# Monitoring Nanoiron Transport in Porous Media Using Magnetic Susceptibility Sensor

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**ABSTRACT** Nanoiron has recently shown to be effective for reduction of recalcitrant organic contaminants such as PCP, DNT and TCE in the environment. This paper investigates the transport of nanoiron through porous media (natural sand) without and with lactate surface modification. Magnetic susceptibility (MS) or κ sensor system was used to monitor the real-time transport of nanoiron in sand column experiments. A series of laboratory experiments was conducted using a Plexiglas® column with an inside diameter of 38 mm and length of 135 mm. Bartington MS2C magnetic susceptibility meter sensor was used to monitor the transport of bare and lactate-modified nanoiron at two different slurry concentrations of 1 g/L and 4 g/L under two different flow rate (hydraulic gradient) conditions. The results showed a linear correlation between the iron concentration and κ. Overall, this study showed that MS can be used for real-time monitoring of nanoiron transport in porous media, and the 4 g/L lactate-modified nanoiron transported better than bare nanoiron.

## INTRODUCTION

Nanoscale iron particles (NIPs) have recently been shown to possess the potential to decontaminate soils and groundwater contaminated by dinitrotoluene (DNT), trichloroethylene (TCE), pentachlorophenol (PCP) and chlorophenol (CP). This is due to their unique properties such as infinitesimal small size and high surface to volume ratio. Reddy and Karri (2008) effectively treated PCP contaminated soils using NIPs. Although the reactivity of NIPs has been established by researchers, there have been limited studies on the mobility or transport of NIPs. USEPA-NSF workshop held in 2006 concluded that there are limited studies on the transport and fate of NIPs (Reddy, 2006). Delivery of NIPs uniformly in required amounts is essential for a successful in-situ remediation of soils and groundwater. Agglomeration and fast settling of NIPs impedes transport of NIPs in soils during in-situ applications. Researchers have tried to modify the surface of the NIPs particles with different types of dispersants such as polymers, surfactants and cyclodextrins (Cameselle et al., 2008; Saleh et al., 2007) to improve transport in subsurface. The dispersants are believed to form a light film around the surface of the particles thereby reducing sticking coefficient and attachment efficiency. The modification changes the hydrodynamic radius and can also alter the surface charge of the particles reducing aggregation (Cameselle et al., 2008, Saleh et al., 2007).

Magnetic susceptibility (MS) is a fast, inexpensive, nondestructive and straightforward system that has been used to monitor and detect iron bearing minerals in rock cores and metal pollution in soils and sediments. It has also been used in mapping and distribution of pollutants in the environment. This is because most of the polluted particles in the environment contains or either attached by magnetic particles. MS is the ratio of magnetization to the applied magnetic field and it measures how a magnetic material will respond to the presence of magnetic field. When the material comes near magnetic field, it gets magnetized according to the amount of iron-bearing minerals available. A material can be paramagnetic, diamagnetic and ferromagnetic due to how they respond to the presence of a magnetic field. The presence of more iron bearing minerals per unit volume in a sample will indicate high MS values. Paradelo et al. (2009) used magnetic susceptibility to determine the presence of metal contamination in eight different composts. The study found a high correlation between MS and total concentration of Cd, Zn, Pb, Cr and Ni present. No studies have been reported to investigate to monitor the mobility of NIPs in soils with magnetic susceptibility system.

NIPs are magnetic and they can respond to the presence of applied magnetic field. In this study, the transport of bare and lactate modified NIPs was examined in column experiments by monitoring the movement of NIPs in natural field sand using Bartington MS2C magnetic susceptibility meter with 130 mm diameter sensor. Bare and lactate-modified NIPs were investigated at two different slurry concentrations of 1 g/L and 4 g/L. Different hydraulic gradient (0.5, 1.0) were examined to find the effect of flow rate. The extent and transport of NIPs were tracked using the magnetic susceptibility as they move through the soil.

