

Nanotechnology for Site Remediation: Dehalogenation of Organic Pollutants in Soils and Groundwater by Nanoscale Iron Particles

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ABSTRACT: Thousands of sites have been polluted with variety of toxic chemicals, posing serious threat to public health and the environment. Emergence of nanotechnology, particularly synthesis of nanoscale iron particles (NIP), has provided opportunities to develop innovative site remediation technologies. The reaction pathways of NIP with target halogenated organic contaminants are similar to that of zero-valent iron (iron filings) commonly used in a permeable reactive barrier technology. However, due to their infinitesimally small size, NIP can be highly reactive due to their high surface to volume ratio and greater number of reactive sites and higher intrinsic reactivity on reactive sites. In addition, NIP can be injected directly into the contaminated zones, making the in-situ remediation faster and effective. NIP exhibit high van der Waal attractions due to high Haymaker constant and also have high magnetic properties which cause the NIP to agglomerate and settle. Therefore, NIP are modified with dispersants to achieve stability in suspensions as well as adequate transport and reactivity in subsurface environment. Our research has developed inexpensive and environmentally-benign lactate-modified NIP that are stable and capable of transporting in soils and groundwater and dehalogenating organic pollutants such as pentachlorophenol and dinitrotoulene. We have also developed pressurized system and electrokinetic system to deliver lactate-modified NIP into high permeability and low permeability soils, respectively. Limited number of field pilot applications showed that modified NIP can significantly reduce the pollutants into non-toxic products quickly and effectively.

INTRODUCTION

Thousands of sites exist in the United States and worldwide where subsurface soils and groundwater have been contaminated with a wide range of toxic organic compounds and heavy metals. In particular, halogenated organic contaminants, such as pentachlorophenol, trichloroethylene, trichloroethane, dinitrotoulene, and trinitrotoluene, are present at several sites, and these contaminants are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their toxicity and carcinogenicity. These contaminants are persistent in the environment and they are transformed or degraded extremely slowly by natural processes (Vogel et al., 1987). There has been public outcry and pressure on regulatory agencies to clean-up such contaminated sites urgently. The conventional methods of treating these contaminants include soil

washing/flushing, thermal desorption, vitrification, and bioremediation (Sharma and Reddy, 2004); however, these methods are relatively expensive, slow, or limited by the production of secondary waste streams that require subsequent disposal or treatment.

Permeable reactive barrier (PRB) technology, using iron metal or zero-valent iron (Fe^0) as reactive media, has shown to be effective in dehalogenation (detoxification) of organic contaminants in groundwater. Essentially, a PRB consists of installing a trench perpendicular to the path of groundwater flow and filling it with Fe^0 (e.g., iron filings). As the contaminant-laden groundwater passes through the PRB, the organic contaminants react with Fe^0 and dehalogenated into non-toxic form (Gillham and O'Hannesin, 1994; Sharma and Reddy, 2004). Several studies

investigated Fe^0 as an effective reductant in treatment of chlorinated ethylenes, halomethanes, nitroaromatic compounds, pentachlorophenol, chlorinated pesticides such as DDT, polychlorinated biphenyls, atrazine, and other organic compounds containing reducible functional groups or bonds. It should be mentioned here that Fe^0 has also been used for transforming redox-sensitive metals such as arsenic into relatively non-toxic and/or immobile forms through adsorption and transformation (reduction) processes; but heavy metals are not within the scope of this paper.

The use of zero-valent iron as an effective reductant in treatment of contaminants 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. Fe^0 is converted to ferrous ions (Fe^{2+}) in the presence of an oxidizing agent and therefore releases electrons and becomes available to reduce other compounds. 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, 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. In aerobic corrosion of iron, Fe^0 reacts with oxygen to form ferrous iron and water and in anaerobic conditions iron reacts with water to form ferrous ions, hydrogen and hydroxide ions. The possible reaction mechanisms for the treatment of organic compounds are dehalogenation, β -elimination, dehydrogenation, hydrolysis, transformation and hydrogenation depending on the type of contaminant.

PRBs have been preferred to remediate groundwater because they are relatively inexpensive due to low cost of Fe^0 (iron filings) and operation and maintenance (Sharma and Reddy, 2004). However, effectiveness of PRBs

depends on the site-specific hydrogeologic conditions, often requiring longer treatment duration. In addition, after a short time period, Fe^0 is liable to form an oxide surface film, which subsequently reduces the reactivity. Once Fe^0 comes in contact with air, even under proper storage conditions, its reactivity toward the target compounds is reduced. There can be considerable variation in the reactivity toward target pollutants by Fe^0 of different origins. The reaction rates can differ by up to three orders of magnitude. These factors limit the application of PRBs using Fe^0 for long-term *in-situ* remediation.

TABLE 1 Reactions of zero-valent iron (Fe^0) with a halogenated organic compound (RX) in water

<i>Reaction</i>	<i>Mechanism</i>
Anaerobic corrosion of iron	$\text{Fe} + 2\text{H}_2\text{O} = \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$
Aerobic corrosion of iron	$2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{Fe}^{2+} + 4\text{OH}^-$
<i>Possible reductive reactions of iron with RX</i>	
Reaction of RX with ferrous ion in the aqueous phase	$\text{RX} + 2\text{Fe}^{2+} + \text{H}^+ = 2\text{Fe}^{3+} + \text{RH} + \text{X}^-$
Reaction of RX at the surface of the metal (electron transfer reaction)	$\text{RX} + \text{Fe} + \text{H}^+ = \text{RH} + \text{Fe}^{2+} + \text{X}^-$
Adsorption of RX to the metal surface and the subsequent surface reaction of the organic radical R^*	$\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ $\text{RX} + \text{e}^- = \text{R}^* + \text{X}^-$ $\text{R}^* + \text{H}^+ + \text{e}^- = \text{RH}$

With the recent advent of nanotechnology, the use of nanoscale zero-valent iron particles (NIP) is shown to have great potential to overcome the problems of using PRB 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. Instead of waiting for the contaminants to pass through the PRB, NIP can be directly injected into the contaminated source zones (soils and groundwater) for rapid and effective detoxification of the contaminants *in-situ*. The infinitesimally small size (nm) and enhanced reactivity due to high surface area to volume ratio make NIP as excellent choice for *in-situ* subsurface remediation.

As compared to the studies dealing with iron filings and PRB, the number of research studies concerning the use of NIP for subsurface remediation is limited. Most of the studies to date have investigated the reactivity of the NIP with different types of contaminants in aqueous solutions. These studies have clearly demonstrated that the performance of NIP is superior to microscale iron (iron filings). For instance, the surface area of the NIP was found 1100 times more than that of the microscale iron and 95% of TCE was dechlorinated by NIP as compared to 86% by microscale iron (Cao et al., 2005).

