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Chapter 8

A Realistic Look at Nanostructured Material as an Innovative Approach for Enhanced Oil Recovery Process Upgrading

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Additional information is available at the end of the chapter

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Abstract

With the continuous rise in energy demand and decline in reserves, the Petroleum Industries are constantly in search of inventive and novel approaches to optimize hydrocarbon recovery despite several decades of deployment of conventional and enhanced strategies. This chapter presents an in-depth analysis of nanomaterial (nanoparticles), their unique characteristics and potentials in relation to smart field development, enhanced oil recovery (EOR) and CO_2 geosequestration. The particles surface functionalities, unique size dependent property, adsorption, and transport behavior were scrutinized. The materials precise role in enhancing reservoir parameters that influences rock–fluid interactions, and reservoir fluid distribution and displacement such as permeability, wettability, interfacial tension, and asphaltene aggregate growth inhibition were evaluated. The study argues that the application of nanoparticle based fluids as novel EOR approach offers more holistic measures, potentials, and opportunities than micro and macro particles and can stimulate the continuous evolution of EOR processes even under harsh reservoir conditions, thus, offering better benefits over conventional surface-active agents. We believe this study will significantly impact the understanding of EOR with respect to nanoparticles, which is crucial for augmenting reservoir processes and to accelerate the realization of nanoparticles for EOR and CO_2 sequestration processes at industrial scale.

Keywords: EOR, nanoparticles, adsorption, Asphaltene, wettability, IFT, permeability, viscosity, CO_2

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1. Overview

It is a fact that the period of cheap hydrocarbon recovery is waning as hydrocarbons are currently been explored in remote regions under harsh reservoir conditions. The accessible hydrocarbon resources are constantly declining with a corresponding increase in energy demand which invariably contributes to the price irregularities in the oil and gas industry. Globally, the growth in energy demand appears to be predominant amidst feasible unconventional energy options (renewable energy). Unarguably, newer energy sources, such as nuclear, wind, geo-thermal and solar are effective measures for addressing energy shortage. However, they are yet to be ample alternatives for substituting the role of oil in meeting the ever-rising energy demand. To date, these demands are currently being substantiated via hydrocarbon sources especially petroleum – oil is still the most valuable product with great global economic impact. Currently, diverse conventional strategies (waterflooding), and enhanced methods (use of chemicals, gases, and microbes) are been deployed in oil fields, regardless, these challenges persist. More efficient, yet cost-effective, environmentally friendly, and novel alternatives are constantly being searched for process feasibility, and to meet the current global high-energy demand. Interestingly, these challenges can be averted through innovative scientific and engineering approaches such as nanotechnology, specifically, via the use of nanostructured materials. Nanostructured materials in the form of nanoparticles or carbon nanotubes have attracted attention for consideration as effective solutions for resolving challenges in the oil and gas industry. Nanoparticles are considered the simplest forms of nanostructured materials categorize as metallic, metal oxides or magnetic nanoparticles; whereas, the carbon nanotubes are carbon allotropes with a cylindrical nanostructure in the form of a tube which can be single, double, or multiple walled nanotubes [1, 2]. These materials have vast application potentials industrially, however, the choice of a specific material type is highly dependent on the application process.

Research has shown that diverse potentials exist for the application of nanostructured materials in the oil and gas industry for smart field development (**Table 1**). The carbon nanotube materials display great unique properties such as stiffness, strength, and tenacity in comparison to other fiber materials, which lacks one or more of these characteristics. Also, the thermal and electrical conductivity of carbon nanotubes is higher in comparison to other conductive materials [1]. Nanoparticles (NP) are characterized by unique thermal, mechanical, and chemical properties thus particularly interesting for the oil and gas industry. For instance, oil and gas tools are manufactured with nanomaterial functionalities; the inner surfaces of pipelines and production facilities can be coated with nano-based paints; nanoparticle based catalysts are been used in the oil and gas downstream for oil refining and petrochemical activities. Currently, complex reservoir rock heterogeneity and microstructures, and the corresponding effect on multiphase flow as well as the reservoir depth information can now be effectively characterized using sensors fabricated with nanoparticle materials. Superparamagnetic nanoparticles can be effectively used for conductive heat generation [3]. Nanoparticles dispersed in solvents are also been used for drilling, exploration, production, and enhanced oil recovery processes. Such fluids can be used for resolving shallow water flow challenges, drilling and production issues such as borehole instability linked to poorly consolidated and

Processes	Material type	Applications	References
Drilling and completion			
Drilling Bits	Carbon nanomaterial - nano-diamond polycrystalline diamond compact (PDC) Technology	• Suitable for functionalization of PDC cutters for drill bits • Effective for the manufacture of advanced drill bits that has good resistance to abrasion and corrosion upon nano-coating	[1, 46, 47]
Logging while drilling (LWD)	Nanostructured glass-ceramics	• Effective neutron detectors - Li-6 scintillation nanostructured glass ceramics shows better efficiency than ordinary Li-6 scintillation materials	[1]
Cementing	Carbon nanotube (CNT)	• Suitable as reinforcement materials for cement instead of conventional fibers	[1]
Drilling fluids	NP	• Control of fluid loss and wellbore stability • Design of drilling fluids suitable for harsh reservoir conditions • Nanoparticle based drilling fluids can be effective for elimination or reduction of drilling problems such as pipe sticking, equipment wear and tear, rig instability and poor hole cleaning issues	[1, 4]
Exploration			
Geothermal production	NP	• Nanoscale metals suitable for delineation of ore deposits during geochemical exploration	[1, 19, 48]
Exploration			
Imaging tool	NP	• Hyperpolarized silicon Np deliver innovative tools for measurement and imaging oil exploration	[1, 29, 49]
Production			
Hydrate Recovery	NP	• Nickel-iron Np can be used for dissociation of hydrates	[1, 29]
Viscoelastic surfactant stimulation fluid (VES)	NP	• Np associates with VES micelles for stabilization of fluid viscosity	[1, 29]
Reservoir characterization and management			
EOR	NP	• Advanced EOR approach - suitable for surface/interfacial modifications and oil recovery	[23, 24, 31, 50, 78, 79]
Inhibition of inorganic scales	NP	• Inhibition can be achieved over long distances from the injection point using synthesized nanoparticles	[42]
Hydrocarbon detection	NP	• Suitable for detection of hydrocarbon in formation rocks	[1, 47, 51]
Oil microbe detection tool	Nano optical fiber	• Suitable for reservoir penetration and for transmission of laser light which enables the detection of stranded or bypassed oil	[1, 47, 52]
Carbon capture and storage	NP/ Nanomembranes	• Enhances improved gas streams separation and for contamination removal from oil	[1, 19, 47]

Table 1. Nanostructured material applications for smart field development in the oil and gas industry.

or reactive shale zones, reduction of the frictional resistance between pipes and borehole well, and for prevention of loss circulation of drilling mud [4]. Despite the relevance of nanoparticles in diverse oil and gas engineering processes, reservoir engineering specifically enhanced oil recovery (EOR) have attracted the most attention in recent times. EOR is mainly driven by the possibilities of increasing the overall oil displacement efficiency which is greatly dependent on microscopic and macroscopic displacement efficiencies [5, 6]. Unarguably, EOR mechanisms augment additional oil recovery potentials than the primary and secondary methods. However, the successful deployment of EOR requires an understanding of the mechanisms that control efficient fluid displacement and distribution, as well as, overall optimal recovery efficiencies. A number of processes and technologies are used in this regard to upsurge or maintain recovery from existing fields which includes the injection of steams (Thermal EOR), fluid(s) (Chemical EOR) and gases into a reservoir (Gas EOR), and recently microbes (Microbial EOR). These processes facilitate effective displacement of oil towards the producing well, thus, production from matured fields are enhanced as the injected fluid, gases, or microbes interact with the formation rock and oil systems thereby creating a favorable condition for better recovery. Comprehensive breakdown of these processes is provided in our previous work [6]. In the face of diverse EOR technological advancements, there exist several challenges that impede process efficiency. The key process challenges among others are:

- Thermal EOR (TEOR): high operational cost, and environmental unfriendliness owing to emissions from surface steam generation.
- Chemical EOR (CEOR): high chemical cost, chemical mismatch, porous media pore-plugging and chemical trapping issues.
- Gas EOR (GEOR): separation issues, inadequate sources of gas on basis of geographical availability, and mobility control issues.
- Microbial EOR (MEOR): complex process mechanisms, and poor oil recovery potential.

