Review Paper

Effects of nanoparticles on wettability: A review on applications of nanotechnology in the enhanced Oil recovery

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ABSTRACT: Recently, a renewed interest arises in the application of nanotechnology for the upstream petroleum industry. In particular, adding nanoparticles to uuids may drastically beneut enhanced oil recovery and improve well drilling, by changing the properties of the ûuid, rocks wettability alteration, advanced drag reduction, strengthening the sand consolidation, reducing the inter-facial tension and increasing the mobility of the capillary trapped oil. In this study, we focus on roles of nanoparticles on wettability. This paper therefore focuses on the reviews of the application of nano technology in chemical flooding process in oil recovery and reviews the application nano in polymer and reviews the application n surfactant flooding on the wettability process.

Keywords: *Chemical flooding; Enhanced Oil recovery; Nano particles; Nanotechnology; Wettability. particles; Nanotechnolog*

INTRODUCTION

Most of the oil uelds around the world have reached
will reach soon the phase where the production rate or will reach soon the phase where the production rate is nearing the decline period. Hence, the current main challenge is how to delay the abandonment by extracting more oil economically. The latest worldwide industries innovation trends are miniaturization and nanotechnology materials. Nanotechnology is deûned as the construction of functional materials, devices, and systems by controlling matter at the nanoscale level (one-billionth meter), and the exploitation of their novel properties and phenomena that emerge at that scale [1]. Nanouuid technology, as a part of nanotechnology, is a new interdisciplinary area of great importance where nanoscience, nanotechnology, and thermal engineering come across. It has developed largely over the past decade and revealed its potential applications in oil and gas industries [2]. Various nanofluids can be designed by the addition of nanoparticles to different base fluids. The stability or dispersion of nanoparticles in solutions relies on the functionality (or surface activity) of the nanoparticles. Extrained 10 June 2015; revised 30 August 2015; accepted 10 September 2015; available online to Pecember 2015, and an and the upstream CF Pecember 2015 and the particular, adding nanoparticles to unids may drastically bene

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Nanotechnology in the petroleum industry has Nanotech gained enormous interest the recent years [3]. Kanj *et* gained en *al.* [4] identified the usable size of nanoparticles in [4] reservoir rocks through Nano-fluid core flooding experiments. Adding nanoparticles to fluids may e significantly benefit enhanced oil recovery and improve well drilling, such as changing the properties of the fluid, wettability alternation of rocks, advanced drag reduction, strengthening sand consolidation, reducing the interfacial tension and increasing the mobility of the capillary-trapped oil [5]. In the past decade, most investigations have shown that nanoparticles (NPs) ouer promise for future enhanced oil recovery (EOR) processes where silica-based NPs have been most commonly used [6-10]. Although the oil displacement mechanism via NPs is not yet clearly understood [11- 13]. The nanotechnology is now chosen as an alternative method to unlock the remaining oil resources and applied as a new enhanced oil recovery (EOR) method in last decade [2, 7, 8 and 14-17]. polymeric micro-spheres and nanospheres have been applied as water mobility control both as a pilot and full-ueld, and showed fantastic results in reducing water cut, increasing sweep efûciency and improving oil recovery [18-20]. Also, Tian *et al.* reported that polymeric microspheres and nanospheres can swell when meet with water and then reduce water permeability due to its ability of reducing the capillary force and change water ûow path. Consequently water goes into bypassed area and enhances displacement efûciency. They also reported that polymeric microspheres and nanospheres have some advantages such as no degradation at high temperature and salinity. Some papers also address experiments where combinations of nanoparticles and surfactant solutions are tested. Li *et al.* studied synergistic blends of SiO₂ nanoparticles and surfactants for EOR in hightemperature reservoirs.

Hamedi Shokrlu and Babadagli, investigated the effects on nano metals on viscosity reduction of heavy oil and bitumen for thermal oil recovery applications. Based on their obtained results, various parameters such as nano particle types, size and concentration could affect on the mechanism of the viscosity reduction of heavy oil/bitumen [21]. In addition to previous applications of nanotechnology in petroleum upstreams, enormous researches have been made on the title of implementing of nano-particles on the enhanced oil recovery (EOR) from petroleum reservoirs [22]. Hence, in some studies the applications of nanoparticles in oil industry have been reported and classiûed based on priority. So, researchers have concluded that nanotechnology has the greatest usage in chemical EOR methods [23]. Therefore, in some studies, the role of nanoparticles in EOR operations has been reported [24-26]. Subsurface applications of nanotechnology seem to be promising in modifying and monitoring reservoir properties, such as wettability and interfacial tension between rock and ûuids. For instance the capability of $SiO₂$ nanoparticles to alter the wettability of reservoir rock and reduce the interfacial tension between crude oil and brine phases has recently been actively investigated to find implementation in enhanced oil recovery (EOR) [27]. e reservoirs.
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The objective of this paper is to investigate the potential of Nano particles in chemical flooding for oil recovery. This study reviewed and assessed some of the recent advances. Specifically, it aims to explain the contributions of Application Nano in the Polymer and Surfactant flooding on the Wettability process.

