A NOVEL FLOW CELL AND INTEGRATED SENSOR TECHNIQUE FOR SIMULTANEOUS MAGNETIC MONITORING OF CORE SAMPLES DURING FLUID FLOW EXPERIMENTS

†Shahjahan Khan, *David K. Potter and †Ergun Kuru

†Department of Petroleum Engineering, University of Alberta, Edmonton, Canada

*Department of Physics, and Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

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ABSTRACT

Magnetic susceptibility characterisation of core samples before and after laboratory water flooding experiments has recently been used to quantify changes in the amounts of permeability controlling clays and other minerals, at various points along the length of core plugs, resulting from the water flooding (Potter et al, 2011). In the cases studied small amounts of the paramagnetic clay illite were washed out of the samples due to the water flooding. These fluid flow experiments were undertaken with the core plugs inserted into a traditional metallic (stainless steel) flow cell. Whilst this flow cell could withstand relatively high pressures, the metallic nature of the cell prevented magnetic measurements being undertaken during the flooding experiments. Instead, the magnetic susceptibility measurements were only possible on the core samples themselves before and after the flooding experiments. In order to avoid this limitation we have now developed a novel non-metallic flow cell integrated with a surrounding magnetic susceptibility sensor. This allows simultaneous magnetic monitoring at various positions along the core whilst the flow experiment is taking place. Such “in-line” magnetic monitoring of the core during a fluid flow experiment represents a significant step forward in characterisation techniques. Monitoring changes in real time along the length of the core is now possible, and provide new insights into fluid flow processes. We report the results of some initial experiments using the new flow cell on simulated unconsolidated cores, where we monitored the progress of injected nanoparticle dispersions and determined the optimum conditions for their stability and transport through the cores. This is important because the potential use of nanoparticle technology is now starting to be explored by a number of groups worldwide in applications ranging from enhanced oil recovery to monitoring the progress of hydraulic fracturing jobs. The new flow cell and magnetic monitoring system have several other potential applications. These include simultaneous monitoring of fines migration along the length of a core plug during various fluid flow experiments. This is likely to help our understanding of how fines transport can cause formation damage and influence changes in permeability.

INTRODUCTION

Conventional flow cells for undertaking fluid flow experiments on core plug samples are usually made of stainless steel in order to withstand the relevant pressures involved (up to reservoir pressures in some cases). These types of flow cell make it difficult to monitor certain kinds of physical properties of the core whilst the flow experiment is taking place. In particular, it is not possible to carry out simultaneous magnetic measurements on the core during the flow experiments. A recent study has demonstrated how magnetic susceptibility measurements on core plugs before and after water flooding was able to quantify small amounts of paramagnetic illite clay that were washed out of the sample due to the flooding (Potter et al, 2011). The stainless steel flow cell, however, prevented measurements from being undertaken as the water flooding was taking place. The ability to monitor the magnetic properties during the flow experiments would be a big step forward. The present paper describes a novel flow cell and integrated magnetic susceptibility sensor technique that allows simultaneous “in-line” magnetic susceptibility monitoring of a core plug or unconsolidated sample as a fluid flow experiment is taking place. We also describe one application of this flow cell to study the transport properties of magnetic nanoparticles injected into simulated unconsolidated clastic reservoir material.

Recent work has identified several potential applications for magnetic nanoparticles in reservoir characterization (Johnson, 2010; Barron et al, 2010). The high magnetic susceptibilities of these particles (compared to most reservoir rocks and fluids) make them ideal potential magnetic contrast agents to mix with proppant and help to monitor the progress of hydraulic fracturing jobs downhole (Barron et al, 2010).

Another potential application is for estimating the *in situ* permeability (and its anisotropy) downhole. For a highly permeable interval these magnetic nanoparticles should easily flow into the formation, whereas for a low permeability interval the nanoparticles will have a tendency to build up on the borehole wall. These two different situations can be identified and monitored using time dependent downhole magnetic susceptibility measurements. In the high permeability case a constant magnetic susceptibility with time near the borehole wall will rapidly be achieved, and in the low permeability case the magnetic susceptibility near the borehole wall will increase with time. This should enable an approximate order of magnitude estimate of the permeability to be made. A first step in demonstrating the potential usefulness of these nanoparticles is to discover the optimum conditions which allow the particles to be easily transported through the reservoir material, without clumping together and causing any formation damage by blocking pore connections. We therefore describe some experiments detailing the effects of various parameters on the dispersion and transport characteristics of these nanoparticles through simulated reservoir material using the new flow cell and magnetic susceptibility sensor system.