## MATERIALS AND METHODS

### Materials

NIPs used in this study were obtained from Toda Kogyo (Japan). The particles had an average diameter of 70 nm (with a range of 50-300 nm), pH of 10.7, and BET surface area of 37.1 $m^2/g$. Based on X-ray diffraction methods, the NIPs are found to consist of an elemental iron core (α-Fe) and a magnetite shell ($Fe_3O_4$). The approximate composition of NIPs is 50 wt.% α-Fe core and 50 wt.% $Fe_3O_4$. The density of the aqueous NIPs particle suspension is 1.27 g/mL at solids concentration of 25.6 wt.%. Due to the presence of magnetic properties of NIPs, the particles will exhibit magnetic susceptibility in the presence of a magnetic field. This indicates that the movement or mobility of NIPs can be tracked or monitored with the help of a magnetic susceptibility sensor. Therefore the use of the magnetic system is to take advantages of the magnetic properties of NIPs to monitor their mobility.

Native field sand was used for this study to represent typical field soils. Most transport studies conducted used glass beads which do not represent real world soil conditions. The sand used is classified as poorly graded sand (SP).

The aluminum lactate was used for the surface modification of NIPs and electrolyte was used in order to simulate groundwater conditions. The electrolyte contained 0.006 M of sodium bicarbonate, 0.002 M of calcium chloride and 0.001 M of magnesium chloride.

### Test Set-up, Variables and Procedures

Series of transport experiments were performed in a one dimensional bench-scale horizontal column set up. A Plexiglas® column of inside diameter of 38 mm and length of 135 mm was used. The set-up consisted of two porous stones, a cell, two 0.45 micron cellulose filter papers, a reservoir, and Tygon tubing. A Marriott tube of diameter 40 mm was used as the inlet reservoir to maintain the desired constant hydraulic head throughout the experiment. The height of the reservoir could be adjusted to apply different constant hydraulic head conditions.

Two different concentrations (1 and 4 g/L) of NIP- slurries were prepared using electrolyte and additional two slurries were prepared with 1 and 4 g/L NIPs containing 10% aluminum lactate (w/w NIPs). Two different gradients (HG) (0.5 and 1) were investigated to check the effect of flow rate. The sand was packed into the cell in uniform layers and compacted using a tamper to ensure uniform initial soil density. Before the start of each experiment, 200 ml of electrolyte alone was flushed to fully saturate the sand column. The electrolyte in the inlet reservoir was replaced with the selected NIP-slurry and allowed to flush through the sand. One liter of NIPs and Lactate-modified NIPs (LM-NIPs) with different concentration solutions were prepared just prior to the start of the testing and were introduced into the inlet reservoir. Care was taken to keep the NIPs in suspension by shaking the inlet solution regularly. The effluent samples were collected in 120 mL bottles (i.e. approximately every 3 pore volumes) for analysis. At the end of each experiment, the soil was extruded from the column and sectioned into four parts. Soil sample from each section was visually observed and photographed, and iron concentrations were measured using acid digestion and atomic absorption spectrometry (AA).

During the experiments, Bartington MS2 magnetic susceptibility system was used for monitoring real-time movement of the NIPs and LM-NIPs in the soil. The system consisted of a MS meter and it was equipped with 130 mm diameter sensor. The sensor was mounted on a specially fabricated retractable stand that can be moved manually freely back and forth. Magnetic susceptibility measurements were taken at 10 mm distance interval with a resolution of 1.0 SI units along the length of the column starting from the inlet. This equipment can measure at lower sensitivity (1.0) or higher sensitivity (0.1) controlled by a switch. The system can measure from 1 to 9999 x $10^{-5}$(SI) or 1 to 9999 x $10^{-8}$ (cgs). Before starting the experiment, the susceptibility meter reading was zeroed. At different locations of the sample, MS measurement was then made to serve as the baseline values in absence of NIP. The measurements were then taken at different time intervels while the NIP-solution was flowing through the soil. Different tests were conducted under two different hydraulic gradient (HG) (0.5 and 1.0) to assess the effects of varying flow rate on NIPs transport. The extent and transport of NIPs were inferred based on the MS variation across the soil sample with respect to the baseline values.

## RESULTS AND DISCUSSION

### Effect of Aluminum Lactate on the Transport of NIPs

The variation of the magnetic susceptibility along the length of the soil column is attributed to changes in concentrations of magnetic materials (in this case NIPs). There was no significant variation or change in magnetic susceptibility from the inlet to the outlet for the baseline condition during which there was no introduction of NIPs into the soil (Fig.1).

