



Nanotechnology for Site Remediation Fact Sheet

INTRODUCTION

This fact sheet presents a snapshot of nanotechnology and its current uses in remediation. It presents information to help site project managers understand the potential applications of this group of technologies at their sites. The fact sheet also identifies contacts, such as vendors or project managers with field experience, to facilitate networking.

Nanotechnology is still relatively in its infancy but it is rapidly evolving. It holds promise in remediating sites cost effectively and addressing challenging site conditions, such as the presence of dense nonaqueous phase liquids (DNAPL). For example, nanoscale iron is 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™), 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 various biological systems.

This fact sheet includes information on sites where nanoscale iron has been tested for site remediation. Because many of the remediation projects using nanoparticles are just beginning 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. However, 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.

The following topics are covered in this fact sheet:

- Background
- Description of Nanoparticles Used in Site Remediation
- Description of Nanomaterials with Potential Remediation Applications
- Chemistry of Selected Nanoparticles
- *In situ* Application of Nanoparticles
- Limitations
- Fate, Transport, and Toxicity Questions
- Performance and Monitoring
- Cost
- List of Identified Vendors for Nanotechnology
- Selected Sites Using or Testing Nanoparticles for Remediation

Other potential environmental applications of nanotechnology are not addressed in this fact sheet.

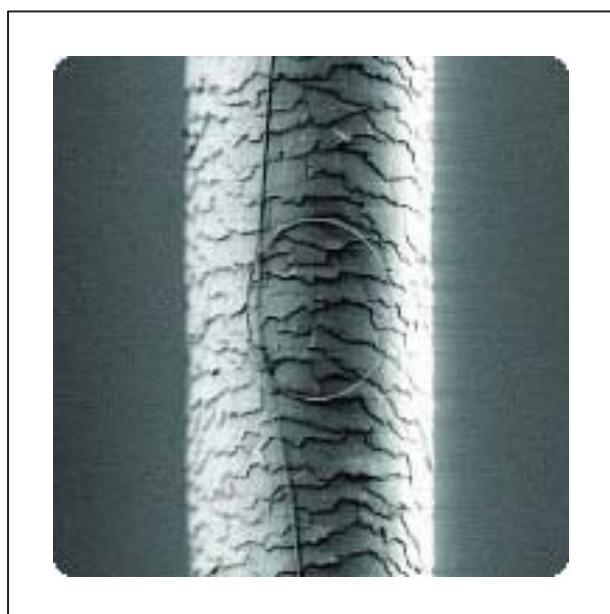
BACKGROUND

The definition of nanotechnology is multifaceted. For the purposes of this fact sheet, it is defined as the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications (NNI, 2008). Figure 1 shows a micrograph of a nanowire compared to a human hair. Nano-sized particles have large surface areas relative to their volumes and may have enhanced chemical and biological

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reactivity (U.S. EPA, 2007). They can be manipulated for specific applications to create novel properties not commonly displayed by particles of the same material at macroscale. Nanoparticles may be produced via a “top down” approach, such as milling or grinding of macroscale material, or, most commonly, via a “bottom up” approach, such as the chloride synthesis method, which creates nanoparticles from component atoms or molecules (Lien, 2006; U.S. EPA, 2007).

Figure 1. Micrograph of a looped nanowire against the backdrop of a human hair (Mazur Group, Harvard University, 2008)



An increasing variety of nanomaterials with environmental applications have been developed over the past several years. For example, NanoScale Corporation is marketing its product, *FAST-ACT®*, as a chemical containment and neutralization system that first responders can use to clean up toxic chemical releases of industrial chemicals or chemical warfare agents (NanoScale, 2008). A group of researchers at the Massachusetts Institute of Technology (MIT) have developed a “paper towel” for oil spills that is comprised 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).

Nanomaterials have also been used to remediate contaminated groundwater and subsurface source areas of contamination at hazardous waste sites. Early treatment remedies for groundwater contamination were primarily pump-and-treat operations. Because of the relatively high cost and often lengthy operating periods for these remedies, the use of *in situ* treatment technologies is increasing.

Since the early 1990s, site project managers have taken advantage of the properties of metallic substances such as elemental iron to degrade chlorinated solvent plumes in groundwater. One example of an *in situ* treatment technology for chlorinated solvent plumes is the installation of a trench filled with macroscale zero-valent iron to form a permeable reactive barrier (PRB) (ITRC, 2005).

Recent research indicates that nanoscale zero-valent iron (nZVI) may prove more effective and less costly than macroscale ZVI under similar environmental conditions. For example, 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, eliminating the need to dig a trench and install a PRB. Research indicates that injecting nZVI particles into areas within aquifers that are sources of chlorinated hydrocarbon contamination may result in faster, more effective groundwater cleanups than traditional pump-and-treat methods or PRBs.

Research indicates that nanoparticles such as nZVI, bi-metallic nanoscale particles (BNPs), and emulsified zero-valent iron (EZVI) may chemically reduce the following contaminants effectively: perchloroethylene (PCE), TCE, cis-1, 2-dichloroethylene (c-DCE), vinyl chloride (VC), and 1-1-1-tetrachloroethane (TCA), along with polychlorinated biphenyls (PCBs), halogenated aromatics, nitroaromatics, and metals such as arsenic or chromium. Two of the important degradation reactions for chlorinated solvents are reductive dechlorination and beta elimination. Beta elimination, which occurs most frequently when the contaminant comes into direct contact with the iron, follows the pathway of $\text{TCE} + \text{Fe}^0 \rightarrow \text{HC Products} + \text{Cl}^- + \text{Fe}^{2+}/\text{Fe}^{3+}$

(U.S. EPA, 2008). Reductive dechlorination, which occurs under the reducing conditions fostered by nZVI in groundwater, follows the pathway of $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{ethene}$ (Elliot, 2006).

