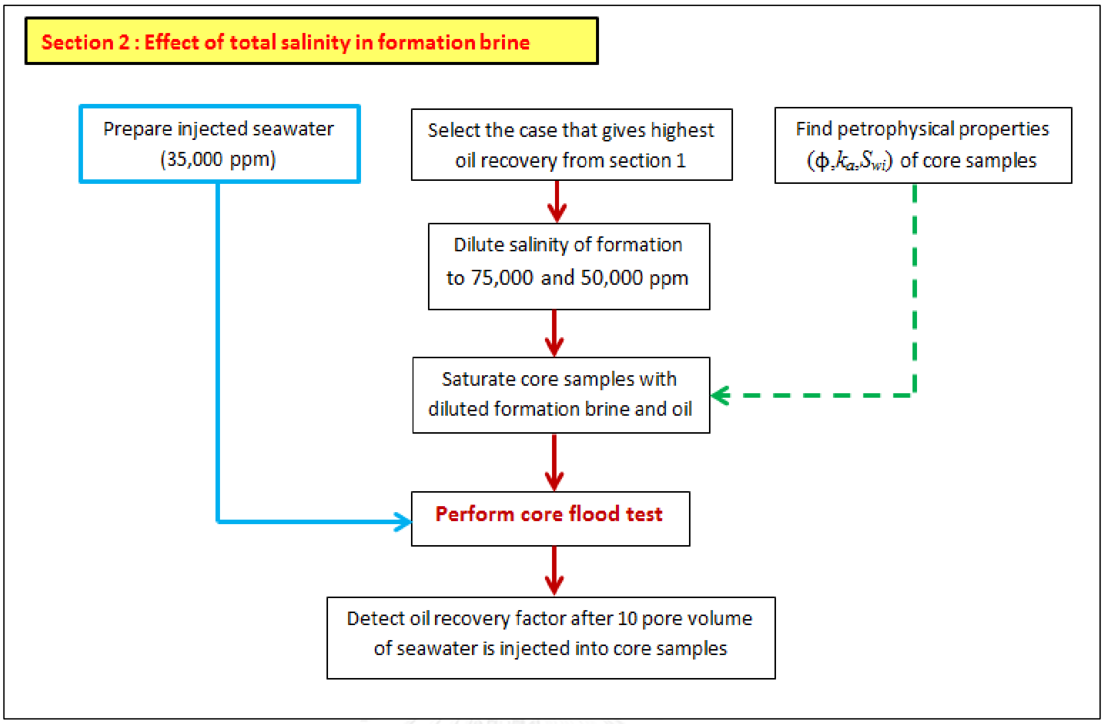


Figure 4.2 Overall process of a study of effects of total salinity in formation brine

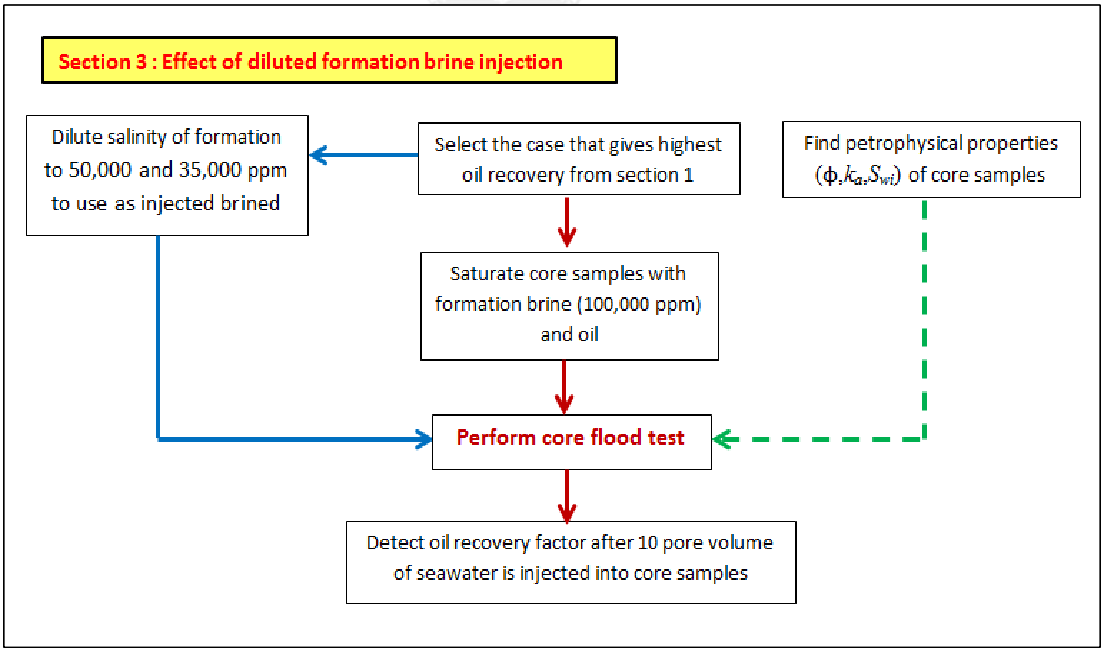


Figure 4.3 Overall process of a study of effects of diluted formation brine injection

4.2 Formation Brine Preparation

4.2.1 Screening of Formation Water Data around the Globe

According to Tables 3.2 and 3.3, total salinity of sandstone oilfields in offshore locations around the globe is varied in the range between 70,000-350,000 ppm [22-24]. Total salinity of formation brine of all cases in this study is therefore fixed at 100,000 ppm to represent the salinity of synthetic formation brine. One reason to select 100,000 ppm is based difficulty of preparation high salinity brine at room temperature. The higher value of formation brine salinity may cause precipitation at room temperature. The prepared formation brine in each experiment is modified for the mass ratio of cations.

Table 4.1 shows the ratio of Sodium ion to Potassium ion of sandstone oilfields located in offshore locations around the globe and Figure 4.4 summarizes distribution of Sodium ion to Potassium ion ratio.

Table 4.1 Mass ratio of Calcium ion to Magnesium ion in sandstone oilfields located in offshore locations around the globe [22-24]

Fluid component	Offshore Angola, North of Launda	Offshore Azerbaijan	Mahakam Basin, Indonesia	Offshore Gulf of Mexico Field 1	Offshore Gulf of Mexico Field 2	Offshore Gulf of Mexico Field 3
Na^+	145	171	120	183	151	129
K^+	1	1	1	1	1	1

Fluid component	Offshore Gulf of Mexico- offshore Louisiana	Onshore Gulf of Mexico- Texas Gulf Coast	San Juan Basin , Colorado/ New Mexico	Miller, North Sea	Statfjord, North Sea	Thames, North Sea
Na^+	163	51	148	158	133	180
K^+	1	1	1	1	1	1

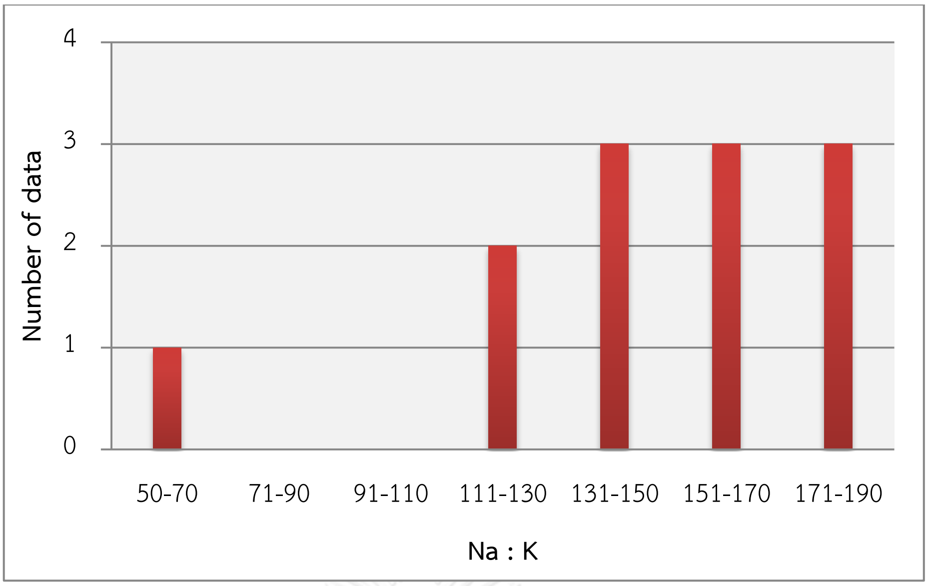


Figure 4.4 Data distribution of Sodium ion to Potassium ion ratio of sandstone oilfields located in offshore locations around the globe [22-24]

Table 4.2 summarizes the ratio of Calcium ion to Magnesium ion in sandstone oilfields located in offshore locations around the globe and Figure 4.5 illustrates the data distribution of Calcium ion to Magnesium ion ratio.

Table 4.2 Mass ratio of Calcium ion to Magnesium ionic sandstone oilfields located in offshore locations around the globe [22-24]

Fluid component	Offshore Angola, North of Launda	Offshore Azerbaijan	Mahakam Basin, Indonesia	Offshore Gulf of Mexico Field 1	Offshore Gulf of Mexico Field 2	Offshore Gulf of Mexico Field 3
Ca^{2+}	9	5	3	5	10	7
Mg^{2+}	1	1	1	1	1	1

Fluid component	Offshore Gulf of Mexico-offshore Louisiana	Onshore Gulf of Mexico-Texas Gulf Coast	San Juan Basin , Colorado/ New Mexico	Miller, North Sea	Statfjord, North Sea	Thames, North Sea
Ca^{2+}	4	9	3	9	6	3
Mg^{2+}	1	1	1	1	1	1

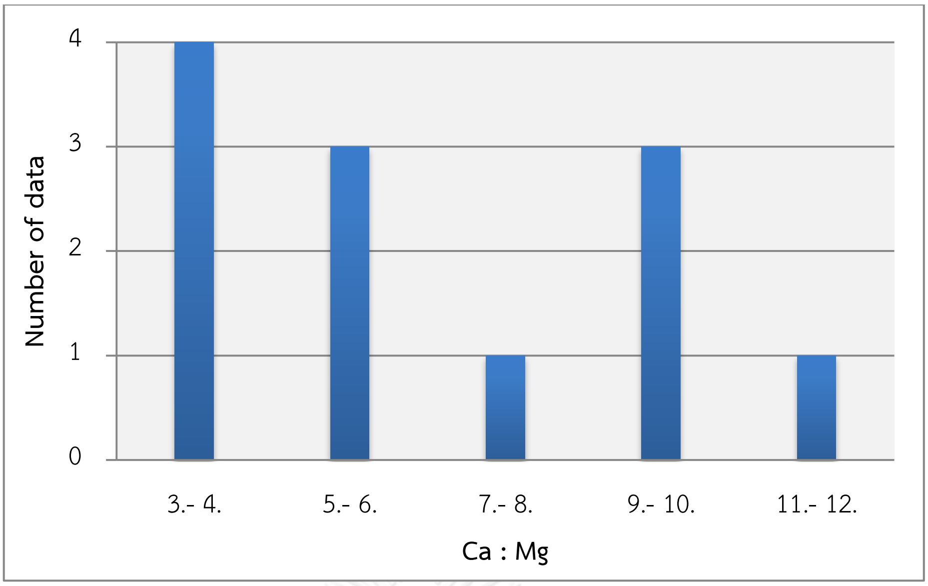


Figure 4.5 Data distribution of Calcium ion to Magnesium ion ratio of sandstone oilfields located in offshore locations around the globe [22-24]

From Tables 4.1 and 4.2 and Figures 4.4 and 4.5, Potassium ion and Magnesium ion which are minorities for monovalent ion and divalent ion respectively are used as base. Numbers of Sodium ion and Calcium ion represent times of ion higher than Potassium and Magnesium ion, respectively. From these data it can be seen that the average ratio of Sodium ion to Potassium ion is around 150:1 and for Calcium ion to Magnesium ion is around 7:1. These ratios are therefore used as base ratio before the modification of ion.

To study effects of divalent ions, the mass ratio of Calcium ion to Magnesium ion is varied from the based value of 7:1 to other four ratios which are 3:1, 5:1, 9:1 and 11:1, whereas the mass ratio of Sodium ion to Potassium ion is varied from average value of 150:1 to other three ratios which are 50:1, 120:1, and 180:1.

4.2.2 Preparation of Base Formation Brine

In this step, each ion from chosen sandstone reservoirs is averaged and trace elements which are assumed to have no effect on low salinity water injection are neglected. The mass ratio of dominant divalent ions (Calcium ion and Magnesium ion) and dominant monovalent ion (Sodium ion and Potassium ion) are modified to desired concentration. Then, the base formation brine is prepared from deionized water and reagent grade chemicals including Sodium Chloride (NaCl), Sodium Sulfate (Na_2SO_4), Sodium Hydrogen Carbonate ($NaHCO_3$), Magnesium Chloride ($MgCl_2$), Calcium Chloride ($CaCl_2$) and Potassium Chloride (KCl).

Basis 1 liter of base formation brine with salinity of 100,000 ppm

Table 4.3 Summary of base formation brine composition (Ca^{2+}:Mg^{2+}=7:1 and Na^{+}:K^{+}= 150:1) at salinity of 100,000 ppm

Fluid component	Molecular weight	Average data of chosen fields			Desired salinity of 100,000 ppm		
		mg/L	ppm	Mass fraction	Mass ratio	ppm	gmol/L
Na^{+}	23	53,774	53,774	0.3493	150	34,691	1.5083
K^{+}	39.1	563	563		1	231	0.0059
Mg^{2+}	24	912	912	0.0406	1	507	0.0211
Ca^{2+}	40	5,404	5404		7	3,552	0.0888
Cl^{-}	35.5	94,359	94,359	0.6064		60,644	1.7083
SO_4^{2-}	96	46	46	0.0003		29	0.0003
HCO_3^{-}	61	535	535	0.0034		344	0.0056
Total		**15,5594**	**15,5594**	**1**		**100,000**	

From Table 4.3, each desired ion composition is prepared from these following chemicals.

a. **Na_2SO_4**

From equation, $2Na^+(aq) + SO_4^{2-}(aq) \rightarrow Na_2SO_4(aq)$

0.0003 moles of SO_4^{2-} requires 0.0006 moles of Na^+ to form Na_2SO_4 of 0.0003 moles

Therefore, **0.0003 moles which is 0.0438 grams** of Na_2SO_4 is used to achieve 0.0003 moles SO_4^{2-} and 0.0006 mol of Na^+ is subtracted from whole amount of Na^+.

b. **$NaHCO_3$**

From equation, $Na^+(aq) + HCO_3^-(aq) \rightarrow NaHCO_3(aq)$

0.0056 moles HCO_3^- requires 0.0056 moles of Na^+ to form $NaHCO_3$ of 0.0056 moles

Therefore, **0.0056 moles which is 0.4740 grams** of $NaHCO_3$ should be prepared to obtain 0.0056 moles HCO_3^- and 0.0056 moles Na^+.

From preparation of Na_2SO_4 and $NaHCO_3$, 0.0062 moles Na^+ has been used and remaining Na^+ is 1.5021 moles.

c. **$MgCl_2$**

From equation, $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow MgCl_2(aq)$

0.0211moles Mg^{2+} requires 0.0422 moles of Cl^- to form $MgCl_2$ 0.0211 moles

Therefore, **0.0211 moles which is 2.0086 grams** of $MgCl_2$ should be prepared to obtain 0.0211moles Mg^{2+} and 0.0422 moles Cl^-.

d. **KCl**

From equation, $K^+(aq) + Cl^-(aq) \rightarrow KCl(aq)$

0.0059 moles K^+ requires 0.0059 moles Cl^- to form KCl 0.0059 moles

Therefore, **0.0059 moles which is 0.4413 grams** of KCl should be prepared to obtain 0.0059 moles K^+ and 0.0059 moles Cl^-.

e. $CaCl_2$

From equation, $Ca^{2+}(aq) + 2Cl^{-}(aq) \rightarrow CaCl_2(aq)$

0.0888 moles Ca^{2+} requires 0.1776moles Cl^{-} to from $MgCl_2$ 0.0888 moles

Therefore, **0.0888 moles which is 9.8572 grams** of $CaCl_2$ should be prepared to obtain 0.0888moles Ca^{2+} and 0.1776 moles Cl^{-}.

From preparation of $CaCl_2$, $MgCl_2$ and KCl, 1.7083 moles Cl^{-} is used and remaining Cl^{-} is 1.4825 mol.

f. NaCl

From equation, $Na^{+}(aq) + Cl^{-}(aq) \rightarrow NaCl(aq)$

1.4825 moles Cl^{-} requires 1.4825 moles of Na^{+} to form NaCl 1.4825 moles

Therefore, **1.4825 moles which is 86.7251 grams** of NaCl should be prepared to obtain 1.4825 moles Na^{+} and 1.4825 moles Cl^{-}.

From the calculation, summary of mass and gram mole of all chemicals required making up base formation brine of total salinity of 100,000 ppm which has the mass ratio of Calcium ion to Magnesium ion equals to 7:1 and the mass ratio of Sodium ion to Potassium ion equals to 150:1 is shown in Table 4.4.

Table 4.4 Weight of chemicals required to make up brine base formation brine with total salinity of 100,000 ppm (Ca^{2+}: Mg^{2+} = 7:1, Na^{+}: K^{+} 150:1)

Chemical	MW	Gram mole	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4825	86.7251
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
Total			**99.5500**

Nevertheless, total salinity of base formation brine is less than 100,000 ppm. In order to keep salinity at 100,000 ppm, amount of NaCl which is abundant is increased 0.45 g. The amount of chemicals is therefore edited and shown in Table 4.5 and ion concentrations are illustrated in Table 4.6.

Table 4.5 Adjusted weight of chemicals required to make up formation brine with total salinity of 100,000 ppm (Ca^{2+}: Mg^{2+} = 7:1, Na^{+}: K^{+} 150:1)

Chemical	MW	Gram mole	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4902	87.1751
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
Total			**100**

Table 4.6 Ion concentrations of base formation brine with total salinity of 100,000 ppm (Ca^{2+}: Mg^{2+} = 7:1, Na^{+}: K^{+} 150:1)

Ion	Mole	Mass
Na^{+}	1.4964	34.4179
Ca^{2+}	0.0888	3.5521
Mg^{2+}	0.0211	0.5074
K^{+}	0.0059	0.2313
Cl^{-}	1.7160	60.9173
HCO_3^{-}	0.0056	0.3442
SO_4^{2-}	0.0003	0.0296
Total		**100**

4.2.3 Modification of Ion Concentration in Formation Brine

Dominant cations are investigated to study effects of ion composition in formation brine affecting effectiveness of low salinity brine injection. Divalent ions including Calcium ion and Magnesium ion are modified in various ratios to observe their major effects. Similarly, monovalent ions which are Sodium ion and Potassium ion are also modified in various ratios to observe their effects of as well. However, total salinity of formation brine is always kept constant at 100,000 ppm for all experiments in order to avoid effects of total salinity.

Modification of Calcium ion and Magnesium ion

To observe effects of divalent ions, the mass ratio of Calcium ion to Magnesium ion is varied in five ratios which are 3:1, 5:1, 7:1 (base ratio), 9:1 and 11:1 for four different Sodium ion to Potassium ion ratios. Preparation method is similar to base formation brine preparation which is described in section 4.2.2. Summary of weight of chemical required for different formation brine as well as ion concentration in formation brines can be found in Appendix A.

