Assessing the Use and Application of Zero-Valent Iron Nanoparticle Technology for Remediation at Contaminated Sites

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LIST OF ABBREVIATIONS

AFCEE	Air Force Center for Engineering and Environment
APGC	amphiphilic polysiloxane graft copolymers
BNI	bimetal nano-iron
BNP	bimetallic nanoscale particles
CMC	carboxylmethyl cellulose
CT	carbon tetrachloride
CY	cubic yard
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
EZVI	emulsified zero-valent iron
Fe	iron
LAI	liquid atomization injection
MSTO	mesothelioma
NAS	Naval Air Station
NASA	National Aeronautics and Space Administration
NEZVI	nano-emulsified zero-valent iron
Nm	nanometer
NPL	National Priorities List
NZVI	nanoscale zero-valent iron
ORP	oxidation reduction potential
PAP	polyaspartate
PCBs	polychlorinated biphenyls, polychlorobiphenyls
PCE	tetrachloroethylene, perchloroethylene
PEG	polyethylene glycol
PPT	pressure pulse technology
PRB	permeable reactive barrier
PV	present value
ROS	reactive oxidation species
TCA	1,1,1-trichloroethane
TCE	trichloroethylene, trichloroethene
TCP	1,2,3-trichloropropane
TOC	total organic carbon
USGS	U.S. Geological Survey
VC	vinyl chloride
VOC	volatile organic compound
ZVI	zero-valent iron

EXECUTIVE SUMMARY

Nanotechnology is one of the fastest growing sectors of the high-tech economy, with more than 800 consumer products using nanomaterials with personal, commercial, medical, and military uses. The term *nanoparticle* is generally used to refer to a small particle with all three dimensions less than 100 nanometers (nm). Its small size and large surface area per unit mass impart characteristics that can be useful in hazardous waste site remediation and contaminant reduction. The main focus of this paper will discuss the use of zero-valent iron nanoparticles. Due to its unique properties, this manufactured nanoparticle is able to effectively eliminate or neutralize certain recalcitrant pollutants that can be found in aquatic environments (*e.g.,* groundwater aquifers). Nanoscale zero-valent iron (NZVI) particles are typically 5–40 nm sized Fe^0/Fe-oxide particles that rapidly transform many environmental contaminants to benign products and are a promising *in situ* remediation agent. Due to their small size and increased reactivity, these manufactured nanoparticles have the potential to be more effective than the microscale ZVI that is already in use for contaminant remediation in soil and groundwater aquifers. However, little is known about the environmental fate of these nanomaterials once they have undergone biological and non-biological processes within a contaminated aquifer. For this reason, it is important to find out what the possible impacts of these nanomaterials are once they enter the environment and how they could potentially affect human health or the environment. Despite these concerns, NZVI technology and its application are a very promising, efficient and cost-effective method for remediating contaminated soil and groundwater aquifer sites.

1. INTRODUCTION

Zero-valent iron has been used successfully in the past to remediate groundwater by construction of a permeable reactive barrier (PRB) of zero-valent iron to intercept and dechlorinate chlorinated hydrocarbons such as trichloroethylene (TCE) in groundwater plumes. Currently, zero-valent iron in both the micro and macro-scale is used in PRBs for the purposes of remediation at contaminated sites. A PRB (Figure 5) most commonly contains granular iron as the reactive medium that degrades chlorinated organics into potentially nontoxic dehalogenated organic compounds and inorganic chloride that precipitates out of the water column and becomes part of the sediment. A PRB, in its simplest form, is a trench built across the flow path of a groundwater plume. The trench is filled with a suitable reactive or adsorptive medium that removes the contamination from the groundwater, thus protecting downgradient water resources or receptors. The treatment media are selected for their ability to clean up specific types of contaminants (ERT2 Multimedia Training Tools, 2008).

The use of nanoscale zero-valent iron (NZVI) instead of using micro/macro-scale Fe^0 (zero-valent iron) materials could potentially eliminate the need for using PRBs and be more effective in both cost feasibility and contaminant remediation. Laboratory studies indicate that a wider range of chlorinated hydrocarbons may be dechlorinated using various nanoscale iron particles (principally by abiotic means, with zero-valent iron serving as the bulk reducing agent), including chlorinated methanes, ethanes, benzenes, and potentially, polychlorinated biphenyls (EPA Nanotechnology White Paper, 2007). Several factors play a role in determining a nanoscale iron product's reactivity, including particle size, the amount of reactive surface area, the presence or absence of hydrogenation catalysts (*e.g.,* palladium), the method of manufacture, the morphology of the particle (porosity), the crystalline structure of the particle, impurities and coating, and whether or not particles have been exposed to acid washing (NZVI synthesis using sodium borohydride [NaBH]) (Dupont Chemicals, 2007). Two potential advantages of nanoscale zero-valent iron over the construction-grade ZVI used in conventional PRBs are that nanoparticles may be delivered to deep contamination zones by injection and that NZVI may be more effective at degrading some contaminants because of a higher reactivity due to increased surface area. Despite the potential for the use of manufactured nanoparticles, there are still particular concerns that must be addressed in regard to the effectiveness and application of this new technology. These issues include the mobility of nanoparticles under subsurface conditions, the kinetics and products of contaminant degradation by NZVI, and whether the NZVI maintains its reactivity during the time period of treatment (Nurmi, J. T. *et al.,* 2005).

2. DESCRIPTION OF NANOPARTICLES FOR SITE REMEDIATION

Nanoscale zero-valent iron particles, with primary particle size less than 100nm, are made by a variety of vendors and shipped as highly concentrated slurries, for use as a reagent to destroy organic contaminants and immobilize inorganic contaminants in groundwater. Several studies have shown that NZVI is very effective for the degradation of halogenated solvents such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes and other polychlorinated hydrocarbons in groundwater (EU paper, 2009). NZVI was also shown to be effective against some pesticides, heavy metals, and dyes. NZVI can be distributed into the subsurface using a variety of carrying fluids. Among the most common are water, nitrogen gas, and vegetable oil. Slurries of water and NZVI powder can be injected into the contaminated zone using nitrogen gas as a carrier. This helps the iron powder disperse in the subsurface and create contact between the contaminants and the iron. Alternatively, NZVI can be mixed with vegetable oil and water to create an emulsion, which is then injected into the contaminant zone (ESTCP, 2006). Researchers hypothesized that chlorinated solvents preferentially diffuse through the vegetable oil and react with the iron inside the emulsion droplet. NZVI will typically be received as stabilized aqueous slurry.

Bare NZVI (Figure 1) is composed of a core which consists primarily of zero-valent or metallic iron while the mixed valent [*i.e.*, Fe (II) and Fe (III)] oxide shell is formed as a result of oxidation of the metallic iron (Figures 1 and 1a.). Iron typically exists in the environment as iron (II)-and iron (III)-oxides, and as such, ZVI is a manufactured material. Thus far, applications of ZVI have focused primarily on the electron-donating properties of NZVI. Under ambient conditions, NZVI is fairly reactive in water and can serve as an excellent electron donor, which makes it a versatile remediation material (Stumm, W. and Morgan, J. J., 1996).

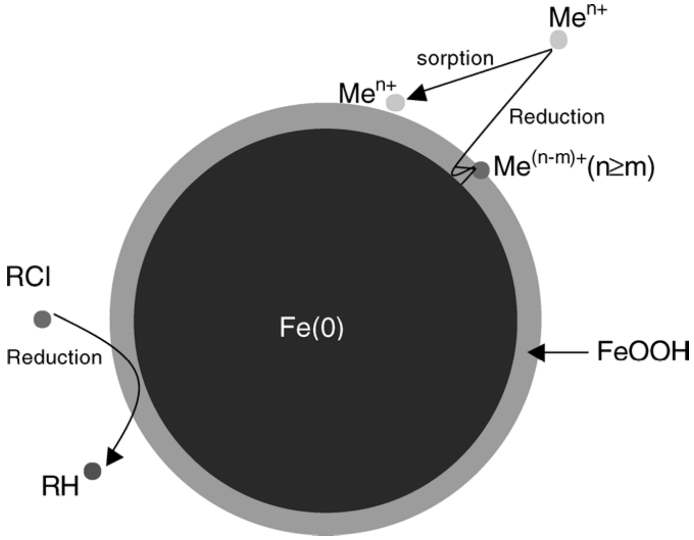


Figure 1: The Core-Shell Model of Zero-Valent Iron Nanoparticles. The core consists of mainly zero-valent iron and provides the reducing power for reactions with environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation of zero-valent iron. The shell provides sites for chemical complex formation (*e.g.*, chemosorption) (Li, Elliot, and Zhang, 2006).

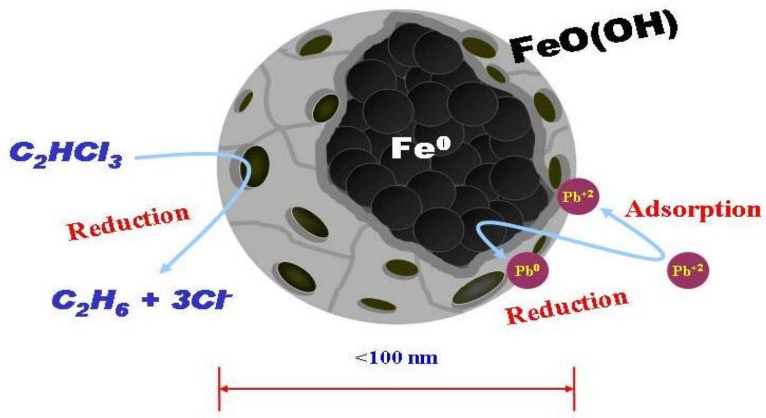


Figure 1a: A More Three-Dimensional View of a Zero-Valent Iron Nanoparticle. This figure also shows the porosity of the nanoparticle, which is also an important factor in physicochemical reactivity. Zero-valent nanoiron can also be coupled with trace metals (*ex*. Pt, Pd, Ag), showing significantly enhanced reaction. Nanoiron is potentially benign to the environment and, ultimately, is mainly transformed into Fe_3O_4 and Fe_2O_3, which are abundant on earth (Copyright © 2007 GeoNano Environ. Tech., Inc.).

According to the core-shell model, the mixed valence iron oxide shell is largely insoluble under neutral pH conditions and may protect the ZVI core from rapid oxidation.

