
Fate, Transport, and Toxicity of Nanoscale Zero-Valent Iron (nZVI) Used During Superfund Remediation

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LIST OF ABBREVIATIONS

Au	Gold
BNP	Bimetallic Nanoscale Particles
Ca²⁺	Calcium Divalent Cation
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFC	Chlorofluorocarbon
CMC	Carboxymethyl Cellulose
Co	Cobalt
CSL	Colloidal Science Laboratory, Inc.
Cu	Copper
DCE	Dichloroethene
DDT	Dichlorodiphenyltrichloroethane
DHHS	Department of Health and Human Services
DNAPL	Dense Non-Aqueous Phase Liquids
DO	Dissolved Oxygen
EPA	United States Environmental Protection Agency
EZVI	Emulsified Zero-Valent Iron
Fe	Iron
Fe⁰	Zero-Valent Iron
Fe²⁺	Ferrous Iron
Fe³⁺	Ferric Iron
GSH	Glutathione
H₂O₂	Hydrogen Peroxide
ISO	International Organization for Standardization
ITRC	Interstate Technology and Regulatory Council
K⁺	Potassium Cation
MDA	Malondialdehyde
Mg²⁺	Magnesium Divalent Cation
mM	Millimoles
MRNIP	Polyaspartate-Modified Nanoscale Zero-Valent Iron
mV	Millivolts
Na⁺	Sodium Cation
Ni	Nickel
nm	Nanometers
NNI	National Nanotechnology Initiative
NPL	National Priorities List
nZVI	Nanoscale Zero-Valent Iron
OH·	Hydroxyl Radical
O₂⁻	Superoxide
ORP	Oxidation Reduction Potential
PAA	Poly Acrylic Acid
PAH	Polycyclic Aromatic Hydrocarbon
PAP	Polyaspartate
PCB	Polychlorinated Biphenyl
PCE	Tetrachloroethene
Pd	Palladium
PRB	Permeable Reactive Barrier
PSS	Polystyrene sulfonate
Pt	Platinum
RNIP	Reactive Nanoscale Iron Product

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ROS	Reactive Oxygen Species
SARA	Superfund Amendments and Reauthorization Act
SDBS	Sodium Dodecyl Benzene Sulfonate
SOD	Superoxide Dismutase
TEM	Transmission electron microscopy
TCA	1,1,1-trichloroethane
TCE	Trichloroethene
VC	Vinyl Chloride
ζ-potential	Zeta Potential
ZVI	Zero-Valent Iron

1. INTRODUCTION

The Superfund program was created in 1980 by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) with the purpose of protecting human health and the environment from the risks posed by abandoned hazardous waste sites (U.S. EPA 2008b). The need to reduce human and environmental exposure to highly contaminated sites was brought to public attention by the discovery of numerous toxic waste disposal sites during the 1970s, such as Love Canal. The Love Canal community in Niagara Falls, New York, which had been established on a former toxic waste dump, had to be relocated due to leaching of hazardous substances into the groundwater after drums filled with chemicals began to corrode (U.S. EPA 2008b; U.S. EPA 2009a). Superfund allows the federal government, specifically the United States Environmental Protection Agency (EPA), to clean up such sites when the responsible parties for the contamination cannot be found or cannot afford the cost of cleanup (U.S. EPA 2008b).

Although approximately two-thirds of the sites listed on the Superfund National Priorities List (NPL) have completed remedy construction, there is still a lot of work that needs to be done (U.S. EPA 2008b). Currently, there are approximately 1,300 abandoned hazardous waste sites undergoing or awaiting remediation efforts on the NPL (U.S. EPA 2009b). The NPL is EPA's list of the most serious uncontrolled or abandoned hazardous waste sites and does not include the more than 450,000 brownfields and other contaminated sites being addressed under other Federal or State programs in the U.S. (U.S. EPA 2008a; U.S. EPA 2008b).

The Superfund program provides two types of response based on the type and severity of an actual or potential release of a hazardous substance, pollutant, or contaminant. Response can either involve removal actions or remedial actions. Removal actions are generally short-term solutions that occur within six months of discovering an issue, such as removal of leaking storage tanks or drums. Remedial actions often involve long-term cleanup that can take years to complete and are intended to be permanent solutions for preventing or minimizing the release of contaminants into the environment (U.S. EPA 2008b). Examples of traditional remedial actions include: solidification/stabilization, soil vapor extraction, incineration of soil, and groundwater "pump-and-treat" (U.S. EPA 2007a). As a result of the Superfund Amendments and Reauthorization Act (SARA) of 1986, EPA has increased consideration and implementation of newer and more efficient innovative technologies to treat wastes rather than the traditional "dig-and-haul" and "pump-and-treat" methods for removing contaminated soils and groundwater from the site (U.S. EPA 2008b). One such emerging field that holds potential for cleaning up Superfund sites in a more cost effective and efficient manner is nanotechnology.

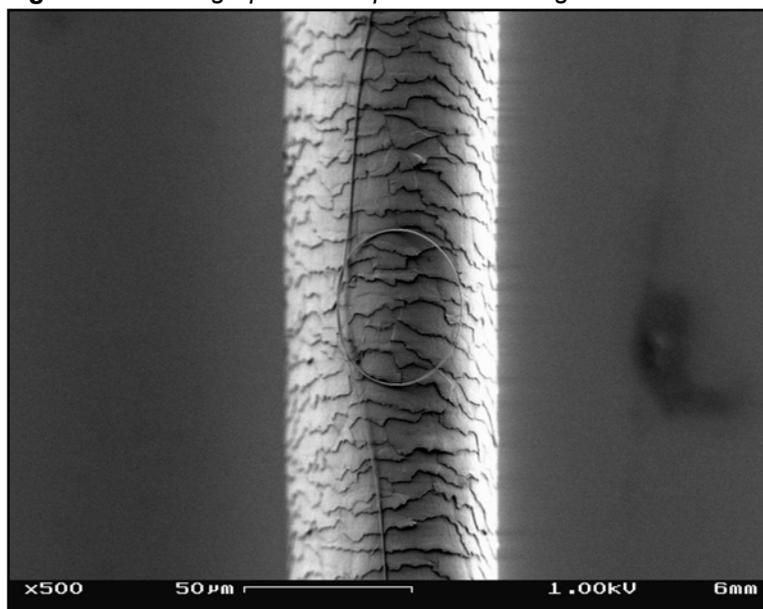
1.1 Introduction to Nanotechnology

The field of nanotechnology involves understanding and controlling matter at the molecular or atomic level where materials, due to their small scale, exhibit unique properties and behaviors when compared to the same material in a larger form (e.g., silver, copper, iron) (U.S. EPA 2008c; Davies 2009). The nanoscale is approximately 1 to 100 nanometers (nm), which is equal to one billionth of a meter. For comparison, an average bacteria cell is approximately 1,000 nm in diameter, there are 10 million nanometers in a centimeter and there are 25.4 million

nanometers in an inch (Zhang 2003; Davies 2009). **Figure 1-1** shows an example of the size scale that nanotechnology works with.

An industry-wide definition for nanomaterial has not yet been agreed upon. However, the British Standards Institution, the American Society for Testing Materials and the Scientific Committee on Emerging and Newly-Identified Health Risks have adopted the definition to be any material with *one* dimension under 100nm (Klaine et al 2008). Within this group of materials are nanoparticles, which are defined by the International Organization for Standardization (ISO/TS 27687:2008) as materials with at least *three* dimensions between 1 and 100nm.

Figure 1-1. *Micrograph of a looped nanowire against a human hair*



Several terms tend to be used interchangeably to describe nanoparticles, including nanomaterials, nanoscale particles, nanoscale materials, nanosized particles, nanosized materials, nano-objects, and nanostructured materials. For the purposes of the remainder of this report, the term “nanoparticles” will be used.

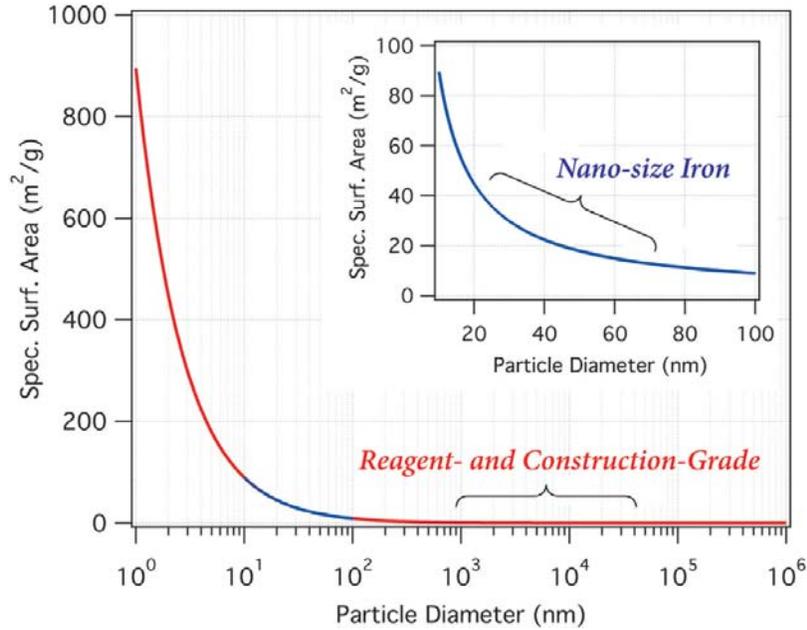
There are three types of nanoparticles: natural, incidental, and engineered. There are many naturally occurring nanoparticles, such as clays, weathered minerals, organic matter, and metal oxides (Watlington 2005; Klaine et al. 2008; NNI 2009). Incidental nanoparticles are generated in a relatively uncontrolled manner and can occur as a byproduct of fuel combustion, manufacturing, agricultural practices, vaporization, weathering, and release into the environment from nanoparticle production facilities (Klaine et al. 2008; DHHS 2009; NNI 2009). Engineered nanoparticles are intentionally designed and manufactured with specific properties or compositions (e.g., shape, size, surface properties, and chemistry) and may be released into the environment through industrial or environmental applications (U.S. EPA 2007b; DHHS 2009; NNI 2009).