Despite the greater reactivity of NIP than microscale iron, the delivery of NIP into the contaminated subsurface soils and groundwater for in-situ applications is limited due to quick aggregation and settling characteristics of NIP. Several investigators have developed surface-modified NIP to overcome this problem and quantify the resulting changes in reactivity with target contaminants.

This paper provides an overview of synthesis, properties and reactivity of bare and modified NIP with organic contaminants, transport behavior of bare and modified NIP in porous media, and engineered methods to enhance transport of NIP in high and low permeability porous media, and lessons learned from a limited number of field applications. The emergence of nanotechnology (specifically synthesis of NIP) has provided opportunities to develop innovative site remediation technologies to address insidious problems of subsurface contamination.

NANOSCALE PARTICLES

In general, nanoscale particles can be defined as particles of size ranging from one to hundred nanometers (nm) in any dimension (Nanotechnology Initiative, 2008). The size of nanoparticles is of several times smaller than even the red blood cells. Nanomaterials can be intentionally (engineered) or unintentionally (non-engineered) produced. Examples of non-engineered nanomaterials include airborne

combustion byproducts, volcanic ash, viruses, and diesel exhaust particles. Some of the different types of engineered nanomaterials include (a) carbon – based materials (composed of carbon), (b) metal – based materials (quantum dot, nanoiron, nanogold, nanosilver and other nanoscale metal oxides), (c) dendrimers (polymers branched units) and (d) composites (combination of different type nanoparticles) (USEPA, 2007). The important characteristics are the size of the particles and their properties which are different from the bulk material. The unique properties of the nanomaterials make them applicable in a wide range of different disciplines. Nanotechnology can be used for medical treatment (medical devices), military installation, pollution sensing and detection, ecosystem monitoring and green chemistry. One field that has received significant benefit with the emergence of nanotechnology is the remediation/decontamination of pollutants in soils and groundwater. The novelty of the technology requires extensive research into safe and beneficial applications of this technology.

Nanoscale metal oxides are considered excellent candidates for subsurface remediation. However, many nanoscale metal oxides (e.g., ZnO and AgO₂) are toxic and are considered unsuitable for injection into subsurface. Nanoscale iron particles (NIP), however, are considered best suited for environmental decontamination due to their environmentally-benign characteristics, favorable chemistry, relatively low cost, and easy use. The reactivity of NIP with target contaminants is shown to be relatively fast, resulting less-toxic or non-toxic transformations or products. Therefore, the use of NIP for site remediation is focused in this paper. In literature, NIP is also referred as *reactive nanoscale iron particles* (RNIP), *nanoiron*, *nanoscale zero-valent iron* (nZVI), etc.

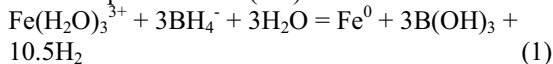
NANOSCALE IRON PARTICLES (NIP): SYNTHESIS, PROPERTIES AND REACTIVITY

Synthesis of NIP

NIP can be synthesized by different physical and chemical methods (Li et al., 2006). The physical

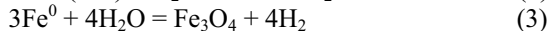
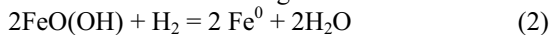
methods consist of inert gas condensation, severe plastic deformation, high-energy ball milling, and ultrasound shot peening. The chemical methods include reverse micelle (microemulsion), controlled chemical coprecipitation, chemical vapor condensation, pulse electrodeposition, liquid flame spray, liquid-phase reduction, and gas-phase reduction. Liquid-phase reduction and gas phase reduction methods are the most widely employed methods for synthesis of NIP that are used for site remediation purposes.

Wang and Zhang (1997) used the liquid-phase reduction method which consists of ferrous iron reduction by a strong reductant, sodium borohydride (NaBH_4), as per the reaction given below to produce NIP (Fe^0):



NIP produced by this method consists of particles in size between 1 nm and 100 nm and the BET surface area of the particles of $33.5 \text{ m}^2/\text{g}$.

Toda America Inc. (Schaumburg, IL, USA) uses the gas-phase reduction method to synthesize NIP in the following steps (Okinaka et al., 2005): (1) acicular goethite ($\text{FeO}(\text{OH})$) is precipitated from oxygenated FeSO_4 solution; (2) the acicular goethite is reduced to α -Fe grains in a heated hydrogen gas atmosphere at high temperature ($350 - 600^\circ\text{C}$); and (3) the α -Fe grains are wet-milled to convert the surface to magnetite:



The NIP produced by this method 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 . Typical properties of NIP are summarized in Table 2. The average particle size determined with a scanning electron microscope (SEM) is 70 nm (Figure 1(b)). The average BET surface area of NIP is $28.8 \text{ m}^2/\text{g}$. 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. It is interesting to

note that the particles possess electromagnetic properties. These particles are manufactured in bulk and available commercially currently (2010) at a cost of US\$25 to \$30 per pound.

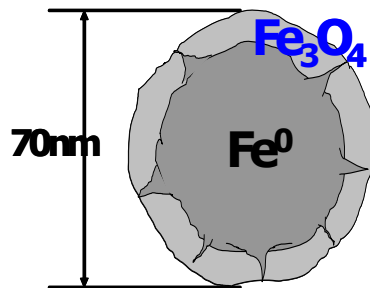


Fig.1(a) Structure of NIP synthesized by TODA

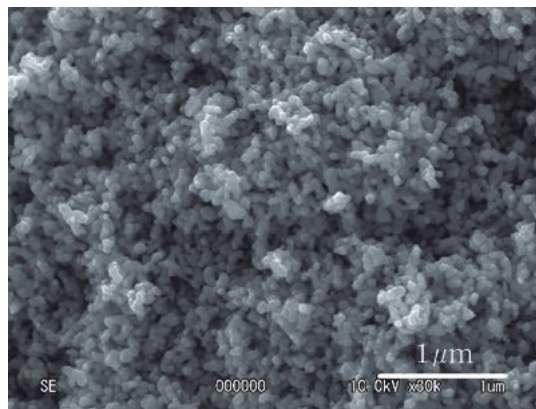


Fig.1(b) SEM image of NIP synthesized by TODA

TABLE 2 Properties of NIP synthesized by TODA

Properties	Value
Coercive Force (Hc)	408 Oe
Mass Magnetization (σ)	149.6 emu/g
σ_p / σ_s (ratio of ferromagnetism and antiferromagnetism)	0.152
pH	10.7
Surface Area (BET)	$37.1 \text{ m}^2/\text{g}$
Electrical Conductivity	$2.29 \times 10^2 \mu\text{S}/\text{cm}$
Particle Size	50-300 nm
Aqueous Suspension	20-30 wt %
Density of Aqueous Slurry	1.2-1.3 g/ml

Properties of NIP

Properties of NIP depend on the synthesis method and can be characterized by several methods and instruments such as transmission electron microscope (TEM), scanning electron microscope (SEM), atomic force microscope (AFM), dynamic light scattering (DLS), S-ray photoelectron spectroscopy (XPS), powder x-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy and matrix- assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF). These instruments help in the quantification of the particle size, shape/morphology and surface area of the particles.

