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Wettability of nanofluid-modified oil-wet calcite at reservoir conditions

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ABSTRACT

Nanofluids, liquid suspensions of nanoparticles (Np), are an effective agent to alter the wettability of oil-wet reservoirs to water-wet thus promoting hydrocarbon recovery. It can also have an application to more efficient carbon storage. We present a series of contact angle (θ) investigations on initially oil-wet calcite surfaces to quantify the performance of hydrophilic silica nanoparticles for wettability alteration. These tests are conducted at typical in-situ high pressure (CO_2), temperature and salinity conditions. A high pressure–temperature (P/T) optical cell with a regulated tilted surface was used to measure the advancing and receding contact angles at the desired conditions. The results showed that silica nanofluids can alter the wettability of oil-wet calcite to strongly water-wet at all operational conditions. Although limited desorption of silica nanoparticles occurred after exposure to high pressure (20 MPa), nanoparticle adsorption on the oil-wet calcite surface was mainly irreversible. The nanofluid concentration and immersion time played crucial roles in improving the efficiency of diluted nanofluids while salinity was less significant at high pressure and temperature.

The findings provide new insights into the potential for nanofluids being applied for improved enhanced oil recovery and carbon sequestration and storage.

1. Introduction

Nanofluids or liquid suspensions of nanoparticles dispersed in deionized (DI) water, brine, or surfactant micelles, have become an elegant solution for many industrial applications including enhanced oil recovery (EOR) [1–5] and potentially carbon geostorage [6]. Various enhanced oil recovery processes have been tested to either accelerate the oil production or improve the recovery factor (e.g. EOR by CO_2 injection, Ameri et al. [7]) from carbonate reservoirs. In this context, the wettability of the fluids/rock system plays a vital role in EOR effectiveness, where water-wet reservoirs are generally more favourable for accelerating oil production [8,9]. One mechanism, which can significantly improve oil production from fractured limestone reservoirs, is to render the oil- (or intermediate-) wet carbonate surfaces water-wet, so that water spontaneously imbibes into the rock and displaces the oil from the matrix pore space [10–12]. Some of these results were supported by Micro-CT images that show the change in the oil clusters size and locations before and after the changes in wettability [12]. Moreover, water-wet formations are also considered more suitable for CO_2 storage (in terms of structural and residual trapping, Iglauer et al. [13,14]). In certain circumstances it may be commercially beneficial to alter the wettability of oil-wet reservoirs to water-wet in order to improve oil production [8,9].

In this context, many studies have observed a significant shift in mineral surface wettability after treatment with nanofluids. Reported data showed that strongly oil-wet surfaces transformed after nanotreatment into strongly water-wet surfaces, e.g. for sandstone [15–19] and for carbonate [4,17,20–23]. In addition, a comparison studies [24–26] between several types (ZrO_2, $CaCO_3$, TiO_2, SiO_2, MgO, Al_2O_3, CeO_2, and CNT) of nanoparticles have previously proved that silica dioxide and, with less degree, zirconium oxide are more efficient in terms of wettability alteration laboratory coreflooding and contact angle experiments.

In this context, several studies reported reduction in contact angle ($-\Delta\theta^\circ$) of mineral surfaces at ambient conditions after nano-treatment with silica nanoparticles. However, only limited amount of literature data have been reported for more relevant conditions (high pressure, temperature and salinity). Table 1 presents a summary of the major experimental variables considered in previous studies, and this work.

Al-Anssari et al. [4] recently observed the variation of the contact

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Table 1
Highest contact angle reduction ($-\Delta\theta°$) of minerals after treatment with nanoparticles.

Reference	SiO_2 conc. wt%	Base fluid	Mineral	Condition	Measurement system	Highest Δθ (°)
Moghaddam et al. [25]	5	Ethanol and brine	Carbonate	Ambient	Decane	− 87°
Roustaei and Bagherzadeh [23]	0.1–0.6	5 wt% brine	Carbonate	Ambient	Crude oil	− 115°
Hendraningrat et al. [17]	0.01–0.1	3 wt% brine	Sandstone	Ambient	Crude oil	− 32°
Bayat et al. [24]	0.005	DI water	Limestone	Up to 333 K, and 0.1 MPa	Crude oil	− 72°
Al-Anssari et al. [4]	0.01–4	0–20 wt% brine	Calcite	Ambient	Decane	− 110°
Al-Anssari et al. [6]	0.01–0.2	0–20 wt% brine	Calcite	Up to 343 K and 20 MPa	CO_2	− 93°
Al-Anssari et al. [27]	0.01–0.2	0–20 wt% brine	Calcite	Up to 343 K and ambient pressure	Decane	− 104°
This work	0.05–0.5	Surfactant-brine (0–20 wt%)	Calcite	Up to 343 K and 20 MPa	Decane	

Table 2
Properties of silicon dioxide nanoparticles used [4].