The characteristics that make most nanoparticles qualitatively different from larger particles is their large surface areas relative to their volumes and/or higher natural reactivity of the reactive surface sites (Tratnyek and Johnson 2006; U.S. EPA 2008c). **Figure 1-2** shows how the specific surface area increases as diameter of the particles decrease (Tratnyek and Johnson 2006). In other words, the particle surface area is inversely proportional to the particle size (CSL 2009). A good way to think about this concept is by imagining a block of sugar versus a pile of powdered sugar with the same volume. Although they have the same proportion of sugar, the powdered version has a greater surface area and therefore a greater ability for each particle that comprises

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the material to interact with outside forces. For example, when water is poured over the pile of powdered sugar it can get into the space in between each particle, but when poured over the block of sugar it cannot reach the particles in the middle of the block, only the particles on the edges.

Figure 1-2. Particle surface area calculated from diameter assuming spherical geometry and density 6.7 g/cm³ (based on the average of densities for pure Fe⁰ and Fe₃O₄)

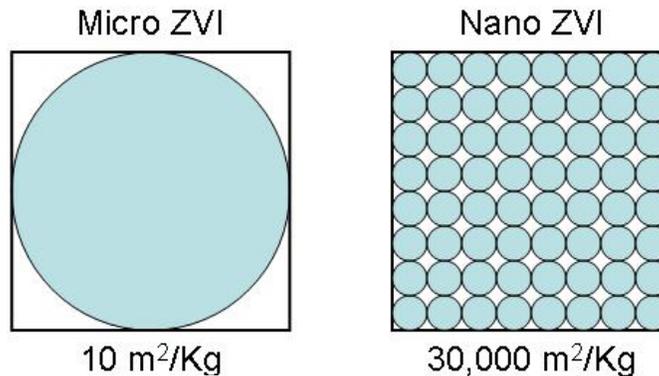


Source: Tratnyek and Johnson 2006

This idea is demonstrated in **Figure 1-3**. The specific surface area of a spherical particle can be calculated by the following equation (Macé et al. 2006):

$$SSA = \frac{\text{Surface Area}}{\text{Mass}} = \frac{\pi d^2}{\rho \frac{\pi}{6} d^3} = \frac{6}{\rho d}$$

Figure 1-3. Comparison of available surface area between micro and nano ZVI



Source: Golder Associates

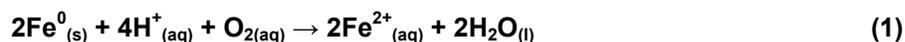
A variety of nanoparticles are currently being used in a wide range of products within the scientific, environmental, industrial, and medical fields. Pharmaceuticals are being reformulated with nanoparticles to increase their absorption and improve administration. Nanoparticles are being used to make commercial products such as tennis rackets, baseball bats, and bicycles lighter. Coatings of nanoparticles are being applied to clothes to make them stain resistant and to eyeglasses to make them scratch resistant and easier to clean. The majority of electronic devices produced in the last decade use nanoparticles to improve sound and picture quality (NNI 2009). The automotive industry uses nanoparticles in part production to enhance mechanical and flame-retardant properties (Watlington 2005). Nanoparticles also are being used to address a variety of environmental issues, including cheaper and cleaner energy production, potable water purification, environmental treatment and remediation of oil spills and hazardous chemical releases and pollution prevention through sensing and early detection (Masciangioli 2003; Balbus 2006; U.S. EPA 2008c; NNI 2009).

Some of the earliest and potentially most beneficial environmental applications of nanotechnology are in the treatment and remediation technologies. Nanotechnology holds the potential of more effective and cost efficient remediation efforts (U.S. EPA 2008). Research has shown that one nanoparticle in particular—nanoscale zero-valent iron (nZVI)—holds potential for effective *in situ* treatment and detoxification of a variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and metal ions (Zhang 2003; Chang et al. 2005; Chang and Kang 2009). Therefore, the specific nanotechnology discussed hereafter solely focuses on site remediation of soil, sediment, and waters using nZVI particles.

1.2 Nanoscale Zero-Valent Iron (nZVI)

Macroscale ZVI (Fe^0) has long been recognized as an excellent electron donor with a tendency to release electrons in aquatic environments regardless of its particle size (Zhang and Elliott 2006). ZVI has been used for site remediation since the early 1990s by creating permeable reactive barriers (PRBs) by filling trenches with ZVI designed to allow groundwater to pass through while “filtering” out the contaminants (ITRC 2005; U.S. EPA 2008c). Research indicates that using the nZVI in place of the macroscale ZVI will accomplish the same remedial work more efficiently and with less cost. A benefit of using nZVI is being able to inject it directly into a contaminated aquifer, which avoids the need to dig a trench for installation of the PRB. Using this injection technique is believed to be faster and more effective for groundwater treatment than either pump-and-treat or PRB methods (U.S. EPA 2008c).

ZVI, or elemental iron, is a moderate reducing reagent that can react with dissolved oxygen (DO) and water resulting in electrochemical/corrosion reactions that oxidize the iron (Zhang 2003). As shown below, the Fe^0 becomes oxidized to ferrous iron (Fe^{2+}) ions and the electrons that are released become available to reduce other compounds (U.S. EPA 2008c). This process can be accelerated or inhibited by changing the solution chemistry and/or solid composition by adding coatings or catalysts (Zhang 2003).



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The chemistry behind nZVI is much the same as with macroscale ZVI. nZVI is highly reducing and generates reactive oxygen species (ROS) through Fenton chemistry. In aqueous environments, nZVI oxidizes over time (i.e., ages) to iron oxides such as magnetite, maghemite, lepidocrocite, and goethite (You et al, 2005; Phenrat et al. 2009c). Research has shown the nZVI can react not only with DO and water, but also with a variety of environmental contaminants, and may prove to be a more effective and less costly remediation alternative. nZVI can either remove contaminants through reduction or adsorption. The treatment of chlorinated solvents, for example, primarily uses reduction, and the removal of arsenic is done by adsorption to iron oxides and hydroxides formed during oxidation (You et al. 2005).

An example that has received a lot of attention is the process of degrading trichloroethene (TCE) and perchloroethylene (PCE), some of the most commonly found contaminants at Superfund sites, to more benign compounds quicker and more completely than when using macroscale ZVI (U.S. EPA 2008c). TCE and PCE were used historically as industrial cleaning and degreasing solvents, as paint removal solvents, and as dry-cleaning solvents (Doherty 2000a; Doherty 2000b). Chlorinated solvents can be degraded through reductive dechlorination or beta elimination. Under the reducing conditions presented by the introduction of nZVI in groundwater, reductive dechlorination follows the pathway of PCE → TCE → DCE → VC → ethane, where DCE is dichloroethene and VC is vinyl chloride (U.S. EPA 2008c).

Table 1-1 shows the environmental contaminants that can be transformed by ZVI and nZVI. This is not intended to be a complete list of all contaminants that may benefit from the use of nZVI for remediation, but is meant to represent the range and variety of contaminants that have shown potential for remediation using nZVI. Of the approximately 1,300 abandoned hazardous waste sites undergoing or awaiting remediation efforts on the NPL, approximately 25 percent are contaminated with PCBs and 40 percent are contaminated with PAHs (U.S. EPA 2009b). **Table 1-1** shows that both of these hazardous chemicals have shown potential for remediation using nZVI.

Table 1-1. Common environmental contaminants that can be transformed by nanoscale iron particles

Chlorinated methanes Carbon tetrachloride Chloroform Dichloromethane Chloromethane	Heavy metal ions Mercury Nickel Silver Cadmium	Other polychlorinated hydrocarbons PCBs Dioxins Pentachlorophenol
Chlorinated benzenes Hexachlorobenzene Pentachlorobenzene Tetrachlorobenzenes Trichlorobenzenes Dichlorobenzenes Chlorobenzene	Organic dyes Orange II Chrysoidine Tropaeolin O Acid Orange Acid Red	Other organic contaminants N-nitrosodimethylamine TNT
Pesticides DDT Lindane	Chlorinated ethenes Tetrachloroethene Trichloroethene <i>cis</i> -Dichloroethene <i>trans</i> -Dichloroethene	Inorganic anions Dichromate Arsenic Perchlorate Nitrate
Trihalomethanes Bromoform		

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Dibromochloromethane Dichlorobromomethane	1,1-Dichloroethene Vinyl chloride	
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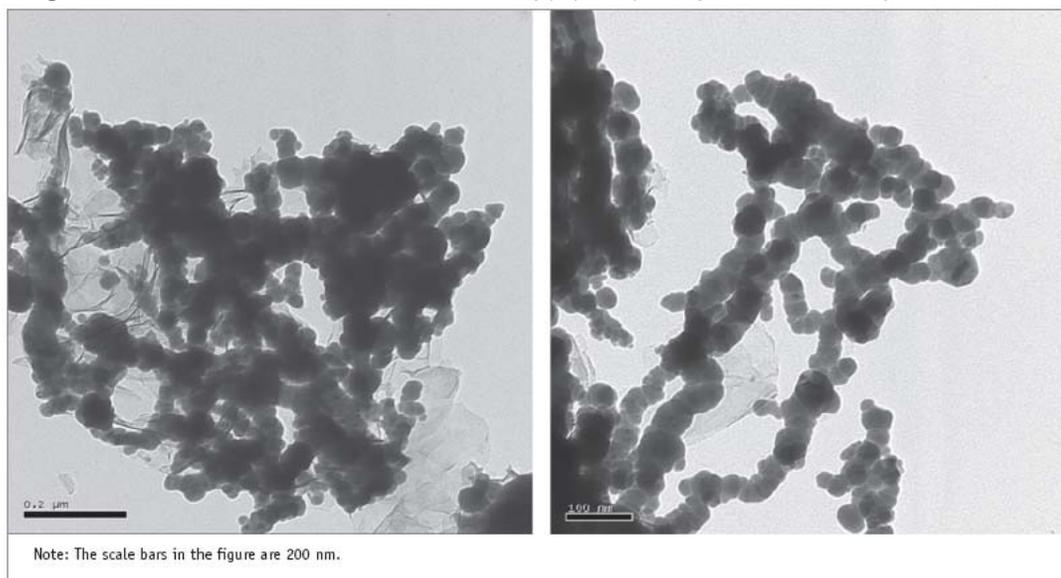
Source: Zhang 2003