Nanoparticles can be highly reactive due to their large surface area to volume ratio and the presence of a greater number of reactive sites. This allows for increased contact with contaminants, thereby resulting in rapid reduction of contaminant concentrations. Because of their minute size, nanoparticles may pervade very small spaces in the subsurface and remain suspended in groundwater, which would allow the particles to travel farther than macro-sized particles and achieve wider distribution. However, as discussed in the 'Limitations' section, bare iron nanoparticles may not travel very far from the injection point.

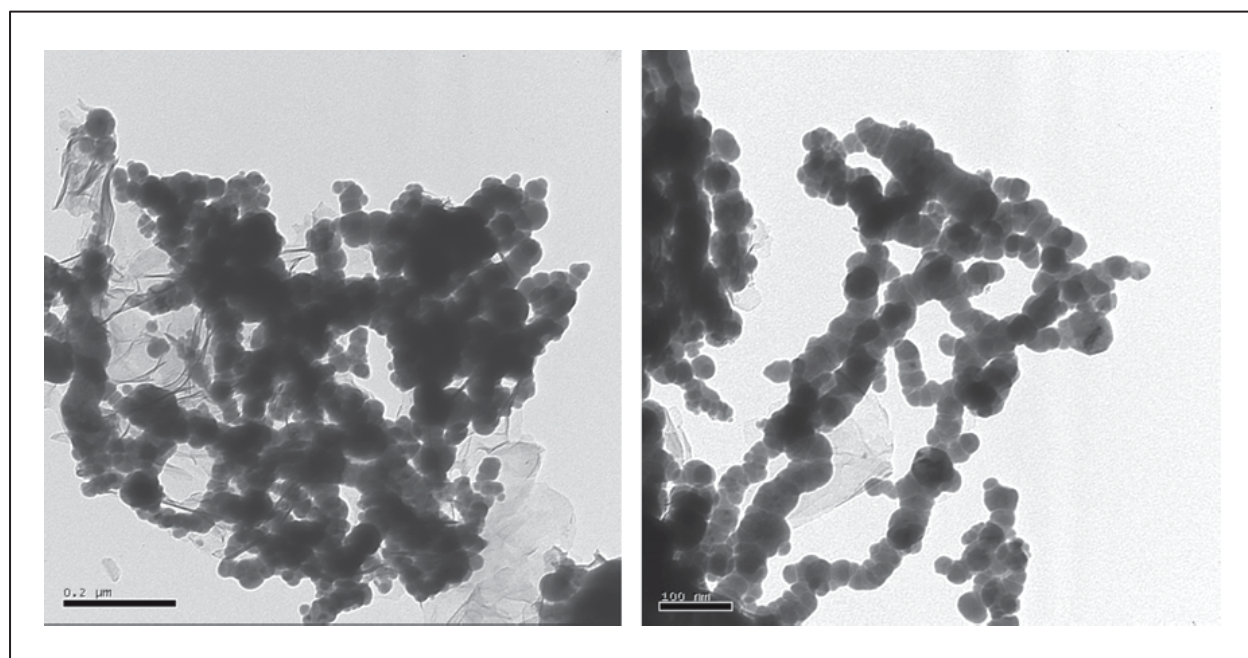
It is important to note that there is variability among iron nanoparticles, even if they have the same chemical composition (Liu, 2005). The properties of particles such as reactivity, mobility, and shelf-life can vary depending on the manufacturing process or the vendor providing the particle (Miehr, 2004).

DESCRIPTION OF NANOPARTICLES USED IN SITE REMEDIATION

Most of the bench-scale research and field application of nanoparticles for remediation at full-scale have focused on nZVI and related products, according to information obtained for this fact sheet. Particles of nZVI may range from 10 to 100 nanometers in diameter or slightly larger. Figure 2 shows transmission electron microscope (TEM) images of nZVI.

An example of a site where nanotechnology showed positive results at full scale is a former fill area in Hamilton Township, New Jersey, which was treated with a nanoiron water slurry (NanoFe Plus™). The groundwater at the site was contaminated with TCE and associated daughter products, with an initial maximum volatile organic compound (VOC) concentration of 1,600 micrograms per liter ($\mu\text{g/L}$). The nZVI was injected in two phases over a total of 30 days. It was reported that post injection monitoring indicated a decrease in the concentration of chlorinated contaminants of up to 90 percent. The site is now in the monitoring phase (Varadhi, 2005).

Figure 2. Transmission electron microscope (TEM) images of iron nanoparticles (Zhang, 2006b)



Note: The scale bars in the figure are 200 nm.

Information on other sites using nZVI can be found in the 'Performance and Monitoring' and 'Selected Sites Using or Testing Nanoparticles for Remediation' sections at the end of this fact sheet.

