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Nanofluids as Novel Alternative Smart Fluids for Reservoir Wettability Alteration

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Abstract

This chapter presents an account of two metal oxide nanoparticles (zirconium and nickel oxide) on basis of their structure, morphology, crystallinity phases, and their wetting effect on solid-liquid interface. As a preliminary step to sound understanding of process mechanisms; wettability, nanoparticles, and their relations thereof were scrutinized. To investigate the nanofluids wetting inclinations, complex mixtures of the nanoparticles and NaCl brine ($ZrO_2/NaCl$; $NiO/NaCl$) were formulated and their technical feasibility as wetting agents tested via contact angle measurement. The result shows that the nanoparticles exhibit different structural and morphological features and capable of addressing reservoir wettability challenges owing to favorable adsorption behavior on the surface of the calcite which facilitated the wetting changes quantified by contact angle. We believe this study will significantly impact the understanding of wetting at solid-liquid interface which is crucial for recovery process optimization.

Keywords: nanoparticles, calcite, zirconium oxide, nickel oxide, carbonate, wettability, EOR

1. Overview of nanomaterials

In the past half century, industrial processes in general have experienced a transition in material applications owing to a shift from conventional bulk materials toward nanoscale materials. This has driven innovative applications in wide-ranging areas of science and technology globally, thus yielding a proliferating interest and investment in nanoscience and nanotechnology fields. The increase possibilities for the manipulation of matter in nanometer-scale have primarily led to this growth with nanomaterials at the leading edge of this fast-developing field. The

potentials for direct control of systems at the same scale as nature such as DNA, cells, mitochondria and even reservoir rock pores can yield effective approaches in a wide variety of industrial processes such as the production of chemicals, materials, and energy [1]. Although nanomaterial appears to be a recent development owing to the current tremendous research growth and diverse applications, this material is not completely new as it has a rather shocking protracted history. The knowledge of the materials commenced as early as the 1950's by Richard Feynman who proposed that fabrications of materials and devices can be performed at atomic scales. Then in the 1980s, the term nanotechnology became even popular as established by Drexler Eric K. The current applications of these materials are not an exclusive result of modern research or laboratory synthesis, or even circumscribed to man-made materials. These materials have long been in existence with traceable applications in the old days. For instance, natural asbestos nanofibers and metal nanoparticles were used several decades ago for the control reinforcement of ceramic matrix and as color pigments in glass and luster technology respectively [2, 3].

Ever since, novel studies of nanoscale fundamentals and principles, design, characterization, production, and application of these materials [4–6] have evolved and remained intriguing and ground-breaking. Since 2000, the nanotechnology industry has experienced a growing trend and the funding of nanotechnology research has also been on the rise (**Figure 1**). For example; in 2013, the global market for nanotechnology was estimated at \$22.9 billion, by 2014, the estimate had grown to about \$26 billion with a further projected growth of about \$64.2 billion by 2019 [7]. This innovative development involves the nanometer (nm) length scale manipulations of the structure of matter, where a nanometer represents a billionth of a meter, a distance that is equivalent to 2–20 atoms positioned next to one another. Nanomaterial has increasingly gained attention for a variety of processes such as electronic cooling and space applications, transportation, biomedicine, cooling of high-power laser diodes and submarines, and heating of buildings [8, 9]. Its wide applicability also extends to the field of environmental protection. This material exhibits great potentials as pollution reduction agent and improves the quality of air, water, and soil [10] and it is also currently being used as novel tools for oil and gas operations. Nanomaterials especially nanoparticles can be used alone

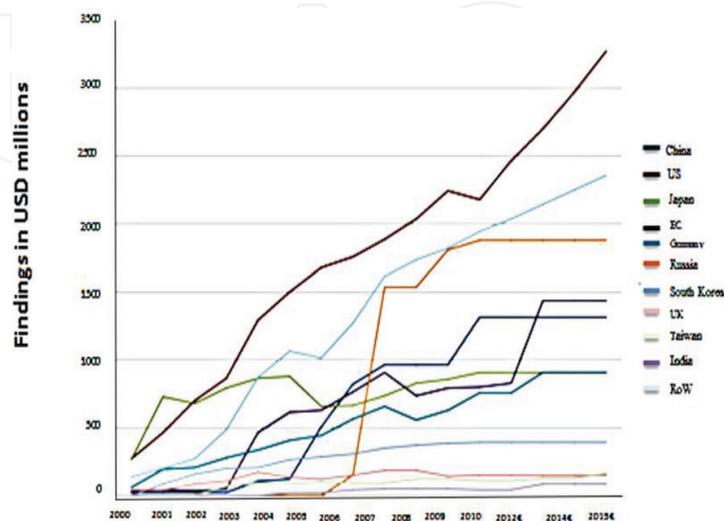


Figure 1. Worldwide nanotechnology research and funding by year [7].

or manipulated for the creation of larger scale materials to facilitate innovative applications. The material allow for clear-cut design and manipulation of atoms and molecules and its industrial applications are cost-effective and efficient [11, 12]. Nanoparticle cut across diverse fields of science and engineering and shows great potentials as effective approach for novel applications with high technological prospects and environmental friendliness. A recent drift in its application is its usage for resolving reservoir engineering challenges.

1.1. Nanoparticles

Nanoparticles are nano-sized structures with dimensions in the range of 1 to 100 nm. These materials exhibit unique properties with better potentials than bulk materials. Nanoparticles application enables the creation of new composites with unique properties which allows for innovative technological advancements. Unarguably, the effectiveness of this material cut across diverse industries such as energy, manufacturing, medicine, electronics, oil and gas industries etc., however, the understanding of the material is still very limited in EOR processes especially in wetting evaluations.

Nanoparticles are categorized as magnetic (iron, cobalt etc. and the oxides) [13–16], metallic (gold, silver, copper, and Platinum) [17, 18] or metal oxides (oxides of aluminum, zinc, silicon, magnesium, zirconium, cerium, titanium) [8, 19–23]. Among these categories, the metal oxides are the most commonly used nanoparticles in EOR [24–28] as the material offers special unique structures, compositions, physical, and chemical properties. These materials display efficient thermal conductivity effect [8], great stability [19] and excellent saline-alkaline tolerance [23]. However, its effectiveness depends greatly on the preparation methods, dispersant and subsequent applicability. Generally, nanoparticles can be prepared via chemical, biological or physical methods, although the preparation method is mainly based on the nature of the material and associated chemical reactions [29], and the applications thereof.

1.2. Nanofluid production and stability control

Nanofluids are colloidal suspensions of solid nanoparticles or nanofibers. These solid-liquid composite materials are typically two-phase systems, consisting of a carrier medium and solid phase. The carrier liquids are often water, polymer solution, oil, ethylene glycol and sodium chloride brine. The solid phases are nanoparticles of chemically stable metals and oxides usually within the range of 1-100 nm [30–39]. Nanofluid has continuously attracted great attention for various processes owing to its great thermal properties at low volume fractions of less than 1%. To achieve the same functionality with conventional suspensions of well-dispersed particles, high concentrations that are greater than 10% of particles is often a requirement. Such high concentrations increase the issues of rheology and stability which has remained a deterrent to the extensive use of conventional slurries as heat transfer fluids [35]. Nanofluid production can be achieved via chemical or physical synthesis. The chemical synthesis involves the use of methods such as thermal spraying, chemical vapor deposition, spray pyrolysis, chemical precipitation, or micro-emulsions. Whereas, the physical synthesis involves inert-gas-condensation technique and mechanical grinding approach. During its production, a one-step or two-step approach can be adopted. The one-step approach allows for the production of nanoparticle and its dispersion

in a fluid in a single combined process, which is suitable for nanofluids with high-conductivity metals contents. Whereas with the two-step method, production process is performed in two separate steps, firstly, the nanoparticle is produced, and then the produced nanoparticle is dispersed in a fluid – this is considered an effective strategy for commercial use [8, 9].

In the face of the diverse functionalities of the nanoparticle, a major impediment in the manipulation and application of nanoparticle is the colloidal stability control. Nanoparticle tends to agglomerate when in suspensions irrespective of its small size. This has remained an issue with the production and utilization of nanoparticle based fluid as this behavior impacts the overall fluid stability. Such agglomeration can impede fluid flow characteristics in porous media as well as in flow based cooling applications [35]. Since nanofluids are typically produced in small quantities at laboratory scale, there is high potentials of yielding sufficiently well dispersed, homogenized, and stable fluids. However, homogeneous nanoparticle dispersion is often a challenge owing to agglomerating or clustering tendencies. The agglomeration inclination or clustering behavior of nanoparticle is dependent on the nanoparticles properties, particle concentrations, production methods, nature of dispersants, fluid homogeneity and stability. The nanofluids stability is vital for process efficiency as instability can influence the particles functionalities. Fedele et al. [19] reported stability evaluation of nanoparticle via a comparison of various preparation methods such as ball milling, sonication, and high-pressure homogenization. The ball milling method produced the least stable fluids when compared to sonication and homogenization, which produced better stable fluid. The use of magnetic stirrer or ball milling method has been shown to be rather insufficient for stable nanofluid formulation [23]. Similarly, Roustaei and Bagherzadeh [20] reported sonication and homogenization [21–23] as the most efficient methods.

An approach to ensure the stability and homogeneity of nanofluids aside the use of additives or stabilizers, is the uniform dispersibility of the particles in the solution. Attaining high-performance heat transfer nanofluids require efficient dispersion of the particles in the base fluid [8, 12, 40, 41] and ensuring an approximately monodispersed or non-agglomerated nanoparticle in liquids during the production of the suspensions. Thus, the fluid stability and excellent particle dispersion in base fluids can be significantly improved by using appropriate dispersants, suitable fluid production methods, and surface treated nanoparticles. Suitable dispersal and fluid production methods are vital to achieving desirable properties and uniform distribution of the particles in the system which can further prevent issues of agglomeration and can also improve the mechanical properties such as strength and ductility of the system [42]. Careful consideration should also be given to the concentration of the nanoparticles, as high particle concentration volume can propel high particle agglomeration.

2. Wettability

Wetting applies to several practical processes and a variety of industries such as energy, marine, manufacturing and materials. Wetting processes often involve the interaction of solids such as porous material, suspensions, or fibers, and liquids - water, ink, dye or lubricants. Typical indications of solid-liquid wetting can be illustrated using standard scenarios to correlate the

dynamics such as: (1) the interaction between porous soil and water - where the water wets the solid components of the soil; (2) enhanced oil recovery processes - where the process permeates water into oil-wet porous media. However, the mineral floatation in these processes is often based on the selective wetting characteristics of the mineral particles [43]. Two key mechanisms [44] governs wettability alteration of surfaces - cleaning and coating. Cleaning involves the use of surface-active agents to desorb surfaces e.g. surfactants induced wettability alteration, where cationic surfactants can desorb the hydrophobic layer on a surface while changing the surface toward hydrophilic condition. Whereas coating involves covering a hydrophobic surface with a hydrophilic material, e.g. hydrophilic zirconium nanoparticle can adsorb on hydrophobic rock surface and form nanotextures capable of coating the hydrophobic surfaces. At large scales, wetting or non-wetting plays an essential role during oil recovery [45]. Inadequate formation wetting can prohibit efficient hydrocarbon flow, which in turn hinders the oil, gas or water movement or distribution through the pore spaces, as such fluids may appear to have flowed whereas its distribution through the pore spaces is hindered owing to poor rock wetting. Assuming a system contains only three phases (solid, liquid, and vapor), for any two of these phases to be in contact, a transitional area of molecular dimensions occurs owing to the compositional alteration of the system that leads to phase changes. For example, if a non-volatile molecular smooth solid is in contact with an inert gas, it is expected that the system will exhibit a transition region thickness of about a molecule, this would cause a change from solid molecules to gas molecules. Whereas, if similar trend occurs on an irregular surface, the transition region would reflect the physical non-uniformity of the surface and a concentration profile of the region would indicate the existence or non-existence of the solid phase. Similar concentration profile phenomenon holds for solid-liquid systems; however, the related specifics are dependent on the solubility of the solid in the liquid or the solubility of the liquid in the solid [46, 47]. In a typical solid-liquid-vapor three-phase system [48], the system would exhibit a completely dry behavior if there is an intrusion of a macroscopic vapor layer between the solid and the liquid; a partial wetting behavior if the droplet is bounded by microscopic thin film that is adsorbed on the surface of the solid; and complete wetting occurs due to macroscopic adsorbed thick wetting layer.

