

U.S. EPA Workshop on Nanotechnology for Site Remediation
U.S. Department of Commerce
Washington, DC
October 20-21, 2005

CONTENTS

DAY 1 – OPENING REMARKS	2
Steve Lingle	2
Ben Wu	2
Can Nanotechnology Thrive in the Environmental Technology “Bazaar”?	3
Navy Strategy to Innovative Technology Implementation	5
STATE OF THE SCIENCE I	6
Nano-Scale Iron Particles: Synthesis, Characterization, and Applications	6
Oxidation of Organic Contaminants on Nanoparticulate Zero Valent Iron (ZVI)	7
Structure and Reactivity of NanoParticles Containing Zero Valent Iron (ZVI): Bridging the Gap Between Ex Situ Properties and In Situ Performance	8
STATE OF THE SCIENCE II	9
Heavy Metal Sequestration Using Functional Nano-Porous Materials	9
Dendritic Nanomaterials for Environmental Remediation	10
Nanotechnology and the Environment: Nano-Scale Research at Temple University	11
CASE STUDIES I	12
Field Performance of Nano-Scale Emulsified Zero Valent Iron (ZVI)	12
Use of Nano- and Micro-Scale Zero Valent Iron (ZVI) at Navy Sites: A Case Study	13
CASE STUDIES II	15
Implementation of a Nano-Scale Iron Source Remediation Demonstration – From Laboratory to Field	15
In Situ Groundwater Treatment Using Nanoiron: A Case Study	17
In Situ Treatments Using Nano-Scale Zero Valent Iron (nZVI) Implemented in North America and Europe	17
Evaluation of the Control of Reactivity and Longevity of Nano-Scale Colloids by the Method of Colloid Manufacture	18
BREAKOUT SESSIONS REPORTS — DAY 1	20
Blue Group	20
Green Group	22
Yellow Group	23
Red Group	25
Orange Group	25

DAY 2 – POLICY AND TECHNICAL ISSUES	27
Why This Workshop: Why Nanotechnology at EPA?	27
Legal/Regulatory/Policy Issues	28
Nanoparticle Transport in Porous Media	30
Nanoiron in the Subsurface: How Far Will It Go and How Does It Change?	31
Health Risk Assessment of Manufactured Nanomaterials: More than Just Size	32
Nano and the Public: Duh, Yuck, and Wow!	34
BREAKOUT SESSIONS REPORTS—DAY 2	35
Red Group	36
Green Group	37
Yellow Group	38
Blue Group	38
Orange Group	39
APPENDIX A – DETAILED NOTES RED GROUP BREAKOUT SESSION – DAY 1	40
APPENDIX B – DETAILED NOTES BLUE GROUP BREAKOUT SESSION – DAY 2	42

DAY 1 – OPENING REMARKS

Steve Lingle

Director, Environmental Engineering Research Division
Office of Research and Development
U. S. Environmental Protection Agency

Steve Lingle opened the session with a welcome to the delegates for this first workshop on nanotechnology and site remediation. He thanked the organizers of the workshop, which included U.S. EPA, other federal agencies of the Federal Remediation Technologies Roundtable, and the National Council for Science and the Environment. He said the meeting included a number of breakout sessions from which EPA hopes to obtain suggestions on research priorities for this emerging area.

Ben Wu

Assistant Secretary for Technology Policy
U.S. Department of Commerce

Ben Wu thanked the organizers of the workshop for beginning a process that involves environmental issues that are often overlooked in the development of nanotechnology policy. The workshop is very timely because the Department of Commerce (DOC) sees nanotechnology as the cutting edge of new commercial opportunities and recognizes that for these to go forward, and for the United States to maintain a leadership role, there needs to be an understanding of potential environmental safety and health concerns.

DOC has sponsored several workshops on moving nanotechnology from the research and development phase into commercialization. Leading this effort is the National Institute of Standards and Technology (NIST), with activities both in the Gaithersburg, MD, office and in Boulder, CO. The administration is committed to having the United States in the forefront of nanotechnology and has invested about 4 billion dollars, since National Nanotechnology Initiative (NNI) began in 2001. The United States, however, is not alone in recognizing the value of nanotechnology; many other countries are also investing in this area. Global public investment in nanotechnology for this year is estimated to be at 5 billion dollars with private venture capital contributing an additional 4 billion dollars. The United States needs to be very vigilant in ensuring a good investment climate to maintain its competitiveness. Nanotechnology has the potential to revolutionize manufacturing processes and may greatly improve pollution abatement and remediation activities.

Given what is at stake, it is imperative that the United States develop a regulatory framework for nanotechnology that is both protective and flexible. This can only be brought about by involving all the stakeholders very early in the process so that issues can be identified and addressed without unduly impeding commercialization of safe products.

In summary, in the United States there is a great deal of concern about the fate and transport of nanomaterials and their potential effects on human health and the environment. The state of knowledge in this area is not great and will require much more research to determine if there are any effects. This research is needed to assure the public that commercialization is occurring responsibly and to earn their trust. Without the public trust, the full introduction of nanotechnologies may not occur. The use of nanotechnologies for environmental applications will need coordinated advocacy if it is to find commercial uses other than nanoiron for chlorinated solvent remediation. These uses, such as radiation, chemical sensors, and treatment technologies, offer huge upsides that would benefit from having a unified voice. Finally, the United States must find ways to sustain commercialization of nanotechnologies while protecting the environment. The Department of Commerce supports EPA in its efforts to address the potential effects of nanotechnologies and will continue to be a partner with the agency in the future.

Can Nanotechnology Thrive in the Environmental Technology “Bazaar”?

Walter Kovalick Jr., Ph.D.

Director

Technology Innovation and Field Services Division

U.S. Environmental Protection Agency

Walter Kovalick talked about the commercialization prospects of nanotechnology in the environmental cleanup marketplace. Unlike other marketplaces, consumers are not anxiously awaiting the newest innovation in environmental cleanup. In fact they are generally suspicious of new products. EPA's Technology Innovation Program acts as an advocate for new technologies and its clients include facility owners or responsible parties, federal and state project managers, and consulting engineers, who mediate the marketplace.

In a market study completed this year, it was estimated that there are between 235,000 and 355,000 sites in the country requiring cleanup at an estimated cost of between 174 and 253 billion dollars. Many of these sites are leaking underground storage tanks and state voluntary

cleanup program sites. The U.S. market is large but is not growing very fast; however, the international market shows more promise.

In the past, the predominant treatment technology for addressing groundwater contamination has been pump and treat. While pump and treat is still the technology of choice, a number of innovative in situ technologies are beginning to be applied. These technologies are gaining acceptance and represent competition for nano-based technologies. The National Research Council put out a table describing the relationship between hydrogeologic conditions and relative difficulty in addressing various contaminants. Researchers looking for markets to break into would be well advised to note that there are many technologies available to address volatile organics in homogeneous sands but very few effective ones to address DNAPL contamination in fractured bedrock. By and large, DNAPLs in general and recalcitrant semivolatile organics tend to pose the most problems. Technologies being used for treating DNAPLs and hence competing for sites include in situ thermal, in situ chemical oxidation, surfactant co-solvent flushing, bioremediation, and nanotechnology.

In a study done by EPA, 15 field scale applications of nanoiron or bimetallic nano-scale iron were identified. In a majority of the field studies, nanoiron was applied by gravity-feed or low pressure injection to a source zone of TCE, TCA, and daughter products. Some of the sites were contaminated with Cr(VI). Issues identified with the use of nanoiron that need to be considered by researchers are:

- Potential rebound of contaminants after in situ injection of nZVI
- Iron passivation
- Agglomeration reducing effective distribution
- Expense
- Incomplete knowledge of mechanism — abiotic versus biotic degradation
- Difficulty projecting particle movement

Most technology development starts at the basic research level and proceeds through scale-up research, commercial evaluation and application, to acceptance. In the environmental field, this process has been found to take approximately 10 years. The environmental marketplace is driven and constrained by regulations and their enforcement. Stakeholders are reluctant to use new technologies because of their inherent risk and the markets are fragmented by state. For instance, acceptance in California does not necessarily lead to acceptance in Florida. In addition, the applications are mediated by locally based consulting engineers. A company wishing to gain access to sites to apply its technology generally has to convince a consulting engineering firm to champion the technology. Marketing directly to site owners is not generally effective. Third party testing of the technology is extremely useful in convincing practitioners of the efficacy of the technology.

