



## Low-salinity water-alternating-CO<sub>2</sub> EOR

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### ABSTRACT

Carbon dioxide flooding is currently the most technically and economically viable enhanced oil recovery (EOR) process in carbonate and sandstone reservoirs. Low-salinity waterflood is a relatively new EOR process; and our experiments in carbonate cores show significant oil recovery improvements with low-salinity waterflood. We propose a new EOR process to improve recovery, which involves low-salinity water-alternating-CO<sub>2</sub>/gas (LS-WACO<sub>2</sub> or LS-WAG) injection.

To evaluate the proposed idea, three core floods and several contact angle and IFT measurements were performed. The core floods include: seawater flood, followed by low-salinity waterflood, followed by CO<sub>2</sub> injection, which yielded fourteen, twenty-five, and thirty-eight percent additional oil recovery by CO<sub>2</sub> from two carbonate and one sandstone experiments.

We performed contact angle measurements on several low-permeability carbonate, medium-permeability Berea sandstone, and ultra-low permeability Three Forks mudstone core discs using different salinities brine with and without CO<sub>2</sub> gas. The contact angle measurements confirmed that favorable wettability alteration is achievable with the proposed EOR process. In addition, visual observations suggested that the proposed EOR process could be effective for cleaning the matrix-fracture interface in conventional and unconventional reservoirs. Interfacial tension (IFT) measurements and correlation relevant to the EOR process is also included in this study.

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### 1. Introduction

By combining low-salinity waterflood EOR and gas injection EOR, a new EOR process is proposed. The new EOR process is low-salinity water-alternate-gas EOR. We will first review both low-salinity waterflood and gas injection (mainly CO<sub>2</sub> injection EOR processes); then we will introduce the theoretical background of the new hybrid of low-salinity and CO<sub>2</sub> EOR. Finally, we will discuss our experimental observations and provide conclusion and recommendations.

#### 1.1. Low-salinity waterflood EOR

Waterflooding is by far the most widely used method to increase oil recovery. Recent studies show that, by modifying the ionic content of water, wettability of reservoirs can be altered. When using seawater to alter wettability, there are different chemical mechanisms in effect between sandstone and carbonate

formations. The polar components in the crude oil reacts with the positively charged carbonate rock surface differently from the negatively charged quartz/clay in sandstone formations, indicating different chemical bonding reaction mechanisms. In general, wettability alteration can be improved by modifying the ionic composition of the injected sea water (Jadhunandan and Morrow, 1995; Tang and Morrow, 1997; Strand et al., 2006; Zhang and Austad, 2006; Karoussi and Hamouda, 2007; RezaeiDoust et al., 2009; Cissokho et al., 2010; Austad et al., 2010; Morrow and Buckley, 2011; Zekri et al., 2012; Al-Harrasi et al., 2012; Nasralla et al., 2011; Alameri et al., 2014; Awolayo et al., 2014; Alameri 2015; Alameri et al., 2015a, 2015b; and references cited in these studies).

Several mechanisms have been proposed in the literature for low-salinity waterflooding EOR. These include: fines migration and rock dissolution (Tang and Morrow, 1999; Pu et al., 2010; Yousef et al., 2011; Yi and Sarma, 2012), pH increase (Morrow and Buckley, 2011; McGuire et al., 2005), multi-component ion exchange (Lager et al., 2008; Austad et al., 2010; Zahid et al., 2012; Austad et al., 2012), and a double layer expansion (Ligthelm et al., 2009; Lee et al., 2010; Fathi et al., 2010). Combinations of these mechanisms is believed to promote favorable wettability alterations, hence improved oil recovery (Alotaibi et al., 2011; Yousef

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## Nomenclature

SW	Seawater
LS <sub>1</sub>	Low salinity with diluting the synthetic seawater 2 times
LS <sub>2</sub>	Low salinity with diluting the synthetic seawater 4 times

LS <sub>3</sub>	Low salinity with diluting the synthetic seawater 50 times
LS-WACO <sub>2</sub>	Low-salinity water-alternate-CO <sub>2</sub> gas
LS-WAG	Low-salinity water-alternate-gas, where the gas can be CO <sub>2</sub> , NGL, or mixture of NGL with CO <sub>2</sub> / N <sub>2</sub>
IFT	Interfacial tension

et al., 2011; Yi and Sarma, 2012; Emadi and Sohrabi, 2013; Alameri et al., 2014; Teklu et al., 2015a).

### 1.1.1. Fines Migration and Rock Dissolution

Tang and Morrow (1999) performed low-salinity waterflood experiments using sandstone core. They reported a reduction in the absolute permeability of the core samples during low salinity waterflood. They concluded that this might due to the fines migration when low-salinity water was injected. Hence, they suggest that this can lead to improved oil recovery as some pore throats were blocked allowing the water flood changes the path to unswept zones. Similarly, Pu et al. (2010) studied the effect of low-salinity waterflooding through coreflood experiments using sandstone core sample. An increase in anhydrite dissolution was observed when low-salinity water was used. Moreover, an increase in sulfate concentration was observed in the effluent samples due to anhydrite dissolution. Based on surface complexation modeling, Hiorth et al. (2010) concluded that calcite dissolution could be the main mechanism of low-salinity water EOR. Based on NMR study of before and after low-salinity waterflood of carbonate cores, Yousef et al. (2011) suggest that rock dissolution of carbonate cores could also be one of the contributing mechanism.

