LABORATORY INVESTIGATION OF POROSITY AND PERMEABILITY IMPAIRMENTS IN BEREA SANDSTONES DUE TO HYDROPHILIC NANOPARTICLE RETENTION

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ABSTRACT

Nanotechnology, especially nanoparticles suspension (nanofluid), is one of the most interesting in the last decade to unlock the remaining oil resources when applied as a new Improved/Enhanced Oil Recovery (IOR/EOR) method. However, prior to doing nanofluid experiments for IOR/EOR, its transport behaviour and other essential parameters influencing the IOR/EOR method should be clearly understood.

This paper presents the effects of injected nanofluid concentration (range 0.5 to 0.01 wt.%), injection rate (0.1 - 4 cm^3/min), and pore volume (0.2 – 3.5 PV) on permeability and porosity during nanoparticles transport through Berea sandstone. A hydrophilic silica nanoparticle with average primary particle size of 7 nm was employed. Synthetic seawater with 3.0 wt.% sodium chloride was applied.

The retention of nanoparticles during flooding experiment in several water-wet Berea cores was investigated in 3 different ways: continuously increasing pressure during single-phase coreflood experiment, microscopic visualization under Scanning Electron Microscope (SEM) integrated with Energy Dispersive X-Ray Spectroscopy (EDX) to distinguish nanoparticles with other elements, and particle measurement between influent and effluent. The liquid permeability and porosity measurement showed the impairment range from 5 to 88% and 1 to 11% respectively. If impairment is high, oil might be trapped in the pore medium and cannot be recovered. Based on these experiments, we obtained essential understanding of how silica nanoparticles are behaving during transport through Berea sandstone.

INTRODUCTION

Nanotechnology through nanoparticles has potentially interesting to transform EOR mechanisms and processes [1]. Because it influences surface tension in surfactant solution, surface adsorption process, wettability rheological properties of non-suspension, oil displacement material and finally the oil recovery [2]. However particle movement in porous media is a very complex process [3]. Adsorption of particles onto rock surface because of the Brownian motion and the electrostatic interaction between the migrating particles and the solid surface of the pores is one of the mechanisms [4]. Mechanical entrapment in small pores has been recognized as another element of retention [5]. The mechanism, also known as straining, leads to blocking of narrow pore throats by larger particles.

Our previous study [6] of lipophobic and hydrophilic polysilicon (LHP) transport through a silica glass micromodel (porosity 44% and permeability 25 D) observed permeability impairment. It was shown that if some nanoparticles have been adsorbed inside a glass micromodel under microscopic visualization that might reduce the pore volume. Yu et al. [7] studied adsorption and transportation in three different core plugs as porous media: Berea sandstone, Indiana limestone and dolomite. However, their observation showed no evidence of permeability and porosity impairment while injecting a silica nanoparticle dispersion of 5000 ppm and it could easily pass through the sandstone core. They did not mention the type of nanoparticles either hydrophilic or hydrophobic and the wetting phase of Berea sandstones. Therefore their nanoparticle transport process is not clearly understood.

Based on these contradictory facts above, we initiated a nanoparticle transport study. We were using a smaller average single nanoparticle size of 7 nm and studied effect of various injection rates, nanoparticle concentration, injected PV, and filtering effect to reveal hydrophilic nanoparticle transport behaviour.

EXPERIMENTAL

A LHP from Evonik Industries with an average single particle size of 7 nm and specific surface area of 300 m^2/g was used. It consists of silicon dioxide (SiO_2) more than 99 %. The LHP has acidity with pH range from 3.70 to 4.70. Synthetic sea water (brine) with sodium chloride (NaCl) 3.0 wt.% was employed. Nanofluid with various weight concentrations (0.01 to 0.5 wt.%) were synthesized using that brine and LHP.

Several dried Berea sandstone cores were applied in this study with initial porosity 18-21% and permeability 125-420 mD. The Berea sandstone is commonly used as a porous medium in experimental oil and gas research.

The following experimental procedures were performed at room condition:

1. The dried core plugs were obtained by cleaning with methanol through soxhlet extraction apparatus at 65-70 ^oC and heated in the oven at 70 ^oC for a day.
2. The porosity of the dried core plugs was measured using a helium porosimeter and a vacuum container was used to saturate core plugs with 100% brine and run vacuum pump about 1-2 hour at a pressure of approximately 100 mbar.
3. The core plugs were put into a core holder with a sleeve pressure of 20 bar and injected with brine with different flowrates: 0.5, 1.0, 2.0 and 4.0 cm^3/min. The pressure was recorded using a Keller PD-33X pressure gauge. In some cases, brine was injected at a single rate 0.1 cm^3/min at this pre-nanofluid injection (see all injection scenarios in Table 1).
4. Nanofluid of a particular concentration was injected at 0.5 cm^3/min from 0.2 to 3.5 PV. In particular cases nanofluid was injected at 0.1 cm^3/min and in another case it was injected using a 25 nm filter.
5. Procedure number 3 was repeated post-nanofluid injection for re-measuring differential pressure of post nanofluid injection.

