

Nanoparticles influence on wetting behaviour of fractured limestone formation

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ABSTRACT

Nanoparticles have gained considerable interest in recent times for oil recovery purposes owing to significant capabilities in wettability alteration of reservoir rocks. Wettability is a key factor controlling displacement efficiency and ultimate recovery of oil. The present study investigates the influence of zirconium (IV) oxide (ZrO₂) and nickel (II) oxide (NiO) nanoparticles on the wetting preference of fractured (oil-wet) limestone formations. Wettability was assessed through SEM, AFM and contact angle. The potentials of the nanoparticles to alter oil-wet calcite substrates water wet, was experimentally tested at low nanoparticle concentrations (0.004-0.05 wt%). Quite similar behaviour was observed for both nanoparticles at the same particle concentration; while ZrO₂ demonstrated a better efficiency by altering strongly oil-wet (water contact angle $\theta = 152^\circ$) calcite substrates into a strongly water-wet ($\theta = 44^\circ$) state, NiO changed wettability to an intermediate-wet condition ($\theta = 86^\circ$) at 0.05 wt% nanoparticle concentration. We conclude that ZrO₂ is very efficient in terms of inducing strong water-wettability; and ZrO₂ based nanofluids have a high potential as EOR agents.

Keywords: Nanoparticles, Wettability, Zirconium oxide, Nickel oxide.

1 Introduction

Fractured carbonate formations hold large amounts of global oil reserves; 60% oil and 40% gas (Ahmed, 2010) and these formations are typically oil-wet. The oil is often located in the tiny pores of the rock or as a thin film on the surface of the rock thereof (Anderson, 1987). The main mechanism for hydrocarbon recovery, spontaneous imbibition of water into the matrix blocks, is often disrupted due to the oil-wet or intermediate-wet character of the limestone (Chabert et al., 2010; Rezaei Gomari and Hamouda, 2006; Thomas et al., 1993) and associated low (water) suction pressures (Strand et al., 2006). Consequently, poor recovery is typically attained when conventional waterflooding methods are adopted (Anderson, 1986a, 1986b, 1986c; Buckley et al., 1998; Iglauer et al., 2010; Standnes and Austad, 2000) in limestone formation. Capillary pressure mainly controls fluid distribution in such porous media. The magnitude and direction of the capillary forces is influenced by the formation pore size, fluid saturation, interfacial tension and wettability (Dawe et al., 2011). Diverse approaches have been employed through the use of additives - surfactants, polymers, alkaline and the combinations thereof, to improve sweep efficiency, interfacial tension reduction, mobility control and optimal oil recovery. However, these mechanisms are often impeded by factors such as large volume of additives which impacts operation cost, chemical incompatibility with the reservoir fluids and conditions, scale formation, and susceptibility to high temperature and salinity formations (Nwideo et al., 2016, 2016a). For feasibility of enhanced oil recovery amid unremitting increase in energy demand and inaccessible oil reserves, it is imperative that efficient economical and environmentally friendly alternatives are considered. Nanoparticles (nanofluids) - though still in its early stages - are promising alternatives, especially metal oxide nanoparticles.

Prior to the recent interest in nanoparticle for EOR processes, nanoparticles have been used in fields such as medicine, energy and electronics, aerospace, manufacturing and

materials. This is due to its special chemical, thermal and mechanical properties in addition to the small particle size and associated unique transport behaviour (Li et al., 2007; Xin et al., 2007, Suleimanov et al., 2011). The small particle size of nanomaterials (1-100nm) can facilitate easy penetration through formations since its size is relatively smaller than the conventional rock pores. As particle size approaches nanoscale, the properties of the nanomaterial become different from the bulk material yielding wide-ranging applications (Guo et al., 2014). The surface area of nanoparticles is also higher than the bulk particles. This large surface area enhances surface energy of the particles which causes structural transitions (Tsuzuki, 2013) and permits favourable particle adsorption at the surface boundaries and can also exhibit high tendencies of being in contact with other neighbouring materials. Interestingly, the surface functionalities of nanoparticles can be engineered (Nassar et al., 2011; Pereira-Almao, 2012) with potential applications also in subsurface engineering. Nanoparticles have also been shown to be interfacially active and good rock wettability modifiers (Ju et al., 2006; Ju and Fan, 2009; Giraldo et al., 2013; Al-Anssari et al., 2016; Roustaei et al., 2013; Nwidae et al., 2016a; Hendraningrat et al., 2013) at laboratory scale. Changing wettability towards water-wet has proven very effective in this context. As such nanoparticle have considerable prospect in carbon geo-sequestration as water-wet formations can store more CO₂ than oil-wet formations (Iglauer et al., 2015a, 2015b).

Wettability has remained a crucial factor controlling efficient fluid displacement at pore-scale and optimal oil recovery. Ju et al. (2006) evaluated wettability effect on porous media using lipophobic-hydrophilic polysilicon nanoparticles and reported that flooding with lipophobic- hydrophilic polysilicon nanoparticles increased oil recovery significantly. Mohajerian et al. (2015) investigated the displacement efficiency of heavy oil using a ZrO₂ surfactant formulation in a fractured 5-spot model in a flooding test and found that these formulations are effective additives for the control of mobility ratio. Roustaei et al. (2013)

examined the efficiency of modified silica nanoparticles on EOR in sandstone cores and detailed that the total oil recovery increased upon exposure to the silica nanoparticles. The focus here is on Nickel (II) oxide (NiO) and Zirconium (IV) oxide (ZrO₂) nanoparticles. Zirconium oxide nanoparticles are materials with high mechanical strength and temperature resistance (Pareja et al., 2006). ZrO₂ has been employed in adsorption and conductivity studies in the presence of surfactants, where ZrO₂ nanoparticle and surfactant formulations enhanced surface activity and adsorption behaviour (Esmailzadeh et al., 2011). NiO nanoparticles are standard materials in the fabrication of magnetic materials, gas sensors, films and cathodes of alkaline batteries (Wu et al., 2007; Thota and Kumar 2007; Hotovy et al., 2006; Min et al., 2007); however, no study investigated the capabilities of NiO with respect to wettability alteration of fractured limestone formations. Hence, the influence of diverse ZrO₂ and NiO formulations was systematically examined in terms of wettability alteration efficiency and the nanoparticles potentials as EOR agents.