Modification Sodium ion to Potassium ion

Similarly, to observe effect of monovalent ions, the mass ratio of Sodium ion to Potassium ion is varied in four ratios which are 50:1, 120:1, 150:1 (base ratio) and 180:1 for five different Calcium ion to Magnesium ion ratios. Preparation method is similar to base formation brine preparation which is described in section 4.2.2. Summary of weight of chemical required for different formation brine as well as ion concentration in formation brines can be found in Appendix A.

4.3 Injected Brine Preparation

Average salinity of seawater is found around 35,000 ppm which is less than salinity of formation brine in some fields especially those from very deep reservoirs. Since benefit of low salinity brine has been observed, seawater and produced water are considered to be used as injected fluid in case of waterflooding in offshore field. The preparation method of injected brine is similar to base formation brine preparation. Table 4.7 shows the average ion composition in seawater around the globe and Table 4.8 summarizes chemical required for preparing seawater with total salinity of 35,000 ppm.

Table 4.7 Average ion composition in seawater around the globe [19, 24]

Ion	MW	Gmol	Mass(ppm)
Na^+	23	0.1343	10,813
K^+	39.1	0.0026	369
Mg^{2+}	24	0.0138	1,157
Ca^{2+}	40	0.0022	304
Cl^-	35.5	0.1399	17,386
SO_4^{2-}	96	0.0144	4,844
HCO_3^-	61	0.0006	127
			35,000

Table 4.8 Weight of chemicals required to make up seawater with total salinity of 35,000 ppm

Chemical	MW	Mass(g)	Gram mole
$MgCl_2$	95	4.58	0.0482
$CaCl_2$	111	1.02	0.0092
KCl	74.6	0.58	0.0078
NaCl	58.5	21.48	0.3671
Na_2SO_4	142	7.17	0.0505
$NaHCO_3$	84	0.18	0.0021
Total		**35.00**	

Table 4.9 summarizes density and viscosity of formation brine at ambient temperature ($25^{o}C$) and injected seawater at flooding temperature ($50^{o}C$) Determination method of these two properties is described in appendix C.

Table 4. 9 Properties of formation brine and Injected seawater

Fluid	**Salinity (ppm)**	**Temperature (^{o}C)**	**Viscosity (cP)**	**Density (g/cm^3)**
Formation brine	100,000	25	1.065	1.054
Seawater	35,000	50	0.607	0.988

4.4 Core Samples Preparation

In this study, three Berea sandstone outcrop cores are utilized for waterflooding. The petrophysical properties of Berea cores are measured using coreflooding apparatus and high salinity Formation Brine (FB) at ambient temperature by theses following steps;

1. Sandstone cores were dried, weighed, and measured their bulk volumes using dimensions (diameter and length).
2. Core samples were fully saturated in coreflooding apparatus by injecting formation brine at four different flow rates (2, 4, 6 and 8 cm^3/min) until no gas bubble is detected at the outlet. At the same time difference pressure drop must be stabilized or increment of pressure difference must be proportionate with injection rate. That means, there is no more gas remained in core sample. The difference pressure drop across core samples are monitored at different injection rates and used for calculation of absolute permeability (k_a).
3. Saturated cores are weighed and effective porosities (ϕ_{eff}) are calculated.
4. Dodecane (C12) which is used as oil phase throughout this study is prepared to have Acid Number of 5.0 by mixing with Oleic acid. Preparation of acid oil is described in section 4.5. The acid oil is injected to displace formation brine inside saturated core with four different flow rates (2, 4, 6 and 8 cm^3/min) until no water is detected at the outlet and difference pressure drop is stabilized. The difference pressure drop across core samples is monitored and

used for calculation of relative permeability to oil (k_{ro}) at irreducible water saturation (S_{wi}).

5. Volume of produced water is measured and is used for calculation of S_{wi}.
6. Saturated core samples are aged in beaker filled up with acid oil for a week to ensure completion of wettability alteration mechanism.

The petrophysical properties of Berea sandstone cores which are used in this study are summarized in Table 4.10.

Table 4.10 Physical properties of Berea sandstone core samples

Core ID	Length (cm.)	Diameter (cm)	Dry weigth (g)	PV (cc)	Porosity (%)	k_a (md)	S_{wi}	k_{ro} at S_{wi} (md) before aging	k_{ro} at S_{wi} (md) after aging
B-1	12.68	0.378	296.47	28.26	20.09	83.01	0.35	49.63	34.86
B-2	12.68	0.378	299.01	27.78	19.63	53.85	0.40	35.43	21.54
B-3	12.68	0.378	298.86	27.65	19.54	69.91	0.39	41.41	31.46

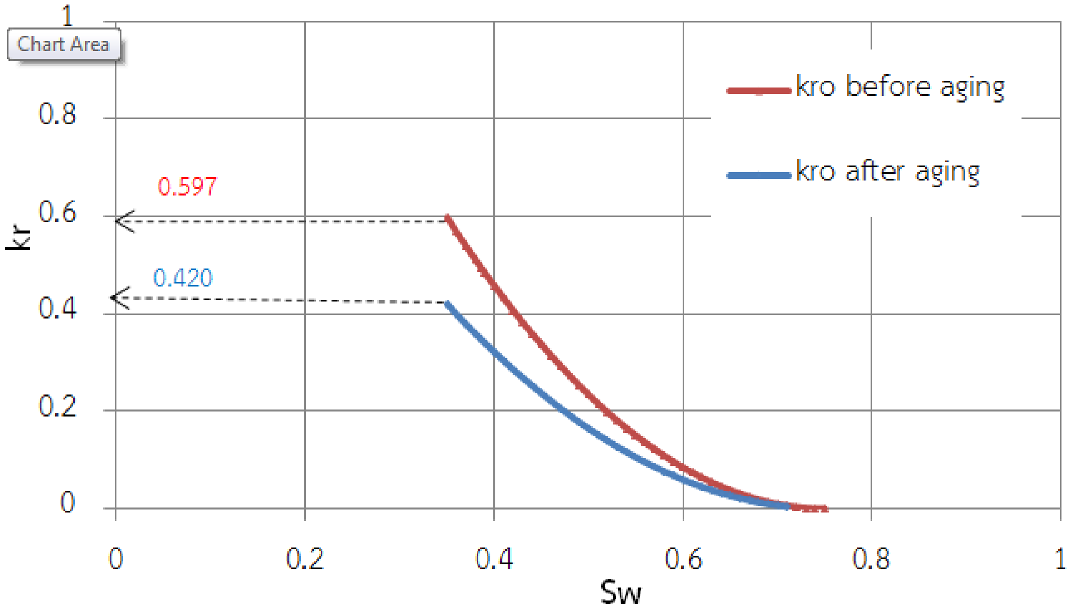


Figure 4.6 Comparison of relative permeability to oil before and after acid treatment of core B-1

According to step 4 in core sample preparation method, the saturated core sample is displaced with acid oil with acid number of 5.0 until no more displaced water can be observed. At this point, pressure drop across the core sample is detected to calculate relative permeability of oil. After aging period of 1 week, acid oil with acid number of 1.0 is flushed into core sample in order to remove excess oleic acid as this could cause saponification with other compound in injected brine. Again pressure drop across the core sample is detected and relative permeability of oil after wettability alteration process is measured. Figure 4.6 illustrates comparison of relative permeability to oil before and after acid treatment of core B-1. It can be observed that relative permeability to oil after acid treatment is smaller than the state prior to acid treatment. This is a confirmation that oleic acid is adsorbed onto rock surface through ion binding and the core sample turns more an oil-wet condition as oil has more affinity to rock surface and hence its flow ability is decreasing.

4.5 Oil Preparation

Generally, crude oil contains polar organic compounds such as acid and base and these compounds are responsible for alteration of natural wettability. The carboxylic compounds (-COOH) in oil are usually found as majority of heteroatoms and they can bond with sandstone surface through divalent ions including Ca^{2+} and Mg^{2+} in formation brine.

Acid number (AN) is defined as the amount of Potassium Hydroxide (KOH) in milligrams, required for neutralizing 1 gram of crude oil. Larger acid number refers to higher amount of carboxylic compounds (-COOH). Usually, range of acid numbers in crude oil in sandstone reservoir fall in between 0.17 and 2.07 mg-KOH/g [19].

In this study, Dodecane with Acid Number (AN) of 5.0 is prepared by adding Oleic acid. The reason to use high acid number of oil is to enhance the adsorption of carboxylic compounds onto sandstone surface through Calcium ion and Magnesium ion in formation brine. Core samples which are flushed by acid oil are aged under acid Dodecane for one week to ensure wettability at room temperature. After one week of aging period, samples are flushed by acid oil with acid number of 1.0 to remove excess oleic acid and also to adjust the surface equilibrium at test temperature (50°C). Table 4.11 summarizes the amount of Oleic acid used in preparation of acid oil and calculation of amount of Oleic is described in appendix B.

Table 4.11 Amount of Oleic acid used in preparation of acid oil

Acid oil	Dodecane (g)	Oleic acid(g)
Acid number of 5.0	1,000	25.17
Acid number of 1.0	1,000	5.03

After acid oil is prepared, oil density is measured by using pycnometer and oil viscosity is also measured by Cannon-Fenske viscometer. Both glass wares are illustrated in Figure 4.7. Oil density is used in calculation of oil viscosity and oil viscosity is also used for application of Darcy’s equation.

Pycnometer

Cannon-Fenske viscometer

Figure 4.7 Pycnometer (left) and Cannon-Fenske viscometer (right)

Table 4.12 summarizes density and viscosity of acid oil used during aging process and Table 4.13 summarizes density and viscosity of acid oil in flooding process. Determination method of these two properties is described in appendix C.

Table 4.12 Properties of acid oil (AN=5.0) in aging process

Process	Acid number	Temperature (^{o}C)	Viscosity (cP)	Density (g/cm^3)
Aging	5.0	25	1.25	0.745

Table 4.13 Properties of acid oil (AN=1.0) in flooding process

Process	Acid number	Temperature (^{o}C)	Viscosity (cP)	Density (g/cm^3)
Pre-flush	1.0	25	1.21	0.730
Flooding	1.0	50	0.90	0.694

4.6 Coreflood Apparatus

The coreflooding apparatus in this study is shown in Figure 4.8. This set of apparatus consists of a core-holder, three fluid accumulators, four syringe pumps, a separator, and an oven. Core sample is placed in the core-holder by an assist of core sleeve which is used to prevent contact with confining fluid. Two syringe pumps are responsible for displacing the working fluid to displace desired fluids in accumulators into the core sample at constant rate or constant pressure. Confining pressure is applied to prevent bypassing of injecting fluid across core sample and this pressure is applied on core sample by using another syringe pump to inject distilled water into the annulus space between core holder and rubber sleeve that cased the core sample. The confining pressure in this study set at 1,500 psia which is appropriate for desired flow rate and permeability of core samples. The remaining syringe pump is used to pump nitrogen gas to control the back pressure regulator which has a function to control pressure at the out flow. In this study, nitrogen pump is set around 520 psia in order to have back pressure regulator functioned at 500 psia. Two pressure transducers are used to measure the pressure drop across core sample and pressure difference can be reported with different resolution depending on permeability of samples. The schematic of coreflooding setup is illustrated in Figure 4.9.

Figure 4.8 Coreflood apparatus

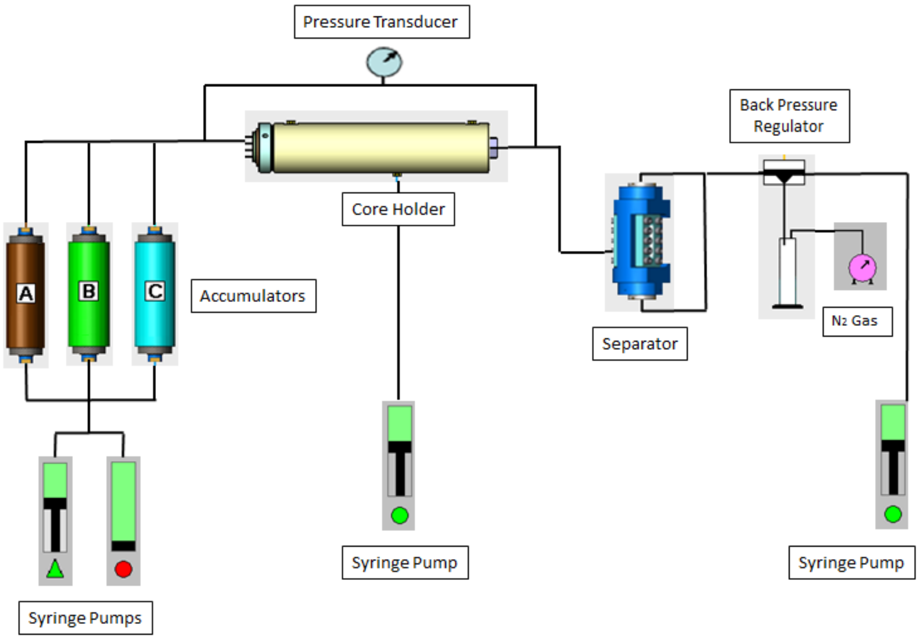


Figure 4.9 Schematic of coreflood apparatus

4.7 Detection of Produced Oil by Coreflood Apparatus

The volume of produced oil is required to calculate oil recovery factor and it is detected through the use of liquid separator. This part of coreflood apparatus contains inlet tube to the labyrinth paths to stabilize phase of fluid before entering the crystal chamber. Detection of fluid level requires two different fluids inside the chamber and movement of interface is controlled by type of fluid entering together with choosing to open superior or inferior vales. In order to detect volume of oil, the inferior valve is opened while superior valve remained closed. By means of this configuration, oil which is lighter than water will cause the lowering down of interface. Figure 4.10 illustrates the change of liquid level in separator. During the process of displacement mechanism where brine is injected into core sample, produced oil firstly come out from the saturated core sample and then flow to separator. When produced oil reaches separator, the liquid level will be decreased due to increasing of oil volume. As oil production rate declines from water breakthrough, interface is slightly changed and as no more oil is produced, interface stops moving. Finally, difference of volume between before and after displacement mechanism can be detected from calibration data (between height of fluid and fluid volume).

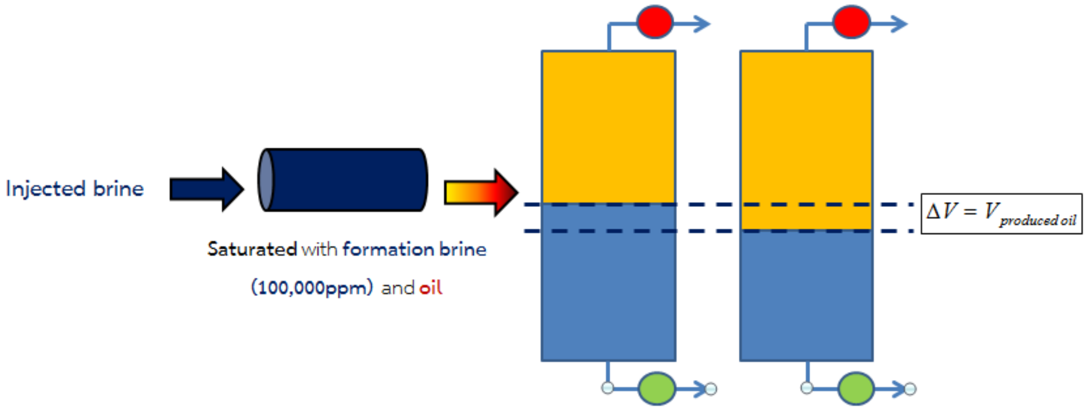


Figure 4.10 Illustration of detection of liquid level in fluid separator

However, when considering the schematic of coreflooding setup which is illustrated in Figure 4.9, it can be seen that the detected oil volume includes volume of oil during pre-flushing process remained in pipe between core holder and separator. This volume is so-call “dead pore volume” that should be subtracted out from detected oil volume before calculation of oil recovery factor.

Prior to performing experiment, dead pore volume must be firstly measured by using “test core plug” together with fixed length outlet tube which is shown in Figure 4.11. The pore volume of test core plug is 0.1 cm^3. In this process, oil and water is alternately injected to identify dead pore volume of the system. Oil is firstly filled in the whole system, occupying three different zones which are 1) inside the test core plug, 2) known volume tube and 3) unknown dead pore volume. Water is alternately injected and total change of oil volume is detected through height of liquid volume.

Figure 4.11 Test core plug and known-volume tube from the outlet of core holder

Dead pore volume can be calculated from equation 4-1. And in this coreflood apparatus, dead pore volume is 1.98 cm^3. Figure 4.12 shows the volume of three parts as mentioned before which are used to identify dead pore.

$$\textit{Dead Pore Volume} = V_{produced\ oil} - V_{Test\ core\ plug} - V_{known\text{-}volume\ tube} \qquad (4.1)$$

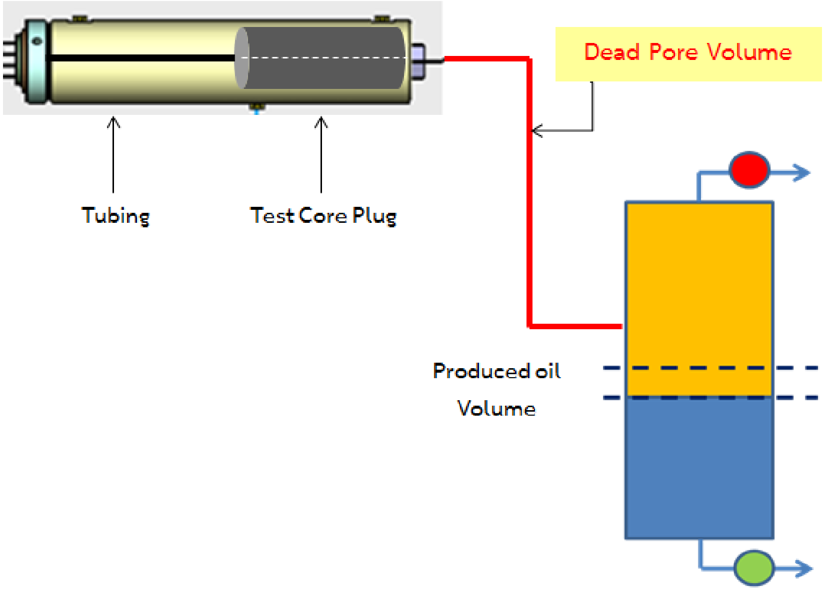


Figure 4.12 The volumes of three parts which are used to identify dead pore volume

4.8 Summary of Experimental Study

The experiments are conducted by the use of coreflooding machine. Berea sandstone cores are used to represent sandstone surface in this study. First, basic rock properties and petrophysical properties including porosity, permeability, wettability and residual phase saturations are measured. The experiments relating to efficiency of low salinity waterflooding are mainly divided into four sections.

4.8.1 Blank Coreflood Test

In this section, two corefood experiments are performed to compare the effect between conventional waterflooding and low salinity waterflooding. Two core samples are saturated with formation brine with total salinity of 100,000 ppm and displaced by oil containing carboxylic acid. After aging period of a week, formation brine is injected to displace oil from core sample with constant flow rate 2 cm^3/min at 50 °C for conventional waterflooding case. On the other hand, for low salinity case, synthetic seawater with total salinity of 35,000 ppm is used as injected brine after aging process. Figure 4.13 shows the diagram of two coreflood experiments in this section.