EQUIPMENT, SAMPLES AND EXPERIMENTAL SET UP

Acrylic Flow Cell and Integrated Magnetic Susceptibility Sensor

A non-metallic flow cell (Figures 1 and 2) made from acrylic tubing and acrylic blocks was designed and constructed for fluid flow experiments to observe the transport behaviour of nanoparticles through glass beads, sand packs or core plug samples. Acrylic blocks were machined to fit into the internal diameter of the tubing, as push-in type end caps. Filter papers were used at the inlet and outlet end of the flow cell to prevent the flow of glass beads or sand from the cell. The dimensions (inner diameter 57 mm, outer diameter 63.5 mm, and length 200 mm) of the flow cell were selected to ensure a measureable magnetic susceptibility signal, a reasonable number of measurement points along the cell, and ease in flow cell handling and packing or unpacking the simulated or real reservoir material. A much smaller diameter flow cell would have resulted in a lower magnetic susceptibility response, which would amplify any uncertainty in the susceptibility measurements. The length of the flow cell provided sufficient measurement points to closely monitor the transport behaviour of the nanoparticle suspensions with distance from the injection to the outlet ends. We commissioned a low field magnetic susceptibility sensor and measuring system from Bartington Instruments that could be used in conjunction with our flow cell to enable measurements of several volume slices to be taken at different positions along the flow cell during the fluid flow experiments. The system comprises an MS2C coil like sensor which applies a weak magnetic field producing a magnetization in the sample being measured. The magnetic susceptibility (magnetization/applied magnetic field) is displayed on an MS2 meter that is connected to the sensor via a signal transmission cable. The meter has a high resolution magnetic susceptibility reading option (allowing measurements to be taken in 11 seconds) and a low resolution option (allowing measurements to be taken in just 1.1 seconds). The volume magnetic susceptibility measuring range of the MS2 system is 1-9999 x 10^{-5} SI. This type of sensor has been previously used to measure whole core magnetic susceptibility (Lees et al, 1998), and more recently to monitor the transport of iron nanoparticles in a vertical sand column for applications related to the reduction of recalcitrant organic contaminants (Darko-Kagya and Reddy, 2010).

In our flow experiments the size of the aperture of the MS2C sensor (80 mm diameter) was selected relative to the outer diameter of the flow cell (63.5 mm) to provide sufficient clearance. This clearance was needed to avoid any obstruction during movement of the MS2C sensor along the full length of the flow cell and also to keep the option for installation of any pressure or temperature ports open. Moreover, the internal diameter of the flow cell to sensor aperture ratio meant that no correction was required to the magnetic susceptibility measurements. The system gives the true magnetic susceptibility in a homogenous medium over a distance greater than the aperture of the MS2C sensor either side of the measurement point. The flow cell was held in a wooden stand, which kept it concentric to the aperture of MS2C sensor, and meant that the flow cell and support stand did not contribute significantly to the total magnetic susceptibility signal.

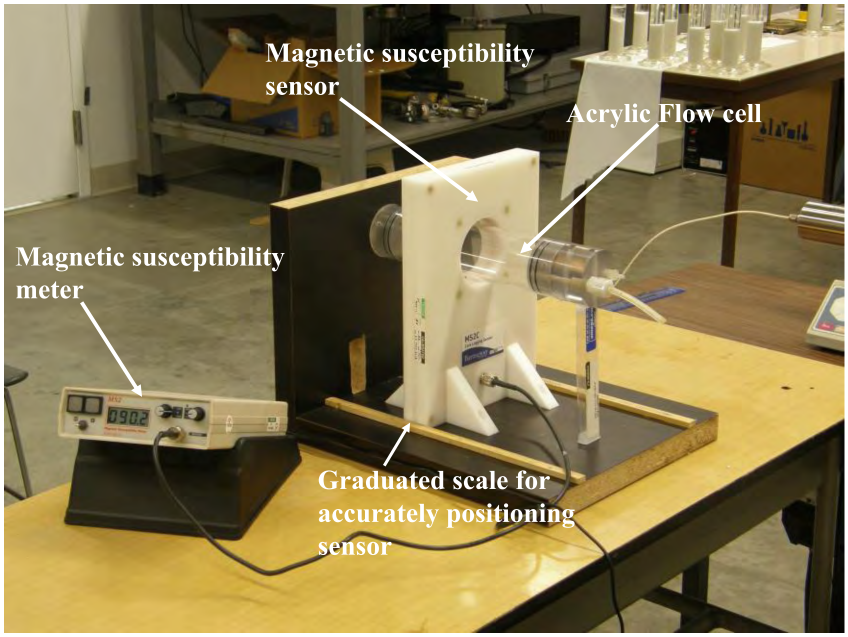

Figure 1. Photograph showing the acrylic flow cell and the integrated magnetic susceptibility sensor.

