Nanotechnology for Site Remediation

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As a remediation tool, nanotechnology holds promise for cleaning up hazardous waste sites cost-effectively and addressing challenging site conditions, such as the presence of dense nonaqueous phase liquids (DNAPLs). Some nanoparticles, such as nanoscale zero-valent iron (nZVI) are already in use in full-scale projects with encouraging success. Ongoing research at the bench and pilot scale is investigating particles such as self-assembled monolayers on mesoporous supports (SAMMS\textsuperscript{TM}), dendrimers, carbon nanotubes, and metalloporphyrinogens to determine how to apply their unique chemical and physical properties for full-scale remediation. There are many unanswered questions regarding nanotechnology. Further research is needed to understand the fate and transport of free nanoparticles in the environment, whether they are persistent, and whether they have toxicological effects on biological systems.

In October 2008, the U.S. Environmental Protection Agency’s Office of Superfund Remediation and Technology Innovation (OSRTI) prepared a fact sheet entitled “Nanotechnology for Site Remediation,” and an accompanying list of contaminated sites where nanotechnology has been tested. The fact sheet contains information that may assist site project managers in understanding the potential applications of this group of technologies. This article provides a synopsis of the US EPA fact sheet, available at http://clu-in.org/542F08009, and includes background information on nanotechnology; its use in site remediation; issues related to fate, transport, and toxicity; and a discussion of performance and cost data for field tests. The site list is available at http://clu-in.org/products/nanozvi. © 2008 Wiley Periodicals, Inc.

INTRODUCTION

The definition of nanotechnology is multifaceted. As used here, it is defined as technology at the scale of one to one hundred nanometers (nm) in any dimension; the creation and use of structures, devices, and systems with novel properties and functions due to their size in this range; and the ability to control or manipulate matter on an atomic scale (National Nanotechnology Initiative [NNI], 2008). Nanosized particles have large surface areas relative to their volumes and may have enhanced chemical and biological reactivity (US EPA/Science Policy Council, 2007). They can be manipulated for specific applications to create novel properties not commonly displayed by particles of the same material at macroscale. Several nanomaterials with environmental applications have been developed in recent years. For example, NanoScale Corporation (Manhattan, Kansas) is marketing its product, FAST-AC\textsuperscript{T}1, as a chemical containment and neutralization system that first responders can use to clean up releases of industrial chemicals or chemical warfare agents (NanoScale Corporation, 2008). In addition, a group of researchers at the Massachusetts
Institute for Technology (MIT) have developed a “paper towel” for oil spills that is composed of a membrane or mat of potassium manganese nanowires. According to the researchers, the nanowire membrane selectively absorbs oil with high efficiency. The oil can be recovered by heating the mat, which can then be reused. The membrane, which appears to be impervious to water, may have additional uses in water filtration (Thomson, 2008).

For many years, iron has been used to remediate contaminated groundwater at hazardous waste sites. For example, iron granules or other iron-bearing minerals may be used in a permeable reactive barrier (PRB) to treat an intercepted groundwater plume (Interstate Technology & Regulatory Council [ITRC], 2005). Nanoscale zero-valent iron (nZVI) may prove more effective than macroscale ZVI under similar environmental conditions. Nanoparticles can be highly reactive due to their large surface area-to-volume ratio and the presence of a greater number of reactive sites. In laboratory and field-scale studies, nZVI particles have been shown to degrade trichloroethene (TCE), a common contaminant at Superfund sites, more rapidly and completely than larger ZVI particles. Also, nZVI can be injected directly into a contaminated aquifer, which could result in faster, more effective groundwater cleanups than traditional pump-and-treat methods or PRBs.

Research indicates that nanoparticles such as nZVI, bimetallic nanoscale particles (BNPs), and emulsified zero-valent iron (EZVI) may chemically reduce the following contaminants effectively: perchloroethylene (PCE), TCE, cis-1,2-dichloroethene (cis-DCE), vinyl chloride (VC), and 1,1,1-trichloroethane (TCA), along with polychlorinated biphenyls (PCBs), halogenated aromatics, nitroaromatics, and metals such as arsenic or chromium. The beta elimination degradation pathway, which occurs most frequently when the contaminant comes into direct contact with the iron, follows the pathway of TCE + Fe⁰ → HC Products + Cl⁻ + Fe²⁺/Fe³⁺ (US EPA/Office of Superfund, Remediation and Technology Innovation, 2008).