Although nZVI particles can exist naturally, remediation techniques generally use engineered nanoparticles. nZVI can be created in a variety of different ways. Researchers at Lehigh University discovered three distinct methods for producing nZVI through the reduction and precipitation of ZVI from an aqueous solution using sodium borohydride for the chemical reduction of ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions (Zhang and Elliott 2006). nZVI also can be produced by hydrogen reduction of iron oxides or hydroxides (Macé et al. 2006). The following equations illustrate some of the reactions that can take place to produce nZVI (Wang and Zhang 1997; Zhang and Elliott 2006):



When performing remediation work, it is important to know how the nanoparticles that are being used were produced. Even particles with the same chemical composition will have different reactivity, mobility, and active life due to the process or vendor used to obtain the nanoparticles (U.S. EPA 2008c). Contamination also can be an issue for reactivity. The greater the percentage of ZVI present in the resulting nanoscale powder, the more reactive it will be. When Fe^{2+} or Fe^{3+} ions are present in the nZVI powder it will be less reactive due to the decreased availability of electrons (Macé et al. 2006). **Figure 1-4** shows example photos of engineered nZVI particles obtained through transmission electron microscopy.

Figure 1-4. *Transmission electron microscopy (TEM) images of iron nanoparticles*



Source: Zhang and Elliott 2006

There are three main forms of nanoscale iron that can be used during remediation efforts – nZVI, bimetallic nanoscale particles (BNP) and emulsified zero-valent iron (EZVI). According to the EPA, nZVI is the most common nanoparticle that has been tested and field applied. BNPs are particles of nZVI that have been coated with a catalyst, such as platinum, gold, nickel, or palladium, to increase mobility and enhance reduction reactions (U.S. EPA 2008c; CLU-IN 2009). EZVI are nZVI particles that have been coated with a membrane made from biodegradable oil and water to facilitate the treatment of chlorinated hydrocarbons by making the particles more hydrophobic. This allows the particles to mix directly with dense non-aqueous phase liquids (DNAPL), such as TCE, to increase mass transfer between the DNAPL and the nZVI through the emulsion membrane (CLU-IN 2009).

1.3 Objective

The goal of this document is to provide information about the fate, transport, and toxicity associated with the use of nZVI for Superfund remediation. Specific and unique site conditions are likely to determine the usefulness and influence the fate and transport of nZVI particles during remediation efforts. Factors to consider prior to application include: effects of geochemistry on the mobility of nanoparticles, use of metal catalysts and coatings on the movement of nZVI particles and other variables affecting the fate and transport of nZVI in the environment. Other considerations include potential environmental and human health effects as a result of the fate and transport of nZVI in the environment.

This document is one of two reference reports that were created for the EPA regarding the applications and implications of nZVI for Superfund remediation. These two complementary reference documents were created with the goal of helping EPA Superfund project managers assess the best method of remediation for their sites. While this document focuses on the fate, transport, and toxicity associated with the use of nZVI for Superfund remediation, the other

reference document focuses on the practical application considerations, such as technology performance, monitoring and cost.

2. METHODS

Research for this document primarily focused on articles from peer-reviewed journals and publications from experts in the field of nanotechnology. The literature review collected information concerning issues that may limit or enhance the mobility and toxicity of nZVI particles in the groundwater and soil. The results of the literature review have been presented in a report that can be used by EPA employees and other members of the nanotechnology and remediation fields to guide project management and remedial plans. This document summarizes the results from laboratory studies, pilot field studies, and full-scale, implemented remediation projects.

No laboratory work, field sampling, or monitoring was performed as part of this project. All information gathered and conclusions generated are based on work performed by others in the academic field and experts within nanotechnology organizations. This document serves as a review and summary of existing information and does not present any new experimental data.

3. RESULTS

Limited data exists concerning the fate, transport, and toxicity specific to nZVI. The majority of review papers and fact sheets that exist concerning this topic focus on nanoparticles as a whole, and not specifically on nZVI particles (Kreyling et al. 2006; U.S. EPA 2008c; Klaine et al. 2008). This document compiled available information concerning the fate, transport, and toxicity specific to nZVI particles that should be considered when choosing the best method for Superfund and other remediation efforts. Understanding the fate and transport of nZVI is just as important to *in situ* remediation as the high reactivity of the nanoparticles. The nZVI must be readily dispersible in the groundwater column so that it will reach the targeted zone of contamination without further polluting the environment (Phenrat et al. 2007). There are multiple information gaps concerning fate, transport, and toxicity. Therefore, recommendations have been provided throughout this document concerning research that needs to be performed to make nZVI particles a reliable tool for remediation efforts.

3.1 Fate and Transport

The fate and transport of nZVI within groundwater and soil is very site specific because it is highly affected by the geochemistry of a system. There is much debate over whether or not nZVI can be effectively transported by groundwater to impact an entire contamination plume, and if increasing mobility too much will add to concerns about particles moving offsite and becoming a toxicological issue. Some of the issues affecting the fate and transport include the contaminant concentration, the nZVI synthesis process, particle agglomeration, age of the nZVI particles, improper handling during application, particle density, the soil matrix, ionic strength of the groundwater, hydraulic properties of the aquifer, depth to the water table, presence of organic matter, and other geochemical properties, such as pH, DO, oxidation reduction potential (ORP), and concentrations of competing oxidants (e.g., nitrate) (U.S. EPA 2008c). In order to overcome

some of the obstacles of mobility and reactivity, researchers have been examining the potential uses of different coatings and catalysts to increase the effectiveness of the nZVI.

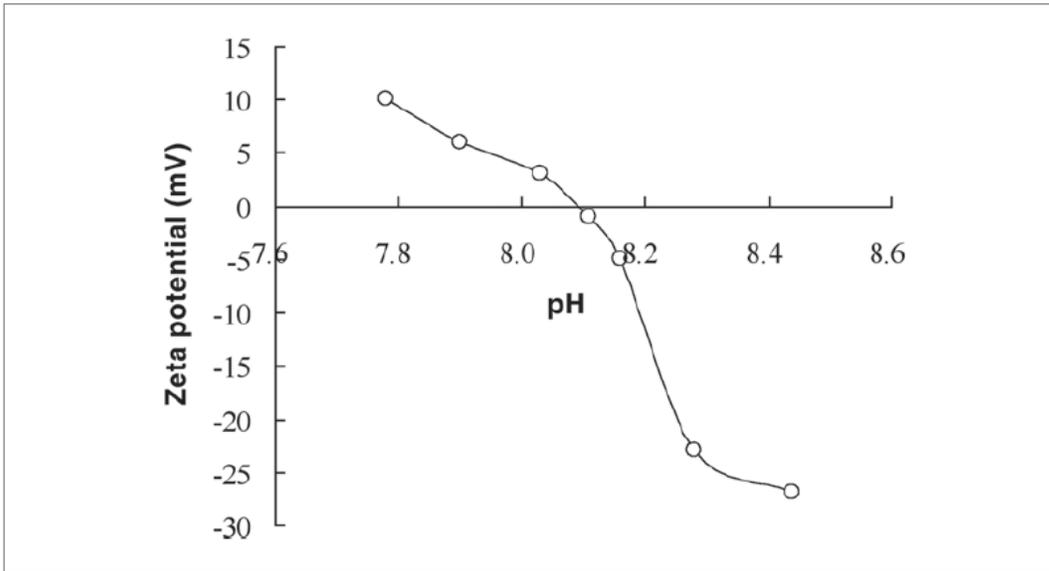
3.1.1 Agglomeration and Zeta Potential

Bare nZVI particles tend to agglomerate (or aggregate), meaning the separate particles cluster together to form larger particles or adhere to soil particles. This decreases the surface area of the nZVI, which decreases the mobility and reactivity, thereby limiting the radius of influence (He et al. 2007). Several conditions can cause the nZVI particles to agglomerate, including the nZVI particle concentration, the magnetism of the particles, size distribution, and zeta (ζ) potential (Phenrat et al. 2007; Phenrat et al. 2009b).

Application of the nZVI particles at too high of a concentration may increase the chances of particle agglomeration (Saleh et al. 2007). Recent research shows that particles are mobile at low concentrations (e.g., 30 mg/L) regardless of the size distribution and magnetic forces (Phenrat et al. 2009b). Larger particles with higher ZVI content are more magnetically attracted to each other and soil grains, which may also increase the nZVI deposition potential. Smaller particles with low ZVI content travel farther than those with high ZVI content because they are less likely to agglomerate (Phenrat et al. 2009b). However, ZVI is essential for the actual contaminant reduction, removal, and/or immobilization; therefore, a balance between all of these variables needs to be found in order to maximize the effectiveness of this technology.