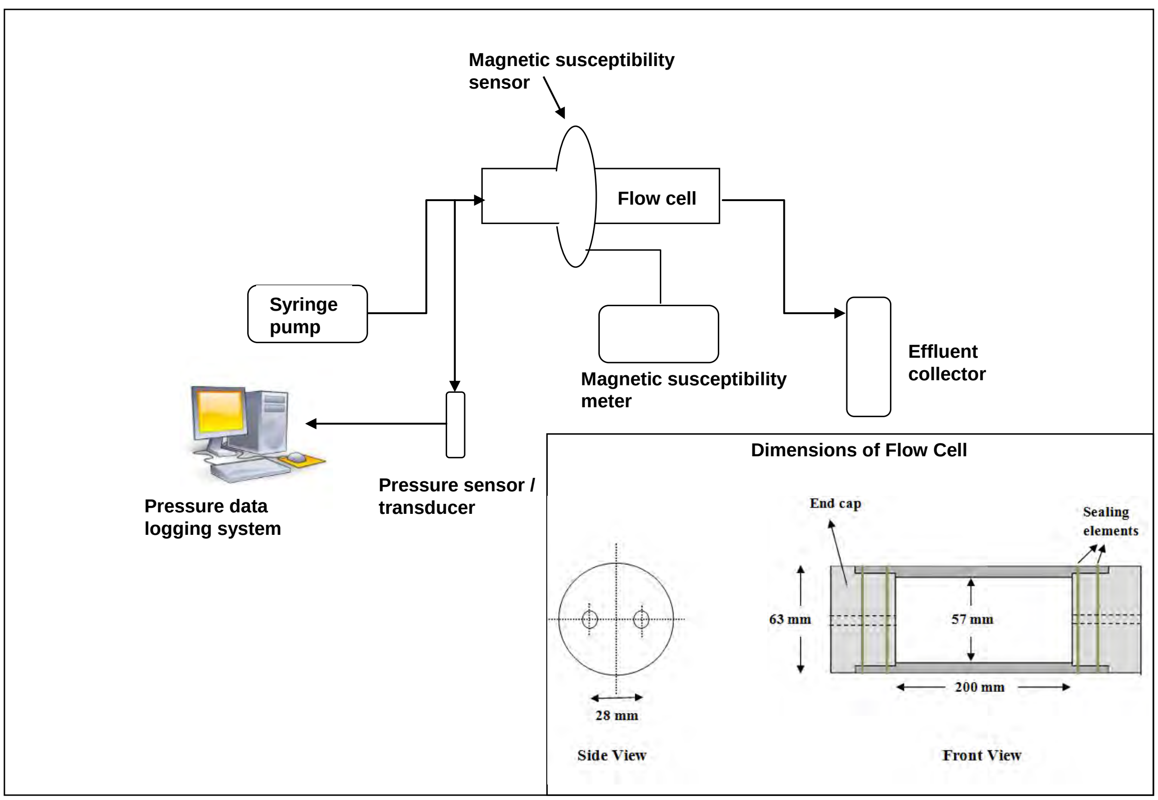

Figure 2. Schematic of the experimental set up. Inset shows details of the flow cell.

Details of flow experiments to analyse the transport characteristics of magnetic nanoparticles injected into simulated or real reservoir core material

In our flow experiments magnetic nanoparticle suspensions and later water (during subsequent water flooding) were injected using a syringe pump. Simultaneous "in line" magnetic susceptibility measurements were taken at different points along the length of the flow cell. The centre of the magnetic sensor could easily be positioned to the nearest millimetre using the graduated scale at the base of the wooden stand (Figure 1). Pressure sensing was performed to measure the absolute permeability of the simulated or real reservoir material (glass beads or sand pack), and also any variation due to the injection of the magnetic nanoparticle suspensions. The effluent was collected at the outlet end of the flow cell. Since non-metallic (dominantly diamagnetic acrylic and wood) equipment was used, a large increase in magnetic susceptibility was observed when the nanoparticle suspensions were injected into the flow cell. The purpose of the flow experiments was to etermine the optimum conditions for the transport of the magnetic nanoparticles through the porous media to minimize agglomeration of the particles or adhesion to the surfaces of the porous media. The flow experiments were performed under different conditions, and different suspension recipes, to understand the effect of individual parameters on the transport characteristics of the magnetic nanoparticle suspensions. Static stability experiments in glass tubes (without flow) had already been performed (Khan, 2012). The following procedure was implemented to perform the flow experiments:

1. The flow cell was packed with glass beads or sand of known grain size and saturated with de-ionized water by inserting one end cap of the flow cell, pouring in a small amount of glass beads or sand, adding some de-ionized water until the porous medium was covered, then adding more glass beads or sand followed by more de-ionized water, and repeated until the flow cell was full. This procedure helped to eliminate air being trapped in the glass bead or sand packs. The porosity was determined using the volume of the flow cell and the known amount of de-ionized water that was added. Background magnetic susceptibility measurements were then taken at 1 cm intervals along the length of the flow cell using the magnetic sensor.
2. A pressure transducer was attached at the inlet of the flow cell and de-ionized water of known viscosity was injected. Pressure measurements at different flow rates were taken and the absolute permeability of the glass beads or sand pack was determined.
3. The magnetic nanoparticle suspensions were prepared by mixing the desired weight of nanoparticles in 600 ml of de-ionized water, adding dispersant, and finally sonicating the suspensions. (A few initial flow experiments were performed with the nanoparticle suspensions prepared by first sonicating and then adding the dispersant).
4. Three pore volumes (PV) of nanoparticle suspensions were pumped through the porous medium at a certain flow rate and the magnetic susceptibility was rapidly measured (without stopping the flow) at 1 cm intervals along the flow cell's length after every PV injection. The background values were subtracted from these readings.
5. After injection of the 3 PV nanoparticle suspensions, the flow cell (containing the glass beads or sand pack) was flushed with 4 PV of de-ionized water at the same flow rate. Magnetic susceptibility measurements were taken after 1 PV and 4 PV injections of de-ionized water to estimate the retention of nanoparticles in the flow cell.

Properties of the magnetic nanoparticles, dispersants and porous media
For most of the flow experiments described here we used spherical maghemite (γFe_2O_3) particles that were 20nm in diameter. Magnetic hysteresis measurements indicated that these were superparamagnetic (such particles have a very short relaxation time so that they don't acquire a remanent magnetization). For some of the experiments we used spherical superparamagnetic magnetite (Fe_3O_4) particles that were also 20nm in diameter in order to see the effect of using a different composition. We tested the effect of using two different types of dispersant. One was a cationic dispersant cetyltrimethyl ammonium bromide (CTAB), whilst the other was an anionic dispersant sodium dodecylbenzeno sulfonate (DDBS). For the porous media in these initial experiments we used a range of well characterized glass beads or sand with characteristic sizes as shown in Table 1.

Table 1. Description and sizes of the porous media.

Material Description	Mesh Size	Equivalent Grain Size (µm)
SIL 40-70 glass beads	40-70	210-400
SIL 100-170 glass beads	100-170	88-149
SIL 170-325 glass beads	170-325	44-88
SIL-4 sand	30-60	250-595

RESULTS AND DISCUSSION

Effect of magnetic nanoparticle suspension preparation method
Figure 3 shows the volume magnetic susceptibility measurements of an experiment where a maghemite nanoparticle suspension was injected into a porous medium consisting of 44-88µm glass beads. The suspension was sonicated and then dispersed using the cationic dispersant CTAB prior to injection. Further details regarding the suspension recipe, injection rate, sonication, and porosity and permeability of the porous medium are given in the Figure 3 caption. It is clear from the magnetic susceptibility results that the maghemite particles merely collected near the injection inlet of the flow cell and did not flow through the porous medium. Therefore it appears that sonication followed by dispersion using CTAB is not very effective at dispersing the particles, and they agglomerated together (thus blocking further transport through the pore space) and/or adhered to the glass beads. Figure 3 shows that subsequent water flooding also did not move the maghemite particles from the inlet end of the flow cell. Figure 4, which is an image of the flow cell after nanoparticle injection and subsequent waterflooding, confirms this and is consistent with the magnetic susceptibility observations.

