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The Potential of Temperature-activated CO2 Production In Situ as an Enhanced Oil Recovery Process

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Summary

Recent literature has brought up the combination of carbonated water and low salinity water to increase oil recovery from carbonates. In this study, we investigate the effect of bicarbonate on enhanced oil recovery by adding sodium bicarbonate to brine. By changing the temperature to more than 50 °C, the sodium bicarbonate is converted to CO2. Therefore, we can produce CO2 in situ. It is noteworthy to say that at the high pressure found in the reservoir, the analysis from the PHREEQC software shows that CO2 will be dissolved in the brine in low salinities. Several experiments have been conducted to investigate the effect of ionic composition of smart water. Mg2+, Ca2+, and SO42- are among the divalent ions which has a potential effects on the increased oil recovery, while the monovalent ions like Na+, Cl- and K+ does not show any effects. However, in some cases researchers have reported negative effects for the latter types. Among the experiments, there is a lack of experiments investigating the influence of bicarbonate. Dissolved NaHCO3 in the water produces carbon dioxide in-situ in the core plug. This means that injection of corrosive carbonated seawater can be avoided, since carbon dioxide can be produced in-situ.

Introduction

One of the most popular techniques for enhancing oil recovery from oil reservoirs is low salinity and smart water flooding. Water is easy to inject and has low operation cost and capital investment, inexpensive, available and an effective fluid to displace oil. Low salinity and smart water flooding has appeared since more than two decades ago. It was begun with conducting laboratory tests in sandstones and continued with carbonate rocks until today. This method changes the fluid and rock/fluid characteristics to improve the conditions in a positive way to enhance oil recovery from carbonate rocks. Recently, the combination of carbonated water with low salinity water had an increased interest. In this study, we investigate the effect of bicarbonate on enhancing the oil recovery by adding sodium bicarbonate to brine.

In designed water flooding, all the components such as crude oil, rock type, formation and the injected water has their own roles in oil recovery in contact with the others (Gachuz-Muro et al., 2016). The positive charge of carbonate rock surfaces is available for adsorption of deprotonated carboxylic acids in the oil, which may lower the oil recovery potential, since it may prevent oil from flowing. The surface charges of the oil and rock is believed to be an important parameter (Buckley et al., 1998). The total acid number (AN) is an indication of the amount of carboxylic groups in the oil.

The interface between the injected fluid and the oil is charged which depends on the acidity of the oil and composition of injected brine. By an increasing acid number (AN) of the oil, oil recovery from the carbonates might be reduced and oil tends to stick to the rock surface. A set of experimental work of spontaneous imbibition (SI) tests have been done by Standnes et al. (Standnes and Austad, 2000). They indicated that by changing acid number from 0 to 1.7, the oil recovery is reduced by 70%. This AN is an major parameter in describing the importance of the functional groups in the oil on the wettability (Zhang and Austad, 2005). It is noteworthy to say that before using low salinity/smart water injection method as an EOR technique, the effect of using this method in the rock should be evaluated (Austad, 2013).

Several experiments have been conducted to investigate the effect of ionic composition of smart water. Mg^{2+}, Ca^{2+}, and SO_4^{2-} are among the divalent ions which has a potential effects on the increased oil recovery (Andersen et al., 2012; Mohanty and Chandrasekhar, 2013; Strand et al., 2008), while the monovalent ions like Na^+, Cl^- and K^+ does not show any effects (Fathi et al., 2010; Fathi et al., 2011). However, in some cases researchers have reported negative effects for the latter types. Among the experiments, there is a lack of experiments investigating the influence of bicarbonate. Bicarbonate can be converted to CO_2 above 50 °C as shown in equation (1). Therefore, dissolved $NaHCO_3$ in the water produce carbon dioxide in-situ in the core plug. This means that injection of corrosive carbonated seawater can be avoided, since carbon dioxide can be produced in situ.

$$2NaHCO_3 \xrightarrow{50°C} CO_2 + H_2O + Na_2CO_3 \qquad (1)$$

According to the PHREEQC software, CO_2 is dissolved in the water phase and does not exist as a gas phase at high pressure and temperature in low salinities. According to equations 2 and 3, addition of bicarbonate shifts the equilibrium in equation 3 to the left, meaning that calcite (calcium carbonate) in equation 2 is not dissolved.