A failure often observed in the environmental technology research community is in reporting their findings in context. Journal articles often are not clear about whether the results reported merely fill a data gap in a developing framework or is the final piece in the process that readies the work for application to a specific problem. Someone needs to take responsibility and report the results in terms of a time scale that clarifies whether the technology is ready for prime time or not. The point being that this should not be left to the customer to decide.

The Innovative Technology Program uses a variety of approaches to getting information into the hands of users. These include: exhibit booths at remediation conferences, fact sheets, a 6-page/bimonthly newsletter called Technology News and Trends, biannual CD ROM collection of all publications to date, Clean-Up Information web site (clu.in.org), Tech Direct (a 22,000 person list service for remediation professionals with 1-3 page summary of new documents and training), and internet seminars.

In summary, researchers should remember:

- “Getting the word out” is NOT the audience’s problem
- Not all results are created equal
- Interpreting CONTEXT is a critical function
- Be aware of your audience
- Successful information transfer requires thoughtful planning and execution
- Consider multiple channels of transfer

Navy Strategy to Innovative Technology Implementation

Richard Mach

Naval Facilities Engineering Command

The Department of the Navy has approximately 3,700 environmental restoration sites. This is up from the baseline set in 1996 of 3,256. About 74% of the 3,700 sites are in the remedy-in-place or response-complete stage. The Navy expects to have all its sites in a remedy-in-place status by 2014. Long term management activities will continue after this date. For emerging innovative technologies to be used at Navy facilities, they have to be commercially available before 2014. The Navy invests about \$300 million a year in environmental restoration.

Unlike the Army and Air Force, the Navy’s environmental program is centrally managed. As the program progresses, a greater amount of their budget has been going to operation, maintenance activities, and long-term monitoring. This trend led them in 2004 to adopt an optimization policy. The policy requires the use of the three NAVFAC optimization guidance documents, headquarters approval for all new pump and treat systems, third-party evaluation of cleanup plans to ensure all options have been considered, and tracking of project progress through a central computer system. The tracking process involves providing information on any optimization studies that are being done or are anticipated and their results and costs.

The Navy’s review of their in-place pump and treat systems resulted in the requirement that any new pump and treat system be approved by headquarters and that the request for approval show that pump and treat would be the most effective system in meeting cleanup goals.

About 2 years ago, the Navy formalized their environmental restoration technology transfer program. The objectives of this program are to transfer information on new technology developments and Navy-sponsored research, provide information on cost saving strategies for site cleanup, and share lessons learned between RPMs at other FECs. The program seeks a two-way information exchange and the technical content is driven by RPM needs. It uses web-based tools (www.ert2.org) for easy access and updates and features periodic reporting of milestones and technology transfer feedback.

To facilitate their Environmental Restoration work, the Navy has established workgroups in six key areas:

Meeting Summary EPA Workshop on Nanotechnology for Site Remediation

- Alternative Restoration Technology Team (ARTT)
- Cost To Complete (CTC) Workgroup
- Munitions Response Workgroup
- Risk Assessment Workgroup (RAW)
- Optimization Workgroup
- Geographic Information System (GIS)/Data Management Workgroup

The Navy has developed an approach for addressing DNAPL sites. This approach involves identifying target treatment zones and remedial action objectives for each zone. Treatment trains are then used to address each zone. Multiple remedial technologies can be used over time. For many cases, nanoiron may have a role to play during some part of the remediation. The approach also sets performance objectives for each technology considering its limitations and establishes an exit strategy. Frequent observation of results allows for optimization of the system by changing or modifying the technologies.

The Navy has introduced the concept of selecting the "right" technology. A "right" technology either reduces life-cycle cost or reduces risk of the overall remedy compared to not using the technology. In most cases, there are multiple right technologies that can be used. These technologies might include treatment trains used sequentially over time; treatment trains used simultaneously as part of a single treatment process; or treatment trains used in different target treatment zones.

The Navy needs more information on the performance of nanotechnologies in order to be able to properly evaluate them. There is a concern that the public and communities have issues with nanotechnologies in general. Mach has not seen this to be the case with nanoiron since they have been using zero valent iron (ZVI) for years starting with iron filing and moving to microiron and now nanoiron. While the Navy has not seen any problems with the nanoiron they have used on sites, there is still a question about its fate and transport that needs to be better answered. He encourages more research into this issue.

STATE OF THE SCIENCE I

Nano-Scale Iron Particles: Synthesis, Characterization, and Applications

Wei-Xian Zhang
Lehigh University

Particle size is a relatively important transport property in porous media. In theory, single particles that are around 100-150 nm have the highest mobility. Mobility falls off with both smaller and larger particles. Nanoiron particles have a tendency to aggregate so the individual particles optimally should be between 20 and 50 nm.

One method of making nano zero valent iron (nZVI) is by reacting ferric chloride in water with sodium borohydride, which yields Fe^0 , $\text{B}(\text{OH})_3$, H_2 , and NaCl . The general properties of this nZVI are 10-100 nm with a mean size of 50 ± 15 nm and a specific surface area of 10-50 m^2/g . If iron pentacarbonyl is heated to 200-250°C, it will disassociate into nZVI and carbon monoxide. The nanoparticles formed in this reaction are approximately 5 nm. Finally, reacting iron oxides with hydrogen will yield nZVI particles in the 200-300 nm size.

In terms of reactivity, if nZVI is placed in water, it will rapidly bring the redox value down. At concentrations as low as 0.031 g/L the redox will reach a value of less than -0.4 Eh (volts). nZVI has been found to be a very effective agent in dechlorinating chlorinated solvents.

In an experiment at a site containing chromite ore processing residue (COPR) two types of zerovalent iron were tested to determine their effectiveness in remediating contaminated water. COPR (10 g) was placed in water and 6 g of micro-scale ZVI was added to the solution. The micro-scale iron, while moderating the increase of Cr(VI) into the water was unable to prevent the concentrations from increasing. When 0.24 g of nano-scale iron was added to a solution containing 10 g of COPR the reaction was relatively rapid and in 10 days reduced the concentration of Cr(VI) from 50 mg/L to about 10 μ m/L showing the vast difference in reactivity between nano- and micro-scale iron. nZVI has also been used to reduce perchlorate, but the reaction is slow.

The surface area physics of nZVI is also important to its effective reactivity. For example, in typical nZVI, the larger the particle the lower the percentage of surface iron atoms as compared with the total number of atoms in the particle. For example a 50 nm particle has about 4% of its total number of atoms on the surface. While this compares favorably with the granular iron typically used in permeable reactor wall construction, (0.5 mm with a surface area of about 0.0004% of its atoms) it can be made better by constructing a porous iron nanoparticle.

Zhang has constructed porous nanoparticles using resin and template- directed synthesis. A 0.4 mm porous nanoparticle has an effective surface area of 2,100 m²/g as compared with that of a 0.4 mm nanoparticle's 1.9 m²/g. nZVI can also be made more reactive by including other metals in its construction (most notably palladium).

Untreated nZVI has a tendency to aggregate and settle out of solution over time. This settling reduces its effectiveness in treating plumes. The particles can, however, be treated with dispersants that effectively keeps them in solution. The presence of the dispersant reduces the effective surface area somewhat but also keeps the particles unaggregated and small and allows for more interaction with dissolved phase contaminants.

Oxidation of Organic Contaminants on Nanoparticulate Zero Valent Iron (ZVI)

David Sedlak

University of California, Berkeley

Not all contaminant problems can be solved by reduction. Some will require oxidation. These contaminants include the organics that are not readily amenable to biodegradation and metals and semi- metals that are best addressed by oxidative precipitation.

ZVI has been used extensively in permeable reactive barriers to reduce (dehalogenate) chlorinated solvents and sequester metals, and nanoparticles are beginning to be used for in situ remediation. In all of these applications, oxygen is undesirable.

