REMEDIATION OF CONTAMINATED SUBSURFACE USING NANOSCALE IRON PARTICLES

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ABSTRACT

Through the accidental or improper release of chlorinated organic pollutants, numerous sites have become contaminated. Lately, success has been achieved by using iron filings (zerovalent iron, Fe^0) as a reactive material in permeable reactive barriers to remediate such contaminants in groundwater. Nanoscale zerovalent iron (NIP) particles have the potential to be superior to iron filings, both in terms of initial rates of reduction and total moles of contaminants reduced per mole of iron. Instead of waiting for the contaminants to pass through the permeable reactive barriers, the NIP can be injected into the contaminated source zones for rapid and effective detoxification of the contaminants. The reactivity of the NIP has been well documented, but there is only sparse data on the fate and transport of NIP in different subsurface conditions. The delivery of NIP into the contaminated zones uniformly and in required amounts in a controlled manner is essential for effective remediation. This paper presents a comprehensive research program to investigate reactivity and transport of NIP and methods to enhance the transport of NIP in subsurface soils and corresponding changes in reactivity of NIP. Despite high reactivity, bare NIP is found to have limited mobility in soils due to agglomeration and settlement of NIP within short time interval. Surface modification using environmentally benign green compounds such as aluminum lactate is found to enhance transport of NIP in soils. The reactivity of NIP is found to reduce due to surface modification by lactate. Therefore, optimization of NIP and lactate concentrations is necessary to achieve both adequate transport and reactivity to achieve effective in-situ remediation. Innovative enhancement/delivery strategies are required to transport NIP and remediate contaminants under difficult subsurface conditions, including low permeability and heterogeneous subsurface. These strategies may include the use of novel dispersants, pressurized systems, electrokinetic systems, or a combination of these.

INTRODUCTION

Numerous sites are contaminated with chlorinated organic compounds such as trichloroethylene (TCE), trichloroethane (TCA) and pentachlorophenol (PCP) across the United States and worldwide. Once introduced into the subsurface, these contaminants tend to be mobile, and they are only reduced/degraded/transformed by slow natural processes (Vogel et al., 1987; Reddy et al., 2001). Chlorinated organic compounds are priority pollutants due to their detrimental effects on public health and the environment (Verschuren, 1983; Mulligan et al., 2001; Cook et al., 2002). Without appropriate cleanup measures, these organic pollutants can persist in soils and endanger groundwater resources and public health. Therefore, there is considerable public interest and regulatory pressure to clean up contaminated sites. Several physicochemical,

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thermal and biological processes have been proposed for this purpose (Sharma and Reddy, 2004). However, traditional treatment processes are ineffective, relatively expensive to operate, or limited by the production of concentrated waste streams that may pose disposal problems.

Recently, encouraging results in laboratory and field experiments have stimulated a rapid increase in the use of iron filings (zero-valent iron, Fe^0) as a reactive material in permeable reactive barriers to remove redox-sensitive contaminants from groundwater. This essentially involves placing iron filings in the path of a migrating contaminant plume, either in a trench or buried as a continuous permeable wall (Gillham and O'Hannesin, 1994; Blowes et al., 1995; Cantrell et al., 1996). The surface of the iron reacts with the contaminants and converts them into nontoxic chemical forms. In addition, such treatment has low operating and maintenance costs and has the potential to be much less expensive than other conventional cleanup methods. This *in-situ* permeable reactive barrier approach using Fe^0 has been used to successfully remediate chlorinated solvents (Gillham and O'Hannesin, 1994; Johnson et al., 1996).

The remediation of contaminated groundwater by the *in-situ* permeable reactive barrier approach with Fe^0 relies on the redox reaction between the iron and a reducible contaminant. In general, the reduction/dehalogenation process by Fe^0 includes multiple chemical processes:

- The Fe^0 acts as a reductant by supplying electrons directly from the metal surface to an adsorbed target compound.
- Hydrogen gas is generated by the anaerobic corrosion of the iron by water.
- Theoretically, the hydrogenation processes are kinetically feasible only in presence of a catalyst, and it is thought that impurities in the iron ore or surface defects on the iron particles are possible catalysts for the reaction.

Recent laboratory and field studies have shown that using Fe^0 may have drawbacks for practical applications:

- After a short time period, Fe^0 is liable to form an oxide surface film, which subsequently reduces the reactivity (Wang and Zhang, 1997).
- It is difficult to maintain Fe^0 surface reactivity. Once Fe^0 comes in contact with air, even under proper storage conditions, its reactivity toward the target compounds is reduced (Cheng and Wu, 2000).
- There is a considerable variation in the reactivity toward target pollutants of Fe^0 of different origins. The reaction rates can differ by up to three orders of magnitude (Su and Puls, 2001).

These factors restrict the application of zero-valent iron to *in-situ* remediation. Nanoscale zero-valent iron (NIP) particles have the potential to overcome these problems and to be superior to iron filings, both in terms of initial rates of reduction and total moles of contaminants reduced per mole of iron. The infinitesimally small size (nm) and enhanced reactivity due to high surface area to volume ratio should make them good candidates for use in subsurface remediation.