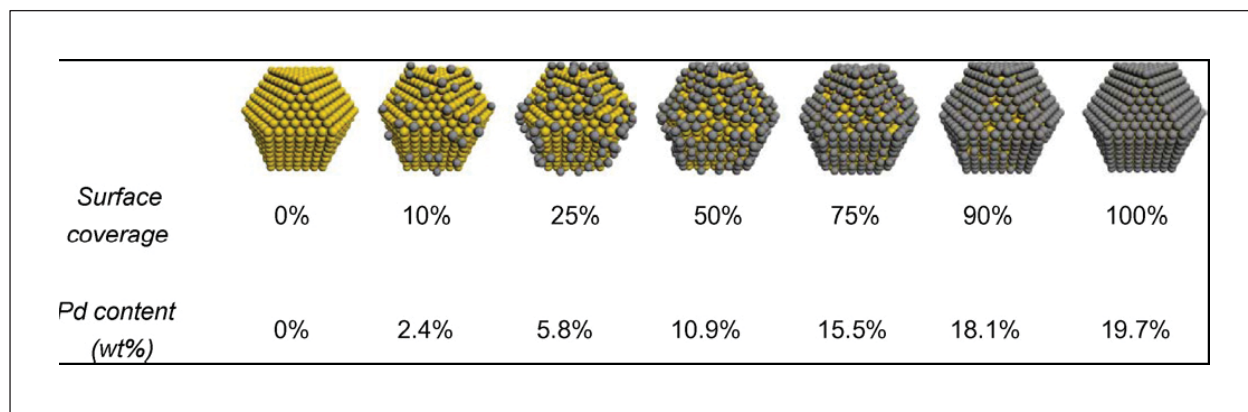
Nanoscale iron particles can be modified to include catalysts such as palladium (Pd), coatings such as polyelectrolyte or triblock polymers (Saleh, 2007), or can be encased in emulsified vegetable oil droplets (Hydutsky, 2007; He, 2007). Some nanoparticles are made with catalysts that enhance the intrinsic reactivity of the surface sites (Tratnyek, 2006). BNPs have been used for the remediation of contaminants in soil and groundwater. 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, 2006b). These particles were 99.9 percent iron and less than 0.1 percent palladium. Palladium can catalyze

the direct reduction of TCE to ethane without producing other intermediate by-products such as vinyl chloride (Nutt, 2005). Research is ongoing using gold and palladium BNPs to degrade TCE and other chlorinated compounds (Nutt, 2005); however, unlike nanoiron, these nanoparticles require a source of reductant such as dissolved hydrogen. They may be used in conjunction with nZVI to supply hydrogen, or an external source of reductant must be applied. Figure 3 shows a schematic of gold and palladium BNPs from a study where the amounts of palladium were varied to optimize the contaminant degradation rate by maximizing the percentage of surface cover. In that study, the TCE reaction rate was maximized at 12.7 percent palladium content. Using palladium in BNPs may improve the reaction kinetics and more effectively distribute the injected slurry or mixture.

BNPs can be injected by gravity or by pressure feed (Gill, 2006). BNPs were used in an application at the Naval Air Engineering Station in Lakehurst, New Jersey, where the soil and groundwater were contaminated with PCE, TCE, and other daughter products. Data indicate that the BNP treatment resulted in a decrease in the average total VOC concentration by 74 percent within six months (NAVFAAC, 2005).

Figure 3. Schematic of Pd/Au BNPs idealized as clusters, with a 4-nm Au core and variable Pd surface coverage from 0 to 100 percent (with corresponding Pd content). (Nutt, 2006)

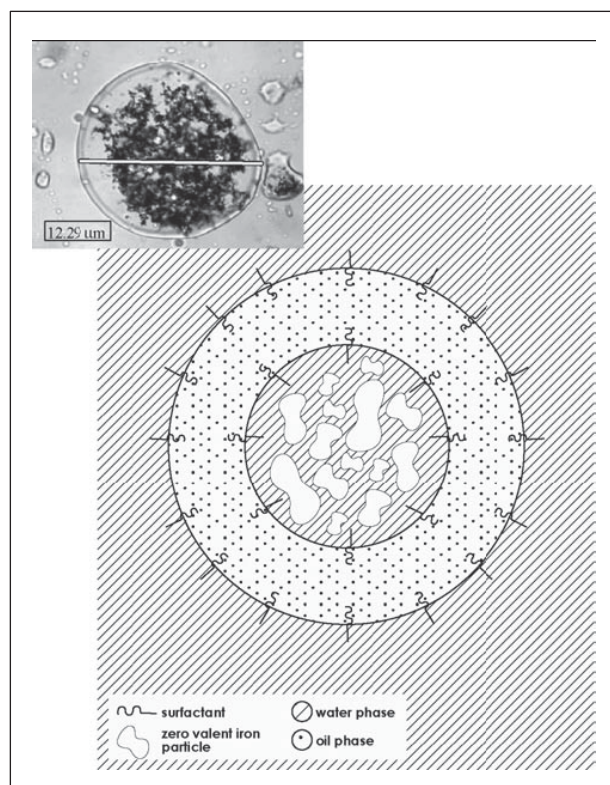


Another product, EZVI, is also commercially available and has been used for the remediation of chlorinated solvents. The product consists of ZVI surrounded by an oil-liquid membrane that facilitates the treatment of chlorinated hydrocarbons. EZVI is made from food-grade surfactant, biodegradable oil, water, and either

nanoscale or microscale iron to form emulsion droplets. Figure 4 illustrates the structure of an EZVI particle. The exterior oil membranes of the droplets are hydrophobic, as are DNAPL contaminants such as TCE. The droplets are therefore miscible with the DNAPL, allowing increased contact between the TCE DNAPL and

the ZVI within the droplets. It is believed that when the emulsion droplets combine with the TCE, the contaminant dissolves and diffuses into the droplet where it comes into contact with the ZVI and is degraded. A concentration gradient is established from the migration of the TCE molecules into the aqueous emulsion droplet and by the migration of the by-products out of the particles and into the surrounding water phase, further driving the degradation reactions (O'Hara, 2006). While both nZVI and EZVI have been shown to reduce TCE DNAPL, according to one researcher, EZVI appears to be more effective in treatment, lowering TCE concentrations to a greater extent than nZVI. The vegetable oil also enhances biological activity, which contributes to the destruction of the contaminant (Quinn et al, 2005).

