Full Length Article

Dependence of wettability on brine composition in high temperature carbonate rocks

Sriram Chandrasekhar, Himanshu Sharma, Kishore K. Mohanty*

The University of Texas at Austin, United States

ABSTRACT

Laboratory experiments and small-scale field tests have shown that injection of low salinity brine can improve oil recovery from carbonate rocks. Contact angle studies, spontaneous imbibition and core flood experiments indicate that wettability alteration is responsible for this process. In this study, the core-scale manifestation of wettability mechanisms is evaluated, and a geochemical model is developed for further insight into reaction pathways. Brines of different compositions were injected into carbonate cores with no oil and the effluent was analyzed for ionic composition. Seawater, sulfate-rich seawater, and dilutions of seawater were tested. A mechanistic model was developed using our in-house reservoir simulator UTCHEM-IPHREEQC for the wettability alteration process. The model changes core wettability according to the adsorbed naphthenic acid concentration on the rock surface, which is controlled by the brine composition. The model was used to match previously published two-phase flow experiments. The single-phase core floods with test brines indicate retention of SO_4^{2-} within the core. Calcite dissolution is prominent in ultra-dilute seawater injection. The relative permeability parameters for oil-wet and water-wet conditions were different, but the same for all the core floods. Model results were in good agreement with single-phase core floods and oil recovery experiments. Sulfate adsorption and calcium dissolution led to naphthenic acid desorption which in turn altered core wettability. Single-phase core floods reached equilibrium within 2 pore volumes (PV) of injection. Two-phase core floods with seawater and sulfate enriched seawater took longer to reach equilibrium, only after 3–4 PV. Oil-displacing ultra-dilute brine injection experiments did not reach equilibrium in 5 PV, particularly the Ca^{2+} ions, due to slow calcite dissolution.

1. Introduction

Carbonate reservoirs are estimated to hold approximately 60% of the world's oil. Primary recovery and conventional waterflooding of these reservoirs recover only about 30–40% of the oil in place leaving behind a large volume of remaining oil [1]. Carbonate reservoirs at high temperatures tend to be oil-wet or mixed-wet [2]. If the oil has acid groups, they exist in the dissociated state at the oil/brine interface and make it negatively charged. The formation brine salinities are often high in carbonate reservoirs and the rock/brine interface is typically positively charged. Thus there is an attractive force between the rock/brine and brine/oil interfaces leading to adsorption of organic acids on the solid that makes the rock oil-wet or mixed-wet [3]. Reservoir wettability can adversely affect waterflood recovery. However, past studies have shown wettability alteration by systematically changing the ionic composition of brine [4–6], using anionic, cationic and nonionic surfactants as well as chelating agents [2,7–9].

Many laboratory studies have been published which show improved oil recovery from cores using ionically modified brines [4,5]. Typical experiments include spontaneous imbibition and core flooding. Literature has shown carbonate rocks to respond positively to seawater and its dilutions [5], seawater with increased SO_4^{2-} concentration [10], and other brine compositions [11,12]. The improved oil recovery effect of low salinity brines has been seen in many carbonate types including Stevns Klint chalk, Indiana Limestone, Silurian Dolomite, and various reservoir cores from Middle East and North Sea reservoirs [13]. However, it has also been unsuccessful in some chalks absent of anhydrite [12] and Estaillades Limestone [14].

Studies in the last few years have been targeted at understanding the mechanisms by which carbonate wettability is changed in the low salinity condition. Mineral dissolution was proposed by Hiorth et al. [15] who history matched spontaneous imbibition experiments in chalk using a surface complexation model where the oil recovery was tied to the extent of calcite dissolution. The idea is that surface layers of the rock or mineral would dissolve and organic material adsorbed to those locations would accordingly desorb from the surface. Yousef et al. [6]

---

* Corresponding author.
  E-mail address: mohanty@mail.utexas.edu (K.K. Mohanty).

Nomenclature

CaMg4S	seawater brine with four times increased sulfate content
FB	formation brine
N_{cap}	Dimensionless capillary number
OOIP	original oil in place
PVI	pore volumes injected
SW	seawater
SW/20	seawater diluted by a factor of 20
SW/50	seawater diluted by a factor of 50

published experimental NMR data indicating enhanced micro and macro pore connectivity in cores flooded with low salinity brine, attributed to dolomite dissolution. Anhydrite dissolution was the main mechanism suggested by Austad et al. [12] which increases sulfate concentration and ion exchange on the surface. Den Ouden et al. [16] performed static tests and single/two phase core floods to evaluate the calcite dissolution contribution by the low salinity effect in chalk and limestone cores. It was concluded that equilibrium was reached quickly in static tests, single phase core floods reached equilibrium at 1 ft/day but not at higher injection rates, the presence of oil slowed down the dissolution rate, and the increase in Ca^{2+} concentration from dissolution was not significant enough to hinder the low salinity effect. The dissolution increased the pH which can subsequently affect interfacial and surface charges. Nasralla et al. [17] modeled the calcite-brine interaction in their PHREEQC-coupled reservoir simulator, and showed that the calcite dissolution effect is only a near-well bore effect that cannot be propagated throughout the field. However, changes in pH (increase up to pH 8–9) and brine composition can still impact the oil recovery at the field scale.