Instead of waiting for the contaminants to pass through the permeable reactive barriers, it is prudent to inject the NIP into the contaminated source zones (soils and groundwater) for rapid and effective detoxification of the contaminants. In addition, contaminants such as chloroethanes that are not susceptible to oxidation by permanganate can be treated with NIP. The injection of NIP has therefore the potential to treat both chloroethenes and chloroethanes.

Recently held USEPA-NSF workshop has concluded that the reactivity of the NIP has been well documented, but there is only sparse data on the fate and transport of NIP in different subsurface conditions (USEPA, 2005). The delivery of NIP into the contaminated zones uniformly and in the required amounts in a controlled manner is essential for effective remediation. Any potential changes in reactivity of NIP during their transport in the subsurface are also critical to quantify and to ensure adequate contaminant reduction.

This paper presents a comprehensive research program to investigate the transport and reactivity of NIP and identify promising strategies for the enhanced transport of NIP. An overview of previous research studies using NIP for contaminant remediation is presented first and then summarizes the reactivity and transport of bare NIP. Finally, surface modifications to enhance transport of NIP in soils and consequent effects on PCP remedial efficiency are presented. Overall, this research is aimed at developing innovative system that has the potential to deliver the NIP efficiently into subsurface environments for effective *in-situ* remediation of contaminants.

PREVIOUS STUDIES

Permeable reactive subsurface barriers have been used in full-scale field applications for the treatment of plumes of chlorinated hydrocarbons and chromate. Several laboratory and field research studies have been reported that investigated the effectiveness of a variety of reactive materials. Many of these studies have dealt with zero-valent iron and have shown encouraging results with respect to the capacity of zero-valent iron to reduce the contaminants to non-toxic end products.

The introduction of zero-valent iron in environmental remediation of contaminated sites has met with increasing success and novelty as a treatment alternative. The novelty of iron metal holds especially true in in-situ applications of the zero-valent metal. The iron metal (zero-valent iron) has been used for the remediation of contaminated groundwater, and municipal and industrial waters. Iron has been used as an effective reductant in treatment of chlorinated ethylenes (Roberts et al., 1996; Schreier and Reinhard, 1994), halomethanes (Lien and Zhang, 1999; Kenneck and Weber, 2003), nitroaromatic compounds (Agrawal and Tratnyek, 1996; Devlin et al., 1998; Oh et al., 2002a,b), pentachlorophenol (Kim and Carraway, 2000), chlorinated pesticides such as DDT (Sayles et al., 1997), polychlorinated biphenyls (Arienzo et al., 2001; Chuang et al., 1995), atrazine (Dombek et al., 2001; Singh et al. 1998; Ghauch et al., 1999), and other organic compounds containing reducible functional groups or bonds (Ghauch, 2001; Ghauch et.al., 2001).

The utility of zero-valent iron as an effective reductant in treatment of contaminated waters is due to the generation of several types of reducing species during iron corrosion. The standard reductive potential of zero-valent iron is 447 mV. For iron, the possible reduction reactions involving a halogenated organic compound RX dissolved in the aqueous phase are shown in Table 1. The predominant reactions between dissolved RX and zero-valent iron are the heterogeneous reactions occurring at the surface of the metal rather than the reactions with hydrogen and ferrous iron in the aqueous phase (Matheson and Tratnyek, 1994; Burrow et al., 2000), although the corrosion reactions (generation of ferrous ion from iron metal) are the major source of reducing species for subsequent reactions for reduction of the halogenated compound.

Table 1. Reactions of zero-valent iron with a halogenated organic compound RX in water

Reaction	*Mechanism*
Anaerobic corrosion of iron	$Fe + 2H_2O = Fe^{2+} + H_2 + 2\,OH^-$
Aerobic corrosion of iron	$2\,Fe + O_2 + 2\,H_2O = 2\,Fe^{2+} + 4\,OH^-$
Possible reductive reactions of iron with RX	
Reaction of RX with ferrous ion in the aqueous phase	$RX + 2Fe^{2+} + H^+ = 2\,Fe^{3+} + RH + X^-$
Reaction of RX at the surface of the metal (electron transfer reaction)	$RX + Fe + H^+ = RH + Fe^{2+} + X^-$
Adsorption of RX to the metal surface and the subsequent surface reaction of the organic radical R*.	$Fe = Fe^{2+} + 2e^-$ $RX + e^- = R^* + X^-$ $R^* + H^+ + e^- = RH$

While zero-valent iron has been hailed as an inexpensive and environmentally safe alternative to other in-situ treatment technologies, its implementation at the nanoscale in the form of nanoparticles of zero-valent iron promises to be more effective and successful than at the larger particle size scales (Masciangioli and Zhang, 2003). The greater effectiveness of nanoscale iron is mainly due to the greatly enlarged surface areas of the nanoparticles, hence its enhanced reactivity toward organic and inorganic contaminants.