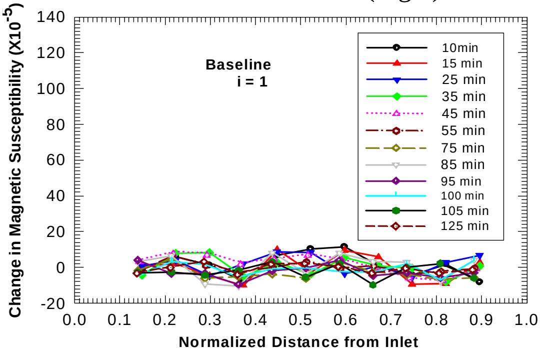


**Fig.1** MS values along the column at different time periods for the baseline test without NIPs and HG=1

(For colour figure, refer to CD)

Figure 2 shows the MS values at different time periods for the test with NIPs and LM-NIPs at HG of 1. In these experiments, high MS values were observed at the inlet sections of the column and then they reduced near the outlet. It can be inferred that NIPs were able to transport pass the mid point of the LM-NIPs column than that of the bare NIPs column from the point of inlet. For example, at normalized distance of 0.5, the MS value measured for 4g/l LM-NIPs test was 45x$10^{-5}$ SI units compared to 24x$10^{-5}$ SI units for 4 g/l NIPs test.

Similarly for HG of 0.5, the MS value at normalized distance of 0.5 for 4 g/L LM-NIPs was 36x$10^{-5}$ SI units whereas that of 4 g/L NIPs was 8x $10^{-5}$ SI units (results not shown). High MS values at a point is an indication that more NIPs have traveled to that point, while low MS measurements implies that less amount of NIPs transported to that point. Aluminum lactate enhanced the transport or mobility of NIPs through the soil. This can be attributed to the fact that the lactate forms a film around the NIPs, thereby reducing sticking coefficient, aggregation and attachment to soil particles. For 10% Aluminum lactate, the surface charge of the NIPs also reduces from a positive value to negative value. The negative charge reduced the sorption/absorption of NIPs to the negatively charged soil particles.

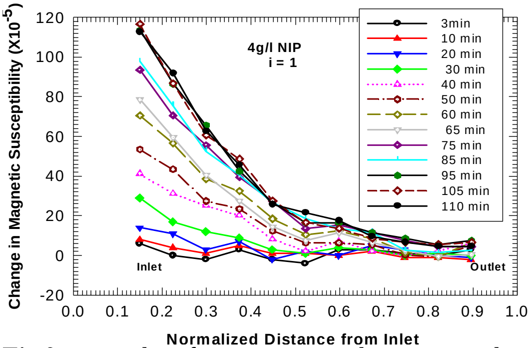


**Fig.2a** MS values for 4 g/L NIP and HG=1 test along the column at different time periods
(For colour figure, refer to CD)

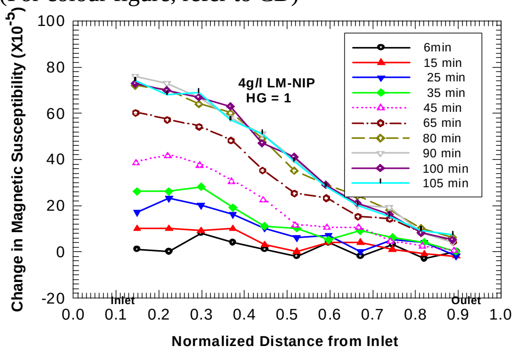


**Fig. 2b** MS values for 4 g/L LM-NIP and HG=1 test along the column at different time periods
(For colour figure, refer to CD)

The MS of NIPs was measured at the end of each test and all the results are plotted together (Fig.3). It can be seen that all the higher NIPs concentration (4g/l NIPs and LM-NIPs) conditions yielded higher magnetic susceptibility values than the lower NIP concentrations (1g/l NIPs and LM-NIPs) which indicates the fact that the presence of higher amount of NIPs caused higher values of MS. This can be observed in Fig 3 as the MS value near the inlet at HG of 1 for 4 g/L NIPs was $118 \times 10^{-5}$ SI units and that of 1 g/L NIPs was $38 \times 10^{-5}$ SI units. This shows that MS system can be used to quantify the extent of transport of NIPs in soils. It can also be seen that the MS values for 4 g/L NIPs were high near the inlet, but the values drop drastically just before the mid section of the soil column. However in the case of 4 g/L LM-NIPs, the MS at the inlet was initially lower than that of the NIPs test but there was gradual decrease of MS measurement away from the inlet indicating that the particles have been transported relatively more and uniformly than that of NIPs. There was not much difference between the two lower NIP concentration tests in-terms of their MS values.

