The Influence of Nano Fluid Compared With Polyethylene Glycol and Surfactant on Wettability Alteration of Carbonate Rock

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Abstract: The purpose of this research is to enhance oil recovery of the carbonate rock by wettability alteration using silica suspended in brine, polyethylene glycol (PEG), and sodium dodecyl sulfate (SDS). Hydrophilic silica with a different mean Nano size 52, 65 nm was synthesized from local sand by a chemical method. The synthesized Nano silica was characterized by AFM to determine the average particle size and distribution, and surface area was measured by physical adsorption of nitrogen. The wettability alteration was studied by dipping the carbonate rock in different concentrations of Nano silica (0.01-1wt. %) for a certain silica size suspended in brine for different dipping times as well as for PEG and SDS. The contact angle was measured before and after each run in order to recognize the extent of affinity change (wettability) of the carbonate. The results showed that the Nano particles were more reactive due to their high surface area these particles had the highest potential for wettability alteration. The contact angle decreased with decrease particle size and increase concentration. The PEG polymer and SDS surfactant showed less influence on wettability alteration compared with Nano fluids.

Keywords: Carbonate; EOR; Nano Silica; Wettability alteration

1. Introduction

The importance of Carbonate (Limestone and dolomite) reservoirs constitutes one of the largest sources of crude oil supply in the world now a day, for enhancing oil recovery, industry focused on finding new and alternative technology to increase production of oil at less cost and environmental friendly. Nanotechnology in the petroleum industry has gained enormous of interest the recent years. The wide spectrum of environments in which carbonates are deposited and subsequent diagenetic alteration of the original rock, causes heterogeneity in carbonate reservoir [1]. Furthermore, Heterogeneous wettability drastically affects the macroscopic characteristics and transport properties. Also, related to heterogeneous permeability, in which role the flow properties [2]. Reduction in the oil production in carbonate reservoir caused due to reservoir heterogeneity (different permeability zones, channels and fractures) [3]. Viscosity and density differences between injected and connate fluids can cause injection fluid fingering deep in the reservoir during the sweep process causing the water production [4]. The wetting properties of carbonate reservoirs are fundamental to the understanding of fluid flow through the porous media, and can affect the production characteristics greatly during water flooding. So, knowledge of the preferential wettability of reservoir rock is of upmost importance to researchers (Okasha, Funk, and Rashidi 2007).
In Iraq, Mishrif Formation characterized by high degree of heterogeneity formation (Porosity of the formation is up to 22%, and permeability ranges from 23 to 775 md). Originally described as organic detrital carbonate with beds of algal, rudist, and coral-reef carbonate, capped by limonitic fresh water limestone [5]. Enhanced oil recovery (EOR) is a common term for tertiary recovery methods that increase the quantity of produced crude from a reservoir after conventional methods of recovery. There are many types of EOR techniques that can be used to improve oil Recovery through the application of heat, chemicals or solvents after primary and secondary recovery have been deployed [6]. Nano-fluid may significantly benefit enhanced oil recovery and improve well drilling, such as changing the properties of the fluid, wettability alternation of rocks, advanced drag reduction, reducing the interfacial tension and increasing the mobility of the capillary-trapped oil[7]. Nanoparticles can travel easily through a reservoir so long as they do not aggregate and/or agglomerate to form larger structures or adsorb unto the rock surface due to its small size (1-10nm) compared with reservoir channel in micrometers as size[8].

