



Full Length Article

Laboratory investigation of chemical mechanisms driving oil recovery from oil-wet carbonate rocks

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ARTICLE INFO

Keywords:

Chemically tuned waterflooding
 Potential determining ions
 Zeta potential
 Trace element analysis
 Wettability alteration

ABSTRACT

The purpose of this work is twofold; to improve current understanding of the oil recovery mechanism behind chemically tuned waterflooding in oil-wet carbonate rocks, and to propose a set of governing chemical reactions consistent with this mechanism. For this, a series of waterflood experiments were conducted at 90 °C with synthetic seawater type brine solutions with varying compositions of potential determining ions (Ca^{2+} , Mg^{2+} , and SO_4^{2-}). Characterization techniques like zeta potential, contact angle, and trace element analysis were implemented to account for the ionic interactions taking place among the rock, the brine solution, and the crude oil. Additionally, relative permeabilities were estimated using the Brooks and Corey model where the wettability exponents were tuned against the experimental fractional flow data. Zeta potential measurements highlight the affinity of Mg^{2+} , Ca^{2+} , and SO_4^{2-} ions toward the rock surface in chemically tuned brines where an increase in the magnitude of zeta potential was observed corresponding to the increase in the concentration of each of these ions in the suspension. Oil recovery measurements show an increase for all chemically tuned brines when compared to plain seawater injection. Relative permeability estimations and contact angle measurements show corresponding trends of increasing water-wetness, suggesting the alteration of wettability. Maximum recovery of ~76% original oil in place (OOIP) was observed for the brine with increased Mg^{2+} ion concentration due to higher activity of Mg^{2+} ions and their ability to replace Ca^{2+} ions from the rock surface. A lower recovery of ~64% OOIP was seen for the brine with increased Ca^{2+} ion concentration due to lower activity of Ca^{2+} ions as opposed to Mg^{2+} ions. Further lower recovery of ~59% OOIP was seen for the brine with increased SO_4^{2-} ion concentration due to the increased precipitation of these ions on the rock surface. These chemical reactions including salt precipitation, crude oil desorption/solubilization, and mineral dissolution were confirmed through ionic analysis of the effluent brine during each waterflooding experiment. The presented experimental results and the proposed sequence of chemical reactions can be used for the development of an appropriate reaction model for predicting oil recovery via wettability alteration.

1. Introduction

Chemically Tuned Waterflooding (CTWF) is a widely researched field of study in the petroleum industry, which has evolved significantly in the past two decades. This waterflooding scheme was initially found useful for improving oil recovery from rocks of simpler wetting characteristics like sandstone reservoirs that are usually water-wetting or intermediate-wetting in nature. Early attempts were performed by Morrow and coworkers (1995, 1996, 1999) in mixed-wetting sandstone rocks [1–3]. For example, in the experiments conducted by Yildiz and Morrow (1996) on Berea sandstone cores, the effect of changing brine injection compositions with NaCl and CaCl_2 salts led to improvements

in oil recovery [2]. Later, Tang and Morrow (1999) studied the effect of low-salinity waterflooding in similar cores and observed an increase in oil recovery together with the generation of fine particles upon the injection of a low-salinity brine. They attributed the improvement in oil recovery to the liberation of mixed-wet fines which assisted in the removal of attached crude oil causing alteration of wettability [3]. This was termed as the ‘fines migration’ mechanism of wettability alteration in sandstone cores and was also observed by Pu et al. (2010) in their waterflooding experiments, after observing an increase in the differential pressure due to blockage of pores with the migration of fines [4].

However, Lager et al. (2008) recognized that ‘fines migration’ did not support their oil recovery experiments and advocated for a different

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Nomenclature

<i>CTB</i>	chemically tuned brine
<i>CTWF</i>	chemically tuned waterflooding
<i>EC</i>	electrical conductivity; ($\mu\text{S}/\text{cm}$)
<i>FW</i>	formation water
<i>IS</i>	ionic strength (mol/L)
<i>OOIP</i>	original oil in place
<i>PDI</i>	potential determining ion
<i>SW</i>	seawater
<i>SW2C</i>	seawater with 2 times Ca^{2+} ion concentration
<i>SW2M</i>	seawater with 2 times Mg^{2+} ion concentration
<i>SW2S</i>	seawater with 2 times SO_4^{2-} ion concentration
<i>SW4C</i>	seawater with 4 times Ca^{2+} ion concentration
<i>SW4M</i>	seawater with 4 times Mg^{2+} ion concentration
<i>SW4S</i>	seawater with 4 times SO_4^{2-} ion concentration
<i>XRD</i>	x-ray diffraction

Equation symbols

A_i	temperature dependent constant; ($\text{mol}^{-1/2}/\text{L}^{1/2}$)
α_i^o	constant dependent on radii of ionic species; 5 for Ca^{2+} ion and 5.5 for Mg^{2+} ion (A^o)

