AN EXPERIMENTAL INVESTIGATION OF NANOPARTICLES ADSORPTION BEHAVIOR DURING TRANSPORT IN BEREA SANDSTONE

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ABSTRACT

Nanoparticles fluid (nanofluid) has shown its potential for increasing oil recovery during last few years. Due to very small size (D~ 1 to 100 nm), nanoparticles can pass through reservoir, while the huge specific surface area of porous media and nanoparticles result in significant adsorption of nanoparticles inside reservoir. The behavior of this adsorption plays very important role for enhanced oil recovery (EOR) mechanisms of nanofluid, it can alter reservoir wettability and change permeability. Investigation of nanoparticles adsorption behavior leads to better understanding of nanofluid EOR process.

The objective of this experimental study is to investigate nanoparticles adsorption behavior during transport in Berea sandstone, analyses of pressure drop and nanoparticles concentration of effluent fluid were used to evaluate nanoparticles adsorption. Three different wettability core plugs (water, oil, and neutral wet) with 8cm length and 3.8 cm diameter were employed. Hydrophilic nano-structure particle and colloidal nanoparticle were used in this experiment and they were dispersed in 3 wt. % brine. Nanofluid was injected into each core plug saturated with brine for several pore volumes, and brine was injected afterwards for post-flush. Pressure drop across core was recorded during whole injection process. Nanoparticles concentration of effluent fluid was measured to plot adsorption curve.

The results showed that nano-structure particle and colloidal nanoparticles undergo adsorption during transport inside core, but nano-structure particle has larger adsorption amount than colloidal nanoparticle. For nano-structure particle more nanoparticles can be adsorbed if the core is neutral wet, nanoparticles desorption was not observed inside water wet cores. Injection of high concentration of nano-structure particle fluid can block core channels and result in permeability impairment, while for colloidal nanoparticles fluid injection does not reduce permeability dramatically, on the contrary it makes core more permeable for some cases.

INTRODUCTION

During last decade nanotechnology was proposed can be utilized in oil and gas industry for different disciplines [1]. Particles can show some special properties when size reduce down to nanoscale, like surface activity and huge specific surface area, so nanoparticles have promising future to be a new EOR agent. The nanoparticles suspension fluid, so called nanofluid, is a fluid containing nanometer-sized particles, and the dispersing liquids can be water for hydrophilic nanoparticles. Based on many publications [2, 3, 4, 5] addressed on this topic, nanofluid has already been proven to have good potential for EOR.

Miranda et al. [6] have mentioned that 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) nanoparticles dispersion has good stability because surface forces easily counterbalance the force of gravity; 3) the properties of thermal, stress–strain and rheology strongly depend on size and shape of the nanoparticles, and can be tailored during their production; 4) 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; 5) the price of silica nanoparticle is cheaper than chemical, which makes silica nanoparticle can be widely applied for EOR at oil field.

The EOR mechanisms for nanofluid have already been discussed in previous author's papers [7, 8], which include disjoining pressure, interfacial tension reduction, wettability alteration, pore channels plugging and emulsification. The effect of nanoparticle adsorption inside core on wettability alteration is highlight of these mechanisms, since hydrophilic nanoparticles can alter oil wet and neutral wet core to water wet [9, 10]. The adsorption of nanoparticles might also affect permeability of core, so this paper focuses on adsorption behavior of hydrophilic silica nanoparticles inside different wettability core and its effect on permeability.

Adsorption and Transport of Nanoparticles inside Porous Medium

After hydrophilic nanofluid is injected into porous medium, five phenomena will occur: adsorption, desorption, blocking, transportation and aggregation of nanoparticles. Since the particle size of nanoparticle is less than 1 micron, so they are Brownian particles, and five forces dominate the interactions between nanoparticles and pore walls: the attractive potential force of van der Waals, repulsion force of electric double layers, Born repulsion, acid-base interaction, and hydrodynamics. When the total force of five forces is negative, the attraction is larger than repulsion between nanoparticle and pore walls, which leads to adsorption of nanoparticle on the pore walls. Otherwise desorption of nanoparticle from the pore walls will occur at the same time. Adsorption and desorption is a dynamic balance process controlled by the total force between nanoparticle and pore walls. Zhang et al., [11] discussed that both reversible and irreversible adsorption of nanoparticles occurs during transport through porous medium. Blocking will take place if the diameter of the particle is larger than the size of pore throat, or when some nanoparticles aggregate to form bigger particle at the pore throat. The aggregation of nanoparticles happens if the previous equilibrium of the nanoparticle dispersion system breaks up and nanoparticles form clusters to block some pore channels. Some images of adsorption and aggregate of nanoparticles in porous medium are shown in Figure 1.