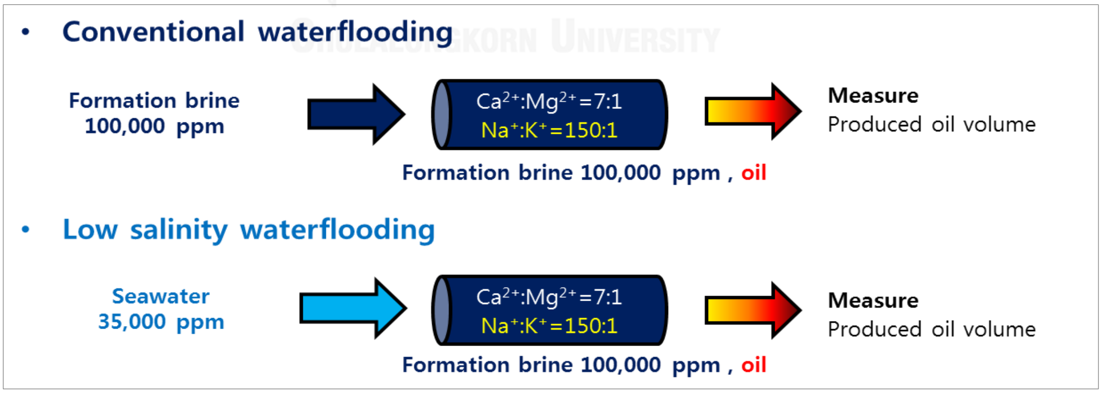


Figure 4.13 Illustration of two coreflood experiments in blank coreflood test; Conventional Waterflooding (upper) and Low Salinity Waterflooding (below)

4.8.2 Effects of Ion Composition in Formation Brine through Seawater Injection

To study effects of divalent ions in formation brine, mass ratio of Calcium ion to Magnesium ion in formation brine are varied in five different ratios (3:1, 5:1, 7:1, 9:1 and 11:1) while mass ratio of Sodium ion to Potassium ion are varied into four different ratios (50:1, 120:1, 150:1 and 180:1) to study effects of monovalent ion. Core samples are first saturated with formation brine at different each ratio and consecutively with acid oil at desired aging time. Then core samples are displaced by simulated seawater with constant flow rate 2 cm^3/min at 50°C. Figure 4.14 shows the diagram of coreflood experiment in this section.

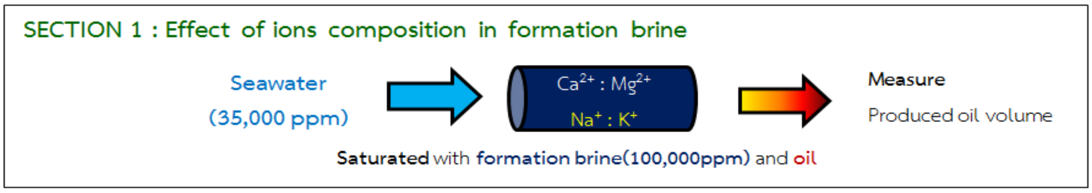


Figure 4.14 Illustration of coreflood experiment to study effects of ion compositions in formation brine through seawater injection

4.8.3 Effects of Total salinity of Formation Brine through Seawater Injection

Formation brine concentration which yields the highest oil recovery factor from first section is diluted to 75,000 ppm and 50,000 ppm to study effects of total salinity of formation brine. Figure 4.15 illustrates coreflood experiment this section.

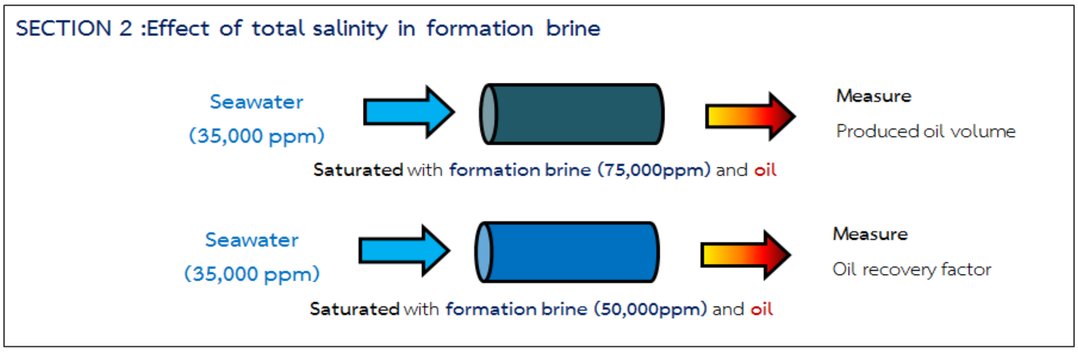


Figure 4.15 Illustration of coreflood experiment to study effects of total salinity of formation brine through seawater injection

4.8.4 Effect of Diluted Formation Brine

Formation brine concentration which yields the highest oil recovery factor from first section is diluted to 50,000 and 35,000 ppm and they are used as injected brined instead of using simulated seawater. Figure 4.16 summarizes coreflood experiment in this section.

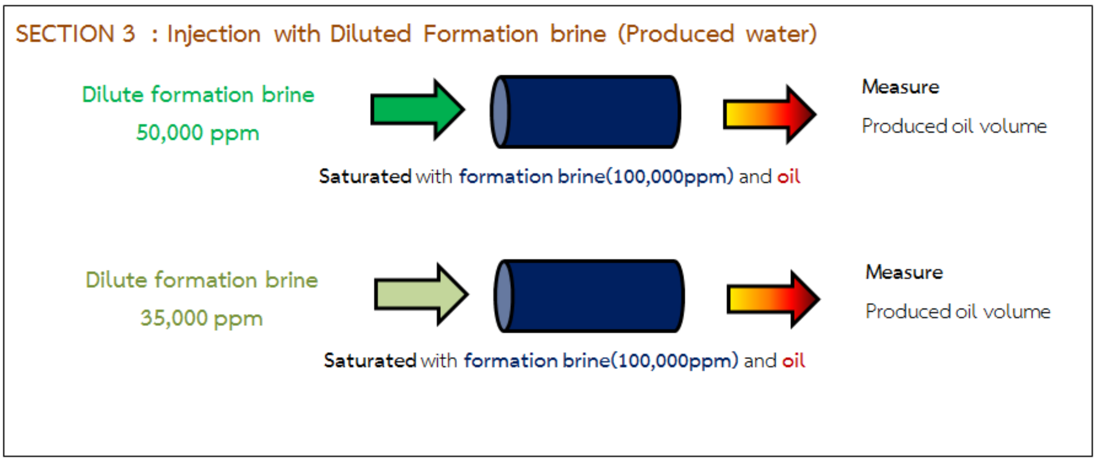


Figure 4.16 Illustration of coreflood experiment to study effects of using diluted produced water instead of seawater injection

Results obtained from each section are compared in terms of rate of oil recovery as well as oil recovery factor as a function of injected pore volume of brine. At the end of the study, the most suitable criteria concerning formation brine is summarized for seawater injection and low salinity brine injection (diluted produced water).

CHAPTER V

RESULTS AND DISCUSSION

This chapter presents the results and discussion from laboratory experiment for each interest study. First, the results between conventional waterflooding and low salinity waterflooding are compared. Next, the effects of ion composition in formation brine on effectiveness of low salinity seawater injection are discussed. Then, discussion is continued with effects of total salinity of formation brine and effects of injection of diluted formation brine, respectively. The results are mainly investigated on aspects of oil recovery rate and total oil recovery factor.

5.1 Blank Coreflood Test

This section is performed to compare the effect between conventional waterflooding and low salinity waterflooding. The average ratios of Calcium ion to Magnesium ion (7:1) and the average Sodium ion to Potassium ion ratio (150:1) are selected to prepare the base formation brine solution. The first experiment is performed to draw a base line obtained from waterflooding process. This experiment represents conventional waterflooding where the salinity of injected water is equal to that of formation water. Hence, the base formation brine with salinity of 100,000 ppm is utilized as injected brine. The second experiment is performed to represent low salinity waterflooding case by using synthetic seawater with salinity of 35,000 as injected brine. Oil recovery factor is detected until 10 pore volume of injected brine is injected and the chosen injection rate in this study is fixed at 2 cm^3/min as this rate would provide adequate force to displace oil in every pore size [25].

The results from coreflood experiment are mainly investigated from rate of oil recovery and total oil recovery factor which are illustrated in Figures 5.1, whereas summary of oil recovery factor, final phase saturation, and relative permeability to water are compared in Table 5.1.

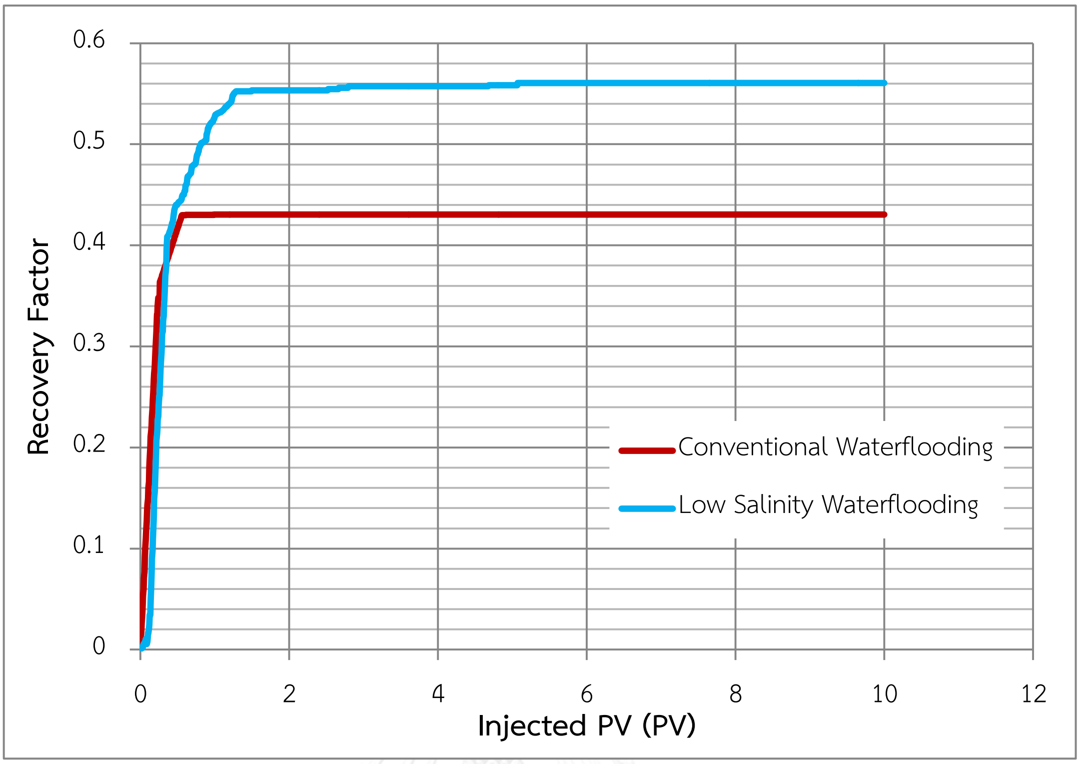


Figure 5.1 Oil Recovery factors obtained from conventional waterflooding case as a function of injected pore volume of base formation brine and low salinity waterflooding case as a function of injected pore volume of seawater

Table 5.1 Comparison of final phase saturation, relative permeability to water and oil recovery factors between conventional waterflooding case and low salinity waterflooding case

Case	Relative Permeability to water at 1-S_{or}	Residual oil saturation (S_{or}) (fraction)	Recovery factor (RF) (%)
Conventional Waterflooding	0.25	0.39	43.04
Low Salinity Waterflooding	0.20	0.28	56.07

According to Figure 5.1, the result shows that 56.06% of OOIP can be obtained from low salinity waterflooding case whereas only 43.04% of OOIP is obtained from conventional waterflooding case. It means that approximately 16% of OOIP can be additionally obtained by effects of low salinity water.

From Table 5.1, it can be seen that both of relative permeability to water and residual oil saturation are decreased after performing with low salinity waterflooding compared to conventional waterflooding. This can be explained that low salinity water can alternate rock wettability to a more water-wet condition. Therefore end point of relative permeability changes by reducing residual oil saturating as well as decreasing flow ability of water. According to this, additional oil recovery is obtained. The effects of formation brine supposed to affect oil recovery mechanism by low salinity waterflooding are studied in the next section.

5.2 Effects of Ion Composition in Formation Brine on Low Salinity Seawater Injection

This section emphasizes on effects of ion concentration in formation brine on low salinity seawater injection. Both of monovalent ions and divalent ions are mainly considered in this study. For monovalent ions, the summation of mass of Na^+ to K^+ is kept constant while their relative ratio is varied in four different values including 50:1, 120:1, 150:1 and 180:1 in order to study the effects of monovalent ions. As explained in Chapter 4, these numbers are based on the fact that Sodium ion is more abundant than Potassium in most brine around the globe. Similarly, effects of divalent ions are studied by varying the mass ratio of Ca^{2+} to Mg^{2+} in five different ratios which are 3:1, 5:1, 7:1, 9:1 and 11:1. It can be obviously seen that in nature Calcium ion is more enriched in formation brine compared to Magnesium ion. However, the difference is not as large as Sodium and Potassium ions which is due to extra abundance of Sodium ion on earth.

5.2.1 Effects of Divalent Ions in Formation Brine on Low Salinity Seawater Injection.

After oil migration is completed, oil is not in direct contact with sandstone surface. But with long geological time frame together with additional factors such as presence of carboxylic acid in oil and presence of divalent ions in formation brine, oil starts to have affinity with sandstone surface. Oil is adsorbed through divalent cations covering on the sandstone surface. Figure 5.2 illustrates the condition in sandstone porous media after oil starts having affinity onto rock surface, causing rock to become more oil-wet condition. Oil is majorly adsorbed through two important divalent cations found in brine which are Calcium ions and Magnesium ions. Due to difference in ionic radius, the larger ionic radius will cause less ionic strength when bonding with oppositely charged ions. In other words, oil is kept longer distance from rock surface. The ionic radius of cations in this study is compared in Table 5.2.

Table 5.2 Ionic radius and hydrated radius of cations [20]

Ion	Ionic Radius (pm)	Hydrated Radius (pm)
Sodium (Na^+)	116	450
Potassium (K^+)	152	300
Magnesium (Mg^{2+})	86	800
Calcium (Ca^{2+})	114	600

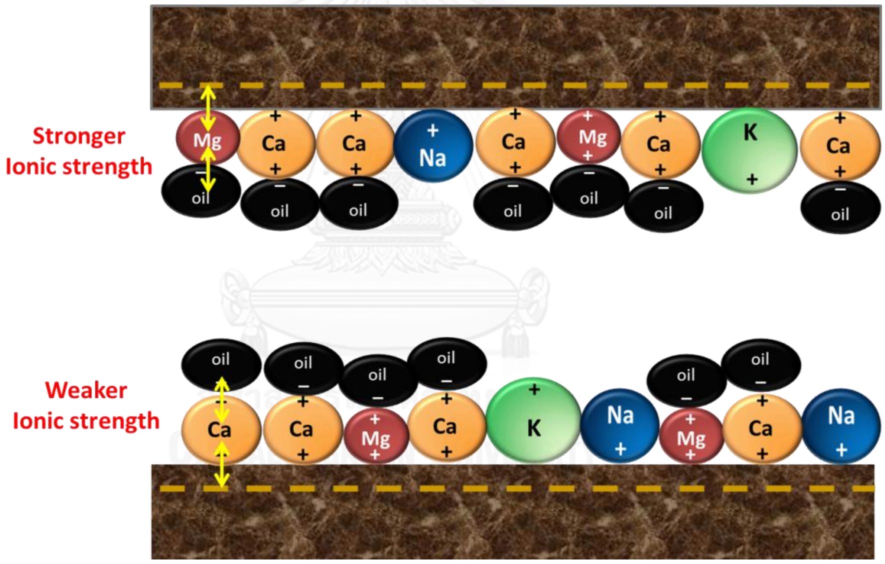


Figure 5.2 Illustration of oil-wet condition on sandstone surface through ion binding mechanism

From ionic bonding theory, radius of cation is inversely proportional to the strength of its bonding with oppositely charged ions. This can be described that an ion with smaller crystal radius possesses higher positive charge density per unit volume, therefore this ion will attract more negatively charged ion and its ionic strength is much stronger than that of an ion with larger crystal radius. According to this explanation, Magnesium ions create bonding between sandstone surface and oil with stronger ionic force than Calcium ion. This results in different degree of oil-wet condition when ratio of Magnesium and Calcium ions is altered. This explanation is used to describe the results in this section later on.

In this section, mass ratio of Calcium to Magnesium ions in formation brine is varied whereas mass ratio of Sodium to Potassium ions is fixed constant and total salinity is also kept constant at 100,000 ppm. Hence, the effects from other variations are neglected. Tables 5.3 to 5.6 show the amount of each ion composition in formation brine when mass ratio of Calcium ion to Magnesium ion varied in five different ratios (3:1, 5:1, 7:1, 9:1 and 11:1) for four different Sodium ion to Potassium ion ratios.

Table 5.3 Ion composition in formation brine which mass ratio of Calcium ion to Magnesium ion is varied whereas the mass ratio of Sodium ion to Potassium ion is fixed at 50:1

$Na^+ : K^+ = 50 : 1$						
Composition	**Seawater**	$Ca^{2+} : Mg^{2+}$				
		3 : 1	**5 : 1**	**7 : 1**	**9 : 1**	**11 : 1**
Na^+	10,813	34,250	34,250	34,250	34,250	34,250
K^+	304	685	685	685	685	685
Ca^{2+}	369	3,045	3,382	3,552	3,654	3,721
Mg^{2+}	1,157	1,014	677	507	406	338

Table 5.4 Ion composition in formation brine which mass ratio of Calcium ion to Magnesium ion is varied whereas the mass ratio of Sodium ion to Potassium ion is fixed at 120:1

Na$^+$: K$^+$ = 120 : 1						
Composition	Seawater	Ca^{2+} : Mg^{2+}				
		3 : 1	5 : 1	7 : 1	9 : 1	11 : 1
Na$^+$	10,813	34,139	34,296	34,375	34,422	34,454
K$^+$	304	289	289	289	289	289
Ca^{2+}	369	3,045	3,383	3,552	3,654	3,721
Mg^{2+}	1,157	1,015	677	507	406	338

Table 5.5 Ion composition in formation brine which mass ratio of Calcium ion to Magnesium ion is varied whereas the mass ratio of Sodium ion to Potassium ion is fixed at 150:1

Na$^+$: K$^+$ = 150 : 1						
Composition	Seawater	Ca^{2+} : Mg^{2+}				
		3 : 1	5 : 1	7 : 1	9 : 1	11 : 1
Na$^+$	10,813	34,183	34,339	34,418	34,465	34,494
K$^+$	304	231	231	231	231	231
Ca^{2+}	369	3,045	3,383	3,552	3,654	3,721
Mg^{2+}	1,157	1,015	677	507	406	338

Table 5.6 Ion composition in formation brine which mass ratio of Calcium ion to Magnesium ion is varied whereas the mass ratio of Sodium ion to Potassium ion is fixed at 180:1

$Na^+ : K^+ = 180 : 1$						
Composition	**Seawater**	**$Ca^{2+} : Mg^{2+}$**				
		3 : 1	**5 : 1**	**7 : 1**	**9 : 1**	**11 : 1**
Na^+	10,813	34,211	34,368	34,447	34,494	34,525
K^+	304	193	193	193	193	193
Ca^{2+}	369	3,045	3,383	3,552	3,654	3,721
Mg^{2+}	1,157	1,015	677	507	406	338

The results from coreflood experiment in every case in this section are mainly investigated on rate of oil recovery and total recovery factor which are illustrated in Figures 5.3 to 5.6.