A report by Tratnyek and Johnson (2006) stated that the greater reactivity that is often ascribed to nanoparticles can be the result of larger overall surface area, greater density of reactive sites on the particle surfaces, and/or higher intrinsic reactivity of the reactive surface sites. Together, these factors have produced three operationally distinct results for NZVI: (1) degradation of contaminants that do not react detectably with larger particles of similar material (*e.g*., polychlorinated biphenyls); (2) more rapid degradation of contaminants that already react at useful rates with larger particles (e.g., chlorinated ethylenes); or (3) more favorable products from contaminants that are rapidly degraded by larger materials but that yield undesirable byproducts (e.g., carbon tetrachloride) (Tratnyek and Johnson, 2006).

Elemental iron slowly oxidizes to ferrous iron and releases two electrons. These electrons begin to function in a variety of reactions that lead to the transformation of target contaminants. It is intended that toxic contaminants (*e.g*., tetrachloroethylene, tricholoroethylene) would be reductively dechlorinated to an essentially nontoxic mixture of ethane, ethene, and acetylene. Elemental iron can be oxidized by many substances in the environment in accordance with the following oxidation half reaction:

$$\mathbf{Fe^0\ (s) \rightarrow Fe^{2+}\ (aq) + 2e\text{-}\ (aq)}$$

Contaminants such as polychlorobiphenyls, or PCBs, and chlorinated benzenes can accept the electrons and be reduced to hydrocarbon compounds. For example, tetrachloroethene (C_2Cl_4) can be reduced to ethene in accordance with the following stoichiometry:

$\mathbf{C_2Cl_4 + 4Fe^0 + 4\ H+ \rightarrow}$

$\mathbf{C_2H_4 + 4Fe^{2+} + 4Cl^-}$

These reactions proceed in two known pathways: (1) Beta-elimination pathway, in which the formation of partially dechlorinated products such as dichloroethene and vinyl chloride (VC) is avoided, and trichloroethene (TCE) is transformed directly to ethane via the production of some short-lived intermediates, such as chloroacetylene and acetylene; and (2) Hydrogenolysis or sequential degradation pathway, which occurs when one chlorine atom is removed in each step, so that TCE degrades to *cis*-1,2 DCE, then to VC, and finally to ethene and ethane. It is believed that chlorinated solvents degrade primarily through the beta-elimination pathway when exposed to iron (Tratnyek and Sarathy, 2008). Beta-elimination is the preferred pathway because it occurs under abiotic-reducing conditions and degrades TCE without producing the environmentally persistent intermediate products DCE and VC.

The pH of the aqueous solution containing the NZVI is an important factor in the degradation, the rate of which is slightly faster at pH 4 than at pH 8.1. Degradation also continues at pH 4, while at pH 8.1 the degradation rate slows down and seems to plateau (McDowall, 2005). This is consistent with the mechanisms in that the production of hydrogen peroxide at pH 8.1 is initially smaller than that at pH 4 and decreases to below detection limits at about the time the degradation plateaus (McDowall, 2005). This next reaction shows ZVI reduction as an enhancement to Fenton Reagent Oxidation:

$\mathbf{Fe^0 + O_2 \rightarrow\ >O_2}$
$\mathbf{Fe^0 + >O_2 \rightarrow >Fe^{2+} + 2>e-}$
$\mathbf{>O_2 + >e- \rightarrow >O_2}$

$\mathbf{>Fe^{2+} \rightarrow\ Fe^{2+}}$
$\mathbf{>O_2^{\bullet-} \rightarrow O_2^{\bullet-}}$

$\mathbf{O_2 + O_2^{\bullet-} + 2H+ \rightarrow H_2O_2 + O_2}$
$\mathbf{Fe^{2+} + O_2 + H_2O \rightarrow FeOH^{2+} + O^{2\bullet-} + H^+}$
$\mathbf{Fe^{2+} + H_2O_2 \rightarrow\ FeOH^{2+} + OH^\bullet}$
$\mathbf{Fe^{2+} + OH^\bullet \rightarrow\ FeOH^{2+}}$
$\mathbf{FeOH^{2+} + OH^- \rightarrow Fe(OH)_3(s)}$
$\mathbf{Molinate + OH^\bullet \rightarrow Mol^\bullet + H_2O}$
$\mathbf{Mol^\bullet + O_2 \rightarrow keto\text{-}molinate\ isomers}$

Oxygen reacts with ZVI in two fashions. In the first, Fe^0 reacts with O_2 to form Fe^{+2} and O_2^{-2}. The O_2^{-2} reacts with hydrogen to form hydrogen peroxide, which reacts with more Fe^0 to form water. This is not a particularly useful reaction (USEPA, 2005a). In the second pathway, Fe^0 reacts with O_2 to form Fe^{+2} and O_2^{-2}. The O_2^{-2} reacts with hydrogen to form hydrogen peroxide, which reacts with Fe^{+2} to form Fe^{+3} and hydroxyl radicals (Fenton's reaction) that are highly reactive oxidants. The usefulness of the reaction depends on the efficiency of the branching process to favor hydroxyl radical formation (USEPA, 2005a). A study, performed by Chen *et al.* 2001, showed that Fenton's reagent was able to degrade aqueous phase TCE by 90 to 100 percent at a pH of 3. The experiments were also conducted in a sandy soil column and showed that Fenton's reagent with iron addition was able to oxidize TCE in the presence of the soil (Chen *et al*., 2001). For contaminants that are difficult to either oxidize or reduce, a combination of ZVI reduction and Fenton reagent oxidation may be useful. One main disadvantage to using Fenton reagent is that the pH has to be lowered to less than 4 to keep the iron in solution (Chen *et al*., 2001). There is a significant cost for acid addition, and subsequent base addition to raise the pH back up to neutral. Also, competition by other natural electron donors with target contaminants in these reactions can inhibit contaminant transformation to less toxic or non-toxic products. Other factors that can affect NZVI reactivity are oxidation reduction potential (ORP) and dissolved oxygen (DO).

NZVI works best under anaerobic conditions, especially in the case of beta-elimination reactions. Decreased DO levels and increased ORP ($\leq$ -400mV) are ideal conditions to facilitate target contaminant degradation (USEPA, 2005b). ORP depends on the transfer of electrons between chemical species and determines the reduction potential of an aqueous solution. Like pH, the reduction potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction in much the same way that pH does not necessarily characterize the buffering capacity. Reduction potential measurement is useful as an analytical tool in monitoring changes in an aqueous system rather than determining their absolute value.

Besides toxic chlorinated compounds such as TCE, NZVI has been shown to able to degrade other compounds found at contaminated sites such as the organic contaminant trinitrotoluene (TNT), pesticides (DDT), heavy metals (Hg, Ni, Cd, etc.), organic dyes (chrysoidin), and inorganic anions (Table 1) (Li, Elliot, and Zhang, 2006).

Table 1. Common Contaminants That Can Be Remediated by Iron Nanoparticles (Li, Elliot, and Zhang, 2006)

Chlorinated Methanes
- Carbon tetrachloride (CCl_4)
- Chloroform ($CHCl_3$)
- Dichloromethane (CH_2Cl_2)
- Chloromethane (CH_3Cl)

Chlorinated Benzenes
- Hexachlorobenzene (C_6Cl_6)
- Pentachlorobenzene (C_6HCl_5)
- Tetrachlorobenzenes ($C_6H_2Cl_4$)
- Trichlorobenzenes ($C_6H_3Cl_3$)
- Dichlorobenzenes ($C_6H_4Cl_2$)
- Chlorobenzene (C_6H_5Cl)

Trihalomethanes
- Bromoform ($CHBr_3$)
- Dibromochloromethane ($CHBr_2Cl$)
- Dichlorobromomethane ($CHBrCl_2$)

Chlorinated Ethenes
- Tetrachloroethene (C_2Cl_4)
- Trichloroethene (C_2HCl_3)
- *cis*-Dichloroethene ($C_2H_2Cl_2$)
- *trans*-Dichloroethene ($C_2H_2Cl_2$)
- 1,1-Dichloroethene ($C_2H_2Cl_2$)
- Vinyl Chloride (C_2H_3Cl)

Pesticides
DDT ($C_{14}H_9Cl_5$)
Lindane ($C_6H_6Cl_6$)

Organic Dyes
Orange II ($C_{16}H_{11}N_2NaO_4S$)
Chrysoidin ($C_{12}H_{13}ClN_4$)
Tropaeolin O ($C_{12}H_9N_2NaO_5S$)

Heavy Metals
Mercury (Hg^{2+})
Nickel (Ni^{2+})
Cadium (Cd^{2+})
Lead (Pb^{2+})
Chromium (Cr(VI))

Other Polychlorinated Hydrocarbons
PCBs
Pentachlorophenol
1,1,1-trichloroethane

Other Organic Contaminants
N-nitrosodiumethylamine (NDMA) ($C_4H_{10}N_2O$)
TNT ($C_7H_5N_3O_6$)

Inorganic Anions
Perchlorate (ClO_4^-)
Nitrate (NO_3^-)

3. BIOGENICALLY ENHANCED NZVI CONTAMINANT DEGRADATION

In situ biogeochemical transformation refers to processes in which contaminants are degraded by abiotic reactions with minerals formed that are either naturally occurring or are biogenically produced in the subsurface (AFCEE, 2008). Natural aquifer systems are complex ecosystems with a plethora of microbial communities. These microbial communities are subject to a wide variety of changes as the environment of the aquifer is altered. NZVI, with the proper substrate, could be used to take advantage of the degradation capabilities of these microbial communities for a synergistic degradation effect of target contaminants present in the aquifer. An ESTCP report in 2006 stated that a variety of different substrates have been used to stimulate anaerobic bioremediation. In practice, the added organic substrates are first fermented to hydrogen (H_2) and low-molecular weight fatty acids. These short-chain molecules, such as acetate, lactate, propionate, and butyrate, in turn provide carbon and energy for anaerobic bioremediation. The substrates can be broadly categorized into four types: soluble substrates, viscous or low viscosity substrates, solid substrates, and miscellaneous experimental substrates. All of these substrates are biodegraded and ultimately yield (or “release”) hydrogen (ESTCP, 2006).