**DESCRIPTION OF NANOPARTICLES USED IN SITE REMEDIATION**

The majority of bench-scale research and field applications of nanoparticles for remediation at full scale has focused on nZVI and related products. Nanoscale iron particles can be modified to include catalysts, such as palladium (Pd); coatings, such as polyelectrolyte or triblock polymers (Saleh et al., 2007); or can be encased in emulsified vegetable oil micelles (He et al., 2007; Hydutsky et al., 2007). Some nanoparticles are made with catalysts that enhance the intrinsic reactivity of the surface sites (Tratnyek & Johnson, 2006).

BNPs consist of particles of elemental iron or other metals in conjunction with a metal catalyst, such as platinum (Pt), gold (Au), nickel (Ni), and palladium. The combination of metals increases the kinetics of the oxidation-reduction (redox) reaction, thereby catalyzing the reaction. Palladium and iron BNPs are commercially available and currently the most common.

In bench-scale tests, BNPs of iron combined with palladium showed contaminant degradation two orders of magnitude greater than microscale iron particles alone (Zhang & Elliott, 2006). Palladium can catalyze the direct reduction of TCE to ethane without producing other intermediate by-products, such as vinyl chloride (Nutt et al., 2005). Research is ongoing using gold and palladium BNPs to degrade TCE and other chlorinated compounds (Nutt et al., 2005).
Another product, EZVI, consists of ZVI surrounded by an oil-liquid membrane that facilitates the treatment of chlorinated hydrocarbons. EZVI is made from food-grade surfactant, biodegradable oil, water, and either nanoscale or microscale iron to form emulsion droplets. Exhibit 1 illustrates the structure of an EZVI particle. The exterior oil membrane of the emulsion is hydrophobic, as are dense nonaqueous-phase liquid (DNAPL) contaminants, such as TCE. The emulsion is therefore miscible with the DNAPL, allowing increased contact between the TCE DNAPL and the ZVI within the droplet (O’Hara et al., 2006). The vegetable oil also enhances biological activity, which contributes to the destruction of the contaminant (Quinn et al., 2005).

Like other iron nanoparticles, the size of EZVI particles ranges into the microscale (larger than 100 nm), which might make them hard to emplace. Because microscale particles are less costly to produce than nanoscale EZVI, using a mixture of nano- and microscale particles provides cost savings while maintaining the benefits of nanoscale iron. Information on EZVI applications, along with information on other sites using or testing nanoparticles for remediation is available at http://clu-in.org/products/nanozvi.

**DESCRIPTION OF NANOMATERIALS WITH POTENTIAL REMEDIATION APPLICATIONS**

Researchers are developing a variety of nanomaterials for potential use to adsorb or destroy contaminants as part of either *in situ* or *ex situ* processes. These particles include
self-assembled monolayers on mesoporous supports (SAMMS™), ferritin, dendrimers, and metalloloporphyrinogens. The stage of development ranges from bench to pilot scale. More information on these materials and their uses can be found in the US EPA fact sheet at http://clu-in.org/5+2F08009.

Researchers are also using nanotechnology to develop membranes for water treatment, desalination, and water reclamation. These membranes incorporate a variety of nanomaterials, including nanoparticles made of alumina, zero-valent iron, and gold (Theron et al., 2008).

CHEMISTRY OF ZERO-VALENT IRON NANOPARTICLES

Zero-valent, or elemental, iron is a reducing reagent that can react with both dissolved oxygen and water (Zhang, 2003). In the presence of an oxidizing agent, Fe⁰ becomes oxidized to ferrous ions (Fe²⁺), and the two released electrons become available to reduce other compounds. In aerobic conditions, Fe⁰ reacts with dissolved oxygen to form ferrous ions and water. Fe⁰ can also reduce water to form ferrous ions, hydrogen, and hydroxide ions. These reactions are:

\[
2\text{Fe}^0 + 4\text{H}^+ + \text{O}_2 \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (\text{Matheson & Tratnyek, 1994})
\]

\[
2\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (\text{Matheson & Tratnyek, 1994})
\]

In addition to the above reactions, ZVI can also react with contaminants. Exhibit 2 illustrates a reaction that shows the reducing ability of elemental iron with a chlorinated hydrocarbon. In this example, the Fe⁰ (in the form of a BNP) transforms TCE to ethane, releasing Fe²⁺ ions and chloride ions.