Among these challenges is the need for more economically feasible approach that will reduce operational cost and improve the quality and amount of recoverable oil to meet the global market demands with less environmental footprints.

2. Nanoparticles

Nanoparticles are nano-sized structures with at least a phase of one or more dimensions in the nanometer size range (typically 1–100 nm). The uniqueness of the properties of the material dates to several centuries (ninth century AD). The first optical property of nanoparticle was discovered from a luster technology on a glazed ceramic in Mesopotamia at the time, which later became popular in Egypt, Spain, and Persia. An archeomaterial of this material indicted the optical properties were as a result of the metallic nanoparticles that were dispersed on the outermost layers of the glaze [7]. With the advent of time, practicalities of nanoparticle have become even more prevalent owing to their physical and chemical properties. Nanoparticles cut across a wide variety of materials such as; (a) materials with surface protrusions spatially

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separated by distances in the order of nanometers; (b) porous materials with particle sizes in the nanometer range or nanometer sized metallic clusters dispersed within a porous matrix; (c) polycrystalline materials with nanometer sized crystallites. Quantization of the electronic states of nanoparticles, and the possible state manipulation through shape and size control are the key drivers for research in nanoscience or nanotechnology. At nano-scale, the property changes that occur are based on the nature of the material and the applied mechanisms. For instance, when metallic nanoparticles transition from bulk metal to a much smaller metallic nanoparticle, the bulk metal energy continuum changes to produce even more discrete energy levels – an indication of a decrease in the density of the electronic states [8].

2.1. Characteristics of nanoparticles

Nanoparticle application though in its early stage have emerged a novel EOR pathway owing to its unique properties and transport behavior that can address the underlying mechanisms that influence reservoir behavior and the corresponding effect on efficient recovery. Nanoparticles are considered suitable for EOR due to their strong particle surface interaction with solvents, which helps to overcome density difference that make materials float or sink in a system This material has an extensive range of unique characteristics for varied functionalities such as surface plasmon resonance, superior catalytic activity, intrinsic reactivity, quantum confinement, great adsorption affinity and dispersibility [9–11]. Interestingly, the particles surface functionalities can be engineered with potentials for subsurface engineering applications.

Comparison of the exceptional properties of nanoparticles to their bulk material counterpart shows that nanoparticles display quite different properties and superior behavior. Its applications enable the creation of new composites with unique properties, which allows for innovative technological advancements. Typically, nanoparticles are characterized by thermal, mechanical, physical, and chemical properties. These properties span through material's grain boundary, particle size, surface area per unit volume, size of the particles, purity, thermal conductivity etc. On basis of their thermal properties, nanoparticle based fluids exhibit high thermal conductivity and high surface area than conventional base-fluids. The thermal conductivity of conventional base liquid can be improved by addition of nanoparticles as heat transfer occurs at the surface of the particles [12]. The high surface area increases the thermophysical properties and the small particle size enhances their potentials as absorber fluids due to high potential of large surface coverage in heat transfer processes. Lee et al. [12], Choi [13], and Eastman et al. [14] reported that nanoparticle based fluids exhibit higher thermal conductivity with great dependency on factors such as the material type, size, shape, surface area, particle volume fraction, base fluid material and temperature. For example; the thermal conductivity of ethylene glycol – a conventional base fluid with thermal conductivity of approximately 0.258 (W/m K), can be significantly enhanced (20% increase) upon addition of about 4% volume CuO of 35 nm particles. On the mechanical properties, nanoparticles exhibit high ductility, high average hardness, and maximum strain in comparison to the other composite materials, thus, considered suitable for improving fracture toughness. However, the particles geometry can influence the mechanical properties of nanoparticles such as tensile modulus, tensile strength, and fracture toughness [15]. Zhang and Singh [16] showed that the

addition of 4.5% volume fraction of well-bonded Al_2O_3 particles to unsaturated polyester led to a 100% increase in fracture toughness. It has also been reported [17, 18] that nanoparticles are suitable filler materials for improving the mechanical properties of composites. The addition of small amount of rattan nanoparticles (0–5%) to polymer matrix (polypropylene) as fillers enhanced the mechanical performance of composites.

With respect to the physical and chemical properties, these span through shape, size, structure, quantum confinement, lattice parameter and symmetry, charge, solubility, and surface coating [19–21]. The enhanced physiochemical properties and superior performance of nanoparticles is mainly based on the overriding effect of surface forces from the particles atomic scale size rather than the mass forces. The physical and chemical properties of the bulk materials are typically constant irrespective of the material size; and the number of surface atoms is substantially smaller than atoms in the bulk phase. This is not the case with nanoparticles owing to the small particle size, high surface area, and unique transport behavior that enhances surface performance. Nanoparticles yield applications that are even more extensive with the particle size approaching nanoscale. The particles coalesce into the structure of materials and display strength. The atoms of conventional materials are located in the interior of the particle, whereas, the atoms of nanoparticles are located on the particles surface [22–25]. A dramatic change in properties such as thermal resistance, chemical and catalytic activities, melting point, internal pressure, magnetism, and optical behavior occurs as the atoms at the surface of the material become even more significant owing to the large surface area to volume ratio. The surface area to volume ratio appears exponentially larger, and the number of surface atoms becomes even more substantial with respect to that in the bulk phase [2, 10, 11, 26–29]. Amanullah and Al-Tahini [4] reported a comparison between the surface area to volume ratio of spherical particles of the same nanomaterial in micrometer, millimeter, and nanometer. Nanoparticle surface area to volume ratio is over a million times higher than the conventional scales and the particle surface area is also higher than the bulk particles – micro and macro materials of the same mother source, which enhances their increased potentials even with a significantly low concentration of the materials in the system. Such high surface area increases the particles surface energy which leads to structural transitioning [30]. This behavior allows for favorable particle adsorption at the surface boundaries and permits high particles contact tendencies with nearby materials or solvent molecules in suspensions [23], and the particles boundaries facilitate their enhanced quantum effects. A key benefit of nanoparticles in EOR is the ability to alter reservoir rock surfaces – where strongly hydrophobic surfaces can be rendered hydrophilic upon contact with nano – based systems [23, 24, 31–38] thus interesting for engineering and subsurface processes, EOR, and carbon geo-sequestration process efficiency.

2.2. Nano-based smart fluids

Nanoparticle based fluids otherwise called smart fluids are fluid systems containing nano-additives, and the systems exist in the form of suspensions or emulsions known as nanofluids, nano-catalyst suspensions or nanoemulsions. The nano-emulsions are emulsions that exhibit unique characteristics such as great stability in comparison to micro-emulsions. Anton et al. [99] established that nano-emulsions are kinetically stable irrespective of temperature changes

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in comparison to other emulsions that are thermodynamically unstable systems with free energy of emulsion formation greater than zero. Since nanoparticles are active emulsifiers of oil and water [39, 40], preparation of ultra-stable emulsion is attainable by the control of the degree of surface charges. The emulsions are not subject to gravity driven separation as the dispersed droplets are relatively small size which eliminates separation processes owing to phase density difference. The particle dispersals are typically mixtures of water, oil, surfactant, or brine. It has been reported that nano-emulsions upsurge additional oil recovery [41]. Zhang et al. [42] reported that nanoparticles form stable emulsions, however, the level of stability depends on the oil polarity as the formation of oil-water stable emulsions are more favorable to non-polar oils and water oil emulsions are preferable with polar oil. Another relevant system suitable for EOR processes in porous media is the nano-based catalysts suspensions, which demonstrates high efficiency for heavy oil recovery. The presence of nanocatalyst in porous media has been reported to enhance bitumen conversion to lighter products [10, 43, 45]. Nanofluids are colloidal suspensions of solid nanoparticles or nanofibers consisting of a carrier medium and solid phase. A key advantage of nanofluids over conventional fluids in EOR is that nanoparticles improve the property of its dispersals even at very low particle concentrations in the suspension. The particles in suspension enhance the performance of the carrier fluid during production owing to high dependency on the unique electrical, rheological, and magnetic properties of the nanoparticles. Since the carrier fluids are normally conventional heat transfer liquids, the particles also enhance the thermal conductivity and convective heat transfer performance of this base liquids as its thermal conductivities are typically an order-of-magnitude higher than that of the base fluids [9, 63]. The nano-based smart fluids display significantly high functional abilities in different systems while reducing the overall fluid cost irrespective of high cost of individual additives [4].