Another condition that can cause agglomeration is the ζ -potential of the particles. Each of the different processes available for generating nZVI will create particles with different ζ -potentials. The ζ -potential, or the electric potential, of a particle determines how attracted it will be to other particles, and therefore, how likely they are to agglomerate. As the ζ -potential approaches zero, particles tend to agglomerate, making them less mobile and decreasing reactivity. Particles with ζ -potential values greater than +30 mV (millivolts) and less than -30 mV are considered stable, with maximum instability, or agglomeration, taking place at zero (Zhang and Elliott 2006). Surface modification using charged polymers (polyelectrolytes) or surfactants also changes the ζ -potential by increasing surface charge and repulsion between particles to reduce agglomeration (Saleh et al. 2008). The pH of a solution also influences the ζ -potential. As the pH of a solution increases, particles tend to acquire negative charge, which results in a negative ζ -potential (Zhang and Elliott 2006). This implies that the pH of the groundwater at a remediation site will directly influence the usefulness of injecting nZVI particles into the system based on the effect it has on ζ -potential and, therefore, agglomeration. **Figure 3-1** shows that a pH between approximately 8.0 and 8.2 may result in a ζ -potential of zero, which could render the nZVI particles useless during the remediation process.

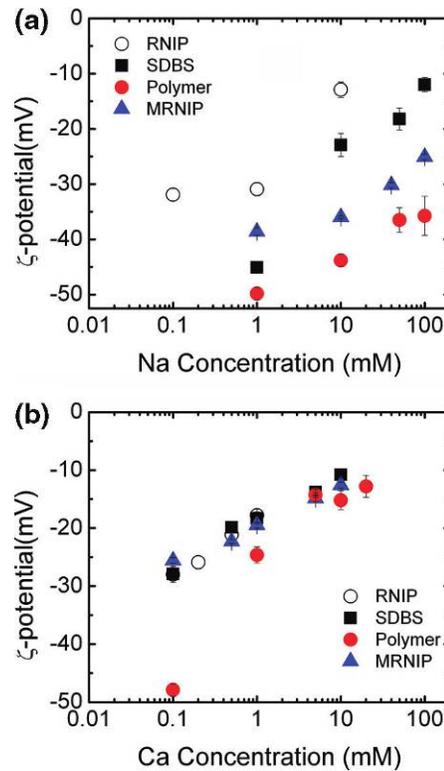
Figure 3-1. Titration of zeta potential versus pH using 2.0 N sulfuric acid for a 10 g/L suspension of nZVI in water



Source: Zhang and Elliott 2006

The ionic strength of the groundwater also has an effect on the ζ -potential, and therefore, on the mobility of nZVI in a system. Most of the studies on transport and mobility of nZVI used either deionized water or water at low ionic strength to test the dispersion stability, which is not representative of actual groundwater (Saleh et al. 2008). According to Saleh et al., in groundwater, the concentration of monovalent cations (e.g., Na^+ , K^+) is typically 1-10 mM (millimoles) and the concentration of divalent cations (e.g., Ca^{2+} , Mg^{2+}) is typically 0.1-2 mM. Research that used water within “natural” concentrations of ions to better represent the actual conditions of groundwater showed that the ionic strength of the water affects the ζ -potential and therefore decreases the mobility of nZVI within porous media (Saleh et al. 2008). As shown in **Figure 3-2**, as the concentration of positively charged ions increased in the water, the ζ -potential approached zero, which leads to greater agglomeration of the nZVI particles. The mobility of several particles with surface modifications were also tested in relation to ionic strength of the water as shown in **Figure 3-2**.

Figure 3-2. Measured apparent ζ -potential as a function of ionic strength



Note: a) Na⁺, b) Ca²⁺; pH = 7.7 ± 0.4, particle concentration = 15mg/L. Error bars represent one standard deviation of triplicate measurements
Source: Saleh et al. 2008

Recent research indicates that the ζ -potential of bare nZVI particles is approximately -30 ± 3 mV and is virtually immobile (Zhang and Elliott 2006; Saleh et al. 2008). Tests indicated that triblock copolymer-modified nZVI had the highest ζ -potential at -50 ± 1.2 mV and therefore was the most mobile in the porous media under consideration (i.e., water-saturated sand columns). The high mobility is thought to be an effect of the electrosteric stabilization provided by the triblock copolymer, but not the electrostatic stabilization provided by the other modifiers tested (i.e., polyaspartate-modified nZVI [MRNIP] and sodium dodecyl benzene sulfonate [SDBS]-modified nZVI) (Saleh et al. 2008). The electrosteric stabilization provided the best resistance to changing electrolyte (e.g., Na⁺ and Ca²⁺) concentrations that occur in real groundwater and provided transport distances of tens to hundreds of meters in sandy aquifers (Saleh et al. 2008).

3.1.2 Particle-Grain Interactions

Other research implies that the transport of nZVI particles is directly correlated to particle-grain interactions rather than the ζ -potential or colloidal stability (Saleh et al. 2007). In other words, rather than low mobility potential being affected by the attraction between the nZVI particles themselves, transport may be determined by attraction of nZVI particles to non-target soil grains in the groundwater. After application of nZVI occurs, the particles can do several things – agglomerate, attach to soil grains, or “stick” to the targeted contaminant of concern (Saleh et al.

2007). The agglomeration and attraction to soil grains can lead to clogging of the soil pores and reduction of nZVI transport. **Figure 3-3** shows how attraction to soil grains and agglomeration work together to decrease nZVI transport through a system. Surface modification (e.g., coating the particles) can enhance transport by decreasing the particle-grain attraction and increasing the colloidal stability (Saleh et al, 2007).

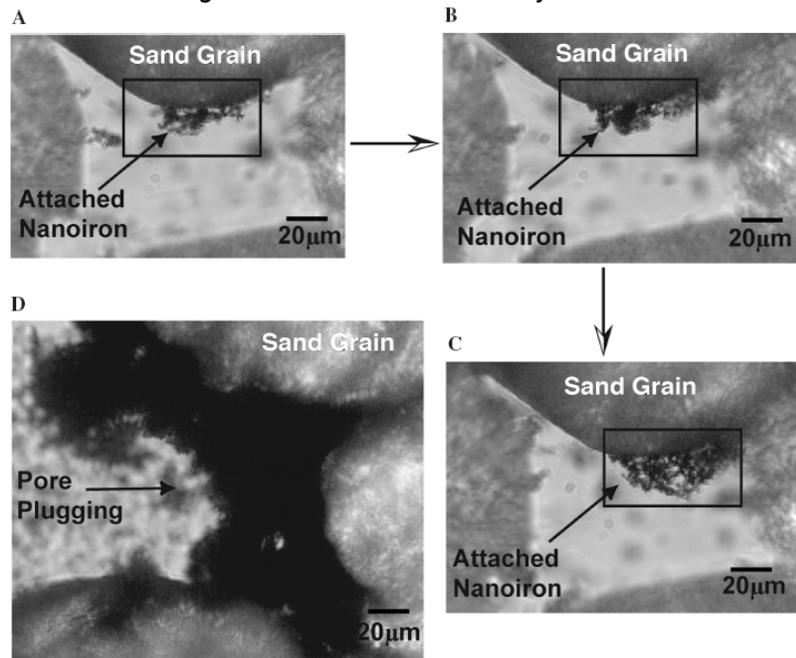
3.1.3 Geochemistry

The transport of nZVI particles in the soil and groundwater is strongly influenced by the geochemistry found in the aquifer, such as the ionic strength, ionic composition, ORP, DO, and pH, and vice versa (i.e., addition of nZVI can also alter the geochemistry of a system). Changes in inorganic indicators, such as ORP, pH, chloride, and alkalinity, can be measured to determine if the application of nZVI is affecting the contamination plume (Gavaaskar et al. 2005). Studies comparing the rate of reaction between nZVI and macroscale ZVI noted that the pH and ORP values changed significantly more when using nZVI. pH increased from 4.8 to 8.5 due to hydroxide production during remediation reactions and ORP decreased from +400 to -550 mV and continued to decline to -700 mV when additional nZVI was added. These results indicate that the nZVI can produce strong reducing conditions conducive to remediation of a variety of contaminants (Chang and Kang 2009).

The pH of the groundwater into which the nZVI is injected will affect the fate and transport of the particles. The sorption strength, agglomeration, and mobility of the particles are all affected by the pH. As indicated in Section 3.1.1, as the pH of a solution increases, particles tend to acquire negative charge, which results in agglomeration (Zhang and Elliott 2006). Factors such as ionic strength and ionic composition of the surrounding media can also lead to agglomeration or attraction of the nZVI particles to soil grains and ions that are not part of the contaminant of concern.

ORP and DO can affect the rate of the reduction reactions and limit the mobility of nZVI by reducing or increasing the amount of oxidation taking place (e.g., high amounts of DO will significantly increase oxidation rates, which will decrease the mobility of the particles).

Figure 3-3. Reactive nanoiron particles (RNIP) straining as an aqueous suspension of 3 g/L of PMAA₄₁-PMMA₂₆-PSS₄₆₂ modified RNIP flows through a water-saturated monolayer of silica sand



Note: a) t = 1 min, b) t = 5 min, c) t = 10 min, and d) example of pore plugging that occurred after longer times
Source: Saleh et al. 2007

3.1.4 Delivery Method

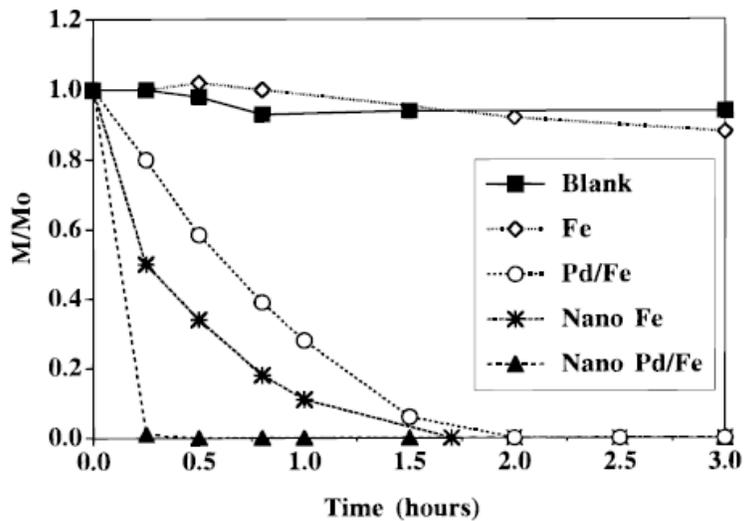
nZVI is typically introduced to a system through the injection of a slurry that is made by combining nZVI powder and water (Gavaskar et al. 2005). Improper handling of the nZVI slurry prior to or during the application process can also limit reactivity and mobility of nZVI particles. Exposure to the air during application can cause the water to become oxygenated, leading to oxidation and passivation of the nZVI prior to reaching and reacting with the contamination plume. Generally, to prevent passivation from occurring, injection methods should limit the amount of aerated water used in the slurry and during injection to limit the particles' exposure to oxygen and other oxidants (Gavaskar et al. 2005; U.S. EPA 2008c).

