

## Effect of Formation Brine Compositions on Low Salinity Waterflooding using Seawater

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### Abstract

To study the effects of ion compositions in formation brine on effectiveness of seawater injection in sandstone reservoir and to provide guideline for selecting candidate field for low salinity seawater injection based on formation brine of the field. The compositions of in formation brine (salinity of 100,000 ppm) was modified in various ratios. First, physical properties of sandstone core samples were measured before saturating core samples with different formation brines. After that, samples were altered to oil-wet condition by displacing organic acid oil. Then, sandstone core samples were displaced with synthetic seawater using coreflooding apparatus. The results indicated that the rate of oil recovery was improved when the ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  was increased. Due to the larger ionic size of  $\text{Ca}^{2+}$  compared to  $\text{Mg}^{2+}$ , the ionic strength between oil and  $\text{Ca}^{2+}$  is weaker than  $\text{Mg}^{2+}$ . However, if  $\text{Ca}^{2+}$  is excessively increased, the abundant  $\text{Ca}^{2+}$  will obstruct the substitution of monovalent ions from injected seawater to absorbed divalent ions on surface, resulting in decreasing oil recovery rate. Meanwhile, low  $\text{K}^+$  concentration in formation brine resulted in diffusion of  $\text{K}^+$  from injected seawater to formation brine, substituting absorbed divalent ions bridging between oil and surface which results in increasing oil recovery rate. Ion compositions in formation brine affected the efficiency of low salinity water injection. High  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  ratio and high  $\text{Na}^+$  to  $\text{K}^+$  are considered as favorable conditions for seawater injection.

**Keywords:** low salinity water injection, seawater injection, ion substitution, formation brine compositions

### บทคัดย่อ

วัตถุประสงค์ของงานวิจัยเพื่อศึกษาผลกระทบขององค์ประกอบของน้ำในแหล่งกักเก็บหินทราย ที่มีต่อกระบวนการฉีดอัดน้ำเกลือที่มีความเข้มข้นต่ำโดยใช้น้ำทะเล และศึกษาคุณสมบัติของน้ำในแหล่งกักเก็บที่เหมาะสมต่อกระบวนการฉีดอัดน้ำเกลือที่มีความเข้มข้นต่ำโดยใช้น้ำทะเล ดำเนินการวิจัยโดยทำการศึกษารูปแบบของน้ำในแหล่งกักเก็บ ซึ่งถูกปรับเปลี่ยนตามสัดส่วนต่างๆ โดยมีความเข้มข้นรวม 100,000 ส่วนในล้าน ตัวอย่างหินทรายถูกนำไปวิเคราะห์คุณสมบัติทางกายภาพก่อนทำให้อิ่มตัวด้วยน้ำในแหล่งกักเก็บและน้ำมันตามลำดับ เพื่อเปลี่ยนสภาพความเปียกให้เป็นสภาพความเปียกด้วยน้ำมัน โดยการฉีดอัดน้ำมันที่มีกรดอินทรีย์ จากนั้นหินตัวอย่างถูกนำมาแทนที่ด้วยน้ำทะเลสังเคราะห์ด้วยอุปกรณ์จำลองการแทนที่ในแหล่งกักเก็บ ผลการวิจัยพบว่าเมื่ออัตราส่วนของแคลเซียมไอออนต่อแมกนีเซียมไอออนของน้ำในแหล่งกักเก็บเพิ่มขึ้น อัตราการเพิ่มผลผลิตน้ำมันจะมีค่าเพิ่มขึ้น เนื่องจากแรงดึงดูดระหว่างแคลเซียมไอออนกับน้ำมันมีค่าน้อยกว่าเมื่อเทียบกับแมกนีเซียมไอออน แต่เมื่อปริมาณแคลเซียมไอออนเพิ่มมากเกินไป จะส่งผลให้เกิดการกีดกันการแทนที่ของไอออนประจุเดี่ยวที่เข้าแทนที่ไอออนประจุคู่ที่ตรงน้ำมันอยู่ อัตราการเพิ่มผลผลิตน้ำมันจึงลดลง เมื่อพิจารณาอัตราส่วนระหว่าง โซเดียมไอออนต่อโพแทสเซียมไอออนของน้ำในแหล่งกักเก็บ เมื่อปริมาณโพแทสเซียมไอออนในแหล่งกักเก็บน้อยลง โพแทสเซียมไอออนจากน้ำทะเลที่ฉีดอัดจะแพร่มาขังน้ำในแหล่งกักเก็บ และเข้าแทนที่ไอออนประจุคู่ที่ตรงน้ำมันอยู่ ส่งผลให้อัตราการเพิ่มผลผลิตน้ำมันเพิ่มมากขึ้น ข้อสรุป คือ องค์ประกอบของน้ำในแหล่งกักเก็บเป็นปัจจัยหนึ่งที่มีความสำคัญต่อการเลือกใช้กระบวนการฉีดอัดน้ำที่มีความเข้มข้นต่ำโดยอัตราส่วนของแคลเซียมไอออนต่อแมกนีเซียมไอออน และอัตราส่วนของโซเดียมไอออนต่อโพแทสเซียมไอออนควรมีค่ามาก