3. Definite role of nanoparticles in porous media applications for process enhancement

3.1. Adsorption/transport potentials

Nanoparticles injected into porous media can exhibit different phenomenal behaviors; adsorption, desorption, transport, and blocking inclinations. The interactions between nanoparticles and the walls of the porous media can lead to adsorption if the force of attraction is higher than the repulsive with the reverse leading to desorption, however, adsorption and desorption is a dynamic balance process that is controlled by the total force existing between the porous media wall and nanoparticle. Blocking can occur if the nanoparticle diameter appears bigger than the size of the pore throat or due to particle to particle aggregation at the pore throat which can inhibit efficient transport of nanoparticle based fluids through the porous media [44, 54–59]. Generally, nanoparticles regardless of their small particle sizes are easily susceptible to aggregation in liquid suspensions, which promotes surface adsorption of neighboring particles or molecules. This behavior is due to the particles large surface-to-volume ratio and poor wettability in the metal matrix [2, 60, 61, 63]. However, a recent study on nanoparticle adsorption and transport behavior shows that nanoparticle based fluids can efficiently flow

through the porous media without excessive adsorption and retention inclinations with an equilibrium adsorption estimation of 1.27 mg/g for 5000 ppm nanofluid [62]. More so, when the particle size of nanomaterial is reduced to near or less than the wavelength of electrons conductivity, the property of the material changes. Since oil is typically recovered from formation rocks with micron-sized pores, nanoparticles are much smaller fine particles with unique size dependent physical and chemical properties that enhance easy penetration through the reservoir pores since the particle size is much smaller than the conventional rock pores [22–24]. Thus, fluid flow through the reservoir pore spaces can be significantly improved with little or no negative impact on the formation permeability, or porous media pore-plugging or chemical trapping related issues that are commonly associated with conventional EOR processes. Shen et al. [63] and Zhang et al. [64] also reported the excellent transport, diffusion, retention, and releasing properties of nanoparticles in porous media.

3.2. Asphaltene growth inhibition

Nanoparticles exhibit strong chemical stability, irrespective of harsh reservoir conditions and great selective adsorption behavior in the presence of heavy components in crude oil such as asphaltenes. Asphaltenes are common petroleum macromolecules which poises challenges such as well bore plugging, adsorption, pipeline deposition, and sedimentation issues. Asphaltenes [65, 66] exist in forms of solid deposits and usually self-associate with resins in crude oil and are often problematic during production as they can plug wellbore tubing and valves, and contribute to undesirable formation rock surface coating. Such asphaltenes – polydispersed [67] can exist in the form of colloidal suspensions or micelles which form deposits when the wettability conditions of the reservoirs are altered. A study by Franco et al. [68] on the adsorption behavior of nanoparticles on heavy components in crude oil such as resins and asphaltenes shows that nanoparticles in contact with crude oil is capable of adsorbing resins and (or) asphaltenes, however, nanoparticles exhibit great selectivity and preferential affinity for adsorption of asphaltenes (n-C_7) compared to resins. This behavior is also confirmed by an earlier report by Nassar et al. [56, 57], which shows that nanoparticles have great affinity for asphaltenes—where alumina nanoparticles adsorbed asphaltenes more readily than micro porous alumina particles with similar acid content. Taborda et al. [69] investigated nanoparticles effect on adsorption isotherms of n-C_7 asphaltenes at 298 K temperature in complex crude oil systems. The authors compared the performance of different ranges of SiO_2 and Al_2O_3 nanoparticles. The SiO_2A nanoparticles showed better adsorption capacity than others as the adsorption potential to capture n-C_7 asphaltenes is in the order of SiO_2A > SiO_2 > Al_2O_3. The acidic silica exhibited better adsorptive capacity especially at low concentrations owing to increased surface acidity of the nanoparticles as n-C_7 asphaltenes adsorption increases concurrently with increase in surface acidity [70].

Heavy oils are typically known for their high asphaltene content (> 5 wt.%), such asphaltenes [71, 72] forms viscoelastic network of large size nanoaggregate clusters and promote formation damage as a result of self-association, and if sub-saturated oil reservoirs exist at pressures above the bubble point. The asphaltene becomes excluded from the oil matrix and then forms deposits on the reservoir rock. This behavior causes blockages of the porous media and wettability challenges. Reduction of large asphaltene aggregates using nanoparticles by breaking the attachment points within the viscoelastic network is thus necessary to improve their

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configuration and distribution in the oil matrix. Taborda et al. [69] examined the behavior of n-C_7 asphaltenes in the presence and absence of nanoparticles as a function of time at 298 K temperature. An initial increase in the mean size of asphaltene aggregates (d_{asp}) occurred with time, followed by a decrease in size in the absence of nanoparticles with a notable stabilization of approximately 300 min. This was attributed to the aggregation-fragmentation forces that exist under shear conditions which has a direct growth / reduction effect on d_{asp}. Similar behavior was also observed in the presence of the diverse nanoparticles (Al_2O_3, SiO_2 and SiO_2A) tested, however, a lower d_{asp} and faster stabilization (180 min) was attained in a decreasing order of $SiO_2A < SiO_2 < Al_2O_3$. Franco et al. [73] conducted an asphaltene displacement and adsorption test to inhibit formation damage using nanoparticles at reservoir conditions. The authors reported a significant increase in oil production level owing to the presence of nanoparticles. 80% increase in oil recovery occurred after the injection of nanoparticle based fluids in damage systems owing to efficient inhibition of the growth of asphaltene aggregates and the swift capture of asphaltene through adsorption.

3.3. Permeability improvement

Permeability plays a major role in oil recovery processes as adequate permeability can improve reservoir fluid displacement. High permeable formations permit high fluid displacement alongside other essential factors, such as capillary pressure and formation wettability. Relative permeability is considered the ratio of the phase permeability to the absolute permeability *k*. The phase permeability primarily exists as a water, gas, or oil phase as shown in Eqs. (1)–(3):

$$\text{Water phase relative permeability} : k_{rw} = k_w/k \tag{1}$$

$$\text{Gas phase relative permeability} : k_{rg} = k_g\ /k \tag{2}$$

$$\text{Oil Phase relative permeability} : k_{ro} = k_o/k \tag{3}$$

Nanoparticles have the potentials of enhancing the reservoirs permeability for achieving higher recovery factor. Nanoparticles can efficiently expand the pore radius, enable the reduction of flow resistivity of the water injected into the pores, promote water permeability enrichment, promote reduction in injection pressure and enhance injection volume as well as recovery potentials. Wang et al. [74] reported that the injection of 0.5 wt.% of SiO_2 nanoparticle concentration led to over 10% increase in oil recovery. The small particle size of this material enabled penetration into the low-permeability layers while averting hydration occurrences from water-rock contact, and promoted injection and subsequent augmentation of oil recovery even in low permeable regions. Guzmán et al. [75] performed a core flooding test in bauxite porous media, relative permeability was measured in the presence and absence of fracturing fluid containing nanoparticles. Injection of fracturing fluids into reservoirs can induce formation damage, where the original K_{ro} values appears lower than the base system due to some degree of formation damage. However, with optimized fracturing fluid containing nanoparticles, K_{ro} becomes higher than the base system with mobility range of 0.42–0.80. Formation damage reduction from 55 to 16% occurred which was about 71% reduction upon addition of nanoparticles to the optimized fracturing fluid, thus, an indication that the presence of nanoparticles improved the fluids performance and inhibits the associated formation

damage which may be due to the porous media wettability alteration as nanoparticle inclusion changes the rock wettability from oil-wet to water-wet.

3.4. Wettability alteration

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. Wettability is however influenced by the degree to which the crude oil polar components deposits or adsorbs on the mineral rock surface, hence, an understanding of fluid–rock interaction is vital for efficient EOR processes. Quantification of reservoir wettability in relation to nanoparticles are analyzed by contact angle, imbibition etc.