$$CaCO_3 \Leftrightarrow Ca^{2+} + {CO_3}^{2-} \qquad (2)$$

$${CO_3}^{2-} + H_2O \Leftrightarrow {HCO_3}^{-} + OH^- \qquad (3)$$

Proposed Mechanisms in Modified Water Injection into Carbonates

One of the first proposed mechanism in low salinity flooding and smart water flooding in carbonate oil reservoirs is wettability alteration of rock surface. As it is shown in figure 1, magnesium is substituted by calcium at the surface and releases the carboxylic acid sticking into the positive charge of the surface (calcium ion). Although, this mechanism is favored by many researchers, the impact of other mechanisms such as ion exchange, IFT reduction between injected fluid and oil, mineral dissolution, and changes in surface charge should not be underestimated. Actually, low salinity effect in carbonates is most like the result a combination of mechanisms. A common factor in the mechanisms is that they release carboxylic acids of the oil from positive carbonate surface, which improve mobility of trapped oil.

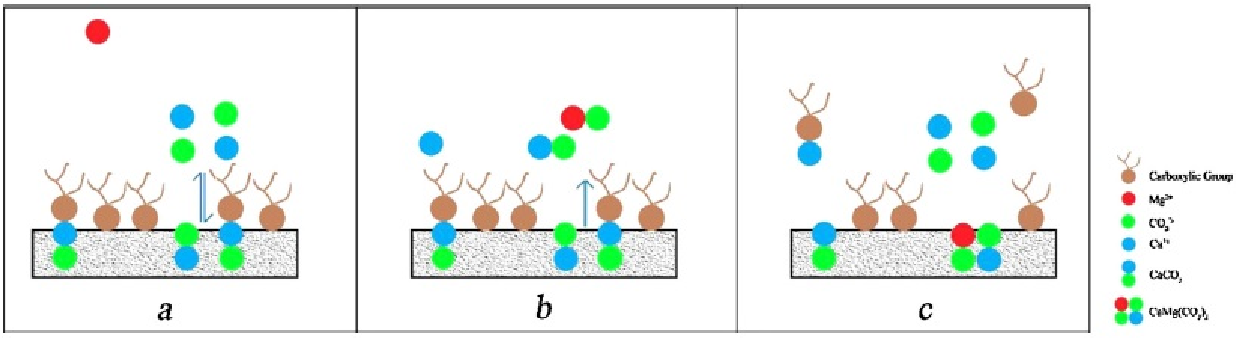

Figure 1 *Proposed mechanism of wettability alteration of a carbonate rock surface by* Mg^{2+} *(from Rashid et al.(Rashid et al., 2015)).*

Khaksar Manshad et al. have studied the effects of smart water with selected active ions on the interfacial tension between oil and water for EOR application. As shown in figure 2, a number of specific salts like NaCl, KCl, $MgCl_2$, $NaHCO_3$ were dissolved in distilled water at different concentrations at reservoir temperature and atmospheric pressure. They concluded that each salt had a specific optimum concentration with an IFT minimum, and in general an optimum salinity for creating a low IFT (Khaksar Manshad et al., 2016). Apart from K_2SO_4 which has the minimum IFT in 2000 ppm, $NaHCO_3$ has the lowest IFT above 1000 ppm in comparison with the other salts studied.