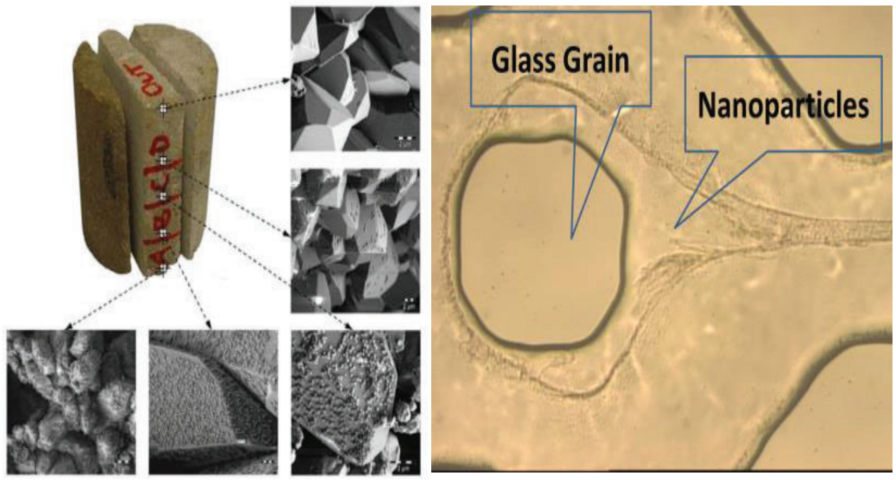


Figure 1 Nanoparticles adsorption inside porous medium.
Left: ESEM image of nanoparticle adsorption inside core [12]; right: Microscope image of nanoparticles adsorption in glass micromodel

Transportation of nanoparticles in porous medium is governed by diffusion, convection and hydrodynamics. After adsorption and desorption reach the equilibrium state, nanofluid can flow through the porous medium without too much adsorption and retention. The equilibrium adsorption is estimated to be 1.27 mg/g for 5000 ppm nanofluid [13].

EXPERIMENTAL MATERIALS

Nanoparticle

Both hydrophilic silica Nano-Structure Particles (NSP) and hydrophilic silica Colloidal NanoParticles (CNP) were employed in this experimental study. They are produced by Evonik Industries. NSP and CNP are supplied as powder and highly concentrated dispersion fluid respectively. They have been characterized by Transmission Electron Microscope (TEM) and TEM images are shown in Figure 2. NSP have average primary particle size of 7 nm and specific surface area of 300 m^2/g, but they can aggregate to form bigger particles, where particle size might be higher than 100nm. CNP have average single particle size of 18 nm and specific surface areas of 350 m^2/g, and this type of nanoparticles don't aggregate in dispersion due to adding of special stabilizer. The reason for NSP and CNP looking similar in Figure 2 is that CNP dispersion fluid was dried before TEM imaging, so nanoparticles reaggregated and formed soft agglomerate, while NSP always form hard agglomerate both in dispersion and powder status.

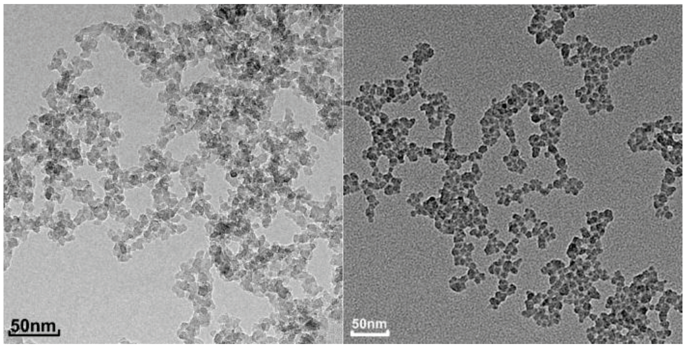


Figure 2 TEM images for NSP (left) and CNP (right) (Provided by Evonik)

Nanofluid

Three nanoparticles concentrations (0.05 wt. %, 0.2 wt. % and 0.5 wt. %) were utilized for nanofluid, and 3 wt. % NaCl brine was used as dispersion fluid. NSP was weighed and dispersed in brine by sonicator, while CNP nanofluid was diluted from concentrated dispersion. Two types of nanofluid with different concentration are shown in Figure 3, as we can see there is no big difference between different concentrations of CNP nanofluid due to good nanoparticle dispersion, but for NSP the higher concentration the milkier nanofluid will be. Fluid properties of each fluid are shown in Table 1.