Figure 4. Structure of an EZVI particle (modified from O'Hara, 2006)



EZVI can be made from nanoscale ZVI, microscale ZVI (larger than 100 nm), or a combination. Using larger particles could make the emulsion more difficult 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.

EZVI has been used to clean up TCE-contaminated soil and groundwater at an industrial site on Patrick Air Force Base in Florida. The particles were introduced via high-pressure pneumatic injection. While initial TCE concentrations were as high as 150,000 µg/L, the highest concentration measured after treatment was 3,580 µg/L. The remediation project was still in operation at the time this fact sheet was prepared. More information on EZVI applications can be found at the Web site link provided in the 'Selected Sites Using or Testing Nanoparticles for Remediation' section at the end of this fact sheet.

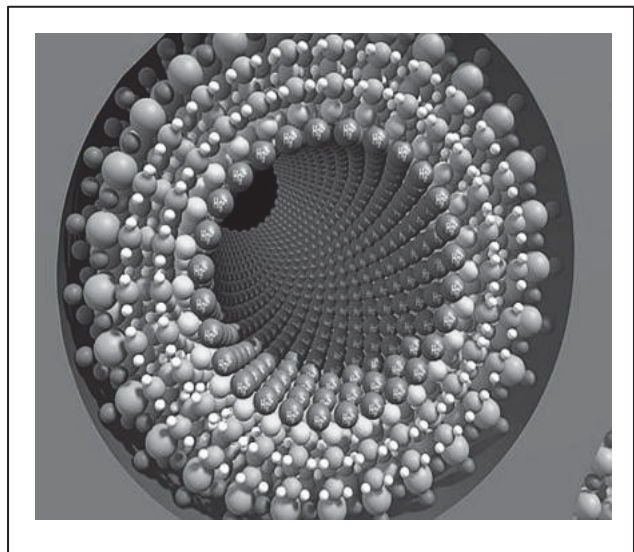
DESCRIPTION OF NANOMATERIALS WITH POTENTIAL REMEDIATION APPLICATIONS

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 SAMMS™, ferritin, dendrimers, and metalloporphyrinogens. The stage of development ranges from bench to pilot scale.

Some materials can be made with surface functional groups to serve as adsorbents to scavenge specific contaminants from waste streams. SAMMS™ particles consist of a nanoporous ceramic substrate coated with a monolayer of functional groups tailored to preferentially bind to the target contaminant. The functional molecules covalently bond to the silica surface, leaving the other end group available to bind to a variety of contaminants. According to researchers, SAMMS™ particles maintain good chemical and thermal stability and can be readily reused or restored (Fryxell, 2007). Figure 5 shows a schematic of a functionalized nano-sized pore within a SAMMS™ particle. The particle has a large surface area to allow for quick sorption kinetics.

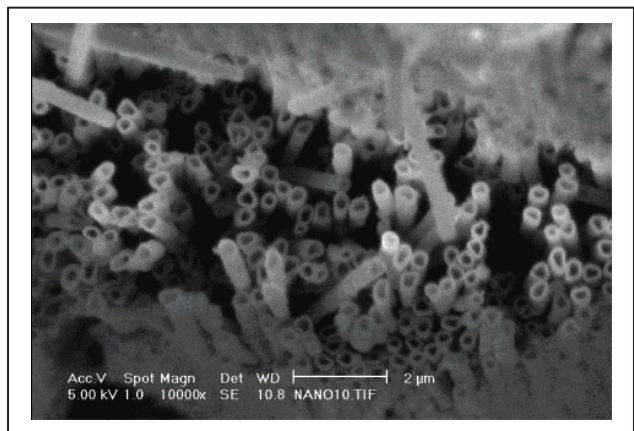
Contaminants successfully sorbed to SAMMS™ particles include radionuclides, mercury, chromate, arsenate, pertechnetate, and selenite (Mattigod, 2003; Tratnyek, 2006). According to the SAMMS™ Adsorbents Web site (<http://sammsadsorbents.com/page/resource-center>), SAMMS™ has shown positive results in pilot scale tests in the remediation of mercury in well water with a high concentration of dissolved solids, aqueous mercury in low concentrations, highly radioactive mercuric waste, and gaseous elemental mercury.

Figure 5. Schematic of functionalized nano-sized pore within a SAMMS™ particle (modified from Mattigod, 2004)



Nanotubes are engineered molecules most frequently made from carbon. They are electrically insulating, highly electronegative and easily polymerized. Nanotubes have also been made from titanium dioxide (see Figure 6) and have demonstrated potential for use as a photocatalytic degrader of chlorinated compounds (Chen, 2005). Bench-scale research has shown titanium dioxide nanotubes to be particularly effective at high temperature, capable of reducing contaminant chemicals by greater than 50 percent in three hours (Xu, 2005).