2 Experimental procedure

2.1 Materials

Calcite crystal from Wards Science was used as representative of limestone formation. Toluene (Sigma Aldrich, purity 99.9 mol%) was used as model oil. Ultrapure de-ionised water (from David Gray, conductivity 0.02mS/cm) and NaCl (purity \geq 99.5 mol%, from Rowe Scientific) brine was used as dispersing agents for all tests. Nanoparticles: Zirconium (IV) oxide (ZrO₂) {Purity: 99.5 wt%; density: 5.89 g/mL at 25 °C (lit.)} and Nickel (II) oxide (NiO) {Purity 99.5 wt%; density: 6.67 g/mL at 25 °C} (Sigma Aldrich) were used (Table 1). Dodecyltriethoxysilane (C₁₈H₄₀O₃Si, from Sigma Aldrich; purity >99.0 mol%; boiling point: 538.4k; Density: 875kg/m³ – Fig. 1) was used to render the calcite crystals oil-wet.

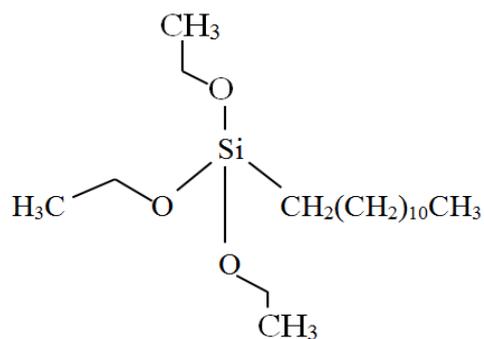


Fig. 1 Structure of Dodecyltriethoxysilane

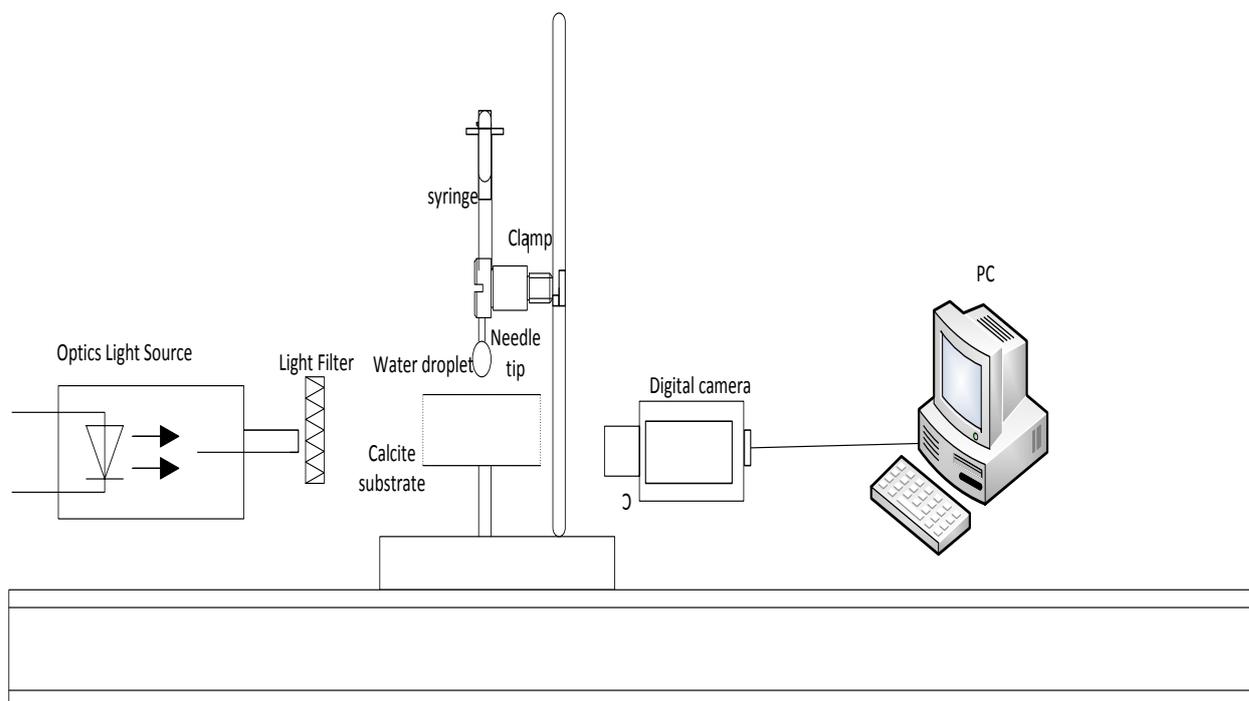


Fig. 2 Schematic of Experimental Setup.

Table 1 Properties of Nanoparticles

Modifiers	Concentration (Wt. %)	Chemical formula	Molecular Weight (g/mol)	Form	Particle Size (nm)
Zirconium Oxide	(0.004-0.05)	ZrO ₂	123.22	Nanopowder	<50
Nickel Oxide	(0.004-0.05)	NiO	74.69	Nanopowder	<50

2.2 Sample preparation

The calcite substrates were initially cleaned with analytical reagent grade acetone and methanol (Rowe Scientific pty. Ltd) and de-ionised water (David Gray & Co. Ltd) to remove surface impurities. The substrates were then dried and further cleaned in air plasma for 15 min to remove any residual organic contaminants (Love et al., 2005; Iglauer et al., 2014, Sarmadivaleh et al., 2015). The clean substrates were rendered oil-wet by aging them in dodecyltriethoxysilane for 12 h at 90°; thereafter, the aged substrates were cleaned again with acetone, methanol and deionised water to remove excess amount of silane from the calcite surface (Al-Anssari et al., 2016; Nwidee et al., 2016a) then dried in air. Then the reference contact angles were measured as a baseline and to ensure oil-wetness was attained; a 90° and 152° water contact angle in air and in toluene was measured indicating intermediate-wet and strong oil-wettability, respectively. The nanofluids were formulated by homogeneously dispersing nanoparticles (NP) in base fluid (NaCl brine). Specifically, ZrO₂ and NiO nanoparticles (concentrations: 0.004 – 0.05 wt%) and NaCl brine (3-20 wt%) were sonicated for 90min using a 300VT Ultrasonic homogenizer. Then the formulations were kept in a cool place away from heat and light and subject to virtual monitoring. The densities of the nanofluids (ZrO₂, NiO), model oil (Toluene) and brine (NaCl) were also measured at 296 K and atmospheric pressure: ($\rho(\text{ZrO}_2 \text{ nanofluid}) = 980 \text{ kg/m}^3$; ($\rho(\text{NiO nanofluid}) = 950 \text{ kg/m}^3$; ($\rho(\text{toluene}) = 850 \text{ kg/m}^3$; ($\rho(\text{NaCL brine}) = 997 \text{ kg/m}^3$).