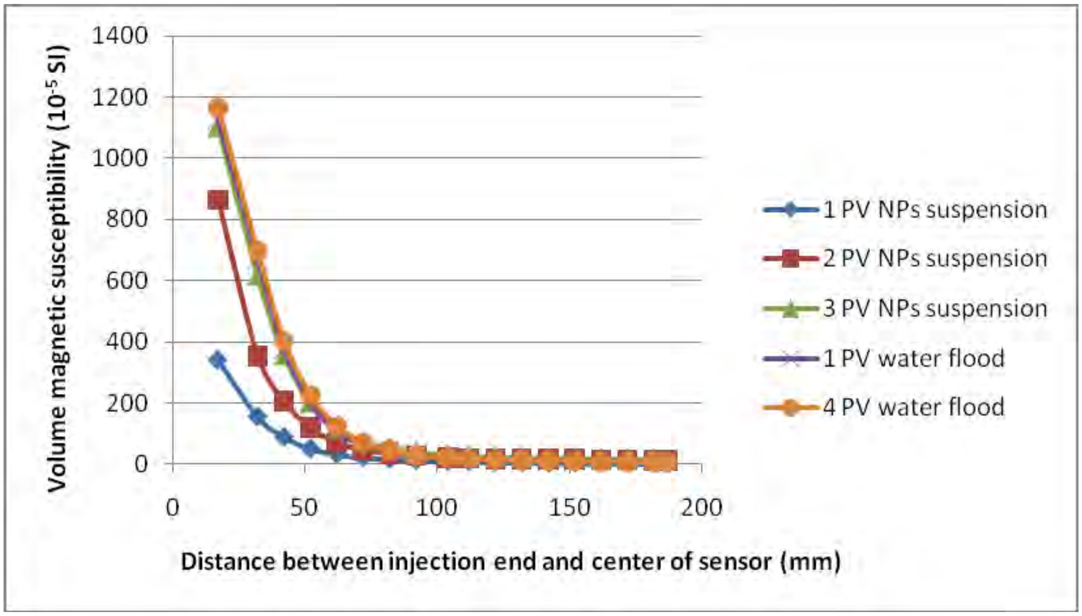

Figure 3. Volume magnetic susceptibility after different pore volumes (PV) of a maghemite nanoparticle (NP) suspension were injected into a porous medium comprising 44-88µm glass beads. The suspensions consisted of 3.0 g maghemite + 600 ml de-ionized water + 1 g CTAB dispersant. The suspensions were prepared by sonicating then dispersing using the CTAB prior to injection. Sonication power: 120W. Sonication time: 40 min. Injection rate: 20cc/min. Measured porosity: 0.33. Measured permeability: 2.2 D. The results for subsequent waterflooding are also shown.

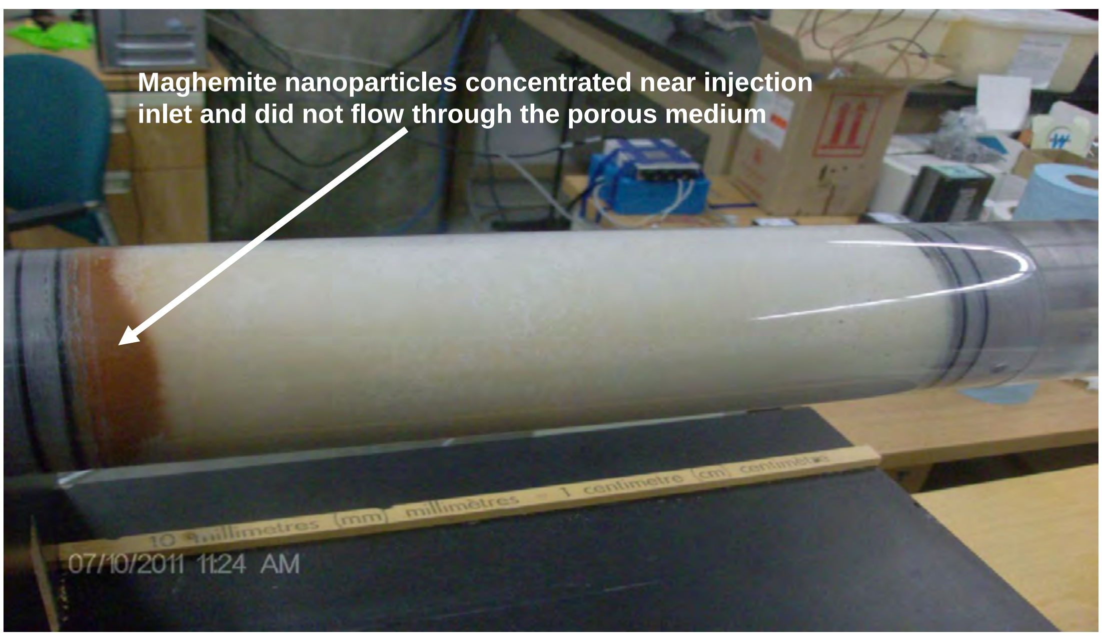

Figure 4. Photograph of flow cell after the injection of the maghemite nanoparticle suspension and the subsequent water flooding under the conditions described in Figure 3. The maghemite nanoparticles concentrated near the injection inlet and did not flow through the porous medium.