Figure 6. Scanning electron microscope image of titanium dioxide nanotubes (Chen, 2005)



Bench-scale tests using ferritin, an iron storage protein, have indicated that it can reduce the toxicity of contaminants such as chromium and technetium in surface water and groundwater to facilitate remediation (Temple University, 2004). Like titanium dioxide, ferritin is photocatalytic; in one bench-scale project, the addition of visible light caused ferritin to reduce toxic, water-soluble hexavalent chromium to the less toxic trivalent chromium, which is not water soluble and precipitates out of solution.

Dendrimers are hyper-branched, well-organized polymer molecules made up of three components: core, branches, and end groups. Dendrimer surfaces terminate in several functional groups that can be modified to enhance specific chemical activity. Fe^0/FeS nanocomposites, synthesized using dendrimers as templates, could be used to construct permeable reactive barriers for the remediation of contaminated groundwater. Bench-scale research has indicated that dendrimers have flexible delivery options (Diallo, 2006).

Metalloporphyrinogens are complexes of metals with naturally occurring, organic porphyrin molecules. Examples of biological metalloporphyrinogens are hemoglobin and vitamin B_{12} . Batch-reactor experiments have shown that metalloporphyrins are capable of reducing chlorinated hydrocarbons such as TCE, PCE, and carbon tetrachloride under anoxic conditions to remediate contaminated soil and groundwater, with some structures showing a reduction of TCE and PCE by greater than 990 percent from the original concentration (Dror, 2005).

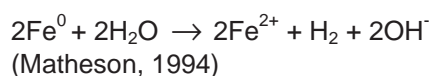
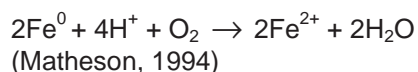
Researchers are also using nanotechnology to develop membranes for water treatment, desalination, and water reclamation. These membranes incorporate a wide variety of nanomaterials, including nanoparticles made of alumina, zero-valent iron, and gold (Theron, 2008). Carbon nanotubes can be aligned to form membranes with nanoscale pores to filter organic contaminants from groundwater (Mauter, 2008; Meridian Institute, 2006).

These and other types of nanoscale materials are chemical substances as defined under the Toxic Substances Control Act (TSCA). Pursuant to TSCA section 5(a)(1), any person manufacturing (including importing) a new chemical substance must file with EPA a

premanufacture notice (PMN) at least 90 days prior to manufacture, unless the substance is exempt from PMN reporting.

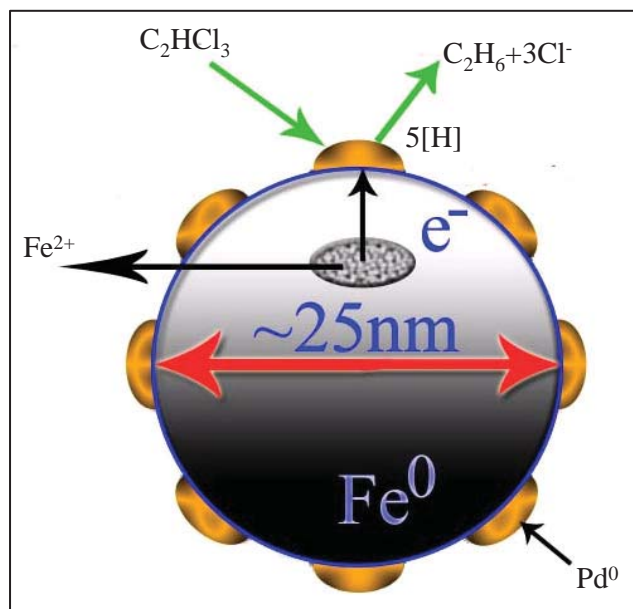
CHEMISTRY OF SELECTED NANOPARTICLES

Zero-valent, or elemental, iron is a reducing reagent that can react with both dissolved oxygen (DO) and water (Zhang, 2003). In the presence of an oxidizing agent, Fe^0 becomes oxidized to ferrous ions (Fe^{2+}), and the two released electrons become available to reduce other compounds. In aerobic conditions, Fe^0 reacts with dissolved oxygen to form ferrous ions and water. Fe^0 can also reduce water to form ferrous ions, hydrogen, and hydroxide ions. These reactions are shown below:

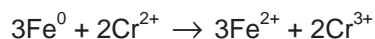


In addition to the above reactions, ZVI can also react with contaminants. Figure 7 illustrates a reaction that shows the reducing ability of elemental iron with a chlorinated hydrocarbon. In this example, the Fe^0 (in the form of a BNP) transforms TCE to ethane, releasing Fe^{2+} ions and chloride ions.

Figure 7. Reaction of iron in a bimetallic nanoscale particle with TCE (image courtesy of Wei-Xian Zhang, Lehigh University)



The reductive capacity of Fe^0 when it comes into contact with chromium contamination in soil and groundwater can be seen in the following equation, where iron is oxidized to its ferrous form and chromium is reduced from chromium (VI) to the less toxic chromium (III) (Cao, 2006):



Nanosized titanium dioxide has been shown to mineralize a variety of herbicides, insecticides, and pesticides via photocatalysis and can convert other contaminants to less toxic compounds (Konstantinou, 2003). When aqueous titanium dioxide suspensions are irradiated with light energy greater than 3.2 eV, titanium dioxide is activated and can combine with water and/or dissolved oxygen to form highly reactive species, including the hydroxyl radical and the superoxide radical anion, which can oxidize many contaminants.