Wang and Zhang (1997) used TEM to analyze the morphology of the particles and found that the BET surface area of NIP and microscale iron particles was 33.5 m²/g and 0.9 m²/g, respectively. Liu et al. (2005a) compared Fe particles synthesized from sodium borohydride reduction of ferrous iron (Fe/B) with NIP produced by Toda America (RNIP) (Table 3).

TABLE 3 Properties of Fresh Nanoparticles before

Reaction	Nanoiron	
	Fe/B	RNIP
Average primary size (nm)	30-40	40-60
Shape	Spherical	Spherical
Boron (wt%)	5	<10 ⁻⁴
Specific surface area (m ² /g)	36.5	23
Initial Fe ⁰ Content (wt%)	97±8	26.9±0.3

Shrick et al. (2002) characterized morphology of NIP using X-ray diffraction and transmission electron microscope, and the oxide content of the iron was evaluated using thermogravimetric analyzer. The results showed that the NIP sizes vary from 3 to 30 nm in diameter and they appear like chains of beads. The BET surface area of NIP was 18 m²/g and for Fe fillings was 2.6 m²/g.

Nurmi et al. (2005) also characterized the morphology of Toda NIP (Fe^{H2}), borohydride reduced NIP (Fe^{BH}) and microsized electrolytic Fe⁰ powder (Fe^{EL}) using TEM, XRD and XPS. The results show that the mean particle size as received and after flash dried had no significant difference. It was realized that Fe^{H2} consists of elemental iron (α -Fe⁰) and Fe₂O₄. The α -Fe⁰ is about 30 nm in size and the oxide is ~60nm in size. The surface consists mainly of Fe, O and small amount of S, Na and Ca. The presence of S is due to the use of FeSO₄ and that the sulfur (S) seems to play a role in its reactivity. The ratio of Fe/O ranges from 0.72 to 1.15. The size of the Fe^{BH} is <1.5nm and the particle aggregate diameter is between 20-100nm. They contain less iron and sulfur, but more boron and the Fe/O ratio varies from 0.4 to 0.55. It has a thin oxide layer and an outer layer of mainly sodium borate. The sulfur (S) in the Fe^{BH} is believed to be in an oxide form whereas the S in the Fe^{H2} is in a reduced form.

NIP can be highly reactive due to their high surface to volume ratio and they also have greater number of reactive sites and higher intrinsic reactivity on reactive sites (Tratnyek and Johnson, 2006; Nurmi et al., 2005). Due to their small size, they can be injected into the subsurface to directly react with the contaminants. NIP act as a reducing agent and react with both dissolved oxygen and water. NIP tend to easily agglomerate and settle fast which increases with increase in particle concentration and saturation magnetization (Phenrat et al., 2007; Saleh et al., 2007). The agglomeration changes the size of the particles making them microsize and not nanosize anymore thereby losing their unique properties (Tratnyek and Johnson, 2006). Quantum effects also influence on the chemical and physical properties of the NIP.

Reactivity of NIP

The reactivity of organic compound with NIP is dependant on the concentration of NIP, type and initial concentration of contaminant and reaction time. Factors such as pH, ORP, temperature, and anaerobic or aerobic conditions, affect the reaction

rate. The following steps are presumed to occur during reactivity of NIP: (a) movement of halogenated compounds from the solution to the surface of the iron; (b) The compounds get adsorbed to the surface of the iron; (c) reductive dehalogenation takes place on the surface of the iron; (d) the reduced products get desorbed; and (e) the products are transferred to the bulk solution (Shih et al., 2008). The presence of dissolved oxygen can affect the reactivity of nanoscale iron particles with the target contaminants (Tranyek and Johnson, 2006). The effect of ionic strength on the reactivity of RNIP is minimal at high concentration of mass of iron as compared to low concentration (Okinaka et al., 2005).

Liu et al. (2005a) investigated the reaction mechanism of NIP produced by Toda America (RNIP), and Fe particles synthesized from sodium borohydride reduction of ferrous iron (Fe/B). The study investigated how the two types of nanoiron particles react (reaction mechanism) or dechlorinate TCE. The study shows that given the same concentration of the two types of nanoiron, the amount (mass) of TCE dechlorinated is about the same. In the case of Fe/B about 92% of the iron was available for reaction and TCE is converted to saturated hydrocarbons such as ethane (80%) and C3 – C6 coupling products (20%). On the other hand, about half (54%) of Fe⁰ in RNIP was unavailable during the reaction. Reaction with RNIP converts TCE to unsaturated hydrocarbons such as acetylene and ethene.

Liu et al. (2005b) investigated the effect of structure (crystalline or amorphous) on reactivity and also how they can activate or made use of external addition of hydrogen to hydrodechlorinate TCE. The study made use of high resolution transmission electron (HRTEM) and selected area electron diffraction (SAED) to characterize the morphology of the particles. Nanoiron samples from borohydride reduction (Fe(B)) of dissolved iron(II) in water/methanol solution were used. Fresh Fe/B exhibit amorphous structure while annealed Fe(B)^{cr} and RNIP were crystalline in structure. The rate of dechlorination of the different particles with TCE was evaluated. The

crystalline nanoiron did not produce hydrogen and could also not use external addition of hydrogen and most of their reaction byproducts were unsaturated compounds. However, the non-crystalline particles were able to activate hydrogen and made use of any external addition of hydrogen. The crystalline nanoiron and the less ordered ones reacted differently and this might be due to the weaker atomic interactions in the less ordered nanoiron. The study attributed the activation of hydrogen for dechlorination by Fe(B) to the morphology (less ordered) of the nanoiron. The presence of hydrogen helped in the total hydrochlorination of the reaction. The non-crystalline particles were easily prone to oxidation as compared to the more crystalline nanoiron particles.