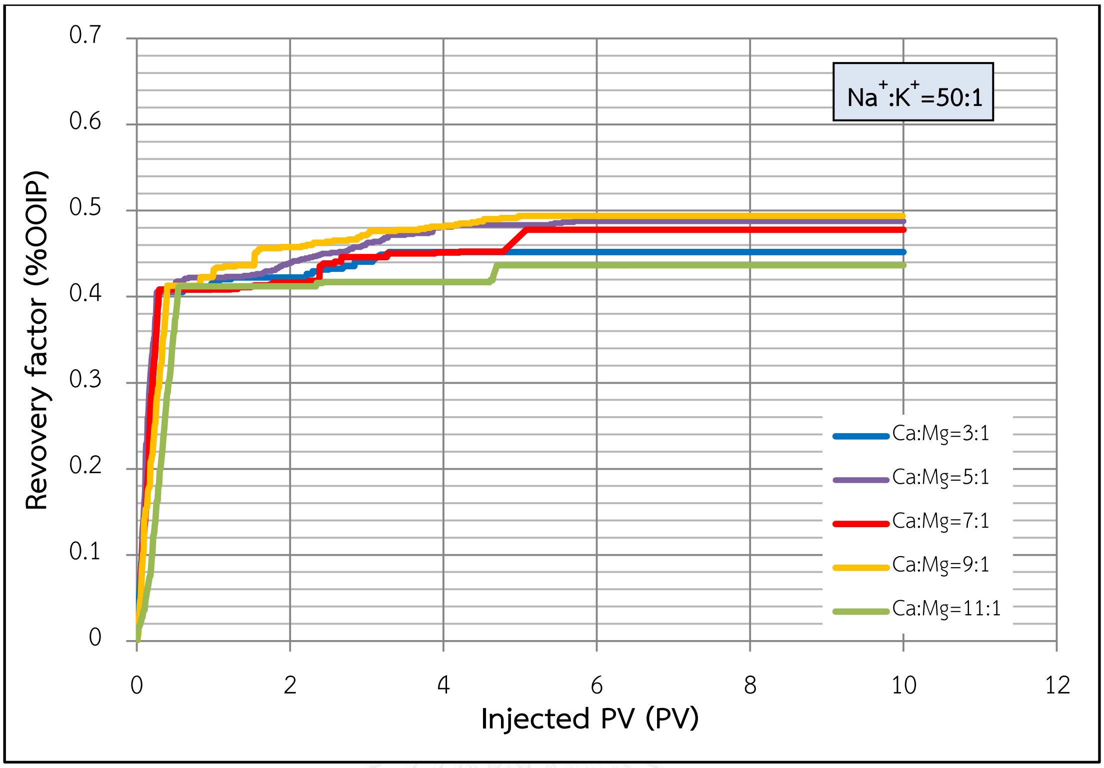


Figure 5.3 Oil Recovery factors obtained from seawater injection in cases with variation of Calcium ion to Magnesium ion ratios and Sodium ion to Potassium ion ratio is fixed at 50:1 as a function of injected pore volume of seawater

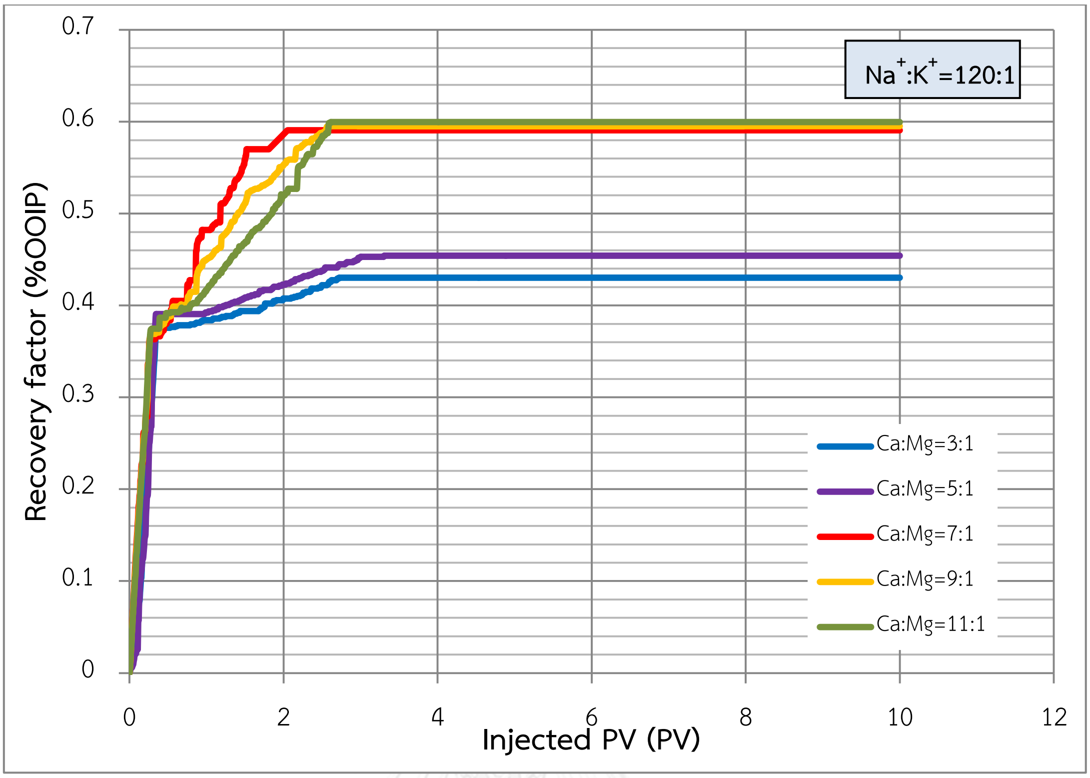


Figure 5.4 Oil Recovery factors obtained from seawater injection in cases with variation of Calcium ion to Magnesium ion ratios and Sodium ion to Potassium ion ratio is fixed at 120:1 as a function of injected pore volume of seawater

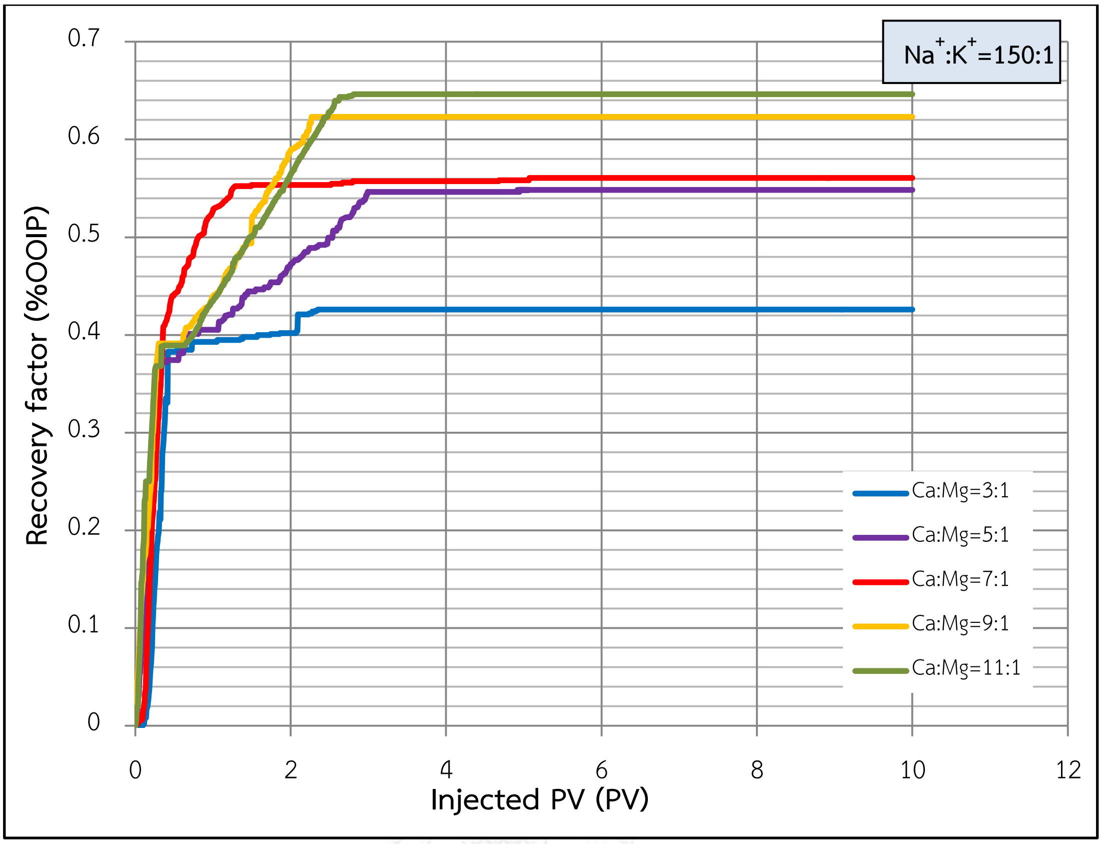


Figure 5.5 Oil Recovery factors obtained from seawater injection in cases with variation of Calcium ion to Magnesium ion ratios and Sodium ion to Potassium ion ratio is fixed at 150:1 as a function of injected pore volume of seawater

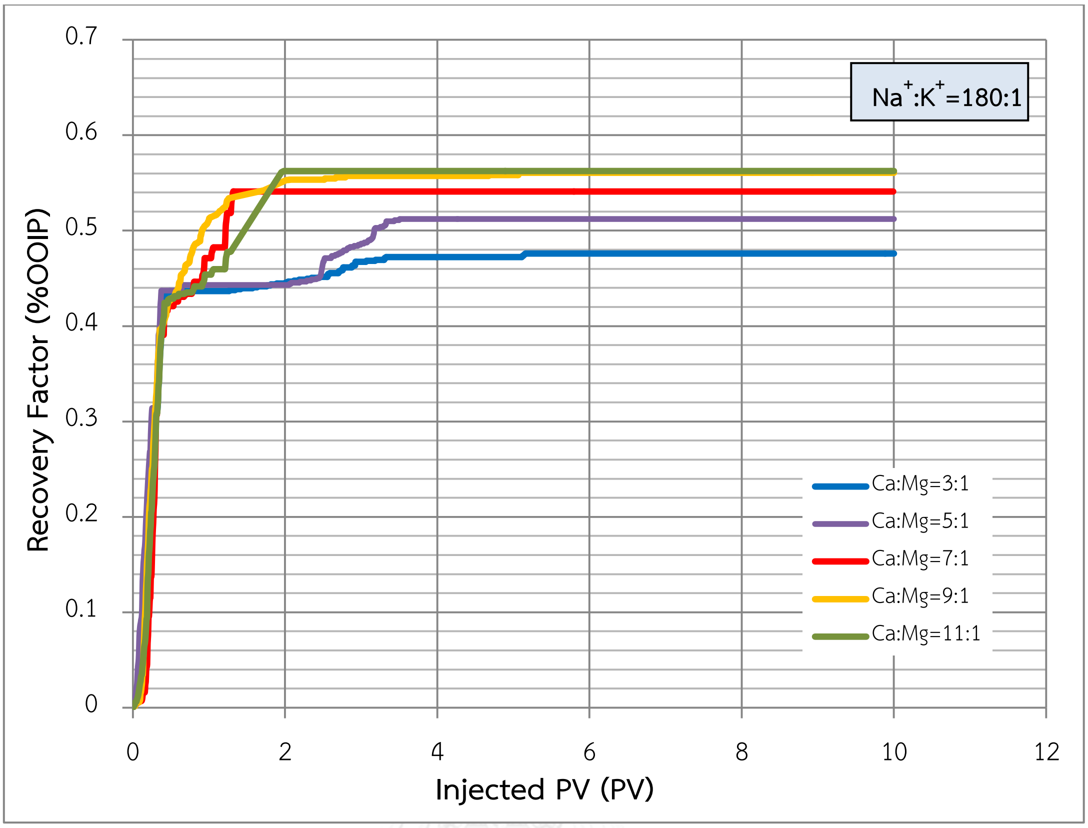


Figure 5.6 Oil Recovery factors obtained from seawater injection in cases with variation of Calcium ion to Magnesium ion ratios and Sodium ion to Potassium ion ratio is fixed at 180:1 as a function of injected pore volume of seawater

According to Figures 5.4 to 5.6, these cases are considered as high Sodium ion to Potassium ion ratio (120:1, 150:1 and 180:1). Among these cases, the rate of oil recovery is slow when Calcium ion concentration is low as can be observed from flat increment of oil recovery as a function of pore volume of seawater injected. This slow rate of oil recovery could be a result from difficulty of dissolution of Magnesium ions that link sandstone surface and oil. When Calcium ion to Magnesium ion ratio is 3:1, the amount of Magnesium ion on sandstone surface is the highest among other cases. Due to the smaller ionic size of Magnesium ion, the ionic strength between attached oil and Magnesium ion is stronger than that oil and Calcium ion, resulting in difficulty in liberation of attached oil. Moreover, the ionic strength between absorbed Magnesium ion and sandstone surface is also stronger than absorbed Calcium ion and sandstone surface and hence, substitution of monovalent ions from injected brine through MIE mechanism is difficult. This combination results in slow rate of oil recovery.

At higher concentration of Calcium ions (ratios of 5:1 and 7:1), the rate of oil recovery is improved compared to the previous case according to more amount of Calcium ion which is easier for detaching oil as well as monovalent ion substitution. Figure 5.7 compares the formation brine system in case of higher concentration of Calcium ions and lower concentration of Calcium ions (or higher concentration of Magnesium ion) and their responses after seawater injection.

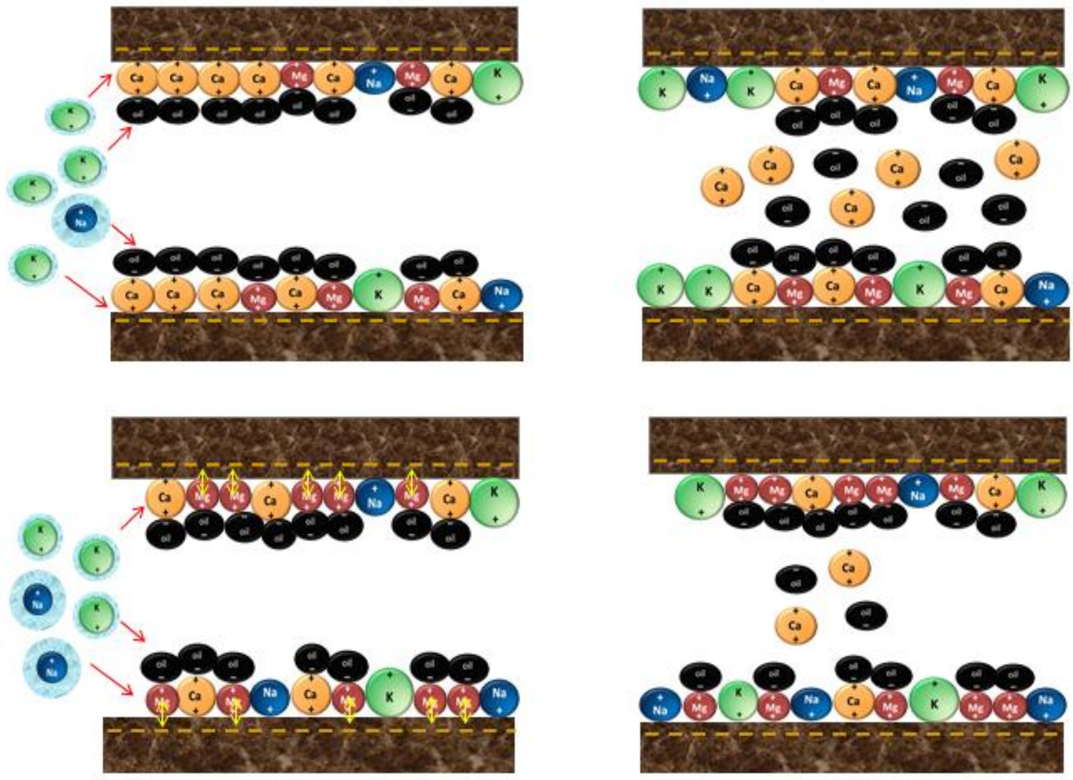


Figure 5.7 Formation brine system in case of higher concentration of Calcium ions (upper) and lower concentration of Calcium ions (lower) and the results after low salinity seawater injection.

However, in the case of excessive Calcium ion in formation brine, dissolution of Calcium ion occurs quickly and oil is liberated from rock surface. The abundant Calcium ions which are newly liberated start to prevent the forward MIE mechanism. This also results in low rate of oil recovery rate. Reduction of rate of oil recovery with increment of Calcium ion can be observed from a decrease of slope after breakthrough of injected seawater. Although the rate of oil recovery tends to be slow with an increment of Calcium ion, the obtained final oil recovery factor is still higher than other cases due to the higher amount of Calcium in formation brine system. The formation brine system in case of excessive Calcium ion is illustrated in Figure 5.8.

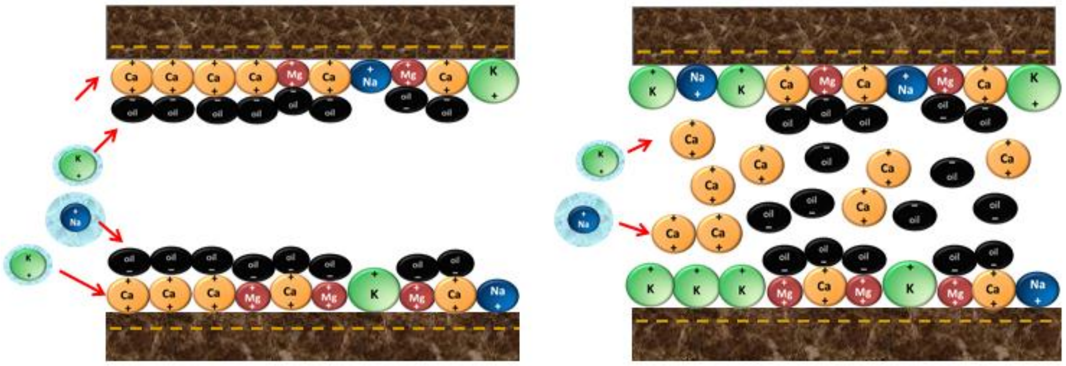


Figure 5.8 Formation brine system in case of excessive Calcium ion; the result after low salinity seawater injection

From Figure 5.3, this is the only case which is considered as low Sodium ion (compared to usual number) and the ratio of Sodium ion to Potassium ion 50:1. From the figure, it can be seen that the results obtained in this case are not in the same direction as other cases with higher Sodium ion ratios (120:1, 150:1 and 180:1). The results of every Calcium ion to Magnesium ion ratio yield very small difference in rate of oil recovery as well as oil recovery factor. Although Calcium ion in formation brine is increased, rate of oil recovery rate and oil recovery factor is not significantly increased. It is could be possible that, the effect of divalent ions is less dominant compared to effect of monovalent ions. In cases of higher Sodium ion concentration (120:1, 150:1 and 180:1), although the effects of Calcium ion and Magnesium ion in every fixed ratio of Sodium ion to Potassium ion show the similar direction, rate of oil recovery from every ratio of Sodium ion to Potassium is still different. This means that Sodium ion and Potassium ion in formation brine also affect the efficiency of low salinity seawater injection and this is explained in the following section.