3.1.5 Catalysts

nZVI particles can be made with coatings of other metals (e.g., platinum, gold, nickel, and palladium) that act as catalysts during the reduction of contaminants. These bimetallic nanoscale particles, or BNPs, are generally more reactive than the bare nZVI because the combination of metals increases the kinetics of the oxidation-reduction (redox) reaction (U.S. EPA 2008c). This implies that the fate of the nZVI will be very different when a catalyst is used versus the bare nZVI. If reactions with contaminants are happening quicker, there is less nZVI that will escape the system. Generally, catalysts do not reduce the chances of agglomeration. Often other coatings have to be used in addition to the metal catalysts to stabilize the particles to reduce attraction (He et al. 2007).

Not all surface modifications enhance reaction at the same rate. One study observed that the reduction of 1,1,1-trichloroethane (TCA) not only showed different reaction rates with different catalysts, but there was also no obvious periodic trend in reactivity where: Ni/Fe \approx Pd/Fe > Cu/Fe > Co/Fe > Au/Fe \approx Fe > Pt/Fe (Cwiertny et al. 2006). The most commonly used BNP is palladium and iron (U.S. EPA 2008c). **Figure 3-4** demonstrates the produced effect of using palladium as a catalyst on nZVI to treat TCE.

Figure 3-4. Reactions of TCE with commercial Fe powders (Fe), pd-modified commercial Fe powders (Pd/Fe), nanoscale Fe particles (Nano Fe, and nanoscale Pd/Fe particles (Nano Pd/Fe)



Note: Initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL

Source: Wang and Zhang 1997

3.1.6 Coatings

In order to overcome the attraction of nZVI particles to each other or soil grains and enhance reactivity by reducing agglomeration, sedimentation, and corrosion, surface coatings can be

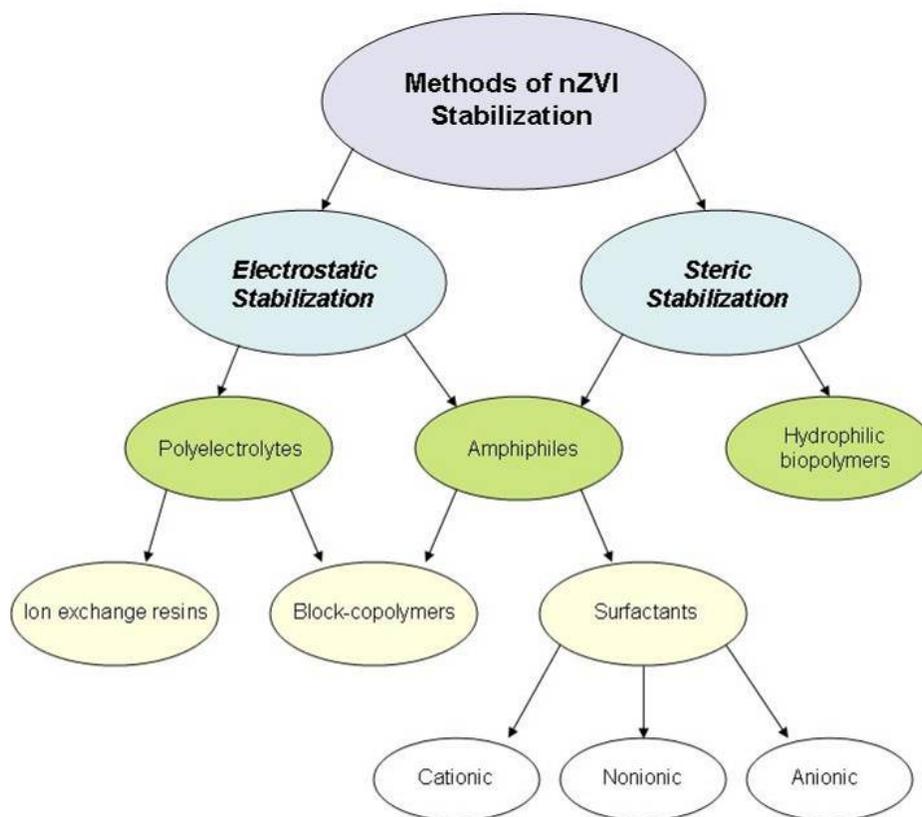
added to the particles to increase the surface charge to provide electrostatic stabilization or steric repulsion. Surface coatings also have been shown to reduce the interaction between the highly reactive surface of the bare nZVI particles and the geochemical conditions of the surrounding media (e.g., DO and water) (He et al. 2007).

The majority of engineered nZVI particles are produced with a coating to provide a specific function, such as stabilization. Particles also can gain a coating, such as natural organic matter, after release into the environment, which has been shown to increase the particle mobility (Phenrat et al. 2009a; Johnson et al. 2009). Ideal coatings are biodegradable to reduce introducing additional contamination at a site (He et al. 2007). According to Phenrat et al., there are three main ways that surface coatings may affect the reactivity of the nZVI particles: 1) by inhibiting diffusion and adsorption of substrates to reactive surface sites, 2) by decreasing the reaction rate at the surface by blocking access to reactive sites, or 3) by inhibiting the desorption and diffusion of reaction products from the surface. Different coatings have been shown to enhance, reduce, and have no affect on the particle reactivity. Examples of investigations that have been performed on coatings include the following (Kustov et al. 2009):

- Hydrophilic biopolymers such as starch, guar gum, alginate, and aspartame (He and Zhao 2005; Tiraferri et al. 2008; Saleh et al. 2008; Tiraferri and Sethi 2009; Bezbaruah et al. 2009);
- Carboxymethyl cellulose (He et al. 2007; Phenrat et al. 2008);
- Chitosan (Zhu et al. 2006; Geng et al. 2009);
- Natural organic matter such as humic acid (Xie and Shang 2005; Zhu et al. 2008);
- Polyelectrolytes such as polyacrylic acid, ion-exchange resins, and block copolymers (Kanel and Choi 2007; Zhao et al. 2008; Sirk et al. 2009);
- Amphiphiles including various surfactants, which can be anionic, cationic, or nonionic (Hydutsky et al. 2007; Kanel et al 2007; Zhu et al. 2008) and block copolymers (Saleh et al. 2005; Saleh et al. 2007; Saleh et al. 2008);
- Various oil-based microemulsions (Quinn et al. 2005).

Figure 3-5 shows some of the different types of coatings that have been researched thus far on nZVI particles. Each type of coating will have a different effect on the nZVI particles' ability to transport within the subsurface environment. For example, surface modifications have been shown to decrease particle-grain attraction on average by two to four times, but depending on the coating, as high as nine times (Saleh et al. 2007). These results are based on laboratory column tests that assessed the particle mobility under different conditions. Although the study is useful for evaluating the significance of using coatings, it is limited in its usefulness because of the difficulty of reproducing the subsurface conditions and groundwater differences unique to each potential remediation site. Further investigation needs to be performed to determine the best coatings to use under certain environmental conditions.

Figure 3-5. Possible methods of nZVI stabilization



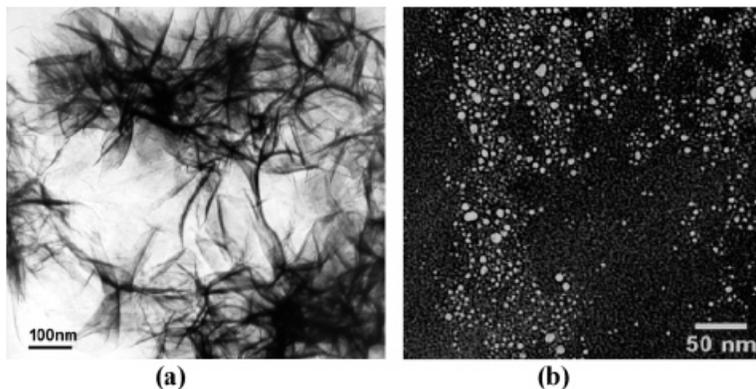
Source: Kustov et al. 2009

Certain coatings have been shown to also increase the length of time particles remain mobile in the environment. Particles enhanced with certain polyelectrolytes have proven to be more mobile than bare nZVI even after aging. The polyelectrolytes slow deposition of the particles by reducing the magnetic attraction of the nZVI to each other and soil grains. nZVI coated with certain polyelectrolytes (e.g., polyaspartate [PAP], carboxymethyl cellulose [CMC], polystyrene sulfonate [PSS]) can remain mobile for at least eight months after the original injection depending on the hydrochemistry and geochemistry found at a site (Kim et al. 2009).