A report done by the AFCEE in 2008 stated that there are four mediated transformations that are facilitated by biogenically produced reactive iron minerals; these reactive minerals are thought to include reduced sulfide minerals such as iron monosulfide (Butler and Hayes, 2001); green rusts which are layered structures composed of mixed divalent and trivalent iron oxides interspersed with water and anions, including sulfate, chloride, and carbonate (Christianson and Stipp, 2003; and Lee and Batchelor 2002); and magnetite. Magnetite is a ferromagnetic mineral composed of mixed divalent and trivalent iron with the formula Fe_3O_4 (Ferrey *et al.*, 2004; and AFCEE, 2008). Figure 2 shows how both biochemical and geochemical reactions can be linked to result in the generation of reactive surfaces that facilitate contaminant degradation, and provides an example of these synergistic reactions. The end products of these biogenically produced reactive iron mineral transformations of chlorinated pollutants such as TCE are CO_2 and H_2O. These reactions may be important in understanding the fate of NZVI once it enters the aqueous environment and when physicochemical and geochemical transformation occurs. The interplay of these reactions and their implications for remediation of contaminated environments is just beginning to become understood (AFCEE, 2008).

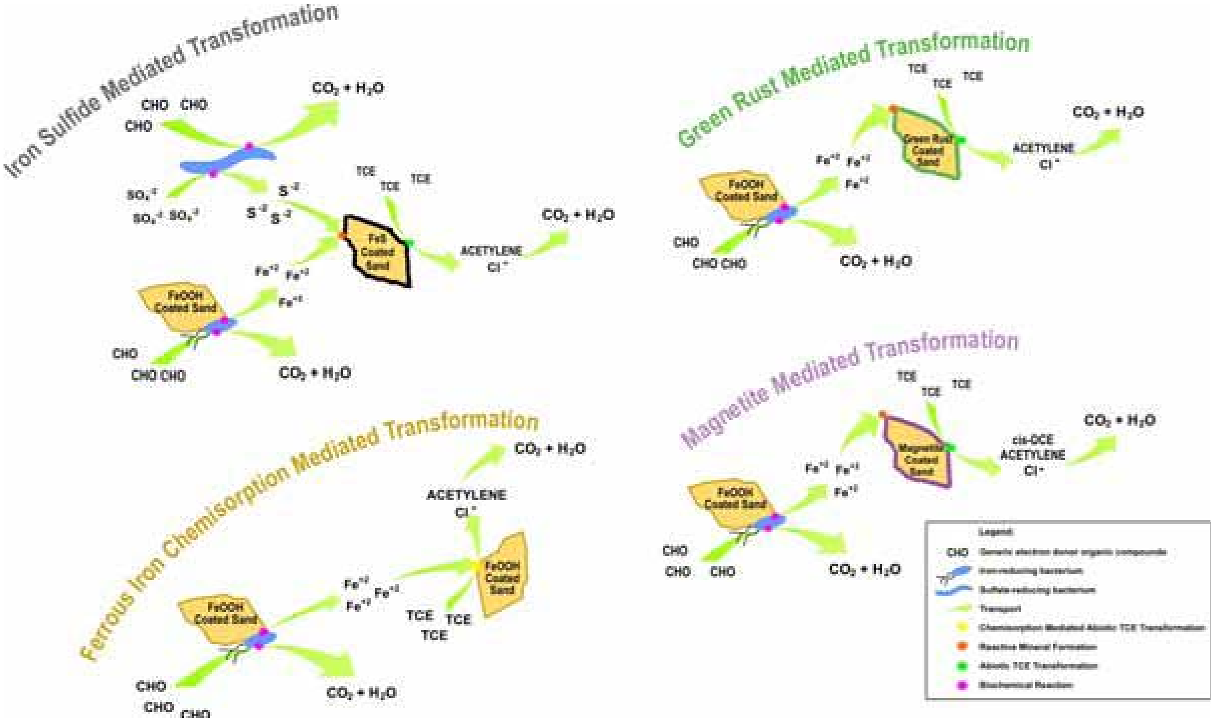


Figure 2: Four Mediated Transformations by Reactive Iron Compounds. (Iron sulfide, green rust, ferrous iron chemosorption, and magnetite) on the contaminant TCE (AFCEE, 2008).

3.1 Metal Catalyst: Bimetal Nanoparticles

Bimetallic nanoscale particles (BNPs) increase the kinetics of the redox reactions involved in contaminant remediation, and thus perform as a catalyst to this reaction. Palladium and iron BNPs are commercially available and currently the most commonly used in site remediation. The reactivity of the nanoscale iron particles can be significantly enhanced by depositing a small amount (less than 0.1 percent) of a noble metal (palladium, platinum, nickel, silver, etc.) on the surface of the iron, which creates bimetallic nanoscale particles (USEPA, 2008). Tee (2006), using Fe^0/Ni and Fe^0/Pd BNPs, observed a TCE degradation rate constant that was two orders of magnitude higher than bulk iron and NZVI, indicating that the bimetallic nanoparticles are more efficient at degrading TCE when compared to the monometallic iron nanoparticles. It has been postulated that atomic hydrogen adsorbed on the reductant surface (H_{ads}) is responsible for bimetal reactivity (Schrick *et al*., 2002 and Cirwertny *et al.,* 2007). In bimetallic systems, H_{ads} could be generated through the dissociative chemisorption of H_2, itself generated *in situ* via water reduction. Alternatively, H_{ads} could be produced as an intermediate to H_2 (Cirwertny *et al.,* 2007). It was also suggested that *ab*sorbed atomic hydrogen (H_{abs}) within the metal additive lattice, rather than surface-*ad*sorbed atomic hydrogen (H_{ads}), represents the reactive entity in iron-based bimetallic systems. Differences in the reactivity of Pd and Pt electrodes toward 4-chlorophenol have been attributed to the substantially greater solubility of atomic hydrogen in Pd relative to Pt (Zhang, 2003).

Laboratory research on TCE degradation at Oak Ridge National Laboratory (ORNL) led to the first reported observation of degradation byproducts, including vinyl chloride (VC), when using monoiron nanoparticles (Li, Elliot, and Zhang, 2006; and USEPA, 2006). In order to enhance dechlorination reaction rates and minimize byproduct formation, (BNP) systems of palladized iron were developed (and patented). It has been observed that the surface area normalized rate constant (K_{sa}) of Fe/Pd nanoparticles for the degradation of tetrachloromethane is over two orders of magnitude higher than that of microscale iron nanoparticles (Li, Elliot, and Zhang, 2006). Zhang (2003) has given an overview of the synthesis, characterization and use of NZVI particle and BNPs such as Fe^0/Pd^0, Fe^0/Pt^0, Fe^0/Ag^0, Fe^0 /Ni^0, Fe^0/Co^0, and Fe^0/Au^0 in environmental remediation. These nanoparticles can reduce a variety of organic pollutants (*e.g*., chlorinated alkanes and alkenes, chlorinated benzenes, pesticides, organic dyes, nitro aromatics, PCBs) and inorganic anions (*e.g*., nitrates) in aqueous solutions to less toxic and less recalcitrant by-products. NZVI and bimetallic NZVI nanoparticles have also been successfully used to reduce redox-active metal ions such as Cr(VI) to less toxic and less mobile Cr(III) species (Zhang, 2003).

Work done by Liu and Zhao (2007) and Xu and Zhao (2007) indicated the potential of using stabilized NZVI and phosphate-based nanoparticles as soil amendments, to reductively immobilize Cr(VI) and also reduce the bioaccessibility of Cu in soils (Cundy, Hopkinson, and Whitby, 2008). The Naval Air Engineering Station (NAES) in Lakehurst, NJ, conducted a series of bimetallic nanoscale particle (BNP) applications from 2001 to 2003 to treat groundwater containing chlorinated solvents. Based on successful results, a full-scale application was completed in 2003 to treat two contaminant source areas at the facility. The plumes consist primarily of tetrachloroethene (PCE), TCE, and 1,1,1- trichloroethane (TCA), and degradation products such as *cis*-dichloroethene (*cis*-DCE) and vinyl chloride. The selected BNP slurry contained iron particles averaging 50 nm in diameter and coated with trace (0.1 percent by weight) palladium that served as a catalyst for redox reactions. The slurry was injected directly into the aquifer across the treatment area over a period of 13 days using direct-push technology at 15 injection points. Overall, TCE and DCE concentrations decreased an average of 79 and 83 percent, respectively, and the average total volatile organic compound (VOC) concentration decreased 74 percent. Presence of the hydrogenation catalyst (Pd, Pt, Sn, Ni, Ag, etc.) is likely to be the object of regulatory scrutiny (USEPA, 2005b and Gavaskar *et al.,* 2005). Many of these metals were used historically in ways that foster human oral exposure such as dentistry and food preservation.

The use of palladium is the most extensively researched metal as a catalyst for BNP with zero-valent iron. Tratnyek and Sarathy in 2008 found that, in general, 1,2,3-trichloropropane (TCP) exhibits little or no reaction with mild reductants (including construction-grade ZVI) but is dechlorinated by strong reductants (like palladized NZVI). Figure 3 shows a summary of degradation pathways that are most promising for TCP degradation in soil and groundwater.