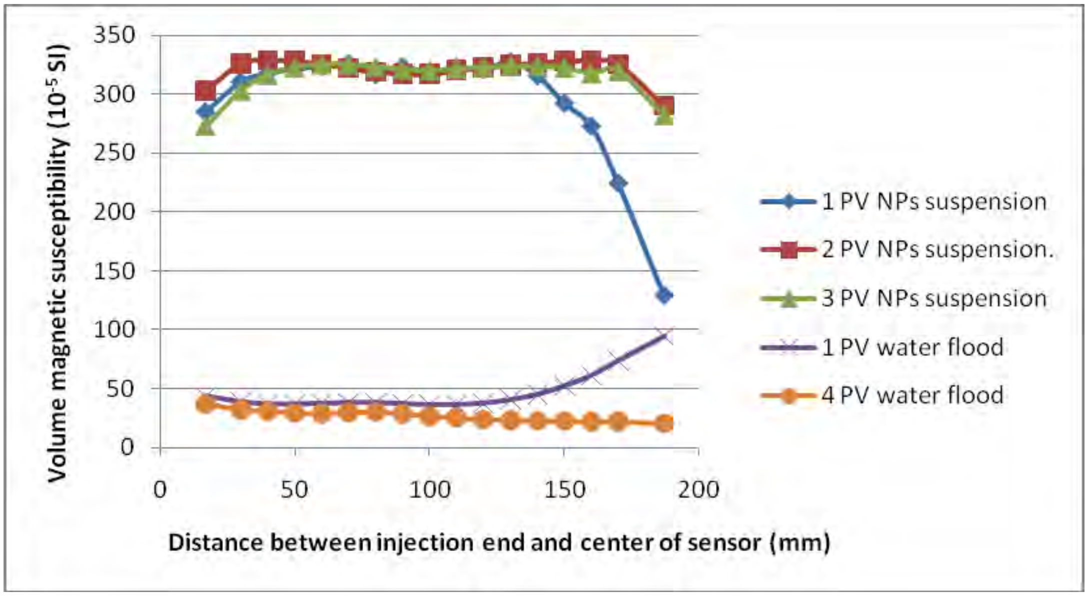

Figure 5. Volume magnetic susceptibility after different pore volumes (PV) of a maghemite nanoparticle (NP) suspension were injected into a porous medium comprising 44-88µm glass beads. The suspensions consisted of 3.0 g maghemite + 600 ml de-ionized water + 2 g DDBS dispersant. The suspensions were prepared by dispersing with the DDBS then sonicating prior to injection. Sonication power: 120W. Sonication time: 40 min. Injection rate: 20cc/min. Measured porosity: 0.34. Measured permeability: 2.3 D. The results for subsequent waterflooding are also shown.

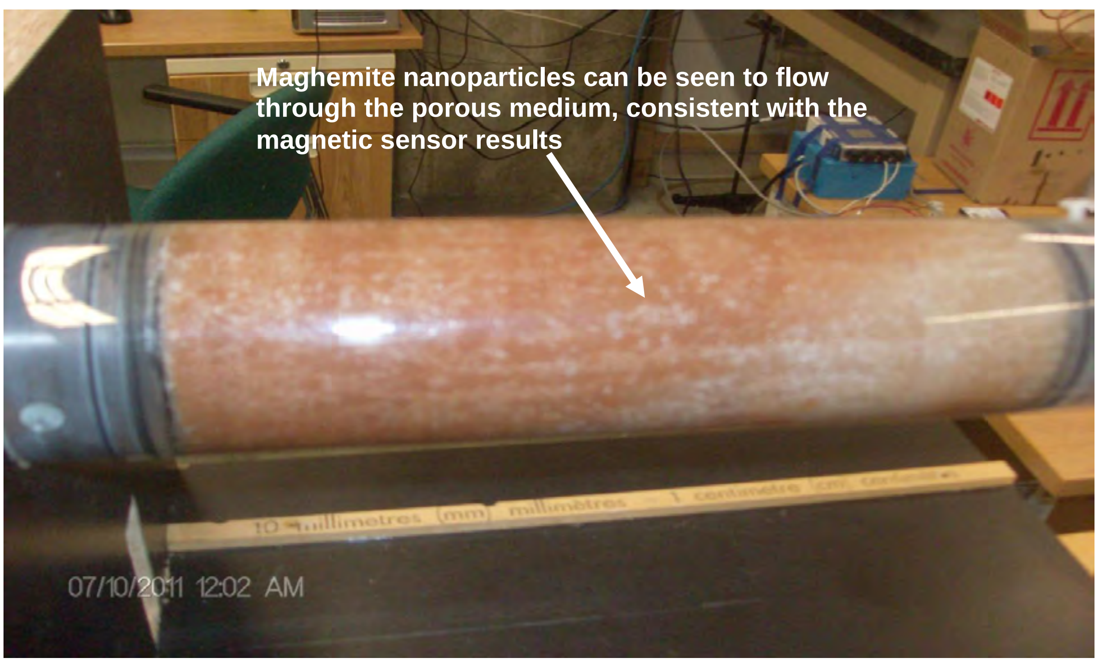

Figure 6. Photograph of flow cell after the injection of the maghemite nanoparticle suspension and the subsequent water flooding under the conditions described in Figure 5. The maghemite nanoparticles did flow through the porous medium in this case.