α_i	free ion activity of species i ; (mol/kg)
B_i	temperature dependent constant; ($\text{mol}^{-1/2}/\text{L}^{1/2}/\text{A}^o$)
b_i	empirical constant for ionic species; 0.165 for Ca^{2+} ion and 0.2 for Mg^{2+} ion ($\text{mol}^{-1/2}/\text{L}^{1/2}$)
ϵ	dielectric constant of the solution; 72 for SW (F/m)
γ_i	activity coefficient
I	ionic strength; 0.6575 for SW (mol/L)
K_{abs}	absolute brine permeability; (mD)
K_{ro}	relative permeability to oil
K_{ro}^o	relative permeability to oil at initial water saturation
K_{rw}	relative permeability to water
K_{rw}^o	relative permeability to water at residual oil saturation
M	molarity of the solution; (mol/L)
m_i	molality of species i ; (mol/kg)
n_o	exponent for relative permeability of oil
n_w	exponent for relative permeability of water
S_{orw}	residual oil saturation
S_w	water saturation
S_{wirr}	irreducible water saturation
T	temperature; ($^{\circ}\text{C}$ or K)
V_p	pore volume; (ml)
Z_i	charge of species i

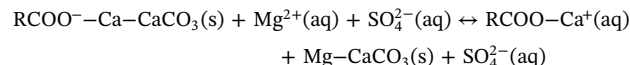
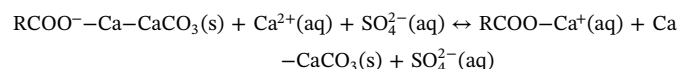
mechanism of wettability alteration to reason the improvements in oil recovery [5]. They proposed a mechanism called the ‘multi-ion exchange’ based on the competitive interactions among the ions (from injection brine and connate water), crude oil, and the rock surface. They suggested that primarily 8 different types of interactions could occur including cation bridging, cation exchange, anion exchange, ligand exchange, water bridging, protonation, hydrogen bonding, and Vander Waal’s attraction based on the type of mineral/clay content of the rock and the types of organic functional groups present in the crude oil. They suggested that the availability of multi-valent ions in the injection brine could result in stronger ligand bonding between these ions and crude oil, which could overcome weaker ion bridging interactions between the rock mineral and crude oil. This would result in the release of the crude oil from the rock surface, improving oil recovery and altering the wettability of the rock [5].

More recently research has been done to investigate the effect of CTWF in carbonate reservoirs. This is largely due to the abundant oil reserves that carbonate reservoirs hold and due to the higher oil recovery potential from carbonate rocks owing to their complex wetting characteristics. With the success of seawater and low-salinity seawater injection to alter wettability in carbonate rocks, research has been done to investigate the importance of the primary ions present in seawater [6–10]. Austad and coworkers (2006, 2007) identified the potential determining ions (PDIs), namely, Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions, useful for achieving wettability alteration in carbonate rocks by conducting zeta potential measurements in NaCl brine environments at seawater pH and room temperature [6,9,10]. They validated the importance of these ions toward oil recovery by conducting spontaneous imbibition recovery experiments in chalk reservoirs and proposed a chemical mechanism similar to the multi-ion exchange mechanism proposed by Lager et al. (2008) [5] to reason the increase in oil recovery [10–12].

Some researchers have theorized other mechanisms such as ‘mineral/rock dissolution’ and ‘salting-in’ to support the changes in oil recoveries from carbonate reservoirs upon the injection of CTBs [11,13,14]. Austad et al. (2012) [13] suggested that the injection of a low-salinity brine could lead to anhydrite (CaSO_4) dissolution from the carbonate surface, which would facilitate the availability of SO_4^{2-} ions to achieve wettability alteration, whereas, Yousef et al. (2012) [15] suggested that the injection of a CTB, different in ion composition to the formation water (FW), could disturb the chemical equilibrium between

the rock surface and the originally present ions, which would lead to the consequential migration of surface ions to reestablish the chemical equilibrium resulting in wettability alteration.

According to Lager et al. (2008) [5], oil-wetness in a rock can be induced by two types of interactions between the crude oil and the mineral/rock surface. These include the formation of an ion-bridged organo-metallic complex between the polar component of the crude oil and the cations in the FW, or the direct adsorption of the polar component of the crude oil onto the mineral/rock surface. Rezaeidoust et al. (2009) [11], proposed the following chemical reactions to explain wettability alteration in carbonate rocks considering that oil-wetness is induced due to the formation of ion-bridged organo-metallic complexes.



In these reactions, the reactant on the left is the carboxylic group of the crude oil attached to the rock surface in the form of an ion-bridged organo-metallic complex. However, the reason for the formation of organo-metallic complexes binding to the carbonate rock surface was not clearly explained by the authors. It may be due to the availability of $> \text{CO}_3^{2-}$ (here, $>$ represents the surface ions) moieties (less abundant at seawater pH) on the rock surface that enable the cations from the formation brine to create a complex with crude oil. The Ca^{2+} ions participate in ion-bridging due to their availability in the formation brine and the SO_4^{2-} ions act as a catalyst for lowering the surface potential, enabling the interaction of the positive ions with the rock surface necessary for wettability alteration.

In a carbonate rock/oil/brine system, among the PDIs participating from the injecting brine and the formation brine, and the surface ions ($> \text{Ca}^{2+}$ and $> \text{CO}_3^{2-}$) participating from calcite mineral (usually the most abundant mineral present in carbonate rocks), several possible reactions can occur during wettability alteration. These may include salt precipitation, mineral dissolution, and crude oil desorption. There have been few attempts by various authors to understand these supporting/competing chemical reactions that occur simultaneously on the oil/rock/brine interfaces for facilitating/hindering oil recovery

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