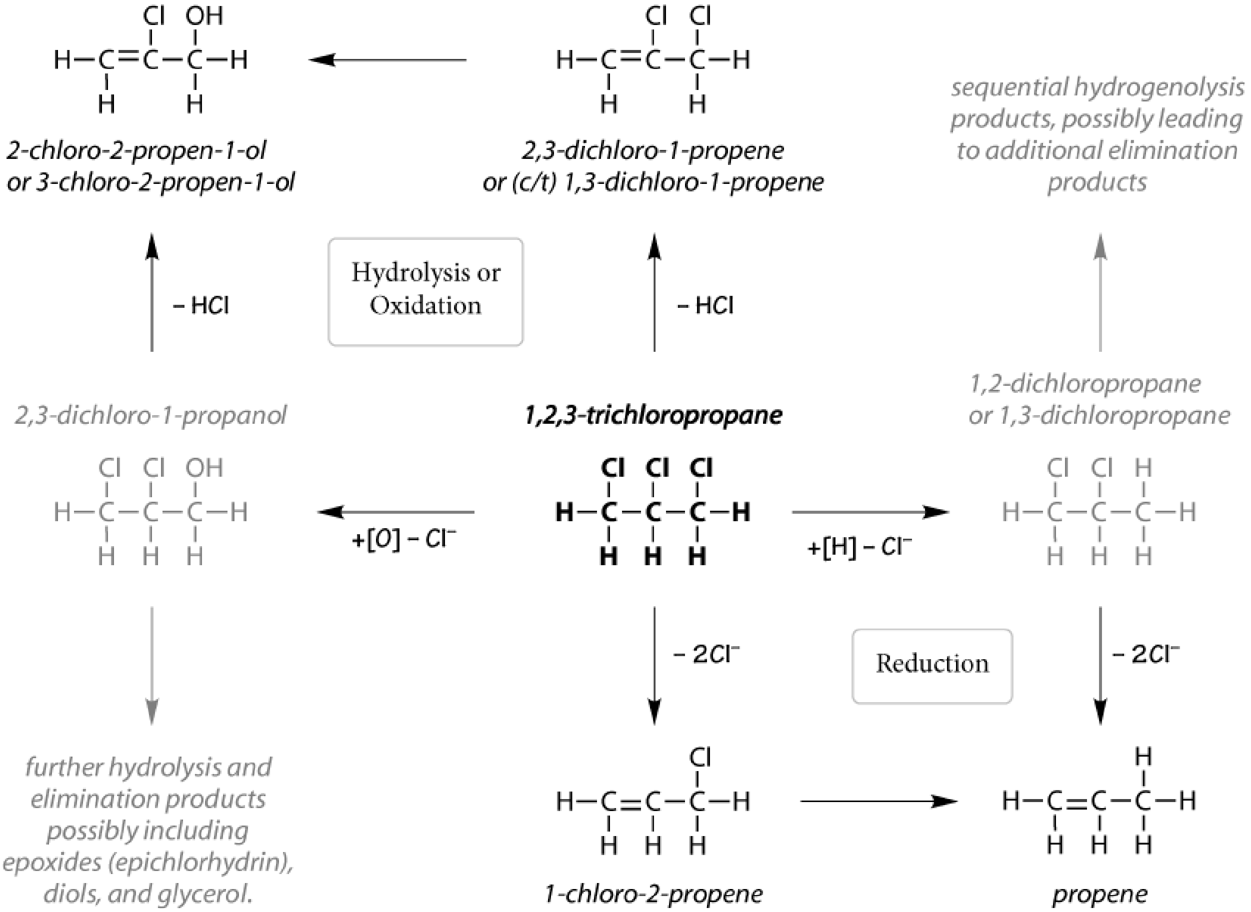


Figure 3. Anticipated Primary Reaction Pathways for Degradation of TCP. Oxidation, hydrolysis, and hydrogenolysis are represented by the horizontal arrows. Elimination (dehydrochlorination) and reductive elimination (reductive ®-elimination) are shown with vertical arrows. [O] represents oxygenation (by oxidation or hydrolysis), [H] represents reduction. Gray indicates products that are likely to be of lesser significance (Tratnyek and Sarathy, 2008).

Doping palladium on the surface sets up a galvanic couple, which increases the rate of corrosion of the iron, thus increasing the rate of dechlorination (Lien and Zhang, 2001). Palladium and nickel have also been found to significantly enhance the dechlorination of perchloroethylene (PCE) in a zero-valent silicon/water system (Doong, Chen, and Tsai, 2003).

Geochemistry literature analysis shows that Pd introduced into the environment through the application of bimetal nano-iron (BNI) will remain insoluble rather than dissolving and migrating down-gradient in aquifer environs. Nanoscale particles can be readily incorporated onto/into various supports, thus widening their scope of applications. Lin, Liou, and Lo (2009) studied nano- Pd/Sn bimetallic cation resin. Their results showed that it was possible to successfully synthesize these resins to enhance the removal of TCE from contaminated water. Although DO (dissolved oxygen), nitrate, and sulfide had a significant negative effect on the rate of degradation of TCE, a regeneration process using wet chemical method effectively restored the reactivity of the Pd/Sn/resin (Lin, Liou, and Lo, 2009).

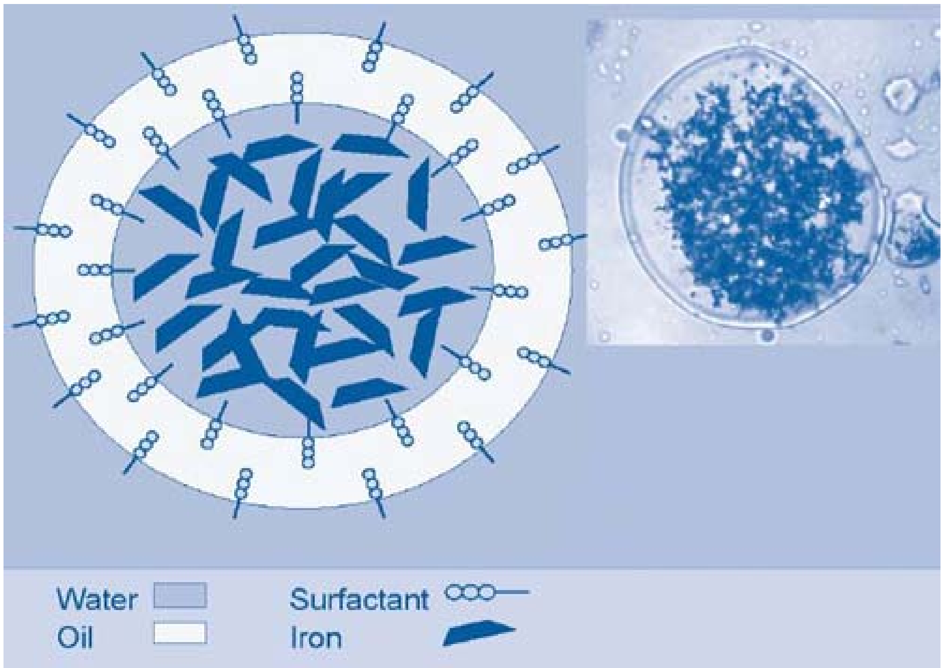
Research conducted by Liu *et al.* (2009) showed a more green approach in creating Fe^0/Pd BNPs, using nontoxic ascorbic acid and sodium carboxymethyl cellulose (CMC) as a reducing agent and capping agent. They found that adsorbed CMC molecules did not inhibit the addition of Pd atoms onto the seeds during the growth but provided stabilization of the Pd nanoparticles in aqueous solution after the growth. Along with the advantage of this seed growth process providing stoichiometric control over the size of the Pd nanoparticles by simply varying Pd^{2+} added during the growth stage, the use of ecologically friendly reagents, such as water (solvent), CMC (capping agent), and ascorbic acid (reducing agent), in both the seed synthesis and subsequent seed-mediated growth provide both “green” and economic attributes to this process.

3.2 Emulsified Zero-Valent Iron

Dense non-aqueous phase liquid (DNAPL) at the source zone of contaminated areas has been a major problem that inhibits the remediation process at contaminated sites and prevents site closure. DNAPLs are a common cause of environmental contamination at thousands of Department of Energy, Department of Defense, National Aeronautics and Space Administration (NASA), and private industry facilities around the country (AFCEE, 2008). To deal with this ongoing problem, researchers have developed emulsified zero-valent iron, or EZVI (Figure 4). EZVI is a surfactant stabilized emulsion with NZVI that is also biodegradable. The surfactant surrounds the nanoparticle to form very small colloid droplets consisting of an oily membrane around the zero-valent iron nanoparticle while suspended in water. The surfactant emulsion is commonly made of some type of vegetable oil. Edible oils have been used in a variety of locations throughout the United States to stimulate anaerobic biodegradation of chlorinated solvents and other contaminants (ESTCP, 2006). Not only would these particular emulsifiers stimulate microbial activity, but they would also allow for better mobility while forming a hydrophobic membrane around the NZVI, making them miscible to the DNAPL, such as trichloroethene (TCE), which is also hydrophobic. By using surfactants that attract the organic species to the surface of the NZVI, the contact time can be increased, thus allowing a more complete reaction. This is particularly important when using NZVI in a permeable barrier where the contaminated water usually flows through (McDowall, 2005).

Encapsulating NZVI in a hydrophobic membrane protects the nanoscale iron from other groundwater constituents such as inorganics that might otherwise use some of the iron’s reducing capacity, thereby reducing the mass of NZVI available to treat target contaminants, and affect overall project costs. According to researchers, when using EZVI, TCE diffuses through the oil membrane into the interior aqueous phase of the emulsion particle. There it will undergo reductive dechlorination facilitated by the zero-valent iron particles (USEPA, 2006). This will maintain a concentration gradient across the oil membrane and provide a driving force for TCE molecules to continue entering the micelle. The final by-products of non-chlorinated hydrocarbons from the reaction can then diffuse out of the emulsion into the surrounding groundwater. It is expected that increased destruction of chlorinated solvents can be achieved using EZVI through increased contact between the DNAPL and the nano-sized iron and through providing vegetable oil and surfactant components, which enable the material to serve as a long-term electron donor and to augment biological degradation.

In a three-year study conducted by the U.S. EPA (from 2002 to 2005), EZVI was introduced to an aquifer during a single injection occurring over five days in October 2002. Based on earlier laboratory evaluations, the selected injectant contained 44.3 percent water, 37.2 percent oil, 1.5 percent surfactant, and 17 percent (100 to 200 nm-sized particles) iron by weight (AFCEE, 2008). Geostatistical analysis indicated 58 to 85 percent reductions in total TCE and TCE DNAPL mass from initial pre-treatment estimates of 17.8 kg and 3.8 kg, respectively, in the upper sand unit (USEPA, 2006). Analysis of TCE in groundwater samples collected from wells located in the center and downgradient portions of the treatment area indicated 57 to 100 percent reductions of TCE at all targeted depths and significant reductions in TCE degradation products. Analysis of TCE and biodegradation products suggested that TCE reductions in the demonstration area were caused by contaminant destruction rather than mobilization. Nearly three years of monitoring following the demonstration suggests that biodegradation enhanced by the presence of oil and surfactant in the EZVI emulsion has contributed to TCE reductions. Surfactants can be ionic or nonionic. Research conducted showed that ZVI modified by nonionic surfactants has less positive synergistic effects than ZVI modified by cationic surfactants on carbon tetrachloride (CT) (USEPA, 2005b). Meng, Y. *et al.* (2007) indicate that the best degradation results were facilitated at near critical micelle concentrations.