With respect to petroleum reservoir rocks, wetting is ascribed to the measurement of the reservoir rocks affinity for water or oil in a typical rock-fluid-oil system. An understanding of the wetting preference of rock is vital, as it unveils the mechanisms behind fluid flow in porous media, soil decontamination process evaluations, and ultimately promotes recovery efficiency. Reservoirs exhibit different wetting inclinations: water-wet, oil-wet, or intermediate-wet (**Figure 2**). Reservoir rocks considered as water-wet have high affinity for water and water predominantly occupies the tiny rock pores as well as the surface of the formation rock. Whereas, oil-wet reservoir rocks have high affinity for oil and such oil mainly occupies the tiny rock pores and the formation rock surface. For example; in controlled laboratory experiments involving the manipulations of cores or rock samples, the samples are usually cleaned and modified to a preferential wetting state. If such samples have high affinity for water or were originally water wet, then saturated to a suitable oil-wet state, the rock surface becomes even more oil-wet or hydrophobic upon exposure to oil under efficient and favorable treatment conditions. However, this does not influence the actual wetting affinity of the rock. The actual wetting affinity can be affirmed by exposing such hydrophobic rock to a water imbibition test. The water imbibing potential of the rock can be used to predict its wetting affinity.

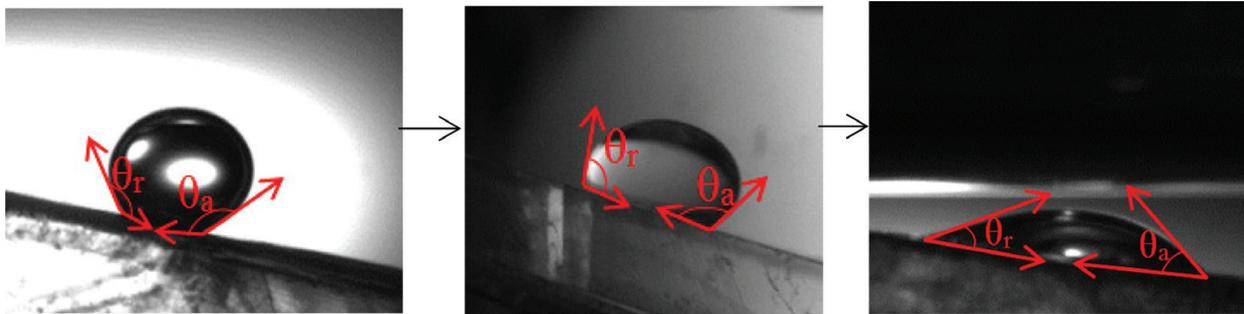


Figure 2. Rock surface wetting transition from hydrophobic to hydrophilic. Left: Oil-wet ($105\text{--}180^\circ$); Center: Intermediate-wet ($75\text{--}105^\circ$); right: Water-wet ($0\text{--}75^\circ$).

Ideally, if the rock has high affinity for water then the oil will be displaced from the surface of the rock by water. Whereas if a rock with high affinity for oil is saturated with water, and then the rock is placed in an oil-wet environment, the oil will displace the water from the rock surface while efficiently imbibing into the rock pores. In the absence of an actual inclination for water or oil, the formation rock is considered intermediate wetting. Aside from these key-wetting preferences, there also exists fractional wetting where the formation rock exhibit different wetting inclination in different sections of the rock [49–53].

2.1. Carbonate porous media and wettability challenges

Reservoir rocks considered as porous media are formations with an interconnected network of pores or voids characterized by the rock's porosity, and physical and textural properties that exhibit a dependency on the formations constituents. Oil recovery exhibits great dependency on the formation wettability as it controls the fluid displacements of the wetting and non-wetting phase at the pore scale. Reservoir wettability is a prime factor for determining the microscopic displacement efficiency in the swept regions of a waterflood. Originally, reservoirs were strongly water-wet, and the formation traps were initially filled with water, thus the surface of reservoir rocks had high affinity for water in the presence of oil. However, overtime, oil migrated into such formations forming firm adsorbed layers of heavy hydrocarbons that pose several challenges and cannot be altered via gasoline or mere solvent applications. The oil migration and accumulation cause water to be retained in the rock pore spaces due to capillary pressure, while the rock pores surface become covered by oil, and water existed on such surfaces in the form of films. Such effect is primarily due to the rock surface wettability changes owing to the ease of invasion by a wetting fluid, which causes lithological variances. The level of oil migration also determines the formations wetting state. For instance, if the migrated oil is negligible, the possibilities are that the neighboring formations will be more oil wetting, while the tight regions of the formation would exhibit more water-wet behavior [49–55]. This behavior is more prevalent in carbonate rocks owing to the oil-wet character of this formation, which is still poorly understood.

It is well established that heterogeneous carbonate rocks are more prevalent globally. Carbonate rocks exhibit complex microstructures [56–58] and its complex nature impacts reservoir wetting preference. These formations are predominantly naturally fractured, and exhibits diverse wetting conditions; intermediate-wet or oil-wet behavior with as high as over 80% oil-wetness. The

oil-wet nature of carbonate formation is due to its surface charges, which tend to attract negatively charged carboxylic acids compounds in crude oils [59–61]. Ideally, the formations positive surface charges attract crude oil acidic components. Carbonate reservoirs are problematic, as the complex wetting characteristics of this reservoir make the production capacity quite different in comparison to other conventional formations. Typically, an enormous capacity of the original oil in place is left stranded in this formation after primary and secondary oil recovery approaches are employed. Such approaches have been implemented for several decades, however, the fraction of recoverable oil from this reservoir is less than two-thirds [39, 62]. Fractured reservoir with enormous oil resources in its matrix requires advanced approaches for efficient recovery. Although water flooding enhances productivity in this reservoir by imbibing water from the formation fractures into the rock matrix, while enhancing oil flow out of the matrix through the fractures to the production well, this is mainly achievable if the capillary driving force is robust and efficient as it influences recovery efficiency, and the interaction between the matrix and the fracture is required for oil recovery from the formation matrix. Capillary forces have a significant effect on recovery capacities, however, its impact is greatly dependent on the nature of the reservoir, whether it is fractured or non-fractured. For non-fractured reservoirs, the presence of strong capillary forces during water flooding traps oil, however, the residual oil saturation becomes relatively high. Hence, the need for a reduction of the oil-water interfacial tension forces in order to remobilize residual oil in such formations. Whereas, for fractured reservoirs such as carbonate, the key driving force for efficient oil displacement in this formation is the spontaneous imbibition of water [63, 64]. Capillary effect and wettability are the underlying mechanisms in this case. This effect is attainable if the formation rock is hydrophilic [65]. Strong capillary effect occurs if the matrix is sufficiently water-wet and the fracture network holds enough water. Ideally, this is not the case with carbonate reservoir, as it is characterized by complex microstructures and poor rock wettability (intermediate-wet or oil-wet). This behavior impedes productivity, hence, harnessing substantial oil from this formation is rather unsatisfactory.

Understanding wettability in oil-wet carbonate reservoir is challenging owing to the complex nature of crude oil, and its characterization is even more difficult. Crude oil contains polar compounds which are normally surface-active and capable of altering reservoir rock surfaces when adsorbed [55, 66–69]. Among such polar compounds, asphaltenes and resins have the most polar oil fractions with high surface activity. Asphaltenes are known for their propensity to self-associate in solution, with high surface adsorption behavior. Surface wettability alteration is mainly caused by the asphaltenes through interaction of its polar functional component with the surface polar sites, which leads to operational problems, and such interaction poses even more complexities [66, 70–75]. Since the distribution of the oil in the reservoir is dependent on the degree of the reservoir rock wettability, it is, therefore, imperative to quantify the balance of forces existing at the line of contacts between the rock, oil, and water. Typically, if the oil and water are in contact with the rock surface, either of these fluids will exhibit displacement tendencies of the other or attain equilibrium as the fluids create an angle of contact with the rock. However, such interactions can be affected by factors such as the mineralogy of the rock surface, brine composition, pore roughness and the nature of the oil.

Contact angle and spontaneous imbibition tests are key approaches for assessing formation wettability among other approaches such as relative permeability, capillary pressure/displacement

capillary pressure or USBM [49–52, 76]. However, there exists a remarkable variation in the test methods, which is primarily based on how much of the rock surface is exposed to the wetting phase or wetted by water. In contact angle tests, only the outer surface area of the sample is exposed to a drop of water without consideration for the inner surface of the rock, whereas, in the spontaneous imbibition tests, the whole sample is exposed to the wetting phase (**Figure 3**). Thus, the inner surface area of the rock can be accounted for upon displacement of the non-wetting phase (oil) by the wetting phase. For example, in an oil-wet carbonate rock, for oil to be displaced by the wetting phase (water/brine solutions etc.) the capillary barriers must be overcome. If the wetting phase penetrates the rock pores, two key possibilities exist; (a) rock wettability change; (b) the presence of a positive capillary due to the wettability change. Such scenarios can enhance recovery especially if the formation rock is hydrophilic. **Figure 3b** (i-ii) shows a typical case of an oil-wet rock or core sample placed in an imbibition cell containing NaCl brine solution (the wetting phase). The brine imbibes into the rock or core pores and pushes out the oil in the cores. Such expelled oil sticks on the rock surface while been collected at the top of the cell simultaneously for estimation of the recoverable oil. Formation rock with a considerable water-wet condition exhibits high potentials for allowing water into the tight rock matrix pores. Thus, more water-wet rocks allow higher rates in spontaneous imbibition with possibilities of improving recovery. However, maintaining water wetness of formation rocks depends on the extent to which the water film on the rock surface is stable. The presence of unstable water films can lead to oil migration to the rock surface (like the behavior observed in **Figure 3b**), thus, changing the rock surface wettability. With respect to a typical crude oil system, such behavior would lead to adsorption of polar compounds on the solid surface which in turn changes the wetting properties of the solid [51]. Usually the brine present in a typical carbonate reservoir exhibits a somewhat basic pH (7–8), very high concentration of Ca^{2+} , and a very small amount of CO_3^{2-} , thus the rock-water interface becomes positively charged [77]. The carboxylic materials present in the crude oil acts as surface-active materials, and partial dissociation of the acidic group leads to negatively charged oil-water interface. This behavior causes instability of the initial water film between the oil and the rock and the oil comes in contact with the rock yielding mixed-wet characteristics. Several wetting studies have been conducted with crude oil used to alter originally water-wet surfaces to oil-wet in different systems [78–89]. For example; Standnes and

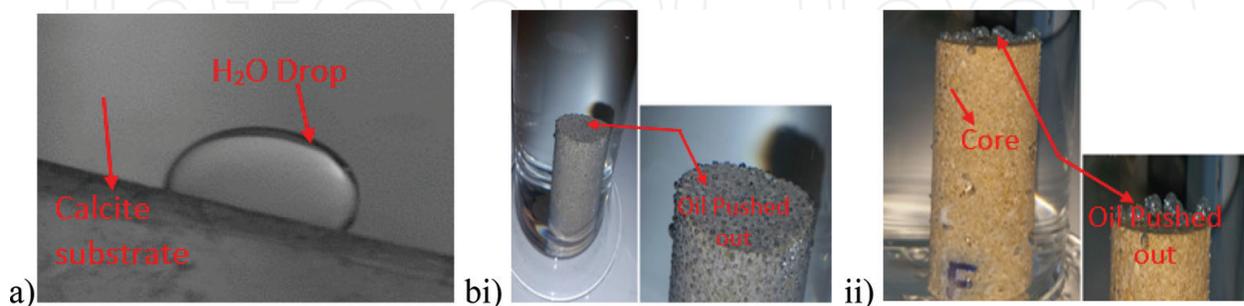


Figure 3. Contact angle versus spontaneous imbibition (a) contact angle: Outer surface area wetted by a drop of water on calcite sample; (b) imbibition: The whole carbonate core sample is wetted by brine (NaCl) in an imbibition cell at different temperature conditions during an imbibition experiment. As the brine imbibes into the cores, the oil is pushed out of the cores to the rock surface and collected at the top of the cell (i) ambient temperature ($22 \pm 1^\circ\text{C}$); (ii) $50 \pm 1^\circ\text{C}$ showing oil droplets that have been pushed out of the cores on the outer surface of the rocks.

Austad [79, 80] performed a wettability test on chalk cores and calcite mineral surfaces altered by crude oil to a sufficient oil-wet state using surfactant as the surface-active agents via spontaneous imbibition. The authors reported that the cationic surfactant changed the wettability of the chalk by desorbing the organic carboxylates from the chalk surface leading to an increased oil recovery of about 70% from the chalk. Buckley and Lord [83] altered mica surface to oil-wet using series of crude oil through atomic force microscopy (AFM), and found that the oils that produce the thickest coatings exhibited the highest water-advancing angles.

3. Nanoparticles and its effect on solid-liquid interface

Based on the wettability issues in carbonate formations mentioned above, here, we investigated two specific metal oxide nanoparticle types of interest; zirconium oxide and nickel oxide. Firstly, their structure, morphology, and crystallinity phases were examined. Then the wetting inclinations of the nanoparticles were further tested to ascertain their solid-liquid interface behavior on basis of wettability owing to the growing interest in understanding reservoir rock wetting.