The majority of studies use a combination of surface modifications (i.e., both a catalyst and a coating). For example, Zhu et al. looked at the influences of amphiphiles (the coating) on dechlorination of trichlorobenzene using palladium (the catalyst) enhanced ZVI (Zhu et al. 2008). It is not clear from the currently available research if all catalysts and coatings will work for all contaminants or if certain surface modifications only can be used for certain contaminants. However, it is likely that when choosing surface modifications, the geochemistry of a site will have to be taken into consideration. **Figure 3-6** shows the difference in agglomeration between Pd/Fe particles and Pd/Fe particles that have been coated with a stabilizer and **Figure 3-7** shows the difference in sedimentation rates of bare nZVI and coated nZVI.

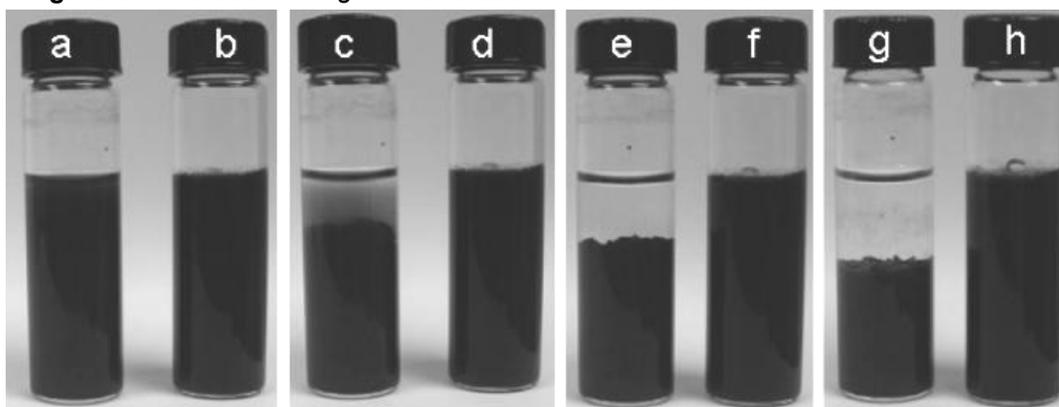
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Figure 3-6. TEM images of 0.1 g/L freshly (a) nonstabilized and (b) 0.2% (w/w) NaCMC-stabilized Fe-Pd nanoparticles



Source: He et al. 2007

Figure 3-7. Vials containing nZVI and stabilized nZVI at various times



Note: (a) and (b) nZVI and S-nZVI after 1 min; (c) and (d) after 10 minutes; (e) and (f) after 2 hours; (g) nZVI after 2 days; and (h) S-nZVI after 60 days

Source: Kanel et al. 2008

3.1.7 Bioavailability and Bioaccumulation of nZVI

Bacteria and living cells have the ability to take up nanoparticles (i.e., nZVI particles are bioavailable). This implies a potential for bioaccumulation in the food web; however, little is known about the actual bioaccumulation of nZVI particles. The bioavailability of iron depends on its free ion concentrations in water (U.S. EPA 2007b). Due to the rapid oxidation of nZVI once exposed to water and/or air, few ions will remain to be transported offsite and expose animals other than microorganisms in the subsurface to nZVI. Microorganisms are the most likely to be exposed to nZVI within the groundwater and soil in the remediation area. Recent research has focused on the bioavailability of nZVI particles in microorganisms, which may affect the toxicity (Lee et al. 2008).

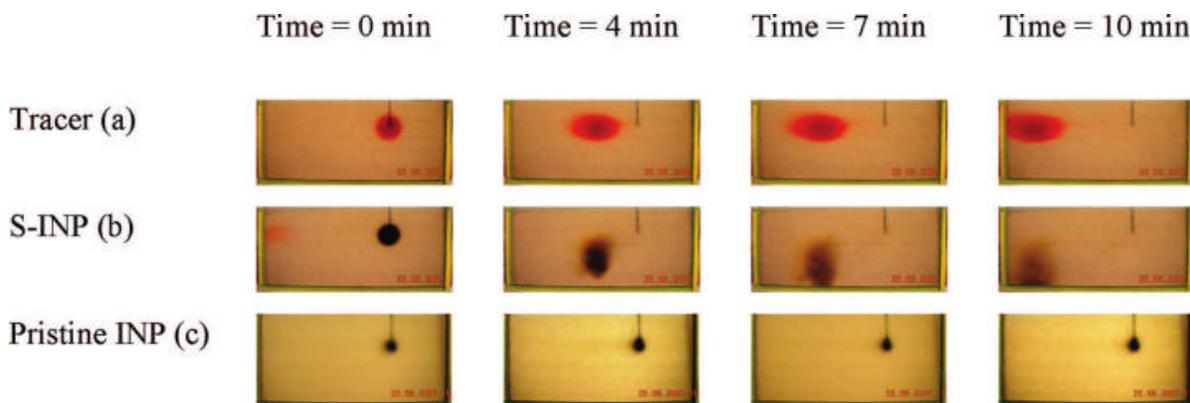
3.1.8 Transport Flow Models

The first study on the two-dimensional transport characteristics of nanoparticles was performed using nZVI and nZVI stabilized with poly acrylic acid (PAA). Data was gathered using the

SEAWAT program, which models the variable-density groundwater flow. This model was significant in demonstrating the importance of density effects on transport that cannot be captured using one-dimensional, column experiments (Kanel et al. 2008). As illustrated in **Figure 3-8**, results showed that nZVI, stabilized nZVI, and a water-based tracer all moved very differently within the test media based on their density compared to the water. Knowing how the nanoparticles move within the water column is not only important for determining if the technology is useful for covering an entire contamination plume, but also for knowing whether or not the material will leave the site. The more contained the particles are, the less likely they are to pose a threat to human health and the environment.

Prior to modeling, the two-dimensional transport of nZVI and the stabilized nZVI were compared to the transport of a tracer within flow containers containing silica beads to represent porous media. The bare nZVI used was assumed to have a positive charge at neutral pH once injected into the test media. Since the porous media had a negative charge, the nZVI was able to attach to the media and become immobilized. As shown in **Figure 3-8**, the stabilized nZVI first moved downward before flowing left and the tracer moved straight left. The differences in transport between the tracer and stabilized nZVI can be attributed to the higher density of the stabilized nZVI (1.036 g cm^{-3}) compared with water (1 g/cm^3) (Kanel et al. 2008). The results from the lab experiment and from the SEAWAT model were compared and indicated that the model accurately predicted the transport of the stabilized nZVI particles. This study is important for demonstrating that an understanding of the effects of density on the transport of nanoparticles is important when choosing the type of nZVI to use during remediation. Based on the density, particles can either move through the entire contamination plume or bypass the plume and leave the system. Knowing the density also can be useful when trying to reach deeper aquifer regions. The full effects of density cannot be demonstrated in conventional one-dimensional column experiments; therefore, the SEAWAT model may be useful when designing future experiments and remediation planning (Kanel et al. 2008).

Figure 3-8. *Transport of tracer, bare nZVI and stabilized nZVI in the flow container*



Source: Kanel et al. 2008

3.2 Toxicity

It is important to understand the fate and transport of a compound when assessing the potential risks or hazard. The toxicity of nZVI cannot be compared directly to macroscale iron particles because the increased surface area, and therefore larger number of reactive sites, may equate to

greater biological activity per unit mass. This implies that research specific to nZVI particles needs to be performed before the technology can be implemented on a mass scale.

Generally, concerns regarding the toxicity of nZVI have been minimal. This is largely due to the formation of iron oxides, which are already present in the ground as rust, during remediation (Watlington 2005). However, this topic is gaining interest within the research and regulatory communities. Although iron is a required nutrient for oxygen transport, electron transfer, and catalysis in the body, it can accumulate to a level that causes DNA damage, oxidative stress, lipid peroxidation, and severe diseases such as hemochromatosis and carcinogenesis. The toxicity of iron is based on its ability to catalyze the formation of hydroxyl radicals (OH[•]) from superoxide (O₂^{•-}) and hydrogen peroxide (H₂O₂) (Li et al. 2009). Free radicals are highly reactive, unstable molecules that are in need of an additional electron for stabilization. Because of this, they can “affect antioxidant enzymatic activities, peroxidation of membrane lipids, modification of nucleic acids, and eventually cause cell death and tissue injury” (Li et al. 2009). Iron toxicity studies have primarily focused on Fe²⁺ and its oxides and little is known about the toxicity specific to nZVI or macroscale ZVI. However, ZVI produces Fe²⁺ and iron oxides through oxidation and ZVI and nZVI can produce free radicals through this transformation process.

Although few studies have been completed, several research groups are currently in the process of analyzing data pertaining specifically to the toxicity of nZVI. Current studies are focusing on the toxicity to microbial communities because these organisms represent the bottom of the food chain. They are also important for the degradation of surface coatings, natural attenuation of contaminants, and the continued degradation of contaminants after the nZVI has lost its reactivity.

3.2.1 Routes of Exposure

Understanding the possible routes of exposure is important when assessing the potential risks presented by a compound and should influence the focus of toxicity-related research. Different routes of exposure will affect different parts and functions of the body. Knowing how a compound could enter the body helps to implement safety measures to reduce exposure.

Human Exposure

Humans can be exposed to nZVI through the following pathways:

- **Dermal Exposure** – The most likely human exposure pathway is accidental skin contact with nZVI powder or slurry during production, application, and decontamination of equipment. Due to their small size, certain nanoparticles may pass into cells directly through the cell membrane with the possibility of interfering with important cell functions. Some nanoparticles may be transported through the bloodstream and may accumulate in organs if they are able to penetrate through all the layers of the skin and into the dermis. The likely oxidation of nZVI particles within the body will also lead to exposure to Fe²⁺ and iron oxide molecules.