However, a reducing system can be converted into an oxidizing system, and the reductive power of iron can be used for oxidation reactions. In an experiment with the pesticide molinate and ZVI, no change was observed in the concentrations of either one when bubbling nitrogen gas through the solution. Air showed a marked reduction in molinate. Oxygen achieved the greatest

reduction. In another experiment, granular iron with EDTA was used to degrade chlorophenol. The EDTA functioned as a restorative by stripping oxidized iron from the granulated iron surface and opening up more ZVI for further reaction.

Oxygen reacts with ZVI in two fashions. In the first, Fe^0 reacts with O_2 to form Fe^{+2} and O_2^{-2} . The O_2^{-2} reacts with hydrogen to form hydrogen peroxide, which reacts with more Fe^0 to form water. This is not a particularly useful reaction. In the second pathway Fe^0 reacts with O_2 to form Fe^{+2} and O_2^{-2} . The O_2^{-2} reacts with hydrogen to form hydrogen peroxide which reacts with Fe^{+2} to form Fe^{+3} and hydroxyl radicals (Fenton's reaction) that are highly reactive oxidants. The usefulness of the reaction depends on the efficiency of the branching process to favor hydroxyl radical formation.

To determine how much hydroxyl radical is formed, an experiment is conducted using benzoic acid as the organic to be oxidized. Hydroxyl radicals react with benzoic acid to form either o-, m- or p-hydroxibenzoic acid, which can be measured. At low pH (<4), the reaction results in a 5-25% production of radical hydroxyls. It does not appear to work well at higher pH although the reaction is still present at pH 8. What is not known at this time is whether the higher pH affects the branching ratio, producing less hydroxyl radicals, or whether the higher pH is slowing the reaction down; hence the same amount of hydroxyl radicals would be produced at the higher pH as at the lower one except it would take significantly more time.

There are several potential applications of using nZVI as a promoter of oxidation reactions. In water containing As(III), nZVI would produce an oxidation reaction that converts the As(III) to As(V) with the As(V) being adsorbed onto the iron oxide product from the reaction. In a laboratory experiment it was demonstrated that zerovalent iron at 6,000 mg/kg sand and gravel would effectively treat molinate contaminated water that was passed through it. This suggests that pesticide contaminated run-off might be effectively treated by collecting and passing it through a sand/ZVI infiltration basin.

Finally, ZVI acting as an oxidizing agent, might be used to treat low concentrations of recalcitrant, miscible, volatile organics, such as MTBE, MTBA, and 1,4-dioxane.

Structure and Reactivity of NanoParticles Containing Zero Valent Iron (ZVI): Bridging the Gap Between Ex Situ Properties and In Situ Performance

Paul Tratnyek

Oregon Health and Science University

nZVI reactivity can be looked at in two ways. The first involves reactions that are unique to nanoparticles and are not observed in construction-grade ZVI, such as the degradation of PCBs. The second is the improvement of a reaction seen in construction-grade ZVI. Improvements include faster reaction rates, such as those found with TCE and more favorable degradation products. For example, in the case of carbon tetrachloride (CCl_4), the construction-grade ZVI is more likely to produce chloroform than other less toxic degradation products. If nZVI shifts the reaction more to the less toxic degradation forms, then it will make iron a more desirable remediation option.

Not all nZVI are created equal and Tratnyek's group has been working with several different sources. There is Toda (RNIP), a nZVI that is created by high temperature reduction of oxides

by hydrogen and has an average size of 70 nm with a surface area of 29 m²/g. Two (Fe/B) are created by precipitation with sodium borohydride (Zhang of Lehigh University and Linehan of Pacific Northwest National Laboratory) and have an average size of 10-100 nm and a surface area of 33.5 m²/g. For reference, a Fisher Chemical product (Fe/elec) that is created by electrolytic processes has an average size of 150 μ m, a surface area of 0.1-1 m²/g, and falls into the micro-scale iron category. Each of these has some impurities. In addition to ZVI, RNIP has magnetite and sulfur fractions and Fe/B has iron oxide and boron. These impurities have some implications for the reactivity of the material.

Examination of the particles by transmission electron microscope (TEM) shows that the RNIP and Fe/B have different structural configurations. The TEM also shows that the two production methods produce different distributions of particle size with the preponderance of RNIP particles falling in the 10-40 nm range and the Fe/B being more evenly distributed over the 10 to 110 nm range. Both have the most particles in the 20 to 40 nm range. Using the distribution determined by the TEM, it is possible to estimate the surface area available for each material. Surface areas can also be calculated using gap adsorption methods. These techniques will not necessarily yield comparable numbers.

Three methods are used in the solution phase studies of nZVI. They are electrochemical, batch reactors, and in situ spectroscopy. The remainder of the talk was devoted to batch experiments with CCl₄.

The reaction of CCl₄ with nZVI produces chloroform, unknown products, chloride and Fe(II). nZVI prepared by Fisher electrolytic, Toda, and Zhang were pretreated by flash drying and reacted with the CCl₄. By measuring the concentrations of chloroform and CCl₄, a mass balance can be calculated that will yield an estimation of the amount of unknown products produced by the reaction.

The results of the experiment show that:

- Specific surface area is an important and challenging property
- nZVI gives greater reactivity than micro-scale iron for normalized mass, but not necessarily greater reactivity for normalized surface area
- Some nZVI gives more favorable products (low YCF [spell this out]) than other nanoFe⁰ (important to test nZVI for site-specific problems)
- Low chloroform yield from nZVI reaction with CCl₄ and injectability offer prospects for remediation

STATE OF THE SCIENCE II

Heavy Metal Sequestration Using Functional Nano-Porous Materials

Glen Fryxell

Pacific Northwest National Laboratory

Glen Fryxell reported on the development of hybrid nanoparticles that are a mixture of organic and inorganic materials for the sequestration of metals and radionuclides. Ideally the nanoparticle will be able to selectively bind specific metals, such as mercury, lead, and arsenic that are found in water or other liquids.

Nanomaterials are excellent for this task since they provide high surface area (capacity), well defined structure, high reactivity, and easy dispersability. Also they can be readily tailored for application in different environments.

The basic fundamental structural building blocks that are exploited in the construction of these nanomaterials are macro-molecular templates. Surfactant/oil/water mixtures provide for the formation of various shapes of micelles. By changing the ratio of the components of the mixture, specific shaped and sized micelles can be made. The micelles that are of interest are made of surfactants that have a rod shape — essentially cationic logs floating in solution. When these logs are exposed to routine sol-gel conditions (silicate anions), an anionic metastasis takes place on the outer surface of the micelle that results in a charge quenching of the micelle surface and a coating of silicate. By controlling the reaction, hexagonal nanoparticles are created that have these surfactant logs embedded in them. The particle structure, while siliceous, is not a true ceramic as it lacks rigidity. Calcining of the particles results in a ceramic structure, and the destruction of the micelles leaves a rigid, porous structure. Care should be taken in the calcining step because destruction of the micelles first will result in the collapse of the structure.

The pore dimensions for the project being discussed are in the 50-60 Å range, which yields a surface area of 900-1,000 m²/g. To make the pore surfaces both selective and reactive, a molecular self assembly technique is used. Self-assembly is driven by Van der Waals interactions between chains, as well as the interaction between the headgroup and the surface. The result is a very high density monomolecular layer binding surface. The name given to this process is Self-Assembled Monolayers on Mesoporous Supports or SAMMS. The value of SAMMS are:

- Extremely high surface area = high capacity
- Rigid, open pore structure provides for fast sorption kinetics (Polymer based structures are prone to swelling and shrinking which can affect the available reactive surfaces—rigid structures are not)
- Chemical specificity dictated by monolayer interface, easily modified for new target species
- Proximity effects allow multiple ligand/cation interactions
- Sequestration can be driven either by metal/ligand affinity or by adduct insolubility.
- Good chemical and thermal stability
- Easily regenerated/recycled

PNNL has been developing a nanoparticle for treating mercury (Hg) in solution. The particle uses a mercaptopropyl siloxane monolayer as its reactive surface. Hg atoms are captured by the sulfur. Silane loading density can be tailored to 4, 5, or 6 silanes/nm² which gives the particle the ability to absorb as much as 2/3 of its own weight in Hg. The particles have been used to treat laboratory waste, scrubber waste, and waste oils.