Exhibit 2. Reaction of iron in a bimetallic nanoscale particle with TCE (image courtesy of Wei-Xian Zhang, Lehigh University)
IN SITU APPLICATION OF NANOPARTICLES

The method of application for nanoparticles is site-specific and dependent on the geology of the treatment zone and the form in which the nanoparticles will be injected. The most direct route of injection utilizes existing monitoring wells, piezometers, or injection wells. Recirculation can be carried out using existing wells to maintain better contact between the nZVI particles and the contaminants. Additional methods and processes to inject the nanomaterials include direct push, pressure-pulse technology, liquid atomization injection, pneumatic fracturing, and hydraulic fracturing. Details regarding these methods can be found in the US EPA fact sheet. Research is ongoing into methods of injection that will allow nanoparticles to better maintain their reactivity and achieve wider distribution in the subsurface.

Creating nZVI on-site reduces the amount of oxidation the iron undergoes, thereby reducing loss in reactivity. Researchers in green chemistry have successfully created nZVI in soil columns using a wide range of plant phenols, which, according to the researchers, allows greater access to the contaminant and creates less hazardous waste in the manufacturing process (Varma, 2008).

Postinjection observations of the subsurface indicate an increase in pH (due to the formation of hydroxyl ions) and a decrease in the oxidation-reduction potential (ORP) (due to the reducing conditions that are created). A lower ORP favors anaerobic bacteria growth, which in turn may promote increased degradation. Other chemicals formed when using nZVI may include hydrogen gas and Fe$^{2+}$ ions, which would further promote microbial growth. After an nZVI injection, the ORP tends to decrease sharply before becoming stable (Zhang, 2003).

LIMITATIONS

Site-specific conditions, such as the site location and layout, geologic conditions, concentration of contaminants, and types of contaminants may limit the effectiveness of nanoparticles (Macá et al., 2006). Prior to injection of nanoparticles, geologic, hydrogeologic, and subsurface conditions should be evaluated to determine whether injected particles would have adequate subsurface infiltration. Factors that affect subsurface mobility of nanoparticles include composition of the soil matrix, ionic strength and types of cations in the groundwater, hydraulic properties of the aquifer, depth to the water table, and geochemical properties (including pH, dissolved oxygen, ORP, and concentrations of nitrate, nitrite, and sulfate), among others. Studies have shown that nanoparticles may not achieve widespread distribution in the subsurface due to agglomeration prior to complete dispersion within the soil or groundwater matrix, limiting the radius of influence. Agglomeration also reduces the exposed reactive surface area of the particles. The pH of the groundwater affects the sorption strength, agglomeration, and mobility of the particles (US EPA, 2007), with the effects varying based on other site-specific subsurface conditions. Passivation also reduces the effectiveness of iron nanoparticles. As a rule, injection mechanisms should limit the volume of water injected along with the iron, to control exposure to oxygen and other oxidants that could passivate the iron before and during injection. If using larger volumes,
deoxygenated water can minimize the iron passivation, but other oxidants may still be present to react with the iron (Gavaskar et al., 2005).

There is variability among iron nanoparticles, even if they have the same chemical composition (Liu et al., 2005). Properties, such as reactivity, mobility, and shelf life, can vary depending on the manufacturing process or the vendor providing the particle (Miehr et al., 2004). Several vendors supply nanomaterials for site remediation. More information about vendors and other types of nanomaterials can be found at http://www.nanovip.com.

A challenge to evaluating the effectiveness of nanoparticle injection is monitoring the distribution of injected particles in the subsurface. Therefore, it is important to identify the appropriate parameters to measure performance. Typically, geochemical measurements, such as ORP, are monitored as a surrogate. Dissolved iron can also be monitored. Reaction kinetics are difficult to monitor; however, postinjection chemical concentrations can be measured using standard approaches to evaluate the effectiveness of the injection process.