2.4 Wettability measurements

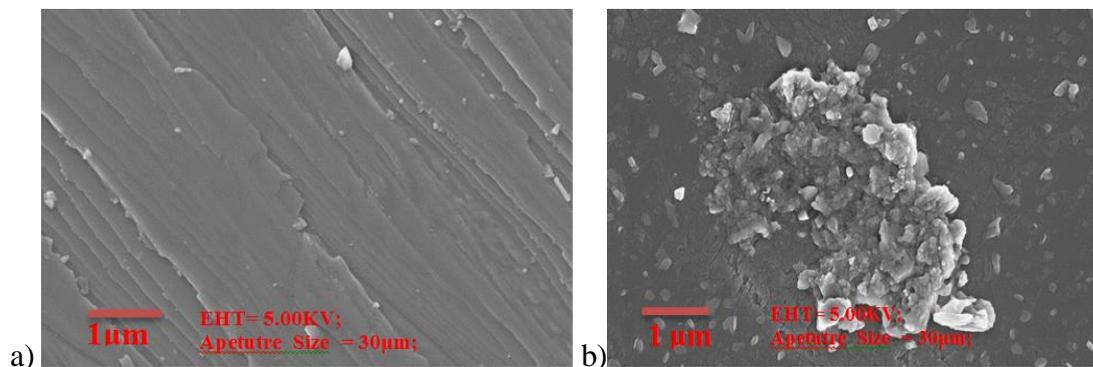
The oil-wet calcite substrates were submerged in nanofluids for a fixed time interval of 60min at room temperature and then dried for wettability assessment. Advancing and receding contact angle (Drummond and Israelachvili, 2002) was measured using the tilted plate technique (Landers et al., 1993) in air and in model oil (toluene). A high performance camera (Basler scA 640–70 fm, pixel size =7.4 μm ; frame rate =71 fps; Fujinon CCTV lens: HF35HA-1B; 1:1.6/35 mm) captured the water drop dispensing process, and advancing (maximum wetting) and receding (minimum wetting) contact angles were measured on the substrate (Fig. 2). All tests were conducted at $296\text{K}\pm 1\text{ K}$. The standard deviation based on replicate measurements is $\pm 3^\circ$. The surface morphology and topography of the unmodified and modified samples was also tested via SEM (-Zeiss Neon 40EsB FIBSEM with an Oxford Instruments x-act Inca SDD x-ray detector and Inca software), and AFM (-Dual Scope TM C-26 Scanning probe and optical microscope with DME software).

3. Results and discussion

3.1 Calcite surface characterization

Characterization with scanning electron microscope (SEM) and atomic force microscope (AFM) was conducted on calcite substrates in pure state, oil-wet state and after exposure to nanofluids (Figure 3 and 10). SEM and AFM are effective tools for wettability alteration studies through morphological and topographical surface evaluation. The particle size of ZrO_2 and NiO nanoparticles were less than 50nm. Particle size is of great relevance as it influences nanoparticle transportation and retention behaviour in limestone formation. Nanoparticles with particle sizes $<100\text{nm}$ inhibits direct plugging and bridging in the micro-pore network systems especially in the subsurface (Li and Cathles, 2014) as such can facilitate transport through the formation. In contrast, large particles have high tendencies of poor

dispersal into the neighbouring rocks (Serres-Piole et al., 2012) and may sediment and erode the channels therein (Rudyak, 2013). SEM test shows the morphological structure of the clean calcite sample (Fig. 3a), before modification with dodecyltriethoxysilane (Fig. 3b). After nanofluid exposure, adsorption of nanoparticles on the surface of the calcite crystals was clearly visible at higher image resolution (200 nm) (Fig. 3d, f) which is consistent with Al-Anssari et al. (2016); Winkler et al. (2011); Nikolov et al. (2010). At lower image resolution, deposits of ZrO₂ (Fig. 3c) and NiO (Fig. 3e) nanoparticles were evident, with better uniform surface adherence of the nanoparticles apparent on Fig. 3c (ZrO₂ coated) than Fig. 3e (NiO coated), thus, indicating better adsorption behaviour. AFM was used to evaluate the topography (Buckley and Lord 2003; Jarrahian et al., 2012; Zargari et al., 2010) of the untreated (Fig. 10a) and treated (Fig. 10b-d) samples. The mean roughness and root mean square of the untreated sample was 8.8 and 11 nm respectively. The topography of the sample aged in silane (Fig. 10b) demonstrates adsorption of dodecyltriethoxysilane on the calcite surface which explains the change in wettability of the calcite surface from its original water-wet condition (Fig. 10a) to an oil-wet (Fig. 10b). This is consistent with the SEM (Fig. 3b) and the measured reference advancing contact angle for silane modified surface which indicates strongly oil wet ($\theta=152^\circ$). Fig. 10(c and d) shows nanoparticle absorption on the aged calcite surface which also shows consistency with the SEM (Fig. 3c and e).