**คำสำคัญ:** การฉีดอัดน้ำที่มีความเข้มข้นต่ำ การฉีดอัดน้ำทะเล การแทนที่ของไอออน องค์ประกอบของน้ำในแหล่งกักเก็บ

### 1. Introduction

The recovery of oil by natural mechanism, so-called primary recovery, is generally decreased 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 recovery method. Waterflooding has been considered as the most widely used secondary recovery method. This technique is implemented by injecting adequate amount of water into injection well to displace movable oil toward production well. Waterflooding is an efficient technique for reservoir containing light to medium oil. Availability and inexpensiveness of water are considered as major benefits of this technique. Moreover, waterflooding involves relatively low capital investment as well as operating costs compared to other

techniques. However, 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 have more concerned on effects from controlling salinity and composition of injected water and this technique is nowadays widely known as Low Salinity Waterflooding (LSW) (Ashraf et al., 2001, Robertson et al., 2007). Modification of water composition has shown to be an excellent way to increase oil recovery from both sandstone and carbonate reservoirs (Zhang et al., 2001, Nasralla et al., 2011, Rivet et al., 2011). The mechanisms associated to this process are still indistinct (Boussour et al., 2009). 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 negative charge of carboxylic acid group in oil (Buckley et al., 1998). Many LSW studies are concluded that when low salinity brine is injected into formation, Multicomponent 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 improvement in oil recovery (Leger et al., 2006, Srisuriyachai and Muchalintamolee, 2013). According to MIE mechanism, ion type in injected water is also considered to be important to the performance of LSW. Normally, different types of ion are also different in size as well as ionic strength. The larger ionic radius causes weaker ionic strength between rock surface and ion. Hence, the liberation of oil bound on rock surface with different ions will occur differently.

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 was performed and sandstone samples saturated with different formation brine were experimented using coreflooding apparatus. This study emphasizes on effects of ion concentration in formation brine on effectiveness of the process which were mainly on oil recovery rate. Results from this study will be useful for implementation of LSW especially in selecting candidate field that would yield great benefit from LSW when injected brine is the limitation of process.

## 2. Objectives

1. To study the effects of ion compositions in formation brine on effectiveness of seawater injection in sandstone reservoir.
2. To provide guideline for selecting candidate field for low salinity seawater injection based on formation brine of the field.

## 3. Materials and methods

### Sample preparation

Core samples: In this study, three Berea sandstone outcrop cores were used for waterflooding. Porosity and permeability of Berea cores were measured using coreflooding apparatus and high salinity Formation Brine (FB) at ambient temperature and a summary is shown in Table 1.

**Table 1** Physical properties of Berea sandstone core samples

Core ID	Length (cm.)	Diameter (cm)	Dry wt. (g)	PV (cc)	Porosity (%)	$k_a$ (md)	$S_{wi}$	$k_o$ at $S_{wi}$ (md) before aging
B-1	12.68	0.378	296.47	28.26	19.97	115.50	0.325	55.23
B-2	12.68	0.378	299.01	27.78	19.63	75.30	0.396	50.02
B-3	12.68	0.378	298.86	27.65	19.54	94.81	0.386	59.70

Oil: Dodecane with Acid Number (AN) of 5.0 was prepared by adding oleic acid. This acid oil was used for saturating the core samples. The density and viscosity of acid oil at ambient temperature were  $0.745 \text{ g/cm}^3$  and  $1.25 \text{ cP}$ , respectively.