As compared to the studies dealing with iron filings, the number of research studies concerning the use of NIP for subsurface remediation is limited (e.g., Lien and Zhang, 1999; Ponder et al., 2000; Elliott and Zhang, 2001; Lien and Zhang, 2001; Schrick et al., 2002; Nikolaidis et al., 2003; Lecoanet et al., 2004). Most of the studies to date have investigated the reactivity of the NIP with different types of contaminants (Okinaka et al., 2005; Liu et al., 2005). Nanoscale zero-valent iron has been used to degrade chlorinated alkenes (Lien and Zhang, 2001), chlorinated methanes (Lien and Zhang, 1999) and trichloroethylene (Li et al., 2003), and to treat chromium and lead (Ponder et al., 2000). These studies have clearly demonstrated that the performance of NIP is superior to microscale iron (iron filings). These studies have investigated reaction pathways and end products in detail.

Very limited studies have been conducted on the transport of NIP in porous media. Even some of these studies used glass beads, not real-world soils. These studies have indicated that the mobility of NIP is limited and have suggested the use of modified NIP such as polyelectrolyte- and surfactant-modified NIP. Unfortunately, such modification of NIP has the potential to reduce the reactivity of the particles as well as increase the material costs. Although the results of these findings are interesting, they may not be applicable to study the transport of NIP in different subsurface environments. The transport of NIP in subsurface is quite complex due to different geologic deposits with different gradation and composition and heterogeneities.

To date, commercially available NIP are shown to have excellent reactivity characteristics to detoxify different types of contaminants. However, the major hindrance to the *in-situ* remediation of contaminated sites is the difficulty of delivering the NIP uniformly and in substantial amounts into the contaminated regions. As explained earlier, the iron filings are placed in trenches when dealing with permeable reactive barrier systems, but the NIP can be injected into the contaminated zone using hydraulic methods such as flushing and pumping. The use of dispersant without or with pressurized systems has potential to prevent agglomeration of NIP and enhance transport and distribution of NIP in subsurface.

SYNTHESIS OF NANOSCALE IRON PARTICLES

The NIP can be synthesized from sodium borohydride reduction of ferrous iron (Wang and Zhang, 1997). However, concerns have been raised regarding the toxicity of these particles due to the presence of boron. The NIP are also commercially available from Toda America, Inc. and these particles are synthesized based on the following process: (1) acicular goethite ($FeO(OH)$) is precipitated from oxygenated $FeSO_4$ solution; (2) the acicular goethite is reduced to α-Fe grains in a heated hydrogen gas atmosphere; and (3) the α-Fe grains are wet-milled to convert the surface to magnetite:

$$2FeO(OH) + H_2 = 2\,Fe^0 + 2H_2O$$
$$3Fe^0 + 4H_2O = Fe_3O_4 + 4H_2$$

Based on x-ray diffraction methods, the NIP are found to consist of an elemental iron core (α-Fe) and a magnetite shell (Fe_3O_4) as shown in Figure 1(a). The approximate composition of NIP is 50 wt.% α-Fe core and 50 wt.% Fe_3O_4. The average particle size is determined with a scanning electron microscope (SEM) and is 70 nm (Figure 1(b)). The average BET surface area of NIP is 28.8 m^2/g. The density of the aqueous NIP particle suspension is 1.27 g/mL at solids concentration of 25.6 wt.%. The sulfur content is approximately 4,500 mg/kg and it originates from the ferrous sulfate starting material used for the production of NIP. These particles are manufactured in bulk and available presently at a cost of $25 to $30 per pound. Because of their nontoxic characteristics and relatively low cost, these particles are suitable for subsurface contaminant remediation.

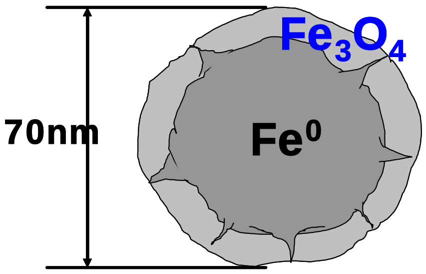


Figure 1(a). Structure of NIP

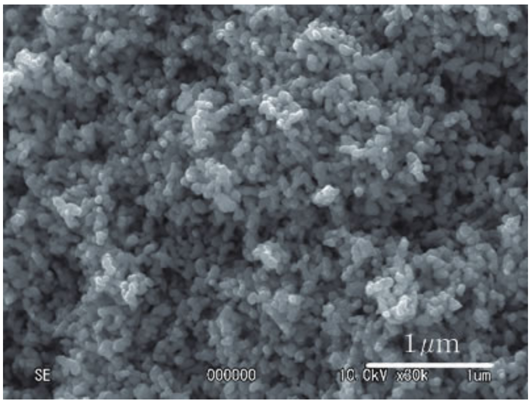


Figure 1(b). SEM image of NIP

The NIP from TODA America Inc. also known simply as nanoscale zerovalent iron particles (nZVI) or reactive nanoscale iron particles (RNIP), and the main properties of these are summarized in Table 2. It is interesting to note that these NIP possess electromagnetic properties. These particles have been chosen for this study because they are commercially available in large quantities at reasonable cost and their reactivity with different contaminants has been well characterized (Okinaka et al., 2005; Liu et al., 2005). The longevity and aggregation aspects of these particles have also been studied by different researchers (e.g., Liu et al., 2005). Saleh et al. (2005) found that the NIP possess negative surface charge with a zeta potential of -46 mV.