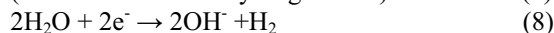
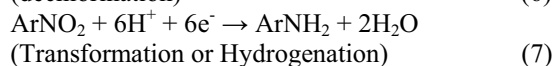
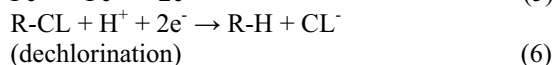
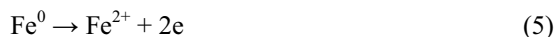
The properties of dry nanoiron particles change with time (aging) and also in contact with suspension and oxygen. The iron concentration available after 5 months of storage was about 14% less than the amount initially reported by the manufacturer. This was attributed to the oxidation of Fe⁰ by water to a more oxidation iron phases (e.g., Fe₃O₄, γ-Fe₂O₃ and γ-FeOOH). Sarathy et al. (2008) investigated the effect of aging on the reactivity of RNIP with carbon tetrachloride (CCl₄). Transmission electron microscope (TEM), X-ray diffraction (XRD) and MCD (mean crystalline diameter) were employed to examine the effect of aging on the composition and morphology of the particles. The study examined H₂ production, electrochemical corrosion potential, Fe⁰ content and morphology as the RNIP ages. Two types of RNIP were used for the experiment, thus the dried nanoparticles (Fe^{H₂(D)}) and the 'flash dried' (Fe^{H₂(W)}) (RNIP was received in a slurry form and dried by vacuum filtration process with acetone). The Fe^{H₂(D)} test was monitored for a 30 days period and Fe^{H₂(W)} sample stored for six months in the slurry form before flash drying and then the test was also monitored for 25 days period.

It was shown that the mole fraction of Fe⁰ in Fe^{H₂(D)} reduced from 0.9-0.75 in 5 days and the decrease was even higher in the presence of CCl₄ thus within 4 hours. Since the Fe^{H₂(W)} was stored

for six months before use its mole fraction was about 0.3 and this reduced gradually in the presence of deoxygenated/deionized water and CCl_4 over a period of 30 days. The MCD analysis of $\text{Fe}_2^{\text{H}_2(\text{D})}$ showed that Fe^0 decreases and iron oxide increases when in contact with dilute suspension after 5 days. In the case $\text{Fe}_2^{\text{H}_2(\text{W})}$, both Fe^0 and iron oxide slightly increased and was attributed to the fact it was in slurry for 6 months and there was modest modification over 20 days in dilute suspension. The TEM and XRD analyses shows that both particles exhibited initial thin oxide shells but becomes thick with time and this was more prominent with the $\text{Fe}_2^{\text{H}_2(\text{D})}$ particles. The study shows that rate of aging will be slower after 20 days but this contradicts earlier findings that $\text{Fe}_2^{\text{H}_2(\text{W})}$ will continue to age (Nurmi et al., 2005). It was shown that hydrogen production increased from 0-1.5 days and start to reduce after two days. The mass of CCl_4 reduced increases with mole fraction but decreases with increase in oxides. Knowing the life time of the particles will help the cleanup after treatment. Due to the importance of aging of NIP, as it affects the properties of the particle, Liu and Lowry (2006) investigated the effect of particle age of RNIP on reactivity of TCE. The study indicated that the initial iron content tend to decrease with time over a period of two years despite been stored in an anaerobic condition.

Tratnyek and Johnson (2006) reported that NIP possess high reactivity due to their high surface area, greater density of reactive sites and higher intrinsic reactivity on reactive sites. Different isomers of chloro phenol (2-CP, 3-CP, 4-CP) were dechlorinated by NIP and removal increased from 4-CP to 2-CP. The percent removal of 4-CP, 2-CP and 3-CP, were respectively 25.6%, 32.0% and 39.9%. The higher removal rate of 2-CP was attributed to having higher potential of accepting electrons. The position of the halogens had an effect on its removal rate. Also temperature affected the rate of removal and reaction pathway as dechlorination was predominant at higher temperature (30°C) whereas adsorption was the leading process at low temperature of 10°C (Cheng et al., 2008; Cheng et al., 2006).

Choe et al. (2001) studied the degradation of trichloroethylene, chloroform, nitrotoulene, nitrobenzene, dinitrobenzene and dinitrotoulene in aqueous solution at ambient and anaerobic conditions using NIP. They predicted degradation of organic contaminants by the following reaction pathways (equations 5 to 9):



The study showed that about 90% of TCE was dechlorinated after 30 minutes and the product was 70% ethane. On the other hand, chloroform was completely dechlorinated within 5 minutes and 80% of the products were methane. All the nitro compounds were transformed within 5 minutes of reaction. All the nitroaromatic compounds produced different reaction products of the amine group. After 30 minutes of reaction, 100% aniline was produced from nitrobenzene, 85% of toluidine from nitrotoulene, 80% of benzene diamine from dinitrobenzene and 70% of diamino toluene was produced from dinitrotoulene. NIP completely removed nitroaromatic compounds within 30 minutes of reaction. The reaction kinetics was pseudo first order and showed an average rate of 0.216 L/min (Welch and Riefler, 2008; Choe et al., 2001).

Shih et al. (2008) was able to dechlorinate 60% of hexachlorobenzene (HCB) after 24 hours reaction with NIP. High energy is required for the degradation of multiple bonds compounds and more functional group compounds results in less reaction rate with the nanoscale iron particles (Choe et al., 2001).

MODIFIED NANOSCALE IRON PARTICLES

Reactivity of NIP with certain contaminants can be slow; therefore, modified NIP is suggested in order to increase the reactivity. In addition, NIP are not stable due to agglomeration and sedimentation;

therefore, modifications are proposed to achieve stable NIP that can be available for reaction with the target contaminants.

Modification to Increase Reactivity

Several studies have reported methods to increase the reactivity of NIP. One approach to increase the reactivity of NIP is to combine NIP with a noble metal to form composite nanoparticles. The particles are called bimetallic nanoparticles and examples are Ag/Fe, Ni/Fe, Pd/Fe, and Cu/Fe. The noble metal acts as a catalyst and does not allow NIP to easily oxidize by protecting the iron core from rapid oxidation (Li et al 2006). Bimetallic particles have the potential to degrade most organic contaminants in aqueous solution.

Wang and Zhang (1997) showed that TCE was completely reduced after 1.7 hours by NIP and 0.25 hours by nano palladized-iron (Pd/Fe). Nano-bimetallics have been used to degrade different contaminants such as dichloromethane (DCM), chloroform (CF), carbon tetrachloride (CT), TCE, lead (Pb(II)), chromium (Cr(VI)), arsenate, VOCs, trichlorobenzene, and sulfur mustard. The particles have catalytic properties and therefore exhibit rapid initial rate of reaction (Wang et al., 2009, Shrick et al 2002). Unfortunately initial faster reaction rate cannot be sustained and the cost of treatment using such bimetallic nanoparticles increases, making it less attractive for use. Another downside of the bimetallic nanoparticles is the toxicity of the metals which may create new metal contamination problem to deal with.