Table 1 Fluid properties

Fluid	Density, g/cm^3	Viscosity, cP
Brine Nacl 3 wt. %	1.022	1.0026
NSP Nanofluid 0.05 wt. %	1.021	1.0858
NSP Nanofluid 0.2 wt. %	1.022	1.1550
NSP Nanofluid 0.5 wt. %	1.022	1.5627
CNP Nanofluid 0.05 wt. %	1.022	1.0331
CNP Nanofluid 0.2 wt. %	1.022	1.0342
CNP Nanofluid 0.5 wt. %	1.022	1.0372

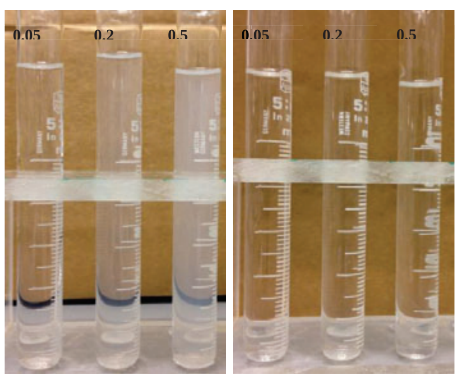


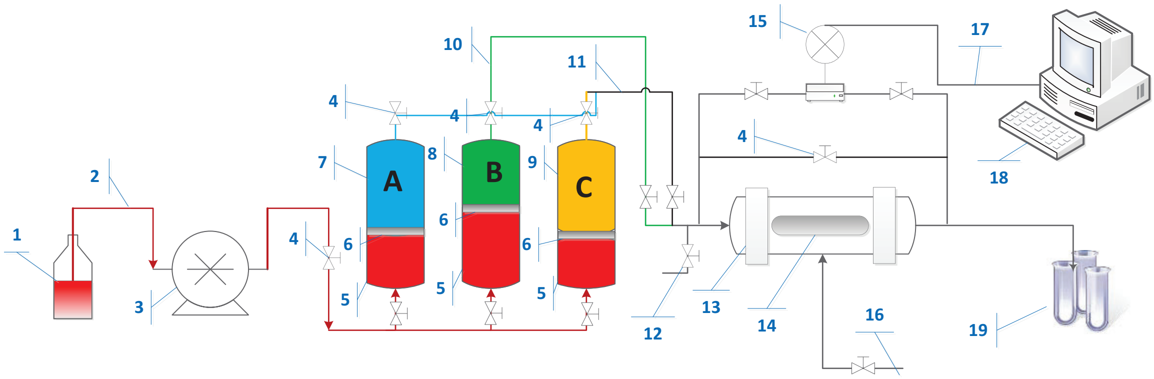
Figure 3 Nanofluid for NSP (left) and CNP (right)

Porous Medium

In total, 18 long core plugs drilled from one block of Berea Sandstone were used for this nanoparticles transport experiment. The average porosity and permeability are 19.5% and 352 mD respectively. The diameter is 3.83cm and length is 8 cm. The pore volume (PV) is about 16ml. Two groups (6 cores for each) were aged to be oil wet and neutral wet under the same condition and the wettability index for oil wet core and neutral wet core is -0.39 and -0.09 respectively. The wettability index for original water wet core is 0.8.

Flooding Setup

Figure 5 shows schematic of flooding setup. The pump injected Exxol D-60 as pumping fluid to push the piston located inside the reservoir. There are 3 reservoirs filled with brine, oil and nanofluid respectively. The pressure drop across the core plug during nanoparticle transport experiments was recorded by precision pressure gauge.