3.1. Nanoparticle characterization

Nickel oxide (NiO) is a metal oxide nanoparticle in the form of dark gray (**Figure 4**) crystalline solid. This material has good chemical stability, excellent electrical properties, large exciton binding energy, and a stable wide band gap >3 eV [90–94]. NiO is considered a p-type semiconductor metal oxide particle, thus, a candidate for p-type transparent conducting films [92, 95, 96]. This material also exhibits good optical and magnetic properties; anodic electrochromism properties, excellent durability, large spin optical density, and displays strong insulating property [92, 97–100]. On the basis of reactivity, NiO surface that is considered imperfect acts as a useful oxidation catalyst, although, a perfect NiO is weakly reactive. The perfect surface inertness of NiO is in accordance with the non-metallic properties of the material bulk system [92]. NiO is suitable for usage in electrochemical super-capacitors, dye-sensitized photo cathodes applications and smart windows applications [92, 97–100]. Other processes where uniform size, well-dispersed NiO nanoparticles are also suitable are in heterogeneous catalytic processes, design of ceramics, magnetic applications, fabrication of gas sensors, films, and cathodes of alkaline batteries [101–109]. Although NiO appears to be suitable for a wide variety of processes, its property and functionality depend on the pore morphology, pore matrix-interface and process application. For instance, a very high specific surface area is required for this material in catalytic applications, whereas a rather dense material is required for cathodic applications [96].

Zirconium Oxide (ZrO_2) is a metal oxide nanoparticle in the form of white (**Figure 4**) crystalline solid. ZrO_2 has high refractive index, high melting point of $2680^\circ C$, wide region of low absorption from the near-UV > 240 nm to mid-IR range < 8 mm and high resistance against oxidation [110, 111]. This material is also characterized by high breakdown field, good thermal stability, large band gap >5 eV, and high-dielectric constant >20 [112–115], thus, the material has been considered a potential challenger of other nanoparticles. In a recent report, it was established that ZrO_2 exhibits superior chemical and thermal stability than alumina and silica nanoparticles [112].

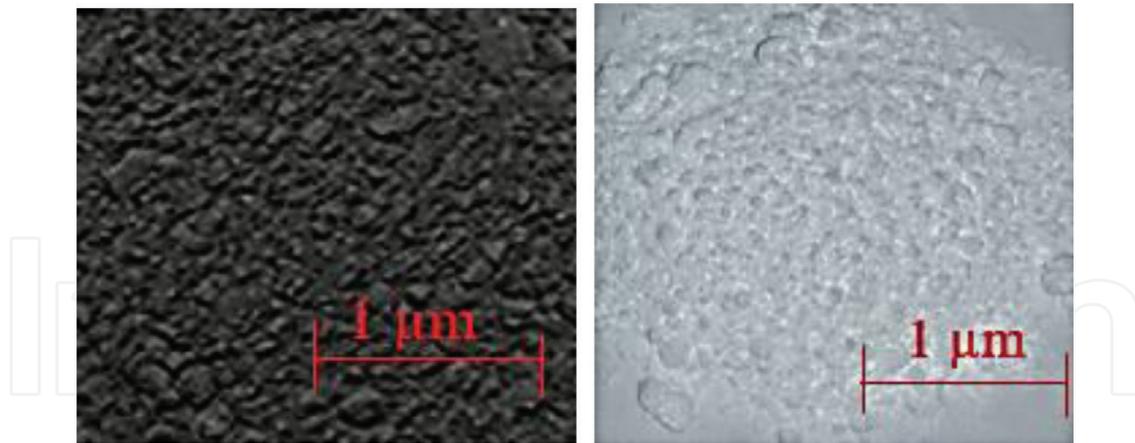


Figure 4. Nanoparticles in powder form (NiO-dark gray green color; ZrO₂-white color).

Similarly, Gopalan et al. [116] earlier reported that silica nanoparticles exhibit limited chemical and physical stability, as such, ZrO₂ nanoparticle was considered as a better alternative and also more chemically stable than γ -alumina or silica. ZrO₂ has an extraordinary high catalytic effect and it is the only metal oxide nanoparticle with four chemical properties on the surface: acidic/basic and reducing/oxidizing properties [117]. ZrO₂ has attracted attention in a wide variety of processes, as the material displays superior mechanical strength, high temperature resistance, high flexural strength, hardness, and low corrosion potential. As such, it can act as a catalyst, refractory, and insulator in transistors in fuel cells, electronic devices, and oxygen sensors, and also suitable for broadband interference filters, laser mirrors, and ionic conductors [118–121].

With respect to wettability, the recent relevance of nanoparticles in wetting processes is mainly due to the particles excellent range of physical and chemical properties as reported earlier. The materials surface and interface properties play an essential role in their overall behavior, whether during preparation or applications. However, there is a lack of understanding of nanoparticles wetting on basis of the solid-liquid interactions, especially, whether strongly hydrophobic surfaces can be rendered hydrophilic, as this is vital for EOR, soil decontamination, and carbon geo-sequestration process efficiency. Since successful oil recovery from fractured carbonate reservoirs show dependency on wettability [122], it is, therefore, necessary to establish an understanding of ZrO₂ and NiO nanoparticles properties, specifically, on the key areas that facilitate their process efficiency and subsequent influence on wetting.

4. Experimental procedure

4.1. Materials

4.1.1. Rock samples

Iceland spar calcite crystals from Ward Science as a representative of carbonate formation as calcite is a predominant mineral constituent of carbonate [38, 58] as also evident in the spectrum analysis of the calcite fraction of a carbonate rock (**Figure 5; Table 1**).

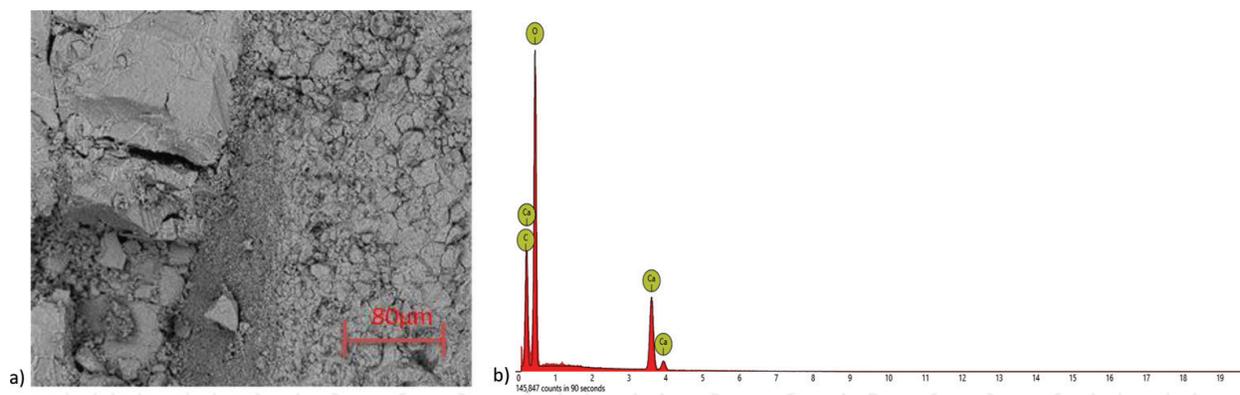


Figure 5. Spectrum analysis of the calcite fraction of the carbonate rock.

Element	Symbol	Atomic concentration (%)	Weight concentration (%)
Calcium	Ca	62.76	57.24
Carbon	C	10.78	24.64
Oxygen	O	26.46	18.12

Table 1. Carbonate rock.

4.1.2. Nanoparticles

Zirconium oxide (Purity: 99.5 wt. %; density: 5.89 g/mL at 25°C (lit.)) and nickel oxide (Purity 99.5 wt. %; density: 6.67 g/mL at 25°C) nanoparticles from Sigma Aldrich were used in this study (**Table 2**).

4.1.3. Oil phase

Dodecyltriethoxysilane obtained from Sigma Aldrich ((C₁₈H₄₀O₃Si) - purity ≥99.0 mol. %; boiling point: 538.4 k; Density: 875 kg/m³ - **Figure 6**) was used for altering samples to sufficiently stable oil-wet state. Toluene (purity 99.9 mol. %) obtained from Sigma Aldrich was used as model oil.

Sample	Concentration (Wt. %)	Chemical formula	Molecular weight (g/mol)	Form	Color	Particle Size (nm)
Zirconium Oxide	(0.005–0.05)	ZrO ₂	123.22	Nano powder	White	< 50
Nickel Oxide	(0.005–0.05)	NiO	74.69	Nano powder	Dark gray	< 50

Table 2. Properties of nanoparticles.

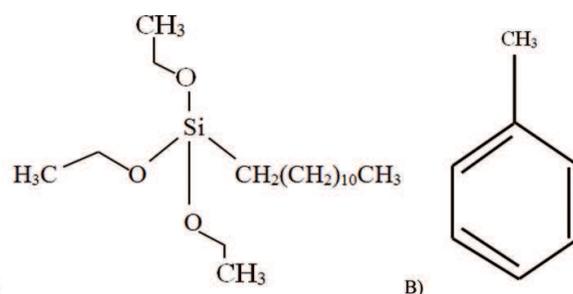


Figure 6. Structure of silane and model oil (A) Dodecyltriethoxysilane; (B) toluene.

4.1.4. Aqueous phase

Sodium Chloride (purity ≥ 99.5 mol. %) from Rowe Scientific and ultrapure de-ionized water from David Gray was used. The sodium chloride was dissolved in deionized water to achieve desired concentrations using a 220 V/50 Hz magnetic stirrer.

4.2. Sample preparation

Sample preparation which accounts for sample treatments and techniques used, is an important requirement in wetting analysis. Proper sample preparation, as well as, adequate sample quality and cleanliness are essential to eliminate any chances of methodical inaccuracies.

4.2.1. Calcite cleaning

The mineral crystals (calcite) originally hydrophilic were cleaned with analytical reagent grade acetone and methanol (Rowe Scientific Pty. Ltd), and de-ionized water (David Gray & Co. Ltd). This was done to remove surface fragments and inorganic contaminants. Subsequently, the samples were exposed to air plasma for 15 mins [123–125] to remove any residual organic contaminants.

4.2.2. Aging

The clean samples were modified to oil-wet by aging in the oil phase (dodecyltriethoxysilane) for 12 h at 90°C . Samples were then separated from the oil phase, cleaned with methanol, and deionized water to remove excess silane from the surface of the rock and dried.

4.2.3. Nanofluid formulation

ZrO_2 and NiO nanoparticles (Concentration - 0.005 - 0.05 wt. %) were mixed with a fixed amount of dispersals. To ensure adequate particle dispersal in the base fluid and the fluid uniformity, all fluids were formulated using high frequency ultrasonic homogenizer (a 300VT ultrasonic homogenizer and a titanium micro tip of 9.5 mm diameter) as also reported in literature [21–23, 126]. The formulations were kept in a cool place away from heat and light and the nanofluids were subjected to visual monitoring for a fixed period to ensure clear and stable solutions.

4.3. Wettability quantification

Wettability quantification was achieved via contact angle measurement and mechanistic approaches.

4.3.1. Contact Angle

Contact angle (θ) was used as the deterministic tool for wettability assessments. The aged samples were exposed to the formulated ZrO_2 and NiO nanofluids for a fixed period of one hour (1 h). Then the substrates were removed from the nanofluids and dried. A water droplet was dispensed on the modified calcite substrate and a high-performance microscopic 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) was used to capture the water drop dispensing process. The advancing and receding contact angles were measured using a tilting stage [127] for water contact angle in air. Further analysis of the drop was done using Image J software and the standard deviation was ± 3 based on replicate measurements.

4.3.2. Mechanistic quantification

Mechanistic investigation of samples was achieved by X-ray powder diffraction, atomic force microscope and scanning electron microscope.

4.3.3. X-ray diffraction (XRD)

Samples were prepared by placing the fine powders in a sample holder that has been well smeared on a glass slide for measurement in a powdered x-ray diffractometer. Diffraction arises through constructive interference due to the illumination of periodic structures of a given spacing with the light of a similar wavelength [128]. The X-ray diffraction patterns of the nanoparticle samples were recorded using powder diffractometer D8 advance (Bruker AXS, Germany), with a copper K alpha radiation source at 40 kV and 40 mA with a LynxEye detector.

4.3.4. Scanning electron microscope (SEM)

The surface morphology of the treated and untreated samples was characterized by scanning electron microscopy - Zeiss Neon 40EsB FIBSEM with an Oxford Instruments x-act Inca SDD x-ray detector and Inca software, and scanning transmission electron microscopy - Tescan Mira3 FESEM instrument. High electron beam was used to scan over the surface of the sample for improved surface characterization. Several researchers have also reported the effectiveness of SEM for morphological evaluations [129–134].