Formation Brine (FB): All the formation brines were prepared in the laboratory using deionized water and reagent grade chemicals. According to the total salinity of sandstone oilfields in offshore locations around the globe, the values are varied in the range between 70,000-350,000 ppm (Houston, 2007). Total salinity of formation brine of all cases in this study was therefore fixed at 100,000 ppm to represent the salinity of synthetic formation brine. This value was still in this range and it was higher than salinity of injected brine (seawater, SW). The prepared formation brine in each experiment was modified for the mass ratio of cations in formation brine. To study effects of divalent ions, the mass ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  was varied in three ratios which were 3:1, 7:1 and 11:1, whereas the mass ratio of  $\text{Na}^+$  to  $\text{K}^+$  was varied in four ratios which were 50:1, 120:1, 150:1 and 180:1 (based on the ratio in real oil fields) to study the effect of monovalent ion.

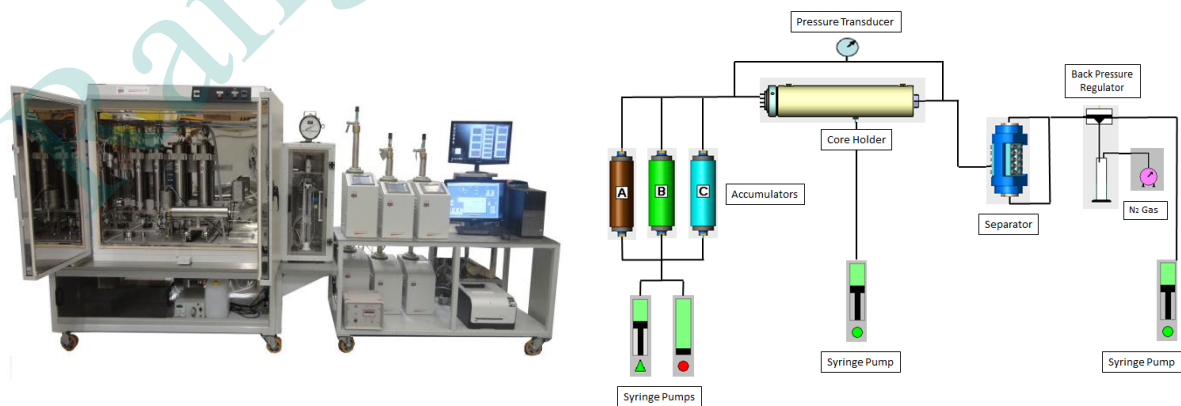
Injected Brine (IB): The injected brine was prepared from the average composition of seawater around the globe which is around 35,000 ppm. The composition of injected brine is shown in Table 2.

**Table 2** Ion composition of injected brine (salinity of 35,000 ppm)

Composition	Mole	Mass (g)
$\text{Na}^+$	0.4667	10.7330
$\text{K}^+$	0.0092	0.3568
$\text{Mg}^{2+}$	0.0482	1.1537
$\text{Ca}^{2+}$	0.0092	0.3676
$\text{Cl}^-$	0.0486	17.3839
$\text{SO}_4^{2-}$	0.0505	4.8297
$\text{HCO}_3^-$	0.0021	0.1270
Total	0.1536	35.00

#### Experimental set-up

The coreflooding apparatus consisted of a core-holder, three accumulators, four syringe pumps, a separator, and an oven is shown in Figure 1. Core sample was placed in the core-holder. Two syringe pumps were used to inject the fluid into the core at a constant rate. Confining pressure on the core was applied by using a syringe pump injecting the deionized water to the annulus space between the core-holder and rubber sleeve that cased the core. The confining pressure was set at 1,500 psia. Another syringe pump was used to pump nitrogen gas to control the core outlet flow at pressure of 500 psia. Two pressure transducers were used to measure the pressure drop across core sample.



**Figure 1** Coreflooding apparatus (left) and schematic of coreflooding setup (right)

### Experiment Procedure

1. Sandstone cores were dried, weighed, and their bulk volumes were measured.
2. Core samples were fully saturated in coreflooding apparatus by injecting formation brine at four different flow rates (2, 4, 6 and 8 cm<sup>3</sup>/min) until no gas bubble was detected at the outlet and different pressure drop was stabilized. The difference pressure drop across core sample was monitored and used for calculation of absolute permeability ( $k_a$ ).
3. Saturated cores were weighed and effective porosities were calculated.
4. Acid oil with AN of 5.0 was injected to saturated core at four different flow rates (2, 4, 6 and 8 cm<sup>3</sup>/min) until no water was detected at the outlet and different pressure drop was stabilized. The different pressure drop across core samples was monitored and used for calculation of relative permeability to oil ( $k_{ro}$ ) at irreducible water saturation ( $S_{wi}$ ).
5. Volume of produced water was measured and used for calculation of  $S_{wi}$ .
6. Saturated core samples were aged in oil for a week to ensure completion of wettability alteration mechanism.
7. Aged core samples were displaced by injected brine at constant flow rate of 2 cm<sup>3</sup>/min at 50 °C. Oil recovery factor was detected until 10 Pore Volumes (PV) of brine was injected into core sample. The different pressure drop across core sample was monitored and used for calculation of relative permeability to water ( $k_{rw}$ ).