Table 2. Properties of NIP

Coercive Force (Hc)	408 Oe
Mass Magnetization (σs)	149.6 emu/g
σρ/ σs (ratio of ferromagnetism and antiferromagnetism)	0.152
pH	10.7
Surface Area (BET)	37.1 m^2g
Electrical Conductivity	$2.29x10^2$ μS/cm
Particle Size	50-300 nm
Aqueous Suspension	20-30 wt %
Density of Aqueous Slurry	1.2-1.3 g/ml

REACTIVITY OF NANOSCALE IRON PARTICLES

Several studies have investigated the reactivity of NIP with chlorinated organic compounds in aqueous systems and in sand; however, no studies have been reported on reactivity of NIP with organic contaminants in clayey soils. Recently, Reddy and Karri (2008) investigated the efficiency of NIP to promote the reductive degradation of PCP in a clayey soil. A series of batch experiments was conducted using kaolin as a low permeability clayey soil that was spiked with PCP at 1000 mg/kg and NIP at different concentrations. Specifically, different contact time (1, 2, 8, 12, 24 and 48h) and different NIP concentrations (1, 2, 4, 5, 8, 10, 20, 40, 60, 80 and 100 g/L) were investigated. PCP concentrations in supernatant and the residual soil for each test were measured. Results shown in Figure 2 reveal that 80 to 98% PCP was removed from the soil within an hour, and PCP reduction was increased from 50 to 78% at 1h contact time to 40 to 90% at 24 h contact time for different NIP concentrations. There was no significant effect of NIP concentration on the PCP removal; however, the amount of PCP reduction increased with increase in concentration of NIP with 30% at 1 g/L to 98% at 100 g/L. There appears to be an optimal NIP concentration beyond which benefits are diminished.

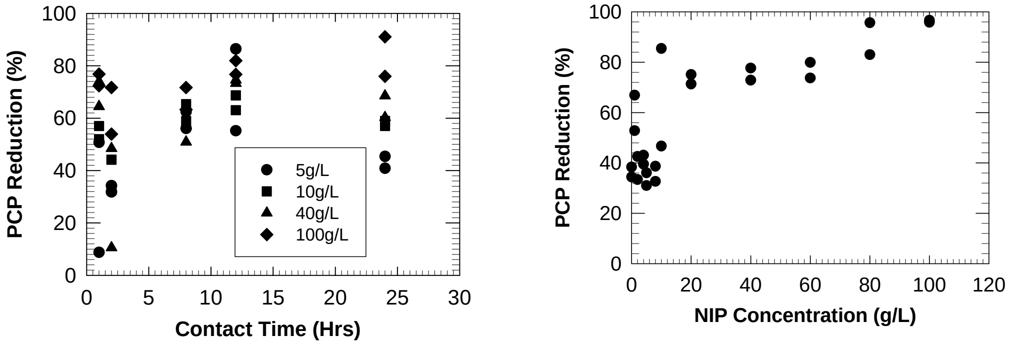


Figure 2. Effect of contact time and NIP concentration on PCP reduction (Reddy and Karri, 2008)

TRANSPORT OF NANOSCALE IRON PARTICLES

Hydraulic delivery of NIP into high permeability soils such as sands has been attempted by a few researchers. However, hydraulic delivery of NIP into clayey soils is not possible; therefore, Reddy and Karri (2007) investigated the potential electrokinetic delivery of NIP in low permeability soils contaminated with chlorinated organic compounds. Kaolin soil was used as a model low permeability soil and it was artificially spiked with PCP (1000 mg per Kg of dry soil). Laboratory electrokinetic experiments were conducted using deionized water or NIP of 50-300 nm particle size at slurry concentrations of 5 g/L and 10 g/L at the anode. All experiments were conducted for 427 hours at a constant voltage gradient of 1 VDC/cm. The experimental results showed that the soil pH decreased near the anode and increased near the cathode. Substantial electroosmotic flow was induced initially and then it decreased, but the flow was not hindered by the NIP. The total iron in the soil increased from the anode to the cathode, indicating that NIP may have transported towards the cathode. However, the transport of NIP in the soil was limited by aggregation and settling of NIP in the anode. In addition, NIP may have transformed into Fe^{3+} ions under the oxygenated and low pH conditions that existed at the anode. Figure 3 shows the PCP distribution in the soil at end of testing. It appears that NIP may not have contributed to PCP degradation. Instead, 47 to 55% of PCP was degraded in the cathode by reductive dechlorination in all tests. Complete PCP degradation did not occur in any of the tests because of limited transport of PCP into the cathode as a result of low solubility of PCP under the low pH conditions induced near the anode and low electroosmotic flow. An electrokinetic system without NIP may be effective for remediation of PCP provided enhanced transport of PCP into the cathode and high electroosmotic flow are achieved.