Surface area [$m^2{\cdot}g^{-1}$]	140
Purity [wt%]	≥99.50
Density [$kg{\cdot}m^{-3}$]	(2200–2600)
Molecular mass [$g{\cdot}mol^{-1}$]	60.08
Boiling point [°C]	2230
Solubility in water	Insoluble

angle with the composition and exposure time of calcite samples to nanofluids. Energy destructive spectroscopy (EDS) and scanning electron microscopy (SEM) verify the adsorption of silica nanoparticles on the calcite samples and the formation of nanotextured surfaces. Their results revealed that all the significant changes in contact angle were happened during the first hour of treatment and no more probable reduction was achieved after 3 h of exposure to the nanofluid. Moreover, the efficiency of nanofluid increased with nanoparticles concentration until reach a minimum θ at 2 wt% SiO_2, where no more reduction were observed with increased concentrations.

Although efforts in studying the influence of nano-treatment on surface wettability, the fundamental aspects related to nanoparticle adsorption characteristics, optimal concentration and effect of exposure time on wettability alteration have not been tested at reservoir conditions before.

Thus, in this work we investigate the wettability of decane/brine and CO_2/brine systems on an oil-wet calcite surface as a function of nanoparticle concentration, exposure time, surfactant addition, salinity and reservoir pressure to understand the influences of nanofluid-treatment on oil reservoirs and other subsurface formations. The results lead to a broader understanding of the potential for application of nanoparticles to enhanced oil recovery and CO_2 storage.

2. Experimental methodology

In this study, to mimic carbonate oil reservoirs, pure calcite samples were treated first with organic materials to achieve oil-wet surfaces. Silica nanofluids were then used to render the wettability of these oil-wet sample water-wet at reservoir conditions. Contact angle measurement for a drop of water on calcite substrate that immersed in decane at elevated pressure and temperature were used to investigate the efficiency of nanofluid in terms of in-suit wettability alteration.

2.1. Materials

Pure calcite (Iceland spar, from Ward's Natural Science) was used as a representative for carbonate reservoir rocks. Deionized (DI) water (Ultrapure from David Gray; conductivity = 0.02 mS/cm) and sodium chloride (≥99.5 mol%, Scharlan) were used to prepare brine solutions (1–20 wt% NaCl, 0.17–4.43 M). The dissolved air was removed from brine by vacuuming for 24 h.

N-decane (> 99 mol%, from Sigma-Aldrich) was used as model oil similar to other published studies [4,28]. Different cleaning agents, toluene (99 mol%, Chem-supply), n-hexane (> 95 mol%, Sigma-Aldrich), acetone and methanol (99.9 mol%, Rowe Scientific) were used to wash pure calcite samples. Nitrogen (> 99.99 mol%, BOC) was used as the ultrapure drying gas. CO_2 (99.9 mol% from BOC, gas code-082) was used to achieve the desired pressure [29] for nano-modification and contact angle measurements processes.

Stearic acid (≥98.5%, Sigma Aldrich) was used to render the original calcite surface as oil-wet. A stearic acid solution (0.01 M) was initially prepared by dissolving 0.285 g of stearic acid in 100 mL of n-decane (> 99 mol%, Sigma-Aldrich).

Silicon dioxide (SiO_2) hydrophilic nanoparticles (porous spherical, Sigma Aldrich) were used to prepare different nanofluids (general properties are listed in Table 2).

An anionic surfactant [Sodium Dodecylsulfate, SDS, Sigma Aldrich, ≥98.5 mol%, Mol.wt = 288.38 $g{\cdot}mol^{-1}$, the critical micelles concentration, CMC = 2450 $mg{\cdot}L^{-1}$ (8.49×10^{-3} $mol{\cdot}L^{-1}$)] was used to improve the stability of nanoparticle suspension in a brine [30–32].

2.2. Equilibration between calcite and brine

In carbonate reservoirs of the geological subsurface, the formation brine is in equilibrium with both calcite and any in-situ CO_2 [33]. Thus, it is essential to ensure an equilibrium between calcite, water, and atmospheric CO_2 to avoid calcite dissolution and associated change in surface charge during measurements.

Experimentally, the equilibrium between calcite and water in the presence of CO_2 is reached when all carbonate ions are turned into bicarbonates [34]. Mechanistically, carbonate minerals are soluble in water and the dissolution yields carbonate ions (CO_3^{2-}) which are likely to react with water to form bicarbonate (HCO_3^-) and hydroxide (OH^-) ions, and this leads to an increase in pH of the solution according to the equilibrium reactions:

$$CaCO_{3(S)} \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{1}$$

$$CO_3^{2-} + H_2O_{(l)} \rightleftharpoons HCO_3^- + OH^- \tag{2}$$

Also, CO_2 dissolves into brine and directly reacts with hydroxide ions to form bicarbonate (HCO_3^-) and thus reduces the pH according to the equilibrium reaction.

$$CO_{2(g)} + OH^- \rightleftharpoons HCO_3^- \tag{3}$$

All brine solutions used in this study were equilibrated with calcite. To achieve equilibrium, the pH of the solution was continuously monitored during immersion of offcuts of calcite in brine solutions. The initial increase in pH is attributed to the formation of hydroxide ions and thus the dissolution of calcite (Eqs. (1) and (2)). However, the later decrease in pH indicates the subsequent formation of bicarbonate (Eq. (3)). Eventually, a stabilized pH (≈8.35) was achieved reflecting the equilibrium condition (with no further calcite dissolution occurring, Venkatraman et al. [35]).

2.3. Calcite surface preparations

The calcite surfaces were then washed with DI water and rinsed