Effect of Silica Nanoparticles Adsorption on the Wettability Index of Berea Sandstone

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ABSTRACT

Nanotechnology has already drawn attentions in the oil and gas industry for its many potential applications in exploration and production processes, especially in the enhanced oil recovery (EOR) area. Nanoparticles, as a part of nanotechnology have been suggested as a promising EOR method in the future. Some EOR mechanisms for nanoparticle have already been proposed, such as disjoining pressure gradient, interfacial tension reduction, wettability alteration and plugging of big pore channels. Hence, the study objective of this paper is to investigate the effect of silica nanoparticle adsorption on the wettability index for Berea sandstone.

In this experimental study, both hydrophilic and hydrophobic silica nanoparticles with 7 nm average particle size were used. Water wet and neutral wet Berea sandstone cores with 250-450 mD permeability were selected as porous media. Three weight percent (3 wt. %) NaCl brine and ethanol were used as suspension fluids for hydrophilic and hydrophobic silica nanoparticles respectively, and the wettability index of Berea sandstone treated by nanoparticle was measured using Amott method.

The results indicated that the hydrophilic nanoparticles can make neutral wet cores more water wet and increase the wettability index of water wet cores about 10%. The hydrophobic nanoparticles can delay the imbibition process for water wet cores but have no significant effect on wettability change. While for neutral wet cores the high concentration hydrophobic nanoparticles suspension can make it more oil wet. The adsorption and retention of nanoparticles in porous media can reduce its porosity and permeability.

INTRODUCTION

The nanoparticle, generally defined as particles with size ranges from 1nm-100nm and single nanoparticle is invisible with naked eyes or optical microscope. Nanotechnology emerged in the 1980s and has already been applied successfully in a lot of industries. Recently nanotechnology was proposed to be utilized in oil and gas industry. The pore channels size of the conventional reservoir rock is in micron magnitude and nanoparticle can flow into the reservoir easily, so nanoparticle has potential to enhance oil recovery in the future. The fluid suspension of nanoparticles, so called nanofluid, is a fluid containing nanometer-sized particles, and the dispersing liquids are water, oil or ethanol. Based on many publications addressed on this topic, nanofluid has already been proved to have potential for EOR.

The nanoparticle used in this experiment is silica nanoparticle. Both hydrophilic and hydrophobic silica nanoparticles were applied to change the wettability of core samples. Silica nanoparticle has many advantages as EOR agent, for instance, 1) 99.8% of silica nanoparticle is silicon dioxide (SiO_2), which is main component of sandstone, so silica nanoparticle is an environmentally friendly material compared to chemical substance; 2) since the silica nanoparticle is made from silicon dioxide, so the raw material (quartz) is easy to be obtained, and the price is cheaper than chemical. This makes silica nanoparticle applicable for EOR in oil field; 3) the chemical behavior of the nanoparticle is correlated to the chemical substance of surface coating. The chemical properties of nanoparticle can be easily controlled by changing surface coating chemical.

The EOR mechanisms for nanofluid has already been mentioned in previous author's paper [1], which includes disjoining pressure, interfacial tension (IFT) reduction, wettability alteration and pore channels plugging. The hydrophilic nanoparticle suspension was found to reduce IFT and contact angle between oil and water even under low concentration (0.1 wt. %), especially for wettability change, 0.1 wt. % nanofluid can reduce contact angle from 54˚ (water and oil) to 22˚. This is a significant reduction, and in this paper the work was focused on the effect of adsorption of silica nanoparticle on the wettability change for Berea sandstone. The main objective is to investigate the phenomenon of wettability alteration during the nanofluid EOR process.

ADSORPTION AND TRANSPORTATION of NANOPARTICLES IN POROUS MEDIA

After hydrophilic or hydrophobic nanoparticle suspension is injected into porous media, five phenomena will occur: adsorption, desorption, blocking, transportation and aggregation of nanoparticles. Since the particle size of nanoparticle is less than 1 micron, therefore it is Brownian particles. Five forces dominate the interactions between nanoparticles and porous walls: the attractive potential force of van der Waals, repulsion force of electric double layers, Born repulsion, acid-base interaction, and hydrodynamics [2]. When the total force for the five forces is negative, the attraction is larger than repulsion between nanoparticle and porous wall, which leads to adsorption of nanoparticle on the porous wall. Otherwise desorption of nanoparticle from the porous wall will occur. Adsorption and desorption is a dynamic balance process controlled by the total force between nanoparticle and porous wall. Blocking will take place if the diameter of the nanoparticle is larger than the size of pore throat, or when some nanoparticles aggregate at the pore throat [3]. The aggregation of nanoparticle happens if the previous equilibrium of the nanoparticle suspension system breaks up and nanoparticles form clusters to block some pore channels. Some pictures of adsorption and aggregate of nanoparticles in porous media are presented in previous author's paper [4].