Modification to Increase Stability

In addition to reactivity, the stability of NIP is also of a major concern. NIP exhibit high van der Waal attractions due to high Haymaker constant and also have high magnetic properties which cause the particles to agglomerate. In addition, NIP are denser than water and tend to settle down quickly in solutions. Due to these properties, NIP are not stable in suspensions for long period of time. The sedimentation and agglomeration of NIP impede the delivery of NIP into the contaminated zones during the in-situ applications. Researchers have been trying to modify the surface of the NIP to

make them more stable in suspension and ensure adequate reactivity as well as mobility to deliver into the contaminated subsurface zones. To achieve this, several different modifiers have been investigated including polyacrylic acid (PAA), guar gum, potato starch, triblock polymer modified and commercially available polymer-modified nanoiron (Saleh et al., 2007; Schrick et al., 2004; Yang et al., 2007; Traferri et al., 2008). Geiger and Quinn (2002) used emulsified NIP and compared its effectiveness with microscale iron particles (EZVI) to dechlorinate TCE. Modifiers can change the properties of NIP both positively and negatively. Modified NIP are more dispersed and homogeneous, stable and exhibit lower rate of sedimentation and aggregation (Yang et al., 2007; Kanel et al., 2008; Shrick et al., 2004; Saleh et al., 2007). However, the hydrodynamic diameter of the modified particles tends to change. For example, the addition of guar gum to 231 mg/l RNIP reduces the hydrodynamic radius but there was no effect when added to 1g/l RNIP. Increase in ionic strength (NaCl) of bare RNIP tends to increase the hydrodynamic radius but it has no effect on RNIP modified with guar gum. However, addition of CaCl₂ increased the hydrodynamic radius of both bare and guar modified RNIP (Traferri et al., 2008).

The surface charge of the NIP changes when they are modified depending on the modifier. Reactivity reduces to about 2 to 10 factors depending on the type of modifier (Saleh et al., 2007). The charge on the particle became negative when modified with anionic polymer (Kanel et al., 2008). Since the particles are surface mediated reaction, a thin film formed on the surface when they are modified can the reactivity negatively.

SUBSURFACE SOIL AND GROUNDWATER REMEDIATION

Many studies are conducted to investigate reactivity of NIP or modified NIP in aqueous systems. These studies are immensely valuable to understand the NIP reactivity with target contaminants in groundwater. Very limited studies have been conducted to investigate reactivity and delivery of NIP under subsurface conditions. In

order to achieve effective subsurface remediation, the NIP should have adequate reactivity with the target contaminants as well as be able to transport into the contaminated zone during in-situ injection applications.

Reactivity of NIP and Modified NIP in Soils

The reactivity of NIP in soils is very important as recalcitrant contaminants often reside within the soils above groundwater (vadose zone). As previously mentioned, due to their small size, NIP slurry can be injected directly into the soil and groundwater to react with the target contaminants *in-situ*. Reactivity in soils can be lower than in aqueous solutions due to rate-limited desorption or solubilization/dissolution of contaminants. For example 90% of PCB in aqueous solution was degraded as compared with 38% of PCB degraded in soils and the difference in reaction rate is due to the difficulty of the PCB in diffusing from the surface of the soil particles to the NIP surface for effective reaction (Varanasi et al., 2007; Wang and Zhang, 1997). Reaction rate in soils also increases with increase in NIP concentration and also by increasing reaction time (Chang et al., 2005; Varanasi et al., 2007; Chang et al., 2007). NIP have the potential of reacting with organic contaminants in soils better than that of microscale size. Chang et al. (2007) reported pyrene removal of 60% from soils in Taiwan by NIP, while microscale iron was able to reduce 11%. The reactivity of pyrene in soil followed pseudo first order. With time, foreign materials such as oxides get deposited on the surface of the iron particles, reducing reactivity.

Very limited studies have been reported on the reactivity of modified NIP in soils. Elliot and Zhang (2001) examined the reactivity of modified nanoscale particles (bimetallic Fe/Pd) with TCE in soils. The laboratory experiments were performed to study the effect of dosage and the products of the reaction. Batch tests were performed using groundwater and aquifer materials from an actual field site in Trenton, NJ. During the test 0.1 or 0.25 g of nanoscale iron and Fe/Pd particles were added to 40 ml groundwater and 40 g of sediment. The results showed a complete reduction of TCE in 12

hours for the 0.25g Fe/Pd, whereas it took 2 days for the 0.1 Fe/Pd to completely remove the TCE.

The surface modification by dispersants can reduce the reactivity of NIP. Reddy and Karri (2008) and Darko-Kagya (2010) investigated the reactivity of NIP and lactate-modified NIP (LM-NIP) with pentachlorophenol (PCP) and 2,4-dinitrotoluene (2,4-DNT) in kaolin and field sand as representative low and high permeability soils, respectively. Aluminum lactate modification was used among other modifiers investigated to achieve enhanced transport in soils (discussed in a follow-up section). Kaolin and sand were spiked, respectively, at concentration of 100 and 89 mg/kg PCP, or 920 and 740 mg/kg of DNT. Batch experiments were conducted with NIP and LM-NIP dosages of 1, 4, 10, 20, 50, 75 and 100g/L for 24 hours. The effect of reaction time was then evaluated using NIP and LM-NIP dosages of 4 g/L for 1, 2, 4, 7, and 14 days. Figure 2 shows the typical results for field sand. Higher NIP and LM-NIP dosages resulted in greater degradation of PCP and DNT in both soils. Greater PCP degradation occurred in bare-NIP systems than in LM-NIP systems where 95 and 98 percent degradation was obtained with bare-NIP for field sand and kaolin, respectively. The difference in PCP degradation between bare NIP and LM-NIP decreased with time for field sand but not for kaolin. For both field sand and kaolin, near complete dechlorination of PCP to phenol occurred with bare-NIP and LM-NIP, with a more rapid dechlorination in field sand than in kaolin. The DNT degradation ranged from 68% to 99% and 67% to 98% in kaolin and sand, respectively, with bare NIP, and it ranged from 65% to 99% and 59% to 98% in kaolin and sand, respectively with LM-NIP. The highest degradation was attained after 14 days in both soils. The reactivity of LM-NIP improved with time to levels as high as the reactivity of bare NIP.