Dendritic Nanomaterials for Environmental Remediation

Mamadou Diallo

California Institute of Technology

Dendritic structures are built starting with an initiator core with covalent linkage of molecular connectors that lead to multiple branching sites. In an uncontrolled state, one obtains a "statistical structure" with random hyperbranched links. Under somewhat better controls, a dendrigrath structure that resembles a linear system of molecular links is produced. High levels

of synthetic control enable the synthesis of nearly monodisperse nano-scale ligands with well defined molecular composition, size and shape such as those found in dendrons and dendrimers. Dendritic structures are built by "generation" and each new generation could double the number of surface groups.

Dendrimers are soft, flexible polymers that can be made with open structures that allow water to pass through. The open structures (flexible scaffolding) are made in the first three generations of construction. Dendrimers can also be constructed as "containers" with accessible interiors that allow materials to enter the structure where they can be trapped. Finally, with generations of seven and above, the dendrimer has a densely packed surface (rigid surface scaffolding) and an inaccessible interior. These surfaces can be constructed to provide for a high capacity and recyclable sorption area for cations. Experiments have shown that dendritic polymers can remove all exchangeable Cu(II) from a water solution. The treatment system uses ultra-filtration for the recovery and regeneration of the polymers. A modified system has also been applied to copper- contaminated soil.

Anions present a somewhat different problem than cations in that they can have different shapes such as spherical (Cl^- , F^-), linear (CN^- , OH^-), trigonal or square planar (CO_3^{2-} , NO_2^- , CH_3COO^-), tetrahedral (SO_4^{2-} , PO_4^{3-} , CrO_4^{2-} , ClO_4^-), and octahedral ($\text{Fe}(\text{CN})_6^{4-}$, SiF_6^{2-}). However, a variety of modified dendrimers have been constructed that are capable of removing these anions and are recyclable. Dendritic macro-molecules can also be fabricated to sorb organic solutes as well as contain catalytic materials (such as those containing palladium) or ZVI to degrade organic molecules.

The ability to design and synthesize water-soluble or solid supported high-molecular weight dendrimer-based functional nanostructures with cation/anion binding functional groups, redox active metal ions and clusters, catalytically active metal ions and clusters, hydrophobic cavities, and bioactive active agents provides a ready tool for water and wastewater purification applications. While there have been numerous dendrimer toxicity and biodistribution studies carried out during the last 5 years, the effects of dendrimer core and terminal group chemistry, size, shape, and hydrophobicity on dendrimer interactions with cell membranes and toxicity are still not well understood. Also only a limited number of studies have been published on the fate and transport of dendrimers in the environment.

Nanotechnology and the Environment: Nano-Scale Research at Temple University

David Kargbo

U. S. Environmental Protection Agency, Region 3

One project at Temple involves the sequestration of metals by nanoparticles. The specific method involves fabricating zeolites by heating ash (municipal or fly) in the presence of sodium hydroxide. These zeolites have a nano-scale channel system ranging in size from 0.4 to 1.4 nm and a high surface area. They are predominantly faujasites, with traces of zeolite Na-P1, and sodalite octahydrate. The municipal solid waste ash and fly ash produced zeolites of similar composition.

The void space structure of the faujasite zeolite consists of an interconnecting three-dimensional network and possesses 8-Å (0.8 nm) pore openings on the external surface and 13-Å (1.3 nm) internal supercages connected by 8-Å pores. With a framework density of 12.7

tetrahedra/1000Å³, this nano-sized channel system provides a size- & shape-selective matrix for absorbed molecules/species. Molecules whose kinetic diameters are greater than the zeolite pore entrances will not be sorbed.

Three ash sources were used for making the zeolites. In sorption tests, it was found that two behaved similarly and satisfactorily (very good removal efficiency for Cr (1.4 Å diameter) and Cd (2.4 Å diameter)). The zeolites from the third source performed poorly. 1,000 ppm of Cr and Cd solution were passed through a column containing 200g of the best performing zeolite with a reduction of both to the 100 ppb range.

Another project uses zeolites to produce electrical gas sensors. Nile Red dye is synthesized in the zeolite supercages. The dye has good absorption and fluorescent characteristics and allows optical sensing of any changes in color that can be used to identify and quantify the presence of toxic gases.

The university is also involved in nanoparticle fabrication for environmental applications using what they call atomic tailoring. nZVI generally has to have a shell (oxide) to prevent agglomeration of the particles. By using this system, they can fabricate nanoparticles without the need to put a coating over the particles. This is done by reducing the particles' kinetic energy to a very low level. A pulsed laser beam is focused on a target into which a plume of gaseous material is injected and the gaseous material is deposited onto an extremely cold surface. The process can create glassy or crystalline materials. It controls the size of the nanoparticles, the active ions in them, and the separation between the ions, which yields a nano-patterned surface of sensor particles with nanometer precision. The technology can be used to produce chemical sensors.

Finally a project on the size-reactivity relationship of iron oxyhydroxide nanoparticles assembled within ferritin was described. The ferritin has 24 structurally similar polypeptide subunits that are self assembled into a spherical protein cage. Iron oxyhydroxide nanoparticles are formed within the cage cavity which is about 80 Å in diameter and accommodates up to 4,500 Fe atoms. These particles have been used to mediate the reduction of Cr.

CASE STUDIES I

Field Performance of Nano-Scale Emulsified Zero Valent Iron (ZVI)

Jacqueline Quinn

National Aeronautics and Space Administration

While ZVI permeable reactive barriers (PRBs) are effective in treating dissolved chlorinated volatile organic carbons (CVOCs), they are dependent on the dissolution and transport of the CVOCs; and do little to reduce the clean up time and long-term monitoring costs. Also, ZVI needs to be in the presence of water to promote reductive dehalogenation. The injection of ZVI into a DNAPL source zone only treats the dissolved phase at the edges of the DNAPL. Emulsified ZVI (EZVI) can be used to enhance the degradation of DNAPLs by enhancing the contact between the DNAPL and the ZVI particles. It works against the dissolved as well as the non-dissolved phase of the DNAPL.

EZVI is composed of food-grade surfactants, biodegradable vegetable oil, and water. The emulsion droplets are held together by the surfactant and contain iron particles in water

surrounded by the hydrophobic oil-liquid membrane. The hydrophobic membrane is miscible with the DNAPL which allows their diffusion through the membrane where they undergo reductive dechlorination in the presence of the ZVI (nano or micro) in the interior aqueous phase. In addition to abiotic degradation due to ZVI, EZVI contains vegetable oil and surfactant which will act as long-term electron donors; promoting anaerobic biodegradation.

Another plus for EZVI is that with the iron core it also is a DNAPL and will move in the subsurface in the same fashion as the target DNAPL. Hence, injecting it in the same area as the source zone will result in it following similar pathways which increase its chances of achieving contact with the DNAPL.

At site LC34, 700-750 gals of EZVI were injected into the aquifer using eight injection wells. The injection was at two discrete intervals between 16 and 24 ft below grade. Multi-level monitoring wells were placed downgradient to measure mass flux changes. Borrowing from the oil industry, they used a pressure pulsing injection technology. Pulsing, applied every $\frac{3}{4}$ of a second, causes a dilation of the pore structure in the subsurface, which allows the pulsed fluid to enter more of the formation. Non-pulsed liquids tend to follow the path of least resistance and result in less infiltration into the formation as a whole. Nevertheless, they encountered some control difficulties in getting the emulsion to the desired depths.

Where EZVI mixed with the TCE, a reduction of 80% of the mass was observed over 4 months. However, because of the injection control problems, which resulted in the EZVI migrating to shallow depths away from the TCE, the average TCE reduction was 58%. Dissolved TCE concentrations were reduced 60 to 100% at target depths and there was a 56% reduction in mass flux. The appearance of cis-1,2-dichloroethene and vinyl chloride suggested that the oil was also contributing to biodegradation of the TCE.

Laboratory tests were also conducted to evaluate EZVI. The tests compared the effects of vegetable oil & surfactant alone, nano-scale zero valent iron (nZVI), and EZVI on a TCE source placed in distilled water. The vegetable oil and surfactant alone resulted in a drop in dissolved TCE concentrations due to sequestering of the TCE within the emulsion but no degradation products. nZVI (Toda product) reduces the mass of the TCE but does not reduce the dissolved phase TCE concentrations, which remain stable at saturation levels. EZVI, because of sequestering of the source as well as destruction, reduced the dissolved phase TCE concentrations to less than 10% of saturation levels. There were no biodegradation effects observed, since the experiment used distilled water, which should not contain appropriate bacteria colonies.