IN SITU APPLICATION OF NANOPARTICLES

The method of application for nanoparticles is usually site-specific and is dependent on the type of geology found in 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 is a technique that involves injecting nanoparticles in upgradient wells while downgradient wells extract groundwater. The extracted groundwater is mixed with additional nanoparticles and reinjected in the injection well. The wells keep the water in the aquifer in contact with the nZVI, and also prevent the larger agglomerated iron particles from settling out, allowing continuous contact with the contaminant.

Additional methods and processes to inject the nanomaterials include direct push, pressure-pulse technology, liquid atomization injection, pneumatic fracturing, and hydraulic fracturing. The direct push method involves driving direct-push rods, similar to small drilling augers, progressively deeper into the ground. This method allows materials to be injected without having to install permanent monitoring wells (Butler, 2000). Pressure pulse technology utilizes large-amplitude pulses of pressure to insert the nZVI slurry into porous media at the water table; the pressure then excites the media and increases fluid level and flow (OCETA,

2003). Liquid atomization injection is a technology that is proprietary to ARS Technologies, a company that specializes in pneumatic fracturing and injection field services. It introduces an nZVI-fluid mixture into the subsurface using a carrier gas. The nZVI liquid-gas combination aerosolizes, allowing for more effective distribution; this method can be used in geologic formations with lower permeability (NAVFAC, 2008). Fracturing injection (pneumatic or hydraulic) is a high pressure injection technique using compressed air (pneumatic) or a water-based, highly viscous slurry containing sand (hydraulic) that fractures rock and allows liquids and vapors to be transported quickly through the channels created. Pneumatic fracturing uses air to create a fracture network of preferential flow paths in rock around the injection point to allow liquids and vapors to be transported quickly through fractured rock. This method of injection improves access to contaminants and allows liquids to flow freely (Pneumatic Fracturing Inc., 2008; Zhang, 2003).

Research is ongoing into methods of injection that will allow nanoparticles to better maintain their reactivity and increase their access to recalcitrant contaminants by achieving 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). Figure 8 illustrates the basic principles of two methods of remediating contaminated groundwater using nanoscale iron. The image at the top shows treatment of DNAPL contamination by injection of nanoparticles. In the second image, a reactive treatment zone is formed by sequential injections of nZVI. This creates overlapping zones of particles that adsorb to the native aquifer material.

Post-injection 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 would most likely favor anaerobic bacteria growth, which in turn may promote increased degradation. Other chemicals formed when using particles such as nZVI may include hydrogen gas and Fe^{2+} ions, which would further

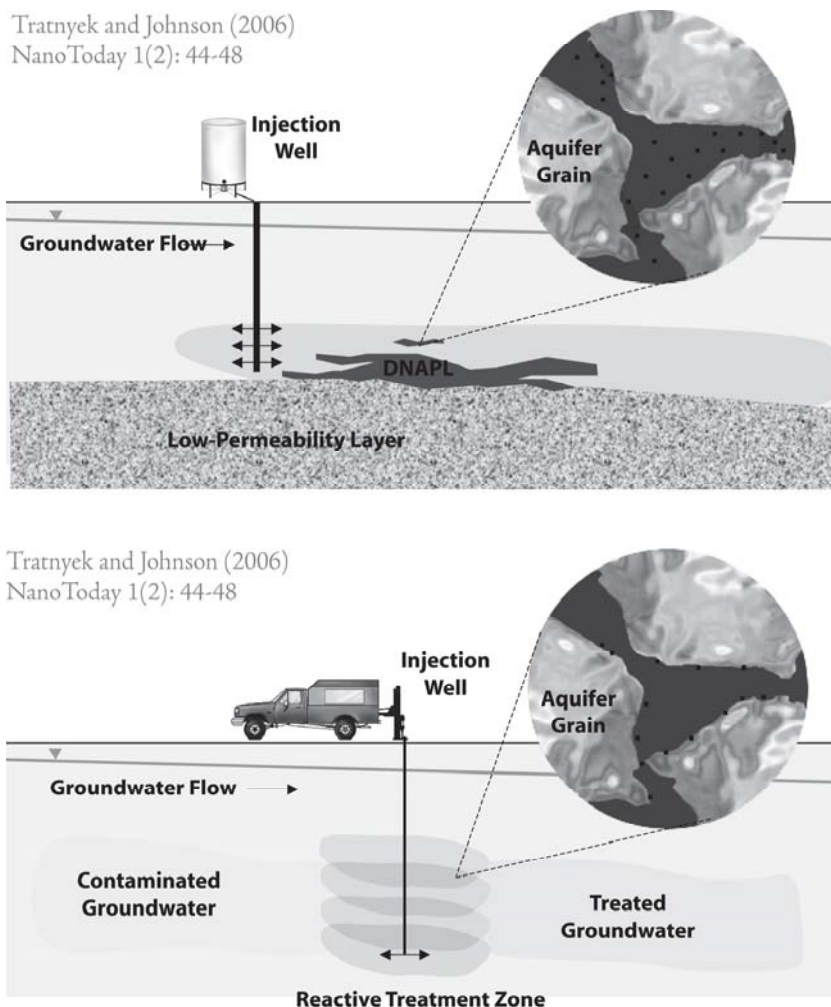
promote microbial growth. After an nZVI injection, the ORP tends to decrease sharply before becoming stable (Zhang, 2003).

