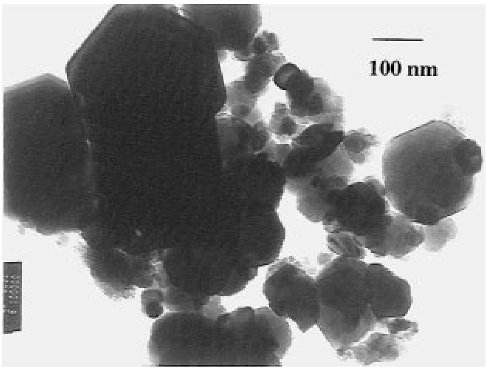

(Wang 1997)

Emerging Nanotechnologies for Site Remediation and Wastewater Treatment

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ABSTRACT

The impacts of nanotechnology are increasingly evident in all areas of science and technology, including the field of environmental studies and treatment. Experts anticipate the development and implementation of environmentally beneficial nanotechnologies in the categories of sensing and detecting, pollution prevention, and treatment and remediation. Of the three, the category of treatment and remediation has seemingly experienced the most growth in recent years. In terms of site remediation, the development and deployment of nanotechnology for contaminant destruction has already taken place. Nanoscale iron particles and the subsequent derivatives (bimetallic iron particles and emulsified iron) represent a viable commercially available nanotechnology for remediation. Currently, over 15 academic and commercial field scale tests involving nano-iron particles are underway or have reached completion. Many more sites have scheduled field studies and consequently the number of vendors supplying this product continues to grow. In addition, a multitude of nanotechnology applications for site remediation and wastewater treatment are currently in the research and development stages. From dendritic polymers to functionalized ceramics, the technologies poised to impact the treatment field are considerably diverse.

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ANSI	American National Standards Institute
BNIP	Bimetallic Nanoscale Iron Particles
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CA	Chloroethane
cDCE	cis-1,2-dichloroethene
COC	Chlorinated Organic Contaminant
CVOC	Chlorinated Volatile Organic Contaminant
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
DCA	Dichloroethane
DCE	Dichloroethene
DNAPL	Dense Non-Aqueous Phase Liquids
DOD	Department of Defense
DOE	Department of Energy
EZVI	Emulsified Zero-Valent Iron
MTBE	Methyl-*tert*-butyl ether
NNI	National Nanotechnology Initiative
NPL	National Priority List
nZVI	Nanoscale Zero-Valent Iron
PAMAM	Poly(amidoamine)
PCB	Polychlorinated Biphenyl
PCE	Tetrachloroethene
PRB	Permeable Reactive Barrier
RCRA	Resource Recovery Conservation and Recovery Act
RNIP	Reactive Nanoscale Iron Product
SAMMS	Self Assembled Monolayers on Mesoporous Silica
SEN	Single Enzyme Nanoparticle
TCA	Trichloroethane
TCE	Trichloroethene
TSCA	Toxic Substances Control Act
UST	Underground Storage Tank
VC	Vinyl Chloride
ZVI	Zero-Valent Iron

1. FORWARD

For the next few decades, at the very least, our country will be faced with serious issues regarding the cleanup of contaminated sites across the country. Despite a significant effort over the past 25 years, the job remains far from complete and as of yet, many sites remain inadequately characterized. A number of contaminated areas await remedial action, and many still await identification. Adhering to the current regulatory standards, an estimated 294,000 sites (range 235,000-355,000) require some form of remediation; this does not include sites with completed or ongoing remediation projects. Contaminated sites can be divided into seven groups based around regulatory and decontamination responsibility: Superfund, Resource Conservation and Recovery Act (RCRA) Corrective Action, Underground Storage Tanks (USTs), Department of Defense (DOD), Department of Energy (DOE), Civilian Federal Agencies, and States (USEPA 2004). Figure 1 shows the breakdown of the 294,000 sites remaining for the various segments (USEPA 2004).

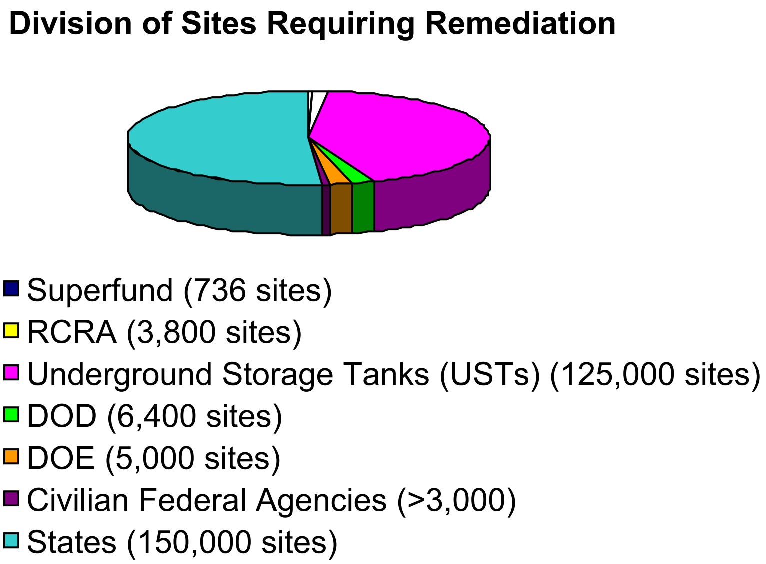

Figure 1. Division of sites still in need of remediation based on regulatory responsibility (USEPA 2004)

The majority of these sites, which are both large and complex, will require the collaboration of multiple stakeholders for successful cleanup as well as the development and implementation of innovative remedial solutions. The drive for novel remediation processes is in high demand. Expedited and efficient processes often reduce costs, thus saving the responsible parties a great deal of money. Successful remediation also allows for the ability to reuse land. Another driver for innovation originated from the 1986 reauthorization of the Superfund law, which added a new emphasis to “permanence and treatment,” (USEPA 2004). While the law only encompasses the National Priority List (NPL)/Superfund sites that comprise a relatively small fraction of the total list of contaminated sites, the Superfund program has greatly influenced the entire field of remediation. The idea of permanence and treatment has largely been adopted by all site divisions. In addition, many new and better remediation technologies implemented at Superfund sites have spread to other sectors due to the interchangeability of innovative technologies across the various segments. The remedial compatibility across site divisions, in turn, has created an extremely large market and, thus, a substantial demand for these new technologies (USEPA 2004).

In the past ten years, emerging technologies such as phytoremediation, bioremediation, and permeable reactive barriers have become popular new tools. These novel treatments have begun to compete with more established technologies such as solidification/ stabilization, soil vapor extraction, and thermal desorption for soil, and pump and treat systems for groundwater (USEPA 2004).

At the very forefront of these emerging technologies lies the development of nanotechnology for site remediation. Nanotechnology represents an extremely broad field, which encompasses a number of materials and technologies spanning multiple disciplines. Currently a wide variety of potential remedial tools employing nanotechnology are being examined at the bench-scale for use in waste water and soil remediation. One emerging nanotechnology, nanosized zero valent iron and its derivatives, has reached the commercial market for field-scale remediation and studies.

2. PURPOSE

While nanotechnology is considered the new buzzword by many in the scientific community, information regarding the subject remains largely dispersed and fragmented due to the relative novelty of the technology. This fact holds true for the specific developments in the field of hazardous waste remediation. While one specific nanotechnology and its derivatives have reached the commercialization process, a majority of the current studies involving nanotechnologies for remedial applications remain on the bench scale. Recent journals and books, such as the *Environmental Science and Technology*'s Special Issue on Nanotechnology and the ACS Symposium Series, Nanotechnology and the Environment, provide a more comprehensive view of the recent advances. However both of these publications present the majority of information as a compilation of peer-reviewed articles. These types of publications often detail the science behind the technology, leaving the overall relevance and connections to field scale applications vague. In general, a lack of assembled information exists on how these individual nanotechnologies might eventually be implemented, the type of sites where they would be appropriate, and the general feasibility for scale-up.

In evaluating the status of this emerging field while also looking ahead to the future, it becomes important to examine both the science behind these nanotechnologies as well as their current and potential applications. This paper seeks to provide a more holistic view of the state of the science. Both the commercialized nanotechnology products and many of the technologies being researched in academia are discussed. Attention is given both to the research itself as well as the remedial capabilities. The toxicity and safety concerns of the individual technologies are also briefly outlined as are the overall toxicity concerns related more generally to the field of nanotechnology. Finally the current state of regulation is addressed.

3. INTRODUCTION TO NANOTECHNOLOGY

"If I were asked for an area of science and engineering (S&E) that will most likely produce the breakthroughs of tomorrow, I would point to nanoscale science and engineering."
~ Neal Lane, testifying before Congress in 1998

In 1959, Richard Feynman, a professor at Cal Tech, introduced the world to the expansive concept of nanotechnology in his lecture, "Plenty of Room at the Bottom," (Feynman 1959). A revolutionary theory at the time, Feynman envisioned a world where scientists like him could, "arrange atoms the way we want, the very atoms, all the way down!" (Feynman 1959). While his lecture incited a great deal of interest in the scientific community, it was the 1980s before Feynman's radical vision became feasible.

The vision of nanotechnology expanded in 1981, when researchers at IBM developed the scanning tunneling microscope (STM), which allowed scientists to "see" atoms and molecules. By 1985, with the aid of the STM, IBM scientists "wrote" the letters IBM using 35 individual xenon atoms (Lane 2005). These developments helped scientists realize the possibilities, thus paving the way for the expansion of nanotechnology research and development (R&D).

Despite a growing interest in the subject, a fixed definition of what constitutes "nanotechnology" remains undeniably elusive. Generally, nanotechnology covers objects on the "nano" scale, or in other words, objects measuring between 1 and 100 nm (NNI 2005). However, basing categorization simply on size does not give an adequate definition of the technology. Many nanosized structures, such as weathered minerals, exist in the environment naturally (Masciangioili 2003). While classified on the nanoscale, these materials do not fall into the category of nanotechnology. The remaining requirements for categorization as nanotechnology include the concept that compounds must possess unique physical, chemical, and/or biological properties, different from those found in the same material on a large scale (NNI 2005). Compounds also must be created on the principle of atomic scale control of the assembly and structure. The National Nanotechnology Initiative (NNI) similarly breaks down the definition into three requirements, of which any "nanotechnology" must involve all three: "1.) Research and technology development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1 - 100 nanometers, 2.) Creating and using structures, devices, and systems that have novel properties and functions because of their small and/or intermediate sizes, and 3.) Ability to be controlled or manipulated on the atomic scale." (NNI 2005).

A significant number of technologies today already fit the definition for "nano" as defined by the NNI. Nanotechnology has contributed to the development of materials used in electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, catalytic, and materials applications. In the manufacturing community, initially, the most profitable avenues for nanoscale particles and materials have been in the areas of sunscreen, magnetic recording tape, automotive catalyst supports, biolabeling, chemical-mechanical polishing, electroconductive coatings, and optical fibers (NNI 2005).

With the many hi-tech functions of nanotechnology, environmental remediation would seemingly prove an unlikely place to find many applications of nanotechnology. However, the emergence of nanotechnology presents a number of potential environmental benefits, both directly and indirectly. In a recent review, Masciangioli et al. divided the potential impact areas for nanotechnology into three categories: treatment and remediation, sensing and detection, and pollution prevention. Of the three environmental categories, treatment and remediation have felt the earliest impacts of the nanotechnology revolution. A variety of nanomaterials are in various stages of research and development, each possessing unique functionalities for treatment. Some nanoparticles destroy contaminants, for instance, while others sequester them (Masciangioli 2003). The specific nanotechnologies discussed hereafter solely focus on site remediation and some waste water treatment. In addition to remedial applications for soil, groundwater, and wastewater, a number of technologies for air remediation are also in development. Carbon nanotubes, for example, have been recognized for their ability to adsorb dioxin much more strongly than traditional activated carbon (Long 2001).

Within the category of sensing and detection, nanotechnology anticipates the capability to provide more sensitive and cost effective technologies for detecting pollution in the ground, water, and air. Smaller particle size enables the development of smaller sensors, which can be deployed more easily into remote locations (Masciangioli 2003). The high surface area to mass ratio, characteristic of nanoparticles, amplifies changes in electrical conductivity and mechanical resonance that occur when pollutants bind to the particle surface. This feature translates into sensing systems able to detect very small amounts of pollutants (Rose-Pehrsson 2004). Array sensors, capable of detecting various pollutants discriminately, also benefit from nanotechnology. Their ability to manipulate the surface chemistry of particles allows a new level of selectivity control (Rose-Pehrsson 2004). Single-wall nanotubes (SWNTs) are exemplary of the potential developments in this field. The unique chemical and electronic features of SWNTs enable them to act as sensors of electrical resistance changes in the presence of a targeted pollutant, such as nitrogen dioxide. Zinc oxide also is being researched as a potential dual-function sensor and remediator (Kamat 2002).

The ability of nanotechnology to abate pollution production is just beginning to be explored and could potentially catalyze the most revolutionary changes in the environmental field (Masciangioli 2003, Karn 2004). From the birth of manufacturing onward, production has been achieved through a top-down approach. In many ways, top-down production parallels stone sculpture, where an artist begins with a huge block of stone, chiseling, grinding, and sanding to reach a finished product. Not only does this approach produce waste, but it requires large energy expenditures (Karn 2004). The "1.7 kg microchip" has recently been adopted as the new spokesmodel for the scientific community when discussing the problems of top-down manufacturing (Masciangioili 2003). A study published in 2002 by Williams et al. determined that the production of a single 2-gram, 32-megabyte chip requires the use of 32 kg of water and 1.7 kg of fossil fuels and chemicals (Williams 2002 and Masciangioli 2003). Nanotechnology claims the ability to revolutionize manufacturing through a bottom-up assembly approach, where products self-assemble from molecular building blocks similar to the biological assembly of proteins (Karn 2004). The idea of molecular manufacturing, however, largely remains theoretical and most likely will for the coming years. Many nanotechnologies on the market today do exhibit a level of self-assembly, just not on the same scale required in manufacturing.

With any new technology, however, come concerns over its misuse and possible negative effects. The great excitement for nanotechnology and its potential applications already has been met by apprehensions over environmental and health effects induced by the unintentional release of nanoparticles into the environment. Because nanotechnology produces substances with such unique properties and functionalities, worker exposure and accidental release pose serious potential threats. Similarly, because of the broadness of the field, regulation of nanoparticles will be difficult. At the moment it is unclear whether current regulations are adequate for these emerging technologies.

4. COMMERCIAL USES OF NANOTECHNOLOGY FOR SITE REMEDIATION: NANO IRON AND ITS DERIVATIVES

4.1. Background

Over the years, the field of remediation has grown and evolved, continually developing and adopting new technologies in attempts to improve the remediation process. One of the most established systems is that termed “pump-and-treat” (USEPA 1998b). Pump-and-treat systems operate on the basis of removing contaminated groundwater from the ground, downstream of the contamination site, and then treating it before returning it to the ground. With this technology “it takes a long time to achieve cleanup goals, it has been demonstrated to spread contamination in some cases, and it is expensive to operate and maintain,” requiring continual energy input (USEPA 2004, 1998b). “A 2001 EPA study found that the average annual operations and management (O&M) costs of pump-and-treat systems at 79 fund-financed sites are approximately $570,000, and the median is $350,000... The periods of operation of these systems as well as the costs vary widely from site to site. The average pump-and-treat system in the EPA study operated for 18 years, for an average cost of $10 million. Pump-and-treat systems at some sites with dense non-aqueous phase liquids (DNAPLs) may need to operate for considerably longer periods.” (USEPA 2004). Despite the number of limitations exhibited by these systems, pump-and-treat remedies still account for 67% of the ground water remedies proposed or in progress at NPL sites (USEPA 2004, 1998b).