Use of Nano- and Micro-Scale Zero Valent Iron (ZVI) at Navy Sites: A Case Study

Nancy Ruiz

Department of the Navy

The classical use of ZVI has been in PRBs to treat dissolved phase contaminants. There are two pathways of degradation using ZVI. The first is hydrogenolysis through sequential dehalogenation (TCE to DCE to VC to ethene). The second is beta elimination (TCE to chloroacetylene to acetylene to ethene). The latter occurs in 70-90% of the reactions with nZVI.

The Naval Air Station in Jacksonville, FL, has been in operation since 1940. The source of the contamination is from a leaking storage tank. Contaminants of concern are TCE, PCE, 1,1,1-TCA, and 1,2-DCE with TCE having a maximum concentration in groundwater of 26,000 µg/L. The areal extent of the contaminated area is about 1,450 yd².

The treatment system used about 300 pounds of a bimetallic nanoparticle consisting of palladized iron with a polymer support that was mixed with water and gravity fed through 10 injection points. Extraction wells were used to pull the treated water through the treatment zone. Extracted water was returned to a holding tank where it was used as make-up water for the feed system.

Initially there was good reduction in TCE levels with the production of nitrates and sulfates as well as ethene and ethane. However, there also was a significant increase in DCE levels, which they attributed to the inability of the system to drop the redox values to an appropriate level. The observed levels were in the -200 mV range (typical iron PRB levels are generally in the -400 to -750 mV range). Without the lower redox levels, abiotic degradation is slow to non-existent. Also they did not see an increase in pH, which is typical at iron barriers, nor did they see a decrease in alkalinity, magnesium, or calcium.

The reason for the poor redox levels may have been due to the recirculation system. It is possible that the system presented the nZVI with an excess oxygen supply that passivated it. In future designs of these systems, care should be taken that no oxidizing agents are introduced to the iron during storage or mixing.

The amount of nZVI chosen was based on a straight stoichiometric calculation of how much would be needed to treat approximately 125 pounds of TCE. It would have been better if the geochemical conditions in the subsurface were also considered to ensure a sufficient amount of nZVI to accommodate non-target reactions.

The next site to be discussed was RU-C4, Parcel C at Hunter's Point Shipyard, San Francisco, CA. The site operated from 1869 to 1986 as a ship repair, maintenance, and commercial facility. The primary contaminant of concern at RU-C4 is TCE. Possible sources for the contamination are a former waste-oil UST, grease trap and associated cleanout, and five steel dip tanks at a former paint shop. The treatment zone is approximately 730 yd³.

Micro-scale ZVI was injected between 10 and 30 ft below ground surface (bgs) at 3-ft intervals. Nitrogen was used as the carry fluid (avoiding oxidation passivation issues) with injection pressures ranging from 55 to 230 psig. The amount of iron needed was calculated to be 16,000 pounds based on an iron to soil ratio rather than an iron to contaminant ratio.

Approximately 99% of the TCE in the source zone was destroyed with no chlorinated daughter products. The ORP was significantly below -200 mV (in many cases below -400 mV) and the pH of the water increased 1 to 2 units. The reaction was definitely abiotic in nature. The highest concentration of dissolved TCE dropped from approximately 87.5 mg/L to under 1 mg/L with no observed rebound. The ORP levels generally remained depressed over time indicating the iron was still active.

Lessons learned at this site included:

- Inject the ZVI mass at a level much greater than stoichiometry

- Include long-term monitoring to ensure there is no rebound occurring
- ORP levels are a good long-term monitoring performance parameter

The principal contaminants at Naval Air Station, Lakehurst, NJ, are PCE, TCE, TCA, cis-DCE, and VC. The contamination extends 70 ft below the groundwater table with the largest mass being in the 45 to 60 ft interval below the groundwater table. About 300 pounds of palladized iron with a polymer support was mixed with about 18,000 gals of water and delivered via submersible pumps and direct push technology.

The results of this effort were similar to those found in Jacksonville. Only a slight decrease in ORP in 3 of 13 wells was observed with some wells having an ORP increase. The pH levels did not increase as expected nor was there a significant increase in chloride. Because there were increased contaminant levels in 50% of the monitoring wells one week after the injection, the large amount of injection water may have pushed the contaminated groundwater radially outward. Also, since the mixing water was not deoxygenated, the nano iron may have been passivated and as was the case in Jacksonville, the mass of iron injected may have been insufficient to create strong reducing conditions necessary for the abiotic reduction of CVOCs.

The cost of iron has decreased in the past year due to the decrease in cost of raw materials, increased manufacturing capacity, and increasing number of suppliers and vendors. The table below provides a representative sample. The prices are 6 months to a year old. Advice to RPMs would be to use granular iron to achieve appropriate redox conditions in the aquifer and the more expensive material to target strategic zones.

Iron Product	Supplier	Cost/Pound
"Catalyzed" BNP (dry nZVI)	PARS environmental	\$31-\$66/lb, depending on type
"Catalyzed" Zloy	OnMaterials, Inc.	\$23/lb
"Catalyzed" PolyMetallix™	Crane Company	\$72-\$77/lb, depending on quantity
"Catalyzed" RNIP	Toda America	\$26-\$34/lb, depending on quantity
Micro-Scale ZVI	ARS Technologies	\$1-\$1.70/lb
Granular Iron	Peerless Metal Products, Master Builders	\$0.40/lb

nZVI works but should be used wisely because of cost. Special care should be taken in its storage and handling to prevent its passivation. Consideration should be given to the amount of ZVI that will be needed to reach the required redox conditions in the treatment zone.

CASE STUDIES II

Implementation of a Nano-Scale Iron Source Remediation Demonstration – From Laboratory to Field

Keith Henn
TetraTech NUS, Inc.

Palladized iron is a nano-scale particle that uses ZVI as a core to provide electrons with a noble metal (palladium) on the surface as a catalyst. The particles are 10-600 nm in diameter.

The site on the Naval Air Station in Jacksonville, FL, is small with an underlying geology of silt to fine sand from 0 to 24 ft bgs and dense clay from 24 to 54 ft bgs. Groundwater, which occurs at approximately 7 ft bgs, flows to the southeast. The site is very well characterized with maximum total VOC concentration in the soil at 550 mg/kg and in the groundwater water at 80 mg/L.

The remedial goal as stated in the work plan was to reduce contaminant mass by 40-50%. This was not expected to achieve maximum contaminant level values, but it may allow for MNA as a follow-on. They estimated they would need between 210 and 1250 pounds of nZVI to achieve their goals. Their calculations were based on reaction to contaminants only and did not include the potential effects of other reactants in the subsurface. Because of budget constraints, they used 300 pounds.

The injection was carried out in two phases. The first targeted specific areas of concern. The second employed a recirculation system that used four injection wells and three extraction wells. Extracted water was pumped to a holding tank where it was mixed with nZVI and reinjected. The purpose of the recirculation system was to keep the iron in the source zone and facilitate mixing. Results in some wells showed a marked decline in TCE concentrations along with a slower decline of DCE followed by an increase in DCE as time went on. Besides monitoring ethene and ethane for evidence of degradation, they also monitored for the beta-elimination route associated with nZVI that includes acetylene, isobutane, and butane.

While ORP decreased in some wells to levels that would sustain abiotic degradation, it did not remain that way for long. Oxygen concentrations dipped somewhat in the source zones indicating anaerobic conditions but showed some rebound with time. During the 3 to 6 months after the injection period, one source showed a marked increase in methane and dissolved iron values, a rise in carbon dioxide concentrations, and a decrease in sulfate, which indicated that an anaerobic biodegradation process was occurring. Analysis for the dehalococcoides bacteria (species that will completely degrade TCE) in the site wells was generally negative.

An examination of contaminant concentrations in soil cores taken after the treatment indicated a general reduction in contaminant levels. Depending upon the estimation used for initial and final mass, the total mass reduction ranged from 16 to 62%.