3.4.1. Contact angle

Contact angle is an effective wettability measurement approach for evaluating rock surface wetting as it enables the valuation of the balance of forces at the contact line. Theoretically, this has been demonstrated by the Young-Laplace equation (Eq. (4); **Figure 1**). Wetting phenomenon is closely related to the reservoir rock surfaces and the imbibing fronts, as such if a liquid wet a solid, the change in wettability can be dramatic even for a slight surface modification of the surface property of the solid. Wetting via nano-modification have been reported in several literatures [23, 24, 31, 36, 37, 76, 77, 80–85], despite the disparity in test methods, a clear trend in nanoparticles wetting efficiency in changing hydrophobic surfaces towards favorable hydrophilic conditions were reported. For example: Ju and Fan [76] tested the wetting inclination of lipophobic and hydrophilic polysilicon nanoparticles in hydrophobic sandstone formation. The authors reported that the presence of nanoparticles caused a change in wettability to hydrophilic state owing to efficient particle adsorption on the surface of the rock. Nwidee et al. [24] assessed nanoparticles surface modification effect on solid-wetting in hydrophobic limestone formation over a wide range of temperatures (22–70°C) using Zirconium oxide—ZrO_2 and Nickel oxide—NiO; concentrations - 0.05 wt.%). To optimize the wetting characteristics of the nanoparticles, appropriate amount of surfactant (cationic - C_{16}TAB) was used, which facilitated the reduction in the solid-nanofluid-oil three-phase contact angle and maximized the structural force from the nanoparticles confinement in the wedge film. The nanoparticles formed a wetting wedge in form of an ordered structure near the three-phase contact line of the droplet on the rock surfaces, which stimulated significant wetting and spreading effect with ZrO_2 system exhibiting better surface wetting over NiO (ZrO_2C_{16}TAB > $NiOC_{16}$TAB) while maintaining great stability at elevated temperature (**Figures 2** and **3**). Cao et al. [77] performed

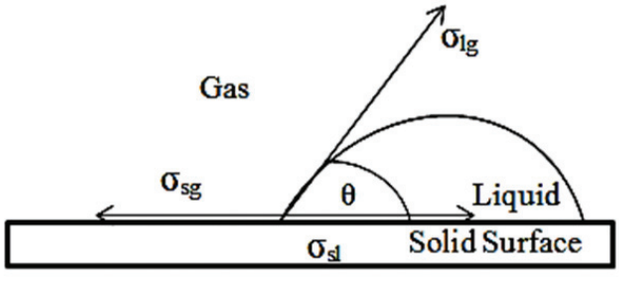


Figure 1. Young's equation illustrating a three-phase contact line.

a wetting investigation in the presence of zirconium oxide, and silicon oxide dispersed in surfactant, alkali and brine solutions. The authors reported that the nanofluids displayed great stability under harsh reservoir conditions of high pressure and high temperature.

$$\sigma_{sg} = \sigma_{sl} + \sigma_{lg}\, cos\theta \tag{4}$$

where σ_{sg} is the solid surface free energy; σ_{sl} is the IFT between the solid and liquid; σ_{lg} is the liquid surface tension; θ is the contact angle.

Notably, although nanoparticles promote formation rock wetting, the extent to which wetting occurs is dependent on the level of contact established between the rock surface and the wetting phase, which can impact the rather immobile fluid on the rock surface while mobilizing such fluids towards the flow lines.

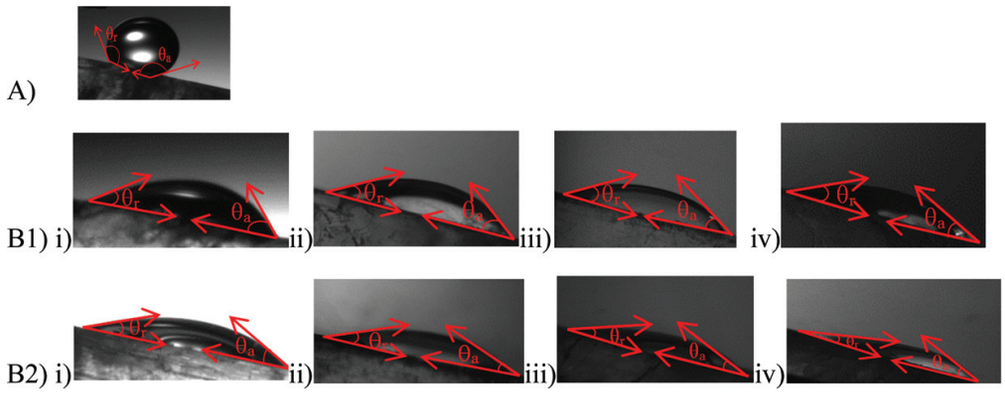


Figure 2. The receding (θ_r) and advancing (θ_a) contact angle images of water droplets (probe liquid) before and after exposure to nanofluid (A) oil modified rock (before nano-modification - high θ - indicates the surface's hydrophobicity - 152° θ_a); (B) nano modified at different temperatures (22–70°C) (B1- $NiOC_{16}TAB$; B2 - $ZrO_2C_{16}TAB$ - low θ - indicates hydrophilic conditions) which represents strong interaction with the rock surface thus exhibiting low surface energies and inclination to wet; I–IV); see graphical representation (**Figure 3**) for θ - values [24]©.

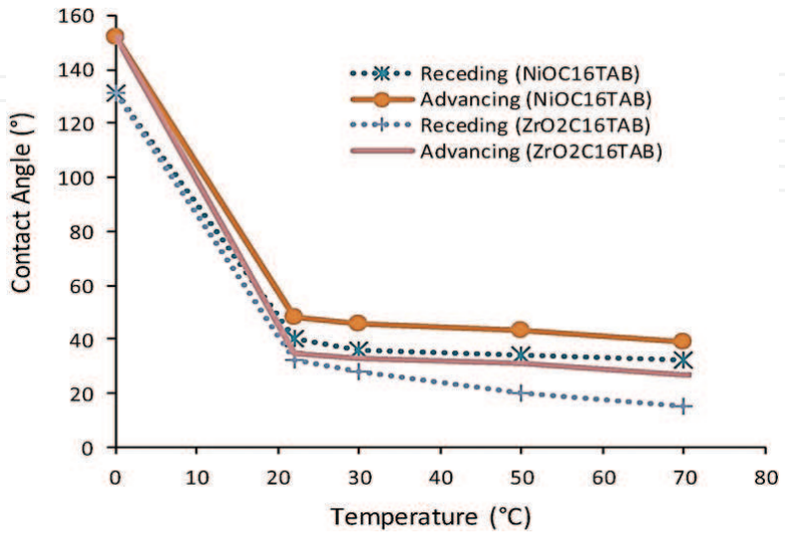


Figure 3. θ_R and θ_A depicting wettability change of NiO, ZrO_2 (0.05 wt.%), $C_{16}TAB$ (0.5 wt.%) blends in toluene (1-hour Exposure time) at different temperatures [24]©.

3.4.2. Imbibition

Imbibition enables an assessment of the displacement capacity of a wetting phase over a non-wetting phase. When immiscible fluids in the rock pore spaces are in contact, there exists possibilities for pressure discontinuity across the interfaces which shows high dependency on interfacial tension, the porous media pore spaces, and the wetting angle. Capillary pressure (the pressure variation between two fluid phases in contact - Eq. (5)) and wetting phase saturation plays a key role in imbibition processes and exhibits great dependency on wettability. For example; if a formation exhibits hydrophobic wetting characteristics, water imbibition in such systems is typically inhibited owing to negative capillarity. Whereas, if a formation exhibits hydrophilic wetting characteristics, such promotes better oil displacement from the rock as water readily imbibes into the rock pores and the presence of positive capillary pressure promotes this behavior. In a typical complex crude oil system, Zhang et al. [86] performed an imbibition test under high temperature, pressure, and high salinity condition using IIT nanofluid to simulate reservoir condition. The nanoparticle dispersion was reported as insensitive to electrolytes or temperature and stable in harsh reservoir environment. Core plugs saturated with crude oil was placed into a glass jar containing the test solution (IIT nanofluid and brine) to test their potentials to displace oil from the cores at 55°C. As the fluids imbibe into the core, oil is expelled which floats on the top of the glass jar. The recovered oil was recorded as a function of percentage of the original oil in place versus time in the presence and absence of nanoparticles. For the brine solution alone in the absence of nanoparticles only about 17% of the crude oil was displaced, whereas, the oil-wet cores exposed to the nanofluid formulations displaced approximately 50% of the crude oil. Youssif et al. [87] conducted a tertiary recovery core flooding test using silica nanofluid after imbibition by water flooding. Black oil (32.5 API and 4.6 cp) from the North Sea was used in the flooding experiments. Oil saturated cores were subjected to imbibition by initial saturation with brine to displace oil at injection rate of 0.5 ml/min and a pore volume of 1.77 PV. Eq. (6) was used for the calculation of the displacement efficiency. The injection of silica nanofluid in the core enhanced oil production with increase in particle concentration (0.01–0.1 wt.%), then decrease in the amount of oil at much higher concentrations (0.5 wt.%) occurred after the optimal concentration (0.1 wt.%), which was attributed to possible permeability impairment. At 0.1 wt.% silica concentration, an increase in the oil recovery factor from 53.1% (waterflooding alone - **Figure 4**) to 66.40% following the nanofluid injection occurred. Better recovery occurred in comparison to water flooding alone, with an initial oil in place increase of 13.28% in the presence of the nanoparticle and low injection rate of the nanofluid decreased permeability impairment.