In the early 1990s, the reducing capabilities of metallic substances, such as zero-valent iron (ZVI), began to be examined for their ability to treat a wide range of contaminants in hazardous waste/water (Zhang 2003). The most common deployment of ZVI has been in the form of permeable reactive barriers (PRBs) designed to intercept plumes in the subsurface and subsequently remediate them (USEPA 1998b). PRBs, first installed at the field-scale in 1994, offer a substitute for the more established pump-and-treat systems (USEPA 1998b). [The first full-scale commercial PRB was approved for use in the State of California by the San Francisco Regional Water Quality Control Board (RWQCB) in 1994. USEPA1998b]. This passive treatment system has been used to treat pollutants, including chlorinated hydrocarbons, nitro aromatics, polychlorinated biphenyls (PCBS), pesticides and even chromate. The reducing capabilities of ZVI can dechlorinate chemicals such as trichloroethene (TCE) and polychlorinated biphenyls (PCBs) (Lien 2001). ZVI can reduce hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)), as well, precipitating it out of solution, thus immobilizing it as Cr (III) hydroxides or chromium-iron hydroxide solid solutions (USEPA 1997, 1998b).

While PRBs can potentially replace pump-and-treat systems as better remedial solutions, the technology itself is not without drawbacks. As compared to pump-and-treat systems, installation costs for PRBs are relatively high and the effective "time to replacement" is often uncertain (USEPA 2004). The installation capabilities only allow PRBs to be inserted up to about 50 ft, which restricts the technology to shallow plumes only. To prevent contaminants from circumventing the PRB, plumes must be carefully characterized and delineated (USEPA 1997). Problems occur from a decrease in iron reactivity caused by the precipitation of metal hydroxides and metal carbonates onto the surface of the iron (Wang 1997). The low reactivity of ZVI toward lightly chlorinated compounds allows the formation and perseverance of hazardous byproducts. Compounds such as cis-1,2-dichloroethane (cDCE) and vinyl chloride often can be observed as products from the reduction of tetrachloroethene (PCE) and trichloroethane (TCE) (Wang 1997).

Just as PRBs were designed to provide a better alternative to pump-and-treat, new technologies are now available to compete with PRBs. As detailed below, nanoscale iron particles and their derivatives offer a potentially more effective and economical alternative to many remedial technologies (Zhang 2003). The small particle size of the nano iron (1-100 nm) facilitates a high level of remedial versatility. This allows a much greater diversity in applications as compared to the traditional ZVI employed in PRBs. The elevated surface area to mass ratio, a common characteristic of nanoparticles, also enhances the reactivity of the iron, making it a promising emerging technology.

4.2. Technology Overview

Nanoscale Zero Valent Iron (nZVI) and Reactive Nanoscale Iron Product (RNIP) comprise the most basic form of the nano iron technology (Zhang 2003, Okinaka 2004). Particles of nZVI, typically about 100 to 200 nm in diameter, consist solely of zero valent iron (Fe^0). The most common route to nZVI synthesis employs sodium borohydride as the key reductant (Zhang 2003). In 1997, Wang et al. first produced the nanoscale iron particles in the laboratory using the method of sodium borohydride reduction. By mixing sodium borohydride ($NaBH_4$) with $FeCl_3·6H_2O$, Fe^{3+} is reduced according to the reaction scheme below:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \qquad \text{(Wang 1997)}$$

In laboratory scale production of nZVI, Wang et al. achieved a particle size distribution of less than 100 nm for 90% of the particles produced. The BET surface area for the particles was determined to be 33.5 m^2/g (Wang 1997). Following the reaction, the reduced particles of iron (Fe^0) created could be directly used for contaminant destruction. The stoichiometry of the reduction of trichloroethene (TCE) to ethane, a typical decontamination reaction, would proceed as follow:

$$C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^- \qquad \text{(Elliott 2001)}$$

RNIP particles vary slightly from nZVI particles, in that RNIP particles consist of approximately a 50/50 wt% mixture of iron and magnetite (Fe_3O_4). The core of the particles consists of the elemental iron (α-Fe), while the Fe_3O_4 surrounds the Fe, forming an outer shell (Okinaka 2004). In a study by Okinaka et al., particle sizes for RNIP were averaged at about 70 nm and mean

BET surface areas were determined to be 28.8 m^2/g (Okinaka 2004). The synthesis method for RNIP particles has been patented and detailed, with ferrous sulfate listed as the starting material. The use of ferrous sulfate as a raw material contributes to a small (~5,000 mg/kg) sulfur content present in the RNIP particles.

A recent study by Liu et al. compared the efficiency and degradation capabilities of nZVI synthesized using sodium borohydride reduction and the RNIP particles produced from ferrous sulfate. The study found that nZVI demonstrated a higher initial surface area and Fe^0 content. It was concluded, though, that the presence of boron and the shell thickness were the most likely explanations for observed differences in reactivity. The nZVI particles demonstrated rapid dechlorination of TCE and no deactivation; however rapid H_2 evolution was observed. This behavior could cause the particles to "burn out" before they could reach the treatment zone. Conversely, RNIP particles showed much slower degradation rates of TCE and a lower accessibility of Fe^0 due to the Fe_3O_4 shell. The shell, however, also protected the particles from reacting with water, thus preventing the "burn out" observed with the nZVI particles (Liu 2005).

Other methods of producing nanosized iron particles also have been developed. Ball milling represents another technique. In this process, micron-size iron powder is reduced to the nanoscale through an attrition or abrasion process using a ball mill (Liles 2004). A vacuum/gas condensation process also has been used to produce nanosized iron and other metals (Canano Technologies 2005).

The production of Bimetallic Nonsocial Iron Particles (BNIP) represents an enhancement of the nZVI technology described above. Grittini et al. reported in 1995 that a bimetallic system of palladium and iron could rapidly degrade PCBs (Grittini 1995). While Grittini used microscale iron particles in his experiments, the discovery of palladium's ability to enhance reductive capabilities proved significant. In 1997, Wang et al. created the first nZVI particles. In the same experiment, they also coated the nZVI particles with palladium. Later Zhang et al. determined that the nanoscale palladium-coated ZVI degraded chlorinated compounds at rates 10 to 100 times faster than microscale particles.

To synthesize the particles, after obtaining Fe^0 as described above, Wang et al. saturated the iron with an ethanol solution of $[Pd(C_2H_3)_2]_3$ leading to the deposition of palladium on the iron surface through the reaction:

$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+} \qquad \text{(Wang 1997)}$$

Initial experiments performed by Wang et al. determined that while nZVI particles dechlorinated TCE and PCB compounds at a higher rate than iron powders, palladium-coated BNIP proved the most reactive and thus the destructive to the chlorinated organic contaminants (COCs) (Wang 1997). Scientists have experimented using other noble metal catalysts, such as plutonium, gold, and nickel; however palladium/iron BNIPs are the only particles commercially available (See section on Bimetallic Particles).

As with the addition of metal catalysts to nZVI particles, the formation of emulsified zero valent iron (EZVI) also represents an enhancement to the existing nZVI technology. Emulsion droplets can be created using a food grade surfactant, biodegradable vegetable oil, water, and nZVI, where a surfactant-stabilized oil-liquid membrane forms around the iron particles in water (Quinn 2005). Figure 2 shows a diagram of an EZVI droplet. Specifically, in a study performed by Quinn et al., Sunlight-brand corn oil, sorbitan triolate (a nonionic surfactant) and RNIP particles from Toda were used to make EZVI. Both nano and microscale iron can be used; however the studies and information described in recent studies involve only nZVI. Emulsions typically have a diameter of about 40 um and a specific gravity of approximately 1.1 (Quinn 2005, O'Hara 2004).

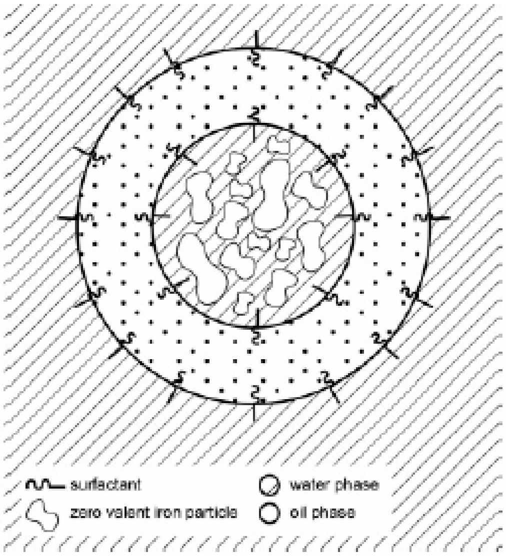

Figure 2. **Diagram of EZVI droplet (Quinn 2005)**

4.3. Remedial Applications

As mentioned previously, the small particle size and high surface area to mass ratio make iron nanoparticles highly reactive and extremely versatile. The high surface area and surface reactivity compared with granular forms enable the nanoparticles to remediate more material at a higher rate and with a lower generation of hazardous byproducts (Zhang 2003). The ability of the nanoparticles to act as strong reducers also enables the remediation of an extremely wide range of contaminants. Table 1 lists many of the pollutants potentially remediated by nano iron. Based on the documented case studies detailed below, the majority of field applications have utilized nano iron to remediate chlorinated organics compounds, such as TCE. A growing number of sites, though, contain metal ions such as chromium (Zhang 2003).

Carbon tetrachloride	Chrysoidine	*cis*-Dichloroethene
Chloroform	Tropaeolin	*trans*-Dichloroethene
Dichloromethane	Acid Orange	1,1-Dichloroethene
Chloromethane	Acid Red	Vinyl Chloride
Hexachlorobenzene	Mercury	PCBs
Pentachlorobenzene	Nickel	Dioxins
Tetrachlorobenzenes	Silver	Pentachlorophenol
Trichlorobenzenes	Cadmium	NDMA
Dichlorobenzenes	Bromoform	TNT
Chlorobenzene	Dibromochloromethane	Dichromate
DDT	Dichlorobromomethane	Arsenic
Lindane	Tetrachloroethene	Perchlorate
Orange II	Trichloroethene	Nitrate

Table 1. Contaminants remediated by nanoscale iron (Zhang 2003)

In conjunction with nano iron's diverse group of target contaminants, the field scale deployment of the particles can be achieved in a variety of ways. Nanoparticles can be mixed with water to form a slurry that can be injected using pressure or gravity into a contaminated plume (Zhang 2003). Once injected, the particles remain in suspension, forming a treatment zone. Particles of iron also can be used in ex situ slurry reactors to treat soil, sediment, and solid waste. In cases of water and/or wastewater treatment, anchoring nanoparticles onto a solid matrix, such as activated carbon, can prove extremely effective (Zhang 2003).

The injection of nano iron into the ground represents the most common deployment of this technology thus far. Overall the process provides a number of remedial benefits. In comparison with PRBs, nanoparticle injection allows remediation at greater depths and in areas unreachable by PRBs (i.e. land covered by a building). Most importantly, this technique facilitates source zone remediation, a clear benefit for site cleanup. The hydrophilic surface of the nano iron particles only permits the remediation of aqueous phases, which excludes DNAPL remediation. However nano iron injections into the source still provide benefits unachievable by downgradient technologies. Remediation at the point of dissolution eliminates the migration distance required for PRBs and pump-and-treat systems. It also has been speculated that the presence of nZVI in the source zone amplifies the concentration gradient between the aqueous phase and DNAPL, which in turn increases the mass transfer of contaminants from DNAPL to the dissolved phase.

To address the significant number of sites across the country contaminated with chlorinated VOCs in the form of DNAPL, researchers developed EZVI. As mentioned previously, NIP injections only work for aqueous phase source zone treatment and while they can enhance DNAPL dissolution, NIP injections cannot directly treat DNAPL. EZVI offers a solution to this problem in the form of an external oil membrane (Quinn 2005, O'Hara 2004). The EZVI, exhibiting a specific gravity of 1.1, can be considered in some ways a DNAPL itself. Similarities between the exterior membrane and DNAPL allow the EZVI to be miscible with the DNAPL (O'Hara 2004). As a result of this miscibility, when EZVI droplets come in contact with pure phase contaminants, the DNAPL dissolves through the exterior oil membrane. Once the DNAPL passes through the oil membrane, the contaminants become trapped. The confinement of the DNAPL to the emulsion facilitates the degradation by the NIPs. This capability thus can potentially allow source zone remediation of chlorinated DNAPLs (Quinn 2005).

4.4. Vendors

In the past five years, a variety of vendors for nZVI and RNIP have appeared. Polyflon Company manufactures a nZVI product called Polymetallix, which is then distributed by Nanitech LLC. PARS Environmental, Inc., manufactures and distributes NanoFe. Wei-xiang Zhang of Lehigh University supplies nZVI particles to many field sites although he does not manufacture his product on a commercial scale. OnMaterials represents the most recent market edition with their product Z-loy. Toda Kogyo Corporation manufactures RNIP, and is the sole producers of this patented technology.
Polymetallix, NanoFe, and Zhang's particles are all prepared in the same manner, using sodium borohydride to reduce Fe3+ to nZVI (Zhang 2003, Bilvey Conversation 2005, PARS 2005). While Zhang achieved particle sizes of less than 100 nm in the lab, for large-scale projects, all three distributors advertise particle sizes of between 100 and 200 nm. The approximate surface area of the nZVI particles is advertised as 37.0-58.0 m^2/g by Polymetallix manufacturers. However, Zhang et al. determined the average surface area of their particles to be approximately 33 m^2/g (Zhang 2003).

OnMaterials employs the second technology outlined above for the manufacture of their product Z-loy. The company website describes the mean particle size as 250 nm and the median particle size as 200 nm, with particle surface areas ranging from 1-30 m2/g (OnMaterials 2005). As described above, Toda's RNIP particles represent a mixture of Fe and Fe304, with an average size of 70 nm and an average surface area of 28.8 m^2/g (Okinaka 2004).

Prices for nZVI and RNIP vary between vendors. Nanitech LLC has quoted the cost of Polymetallix at $77 per pound for orders of 300 lbs, and $72 per pound for orders of 400 lbs including delivery. PARS prices orders exceeding 1,000 pounds at $45 per pound for polymer-supported particles and $31 per pound for unsupported material. OnMaterials quotes pilot scale quantities of the Zloy product at $20 per pound with a shipping charge of $3 per pound. Toda estimates the cost of RNIP from $26 to $34 per pound based on the order amount, where the range is 10,000 lbs to 100 lbs respectively (Gavaskar 2005).

Many of the same vendors that manufacture pure nZVI also offer palladium-coated BNIP as well. PARS Environmental, Inc., manufactures NanoFe Plus. OnMaterials advertises the ability to customize orders of Zloy through choosing the ratio of iron to palladium. Wei-xiang Zang also produces BNIP in his lab in addition to nZVI, with the majority of field tests and treatments using BNIP.

In terms of cost, coating with a catalyst often adds significant expense to an order. PARS quotes polymer supported nZVI at $45 a pound, while an order of palladium-coated (and supported) BNIP costs $66 per pound. The near 50% cost increase accompanying palladium coating must be thus factored into the cost-benefit (Gavaskar 2005).

Currently no vendors exist for EZVI. Case studies and experiments involving the technology have used EZVI prepared on site. As previously noted, nZVI and RNIP particles act as bases when forming EZVI.

4.5. Case Studies

The application of nano iron and its derivatives for site remediation has quickly gained popularity as an option in the field. A number of projects involving some form of nano-iron have been reported, and it appears that these sites represent a variety of the regulatory categories. The following case studies attempt to provide an overview of the field applications. Table 2 provides a more comprehensive list of locations where field studies have been completed, are currently underway, or are in planning.