### 4. Results and Discussion

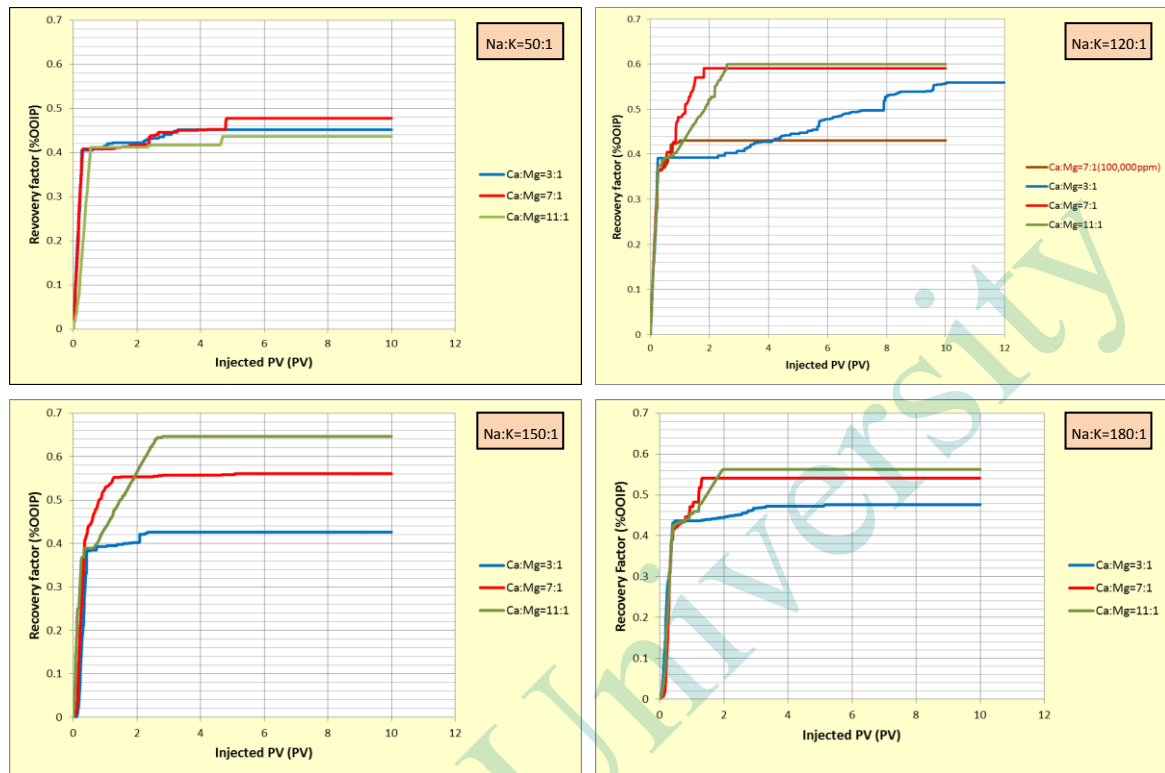
This study emphasizes on effects of ion concentration in formation brine on low salinity seawater injection. Both of monovalent ions and divalent ions are considered in this study. For monovalent ions, the mass ratio of Na<sup>+</sup> to K<sup>+</sup>, the dominant monovalent ion in formation brine, were varied in four different ratios (50:1, 120:1, 150:1 and 180:1) in order to study the effects of monovalent ions. On the other hand, the effects of divalent ions are studied by varying the mass ratio of Ca<sup>2+</sup> to Mg<sup>2+</sup> in three different ratios (3:1, 7:1 and 11:1).

