Effect of salinity, single and binary ionic compounds’ low salinity water on wettability alteration in carbonate rocks

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Abstract. Low salinity water flooding is one of the emerging enhanced oil recovery technologies as it has been proven economical and environmentally friendly. However, the recovery mechanism of low salinity water (LSW) is still under debatable due to the complex effect of low salinity water and its ionic compositions. Therefore, this study aims to discover the optimum seawater dilution salinity and influence of single and binary ionic compounds low salinity water on wettability alteration of carbonate core slices at optimum salinity. To achieve that, a modified Design of Experiments (DOE) has been implemented. Contact angle measurement was carried out to characterize the wettability of core slices at 0 hour, after 24 hours and after 48 hours. The results revealed that dilution of seawater reduced the contact angle of carbonate core slices towards more water wet until the optimum salinity of 1750ppm. Further dilution to 700ppm only shown a slight impact in shifting the wettability of the carbonate slices towards more water wet. In single ionic compound LSW, MgCl₂ showed the greatest ability in altering wettability. In binary ionic compounds LSW, it was found out that MgCl₂ mixed with ionic compounds containing monovalent ion is more effective in altering contact angle than MgCl₂ mixed with ionic compounds containing divalent ion which serve as a new finding in current low salinity water study on carbonate rocks.

1. Introduction
Most of the oil and gas reserves are held in carbonate reservoirs. Its complex nature of characters such as oil wet to intermediate wet, heterogeneous characteristic and highly fractures resulted in large amount of hydrocarbon left untapped in the reservoir [1]. Until last decade, one green popular enhanced oil recovery (EOR) method known as low salinity water flooding (LSWF) is being explored extensively on carbonate reservoirs. Low salinity water flooding is not only eco-friendly and inexpensive; the simplicity of injection into oil bearing formation and capability of sweeping light to medium gravity crude oil leading it more attractive over the other EOR methods [2], [3]. There are different conclusions that have been drawn on the performance of low salinity water flooding in carbonate rocks. In the studies of [3-5], lowering the salinity of water could have lowered the contact angle towards more water wet and thus increasing oil recovery. However, Fathi et al. [6] claimed that low salinity water has negative impact on oil recovery of carbonate rock. Sharifi and Shaikh [7] concluded that there is no direct relationship between contact angle and salinity and Su et al. [8] has revealed that there is an optimum salinity to achieve maximum wettability alteration. On the other hand, many laboratory investigations showed favourable oil recovery by tuning the ionic compositions like types and concentration of ions in low salinity water. Hognesen et al. [9] reported that the increase in SO₄²⁻ concentration in seawater could increase the oil recovery through their spontaneous
imbibition experiment. In the work of Zhang and Austad [10], the authors mentioned that both SO$_4^{2-}$ and Ca$^{2+}$ are the potential determining ions. Zhang et al. [11] were then proved that SO$_4^{2-}$ is required to interact with either Ca$^{2+}$ or Mg$^{2+}$ to improve oil recovery. Contradicting result was found by Al-Attar et al. [5] work who claimed that the increase in Ca$^{2+}$ concentration of water injection has an adverse impact on oil recovery. Interestingly, contact angle measurement on an Iranian carbonate rock carried out by Lashkarbolooki et al. [12] reported that the monovalent ions (K$^+$ and Na$^+$) are able to improve water wettess of carbonate rock compared to divalent ions (Ca$^{2+}$ and Mg$^{2+}$) when tested individually. Conversely, Sodium chloride is known to be a non-active ion by [6], [13]. Therefore, to improve understanding on the effect of low salinity water on carbonate rock, this study aims to investigate further into the optimum salinity and the effect of ions in single ionic compound and the relative effect of ions in binary ionic compounds low salinity water on wettability alteration of Indiana limestone.

2. Experiment Materials and methodology

2.1. Core
Indiana limestone outcrop core was provided by Kocurek Industries Inc. The petrophysical properties of Indiana limestone were measured by Poroperm using Helium gas and are tabulated in table 1.

| Air permeability (mD) | Porosity (%) | Pore volume (cc) | Grain volume (cc) | Bulk Volume (cc) | Grain density (g/cc) | Bulk density (g/cc) |
|-----------------------|--------------|------------------|-------------------|------------------|----------------------|--------------------|
| 66.03                 | 11.571       | 9.418            | 71.976            | 81.394           | 2.540                | 2.246              |

2.2. Oil
Real crude oil has been used in this study. Oil was filtered by using 11miron pore size Whatman filter paper before conducting experiment to eliminate the presence of coarse particles in the oil. The properties of crude oil are as shown in table 2.