Site Name/Description	Classification	Region	Contaminant(s)	Site Characterization	Status	Remediation Scheme	References
Naval Air Engineering Station, Lakehurst, NJ	NPL (DOD)	2	PCE, TCE, TCA, DCE, VC	Groundwater in shallow aquifer	Field-scale test complete	BNIP injection	Gavaskar 2005
Naval Air Station, Jacksonville, FL	NPL (DOD)	4	TCE, DCE, VC		Field-scale test complete	BNIP injection into source zone	Gavaskar 2005
Northeastern USA (ARCADIS)	Private		PCE-Source Zone and DNAPL	Fractured rock aquifer, low permeability siltstone and shale, water table to 100ft bgs	Small field test complete; full-scale test in planning	nZVI in conjunction with molasses	Horst 2004
Defense contractor site, Documented Field Studies, California	RCRA	9	Perchlorate, NDMA, TCE, DCE		Pilot test completed; full-scale test in process	nZVI injection, Wei-xian Zhang's particles	Durant 2004
GlaxoSmithKline Pharmaceutical Facility	Private	4	TCE	Fractured bedrock aquifer	Field-scale test	nZVI injection, Wei-xian Zhang's particles	Glazier 2003
Edison New Jersey Industrial Site	Private	2	TCA, TCE, DCA, DCE, CA, VC	Fractured bedrock	Field-scale test completed; larger-scale treatment in progress	Injection of OnMaterial's Z-loy, an emulsified vegetable oil amendment	Chu 2005
Trane Co. Site	Private	2	TCE	Downgradient plume, surficial aquifer	Field test completed	BNIP injection	Elliot 2001
NASA Launch Complex 34	DOD	4	TCE	Surficial aquifer containing sand, DNAPL present	Field test completed	EZVI injection	Quinn 2005
Public Service Electric and Gas Company (PSE&G), Klockner Road Site, New Jersey	Private	2	TCE, TCA, DCE, DCA	Groundwater contamination in "perched water zone and upper table aquifer"	Field test completed	BNIP injection with PARS's NanoFe into source zone	Varadhi 2005

Table 2. Field studies where nZVI, RNIP, EZVI, or BNIP injections have occurred.

	Name/Description	Classification	Region	Contaminant(s)	Site Characterization	Status	Remediation Scheme	References
Site Sites to Implement Field Scale Studies	Picattiny Arsenal, Dover, New Jersey	NPL Site	2	TCE, PCE, DCE, and other VOCs	No Information	Pilot-scale test completed; possible plans to implement field scale	nZVI tests with PARS	Roach Conversation 2005
	Vanderburg Air Force Base	DOD (ESTCP)	9	COCs-TCE, DCE	No Information	Bench-scale test completed; field-scale test on hold	BNIPs created from ball milling process	Liles 2004
	Nease Chemical, Ohio	NPL Site	5	Mirex, VOC	Fractured Bedrock	Public comment phase decision	nZVI for treating deep ground water in conjunction with pump and treat for shallow groundwater	Cutting Edge Techniques 2005
	BP, Alaska	NPL Site	10	TCA	No Information	Bench-scale test completed; field-scale test planned next June	nZVI injection planned with Wei-xian Zhang's particles	Hideen Conversation 2005
	Sierra Army Depot, Nevada	BRAC Facility	9		No Information	Field-scale tests in planning	nZVI injection with Polymetallix	Bilvey Conversation 2005
	Phoenix-Goodyear Airport (PGA) Area, Unidynamics	NPL Site	9	TCE, PCE, DCE, Carbon Tetrachloride, Chromium	No Information	Field-scale tests in planning	nZVI injection with Polymetallix	Bilvey Conversation 2005

Table 3. Sites where nZVI, RNIP, EZVI, or BNIP injections have been proposed..

4.5.1. Edison New Jersey Industrial Site

The Edison New Jersey location is the site of a retired adhesives manufacturing plant, which operated from 1967 to 2002. Until 1990, the manufacturing process employed trichloroethane (TCA). No major spills or releases were recorded during the operational period. However, contamination has been attributed to small spills incurred during routine transfer of TCA from tanker rail cars to aboveground storage tanks. A number of chlorinated volatile organic contaminants have been detected in the groundwater at the site in high concentrations, primarily TCA and TCE. Degradation products including DCA, DCE, CA, and vinyl chloride also have been identified (Chu 2005).

The contamination area fell under the classification of fractured bedrock, specifically Brunswick Shale. A thin layer (4-6 ft) of soil comprised mainly of silt and clay covered the bedrock. Both a primary source area and secondary release area were identified. Concentrations as high as 37,000 mg/L of TCA indicated the possible presence of DNAPL in the primary source area. A pump and treat system was installed in July 2001 and was operational up to the point of the study (Chu 2005).

The Secondary Source Area served as the location for the pilot study. The contamination in the area was considered relatively localized, and the area was located away from the buildings and utilities on site. Z-loy, produced by OnMaterials, and emulsified vegetable oil were used concurrently to provide an abiotic/biotic remedy. Concentrated iron product and vegetable oil were mixed together on site; a total of 300 pounds of nZVI and 1,500 gallons of emulsified vegetable oil comprised the mixture. Injection took place in two locations. One injection well was converted from a groundwater extraction well, and the other injection point was converted from a shallow bedrock monitoring well. The solution was injected into both wells in approximately equal amounts and at pressures between 25 and 50 pounds psi (Chu 2005).

Following the injections, both injection well and two downgradient monitoring wells were monitored for 13 months. Results indicated that the nZVI produced rapid abiotic degradation in the injection wells while the vegetable oil encouraged a more lasting biological process downstream in the monitoring wells. This was inferred from data collected over the monitoring period. Injection Well 1 experienced a sharp drop in TCA concentration from 10,000 ug/L to a level below the minimum detection limit. DCA concentrations experienced an initial increase due to the degradation of TCA, however levels quickly began to decline. CA, the product of DCA degradation, increased for a longer period of time before finally beginning to decrease. DCE concentrations also decreased with no accumulation of VC or ethene, indicating complete degradation to ethane. Overall ethane concentrations for Injection Well 1 steadily increased. Also of note, alkanes/alkenes and molecular hydrogen were observed in the injection well up to month 7, indicating ZVI activity throughout that time period (Chu 2005).

4.5.2. GlaxoSmithKline, Research Triangle Park, NC

The site detailed in this particular case study was located in Research Triangle Park, NC, and owned by GlaxoSmithKline (GSK). While GSK was supervising the cleanup of the RCRA-regulated site, contamination could be attributed to industrial activities carried out by the former property owners. A waste disposal area was previously located on site but was cleared out prior to the study by waste excavation. Despite the waste removal, residual contaminants remained. While multiple chlorinated volatile organic (CVOCs) were detected at the site, TCE was the primary contaminant of concern. The groundwater concentration of CVOCs reached 14,000 ug/L in the injection well prior to the study. Concentrations in the immediate vicinity of the former waste disposal area most likely exceeded this value (Zhang 2003).

The site was located in the Durham subbasin, an area composed of Triassic age sedimentary bedrock. Groundwater was located approximately 30 feet bgs within the interbedded siltstone and sandstone. The injection site for the case study was located about 125 feet downgradient from the former waste disposal site mentioned previously. Two downgradient monitoring wells were installed approximately 22 and 43 feet from the injection site (Zhang 2003, Glazier 2003).

BNIPs and chemical oxidation were both considered for remediation; however BNIPs were ultimately chosen for the job. Part of the reasoning behind that decision was that the anaerobic bacteria, *Dehalococcoides ethenogenes,* had been detected at the site in early characterization. As mentioned earlier, the lowering of the groundwater ORP has been shown to stimulate the degradation of CVOC by bacteria (Glazier 2003).

The BNIPs used in the study consisted of iron with a palladium coating and were prepared by researchers at Lehigh University. A slurry was mixed on site with a BNIP concentration of 1.9 g/L. The total slurry volume was 6,056 L or 1,600 gallons, which translated to a total of 11.2 kg of iron to be injected. The injection was carried out over a span of three days at an injection rate of 0.6 gallons per minute (gpm) (Zhang 2003).

Following the injection period, the treatment accomplished over a 90% reduction in the total concentration of CVOCs in the injection well. This change occurred within several days of the treatment. A similar reduction in contamination occurred downgradient in the monitoring wells; however the decontamination process took longer (about 40 days to level out). Individual PCE, TCE, and DCE concentrations reached groundwater quality standards within six weeks of remediation and no significant amounts of hazardous daughter products were detected (Zhang 2003, Glazier 2003).

4.5.3. Naval Air Station, Jacksonville, Florida

The Naval Air Station (NAS) located in Jacksonville, Florida, has been operational since 1940. The site of interest for this case study, H1K, was positioned near the center of the NAS. The source of contamination for the site was two underground storage tanks (USTs), Tank A and Tank B. While they were excavated and capped in 1994 along with the associated pipelines, they were expected to be the source of contamination in the area. Prior to removal, two USTs stored waste solvents in addition to other substances received from a wash rack, manhole, and various other operations. Following removal, soil samples taken in 1995 confirmed that the removal of tanks and pipelines accomplished clean closure for unsaturated soil. The main groundwater contaminants detected, TCE and TCA, had accumulated around the former location of Tank A (Gavaskar 2005).

From 2000 to 2001 a chemical oxidation method was used to treat the source area. Rebound of the dissolved phase concentration occurred after each treatment. In 2002, the recharacterization of the site took place to reassess the level of contamination. Maximum soil concentrations of 25,300 ug/kg, 4,369 ug/kg, and 60,100 ug/kg were detected for TCA, PCE, and TCE, respectively. Groundwater maximums reached 173 ug/L, 5,520 ug/L, and 1,350 ug/L for PCE, TCE, and DCE respectively. The concentrations indicated the potential presence of DNAPL, which would lead to the rebound experienced (Gavaskar 2005).

Groundwater was present in a shallow aquifer located approximately 7 to 24 feet bgs. Characterization of the unsaturated zone at the site indicated a fairly uniform composition of medium grained sand and sandy fill. Directly below the water table, between 6 and 12 feet bgs, a thin layer of clayey and/or silty sand rested on a fine to medium silty sand layer positioned 10 to 17 feet bgs. Between 20 to 24 feet bgs, the composition shifts to a larger amount of silt and clay, and then at 24 feet becomes mostly clay to a depth of 54 bgs (Gavaskar 2005).

PARS Environmental's product, NanoFe Plus, was chosen for use. The BNIPs consisted of 99.9% iron and 0.1% palladium by weight. The BNIPs were distributed throughout the site using both direct injection into known "hot spots" and closed loop recirculation. Direct-push technology (DPT) was used for the injections, where a suspension of BNIPs at 10 g/L was pumped directly into the DPT boor holes and allowed to discharge via gravity flow. Four injection and three extraction wells were used for the recirculation system. A BNIP concentration of 2 g/L was implemented initially in the recirculation process and then increased to 4.5 g/L (Gavaskar 2005).

Results of the remedial process varied widely from well to well. The recirculation process appeared to enhance desorption of contaminants into the dissolved phase. Many wells achieved over a 65% decrease in concentrations of parent VOCs within a short period of five weeks. All wells showed the present of "daughter" products, such as DCE, where in some cases the concentration of daughter products rose rapidly after injection and then decreased over time. An increase in ethane and ethane concentrations accompanied decreases in daughter products, indicating complete conversion (Gavaskar 2005).

Some source zone wells however, experienced a rise in both TCE and DCE concentrations after injection. This likely stems from poor distribution of the BNIP slurry and possible displacement of dissolved TCE. Of additional note, while the presence of ethane/ethane and C4-hydrocarbons, such as acetylene, indicate some abiotic degradation, the predominance of anaerobic reductive products such as 1,2-DCE suggests that much of the "parent" degradation occurred through microbial action. However, a well 20 feet downgradient of the source zone reported almost a 99% reduction in contamination, signifying that a significant amount of BNIPs potentially migrated out of the treatment zone (Gavaskar 2005).

Overall, the treatment provided some benefit to the site. In the end though, it was unclear how much of the decontamination that occurred could be attributed to abiotic degradation. nZVI and BNIPs have been identified as microbial enhancers and it is likely that a significant amount of the VOC destruction occurred through microbial pathways. It was speculated that some of the

BNIPs might have become passivated before injection and also that the concentration of BNIPs in the slurry was not high enough (Gavaskar 2005).

4.5.4. Launch Complex 34 at Cape Canaveral Air Force Station, Florida

From 1960 to 1968, Launch Complex 34 (LC34) served as a launch site for Saturn Rockets. Ground contamination most likely occurred during that period and can be attributed to the rocket cleaning methods employed. Documented evidence indicates that rockets were cleaned with solvents including TCE directly on the launch pad. At the time of cleaning, excess solvents were allowed to evaporate, penetrate the subsurface directly, or migrate to surface drainage pits as runoff material. Following the cessation of the rocket launching program at LC34 in 1968, the site was abandoned and became overrun with plant life. The contamination that occurred during the operational period resulted in the presence of DNAPL at the site prior to the study. TCE represented the main component of DNAPL contamination. However, cis-1,2,-dichloroethene (cDCE) and vinyl chloride, both products of the natural biodegradation process of TCE, were also detected in the groundwater. (Quinn 2005).

The study itself was conducted on a small plot of land near the Engineering Support Building, a site of known DNAPL presence. The site contained a surficial aquifer and a semi-confined aquifer, where the groundwater TCE concentrations approached solubility (of TCE). The surficial aquifer, covered by a clay unit, started at the water table, which began at a range of 3-7 feet bgs. Three layers comprised the surficial aquifer, an upper sand unit, a middle fine-grained unit, and a lower sand unit. The upper sand unit extended from the ground surface to between 18 and 25 feet bgs and contained a mixture of medium to coarse-grained sand and crushed shells. At the bottom of the upper sand unit, the middle fine-grained unit began, extending to about 30 feet bgs and comprised of "gray, fine-grained silty/clayey sand," (Quinn 2005). The lower sand unit extended from the middle fine-grained unit to about 45 feet bgs. The injection of EZVI was planned for the upper sand unit (Quinn 2005).

Both soil and ground water samples were collected before the start of the injection to assess contamination levels. Six soil cores were obtained and samples from 21 monitoring wells were taken to provide pre-injection data. In an effort to maintain hydraulic control of the groundwater within the site area, a groundwater control system was installed. The system also served to assess the flux of DNAPL to groundwater during treatment. The EZVI , consisting of 44.3% water, 37.2% oil, 1.5% surfactant, and 17.0% nZVI by weight, was prepared on site. A total of about 670 gallons were injected across the entire pilot test area, which contained eight separate injection wells. The injection volumes across the eight wells were adjusted based on contamination concentration (Quinn 2005).

Based on the soil samples from the upper sand unit, significant reductions of TCE concentrations upwards of 80% were achieved at most of the soil boring locations. Problems in remediation were encountered at two wells, where it appeared that following injections, the EZVI migrated upwards, thus not reaching the contamination zone. It was suggested that the injection technique used, pressure pulse technology, contributed to the upward migration. Linear interpolation and kriging, a "statistical interpolation method for analyzing spatially variable data," also were used to estimate the overall success of DNAPL removal. Linear analysis estimated an initial total mass of 17.8 g of TCE with 3.8 g of DNAPL. This method then approximated an 85% reduction in TCE and TCE DNAPL mass. Kriging produced a value of 28 g of TCE for the initial mass and an average reduction of 58%. It was also observed that the total mass of TCE present below the upper sand unit, in the middle fine-grain unit, also decreased. An increase in "daughter" products however, points to possible biotic degradation in the lower soil unit (Quinn 2005).

Groundwater samples were also measured in the experiment and showed a marked reduction in contamination. A variance of contaminant destruction between 57 and 100% was observed in TCE concentrations between the various observation wells. Samples also displayed considerable increases in cDCE, VC, and ethane. The presence of cDCE and VC in the groundwater indicated the occurrence of biotic degradation. Combining the observation of daughter products in the soil and groundwater implied that biodegradation was responsible for a significant portion of TCE destruction (Quinn 2005).