Transportation of nanoparticles in porous media is governed by diffusion, convection and hydrodynamics. After adsorption and desorption reach the equilibrium state, nanofluid can flow through the porous media without too much adsorption and retention. The equilibrium adsorption is estimated to be 1.27 mg/g for 5000 ppm nanofluid [5].

MATERIAL AND EXPERIMENTAL METHODS

Material

1. Nanoparticle: Both hydrophilic and hydrophobic silica nanoparticles with average single particle size 7 nm were used. They are produced by Evonik Industries and consist of silicon dioxide (SiO_2) ≥ 99.8 %, and have around 300 m^2/g specific surface area. The nanoparticles have been characterized under Scanning Electron Microscope (SEM), and the picture is shown in previous author's paper [1].

2. Nanofluids: The nanofluids with various weight concentrations (0.01, 0.1 and 0.5 wt. %) were prepared by sonicator. 3 wt. % brine was used as dispersion fluid for hydrophilic nanoparticle and ethanol and decane was utilized to make hydrophobic nanofluid for water wet core and more oil wet core respectively.

3. Oil: The oil used in this experiment is decane, and the density is 0.73g/ml.

4. Cores: For wettability index (WI) measurement experiments a total of 22 core plugs were cut to similar dimensions from one contiguous source cores (Berea Sandstone). The average porosity and permeability are 17% and 354 mD respectively. The diameter is 3.83cm and height is 4.07 cm so the average pore volume is 8.14 cm^3. 8 core plugs were aged to be more oil wet by using crude oil, and the others were left in its original water wet state.

5. Amott Cell, Centrifuge: 12 Amott cells and centrifuge were used in this experiment to measure the WI for each core.

Experimental Methods

1. Core Treatment by Nanoparticles

Totally 12 water wet cores were treated by nanoparticles, 3 pairs were treated by 3 different concentrations (0.01, 0.1 and 0.5 wt. %) of hydrophilic nanoparticles suspensions (brine as base fluid) and 3 pairs were treated by 3 different concentrations (0.01, 0.1 and 0.5 wt. %) of hydrophobic nanofluids (ethanol as base fluid). Each pair of water wet cores were saturated with one concentration of nanofluid by using vacuum container, and then the same concentration of nanofluid was injected into the core for 10PVs with 2ml/min rate, finally they were put in the nanofluids under 60 ℃ for 3 days till adsorption and desorption reached equilibrium and dry.

6 more oil wet core plugs were treated the same way. Two groups with 3 cores were treated by different concentration of hydrophilic (brine as base fluid) and hydrophobic (decane as base fluid) nanofluids respectively. The aged cores were cleaned by decane first and then hydrophilic and hydrophobic nanofluids were injected into the cores for 10PVs with 2 ml/min rate, afterwards the cores were put in the nanofluids under 60 ℃ for 3 days and dry.

2. Wettability Index (WI) Measurement

The core saturated with decane is placed in an imbibition cell surrounded by brine. The water is allowed to imbibe into the core displacing oil out of the sample until equilibrium is reached, and the volume of water imbibed (V_{o1}) is measured. Then the core is removed and the remaining oil in the sample is forced down to residual oil saturation by using centrifuge, the volume of oil displaced (V_{o2}) can be determined by weight measurements. The core, now saturated with water at residual oil saturation, is placed in an imbibition cell and surrounded by oil. The oil is allowed to imbibe into the core displacing water out of core, the volume of water displaced (V_{w1}) is measured after equilibrium is reached. And then remaining water in the core is forced out by displacement in a centrifuge. The volume of water displaced (V_{w2}) is measured [6]. The WI of the core is calculated by following equation:

$$\mathrm{WI} = \frac{V_{o1}}{V_{o1}+V_{o2}} - \frac{V_{w1}}{V_{w1}+V_{w2}} \quad (1)$$

RESULTS AND DISCUSSION

Water wet cores

Two water wet cores (W1 and W2) without treatment by nanoparticle were used to measure original WI, and this resulted in an average value of 0.8. Since all the water wet cores were drilled from one core source, so the initial WI of other cores was assumed to be 0.8, which will be used for comparison with the value after treatment with nanoparticle.

Three pairs of core plugs were treated by hydrophilic nanoparticles, core W3 W4, W5 W6 and W7 W8 were treated by 0.01 wt. %, 0.1 wt. % and 0.5 wt. % nanofluid respectively. During the spontaneous water imbibition process, oil volume produced from core was recorded for each time step to plot the imbibition rate curve (Figure 1). In Figure 1, we can see that the imbibition rate of the treated cores is slower than the original cores, which might be due to the reduction of permeability after treatment of nanoparticles. The average permeability reduction is about 50mD, and for core W8 the reduction is up to 220mD. The WI of each treated core plug was calculated and shown in Figure 2. As we can see the hydrophilic nanoparticle can increase the WI of water wet cores about 10% and this phenomenon is independent of the nanofluid concentration.