1) Pump fluid (Exxol D60); 2) injection line; 3) Quzix Pump; 4) Valve; 5) Pump Fluid in reservoir; 6) Piston plate; 7) Brine in reservoir-A; 8) Oil in reservoir-B; 9) Nanofluid in reservoir-C; 10) Oil line; 11) Brine/Nanofluid line; 12) Bypass Valve; 13)Hassler Core Cell; 14) Core plug ; 15) Pressure gauge; 16) Sleeve pressure; 17) connection cable; 18) Computer; 19) Accumulator

Figure 4 Schematic of flooding setup

EXPERIMENTAL METHODS

The core plugs were saturated by 3 wt. % brine using a vacuum pump to ensure there was no trapped air inside. Firstly, about 1 PV of brine was injected to measure core absolute permeability, and then about 4 or 5 PVs NSP or CNP nanofluid injection with different concentrations was followed to evaluate effect of nanoparticles adsorption and retention on permeability. Finally, brine injection was conducted as post-flush to observe desorption of nanoparticles, flow rate of 2 ml/min was utilized. Pressure drop across the core was recorded during whole injection process. Effluent fluid was collected every 4ml (1/4 PV) for NSP nanofluid flooding experiments, nanoparticles concentration was measured by using UV Spectrophotometer afterwards, 4-5 measurements were conducted for one sample to get average result.

RESULTS AND DISCUSSION

Oil Wet Core

Figure 5 shows the pressure drop of oil wet core flooding experiments for NSP and CNP nanofluid with different concentrations. There is big difference of pressure drop curve between NSP and CNP nanofluid injection cases. For NSP injection case pressure drop increased rapidly after nanoflud injection and the higher concentration the higher pressure drop, at end of nanofluid injection pressure was still continuing to climb and far away from equilibrium. During post-flush brine injection of NSP case pressure drop decreased gradually for all of three cores. Compared to adsorption process desorption process is slow but quite significant, pressure drop decreased about 30% during post-flush injection. CNP nanofluid injection showed different pressure drop curves, as Figure 5 right shows. There is no rapid pressure increase after CNP nanofluid injection and pressure still kept the same during post-flush period. The different nanoparticles adsorption behavior indicates the adsorption of NSP nanoparticles is multilayer while CNP might be monolayer.

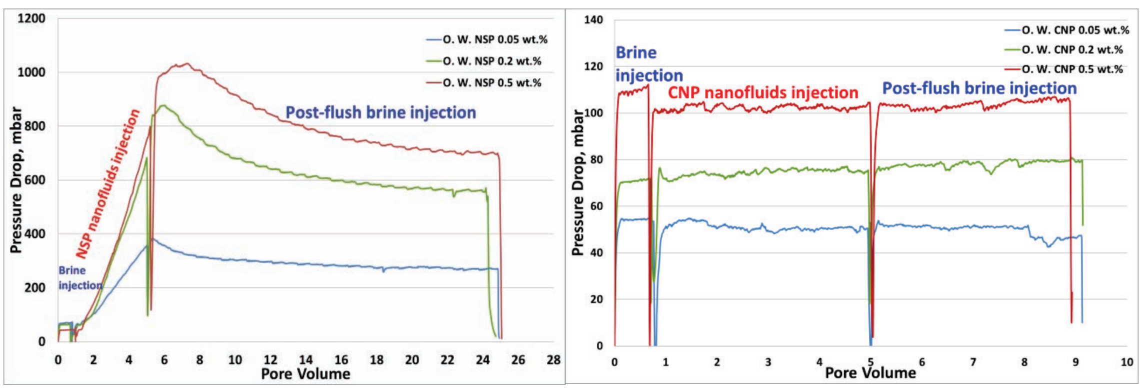


Figure 5 Pressure drop curves for oil wet cores (left: NSP, right: CNP)

Figure 6 shows dimensionless nanoparticles concentration curve of NSP nanoparticles transport through oil wet core plugs, the dimensionless nanoparticles concentration is defined as the ratio of effluent nanoparticles concentration to the injection nanoparticles concentration. As shown in Figure 6, 0.05 wt. % NSP nanofluid have earliest breakthrough while 0.5 wt. % NSP nanofluid have latest breakthrough. Effluent nanoparticles concentration can stay on plateau for about 3 to 4 PV and the lower concentration the longer plateau will be. For 0.2 and 0.5 wt. % cases concentration vibration is observed during plateau, the reason might be due to discontinuous adsorption and desorption, which means for injection of higher concentration nanofluid large amount of nanoparticles adsorbed and trapped inside core and resulted in blocking of pore channels as well as increase of pressure drop. While when pressure drop increased high enough adsorption or retention of nanoparticles can be detached and flushed out of core and then more adsorption and retention will happen again to recover previous balance until next breakthrough, this lead to decline of the effluent concentration. Similar vibration was also observed in pressure drop curve. The effluent concentration of three cases decreased at about 5 PV during post-flushing. A "tail" of concentration curve was shown up after brine breakthrough, which means desorption of nanoparticles during post-flush injection.