6. The influent and effluent of nanofluid were taken to measure particle concentration using the NanoSight instrument (for some cores) and procedure number 1 and 2 were repeated to re-measure porosity of post nanofluid injection. Several core plugs were cut and underwent Scanning Electron Microscope (SEM) and EDX analysis.

The most common types of clay mineral deposited in sandstone reservoirs are kaolinite, smectite, illite and chlorite [8]. The EDX analysis was performed to characterize minerals including clay and nanoparticles in our cores. The result showed that the presence of mineral K and Fe show that we might have illite that is well-known as a non-expanding clay. Therefore the interaction between brine/nanofluid and clay may not be the main cause of permeability and porosity impairment in this study.

RESULT AND DISCUSSION

Several injection scenarios have been performed and summarized in Table 1. The different scenarios of nanofluid injection rate and concentration were performed to observe the effect of entrapped nanoparticles on rock property impairment such as porosity and permeability. We define percentage porosity impairment in this study as follows:

$$\Phi_{imp} = \frac{(\Phi_{post} - \Phi_{pre})x100}{\Phi_{pre}} \tag{1}$$

Permeability is also an important property of a porous medium. Examination of permeability impairment was conducted by comparing the single-phase flow ability of brine into core plugs pre- and post-nanofluid injection. We define average percentage liquid permeability impairment in as follows:

$$k_{imp} = \frac{(k_{post} - k_{pre})x100}{k_{pre}} \tag{2}$$

In this study, entrapped nanoparticles inside porous medium were investigated in three different methods. Firstly, it was observed from continuously increasing pressure during a single-phase coreflood experiment. The real time pressure recording during the core flood experiment was very helpful to detect such particle blocking mostly at the core inlet and some in pore network. The different pressure profile pre-, during and post-nanofluid injection have been observed. During pre-nanofluid flooding, the differential pressure for all core plugs were relatively low and stable under 100 mbar (see Figure 1a). The change of differential pressure was due to the flowrate change from 0.5 cm^3/min to 4.0 cm^3/min. The differential pressure suddenly increased to 200-500 mbar indicating that plugging occurred when injecting 0.1-0.5 wt.% nanofluid concentration to core plugs #1 and #2 respectively (see Figure 1b). The differential pressure was much lower (less than 10 mbar) when injecting nanofluid concentration in the range 0.01-0.05 wt.%. At post-nanofluid flooding as shown in Figure 1c, the differential pressure is higher than in pre-nanofluid injection which is interpreted some nanoparticles have blocked the pore network. After particular time, the differential pressure slightly decreased, which may indicate deportation of nanoparticles. Some can be recovered at post-nanofluid flooding and the rest may be adsorbed inside the core plugs, impairing the rock properties. Continuously increasing pressure did not occur when the nanoparticle concentration decreased to 0.01 - 0.05 wt.%. The pressure profiles of these concentrations were relatively stable.

Secondly, microscopic visualization under SEM was performed to see if there was any nanoparticle retention inside the cores, both in wet and dry conditions. Figure 2 shows images inside the core plugs after the coreflood experiment. We observed some particle retention and agglomeration on the rock surface (Figure 2a).

Lastly, the particle concentration of influent and effluent was measured using the NanoSight instrument. NanoSight is working based on a conventional optical microscope, but uses a laser light source to illuminate nano-sized particles within a sample introduced to the viewing unit with a disposable syringe [9]. Figure 3 shows brine effluent particle concentration together with pressure versus PV from core plug #1 after injecting approximately 3.5 PV of 0.5 wt.% nanofluid at injection rate 0.5 cm^3/min (particle concentration 3.42×10^8 particles/ml) and continued injecting brine with multiple flowrates. Based on measurements, total nanoparticles recovery through brine effluent concentration was 3.14×10^8 particles/ml or 8.2% particles were left behind at core #1.

In summary, the higher velocity in narrow areas such as pore throats may cause particles to accumulate mostly at the inlet and be retained, and in the worst case may block pore throats. It observed that lower nanofluid injection rate (<0.5 cm^3/min) will minimize possibility of formation damage. Hence injection rate is a parameter for transport efficiency as observed by Khan et al. [10].

The effect of nanofluid concentration was also studied. A higher concentration of nanoparticles cause greater impairment to rock porosity and permeability, since more particles can be adsorbed and retained inside the pore network. Consequently blockage phenomena will occur and damage the formation. Mustin and Stoeber [11] also investigated if particle deposition in core as a function of particle concentration.

