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Experimental Investigation of Wettability Alteration in Reservoir Rock Using Silica, Alumina and Titania Nanoparticles

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Abstract

In recent years, several studies have been conducted regarding wettability alteration in petroleum reservoir rock using hydrophilic Silica (SiO_2), Alumina (Al_2O_3) and Titania (TiO_2) nanoparticles in order to improve waterflooding process that results in enhanced oil recovery (EOR). The studies have showed the significant role of these nanoparticles; however, their potential in wettability alteration and enhanced oil recovery as well as stability of them compared to each other have not been cleared yet; thus, an integrated comparison of them seems necessary. In this study, in addition to evaluating stability and price of these nanoparticles, their impacts on wettability alteration and EOR were investigated on oil-wet sandstone core samples. By injecting the nanofluids prepared from these nanoparticles, it could be expected to alter the rock wettability condition from oil-wet to water-wet due to their hydrophilic properties. For this purpose in this research, ten similar slices of the core samples were floated in ten different concentrations of the nanofluids; and their wettability alterations were determined by measuring the contact angles through sessile drop technique at different aging times. Then, brine and the nanofluids were injected to the three similar core samples to evaluate oil recovery caused by injection scenario. The results indicated that Titania, Silica and Alumina nanoparticles, respectively, had the most impacts on wettability alteration in the rock and their impacts incremented by increasing the nanoparticles concentration. After the injections of Titania, Silica and Alumina nanofluids with the optimum concentration at 0.1 wt%, the ultimate oil recovery is enhanced up to 18.27, 15.66 and 12.38 %, respectively, compared to the waterflooding. However, challenges of the use of these nanoparticles including the lack of stability and price of Alumina and Titania which are types of metal oxide-based nanoparticles were more than Silica.

Keywords: Enhanced Oil Recovery, Wettability Alteration, Nanoparticles, Nanotechnology, Core Flooding.

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Introduction

In recent years, several studies have been conducted in attempts to enhance oil recovery through wettability alteration in reservoir rock using Nanoparticles (NPs); and Silica NPs have been used in most of them [1-9]. Also, metal oxide-based NPs have been used in a number of researches in which hydrophilic Alumina and Titania NPs have received more attention than others [1, 9-12]. Although other hydrophilic metal oxide-based NPs have been used in some researches [1, 13]. It should be noted in some of the studies, factors such as oil viscosity reduction and consequently, mobility ratio reduction [1] and oil-water interfacial tension reduction [7-8] have been investigated as well; however wettability alteration is the common key factor among them in order to facilitate oil displacement and enhance oil recovery.

In this study, impacts of three hydrophilic Silica, Alumina and Titania NPs on wettability alteration in ten similar oil-wet sandstone slices have been investigated in homogenous conditions. Also, by using similar injection scenarios, potential of each one of them have been determined in EOR. In addition, challenges of using these NPs in EOR through water/Nanofluid flooding have been discussed. This study draws a clearer perspective of the application of these NPs to make it possible to specify their use in EOR in a more detailed and intelligible form.

Methodology

To determine wettability, contact angles was measured through sessile drop technique. In this method, contact angle of a sessile oil drop on rock surface is measured through water (the denser phase) [14]. In this way, first, initial wettability of the ten core slices was determined in average; then, wettability alterations were surveyed by aging each one of them in ten Nanofluids concentrations for 12, 24, 48 and 96 hours. After determining the wettability of each one of them, to ensure non-blockage of porous medium, a concentration of NPs with highest relative changes of wettability and adequate stability was considered as the optimum concentration to be used in core flooding scenarios.

Also, to create initial saturation conditions in three similar cores for simulating the equilibrium state which is naturally present in reservoir, brine 30000 ppm was injected to them by injection rate 0.2 cc/min to saturate them. After that, 3 PV of the crude oil was injected to the cores with the same injection rate until no water was produced from the cores; in another word, the water saturations in the cores were reached to the initial irreducible state.

According to the injection scenarios, first, 2 PV of the brine was injected to each one of the cores to simulate the primary and secondary oil recovery processes. Then, each one of Nanofluids prepared from the NPs with optimum concentration (which its amount will be described in the next section) were injected to one of the cores, until no excessive oil was produced from them. This scenario was used for all three cores which have same specifications. Injection rate in the all flooding processes was equivalent to 0.2 cc/min. The amounts of accumulated brine/Nanofluid and produced oil were measured from scaled cylinders during the injection scenarios. Hence, oil recovery due to injecting water and Nanofluid could be calculated. In addition, by measuring the pressure difference across the cores, pressure drop was measured during injection processes.

Results and Discussion

Stability of Nanofluids

Visual evaluation of stability of the distributed NPs in fluids was showed that by increase in saline and NPs concentration, stability of the Nanofluids decreases. In addition, Alumina and Titania NPs which are types of metal oxide-based NPs were showed far less stability than Silica NPs in the brine. For example, in temperature 19°C and brine 30000 ppm, Nanofluid 1000 ppm Silica was stable after 48 hours; but Nanofluids Alumina and Titania with 1000 ppm concentration were lose their stability and deposited after 5 and 7 hour, respectively. The cause of this instability should be sought in impact of electrostatic forces such as surface charge; if surface charge is sufficiently large, the Nanofluid will show a desirable stability. However in this research, due to small volume of cores, the Nanofluids were remained stable during the injection scenario and no signs of deposition and accumulation were observed. As a result, to ensure no intervention of other factors in comparing these NPs, no other additives were used and the NPs were injected with the same initial synthetic; but, according to the above-mentioned results, for stability of metal oxide-based Nanofluids for flooding processes in industrial scale, it is necessary to use additives such as surfactants and stabilizer solutions.