Table 5.7 summarizes values of residual oil saturation , oil recovery factor and additional of oil recovery factor from conventional waterflooding obtained from seawater injection with formation brines with different ratios of Calcium ion to Magnesium ion ratios.

Table 5.7 Residual oil saturations ,oil recovery factors and additional of oil recovery factor obtained from seawater injection in cases with variation of ratios of Calcium ion to Magnesium ion

$Na^+ : K^+$	$Ca^{2+} : Mg^{2+}$	Residual oil saturation(*Sor*) (fraction)	Recovery factor (RF) (%)	Additional Recovery factor (%)
50 : 1	3 : 1	0.32	45.19	2.15
	5 : 1	0.33	48.77	5.73
	7 : 1	0.34	47.77	4.73
	9 : 1	0.37	49.38	6.35
	11 : 1	0.36	43.65	0.61
120 : 1	3 : 1	0.30	43.03	(0.1)
	5 : 1	0.33	45.42	2.38
	7 : 1	0.27	59.07	16.03
	9 : 1	0.31	59.52	16.48
	11 : 1	0.27	59.96	16.92
150 : 1	3 : 1	0.40	42.60	(0.44)
	5 : 1	0.24	54.84	11.80
	7 : 1	0.28	56.07	13.03
	9 : 1	0.26	63.73	20.69
	11 : 1	0.23	64.64	21.60
180 : 1	3 : 1	0.37	47.60	4.56
	5 : 1	0.32	51.22	8.18
	7 : 1	0.35	54.10	11.06
	9 : 1	0.38	56.07	13.03
	11 : 1	0.33	56.25	13.21

*** ( ) is the case where seawater injection yields lower oil recovery factor than conventional waterflooding.*

From Table 5.7, when Calcium ion in formation brine is increased, the amount of residual oil saturation tends to significantly decrease, resulting in higher oil recovery factor as well as more additional oil recovery. This is caused by higher amount of weaker ionic strength from Calcium ions. The dissolution of divalent bridging ion through MIE and diffusion are therefore easily occurred. However, oil recovery factor in some cases is lower than conventional waterflooding case. This is caused by low amount of Calcium ion in formation brine system.

5.2.2 Effects of Monovalent Ions in Formation Brine on Low Salinity Seawater Injection

In this section, mass ratio of Sodium ion to Potassium ion in formation brine is varied whereas mass ratio of Calcium ion to Magnesium ion is fixed and total salinity of formation brine is kept constant at 100,000 ppm. Hence, the effects from variables are minimized. Tables 5.8 to 5.12 illustrate the amount of each ion composition in formation brine when mass ratio of Sodium ion to Potassium ion is varied in different four ratios of 50:1, 120:1, 150:1, and 180:1 for four different Calcium ion to Magnesium ion ratios.

Table 5.8 Ion composition in formation brine which mass ratio of Sodium ion to Potassium ion is varied whereas the mass ratio of Calcium ion to Magnesium ion is fixed at 3:1

$Ca^{2+} : Mg^{2+} = 3 : 1$					
Composition	**Seawater**	$Na^{+} : K^{+}$			
		50 : 1	**120 : 1**	**150 : 1**	**180 : 1**
Na^{+}	10,813	33,842	34,139	34,183	34,183
K^{+}	304	685	289	231	231
Ca^{2+}	369	3,045	3,045	3,045	3,045
Mg^{2+}	1,157	1,014	1,014	1,014	1,014

Table 5.9 Ion composition in formation brine which mass ratio of Sodium ion to Potassium ion is varied whereas the mass ratio of Calcium ion to Magnesium ion is fixed at 5:1

$Ca^{2+} : Mg^{2+} = 5 : 1$					
Composition	**Seawater**	**$Na^{+} : K^{+}$**			
		50 : 1	**120 : 1**	**150 : 1**	**180 : 1**
Na^{+}	10,813	33,999	34,296	34,339	34,368
K^{+}	304	685	289	231	193
Ca^{2+}	369	3,382	3,382	3,382	3,383
Mg^{2+}	1,157	677	677	677	677

Table 5.10 Ion composition in formation brine which mass ratio of Sodium ion to Potassium ion is varied whereas the mass ratio of Calcium ion to Magnesium ion is fixed at 7:1

$Ca^{2+} : Mg^{2+} = 7 : 1$					
Composition	**Seawater**	**$Na^{+} : K^{+}$**			
		50 : 1	**120 : 1**	**150 : 1**	**180 : 1**
Na^{+}	10,813	34,078	34,375	34,418	34,447
K^{+}	304	685	289	231	193
Ca^{2+}	369	3,552	3,552	3,552	3,552
Mg^{2+}	1,157	507	507	507	507

Table 5.11 Ion composition in formation brine which mass ratio of Sodium ion to Potassium ion is varied whereas the mass ratio of Calcium ion to Magnesium ion is fixed at 9:1

$Ca^{2+} : Mg^{2+} = 9 : 1$					
Composition	**Seawater**	$Na^{+} : K^{+}$			
		50 : 1	120 : 1	150 : 1	180 : 1
Na^{+}	10,813	34,125	34,422	34,465	34,494
K^{+}	304	685	289	231	193
Ca^{2+}	369	3,654	3,654	3,654	3,654
Mg^{2+}	1,157	406	406	406	406

Table 5.12 Ion composition in formation brine which mass ratio of Sodium ion to Potassium ion is varied whereas the mass ratio of Calcium ion to Magnesium ion is fixed at 11:1

$Ca^{2+} : Mg^{2+} = 11 : 1$					
Composition	**Seawater**	$Na^{+} : K^{+}$			
		50 : 1	120 : 1	150 : 1	180 : 1
Na^{+}	10,813	34,156	34,454	34,494	34,525
K^{+}	304	685	289	231	193
Ca^{2+}	369	3,721	3,721	3,721	3,721
Mg^{2+}	1,157	338	338	338	338

Oil recovery factors plotted as a function of injected pore volume of seawater and are illustrated in Figures 5.9 to 5.13 for different cases with fixed Calcium ion to Magnesium ion ratios of 3:1, 5:1, 7:1, 9:1, and 11:1, respectively.

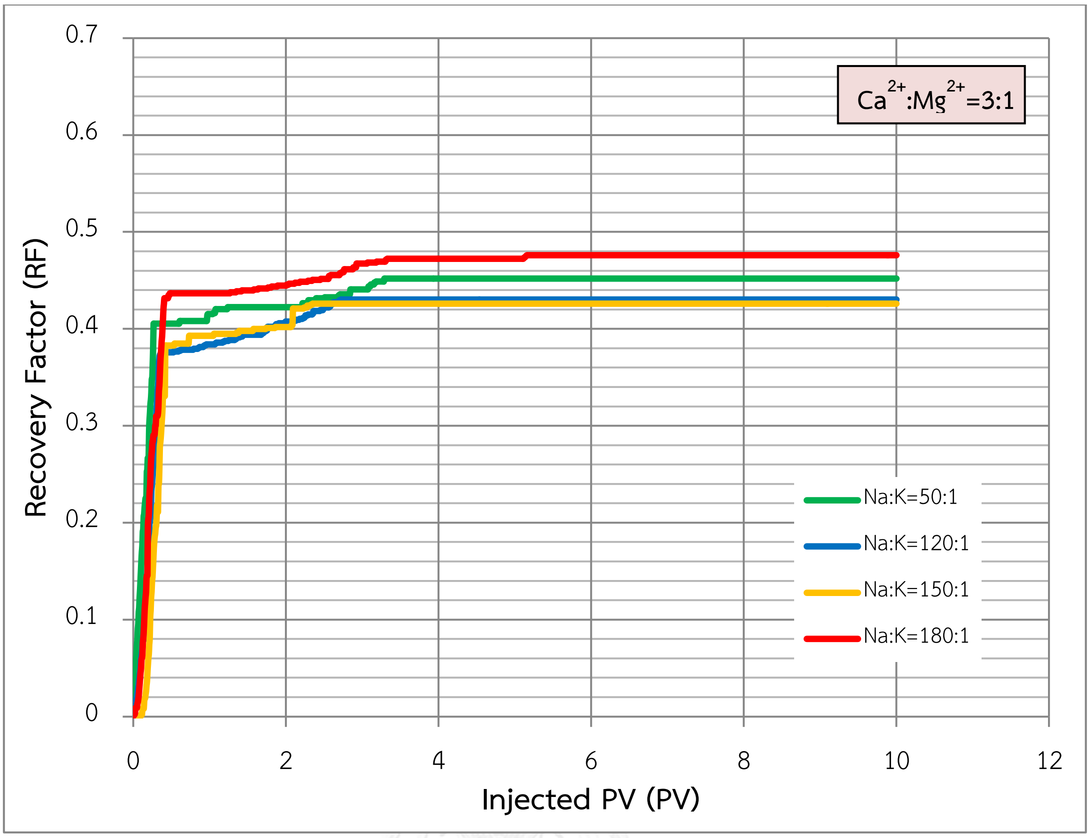


Figure 5.9 Oil Recovery factors obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios and Calcium ion to Magnesium ion ratio is fixed at 3:1 as a function of injected pore volume of seawater

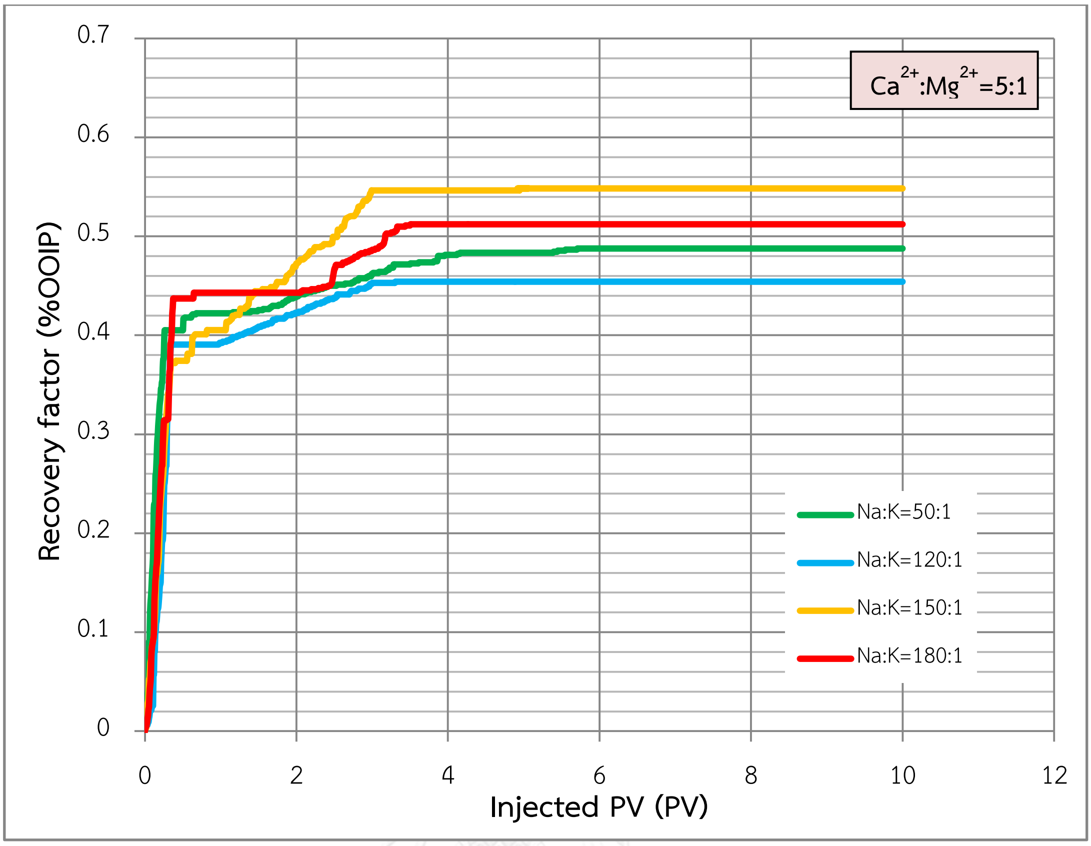


Figure 5.10 Oil Recovery factors obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios and Calcium ion to Magnesium ion ratio is fixed at 5:1 as a function of injected pore volume of seawater

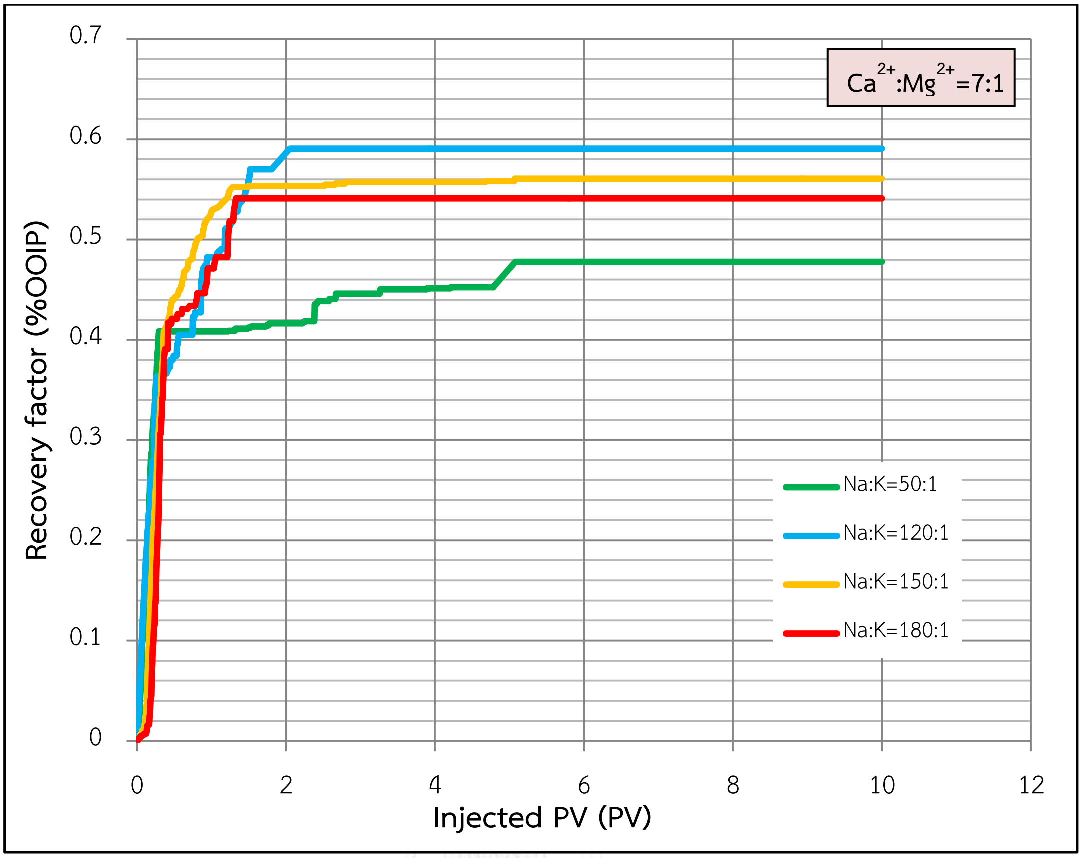


Figure 5.11 Oil Recovery factors obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios and Calcium ion to Magnesium ion ratio is fixed at 7:1 as a function of injected pore volume of seawater

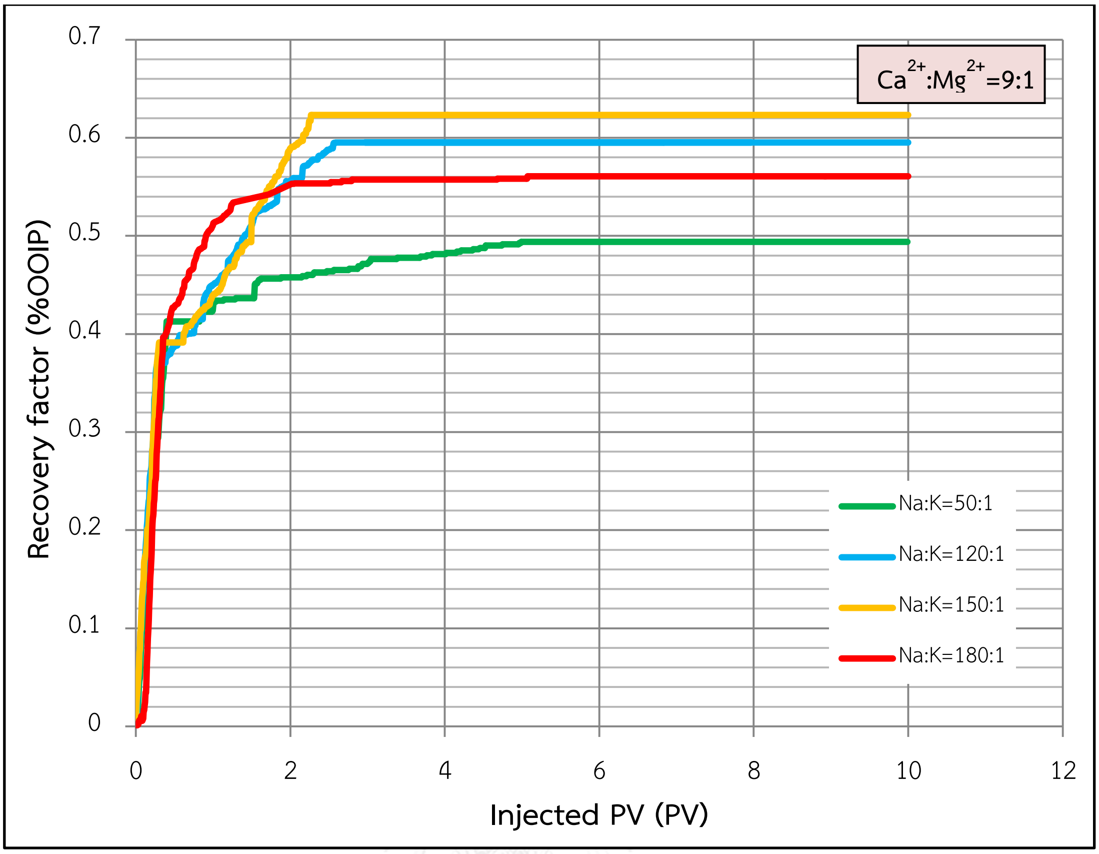


Figure 5.12 Oil Recovery factors obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios and Calcium ion to Magnesium ion ratio is fixed at 9:1 as a function of injected pore volume of seawater