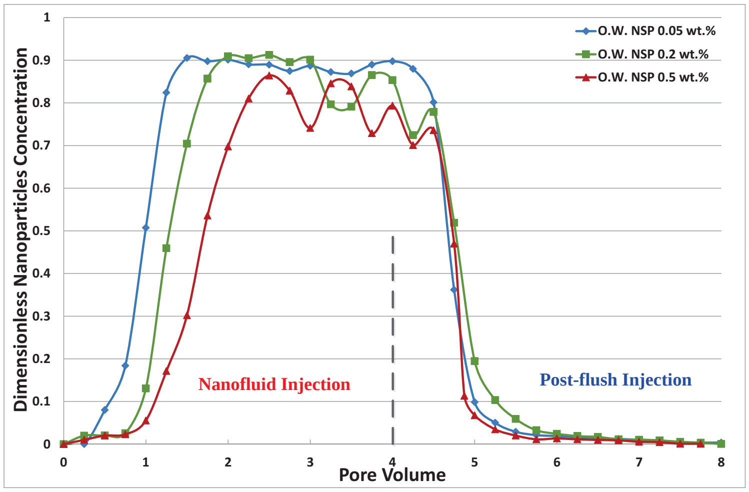


Figure 6 Effluent NSP nanoparticles concentration curves for oil wet cores

Neutral Wet Core

Pressure drop curves were plotted in Figure 7 for neutral wet core NSP nanofluid injection, three curves were plotted separately due to big scale difference. Similar with previous case, pressure drop increase very fast after nanofluid injection. The higher concentration the faster pressure drop increase will be. For 0.5 wt. % case both nanofluid injection and post-flush injection were terminated earlier because pressure almost reached to maximum limit of pressure gauge. Pressure drop decline result from nanoparticles desorption was observed. Permeability change before nanofluid and after post-flush was list in Table 2.

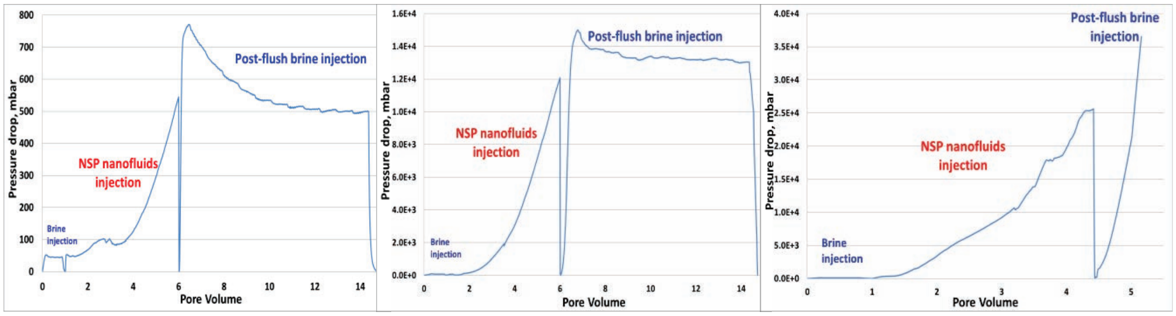


Figure 7 Pressure drop for neutral wet cores NSP nanofluid (left: 0.05 wt.%, middle: 0.2 wt.%, right: 0.5 wt.%)

Figure 8 shows pressure drop for neutral wet CNP injection, the pressure drop didn't change too much before and after nanofluid injection. Which means for neutral wet core adsorption of CNP is still monolayer while NSP adsorption is multilayers. For 0.2 and 0.5

wt. % cases after nanofluid injection pressure drop decrease somehow, which might mean that permeability increased. Table 2 shows that percentage of permeability change.