FATE, TRANSPORT, AND TOXICITY QUESTIONS

While nZVI is the most widely used nanoparticle in site remediation, little research has been conducted on the fate and transport of iron nanoparticles in the environment, or the potential toxicological effects they might pose.

While nZVI is the most widely used nanoparticle in site remediation, little research has been conducted on the fate and transport of iron nanoparticles in the environment, or the potential toxicological effects they might pose. There are insufficient data on the potential for bioaccumulation of nanoparticles in environmentally relevant species (Kreyling et al., 2006), and there have been few studies on the effects of any nanoparticles on environmental microbial communities (Klaine et al., 2008).

Under standard environmental conditions (aerated water, pH 5 to 9), Fe$^{2+}$ will readily and spontaneously oxidize to Fe$^{3+}$ and precipitate out of the groundwater as insoluble iron oxides and oxyhydroxides. Ongoing studies are evaluating surface coatings and other modifications that would maximize subsurface mobility of nZVI (Phenrat et al., 2008). While increased mobility would allow more efficient remediation, it could also result in the possibility of the nanomaterials migrating beyond the contaminated plume area, seeping into drinking water aquifers or wells, or discharging to surface water during the remediation process.

Studies are being conducted on the potential toxicity of various types of manufactured nanomaterials. Substances considered nontoxic at macroscale may have negative impacts on human health when nanoscale particles are inhaled, absorbed through skin, or ingested (Kreyling et al., 2006). Because of the minute size of nanomaterials, the particles have the potential to migrate to or accumulate in places that larger particles cannot, such as the alveoli in the lungs (Grassian et al., 2007), thereby potentially increasing toxicity.

Issues of toxicity and safety have limited the use of nanotechnology for remediation by some private-sector companies. DuPont, for example, has ruled out the use of nZVI for site remediation at any of its sites until issues concerning fate and transport have been more thoroughly researched. The company has cited questions of postremediation persistence and potential human exposure to the particles as areas of particular concern (DuPont, 2007).

The US EPA’s Office of Research and Development published a Draft Nanomaterial Research Strategy (NRS) in January 2008 (US EPA/Office of Research and Development,
The initial emphasis of the NRS will be to evaluate and assess the extent to which nanomaterials and products impact the environment and human health. Results from this research will directly inform future policy decisions regarding how to address possible adverse implications associated with the production, use, recycling, or disposal of nanomaterials and products containing nanomaterials.

PERFORMANCE AND COST

As of September 2008, the US EPA had obtained data exhibiting varying degrees of comprehensiveness for a total of 26 sites using or testing nanoparticles for remediation. Details on these selected sites are available at http://clu-in.org/products/nanozvi, and the US EPA will update the list periodically as new information is received.

One site is located in Quebec, Canada; the remaining 25 sites cover seven states in the United States. Of these 25 sites, data for 16 were independently verified through peer-reviewed sources or by government regulators. Data for the other nine sites were not independently verified. There are seven full-scale remediation applications and 19 pilot-scale projects represented. Thirteen remediation projects used nZVI, eight used BNP, four used EZVI, and one used nanoscale calcium ions with a noble metal catalyst. The most frequently treated contaminants of concern were chlorinated solvents, such as TCE, PCE, TCA, and vinyl chloride.

Of the seven full-scale projects, the points of contact for five projects indicated that site-specific cleanup goals were met. The other two projects demonstrated decreasing trends in contaminant concentrations. Of the 12 pilot-scale projects, six indicated that cleanup goals had been achieved. The other six either did not meet cleanup goals or sufficient information on cleanup goals was not provided to assess performance.

As many of the remediation projects using nanoparticles are recently under way or are ongoing, there are limited cost and performance data at this point. In addition, due to proprietary concerns, information about cost is often not made publicly available. Therefore, a comparison of nanotechnology costs with the costs of traditional technologies cannot be accurately conducted at this time. Available cost data are presented at the Web site referenced earlier. As the technology is applied at an increasing number of sites with varying geologies, more data will become available on performance and cost, providing site managers and other stakeholders additional information to determine whether the technology might be applicable to their sites.

NOTICE

This article is drawn from the US EPA Fact Sheet “Nanotechnology for Site Remediation” EPA 542-F-08-009 (http://clu-in.org/542F08009).

REFERENCES


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