Transport of NIP and Modified NIP in Soils

NIP or modified NIP are shown to have adequate reactivity with target contaminants in soils. As explained previously, iron filings are placed in trenches when dealing with permeable reactive

barrier systems, but the NIP or modified NIP is injected into the contaminated zone using wells or other injection systems (e.g. GeoProbe®) by hydraulic methods such as flushing and pumping. This method is possible due to its nanoscale size of the particles. It is essential that the NIP or modified NIP is transported and distributed through the entire zone of contamination to achieve effective remediation.

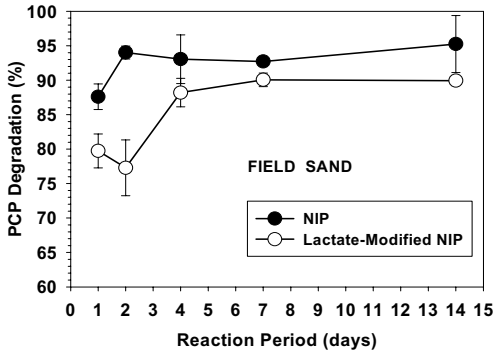


Fig.2 Degradation of PCP in field sand using bare and lactate-modified NIP (Darko-Kagya, 2010)

Transport of NIP or modified NIP can be impeded by hydrophobicity and hydrophilicity interactions, heterogeneity of the subsurface, blocking of deposition sites, presence of other properties, changes in attachment efficiency due to ionic strength and steric stabilization. Attachment efficiency is considered as the ratio of rate of particle deposition on a collector to the rate of collisions with that collector. This is a function of van der Waal forces, electrical double layer interactions, hydration forces and particle hydrophobicity. The particle attachment efficiency can be estimated using the expression below (Lecoante et al., 2004):

$$\alpha = -\frac{2d_c}{3(1-\varepsilon)\eta_0 L} \ln(C/C_0) \quad (10)$$

where d_c is the diameter of collector (assumed to be spherical) in porous medium, ε is the porosity, L is the length of porous medium, C and C_0 are particle concentration present at L and L_0

respectively, and η_0 is the clean bed single collector efficiency. Attachment efficiency is 1 when attachment is favored (Laconet et al., 2004; Yang et al., 2007). The charge of the particle is important during transport and therefore zeta meter was used to investigate the charge of NIP. The zeta potential of the NIP has been found to decrease with increase in pH (Yang and Lee, 2005).

The transport of bare NIP is very limited due to agglomeration; however, particle concentration and ionic strength affects the transport of NIP through porous media. Bare NIP transported only 2 cm in sand packed column but there was no transport when higher ionic strength of 1mM NaHCO₃ solution was used. Particle-particle interactions were more prominent during transport than particle-sand interactions (Saleh et al., 2007). Phanrat et al. (2007) employed a dynamic light system to monitor rate of sedimentation and aggregation of NIP. Magnetic attractive forces between particles are the major cause of aggregation. Two types aggregation occur during agglomeration: (1) iron particles come together to form secluded aggregates to form microsize particles and this tend to occur under 30 mins in solution, and (2) The aggregates link each other to form chains and this starts to form after 30 minutes. Particles tend to settle when they form aggregates since they become heavy. The sticking coefficient of unmodified nanoparticles in Chagrin soil was about 0.14, representing just 20% elution and the low sticking coefficient is due to high cation exchange capacity and high negative surface charge density.

The estimated travel for bare NIP was about 0.25 cm in loamy soil packed in a vertical column (Yang et al., 2007). Diffusion, interception and gravitational sedimentation are the basic mechanisms that control the capture of colloidal particles in a packed bed. Smaller particles of size less than 200 nm are affected by diffusion, and larger particles are affected by gravitational and sedimentation (Hydustsky et al., 2007; Tranyek and Johnson, 2006; Lecoante and Weisner, 2004). Flow rate and length of porous media can affect the delivery of NIP. Increase in flow rate reduces

the breakthrough time (Kanel and Choi, 2007). Kanel et al. (2008) attributed transportability of NIP to advection, dispersion, and density of the medium. Clogging and filtration also affect the transport pattern. Reported sticking coefficient of bare nanoiron particles ranges from 0.14 – 1 and it showed the particles will travel few centimeters in a typical groundwater (Shrick et al., 2004; Tratnyek and Johnson, 2006; Yang et al., 2007). Some of these studies used glass beads, not real-world soils (Kanel and Choi, 2007; Kanel et al., 2008).

Enhanced Transport of NIP and Modified NIP in Soils

As previously explained, NIP requires modification to increase their stability and maintain adequate reactivity. Simultaneously, one should consider that modified NIP should be able to transport through the soils while maintaining adequate reactivity with the target contaminants under subsurface conditions. This has been a challenging task for the remediation professionals. In addition, alternate hydraulic delivery techniques such as pressurized or pulsed pressurized systems may further enhance transport of modified NIP in the subsurface. Since hydraulic delivery methods are ineffective in low permeability clayey soils, electrokinetic methods may offer enhanced transport of modified NIP in such soils.

Modified NIP for Enhanced Transport

Some investigations have suggested the use of modified NIP such as polyelectrolyte- and surfactant-modified NIP to assure stability and adequate reactivity and transport in soils.

Saleh et al., (2007) studied ways to enhance the NIP for effective transport using three different modifiers (triblock polymer modified, surfactant modifier and a commercially available polymer-modified nanoiron). The study evaluated the effect of ionic strength and particle concentration on the transport of the iron particles. Whenever the surface of RNIP is modified with a polymer, its surface charge and stability changes which in turn changes the hydrodynamic diameter of the particles. Transport of bare RNIP through a sand column of low ionic strength showed that very low

amount of iron eluted out about $1.4 \pm 3\%$. Bare RNIP got trapped within the first 1-2 cm of the column. When RNIP was modified, more particles were eluted. Modified RNIP (MRNIP) and Triblock polymer eluted about 98% and 95% respectively while SDBS eluted 48%. The study showed that transport depends on particle concentration and that at low concentration of 180 mg/L RNIP about 50% iron eluted. It was shown that increase in ionic strength decreases the transport abilities of both the bare RNIP and modified RNIP. In the case of bare RNIP there was no transport when the ionic strength was increased more than 1mM NaHCO_3 . There are more particles – particle interactions than the particle – sand interactions. In the case of surface modified RNIP there was no pore plugging and sticking.

Modified NIP exhibit low sticking coefficient due to high cation exchange capacity and high negative surface density which implies there seems to be repulsion among negative clay particles and negative particles of the modifiers (Shrick et al., 2004; Hydustsky et al., 2007). Straining plays a major role than filtration and zeta potential does not always show a relationship with filtration length (Hydustsky et al., 2007; Saleh et al., 2007). Increase in concentration of modifiers (PAA) increases transport. However there is a limit to increase in concentration. When PAA was increased from 3 – 6g/l, an increase in transport was realized but a further increase from 9 – 12g/l decrease the transport. Increase in flow rate also enhances delivery of NIP (Kanel and Choi, 2007). Trafferri et al. (2008) examined the sedimentation rate and aggregation behavior of modified and bare NIP.