This LHP without surface treatment has a tendency to aggregate in polar solvents after a particular time. Hence, we used a 25 nm filter before injecting the nanoparticles into the core plugs to reduce the possibility of pore throat blocking caused by mechanical entrapment. But it did not give any significant improvement of the permeability impairment because the filter size might bigger than the agglomerated nanoparticle size. The effect of injecting the nanofluid into the core plugs was performed with and without using the filter. Decreasing the injected nanofluid PV may lead to lower porosity and permeability impairment.

CONCLUSIONS

Based on the experimental results, the following conclusions can be stated:

1. The retention of nanoparticles inside the core plugs induced porosity and permeability impairment. A higher nanoparticle concentration and injection rate will lead to high impairment. Using a 25 nm filter did not significantly reduce the impairment.
2. Nanofluid concentration in the range 0.01 to 0.05 wt.% and low injection rate (<0.5 cm^3/min) might be favourable for the next stage of the IOR/EOR coreflood experiment to minimize possibility of formation damage.

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Table 1. Porosity and Permeability measurement: Comparison between pre- and post-nanofluid injection

Berea SS #	**Porosity, %**		**Porosity Impairment, %**	**Avg. Liq. Permeability, mD**		**Avg. Liq. Permeability Impairment %**	**Scenario**
	Pre	**Post**		**Pre**	**Post**		
1	18.68	16.67	-10.76	N/A	18.89	N/A	Injected 3 PV Nanofluid **0.5 wt.%**: Nanofluid Qinj 0.5 cm^3/min*
2	18.75	16.63	-11.31	346.92	44.21	-87.99	Injected 3 PV Nanofluid **0.1 wt.%**: Nanofluid Qinj 0.5 cm^3/min*
3	18.88	N/A	N/A	384.22	184.09	-50.46	Injected 0.5 PV Nanofluid **0.01 wt.%**: Nanofluid Qinj 0.5 cm^3/min*
4	19.44	N/A	N/A	415.88	347.23	-17.48	Injected 0.5 PV Nanofluid 0.01 wt.%: Nanofluid Qinj **0.1 cm^3/min***
5	19.18	18.40	-4.07	334.32	229.59	-31.24	Injected **0.2 PV** Nanofluid **0.01 wt.%**: Nanofluid Qinj **0.1 cm^3/min***
6	21.06	N/A	N/A	181.38	172.74	-4.80	Injected 0.2 PV, **filtered** Nanofluid 0.01 wt.%: Nanofluid Qinj 0.1 cm^3/min**
7	18.63	17.93	-3.76	124.49	109.47	-12.10	Injected **1** PV, **filtered** Nanofluid 0.01 wt.%: Nanofluid Qinj & 0.1 cm^3/min**
8	20.64	20.37	-1.31	223.15	210.02	-5.90	Injected **0.2** PV Nanofluid 0.01 wt.%: Nanofluid Qinj 0.1 cm^3/min**
9	19.23	18.69	-2.81	224.67	189.20	-15.80	Injected 0.2 PV Nanofluid **0.05 wt.%**: Nanofluid QInj 0.1 cm^3/min**

* Core plugs were injected with Brine (Pre- and Post- Nanofluid Injection) multiple-rate: **0.5; 1.0; 2.0 and 4.0 cm^3/min**
** Core plugs were injected with Brine (Pre- and Post- Nanofluid Injection) with single rate at **0.1 cm^3/min**