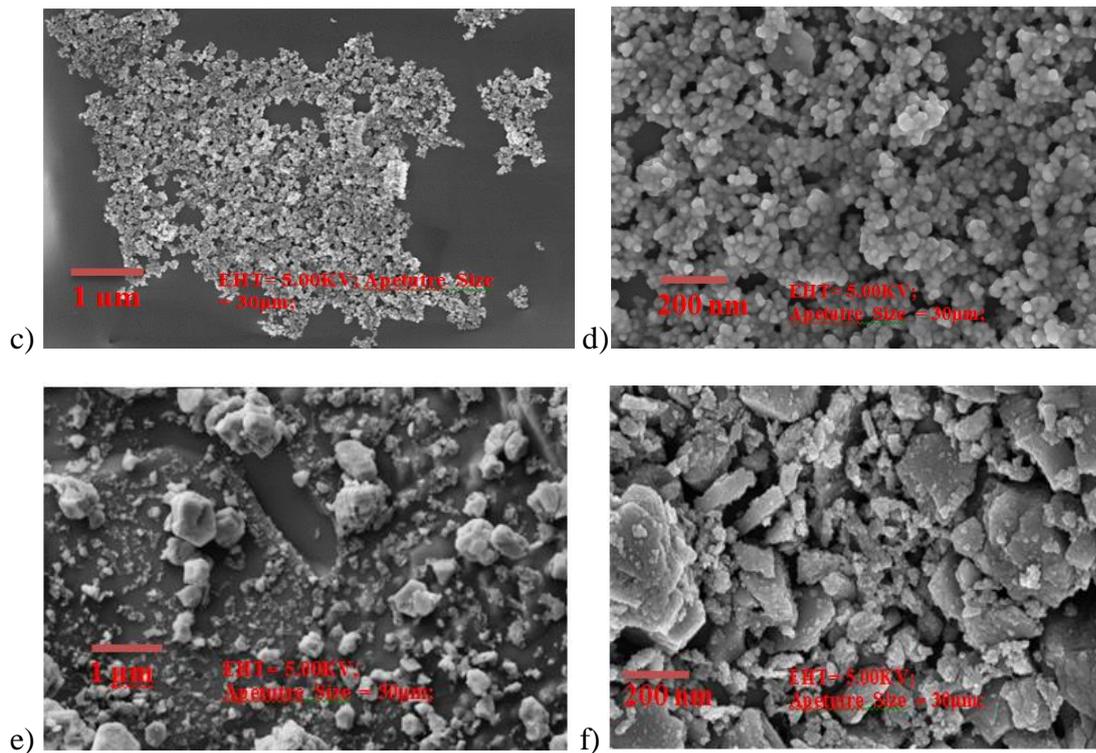


Fig. 3 SEM images of calcite crystals: (a) before coating - untreated state; (b) after coating with silane; (c) and (d) ZrO₂ adsorption on calcite crystals; (e) and (f) NiO adsorption on calcite crystals at different magnifications.

3.2. Contact angle measurements

A comparative study of the influence of Zirconium oxide and Nickel oxide nanofluids on wettability alteration through contact angle (θ) measurement was investigated as a function of nanoparticle (NP) concentration, exposure time and salinity. Reference tests for water contact angles (θ) were initially conducted on cleaned calcite crystals to ensure a completely water-wet state. The water contact angles measured (clean calcite $\theta=0^\circ$) indicate a strongly water wet-state, which supports the reports of Al-Anssari et al. (2016) (clean calcite $\theta=0^\circ$) and Karimi et al. (2012) (clean calcite $\theta=32^\circ$) [although Karimi et al. (2012) reported a relatively high θ value of 32° which may have occurred as a result of insufficient cleaning Iglaier et al. (2014)]. Another reference test was performed after establishment of the oil-wet state and the

water advancing contact angle θ in air was 90° , indicating an intermediate-wet state and 152° in toluene, indicating a strongly oil-wet state.

3.2.1 Influence of nanoparticle-brine interaction on wettability alteration.

Fluid displacements of wetting and non-wetting phase at pore scale are controlled by wettability. However, a shift in the wettability of the porous walls of the oil-wet rock towards water-wet can efficiently enhance fluid flow, as such the effect of nanoparticles concentration on wettability alteration was tested to assess the efficiency of ZrO_2 and NiO nanoparticles. Low nanoparticle concentrations (0.004-0.05 wt% ZrO_2 and NiO) was added to fixed concentration of the displacing fluid (7 wt% NaCl) and stirred ultrasonically over time. The interaction of the nanoparticles with NaCl produced clear and stable solutions. Then the oil-wet calcites were exposed to ZrO_2 and NiO nanofluids at the same specific concentration and a fixed time (3600s). This led to the formation of nanoparticle films or adsorbed layers on the surface of the calcite substrates after exposure to air as evident by the SEM images. Surface energies often dictate the wetting state of the rock, hence the adsorption of the nano-surface active and energetic material on the calcite surface may have led to significant change in the surface energy. Consequently, water spreads more readily on the calcite substrates, hence, the change in wettability towards water wet. This is evident in the results as ZrO_2 nanofluids (0.004wt%) changed the wettability (from 90° in air) to a water-wet condition (62°) in air and from 152° in toluene to intermediate-wet condition (89°) in toluene whereas, NiO nanofluids changed wettability to intermediate-wet (72°) in air and lowered the contact angle to 126° in toluene (which, however, is still oil-wet). At subsequent increase in NP concentration (0.05 wt%), θ decreased to 40° in air and 44° in toluene with ZrO_2 and to 49° and 86° in toluene for NiO (Figures 4, 5). ZrO_2 may have formed better adsorbed nano-layers on the oil-wet calcite surface

when compared to the NiO. As the dispensed water droplets get in contact with the ZrO₂ nano-coated calcite, the contact angle decreases more readily, thus wettability is efficiently changed towards water-wet at minimal particle concentration. We thus conclude that ZrO₂ is a more efficient wettability modifier than NiO based on exhibited efficacy after an hour exposure time.

