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Wettability alteration of oil-wet carbonate by silica nanofluid

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HIGHLIGHTS

- Preparation of nanofluids (different nanoparticles concentration in different brine concentration).
- SEM and AFM images (images taken before and after nano-modification).
- EDS analysis (data were taken after nano-modification of the surfaces).
- Effect of exposure time, brine concentration and nanoparticle concentration on contact angle.
- Efficiency of used nanofluid (sustainability of silica nanoparticles).

GRAPHICAL ABSTRACT
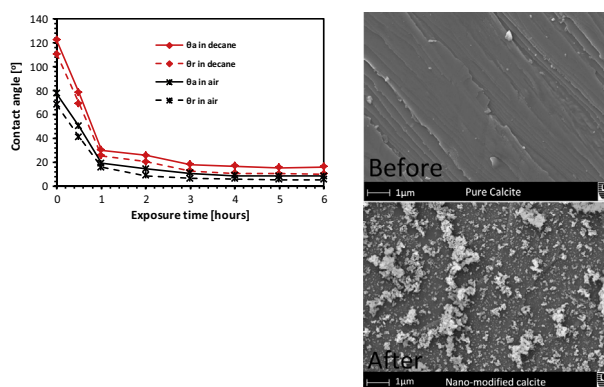
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ABSTRACT

Changing oil-wet surfaces toward higher water wettability is of key importance in subsurface engineering applications. This includes petroleum recovery from fractured limestone reservoirs, which are typically mixed or oil-wet, resulting in poor productivity as conventional waterflooding techniques are inefficient. A wettability change toward more water-wet would significantly improve oil displacement efficiency, and thus productivity. Another area where such a wettability shift would be highly beneficial is carbon geo-sequestration, where compressed CO_2 is pumped underground for storage. It has recently been identified that more water-wet formations can store more CO_2.

We thus examined how silica based nanofluids can induce such a wettability shift on oil-wet and mixed-wet calcite substrates. We found that silica nanoparticles have an ability to alter the wettability of such calcite surfaces. Nanoparticle concentration and brine salinity had a significant effect on the wettability alteration efficiency, and an optimum salinity was identified, analogous to that one found for surfactant formulations. Mechanistically, most nanoparticles irreversibly adhered to the oil-wet calcite surface (as substantiated by SEM–EDS and AFM measurements). We conclude that such nanofluid formulations can be very effective as enhanced hydrocarbon recovery agents and can potentially be used for improving the efficiency of CO_2 geo-storage.

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1. Introduction

The unique properties of designed nanoparticles have shown promising applications in a diverse range of fields, spanning from medicine [1], drug delivery [2], biology [3], food additives

[4], polymer composite [5], metal ions removal [6], corrosion protection [7], heterogeneous catalysis [8], and improved surface properties [9] to enhanced oil recovery [5,10], on which we focus here.

In enhanced oil recovery (EOR), one of the main challenges is hydrocarbon production from fractured limestone reservoirs. These reservoirs contain more than half of the known remaining oil reserves in the world [11], and they are typically intermediate-wet or oil-wet [12]. Secondary recovery (conventional water flooding techniques) is inefficient and productivity is low: mainly oil from the fractures is produced as water does not spontaneously imbibe into the oil-wet rock matrix [13]; however, most oil is stored in the matrix [12], and as a result only 10–30% of the oil is recovered [14].

One mechanism, which can significantly improve oil production, 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 [15]. Several methods have been suggested: surfactant flooding [13,14], polymer flooding [16,17], nanoparticle stabilized emulsions [18], various nanoparticle-surfactant-polymer formulations [19–24], and nanofluids [25–28]. Surfactant EOR has been tested at field scale, but efficiency proved to be poor [29]. However, when polymer was used as cosurfactant, oil recovery was enhanced significantly [29]. The other techniques have not been used at industrial scale as far as we are aware.

Furthermore a wettability change toward more water-wet would be greatly beneficial to Carbon Geo-Storage (CCS) projects, where oil-wet rock surfaces lead to dramatically reduced storage capacity and containment security [30,31]. Specifically, higher water wettability has been shown to increase residual trapping capacities, at the reservoir scale [30], and at the core- or pore-scale (e.g. Spiteri et al. [32], Pentland et al. [33], Iglauer et al. [34] and Iglauer et al. [35] versus Chaudhary et al. [36]). Moreover, higher structural trapping capacities are predicted for strongly water-wet systems [31].