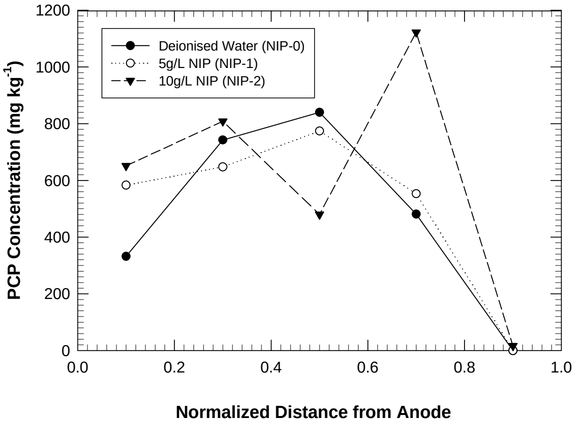


Figure 3. PCP Variation in the soil after testing (Reddy and Karri, 2007)

In a supplemental study, Reddy and Karri (2008) examined the enhanced delivery of NIP amended with surfactant or cosolvent under electric field for the remediation of kaolin soil spiked with PCP (1000 mg/kg of dry soil). Bench-scale electrokinetic experiments were conducted using NIP amended with a nonionic surfactant (5% Igepal CA720) or a cosolvent (5% ethanol) in anode and applying the same electric potential of 1 VDC/cm. Results showed that the electroosmotic flow was not influenced significantly by the amendment; however, the transport of NIP was limited similar to the experiment with bare NIP. PCP was partially degraded in all of the experiments not because of NIP, but mainly due to reductive dechlorination at cathode. The extent of PCP reduction was slightly more in the cosolvent system, possibly due to enhanced solubilization and transport of PCP into cathode. Overall, it is shown that new strategies are needed to prevent aggregation, settlement and oxidation of NIP for effective electrokinetic delivery of NIP and remediation of PCP in low permeability soils.

Reddy and Karri (2009) and Reddy et al. (2007) summarized the entire testing program, including the additional bench-scale electrokinetic experiments at different voltage gradients, as summarized in Table 2. Except for the control test, the anode reservoir was filled with NIP suspension and recirculated with a pump, while the cathode reservoir was filled with deionized water. During the application of electric potential, current and the electroosmotic flow were recorded. At the end of each test, aqueous samples from the electrodes and dissected soil sections were analyzed for pH, iron and PCP.

Table 2. Testing Program to Investigate Electrokinetic Delivery of NIP

Test Date	**Test Designation**	**Voltage Gradient (VDC/cm)**	**Anode Flushing Solution**	**Test Duration (Hours)**	**Pore Volumes**
March 31, 2003-April 18, 2003	NIP0	1.0	Distilled Water	427	1.2
	NIP1	1.0	5 g/L NIP	427	2.1
	NIP2	1.0	10 g/L NIP	427	2.2
August 28, 2003-October 7, 2003	NIP3	2.0	5 g/L NIP	937	0.9
	NIP4	2.0	10 g/L NIP	936	1.5
	NIP5	1.0	5% Igepal CA-720 + 5 g/L NIP	936	2.4
	NIP6	1.0	5% Ethyl Alcohol + 5 g/L NIP	936	2.5

Under all studied testing conditions, the extent of delivery and reactivity of NIP were limited by passivation and aggregation of NIP under the oxygenated and low pH conditions that exist at the anode as well as complex geochemical reactions occurring simultaneously at different rates. The NIP transport may be affected by probable dissolution of substrate minerals and possible precipitation of secondary solids as well as changes in the surface charge of all solids as the solution composition changes. Parameters controlling these reactions include pH, Eh, solution composition, and solid (both NIP and substrate) composition and structure. Besides these considerations, surface modification of NIP, introduction of NIP away from the anode, and the optimization of system parameters such as voltage gradient, mode of voltage gradient application (pulsed versus continuous), and pH control at the anode and cathode should be investigated.

TRANSPORT OF COMMERCIAL SURFACE MODIFIED-NANOSCALE IRON PARTICLES

Recognizing that bare NIP cannot be transported effectively through saturated soils, including high permeability sands, TODA America, Inc. developed three types of modified NIP particles. Reddy (2006) and Reddy and Khodadoust (2007) assessed the transport of the bare and modified NIP in a sandy soil by performing a series of column experiments. The four types of RNIP, provided by TODA America, Inc., were their original RNIP (10 DS) and three polymer coated MRNIP. The procedure for this research involved loading the columns with clean soil to a height of 20 cm, injecting a slug of selected RNIP suspension at 2.0 grams per liter (g/L), flushing with deionized water or simulated groundwater, and analyzing effluent for pH, electrical conductivity, total dissolved solids, and iron. Among the different polymer MRNIP, MRNIP-2 was found to transport relatively better under both deionized water (DI) and simulated groundwater (electrolyte) flushing. Using MRNIP-2, a series of enhanced transport strategies were then tested, including various polymer to RNIP ratios, different levels of pressure and conditions (pulsed and constant), and oxygen-free conditions (oxygen was replaced with nitrogen). Results shown in Figure 4 show that polymer MRNIP, specifically MRNIP-2, can be effectively transported through subsurface soils under pressurized conditions.