The total cost to implement was \$260K (thousand) (2004). This breaks out roughly to \$112K for injection costs, \$37K for nano-scale iron (would be about \$5-\$14K today), and \$111K for monitoring. These costs compare favorably with other in situ remedies, such as chemical oxidation and bioremediation, which at this site would require bioaugmenting to work.

In summary, there was significant reduction in the parent compounds. A significant increase in daughter products (DCE and DCA) suggests a degradation route other than nanoiron. The production of some acetylene indicates nanoiron reactions were taking place. The longevity of the iron appeared to be between 6 and 9 months. Concentrations of dissolved contaminants rebounded in the source areas, which were expected.

In Situ Groundwater Treatment Using Nanoiron: A Case Study

Harch Gill

PARS

This case history involves the in situ treatment of a chlorinated solvents plume (1,1,1-TCA, TCE, PCE, 1,1-DCE, 1,1-DCA) at a former landfill. The groundwater at the site was very acidic (pH 3) and because of the low pH it created a variety of ancillary problems that included mobilization of soil metals (Al, Pb, Ni) and the degradation of a downgradient wetlands. The use of nano-scale iron (bimetallic with noble metal catalyst) resulted in an increase in site pH to over 6.5-7.0, which solved the metals problem as well as the adverse impact on the wetlands.

The site had a pump and treat system and downgradient monitored natural attenuation. These systems were costing about 1 million dollars per year. The new plan was to excavate the source area and treat the plume with nanoiron. The site occupies about 4 acres of land with the nano-treatment covering approximately $\frac{3}{4}$ of an acre. Groundwater occurs at about 2 ft bgs, the subsurface permeability was about 10^{-4} to 10^{-5} cm/sec with a flow rate of about 10-12 ft per year. The approach was to inject the iron in two phases. Phase one would entail injection of 3,000 pounds over 20 days, and some three weeks later, a phase two would be carried out with 1,500 pounds of iron over 10 days. He emphasized that, in their experience, one injection was generally not satisfactory. The iron was injected on a broad grid with 40-45 ft centers. In phase two, a 20-ft grid was used to apply the remaining iron.

In the field application, the nanoiron is delivered in 5-gal pails where it is mixed with water in 300 gal containers to form a slurry. They used two containers to maintain continuous injection. Because of the tightness of the aquifer material, they started off with an injection concentration of 5 g/L. As they became more confident that the aquifer material would "take" the slurry, they increased the concentration to 30 g/L. The initial injection dropped the ORP from 300 plus mV to around -500 mV and, as time went by, the ORP remained in the -200 to 250 mV range. Examination of the plume over time showed that it had shrunk and that the concentration of total VOCs had decreased to the 10s of $\mu\text{g/L}$ from the 1,000s present before treatment. Also, the nanoiron was still active several months after the second injection.

In summary, nanoiron treats dissolved plume and source area(s). There are no depth limitations. It is highly reactive with rapid degradation and no toxic intermediates. It is portable with low capital and operation and maintenance costs, and low ratios of nanoiron to contaminant are needed.

In Situ Treatments Using Nano-Scale Zero Valent Iron (nZVI) Implemented in North America and Europe

Florin Gheorghiu

Golder Associates, Inc.

The nano-scale iron that they used in their applications is a bimetallic material using iron as the base and palladium as the catalyst as developed at Lehigh University. Nano-scale iron (nZVI) provides a large reactive surface area with 2-5 nm particles giving approximately 142,000 m^2/kg . There are many advantages to using this technology:

- nZVI water slurry (no additives)
- Subsurface placement by gravity feed

- No special well construction needed
- Fast reaction time – real time monitoring and reactant dosage changes due to field observations
- Minimum design requirements/permit level design
- Does not eliminate anaerobic bacteria activity
- Flexible remedial system that can be modified with time
- Equipment needed to implement is minimal – data logger, mixing tank and injection well

Before beginning a nano-injection project, a good conceptual site model is needed that includes not only the site hydrogeology but also the geochemistry. Geochemistry is necessary for determining what else the nZVI will react with other than the target compounds.

In a pilot scale case study, 11.2 kg in 6,050 liters of bimetallic nanoiron (BNP) slurry was injected into fractured interbeds of sandstone and siltstone. The result after two days of monitoring was a reduction in TCE from approximately 14,000 µg/L to very low values. ORP values dropped from approximately 75 mV to between approximately -290 to -590 mV with dissolved oxygen concentrations also falling. The lowering of the ORP and dissolved oxygen values is expected to have some impact on the microbial community. However, results of sampling the microbial community before and after injection indicated there were no significant trends due to the injection. This study also showed that changing the amount of palladium used to make the BNP also changes its reactivity (slower). Less reactive nanoparticles will have a longer active period in the aquifer and will travel farther.

In comparing porous media with fractured rock, Gheorghiu thinks that because of the small fracture aperture, the nanoparticles have an opportunity to spread further in rock than in porous media. Also, less nZVI will be required in rock remediation than in porous media because more iron will be needed to address the contaminants dispersed through the pore structure.

In conclusion he has found:

- A dramatic decrease of VOC concentrations over a short time in fractured bedrock aquifers
- A slower, but steady decrease of VOC concentrations in primary porosity aquifers
- Iron particles travel with groundwater and move quicker in fractured media than in unconsolidated sediments
- There is a persistence of VOC treatment over a long period of time (BNP reacts quicker but is spent more rapidly, nZVI reacts slower but has a longer effect)
- nZVI does not eliminate anaerobic bacteria activity

Evaluation of the Control of Reactivity and Longevity of Nano-Scale Colloids by the Method of Colloid Manufacture

David Vance
Arcadis

Not all colloids are created the same. They are currently engaged in an evaluation of nanoparticles created by different manufacturers and manufacturing processes. There are three main processes:

- Bottom-up precipitation with sodium borohydride reduction being the dominant
- Bottom down attrition via ball milling

- bottom down iron oxides with hydrothermal reduction

For a manufacturing technology to be practical, it must produce an affordable product in large lot sizes (tons) in a relatively short time. The delivery of nano-scale particles is generally easier in fractured rock systems than porous systems. The size of the particle has a lot to do with its effective delivery, striking a balance between gravitational settling and attractive forces with 200 to 600 nm being ideal. Longevity is affected by passivation of the iron, dissolved inorganics (nitrates sulfates and possibly carbonates), unproductive hydrogen generation, and kinetic response.

Intrinsic manufacturing controls on colloid longevity include the particle morphology (shape, pits) and its crystal structure (size of crystal domains, kinks, amorphous zones); the deliberate addition of secondary constituents, such as catalysts and the unavoidable introduction of manufacturing impurities; and modifications made to the colloid surface (surfactants, inorganic inhibitors, catalysts). In the borohydride reduction process, a considerable amount of boron impurities remain behind. These impurities have the effect of slowing the iron reaction down, which is not necessarily a bad thing since it may be beneficial for the particles to remain active for longer than a few hours.

In head to head comparisons between a relatively large (400 nm) ball milled particle and a precipitated particle (<100 nm), similar reactivities were observed, implying there is more going on in the reactions than just surface area.

In testing the reactivity of various vendor supplied nanoparticles, they have come across three types of reactions. The first is a very rapid reaction where the material is depleted quickly. The second is a slow reaction that continues to take place over a long time. The third is a reaction that initially starts out rapid but quickly levels off to no reactivity. Note that there does not seem to be any intent on the part of the manufacturer to engineer these behaviors. So what is it about the material that moderates its activity from rapid to none?

They investigated the possibility of an oxidation or coating reaction during transport and storage but found that acid treatment did not regenerate it. The borohydride process leaves percent levels of boron in the colloid, which may affect the reactivity, or there may be some structural annealing or Ostwald ripening effect that is causing the crystal structure to change in an unfavorable fashion. They have found, however, that when they pallidize type two or three materials, the reaction kinetics are more like the first type of reaction, which is rapid and short. It should be kept in mind that these reactions occur and you have to test the product to determine what you have in hand.

Type one and type two each have a valuable niche. Type one colloids are of value for treatment of DNAPL or high concentrations of adsorbed CVOC. Think of the reductive version of strong chemical oxidation with a “champaign effect” being observed with the most extreme examples. Type two colloids are of value for the long-term treatment of dissolved CVOCs under natural flow conditions.