[9] showed that an increase in concentration of bismuth telluride nanoparticles increased the contact angle, until it reached a peak, where it decreased again. [10] investigated the influence of zirconium (IV) oxide (ZrO₂) and nickel (II) oxide (NiO) nanoparticles on the wetting fractured limestone formations and conclude that ZrO₂ is very efficient in terms of inducing strong water-wettability; and ZrO₂ based Nano fluids have a high potential as EOR agents. (Cankara 2005) investigated Oil/water relative permeability, effect of polymer injection on end point relative permeability and residual oil saturations in carbonate reservoirs, where relative permeability increased when polymer solution was used as the displacing phase. Besides, end point hexane relative permeability increased with polymer injection and fracture presence. [12] investigated the effectiveness of Nano fluids of silane coated silica nanoparticles as in situ reservoir agents. They found that Nano fluids of silane coated silica can affect wettability change toward a more water wet state. Around 2 g/L as the optimal concentration for affecting wettability change. [13] investigated the possibility of nanoparticles to be of substantial benefit to EOR, conducted using two metal oxide nanoparticles (zirconium oxide and nickel oxide). The study identified a prime characteristic of nanoparticle in EOR, its ability to improve the property of the dispersal, and its capacity to significantly alter reservoir rock surface towards water-wet conditions, enhanced carbon geo-sequestration, and soil decontamination processes.

In the present work, it was studied the effect of Nano fluids, polymer, and surfactant on wettability alteration of carbonate rock. Nano silica was prepared from local sand and characterized by AFM and physical adsorption of nitrogen molecule. The Wettability alteration of carbonates was detected after treatment with Nano fluids of silica with different concentrations (0.01-1wt. %) in brines (5-20 wt. %.) as well as in polyethylene glycol (PEG) and surfactant (SDS). The contact angle was measured to indicate the effect of wettability alteration.

2. Experimental work:

2.1 Chemicals
Carbonate Rock from mishrif formation-Iraq and Deionized water (1.000 g/ml) was used. Sand was supplied from Al-Anbar-Iraq with 99% silica oxide; Sulphuric acid 98%, Barium chloride 99% anhydrous, and Nano silica (5-15nm) purity 99.99% were supplied from sigma Aldrich. Sodium dodecyl sulfate 98% from Himedia Company, sodium chloride 99.5% from alpha company, and Sodium hydroxide were supplied.

2.2 Preparation of Nano silica
Sand was crashed by ball miller and sieved to 47µm and 37µm. 40 g from each size was mixed with 100g sodium hydroxide. The two samples heated to 500 °C for 30 min. where sodium hydroxide melts coated the sand particles, making the mixture a greyish/white color of The Sodium Silicate as shown in equation (1), then samples cooled to room temperature.
\[ 2NaOH(l) + SiO_2(s) \rightarrow Na_2SiO_3(s) + H_2O(g) \]  \hspace{1cm} \text{… (1)}

Distilled water was added with mixing until sodium silicate completely dissolved, where salicylic acid and sodium oxide formed as shown in equation (2).

\[ 2Na_2SiO_3(s) + 4H_2O(l) \rightarrow 2H_4SiO_4 + 2Na_2O \]  \hspace{1cm} \text{… (2)}

The solution was acidified (pH=1) to precipitate Nano silica by addition of concentrated sulfuric acid. Coagulated Nano silica was separated from the solution by vacuum filtration and then washed with distilled water to remove sulfate ions which controlled with 6% BaCl_2 solution. The separated cake was dried in oven at 100°C for 48hr.

2.3 Preparation of fluids

2.3.1 Brine fluid.

A brine fluid was prepared with different concentrations of sodium chloride (5, 9, and 20 wt. %). A certain amount of salt was added to 100ml of distilled water with stirring until salt completely dissolved.

2.3.2 Nano fluid.

Nano fluids were prepared in two-steps. First, a certain amount Nano silica was added to of a brine fluid (pH 8.6) under mixing condition to obtain concentration from 0.01 to 1wt. %. Second, suspended silica was subjected to sonication using an ultrasonic mixer for 15 min. with high energy to avoid agglomeration.

2.3.3 Polymer and surfactant solutions.

Polyethylene glycol and SDS solutions were prepared by dissolving under mixing condition with a certain amount of brine fluid (9wt. % NaCl) to obtain concentration from (0.1 to 5 wt. %) and (0.01-5wt. %) for polymer and surfactant respectively.