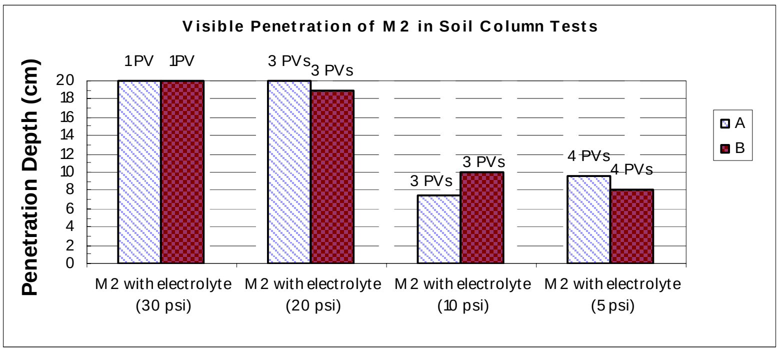


Figure 4. Visible penetration of M2 in soil column tests (Reddy and Khodadoust, 2007)

EVALUATION OF DIFFERENT SURFACE MODIFICATIONS

A systematic study was conducted to evaluate different dispersants to modify the surface characteristics of NIP and enhance their transport in soils. Firstly, the zeta potential of NIP with various surface modifying agents was measured (Cameselle et al., 2008). Eight different dispersants at different concentrations were investigated to determine their ability to modify the surface characteristics and increase the stability of the NIP suspension, minimizing flocculation and precipitation of the NIP. The studied dispersants and their tested concentration ranges (as % of NIP suspension, w/w) were: lactate compounds [aluminum lactate (2-15%), sodium lactate (6-12%) and ethyl lactate (6-12%)], polymers [aspartic acid (2-8%) and polyacrylic acid (2-8%)], and cyclodextrins [2-hydroxypropil-β-cyclodextrin (1-4%), β-cyclodextrin (1-4%) and methyl-cyclodextrin (1-4%)]. Zeta potential of NIP-dispersant suspensions was determined by measuring the electrophoretic mobility through tracking the movement of the charged colloids inside an electrophoresis cell.

Results showed that the zeta potential of bare NIP was 41.7±2.3 mV. The influence of the dispersants was found to vary significantly depending on the chemical nature of the dispersant and the electrical charge of the ions in solution. Aluminum lactate released Al^{3+} into the solution, resulting in a reduction of the modified NIP zeta potential from 37.7±1.8 mV at 2% concentration to 9.5±0.7 mV at 15% concentration. However, sodium lactate affected the zeta potential slightly, while ethyl lactate slightly increased the zeta potential. Among the polymers, aspartic acid showed a significant reduction of zeta potential from 27.5±8.7 mV at 2% concentration to 13.4±3.3 mV at 8% concentration, but the most significant influence was observed with polyacrylic acid. Even small concentrations of polyacrylic acid resulted in large changes in the zeta potential of NIP from positive (for bare NIP) to negative (-20.5±1.2 mV at 2% conc.) and this value remained almost constant at higher polyacrylic acid concentrations. Finally, cyclodextrins had the smallest effect on the zeta potential of modified NIP with a slight increase (up to 49.3±3.2 mV).

In order to directly assess the enhanced transport of NIP in soils, Reddy et al. (2009) conducted column experiments using NIP modified with different dispersants. Eight different dispersants (3 types of lactate, 2 polymers and 3 cyclodextrin) at different concentrations were tested. The dispersants tested were aluminum lactate, sodium lactate, ethyl lactate, polyacrylic acid, aspartic acid, methyl β-cyclodextrin, beta-cyclodextrin and hydroxyl propyl – beta- cyclodextrin. The porous media used was natural fine to coarse sand. During the experiment, the sand was homogeneously packed in a glass vertical column of 2.5 cm inside diameter and a length of 30 cm. The soil was packed at a height of 20 cm and the bottom of the column was plugged with a stopper containing a wire mesh and filter membrane. A slug of NIP amended with dispersant was immediately placed on top of the sand. The top of the column was covered with a plug connected with a tube from a cell containing electrolyte solution under 30 psi pressure. About 20 pore volume of electrolyte is injected into the vertical column by opening the closed valve of the cell. Effluent was collected at the bottom of the column in 60-mL bottles at different time. The time for each bottle collected is recorded and the weight and volume of the solutions were all measured. The permeability, iron concentration eluted, pH, conductivity and total dissolved solids were all determined. Visual observation also helped in determining whether the slug was transported or not. The results depict that higher percentage of NIP modified with aluminum lactate eluted from the soil. 10% aluminum lactate exhibited the highest (93%) elution of the modified iron from the soil media. Aspartic acid and ethyl lactate showed less amount of iron eluted (35-40%). With the bare NIP, only about 50% eluted from the soil media. In the case of aluminum lactate, the amount of iron eluted increased with increased in concentration (2 to 10%) up to 10% then start to reduce with increase in concentration. pH differs due the type of dispersant added to the NIP. The pH turn to decrease with increase in concentration when the dispersant is slightly acidic and the pH turn to increase with concentration when the dispersant is slightly basic. The experiment showed that different dispersant help transport the NIP differently. It also showed that different concentration of the various dispersant shows different characteristics in their transport abilities. Aluminum lactate at 2% showed about 55% elution and 10% aluminum lactate gave about 92% elution. It shows that there is an optimum concentration at which each dispersant perform better. Overall, these results demonstrated that aluminum lactate can increase the stability of RNIP suspension and enhance their transport in subsurface soils. Furthermore, this dispersant is environmentally safe, relatively inexpensive, and practical to use.