NZVI Visible Inside a Vegetable Oil Emulsion Droplet

Figures 4 and 4a: **EZVI Emulsion Droplets Containing Nanoscale Iron Particles in Water Surrounded by an Oil-Liquid Membrane.** EZVI is usually composed of surfactant, biodegradable vegetable oil, water, and nanoscale iron. The emulsion particles (or micelles) that formed from this mixture contain a nucleus of iron suspended in water, surrounded by an oil membrane. The surfactant keeps the micelles intact and well-distributed (dense non-aqueous phase liquids [DNAPLs]) (Treatment Technologies 2005).

3.3 NZVI Mobility/Dispersion: Implications of Technology and Application

In situ degradation of contaminants, when feasible, is often preferred over other approaches because it has the potential to be more cost-effective. However, *in situ* remediation requires delivery of the treatment to the contamination, and this has proven to be a major obstacle to expanded development of *in situ* remediation technologies. With respect to this issue, nanotechnology has special relevance because of the potential for injecting nano-sized (reactive or absorptive) particles into contaminated porous media such as soils, sediments, and aquifers. In this manner, it should be possible to create either: (i) *in situ* reactive zones with nanoparticles that are relatively immobile; or (ii) reactive nanoparticle plumes that migrate to contaminated zones if the nanoparticles are sufficiently mobile. The *in situ* mobility of nanoparticles will be discussed further below. The appeal of NZVI for remediation stems from the potential for improved remediation chemistry and/or expanded options for deployment that complement the already well-developed science and engineering of contaminant remediation with millimeter-sized "conventional" ZVI. This combination of factors has led to very rapid transfer of this technology from preliminary laboratory testing to pilot-scale demonstrations in the field. Full-scale commercial applications of NZVI in remediation are quickly becoming common, and there already are competitive markets among purveyors of NZVI materials and geotechnical service providers with various methods for deploying NZVI.

Even though NZVI has been used for groundwater remediation of various contaminants because of its physicochemical properties, NZVI, however, is not only highly reactive with the contaminants, but also rapidly reacts with surrounding media in the subsurface, such as dissolved oxygen and/or water, and other non-target compounds. This means that there can be a significant loss of NZVI reactivity that occurs before the particles reach the target contaminant. Also, strong magnetic interaction between particles causes agglomeration which can limit colloidal stability and cause reduction in reactive surface. According to a report by Dupont Chemicals in 2007, in order for treatment reactions to occur, there must be direct contact between NZVI particles and the contaminant molecules.

NZVI transports away from the application point; typically on the order of 10 m or more is essential for field application by direct push well injection systems (Henn and Waddill, 2006; and Selah *et al.,* 2008). Safety concerns surrounding the uncontrolled release of nanomaterials into an aquifer are further motivation to determine the mobility of NZVI under natural groundwater conditions. Rapid aggregation and limited mobility in water-saturated porous media limits the ability to deliver NZVI dispersions in the subsurface (Phenrat, T. *et al*., 2007).

Bare NZVI with an apparent zeta-potential of -30 mV ± 3 mV has a relatively low zeta potential due to its zero valence and small size (Selah, N. *et al.,* 2007). This means that these particles are unstable and can become immobile in an aqueous solution (Selah, N. *et al.,* 2007). These particles may adhere to negatively charged minerals or natural organic matter surfaces before reaching target contaminants such as chlorinated dense nonaqueous phase liquids (DNAPL) (Selah, N. *et al.,* 2008). Using an electroacoustic spectrometer, Lien *et al.* (2006) found that the zeta potential of a 0.85 percent (by weight) slurry of NZVI in water was measured to be -27.55 mV at a pH of 8.77. According to this data, NZVI is not stabilized at this pH and begins to aggregate and settle out of the aqueous medium. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. For molecules and particles that are small enough, a high zeta potential will confer stability, *i.e.,* the solution or dispersion will resist aggregation. When the zeta potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. Colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate (American Society for Testing and Materials, 1985). This means that colloidal particles with zeta potential values more positive than +30 mV or more negative than -30 mV are considered stable with the maximum instability (*i.e.,* aggregation) occurring at a zeta potential of near zero or zero. It provides an indication of the stability of the colloidal suspension and is a function of many variables, including the nature of the particle surface, ionic strength, pH, and presence of other substances that can interact with the surface (*e.g.*, surface-active polymers, etc.) (Lien *et al.,* 2006). This can be important information for NZVI technology application.

Incomplete destruction reactions could result from poor contact, from adding insufficient quantities of NZVI, or from aquifer conditions that limit the reaction (*e.g.*, unfavorable pH, low temperature). Also, NZVI may not react with or destroy all groundwater contaminants. Incomplete destruction of target contaminants due to the low mobility of NZVI could result in the generation of toxic partial degradation products. At this stage of development, a laboratory feasibility study, followed by appropriate field studies, are recommended to demonstrate contaminant destruction and treatment mechanisms.

Lower molecular weight polymers or surfactants that afford primarily electrostatic repulsions may provide adequate mobility enhancement needed for placement in groundwater remediation systems (Saleh *et al.,* 2008, and Krajangpan *et al*., 2008). Considering the requirements of an effective delivery system for NZVI, functionalized amphiphilic polysiloxanes may be an ideal class of polymers for this application (USGS, 2008). Also according to the USGS study, present research is targeted toward developing a polymeric delivery vehicle for NZVI which will be cost-effective and efficient. There is also research directed toward making the polymer contaminant-specific. The hydrophobic “tails” of the surfactants physically absorb onto the NZVI surface while the hydrophilic “heads” inhibit flocculation and allow for suspension in the aqueous medium. While surfactants provide colloidal stability in water, the highly reversible nature of surfactant absorption limits its application as a delivery system for groundwater decontamination since desorption will be favored when the nanoparticles are transported through surfactant-free groundwater.

In contrast, high molecular weight, amphiphilic polymers show essentially irreversible absorption and, thus, are more suitable as a delivery system for groundwater remediation (USGS, 2008). Synthesis of amphiphilic polysiloxane graft copolymers (APGC) is achieved through hydrosilyation of hydride functioning polysiloxanes by polyethylene glycol (PEG) and tertiary butyl acrylate (tBA). The PEG grafts are water soluble and allow for colloidial stability and dispersibility in aqueous mediums. The polysiloxane backbone polymer imparts a hydrophobic barrier to the NZVI particles which protects them from excessive oxidation. It also gives an affinity of the coated NZVI for water contaminant interface and allows for permeation of the contaminants to the NZVI surface (Krajangpan *et al.,* 2008). Additionally, the hydrosilylation reaction used to produce the polymers will enable tailoring of the chemical structure to enhance contaminant specificity (Krajangpan *et al*., 2008).

Successful development of a delivery vehicle for iron nanoparticles will have broader ramifications in the field of groundwater remediation. Targeted delivery of the NZVI will save resources and time needed for remediation of contaminants in the subsurface and thus, will help protect water resources. Successful development of a polymeric delivery vehicle (APGCs) can also be pilot tested to create a reactive barrier/wall to contain the contaminant plumes. In addition to possessing the ideal characteristics for NZVI delivery system, this class of polymers can be easily synthesized from a wide variety of commercially available starting materials (USGS, 2008). The downside to this technology is that polymeric coatings are synthetic and may not be desirable in the subsurface. In the case of highly toxic and recalcitrant contaminants (chlorinated solvent sites), this characteristic may be acceptable, but for the purposes of remediating less toxic pesticides, this may not be an acceptable delivery system for NZVI (Thompson *et al*., 2007). Another more acceptable approach would be to encapsulate the NZVI in calcium alginate, though it lacks many of the specialized properties of more advanced polymeric vehicles. This process would impart biodegradability to the nanoparticles and be more economically feasible. Alginate entrapment/encapsulation is a process in which NZVI is captured in an alginate matrix (entrapment) or encapsulated in a thin-walled alginate capsule (encapsulation) (Thompson *et al*., 2007). Emulsified NZVI with an anionic surfactant may be still a more effective process for NZVI dispersal and biodegradability when considering less toxic contaminants at this juncture. When NZVI is injected in a vegetable oil emulsion, it may provide nutrients to indigenous microbial populations, which may increase biodegradation of contaminants as well. Vinyl chloride (VC) may be produced as a by-product and should be monitored, but should not present problems with implementation of this technology. Because injection occurs as an event and not continually through permanent injection wells, fouling is not an issue (USGS, 2008).

The use of CMC as a stabilizer can accelerate nucleation of Fe atoms during the formation of ZVI nanoparticles and, subsequently, forms a bulky and negatively charged layer via sorption of CMC molecules on the ZVI nanoparticles, thereby preventing the nanoparticles from agglomeration through electrosteric stabilization (He and Zhao, 2008, and He, Zhang, Qian, and Zhao, 2009). He, Zhang, Qian, and Zhao (2009) also found that the attachment efficiency for CMC-Fe was found to be one to two orders of magnitude lower than reported for NZVI stabilized with other commercial polymers. The results from this research indicate that the CMC-Fe nanoparticles can be readily delivered into porous media, and their transport distance can be harnessed by manipulating the injection pressure or the injection flow rate.

Research conducted by Phenrat, T. *et al.,* 2008, prepared stable NZVI dispersions using commercially manufactured anionic polyelectrolytes using physisoprtion. They were prepared using 5- 40 nm sized Fe^0 /Fe- oxide nanoparticles along with several different types of polyelectrolytes (polystyrene sulfonate [PSS], carboxymethyl cellulose [CMC], and polyaspartate [PAP]). Results showed that the order of effectiveness for the prevention of rapid aggregation and dispersion stabilization was PSS70K(83 percent) > ≈PAP10K(82 percent) > PAP2.5K(72 percent) >CMC700K(52 percent) respectively (Phenrat, T. *et al.,* 2008).

Polyelectrolyte modified nanoparticles will remain more mobile than their unmodified counterparts even after aging (Kim *et al.,* 2009). A fraction of the particles cannot be stabilized by any modifier and rapidly agglomerates to micron sized aggregates, as is also observed for unmodified NZVI. This nondispersible fraction is attributed to strong magnetic attractions among the larger particles present in the polydispersed NZVI slurry as the magnetic attractive forces increase.