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. For example, the research conducted for this fact sheet documents only two sites that have used nanoparticles in fractured bedrock, although several pilot studies have been undertaken (Macé, 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 include composition of the soil matrix, ionic strength of the groundwater, hydraulic properties of the aquifer, depth to the water table, and geochemical properties (including pH, dissolved oxygen, ORP, concentration of nitrate, nitrite, and sulfate), among others. Performance will be site specific and depend on the presence of competing oxidants such as DO and NO_3^- (nitrate ion), contaminant concentration, and soil/groundwater pH (Liu, 2006; Liu, 2007).

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. Nanoscale zero-valent iron particles are attracted to one another, which can cause them to agglomerate into larger micron-sized particles (greater than 100 nm) (Tratnyek, 2006; Phenrat 2007). Agglomeration also reduces the exposed reactive surface area of the particles. The pH of the subsurface may also limit the effectiveness of nanoparticles because the sorption strength, agglomeration, and mobility of the particles are all affected by the pH of the groundwater (U.S. EPA, 2007). The ionic strength and types of cations in the groundwater, as well as the chemical and physical characteristics of the aquifer materials, also affect the agglomeration and movement of iron nanoparticles (Saleh, 2008).

Figure 8. Schematic of two methods of groundwater remediation using nanoiron (Tratnyek, 2006)



Passivation is another factor that may limit the effectiveness of iron nanoparticles. If nZVI is being used, improper handling can result in the iron becoming oxidized and passivated prior to reacting with the contaminants. As a rule, injection mechanisms should limit the volume of water injected along with the iron, to limit 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, 2005).

A challenge with evaluating the effectiveness of nanoparticle injection is monitoring the distribution of injected particles in the subsurface. It is therefore important to identify the appropriate parameters to measure performance. Typically, geochemical measures such as ORP are monitored as a surrogate. Dissolved iron can also be monitored. Reaction kinetics are difficult to monitor; however, post-injection chemical concentrations are measured using standard approaches. Additionally, the kinetics and reactivity of nanoparticles in a DNAPL source zone may vary from the kinetics and reactivity in a dissolved plume (U.S. EPA, 2008; Liu, 2007).

FATE, TRANSPORT, AND TOXICITY QUESTIONS

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

As described in the 'Limitations' section, agglomeration often affects transport of nanoparticles in the subsurface. The particles may become associated with the aquifer matrix as oxidized iron particles after reacting with contaminants. 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. Researchers have developed methods, some of which are in use commercially, to improve the mobility of iron nanoparticles within aquifers and to optimize contact between the nanoparticle and contaminant. Ongoing studies are evaluating surface coatings and other modifications that would reduce agglomeration of nanoparticles and maximize subsurface mobility (Phenrat, 2008). Preliminary research indicates that polymers and surfactants stabilize nanoparticle suspensions in aquifers, inhibiting their agglomeration and allowing greater dispersal without compromising the ability of the iron to remediate contaminants (He, 2007). Soils high in clay content have been shown to allow greater dispersal of nZVI as well; anionic clay particles appear to function as a natural stabilizer, allowing for more effective transport (Schrack, 2004, Hydutsky, 2007). 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. The increased surface area and larger number of reactive sites of nanomaterials

may equate to greater biological activity per unit mass than micro- or macro-scale particles of the same composition. Substances considered nontoxic at macroscale may have negative impacts on human health when nanoscale particles are inhaled, absorbed through skin, or ingested (Kreyling, 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, 2007), thereby potentially increasing toxicity. Some nanoparticles have demonstrated an ability to increase bioavailability of certain hydrophobic contaminants, for example, by increasing mobility of contaminants bound to soil and sediment surfaces (Tungittiplakorn, 2005).

Issues of toxicity and safety have limited the use of nanotechnology for remediation by some private sector companies. For example, DuPont 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 post-remediation persistence and potential human exposure to the particles as areas of particular concern (DuPont, 2007). As another example of a cautionary approach, the Continental Western Group of insurance companies announced that it will no longer cover injury and/or damage arising from nanotubes or nanotechnology, as used in products or processes. See: <http://cwgingins.com/mike/documents/CW33690608NanotubesExclusion.pdf>.

EPA's Office of Research and Development (ORD) published a Draft Nanomaterial Research Strategy (NRS) in January 2008. 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 nanoproducts (that is, products containing nanomaterials). Initially, a smaller portion of the proposed research will focus on beneficial environmental applications, such as more effective control technologies and enhanced production processes that reduce emissions and releases of conventional pollutants. As the program

evolves over time, ORD will augment its efforts in this area.

In the Draft NRS, ORD identified four key research themes for investigating nanomaterials for EPA:

- Sources, Fate, Transport, and Exposure
- Human Health and Ecological Research to Inform Risk Assessment and Test Methods
- Risk Assessment Methods and Case Studies
- Preventing and Mitigating Risks (USEPA 2008A).

PERFORMANCE AND MONITORING

As of September 2008, data exhibiting varying degrees of comprehensiveness were obtained 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 will be updated 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 BNPs, 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 VC.

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

Details for two projects in the list of sites are provided below.