5. Results and discussion

5.1. Scanning electron microscope

The scanning electron microscope images show the micrograph of ZrO_2 and NiO nanoparticles (**Figure 7**). The ZrO_2 nanoparticle exhibits a distribution of sphere-like shaped particles in the range of 25–40 nm, while the NiO nanoparticle displays hexagonal-like shaped particles in the range of 10–20 nm. The nanoparticles exhibited approximately uniform size distribution and high trends of finely dispersed particles in the bulk state, thus, an indication of low particle-particle agglomeration inclinations. This behavior can be attributed to the intrinsic properties of metal oxide (superior stability) and preparation method (homogenization - Section 1).

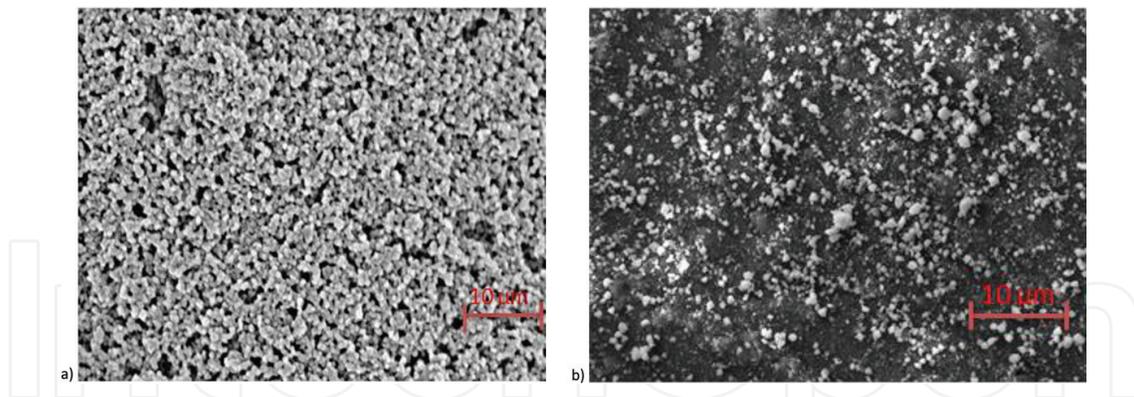


Figure 7. SEM images of: (a) ZrO_2 ; (b) NiO nanoparticles.

5.2. Particle size and surface area

Particle size plays a vital role in the nanoparticle characterization as their physical and chemical properties greatly depend on the particle size. The small particle size of nanoparticles yields important features such as surface area. Nanoparticle size and surface area are interrelated; as the nanoparticle size becomes negligible, the particle surface area increases. Bulk materials as opposed to nanoparticle exhibit larger particle sizes (nanoparticle average diameter: $<100\text{ nm}$; microparticle $>1\ \mu\text{m}$) with tons of atoms on the inside of the particle and limited atoms at the surface, whereas, with nanoparticles more atoms are predominantly on the outer surface of the particles. Such high surface area enables the bonding of other materials on the particle surface and lead to the generation of even much stronger materials that promote better interaction with neighboring atoms or ions. Ascertaining the nanoparticles size is essential as it affects particulate materials properties and can act as an approach to determine the quality and performance of these materials. The particle size of the ZrO_2 and NiO nanoparticles was investigated to obtain more accurate and precise size of the particles. **Figure 8** shows that the ZrO_2 particle size was 21–35 nm and NiO was in the range of 10–12 nm. The average particle diameter for $\text{ZrO}_2 \sim 28\text{ nm}$ and the average value for NiO was $\sim 12\text{ nm}$.

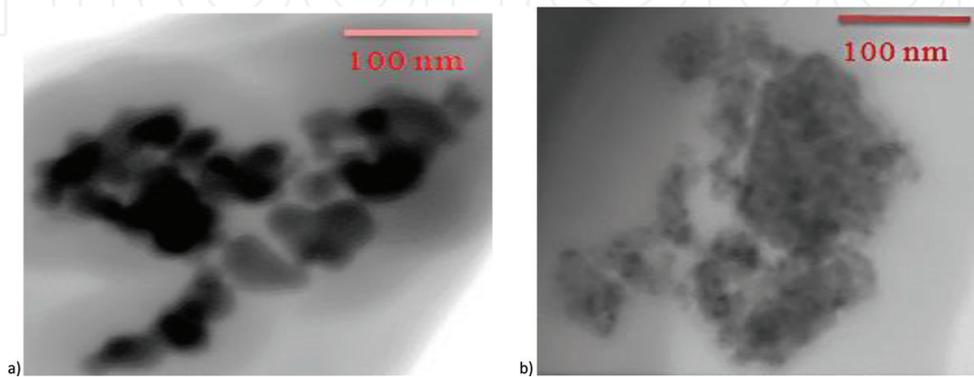


Figure 8. Particle size morphology of a) ZrO_2 ; b) NiO nanoparticles ($<50\text{ nm}$).

5.3. X-ray diffraction analysis

To better understand the crystallographic nature of ZrO_2 and NiO nanoparticles, the materials were further characterized using X-ray Diffraction (XRD). The XRD peaks usually exhibit different patterns and positioning. The pattern of the XRD of a specific sample is mainly dependent on the different arrangements of the atoms. The unit cell dimensions and angles determine the positions of the peaks. Whereas, the types and positions of the atoms within the unit cell determine the intensities of the peaks [128]. **Figure 9** shows the typical XRD patterns of the ZrO_2 (in red) and NiO (black) nanoparticles. The scan parameters used for phase identification were 2theta scan range (degree): 7.5–90; Step size (degree): 0.015; Time/step: 0.7 s and total scan time of approximately 1 hr. The XRD pattern indicates the crystallographic structure of the nanoparticles. Strong and sharp diffraction peaks at 2θ values were observed in both cases (ZrO_2 - in red; NiO - in black), especially, for NiO with precise peaks - 37, 43.5, 63 etc., while the ZrO_2 diffraction Peaks value were 28.5, 31.5, 34.5, 50.5 etc. The peaks are indications of the pure phase formation of the ZrO_2 and NiO nanoparticles. The crystallographic phases of the nanoparticles were also identified. Pure ZrO_2 exhibits a tetragonal phase (**Figure 10 (i)**), and the pure NiO exhibits a cubic phase (**Figure 10 (ii)**), consistent with literature [92, 135].

5.4. Contact angle

An understanding of surface chemistry is imperative for evaluating wetting behavior as porous media wetting are influenced by the rock surface morphology, as well as, the chemical compositions. Surface chemistry modifications of materials facilitate short-ranged chemical interactions. This phenomenon is predominantly governed by the surface and interfacial interactions, which act over the scale of molecules, and electrostatic surface forces that determine the extent to which

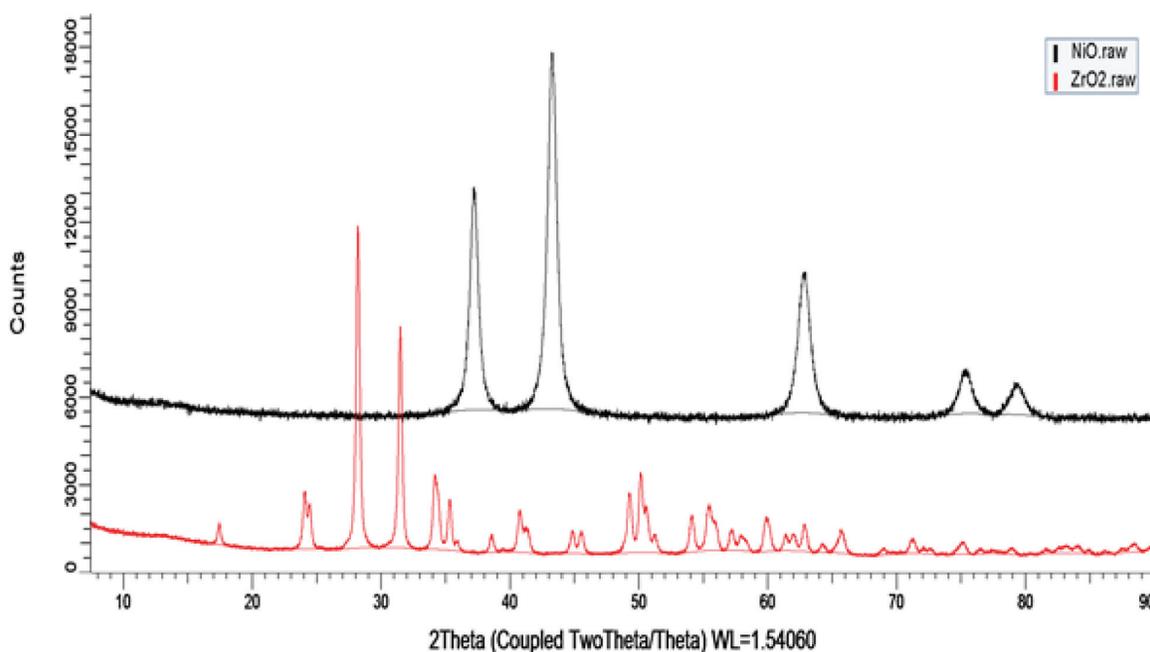


Figure 9. XRD patterns of the ZrO_2 and NiO nanoparticles.

a fluid can wet a surface [48]. Quantification of wettability of solid surfaces was also performed to ascertain the effects of ZrO_2 and NiO nanoparticle on wettability alteration of carbonate rocks. Contact angle tests were conducted at solid-liquid-air interface to ascertain the wetting variances prior and after nano-modifications. Water-advancing and receding contact angles were measured of which the advancing contact angles better defines wettability since its relevant to waterflooding [51]. The understanding of contact angle is complex as it exhibits a dependency on the solid-liquid interaction and the structure of the solid or mineralogy of the rock sample.

Prior to the contact angle measurement, calcite substrates were cleaned and aged based on procedure 4.2.2. The nanofluids were prepared using various nanoparticle concentration (0.005–0.05 wt. %) and fixed NaCl brine concentration (7 wt. %) as dispersing agents based on procedure 4.2.2. The samples were immersed in the nanofluids and subsequently contact

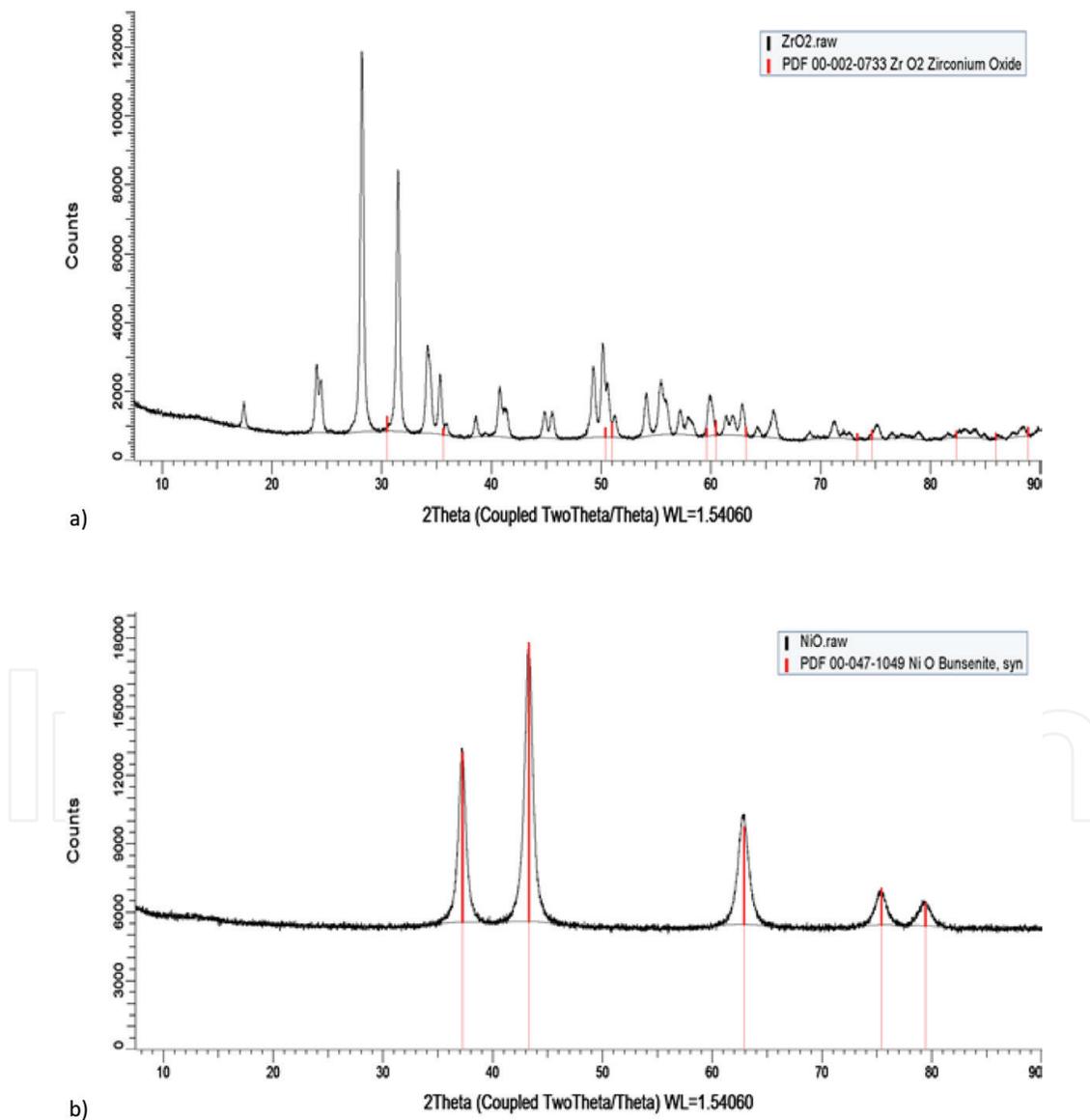


Figure 10. (a) Crystallographic phases of the ZrO_2 nanoparticles exhibiting tetragonal phase. (b). Crystallographic phase of the NiO nanoparticles exhibiting cubic phase.