$$P_c = P_n - P_w \tag{5}$$

where P_c is the capillary pressure (Pa), P_n is the non-wetting pressure (Pa), P_w is the wetting pressure (Pa).

$$E_D = [1 - S_{or2}/S_{Or1}] \times 100 \tag{6}$$

where E_D is the displacement efficiency, S_{or} is the residual oil saturation, S_{or1} is the Sor after brine flooding, S_{or2} is the Sor after nanofluid flooding.

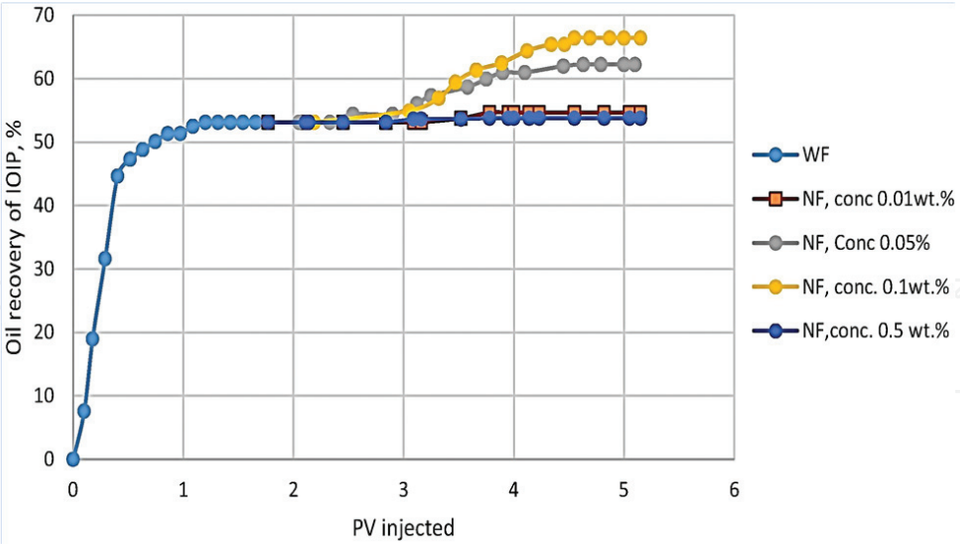


Figure 4. Oil recovery vs. pore volume (PV) injected for oil-wet Berea sandstone before and after nanofluid exposure [87]©.

3.4.3. SEM and AFM imaging

Mechanistic surface imaging tools such as scanning electron microscopy (SEM) and atomic-force microscopy (AFM) are used to characterize porous media wetting, adsorption characteristics of reservoir rocks and their surface roughness. Morphology and roughness are key parameters that influence rock surface wetting. Assessing wettability by contact angle usually does not account for surface roughness and the pore rock structures that impact liquid–solid contact lines. For improved knowledge of wetting and rock surface behavior, it is imperative that these factors are put into considerations. SEM is an approach for micro-analysis of solid materials with high accuracy. SEM produces high-resolution images for even the smallest structures at nano-scale as high magnifications are used during image processing. SEM investigations on rock substrates with respect to wetting have been reported by several researchers [88–90]. AFM also enables imaging of the surface of the samples at extremely high resolutions using a sharp tip for probing the surface features of the samples. These tools enable micro and nano-scale evaluation of solid surfaces, the topographic changes of such surfaces, and their surface roughness. The surface roughness is generally estimated using Eq. (7) and (8). **Figure 5** shows example cases of SEM and AFM images in wetting evaluations [23]. Treating rock surfaces with nanoparticles based fluids have been shown to improve surface wetness confirmed via contact angle examinations owing to efficient adsorption of nanoparticles on rock surfaces and surface roughness increase. Several wetting studies have been performed via this approach and confirms the effectiveness thereof on diverse rock surfaces [23, 24, 46–48, 91–94]. For example, the adsorption and surface roughness behavior of blends of nanoparticles (ZrO_2 and NiO) and surfactants (cetyltrimethylammonium bromide (C_{16}TAB-cationic) and triton X-100 (non-ionic)) were mechanistically assessed by exposing rock substrates to different nanoparticle-surfactant fluids (NiO/C_{16}TAB, NiO/TX-100, ZrO_2/C_{16}TAB, ZrO_2/TX-100) [24]. The treatment of the substrates with surfactant - nanoparticle based fluids enabled favorable adsorption of the particles on the surface of the rock owing to electrostatic interactions, with a corresponding increase in surface roughness (mean

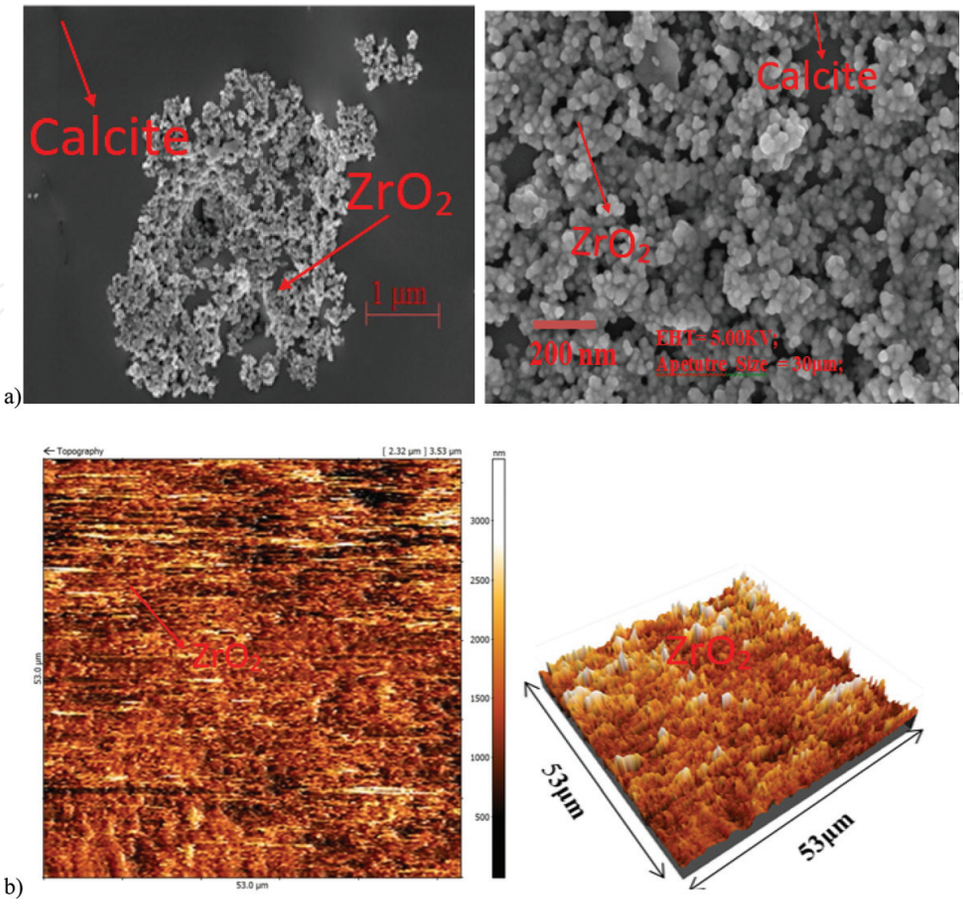


Figure 5. SEM (a) and AFM(b) images of ZrO_2 nanoparticle as uniform nano-spherical particle with mean particle size of 28 nm depicting surface adsorption on calcite substrates [23]©.

