Nanotechnology for Site Remediation: Fate and Transport of Nanoparticles in Soil and Water Systems

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1. Introduction

1.1 Study Purpose

According to an encyclopedic source, nanotechnology is defined as the design, characterization, production, and application of structures, devices, and systems by controlling shape and size at the nanoscale. Nanotechnology is an emerging science that already shows promise in improving various life aspects ranging from medicine to industrial materials. Along with our ambition to move forward with nanotechnology, we as a society must be conscious of the potential environmental and health impacts of nanomaterials. It naturally results that our best interest is in studying the inherent impact of nanomaterials on us as a society, an ecosystem, and an integral part of nature.

This document focuses on the use of nanomaterials in site remediation. As is well known to researchers and scientists of the field, nanotechnology has great potential in performing chemical and physical processes that are useful in toxic chemical remediation. It is observed that otherwise recalcitrant species found in the environment are neutralized at unprecedented rates and efficiencies when treated with specialized nanoparticles such as nanoscale zero-valent iron (NZVI).

With nanotechnology being as cost effective as it is relative to other leading methods, it becomes necessary to understand its potential impact on the environment. Nine current EPA Office of Research and Development (ORD) Science to Achieve Results (STAR) grants aim at increasing our understanding of the fate and transport of nanomaterials as they are used for desirable processes in the environment. The immediate question of concern becomes: do we understand the physiochemical properties of nanoscale materials well enough to effectively apply them towards remediation? This document will attempt to answer this question by providing information on recent research.

1.2 Background of Nanotechnology for Site Remediation

Nanoscale materials have been tested at a number of contaminated sites with preliminary reports of success. The sites mentioned herein contain chlorinated hydrocarbons such as TCE (trichloroethylene), PCE (perchloroethylene), and other recalcitrant compounds often found as contaminants of concern at EPA's National Priorities List sites. The original concept of using metals as a remediation agent is based on a widely known chemical reaction that uses a neutral electron donor (a metal) to chemically reduce an electron acceptor (a contaminant). The overall reaction is called a reduction-oxidation reaction, or simply a "redox" reaction. In its inception, redox-based remediation viewed elemental iron as the ideal electron donor because of its abundance and ease of application and preparation. Scientists immediately became aware of the potential for metals as reducing agents and sought more effective methods of preparation and application.

Where the original treatment was macroscopic and solely iron-based, new treatments utilize "manufactured" iron in which remediation takes place on the nanoscale. One specific method utilizes advanced iron particles coated with noble metals (colloidal bimetallic nanoparticles, or BNP) that act as catalysts in the redox reaction. In many cases, other elements with properties similar to those of iron are used depending upon site-specific remediation requirements. It has been reported that even zinc or silver can be used as an electron donor in the metal-oxide remediation scheme. Ideal properties of a reductive material are that it be metallic (neutral or "zero valent") and that it holds a reductive potential of two standard charges.

While the chemical properties of a redox-based process are vital to remediation, the physical properties are equally important and play an even more important role in a nanoscale environment. Zero-valent iron remediation traditionally is applied via a permeable reactive barrier (PRB). This technology involves placement of reactive media in one or more soil trenches located directly in the path of contaminated ground-water flow, thereby providing direct contact between contaminants and the reducing agent. Depending upon solubility and other characteristics of a target contaminant, as well as site-specific geochemical conditions, redox reactions can occur successfully within the PRB.

An alternate ZVI-based remediation technology employs reactive media in the form of slurry. The slurry is injected directly into the subsurface through one or more injection wells strategically placed within the target treatment zone. This approach helps mobilize aqueous-phase iron and increase distribution of reactive material across the treatment zone. Both methods have advantages; while PRBs are particularly effective where treating a well-defined contaminant plume, injection methods are useful in treating source areas or a relatively immobile contaminant plume.

2. Case Studies of NZVI-Based Remediation

2.1 Nease Chemical, OH

Based on pilot-scale and bench-scale NZVI studies, decision-makers at many sites across EPA's 10 regions are considering use of this technology to remediate contaminated ground water and soil. One example is the Nease Chemical Site in Ohio, where NZVI technology is one of five cleanup options under consideration by EPA Region 5.