angles were measured. **Figures 12 and 13** (SEM) show nano-modified calcites, as compared to the fresh calcite without any nano-modification (**Figure 11**). The ZrO_2 nanoparticle exhibits a spherical-like shape and more uniformly adsorbed behavior on the calcite surface than NiO, while the NiO exhibits a hexagonal-like shape which is consistent with the earlier observation in Section 4.31. **Figure 15** shows the contact angle measurement as a function of nanoparticle concentration for ZrO_2 and NiO nanoparticle respectively in air. It is expected that the exposure of the calcite to a different environment would change its surface property. The calcite upon contact with the ZrO_2 and NiO nanofluids, film-like deposits of the nanofluids were adsorbed on the calcite surface after exposure to air. Such film thickness can vary between a fraction to numerous fractions of a molecule. However, the level of thickness is dependent on the affinity of the molecules to the substrate and the corresponding distance to the bulk critical point. Moreover, the nano-films on the rock surface may appear thinner than others, which is dependent on the nanoparticle type, and their optical and electrical properties. ZrO_2 nano-films are relatively thicker than those of other nanoparticles owing to its material properties such as large band gap $>5\text{eV}$ and high-dielectric constant >20 (Petit and Monot, 2015). This may have formed better-adsorbed ZrO_2 nano-layers on the oil-wet calcite surface when compared to the NiO nanoparticles.

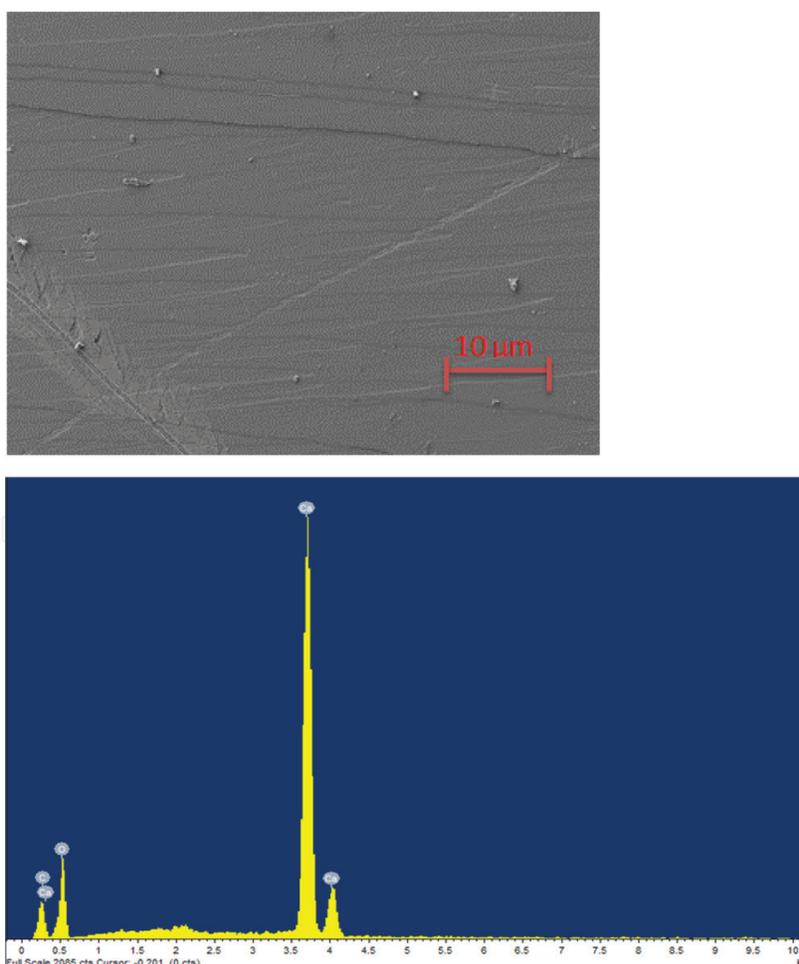


Figure 11. SEM image of pure calcite surface before nano-modification.

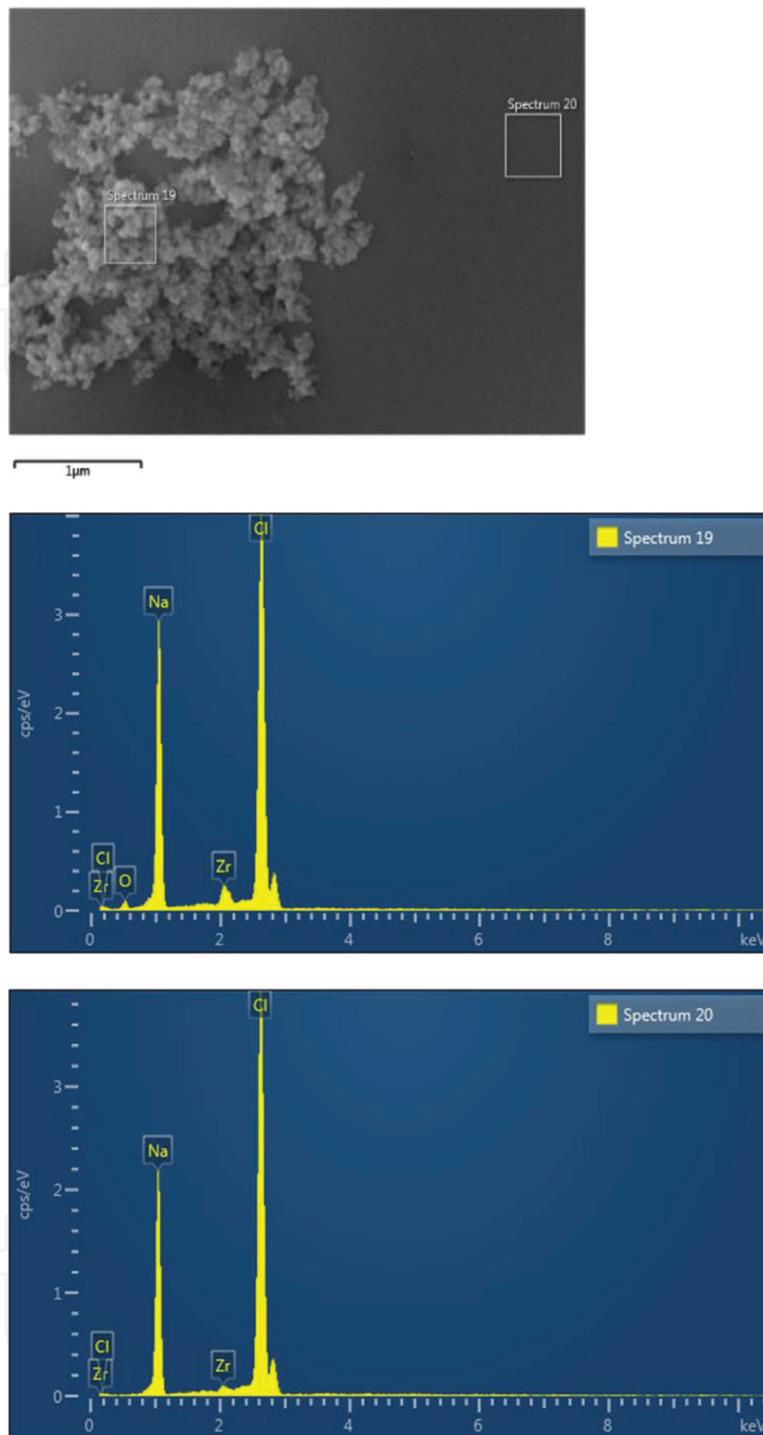


Figure 12. SEM image of calcite surface after ZrO_2 nano-modification.

As the dispensed water droplet comes in contact with the surface of the nano-coated calcite, the contact angle decreases owing to the presence of adsorbed nano-layers. This behavior is attributed to the favorable interaction of the nanoparticles with the dispersing fluid (NaCl brine) and high chemical affinity to the calcite. Such solid-liquid interaction at the interface is mainly due to electrostatic interactions. The presence of the nanoparticle increased the surface activity of the brine (NaCl), thereby modifying the calcite surface wetting propensity upon

contact. The nanoparticles in suspension act as a coating mechanism by self-structuring into layered NPs and changes the entropy of the system. The particles hydrophilic nature facilitates their adsorption on the rock surface in form of a wedge film which in turn displaces the oil on the surface of the rock, yielding a hydrophilic state. Ideally, if wettability is preferentially altered to favorable water-wet condition and the IFT is ultralow, the forces that retain oil in a fractured reservoir can be overcome as capillarity is diminished through the ultralow IFTs.

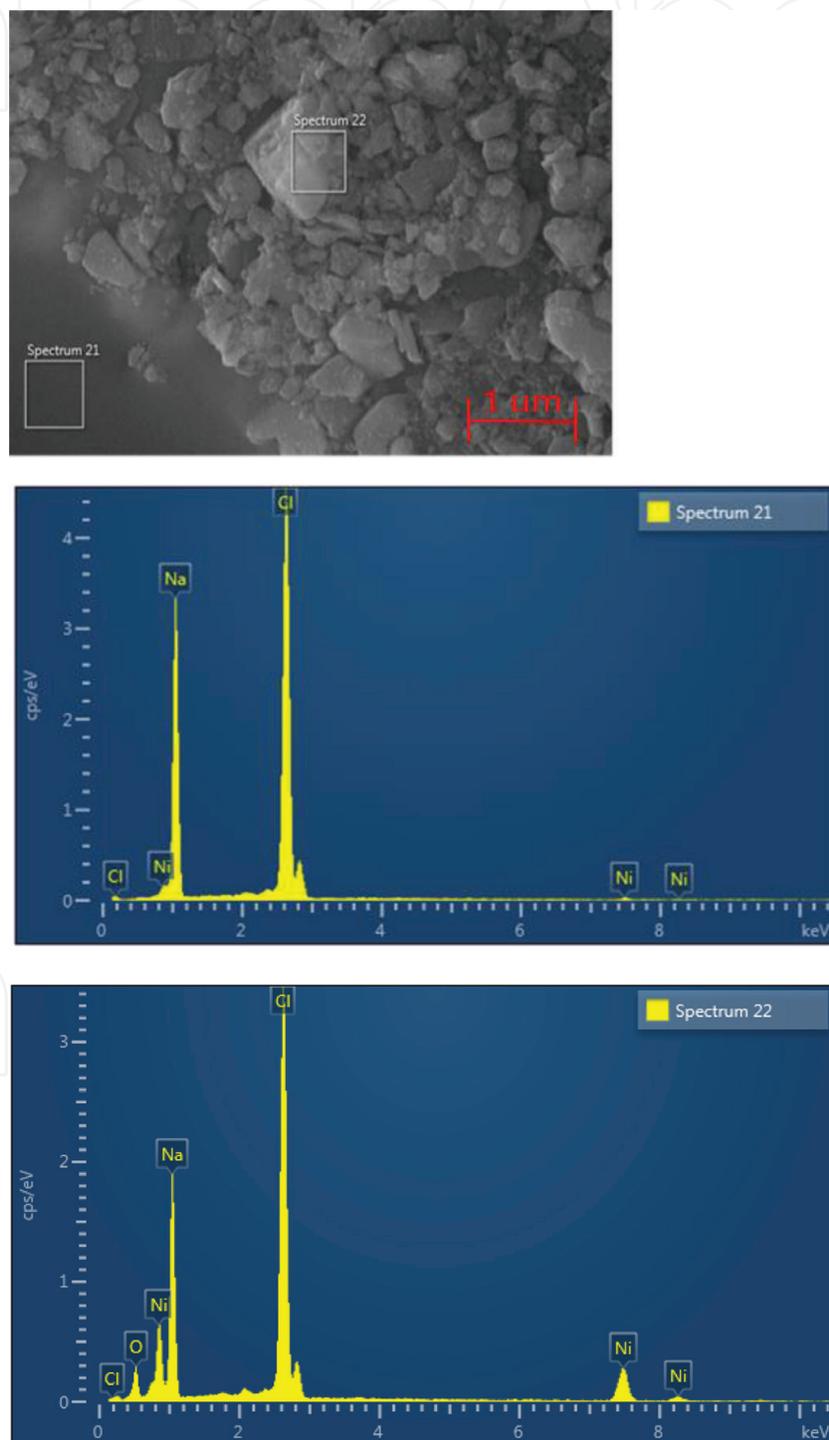


Figure 13. SEM image of calcite surface after NiO nano-modification.