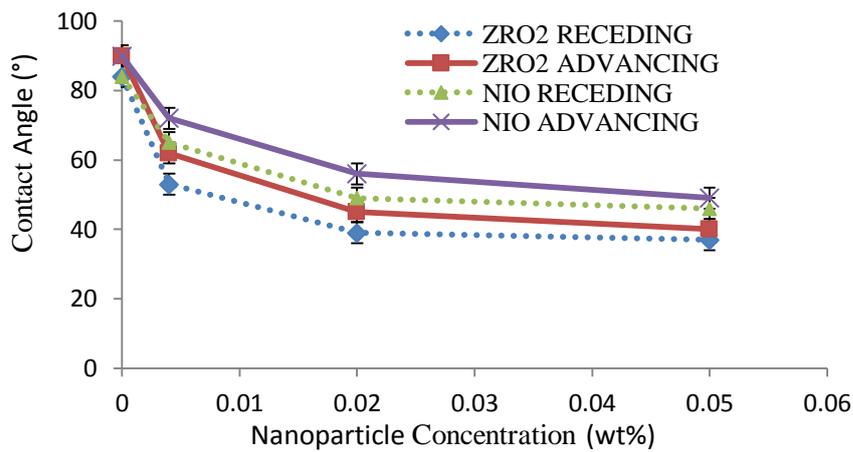


Fig. 4. Receding and advancing water contact angles (versus air) on initially oil-wet calcite as a function of nanoparticle concentration (60 minutes exposure time).

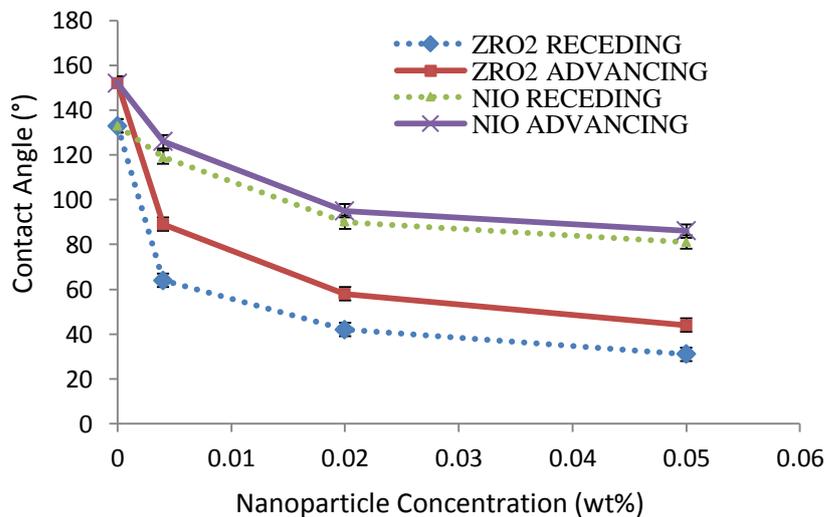


Fig. 5. Receding and advancing water contact angles (versus toluene) as a function of nanoparticle concentration (60minutes exposure time).

3.2.2 Wettability alteration as a function of time

Nanofluid efficiency is vital as fluid displacement and better oil recovery can be achieved over time when a rock is water-wet than oil-wet. Hence, the nanofluid wettability efficiency as a function of time (300-14400 seconds) was tested. ZrO₂ and NiO nanoparticles were at the (fixed) optimum nanoparticle concentration (0.05 wt%; chosen due to its effectiveness; see Fig. 4, 5 above) and at a fixed 7 wt% NaCl concentration. Both, receding and advancing θ in air and in toluene decreased with time (Fig. 6, 7); initially rapidly, and after ~4000s in air and ~6000s in toluene the decrease flattened out and only a smaller incremental drop in θ was observed. ZrO₂ displayed a slightly better performance over NiO. After 300s in air, θ exhibited a small change, θ decreased from 90° to 76° for ZrO₂ nanofluid, and to 82° for NiO nanofluids. However, after 900s a substantial decrease in θ resulted in a water-wet state ($\theta=60^\circ$ for ZrO₂; $\theta=66^\circ$ for NiO). Overall, the decrease in θ was continuous and smooth.

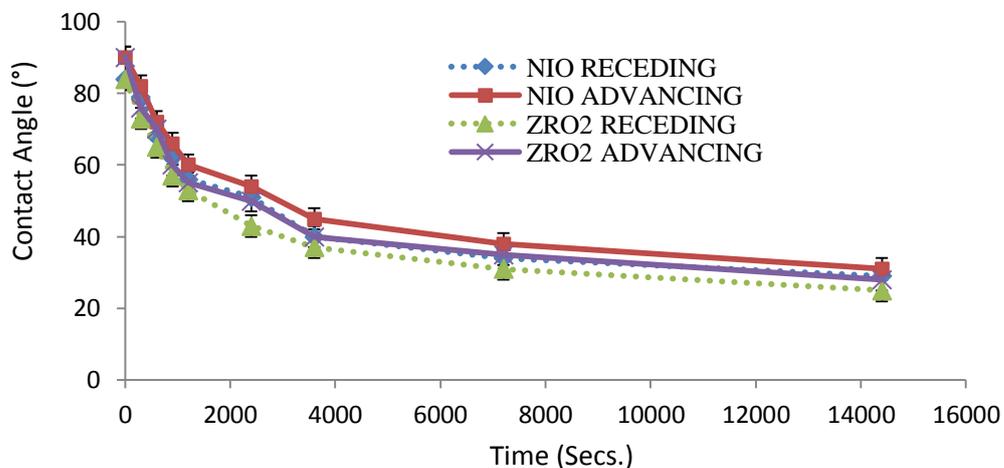


Fig. 6. Receding and advancing water contact angles (versus air) as a function of time (7 wt% NaCl brine; 0.05 wt% nanoparticle concentration).

For oil-wet calcite substrates exposed to ZrO₂ and NiO nanofluid in toluene, θ changed from 152° to 123° for ZrO₂ and to 135° for NiO, thus, still denoting an oil-wet state after 300s. After 900-1200s exposure time, an intermediate-wet state (89°-79°) resulted with ZrO₂, and a

weakly oil-wet state (118° - 109°) was achieved with NiO. With a further substantial increase in exposure time (7200-14400 secs), water-wet conditions were achieved for all substrates (42° and 35° for ZrO_2 ; 62° and 40° for NiO). The continuous change in θ with respect to time for the systems tested is an indication that the addition of a small fixed fraction of the nanoparticles to the dispersing fluid significantly impacted the fluid-rock interaction which led to efficient displacement of oil over time thus the rock surface is rendered more water-wet.