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

In this section, mass ratio of Ca<sup>2+</sup> to Mg<sup>2+</sup> in formation brine was varied whereas mass ratio of Na<sup>+</sup> to K<sup>+</sup> was fixed and total salinity were kept constant. Hence, the effects from other variations were neglected. According to Figure 2, in every mass ratio of Na<sup>+</sup> to K<sup>+</sup>, at low Ca<sup>2+</sup> concentration (Ca<sup>2+</sup>:Mg<sup>2+</sup> = 3:1), the rate of oil recovery is quite slow compared to higher Ca<sup>2+</sup> concentration (Ca<sup>2+</sup>:Mg<sup>2+</sup> = 7:1). The slow oil recovery rate could result from the difficulty of dissolution of Mg<sup>2+</sup>. In case of Ca<sup>2+</sup>:Mg<sup>2+</sup> = 3:1, the amount of absorbed Mg<sup>2+</sup> onto surface is higher than other cases. Due to the smaller ionic size of Mg<sup>2+</sup>, the ionic strength between attached oil and Mg<sup>2+</sup> is stronger than attaching with Ca<sup>2+</sup>, resulting in difficulty in oil liberation and hence, slowing down the oil recovery rate. Moreover, the ionic strength between absorbed Mg<sup>2+</sup> and surface is stronger than absorbed Ca<sup>2+</sup> and surface and substitution of monovalent ions in injected brine through MIE mechanism is more difficult, resulting in slowing down of oil recovery rate. At slightly higher Ca<sup>2+</sup> concentration (Ca<sup>2+</sup>:Mg<sup>2+</sup> = 7:1), the rate of oil recovery is higher according to more amount of Ca<sup>2+</sup> which is easier in oil liberation and monovalent ion substitution.

However, if Ca<sup>2+</sup> is excessively increased in formation brine system (Ca<sup>2+</sup>:Mg<sup>2+</sup> = 11:1), there is no space for Ca<sup>2+</sup> to adsorb onto surface area due to the larger size of Ca<sup>2+</sup>. The abundant Ca<sup>2+</sup> that cannot be absorbed will start to obstruct the substitution of monovalent ions from injected seawater to absorbed divalent ions on surface, resulting in decreasing oil recovery rate.

From Figure 2, although the effect of Ca<sup>2+</sup> and Mg<sup>2+</sup> in every fixed ratio of Na<sup>+</sup> to K<sup>+</sup> is in same direction, the recovery rate from several ratios of Na<sup>+</sup> to K<sup>+</sup> is also different. It means that Na<sup>+</sup> and K<sup>+</sup> in formation brine also affects the efficiency of low salinity seawater injection and this is explained in the following section.