### 1.1.2. pH Increase

McGuire et al. (2005) noticed an increase in pH due to low salinity waterflooding. This is due to reactions with the minerals in the reservoirs; hence pH increases. Similarly, Morrow and Buckley (2011) reported an increase in the pH can contribute to improved oil recovery during low-salinity waterflood. Based on published and their experimental observations, Austad et al. (2010) suggested that, local pH increase caused by desorption of adsorbed cations from clay minerals could be responsible for residual oil mobilization by low-salinity water flooding.

### 1.1.3. Multi-component Ion Exchange

various studies presented in the literature on low-salinity waterflooding in carbonate reservoirs indicated that SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> (divalent ions) played a vital role (key ions) in the wettability alteration (Strand et al., 2006; Zhang and Austad, 2006; Austad et al., 2012). Based on experimental results of Austad et al. (2012), a chemical mechanism was discussed regarding the interactions between Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, and also between Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> at chalk surface (carbonate formation), causing to desorb the carboxylic organic materials. According to Austad et al. (2012), Mg<sup>2+</sup> only has a strong impact on the low-salinity waterflood process when temperature is high. Similarly, Lager et al. (2008) showed that multicomponent ion exchange occurred when low salinity water was injected and improved oil recovery in sandstone reservoirs. They reported that multicomponent ion exchange happens between rock, oil, and brine; hence, oil droplets were detached from the rock surface. From laboratory experiments, Lager et al. (2008) observed a decrease in the concentration of Mg<sup>2+</sup> and Ca<sup>2+</sup> in the effluent samples.

### 1.1.4. Electrical Double Layer (EDL) Expansion

Low-salinity waterflooding can lead to wettability alteration due to the double layer expansion (Ligthelm et al., 2009; Lee et al., 2010; Nasralla et al., 2011). Ligthelm et al. (2009) suggested that reducing the salinity and the multi-valent cations in the brine solution, the EDL surrounding the clay will expand; hence more oil will flow to the surface. Nasralla and Nasr-El-Din (2012) conducted coreflood experiment, contact angle measurements, and zeta potential measurements to test if the electrical double layer expansion is the main mechanism of low-salinity waterflooding. The correlation of zeta potential measurements to the results of the coreflood of Nasralla and Nasr-El-Din (2012) could demonstrate that double layer expansion can be one of the dominant mechanisms by which low salinity water alters the wettability or rock surfaces favorably.

## 1.2. CO<sub>2</sub> Flooding EOR

Hydrocarbon and non-hydrocarbon gas injection in general, and CO<sub>2</sub> floods in particular, is the leading EOR flooding process in light-oil and medium-oil, both in sandstone and carbonate reservoirs (Stalkup, 1978; Holm, 1987; Manrique et al., 2007; Ghedan, 2009; Alvarado and Manrique, 2010; OGJ, 2014). Mostly from Permian basin, by the start of 2014, 300 M bbl/day of oil is produced by CO<sub>2</sub>-EOR in USA and is forecasted to grow to 638 M bbl/day by 2020 (Kuuskraa and Wallace, 2014; OGJ, 2014). Current utilization factor in mature USA CO<sub>2</sub>-EOR projects range from 5 to 15 Mcf of CO<sub>2</sub> injected/bbl of oil produced (DOE/NETL-2014/1648, 2014).

Even though, miscible and immiscible continuous injection, carbonated water flooding, huff and puff injection are among the possible scenarios of CO<sub>2</sub> injection EOR processes, water-alternating-CO<sub>2</sub> (WAG) is the most frequently applied EOR process (Stalkup, 1983; Brock and Bryan, 1989; Hadlow, 1992; Christensen et al., 2001; Rogers and Grigg, 2001; Ghedan, 2009; Alvarado and Manrique, 2010). This is mainly to improve sweep efficiency and minimize cost. Typical incremental oil recovery by CO<sub>2</sub> flooding ranges between 5 to 25% (Holm, 1987; Ghedan, 2009). Recent experimental, theoretical, and modeling studies show that CO<sub>2</sub> injection with appropriate soaking time can be a promising EOR process for unconventional liquid rich shale reservoirs (Hawthorne et al., 2013; Gamadi et al., 2014; Teklu et al., 2014a, 2014b, 2014c; Alharthy et al., 2015; Sheng, 2015).

The mechanisms of residual oil mobilization by CO<sub>2</sub> flooding in conventional reservoirs include – solution gas drive, immiscible drive, first or multiple contact miscible drive processes. These driving processes enhance oil recovery mainly by – (a) promoting oil-swelling, (b) reduce oil viscosity, (c) favorable density change of oil and water phases, where the density difference between oil and water reduces and minimizes gravity segregation, (d) rock wettability alteration towards water wet, and (e) lower IFT between hydrocarbon-enriched CO<sub>2</sub> and CO<sub>2</sub>-saturated oil (Holm and Josendal, 1974; Stalkup, 1987; Rao et al., 1992; Lansangan and Smith, 1993; Srivastava et al., 2000; Ghedan, 2009).

Residual oil mobilization by gas injection EOR is optimal when

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