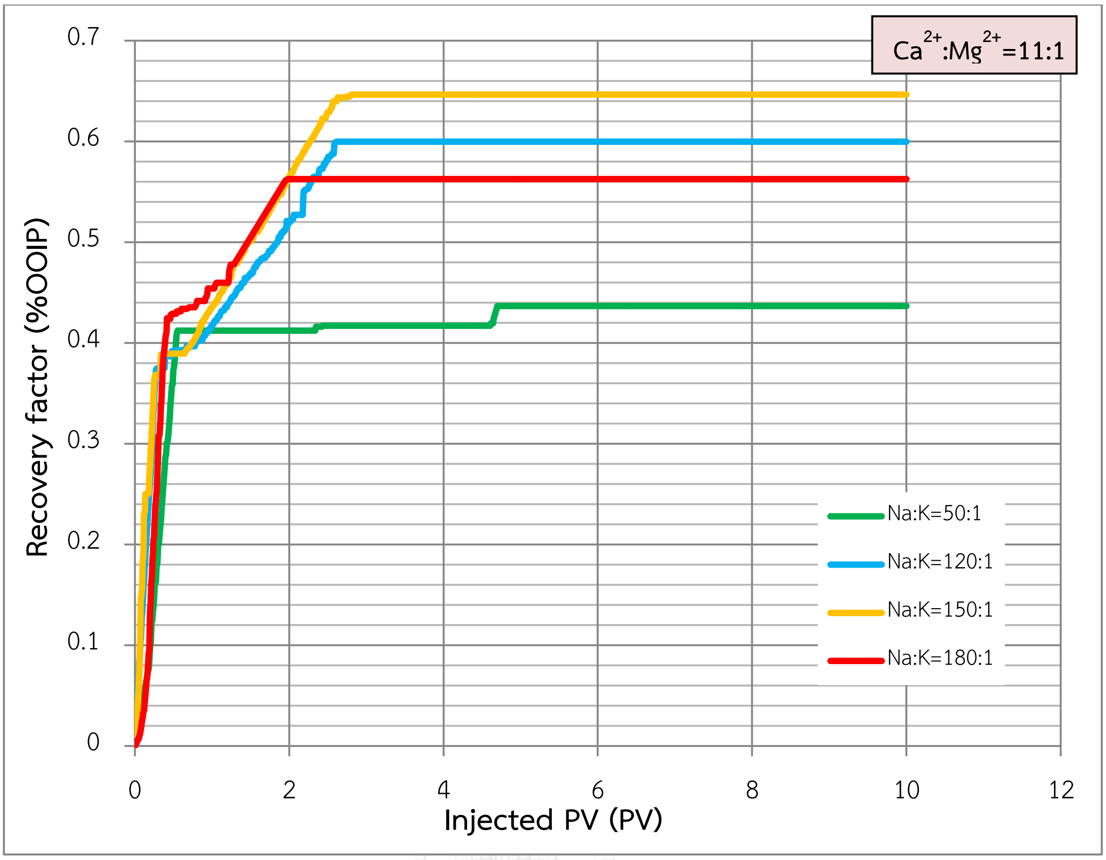


Figure 5.13 Oil Recovery factors obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios and Calcium ion to Magnesium ion ratio is fixed at 11:1 as a function of injected pore volume of seawater

In nature, without bonding with negatively charged ions, free cations are hydrated with water molecules. The smaller the size of the ion, the degree of hydration is greater. Thus, one Sodium ion is bound with higher number of water compared to Potassium ion. It results in stronger ionic strength of hydrated Potassium ion has. Consecutively, hydrated Potassium ion possesses higher capacity of replacement of detached divalent ions during the dissolution mechanism compared to Sodium ion. Moreover, in terms of ionic mobility, larger hydrated ion is lower ionic mobility in water as well. The hydrated size and ionic mobility of Sodium ion and Potassium ion are compared in Table 5.13.

Table 5.13 Ionic radius, hydrated radius and ionic mobility of Sodium and Potassium ion [20]

Monovalent Ion	**Ionic Radius** (pm)	**Hydrated Radius** (pm)	**Ionic mobility** (ohm^{-1}cm^{2}mol^{-1})
Sodium (Na^+)	116	450	43.5
Potassium (K^+)	152	300	64.5

As a result, the hydrated radius and ionic mobility affect efficiency of substitution process of divalent ions by monovalent ion in during MIE mechanism. According to Figures 5.9 and 5.10, at low Calcium ion concentration or Calcium ion to Magnesium ion ratios of 3:1 and 5:1, no matter the ratio of Sodium ion to Potassium ion is changed in formation brine, the rate of oil recovery is mostly constant. Nevertheless, an increment of Calcium ion concentration in formation brine causes more distribution of oil recovery rate. It can be observed in similar direction that increasing of Sodium ion to Potassium ion in formation brine results in better rate of oil recovery as can be observed in Figures 5.11 to 5.13. As explained in previous section, lower amount of Calcium ion in formation brine causes oil-wet condition through ion binding between carboxylic acid and sandstone surface by using Magnesium ion as bridging ion. This results in stronger attraction between oil phase and rock surface and eventually results in more difficulty to liberate oil. In case of low Calcium ion concentration, there is no direct relationship between Sodium ion to Potassium ion ratio with oil recovery. This could be due to the different in total pore volume of each sample that could make slightly different in oil recovery.

From Figures 5.11 to 5.13 which correspond to cases with higher Calcium ion concentration (Calcium ion to Magnesium ion ratios of 7:1, 9:1 and 11:1), it can be obviously seen that the lowest ratio of Sodium ion to Potassium in formation brine of 50:1 results in the slowest rate of oil recovery rate. At this condition, it can be explained that the concentration of Potassium ion in formation brine is much higher than the concentration of Potassium ion in injected seawater. Thereby, Potassium ion in formation brine would rather diffuse to the injected seawater solution, resulting in decreasing of chances that Potassium ion in formation brine will substitute the divalent ion bridging between oil and rock surface. Therefore, rate of oil recovery is slow. This mechanism is illustrated in Figure 5.14.

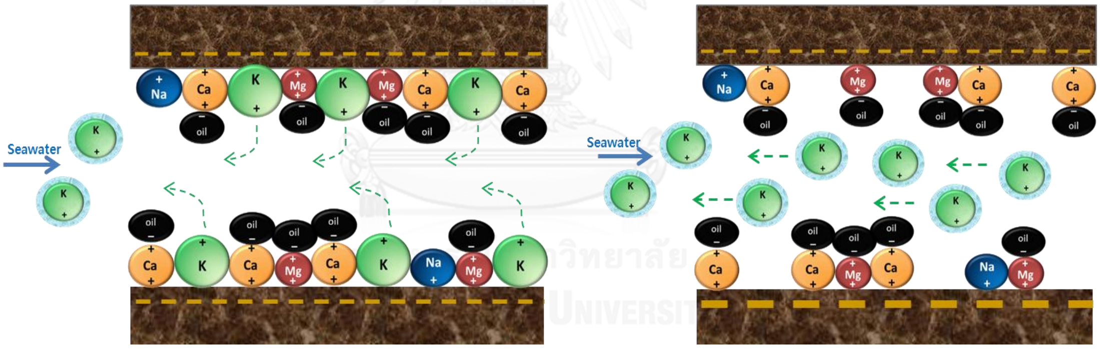


Figure 5.14 Diffusion of Potassium ion from formation brine to injected seawater solution in case of the lowest ratio of Sodium ion to Potassium ion in formation brine

However, if the ratio of Sodium ion to Potassium ion is increased, in cases of ratios of 120:1, 150:1 and 180:1, the amount of Potassium ion in formation brine is lower than Potassium ion in injected seawater. Low Potassium ion concentration in formation brine would result in reverse mechanism, Potassium ion diffusing from injected seawater to formation brine and causing substitution of Potassium ion on sites of divalent ions bridging between oil and surface. This hence, results in increment of oil recovery rate.

When considering oil recovery factors from these three Figures, it can be seen that the highest oil recovery is obtained when Sodium ion to Potassium ion ratio is around 150:1. At the highest ratio of Sodium ion to Potassium ion (180:1), the rate of oil recovery is quite high in general but this results in attaining of equilibrium of Potassium ion between injected brine and formation brine at earlier time compared to other Sodium ion to Potassium ion ratios (120:1 and 150:1).

Table 5.14 summarizes values of residual oil saturation, oil recovery factor and additional of oil recovery factor from conventional waterflooding obtained from seawater injection in cases with different ratios of Sodium ion to Potassium ion in formation brine.

Table 5.14 Residual oil saturations, oil recovery factors, and additional of oil recovery factor obtained from seawater injection in cases with variation of Sodium ion to Potassium ion ratios

Ca^{2+}:Mg^{2+}	Na^{+}:K^{+}	Residual oil saturation(*Sor*) (fraction)	Recovery factor (RF) (%)	Additional Recovery factor (%)
3 : 1	50 : 1	0.32	45.19	2.15
	120 : 1	0.30	43.03	(0.10)
	150 : 1	0.40	42.60	(0.44)
	180 : 1	0.37	47.60	4.56
5 : 1	50 : 1	0.33	48.77	5.73
	120 : 1	0.33	45.42	2.38
	150 : 1	0.24	54.84	11.80
	180 : 1	0.32	51.22	8.18
7 : 1	50 : 1	0.34	47.77	4.73
	120 : 1	0.27	59.07	16.03
	150 : 1	0.28	56.07	13.03
	180 : 1	0.35	54.10	11.06
9 : 1	50 : 1	0.37	49.39	6.35
	120 : 1	0.31	59.52	16.48
	150 : 1	0.26	63.73	20.69
	180 : 1	0.38	56.25	13.03
11 : 1	50 : 1	0.36	43.65	0.61
	120 : 1	0.27	59.96	16.92
	150 : 1	0.23	64.64	21.60
	180 : 1	0.33	56.25	13.21

*** ( ) is the case where seawater injection yields lower oil recovery factor than conventional waterflooding.*

From Table 5.14, in cases of higher Sodium ion to Potassium ion ratio (120:1, 150:1 and 180:1), when the ratio of Sodium ion to Potassium is increased, the amount of residual oil saturation tends to decrease, resulting in higher oil recovery factor and more additional oil recovery. This is caused by diffusing of Potassium ion from injected seawater to formation brine and this helps promoting the substitution of Potassium ion onto the sites of divalent ions bridging between oil and surface. However, oil recovery factor in some cases is lower than conventional waterflooding case. This is caused by low amount of Calcium ion in formation brine system.

From all cases, formation brine with Calcium ion to Magnesium ion ratio 11:1 and Sodium ion to Potassium ion 150:1 is the brine that yields the highest oil recovery factor in this section. Figure 5.15 compares the relative permeability curves between this case and conventional waterflooding case from section 5.1.

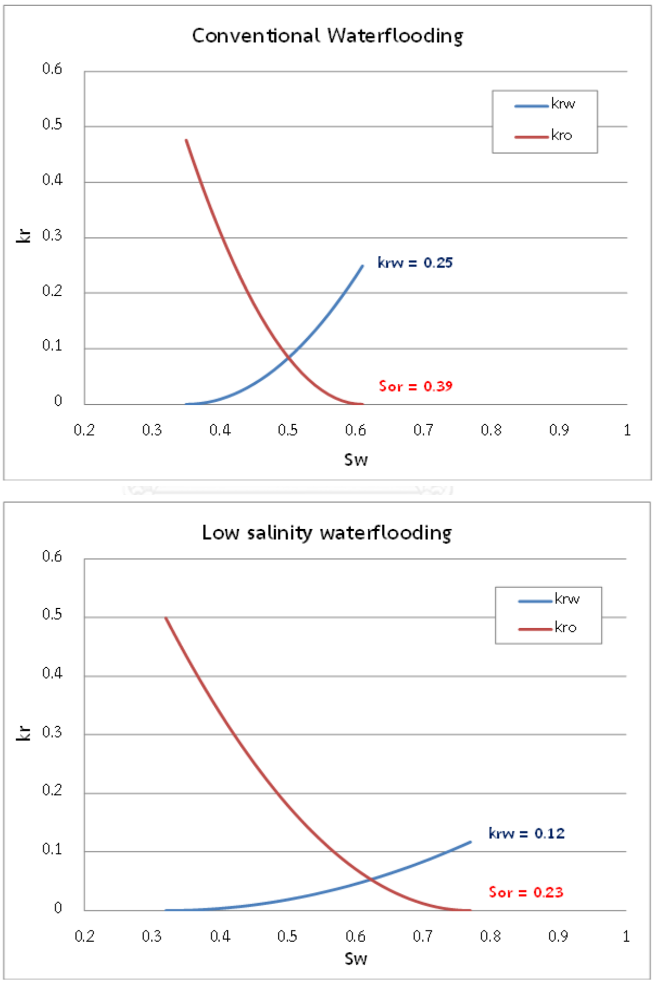


Figure 5.15 Comparison between relative permeability curves of conventional waterflooding case (upper) and low salinity waterflooding case which yields the highest oil recovery factor (below)

According to Figure 5.15, relative permeability to water (k_{rw}) when performing with low salinity waterflooding is lower than the conventional waterflooding case. It means that low salinity waterflooding is effective in wettability alteration which can change the wettability of sandstone surface to a more water-wet condition. Furthermore, residual oil saturation (S_{or}) tends to decrease when performing with low salinity waterflooding.

In this section, it can be seen that amount of cations both divalent and monovalent plays an important role in controlling effectiveness of low salinity seawater injection. MIE mechanism which comes together with high rate of oil recovery and high oil recovery factor is favored by conditions which are: 1) Formation brine contains high ratio of Calcium ion to Magnesium ion. This condition results in oil-wet surface through ion binging that responds low salinity seawater injection. 2) Formation brine contains low Potassium ion to favor diffusion of Potassium ion from injected water to substitute divalent bridging ion at the sandstone surface. 3) Although low Potassium ion in formation brine is considered as favorable condition, lacking of Potassium ion in formation brine would result in shifting of equilibrium quickly and MIE would terminate earlier. 4) Besides considering formation brine, injected water should be low in total salinity, implying low Calcium ion concentration, in order to favor dissolution of divalent ion at bridging layer and at the same time, amount of Potassium ion should be high enough to diffuse to surface zone, causing the substitution of monovalent ion through MIE mechanism.

5.3 Effects of Total Salinity of Formation Brine on Low Salinity Seawater Injection

From section 5.2, concentration of formation brine yielding the highest oil recovery factor is chosen for the experiment in this section. The selected formation brine is diluted from total salinity of 100,000 ppm to 75,000 ppm and 50,000 ppm in order to study effects of total salinity of formation brine on effectiveness of seawater injection. Since total salinity of seawater is 35,000, the minimum total salinity of formation brine in this study must be slightly higher in order to create the dissolution mechanism of several ions from formation brine to injected brine. And hence, the minimum formation brine used in this is section is set up around 50,000 ppm. All saturated core samples with different formation brine concentration in this section are displaced with synthetic seawater.

According to results from section 5.2, the highest oil recovery is obtained from formation brine containing ratio of Calcium ion to Magnesium ion of 11:1 and mass ratio of Sodium ion to Potassium ion of 150:1. This brine formulation is therefore chosen for further modification in this study. Ion composition in mass of three formation brines with difference in total salinity is summarized in Table 5.15.

Table 5.15 Ion composition in mass of three formation brines with difference in total salinity

Composition	Seawater 35,000 ppm	Formation brine salinity (ppm)		
		50,000	75,000	100,000
Na^+	10,813	17,246	25,873	34,494
K^+	304	116	173	231
Ca^{2+}	369	1,861	2,791	3,721
Mg^{2+}	1,157	169	254	338

Results in terms of oil recovery factor from coreflood experiment from these three formation brines are illustrated in Figure 5.16. As explained in previous section, rate of oil recovery is observed through slope after water breakthrough until oil recovery factor becomes constant.

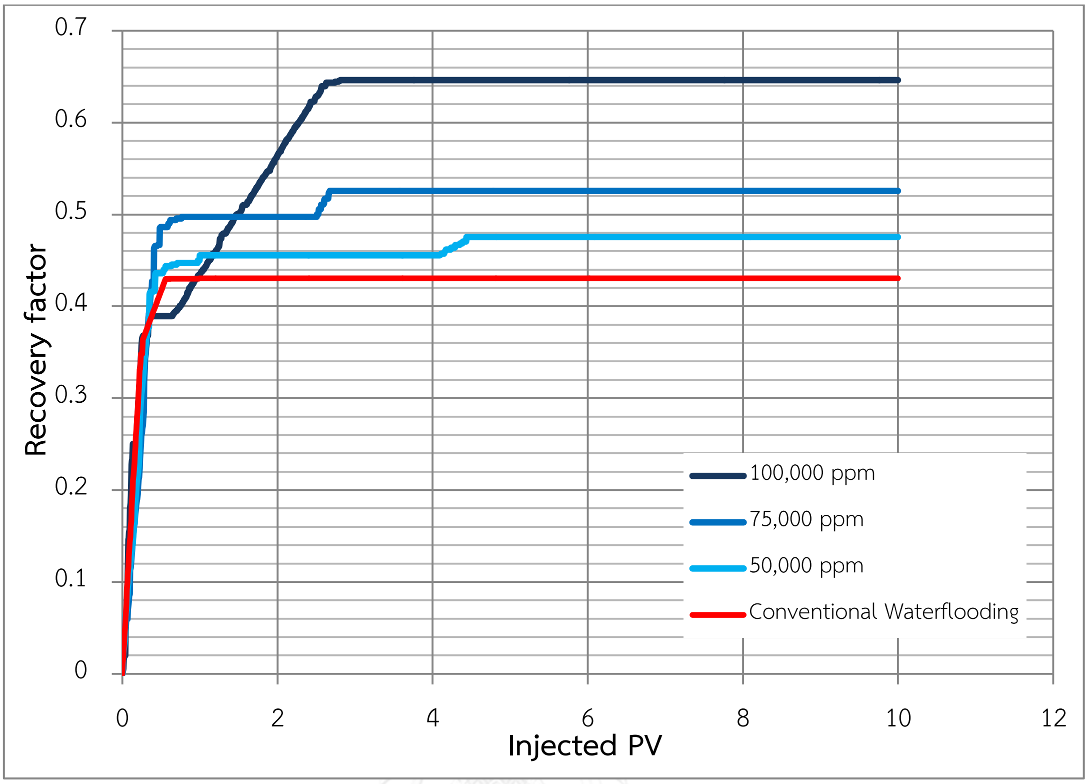


Figure 5.16 Oil Recovery factors obtained from conventional waterflooding and seawater injection in cases with variation of total salinity of formation brine and Calcium ion to Magnesium ion ratios and Sodium ion to Potassium ion ratio are fixed at 11:1 and 150:1 respectively as a function of injected pore volume of seawater

From the figure 5.16, it can be obviously seen that higher salinity of formation brine results in higher oil recovery factor. The core sample that is saturated by the highest salinity formation brine of 100,000 ppm yields the highest oil recovery factor of about 64.6%. On the other hand, core sample that is saturated by the lowest salinity formation brine of 50,000 ppm yields the lowest oil recovery factor only 47.5%. When there is a higher contrast in salinity between formation brine and injected brine, bridging divalent ions can be easier to liberate and together with adequate amount of monovalent ions in seawater, substitution of divalent ions by monovalent ions easily undergoes. This can be explained that higher difference salinity between formation brine and injected brine favors dissolution of bridging divalent ion through Fick’s law of diffusion together with MIE mechanism.

Comparing the rate of oil recovery among three cases, overlaying of oil recovery factors of all three cases in first period explains that only oil is produced and water is not breakthrough yet. Sudden change of slope indicates the breakthrough of injected water. From Figure 5.16 it can be seen that the first breakthrough is found in the case of the highest salinity of 100,000 ppm. This can be explained that, when total salinity of formation brine is high, amount of divalent ion is proportionally, resulting in more bridges to capture oil droplets. Results from section 5.1 also show mostly the same breakthrough point.