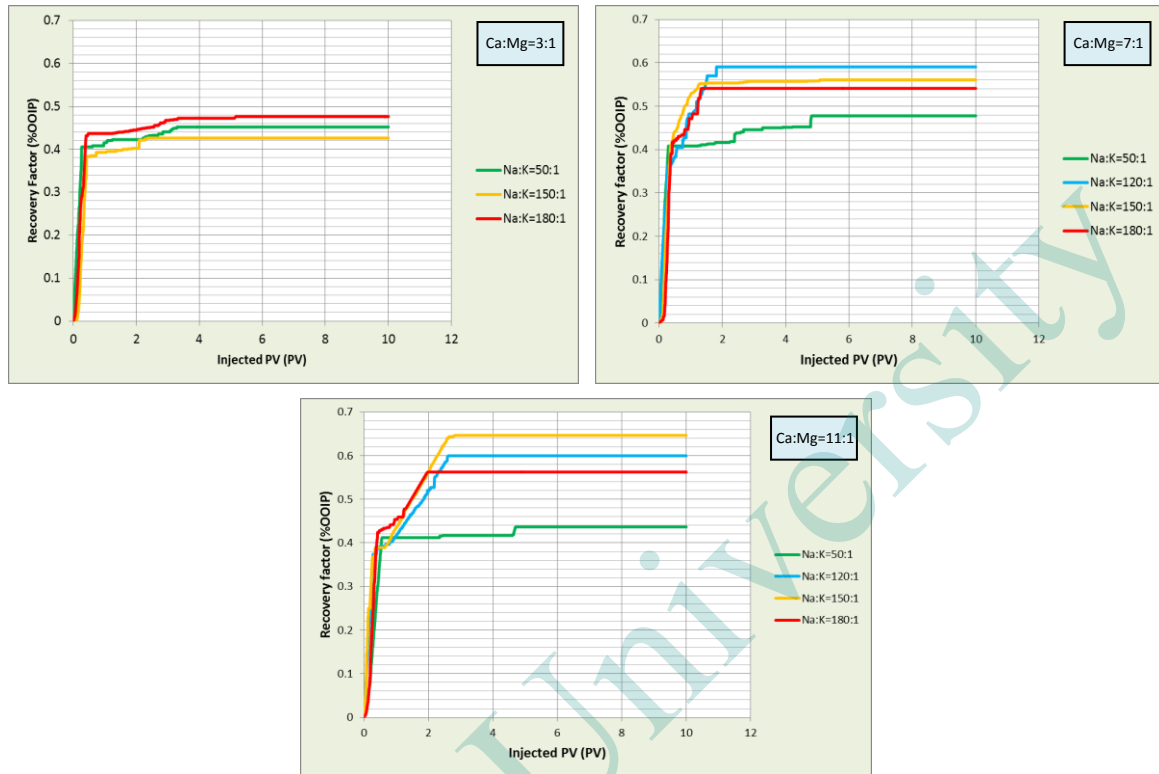


**Figure 2** Oil Recovery factors of seawater injection as a function of injected pore volume when varying the mass ratio of  $\text{Ca}^{2+}:\text{Mg}^{2+}$  in formation brine whereas the mass ratio of  $\text{Na}^+:\text{K}^+$  is fixed at 50:1 (top left), 120:1 (top right), 150:1 (bottom left) and 180:1 (bottom right)

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

In this section, mass ratio of  $\text{Na}^+$  to  $\text{K}^+$  in formation brine was varied whereas mass ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  was fixed and total salinity were kept constant. According to Figure 3 (top left), at low  $\text{Ca}^{2+}$  concentration ( $\text{Ca}^{2+}:\text{Mg}^{2+} = 3:1$ ), no matter the ratio of  $\text{Na}^+$  to  $\text{K}^+$  is increased in formation brine, the rate of oil recovery is slightly constant but it is quite slow when comparing to the case with higher  $\text{Ca}^{2+}$  concentration as can be seen in Figure 3 (top right) and Figure 3 (bottom). This can be explained that the low oil recovery rate could be resulted from the low  $\text{Ca}^{2+}$  concentration as described in the previous section.

From Figure 3 (top right) and Figure 3 (bottom), at higher  $\text{Ca}^{2+}$  concentration ( $\text{Ca}^{2+}:\text{Mg}^{2+} = 7:1$  and  $\text{Ca}^{2+}:\text{Mg}^{2+} = 11:1$ ), it can be obviously seen that the lowest ratio of  $\text{Na}^+$  to  $\text{K}^+$  in formation brine ( $\text{Na}^+:\text{K}^+=50:1$ ) results in slowing down of oil recovery rate. It can be explained that at this condition, the concentration of  $\text{K}^+$  in formation brine is higher than the concentration of  $\text{K}^+$  in injected seawater. Thereby, the  $\text{K}^+$  in formation brine can diffuse into the injected seawater solution which results in decreasing chances of  $\text{K}^+$  in formation brine to substitute the divalent ion bridging between oil and rock surface, and oil recovery rate tends to decrease as well. However, if the ratio of  $\text{Na}^+$  to  $\text{K}^+$  is increased, in case of  $\text{Na}^+:\text{K}^+=120:1, 150:1$  and  $180:1$ , the amount of  $\text{K}^+$  in formation brine is decreased. The low  $\text{K}^+$  concentration in formation brine would result in reversed trend, diffusion of  $\text{K}^+$  from injected seawater to formation brine and substitution of  $\text{K}^+$  on absorbed divalent ions bridging between oil and surface can be occurred, resulting in increasing of oil recovery rate.



**Figure 3** Oil Recovery factors of seawater injection as a function of injected pore volume when varying the mass ratio of  $\text{Na}^+:\text{K}^+$  in formation brine whereas the mass ratio of  $\text{Ca}^{2+}:\text{Mg}^{2+}$  is fixed at 3:1 (top left), 7:1 (top right) and 11:1 (bottom)

## 6. Conclusion

Oil and rock surfaces are linked together by dominant divalent bridging ions in formation brine ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). Due to the weaker ionic strength of  $\text{Ca}^{2+}$  compared to  $\text{Mg}^{2+}$ , the amount of  $\text{Ca}^{2+}$  in formation brine should be high to promote the substitution of monovalent ions in injected brine through MIE mechanism. Nevertheless, the abundance of  $\text{Ca}^{2+}$  in formation brine can obstruct the substitution of monovalent ions and oil recovery rate becomes lower. Presence of lower amount of  $\text{K}^+$  in formation brine is favorable since  $\text{K}^+$  from injected brine can easily diffuse to formation brine and promote the substitution of  $\text{K}^+$  onto absorbed 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  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  ratio and high  $\text{Na}^+$  to  $\text{K}^+$  are considered as favorable conditions for seawater injection.

## 7. Acknowledgements

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