Wettability Alteration

At initial wettability condition, the average of the contact angle measurements of the core slices was 148° that revealed their strong lipophilic wettability. After using the Nanofluids, the contact angle decreased; by increase in NPs concentration as well as increase in aging time, the contact angle decrease was intensified. In another word, the rock wettability was changed into hydrophilic (lipophobic) state. The cause of wettability alteration was physical/chemical interactions including hydrogen-oxygen (hydroxyl group) bound with the NPs absorbed on the rock surface and existence of structural surface, van der Waals and electrostatic forces; and as the NPs concentration was increased, hydrophilic state of the rock was increased as a result of more absorption of the NPs. Titania and Silica NPs, respectively, were shown more potential than Alumina NPs in wettability alteration; however, the interesting point of this survey was similar trend of wettability alteration compared to each other; so that in each one of them, wettability was decreased intensively until concentration 1000 ppm and after that, the wettability alteration intensity was reduced. Therefore, the highest wettability alteration in terms of concentration was occurred for 1000 ppm of the NPs. For this reason, concentration 1000 ppm of NPs, in which they also had suitable stability and where cores floodings did not encounter with the blockage problem and closure of porous medium, was considered as the optimum concentration for injection.

Oil Recovery

After injecting 2 PV of the water, oil recoveries in all three cores were almost the same; and in first, second and third cores, respectively, 43.94, 44.06 and 43.15 % of in-situ oil was produced. Although, according to the results, the highest amounts of oil recovery were occurred in this process, due to previous predicts according to strong lipophilic conditions of the cores, these amounts were not in desirable form. After injecting the Nanofluids, considerable improvement was occurred in oil recovery; as by injecting Silica Nanofluids to the first core, 15.66 %, by Alumina Nanofluids injection to the second core, 12.38% and by injecting Titania Nanofluids to third cores, 18.27% of initial in-situ oil was produced. These results are in agreement with the measure of the wettability alteration due to NPs which were higher in Titania, Silica and Alumina, respectively. In another word, changes in strong lipophilic porous medium to hydrophilic conditions, were led to facilitating oil flow and an increase in the displacement and sweep efficiencies; in an extent that absorption of the NPs was led to water penetration in the small pores and throats which were inaccessible before; and was displaced the oil contents in those small pores. Actually, after waterflooding process, capillary pressure was acted as a barrier for displacement of oil in the porous medium; however, its negative effect was decreased due to the impacts of NPs on rock wettability. As a result, these NPs had a good potential in changing the lipophilic conditions into hydrophilic wettability; and by displacing larger amounts of remaining oil, the NPs were enhanced oil recovery favorably. The difference in amount of oil recoveries, in addition to difference in measure of wettability alterations, is related to other reasons such as changes in interfacial tension, pH of each one of the materials and their possible reactions with the rock or the fluid inside the cores. The density and viscosity of injected fluids were increased by an increase in NPs concentration. The difference in density and viscosity of injected and produced fluids in porous medium, affect the water breakthrough and oil recovery; as the ratio of the density and viscosity of the injected fluid becomes higher than produced fluid, the mobility ratio lowers and the oil recovery increases proportionally. Also, pH was increased by an increase in salt concentration in the brine, and was decreased by an increase in the NPs concentration in the Nanofluids. By decrease in pH, there will be the possibility of asphaltene deposition and consequently, permeability reduction of porous medium; however, injecting optimum concentration of NPs prevents such problems in some extent.

Conclusions

1. Silica, Alumina and Titania hydrophilic NPs were able to alter the wettability of strong lipophilic sand stone core samples into hydrophilic state. Titania and Alumina had the highest and lowest impacts, respectively.

2. In all three cases, by increase in NPs concentration to 1000 ppm, wettability alteration was increased; after that, its intension was reduced. In addition, the stability of 1000 ppm concentration during tests was suitable. For this reason, it was considered as optimum concentration for injection scenarios.

3.Stability of Alumina NPs in brine was less than Titania and stability of these two types of metal oxide-based NPs was less than Silica NPs. By increase in salinity, concentration of NPs and time, their stability was reduced.

4. Ultimate oil recovery by injecting optimum concentration of Silica, Alumina and Titania NPs, was enhanced by a factor of 15.66, 12.38 and 18.27 %, respectively, in comparison to secondary recovery through waterflooding.

5. Pressure drop data trend due to water and Nanofluids injection was almost similar in all three cores. The results were indicate no damage or blockage of porous medium during Nanofluids injection (due to use of optimum concentration

for injection).

6. Although Titania NPs was showed highest impacts in wettability alteration and increase in oil recovery, Silica NPs was proved more suitable in terms of other challenges including stability and price.

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