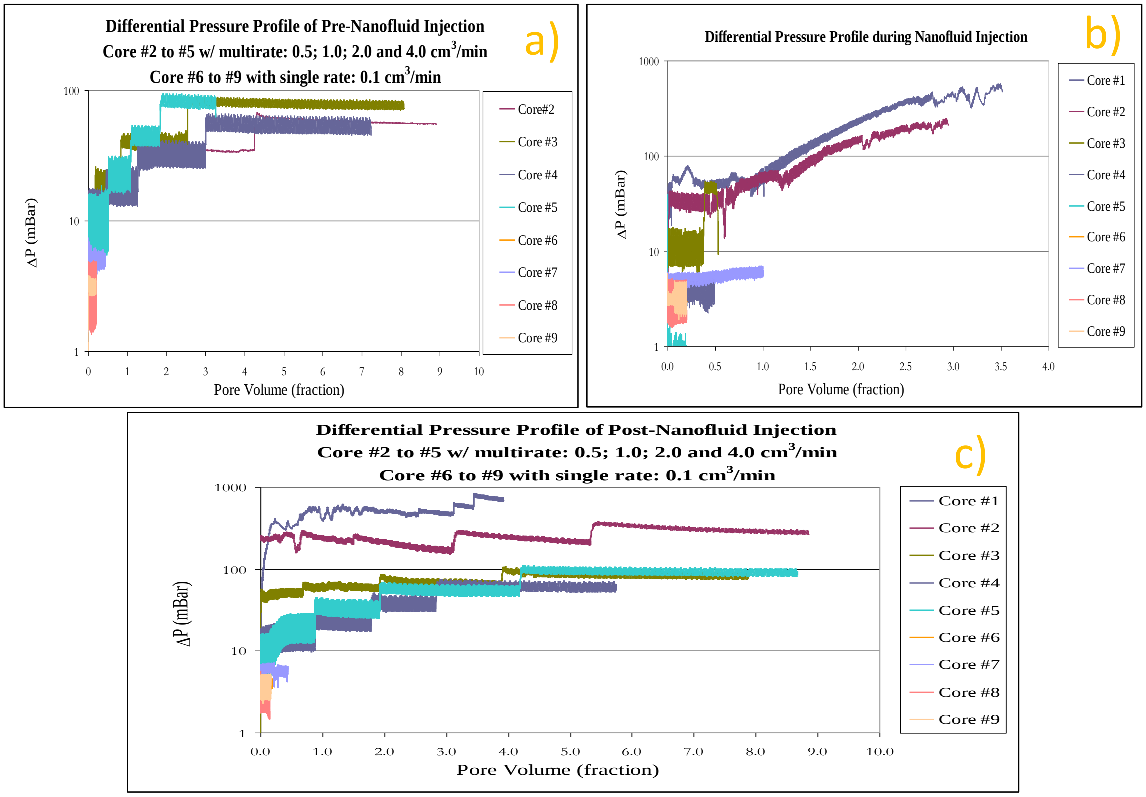

Figure 1 Continuously increasing pressure of Nanofluids: a) Pre-injecting, b) During injecting nanofluids and c) Post-injecting

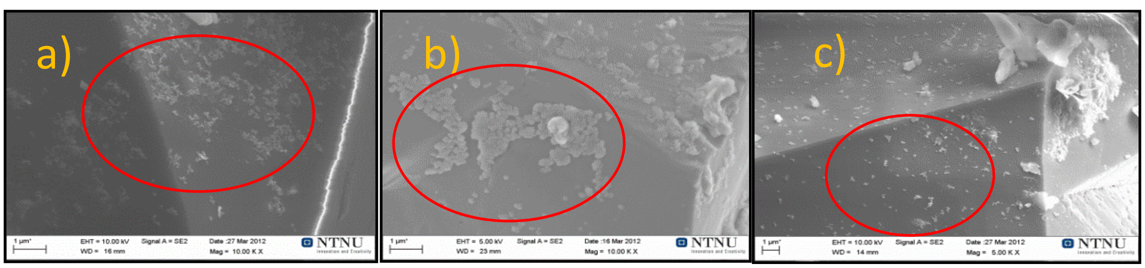

Figure 2 Nanoparticle retention agglomerated inside cores under SEM of: a) Core #2 (cleaned), b) Core #3(wet) and c) Core #4(wet)

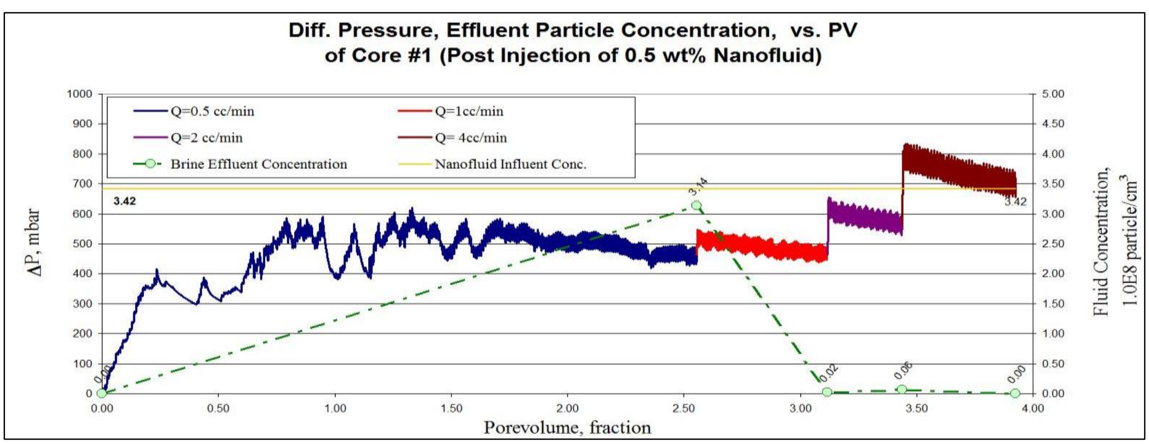

Figure 3 Particle concentration measurement using NanoSight