TRANSPORT OF LACTATE-MODIFIED NANOSCALE IRON PARTICLES

The effect of NIP concentration and type and concentration of lactate amendment on the transport of lactate-modified NIP was investigated by performing a series of column experiments. Khodadoust et al. (2008a,b) present the transport of NIP modified with lactate in 1-

D sand column experiments under pressurized conditions using a natural sandy soil and an electrolyte solution. Sodium lactate and aluminum lactate were considered as lactate species for modification of NIP. Aluminum lactate was mixed with bare NIP at concentrations of 2, 4, 6, 8, 10 and 12%, and introduced at the top of the sand column. As shown in Figure 5, the elution of RNIP from the sand column increased with increasing concentration of aluminum lactate up to 10% using a constant air pressure of 30 psig. Elution of NIP slug through the sand column ranged from 55% for bare NIP to 90% for NIP modified with 10% aluminum lactate using an NIP dosage of 4.8 g/L. Using a constant aluminum lactate concentration of 10%, the elution of NIP through the sand column decreased with increasing dosage of NIP, ranging from 90% for 4.8 g/L to 65% for 12 g/L. Using a dosage of 4.8 g/L of NIP, 10% sodium lactate performed worse than 10% aluminum lactate, resulting in an elution value of 80% versus 90%, respectively.

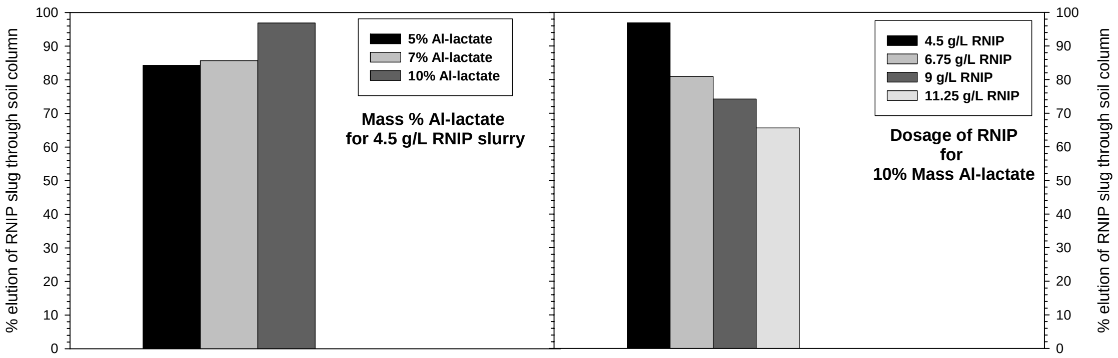


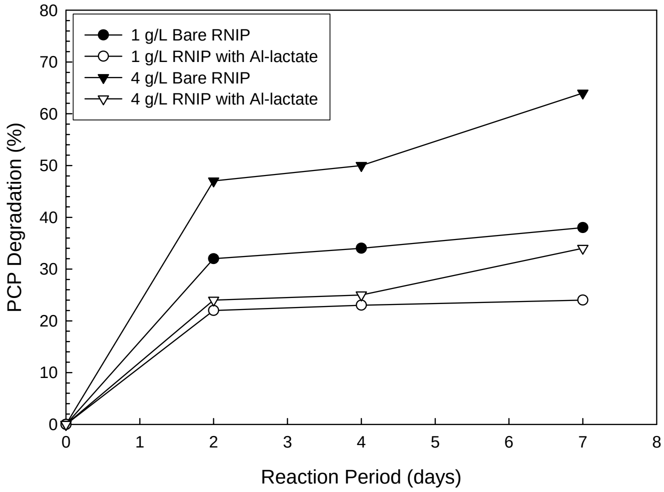
Figure 5. Enhanced transport of nZVI particles using aluminum lactate (Khodadoust et al., 2008a)