Use of nZVI at a former Manufacturing site in Passaic, New Jersey. nZVI was applied at a former manufacturing site in Passaic, New Jersey, where chlorinated solvent contaminants such as TCE had been found in groundwater. A pilot scale test was conducted from September 9 to 13, 2005, to treat a shallow sand aquifer. The technology design included the injection of 108 pounds of nZVI slurry and 1,200 pounds of emulsified oil into 3 points within the silt unit. Pneumatic fracturing injections were used at two of the injection points and hydraulic injection was used at the third. At the end of the pilot-scale test, there was a 90 to 100 percent reduction in TCE concentrations throughout the contaminant plume. Monitoring occurred weekly during the first month of the project and was conducted monthly thereafter (Zhang, 2006a).

Use of nZVI at Fill Area in Hamilton Township, New Jersey. Contaminants at the Klockner Road Site in Hamilton Township, New Jersey were treated using nZVI. The site was a former fill area, where contaminants such as TCE, TCA, DCE, and dichloroethane (DCA) were found in the groundwater. A full-scale project was implemented using nZVI (NanoFe Plus™). NanoFe Plus™ is manufactured by PARS Environmental Inc. and consists of nZVI with an added catalyst to enhance the speed and efficiency of remediation. The nanoscale iron was injected in three phases. Phase I injection contained 3,000 pounds of slurry and was injected at the northern end of the site over a period of 20 days. Phase II injection contained 1,500 pounds of slurry and was injected throughout the northern half of the site over a period of 10 days. Information on Phase III was not available at the time this fact sheet was prepared. The results of the full-scale injections showed up to 90 percent reduction in the overall contaminant concentrations. ORP, pH, and groundwater elevations were monitored during each phase of the injection. The first post-injection monitoring event was conducted one week after the first injection and the second event was conducted two weeks after completion of the Phase II injection. At preparation of this fact sheet, monitoring activities were ongoing and included collecting groundwater samples to monitor trends in any remaining groundwater contamination. Cost information was not available in the materials reviewed to prepare this fact sheet (Gill, 2006).

COST

Three site-specific examples of project costs are shown in Table 1 below. The first two sites achieved their remedial objectives; information on performance for the third site was not available. The cost information that was provided is limited; therefore, a comparison of nanotechnology costs with the costs of traditional technologies cannot be accurately conducted at this time. Factors contributing to the costs include site type, type of contaminants, concentrations of contaminants, extent of the plume, and any challenges that may have occurred during remediation. The factors that were included in the total cost for the Naval Air Engineering Station in New Jersey included monitoring well installation, sampling, nZVI injection, post-injection sampling, and reporting. The components contributing to the total cost at the Naval Air Station in Jacksonville, Florida,

included mobilization, monitoring well installation, nZVI injection, sampling and analysis, and other miscellaneous costs (Gavaskar, 2005). nZVI production is included in the injection costs for both of these sites. The final costs for the Patrick Air Force Base Site include mobilization and site setup, monitoring well installation, recirculation/ injection events, surveying, disposal of demonstration derived waste, and monitoring. Administrative costs associated with project management, work plan generation, and bench-scale treatability study costs were not included.

Additional factors that may increase the total cost of nanoparticle application may include operational requirements connected with any contamination found underneath a building, or the need to treat or dispose extracted fluids (Wilson, 2004).

Table 1. Costs for example projects using nanotechnology for site remediation

Site Name	Cost Components			
	Remediation Cost (Total)	Capital Costs	O & M Costs	Unit Cost
Naval Air Engineering Station Lakehurst, NJ ¹	\$255,500	-	\$213,000	-
Naval Air Station Jacksonville, FL ²	\$260,000	-	\$110,000	\$269/cy
Patrick Air Force Base, FL ³	\$4,000,000	\$2,000,000	\$70,000	\$180/cy

1. O&M costs: Monitoring Well Installation \$24,400, Sampling and Analysis \$58,400, Reporting \$18,100.
2. nZVI cost: \$37,000. O&M costs: Monitoring Well Installation \$52,000, Sampling and analysis \$110,000. 967 cubic yards (cy) soil treated.
3. Capital costs: \$1,000,000 for EZVI, \$1,000,000 for pneumatic injection contractor. 22,222 cy soil treated.

LIST OF IDENTIFIED VENDORS FOR NANOTECHNOLOGY

Several vendors supply nanomaterials for site remediation. Some of the suppliers that were identified and their products are shown in Table 2. This list should not be considered to be comprehensive or as an endorsement by EPA. More information about the vendors and other types of nanomaterials can be found at <http://www.nanovip.com>.

SELECTED SITES USING OR TESTING NANOPARTICLES FOR REMEDIATION

A list of sites using or testing nanoparticles for remediation is available at <http://clu-in.org/products/nanozvi>. This list will be updated periodically as new information is received.

Table 2. Identified nanomaterial vendors

Vendors*	Nanomaterial Produced	Web site
Crane Polyflon	PolyMetallix	www.polymetallix.com
Lehigh University	Fe/B	www.lehigh.edu/nano/environmental.html
Environmental Restoration Services, LLC	Nano-Ox	http://www.ersllccorp.com/index.html
OnMaterials LLC	ZLoy	www.onmaterials.com
PARS Environmental Inc.	NanoFe™ and NanoFe Plus™	www.parsenviro.com
Toda Kogyo Corporation	RNIP	www.toda.co.jp/english/c02-02.html
VeruTEK Technologies, Inc.	Green Chemistry and Nanotechnology	www.verutek.com
Pacific Northwest National Laboratory	SAMMS™	http://samms.pnl.gov/

* Mention of product does not imply endorsement. Vendors that would like to be included in future iterations of this table should submit their request in a comment to the Clu-in Web site at: <http://www.clu-in.org/gbook.cfm>

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