We then tried preparing the maghemite suspensions slightly differently by dispersing with the CTAB first and then sonicating the dispersion (otherwise similar conditions to those in Figure 3). This improved the flow of the particles through the glass beads, but was still not very effective. We then decided to change the dispersant.

Effect of a different dispersant

Figure 5 again shows the volume magnetic susceptibility results after injecting a maghemite nanoparticle suspension into a porous medium consisting of 44-88μm glass beads, but in this case the suspension was dispersed using the anionic dispersant DDBS and then sonicated prior to injection. This shows that the maghemite nanoparticles were dispersed and easily able to flow through the glass bead porous medium. Figure 6 confirmed visually that the nanoparticles were transported through the glass beads. The anionic nature of the surfactant might have increased the electrostatic repulsive forces between glass beads and nanoparticles resulting in lower adhesion. The slight reduction in magnetic susceptibility at the inlet and outlet of the flow cell (where the distance between the injection end and the centre of the sensor is around 20mm and 190mm respectively) is merely due to the sensor sensing a small region beyond the end of the flow cell where there were no maghemite particles. The decrease in magnetic susceptibility of the 1 PV NPs suspension injection trend near the outlet end of the flow cell (beyond about 150mm from the injection end) may be due to a poor sweep efficiency, whereby the suspension doesn't entirely displace the earlier fluid present. Nearly 90% of the nanoparticle suspensions were removed after flooding the glass beads packed flow cell with de-ionized water. Such a high recovery of nanoparticles and excellent stability of the suspensions prepared with this method makes these suspensions a suitable option for application with the fluid and porous media used here. The conditions may vary, however, for other fluid compositions and mixed mineral systems.

Effect of permeability, injection rate, porous medium and nanoparticle type

Figure 7 shows the effect of varying the permeability of the porous media. The permeability was varied (from 2.25 D to 22.8 D) by using different size ranges of glass beads. All other conditions (as detailed in the Figure 7 caption) were identical in each case. The magnetic susceptibility results for all of the examples showed good transport of the nanoparticles through the porous media. The 4 PV water flooding results showed that more of the nanoparticle suspensions were flushed out as the permeability increased. More work needs to be done to establish optimal transport of the nanoparticles in lower permeability conditions.

We tested the effect of a range of other parameters on the transport properties of the nanoparticle suspensions. The nanoparticle suspension injection rate was varied between 5 and 60cc/min. Higher injection rates decreased the final magnetic susceptibility after the 4 PV water flooding, demonstrating that more of the nanoparticles had been flushed from the flow cell. We also tested the effect of using 250-595 μm natural sand instead of glass beads. This gave quite a similar result to Figure 7 (bottom diagram) for the 210-400 μm glass beads.