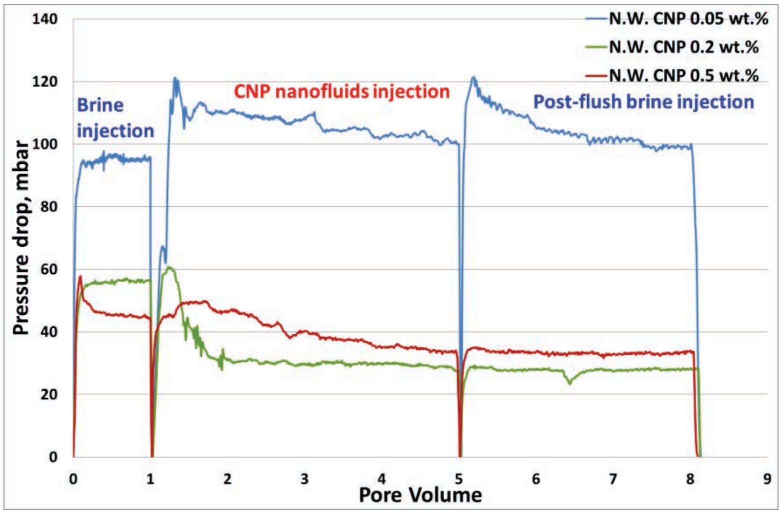


Figure 8 Pressure drop for neutral wet cores CNP nanofluid

Table 2 Permeability of core plugs

Injection scenario	K1, mD (before NP injection)	K2, mD (after NP injection)	K2/K1, %
O.W. NSP 0.05 wt.%	326.2	85.5	26.20
O.W. NSP 0.2 wt.%	361.8	41.1	11.37
O.W. NSP 0.5 wt.%	526.3	33.0	6.27
O.W. CNP 0.05 wt.%	428.9	509.0	118.70
O.W. CNP 0.2 wt.%	321.6	303.2	94.26
O.W. CNP 0.5 wt.%	210.5	228.8	108.66
N.W. NSP 0.05 wt.%	511.4	47.1	9.20
N.W. NSP 0.2 wt.%	326.7	1.8	0.55
N.W. NSP 0.5 wt.%	232.9	0.7	0.29
N.W. CNP 0.05 wt.%	247.6	237.6	95.96
N.W. CNP 0.2 wt.%	427.7	871.3	203.70
N.W. CNP 0.5 wt.%	522.8	691.9	132.35
W.W. NSP 0.05 wt.%	269.3	18.1	6.72
W.W. NSP 0.2 wt.%	463.2	5.9	1.28
W.W. NSP 0.5 wt.%	326.2	1.6	0.48
W.W. CNP 0.05 wt.%	367.6	361.8	98.44
W.W. CNP 0.2 wt.%	165.4	171.5	103.70
W.W. CNP 0.5 wt.%	308.8	361.8	117.19

Figure 9 shows effluent concentration of NSP nanoparticle for neutral wet core, 0.5 wt. % was not presented because not enough effluent samples were collected. 0.05 wt. % case have earlier breakthrough than another one and for both of curves' effluent concentration started to decrease slowly when it reach to the peak. The dimensionless concentration reached only to about 40% maximally, which means most of nanoparticles were trapped inside core. During post-flush large amount of nanoparticles can be measured even at late of post-flush for 0.2 wt. % case.

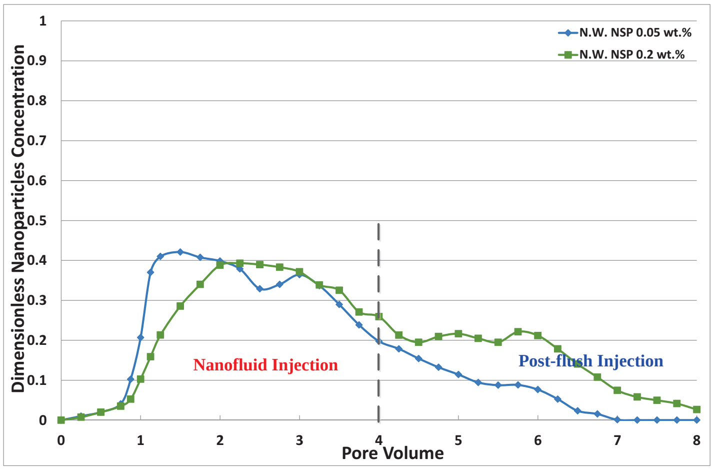
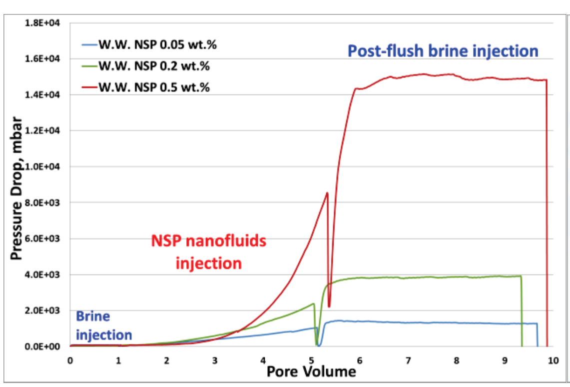