REACTIVITY OF LACTATE-MODIFIED NANOSCALE IRON PARTCLES

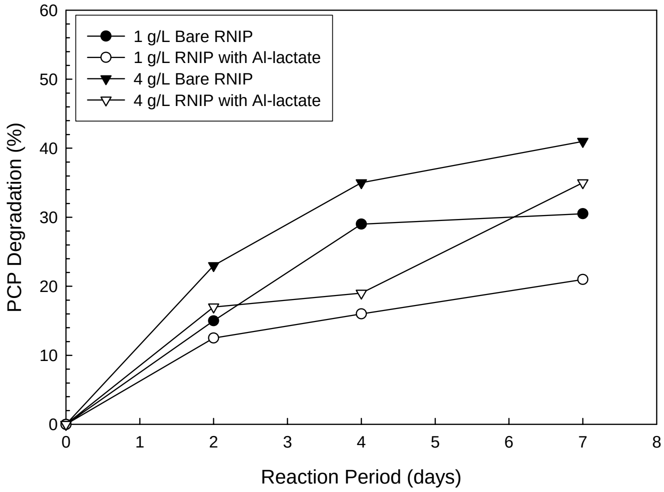
The surface modification by dispersants can affect the reactivity of NIP. As lactate provides better transport, Khodadoust et al (2008b, c) investigated the efficiency of lactate-modified NIP to promote the reductive degradation of PCP in subsurface soils with low permeability and high permeability using clayey and sandy soils, respectively. A series of batch experiments was conducted using kaolin and natural sand soils spiked with PCP at 100 mg/kg and NIP at two concentrations of 1 and 4 g/L. NIP was modified with 10% aluminum lactate (w/w). Typical results are shown in Figure 6. For both soils, the degradation (reduction) of PCP in soil increased with reaction time for all systems, while degradation of PCP in soil was greater for systems without lactate and for systems with the higher concentration of NIP (4 g/L). Higher NIP concentrations resulted in greater degradation of PCP in soil, while longer reaction periods led to greater degradation of PCP in soil (1 and 4 g/L RNIP, with or without lactate). The results show that the greatest degradation after 7 days occurred for the systems with 4 g/L of bare RNIP in both soils. PCP degradation of 35 and 41 percent in natural sand was obtained for NIP with and without lactate, respectively. PCP degradation of 34 and 64 percent in kaolin was obtained for NIP with and without lactate, respectively. PCP degradation was greater for kaolin than for natural sand using 4 g/L bare NIP, while PCP degradation in both soils was comparable using 4 g/L modified NIP.

TRANSPORT AND REACTIVITY OF LACTATE-MODIFIED NANOSCALE IRON PARTICLES

Lactate-modified NIP is shown transport through sand better in column experiments and its reactivity with PCP is decreased as compared to bare NIP. However, it is important to determine the reactivity of modified NIP with PCP as it is transporting through soil. Reddy et al. (2008) compared the transport and reactivity of bare and lactate-modified NIP by conducting horizontal column experiments using field sand contaminated with pentachlorophenol (PCP). Bare NIP and modified NIP with 10% aluminum lactate were investigated at two different slurry concentrations of 1 g/L and 4 g/L. Lactate was found to prevent or slow agglomeration and



(a) Kaolin



(b) Natural Sand

Figure 6. Degradation of PCP in Soils using Bare and Modified NIP (Khodadoust et al., 2008c)

settlement of NIP. NIP slurry was introduced at the inlet of the soil column under a constant hydraulic gradient. Visual observations revealed that the distribution of NIP was uniform in the 4 g/L modified-NIP experiment compared to all other experiments. Hydraulic conductivity of the soil was measured during the course of each experiment- it remained approximately the same in all the experiments except it reduced in the experiment with bare NIP at 4 g/L concentration. Figure 7 shows the distribution of residual PCP in the soil at the end of testing. Transport of NIP in experiments with bare NIP was not uniform and most of the PCP degradation occurred near the inlet where NIP could be transported during the initial stages of testing. The transport of NIP is enhanced by lactate, but the reactivity of NIP with PCP was decreased as compared to the bare NIP experiments. Degradation and the removal of the PCP were found higher (61.2% and 9.7%, respectively) for the 1 g/L lactate-modified NIP; while the degradation and removal were lower (51.6% and 6.4%, respectively) for the 4 g/L lactate-modified NIP. Overall, the results showed that lactate-modified NIP favors relatively uniform distribution of NIP in the soil, but the extent of PCP reduction is lowered by the surface modification. Further research is being performed to optimize the lactate-modified NIP that provides both efficient delivery as well as enhanced reduction of PCP in the soil.

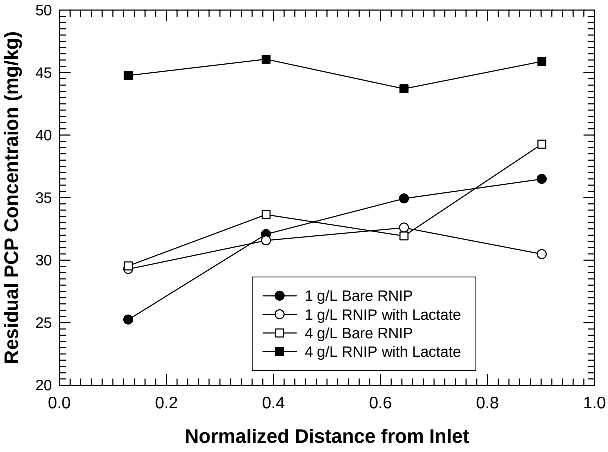


Figure 7. PCP distribution in the soil at the end of testing (Reddy et al., 2008)

SUMMARY AND CONCLUSIONS

Instead of iron filings, nanoscale iron particles (NIP) have great potential to be effective for the remediation of contaminated sites. The advantage of NIP is that they possess a large surface area and extremely high surface reactivity. Based on several series of batch and column experiments, the following conclusions can be drawn from this study:

- Bare NIP can reduce PCP in soils; the amount of PCP reduction increases with increase NIP concentration and with treatment time.
- The transport of bare NIP is found to be limited under hydraulic gradient in high permeability soil (sand) and under combined effects of hydraulic and electrical gradients in low permeability soil (kaolin).