It is thus highly desirable to render such hydrophobic mineral surfaces strongly water-wet; the key to successful EOR and improved CCS is therefore to find formulations, which are very efficient in wettability alteration at very low concentrations (because of economical cost). The economic viability of these processes depends on crude oil prices and carbon tax.

Nanoparticle formulations can meet these requirements as they are active at low concentrations (e.g. compare Mahbubul et al. [37]), and can migrate through the pore space of the reservoir and penetrate into even the smallest pores [24] – note that rock matrix pore sizes in limestone vary between 0.01 and 100 μm [38]. However, the efficiency of such formulations is a complex function of several factors, including the size and type of nanoparticles, nanofluid preparation and stability, the nature of the porous medium, thermo-physical and geological conditions and dwell time in the reservoir [39,40]. Despite the vital importance for limestone reservoirs globally, previous studies focused on sandstone formations [21,25,26,28,41], and only limited information is available for carbonate reservoirs: Roustaei and Bagherzadeh [42] conducted coreflood tests and they demonstrated that nanofluid-EOR can increase oil production by 9–17% depending on ageing time, and Zhang et al. [40] have investigated the adsorption behaviour of silica nanoparticles on calcite powder.

We thus examine the wettability alteration efficiency of silica nanofluids on oil-wet and intermediate-wet calcite surfaces and how various factors influence this efficiency. All experiments were conducted at ambient conditions. At reservoir conditions, however, significantly higher pressures and elevated temperatures prevail, and as pressure and particularly temperature can affect nanofluid properties [28], nanofluid efficiency at reservoir conditions may be different to that measured at ambient conditions; furthermore,

nanofluid efficiency is probably also influenced by rock heterogeneity, which determines nanofluid flow and distribution [5,43] throughout the formation.

2. Experimental methodology

2.1. Materials

N-decane (>99 mol%, from Sigma–Aldrich) was used as a model oil. N-hexane (>95 mol%, from Sigma–Aldrich), nitrogen (>99.99 mol%, from BOC), acetone and methanol (>99.9 mol%, from Rowe Scientific) were used as cleaning agents. Deionized (DI) water (Ultrapure from David Gray; conductivity = 0.02 mS/cm) and sodium chloride ($\geqslant$99.5 mol%, from Scharlan) were used to prepare brines (0–20 wt% NaCl).

Silicon dioxide nano-powder (porous spheres, Sigma Aldrich) was used to prepare the nanofluids (general properties are listed in Table 1).

Iceland spar samples (pure calcite, from WARD'S Natural Science) were used as substrates; the surface topography of the calcite samples was measured with an atomic force microscope (model DSE 95-200), Fig. 4, as surface roughness influences wettability [44] and adsorption rate of nanoparticles [45]. Prior to nano-treatment, all calcite samples were very smooth with root mean square (RMS) surface roughness between 18 and 32 nm.

Pure calcite, however, is strongly water-wet [14,46]. This was confirmed by our contact angle measurements on clean substrates (the water contact angle θ was 0°. We note that in the literature slightly higher contact angles were reported, probably due to insufficient cleaning [47]. Consequently, it was necessary to render the calcite surface oil-wet to simulate an oil (or CO_2 storage) reservoir. To accomplish this, the calcite surfaces were treated with a range of silanes [48,49]: hexamethyldisilazane (HMDS), dodecyltriethoxysilane and (3-aminopropyl) triethoxysilane (Table 2). We note that previously some researchers used naphthenic acids or crude oil for wettability alteration, however, such a wettability change is unstable and leads to only weakly water-wet or intermediate-wet surfaces [14], rather than clearly oil-wet surfaces.

2.2. Calcite surface preparation

The calcite surfaces were flushed with DI water and rinsed with toluene to remove any organic contaminants. Subsequently, the samples were dried for 10 min at 40 °C and exposed to air plasma [47,50]for 40 min to remove any residual contaminants. It is important to properly clean the samples' surfaces as residual contaminations can lead to dramatic systematic errors [47,51,52]. Silanization started directly after surface preparation to minimize any contamination.

Surface modification with silanes

Three different silanes were used to render the calcite surfaces to oil wet (Table 2). Each cleaned calcite substrate was placed in a separate small glass bottle and silane was pipetted gradually over

Table 1
Properties of silicon dioxide nanoparticles (Sigma Aldrich 2015).

Particle size (nm)	5–15
Purity (wt%)	99.5
Density (kg/m³)	(2200–2600)
Boiling point (K)	2503
Melting point (K)	1873
Molecular mass (g/mol)	60.08
Solubility in water	Insoluble