Figure 9 Effluent NSP nanoparticles concentration curves for neutral wet cores

Water Wet Core

Figure 10 left shows NSP nanofluid injection for water wet core, after nanofluid injection pressure drop behavior is similar with previous flooding cases. At end of nanofluid injection pressure curves of 0.5 wt. % case is much higher than another two cases. During post-flush pressure drop increased to plateau and kept constant until end of flooding for all of three concentrations nanofluid cases, which might mean that for water wet core there is no significant desorption of nanoparticles. Figure 10 right indicates that there is no significant pressure drop difference between CNP nanofluid injection and post-flush injection, meaning CNP adsorption is monolayer and will not impair permeability of core. Detail data of effect of nanoparticles adsorption on permeability change can be found in Table 2.



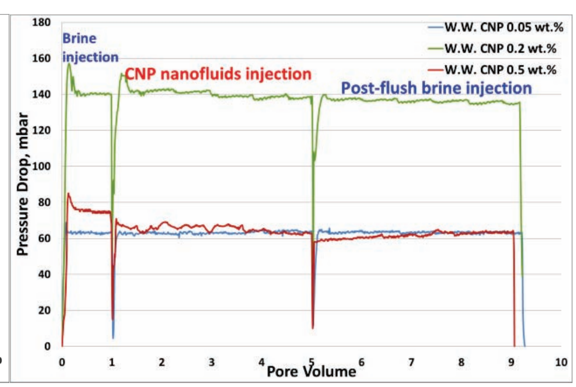


Figure 10 Pressure drop curves for water wet cores (left: NSP, right: CNP)

Effluent NSP nanoparticles concentration curves were plotted versus time and shown in Figure 11. Higher concentration nanofluid case had earlier breakthrough than lower concentration cases, but lower concentration nanofluid curve reached to peak faster than higher cases. The effluent concentration of all the curves decreases immediately after reaching the peak and concentration almost reduced to 0 at 5 PV, which shows a big amount of adsorption and retention of nanoparticles inside the core. The possible reason might be “self-adsorption” of nanoparticles, which means that the previous adsorbed nanoparticles can adsorb nanoparticles injected afterwards, so when adsorbed nanoparticles accumulate more enough the following injected nanoparticles cannot pass through core easily as before. During post-flush injection almost no desorption of nanoparticles after 5 PV, this is consistent with the conclusion from pressure drop.