Overall the case study reported successful results for the remediation of TCE in both soil and groundwater. The study, however, reported inconclusive evidence on the actual mechanism of the TCE degradation and was unable to account for the amount of TCE degraded by the EZVI versus biotic degradation (Quinn 2005).

4.6. Toxicity and Safety Concerns

Generally, concerns regarding the toxicity of this technology have been mild. The confidence in safety is largely due to the fact that iron oxides formed during remediation are already present in the ground as rust, coupled with the fact that nano iron particles do not exhibit radically new properties. No studies reporting the safety and toxicity of iron nanoparticles or bimetallic particles have been published. However a study is due out within the next few months. The preliminary studies in daphnids found that nano-iron exhibited a similar toxicity level to that of the bulk form (Oberdorster conversation 2005). These findings are significant in that they support the previous theories of toxicity. In a recent review, Oberdorster et al. advised that studies not just concern toxicity as related to wildlife and human, but also focus on benthic and soil flora and fauna, "the basis of many food chains, which could be dramatically affected by nanoparticle injections." (Oberdorster 2005).

5. BIMETALLIC PARTICLES AND OTHER METALS

5.1. Technology Overview

While scientists and contractors have developed and tested nZVI and palladium-coated nZVI particles on a large scale, many other metals and bimetallic combinations that can serve as substitutions exist. Metals such as zinc and tin possess similar reduction capabilities of iron (Boronina 1995). Like iron, these metals are converted to metal oxides in the decontamination process. Other metals have been combined with iron as well to produce similar results. Both iron-nickel and iron-copper bimetallic particles have been demonstrated to degrade trichloroethane and trichloroethene (Lien 2001, Schrick 2002). Another example is iron-platinum particles, which possess similar capabilities in degrading chlorinated benzenes (Lien 2001).

In producing bimetallic nanoparticles, inert base metals, such gold and aluminum, also have been used. Unlike iron, aluminum and gold particles are non-reactive or inert. Subsequently, they can only serve as base metals used in conjunction with a catalyst coating. Despite the lack of reactivity, base metals have been shown to increase the catalytic rates of the coating metal (Nutt 2005 and PARS 2005). In terms of metal catalysts able to be applied as coatings, many substitutions exist for palladium. Platinum, silver, cobalt, copper, and nickel represent alternatives tested in the lab (Nutt 2005, Zhang 2003). While these catalysts possess the ability to work alone, coupling with other particles can enhance degradation and catalytic rates. It then follows that the various base metals can be fused with different noble metals to form a multitude of combinations. It should be distinguished that when metal catalysts are coupled with reactive metals such as iron, they serve to enhance the reactive properties of the iron. In contrast, when metal catalysts are coupled with non reactive metals such as gold, they act as the catalysts themselves.

According to the latest information, palladium-coated gold nanoparticles have emerged as the one of the most promising alternatives to nZVI and palladium-coated nZVI. As mentioned previously, palladium-coated gold nanoparticles differ from palladium-coated nZVI in that, palladium-gold particles act as catalysts instead of reactants. The gold particles, which serve as the base metal, do not actually react with organic compounds, nor do they act as catalysts. Gold does, however, augment the catalytic ability of palladium. The enhancing ability of gold, while not yet clearly understood, has been proven by the fact that Pd-on-Au particles generate increased rate constants over 100 times greater than those for palladium alone (Nutt 2005).

In a recent study, Nutt et al. created Pd-on-Au nanoparticles and tested their ability to hydrodechlorinate trichloroethene in water (Nutt 2005). Because the Pd-Au particles catalyze the “hydro”dechlorination of TCE, hydrogen gas is necessary for the reaction to proceed. While scientists have studied gold and palladium particles as catalysts for a variety of other reactions, Nutt et al. appear to be the first in applying the catalytic abilities to remediation. Nutt et al. synthesized the catalysts by first creating gold nanoparticles. Using the citrate reduction method, scientists produced an aqueous fluid containing gold nanoparticle suspensions (Au Sol). To form the bimetallic particles, Nutt et al. added palladium salt in conjunction with a reducing agent to the Au sol (Nutt 2005).

The experiment compared the catalytic ability of palladium nanoparticles, gold nanoparticles, palladium-coated gold nanoparticles, palladium-alumina catalysts, and palladium-gold catalysts on alumina. Within the category of the Pd-on-Au particles, Nutt et al. also compared the effect of palladium coverage on activity. Results concluded that a sub-monolayer of palladium on gold produced the highest catalytic rates. An increase in Pd loading resulted in decreased rate constants, leading to the conclusion that once palladium coverage reached or surpassed one monolayer, the particles behaved as regular palladium particles (Nutt 2005).

5.2. Remedial Applications

At this point in time, the potential remedial applications of palladium-coated gold nanoparticles have been tested only in the lab for the capability to hydrodechlorinate trichloroethene and other chlorinated organic compounds in water. Due to the catalytic nature of the Pd-Au particles, they are not consumed in the reaction, and thus can be reused multiple times (Nutt 2005). This fact differentiates them from nZVI and Pd-nZVI particles, which are oxidized by contaminants such as COCs and subsequently passivated.

The ability to reuse Pd-Au particles multiple times, coupled with the product cost, greatly impacts the potential remedial applications of the particles. In a pound for pound comparison, nZVI particles cost much less than Pd-Au nanoparticles based on the price of the raw materials, but by capitalizing on the reusability of the Pd-Au, a smaller amount of particles can used in comparison to nZVI. Thus, in situ treatments involving slurry injections, where particles dissipate into the ground, work well for nZVI and BNIPs because particle recovery is not necessary. However, these applications would not be cost-effective for Pd-Au particles (Wong Conversation 2005).

Presently, development of remedial applications is focusing on two different innovations. The first technology involves mounting the nanoparticles onto membranes, allowing contaminated ground water or waste water to be pushed through the membranes for remediation. The second technology entails binding the nanoparticles to a powder. This technique enables particle recovery from solution by filtration, a process unachievable with individual nanoparticles (Wong Conversation 2005). Field simulation studies designed to test the ability of Pd-Au particles to remediate groundwater contaminated with TCE are underway at Rice University (Wong Conversation 2005). Plans to expand the study to include other contaminants are also in development. The list of potential contaminants includes other chlorinated compounds, fluorinated compounds, PCBs, nitrates, and potentially inorganic compounds such as arsenic (Wong Conversation 2005, Morello 2005).

5.3. Toxicity and Safety Concerns

Similarly to the cases of nZVI particles and BNIPs, no toxicity studies have yet been published on other bimetallic particles. Conversely, though, it is not apparent that there are any studies in progress. It could be speculated that because of the similarities between particles that they would exhibit similar toxicity levels. None of the bimetallic particles created exhibit radically different properties, and they are created from materials that are non-toxic in the bulk form. However, the persistence of catalytic materials such as the gold-palladium particles needs to be further explored for environmental interactions.

6. FERRITIN

6.1. Technology Overview

In recent years biological systems, namely proteins, have elicited much attention from research and development for their ability to control the formation of mineral structures (Kim 2002). Cage-like protein composites can often function as controlled environments for the assembly and/ or encapsulation of nanosized materials. Synthetic developments of this natural process offer potential applications in drug delivery as well as catalysis (Douglas 1998). A prime example of this occurrence is ferritin, an iron storage protein. Ferritin can be found throughout the animal, plant, and microbial kingdom and plays an integral role in the sequestration and storage of iron. The formation of ferritin occurs when the 24 similarly structured polypeptide subunits comprising the molecule self-assemble into a cage-like protein structure (Douglas 1998). The diameter of the assembled apoferritin (iron-free) is about 12 nm, and the inside cavity is approximately 8 nm. After assembly, iron molecules can diffuse into the cavity through channels in the protein shell, where mineralization converts the molecules into a nanoparticle of ferrihydrite, a ferric oxyhydroxide. The reaction volume of the cage and the .5 nm channel size spatially constrain the iron oxide nanoparticles formed. In vivo, the protein cavity can hold up to 4,500 iron atoms (Chasteen 1999). In vitro, scientists have control over the number of iron molecules entering the shell, producing loadings between 500 and 4,500 molecules. This translates to 5 nm to 7.5 nm iron oxide particles respectively (Kim 2002).

6.2. Remedial Applications

Ferritin offers potential benefits to the field of remediation in multiple areas, the most promising being that of photoreduction of contaminants (Kim 2002). Research has centered on the ability of ferritin to remediate toxic metals and possibly chlorocarbons in the presence of visible light or solar radiation (Moretz 2004). Iron oxides in general have received a significant amount of attention for their potential remedial abilities. While able to carry out significant photochemical processes, however, Fe (III) bearing iron oxide quickly undergoes photoreduction to Fe (II). This transformation renders the catalyst inactive (Strongin 2002). Ferritin naturally converts Fe (II) to Fe(III), thus the encapsulation of iron oxide prevents photoreduction. Despite providing stability, the ferritin cage does not inhibit the photoreduction of environmental contaminants. This factor gives ferritin a significant advantage over the traditional freestanding particles.

Research on this technology is in the early stages. Specifically, scientists at Temple University have demonstrated the ability of ferritin to reduce hexavalent chromium (Cr(VI)) to the trivalent form (Cr(III)) (Kim 2002). Cr(VI), an EPA priority pollutant and a common byproduct of industrial processes, can be toxic to humans and has been identified as a carcinogen. It is regulated by the EPA under a variety of acts, including CERCLA and RCRA (EPA). Cr(III), in contrast, occurs naturally, is less toxic, and is insoluble in water (Moretz 2004). Reducing Cr(VI) to Cr(III) thus reduces the toxicity as well as the mobility, allowing for easier filtration and removal (Kim 2002). Ferritin molecules with loading factors of 100, 500, 1,000, and 3,000 iron molecules have been tested for their ability to reduce Cr(VI). All experiments have been performed on a relatively small scale, of the milliliter order of magnitude. Reactions carried out in the presence of light demonstrated a significant ability to reduce Cr(VI). The results were compared against reactions carried out in no light, as well as reactions with apoferritin (Kim 2002).

This research offers multiple dimensions of expansion. The most immediate area of development includes the testing of ferritin on other toxic metals. Technetium-7, a metal contaminant present at a nuclear waste site in Washington constitutes one such potential metal. If proven applicable, this technology could be used to remediate groundwater that has been contaminated from the slow leakage of the storage canisters containing nuclear waste (Moretz 2004). Besides testing other metals, this technology offers potential remedial capabilities for aromatics and chlorocarbons.

In addition to iron hydroxide, past research has demonstrated that the apoferritin protein cage supports the synthesis of the other metal hydroxides, such as Mn(O)OH, Fe(O)OH, and Co(O)OH (Kim 2002). Exploiting these capabilities could potentially expand this technology, thereby increasing remediation speed and effectiveness as well as expanding the list of contaminants that could be addressed.

Outside of using ferritin to remediate contaminants, this technology also offers a new route to nanoparticle synthesis. A variety of techniques, including laser vaporization, electron beam lithography, and a number of colloidal techniques, currently are being used to produce nanoparticles (Hosein 2004). Despite these technologies, the manufacture of "uniform nanosized, monodispersed transition metal based particles still represents a significant challenge" (Hosein 2004). It has been demonstrated that ferretin could be employed in the production of both metallic and metal hydroxide particles. Scientists recently have developed a fairly straightforward synthesis route for both iron and cobalt metallic- and oxide-based nanoparticles. Using this method, ferritin assembles the particles in solution. Following assembly, the ferritin is dried on a solid support and cleaned with ozone to remove the protein cage. This leaves well-dispersed nanooxide particles. Further exposure of the particles to hydrogen and high temperature can be used to convert the metal oxides to metallic particles. This method allows a relatively high degree of control for particle size between 2 and 8 nm as well (Hosein 2004).

6.3. Toxicity and Safety Concerns

There are no specific toxicity studies concerning the use of ferritin as a remedial tool. However, the natural occurrence of ferritin in the environment points to its lack of toxicity in living animals, plants, and microbes. Concerns about ferritin should be focused on the ecological effects of its deployment in the environment.

7. NANOSCALE SEMICONDUCTOR PHOTOCATALYSTS

7.1. Technology Overview

Semiconductor photocatalysts act much in the same manner as traditional catalysts; however, they obtain their energy from the absorption of light. A number of materials, such as titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe2O3), and tungsten oxide (WO3), act as photocatalysts (Nagaveni 2004). Due to their light absorbing capabilities, they are employed in a variety of applications. Both titanium dioxide and zinc oxide can be used as pigments to provide whiteness for substances, such as paint and paper. The ability of photocatalysts to absorb ultraviolet light makes them useful in sunscreen as well as cosmetics to provide opaqueness to the creams or lotions. These properties also can be exploited for antimicrobial coatings; the photocatalytic properties allow thin coatings to be self cleaning and to have disinfecting properties after exposure to UV radiation. More importantly for this paper, photocatalysts have the ability to oxidize organic pollutants into nontoxic materials. Traditionally, TiO_2 has been used in advanced photochemical oxidation (APO) processes for environmental remediation because of its low toxicity, high photoconductivity, high photostability, availability, and low cost (USEPA 1998a, Nagaveni 2004).

Semiconductors oxidize a variety of organic molecules using light energy. Exposure to light illumination levels with energy greater than the band gap energy level of the photcatalyst result in a charge transfer process. In the charge transfer process, an excited electron moves from the valence band to the conduction band (USEPA 1998a). This process then results in the oxidation of surrounding organic substances. TiO_2, for example, exhibits photoconductivity when illuminated by light with an energy level exceeding 3.2 eV, the band gap for TiO_2 (Nagaveni 2004, USEPA1998a). This energy level translates to light with a wavelength shorter than 387.5 nm, which falls into the category of UV light (USEPA 1998a).

Nanotechnology has enabled the expansion of the field of semiconductor photocatalysis in a number of ways. A greater variety of compounds can be achieved, with increased reactivity and specificity. As with other nanoparticles, increases in surface area enhance reactivity. The ability to form surface modified particles, films, and nanotubes with semiconductor photocatalysts also plays a role in the increased specificity and selectivity of nanoparticles (Chen 2005, Kamat 2002, Nagaveni 2004, NATO 1998).

7.2. Remedial Applications

Conventional semiconductor photocatalysts have been used and tested for a variety of remedial applications. In 1995, a TiO_2 system was tested under the USEPA's SITE program at a Department of Energy (DOE) facility in Oak Ridge. The TiO2 effectively remediated the groundwater contaminated with 1,1-DCA, 1,1-TCA, xylenes, toluene, cis-1,2-DCE, and 1,1-DCE (NATO 1998). Field and pilot scale applications also have demonstrated the ability of TiO_2 to remediate fuel-contaminated groundwater containing benzene, toluene, ethylbenzene, and xylene (BTEX) compounds. In addition, TCE, Methyl-*tert*-butyl ether (MTBE), chloroform, ethylbenzene, and nitrobenzene can be destroyed by semiconductor photocatalysis (NATO 1998, EPA 1998a).

Emerging nanotechnologies and processes have recently enabled the production of a variety of conventional photocatalytic derivatives. Doping particles or modifying the surfaces of the photocatalysts with metal has become an increasingly popular enhancement. While dating back to a pre-nanotech era, the doping of photocatalytic particles is currently being applied to nanoparticles. Metals such as platinum, copper, silver, and gold have been tested for their ability to improve decontamination rates of TiO_2. Coupling with these metals also can induce a sensitivity and subsequent response to visible light. This combats the remediation problems faced by photocatalysts' requirement of UV light, which does not comprise a very large section of solar light (Rajeshwar 2001).