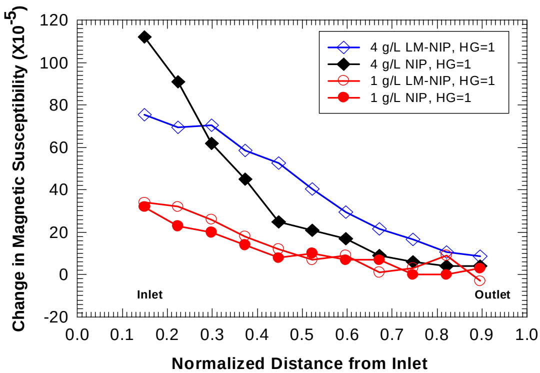


**Fig. 3** MS values along at the end of the testing
(For colour figure, refer to CD)

Figures 4 and 5 show the MS measurements for both 1 g/L NIPs and LM-NIPs tests. It can be inferred from the graph that at normalized distance of 0.5 for HG of 1, the MS value for 1 g/L NIP test was $10 \times 10^{-5}$ SI units which is not significantly different than that of 1 g/L LM-NIP test with a value of $11 \times 10^{-5}$ SI units. This may be attributed to the fact that aggregation is less at lower concentrations; therefore, their mobility is somehow similar. For HG = 0.5, it was observed that the MS values of 1 g/L LM-NIP test are slightly higher than that of 1 g/L NIP test, but the same cannot be said for the test with HG=1 . This can be also attributed to the high flow rate in the case of HG=1, causing similar NIPs transport.

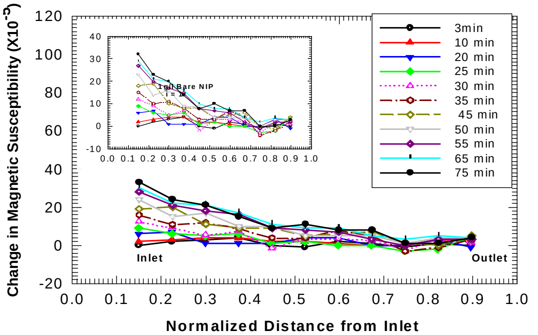


**Fig.4** MS values for 1 g/L NIP and HG=1 test along the column (For colour figure, refer to CD)

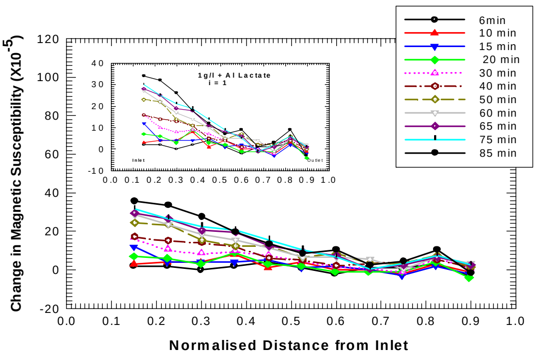


**Fig. 5** MS values for 1 g/L LM-NIP and HG=1 test along the column at different time period
(For colour figure, refer to CD)

## Effect of Hydraulic Gradient (HG)

In assessing the transport of NIPs in subsurface for effective remediation, one parameter such as the flow rate (or HG=1) cannot be overlooked. Increase in flow rate or HG also increases the extent of transport of NIPs. For example, for 4 g/L NIP tests, at a normalized distance of 0.6, the MS value for HG=1 was $18x10^{-5}$ SI units as compared to a lower MS value of $6x10^{-5}$ SI units at the same point with a HG of 0.5. Similarly for HG=1, 4 g/L LM-NIP test, MS value at normalized distance of 0.6 yields 32e-5 SI units, whereas it is $20x10^{-5}$ SI units for HG=0.5.