Figure 14 shows the image representation of the transition phase toward water-wet in air from $88^\circ \theta_a$ to $48^\circ \theta_a$ (NiO/NaCl) and $38^\circ \theta_a$ (ZrO₂/NaCl). A decrease in contact angle was observed for all the systems tested with an increase in the nanoparticle concentration (**Figure 15**) consistent with literature [36–38, 136–139]. Calcite substrates coated with ZrO₂/NaCl fluids demonstrated better wetting propensities than the NiO/NaCl system. The efficiency of the systems is due to efficient surface adsorption of the particles on the pore walls of the rock, which invariably rendered the rock surface sufficiently water wet upon contact.

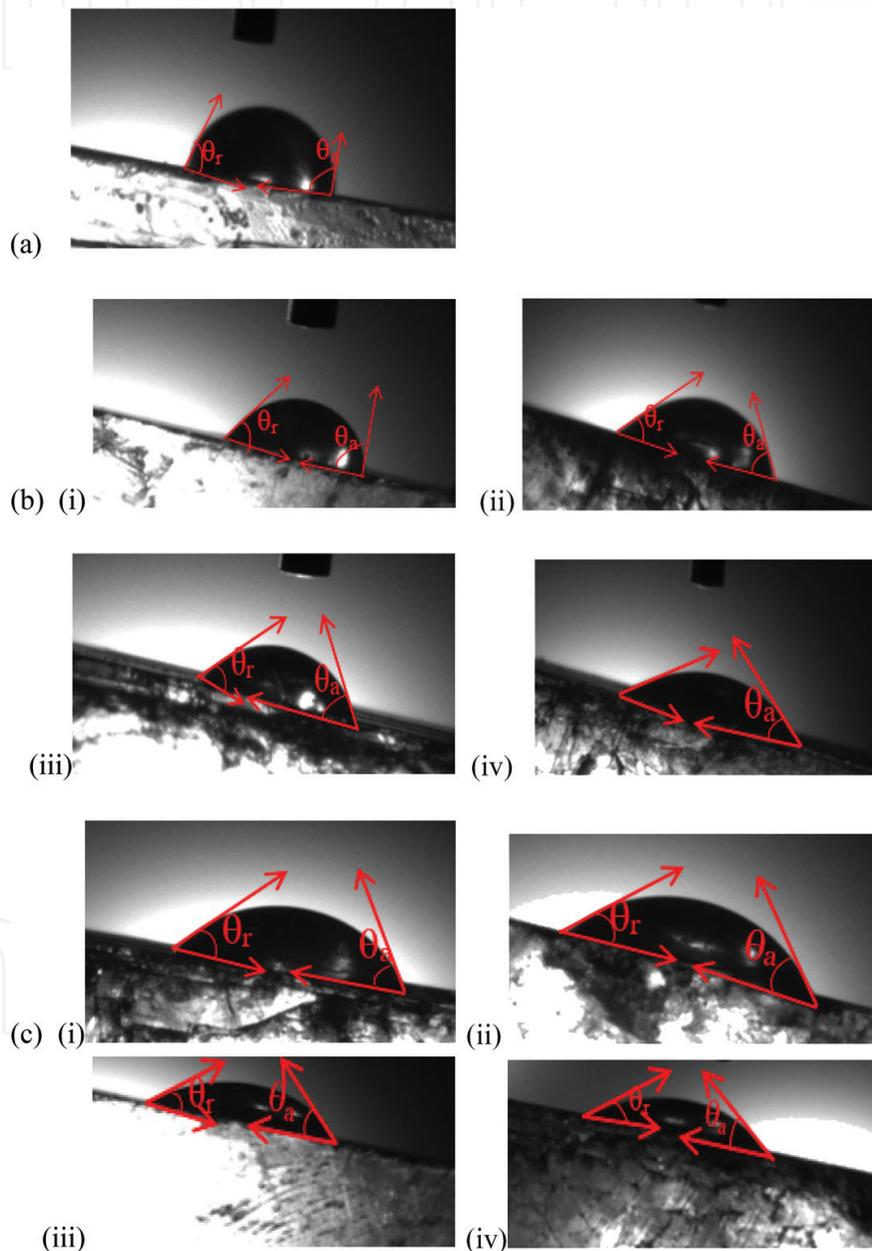


Figure 14. Contact angle images showing variation with increase in nanoparticle concentration (a) unmodified (high θ -indicating an intermediate-wet state— $88^\circ \theta_a$); (B, C) nano-modified—(B) NiO/NaCl modified (NiO concentration—0.005–0.05); (C) ZrO₂/NaCl nano-modified (ZrO₂ concentration—0.005–0.05) (B and C indicates low θ which represents strong interaction with the rock surface, and inclination to wet; I–IV); see graphical representation for θ values.

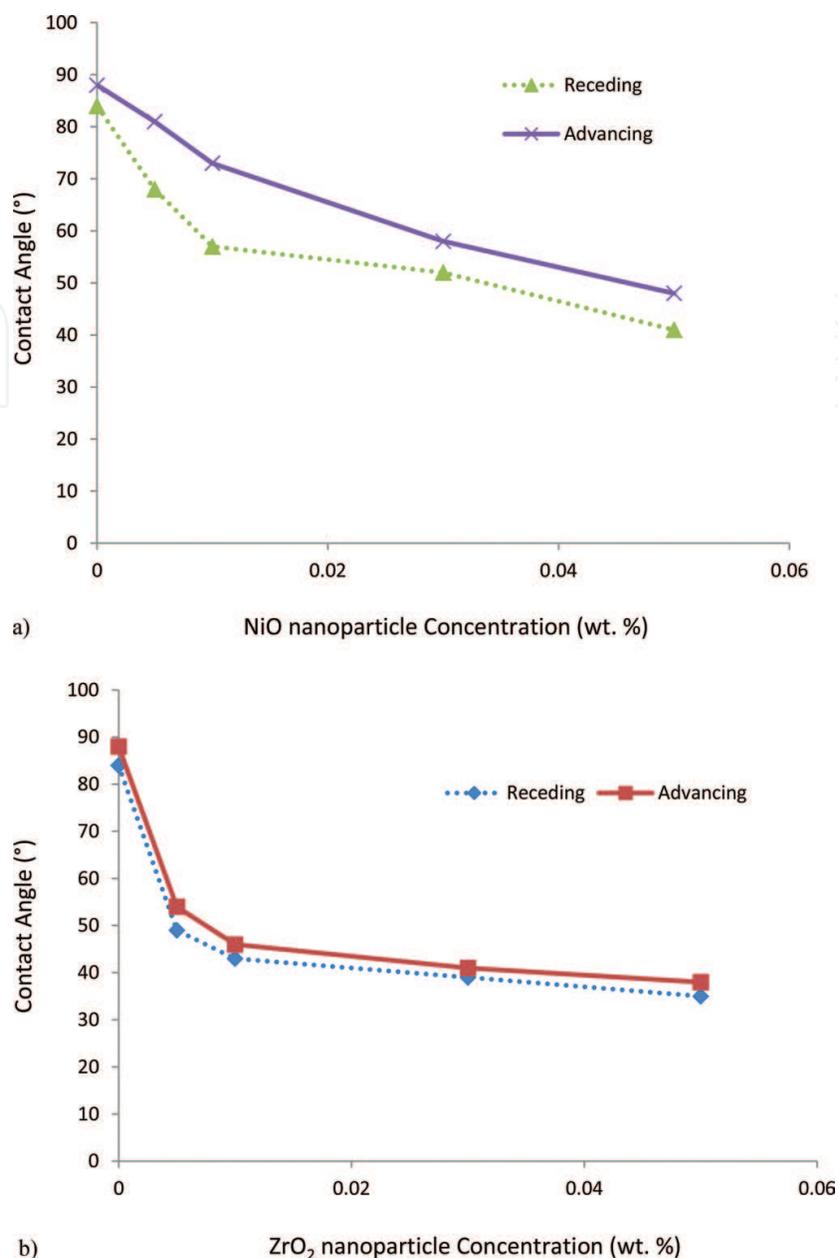


Figure 15. Receding and advancing water contact angles in air (1 h exposure time) (a) NiO; (b) ZrO₂ at ambient condition.

6. Conclusions

The interfacial behavior of nickel oxide and zirconium oxide nanoparticles at solid-liquid interface was studied on their propensity to alter oil-wet surfaces toward water-wet conditions. The ZrO₂ and NiO nanoparticles exhibited very different structural and morphological features, as well as crystallinity phases. The nanoparticles exhibited particles size in ranges below 50 nm (< 50 nm) and different shape patterns. The ZrO₂ nanoparticles are sphere-like shaped particles while the NiO displayed hexagonal-like shaped particles (Figures 7, 12 and 13). The XRD crystallographic structure and phase identification shows the tetragonal phase of the ZrO₂,

whereas, the NiO nanoparticle has a cubic phase orientation. The nanoparticles also displayed favorable adsorption behavior on the calcite surface as evident in the SEM images, which facilitated the wetting change quantified by contact angle measurement, however, the ZrO₂ based systems exhibited more uniform surface distribution and better wetting than NiO. Thus, nanoparticles are considered efficient modifiers for wettability alteration of surfaces toward a suitable hydrophilic condition.

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References

- [1] Campelo JM, Luna D, Luque R, Marinas JM, Romero AA. Sustainable preparation of supported metal nanoparticles and their applications in catalysis. *ChemSusChem*. 2009; **2**(1):18-45
- [2] Colombari P. The use of metal nanoparticles to produce yellow, red and iridescent colour, from bronze age to present times in lustre pottery and glass: Solid state chemistry, spectroscopy and nanostructure. *Journal of Nano Research*. 2009; **8**:109-132 Trans Tech Publications
- [3] Heiligtag FJ, Niederberger M. The fascinating world of nanoparticle research. *Materials Today*. 2013; **16**(7):262-271
- [4] Kaminsky R, Radke CJ. Asphaltenes, water films and wettability reversal. *Society of Petroleum Engineers Journal*. 1997; **2**(4):458-493
- [5] Kamyshny AS, Magdassi S. Aqueous dispersions of metallic nanoparticles. *Colloidal Interfacial Aspects*. 2010:747-778
- [6] Edmunds N, Chhina H. Economic optimum operating pressure for SAGD projects in Alberta. *Journal of Canadian Petroleum Technology*. 2001; **40**(12):13-17
- [7] Nanotek. Pioneering Expansion in the world of Nanotechnology. 19th International Conference on Nanotechnology and Expo. Atlanta, Georgia, USA. 2017. Retrieved on 15 April, 2017 from <http://nanotechnologyexpo.conferenceseries.com/>