In a study coupling TiO_2 with copper for the remediation of Cr(VI), Rajeshwar et al. reported that the combination produced a "synergistic photocatalytic effect." (Rajeshwar 2001). This effect causes the acceleration of Cr(VI) reduction, as well as the reduction of Cu(II) ions, catalyzed by the Cr(VI) (Rajeshwar 2001). Coupling of TiO_2 with gold and silver produced similar reductive capabilities to that of TiO_2 and copper (Rajeshwar 2001). Scientists at Clemson University are currently exploring the reverse of metal doping on TiO_2 particles, instead coating silver and gold particles with a TiO_2 shell. This research also aims at achieving enhanced photocatalytic activity and an increase in light absorbing capabilities (Kumbhar 2004).

The development of TiO_2 based nanotubes represents a separate area of photocatalytic nanotechnology. Recently, Chen et al. reported the production of a TiO_2-based p-n junction nanotubes containing platinum on the inside and TiO_2 on the outside. The nature of the p-n junction allows the outside of the tube to act as an oxidizing surface, while the inside of the tube acts as a reductive surface. Chen et al. tested the ability of the nanotubes to destroy toluene, finding the p-n nanotube catalyst to have a much higher destruction rate than nonnanotube structured material. While still in the very early stages of research, Chen et al. projected the ability of this technology to be used in sensors, light emitting diodes, nanofiltration membranes for air, and water treatments (Chen 2005).

As mentioned previously, characteristics of $TiO_{2,}$ such as low cost, low toxicity and high reactivity, make the compound more popular than other semiconductor photocatalysts. Recently, however, ZnO has been proposed as a dual function photocatalytic material. In 2002, Kamat et al. reported that ZnO possessed both sensing and remediating capabilities for organic contaminants in water (Kamat 2002). By creating nanostructured ZnO films, Kamat et al. tested the ability of ZnO to both detect and treat 4-chlorocatechol. The study concluded that the ZnO films showed a high degree of sensitivity on the order of 1 ppm to aromatic compounds such as chlorinated phenols. Under UV lighting, the films degraded the aromatic compounds. The coupling of these two features also facilitated the monitoring of the degradation process, because as decontamination occurred, a direct change in the emission intensity followed (Kamat 2002).

7.3. Toxicity and Safety Concerns

The toxicity and safety concerns related to semiconductor photocatalysts have been studied fairly extensively, especially for titanium dioxide and zinc oxide. Because of their use in sunscreen and other direct use human products, testing for these materials has likely exceeded that for all other nanoparticles. Inhalation in the workplace presents a greater area of toxicity concern, largely because photocatalyst nanoparticles already have been approved for use in dermal applications, such as sunscreen.

In 2000, a study compared the respiratory effects of TiO_2 particles 20 nm and 250 nm in size. Rats and mice were used as test species. The study found that the smaller particles induced a greater pulmonary-inflammatory neutrophil response as compared to the larger particles when introduced to the rats and mice at the same mass doses. A second study comparing particle surface area (instead of mass) to response, though, found the results to be similar for both particle sizes (Oberdorster 2005). Other studies, however, have found that smaller photocatalyst particle size does not necessarily indicate a greater level of toxicity. At the 2004 American Chemical Society conference, a study was presented comparing the respiratory effects in rats of micron-sized quartz to nano-sized quartz particles and the effects of fine titanium dioxide to nano-sized TiO_2 rods and dots. Preliminary data indicated no difference between the effects of TiO_2 nanodots and rods and fine-sized TiO_2 particles. The preliminary data indicated that the nano-sized quartz actually caused less of an inflammatory response compared to the micron-sized quartz (Warheit 2004).

8. SELF ASSEMBLED MONOLAYER ON MESOPOROUS SUPPORTS-SAMMS

8.1 Technology Overview

As suggested by their name, Self Assembled Monolayers on Mesoporous Silica, or SAMMS, can most simply be described as functionalized nanoporous ceramics or the “marriage of mesoporous ceramics with self-assembled monolayer chemistry” (Mattigod 1999). The overall ceramic structure resembles a hexagonal honeycomb, as seen in Figure 3. The monolayers, formed within the porous surfaces actually adsorb or bind molecules. The nature of the SAMMS, namely the ability to alter the exposed functional group of the monolayer, allows this class of highly sorbent materials to potentially bind a broad range of molecules, and in the case of environmental remediation, contaminants (Fryxell 2005, SAMMS Technical Summary 2005).

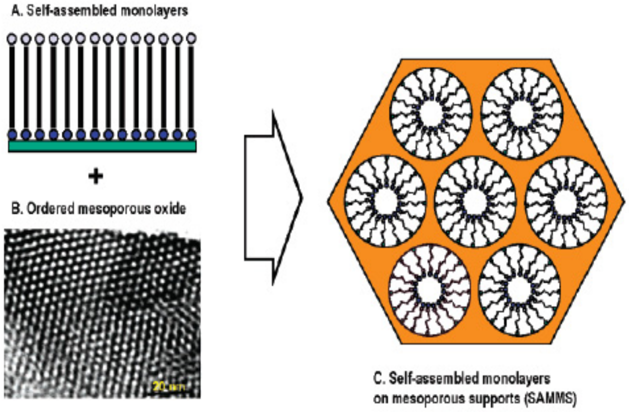

Figure 3. Diagram of SAMMS structure (Fryxell 2005)

Construction of both the ceramic and the monolayer include multiple steps, many reliant on the method of molecular self-assembly. In the first step of production, the starting surfactant molecules aggregate to form micelle templates of ordered liquid crystalline structures “such as hexagonally ordered rodlike micelles” (Mattigod 1999). This aggregation represents the first phase of self assembly (Fryxell 2005). Oxide materials are then precipitated onto the surface of the micelles in the presence of solvents and under mild hydrothermal conditions (Mattigod 1999). The formation of the preliminary mesoporous backbone represents the second phase of self-assembly (Fryxell 2005). The final step in creating the mesoporous ceramic requires the calcination of the organic-oxide material to remove the surfactants. Functionalized silane molecules are then mixed in excess with the mesoporous ceramics and self assemble in an ordered monolayer on the pore surfaces of the ceramic (Fryxell 2005). The bifunctional silanes used in the process can be engineered to have hydrophilic head groups that bind the target materials and hydrophobic tail groups, which covalently bind to the ceramic substrate (Yantassee 2003).

Upon their creation, SAMMS can be mixed with aqueous solutions where they bind to the target of interest. Following sequestration of the targeted molecules, SAMMS can be filtered from solution and recycled. Acid stripping causes SAMMS to release bound compounds, at which point they can be separated out of solution and reused.

8.2 Remedial Applications

As mentioned earlier, the ability to alter the exposed functional group of the SAMMS monolayer enables the potential remediation of a very broad range of contaminants. A multitude of different SAMSS classes have been developed at this point. The first and most widely studied material is termed thiol-SAMMS. Designed mainly for the sequestration of mercury, thiol-SAMMS can also bind other metallic cations, such as silver, cadmium, lead, and thallium (Mattigod 1999). Anion-SAMMS or metal-capped ethylenediamine (EDA) SAMMS have been developed to absorb anions, such as chromate and arsenate. Their derivative, chelate-SAMMS, contain only the EDA functional group, and can bind metals, such as copper, nickel, cobalt, and zinc (SAMMS Technical Summary). Cu-EDA-SAMMS (a type of anion-SAMMS) has been further functionalized to bind cesium by incorporating ferrocyanide-forming Cu-Ferrocyanide-SAMMS (Lin 2001). Finally, a variety of phosphonate and hydroxypyridone (HOPO) functionalized SAMMS have been created and tested for the sequestration of actinides and lanthanides (Fryxell 2004, Fryxell 2005, Lin 2005).

The majority of the SAMMS have only been tested on the bench-scale level, with the exception of thiol-SAMMS. Both bench-scale and pilot-scale tests have been carried out to test the ability of thiol-SAMMS to remediate mercury. Initial studies indicated thiol-SAMMS could remove dissolved mercury from smelter condensate to meet the EPA regulatory standard of .15 mg/L (Mattigod: Bench-Scale2). Following bench-scale studies, a total volume of 160 L of smelter waste containing mercury at a concentration 10.55 mg/L was used in a scaled-up pilot test. The study concluded that three consecutive treatments with approximately 200g of thiol-SAMMS each were required to meet regulatory standards (Mattigod: Pilot-Scale2). In this study, SAMMS used in each consecutive treatment could be recycled and reused. While this is an attractive feature in terms of cost, studies have also indicated that mercury-laden SAMMS are bound tightly enough for landfilling. Mattigod et al. tested the stability of thiol-SAMMS and mercury using the USEPA's Toxicity Characteristics Leaching Procedure (TCLP). The TCLP test indicated that the concentration of mercury released into solution was in the range of 0.0002-0.001 mg/L, an extremely low value. The EPA only requires less than .2 mg/L be released, indicating that the stability of mercury loaded SAMMS allows for easy disposal (Mattigod: Pilot-Scale2).

In addition to mercury removal from waste water, thiol-SAMMS have been shown to remediate mercury-contaminated soil as well. A proprietary lixiviant system has been developed that would allow the removal of mercury and potentially other metals, such as cadmium, silver, and molybdenum from soils and sludges (SAMMS Technical Summary 2005).

Currently, scientists at Pacific Northwest National Laboratory are working with Perry Equipment Corp. on the commercialization of thiol-SAMMS. The industrial development of this technology aims to target ocean-based petroleum operations. The ocean drilling sometimes produces mercury-contaminated sea water, which cannot be returned to the ocean without treatment. Current procedures routinely require the shipment of contaminated water back to land for remediation, which is a costly procedure. Thiol-SAMMS are being developed in an effort to target this problem and permit remediation on-site (Fryxell Conversation 2005).

8.3 Toxicity and Safety Concerns

Because the actual ceramic supports that comprise SAMMS are not on the nano scale—rather the functionalized pores are nanosized—they do not carry the same toxicity concerns of nanosized particles (Fryxell Conversation 2005).

9. DENDRIMERS

9.1. Technology Overview

Dendrimers represent a novel class of three-dimensional, highly branched, globular macromolecules, which fall into a broader category deemed dendritic polymers. This category includes hyperbranched polymers, dendrigraft polymers, and dendrons. Three covalently bonded components comprise dendrimers: a core, interior branch cells, and terminal branch cells (Diallo 2005). Both architecture and composition can be highly controlled in these monodisperse polymers. Synthesis techniques allow molecular design parameters, including size, shape, surface/interior chemistry, flexibility, and topology to be almost completely ordered (Cagin 2005). The size of dendrimers ranges between 2 and 20 nanometers; common shapes include cones, spheres, and disc-like structures. Altering the surface and interior chemistry allows functionalization, where, for example, particles can be designed to be soluble in certain media or bind appropriate molecules (Diallo 2005).

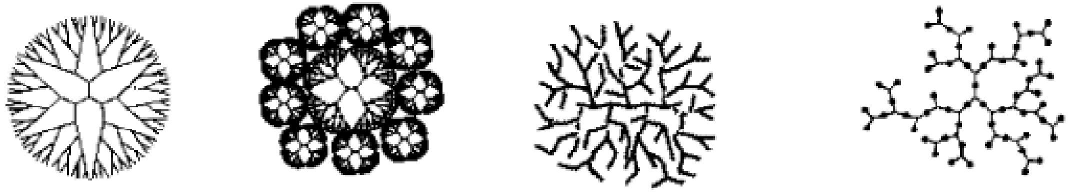

Figure 4. Different dendritic polymers: dendrimer, core-shell tecto(dendrimer), dendrigraft polymer, hyperbranched polymer (Diallo 2005)

9.2. Remedial Applications

Because dendrimers encompass such a broad technology, the potential remedial applications are expansive. Currently, poly(amidoamine), or PAMAM, dendrimers have been developed for use in the remediation of waste water and soil contaminated with a variety of transition metal ions such as copper (Cu(II)). Diallo et al. first reported on the use of PAMAM dendrimers for copper removal in 1999.

In general, PAMAM dendrimers represent an extremely broad class of materials, with a diversity of applications. As mentioned above, dendrimers are comprised of a core, interior branch cells, and terminal branch cells. The term PAMAM refers to the interior branch cells. In the case of PAMAM dendrimers, that includes functional nitrogen and amide groups repeatedly attached in radially branched layers (Diallo 2004). While the interior branch dictates the classification as "PAMAM," dendrimers falling into this class can have a wide range of core compounds and terminal functional groups. Dendritic Nanotechnologies, Inc., for example, offers over 40 variations of PAMAM dendrimers with varying cores and terminal groups. Diverse cores and functional groups translate into broad applications. Beside remedial uses, dendrimers have been commercialized for HIV prevention and anthrax detection (Dendritic Nanotechnologies, Inc., 2005).

For the specific development of metal-remediating dendrimers, researchers have employed an ethylenediamine (EDA) core. The high concentration of nitrogen ligands within the interior branches makes PAMAM dendrimers useful as chelating agents for metal ions (Diallo 2004, Xu 2005). The ability to choose a multitude of functional groups as terminal cells also contributes to functionality as metal chelators. Surface terminal groups, including primary amine, succinamic acid, gycidol, hydroxyl and acetamide, have been tested (Diallo 2004, Xu 2005).

Expanding on initial research developing EDA core PAMAM dendrimers for copper remediation, Diallo et al. devised a dendrimer-enhanced ultrafiltration (DEUF) method to recover copper from aqueous solutions. DEUF is a variation of polymer-enhanced ultra filtration (PEUF), a remedial tool that has emerged in the past 10 years as a promising technology for metal ion removal from waste streams. PEUF and DEUF work on the same principles, where the binding of metal ions to the polymers or dendrimers allows the removal of contaminants though membrane filtration. In the first step of the process, either linear polymers or dendrimers are mixed with contaminated waste water, where they subsequently bind to metal ions present. The solution is then pushed through an ultra filtration (UF) membrane, which prevents the passage of the polymer/dendrimer-metal ion complexes. The metal-laden polymers or dendrimers can then be sent to a second location where the metal is detached from the polymers or dendrimers so that they can be reused (Diallo 2005). Diallo et al.'s proposed process consisting of a clean water recovery unit and a dendrimer recovery unit can be seen below in Figure 5. Diallo et al. are currently working on the engineering development of this process with hopes of having pilot-scale demonstration in the next four years (Diallo Conversation 2005).

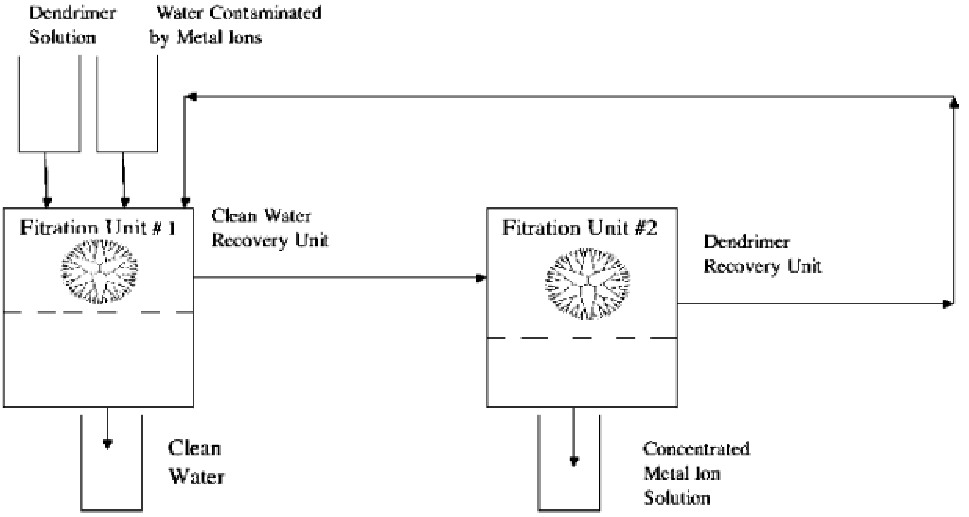

Figure 5. Diagram of Dendrimer Enhanced Ultrafiltration Unit (Diallo 2005)

The ability of EDA-core PAMAM dendrimers to remove copper from soil also has been examined. Laboratory-scale testing by Xu et al. revealed that dendrimers could achieve up to a 54% removal of copper from the soil. In comparison to other extracting agent such as EDTA, the larger molecule size of dendrimers proves advantageous for separation (Xu 2005). Currently, however the price of dendrimers restricts their usefulness as soil remediators (Diallo Conversation 2005).