An alternative to using different dispersion media is the incorporation of NZVI and BNPs into a nanocomposite membrane system, which adds the advantage of preventing the agglomeration of the nanoparticles in the membrane matrix, to minimize the loss of precious metals into the bulk solution phase, and to prevent the formation of precipitated Fe^{3+} hydroxide (Tee, 2006). Tee (2006) used Ni/Fe and Pd/Fe bimetallic nanoparticles immobilized into a chitosan matrix for the synthesis of a nanocomposite membrane reactor to achieve membrane-phase destruction of chlorinated organics under convective flow condition. The membrane-phase degradation results demonstrated similar trends with previous solution phase analysis with the observed enhanced reaction rates. A longevity study through repeated cycle experiments showed minimum loss of activity, which is significant when considering cost and feasibility of using this particular application of BNPs.

4. ESTIMATE OF FACTORS FOR SITE MODELING

Developing a conceptual site model includes conducting a preliminary assessment of the available data to determine whether NZVI injection would be an appropriate technology. Factors that can determine whether NZVI injection is a suitable remedial action at a site include: hydrogeology of the aquifer, geochemistry of the groundwater, type and distribution of contaminants, above ground features and access, and depth of contamination. Geologic and geochemical modeling of the site takes into account the long-term changes that may affect ZVI performance such as pH and the presence of electron donors. A pH below 7 can cause precipitation of the iron particles before contact with the target contaminant due to NZVI high reactivity to other natural electron donors present in the aquifer. Also, the presence of electron donors, especially in aquifer sites that have glacial outwash sediment from bedrock, can cause precipitation and cementation (Klapperich and Korom, 2008). These electron donor elements and the percentages at which they can begin to affect NZVI in groundwater include Ca (23.3 percent); Mg (3.5 percent); Al (1.9 percent); Si (15.3 percent); Fe in the form of ferrous compounds, magnetite and pyrite (18.7 percent); Ti (0.5 percent); Mn (1.7 percent); S in the form of pyrite (2.1 percent); and oxygen (32 percent) (Klapperich and Korom, 2008). All of these elements can cause precipitation and cementation in PRBs containing ZVI, and precipitation can affect the mobility and the reactivity of injected manufactured NZVI before they can reach the target contamination zone.

Cementation is a heterogeneous process in which ions are reduced to zero-valence at a solid metallic interface. The process is often used to refine leach solutions. Cementation is the process of deposition of dissolved mineral components in the interstices of sediments. It is the sticking together of sediment to form a new rock and is an important factor in the consolidation of coarse-grained clastic sedimentary rocks such as sandstones, conglomerates, or breccias during diagenesis or lithification. Cementing materials may include silica, carbonates, quartz, iron oxides, or clay minerals. Cementation is also continually going on in the groundwater zone, so much so that the term “zone of cementation” is sometimes used. Cementation occurs in fissures or other openings of existing rocks and is a dynamic process more or less in equilibrium with dissolution or dissolving process. This has been one of the major problems that inhibit, over time, the remediation of contaminated plumes intercepted in groundwater by permeable reactive barriers (see Figure 5) containing micro and macro sized zero-valent iron particle slurries.

Figure 5: **Permeable Reaction Barriers.** These types of passive treatment technologies are designed to be placed on the down-gradient side of a plume to intercept groundwater flow prior to its migration off-site. As the dissolved phase contamination flows through the permeable reaction wall, reduction of the hydrocarbons and heavy metals occurs. Though these types of passive treatment systems are simple to apply at shallow depths and for low concentration levels of chlorinated organics, their applicability and cost-effectiveness are greatly limited at deeper depths and higher concentrations. (ARS Ferox Technology, 2009).

NZVI dispersion via injection (Figure 6) at the point source of a contamination plume may be a more feasible method of taking advantage of ZVI particles' special properties at the nanoscale.

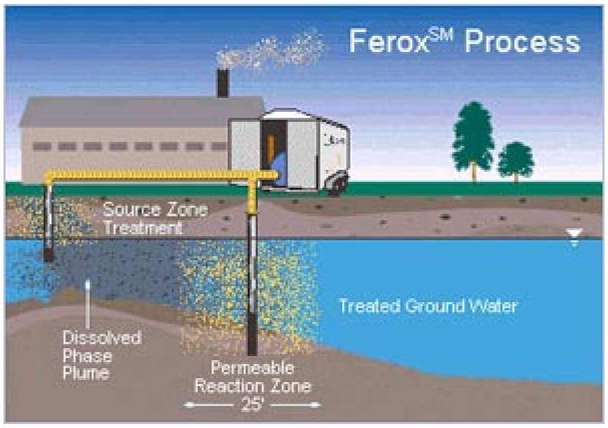


Figure 6: **NZVI Dispersion Via Injection.** An open borehole or direct-push injector assembly casing is used to position the downhole apparatus into the subsurface. Once in place, zero-valent iron powder is injected into the formation as a slurry or as a dry material. Nitrogen gas or compressed air is used as the carrier fluid (ARS Ferox Technology, 2009).

One important parameter to determine for NZVI injection application when looking at soil and sediment properties is the hydraulic conductivity. Hydraulic conductivity, symbolically represented as *K*, is a property of vascular plants, soil or rock, which describes the ease with which water can move through pore spaces or fractures. It depends on the intrinsic permeability of the material and on the degree of saturation. Saturated hydraulic conductivity, K_{sat}, describes water movement through saturated media. One application of this is the Starling equation, which calculates flow across walls of capillaries. Direct estimation of hydraulic conductivity can be measured by applying Darcy's law on the material. Such experiments can be conducted by creating a hydraulic gradient between two points, and measuring the flow rate. There are also *in-situ* methods for measuring the hydraulic conductivity in the field.

One example is when the water table is shallow, the augerhole method can be used for determining the hydraulic conductivity below the water table.

The method uses the following steps:

1. An augerhole is perforated into the soil to below the water table.
2. Water is bailed out from the augerhole.
3. The rate of rise of the water level in the hole is recorded.
4. The K-value (hydraulic conductivity) is calculated from the data thus obtained, using an appropriate equation (ERT2 Multimedia Training Tool, 2008).

Soil mobility tests conducted (He and Zhao, 2005) on CMC-stabilized Fe^0/Pd nanoparticles by measuring the breakthrough behaviors of the nanoparticles through a 2.7 mL of a loamy sand soil bed (obtained from Auburn, AL, an EPA National Priorities List [NPL] site) packed in a glass column (1 cm I.D.). The results showed that the nanoparticles can be easily introduced into the contaminated aquifer under gravity.

4.1 Considerations When Using ZVI and NZVI Remediation Protocols

It is necessary to follow several steps in order to ensure the efficient design and effective performance of an NZVI injection system. The success of any *in situ* technology largely depends upon achieving a good understanding of the contaminated subsurface and preparing a suitable design that takes into account the variabilities inherent in aquifer systems. This is especially important for NZVI injection systems because the NZVI is targeted to a source zone rather than a dispersed plume. This begins with: 1.) Conceptual modeling, 2.) Site characterization, 3) Treatability testing, 4.) Design, 5.) Construction, and 6.) Monitoring (ERT2 Multimedia Training Tool, 2008).

Application methods for *in situ* treatment of contaminated groundwater sites with ZVI and NZVI are site-specific, and a site manager should consider the physicochemical characteristics of a contamination site before establishing a protocol for remediation. A site manager should consider factors such as seasonal fluctuations and conduct evaluations of site characteristics. The characteristics that are relevant for remediation of a contaminated groundwater aquifer include: aquifer type, materials within the aquifer, depth (feet), conductivity (feet/day), aquifer hydraulic gradient (feet/feet) (direction of greatest flow), and velocity and direction of flow rate of the groundwater aquifer (feet/day). Depth by itself is not a limitation for any of the injection technologies. However, greater depth may involve higher injection pressures and bigger equipment, which could make cost the limiting factor. The geology of the aquifer can be a challenge. Subsurface utilities, cobblestones, highly consolidated sediments, and other subsurface obstacles may affect the proposed location of injection points for the NZVI technology, although most vendors use a relatively aggressive injection method, often involving fracturing of the medium with air or water or nitrogen to facilitate movement of the NZVI into soil pores (USEPAa, 2005). To conduct a proper site evaluation, a site manager should map out all geologic and plume heterogeneities, along with providing a model for the range of all the hydraulic parameters.

Once this is done, the site manager must then determine a suitable location for orientation and the dimensions of the dispersion apparatus (*e.g.,* injection wells for NZVI application) while incorporating appropriate safety factors when calculating construction techniques to minimize smearing (*e.g.*, continuous trencher or biodegradable slurries).

Fracturing the medium allows for the creation of pathways for the distribution of NZVI into silty or clay, as well as sandy soils (ERT2 Multimedia Training Tools, 2008). However, once these fractures are filled with NZVI, any additional movement of NZVI may be restricted by the soil type, with slightly better distribution in sandy soils than in silty or clay soils (Grolimund, Elimelech, and Borkovec, 2001; Lecoanet, Bottero, and Wiesner, 2004; and Saleh *et al.,* 2008). Therefore, although aggressive injection methods can overcome some of the limitations imposed by aquifer heterogeneity and finer soils, the soil type and degree of heterogeneity may necessitate more intensive fracturing to obtain adequate contact between NZVI and the contamination (ARS Ferox Technologies accessed July 8, 2009). The horizontal and vertical distribution of contamination can affect the decision to use NZVI injection, which is designed for source zone treatment rather than widespread plumes. The distribution of contamination also can affect the depth of injection and the spacing between injections. Groundwater flow velocity, direction, and other characteristics affect placement of the injection points.

Predicted longevity of the NZVI system is another consideration. Implications for longevity can include: 1.) Whether or not the NZVI becomes dormant sometime in the future unless rejuvenated or replaced in some manner; 2.) Accuracy of the flow estimates (hydraulics); 3.) Colloidial flow and deposition in monitoring wells may be factors that mitigate precipitate buildup in reactive medium; and 4.) Will payback on the capital investment in the injection system pay off before reactivity is exhausted? Fracturing the medium does allow the vendors to create pathways for the distribution of NZVI into silty or clay, as well as sandy soils.