The Nease site is geographically sectioned into areas, or "operable units," needing specific treatment. The property consists of relatively flat terrain with unlined ponds that serve as a source of chemical seeps. The treatment areas are known as "ponds 1 and 2," "remaining ponds and soil," and "shallow and deep ground water." A June 2005 proposed remediation plan and site description specifies NZVI technology employing palladium-coated colloidal iron. The reactive medium will be administered through injection wells reaching deep ground water containing a plume of volatile organic compounds (VOCs).

2.2 RCRA Site, AK

Another site where NZVI is being considered for remediation purposes is an Alaskan facility regulated under EPA's Resource Conservation and Recovery Act (RCRA) program. The site contaminants include VOC constituents of diesel fuel, which was released during an earlier tanker spill, in addition to PCE and TCE. Research indicates that ZVI may effectively reduce the chlorinated compounds in ground-water plumes as well as soil. Field-scale tests will be conducted in both shallow and deep treatment zones. If field-scale tests yield the anticipated positive results, the project will be expanded to full-scale operation.

2.3 Manufacturing Plant, Trenton, NJ

The site of a manufacturing plant in Trenton, NJ, was selected for testing of emulsified zero-valent iron (EZVI) technology to address a contaminant plume that had migrated downgradient from the facility. The test employed ZVI in the form of nanoscale particles suspended in a hydrophobic fluid, thus providing micelles to act as a means of transporting NZVI to non-aqueous phase liquid (NAPL). The micelle membranes are bound by a surfactant that allows cell transport through the ground-water plume (Figure 1).

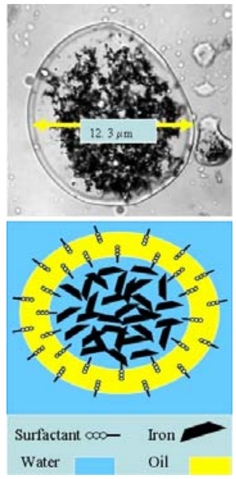

Figure 1. EZVI Agglomerated Particle

EZVI was injected in a water-based slurry through an injection well ("DGC-15") also serving as a monitoring well. Three multi-depth monitoring wells, or piezometers ("PZ-1," "PZ-2," and "PZ-3") also were installed (Figure 2). After the injection process, researchers noted significant TCE reductions in ground water of the second monitoring well but little concentration change in the third.

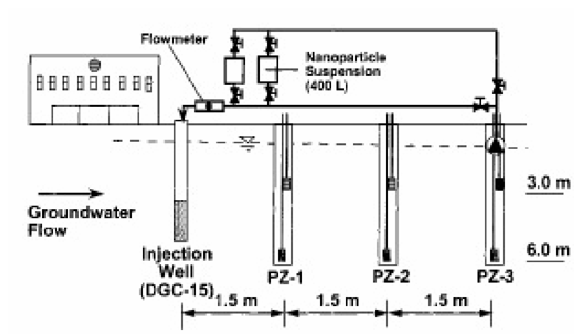

Figure 2. Injection Setup at Trenton Manufacturing Plant

According to an associated *Environmental Science & Technology* journal article, the primary purpose of this field study was to obtain NZVI "proof of concept," i.e., evidence that ZVI administered in the slurry was nanoscale in dimension. The following redox reaction was provided by the authors to show how BNP are manufactured on the nanoscale through the process of reductive deposition:

$$Fe^0 + Pd^{2+} \rightarrow Fe^{2+} + Pd^0$$

Reduction of a chlorinated compound can then proceed via the following reaction:

$$C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^-$$

In some cases, up to 96% reductions in TCE concentrations were observed. Other studies show similar results from ZVI-based treatment, and significant reductions in typical contaminant plumes (Figures 3 and 4).

Figure 3. Typical Contaminant Plume

Figure 4. Typical Contaminant Plume, Post Injection

2.4 Klockner Road Site, Hamilton Township, NJ

This site also is known as the “PSE&G Site” due to its proximity to the PSE&G Trenton (NJ) Switchyard. The area of contamination covers approximately four acres of uncultivated and vacant property historically used as a disposal area for various industrial wastes. Geologically, the site exhibits a perched water aquifer 2-8 feet below ground surface (bgs) and a bedrock formation 130-160 feet bgs.