While the current status of dendrimer research for remediation only includes EDA core PAMAM dendrimers for copper and other metal ion recovery, the technology possesses potential for expansion. PAMAM dendrimers can be functionalized with redox active metal clusters of FeS. These dendrimers could then be used for reductive decontamination of organic pollutants, such as chlorinated compounds and poly(nitroaromatics) (Diallo Conversation 2005).

9.3. Toxicity and Safety Concerns

Toxicity concerns of the developed remedial dendrimers are currently being researched. In general dendrimers encompass such a broad range of materials that a blanket statement about their toxicity would be inappropriate. Some PAMAM dendrimers already are being used in pharmaceutical applications as mentioned above, which would indicate that those dendrimers are nontoxic. However, analysis must be performed on an individual basis.

10. POLYMERIC NANOPARTICLES

10.1. Technology Overview

Polymeric nanoparticles embody an extremely broad category of molecules or molecular aggregates that can be used in a variety of applications, from drug delivery to sunscreen. Similar to surfactant micelles, polymeric nanoparticles possess amphiphilic properties that originate from the properties of each polymer present in the particle. Individual polymers contain a hydrophobic as well as a hydrophilic section. In the presence of water, the molecules self-assemble to form polymer vesicles with diameters in the nanometer range, where the hydrophobic segments are oriented inwards, and the hydrophilic segments form the outer layer (Goho 2004). Polymeric nanoparticles differ from surfactant micelles in synthesis. Cross-linking of the particle precursor chains following aggregation enables the particles to maintain stability regardless of precursor chain concentration (Tungittiplakorn 2004, 2005). Surfactant micelles on the other hand, can only maintain their structure when the concentration of the individual surfactant reaches or exceeds the critical micelle concentration (CMC) (Tungittiplakorn 2004, 2005).

Amphiphilic polyurethane (APU) nanoparticles represent the specific molecular-type of particles in development for remedial applications. Just in the beginning stages of research, scientists have synthesized a number of particles using polyurethane acrylate anionomer (UAA) and poly(ethylene glycol)-modified urethane acrylate (PMUA) as precursor chains (Tungittiplakorn 2004, 2005). The precursor chains influence the structure and properties of the particles. In the case of UAA derivatives, the non-polar backbones remain in the interior of the particle and the carboxylic side chains form the particle surface. On the other hand, the hydrophilic poly(ethylene oxide) portions of the PMUA derived particles form pendant side chains on the particle surface. These structures are seen in Figure 6. Further variation in the nanoparticles structure and functionality can be achieved by altering the properties and synthesis techniques for the precursor chains. For example, varying the size of poly(tetramethylene glycol) (PTMG), a chemical used in synthesizing both UAA and PMUA chains, can alter the structure of the end particle (Tungittiplakorn 2004).

Figure 6. Structure of polyurethane acrylate anionomer (UAA) and poly(ethylene glycol)-modified urethane acrylate (PMUA) derived nanoparticles (Tungittiplakorn 2004)

10.2. Remedial Applications

For remedial techniques, polymeric nanoparticles offer a potential replacement for traditional surfactants commonly used to enhance the remediation of hydrophobic organic contaminants (HOCs) using pump-and-treat systems. Contaminants falling into this category often sorb strongly to soils or form nonaqueous phase liquid (NAPL) (Yeom 1996). Their overall persistence causes a large problem for successful pump-and-treat remediation where "low recoveries can result from: (1) slow dissolution of NAPLs into the ground-water, (2) slow diffusion of contaminants from low conductivity zones to high conductivity zones, (3) slow desorption of sorbed contaminants, and (4) hydrodynamic isolation in dead-end zones," (Jafvert 1996, Yeom 1996) The implementation of surfactants largely has been used to combat the inefficiencies of the pump-and-treat-systems (Yeom 1996). Surfactants can mobilize and solubilize NAPL, as well as solubilize sorbed contaminants (Yeom 1996, Jafvert 1996). This greatly increases the mass recovery rate of pump-and-treat remediation and, in cases of dual remediation, can enhance biodegradation (Yeom 1996).

APU nanoparticles display very similar properties to those of surfactant micelles. Scientists have demonstrated in laboratory-scale research that UAA- and PMUA-derived nanoparticles potentially can be used to enhance pump-and-treat remediation of polycyclic aromatic hydrocarbons (PAHs). Specifically, scientists at Cornell have tested the ability of UAA and PMUA nanoparticles to remove phenanthrene (PHEN), a PAH found in coal tar, from a sandy aquifer media (EST Science). Four different variations of nanoparticles were tested: UAA2K, UAA1K-1, UAA1K-2, and PMUA (EST). The UAA-derivative particles averaged approximately 40 nm in size, while the PMUA particle averaged 80 nm (Tungittiplakorn 2004). Scientists tested each particle type for its affinity for PHEN, the adsorption of the nanoparticles on the sandy material, and the tendency of particles to aggregate (EST). The study concluded that the particles would effectively compete with sand for the sorption of PHEN. It was also determined that changes in functionality can be achieved through particle modifications.

Increasing the length of the hydrophobic backbone can increase PHEN affinity, for example (Tungittiplakorn 2004, 2005).

Currently, in the beginning of the research phase, the scale-up of this project is being examined. Certain hurdles would still need to be crossed before larger tests could begin, such as determining suitability of the particles for treating various soil types, and the development of a recovery and recycling process for the particles. Researchers also plan to further examine the bioavailability of contaminants in the nanoparticles and the potential dual treatment remediation approach (Lion Conversation 2005).

10.3. Toxicity and Safety Concerns

Currently no toxicological studies of the polymeric nanoparticles designed for soil remediation have taken place (Lion Conversation 2005). This represents another research need in the progression to pilot-scale testing of this technology.

11. SINGLE-ENZYME NANOPARTICLES

11.1. Technology Overview

Enzymes offer vast capabilities in the areas of chemical conversions, biosensing, and bioremediation. Their specificity and targeted effectiveness make them much more effective than synthetic catalysts. However, the lack of stability and relatively short life of enzymes inhibit their ability to provide cost effective options (Kim 2003, Kim 2004). Researchers have experimented with methods, such as enzyme immobilization, enzyme modification, and genetic modification, to improve the stability and subsequent persistence of enzymes.

Nanotechnology has recently provided a new method of enzyme stabilization in the form of single enzyme nanoparticles (SENs). In laymen's terms, SENs can be described as armored enzymes surrounded by a protective cage a few nanometers thick (PNL). The "cage" is actually a silicate shell, linked with the surface of the enzyme. While it covers most of the enzyme, the active site remains chemically accessible, maintaining the functionality of the enzyme (Kim 2003, Kim 2004).

Kim et al. assembled the first SENs in 2003, using chymotrypsin as a model enzyme. Synthesis of SENs involves a three part process. The first step requires covalent modification of the enzyme surface creating vinyl group functionality and solubilization of the enzyme in a non-polar/hydrophobic solvent such as hexane. In the second step, silane monomers with both vinyl and trimethoxysilane groups are mixed with the modified enzymes. Vinyl group polymerization creates linear polymers with free trimethoxysilane groups attached to the enzyme surface. The third and last step requires the hydrolysis of the trimethoxysilane groups and the subsequent condensation of the silanols. This final step creates the cross-linked silicate shell resembling armor (Kim 2003, Kim 2004). Figure 7 shows the various stages of formation and the chemistry for synthesis.

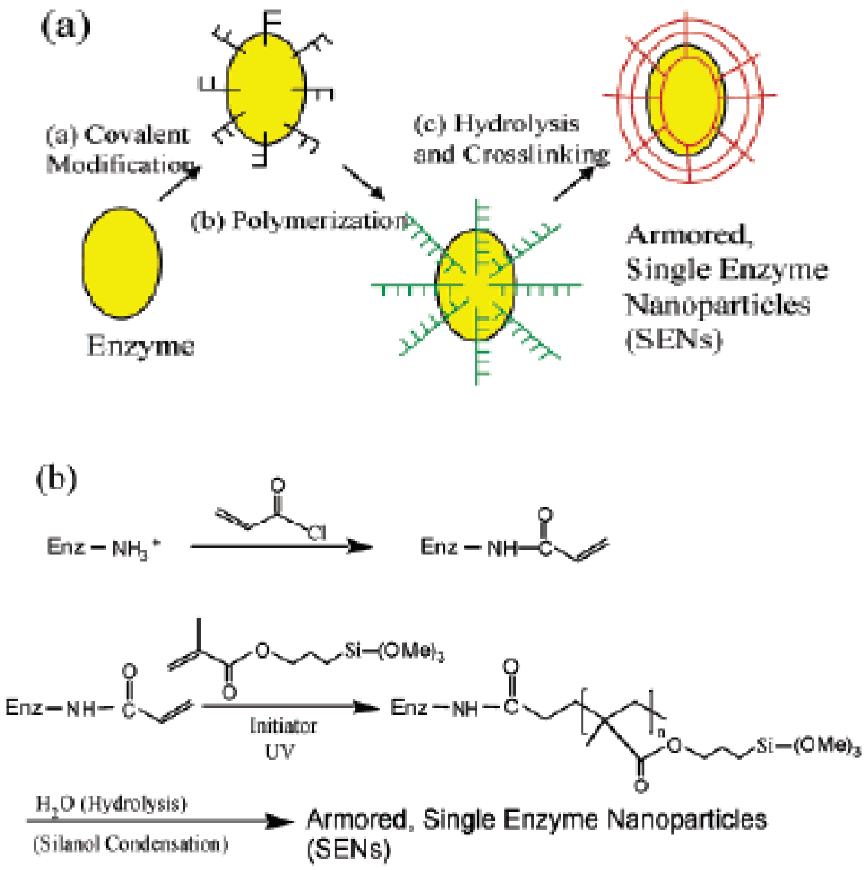

Figure 7. Diagram of the modification process (a), and chemical reactions in the process (b) of creating SENs (Kim 2003)

11.2. Remedial Applications

The use of single enzymes offers potential decontamination methods for a range of compounds. Compared to traditional microbial remediation, the use of individual enzymes offers a variety of advantages. Single enzymes can be used to remediate recalcitrant compounds, for example. They can withstand more extreme conditions, such as high/low pH, high contaminant concentration, high salinity, and high/low temperature. Enzymes also do not require nutrients and biomass acclimation. Metabolic intermediates and byproducts, as well as mass transfer limitations due to cellular transport, are avoided as well. Generally, it is a much easier process to control than whole cell degradation (Kim 2004).

The contaminant of interest dictates the type of enzyme employed for remediation. Peroxidases, polyphenol oxidases such as laccase and tyrosinase, dehalogenases, and organophosphorous hydrolases are examples of applicable enzymes. The plethora of enzymes to choose from allows the potential remediation of an extremely broad class of organic contaminants. Phenols, polyaromatics, dyes, chlorinated compounds, organophosphorous pesticides or nerve agents, and explosives all can be degraded using enzymes (Kim 2004).

Despite the benefits achievable through enzymatic remediation, as mentioned above, enzyme stability and lifetime proves a cost limiting factor for large-scale remedial purposes. While SEN research only has been conducted on the enzyme chymotrypsin, the technology is transferable across all enzymes, thus potentially allowing enzymatic remediation to be cost effective.

11.3. Toxicity and Safety Concerns

No specific toxicity studies or safety concerns have been reported for SENs. Their enzymatic basis would initially point to a lack of toxicity. However, their potential persistence in the environment and/or in mammals if absorbed or ingested should be more clearly detailed.

12. TUNABLE BIOPOLYMERS

12.1. Technology Overview

Tunable biopolymers can be best described as artificial or synthetic protein polymers that exhibit novel organization and control at the molecular level. Genetic engineering and recombinant DNA techniques allow the design and production of nanoscale biopolymers through the creation of a synthetic genetic template. The ability to design these genetic templates allows the sequence, size, composition, and function of the biopolymers to be pre-determined.

Elastin-like polypeptides (ELP) are biopolymers that possess structurally similar characteristics to the mammalian protein elastin (Kostal 2001). Their unique characteristics render them good candidates for base formation of tunable biopolymers. Comprised of the repeating pentapeptide VPGVG, they undergo a reversible phase transition from water soluble forms or polymer solutions into aggregates with increases in temperature. The transition temperature of the ELP can be tuned/controlled by altering the chain length and sequence (Kostal 2001, Kostal 2003). It also fluctuates with changes in pH, ionic strength, pressure, and covalent modifications. ELP can be produced in mass quantities through overexpression in *E. coli*. Purification to homogeneity is readily achievable through exploitation of the temperature responsive trait of ELP. This factor makes it an attractive candidate for biopolymer production. Fusion with other peptides and/or proteins allows functionalization of the ELP, while still maintaining the temperature responsive characteristic (Kostal 2001, Kostal 2003).

12.2. Remedial Applications

Tunable biopolymers have been synthesized on a laboratory scale to specifically bind to heavy metals, making them useful for the removal of heavy metals from waste streams and soil. Through the fusion of ELP with proteins that specifically target metals, such as cadmium, mercury, arsenic and lead, biopolymers that target individual metals can be created. Currently, tunable biopolymers that bind to cadmium and mercury have been developed (Kostal 2001, Kostal 2003).

In 2001, Kostal et al. created a tunable biopolymer useful for the remediation of heavy metals and tested its binding ability for cadmium. An ELP comprised of a repeating VPGVG was used. A hexahistidine tail was also incorporated to serve as the metal binding moiety. The metal binding capabilities of the biopolymer was tested in a buffer solution containing Cd2+. The biopolymers were found to bind to cadmium at a 1:1 ratio. As mentioned above, upon addition of the biopolymers to solution, the nature of the ELP allows them to be precipitated out of solution by increases in temperature or salt solution (Kostal 2001).

Besides testing the ability of ELPs with polyhistidine moieties to remediate waste water, Prabhukumar et al. tested the capacity of the polypeptide to remediate cadmium contaminated soil. Using mostly sandy soil soaked with cadmium nitrate, solution containing the biopolymers was added and cadmium removal measured. The study concluded that cadmium removal increased with the added concentration of biopolymers, and a modest maximum of 55% cadmium removal was achieved. The study noted that other proteins with a stronger cadmium affinity could be employed as replacements for the polyhistidine moiety to increase recovery (Prabhukumar 2004).

In a separate study, Kostal et al. created a tunable biopolymer with a specific affinity for mercury. The protein MerR was used as the metal-binding moiety fused with an ELP. MerR is a bacterial metalloregulatory protein that has a very high affinity and specificity for mercury, even in the presence of other heavy metals, such as cadmium and zinc. The synthesized biopolymers demonstrated the ability to remediate mercury in buffered solutions to ppb levels. Following separation, the mercury could be removed and the biopolymers recycled. The study also tested the ability of the biopolymers to remediate mercury-contaminated lake water (with a higher pH and turbidity) and found that the efficiency was maintained (Kostal 2003).

12.3 Toxicity and Safety Concerns

No specific toxicity concerns have been reported for bioploymers. Their biological basis makes the technology potentially less of a concern than other inorganic nanotechnologies. As mentioned for other nanotechnologies, ecological interactions should be further examined.