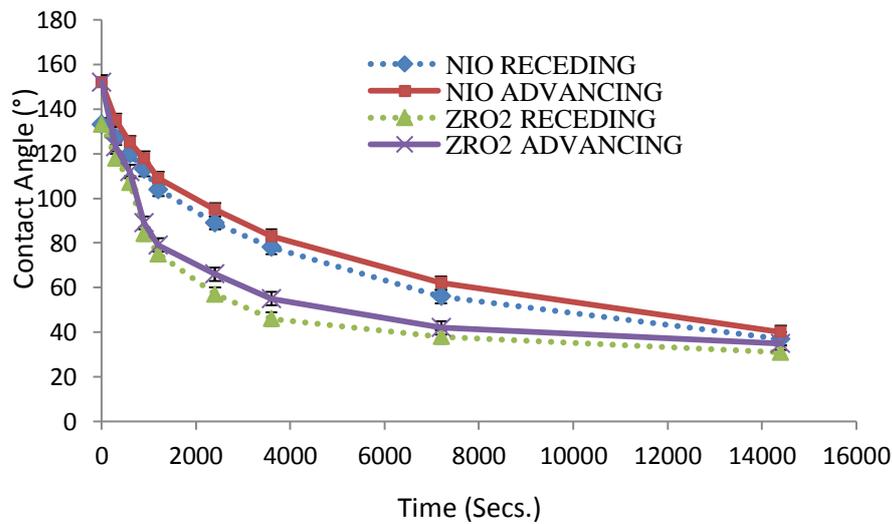


Fig. 7 Receding and advancing water contact angles (versus toluene) as a function of time (7 wt% NaCl brine; 0.05 wt% nanoparticle concentration).

3.2.3 Influence of salinity on wettability alteration efficiency of nanofluids

The saline nature of oil reservoirs influence the fluid-rock interaction, consequently, the fluid-rock surface charges change in the presence of ions and the change is dependent on the solution chemistry of the aqueous fluid that the rock is exposed to. The mechanism behind this behaviour was reported by Li and Cathles (2014), who also asserted that increase in NaCl concentration influences nanoparticle behaviour. Thus, different NaCl concentration (3-20 wt%) at the optimum ZrO_2 and NiO nanoparticle concentration (0.05 wt%) and time interval

(3600 secs), see above, was tested. Increased salt concentration clearly decreased θ (Fig. 8 and 9) for both, ZrO_2 and NiO nanofluids in air and in toluene. Again, ZrO_2 exhibited good wettability alteration efficiency: θ changed from an intermediate wet-state (90° in air) to water-wet (60°) in 3 wt% NaCl brine but remained intermediate-wet (81°) in the presence of NiO . At 5wt% NaCl concentration, water-wetness was achieved in the presence of both nanofluids (49° for ZrO_2 and 68° for NiO in air). A similar scenario, albeit with higher absolute θ values, was observed for toluene: the strongly oil-wet state ($\theta = 152^\circ$) changed to intermediate-wet (8°) in ZrO_2 nanofluid and weakly oil-wet (112°) in NiO nanofluid at 3 wt% NaCl concentration. Highest water-wettability was achieved at the highest salinity (20 wt% NaCl, $\theta = 19^\circ$ in ZrO_2 nanofluid and 34° in NiO nanofluid).

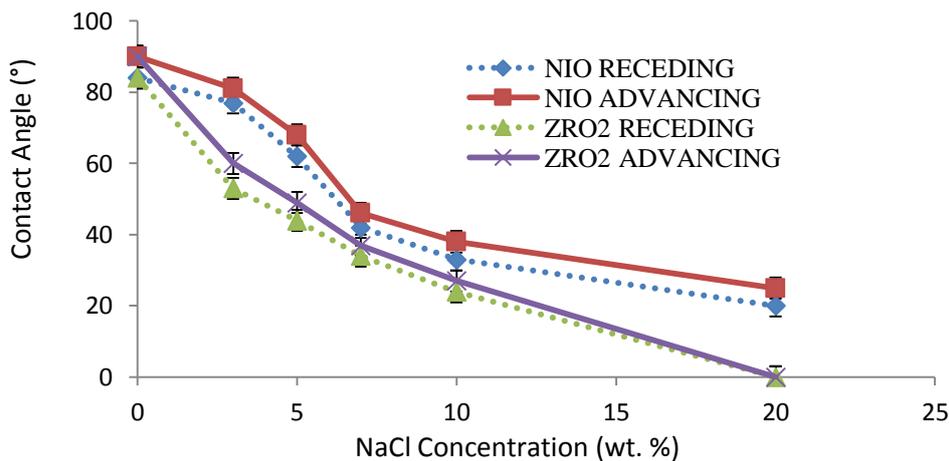


Fig. 8 Receding and advancing water contact angles (versus air) as a function of NaCl concentration (0.05 wt% nanoparticle concentration; 60minutes exposure time).

The decrease in θ with increase in salt concentration is consistent with the report of Al-Ansari et al., (2016), Moghaddam et al., (2015), Nwidee et al., 2016a, and Li and Cathles (2014). The particle adsorbed on the calcite surface with increase in NaCl concentration which can be attributed to the physiochemical interactions or electrostatic forces (Li and Cathles 2014; Zhang et al., 2013) between the nanofluid and calcite. However, extreme salinity can weaken the electrostatic repulsion between the particle and the mineral surface which can lead to high

particle adsorption on the rock surface (Bagaria et al. 2013). This can be unfavourable for nanoparticle transportation, as such, low particle adsorption may be essential for efficient transportation of nanoparticle through the porous media and to achieve low formation damage. Notably, zirconium oxide when compared to other nanoparticles demonstrate better wettability alteration efficiency at very minimal concentration (0.04 - 0.05wt%). This is much lower than the effective concentrations reported for other nanoparticles in wettability alteration studies such as silica-concentration range: 0.1-0.5[wt%] (Ju et al., 2012; Al-Anssari et al., 2016; Maghzi et al., 2012); Alumina-concentration range: 0.01–1[wt%] (Giraldo et al., 2013) and NiO-concentration range: 0.004-0.05 [wt%]. We thus conclude that ZrO₂ is a better efficient wettability modifier than SiO₂, Al₂O₃ and NiO as ZrO₂ base fluid consistency changed water contact angle towards water-wet at minimal particle concentrations, and over longer exposure time. This behaviour may be attributed to the favourable interaction of ZrO₂ with the dispersing fluid (NaCl brine) and high chemical affinity to the calcite.