Despite the success of using PRBs containing ZVI, there has been a trend toward point source decontamination of toxic plumes in groundwater aquifers. Granular ZVI has been used in the form of reactive barriers at numerous sites all over the world for the removal of organic and inorganic contaminants. But the smaller size of NZVI promises new advantages compared with granular ZVI (EU Project paper, 2009). This trend has led to the preferred delivery of NZVI to point source contamination sites via injection wells. A monitoring plan is required to determine how well the NZVI injection met the design objectives of the project. The iron particles are mixed into water and then injected into subsurface aquifers through small diameter wells. The injection method used depends on the type of geology found in the treatment zone and the form in which the NZVI will be injected. Typically four methods have been used to inject NZVI into the subsurface:

1. Direct push techniques involve a direct push rig or stationary injection point to introduce NZVI into the treatment zone.
2. Pneumatic fracturing uses air to create a fracture network of preferential flowpaths around the injection point and enhance NZVI distribution (Figure 7).

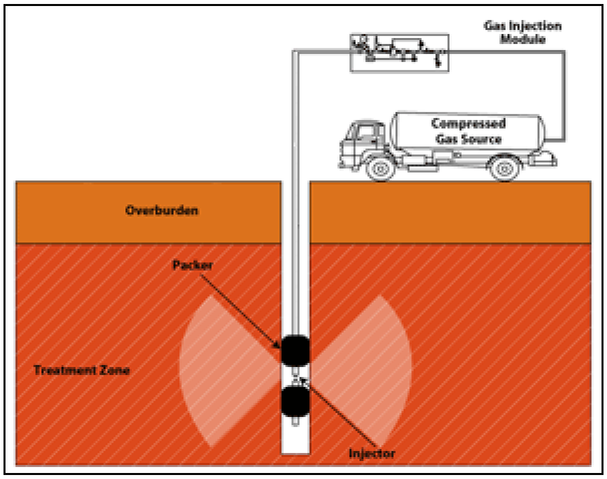


Figure 7: Pneumatic Fracturing. Pneumatic fracturing can best be described as a process whereby a gas is injected into the subsurface at pressures exceeding the natural *in situ* pressures present in the soil / rock interface (i.e., overburden pressure, cohesive stresses, etc.) and at flow volumes exceeding the natural permeability of the subsurface (ARS Ferox Technology, 2009).

3. Pressure pulse technology (PPT) uses regular pulses of pressure while injecting the NZVI slurry, which forces the slurry forward through the subsurface.
4. Liquid atomization injection combines an NZVI-fluid mixture with a carrier gas to create an aerosol that can be dispersed into the treatment zone (Figure 8).

Figure 8: **Liquid Atomization Injection.** Liquid atomization injection (LAI) is a very effective method for injecting liquids uniformly within all types of geology. In addition, injection radii of influence are considerably greater than that achievable using conventional hydraulic injection. LAI relies upon the premise that it is more effective to inject gases or "aerosols" into the subsurface than it is to inject an incompressible liquid into the subsurface (ARS Ferox Technology, accessed July 8, 2009).

Two main types of monitoring are typically required: compliance monitoring and performance monitoring. Compliance monitoring usually consists of collecting groundwater samples downgradient of contamination on a regular basis. Performance monitoring includes groundwater monitoring and soil sampling that can be used to determine the effectiveness of the NZVI treatment. Groundwater monitoring may include collection of contaminant levels, total organic carbon (TOC), oxidation reduction potential (ORP), pH, manganese, iron, and dissolved gases, including ethene and acetylene. Soil sampling can provide both quantitative data on contaminant levels after treatment and visual confirmation of NZVI in the designated treatment area (ERT2 Multimedia Training Tools, 2008).

4.2 Cost Feasibility

Cost feasibility is also very important in the implementation of NZVI technology. The cost of using NZVI at a site depends to a large extent on the scale of the application, in particular, the size of the treatment zone and the amount of iron needed to achieve reductive dechlorination. Unit costs are reported to range from $117 to $286 per cubic yard of contaminated soil in the identified treatment zone. Field-scale demonstrations have found NZVI injections to be cost-competitive when compared to *in situ* chemical oxidation applications at Hunters Point Shipyard (HPS), San Francisco, California (ERT2 Multimedia Training Tools, 2008 and Tetra Tech, Inc., 2003). For this site and others, the primary factors affecting unit costs include:

- The size of the contaminated zone
- Reagent cost (*e.g.,* ZVI)
- Field implementation goals, such as drilling and infrastructure
- Monitoring requirements
- Cleanup goals

A cost summary comparison done for a small field-scale application of the Ferox technology was estimated based on the HPS demonstration and compared to *in situ* chemical oxidation, another injection technology. The total cost of the field-scale application at HPS was $289,274, or $172 per cubic yard of the treatment zone. Excluding sampling, analytical, and demonstration-derived waste management costs, the total cost was $196,665, or $117 per cubic yard. The unit costs for *in situ* chemical oxidation by injecting potassium permanganate (the most common oxidant) were reported to range from $31 to $183 per cubic yard treated (ERT2 Multimedia Training Tools, 2008 and Gavaskar, Tatar, and Condit, 2005).

The cost range/cubic yard (CY) for *in situ* chemical oxidation reflects three different delivery methods:

- $31/CY for soil fracturing with potassium permanganate oxidative particle mixture
- $130/CY for soil mixing with potassium permanganate injection
- $183/CY for horizontal well flushing with potassium permanganate

The cost estimation for the EZVI technology demonstration performed at Cape Canaveral Air Force Station, Florida, Launch Complex 34, involved three major components:

- The application cost of EZVI was $327,000;
- The site preparation and waste disposal cost was $25,000; and
- The site characterization and performance assessment costs were $250,000 and $275,000 respectively.

An economic present value (PV) analysis of the EZVI technology and a groundwater pump-and-treat system was conducted as part of the performance assessment report. The PV of the pump-and-treat costs over 30 years was estimated to be $1,365,000. An equivalent treatment cost for full-scale deployment of the EZVI treatment technology was estimated to be $452,000 (Gavaskar, Tatar, and Condit, 2005). Gavaskar, Tatar, and Condit (2005) also reported that larger particle sizes also are likely to be more persistent in the aquifer, as evidenced by the fact that the microscale iron lasted longer at a contaminated aquifer at Hunters Point Shipyard in San Francisco, CA, than NZVI that was used at a contaminated aquifer site at Naval Air Station (NAS) Jacksonville, FL. This is the case as long as there are no limitations on injectability due to particle size (the oxidation-reduction potential of the treated aquifer remained lower longer at Hunters Point than NAS Jacksonville, where NZVI was used). This indicates that granular ZVI (−8 to +50 mesh), of the type used in permeable reactive barriers, could be very cost-effective and have longer lasting effects on eliminating persistent contaminants for source zone application, as it is much lower in price than either NZVI or microscale iron. If pneumatic fracturing is the method of injection, as it was at the contaminated site at Hunters Point, it may be possible to inject granular ZVI into the fractures by this method (Gavaskar, Tatar, and Condit, 2005 and USEPAa, 2005). However, granular ZVI may not be injectable by simple direct push or recirculation as NZVI was done at the contaminated site in NAS Jacksonville (Gavaskar, Tatar, and Condit, 2005; and USEPAa, 2005). NZVI works but should be used wisely because of cost (USEPA, 2005a). NZVI's degradation capabilities may be maximized when used at injection points where contamination levels are at their highest.

In a USGS report (2007), CMC-stabilized ZVI nanoparticles, synthesized on site and on a relatively large scale, were found to be practical and feasible. The report also stated that the resultant nanoparticles can be easily introduced into the contaminated aquifer under gravity. The CMC-stabilized nanoparticles exhibited unprecedented soil mobility and reactivity for destroying primary contaminants such as PCE, TCE and PCBs under field conditions. The concentrations of PCE, TCE and PCB1242 were lowered by up to 77, 85, and 83 percent, respectively, after deducting dilution effect in the first 10 days and continuously reduced by 59, 96, and 10 percent at the end of 29 days. The introduction of the engineered nanoparticles also greatly boosted and sustained biodegradation. Steady degradation of all three chlorinated compounds was continuously observed four months after the treatment (USGS, 2007). This is a good example of the feasibility benefits in using this type of *in situ* technology for the remediation of groundwater contaminants. That is why a comprehensive site evaluation is needed to access what type of NZVI technology is best suited for the most effective groundwater site contaminant remediation.

There is one important long-term cost benefit to using a DNAPL source remediation technology such as EZVI and NZVI injection. Even if the contaminant source zone is only partially removed by these particular treatments, and natural attenuation is insufficient to meet downgradient cleanup goals, it is anticipated that the weakened source will lead to a weakened plume that can be contained in a cost-effective fashion (ERT2 Multimedia Training Tools, 2008; Gavaskar, Tatar, and Condit, 2005).

4.3 Impact on Human and Environmental Health

Some nanomaterials that enter animal tissues may be able to pass through cell membranes or cross the blood-brain barrier. This may be a beneficial characteristic for such uses as targeted drug delivery and other disease treatments, but could result in unintended impacts in other uses or applications. Inhaled nanoparticles may become lodged in the lung or be translocated, and the high durability and reactivity of some nanomaterials raise issues of their fate in the environment. It may be that in most cases, nanomaterials will not be of human health or ecological concern. However, at this point, not enough information exists to assess environmental exposure for most engineered nanomaterials. This information is important because EPA will need a sound scientific basis for assessing and managing any unforeseen future impacts resulting from the introduction of nanoparticles and nanomaterials into the environment. A nanomaterials risk assessment work sheet by the DuPont Chemical company in 2007 stated that toxicity, human hazard, and environmental fate and effects data available from potential suppliers of NZVI are highly variable in both quality and completeness. It also stated that in many cases, it is not clear from the information provided whether the Environmental Health and Safety (EHS) data are based on the NZVI or on larger sized iron powder. Typical warnings include:

- Skin irritation
- Eye irritation
- Harmful if inhaled – irritating to mucous membranes and upper respiratory tract.
- May be harmful if swallowed. Large doses will produce a laxative effect.
- Toxicological properties have not been thoroughly investigated.
- Dissolved iron and manganese concentrations in groundwater may increase.