13. NANOCRYSTALLINE ZEOLITES

13.1. Technology Overview

The term zeolite represents a very broad group of crystalline structures generally comprised of silicon, aluminum, and oxygen (Song 2005a, Song 2005b). Offering a diversity of potential applications in catalysis and separations, zeolites have become especially popular for use as catalysts in petrochemical processing (Song 2005a, Alwy 2005). Properties of zeolites include high cation exchange capacities, high specific surface areas, and high hydrothermal stability (Song 2005a, Bowman 2002). The specific surface areas of zeolites can be attributed to their porous crystalline structure. Conventional synthesis methods produce zeolites on the scale of 1,000 to 10,000 nm, or 1 to 10 um. However, because the pores fall into the molecular size range (.4 to 1 nm), zeolites are considered nanomaterials.

Recently, researchers have begun to synthesize nanocrystalline zeolites as a way to explore a new avenue relating zeolites and nanotechnology. Nanocrystalline zeolites are comprised of "discrete, uniform crystals with dimensions of less than 100 nm" (Song 2005b). The nano-sized particles often exhibit unique properties in comparison to the same micro-sized structures. Advantages, such as greater external surface areas, smaller diffusion path lengths, and a greater aversion to coke formation make nanocrystalline zeolites superior to traditional micron-sized zeolites (Song 2005a, Song 2005b). In addition, enhanced absorbency capacities of up to 50% greater than those for micron-sized zeolites have been reported (Song 2005b). The ability to assemble nanocrystalline zeolites into thin films and other nanostructures facilitates the potential formation of separation membranes (Song 2005b, Alwy 2005).

13.2. Remedial Applications

It has been projected that the enhanced properties of nanocrystalline zeolites will lead to an increase in the total number of applications for this technology (Song 2005a). Regular-sized zeolites already have been tested for a variety of environmental applications. Zeolites have the ability to remediate water containing cationic species, such as ammonium and heavy metals, as well as chemicals, such as ^{137}Cs and ^{90}Sr. These radioactive species are found in nuclear plant wastewater and polluted groundwater (Bowman 2002). MTBE, a contaminant used as a gasoline additive, also has been reported as a potential target of zeolites. H-ZSM-5, a type of zeolite, converts MTBE to biodegradable chemicals in aqueous solutions, for example (Centi 2002). In addition, surfactant modified zeolites (SMZ) have been researched as potential remedial agents. In 2003, Bowman reported the creation of an SMZ permeable barrier to adsorb the contaminants PCE and chromate from groundwater. Bowman also evaluated the ability of the modified zeolites to remove petroleum hydrocarbons such as BTEX from oilfield wastewater (Bowman 2002).

Currently, nanocrystalline zeolites are still in the research phase, and no specific soil or water remediation processes have been proposed. However, as mentioned previously, the advantages of nano-sized zeolites is compared to micron-sized, will likely lead to an increase in technological applications. This will translate to a growth in environmental applications as well.

13.3. Toxicity and Safety And Concerns

No specific toxicity concerns involving nanocrystalline zeolites have been reported. Studies, however, are currently underway.

14. OVERALL TOXICITY AND SAFETY CONCERNS

Human exposure to nanosized particles does not represent an emerging problem, necessarily. Nanosized particles have been naturally present in the environment for millennia. Examples of these particles include viruses, volcanic ash, forest fire ash, and naturally occurring ferritin. Anthropogenic exposure to nanosized particles is also not a new concept. Since the start of the Industrial Revolution, human contact with nanosized particles has increased dramatically. Internal combustion engines, incinerators, metal fumes, and polymer fumes all represent sources of nanoparticles. These particles, however, are produced unintentionally as byproducts to reactions. The recent emergence of nanotechnology, though, has ushered humans into an era of exposure to intentionally created nanosized particles. As seen throughout this report, these new "manufactured" particles have unique properties, including shape, functionality, and reactivity. While the term "manufactured" does not necessarily indicate toxicity, the increasing number of particles in production increases routes and means of human exposure (Oberdorster 2005).

Human exposure to nanoparticles can occur in a variety of different ways, including through ingestion, inhalation, injection, and dermal exposure (Oberdorster 2005). Thus, the toxicology of nanoparticles must be studied across a variety of exposure routes and test organisms. Inhalation, however, is expected to be the most predominant route of human exposure, particularly in the workplace (Hood 2004). Currently, a number of different laboratories and researchers are conducting toxicity studies involving nanoparticles. A number of studies already have been published, and significantly more data are being generated. In November 2003, the EPA awarded 12 grants to various universities to investigate the potential health and environmental impacts of nanomaterials. In addition, EPA, NSF, and NIOSH have jointly funded an additional grant program this year for further toxicological studies.

The majority of the studies published thus far have centered on carbon nanotubes, fullerenes, and photocatalytic particles. Carbon nanotubes represent a cause for concern due to their similarities to asbestos. A number of studies have already demonstrated the negative impacts that nanotubes have on the respiratory tracts of rats and mice. One study, completed by scientists at NASA compared the effects of soot-like carbon particles to carbon nanotubes on the respiratory tracts of mice. The mice exposed to the nanotubes sustained significant lung damage, while the mice exposed to carbon soot did not show any negative effects. Mice exposed to the carbon nanotubes also showed signs of granuloma formation, a common side effect to particulate exposure (Raloff 2005). These findings have been supported by other similar studies (Oberdorster 2005). While these studies present cause for alarm, it should be noted that exposure levels influence toxicity in humans, and safe handling of these materials can reduce exposure to allowable levels (Raloff 2005).

Outside of carbon nanotubes, carbon nanospheres, such as fullerenes, also have been studied. Most notably, ecotoxicological studies with fullerenes have been conducted using the test organism *Daphnia magna*, as well as largemouth bass. A median lethal concentration of 800 ppb was established for *D. magna.* Similarly, fullerene concentrations as low as 0.5 ppm have been shown to cause glutathione depletion in the gills of largemouth bass, as well lipid peroxidation in the brain over 48-hour exposure periods (Oberdorster 2005). Movement of nanospheres from the lungs to the blood in inhalation studies also has been reported. Once in the blood stream, nanoparticles can attach to red blood cell causing an increased susceptibility to clotting (Raloff 2005).

While a number of studies involving various nanotechnologies already have been performed, adequate risk assessments will ultimately require more studies. Many of the studies thus far have focused on carbon-based nanotechnologies. And of these studies, a majority of them have focused on inhalation as a means to exposure. In terms of understanding the environmental impacts of nanotechnologies, an increasing number of studies will need to focus on the ecological impacts of nanotechnologies used in product production as well as for remedial purposes.

15. REGULATORY NEEDS

"We recommend that the use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications such as remediation be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risks." ~The Royal Society of the United Kingdom

Fearing that nanotechnology will suffer fates similar to those of genetically modified foods, nuclear power, or asbestos, experts are currently scrambling to adequately address the regulatory questions raised by nanotechnology. The sheer vastness of the various materials and technologies encompassed in the term "nanotechnology" represent the main source of the regulatory problem. Evident throughout this paper, the technologies currently available, as well as those in development, possess unique characteristics and subsequently very individualized toxicity capacities. In a recent editorial, *Nature* magazine reaffirmed this position, stating that "nanotechnology is a diverse field united only by a factor of scale. So it is not even clear how one would go about regulating nanotech in a manner unique to the discipline" (Nature 2003). As with the regulation of any technology or process, regulating nanotechnology will require a balancing act. Too much regulation could stifle progress and innovation, while too little could create a number of consequences.

Currently, nanotechnology regulations in the US fall on the minimal side. European countries, while also lacking specific regulations, have taken a much more preventative approach to nanotechnology. For example, the Royal Society and the Royal Academy of Engineering has advised the prohibition of nanoparticle deployment into the environment in the United Kingdom until more conclusive safety data is generated (The Royal Society 2004).

The need for more explicit regulations in the US is increasing. The field of nanotechnology in general is growing very rapidly across a number of disciplines. In the absence of greater regulations, some scientists and policy makers fear that nanotechnology will become the next "Frakenfood." Experts such as Julia Moore, a senior advisor in the NSF's Office of International Science and Engineering, have expressed concern that the news of a single environmentally detrimental nanotechnology could ignite public opposition to the entire field similar to that of genetically modified foods (Service 2004). In reality, nanotechnology covers an imminently broad group of technologies and products with widely varying safety concerns; however a negative public perception of the term "nanotechnology" could hinder future progress across all disciplines.

Calls for more stringent regulations are also appearing from the less obvious sectors. Industry and industry consultants are increasingly pushing for a more defined regulatory strategy. On June 29th, 2005, Matthew Nordan of Lux Research, Inc., testified at a hearing of the House Science research subcommittee that "based on [Lux's] contact with individuals driving nanotech initiatives at America's largest corporations, it's clear to us that ambiguity surrounding environmental, health, and safety regulation of nanoparticles is hampering commercialization." According to Nordan, companies are "reluctant to play a game whose rules may change at any time." (InsideEPA 2005). Lux Research, Inc., is a consulting firm focused on nanotechnology industry.

At the moment, a number of steps have been taken by various federal agencies to begin the process of generating concrete regulations and standards. In August 2004, the American National Standards Institute (ANSI) formed the Nanotechnology Standards Panel (ANSI-NSP). The primary focus of ANSI-NSP is "nomenclature and terminology" for nano-materials, although later work may be extended to testing methodology and material properties (ANSI [No Date]).

The USEPA stands to serve as the primary regulator of nanotechnology. Currently, however, the USEPA is only asking nanomaterials producers to voluntarily provide information about the types of materials they are making and at what volumes. While this information is helpful at a preliminary level, requirements will need to be ramped up quickly to meet the growing production of nanomaterials (Service 2005). The existing regulatory framework for chemicals and now nanomaterials is the Toxic Substances Control Act (TSCA). It is unclear, however, that TSCA has the ability to adequately regulate nanomaterials. TSCA gives EPA the authority to regulate new chemicals. Unfortunately though, there are no provisions in TSCA to distinguish between nanosized materials and their larger-scale counterparts. Because of the nature of nanotechnology, even when chemical compositions remain the same, the functionality of the material can change (Wardack 2003). Recently, EPA received a request for exemption from submitting a full Pre-Manufacture Notice (PMN) for single-walled carbon nanotubes. The request was for a Low-Volume Exemption (LVE). This request again raised the question of whether or not a carbon-based particle can be considered a new chemical (InsideEPA 2005).

With numerous nanoparticles being manufactured, and nZVI injections already taking place, it is clear that, at the moment, the regulations lag behind the technology. As applications and uses of these technologies continue to arise, it will become increasingly important for voluntary programs to become definitive about rules and regulations. With support from both regulatory agencies and industry, alike, a clear incentive exists for establishing better regulations and addressing the deficiencies in the current policies of TSCA.

16. CONCLUDING REMARKS: THE FUTURE OF NANOTECHNOLOGY FOR ENVIRONMENTAL REMEDIATION

The United States, as well as the greater world, is faced with the serious problem of cleaning up polluted lands and waters. With a growing population and growing land requirements, past efforts to sequester contaminants are not adequate. Increasing importance is falling on technologies that can treat pollution and decontaminate sites. With technologies such as bioremediation and phytoremediation gaining popularity, nanotechnology offers a number of emerging technologies that could work to treat contaminants. While one nanotechnology is already commercially available for use in remediation, it is inevitable that other technologies currently on the bench scale will gradually move into field-scale trials. These technologies will hopefully open the door to more effective and less costly toxicant treatments. As can be seen, though, the success of these technologies is reliant on a better understanding of their potential health impacts. Success in the public eye is also dependent on maintaining a positive image for the entire field of nanotechnology. In the end, it likely will be the next few years that dictate the direction of nanotechnologies for environmental remediation.

17. REFERENCES

"Analysts say EPA regulations would help nanotechnology research". 2005. *InsideEPA* July 5.

Alwy, H., G. Li, V.H. Grassian, S.C. Larsen. 2005. Development of Nanocrystalline Zeolite Materials as Environmental Catalysts. Nanotechnology and the Environment. American Chemical Society Symposium Series 890.

ANSI. No Date. [Nanotechnology Standards Panel Brochure]

Bilvey, Al. 2005. Phone Conversation. July.

Boronina T., K. Klabunde, G. Sergeev. 1995. Destruction of Organohalides in Water Using Metal Particles- Carbon Tetrachloride/Water Reactions with Magnesium, Tin and Zinc. *Environmental Science and Technology* 29 (6): 1511-1517

Bowman, Robert S. 2002. Applications of Surfactant-Modified Zeolites to Environmental Remediation. *Microporous and Mesoporous Materials.* 61: 43-56.

Cagin, Tahir, Guofeng Wang, Ryan Martin, William Goddard III. 2005. Molecular Modeling of Dendrimers for Nanoscale Applications. *Seventh Foresight Conference on Molecular Nanotechnology.*

Canano Technologies. Accessed July 2005. http://www.cananopowders.com/index.html

Centi, G., P. Ciambelli, S. Perathoner, P. Russo. 2002. Environmental Catalysis: Trends and Outlooks. *Catalysis Today* 75: 3-15.

Chasteen, N. Dennis, Pauline M. Harrison. 1999. Mineralization in Ferritin: An Efficient Means of Iron Storage. *Journal of Structural Biology* 126: 182-194.

Chen, Yongsheng, John Crittenden, Stephen Hackney, Larry Sutter, David Hand. 2005. Preparation of a Novel TiO2-Based p-n Junction Nanotube Photocatalyst. *Environmental Science and Technology* 39(5):1201-1208.

Chu, Peylina, John Mateo, Sam Fogel, John Freim, Clint Bickmore, William Newman, David Crisman. 2005. Rapid In-situ Dechlorination of Solvents by Abiotic and Biotic Mechanisms.

Contaminant Focus: Chromium VI http://www.clu-in.org/contaminantfocus/default.focus/sec/chromium_VI/cat/Overview/

"Cutting edge techniques proposed for Nease Cleanup". 2005.*Region 5 Factsheet.* http://www.epa.gov.region5/sites/neasefs200506.pdf.

Dendritic Nanotechnologies, Inc., http://dnanotech.com/index.php. Accessed July 2005.

Diallo, Mamadou. 2005. Phone Conversation. June.

Diallo, Mamadou, Simone Christie, Pirabalini Swaminathan, James Johnson Jr., William Goddard III. 2005. Dendrimer Enhance Ultrafiltration. 1. Recovery Cu(II) from Aqueous Solutions Using PAMAM Dendrimers with Ethylene Diamine Core and Terminal NH2 Groups. *Environmental Science and Technology* 39(5):1366-1377.

Diallo, Mamadou, Simone Christie, Pirabalini Swaminathan, Lajos Balogh, Xiangyang Shi, Wooyong Um, Charalambos Papelis, William Goddard III, James Johnson Jr. 2004. Dendritic Chelating Agents. 1. Cu(II) Binding to Ethylene Diamine Core Poly(amidoamine) Dendrimers in Aqueous Solutions. *Langmuir* 20(7):2640-2651.

Diallo, Mamadou, Lajos Balogh, Abdul Shafagati, James Johnson Jr., William Goddard III, Donald A. Tomalia. 1999. Poly(amidoamine) Dendrimers: A New Class of High Capacity Chelating Agents for Cu(II) Ions. *Environmental Science and Technology* 33(5): 820-824.

Douglas, Trevor, Mark Young. 1998. Host–guest encapsulation of materials by assembled virus protein cages. *Nature* 393(6681): 152-155.

Durant, Neal, Evan Cox, Sandra Dworatzek, Wei-xian Zhang, Scott Neville, and Chris Fennessey. 2004. Simultaneous treatment of perchlorate, NDMA, and chlorinated solvents using nanoscale iron. *The Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds.*

Elliot, Daniel, Wei-Xian Zhang. 2001. Field Assessment of Nanoscale Bimetallic Particles for Groundwater Treatment. *Environmental Science and Technology* 35(4): 4922-4926.

Feynman, Richard P. 1959. Plenty of Room at the Bottom. California Institute of Technology Archives. http://www.its.caltech.edu/~feynman/plenty.html.