surface roughness, S_a and root mean square, RMS). The C_{16}TAB - nanoparticle systems exhibited better surface adsorption, higher surface roughness, and wetting inclinations than the TX-100 - nanoparticle systems in the order of ZrO_2/C_{16}TAB (Sa −120 nm; RMS -200 nm) > NiO/C_{16}TAB (Sa −100 nm; RMS -190 nm) > NiO/TX-100 (Sa −78 nm; RMS - 180 nm) > ZrO_2/TX-100 (Sa - 60 nm; RMS - 83 nm) [24]. Similarly, the irreversibly adsorption behavior of silica nanoparticles through SEM and AFM have also been reported [37]. Nano-modified substrates were exposed to different cleaning fluids at temperatures of 296 and 323 K. The authors reported that SiO_2 nanoparticle homogeneously adsorbed on the rock surface with increase in temperature and rock surface roughness (RMS from 18–580 nm at 296 k; 2700 nm at 323 K) which also stimulated better wetting.

$$S_a = \frac{1}{N} \sum_{j=1}^{N} /Zj/ \tag{7}$$

where N is the total data points in the measurement; Z_j is the vertical deviations measured from the average height of the surface.

$$RMS = \sqrt{\frac{\sum (Zj)^2}{N}} \tag{8}$$

where N is the data points; Z_j is the vertical deviation of j- point with respect to the mean line.

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3.4.4. Zeta potential

Zeta potential is a simple, rapid, direct-on-particle approach that permits the characterization of particle modification. This electro kinetic potential allows for estimation of the potential difference in colloidal systems that exist between the dispersion medium and stationary layer of the fluid that attaches to particles. It is closely related to the morphology of the particle surface and the suspension stability as the colloidal dispersions stability is dependent on the zeta potential value. The zeta potential of the rock-water interface and oil–water interface charges can be estimated based on the properties of the particles and suspension conditions (ionic type and strength, pH, and temperature). For example, in carbonate formation; pH and potential ions that forms a part of the carbonate structure such as Ca_2^+ and CO_3^{2-} enables the determination of carbonate-water interface via zeta potential [95]. With respect to nanoparticles, zeta potential enables estimation of the electric potential of particles on the inner boundary of the diffuse layers and surface charge of nanoparticles, since surface charges impact their reactivity, toxicology, and agglomeration behaviors [96, 97]. However, the agglomeration inclinations of nanoparticles can promote colloidal instability. Manan et al. [98] reported that different types of nanoparticles behaves differently owing to their zeta potential. In their study, the zeta potential of four different nanoparticles were compared and reported with varied zeta potential ranges (10–24 mv); where the zeta potential of Aluminum oxide(Al_2O_3) was 24 mv, Silicon dioxide (SiO_2) - 19 mv, Titanium dioxide (TiO_2) -13 mv, and Copper oxide 10 mv. The higher the zeta potential value whether positive or negative, the higher the stability potentials of the NP suspensions. Low zeta potential of colloidal fluids indicates that the repulsive force is lower than the forces of attraction which promotes precipitation and flocculation. However, such flocculation of nanoparticle based fluids like nano-emulsions can be prevented via steric stabilization owing to their droplet size which is sub-micrometric. Overlapping of interfacial droplet layers causes steric repulsion due to the unfavorable mixing of the stabilizing chain of the adsorbed layer which is dependent on the interfacial layer thickness, density and interactions between the interfacial layer and solvent [99–102]. Theoretically, Derjaguin and Landau [103] and Overbeek and Verwey [104] through the DLVO (Derjaguin, Landau, Verwey, and Overbeek) have shown that the stability of colloidal particles in solution is governed by their total energy of interactions (attractive and repulsive) when the particles are near each other. Nanoparticle as colloidal particle interacts with its carrier fluid or dispersal due to van der Waals attraction or electrostatic repulsion forces, of which the effects of the attraction forces can be higher than the repulsive. A comparative zeta potential tests was conducted by Ahmadi et al. [105] to examine the interactions between fines and pore surfaces and the change in total energy of the interactions due to colloidal forces of alterations in the presence of nanoparticles. The pore surfaces were coated with MgO (magnesium oxide), aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2). The pore surfaces changes in potential was tested and the total interaction energy was used to estimate the effects of the nanoparticles on surface properties and fines migration reduction. Upon comparison of the effects of the different nanoparticles, the authors reported that MgO displayed the highest propensity to attach fines to the surface and significantly reduced fines migration than Al_2O_3 and SiO_2, thus considered more efficient.

3.5. Interfacial tension reduction

For two liquid phases (e.g. gas-water, gas-oil or oil–water) to be in existence, there is usually an interplay of interfacial tension (IFT), which is the force that binds the surfaces of two distinct

phases. During oil recovery, reduction in such IFT is essential for better fluid mobilization and efficient recovery process. More so in the presence of negative capillary pressure, a favorable reduction in IFT can be achieved owing to a reduction in the resistance forces that impedes efficient oil production. Nanoparticles exhibit great potentials as IFT reduction agents when in combination with efficient dispersals as the particles display effective adsorption tendencies on the surface of liquids, creating separation layers that permits IFT reduction. This behavior is mainly governed by the nanoparticles surface adsorption, which is reliant on the phase concentration and efficient IFT reduction rate, however, the production of a stable process is dependent on the injected particle concentration. Several studies have been conducted in this regard [23, 68, 69, 83, 106–110]; Sharma and Sangwai [110] investigated the effect of temperature (30–90°C) on IFT of four paraffin oil (n-decane, n-hexane, n-pentane, n-heptane) using nanoparticle-polymer (NP) and nanoparticle-surfactant-polymer (NSP). Nanofluids IFT decreased with temperature increase for n-decane and n-heptane; n-hexane and n-pentane decreased with subsequent increase after reaching a minimum value owing to their low molecular weight that causes volatile losses at high temperature (>70°C). Vatanparast et al. [106] investigated the dynamic IFT of *n*-heptane/water in the presence nanoparticle (SiO_2 concentration - 0–2 wt.%) and surfactants. A sharp reduction in IFT occurred in the absence of nanoparticle and equilibrium was attained in 30 s and from a notable point of about 39 mN/m. For nanoparticle based systems, a rather gradual and steady decrease in IFT occurred over longer time interval (>1500 s). The IFT commenced at about 51 mN/m (close to pure water/heptane IFT) and decreases gradually with increase in the nanoparticle concentration - an indication of the existence of a negligible amount of free surfactant molecules in the system at this point, the nanoparticles did not promote rapid IFT reduction as with the case of the pure surfactant. The exchange of surfactant between the nanoparticle and the interface promoted decrease in IFT as each nanoparticle carries certain amount of surfactant molecules. With the increase in nanoparticle concentration, even more surfactant-nanoparticle complex occurs in the bulk phase which adsorbs to the interface, thus promoting further decrease in IFT at equilibrium condition. A much lower IFT reduction was attained compared to that of surfactant alone. Zargartalebi et al. [83] and Vashisth et al. [111] also reported better IFT reduction occurs in the presence of nanoparticles due to the adsorption of nanoparticles at the aqueous suspension/oil interface.

3.6. Heavy oil recovery enhancement

The upgrading of bitumen and heavy crude oil has remained a challenge. The associated high viscosity and density makes handling and transportation processes even more complex. The unique properties of nanoparticle make it effective as adsorbent and catalysts for enhancing heavy oil upgrading. The presence of nanoparticles in reservoirs improve oil recovery through the production of lighter components achieved by catalytic hydrocracking of heavy oil and by altering the rock surface wettability when the porous medium surface is coated with nanoparticles. Hashemi et al. [45] tested nano-catalysts suspended in heavy oil matrices containing vacuum gas oil (VGO) in oil sands at high temperature and pressure. This was done to ascertain the transport behavior of nanoparticles in oil-reservoirs during heavy oil recovery and upgrading. It was found that nanoparticles specifically, UD multimetallic nanoparticles, can be transported through oil sands porous media into heavy oil reservoir as catalysts for heavy oil upgrading. Similar effects have also been reported in literature [10, 43, 44, 112, 113].