Chemical flooding

Oil production has three different stages; primary (production by natural reservoir energy), secondary (on the supply of external energy into the reservoir in the

form of injecting fluids to increase reservoir pressure) and tertiary production (enhanced oil recovery methods increase the mobility of the oil in order to increase production). Chemical injection or usually known as chemical flooding was, up to 2000's, less common EOR method than thermal and gas but now, huge projects are initiated or revisited. This involves injection of three kinds of chemicals that are alkaline, surfactant and polymer. Each chemical has unique functions and usually isused coincide. Three methods involving these chemicals are polymer, surfactant-polymer (SP) and c alkaline-surfactant-polymer flooding (ASP), and surely the most important substance in these methods is polymer [28].

Polymer

Polymer ûood is the most widely used chemical EOR method. By adding polymers to water, the water–oil By adding polymers to mobility is lowered. Such a change can lead to better sweep efuciency. It is generally believed that polymer ûooding cannot reduce the residual oil saturation, but ûooding cannot reduce it can help to reach residual oil saturation in shorter time [29]. time

Polymer flood was proved technically and economically successful in many EOR projects economica worldwide [30-31]. In ueld applications, polymer worldwi uoods increased recovery by 12–15% [32]. The ueld uood experiences in China showed that polymer ûood was ex cheaper than water uood, due to increased oil output and reduced costs in water injection and treatment [33]. Currently, polymer ûooding is considered as one of the most promising technologies in EOR process because of its technical and commercial feasibility. Particularly, the interest on polymer uooding applications worldwide has been stimulated by the outstanding results reported from the large-scale polymer flooding application in the Daqing oil ueld in China, with incremental oil productions of up to 300,000 barrels per day [34].

In practice, two commercial polymers, hydrolyzed polyacrylamides (HPAM) and xanthan gums, are commonly used in oil field applications. HPAM is a water-soluble polyelectrolyte with negative charges on the polymer chains. Xanthan gums, which are polysaccharides, show excellent viscosifying ability, high tolerance to salinity, and temperature [35].

However, the current widely used polymers, polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM), cannot completely meet the requirements due to the hydrolysis, degradation, and others under high temperature or high salinity [36]. Furthermore, PAM and HPAM have poor shear resistance [37-40]. Polymer molecular chains will be cut oû when polymer solution passes through the pump, pipeline, perforation, and porous medium at high speed, so the viscosity of polymer solution will be greatly reduced [40-41]. Polymer viscosity was seriously affected by salinity. The effect of shearing on polymer viscosity and oil recovery was significant. Thus, high concentration of polymer was utilized to maintain high viscosit [42].

Surfactant

The surfactant-based chemical flooding processes are normally employed to recover the trapped, residual oil after the waterflooding. Numerous patents exist on evaluating different factors, which may affect the performance of these processes [43].

Surfactant ûooding is one of the main mechanisms of reducing interfacial tension between oil and water for the purpose of enhancing oil recovery. Essentially, two different approaches have been developed for using surfactants to enhance oil recovery.

In the ûrst approach, a solution containing a low concentration of surfactant is injected. The surfactant is dissolved in either water or oil and in equilibrium with aggregates of the surfactant known as micelles. Large pore volumes (about 15–60% or more) of the solution are injected into the reservoir to reduce interfacial tension between oil and water and, thereby, increase oil recovery. Oil may be banked with the surfactant solution process, but residual oil saturation at a given position in the reservoir will only approach zero after passage of large volumes of surfactant solution. In the second approach, a relatively small pore volume (about $3-20\%$) of a higher surfactant concentration solution is injected into the reservoir. The high surfactant concentration allows the amount of dispersed phase in the micro emulsion to be high as compared with the low value in the dispersed phase of the micelles in the low concentration surfactant solutions. The infected slug is formulated with three or more components. The initial components (hydrocarbon, surfactant, and water) are sufucient to form the micellar solutions. A co-surfactant as the fourth component (usually alcohol) can be added. Electrolytes, normally inorganic salts, form a ufth component that may be used in preparing the micellar **Archain the statistic of the statistic of the statistic or the statistic or distinguish (yerm) yerm) by employed to recover the trapped, residual manoparticles in an aqueous phase computer and water in our metric and wate**