Fryxell, Glen E., Hong Wu, Yuehe Lin, Wendy J. Shaw, Jerome Birnbaum, John C. Linehan, Zimin Nie, Ken Kemner, and Shelly Kelly. 2004. Lanthanide selective sorbents: self assembled monloayers on mesoporous supports (SAMMS). *Journal of Materials Chemistry* 14: 3356-3363.

Fryxell, Glen E., Yuehe Lin, Sandy Fiskum, Jerome C. Birnbaum, Hing Wu. 2005. Actinide Sequestration Using Self-Assembled Monolayers on Mesoporous Supports. *Environmental Science and Technology* 39(5):1324-1331.

Fryxell, Glenn. 2005. Phone Conversation. June.

Gavaskar, Arun, Lauren Tatar, Wendy Condit. 2005. Cost and Performance Report: Nanoscale Zerovalent Iron Technologies for Source Remediation. *BATTELLE.* Navale Facilities Engineering Service Center.

Glazier, Robert, Ramesh Venkatakrishnan, Florin Gheorghiu, Lindsey Watala, Robert Nash, Wei-xian Zhang. 2003. Nanotechnology Takes Root. *Civil Engineering* May: 64-69.

Goho, A. 2004. Nanosponges: Plastic Particles Pick Up Pollutants. *Science News* February 21.

Grittini, Carina, Mark Malcomson, Quintus Fernando, Nic Korte. 1995. Rapid Dechlorination of Polychlorinated Biphenyls on the Surface of a Pd/Fe Bimetallic System. *Environmental Science and Technology* 29(11):2898-2900.

Hideen, Roberta. 2005. Phone Conversation. July.

Hood, Ernie. 2004. Nanotechnology: Looking As We Leap. *Environmental Health Perspectives* 112(13): 740-749.

Horst, John F., F. Lenzo, David Liles, David Vance, Jennifer Martin. 2004. Nano-scale ZVI-Enhanced reductive dechlorination of PCE DNAPL in fracture bedrock. *the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*

Hosein, Hazel-Ann, Daniel R. Strongin, Mark Allen, Trevor Douglas. 2004. Iron and Cobalt Oxide and Metallic Nanoparticles Prepared from Ferritin. *Langmuir* 20: 10283-10287.

Jafvert, Paul. 1996. Surfactants/Cosolvents. Ground-Water Remediation Technologies Analysis Center. http://www.clu-in.org/download/remed/surf_co.pdf

Kamat, Prashant, Rebecca Huehn, Roxana Nicolaescu. 2002. A "Sense and Shoot" Approach for Photocatalytic Degradation of Organic Contaminants in Water. *Journal of Physical Chemistry B.* 106(4): 788-794.

Karn, Barbara. 2004. Environmental Applications and Implications: How does nanotechnology relate to the environment?. Nanotechnology and the Environment: Applications and Implications. Oxford University Press.

Kim, Ivan, Hazel-Ann Hosein, Daniel R. Strongin, Trevor Douglas. 2002. Photochemical Reactivity of Ferritin for Cr(VI) Reduction. *Chemical Materials* 14: 4874-4879.

Kim, Jungbae, Jay Grate. 2004. Nano-Biotechnology in Using Enzymes for Environmental Remediation: Single Enzyme Nanoparticles. Nanotechnology and the Environment: Applications and Implications. Oxford University Press.

Kim, Jungbae, Jay Grate. 2003. Single-Enzyme Nanoparticles Armored by a Nanometer-Scale Organic/Inorganic Network. *Nano Letters* 3(9):1219-1222.

Kostal, Jan, Ashok Mulchandani, Katie Gropp, Wilfred Chen. 2003. A Temperature Responsive Biopolymer for Mercury Remediation. *Environmental Science and Technology* 37(19): 4457-4462.

Kostal, Jan, Ashok Mulchandani, Wilfred Chen. 2001. Tunable Biopolymers for Heavy Metal Removal. *Macromolecules* 34(7): 2257-2261.

Kumbhar, A., G. Chumanov. 2004. Synthesis and Characterization of Titania-coated Silver Nanoparticles. *Journal of Nanoscience and Nanotechnology* 4(3):299-303.

Lane, Neal, Thomas Kalil. 2005. The National Nanotechnology Initiative: Present at the Creation. *Issues in Science and Technology.* Summer 2005.

Lien, Hsing-Lung, Wei-xian Zhang. 2001. Nanoscale Iron Particles for Complete Reduction of Chlorinated Ethenes. *Colloids and Surfaces*. 191: 97-105.

Liles, David, Andrea Leeson. 2004. ESTCP Evaluates Bimetallic Nanoscale Particles in Treating CVOCs. *Technology News and Trends* 11:3-4.

Lin, Yuehe, Sandra K. Fiskum, Wassana Yantasse, Hong Wu, Shas V. Mattigod, Erich Vorpagel, Glen E. Fryxell. 2005. Incorporation of Hydroxypyridinone Ligands into Self-Assembled Monolayers on Mesoporous Supports for Selective Actinide Sequestration. *Environmental Science and Technology* 39(5):1332-1337.

Lin, Yuehe, Glen E. Fryxell, Hong Wu, Mark Engelhard. 2001. Selective Soprtion of Cesium Using Self-Assembled Monolyaers on Mesoporous Supports. *Environmental Science and Technology* 35(19):3962-3966

Lion, Leonard. 2005. E-mail Conversation. June.

Liu, Yueqiang, Sara A Majetich, Robert D. Tilton, David S. Sholl, and Gregory V. Lowry. 2005. TCE Dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. *Environmental Science and Technology* 39(5): 1338-1345.

Long, Richard Q., Ralph T. Lane. 2001. Carbon Nanotubes as Superior Sorbent for Dioxin Removal. *Journal of the American Chemical Society*. 123(9): 2058-2059.

Masciangioli, Tina, Wei-Xian Zhang. 2003. Environmental Technologies at the Nanoscale. *Environmental Science and Technology.* 37(5):102A-108A.

Mattigod, Shas V., Glen Fryxell, Richard Skaggs, Kent Parker. Mercury Removal from Melter Condensate Waste with Thiol-SAMMS Sorbent. Bench-Scale Treatability Test 2.

Mattigod, Shas V., Glen Fryxell, Richard Skaggs, Kent Parker. Mercury Removal from Melter Condensate Waste with Thiol-SAMMS Sorbernt. Pilot-Scale Treatability Test 3.

Mattigod, Shas V., Glen Fryxell, Richard Skaggs, Kent Parker, Sam Juraich. Mercury Removal from Melter Condensate Waste with Thiol-SAMMS Sorbent. Pilot-Scale Treatability Test 2.

Mattigod, Shas V., Glen Fryxell, Richard Skaggs, Kent Parker, Jun Liu, Xiangdong Feng. Mercury Removal From Waste Streams Using a Novel Synthetic Nanoporous Solvent. http://samms.pnl.gov/index.stm

Mattigod, Shas V., Xiangdong Feng, Glen E. Fryxell, Jun Liu, Meiling Gong. 1999. Separation of Complexed Mercury from Aqueous Wastes Using Self-Assembled Mercaptan on Mesoporous Silica. *Separation Science and Technology* 34(12):2329-2345.

Morello, Lauren. 2005. Tiny Particles Show Big Promise in Pollution Cleanups. *E&E Publishing: Greenwire* 4/28/2005. http://www.eenews.net/Greenwire/searcharchive/test_search-display.cgi?q=Nanotech&file=%2FGreenwire%2Fsearcharchive%2FNewsline%2F2005%2FApril28%2F04280523.htm

Moretz, Preston. 2004. Nanoparticles Developed That Could Clean Environment. *Temple Times*. http://www.temple.edu/temple_times/9-9-04/nanoparticles.html

“Nanotech is not so scary.” *Nature* 421(6921): 299. 2003.

NATO. 1998. NATO/CCMS Pilot Study: Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater. EPA 542-R-98-001c. Committee on the Challenges of Modern Societies. http://www.clu-in.org/download/partner/append-4.pdf.

Nagaveni, K., G. Sivalingam, M.S. Hegde, Giridhar Madras. 2004. Photocatalytic Degradation of Organic Compunds over Combustion-Synthesized Nano-TiO2. *Environmental Science and Technology* 38(5):1600-1604.

NNI (National Nanotechnology Initiative) What Is Nanotechnology?. Accessed July 2005. http://www.nano.gov.

Nutt, Michael O., Joseph B. Hughes, Michael S. Wong. 2005. Designing Pd-on-Au Bimetallic Nanoparticles for Trichloroethene Hydrodechlorination. *Environmental Science and Technology* 39(5):1346-1353.

O'Hara, Suzanne, Thomas Krug, David Major, Jacqueline Quinn, Cherie Geiger, Chris Clausen, Sam Yoon. 2004. Performance Evaluation of Dehalogenation of DNAPLs Using Emulsified Zero-Valent Iron. *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*

Oberdorster, Gunter, Eva Oberdorster, Jan Oberdorster. 2005. Nanotoxicology: An Emerging Discipline Evolving From Studies of Ultrafine Particles. *Environmental Health Perspectives* 113(7):823-839.

Okinaka, Kenji, Andreas Jasdanian, Hisashi Shimizu, Tomoko Okita, Koji Kakuya. 2004. Treatment of 1,1,1- Trichloroethane with Reactive Nanoscale Iron Products in Simulated

Groundwater. *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*. Paper 2E-01.

OnMaterials, Manufacturers of Zloy. Accessed July 2005. http://www.onmaterials.com/

Pacific Northwest National Laboratories. Accessed July 2005. Nanoparticles May Mean Longer Life for Enzymes. http://www.pnl.gov.

PARS Environmental. Accessed July 2005. http://www.parsenviro.com/index.html.

Prabhukumar, Giridhar, Mark Matsumoto, Ashok Mulchandani, Wilfred Chen. 2004. Cadmium Removal from Contaminated Soil by Tunable Biopolymers. *Environmental Science and Technology* 38(11): 3148-3152.

Quinn, Jacqueline, Cherie Geiger, Chris Clausen, Kathleen Brooks, Sam Yoon, Suzanne O'Hara, Thomas Krug, David Major, Woong-Sang Yoon, Arun Gavaskar, Thomas Holdsworth. Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. *Environmental Science and Technology* 39(5): 1309-1318.

Rajeshwar, Krishnan, C.R. Chenthamarakshun, Scott Goeringer, Milijana Djukic. 2001. Titania-based Heterogeneous Photocatalysis. Materials, Mechanistic Issues and Implications for Environmental Remediation. *Pure and Applied Chemistry.* 73(12):1849-1860.

Raloff, Janet. 2005. Nano Hazards: Exposure to minute particles harms lungs, circulatory system. *Science News* 167(12): 179

Roach, Bill. 2005. Phone Conversation. July.

Rose-Pehrsson. 2004. Sensors and Sensor systems: An Overview. Nanotechnology and the Environment: Applications and Implications. Oxford University Press.

SAMMS Technical Summary. 2005. http://samms.pnl.gov/samms.pdf. Accessed June 2005.

Schrick, Bettina, Jennifer Blough, Daniel Jones, Thomas Mallouk. 2002. Hydrodechlorination of Trichloroethylene to Hydrocarbons Using Bimetallic Nickel-Iron Nanoparticles. *Chemical Materials* 14(12):5140-5147.

Service, Robert F. 2005. EPA Ponders Voluntary Nanotechnology Regulations. *Science* 309: 36.

Service, Robert F. 2004. Nanotechnology Grows Up. *Science* 304: 1732-1734.

Song, Weigu, Vicki H. Grassian, SarahC. Larsen. 2005a. High Yield Method for Nanocrystalline Zeolite Synthesis. *Chemical Communications*. 20:2951-2953.

Song, Weigu, Gonghu Li, Vicki H. Grassian. Sarah C. Larsen. 2005b. Development of Improved Materials for Environmental Applications: Nanocrystalline NaY Zeolites. *Environmental Science and Techology.* 39(5): 1214-1220.

Strongin, Daniel R. 2002. Photochemical Reactivity of Ferritin for Cr(VI) Reduction. *Nanotechnology and the Environment: Applications and Implications STAR Progress Review Workshop.* http://es.epa.gov/ncer/publications/workshop/nano_proceed.pdf

The Royal Society. 2004. Nanoscience and nanotechnologies: opportunities and uncertainties. RS 19/04. Royal Academy of Engineering.

Tungittiplakorn, Warapong, Leonard W. Lion, Claude Cohen, Ju-Young Kim. 2004. Engineered Polymeric Nanoparticles for Soil Remediation. *Environmental Science and Technology* 38(5):1605-1610.

Tungittiplakorn, Warapong, Claude Cohen, Leonard W. Lion. 2005. Engineered Polymeric Nanoparticles for Bioremediation of Hydrophobic Contaminants. *Environmental Science and Technology* 39(5):1354-1358.

U.S. EPA. 1997. Permeable Reactive Subsurface Barriers for the Interception and Remediation of Chlorinated Hydrocarbon and Chromium(VI) Plumes in Ground Water. EPA/600/F-97/008. National Risk Management Research Laboratory. Office of Research and Development. http://www.clu-in.org/download/toolkit/remediat.pdf

U.S. EPA. 1998a. Advanced Photochemical Oxidation Processes. EPA/625/R-98/004. National Risk Management Research Laboratory. Office of Research and Development. http://www.epa.gov/ORD/NRMRL/Pubs/1998/625R98004.pdf.

U.S. EPA. 1998b. Permeable Reactive Barriers for Contaminant Remediation. EPA/600/R-98/125. Remedial Technology Development Forum Report. Office of Research and Development. http://www.clu-in.org/download/rtdf/prb/reactbar.pdf

U.S. EPA. 2004. Cleaning Up the Nations Waste Sites: Markets and Technology Trends. EPA 542-R-04-015. Technology Innovation and Field Services Division. Office of Solid Waste and Emergency Response. http://www.epa.gov/tio/download/market/2004market.pdf

Varadhi, Satya, Harch Gill, Louis J. Apoldo, Kaiti Liao, Richard Blackman, Wayne K. Wittman. 2005. Full-scale nanoiron injection for treatment of groundwater contaminated with chlorinated hydrocarbons. *The Natural Gas Technologies 2005 Conference.*

Wang, Chuan-Bao, WeiXian Zhang. 1997. Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs. *Environmental Science and Technology* 31(7):2154-2156.

Warheit, D.B., T.R. Webb, K.L. Reed, C.M. Sayes, and V. Colvin. 2004. Assessing the Pulmonary Hazards and Health Risks of Nano (Ultrafine) Particles and Carbon Nanotubes: Lung

Toxicity Studies in Rats and Relevance of these Findings for Humans. 227th ACS National Meeting Environmental Nanotechnology Symposium: Abstracts.

Williams, Eric, Robert Ayres, Miriam Heller. 2002. The 1.7 Kilogram Microchip: Energy and Material Use in the Production of Semiconductor Devices. *Environmental Science and Technology* 36(24):5504-5510

Wong, Michael S. Phone Conversation. 07/26/05.

Xu, Yinhui, Dongye Zhao. 2005. Removal of Copper from Contaminated Soil by Use of Poly(amidoamine) Dendrimers. *Environmental Science and Technology* 39(7): 2369-2375.

Yantasee, Wassana, Yuehe Lin, Glen E. Fryxell, Brad Busche, and Jerome C. Birnbaum. 2003. Removal of Heavy Metals from Aqueous Solution Using Novel Nanoengineered Sorbents: Self Assembled Carbamoylphosphonic Acids on Mesoporous Silica, *Separation Science and Technology* 38(15):3809-3825

Yeom, Ick Tae, Mriganka Ghosh, Chris Cox. 1996. Kinetic Aspects of Surfactant Solubilization of Soil-Bound Polycyclic Aromatic Hydrocarbons. *Environmental Science and Technology* 30(5): 1589-1595.

Zhang, Wei-xian. 2003. Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research.* 5: 323-332.