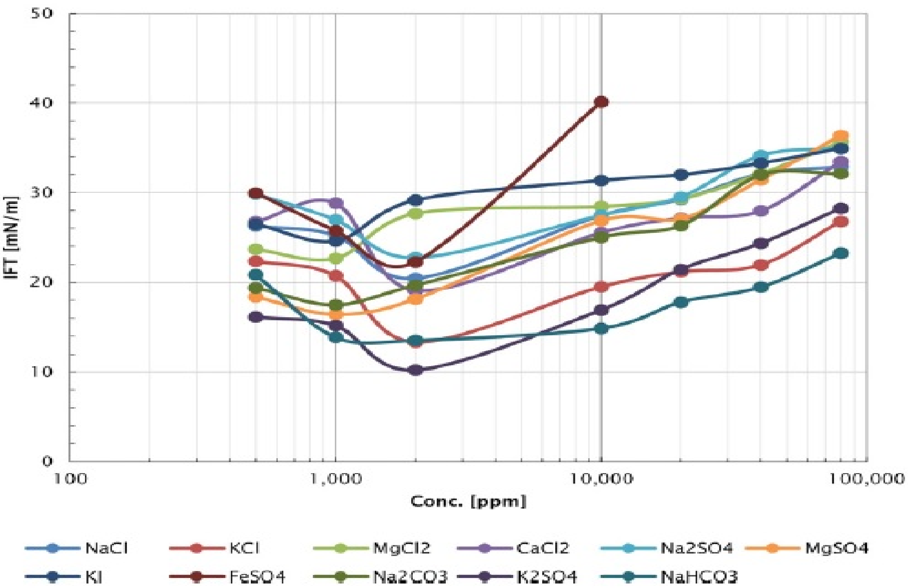

Figure 2 *The interfacial tension (IFT) between oil and salt solutions against concentration at reservoir temperature and atmosphere pressure (from (Khaksar Manshad et al., 2016)).*

Besides of this fact, it also has been observed that interactions between oil and brine affect the oil viscosity. Gachuz-Muro et al. experimentally investigated the effect of brine on heavy oil viscosity.

After examination of crude oils which has been contacted with the injected brines (seaweater with 37198 ppm salinity and diluted seawater) they concluded that the composition of the oil differs from the original one. Their results (% weight versus carbon number distribution) has been measured for oil samples from C_{30} to C_{70} and the composition of the crude oil has changed after being in contact with different brines (Gachuz-Muro et al., 2016). Apart from IFT reduction and oil viscosity reduction, oil swelling and CO_2 expansion lead to produce more oil when CO_2 is among the components in smart water.

Procedure and materials

In this study, different brines are used to evaluate the effect of bicarbonate on enhanced oil recovery. First step has been to evaluate the effect of this special ion, where brines have been contacted with crude oil. Viscosity of crude oil, brine pH and IFT between the crude oil and brine has been measured. The internal proportion ion is the same as in seawater. The brines are:

- FW: Formation water
- SW: Seawater
- 0.5SW+extra BC: water with the molar concentration equal to half of the seawater and with higher bicarbonate concentration (BC: bicarbonate)
- Pure1: water with molar concentration of bicarbonate as the previous brine. Other ions have been omitted
- DSW+ extra BC: which contains mole contents equal to 0.15 of the seawater with higher bicarbonate concentration (~5000 ppm)
- Pure2: water with molar concentration of bicarbonate as the previous brine. Other ions have been omitted
- DSW-BC: water with the molar concentration equal to 0.15 of the seawater without bicarbonate.
- DW: deionized water as reference.

The purpose of using this scenario is evaluation of the effect of brines in three different conditions:

1. The effect of ion contents in the absence of $NaHCO_3$ (i.e. FW and DSW-BC).
2. In a pure solution. (i.e. Pure1 and Pure2)
3. In the presence of other ions. (i.e. SW, 0.5SW+ extra BC and DSW+ extra BC)

After preparation of the brine solutions, they are put in the same container in contact with crude oil (20 cc crude oil and 40 cc of brine). The containers have been in the oven at 60 °C for one week. They were shaken every day, periodically (two times per day). Crude oil density, viscosity and total acid number which is used in this study at 60 °Care d=0.8407 g/ml, μ=4.45 cP and TAN=0.504 mg KOH/g.

Conclusions

Recent literature has brought up the combination of carbonated water and low salinity water to increase oil recovery from carbonates. In this study, we investigate the effect of bicarbonate on enhanced oil recovery by adding sodium bicarbonate to brine. By changing the temperature to more than 50 °C, the sodium bicarbonate is converted to CO_2. Therefore, we can produce CO_2 in situ. It is noteworthy to say that at the high pressure found in the reservoir, the analysis from the PHREEQC software show that CO_2 will be dissolved in the brine at low salinities.

The effect of the bicarbonate ion alone and in the presence of other active ions (Mg^{2+}, Ca^{2+} and SO_4^{2-}) and the non-active (Na^- and Cl^-) ions has been investigated. The preliminary tests were found important for interpreting the results. The results indicate the potential of the temperature activated carbon dioxide production in situ as an enhanced oil recovery process.

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