| Density at 80°C (g/cm$^3$) | API @ 60°F | Viscosity at 80°C (cP) |
|----------------------------|------------|------------------------|
| 0.7937                     | 36.87      | 1.6065                 |

2.3. Brines
Synthetic seawater, low salinity waters and formation water were prepared by dissolving Merck reagent grade salts with purity of more than 99.0% into distilled water such as Sodium Chloride, Calcium Chloride, Magnesium Chloride, Potassium Chloride, Sodium Sulphate and Sodium Bicarbonate. Seawater was synthesized closed to the compositions of typical seawater [14]. Formation water was synthesized based on the formation water of a reservoir limestone at which the air permeability is roughly the same as the air permeability of the core used in this study [15]. Through employing the modified design of experiment (DOE), the brine formulations in this study have been made possible as in table 3. Seawater (SW) was diluted to 5, 10, 20 and 50 times and are represented as SW/5, SW/10, SW/20 and SW/50 respectively. Binary ionic compounds are made up of 50%
MgCl₂ and 50% other ionic compounds (KCl, NaCl, CaCl₂ and Na₂SO₄) at a fixed salinity of 3500ppm. Therefore, there are a total of 14 samples that were used to investigate the low salinity water effect on wettability alteration of Indiana limestone. Density of brines were measured at both 25°C and 80°C by using Mettler Toledo density meter (DM40).

**Table 3.** Formulation of brines.

| Composition | Na⁺ (mg/L) | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | K⁺ (mg/L) | SO₄²⁻ (mg/L) | HCO₃⁻ (mg/L) | Cl⁻ (mg/L) | TDS (mg/L) | Ionic Strength (mol/L) | Density at 25°C (g/cm³) | Density at 80°C (g/cm³) |
|-------------|------------|-------------|-------------|-----------|--------------|--------------|------------|------------|------------------------|--------------------------|--------------------------|
| SW/5        | 2634       | 3480        | 255        | 193       | 2358         | 1794         | 3500       | 3500       | 0.00693               | 1.00945                  | 0.9727                   |
| SW/10       | 2236       | 3050        | 222        | 173       | 2307         | 1783         | 3500       | 3500       | 0.00515               | 1.00875                  | 0.9738                   |
| SW/20       | 2134       | 2849        | 213        | 164       | 2234         | 1764         | 3500       | 3500       | 0.00475               | 1.00825                  | 0.9727                   |
| KCl         | 0          | 0           | 0           | 78        | 0            | 0            | 3500       | 3500       | 0.00273               | 1.0005                   | 0.9926                   |
| NaCl        | 0          | 0           | 0           | 69        | 0            | 0            | 3500       | 3500       | 0.00195               | 1.0000                   | 0.9999                   |
| MgCl₂       | 0          | 0           | 0           | 58        | 0            | 0            | 3500       | 3500       | 0.00147               | 0.9999                   | 0.9755                   |
| CaCl₂       | 0          | 0           | 0           | 48        | 0            | 0            | 3500       | 3500       | 0.00105               | 0.9999                   | 0.9755                   |
| Na₂SO₄      | 0          | 0           | 0           | 38        | 0            | 0            | 3500       | 3500       | 0.00082               | 0.9999                   | 0.9755                   |
| MgCl₂ + KCl | 0          | 0           | 0           | 28        | 0            | 0            | 3500       | 3500       | 0.00060               | 0.9999                   | 0.9755                   |
| MgCl₂ + NaCl| 0          | 0           | 0           | 18        | 0            | 0            | 3500       | 3500       | 0.00032               | 0.9999                   | 0.9755                   |
| CaCl₂ + KCl | 0          | 0           | 0           | 9         | 0            | 0            | 3500       | 3500       | 0.00012               | 0.9999                   | 0.9755                   |

2.4 Experimental Procedures

Core sample was cut into 14 core slices (length of 2cm, width of 2cm and thickness of 3mm-5mm) by using Geological cutting machine. To produce a smooth surface of core slices for contact angle measurement, core slices were polished by using Forcipol 300-1V Grinder and Polisher before they were cleaned with methanol by using Soxhlet Extraction Apparatus. Core slices were then dried in oven for 24 hours at 90°C. To establish the initial water condition of core, core slices were saturated with formation water using Vacuum pump connected to Desiccator until no gas bubbles were released from the core slices. The core slices immersed in formation water were then placed into oven for 3 days at 80°C before it was aged in crude oil for 5 days at 80°C to create initial oil wet condition of core slices. The initial contact angle on aged core was then determined by dropping a water droplet on the cleaned and polished rock surface and the contact angle between the solid surface and tangent of wetting fluid from the surface of solid was then recorded at atmospheric condition. Finally, each aged core slice was immersed in each low salinity waters at 80°C before subsequent contact angle measurements were conducted after core slices being immersed for 24 hours and 48 hours. Contact angle measurement was performed by using Vinci Technologies IFT 700. The method of contact angle measurement is similar to what has been described in literature [16], [17].