However, when core sample is saturated with diluted formation brine, amount of divalent ion is less. Hence, oil-wet condition occurred through ion binding is weaker compared to the higher formation brine salinity. Water breakthrough of both cases with formation brine salinity of 75,000 and 50,000 ppm occurs at later time as rock sample is less oil-wet, shifting toward the water-wetness. Nevertheless, not only the physical displacement mechanism occurs during this period. Effects from low salinity waterflooding can also occur. As oil is less trapped from ion binding in case of formation brine of 50,000 ppm, the breakthrough time should occur after the case of formation brine salinity of 75,000. The case with formation brine salinity of 75,000 ppm may obtain benefit from salinity contrast and hence, MIE occurs more than case of 50,000 ppm. More oil is therefore liberated and this results in late arrival injected water.

After the first recovery period is accomplished, no more oil is recovered for certain period. This period is quite different based on different formation brine. Although breakthrough occurs very early due to higher amount of oil that is trapped on sandstone surface through ion binding in case of high salinity formation brine of 100,000 ppm, there is still high amount of remaining oil that can be recovered by dissolution and MIE mechanisms and this results in short period of no oil production. Sudden increment of oil production is observed. As remaining oil saturation is very high and salinity contrast is very favorable, oil recovery increases rapidly in this period and due to extremely high salinity different, longer time to attain salinity equilibrium results in continuity of recovering remaining oil that can be further reduced. At the end, oil recovery factor reaches highest value at around 64.64 % and lowest residual oil saturation as shown in table 5.16.

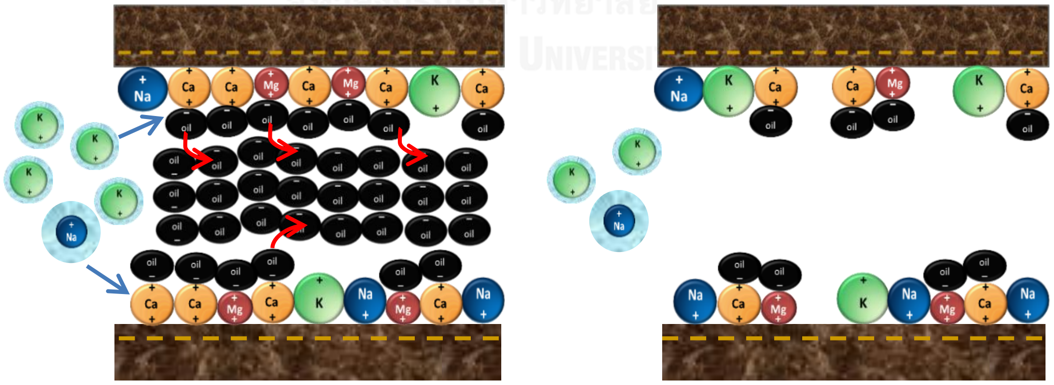
For cases of formation brine salinity of 75,000 and 50,000 ppm, the salinity contrast with injected brine, which is seawater, of 35,000 ppm maybe not high enough. After arrival of first breakthrough, the remaining oil is still facing difference in salinity of formation and injected brine. As difference in salinity between 75,000 and 35,000 is greater than the case of 50,000 and 35,000, dissolution of bridging ions and MIE occur earlier in case of higher salinity contrast. Arrival of second oil bank is observed for both cases but earlier arrival is found in case of higher salinity contrast. As salinity contrast is lower compared the case of formation brine of 100,000 ppm, surface equilibrium is attained earlier and hence, ion concentration at surface and formation water reaches their equilibrium. No more oil is recovered due to determination of dissolution mechanism as well as MIE. Therefore, oil recovery factor is the lowest in case of formation brine salinity of 50,000 ppm and is the highest in case of 100,000 ppm.

Table 5.16 summarizes values of residual oil saturations, oil recovery factor and additional oil recovery factor from conventional waterflooding obtained from seawater injection in cases with different of formation brine salinity.

Table 5.16 Residual oil saturations, oil recovery factors, and additional of oil recovery factor obtained from seawater injection in three cases with difference of formation brine salinity

Formation brine salinity (ppm)	Residual oil saturation(*Sor*) (fraction)	Recovery factor (RF) (%)	Additional Recovery factor (%)
100,000	0.23	64.64	21.60
75,000	0.29	52.55	9.51
50,000	0.35	47.33	4.49

In order to understand oil recovery mechanisms from low salinity waterflooding, phase of oil recovery can be distinguished in two distinct periods. Illustrations of oil recovery mechanisms are proposed. In the first period, oil recovery mechanism is dominated by physical force from mass of brine itself (which is considered as viscous force). However, since there is salinity contrast in the period, dissolution of bridging ion can also occur together with MIE. This is so-called chemical displacement (which is considered as mechanisms occurred through the changes of chemical elements). Figure 5.17 illustrates stages before and after the displacement mechanisms in first period after low salinity water is injected into the formation.

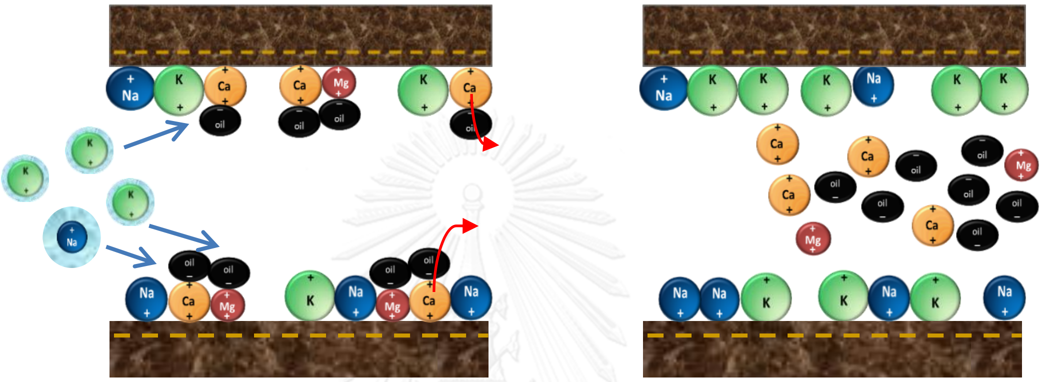


Physical and chemical displacement

Result after first recovery period

Figure 5.17 Oil recovery mechanism during first period which is mainly dominated by physical displacement

Subsequently, the second recovery period starts. Within this period, oil is recovered mainly through chemical displacement which occurs through dissolution of divalent bridging with an assist of MIE. As explained previously, the result of this period is shown as second steep slope as shown for all three cases in Figure 5.16. This period could be seen from the declining slope. Figure 5.18 shows the process of oil recovery mechanisms in second period which is dominated by chemical displacement.



Chemical displacement in second recovery period

Result after second recovery period

Figure 5.18 Oil recovery mechanism during second period which is mainly dominated by chemical displacement

It can be observed that the contrast in salinity between formation brine and injected brine controls both rate of oil recovery and total oil recovery factor. High salinity of formation brine may adversely result in high remaining oil after physical displacement mechanism due to higher amount of divalent ions that can capture oil through ion binding. However, oil recovery can be further increased due to difference in salinity and as salinity difference gap is large, equilibrium may take longer time to be attained and as a result, oil recovery is kept increasing through dissolution of Calcium ion and MIE. In cases where salinity contrast is less, benefit from low salinity water injection maybe obscured. As amount of oil captured through bridging ion is less, physical displacement may already yield good result. Moreover, since the gap of salinity contrast is small, equilibrium of potential ion may attain very quickly and as a result, oil recovery is relative low compared to cases with higher salinity contrast.

Another observation made in this section is that the period between first and second oil bank also has a relationship with salinity contrast. A smaller gap is observed when high salinity contrast is present as difference in salinity can speed up chemical displacement to follow up the physical one. Oppositely, long gap is found in case of low salinity contrast. Accumulation of liberated oil from dissolution mechanism and MIE results in second oil bank arriving after the first oil displaced from mass of water. Nevertheless, separation gap between first and second period of oil recovery mechanisms by means of low salinity waterflooding may be differed if injection rate is changed. It can be expected that smaller injection rate may result in higher retention time and as a consequent, arrival of first and second oil banks may merge together.

5.4 Effect of Diluted Formation Brine Injection

In general, water produced from oil production comes from formation water in reservoir and this is so-called “produced water”. Produced water can be mobile connate water or water from bottom aquifer. In most countries, produced water cannot be disposed to environment and it is strictly forced to re-inject back to the reservoir for water disposal or for maintaining reservoir pressure in secondary recovery. This section emphasizes on the efficiency of using produced water as part of injectant compared to solely seawater injection.

From section 5.2, concentration of formation brine that yields the highest oil recovery factor is chosen for the experiment in this section. The selected formation brine is diluted from total salinity of 100,000 ppm to 50,000 ppm and 35,000 ppm in order to study effects of diluted formation brine injection on effectiveness of seawater injection. This reduction of total salinity is performed to simplify deionization of all the ions inside formation brine and hence, proportion of each ion still remains the same. Core samples are saturated with the same formation brine at concentration of 100,000 ppm and then are displaced with different diluted formation brine concentrations.

According to results from section 5.2, the highest oil recovery is obtained from formation brine containing Calcium ion to Magnesium ion ratio of 11:1 and Sodium ion to Potassium ion ratio of 150:1. This brine formulation is therefore chosen to represent formation brine composition in this section. The ion compositions in formation brine and two injected brine concentration (diluted formation brine) are summarized in Table 5.17, whereas the comparison between ion compositions of injected brine in this study and seawater from previous sections are shown in Table 5.18.

Table 5.17 Potential ion compositions of formation brine and ion compositions of two diluted formation brines

Composition	Formation brine 100,000 ppm	Diluted formation brine	
		50,000	35,000
Na^+	34,494	17,246	12,074
K^+	231	116	81
Ca^{2+}	3,721	1,861	1,302
Mg^{2+}	338	169	118

Table 5.18 Comparison of potential ion compositions of seawater and diluted formation brine

Composition	Seawater 35,000 ppm	Diluted formation brine 35,000
Na^+	10,813	12,074
K^+	304	81
Ca^{2+}	369	1,302
Mg^{2+}	1,157	118

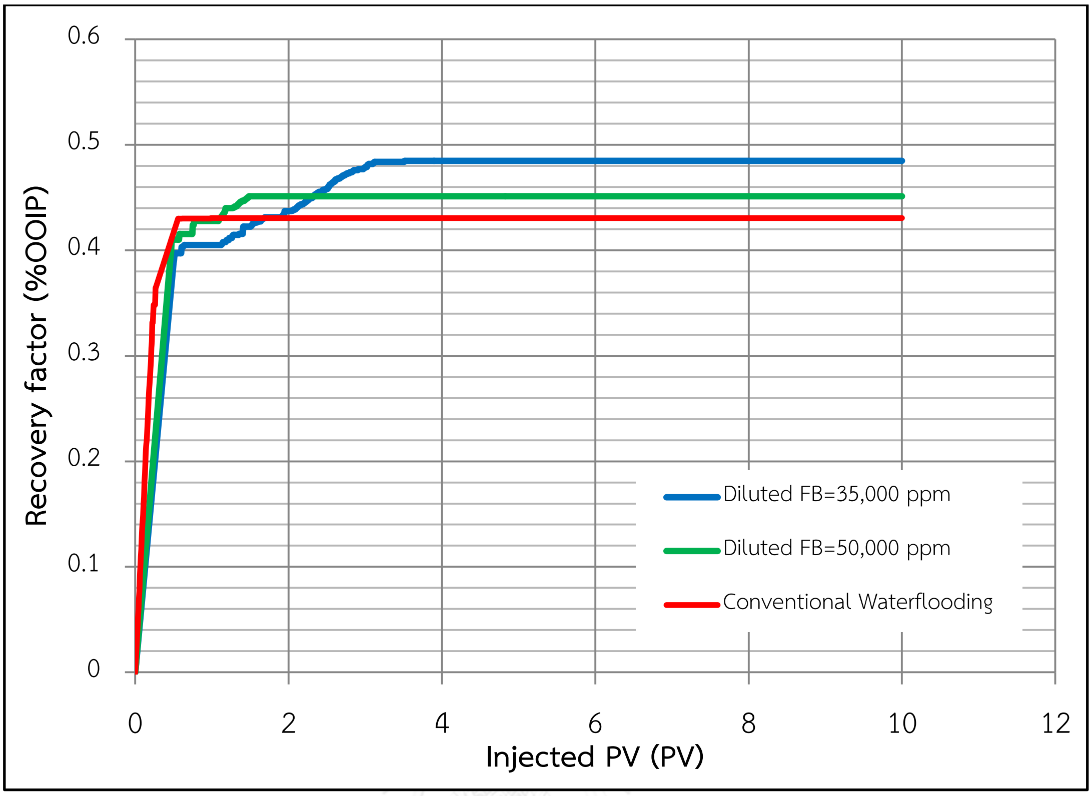


Figure 5.19 Oil Recovery factors obtained from conventional waterflooding and diluted formation brine injections as a function of injected pore volume

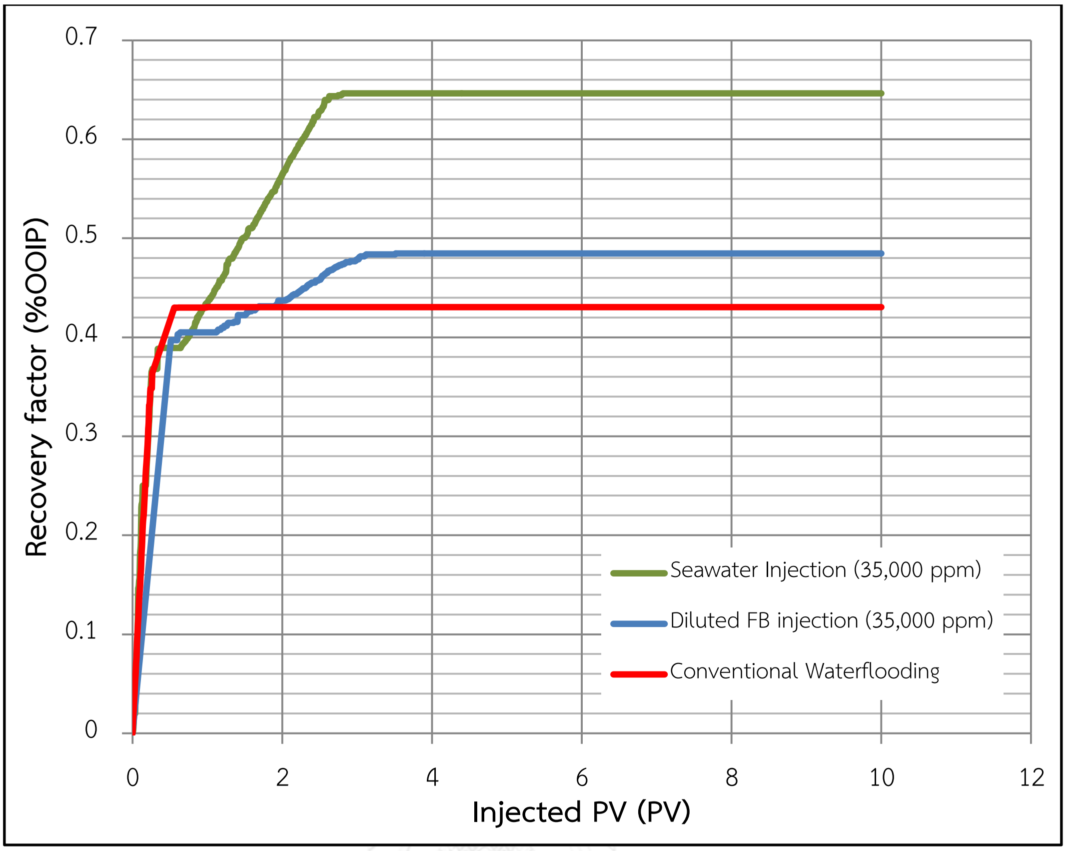


Figure 5.20 Oil Recovery factors obtained from seawater injection, diluted formation brine injection and conventional waterflooding as a function of injected pore volume

From Figure 5.19, the result shows that injection of diluted formation brine at 35,000 ppm yields higher oil recovery factor than injection of diluted formation brine of 50,000 ppm. This can also confirm the results obtained from section 5.3 that higher difference in salinity between formation brine and injected brine favors dissolution of bridging divalent ion through MIE mechanism together diffusion of ions. However, the rate of oil recovery is faster in case of diluted formation brine of 50,000 ppm. As Calcium ion is a major cause of oil-wet condition in this sample, dissolution mechanism of Calcium ion that link between sandstone surface and carboxylic in oil can be very favored. From Table 5.17, amount of Potassium ion which is one of the key factors is slightly higher in case of diluted brine of 50,000 ppm, this helps preventing dissolution of Potassium ion from formation brine back to injected brine and hence, there is still adequate ion of Potassium to complete the MIE mechanism. Nevertheless, since difference between formation brine and injected brine is smaller in case of diluted brine of 50,000 ppm, the equilibrium is attained earlier and oil recovery mechanism through MIE is terminated. The case of diluted brine of 35,000 ppm may be punished from small quantity of Potassium ion in formation brine but it gains the benefit from large different between formation brine and injected brine. This results in low oil recovery rate but at the end larger in oil recovery factor compared to the case of diluted brine of 50,000 ppm.

However, when comparing effects from seawater and diluted formation brine at the same concentration in Figure 5.20, it can be seen that using seawater as injected brine yields much higher oil recovery factor than using diluted formation brine. This result can be explained by Table 5.18. First, the amount Calcium ion in seawater is less than in diluted formation brine. So, dissolution of Calcium ion is more favored by using seawater. Second, the amount Potassium ion in seawater is larger than the amount Potassium ion in diluted formation brine. Moreover, this Potassium ion concentration in seawater is even higher than that of formation brine. Hence, using seawater is a favorable condition for MIE mechanism and this results in high oil recovery rate, high oil recovery factor and low residual oil saturation at the end of oil recovery process. Table 5.19 summarizes the value of residual oil saturation, oil recovery factor and additional oil recovery factor compared to conventional waterflooding obtained from diluted formation brine injection and seawater injection.

Table 5.19 Residual oil saturation and oil recovery factors obtained from diluted formation brine injection and seawater injection.

Injected brine	Residual oil saturation(*Sor*) (fraction of PV)	Recovery factor (RF) (%OOIP)	Additional Recovery factor (%OOIP)
Diluted FB 50,000 ppm.	0.34	45.11	2.07
Diluted FB 35,000 ppm.	0.37	48.47	5.43
Seawater 35,000 ppm.	0.23	64.64	21.60

In conclusion, it can be seen that compositions of both formation brine and injected brine play an important role in controlling effectiveness of low salinity waterflooding. From this chosen formation brine, seawater causes the most favorable conditions due to large difference in Calcium ion concentration and high amount of Potassium ion concentration and these conditions favor MIE mechanism. However, if produced water must be re-injected into the reservoir to avoid disposing water to environment, a mixture of seawater and produced water could be an answer to obtain benefit from both points of view.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

In this chapter, new findings from experiments are concluded. Conclusion is subdivided into three parts according to three discussed sections, starting with the effect of formation brine composition. Subsequently, effects of total salinity in formation brine and effects of diluted formation brine injection are made. Finally, several recommendations are also provided after conclusion for future study.