Another three pairs of cores were treated by hydrophobic nanoparticles, core W9 W10, W11 W12 and W13 W14 were treated by 0.01 wt. %, 0.1 wt. % and 0.5 wt. % nanofluids respectively. Spontaneous imbibition curve is plotted in Figure 3, and we can see that the spontaneous imbibition process was delayed about 1-2 hours due to the wettability change and generally the higher concentration of nanofluid the longer delay. As we can find in Figure 3 the final imbibition volume of treated cores is quite similar with original water wet core (the final imbibition volume for W14 is 3.1ml). The reason is that the hydrophobic nanoparticle can disperse in the oil, so when oil was produced out from core the hydrophobic nanoparticles desorbed from pore wall and were transported out of the core. Hence core plug was becoming more water wet during the imbibition process, which resulted in no water produced during spontaneous oil drainage process. The wettability of core was becoming from less water wet to more water wet during spontaneous imbibition process as hydrophobic nanoparticles desorbed and transported out with oil. The WI for core treated by hydrophobic nanoparticle is shown in Figure 4. As shown most of treated cores have slightly higher WI than original one, and the reason might be that IFT between oil and water was reduced due to the presence of nanoparticle in the oil phase, so more oil can be produced out during spontaneous imbibition process. .

Neutral wet core

Two cores (N1 and N2) aged with crude oil were used to measure original WI for aged cores, the average value is 0.05, which shows that the aged cores are neutral wet. Because all the aged cores were aged with the same crude oil and under the same temperature, so the original WI of other aged cores was assumed to be 0.05.

Three aged cores were treated by hydrophilic nanoparticles, core N3, N4 and N5 were treated by 0.01 wt. %, 0.1 wt. % and 0.5 wt. % nanofluids respectively. The pictures of spontaneous imbibition curve and WI of each core are plotted in Figure 5 and 6. As shown in Figure 5 for the high concentration nanofluid (0.1 wt. % and 0.5 wt. %) treatment cores, final imbibition volume is much higher than original aged cores. The WI of N4 and N5 increased to 0.7 and 0.84 after treated by hydrophilic nanofluid, which means the wettability has already changed to water wet, and the higher concentration of nanofluid, the more water wet of the core.

Another three aged cores were treated by hydrophobic nanoparticles, core N6, N7 and N8 were treated by 0.01 wt. %, 0.1 wt. % and 0.5 wt. % nanofluids respectively. The comparison of imbibition curve and WI between original cores and nanoparticles treatment cores are shown in Figure 7 and 8. As we can see in Figure 7, about 1.1ml water can imbibe into the N6, while for N7 and N8 there was no oil produced during spontaneous imbibition process. In Figure 8, for the high concentration nanofluid treatment cores (N7 and N8), the wettability have already changed to oil wet. The WI of N7 is higher than N8, based on previous results the higher concentration nanofluid should have more obvious effect on wettability change, the reason for disaccord might be core properties difference or plugging of pore channel of N8 by nanoparticles. So that more core samples should be prepared in the future to avoid the errors.

CONCLUSIONS

The WI measurement experiments of different wettability cores showed that nanoparticles can adsorb on the pore wall and resulted in the reduction of porosity and permeability. And the adsorption of different nanoparticles also can change the wettability of cores, for water wet core hydrophilic nanoparticles can increase the WI somewhat, while the hydrophobic nanofluid delayed the spontaneous imbibition process of water wet core but has no significant effect on final WI result; for neutral wet core high concentration of hydrophilic nanoparticles suspension can change the wettability to strongly water wet, and high concentration of hydrophobic nanofluid can alter the wettability from neutral wet to oil wet. More core samples need to be prepared for each case to avoid the errors from cores and more accurate results can be obtained in the future.

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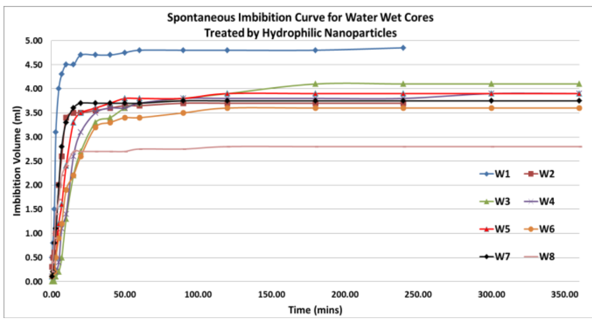