3. Results and Discussions

3.1. Seawater and its dilution low salinity water (LSW)

Based on figure 1, the contact angles decrease with time, which indicating that wettability is shifted towards more water wet; hence improving oil recovery. This result is in line with literature as
illustrated by [3], [4], [5]. Seawater however could not alter the wettability of core slice. Interestingly, it is found out that diluting seawater to 1750ppm is the minimum concentration of low salinity water to have the greatest change in contact angle for Indiana limestone as depicted in figure 2. Further dilution to 700ppm only shows a slight impact in shifting the wettability, which also means additional cost is needed to desalinate seawater with minimum impact on recovery. The reason is deemed to be lack of potential determining ions concentration [6]. Therefore, there is a certain dilution extent for maximum wettability alteration to occur. A similar trend of the result was also obtained by Su et al. [8]. Due to significant change in contact angle has been observed when 7000ppm low salinity water is diluted to 3500ppm and only marginal changes when 3500ppm is diluted to 1750ppm, therefore 3500ppm is marked as the model concentration of low salinity water for subsequent contact angle measurements.

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Contact angle measurement for seawater and its dilution with time.

**Figure 2.** Total cumulative reduction of contact angle for seawater and its dilution after 24 hours and 48 hours.

3.2. Single ionic compound low salinity water (LSW)

Figure 3 presented the contact angle reducing with time for single ionic compound low salinity waters at a salinity of 3500ppm. Relatively appreciable change in contact angle is notable for MgCl₂ composition as illustrated in figure 4. The contact angle has changed from 84.9° to 78.2° with total of 6.7° change in contact angle. Comparable results can be seen for Na₂SO₄ and CaCl₂ composition which has the total change in angles of 4.7° and 3.5° respectively. The results are analogous with the low salinity water contact angle measurements conducted by other researchers [18], [19] who found out that Magnesium ions can shift the wettability towards more water wet than Sulphate ions. Ionic compounds like NaCl and KCl showed the least impact on contact angle changes in carbonate rock. Contradiction was found in the work of Lashkarbolooki et al [12] who mentioned NaCl and KCl have higher capability in wettability alteration than MgCl₂ and CaCl₂. The effect and mechanism of low salinity water are not well understood yet.
3.3 Binary ionic compounds low salinity water (LSW)

Like figure 3, figure 5 shows the contact angle of binary ionic compounds LSW fixed at 3500ppm is observed to be reducing with time. From figure 6, it is apparent that the effect of the combination of 50% MgCl₂ + 50% KCl on wettability is tremendous amongst others. The results revealed that binary ionic compounds of 50% MgCl₂ + 50% KCl or 50% NaCl which has monovalent ion resulted in greater contact angle modification compared to binary ionic compounds of 50% MgCl₂ + 50% Na₂SO₄ or 50% CaCl₂ which has divalent ion. In other words, replacing 50% of single ionic compound such as KCl and NaCl with MgCl₂ increases the reduction of contact angle while replacing 50% of single ionic compound such as Na₂SO₄ and CaCl₂ with MgCl₂ decreases the reduction of contact angle.

4. Conclusions

In this study, it has been demonstrated that the dilution of seawater as well as tuning ionic composition low salinity water could affect the wettability of carbonate rocks. The more the salinity is reduced, the greater the alteration of contact angle and thus improving the wettability of carbonate rock towards water wet. However, there is an ideal salinity below which diluting the water reduces the change in contact angle. Overly dilution leads to a total change in contact angle reduces. In single ionic compound LSW, MgCl₂ has the greatest ability in shifting wettability towards more water wet followed by ionic compounds containing divalent ion (Na₂SO₄ and CaCl₂) which are more capable to alter contact angle compared to ionic compounds containing monovalent ion (NaCl and KCl).
However, in binary ionic compounds LSW, the final wettability for 50% MgCl₂ + 50% ionic compounds containing monovalent ion (NaCl or KCl) tends to be more water-wet than 50% MgCl₂ + 50% ionic compounds containing divalent ion (NaSO₄ or CaCl₂). Overall, from these 14 samples, reducing seawater salinity to 1750ppm has the greatest change in contact angle (from 86.9° to 72.5°), therefore for future work further tuning of types and concentration of low salinity water ions is vital to obtain higher wettability alteration to improve this eco-friendly enhanced oil recovery method.

5. References

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