- [8] Yu W, France DM, Routbort JL, Choi SU. Review and comparison of nanofluid thermal conductivity and heat transfer enhancements. *Heat Transfer Engineering*. 2008;**29**(5):432-460
- [9] Ramakoteswara RN, Gahane L, Ranganayakulu SV. Synthesis, applications and challenges of nanofluids-review. *IOSR Journal of Applied Physics*. 2014:21-28
- [10] Biswas P, Wu CY. Control of toxic metal emissions from combustors using sorbents: A review. *Journal of the Air & Waste Management Association*. 1998;**48**(2):113-127
- [11] Serrano E, Rus G, Garcia-Martinez J. Nanotechnology for sustainable energy. *Renewable and Sustainable Energy Reviews*. 2009;**13**:2373-2384
- [12] Khalil M, Jan BM, Tong CW, Berawi MA. Advanced Nanomaterials in oil and gas industry: Design, application, and challenges. *Applied Energy*. 2017;**191**:287-310
- [13] Jun YW, Choi JS, Cheon J. Heterostructured magnetic nanoparticles: Their versatility and high-performance capabilities. *Chemical Communications*. 2007;**12**:1203-1214
- [14] Pastrana-Martínez LM, Pereira N, Lima R, Faria JL, Gomes HT, Silva AMT. Degradation of diphenhydramine by photo-fenton using magnetically recoverable iron oxide nanoparticles as catalyst. *Chemical Engineering Journal*. 2015;**261**:45-52
- [15] Avendano C, Lee SS, Escalera G, Colvin V. Magnetic characterization of nanoparticles designed for use as contrast agents for downhole measurements. In: SPE 157123 presented at the SPE international oilfield nanotechnology conference and exhibition, Noordwijk, The Netherlands. 12-14 June 2012
- [16] Morrow L, Potter DK, Barron AR. Detection of magnetic nanoparticles against proppant and shale reservoir rocks. *Journal of Experimental Nanoscience*. 2015;**10**(13):1028-1041
- [17] Hyne JB, Greidanus JW, Tyrer JD, Verona D, Rizek C, Clark PD, Clarke RA, Koo J. Aquathermolysis of heavy oils. The Second International Conference on Heavy Crude and Tar Sands, in Caracas, Venezuela, Feb 7-17, 1982
- [18] White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ. Supported metal nanoparticles on porous materials, methods and applications. *Chemical Society Reviews*. 2009;**38**(2):481-494
- [19] Fedele L, Colla L, Bobbo S, Barison S, Agresti F. Experimental stability analysis of different water-based nanofluids. *Nanoscale Research Letters*. 2011;**6**(1):300
- [20] Roustaei A, Bagherzadeh H. Experimental investigation of SiO₂ nanoparticles on enhanced oil recovery of carbonate reservoirs. *Journal of Petroleum Exploration and Production Technology*. 2015;**5**(1):27-33
- [21] Tjong SC. Novel nanoparticle-reinforced metal matrix composites with enhanced mechanical properties. *Advanced Engineering Materials*. 2007;**9**(8):639-652
- [22] Yang Y, Lan J, Li X. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Materials Science and Engineering A*. 2004;**380**(1):378-383

- [23] Mao H, Qiu Z, Shen Z, Huang W. Hydrophobic associated polymer based silica nanoparticles composite with core-shell structure as a filtrate reducer for drilling fluid at ultra-high temperature. *Journal of Petroleum Science and Engineering*. 2015;**129**:1-14
- [24] Salem RAM, Hannora AEA. Comparative investigation of nanoparticle effects for improved oil recovery-experimental work. In: *Proceedings of the SPE Kuwait Oil and Gas Show and Conference, Mishref, Kuwait, 11-14 October 2015*
- [25] Metin CO, Baran JR, Nguyen QP. Adsorption of surface functionalized silica nanoparticles onto mineral surfaces and decane/water interface. *Journal of Nanoparticle Research*. 2012;**14**(11):1246
- [26] Hendraningrat L, Torsæter O. Metal oxide-based nanoparticles: Revealing their potential to enhance oil recovery in different wettability systems. *Applied Nanoscience*. 2015;**5**(2):181-199
- [27] Ahmadi MA, Shadizadeh SR. Induced effect of adding nano silica on adsorption of a natural surfactant onto sandstone rock: Experimental and theoretical study. *Journal of Petroleum Science and Engineering*. 2013;**112**:239-247
- [28] Bayat AE, Junin R, Shamshirband S, Chong WT. Transport and retention of engineered Al_2O_3 , TiO_2 , and SiO_2 nanoparticles through various sedimentary rocks. *Scientific Reports*. 2015;**5**:14264
- [29] Saravanan P, Gopalan R, Chandrasekaran V. Synthesis and characterization of nanomaterials. *Defence Science Journal*. 2008;**58**(4):504-516
- [30] Rudyak VY. Viscosity of nanofluids-why it is not described by the classical theories. *Advances in Nanoparticles*. 2013;**2**(3):266-279
- [31] Choi S. Enhancing thermal conductivity of fluids with nanoparticles. In: Siginer DA, Wang HP, editors. *Developments Applications of Non-Newtonian Flows*. New York: 231, ASME; 1995. pp. 99-105
- [32] Yu W, Xie H. A review on nanofluids: Preparation, stability mechanisms and applications. *Journal of Nanomaterials*. 2012:1-17
- [33] Al-Anssari S, Barifcani A, Wang S, Maxim L, Iglauer S. Wettability alteration of oil-wet carbonate by silica nanofluid. *Journal of Colloid and Interface Science*. 2016;**461**:435-442
- [34] Al-Anssari S, Wang S, Barifcani A, Iglauer S. Oil-water interfacial tensions of silica nanoparticle-surfactant formulations. *Tenside, Surfactants, Detergents*; **54**:6
- [35] Keblinski P, Prasher R, Eapen J. Thermal conductance of nanofluids: Is the controversy over? *Journal of Nanoparticle Research*. 2008;**10**(7):1089-1097
- [36] Nwideo LN, Al-Anssari S, Barifcani A, Sarmadivaleh M, Iglauer S. Nanofluids for enhanced oil recovery processes: wettability alteration using zirconium oxide. *Offshore Technology Conference (OTC-26573-MS)*. Kuala Lumpur, Malaysia, 22-25 March 2016a
- [37] Nwideo LN, Al-Anssari S, Barifcani A, Sarmadivaleh M, Lebedev M, Iglauer S. Nanoparticles influence on wetting behaviour of fractured limestone formation. *Journal of Petroleum Science and Engineering*. 2017a;**149**:782-788

- [38] Nwidee LN, Al-Anssari S, Barifcani A, Sarmadivaleh M, Lebedev M, Iglauer S. Wettability alteration of oil-wet limestone using surfactant-nanoparticle formulation. *Journal of Colloid and Interface Science*. 2017b;**504**:334-345
- [39] Nwidee LN, Theophilus S, Barifcani A, Sarmadivaleh M, Iglauer S. EOR processes, opportunities and technological advancements. In: *Chemical Enhanced Oil Recovery (cEOR)-a Practical Overview*. InTech; 2016
- [40] Wang XQ, Mujumdar AS. A review on nanofluids-part I: Theoretical and numerical investigations. *Brazilian Journal of Chemical Engineering*. 2008;**25**(4):613-630
- [41] Yang Y, Lan J, Li X. Study on bulk aluminum matrix nano-composite fabricated by ultrasonic dispersion of nano-sized SiC particles in molten aluminum alloy. *Materials Science and Engineering A*. 2004;**380**(1):378-383
- [42] Guo D, Xie G, Luo J. Mechanical properties of nanoparticles: Basics and applications. *Journal of Physics D: Applied Physics*. 2014;**47**(1):013001
- [43] De Gennes PG. Wetting: Statistics and dynamics. *Reviews of Modern Physics*. 1985; **57**(3):827-863
- [44] Mohammed M, Babadagli T. Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems. *Advances in Colloid and Interface Science*. 2015;**220**:54-77
- [45] Bertrand E, Bonn D, Broseta D, Dobbs H, Indekeu JO, Meunier J, Ragil K, Shahidzadeh N. Wetting of alkanes on water. *Journal of Petroleum Science and Engineering*. 2002; **33**(1):217-222
- [46] Myers D. *Surfaces, Interfaces and Colloids*. Wiley-Vch: New York; 1990
- [47] Craig FF. *The Reservoir Engineering Aspects of Waterflooding*. SPE, Richardson, Texas: Monograph Series; 1971
- [48] Bonn D, Eggers J, Indekeu J, Meunier J, Rolley E. Wetting and spreading. *Reviews of Modern Physics*. 2009;**81**:739-805
- [49] Anderson WG. Wettability literature survey - part 1: Rock/oil/brine interactions and the effects of core handling on wettability. *Journal of Petroleum Technology*. 1986; **38**(10):1125-1144
- [50] Anderson WG. Wettability literature survey part 2: Wettability measurement. *Journal of Petroleum Technology*. 1986;**38**:1246-1262
- [51] Anderson WG. Wettability literature survey-part 3: The effects of wettability on the electrical properties of porous media. *Journal of Petroleum Technology*. 1986;**38**(12):1371-1378
- [52] Morrow NR. Wettability and its effect on oil recovery. *Journal of Petroleum Technology*. 1990;**42**(12):1-476
- [53] Abdallah W, Buckley J, Carnegie A, Edwards J, Herold B, Fordham E, Graue A, Habashy T, Seleznev N, Signer C, Hussain H. Fundamentals of wettability. *Oilfield Review*. 2007:44-61

- [54] Nutting PG. Some physical and chemical properties of reservoir rocks bearing on the accumulations and discharge of oil. In: Wrather WE, Lahee FH, editors. Problems of Petroleum Geology. American Association of Petroleum Geologists; 1934. pp. 825-832
- [55] Benner FC, Bartel FE. The effect of polar impurities upon capillary and surface phenomena in petroleum production. Drilling and production practice. American Petroleum Institute, New York, New York, 1 January 1941
- [56] Moore CH. Carbonate Reservoirs Porosity Evolution and Diagenesis in a Sequence Stratigraphic Framework. Amsterdam: Elsevier; 2001
- [57] Tucker ME, Wright VP. Carbonate sedimentology. John Wiley and Sons; 2009
- [58] Lebedev M, Wilson ME, Mikhaltsevitch V. An experimental study of solid matrix weakening in water-saturated Savonnières limestone. Geophysical Prospecting. 2014; 62(6):1253-1265
- [59] Treiber LE, Archer DL, Owens WW. A laboratory evaluation of the wettability of fifty oil-producing reservoirs. Society of Petroleum Engineers Journal. 1972;12(6):531-540
- [60] Chilingar GV, Yen TF. Some notes on wettability and relative permeabilities of carbonate reservoir rocks II. Journal of Energy Sources. 1983;7(1):67-75
- [61] Buckley JS, Liu Y, Monsterleet S. Mechanisms of wetting alteration by crude oils. Society of Petroleum Engineering Journal. 1998;3(01):54-61
- [62] Thomas S. Enhanced oil recovery-an overview. Oil & Gas Science and Technology. 2008;63(1):9-19
- [63] Babadagli T. Scaling of co-current and counter-current capillary imbibition for surfactant and polymer injection in naturally fractured reservoirs. SPE/AAPG western regional meeting, Long Beach, California, 19-22 June 2000
- [64] Cheraghian G, Hemmati M, Masihi M, Bazgir S. An experimental investigation of the enhanced oil recovery and improved performance of drilling fluids using titanium dioxide and fumed silica nanoparticles. Journal of Nanostructure in Chemistry. 2013;3(1):1-19
- [65] Delshad M, Najafabadi NF, Anderson G, Pope GA, Sepehrnoori K. Modeling wettability alteration by surfactants in naturally fractured reservoirs. SPE Reservoir Evaluation & Engineering. 2009;12(3):361-370
- [66] Buckley JS, Liu Y, Monsterleet S. Mechanisms of wetting alteration by crude oils. Society of Petroleum Engineering Journal. 1998;3(01):54-61
- [67] Yu L, Buckley JS. Evolution of wetting alteration by adsorption from crude oil. Society of Petroleum Engineers Formation Evaluation. 1997;12(01):5-12
- [68] Tong Z, Xie X, Morrow NR. Crude oil composition and the ability of mixed wettability in sandstones. SCA International Symposium of the Society of Core Analysts, Monterey, CA, USA, 30 September 2002

- [69] Lord DL, Buckley JS. An AFM study of the morphological features that affect wetting at crude oil-water-mica interfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2002;**206**(1):531-546
- [70] Acevedo S, Escobar G, Ranaudo MA, Piñate J, Amorín A, Díaz M, Silva P. Observations about the structure and dispersion of petroleum asphaltene aggregates obtained from dialysis fractionation and characterization. *Energy & Fuels*. 1997;**11**(4):774-778
- [71] González G, Moreira MB. The wettability of mineral surfaces containing adsorbed asphaltene. *Colloids and Surfaces*. 1991;**58**(3):293-302
- [72] Andersen SI, Christensen SD. The critical micelle concentration of asphaltene as measured by calorimetry. *Energy & Fuels*. 2000;**14**(11):38-42
- [73] Kaminsky R, Radke CJ. Asphaltene, water films and wettability reversal. *Society of Petroleum Engineers Journal*. 1997;**2**(4):458-493
- [74] Liu L, Buckley JS. Alteration of wetting of mica surfaces. *Journal of Petroleum Science and Engineering*. 1999;**24**(2):75-83
- [75] Standal S, Haavik J, Blokhus AM, Skauge A. Effect of polar organic components on wettability as studied by adsorption and contact angles. *Journal of Petroleum Science and Engineering*. 1999;**24**(2-4):131-144
- [76] Donaldson EC, Thomas RD, Lorenz PB. Wettability determination and its effects on recovery efficiency. *Society of Petroleum Engineering Journal*. 1969;**9**(1):13-20
- [77] Zhang P, Austad T. Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006;**279**(1):179-187
- [78] Standnes DC, Austad T. Nontoxic low-cost amines as wettability alteration Chemicals in Carbonates. *Journal of Petroleum Science and Engineering*. 2003;**39**(3):431-438
- [79] Standnes DC, Austad T. Wettability alteration in chalk: 1. Preparation of core material and oil properties. *Journal of Petroleum Science and Engineering*. 2000;**28**(3):111-121
- [80] Standnes DC, Austad T. Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. *Journal of Petroleum Science and Engineering*. 2000;**28**(3):123-143
- [81] Standnes DC, Austad T. Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2003;**216**(1):243-259
- [82] Standnes DC, Nogaret LA, Chen HL, Austad T. An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a nonionic and a cationic surfactant. *Energy and Fuels*. 2002;**16**(6):1557-1564