- **Oral Exposure** – Another possible route of exposure is through consumption of contaminated groundwater or surface water from drinking wells, streams, and lakes. However, due to poor mobility, this route is not likely, assuming proper care is taken during remediation efforts to inject the nZVI slurry in areas where the radius of influence does not include groundwater drinking wells or other sources of drinking water. This route could also lead to exposure to Fe^{2+} and iron oxide molecules through oxidation of nZVI particles in the body.
- **Inhalation Exposure** – Inhalation is the least likely source of exposure to nZVI if handled properly and manufactured in its slurry form. Inhalation exposure is most likely possible during the manufacturing of both the nZVI powder and slurry; therefore, it should not be a concern for the general public.

Wildlife Exposure

The main exposure route for wildlife is through consumption of contaminated water or food. Organisms found in the soil and groundwater are at highest risk of exposure to nZVI that is introduced into a subsurface ecosystem for remediation. High rates of oxidation and currently low transport ability will limit the exposure to higher organisms by limiting the amount of nZVI particles that reach the surface water. In remediation scenarios where nZVI would be directly introduced to lakes or streams for surface water remediation, there would be a higher risk of exposure to wildlife through consumption and respiration.

3.2.2 Bactericidal Effect of nZVI

Due to all of the unanswered questions regarding nZVI toxicity, there is currently a significant amount of research being performed. A study performed by Lee et al. observed that nZVI particles exhibited a bactericidal effect on *Escherichia coli* that was not observed with other types of iron-based compounds, such as iron oxide nanoparticles, microscale ZVI, and Fe^{3+} ions. Bacteria exposed to 9 mg/L of nZVI under deaerated conditions exhibited significant physical disruption of the cell membranes. A higher quantity of nZVI (60 to 70 mg/L) was required to reach the same results in oxygenated conditions due to higher rates of corrosion. Inactivation of *E. coli* was also observed by Fe^{2+} ions under deaerated conditions, which suggests that Fe^{2+} ions released during oxidation of nZVI may contribute to the bactericidal effects of the nZVI. However, due to high rates of oxidation in the air-saturated solution, the bactericidal activity of Fe^{2+} ions were not observed (Lee et al. 2008). **Figure 3-9** shows the different morphological changes produced by Fe^{2+} ions and nZVI particles and provide insight into the possible mechanism of inactivation. **Figure 3-9 c** and **d** show that iron oxide was formed by the oxidation of Fe^{2+} ions that passed into the cells and likely produced reactive oxygen species (through the Fenton reaction) to induce oxidative stress. **Figure 3-9 e** and **f** show significant disruption of the cell membranes and leakage of the intracellular content from interaction with nZVI. Lee et al. hypothesized that the nZVI “induced reductive decomposition of the functional groups in the proteins and lipopolysaccharides of the outer membrane. Alternatively, nZVI may have been oxidized by intracellular oxygen, leading to oxidative damages via the Fenton reaction.”

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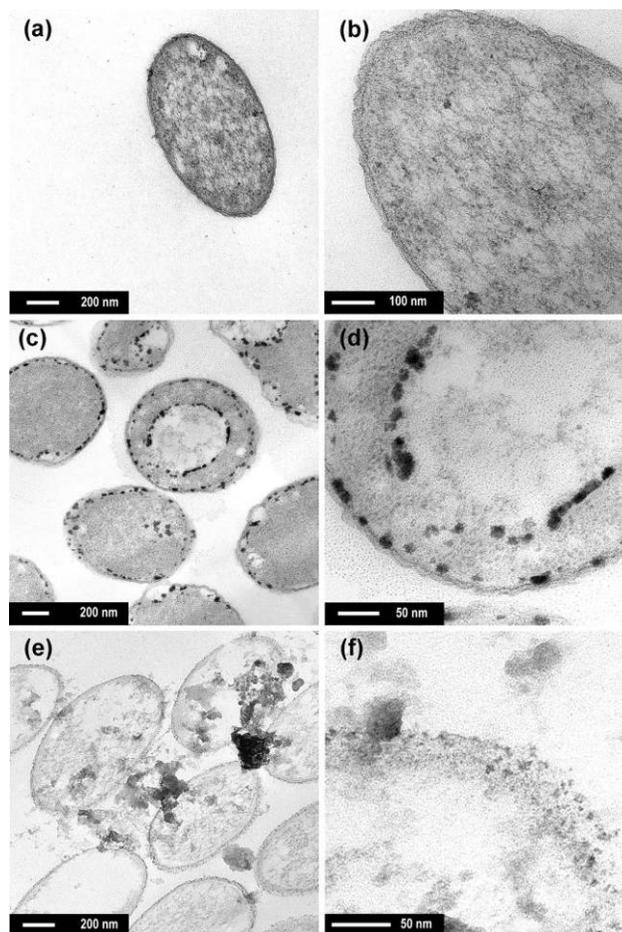
Researchers at Carnegie Mellon University are currently studying the effects of nZVI on microbial diversity and geochemistry in soil microcosms. Recent experiments indicate that although a significant amount of diversity change initially occurs in the microbial community, the overall bacterial abundance does not change. Due to the ever changing diversity of microcosms, the long term impacts of nZVI are minimal and populations easily recover to pre-nZVI conditions after all of the nZVI particles have been oxidized. Preliminary results also indicate that the reducing conditions produced from the corrosion of the nZVI may be conducive for dechlorinating contaminated microorganisms (Kirschling et al. 2009).

Another study that is currently underway at the University of Reading is examining the diversity and activity of soil microbial communities and the effect that nZVI has on microbially mediated soil biogeochemical functions and long-term revegetation of a remediation site. Data is currently being analyzed to determine the effects within the microbial communities. Preliminary results from vegetation experiments indicate that nZVI particles do not have a significant negative effect on the germination and subsequent establishment and survival of certain plant species (e.g., *Trifolium repens* and *Lolium perenne*). nZVI-induced increases in nitrate concentrations in the soil are thought to have led to a depression of nodulation and increased mean shoot mass in *Trifolium repens* (Tilston et al. 2009).

3.2.3 Toxicity to Mammalian Nerve Cells

Studies have indicated that various nanoparticles have the ability to cross biological barriers (i.e., alveolar, intestinal, dermal) when ingested or inhaled and can migrate within the body to various organs and tissues where they have the potential to cause oxidative stress. In order to determine if nZVI particles also have this ability, Phenrat et al. conducted a study on rodent brain cells (BV2 microglia from mice and N27 neurons from rats), which examined the potential for nZVI to produce oxidative stress. The study compared fresh nZVI particles, aged nZVI (partially oxidized >11 months), magnetite (an iron oxide), and two kinds of polyaspartate surface-modified nZVI (i.e., commercially available and laboratory generated).

Figure 3-9. TEM images of (a,b) native *E.coli* cells and treated cells with (c,d) FeSO_4 and (e,f) nZVI



Source: Lee et al. 2008

Results indicate that mice microglia suffered from oxidative stress in response to exposure to fresh nZVI and aged nZVI but did not exhibit signs of oxidative stress when exposed to either surface modified forms of nZVI. Indications of apoptosis (i.e., cell death) only occurred in response to fresh nZVI (≥ 5 ppm, 40 minutes); however, other forms of nZVI appeared to reduce the ATP of the microglia. ATP (or adenosine triphosphate) is an important nucleotide that acts as a coenzyme to provide energy to the cells for metabolism. The ATP was reduced in the following rank order: fresh nZVI (5 ppm, 3 hours) > aged nZVI (20 ppm, 3 hours) > magnetite (20 ppm, 24 hours). Levels of ATP also were reduced in the rat neurons in the following rank order: fresh nZVI (≥ 5 ppm, 1 hour) > surface modified nZVI (20 ppm, 1 hour) > aged nZVI = magnetite (20 ppm, 6 hours) (Phenrat et al. 2009c).

These results demonstrate that different forms of nZVI (i.e., fresh, aged, and surface modified) are differentially toxic to rodent nerve cells (Phenrat et al. 2009c). Generally, “unmodified, relatively immobile nZVI particles oxidize in water and age over months into nontoxic magnetite and/or maghemite, suggesting low risk to encountered ecosystems.” Toxicity appeared to decrease with surface modification, indicating that although they are more mobile, certain surface modified nZVI particles will be a low risk to encountered ecosystems (Phenrat et al. 2009c).

3.2.4 Toxic Effects to Fish

Another recently published study examined the effects of nZVI on medaka fish (*Oryzias latipes*) and their embryos. Both the exposed embryos and medaka adults were exposed to different doses of nZVI (0.5, 5, and 50 $\mu\text{g}/\text{mL}$) in water to determine if observed effects were dose-dependent. Results indicate that oxidative damage was induced in the embryos by measuring antioxidant enzymatic activities and lipid peroxidation. A dose- and time-dependent decrease in superoxide dismutase (SOD) and malondialdehyde (MDA) activities was observed in the embryos. A significant decrease of SOD and glutathione (GSH) activity was observed in liver and brain samples taken from the adults, but as the exposure time increased, the adults appeared to recover from the exposure by adjusting the levels of antioxidant enzymes (Li et al. 2009).

The adults were also examined for possible histopathological and morphological changes. Liver and brain samples did not show significant change, but gill and intestine samples showed considerable change. At exposures of 5 and 50 $\mu\text{g}/\text{mL}$ of nZVI, gill samples were observed with swollen epithelium cells, missing scales, black particles deposited on the surface, and few tactile pillar cells. Morphologic changes were also observed in the gills at exposures of 5 and 50 $\mu\text{g}/\text{mL}$ of nZVI, such as gill lamellae breakage and attachment of black particles on the surface. Exposures also resulted in swelling of the gill arches leading to diminished microridges. Black particle accumulation and swelling were also observed in the intestines (Li et al 2009). **Figure 3-10** shows dose-dependant morphological changes that took place in the gills of the exposed medaka. Pilot remediation tests have previously used concentrations of approximately 4.5 to 10 g/L of nZVI slurry (i.e., 4,500 to 10,000 $\mu\text{g}/\text{mL}$) (Gavaskar et al. 2005). If slurries with nZVI concentrations at these levels come into direct contact with fish they may induce the aforementioned histopathological and morphological changes. Additional studies should be performed on other fish species to determine if results are replicable and/or if different species are affected in different ways.