NZVI that is released into the air in the form of particulate matter could cause the first three aforementioned effects. Particulate matter triggers an acute inflammatory response in the lung, thus stimulating the secretion of cytokines, chemokines, ROS (reactive oxidation species), and transcription factors (Gwinn and Vallyathan, 2006). Naturally occurring and engineered nanoparticles can remain airborne over a long period because of the small size and light weight (Biswas and Wu, 2005). Therefore, an increased likelihood that they will travel long distances, and interact with gases and other airborne particles is possible. When considering the fact that most nanoparticles are suspended in some type of liquid, surfactant medium, or pumped directly into the soil and water for contaminated groundwater remediation purposes, this may not be an important factor.

There has been some toxicological research done on nanomaterials but not NZVI directly. It has been proposed that the induction of intracellular oxidative stress seems to be a key event of the biological effects of many nanomaterials. Once inside the cell, nanomaterials may induce intracellular oxidative stress by disturbing the balance between oxidant and antioxidant processes. A study by Hu *et al*. (2009) found that certain nano-sized metal oxides exhibited toxicity according to their ionic charge. Lethal dose at 50 percent mortality rate (LD_{50}) was calculated after certain metal oxide nanoparticles were exposure to *E. coli* bacteria. This particular bacteria strain was used as the test organism because it commonly exists in the environment and in the human body. *E. coli* also is simple to culture and easy to use in operation. Table 2 gives a brief summary of those results.

Table 2. LD_{50} of *E. coli* After Exposure to Nano-Sized Metal Oxides. There is a correlation with the cation charge of the metal oxide nanoparticles and their toxicity. ZnO is the most toxic to *E. coli* at 21 mg/L and TiO2 is the least toxic at 1104.8 mg/L (Hu *et al.,* 2009).

Nanoparticles	Cation Charge	FW	LD_{50} mg/L
ZnO	2+	81.39	21.1
CuO	2+	79.54	64.5
Al_2O_3	3+	101.96	326.1
La_2O_3	3+	325.82	456.9
Fe_2O_3	3+	159.69	638.3
SnO_2	4+	150.69	1045.6
TiO_2	4+	79.9	1104.8

The induction of intracellular oxidative stress seems to be a key event of the biological effects of many nanomaterials. Hydrophobic nanomaterials (*i.e.,* nano-sized EZVI) can penetrate through tissue and pass into the lymphatics (Gwinn and Vallyathan, 2006). Once inside the cell, nanomaterials may induce intracellular oxidative stress by disturbing the balance between oxidant and antioxidant processes. Microorganisms typically have an overall negative charge associated with their surface particles at neutral pH in solution (Desai and Armstrong, 2003). The negatively charged cell membrane surface can associate with the positively charged metal oxide particles, resulting in electrostatic condensation. Assumably, *E. coli* will attract lower charged cations on per cell basis; therefore, greater cytotoxicity is exerted via the lower valent cations (Hu *et al.,* 2009). A trend that can be observed in Table 2 is that there is a correlation with the ionic charge and the toxicity of the metal oxides, with ZnO being the most toxic with a cation charge of 2+ and TiO_2 being the least toxic with a charge of 4+. Fe_2O_3, which is one of the precipitates of zero-valent iron during exposure to certain contaminants and in the presence of oxygen, was also found to be one of the less toxic metal oxides with a cation charge of 3+. Table 2 indicates that as the cationic charge increases, the toxicity of the metal oxide nanoparticles decreases. Thus it can be surmised that there is a decrease in toxicity (reactivity) as the cationic charge begins to increase. In the case of NZVI, cationic charge increases as it goes from Fe^0 to Fe^{2+} and finally to Fe^{3+} (ferric oxide) during chemical transformation once entering a groundwater aquifer.

Treatment of cell cultures with nano-sized uncoated iron oxide (Fe_2O_3) revealed a cell-type specific response when exposed to human mesothelioma cells and a rodent fibroblast cells (Brunner *et al.,* 2006). Slower proliferating 3T3 (rodent fibroblast) cells were only slightly affected by addition of up to 30 ppm iron oxide, while the cell parameters MTT-conversion and DNA content of faster growing MSTO (human mesothelioma) cells were drastically reduced upon exposure to as little as 3.75 ppm iron oxide(Brunner *et al.,* 2006). This information has significance in the treatment of particular types of cancer, as well understanding the environmental fate of nano-sized iron particles.

In soil, nanoparticles could be partitioned in ways that could influence where they reside and how they get there. Some nanoparticles may bind chemically to soil particles while others could remain separate or reside on the surface of soil particles or in pore spaces between soil particles (Wan *et. al,* 2005). Nanoparticles in water tend to aggregate, eventually becoming large enough to precipitate out. Precipitation that occurs in groundwater aquifers may inhibit reactivity and therefore toxicity because these hydrophobic nanoparticles begin to aggregate and become denser material, which settles out of the water and is sequestered in the soil and sediment. Toxicity may also be a measure of the reactivity of the particular nanoparticle once it enters the aqueous environment. Once NZVI are exposed and begin transformation reactions, their inherent reactivity begins to decrease and thus, theoretically, so would their exposure and toxicity to organisms.

The question is how long would NZVI exist in its original state, especially when one considers modified nanoparticles like nano-emulsified zero-valent iron (NEZVI) and BNPs. When considering cost and remediation efficiency, the longer the NZVI lasts and continues to eliminate or mitigate contaminants, the better. A pilot-scale testing at a RCRA-regulated facility in Research Triangle Park, NC, was conducted in 2002 to test the effectiveness of *in situ* injections of nanoscale zero-valent iron in removing chlorinated hydrocarbons from bedrock groundwater (USEPA Newsletter, 2005). Chlorinated volatile compounds were reduced by 90 percent after a seven-day period and TCE concentrations by 99 percent after five weeks. Microbiological testing of groundwater samples from the monitoring wells indicated that BNP injection had no detrimental effect on the total biomass and microbial community structure at the injection well, suggesting that bioremediation may serve as a final cleanup step (USEPA Newsletter, 2005).

There has actually been some extensive research on the ZVI and NZVI technology concerning application and fate when used for remediation purposes. There is just not a consolidated database that has been compiled for use and regulation. In a literature review done from 2000 to 2007 by Otrowski *et al*. (2008), it was found that there has been a lack of systematic approaches to assessing the toxicology of nanomaterials and that there is a need for standard methodologies to examine the human health and environmental implications of novel nanomaterial characteristics. The literature review also found that peer-reviewed research on nanomaterials and their toxicology has grown nearly 600 percent since the year 2000, increasing almost exponentially across the seven-year period. The problem is that the research being done is scattered over many disciplines (*e.g.,* biology, chemistry, physics, and engineering) and in many different countries, with the United States and China being the leading two respectively. As stated earlier, there is not a universal consolidated body of data to reference for those who have concerns about human exposure, environmental fate, and regulation of nanomaterials, nanoparticles, and their technological application/implications. Also, most toxicity studies have been in acute toxicity and not in characterization of the complex interactions that would involve a whole organism such as human beings (Otrowski *et al*., 2009).

5. CONCLUSION

The NZVI technology can be a suitable remedy for eliminating or mitigating a contaminant source zone (*i.e.*, DNAPL). The technology is *in situ* and the injections may be repeated as necessary. Although the NZVI injection technology itself is fairly young, the use of zero-valent iron to treat chlorinated contaminants is well-established and accepted. As the technology is validated and more widely applied, guidelines for compliance should follow. Injection techniques that minimize the volume of water used to prepare the iron slurry are likely to better preserve the reactivity of the iron than delivery techniques that depend on injection of iron with large volumes of water. If large volumes of water have to be used, an effort should be made to de-oxygenate it, for example, by sparging nitrogen (ERT2 Multimedia Training Tool, 2009). However, other oxidized species (*e.g.*, nitrates and sulfates) may persist and contribute to passivation of the iron. The use of NZVI and ZVI is site-specific and should be utilized at contamination sites where the NZVI's unique contaminant reducing properties are maximized. Contaminated site characteristics have to be determined in order to decide what type of NZVI technology should be used, and how these characteristics will affect the physiochemical and geochemical fate. In some cases, ZVI at the macro and micro size scale is more cost-effective and more efficient than NZVI in terms of reduction of contaminant concentrations and longevity. In contrast, the cost of manufactured NZVI technology designed with more efficient and specific reactive capabilities (*i.e.* BNP, EZVI, APGC-NZVI, CMC-NZVI, and nanocomposite membrane reactors, etc.), for the elimination of target contaminants, continues to decrease. NZVI can also potentially remediate contaminated groundwater sites in a faster period of time than using larger sized ZVI materials in PRBs. This will also contribute in making utilization of NZVI technology and materials at contaminated sites more feasible than protocols using larger scale ZVI materials.

Furthermore, NZVI seems to be better suited for remediation after the delineation of the source of the contamination is determined in deep aquifer zones and where the soil and sediment medium is less porous, thus inhibiting distribution of larger scale ZVI particles. Creating a strongly reducing environment is essential for promoting and fostering abiotic reactions and minimizing the generation of partially dechlorinated byproducts that tend to persist longer in the aquifer. Designing the NZVI mass injected to achieve an oxidation reduction potential below −400 mV is more important than trying to match the NZVI mass stoichiometrically to the estimated mass of contaminants in the target aquifer region (Gavaskar, Tater, and Condit, 2005; and USEPA, 2005b). New innovations in NZVI dispersion technology such as the development of EZVI, BNP zero-valent iron, CMC-Fe^0, Alginated Fe^0 and APCG-Fe^0 could improve NZVI remediation potential and also could stimulate bioremediation as well for a more complete elimination of groundwater pollutants at contaminated sites. NZVI remediation technology is more cost-effective when compared to more traditional remediation methods such as pump and treatment. The benefits from use of nanomaterials for remediation could include more rapid or cost-effective cleanup of wastes relative to current conventional approaches. Such benefits may be derived from the enhanced reactivity, surface area, subsurface transport, and/or sequestration characteristics of nanomaterials.

This *in situ* technology is technically highly feasible and can potentially save millions of dollars in remediation costs. Given the current and future impacts of chlorinated organic contaminants on the economy and human health, the successful implementation of this low-cost cutting-edge technology could save millions of dollars for the United States. Further and more consolidated studies need to take place in order to assess the potential impacts of these particular nanoparticles on human health, their environmental fate, and full-scale ecosystem-wide impacts over time. Using balanced and well thought out approaches will maximize benefits of the use of NZVI technology while minimizing the risks for the purposes of groundwater contaminant remediation.

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