6.1 Effect of Formation Brine Composition

Oil and sandstone surface are linked together through divalent bridging ions in formation brine which can be Calcium ion and Magnesium ion. This turns the surface oil-wet through ion binding and this is the condition that favors low salinity seawater injection.

With respect to effects of divalent ions in formation brine, due to weaker ionic strength of Calcium ion compared to Magnesium ion, the amount of Calcium ion in formation brine should be high to facilitate the substitution of monovalent ions in injected brine through MIE mechanism and diffusion based on Fix's law of diffusion. Nevertheless, if Calcium ion is excessive in formation brine system, the abundance of Calcium ion in formation brine will result in liberation of free Calcium ions, increasing concentration of Calcium ion in injected brine and eventually this can obstruct dissolution of Calcium ion itself and rate of oil recovery becomes low.

When considering the dominant monovalent ions in injected brine, due to smaller hydrated size of Potassium ion compared to Sodium ion, the efficiency in substitution onto divalent bridging ions of Potassium ion is much higher than Sodium ion. Adequate amount of Potassium ion in seawater would facilitate the MIE mechanism. Presence of lower amount of Potassium ion in formation brine is favorable since Potassium ion from injected seawater can easily diffuse to formation brine and promote the substitution of Potassium ion onto divalent bridging ions.

Consequently, the amount of each ion in formation brine should be appropriate to promote the substitution of monovalent ions in injected brine through MIE mechanism. From this study, high amount of Calcium ion and low amount of Potassium ion in formation brine system are considered as favorable conditions for seawater injection.

6.2 Effect of Total Salinity Formation Brine

The contrast of salinity between formation brine and injected brine controls both rate of oil recovery and total oil recovery factor. Higher salinity of formation brine results in higher remaining oil which is captured through ion binding after physical displacement mechanism. Then, the amount of oil which can be recovered in the first recovery period is lower when comparing to the case of less salinity contrast. Nevertheless, oil recovery can be further increased especially in case of high salinity contrast because difference in salinity between formation brine and injected brine helps promoting the dissolution of bridging divalent ions through MIE mechanism together with diffusion of ions.

In cases where salinity contrast is small, the amount of oil captured through bridging ion is less than the case with high salinity contrast and physical displacement may already yield good result. However, since the gap of salinity contrast is small, equilibrium of potential ion may attain very quickly and as a result, oil recovery mechanism can be terminated earlier and as a consequence, oil recovery factor is relative low compared to cases with higher salinity contrast.

In summary, high salinity formation brine should be recommended for seawater injection in order to promote the long lasting dissolution of bridging divalent ion through Fick’s law of diffusion and MIE mechanism.

6.3 Effect of Diluted Formation Brine Injection.

Injection of diluted formation brine which has lower salinity shows the positive effect on additional oil recovery factor due to difference in salinity between formation brine and injected brine. However, when comparing with the use of seawater as an injectant, it can be seen that seawater yields much more benefit in terms of higher oil recovery factor as well as rate of oil recovery than using diluted formation brine. This is because there is more suitable amount of potential ions in seawater. Low amount of Calcium ion in seawater helps promoting the dissolution of Calcium ion. Moreover, enrichment of Potassium ion in seawater which is higher than in diluted formation brine results in a complete cycle of MIE mechanism.

In this study, seawater which is impoverished in Calcium ion and enriched in Potassium ion is recommended as injected fluid over diluted formation brine.

6.4 Recommendations

The following recommendations are provided for future low salinity waterflooding study.

1. Even though potential ions in produced water are improper, produced water must be re-injected back into the reservoir to avoid disposing water to environment. The future study should emphasize on a mixture of seawater and produced water in order to obtain benefit from both points of view.
2. Due to significantly large amount of anions, the future study should emphasize on interference from anions in both injected brine and formation brine.

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APPENDIX A
Formation Brine Preparation

The ion composition in formation brine in every various ratio of Calcium ion to Magnesium ion and Sodium ion to Potassium ion are shown in this section and the amount of chemical; Sodium Chloride (NaCl), Sodium Sulphate (Na_2SO_4), Sodium Hydrogen Carbonate ($NaHCO_3$), Magnesium Chloride ($MgCl_2$), Calcium Chloride ($CaCl_2$) and Potassium Chloride (KCl), which are used to prepared formation brine are also illustrated.

Ratio of Calcium ion to Magnesium ion =3:1 and Sodium ion to Potassium ion = 50:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4714	33,842
K^+	39.1	0.0175	685
Mg^{2+}	24	0.0423	1,15
Ca^{2+}	40	0.0761	3,045
Cl^-	35.5	1.7194	61,040
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0423	4.0173
$CaCl_2$	111	0.0761	8.4490
KCl	74.6	0.0175	1.3065
NaCl	58.5	1.4651	85.7094
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion = 3:1 and Sodium ion to Potassium ion = 120:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4843	34,139
K^+	39.1	0.0074	289
Mg^{2+}	24	0.0423	1,015
Ca^{2+}	40	0.0761	3,045
Cl^-	35.5	1.7222	61,139
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0423	4.0173
$CaCl_2$	111	0.0761	8.4490
KCl	74.6	0.0074	0.5507
NaCl	58.5	1.4780	86.4652
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =3:1 and Sodium ion to Potassium ion = 150:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4862	34,182
K^+	39.1	0.0059	231
Mg^{2+}	24	0.0423	1,015
Ca^{2+}	40	0.0761	3,045
Cl^-	35.5	1.7226	61,153
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0423	4.0173
$CaCl_2$	111	0.0761	8.4490
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4799	86.5746
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =3:1 and Sodium ion to Potassium ion = 180:1

Ion	**MW**	**Gmol**	**Mass(ppm)**
Na^+	23	1.4874	34,211
K^+	39.1	0.0049	193
Mg^{2+}	24	0.0423	1,015
Ca^{2+}	40	0.0761	3,045
Cl^-	35.5	1.7229	61,163
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0423	4.0173
$CaCl_2$	111	0.0761	8.4490
KCl	74.6	0.0049	0.3681
NaCl	58.5	1.4812	86.6477
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =5:1 and Sodium ion to Potassium ion = 50:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4782	33,999
K^+	39.1	0.0175	685
Mg^{2+}	24	0.0282	677
Ca^{2+}	40	0.0846	3,383
Cl^-	35.5	1.7150	60,883
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0282	2.6782
$CaCl_2$	111	0.0846	9.3878
KCl	74.6	0.0175	1.3065
NaCl	58.5	1.4720	86.1097
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =5:1 and Sodium ion to Potassium ion = 120:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4911	34,296
K^+	39.1	0.0074	289
Mg^{2+}	24	0.0282	677
Ca^{2+}	40	0.0846	3,383
Cl^-	35.5	1.7178	60,982
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0282	2.6782
$CaCl_2$	111	0.0846	9.3878
KCl	74.6	0.0074	0.5507
NaCl	58.5	1.4849	86.8655
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion and Sodium ion to Potassium ion = 150:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4930	34,339
K^+	39.1	0.0059	231
Mg^{2+}	24	0.0282	677
Ca^{2+}	40	0.0846	3,383
Cl^-	35.5	1.7182	60,996
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0282	2.6782
$CaCl_2$	111	0.0846	9.3878
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4868	86.9749
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =5:1 and Sodium ion to Potassium ion = 180:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4943	34,368
K^+	39.1	0.0049	193
Mg^{2+}	24	0.0282	677
Ca^{2+}	40	0.0846	3,383
Cl^-	35.5	1.7185	61,006
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0282	2.6782
$CaCl_2$	111	0.0846	9.3878
KCl	74.6	0.0049	0.3681
NaCl	58.5	1.4880	87.0480
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =7:1 and Sodium ion to Potassium ion = 50:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4816	34,078
K^+	39.1	0.0175	685
Mg^{2+}	24	0.0211	507
Ca^{2+}	40	0.0888	3,552
Cl^-	35.5	1.7128	60,804
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0175	1.3065
NaCl	58.5	1.4754	86.3099
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =7:1 and Sodium ion to Potassium ion = 120:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4946	34,375
K^+	39.1	0.0074	289
Mg^{2+}	24	0.0211	507
Ca^{2+}	40	0.0888	3,552
Cl^-	35.5	1.7156	60,903
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0074	0.5507
NaCl	58.5	1.4883	87.0657
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =7:1 and Sodium ion to Potassium ion = 150:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4964	34,418
K^+	39.1	0.0059	231
Mg^{2+}	24	0.0211	507
Ca^{2+}	40	0.0888	3,552
Cl^-	35.5	1.7160	60,917
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4902	87.1751
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =7:1 and Sodium ion to Potassium ion = 180:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4977	34,447
K^+	39.1	0.0049	193
Mg^{2+}	24	0.0211	507
Ca^{2+}	40	0.0888	3,552
Cl^-	35.5	1.7163	60,927
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0211	2.0086
$CaCl_2$	111	0.0888	9.8572
KCl	74.6	0.0049	0.3681
NaCl	58.5	1.4914	87.2482
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =9:1 and Sodium ion to Potassium ion = 50:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4837	34,125
K^+	39.1	0.0175	685
Mg^{2+}	24	0.0169	406
Ca^{2+}	40	0.0913	3,654
Cl^-	35.5	1.7115	60,757
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0169	1.6069
$CaCl_2$	111	0.0913	10.1388
KCl	74.6	0.0175	1.3065
NaCl	58.5	1.4774	86.4300
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =9:1 and Sodium ion to Potassium ion = 120:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4966	34,422
K^+	39.1	0.0074	289
Mg^{2+}	24	0.0169	406
Ca^{2+}	40	0.0913	3,654
Cl^-	35.5	1.7142	60,856
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0169	1.6069
$CaCl_2$	111	0.0913	10.1388
KCl	74.6	0.0074	0.5507
NaCl	58.5	1.4904	87.1858
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =9:1 and Sodium ion to Potassium ion = 150:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4985	34,465
K^+	39.1	0.0059	231
Mg^{2+}	24	0.0169	406
Ca^{2+}	40	0.0913	3,654
Cl^-	35.5	1.7147	60,870
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0169	1.6069
$CaCl_2$	111	0.0913	10.1388
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4922	87.2952
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =9:1 and Sodium ion to Potassium ion = 180:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4997	34,494
K^+	39.1	0.0049	193
Mg^{2+}	24	0.0169	406
Ca^{2+}	40	0.0913	3,654
Cl^-	35.5	1.7149	60,880
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0169	1.6069
$CaCl_2$	111	0.0913	10.1388
KCl	74.6	0.0049	0.3681
NaCl	58.5	1.4935	87.3683
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 50:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4851	34,156
K^+	39.1	0.0175	685
Mg^{2+}	24	0.0141	338
Ca^{2+}	40	0.0930	3,721
Cl^-	35.5	1.7106	60,725
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0141	1.3391
$CaCl_2$	111	0.0930	10.3266
KCl	74.6	0.0175	1.3065
NaCl	58.5	1.4788	86.5100
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 120:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4980	34,454
K^+	39.1	0.0074	289
Mg^{2+}	24	0.0141	338
Ca^{2+}	40	0.0930	3,721
Cl^-	35.5	1.7134	60,824
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0141	1.3391
$CaCl_2$	111	0.0930	10.3266
KCl	74.6	0.0074	0.5507
NaCl	58.5	1.4917	87.2658
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 150:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.4999	34,497
K^+	39.1	0.0059	231
Mg^{2+}	24	0.0141	338
Ca^{2+}	40	0.0930	3,721
Cl^-	35.5	1.7138	60,839
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0141	1.3391
$CaCl_2$	111	0.0930	10.3266
KCl	74.6	0.0059	0.4413
NaCl	58.5	1.4936	87.3752
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 180:1

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.5011	34,525
K^+	39.1	0.0049	193
Mg^{2+}	24	0.0141	338
Ca^{2+}	40	0.0930	3,721
Cl^-	35.5	1.7140	60,848
SO_4^{2-}	96	0.0003	30
HCO_3^-	61	0.0056	344
			100,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0141	1.3391
$CaCl_2$	111	0.0930	10.3266
KCl	74.6	0.0049	0.3681
NaCl	58.5	1.4948	87.4484
Na_2SO_4	142	0.0003	0.0438
$NaHCO_3$	84	0.0056	0.4740
			100.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 150:1 (75,000 ppm)

Ion	MW	Gmol	Mass(ppm)
Na^+	23	1.1249	25,872
K^+	39.1	0.0044	173
Mg^{2+}	24	0.0106	254
Ca^{2+}	40	0.0698	2,791
Cl^-	35.5	1.2853	45,629
SO_4^{2-}	96	0.0002	22
HCO_3^-	61	0.0042	258
			75,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0106	1.0043
$CaCl_2$	111	0.0698	7.7449
KCl	74.6	0.0044	0.3309
NaCl	58.5	1.1202	65.5314
Na_2SO_4	142	0.0002	0.0329
$NaHCO_3$	84	0.0042	0.3555
			75.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 150:1 (50,000 ppm)

Ion	MW	Gmol	Mass(ppm)
Na^+	23	0.7499	17,248
K^+	39.1	0.0030	116
Mg^{2+}	24	0.0070	169
Ca^{2+}	40	0.0465	1,861
Cl^-	35.5	0.8569	30,419
SO_4^{2-}	96	0.0002	15
HCO_3^-	61	0.0028	172
			50,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0070	0.6695
$CaCl_2$	111	0.0465	5.1633
KCl	74.6	0.0030	0.2206
NaCl	58.5	0.7468	43.6876
Na_2SO_4	142	0.0002	0.0219
$NaHCO_3$	84	0.0028	0.2370
			50.00

Ratio of Calcium ion to Magnesium ion =11:1 and Sodium ion to Potassium ion = 150:1 (35,000 ppm)

Ion	MW	Gmol	Mass(ppm)
Na^+	23	0.5249	12,074
K^+	39.1	0.0021	81
Mg^{2+}	24	0.0049	118
Ca^{2+}	40	0.0326	1,302
Cl^-	35.5	0.5998	21,294
SO_4^{2-}	96	0.0001	10
HCO_3^-	61	0.0020	120
			35,000

Chemicals	MW	Gmol	Mass(g)
$MgCl_2$	95	0.0049	0.4687
$CaCl_2$	111	0.0326	3.6143
KCl	74.6	0.0021	0.1544
NaCl	58.5	0.5228	30.5813
Na_2SO_4	142	0.0001	0.0153
$NaHCO_3$	84	0.0020	0.1659
			35.00

APPENDIX B

Oil Preparation

1. CALCULATION OF ACID NUMBER MODIFICATION

For the oil preparation, the acid number modification can be done by adding the quantity of oleic acid. This appendix describes the calculation of acid quantity to obtain the desirable acid number.

In order to calculate acid quantity, some parameters are required: mass of oil portion (*m*), molecular weight of oleic acid (MW_{oleic}) and desire acid number (AN). From the calculation of acid number's equation

$$AN = \frac{(V_{KOH} \times c_{KOH} \times 56.1)}{m_{oil\,portion}} \tag{1}$$

the equation can be rearranged as

$$V_{KOH} = \frac{(AN \times m_{oil\,portion})}{(c_{KOH} \times 56.1)} \tag{2}$$

where V_{KOH} is the volume, in milliliters, of potassium hydroxide solution required for titration and c_{KOH} is the concentration, in mole per liter, of the standard volumetric potassium hydroxide solution.

Then, mass of acid can be expressed in this following equation

$$m_{acid} = \left[\frac{(c_{KOH} \times V_{KOH})}{1000}\right] \times MW_{oleic} \tag{3}$$

Then, substitute equation (2) to equation (3) and the equation becomes

$$m_{acid} = \left[\frac{(AN \times m_{oil\,portion})}{1000 \times 56.1}\right] \times MW_{oleic} \tag{4}$$

where molecular weight of oleic acid (MW_{oleic}) is 282.46 g/mol, then equation (4) becomes

$$m_{acid} = 0.005035 \times AN \times m_{oil\,portion} \qquad (5)$$

Then, in order to prepare acid oil which has acid number of 5.0, 25.17 g of oleic acid is used to mix with 1,000 g of Dodecane. On the other hand, 5.03 g of oleic acid is used to mix with 1,000 g of Dodecane to prepare acid oil which has acid number of 1.0.

APPENDIX C

Density and Viscosity Determination of Fluid

1. Determination of fluid density by using Pycnometer

The density, $\boldsymbol{\rho}$, is one of the physical properties of matters. Density is defined as the ratio of mass (m) to volume (V).

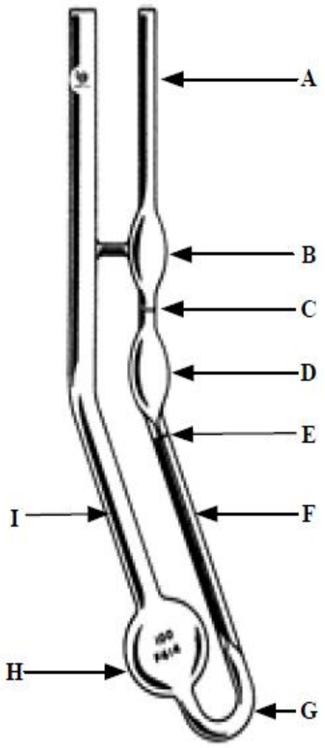
$$\rho = \frac{m}{V} \tag{6}$$

Density determination by pycnometer is a very precise method. The pycnometer is a glass flask with a close-fitting ground glass stopper with a capillary hole through it. This fine hole releases a spare liquid after closing a top-filled pycnometer and allows obtaining a known volume of measured liquid with very high accuracy. Measurement of density by pycnometer is performed by:

1. Weigh the dry flask and stopper on the analytical balance,
2. Fill fluid in pycnometer and close with stopper.
3. Weigh the full pycnometer on the analytical balance.
4. Calculate the mass of fluid by subtract the weight in step 3 with dry weight in step 1
5. Calculate the fluid density by using equation 6 and use the labeled volume at pycnometer.

2. Determination of fluid viscosity by using Cannon-Fenske viscometer

Fluid viscosity is one of the important parameters related to flow characteristics. In general fluid viscosity can be classified as kinematic viscosity and dynamic viscosity. Cannon-Fenske viscometer is used to measure kinematic viscosity and the value is changed to dynamic viscosity by multiplying with fluid density. Measurement of viscosity is performed by:



1. Fill the measured fluid in tube “A” and apply suction to tube “I”, which causes the sample to flow to line “E”. Then turn the viscometer to normal position and wipe tube “A” cleaned.
2. Insert the viscometer into a holder and place in constant temperature bath.
3. Apply suction to tube “A” and bring sample into bulb “B” until reaching a short distance above mark “C”.
4. Flow freely the sample through mark “C”, then measure the efflux time for when the sample pass from “C” to “E”.
5. Repeat steps 3 and 4 for more accuracy.
6. The kinematic viscosity is calculated by multiplying the efflux time by the viscometer constant.
7. Dynamic viscometer can be calculated by

Dynamic viscosity (cP) =
kinematic viscosity (cSt) × density (g/cm^3)

Constant at 40 °C	0.01509	cSt/s
Constant at 100 °C	0.01502	cSt/s

VITA

Chatchanakorn Peerakham was born on November 12th, 1990 in Chiangmai, Thailand. He received his Bachelor Degree in Chemical Engineering from Faculty of Science, Chulalongkorn University in 2013. After obtaining first degree, he continued his study in the Master’s Degree Program in Petroleum Engineering at Department of Mining and Petroleum Engineering, Chulalongkorn University since the academic year 2014.