solutions or microemulsions. The high concentration surfactant solutions displace both oil and water. As the high concentration slug moves through the reservoir, it is diluted by the formation's uuids and the process reverts to a low-concentration uood. There are numerous mathematical modeling and experimental studies of various aspects of surfactant uooding in the literature [44-50].

Le and his colleagues performed experiments blending different types of surfactants with $SiO₂$ nanoparticles. Some of the blends showed great potential for EOR application because of their resistance to adsorption onto the rock surface, and thermostability at 91°C [51]. Suleimanov *et al.* carried out experiments which showed how dispersed nanoparticels in an aqueous phase could modify the interfacial properties of a liquid/liquid system, if their surface were modiued by the presence of an ionic surfactant. The application of nanosuspension in their study permitted signiûcant increase in the effciency of oil displacement uow rate. In homogeneous pore media, oil displacement uow rat oil recovery before water breakthrough was increased oil recovery before w by 51 % and 17 % for surfactant aqueous solution with nanoparticle addition respectively to water and nanoparticle surfactant aqueous solution [52].

Surfactant–polymer Surfa

Surfactant–polymer (SP) uooding processes involve the injection of a surfactant–polymer slug followed by a polymer buffer and chase water injection. If designed correctly, the surfactant increases the capillary number, which is crucial for the mobilization and recovery of tertiary oil. Polymer increases the sweep efuciency by lowering the mobility ratio. If the reservoir crude oil has sufucient saponiuable components, soap (surfactant) is generated in situ by the reaction of these components with the injected alkali, thus adding more surfactant to the uood [53]. Surfactant-polymer interactions in solution are important with regard to the flow behavior in the porous media and the potential to displace the oil [54, 55]. Furthermore, the surfactantpolymer interaction at the solid/liquid interface is extremely important with respect to the loss of chemicals by adsorption onto the minerals of the rock material. The loss of surfactant by adsorption is one of the main factors prohibiting, on economic grounds, the use of surfactants in field applications. In recent years, much attention, both experimen tal and theoretical, has been focused on surfactant- polymer

interactions in solution, and several reviews have been published [56-59]. Alkali free SP uooding avoids the drawbacks associated with alkali. Surfactants with concentrations higher than the critical micelle concentration (CMC) can achieve ultra-low IFT. However, such surfactants are expensive. The use of a hydrophilic surfactant mixed with a relatively lipophilic surfactant or a new surfactant was also investigated [60-62]. However, studies on SP uooding only focused on the screening and evaluation of the polymer and surfactant and their interaction. Reduction in mobility ratio and IFT is inuuenced by reservoir brine salinity, reservoir temperature, concentration of chemical ingredients an oil components, and others [63-66].

Wettability

Wettability is defined as the tendency of one fluid to spread on, or adhere to, a solid surface in the presence of other immiscible fluids. This is a major factor controlling the location, flow, and distribution of fluids in a reservoir. Many investigations of wettability and its effects on oil recovery have come to the conclusion that there is a favorable reservoir wettability for operators to recover maximum crude oil from a given subterranean reservoir [67-77]. Also, wetting properties are fundamental for the understanding of multiphase flow in all aspects of oil formation and production, and can affect the production characteristics greatly during waterflooding. Due to this importance, many reviews of wettability and its effect on oil recovery have been published [78-79]. The wetting properties of a reservoir are determined by the interactions between rocks and fluids. The type of minerals, pore size distribution and pore surface area are believed to be important, as well as fluid composition and temperature. The wettability can vary from strongly water-wet to strongly oil-wet [80].