The second main mechanism suggested in the past is the change in mineral surface charge (or zeta potential) due to the change in the ionic composition of brines. This effect can be propagated through reservoirs. Many have studied the effect of brine composition (from simple NaCl or complicated, multiple potential determining ion compositions) on calcite, dolomite, and crushed outcrop and reservoir rocks, with model and crude oils [4,18–20]. Mahani et al. [21] conducted a zeta potential study on limestone and dolomite at several brine compositions and related it to contact angles; the surface charge decreased and contact angles changed to the water-wet range, even when calcite-equilibrated brines were used. Limestone responded more readily than dolomite, which was more stable carrying a positive rock/brine interface charge at comparable conditions. The rock/brine surface charge was positive with the formation brine and became increasingly negative for seawater and lower salinity brines. Alroudhan et al. [22] used the streaming potential to show logarithmic dependence of zeta-potential on Ca^{2+} and Mg^{2+} concentration changes, but a saturation dependence on SO_4^{2-} concentration. Mahani et al. [23] further observed the sensitivity of the interface charge to pH and rock type; the zeta-potentials were less negative (more positive) for higher pH conditions. This effect was much higher for seawater and lower salinities than for the formation brine salinity; it was also true for sulfate-enriched seawater. Zhang et al. [4] proposed sulfate and oil acid group competitive exchange to explain interface charge.

Surface complexation models have been developed to capture effects of laboratory scale experiments and suggested mechanisms. Hiorth et al. [15] suggested the basic surface complexation model. Brady et al. [24] captured oil adhesion to calcium carbonate through (oil $-COO^-$ adhesion at) $> CaOH_2^+$ sites and to a smaller extent through (oil–NH^+ adhesion at) calcite $> CO_3^-$ sites. Sulfate-enriched brine was shown to eliminate $> CaOH_2^+$ sites through sulfate sorption, and divalent cations can reverse the oil-water interface $-COO^-$ charge through sorption. Qiao et al. [25,26] coupled the surface complexation model to

multiphase flow to understand dynamic effects on wettability alteration, applying their work to spontaneous imbibition results in chalk and flow experiments in various carbonates. Their model assumes that the wettability alteration is due to the interaction of potential determining ions with the acidic components attached on the rock surface. Mahani et al. [23] have developed a larger set of surface complexation pathways against calcite, and adjusted the SO_4^{2-} complexation reaction to model surface-potential vs. pH trends observed experimentally. This model correlated well with the group's zeta-potential measurements and to previously observed contact angle and oil recovery trends.

In this study, we investigate the validity of wettability alteration mechanisms at the core-scale through experiments and modeling on high temperature limestone reservoir cores. We conduct single-phase experiments with several brines. Effluent brine ionic composition is monitored to understand the changes on the rock surface. A mechanistic model for the wettability alteration process is developed using our in-house reservoir simulator, UTCHEM, coupled to IPHREEQC [27]. Both single-phase core floods and oil recovery experiments from the literature [29,31] are then modeled and compared to experiments.

2. Methods

2.1. Materials

2.1.1. Rock

Core plugs were obtained from a limestone reservoir. A composite core (15.3 cm long) was assembled of several (3.8 cm diameter) clean core plugs. 5-μm filter papers were placed between different plugs to establish capillary continuity. The porosity of the composite was 17% and the brine permeability was 25 mD. The systematic procedure to measure porosity and permeability is given elsewhere [32]. X-ray diffraction analysis on two core plugs (Table 1) indicated that the rock was mainly calcite (> 98%). Other minerals present in small quantities are given in Table 1.

2.1.2. Brines

Synthetic brines were prepared with reagent-grade salts from Fisher Scientific. Deionized (DI) water with resistivity 18.2 MΩ-cm (ASTM D1193 standard) was used to dissolve salts and to dilute synthetic brines. The ionic compositions of brines used for each experiment are listed in Table 2. The formation brine had a salinity of approximately 180,000 ppm. The seawater salinity was approximately 44,000 ppm. The ratios of the potential determining ions in formation brine, seawater, and other prepared brines are significantly different and contribute strongly to the low salinity brine effect investigated in this study. The same core was used in all single-phase experiments. Note that, another similar study showed repeatable results when the same core was reused for different single phase corefloods [32]. A standard initial condition was ensured by injecting formation brine during each reconditioning step until the pH was stable at the same value. Note that the effluent pH value was used only as an approximate indicator of achieving equilibrium. Effluent ions were measured using ion chromatograph in each experiment to confirm if the equilibrium was achieved at the beginning of the experiment.

An ion chromatograph (Dionex ICS 3000) was used to analyze the ionic composition of aqueous samples. The ion chromatograph was able to measure concentration of as low as 1 ppm. The effluent samples were diluted so that a given ion concentration can be measured accurately.

Table 1
Mineralogy of the cores from X-ray diffraction, in percent.

Core	Calcite	Dolomite	Fluorapatite	Quartz	Pyrite	Kaolinite	Chlorite
A	98.3	0.2	1.0	0.4	0.0	0.1	0.1
B	98.1	0.6	0.8	0.2	0.1	0.0	0.3