3.2.5 Toxic Effects to Viruses

nZVI has been shown to be capable of removing viruses (e.g., ϕ X174 and MS-2) from water by inactivating them and/or irreversibly adsorbing the viruses to the iron (You et al. 2005). Although toxicity to viruses is not usually a primary concern, the information could be indicative of how the nZVI will interact with other organisms. Traditionally used disinfectant chemicals, such as chlorine, have been shown to be more effective for killing bacteria than viruses. If the same holds true with the toxicity of nZVI, this information would support the evidence presented in Section 3.2.2 that bacteria communities may be at risk of deleterious effects from exposure to nZVI.

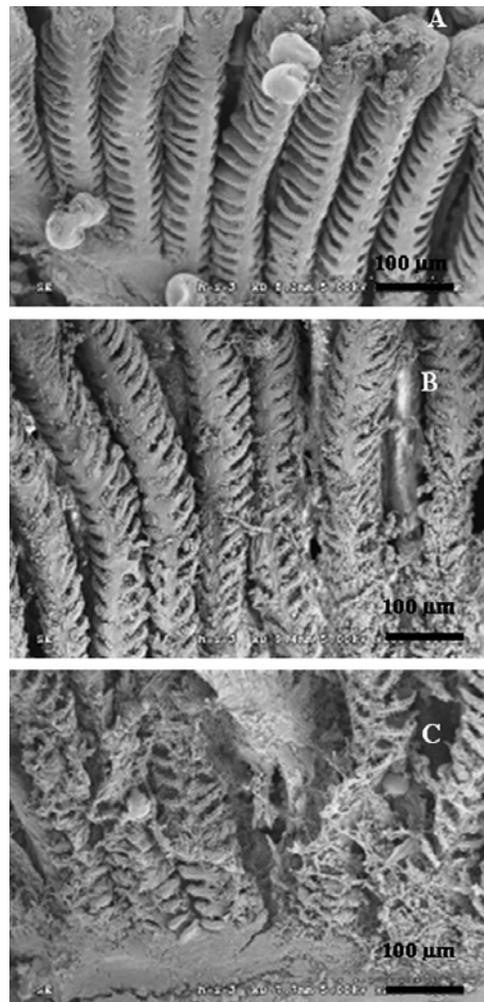
3.2.6 Incomplete Degradation

A potential issue during remediation is incomplete degradation of contaminants to benign products. Some of the byproducts of degradation can be just as or more harmful than the original contaminant. For example, one of the intermediates during TCE degradation is vinyl chloride. Depending on how effectively the nZVI is deployed, TCE may not be completely degraded and the resulting vinyl chloride could cause just as serious a problem for human health and the environment as the TCE would have caused. Another example from a recent study on degradation of lindane by nZVI found biphenyl and trace amounts of benzene as byproducts, both of which are known toxicants (Elliott et al. 2009). Producing a strong reducing environment, meaning an ORP below -400 mV, will promote abiotic reactions and reduce the generation of byproducts that might persist longer in the environment than the original target contaminant. In order to achieve such a reducing environment, application should achieve an iron-to-soil ratio of 0.004 to the target aquifer (Gavaskar et al. 2005). When assessing the pros and cons of using nZVI for remediation, the toxicity of the potential byproducts needs to be considered. If the contaminant cannot be completely degraded (e.g., due to time and money constraints) and the byproducts are a greater environmental concern than the original contaminant, then using nZVI may not be the best solution for remediation.

3.2.7 Mobilizing Contaminants

Another potential issue to consider when evaluating the potential use of nZVI is the possibility of mobilizing contaminants. Although the nZVI particles themselves may be proven to not pose a

Figure 3-10. The morphological alterations in the gill filament of adult medaka due to nano-sized iron exposure



Note: A) control, B) 5 µg/mL of nano-iron, C) 50 µg/mL of nano-iron
Source: Li et al. 2009

threat to human health or the environment, the particles may be capable of binding with contaminants (or byproducts) and transporting them offsite. This may, in the end, increase the problem at hand rather than add to the solution. Naturally occurring nanoscale iron oxide particles (which is a product of nZVI oxidation) have been found with metals, such as copper, bound to their surface many kilometers downstream from mining sites (Hochella et al. 2005). This indicates that introduced engineered iron nanoparticles, either in ZVI or iron oxide form, may be capable of transporting sorbed contaminants. While the nZVI particles themselves may not possess toxic properties, the pollutants they could carry with them may (Karn et al. 2009).

3.2.8 *Iron Oxide Nanoparticles*

Since research concerning the toxicity of nZVI is still in its infant stages, the industry tends to look at the more well known toxicity information for one of the oxidation products of nZVI, iron oxides. Since the two forms of nano iron tend to go hand in hand, the toxicity of nanosized iron oxide cannot be ignored; however, it cannot be the sole concern when considering toxicity. Results from the previously mentioned (Section 3.2.3) study on rodent nerve cells indicate that nZVI particles may be more toxic than nanoscale iron oxide (Phenrat et al. 2009c).

4. DISCUSSION AND CONCLUSIONS

nZVI particles hold great potential to be a valuable tool for *in situ* remediation at Superfund and other contaminated sites. Responsible use of nZVI in environmental applications and careful management of the associated risks requires a fundamental understanding of their mobility, potential bioavailability/bioaccumulation, and impacts on a wide variety of organisms. Currently this fundamental understanding of the environmental fate of nZVI and its oxidation products is not well understood for the variety of environmental conditions that may occur.

4.1 Implications of Fate and Transport of nZVI

The high tendency of bare nZVI to agglomerate indicates that migration in the groundwater should not be an issue for groundwater drinking wells, streams, and other bodies of water. The chance of bare nZVI reaching offsite water is slim, assuming that there is enough of a buffer around the contaminated area to allow for some mobility. Even with coatings that increase mobility and decrease the ζ -potential (i.e., make more negative), the nZVI is not predicted to go much farther than 100 meters from the injection location and much shorter distances when site conditions limit mobility (Saleh et al. 2008). Before the nZVI has an opportunity to move offsite, the majority of the particles will oxidize to form Fe^{2+} , Fe^{3+} , and/or iron oxides and will precipitate out of the groundwater.

There is a fine line between helpful and detrimental transport of nZVI particles. Unfortunately the properties and reactions that may make nZVI harmful to human health and/or the environment are the very same properties that make the particles a valuable remediation tool (Karn 2009). The goal of much current research is to increase the reactivity and mobility of nZVI particles in order to improve contamination reduction. Before allowing mass application of some of the more mobile versions of nZVI, the full toxic effects need to be assessed.

One of the largest remaining questions regarding the fate and transport is how to track nZVI particles in the environment. Because of their small size, the ability to track nanoparticles in the macroenvironment is limited. Methods used to track the mobility under laboratory conditions are not applicable to the natural environment. Current methods of monitoring the presence of nZVI in the environment simply measure changes in the hydrochemistry and geochemistry (e.g., ORP, pH, total iron). This indirect method, though useful for predicting the presence of nZVI, and therefore how far it has traveled, does not measure the concentration of particles. It is therefore difficult to determine how much of the material is mobile in the environment and the concentrations to which humans and wildlife will be exposed. Determining a better method of monitoring the concentrations of nZVI in the environment will help to control unwanted exposures to human and wildlife populations.

4.2 Implications of Current Toxicological Data

Current research seems to indicate that the fate and transport of nZVI should not be an issue for human health and the environment. Based on the limited mobility of nZVI, the chances of bare nZVI reaching the limits of contamination are unlikely. Exposure to nZVI is likely to be insignificant to human health and the environment if it does the job it is intended to do on a given site. If the nZVI properly reacts with the contaminant of interest, the chances of it leaving the site in its original form are minimal. Issues, however, may exist for organisms in the environment that are directly exposed to the nZVI before much oxidation takes place. Concerns may also exist with incomplete conversion of certain contaminants and the offsite mobilization of contaminants that bind to the nZVI.

nZVI fate and transport in the environment, negative interactions with soil bacteria, and reactivity with soil contaminants can be controlled by particle surface chemistry and the geochemistry of the surrounding media. Surface modifications, therefore, determine the interactions of nZVI particles with environmental media and microbes and can be used to control their fate, toxicity, and potential synergistic interactions of nZVI with microbes. However, the full effects of catalysts and surface coatings on the rate and extent of nZVI oxidation, the mobility after reaction, their interactions with microbes, and their effect on human health and wildlife are not well understood (Kustov et al. 2009).

Research indicates that nZVI particles produce detrimental effects in bacteria, viruses, fish embryos, adult fish, and mammalian nerve cells at certain concentrations. Further research should be performed to determine if these results can be replicated for other test species and to establish acceptable exposure limits. Determining exposure limits will help with the management of remediation to ensure that humans and wildlife are not exposed to concentrations that might be detrimental to their health. Widespread use of nZVI as a remediation tool should not be promoted until after acceptable exposure limits are determined. Almost everything is toxic at a certain level; therefore, proper assessment needs to be performed to establish acceptable exposure limits and to determine whether the risks may be greater from exposure to a contaminant or nZVI.

By exploring the fate, transport, and toxicity while the use of nZVI is in its early phases, the industry and governmental agencies can avoid mistakes that have been made in the past with the marketing and use of chemicals prior to understanding the implications. Many products, such as

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asbestos, chlorofluorocarbons (CFCs), dichlorodiphenyltrichloroethane (DDT), leaded gasoline, and PCBs, were used extensively before their toxicity was really understood and created enormous environmental problems that are still affecting the world today. Thoroughly assessing the implications of nZVI could not only prevent harm to human health and the environment, but also reduce the need for additional costly clean-up, legal battles, and damage to public image (Balbus et al. 2005).

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