Figure 1 Brine imbibition volume versus time

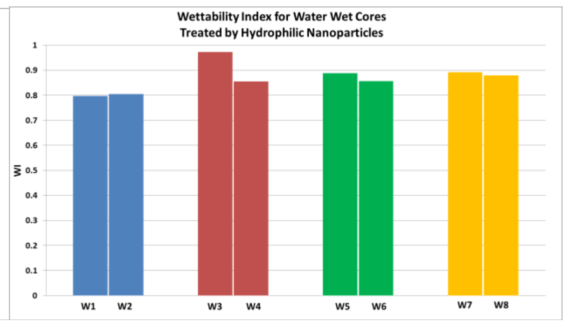

Figure 2 Wettability Index

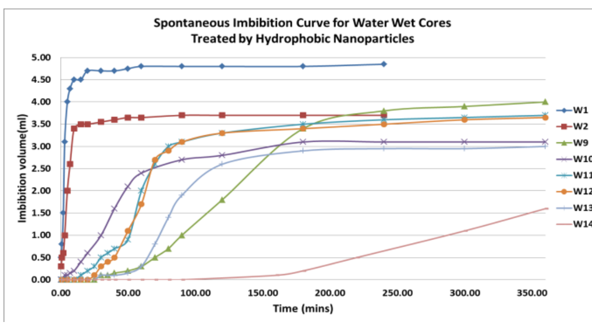

Figure 3 Brine imbibition volume versus time

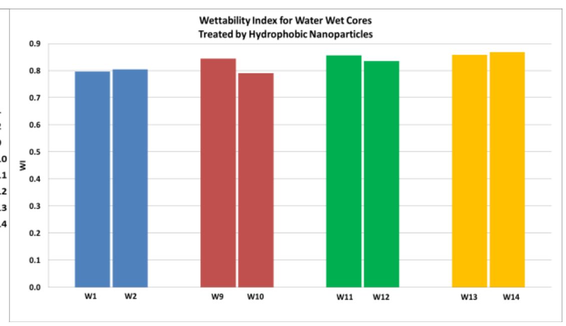

Figure 4 Wettability Index

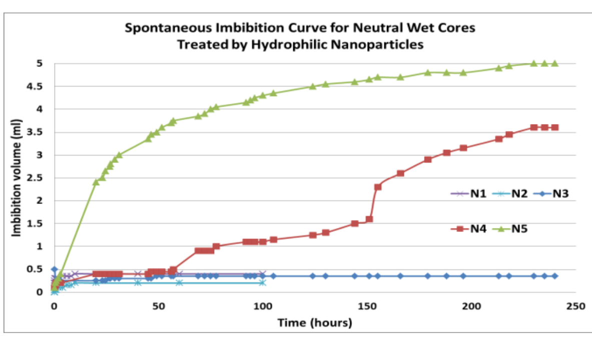

Figure 5 Brine imbibition volume versus time

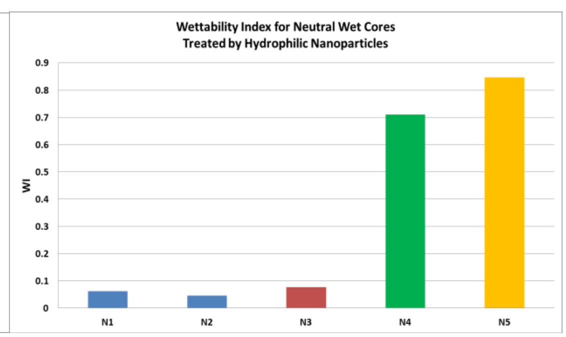

Figure 6 Wettability Index

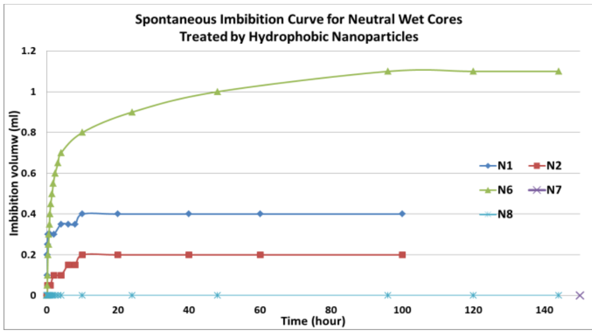

Figure 7 Brine imbibition volume versus time

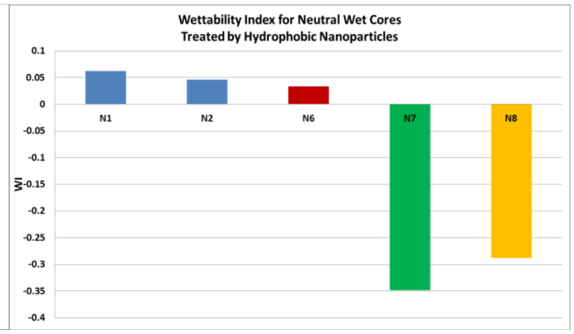

Figure 8 Wettability Index