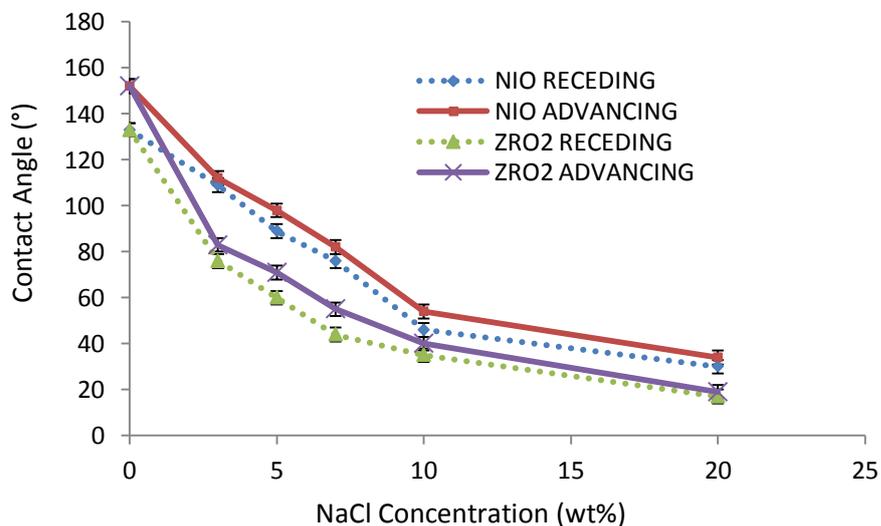
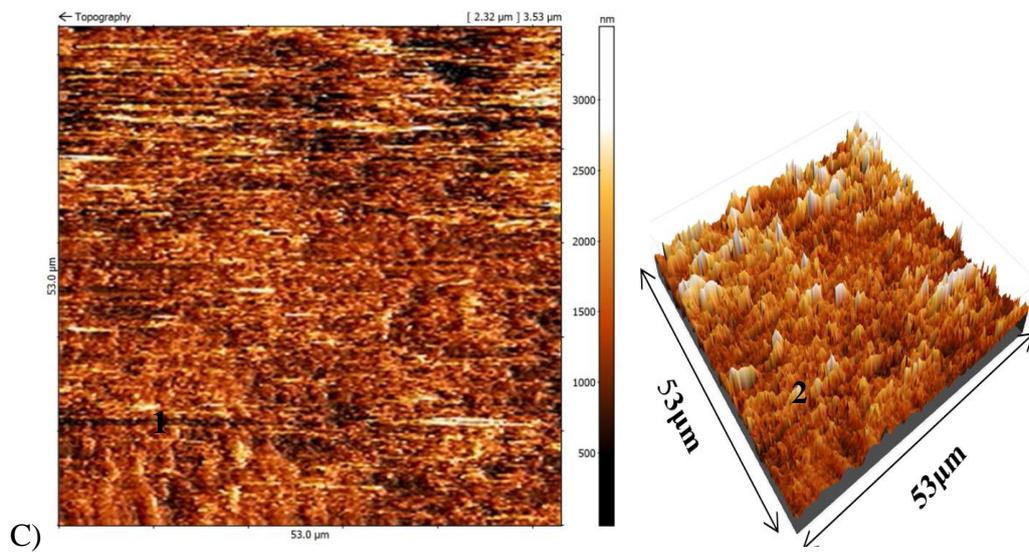
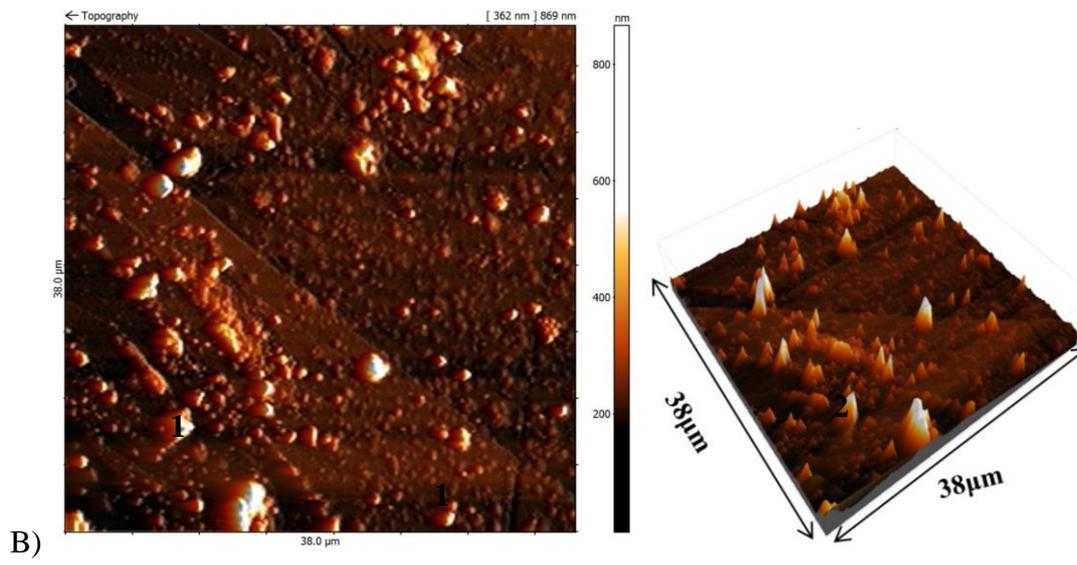
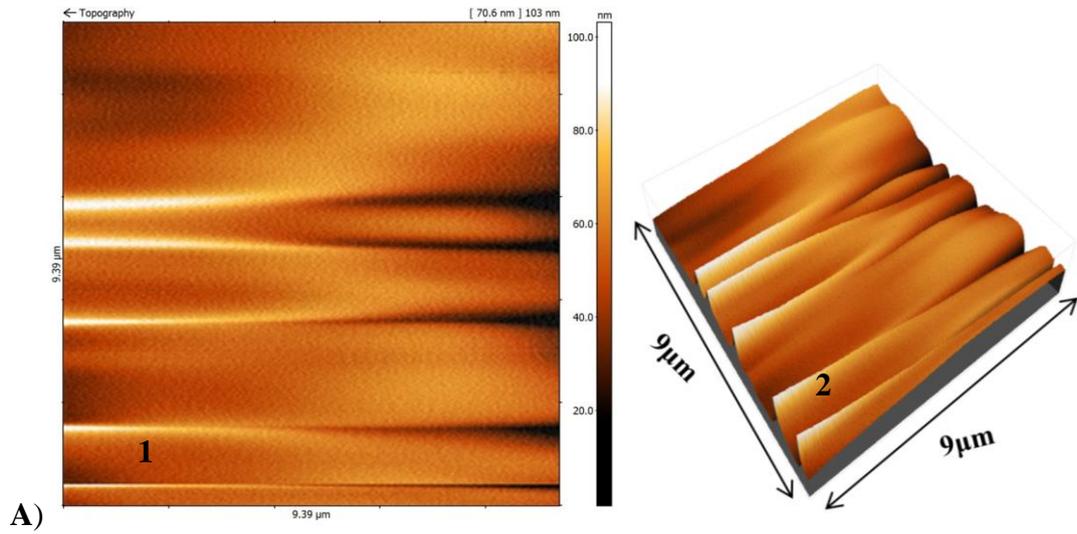