2.3.4 Preparation of carbonate rock.

Slices of carbonate rock were prepared by cutting and polishing, and then dried at 100 °C for 1hr. The carbonate slices as shown in figure (1) were dipped in a 20 ml of different Nano fluid concentrations (0.01-1wt. %) for dipping time range 1-4h under vacuum circumstance. Then slices were dried at 100°C for 1 hour. The same procedure was applied in case of PEG and SDS.

2.4 Nano silica characterization
2.4.1 Atomic Force Microscope (AFM).

The Atomic Force Microscope (AFM) allows for 3D characterization of nanoparticles with sub-nanometer resolution. Nanoparticle characterization using Atomic Force Microscopy has a number of advantages over dynamic light scattering, electron microscopy and optical characterization methods. A 3D rendering type of the surface topography was presented in Fig. 2a and 2b respectively with good resolution scan was achieved for a surface of 3051.48nm × 1550.41nm for sample 1, as it has smaller nanoparticles and of 1606.8nm × 1611.44nm for sample 2.

![AFM 3D images in topography](image1.png)

(a) (b)

**Figure 2.** AFM 3D images in topography for (a) avg. particle size 65nm (b) avg. particle size 52nm

Using data from the image analysis software module, a histogram of the nanoparticle distributions was calculated as shown in figure 3. Figs. 3a and 3b showed that the average particle size was 65nm and 52.4nm for sample 1. Also showed that the particle size distribution is not quite a perfect Gaussian line, where the smaller number of objects that were present on the surface and were therefore subject of the statistical analysis.

![Granularity Cumulation Distribution Chart](image2.png)

(a) (b)

**Figure 3.** relative size distribution built up from AFM image for (a) sample 1 (b)

2.4.2 Accelerated Surface Area and Porosimetry System.

The Micromeritics ASAP 2020 Plus integrates a variety of automated gas sorption techniques into a single as shown in figure (4). The system provides high-quality surface area, porosity, chemisorption and physisorption isotherm data to materials analysis laboratories with ever-expanding analytical requirements. Physical adsorption of nitrogen molecules on a solid surface analysis was applied for the measurement of the specific surface area of prepared Nano silica. For silica particle
size 52nm, the Surface Area: 474.9429 m²/g also Nano silica with 65nm have surface area of 440m²/gm,

2.5 Wettability alteration test
Theta Lite optical tensiometer is a compact and accurate contact angle meter for simple measurements of contact angle and surface free energy as shown in figure (4). It also measures surface and interfacial tension. Wettability was evaluated by measuring contact angle between water drop and rock slice in synthetic brine for several systems. The contact angle measurements were repeated as mentioned before and supreme variation between the measured data for each case was about 10°; thus contact angle data contain a maximum error of ±5°.

Figure 4. optical tensiometer instruments

3. Result and discussion

3.1 effect of Nano fluid
Porous rocks saturated with more than one liquid are a complex system of constant interactions between all existing liquids and between liquids and rock minerals. Wettability is the tendency of the liquid to spread to a solid surface in the presence of another immiscible liquid. This is due to the interfacial tension between the current fluid phases and their individual adhesion to the solids. The wettability of the pore wall depends on the chemical composition of the liquid and the composition of the rock metal.

The oil/water contact angle for oil-wet rock slice before the employment of Nano fluid was about 119° as shown in Figure 5a, which proved oil-wet conditions. On other hand after treatment of sample with Nano fluid (0.065wt.%) contact angle significantly reduced as shown in figure 5b

Figure 5. Tensiometer image (a) water drop on rock slice before treatment (b) water drop on rock slice after treatment with Nano-fluid 0.065% Nano silica
Figure 6 showed direct proportion between nanoparticle size and contact angle. So it is interesting to note that particle size inversely proportional to the surface area /volume ratio, which leads to a decrease in the ability to perform surface interactions [8]. Because the smaller size, technically more chemically reactive, it appears that a mechanical, rather than a chemical, mechanism is the driver for enhanced oil recovery. Furthermore, figure 6 showed the effect of Nano-particle concentration on wettability alteration. In which contact angle decreased with increasing the concentration gradually also it seen that from 0.1-1 wt. %Nano-particle, decreasing in contact angle becomes approximately smaller. The effect of nanoparticle size on contact angle Attributable to the surface energy, in which the surface to volume ratio increases with smaller sized nanoparticles, which lead to increase the surface free energy so that contact angle decreased. Other factors such as surface roughness and nanoparticle distribution on the surface which can be also control the contact angle. The difference in the areal density of the nanoparticles on the surface for different nanoparticle sizes may cause the observed deviation in the values of contact angles, particularly for intermediate sized nanoparticles [14].