QUESTION AND ANSWER SESSION

Question: Will the generation of hydrogen in the treatment of arsenic produce arsine gas and pose a safety hazard to technical personnel?

Answer 1: Temperatures and pressures not generally found in the subsurface are required to produce arsine in this fashion needs.

Answer 2: High generation of hydrogen gas is a relative term. The small concentrations produced by these reactions should not be a problem even if some arsine is produced.

Question: I have a tetrahydrofuran in groundwater water problem. We have been using pump and treat but have switched to air sparging; however the air sparging does not seem to be able to reduce the concentrations below 2,000 ppb. Would ZVI work?

Answer: It is not likely to work through a reductive process, but you might be able to use the system being investigated by David Sedlak to produce an oxidation reaction.

Question: In the presentation by Keith Henn, he showed reduction of TCE in the plume as well as mass reduction at the source, but there was rebound. Is there an explanation for the rebound?

Answer: The nanoiron greatly concentrated in the plume and attacked the DNAPL source; however, not the entire source was reached, and it remained sufficiently strong to produce a rebound similar to original concentrations.

Comment: Also measuring the concentration in the water alone may not tell you much. You need to look to see if you have reduced the flux to determine how successful you have been.

BREAKOUT SESSIONS REPORTS — DAY 1

On day 1 of the workshop, five simultaneous breakout groups discussed research needs and data gaps and reported their findings to the plenary.

Blue Group

Jacqueline Quinn

National Aeronautics and Space Administration

Enhance Remediation

- Field Work – limitations of getting material where wanted with regards to DNAPL

- Injection techniques

- Need more data that can be used to validate modeling and QA/QC

- Use/set up national test sites

 - Need 4-5 major geologic groups

 - Examine placement and movement (F&T) of NP[spell out] (impartial documentation)

 - Emphasize treatment train (NP not only option) approach

 - Key site conditions to evaluate when to change technologies

 - Bench to pilot – permeability changes over time with injections OC[spell out]

- Broaden contaminant suite to include:

 - Energetics, radioactive, chemical weapons

 - Positive/negative synergies of multiple contaminants “cocktail treatment”

 - Examine where oxidation and reduction are required (treatment train) by-product production, metals mobilization

- Nanoparticles to Treat Vadose Zone and Above

Priority research for fate and transport

- Detection:

Assessing – no new requirement (remediation)
Need to understand fate and transport for potential negative impact of nanoparticles
Toxicology – acute/chronic
Material transformation
Durability of material
Agglomeration
Modeling colloidal transport – start in lab and verify/improve w/ field results

Detecting/assessing performance of nanoparticles and nano-structured materials in subsurface
Guidance for QA/QC for data validation
Statistical validity - no new methods required
Size, shape, properties of nanoparticles

Health/environmental hazards

Inhalation and Dermal Exposure – 70 nm – health impact
Threshold Size for Mobility Versus Human Health Risk (Toxicological Impact)
Environmental Toxicity

Four Top Priorities:

1. Sponsor national test sites

Suggest that in the process of cleaning up BRAC sites, which are all over the country, that several be chosen due to geology and contamination as test sites in the process of moving them from military installations to the private/local public sector. These sites could be used to address the fate and transport research needs listed below.

Fate and transport

Different hydrogeologic environments, including

vadose zone
surface soil
sediments
surface water

Injection technique optimization— injection technologies need to be more completely explored. What are the best techniques for getting nanoparticles where you want them? What are the best ways to control their movement in the subsurface?

Different contaminants

Laboratory data to support modeling with follow on field calibration and QA/QC guidelines would include validation of modeling results at national test sites.

2. Toxicological impacts

The group thought there was a large data gap in the toxicological effects of nanoparticles on humans or other environmental species. There is not much information on whether the nanoparticles will transform into something that is toxicologically dangerous. Do we understand the materials stability/durability, especially with regards to metals sequestration? An evaluation needs to be done on what the relationship of the size of a nanoparticle is to its potential toxicological impact. Is there an optimal size that meets remedial transport needs but is not so small as to present toxicological problems? An example of a 100-200 nm "macro-nanoparticle" was given.

3. Removal of nanoparticles if necessary in waste water and drinking water facilities
If these particles are going to be deployed to address water quality issues do we have the technology to ensure that we can recover them if it becomes known that they are harmful?
4. Treatment trains
Options available for combination
Optimization of combinations
Are there cost savings from using treatment trains, and how do the various combinations compare?
Positive/negative impacts

Comments:

Richard Mach. Since the mission statement for BRAC sites is to transfer them to productive use as soon possible, it is probably not possible to use them as test sites. If EPA or another entity take possession of a part of a BRAC base for this purpose, then that might be possible. Federal Agencies do have a right to claim a property before it is transferred but the window of opportunity is small. The bottom line is DoD cannot hold the property themselves for this purpose.

A discussion of whether the current national test site program (e.g., Dover Air Force Base) would meet the proposed testing needs ensued and it was concluded that the current program is very small and would not serve this purpose.

Green Group

David Vance
Arcadis

Key Data Gaps and Research Needs:

1. Risk

Fate and transport. While this may not be an issue in porous media, it is in fractured media. The key question is how to measure it. After the nanoparticle has been injected, how do you know where it ended up and how long it will remain active? The crustal abundance of iron is around 5%, so standard chemistry generally cannot distinguish between injected and naturally occurring iron. A technology is needed that can specifically identify low concentrations of metallic iron colloids.

2. Toxicity and exposure

There is a need to determine the toxicity of nanoparticles on flora and fauna as well as humans. Research into this area should result in toxicity risk numbers. If these are very low, how will we measure them in the environment?

3. Performance metrics/standards of the nanoparticles themselves

Currently there are no standards for nanoparticle manufacturing. One doesn't know how reactive a given batch of particles will be or how long they will last. Also there is no metric for measuring the success of an application.

4. Performance assessment of the contaminants being remediated, and rebound potential

5. Fate of bimetallic nanoparticle

This is an issue with particles using palladium. Palladium is a recognized carcinogen. There is a very small concentration in bimetallic particles that use palladium; however at low pH, it will solubilize. Under normal pH conditions, the palladium will just be a small colloid and may be immobile because it is so small, but we don't know what its mobility is.

4. Surface coatings for dispersal

This is a developing market that will aid in delivering the particles to the contaminants; however, there is some concern as to how well these techniques work and whether or not they will allow the nanoparticles to travel much further than normal (like off-site). Currently there is no way to predict this, and since the market is very proprietary, each vendor can be a little bit different and the toxicity of the coating is also unknown.

5. Emulsions

More evaluation of contaminant behavior in nanoparticle emulsions is needed. How much of the contaminant is eventually destroyed? Is there a portion of contaminants that partition into the emulsion but do not react with the nanoparticle or if they do react, how long does this process take?

Yellow Group

Carlos Nunez

Office of Research and Development

U.S. Environmental Protection Agency

1. Performance

Define when passivation of iron occurs

How to optimize purchase, storage and delivery mechanisms

Define agglomeration and ways to optimize it. How to keep nano as nano and not allow agglomeration that will reduce reactivity and transport?

What are the impacts of co-generated and co-located waste on performance?

2. Fate and Transport

Toxicity

What are the impacts of ZVI in the environment? For example the toxicity to Daphnia – upcoming Woodrow Wilson Center report

Are there human health impacts?

How to put into context of risk-based decisionmaking?

Key issue is in situ treatment in groundwater – what are the risks? What is the level of uncertainty?

Is nanotech really reducing the risk over the long term? Or only reducing mass and degrading the particles in the short term?

What are the perception issues (more concern w/ palladium than with nanoiron) and what science is needed to deal with perceptions?

Delivery systems and particle construction

Comparison of delivery techniques

How to make more particles effective in reaching the contamination (surfactants, emulsions)?

How to make a longer lasting iron?

Corrosion – can be high levels of colloids. Can nanoparticles be used in these conditions?

Monitoring

Need to measure the dispersion of the iron directly (this is an issue of cost and of public perception). More research on remote sensing as well as radionuclides.