Cameselle et al. (2008) investigated different modifiers or dispersants to enhance transport of NIP in soils. 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. Firstly, the zeta potential of NIP with various surface modifying

agents was measured. 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. The study 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. After their characterization, the relative effectiveness of each dispersant on the transport of NIP was investigated in column experiments. The porous media used was a clean natural fine to coarse sand. During the experiments, 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 was 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 study showed that 10% aluminum lactate exhibited the highest (93%) elution of the modified iron from the soil media (Figure 3). Based on the column experiments and zeta potential measurement results, aluminum lactate was selected as suitable dispersant for NIP to enhance transport in soils. Lactate is considered as a green compound (environmentally friendly) and cheap. Moreover, it also enhances bioremediation of contaminants in soils, making it a best choice if long-term residual treatment is relied on biodegradation. As previously explained, lactate modification also assures stability and adequate reactivity of NIP.

Reddy et al. (2008) investigated the transport and reactivity of bare and lactate-modified NIP by conducting horizontal column experiments using field sand contaminated with PCP.

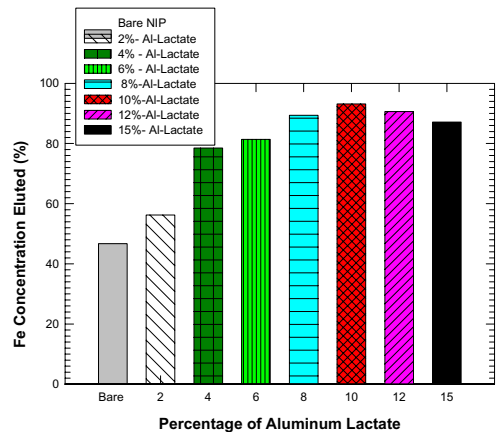


Fig.3 Elution of bare and modified nanoscale iron particles (Darko-Kagya 2010)

(For colour figure, refer to CD)

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 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 4 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.

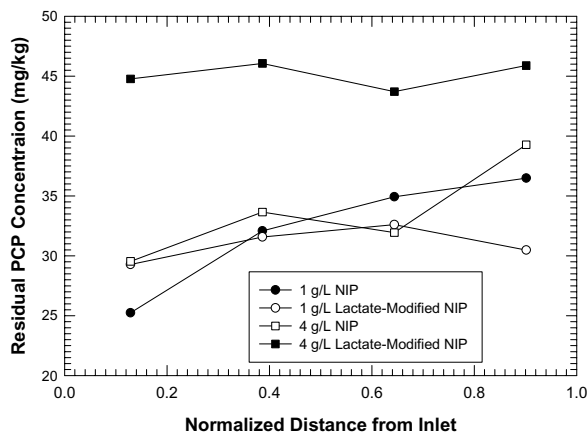


Fig.4 PCP distribution in the soil at the end of testing (Reddy et al., 2008)

Recently, Darko-Kagya (2010) performed a complementary study to investigate the transport and reactivity of LM-NIP in sand soil spiked with 740 mg/kg DNT. A magnetic susceptibility (MS) system that is capable of detecting and monitoring iron in the soil was used to monitor the transport of NIP in contaminated sand. Two NIP concentrations of 1 g/L and 4 g/L (of both bare and lactate modified NIP) and two hydraulic gradients (0.5 and 1.0) were applied to determine the effect of NIP concentration and solution flow rate on the transport and reactivity of NIP. The MS values changed across the length of the sand column due to the variation of iron concentration along the soil column. The data showed that 4 g/L of lactate modified NIP was more effective than 4g/L of bare NIP in transporting the NIP, evidenced by an increase in the MS values at the mid-section of the soil column over that of the bare NIP. There was no significant difference between the bare and lactate modified NIP at 1 g/L NIP. As a result of

enhanced transport of 4 g/L lactate modified NIP, greater degradation of DNT occurred in the sand. The larger flow rate increased the mobility of the NIP particles, thus increasing their reactivity.

Pressurized/Pulsed Hydraulic Delivery

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. The four types of RNIP, provided by Toda America, were their original RNIP (10 DS) and three polymer coated MRNIP. Reddy (2006) assessed the transport of the bare and these modified NIP in a sandy soil by performing a series of column experiments. 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 show that polymer MRNIP, specifically MRNIP-2, can be effectively transported through subsurface soils under pressurized conditions.

Darko-Kagya (2010) also demonstrated through two-dimensional bench-scale experiments that pressurized system is effective for the transport of lactate-modified NIP through different types of sand.

Electrokinetic Delivery

Hydraulic delivery of NIP, even under pressurized conditions, will not be effective in delivering NIP or modified NIP into low permeability clayey soils. Reddy and Karri (2007) investigated the potential electrokinetic delivery of NIP in low permeability soils contaminated with PCP and

DNT. Kaolin soil was used as a model low permeability soil and it was artificially spiked with PCP (1000 mg per Kg of dry soil). 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. About 47 to 55% of PCP was degraded in the cathode by reductive dechlorination in all tests. It appears that NIP may not have contributed to PCP degradation. 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.

Darko-Kagya (2010) investigated the transport and reactivity of NIP and lactate modified NIP (LM-NIP) in low permeability clayey soils contaminated with dinitrotoluene (DNT) under applied electric potential. Bench-scale electrokinetic experiments were performed at constant voltage gradient (1 VDC/cm) with DNT spiked kaolinite at a concentration of 1000 mg/kg. A cylindrical Plexiglas cell (3.81 inner diameter, 13.5 cm length) specially designed for this study was used. NIP or LM-NIP at a concentration of 4 g/L was injected at location 3 cm from the anode. Aluminum lactate 10% (w/w) was used as modifier for LM-NIP. The results showed 41 to 65% of DNT degradation in the soil near the anode, while it was lower at 30 to 34% near the cathode. The highest DNT degradation was achieved using LM-NIP. The total degradation of DNT was attributed to both NIP and electrochemical process. Overall it was found that electrokinetic system can enhance the delivery of LM-NIP in low permeability soils for the degradation of energetic organic contaminants such as DNT.

Yang et al. (2007) reported a sticking coefficient of PAA-modified NIP through a vertical loamy sand column to be 0.0061; however, with the

application of an electric potential across horizontal loamy sand the sticking coefficient was reduced to 0.00034. The estimated travel of NIP through loamy sand with the aid of an electric current was reported to be 2.5 m whereas it is 0.25 m in the absence of electric potential when the soil is in a vertical position.