Effects of nanoparticles on Wettability

In recent years there has been an increasing interest in application of nanotechnology in petroleum industry. Reservoir engineering, however, have received the most attention for nanotechnology applications. Nanoparticles have been implemented in different enhanced oil recovery processes. Wettability alteration effects and considerable oil recovery were observed for hydrophilic poly-silicon nanoparticles [81]. Yu *et al.* [82] introduced iron-oxide cored particles with paramagnetic properties as potential EOR agents of

which the behavior can be controlled by imposing an external magnetic ueld. Onyekonwu and Ogolo [83] studied capability of three different polysilicon nanoparticles as an agent for wettability alteration and oil recovery purposes. Skauge *et al.* investigated the oil mobilization properties of nano-sized silica particles and discussed the underlying mechanism of microscopic uow diversion by colloidal dispersion gels. Surface-coated silica nanoparticles have been used to stabilize both water-in-oil and oil-in-water emulsions (2010). Hendraningrat performed several experimental studies to investigate oil recovery using hydrophilic silica nanoparticle injection. Both secondary and tertiary processes were evaluated. Also Hendraningrat et al. determined the optimum nanoparticle concentration range for enhanced oil recovery purpose in low permeability sandstone reservoirs. Polysilicon nanoparticles (PSNP) have been considered as an EOR agent by Onyekonwu and Ogolo. One important by Onyekonwu and O characteristic of polysilicon nanoparticles is its ability to change rock wettability. Onyekonwu and Ogolo to change rock wettabi discuss three different PSNP which alter the rock discuss three differ wettability in different manners. Their results showed that silane treated NWPN, and hydrophobic and lipophilic polysilicon nanoparticle (HLPN) which is lipophilic p treated by a single layer organic compound, had an b improvement of over 50 % after primary and secondary impro recovery on a water-wet rock [83]. Ju and Fan address re the challenges relating to the application of nanopowder in oilûelds to enhance water injection by the effect of changing wettability through adsorption on porous walls of sandstone. Their result revealed that wettability of surface sandstone can be changed from oil-wet to water-wet by adsorption of untreated polysilicon nanoparticle, lipophobic and hydrophilic polysilicon nanoparticle (LHPN). Furthermore, the sandstones' effective permeability of water was improved, while a decrease in absolute permeability was observed [81]. FT is inuuenced by reservoir brine salinity,
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> In Roustaei and Bagherzadeh work, the impact of SiO₂ Nanoparticles on the wettability of a carbonate reservoir rock was experimentally studied. Accordingly, $SiO₂$ Nanoparticles are wettability modiuers for carbonate systems, and they can change the wettability of carbonate rocks from strongly oilwet to strongly water-wet condition [84].

> Safari [85] investigated the effect of different concentration of lipophobic-hydrophilic polysilicon nanoparticles (LHPN) on rock surface. he used

carbonate rocks in our experiments. The contact angle between oil droplet and rock surface was measured. Finally, results showed that the hydrophilicity and wettability will be increased with increasing nanoparticle concentration and also cores saturated with oil and water were initially mixed-wet, and nanoparticles injection made them water-wet. Water wettability increases at higher concentrations. The SEM image of the carbonate core after and before injecting with nanoparticles is shown in Fig. 1a and b. The pictures are taken with 10000 magnifications.

Fig. 1: (a). SEM images of carbonate cores before injecting with nanoparticles suspension, (b). SEM images of carbonate cores after injecting with nanoparticles suspension [85].

Nanoparticles have properties that are potentially useful for certain oil recovery processes, as they are solid and two orders of magnitude smaller than colloidal particles. The nanoparticle stabilized emulsions droplets are small enough to pass typical pores, and ûow through the reservoir rock without much retention. Spherical

fumed silica particles with a diameter in the range of several to tens of nanometers are the most commonly used. Their wettability is controlled by the coating extent of silanol groups on the surface, and are considered to be hydrophilic if over 90 % of the surface is covered by silanol groups. With these hydrophilic properties, they will consequently form a stable oil-in-water emulsion. Conversely, if the silica particles are coated with only 10 % of silanol groups on the surface, they are hydrophobic, and will form a water-in-oil emulsion [86]. The wettability of a formation can be changed by nanoparticles. The use of nanoparticles to alter rock nanopa wettability and its following effect on oil recovery has been published by several authors [81, 83, 87]. Ju *et* al. reported nanometer polysilicon materials that could change the wettability of porous surfaces. Polysilicon, of which $SiO₂$ is the main component, is obtained by adding an additive activated by γ -ray to form a kind of modified ultra-fine powder with particle size ranging from 10 to 500 nm [88].

om 10 to 500 nm [88].
A reason for uuid uow behavior during nanosurfactant uooding is the adsorption of ZrO_2 nanoparticles onto medium surface and their ability to nanoparticles ont change the surface wettability from oil-wet to waterwet. It is obvious that, among the many features wet. It is affecting the ûuid distribution and oil recovery in affectin porous media, wettability is proven to be a crucial porou factor [89, 90]. Because of wettability alteration from fa oil-wet to water-wet by silica nanoparticles, oil recovery after dispersed silica nanoparticles in polyacrylamide solution uooding caused more of the pore space to become saturated with the dispersed silica nanoparticles in polyacrylamide solution resulting in 10% higher oil recovery than after polymer uooding.