- [83] Buckley JS, Lord DL. Wettability and morphology of mica surfaces after exposure to crude oil. *Journal of Petroleum Science and Engineering*. 2003;**39**(3):261-273
- [84] Zhang DL, Liu S, Puerto M, Miller CA, Hirasaki GJ. Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering*. 2006;**52**(1):213-226
- [85] Seiedi O, Rahbar M, Nabipour M, Emadi MA, Ghatee MH, Ayatollahi S. Atomic force microscopy (AFM) investigation on the surfactant wettability alteration mechanism of aged mica mineral surfaces. *Energy and Fuels*. 2010;**25**(1):183-188
- [86] Kathel P, Mohanty KK. Wettability alteration in a tight oil reservoir. *Energy and Fuels*. 2013;**27**(11):6460-6468
- [87] Bera A, Ojha K, Kumar T, Mandal A. Mechanistic study of wettability alteration of quartz surface induced by nonionic surfactants and interaction between crude oil and quartz in the presence of sodium chloride salt. *Energy and Fuels*. 2012;**26**(6):3634-3643
- [88] Hou BF, Wang YF, Huang Y. Mechanistic study of wettability alteration of oil-wet sandstone surface using different surfactants. *Applied Surface Science*. 2015;**330**:56-64
- [89] Hou BF, Wang YF, Huang Y. Relationship between reservoir wettability and oil recovery by waterflooding. In: *In Advances in Energy Science and Equipment Engineering*, Edited by Zhou, Patty and Chen. London: Taylor Francis Group; 2015
- [90] Kamal H, Elmaghraby EK, Ali SA, Abdel-Hady K. Characterization of nickel oxide films deposited at different substrate temperatures using spray pyrolysis. *Journal of Crystal Growth*. 2004;**262**(1):424-434
- [91] Choi JM, Im S. Ultraviolet enhanced Si-photodetector using p-NiO films. *Applied Surface Science*. 2005;**244**(1):435-438
- [92] Kunz AB. Electronic structure of NiO. *Journal of Physics C: Solid State Physics*. 1981;**14**(16):L455
- [93] Adler D, Feinleib J. Electrical and optical properties of narrow-band materials. *Physical Review B*. 1970;**2**(8):3112
- [94] Irwin MD, Buchholz DB, Hains AW, Chang RP, Marks TJ. P-type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells. *Proceedings of the National Academy of Sciences*. 2008;**105**(8):2783-2787
- [95] Sato H, Minami T, Takata S, Yamada T. Transparent conducting p-type NiO thin films prepared by magnetron sputtering. *Thin Solid Films*. 1993;**236**(1):27-31
- [96] Bahadur J, Sen D, Mazumder S, Ramanathan S. Effect of heat treatment on pore structure in nano-crystalline NiO: A small angle neutron scattering study. *Journal of Solid State Chemistry*. 2008;**181**(5):1227-1235
- [97] He J, Lindström H, Hagfeldt A, Lindquist SE. Dye-sensitized nanostructured p-type nickel oxide film as a photocathode for a solar cell. *The Journal of Physical Chemistry B*. 1999;**103**(42):8940-8943

- [98] Srinivasan V, Weidner JW. An electrochemical route for making porous nickel oxide electrochemical capacitors. *Journal of the Electrochemical Society*. 1997;**144**(8):L210-L213
- [99] Liu KC, Anderson MA. Porous nickel oxide/nickel films for electrochemical capacitors. *Journal of the Electrochemical Society*. 1996;**143**(1):124-130
- [100] Chakrabarty S, Chatterjee K. Synthesis and characterization of nano-dimensional nickelous oxide (NiO) semiconductor. *Journal of Physical Science*. 2009;**13**:245-250
- [101] Wu Y, He Y, Wu T, Chen T, Weng W, Wan H. Influence of some parameters on the synthesis of nanosized NiO material by modified sol-gel method. *Materials Letters*. 2007;**61**(14):3174-3178
- [102] Thota S, Kumar J. Sol-gel synthesis and anomalous magnetic behaviour of NiO nanoparticles. *Journal of Physics and Chemistry of Solids*. 2007;**68**(10):1951-1964
- [103] Hotovy I, Huran J, Spiess L, Romanus H, Buc D, Kosiba R. NiO-based nanostructured thin films with Pt surface modification for gas detection. *Thin Solid Films*. 2006;**515**(2):658-661
- [104] Min KC, Kim M, You YH, Lee SS, Lee YK, Chung TM, Kim CG, Hwang JH, An KS, Lee NS, Kim Y. NiO thin films by MOCVD of Ni (dmamb)₂ and their resistance switching phenomena. *Surface and Coatings Technology*. 2007;**201**(22):9252-9255
- [105] Tao D, Wei F. New procedure towards size-homogeneous and well-dispersed nickel oxide nanoparticles of 30nm. *Materials Letters*. 2004;**58**(25):3226-3228
- [106] Dooley KM, Chen SY, Ross JRH. Stable nickel-containing catalysts for the oxidative coupling of methane. *Journal of Catalysis*. 1994;**145**(2):402-408
- [107] Yang HX, Dong QF, Hu XH, Ai XP, Li SX. Preparation and characterization of LiNiO₂ synthesized from Ni (OH)₂ and LiOH·H₂O. *Journal of Power Sources*. 1999;**79**(2):256-261
- [108] Miller EL, Rocheleau RE. Electrochemical behavior of reactively sputtered iron-doped nickel oxide. *Journal of the Electrochemical Society*. 1997;**144**(9):3072-3077
- [109] Ichianagi Y, Wakabayashi N, Yamazaki J, Yamada S, Kimishima Y, Komatsu E, Tajima H. Magnetic properties of nio nanoparticles. *Physica B: Condensed Matter*. 2003;**329**:862-863
- [110] Venkataraj S, Kappertz O, Weis H, Drese R, Jayavel R, Wuttig M. Structural and optical properties of thin zirconium oxide films prepared by reactive direct current magnetron sputtering. *Journal of Applied Physics*. 2002;**92**(7):3599-3607
- [111] Gao P, Meng LJ, dos Santos MP, Teixeira V, Andritschky M. Characterisation of ZrO₂ films prepared by rf reactive sputtering at different O₂ concentrations in the sputtering gases. *Vacuum*. 2000;**56**(2):143-148
- [112] Petit M, Monot J. Functionalization of Zirconium Oxide Surfaces. *Chemistry of Organo-Hybrids: Synthesis and Characterization of Functional Nano-Objects*. 2015. pp. 168-199

- [113] Balaram N, Reddy MSP, Reddy VR, Park C. Effects of high-k zirconium oxide (ZrO_2) interlayer on the electrical and transport properties of au/n-type InP Schottky diode. *Thin Solid Films*. 2016;**619**:231-238
- [114] Lopez CM, Suvorova NA, Irene EA, Suvorova AA, Saunders M. ZrO_2 film interfaces with Si and SiO_2 . *Journal of Applied Physics*. 2005;**98**(3):033506
- [115] Zhang HH, Ma CY, Zhang QY. Scaling behavior and structure transition of ZrO_2 films deposited by RF magnetron sputtering. *Vacuum*. 2009;**83**(11):1311-1316
- [116] Gopalan R, Chang CH, Lin YS. Thermal stability improvement on pore and phase structure of sol-gel derived zirconia. *Journal of Materials Science*. 1995;**30**(12):3075-3081
- [117] Tanabe K. Surface and catalytic properties of ZrO_2 . *Materials Chemistry and Physics*. 1985;**13**(3-4):347-364
- [118] Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials*. 1999;**20**(1):1-25
- [119] Muhammad S, Hussain ST, Waseem M, Naeem A, Hussain J, Jan MT. Surface charge properties of zirconium dioxide. *Iranian Journal of Science and Technology*. 2012;**36**(A4):481
- [120] Manicone PF, Iommetti PR, Raffaelli L. An overview of zirconia ceramics: Basic properties and clinical applications. *Journal of Dentistry*. 2007;**35**(11):819-826
- [121] Pareja RR, Ibáñez RL, Martín F, Ramos-Barrado JR, Leinen D. Corrosion behaviour of zirconia barrier coatings on galvanized steel. *Surface and Coatings Technology*. 2006;**200**(22):6606-6610
- [122] Puntervold T, Strand S, Austad T. Water flooding of carbonate reservoirs: Effects of a model base and natural crude oil bases on chalk wettability. *Energy and Fuels*. 2007;**21**(3):1606-1616
- [123] Love JC, Estroff LA, Kriebel JK, Nuzzo RG, Whitesides GM. Self assembled monolayers of thiolates on metals as a form of nanotechnology. *Chemical Reviews*. 2005;**105**(4):1103-1170
- [124] Iglauer S, Salamah A, Sarmadivaleh M, Liu K, Phan C. Contamination of silica surfaces: Impact on water- CO_2 -quartz and glass contact angle measurements. *International Journal of Greenhouse Gas Control*. 2014;**22**:325-328
- [125] Sarmadivaleh M, Al-Yaseri AZ, Iglauer S. Influence of temperature and Pressure on quartz-water- CO_2 contact angle and CO_2 -water interfacial tension. *Journal of Colloid Science*. 2015;**441**:59-64
- [126] Mahdi Jafari S, He Y, Bhandari B. Nano-emulsion production by sonication and microfluidization-a comparison. *International Journal of Food Properties*. 2006;**9**(3):475-485
- [127] Lander LM, Siewierski LM, Brittain WJ, Vogler EA. A systematic comparison of contact angle methods. *Langmuir*. 1993;**9**(8):2237-2239

- [128] Ingham B. X-ray scattering characterisation of nanoparticles. *Crystallography Reviews*. 2015;**21**(4):229-303
- [129] Winkler K, Paszewski M, Kalwarczyk T, Kalwarczyk E, Wojciechowski T, Gorecka E, Pociecha D, Holyst R, Fialkowski M. Ionic strength-controlled deposition of charged nanoparticles on a solid substrate. *The Journal of Physical Chemistry C*. 2011;**115**(39):19096-19103
- [130] Nikolov A, Kondiparty K, Wasan D. Nanoparticle self-structuring in a nanofluid film spreading on a solid surface. *Langmuir*. 2010;**26**(11):7665-7670
- [131] Ershadi M, Alaei M, Rashidi A, Ramazani A, Khosravani S. Carbonate and sandstone reservoirs wettability improvement without using surfactants for chemical enhanced oil recovery (C-EOR). *Fuel*. 2015;**153**:408-415
- [132] Eshed M, Pol S, Gedanken A, Balasubramanian M. Zirconium nanoparticles prepared by the reduction of zirconium oxide using the rapet method. *Beilstein Journal of Nanotechnology*. 2011;**2**(1):198-203
- [133] Son HA, Yoon KY, Lee GJ, Cho JW, Choi SK, Kim JW, Im KC, Kim HT, Lee KS, Sung WM. The potential applications in oil recovery with silica nanoparticle and polyvinyl alcohol stabilized emulsion. *Journal of Petroleum Science and Engineering*. 2015;**126**:152-161
- [134] Zargartalebi M, Kharrat R, Barati N. Enhancement of surfactant flooding performance by the use of silica nanoparticles. *Fuel*. 2015;**143**:21-27
- [135] Mercera PDL, Van Ommen JG, Doesburg EBM, Burggraaf AJ, Roes JRH. Stabilized tetragonal zirconium oxide as a support for catalysts evolution of the texture and structure on calcination in static air. *Applied Catalysis*. 1991;**78**(1):79-96
- [136] Li YV, Cathles LM. Retention of silica nanoparticles on calcium carbonate sands immersed in electrolyte solutions. *Journal of Colloid and Interface Science*. 2014;**436**:1-8
- [137] Zhang T, Murphy M, Yu H, Bagaria H, Nielson B, Bielawski C, Johnston K, Huh C, Bryant S. Investigation of nanoparticle adsorption during transport in porous media. SPE Annual Technical Exhibition, New Orleans, Louisiana, 30 September-2 October. 2013
- [138] Ju B, Fan T, Li Z. Improving water injectivity and enhancing oil recovery by wettability control using nanopowders. *Journal of Petroleum Science and Engineering*. 2012;**86**:206-216
- [139] Maghzi A, Mohammadi S, Ghazanfari MH, Kharrat R, Masihi M. Monitoring wettability alteration by silica nanoparticles during water flooding to heavy oils in five-spot systems: A pore-level investigation. *Experimental Thermal and Fluid Science*. 2012;**40**:168-176