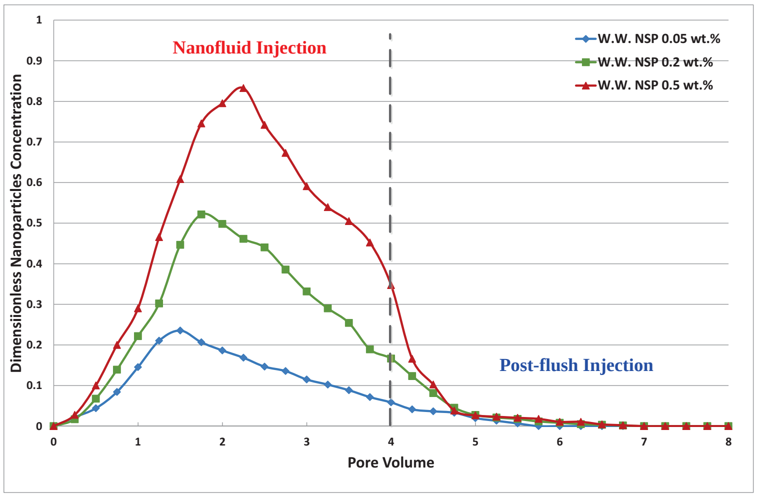


Figure 11 Effluent NSP nanoparticles concentration curves for water wet cores

Comparison of Nanoparticles Adsorption Behavior Against Different Wettabilities

As shown in above figures nanoparticles adsorption behavior is different for different wettability core. First of all, for higher concentration NSP nanofluid injection, neutral wet cores have higher pressure drop than other wettability cores at the same injection volume, while oil wet cores have lowest pressure drop during nanofluid injection. As shown in Figure 12 oil wet cores have highest recovery for nanoparticles, 80 to 90% nanoparticles can pass through core plug. Water wet cores have different recovery for various concentrations of nanofluid, the higher concentration of nanofluid the more nanoparticles can be recovered. While the neutral wet cores have lower dimensionless concentration, the maximum value is only 40%. Based on all of pressure drop data and effluent concentration curves, we can conclude that oil wet cores have lowest adsorption ability for nanoparticles and for higher concentration nanofluid neutral wet cores have highest adsorption ability of nanoparticles but for lower concentration of nanofluid water wet core can adsorb more than others. Desorption of nanoparticles was observed in oil wet and neutral wet cases, but was not presented in water wet cores as discussed above. The core permeability for each core at end of post-flush injection was calculated and listed in Table 2. The permeability for all of core plugs injected by NSP nanofluid has been impaired dramatically, some of them reduced to less than 1% compared with original value.

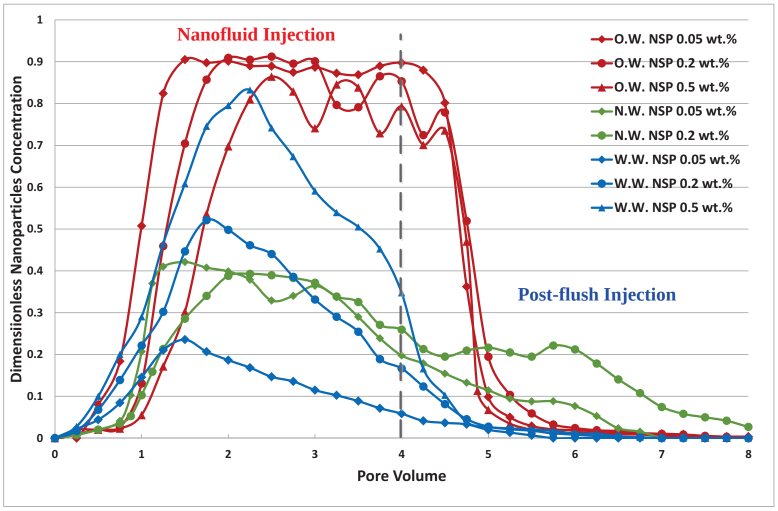


Figure 12 Comparison of effluent nanoparticles concentration curves for different wettability

For CNP nanofluid injection, nanoparticles adsorption is monolayer and will not impair core plug's permeability significantly, which means that after nanoparticles breakthrough most of particles can recovered. During post-flush pressure drop didn't change too much meaning desorption of CNP might be minor. There is no significant difference of CNP adsorption for all three different wettability core plugs. Permeability of cores was calculated and shown in Table 2, as we can see for some core plug permeability increased significantly, especially for neutral wet 0.2 wt. % case permeability double increase. The reason is still unclear, more experiments need to be done to find out the mechanism.

CONCLUSION

1. NSP and CNP have different adsorption behavior inside core plug. Adsorption of NSP is multilayer while CNP adsorption is monolayer. Amount of NSP adsorption is much larger than CNP and result in permeability impairment.
2. Adsorption behavior of NSP is various with different wettability of core. For oil wet core, most of nanoparticles can pass through core and plateau was present in concentration curves. However, neutral wet core adsorbs a large amount of nanoparticles resulting in high pressure drop. For water wet the higher nanoparticles concentration the more nanoparticles can be recovered, and nanoparticles "self-adsorption" was observed.
3. NSP has different desorption behavior against different wettability core plug, desorption happened during post-plush for both oil wet and neutral wet core, but there is no significant desorption of nanoparticles was observed for water wet core.
4. CNP adsorption is independent of wettability and nanoparticles concentration. Injection of CNP nanofluid will not impair core permeability, on the contrary it will increase permeability for some cores.

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