Fig. 9 Receding and advancing water contact angles (versus toluene) as a function of NaCl concentration (0.05 wt% nanoparticle concentration; 60mins exposure time).



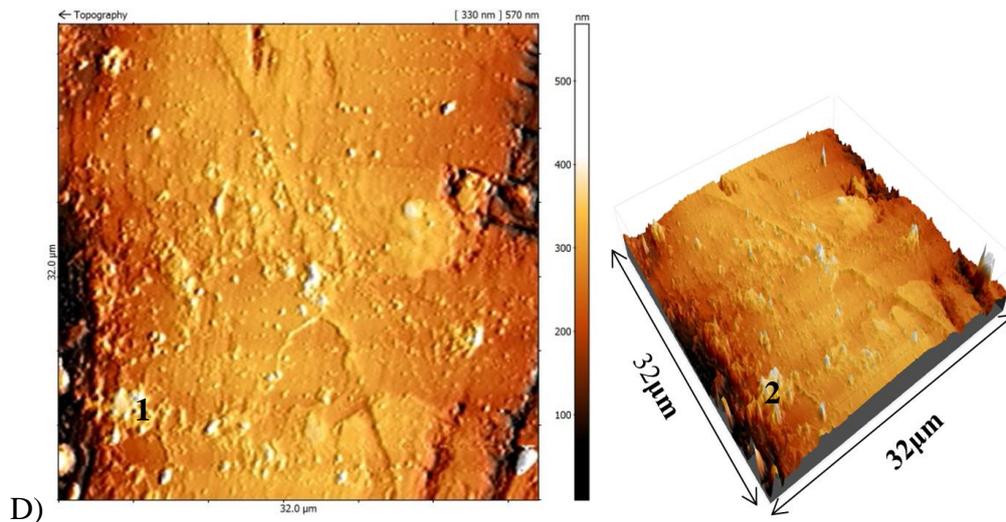


Fig. 10 AFM height images [2D (1) and 3D (2)] of calcite crystals: A) Untreated calcite; B) Silane treated calcite; C) ZrO₂ modified; D) NiO modified. The different colours indicate variation in height of the surface with high Z-values (higher features appearing as white) and low Z-values (lower features appearing as dark shades).

4. Conclusions

The wetting preference of oil-wet calcite substrates was measured to assess nanofluid wettability alteration efficiency. Results from the extensive contact angle measurements indicate NiO demonstrate potentials in wettability alteration, although NiO is less efficient in comparison to ZrO₂ under same condition and particle concentration. Poor oil displacement tendencies were observed at minimal particle concentration (0.004 wt%) and short exposure time (60 min; refer to Fig. 4). However, oil displacement was attained over longer exposure time at higher particle concentration (0.05 wt%; refer to Fig. 6). Furthermore, ZrO₂ even at minimal nanoparticle concentrations (0.05 wt%) significantly decreased the water contact angle and thus rendered the substrate significantly more water-wet which is consistent with Karimi et al. (2012). ZrO₂ consistently displayed higher performance in changing wettability from oil-wet to water-wet, thus, ZrO₂ was considered a better wettability modifier over NiO.

ZrO₂ nanofluids exhibited also better performance than SiO₂ and Al₂O₃ nanofluids (Al-Anssari et al., 2016; Ju et al., 2012; Maghzi et al., 2012; Giraldo et al., 2013). Despite the difference in the wetting behaviour of ZrO₂ and NiO nanoparticles, similarities exist for both nanoparticles potentials to change wettability from oil-wet to water wet for all three variables tested (nanoparticle concentration, exposure time and salinity). A continuous decrease in contact angle with increase in nanoparticle concentration, increase in exposure time and increase in salinity occurred for all tests. Mechanistically, the nanoparticles adsorbed on the calcites substrate surfaces (as observed by SEM -Figure 2 and AFM -Figure 9). Inferring from the study, the following deductions were made:

- ZrO₂ and NiO nanofluids decrease the water contact angle with increase in time, concentration and salinity in a continuous trend especially at suitable particle concentrations (0.004-0.05 by weight of the solution).
- Nanoparticles adsorbed on the surface of the calcite crystals promote oil displacement thus contributing to inevitable change in wettability from oil-wet to water-wet in a very efficient way.
- Application of nanofluids in oil-wet or intermediate-wet formations such as fractured limestone may substantially increase oil recovery efficiency through wettability alteration.

We conclude that NiO and particularly ZrO₂ nanofluids are efficient wettability modifiers (changing oil-wet to water-wet conditions), and are thus potentially very efficient EOR agents.

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