In an attempt to employ different ways to successfully transport NIP, Pamukcu et al. (2008) investigated the transport of modified NIP with the use of electrokinetics. The NIP was coated with polyvinyl alcohol-co-vinyl acetate-co-itaconic acid its iso-electric potential was found to be at pH-8.3. The particles were positively charged and will inturn move from the anode to the cathode under an electric potential. A thin bed of 60% moisture clay was used and a groove was created near the anode. The study showed that ORP reduces from the anode to the cathode and the initial pH at the anode and cathode were respectively 4 and 10 but was later changed to 2.3 and 12.5 after 46 hours. It was shown that electric field assisted the transport of surface charged NIP from the anode to the cathode. However diffusion did not help the migration of the NIP as it was still stacked in the grove. Corrosion occurs at low pH and high ORP, whereas passivity occurs at the cathode end of the clay with high ORP.

FIELD APPLICATIONS

Varadhi et al. (2005) applied modified NIP to remediate contaminated groundwater in Hamilton Township, NJ in *in-situ*. The site area was contaminated with 1,1- dichloroethane, 1,1-dichloroethene, 1,1,1- trichloroethane, 1,2 – dichloroethane and trichloroethane(TCE). Nanoiron concentration of 30 g/l was injected on a 20 foot grid pattern. The NanoFe Plus™ used was nanoiron particles modified to include a catalyst and support additive. Treatment was done in two phases and 3000 pounds and 1500 pounds were injected respectively. Geologically the site consisted of 6 feet fill, underlain by 20 ft interbedded silt, clay and lenses. The water table was at 21 ft below ground surface with perched water also at 2-8 ft below ground surface. The perched water zone contains high concentrations of

dissolved hydrocarbons and metals, while the water table contains lower concentration. The pH was less than 4 and this was solubilizing heavy metals present in the groundwater. The addition of nanoiron increased the pH to between 6 and 7 which helped to reduce the heavy metal concentrations. GeoProbe™ and truck mounted drilling equipment was used for the injection and on site mixing. Injection was performed at a pressure of 20 psi, and nine monitoring wells were used for monitoring. Injection in the central portion of the site was easy due to the presence of mainly sandy soil as compared the western and eastern portions where they experienced some difficulties due to the presence of silt and clay. The study reported 90% degradation of the dissolved contaminants after two weeks of injection and this was confirmed by increase in ethane and ethane concentrations. High degradation was observed at the central portion which consisted of sand where nanoiron slurry was easily delivered. The pH was increased and ORP potential reduced.

Quinn et al. (2005) performed field application of the dehalogenation of TCE using emulsified nanoscale zero valent iron (EZVI) in-situ. EZVI was injected into the saturated zone within five days. The team chose emulsified for the modification since it forms droplets oil-liquid membrane around the particle its biodegradable part will help degradation in the long-term by donating electrons. The hydrophobic droplets prevent the reaction with unwanted target. The RNIP was modified on site by the emulsifier. The lithology was characterized and slug tests were performed before injection. Soil and groundwater samples were analyzed before and after injection for concentration of TCE. The study showed that more than 80% of TCE was degraded from the soil and about 68% was removed from the groundwater. Degradation was confirmed with the observation of increase in concentration of cis-dichloroethene, vinylchloride, and ethane. However, the byproduct of laboratory analyses was ethane. The difference was attributed to the fact degradation of TCE was not only due to dehalogenation but also biodegradation. The hydraulic conductivity before and after were 43

ft/day and 38.2 ft/day, respectively. The pressure pulse technology used for injection did not help the delivery of EZVI and therefore pneumatic and direct push method was recommended.

Logan and Pastor (2007) performed a field pilot study experiment for the decontamination of VOCs using nanoscale zero valent iron particles (NZVI). The site was Nease chemical superfund site in Ohio. The facility operated between 1961 – 1973 whereby they produced household cleaning products, fire retardants and pesticides. Mirex was the common chemical used. The soils had a mirex concentration of 2.080 ppm and the VOCs in the groundwater had a concentration of 100 ppm and consist mainly of chlorinated ethane and ethene with other chemicals such as benzene and toluene. The site geology consisted of fractured sedimentary bedrock that is overlain by glacial till. The area is hydraulically connected and the groundwater is about 1 to 9 ft below the ground surface. The NZVI containing 20% organic dispersant and 1% palladium was injected in batches. A total of 100 kg NZVI was injected at a rate of 0.15 – 1.54 gpm within 22 days. The volume of injection was about 2665 gallons. Pressure injection systems were used and mixing was performed onsite. Water levels and geochemical parameters such as conductivity, pH, ORP, DO, temperature, potentiometric head were monitored in four wells that were close by the injection area. The study had a bench scale tests prior to the field pilot tests. The bench scale test was to provide the engineers the concentration to use and also to help them know the byproducts of the dechlorination. After two weeks of the bench scale test, almost all the contaminants were degraded with the exception of benzene. The pilot study showed 33 to 88% degradation of PCE and 30 to 70% TCE degradation after 4 weeks of injection. Methane, ethane and ethene were the major product but cis-DCE was also produced as a partial dechlorination of the compound. After 8 to 12 weeks of monitoring, the concentration was about the same or it had increased. The increase in concentration was attributed to the fact that the upper gradient was not treated and was polluting

the lower gradient area. There is on-going monitoring as benzene was still not degraded.

CONCLUSION

Nanotechnology has emerged to enhance *in-situ* remediation of toxic contaminants in our environment. Among the different nanoparticles, nanoscale iron particles (NIP) have the ability to decontaminate a wide range of contaminants in soils and groundwater in a safe and effective manner. NIP is able to reduce contaminants in a very short time due to their high surface to volume ratio and the byproducts are benign compared to conventional treatment. NIP tend to agglomerate and settle; therefore, modification of NIP is needed to maintain their stability. The selected modification must also ensure adequate transport and reactivity with the target contaminants under subsurface conditions. Research conducted at the University of Illinois at Chicago resulted in the development of lactate-modified NIP that has potential to be used for safe and effective *in-situ* remediation. Pressurized systems is shown to be effective for the delivery lactate-modified NIP in high permeability soils, while electrokinetic delivery system is shown to be effective for the transport of lactate-modified NIP in low permeability soils. Limited field applications demonstrate that modified NIP can reduce the target contaminants. Efforts are being made to predict transport and fate of NIP or modified NIP under field conditions for both optimal remediation and to reduce environmental risk associated with uncontrolled migration of particles.

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