Administration of ZVI reactive agent is performed through a 20-point injection system on a square grid. Monitoring is conducted on the same grid system to gain a better understanding of chemical reduction that is anticipated to occur via the following reactions:

$$3Fe^0 + 3Fe^{2+} + 6e^- \rightarrow CCl_3CH_3 + 6e^- + 3H^+ C_2H_6 + 3Cl^-$$
$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$
$$CCl_3CH_3 + 3H_2 \rightarrow C_2H_6 + 3HCl$$

2.5 NASA Launch Complex 34, Cape Canaveral, FL

This site is well known for its historical use as a launch pad for shuttle craft and other space-bound vehicles using rocket propulsion. Typical with the use of rocket fuel, chlorinated compounds such as TCE exist in the site’s ground water, soil, and sediment. Field studies suggest that bioremediation via natural attenuation will enhance the results of active treatment technologies implemented at this site.

Three methods of administering NZVI will be field-tested at Launch Complex 34 as alternatives to the direct-injection method: pressure pulsing, pneumatic fracturing, and hydraulic fracturing. Pressure pulsing involves forced administration of NZVI particles to various and relatively predictable subsurface depths. Pneumatic fracturing employs compressed air to create subsurface crevices and small pathways that facilitate distribution of the reactive medium. In a way similar to pneumatic fracturing, hydraulic fracturing uses high-pressure liquids to enhance reagent distribution in the subsurface. Each of these methods is anticipated to show reductions in ground-water contaminant plumes.

Typical changes in concentration reductions in the area of NZVI injections are shown in Figures 5-7.

Figure 5. NAPL Plume

Figure 6. Two-Week Post Injection NAPL Plume

Figure 7. Four-Week Post Injection NAPL Plume

3.0 FOCUS ON NANOPARTICLE FATE AND TRANSPORT

3.1 Issues

Additional research is needed to address specific questions on fate and transport. Although funding and individuals conducting research in this area exist, nanoscale technology is novel and extensive knowledge about nanoparticle fate and transport does not exist. The question regarding "where the particles go" after serving their remediation purpose is significant, particularly as vendors increasingly produce nanoscale metal products and site managers increasingly show interest in using nanotechnology for site remediation. An alternate approach to answering this question is to pose a related question: how can researchers track these nanosized particles in a macroscopic environment? To approach a solution, material scientists are trying to understand the behavior of nanoscale materials in sedimentary environments.

3.2 Research

Many ORD-grant research teams studying nanotechnology fate and transport focus their efforts on soil systems. Some researchers focus on nanotechnology applications in the environment (as nanoparticles occur naturally), while yet others work to increase the understanding of nanoparticle bioaccumulation. Additionally, many research teams have shown that nanoparticles may aggregate or agglomerate to form larger macro-scale metal particles with better known impacts on the environment. These agglomerated nanoparticles may pose concern regarding uptake in wildlife and bioaccumulation. In this sense, the prominent concern becomes the physical interactions between the particles themselves and the environment.

4.0 Case Studies of Fate & Transport of Nanoparticles for Site Remediation

4.1 Manufacturing Plant, Trenton, NJ

This manufacturing plant synthesizes bimetallic particles through use of a process based on the following chemical reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2$$

In order to achieve the bimetallic catalytic effect, iron and palladium are combined in a weight ratio of 1:300. The reactive catalyst coating is applied via the following reaction:

$$Fe^0 + Pd^{2+} \rightarrow Fe^{2+} + Pd^0$$

BNP material is introduced to the contaminated ground-water plume via injection wells, and the reactive agent is distributed throughout the target area via simple suspension in ground water. Monitoring at the piezometers suggests a significant discrepancy in migration rates of the plumes after BNP injection. (Piezometers use pressure differences between at least two subsurface levels to generate a correlation of relative water levels. This method relies on the fact that different plumes exert different pressures although their linear velocities may be the same.) Data provided by PARS Environmental suggest that the contaminant plume continued to move at a rate of 0.3 m/day while the nanoparticles were observed to travel at a rate of 0.8 m/day. Although the relative rates show discrepancy, the impact of the difference is negligible when considering the benign nature of iron particles in soil and water systems.