In polymer ûooding, adding silica nanoparticles to polymer solution can be an acceptable method to enhance oil recovery because besides increasing sweep efûciency by means of polymer, nanoparticles which are present in polymer solution can alter the surface wettability. The ûuid behavior in porous media, especially in the wall of pores and throats shows medium wettability of the surface by the dispersed silica nanoparticles in polyacrylamide solution. In parts, the polymer phase has been trapped and oil on the wall of pores and throats has remained and the surface remains oil wet. In some parts, where the polymer phase existed on the wall of pores and throats, no significant oil is existent in pores and throats, and water-wet wettability is dominant [91].

Multi walled carbon nanotube (MWCNT)-Silica nanohybrid structures are very suitable material for enhanced oil recovery in order to their excellent interfacial activity. In the O/W interface, they could change the oil properties to mobilize the oil in the reservoir. The effect of nanouuid include MWCNT– Silica nanohybrid on the wettability of carbonate and sandstone rocks was investigated by Ershadi *et al.*. Results were shown that the nanouuid can signiucantly change the wettability of the rock from oil-wet to waterwet condition.

Fig. 2a and b show the XRD pattern and FE-SEM image of SiO₂ nanoparticles respectively and Fig. 2c and d show the XRD pattern and SEM image of MWCNT–SiO₂ nanohybrid respectively [92].

Modiûed silica nano ûuid improved oil recovery through major mechanisms of interfacial tension reduction and wettability alteration toward oil-wet condition. Based on contact angle and interfacial experiments, the concentration of 3 g/L showed a signiucant share of interfacial tension reduction and high capability in the transformation of wettability toward oil-wet condition. It was considered as the optimum concentration and was employed in coreuood experiments for both light and intermediate oil systems. Modiued silica nanoparticles are more capable in the reduction of interfacial tension and the alteration of wettability in the case of light oil reservoir [8].

Experimental unsteady state displacement tests of water/water saturated by dispersed nanopartcles-light crude oil systems were performed on a sandstone core sample and relative permeability curves of both water and oil phases were determined for two successive cycles of both imbibitions and drainage processes. Based on the results Nano-Particles additives have more effect on changing the non-wetting phase relative permeability curves than the wetting-phase [93-95]. The nanoûuids change the rock wettability from water wet to neutral wet state and decrease oil-water interfacial tension [96]. γ -Al₂O₃ nanoparticles (Fig. 3) can be considered as an effective agent in the changing the wettability of carbonate rock surface from oil-wet he wettability of carbonat to water-wet. Fig. 1 shows the construction of nanostructures on the rock surface, which changes the nanostructures on th wettability to water-wet conditions [97].

Fig. 2: (a and c) XRD patterns of SiO, nanoparticles and MWCNT–SiO, nanohybrid respectively (b and d) FE-SEM images of SiO₂ nanoparticles and MWCNT–SiO₂ nanohybrid respectively [92].

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Fig. 3: SEM images γ -Al₂O₃ nanoparticles adsorption on calcite surface with a magnification of (a) 1000 and (b)

CONCLUSION

A review of the effect of NPs on wettability for enhanced oil recovery processes have been presented. Several cases as well as laboratory studies were discussed. Nanotechnology has the potential to have a positive effect on the chemical EOR process. The aims of this paper were firstly to compilean up-to-date data base for wettability with NPs projects reported in the literature over the last 15 years. Altogether, nanotechnology can be an effective enhancement option for an oil recovery method in a oil reservoir which is technically sensitive to the chemical recovery method. Although the future of nanotechnology is completely uncharted territory, but certainly nanotechnology will
revolutionize the oil industry in several important ways. revolutionize the oil industry in several important ways. **EXERCT:** Content of the Content of the Content of the SIC is $\frac{1}{2}$ Nanoparticles adsorption on calcite surface with a magnification of (a) 1000 and (b) 5000 [97].
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