The effect of dipping time of slices in Nano fluids shown in Figures 7-9 the contact angle decreased with increase dipping time. The contact angle decreased with increase dipping time due to Increase the adsorption layer of Nano particles in the other hand porosity of the rock unchanged because of the size of rock channel in micron in spite of Nano particle.
Figure 7. Contact angle versus dipping time at different Nano fluid concentration of 65 nm particle size

Figure 8. Contact angle versus dipping time at different Nano fluid concentration of 10 nm particle size
Wettability alteration of limestone rock can depend on parameters like brine salinity, and concentration of Nano silica. In this part of research, alterations of contact angle due to using different salinity of Nano fluids on the limestone sample. Figure 11 shows the effect of Nano silica concentration at different salinities. It was found that fluids with different salinity had the same effect on contact angle which decreased with increasing the concentration of Nano fluids. Moreover, the Nano silica led to alter the limestone rock wettability from oil wet to water wet. Best result in order to wettability alteration (30°-29°) observed in a concentration of Nano fluid 0.01 wt. % for all brines. [15]

3.2 effect of PEG polymer and SDS surfactant
Figure 11 shows the effect of the PEG polymer and surfactant on wettability alteration of carbonates. The contact angle was decreased with decreased with increasing surfactant concentration; surfactants...
tend to stay in the aqueous phase at low salinities and move to the oil phase at high salinities due to the 
electrostatic interactions between electrolytes and surfactants in the case of SDS, the repulsion 
forces between the surface charge and the SDS head charge are increased. Therefore, the adsorption 
of anionic surfactants onto carbonate rocks reduced and causes a poor wettability alteration by SDS;[16]. 
Polymer adsorption/retention mechanisms in porous media are mainly physical interaction, e.g., 
electrostatic attraction due to the charge differences between the solid surface and polymer or Van der 
Waals dipole–dipole interactions. Polymer retention is more general, and consists of three main 
mechanisms: polymer adsorption, mechanical entrapment and hydrodynamic[17]. Figure 11 showed 
decreasing of contact angle with increasing polymer concentration due to the increase in the 
adsorption layer. In which the change in the adsorption layer thickness in the initial segments of the 
isotherms suggests that at low concentrations of polymer, the molecules on the surface of sample are 
distributed and bound with a small number of segments. The increase in concentrations of polymer 
causes a rearrangement of the structure of the adsorbed layer. The adsorbed molecules break 
previously formed bonds so that they straighten and exposed so that the layer thickness increases. At 
higher concentrations of polymer, number of polymer molecules increases, which in turn increase 
interaction between the carbonate surface and polymer molecule. Constant contact angle at 
concentration of polymer up to 1% Attributed to saturation of the adsorption capacity of the active 
adsorption sites after certain concentration so that no further adsorption takes place [18]

![Figure 11. SDS surfactant and polymer effect on contact angle](image)

4. Conclusion

Nanotechnology can be an effective enhancement option for an oil recovery method in an oil reservoir. 
Nano silica had an axial role in wettability alteration (increase hydrophilicity) of carbonate rock. The 
wettability was increased with increasing Nano silica concentration and decreasing particle size. While 
salinity had an insignificant effect on wettability with Nano fluids. Polyethylene glycol (PEG) and 
surfactant (SDS) had alteration wettability but with a high concentration in which probably reduces 
rock permeability due to the thickness of adsorption layer also hydrodynamic and mechanical 
entrapment.

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