4.2 Klockner Road Site, Hamilton Township, NJ

A patented BNP-based product known as NanoFe Plus™, developed by PARS Environmental, Inc., is used for remediation at the Klockner Road Site. PARS Environmental, Inc., reports that the reactive agent is administered in a water-based slurry containing one pound of reactive material in each 3.994 gallons of solution.

Currently, little information is available on the fate and transport of NanoFe Plus particles in the subsurface environment at this site. The injection phases and quantities of the injections are known, and two monitoring sessions are scheduled to take place after two injection phases. Monitoring will be conducted to determine the amount of dense nonaqueous-phase liquid reduced by the nanoscale iron, and to estimate the quantity of iron remaining in the aquifer. According to PARS Environmental, little evidence exists showing that the iron plume has traveled farther than the contaminant plume.

4.3 NASA Launch Complex 34, Cape Canaveral, FL

A slightly different application method is used for EZVI technology targeting chlorinated solvents at Launch Complex 34. This method involves the mixing of nanoscale reactive particles with edible oil to form an emulsion that enhances particle mobility within the contaminant plume. EZVI nanoparticles are made using a 1:55 (weight) ratio of palladium and iron. NASA Kennedy Space Center reports that measures of oxidation-reduction potential indicate rates of EZVI migration are negligible.

5.0 CONCLUSIONS

5.1 Understanding the Results

Preliminary results in the case studies indicate that NZVI-based technology has potential as a means of site remediation. When accompanied by sound environmental safeguarding, the technology may prove to be safe and reliable. Currently, more research is needed regarding potential impacts of nanoparticles and their fate and transport in environmental media. According to researchers and developers, nanoparticles will become more complex in their design and use. This raises the same question regarding the extent to which nanoparticles will be environmentally benign when developed through use of synthetic materials such as polymers.

What is known is that the use of complex nanoparticles in remediation is still in the research phase. Remediation technology developers need to recognize that the release of synthesized materials with complex multi-molecular nanoscale structures will generate questions concerning potential ecological and environmental threats.

Based on the information available, the current methods of nanoscale site remediation do not appear to pose a threat to humans and the environment. Transport data indicate that nanoscale particle plumes may travel slightly faster than the natural migration rate of contaminant plumes. Many case studies found the migration rate of iron plumes is insignificant when compared to the rate of contaminant reduction.

5.2 Questions To Be Answered

This section highlights questions arising during this research. The greatest priority at this stage in nanotechnology is concern about the advent of complex nanoparticles and the extent of their propagation in (and potential impacts to) the environment. To date, there have been only bench-scale studies using nanoparticles formulated from the study of polymer synthesis. The questions to be answered are:

- What impacts, if any, would polymer-based nanoparticles have on the environment and human health?
- What time frame should be considered for full-scale production of polymer nanoparticles?
- What is the potential benefit of using complex nanoparticles versus species such as nanoscale iron or zinc?

5.3 Further Research Needs

This section highlights the need for study on other aspects of current nanoscale applications in hopes of inspiring new grants and grantees for research. Specific research is needed to:

- Assess the extent to which nanotechnology implications reach soil and water systems beyond immediate application areas,

- Evaluate the potential impact of nanoparticles on specific and immediate environmental media,

- Determine whether, and the degree to which, nanoparticles may travel through the food chain; preliminary research already indicates that some nanoparticles may be taken up by bacteria in trace amounts, and

- Examine the uptake of nanoparticles in animal species.

References

"Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment," *Environmental Science & Technology*, Vol. 35, No. 24, 2001.

"Full-Scale Nanoiron Injection for Treatment of Groundwater Contaminated With Chlorinated Hydrocarbons," http://www.parsenviro.com/reference/klockner-NGT-III-2005.pdf.

Wilson, Greg. "Demonstration of In Situ Dehalogenation of DNAPL Through Injection of Emulsified Zero-Valent Iron at Launch Complex 34 in Cape Canaveral Air Force Station, FL," Battelle Conference on Nanotechnology Applications for Remediation: Cost-Effective and Rapid Technologies Removal of Contaminants From Soil, Ground Water and Aqueous Environments, September 10, 2004.

U.S. Environmental Protection Agency, "Nanotechnology White Paper" external review draft, December 2, 2005.

"Operation of Piezometers," http://www.slopeindicator.com/instruments/piezo-vw.html.