This indicates that the particles are able to transport more distance at higher flow rate than lower flow rate and this was affirmed by Kanel and Choi (2007). The effect of lactate can also be observed at lower concentrations. The MS values for HG of 0.5 at normalized distance of 0.5 for 1 g/L NIP test and 1 g/L LM-NIP test are $6x10^{-5}$ SI units and $15x10^{-5}$ SI units, respectively. This indicates that lactate modified NIPs were better, but at higher gradient the mobility of 1 g/L NIPs is almost the same as 1 g/L LM-NIPs.

## Correlation of Magnetic Susceptibility and Iron Concentration

At the end of the experiments, the soil samples were extruded from the columns, divided into four sections and chemical analysis was performed to determine the concentration of the iron in each section based on acid digestion and atomic absorption (AA) analysis.

Figure 6 shows the iron concentrations at the end of each test in different sections from inlet to outlet. It can be observed that higher concentration of iron at the inlet section and then reduced with distance away from the inlet. For the 4 g/L NIP tests, almost all the particles accumulated in the section close to the inlet and then reduced drastically away from the inlet indicating that the NIPs were not able to transport far away from the inlet. However, in the case of 4 g/L LM-NIP tests, the iron was higher throughout the column, indicating high transport. This was attributed to the presence of lactate. Results in Fig. 6 follows similar trend as the results shown in Fig 3. This shows that magnetic susceptibility can be used as a proxy measurement to estimate the transient transport/mobility of NIPs.

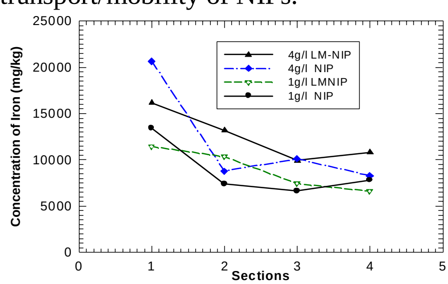


**Fig. 6** Iron concentrations at end of testing (section 1 near inlet) of the column tests with HG=1
(For colour figure, refer to CD)

The iron concentrations and the MS values just before the termination of the tests were used determine any correlation between iron concentration and MS values in the soil. Significant correlation was observed for each test with a correlation coefficient ($R^2$) greater than 0.76 (data not shown). Figure 7 shows results from all of the tests, also demonstrating even better correlation between MS and iron

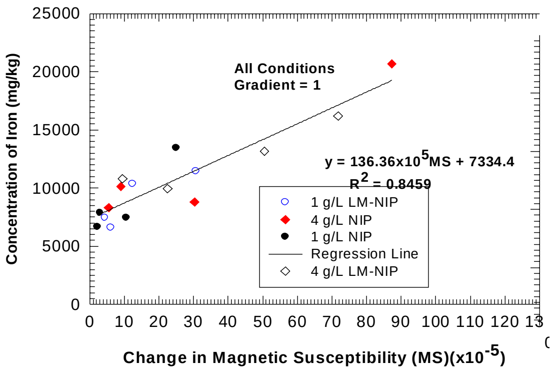


**Fig. 7** Correlation of MS and iron concentrations in soil based on all column tests

(For colour figure, refer to CD)

## CONCLUSIONS

This study investigated if magnetic susceptibility can be used as a rapid, simple, reliable and nondestructive method to estimate the existence and movement of NIPs through soils. Laboratory tests were conducted using NIPs and LM-NIPs in sand columns under different hydraulic gradient conditions. MS measurements were made during the testing, and the iron concentrations were determined at the termination of testing and were correlated with the MS measurements made just before the test termination.

Based on the experiments performed, the following conclusions can be drawn:

1. Tests using aluminum lactate modified NIPs showed enhanced transport of NIPs through the sand.
2. Aluminum lactate reduces agglomeration of NIPs, thereby enhancing dispersivity and transport of NIPs in sand. The transport of NIPs was found to be higher in the 4 g/L LM-NIP test.
3. A significant correlation was observed between magnetic susceptibility and iron concentration in both NIPs and LM-NIPs tests. Therefore, MS monitoring can provide real-time data on the transport and distribution of NIPs in soils.
4. Increase in flow rate (hydraulic gradient) caused increase in the transport of NIPs.

## ACKNOWLEDGEMENT

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