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3.7. Thermal conductivity

The thermal conductivity of a material is an essential characteristic for evaluation of the heat conduction and transmission capacity of the specific material. Nusselt number usually denotes the resistance of a flowing fluid to the heat transfer since it directly considers the thermal conductivity of the fluid and indirectly by the Prandtl number. Interestingly, nanoparticle based fluids exhibits high thermal conductivity and large surface area than conventional base-fluids, although, the physical mechanism that accounts for its potential to enhance thermal conductivity is still not well understood [53, 113–115]. The thermal conductivity of conventional base liquid can be improved by addition of nanoparticles. The high surface area increases the thermophysical properties of nanoparticle based fluids and the small particle size enhances their potentials as absorber fluids as it has high potential of large surface coverage in heat transfer processes. Lee et al. [12], Choi [13] and Eastman et al. [14] reported that nanoparticle based fluids exhibits higher thermal conductivity with great dependency on factors such as the material type, size and shape, surface charge, particle volume fraction, the base fluid containing the particles and temperature.

3.8. Stabilization of viscoelastic surfactant (VES) fluids

Viscoelastic surfactant fluids are fluids composed of low molecular weight surfactants that create elongated micelle structures, which display viscoelastic behavior for fluid viscosity increase [116–120]. Huang and Clark [121] reported that the addition of small amount of nanoparticles to VES solutions leads to a pseudo crosslink between the nanoparticle and the VES micelles owing to charge attraction and surface adsorption, as nanoparticles have high surface area. The nanoparticle stabilizes the VES micelles even at high temperature conditions, while minimizing the VES fluid leakage potential in the porous media.

3.9. Control of formation fines migration

Formation fines migration can be controlled in the presence of nanoparticles to enhance reservoir productivity and oil recovery. Nanoparticles show great potentials as possible formation damage remediation measures, as they are capable of sticking fines together while holding them in place to prevent their movement in porous media. Huang et al. [120] showed that in fracture packing operations, nanoparticles coated on proppants exhibit great potentials in holding formation fines in the proppant fractures. The high surface forces of nanoparticles enable the attachment of the particles on the proppant surface during proppant fracturing pumping treatments. Movement of the formation fines to the near-wellbore region is hindered owing to the surface forces of the nanoparticles, which captures the formation fines as it migrates through the nanoparticle treated regions.

3.10. Viscosity and reservoir sweep efficiency improvement

Improving formation viscosity and sweep efficiency is of great necessity for efficient hydrocarbon flow so as to avoid poor oil, gas or water movement or distribution through the pore spaces. The addition of nanoparticles to injection water can increase contact with more swept zones and upsurge the formations sweep efficiency. Typically, the reservoirs pores are filled with hydrocarbons, the flow of water containing nanoparticles through such pores can control

the movement and swelling tendencies of the local clays and other formation fines therein. This will in-turn reduce the accumulation of formation-particles and pore throats plugging in the flow channels, which can enhance better water sweep efficiency and subsequent oil recovery [121]. Maghzi et al. [122] investigated the effect of nanoparticles on the rheological behavior of polymer in promoting oil recovery. The authors reported that the presence of low concentration of nanoparticles in the polymer suspension improved the viscosity of the system and the system exhibited better viscosity with much higher oil recovery potential than the polymer system without nanoparticle.

3.11. CO_2 storage and leakage inhibition

For several decades, the excessive use of fossil fuels has contributed immensely to the increase in the atmospheric concentration of greenhouse gases. Carbon capture and storage (CCS) [123–128] is considered the most direct carbon management strategy for long-term reduction of such greenhouse gases. However, the capturing and storage process of CO_2 in geological formations such as deep saline aquifers or depleted reservoirs pose potential leakage threats, which has raised several concerns about the feasibility and long-term storage fate of such CO_2. Interestingly, when reservoirs are primed with nanoparticle based fluids, the systems demonstrate potentials of improving storage efficiency and also inhibit CO_2 leakage tendencies thus providing containment security and storage capacity improvement. Al-Anssari et al. [129] investigated the influence of pressure on the wettability of calcites treated with and without nanoparticles in the presence of CO_2 to account for pressure variation with injection depth. An increase in pressure with increase in contact angle occurred for all surfaces tested which is attributed to an increase in intermolecular interactions between CO_2 and calcite, which increased significantly with increasing CO_2 density thus an implication of a reduction in structural and residual trapping capacities at reservoir conditions [126–128, 130–133]. At ambient condition, oil-wet calcite was weakly CO_2-wet (115° θa - 0.1 MPa and 323 K) and strongly CO_2-wet at storage conditions (148° θa - 20 MPa and 323 K) - the high contact angle is an indication of possibilities of CO_2 leakage. However, the CO_2-wet surfaces were significantly rendered water -wet (41° θa - 15 MPa and 323 K) upon exposure to nanofluids. Aminzadeh et al. [134] investigated CO_2 leakage prevention mechanism through nanoparticle application. The study proffers a remediation strategy where injection of nanoparticle dispersion into a leakage pathway after CO_2 escape has been revealed can create a passive barrier against CO_2 leakage whether driven by viscous forces such as pressure, or by buoyancy. Core floods test was performed to measure the flow pattern and pressure drop in which CO_2 or a CO_2-analogue fluid displaced brine with and without dispersed nanoparticles. The in-situ saturation distribution of the phases was captured in real time for cores positioned horizontally in a modified medical scanner, and the pressure gradient during displacement was measured using pressure transducers. CT scans was used to evaluate water saturation distribution along the core after injection of 0.1 PV n-octane with and without nanoparticles. Lateral CT scans with brine (2 wt.% salinity) as the initial fluid demonstrates non-uniform displacement front. In comparison, the system containing nanoparticle suspension depicts a more distinct and uniform front with slower displacement front and more uniform CO_2 saturation near the inlet and less gravity override. The authors emphasized that the dispersion of nanoparticles on or above potential CO_2 leakage paths such as faults, abandoned wells or

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fractures can allow the formation of CO_2/brine foam when CO_2 enters the path, which can avert the possibilities of leakage.

3.12. CO_2 Foamability, stabilization and mobility control

Surfactants have been used as a common approach for stabilizing CO_2 foams. CO_2-in-water foams permit the reduction of the mobility of CO_2 which upsurges better sweep efficiency. Despite the process efficiency, the key limitation with this process is that, constant regeneration of surfactant based foams is required for efficient process implementation. Nanoparticle is currently being used to stabilize CO_2 instead of surfactant owing to its unique chemical properties as it offers several advantages over bulk material especially with respect to stability. CO_2 injected with nanoparticle dispersion stabilizes nanoparticle foam, although, at a threshold shear rate, since high shear rates are usually connected with preferential flow through high permeability zones in typical field cases. This promotes the tendencies for the creation of self-guiding fluids that selectively reduces the mobility of CO_2 via foam generation in fractured and gravity override regions with rapid CO_2 flow, which normally contains less oil. In the presence of the oil, the foam breaks to facilitate high recovery via contact with the mobile CO_2. AttarHamed et al. [135] assessed nanoparticle size effect on foamability, foam stability, and synergistic effect. To evaluate the foam stability, a glassware test was conducted at ambient temperature and atmospheric pressure using amorphous hydrophilic silica nanoparticle with particle size ranges of 15, 70, and 250 nm (concentration: 0.1–1.0 wt.%) and alpha olefin sulfonate—AOS (anionic surfactant). The CO_2 foam behavior was assessed by injecting CO_2 into 400 ml prepared solution in a visual cell at a constant rate of 7.9 mL/min, thereafter, the foam volume and the break time were measured and the normalize foam height estimated using Eq. (9) and the synergistic effect were also evaluated. The authors reported that the particle size, concentration, and hydrophobicity have significant effect on foam stability. The silica nanoparticles displayed an antagonism effect on foamability with an initial foam height reduction irrespective of their particle sizes - 15, 70, and 200 nm. However, for the synergistic effect on basis of foam stability, only systems containing small size nanoparticles (15 nm) and low particle concentration (0.3 and 0.5 wt.%) displayed better effect in stabilizing CO_2 in water foams over 70 and 250 nm particle size and 1 wt.% concentration and improved CO_2 in water foams stability by 25% at an initial foam volume of 20%. On basis of the particles hydrophobicity, for high stability to be achieved, nanoparticles should be designed with efficient surface coatings for adequate hydrophobicity and formation of CO_2 in water foams.

$$\text{Normalized foam height} = \text{foam height}(t)/\text{foam height}\ (t = 0) \tag{9}$$

where, t is the time (minutes).