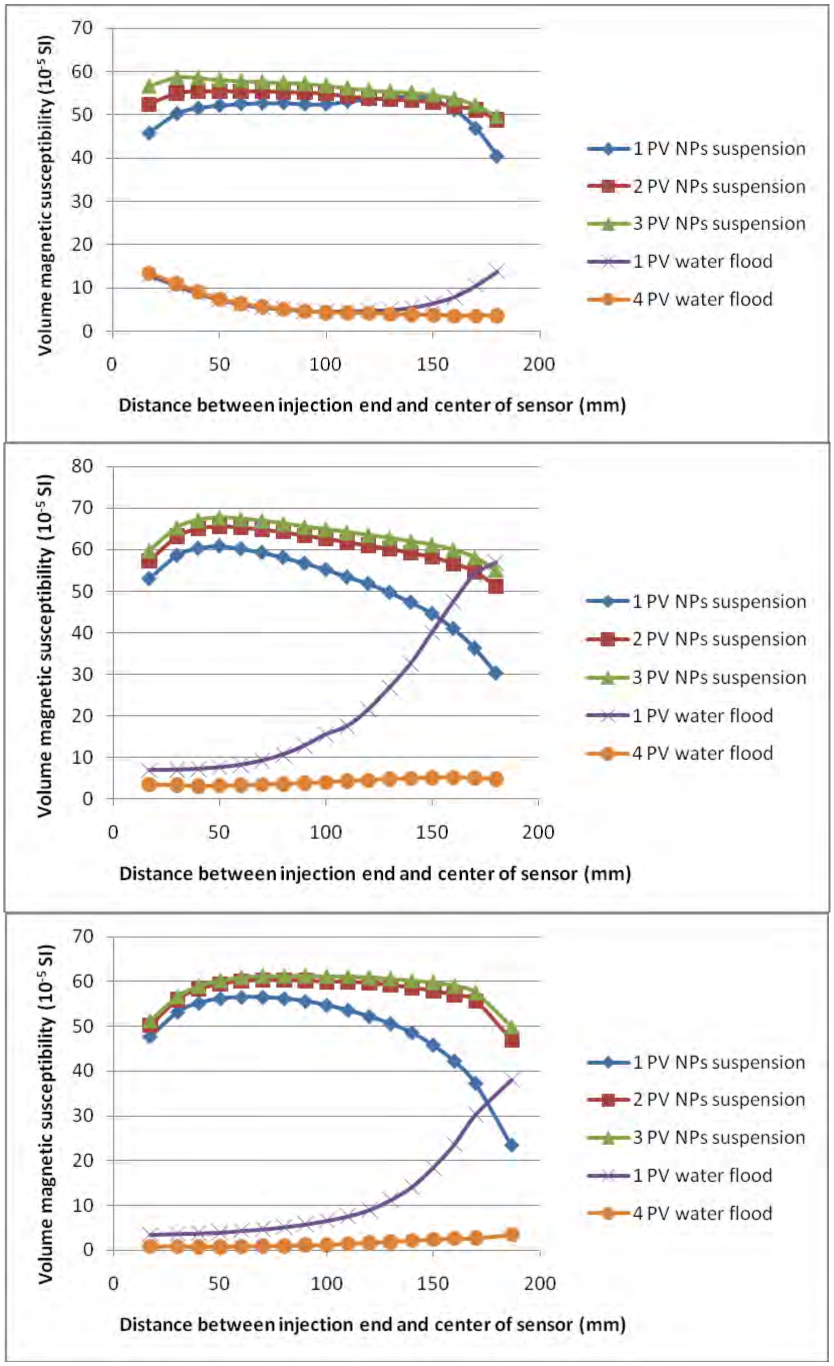

Figure 7. The effect of varying the permeability of the porous medium. Volume magnetic susceptibility after different pore volumes (PV) of a maghemite nanoparticle (NP) suspension were injected into a porous medium comprising **Top:** 44-88µm glass beads, permeability 2.25 D, porosity 0.34, **Middle:** 88-149µm glass beads, permeability 6.35 D, porosity 0.37, **Bottom:** 210-400µm glass beads, permeability 22.8 D, porosity 0.37. In each case the suspensions consisted of 0.4 g maghemite + 600 ml de-ionized water + 2 g DDBS dispersant. The suspensions were prepared by dispersing with the DDBS then sonicating prior to injection. Injection rate: 60cc/min. Sonication power: 120W. Sonication time: 40 min. The results for subsequent waterflooding are also shown.

We also tested the effect of using different types of nanoparticles, and some other parameters too numerous to include here. Magnetite (Fe_3O_4) particles, which were also spherical and 20 nm in diameter like the maghemite particles, gave quite similar results to the maghemite particles.

OTHER POTENTIAL APPLICATIONS OF THE FLOW CELL

Whilst the present experiments concentrated on unconsolidated and relatively high permeability samples, the flow cell can potentially be used to study fines migration in consolidated core plugs during fluid flow experiments. This would allow simultaneous monitoring of fines migration (without the need to cut the sample) during fluid flow experiments, which would complement the recent interesting work by Fogden et al (2011) and Kumar et al (2011) on the mobilization of fine particles during fluid flooding. Note that the thickness of the acrylic tubing for the flow cell can be increased in order to withstand higher pressures. The flow cell is made of a diamagnetic material and will not generally dominate the magnetic susceptibility signal when there is core material in the flow cell. In any case the background magnetic susceptibility signal of the flow cell is measured and subtracted from the signal when the flow cell contains core material. There are also two ports at both ends of the flow cell (i.e. at the end caps) for future potential studies of the simultaneous flow of two fluids.

CONCLUSIONS

The main conclusions from this work can be summarised as follows:

- A novel flow cell and integrated magnetic sensor technique has been developed which allows simultaneous “in-line” monitoring of the magnetic susceptibility during fluid flow experiments, thus allowing the movement of certain fine particles to be tracked.
- The flow cell and magnetic sensor were used to help elucidate the optimum conditions for the transport of magnetic nanoparticle suspensions through porous media (glass bead or sand packs) for potential reservoir applications. Dispersing the particles with an anionic dispersant DDBS followed by sonication prior to injection was found to be a very effective means of ensuring good transport through these porous media.
- The transport efficiency of the nanoparticle suspensions was further found to be dependent upon the permeability of the porous media, the injection rate, the type of magnetic nanoparticles and other parameters.

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