Similarly, Singh and Mohanty [136] reported that nanoparticle-surfactant solutions containing only about 0.3 wt.% nanoparticles significantly modified foam mobility ratio. The increase in nanoparticle concentration (0–5 wt.%) increased the mobility reduction factor from 4000 to 8700 and increased foam stability. It has also been experimentally proven that the presence of nanoparticle creates better foam stability than surfactant or VES fluids and even polymer, and improves mobility control; and efficient for enhancing oil recovery owing to high sweep efficiency and effective viscosity [137–142] (**Table 2**).

Nanoparticle (NP)	Nanoparticle concentrations	Dispersals/reagents	Tests	Oil/formation type	Results and remarks	References
SiO_2	100–200 mg L^{-1}	Fracturing fluid (FF)	Core flooding	Crude oil (43° API); Bauxite porous media	• Enhanced porous media wetting towards water-wet condition • Reduction of formation damage by 71% • Optimized fracturing fluid for operations and modified water relative permeability by 82%	[89]
Naked TiO_2, Fe_3O_4, Fe $(OH)_3$, Al_2O_3-coated TiO_2	0.5–100 mg L^{-1}	$FeSO_4{\cdot}7H_2O$; $NaHCO_3$; $FeCl_3{\cdot}6H_2O$; NH_4OH; $CaCO_3$; NaOH; HCl; NaCl; D1 water	Zeta potential		• Zeta potential exhibits great dependency on the nanoparticle concentrations in solution • Excessively high particle concentration can create unreliable results when in the diluted dispersion owing to multiple scattering and turbidity effects	[97]
SiO_2	150–600 ppm	Synthetic polyacrylamide (Flopaam 3630S); Colloidal dispersion gel (CDG) NaCl brine; Aluminum citrate (AlCit)	Core flooding	Sandstone cores	• No oil mobilization occurred in Berea sandstone cores in the presence of the SiO_2, and polymer alone as the capillary number based on differential pressure and viscosities associated with polymer and silica floods were below critical capillary number or oil mobilization threshold • Systems containing blends of hydrolyzed polyacrylamide (HPAM) and silica (300 ppm SiO_2 dispersed in polymer 600 ppm) and NaCl (0.5%) (600/300Si/0.5) yielded oil mobilization with a reduction in Sor (21–24%) on microscopic level and generated an oil bank on the macroscopic level	[149]
SiO_2	0.01–0.10 wt.%	$C_{20}H_{44}BrN$ surfactant; CO_2; D1 water	CO_2 foam stability and mobility control		• Blends of nanoparticle and surfactant promoted higher foam stability and better viscosity than the surfactant-stabilized foam alone • NPS solution exhibited better efficiency in mobility control than the surfactant stabilized foam	[143]
SiO_2	1–25 g/L	NH_4OH; HCl; n-heptane; Toluene; n-C7 asphaltenes; TEOS (tetraethyl orthosilicate)	Formation damage inhibition	crude oil (6.8° API, 6.9×10^5 cP viscosity)	• Increased effective permeability to oil • Promoted increase in the recovery factor by 11% • Enabled the inhibition of n-C_7 asphaltene aggregate growth especially nanoparticles with the high adsorptive capacity	[144]
TiO_2, ZrO_2, SiO_2	0.07–0.5 wt.%	Paraffin, HNO_3 or $C_2H_8N_2$; n-heptane; Toluene; asphaltenes	Asphaltene stability/	crude oil (19° API)	• Nanoparticles do not act as asphaltene precipitant in strongly acidic conditions rather as dispersant for enhancing asphaltene stability	[145]

Nanoparticle (NP)	Nanoparticle concentrations	Dispersals/reagents	Tests	Oil/formation type	Results and remarks	References
			precipitation inhibition		• TiO_2 exhibited better performance over ZrO_2, SiO_2 in stabilizing asphaltenes under acidic conditions, and contributed to a higher precipitation onset point	
SiO_2; Al_2O_3; SiO_2 with acid surface (SiO_2A)	1–4 wt.%	Tween 80 surfactant; distilled water; TEOS (tetraethyl orthosilicate); NH4OH; H_2SO_4	Viscosity reduction of heavy crude oil	crude oil (13° API; of 1.2×10^5 cP viscosity)	• Addition of nanoparticles reduced the asphaltene mean aggregate size and promoted adsorption of n-C_7 asphaltenes onto the nanoparticles dispersed in the nanofluid • Viscosity decreases with increase in the temperature of crude oil; and increase in nanofluid concentration in the mixture enhanced higher degree of viscosity reduction • Significant reduction in viscosity (>90%) of heavy oil by addition of active component - SiO_2A nanoparticles	[69]
ZrO_2; NiO	0.004–0.05 wt. %	NaCl brine; D1 water; C_{16}TAB and TX-100 Surfactant	Contact Angle/ spontaneous imbibition	Toluene; limestone	• Nanoparticle based systems act as novel surface-modifiers with better impact in promoting formation wetting. Water contact angle decreased with increase in time, concentration, salinity, surface roughness and temperature in the presence of the nanofluids • Surfactant - nanoparticle systems (ZrO_2/C_{16}TAB; NiO/ C_{16}TAB; ZrO_2/TX-100; NiO/TX-100) exhibited faster water imbibition capabilities and wetting potential than the surfactant system alone (C_{16}TAB and TX-100)	[23, 24, 31]
SiO_2	0.005–0.1 wt.%	NaCl brine; D1 water	Core flooding	Limestone cores	• Particle size influences porous media retention and transport behavior; SiO_2 with small particle size promote efficient penetration through the porous media • Nanoparticle transport can be negatively impacted by salinity owing to screening effect of salts on the repulsion forces between particles in the injected fluid which can lead to particle clustering or large agglomeration effect • Retention of the nanoparticles can be significantly reduced with temperature increase due to the surface charge changes between the SiO_2 and carbonate surface	[148]
SiO_2	0.1 wt.%		Spontaneous imbibition	Dehydrated crude oil and kerosene	• Nanofluid systems demonstrated higher recovery potential than alkaline water and NaCl solutions	[146]

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Nanoparticle (NP)	Nanoparticle concentrations	Dispersals/reagents	Tests	Oil/formation type	Results and remarks	References
		alkaline water (pH 10), and NaCl brine			• Higher displacement efficiency and ultimate oil recovery was attained in the presence of nanofluid • Nanoparticle based systems recovered approximately 38% of oil within 12 days, whereas, alkaline water and NaCl solution recovered only about 12 and 6% of oil respectively	
SiO_2	0–2 wt.%.	CTAB, SDS, double distilled water	Surface tension, foamability, and foam stability		• Pure hydrophilic SiO_2 in the absence of surfactants have no effect on the surface tension/surface elasticity at air-water interface • Surface activity of the surfactant is increased significantly with increase in the nanoparticle concentration • The foam stability and foamability is greatly improved with more stable foams achieved in the presence of nanoparticles than pure surfactant solution alone	[147]

Table 2. A selection of published studies on the effect of nanoparticle based systems on process efficiency.

4. Conclusion

In hydrocarbon reservoirs, fluid–rock interactions are predominant occurrences owing to the existence of surface forces between molecules. The presence of oil, water and even gas is an indication that concurrent flow of fluids at the production stage of a reservoir often occurs. Fluid displacement in reservoirs, especially when more than one fluid is involved can contribute to poor oil recovery as the oil gets trapped owing to factors such as IFT between fluids, fluids immiscibility and rock surface wetting challenges. The role of nanomaterial in addressing these issues have been evaluated; the material displays great potentials as excellent particles for the design and formulations of smart fluids for applications in high temperatures-high pressures regions. The surface functionalities and excellent properties of nanomaterial such as their enhanced thermal conductivity and stability, unique particle size, high surface area, great adsorption affinity, and unique transport behavior in porous media influences their superior efficiency over the micros and macros bulk counterpart even under harsh reservoir conditions. Nanoparticles show great potentials as effective novel tools for permeability enhancement; IFT reduction, rock wettability alteration from oil-wet to water-wet, oil mobility and recovery enhancement, and CO_2 stabilization. The study identifies a prime characteristic of nanoparticles in EOR, which is its ability to improve the property of the dispersal even at low particle concentrations in the suspensions owing to high dependency on the materials unique properties. The addition of nanoparticle changes the rheological property of the fluid and the particles in suspension enhanced the performance of the carrier fluid during production and inhibits any associated formation damage. Thus nano-smart fluids are highly recommended for EOR project design as potential stabilizer of dispersed systems for hydrocarbon production augmentation, CO_2 geo-storage, and soil de-contamination processes.

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