Need methods for monitoring the fate of nanoparticles and direct and indirect measurements in different environments

Is intensive monitoring of particular demo sites sufficient or is there a need for a broader protocol for monitoring for all uses? Need to take into account the site characteristics

How to distinguish between attenuation and natural dispersion?
(need groundwater monitoring over an area)

Fate

What happens to disinfectants in drinking water (e.g. fullerenes and chlorines)?

How would you remediate the particles if you need to? (if a problem was found)

Push-pull tests – using surrogates for contaminants

Full life cycle analysis of the technology

Sequestering metals – a big problem for remediation. How can metals be minimized?

Is the degradation of ZVI the same as degradation of micro-scale iron and other forms of iron?

3. New technologies – additional nanomaterials

What is the next new material? (after iron)

The federal government should invest in developing additional nanomaterials.

On site generation of materials.

What are other materials that may be used?

Is ZVI the best (or just what is being used now)?

4. What are additional uses of existing nanotech?

What are opportunities for cleaning up other types of contaminants?

What is happening to other contaminants when nanotech is introduced to a site?

Need bench scale demonstration research for additional uses.

How to handle DNAPL in fractured bedrock?

How to design a system where one or two applications will be sufficient to reduce mass and transform contaminant?

5. Cost

What is the cost to remediate a site? Need a common metric to evaluate costs of different techniques.

What is the project cost per unit compared with other techniques?

How much of costs are performance indicators?

How can costs be reduced (a data gap)

Is cost related to performance?

6. Knowledge summaries/synthesis

Critical review – summarize the state of knowledge.

What is known now? Where are the data gaps? What are the research needs?

SERDP and others could do a directed call for research and data on nanotech for remediation.

Red Group

Jon Josephs
Office of Research and Development
U.S. Environmental Protection Agency

On day one, the Red Group selected the following research needs as the highest priorities:¹

1. Research on the fate and transport of nanoparticles and nanoparticle-sequestered contaminants
2. Research on toxicity (to humans and biota) of nanomaterials and derivatives formed after their release to the environment
3. Research on the best delivery methods for different nanomaterials/site conditions
4. Research to lower the cost of nano remediation (although this research should be conducted/funded chiefly by the private sector, rather than the government).
5. Research to develop nanomaterials with appropriate reactivity and mobility for different site conditions and contaminants
6. Research to extend nano remediation to other media (e.g., unsaturated soil and sediments)
7. Research to develop a tool or methodology for determining whether the use of nanotechnology is appropriate given site condition

Orange Group

Todd Anderson
Office of Science
Department of Energy

What research is needed to enhance remediation of contaminated sites using nanotechnology for in situ remediation?

1. Need a Better Understanding of Nano-Scale Chemistry and Physics – quest for intrinsic nano-scale processes and mechanisms – do they exist?
 Surface area vs. electronic effect
 Bulk properties vs. surface effect

¹ See Appendix A for detailed notes on the Red Group breakout session on Day 1.
Meeting Summary EPA Workshop on Nanotechnology for Site Remediation

Extrapolating current understanding from macro-scale and micro-scale to nano-scale – is it feasible or appropriate?

Is there a unique nano-scale physico-chemistry that cannot be identified at the macro-scale?

2. Research on methods for effective delivery of nanoparticles
Technology deployment and platform needs – scaling up to field scale application
3. The next generation (beyond nZVI)
Future nanomaterials for in situ remediation – technology development.
Emerging technologies/applications
Develop nanoparticles for treating emerging contaminants (NDMA, 1,4-dioxane, pharmaceuticals)
4. Fate and permanence of inorganics treated by nano metallic particles in the subsurface
Precipitated constituents (e.g., $\text{CrIII}(\text{OH})_3(\text{s})$)
Sorbed/sequestered constituents (e.g., AsIII)
5. Competitive inhibition and synergism (e.g., passivation of nZVI surface; anion inhibition of perchlorate degradation by ZVI, effects of multiple contaminants on nanoparticle reactions)

What are the priority research needs for assessing the fate and transport of nanoparticles in subsurface environments and for detecting nanoparticles in these environments?

1. Factors controlling fate and transport of metallic nanoparticles in the subsurface
Chemical
Physical
2. Develop monitoring and detection technologies for nanoparticles
3. Development and validation of multi-scale modeling of nano-scale transport and reactivity
Bench scale (columns)
Pilot scale, natural and forced gradient

What are the priority research needs for detecting and assessing the performance of nanoparticles and nanostructured materials in subsurface environments?

1. Need for rigorous, controlled-condition, field demonstration, complete with intensive monitoring, attempted mass balances, and modeling
2. In situ sensors, real-time techniques, and analytical methods for detection of nanoparticles

What research is needed to assess the potential human health and environmental effects of nanoparticles and nanostructured materials developed for hazardous waste remediation?

1. Potential intrinsic toxic properties at the nano-scale (can material toxicity properties known for traditional systems be extrapolated to nano-scale) due to size, shape, chemistry
2. Fate and transport
Studies to elucidate speciation of nanoparticle degradation intermediates and products—what happens if nanoparticles breakdown?
3. Secondary water quality impacts
Ecotoxicology effects
Facilitated contaminant transport—if a material is sequestered in a nanoparticle does this allow it to move better?
Effect do nanoparticles have on natural systems—would they affect the normal operation of natural attenuation?

DAY 2 – POLICY AND TECHNICAL ISSUES

Why This Workshop: Why Nanotechnology at EPA?

Barbara Karn
Office of Research and Development
U. S. Environmental Protection Agency

Barbara Karn opened the second day of the workshop by thanking all of the workshop organizers and crediting David Blockstein of the National Council for Science and the Environment for initially suggesting the idea of the workshop.

Karn explained that bringing attention to environmental nanotechnology applications and implications and building and sustaining a community of nanotechnology researchers has taken considerable effort over the last four years. A part of that effort involves embedding nanotechnology into EPA's overall mission to protect the environment and human health. She described EPA as the conscience of other government agencies, ensuring that they consider the environment and human health in their nanotechnology research programs. EPA also works with industry to foster the environmentally responsible development of nanotechnology and reaches out to the public to promote an understanding of the implications of nanotechnology on the environment and human health. EPA provides international leadership as well.

EPA has categorized its nanotechnology research as application and implication research. Applications research addresses existing environmental problems or the prevention of future problems. It mainly encompasses the use of nanotechnology in treatment, site remediation, environmental monitoring, and green manufacturing to clean up current industries. While EPA does not support green energy research, it certainly promotes it. Implications research addresses the interactions of nanomaterials with the environment and the potential risks their release might pose. This research encompasses toxicology; natural nano-processes; life-cycle aspects; fate, transport, and transformation; and exposure, bioavailability, and bioaccumulation. Much of the research until recently has focused on application issues, which EPA hopes to continue while building the implications research arm of the program.

EPA's external grants program, referred to as the STAR program, funds the majority of EPA's external nanotechnology research. Last year, EPA partnered with NIOSH and NSF in joint solicitations to award 19 grants related to the health and environmental effects of nanoparticles. The next solicitation, which is due out shortly, is a joint solicitation with NIOSH, NSF, and NIEHS on the health and environmental effects of nanoparticles. On November 2, EPA will hold its third grantees' workshop, during which grantees will discuss their research. A few Small Business Innovative Research (SBIR) program grants on nanotechnology are available. The Greater Research Opportunities is a smaller research program for universities with small research programs.

One of the largest programs increasing the research community is the American Chemical Society (ACS) symposia, which are 5-day meetings that include presentations on 65-70 research papers related to nanotechnology. The March 2006 ACS symposium will emphasize green chemistry (pollution prevention and sustainability). The due date for the call for papers is November 28, 2005. For more information see <http://www.scgcorp.com/2005nano/index.asp>.

EPA maintains internal coordinating groups and participates on government-wide committees. EPA's "Nanomeeters" helps coordinate intra- and inter-agency research activities. EPA's Science Policy Council is preparing a white paper on research needs and policy, which is due out in December 2005. EPA participates on the National Nanotechnology Initiative (NNI), including the Subcommittee on Nano-Scale Science, Engineering, and Technology and the Subcommittee on Nano-Scale Environmental and Health Implications (NEHI). NEHI is preparing a research document on nanotechnology implications.

Legal/Regulatory/Policy Issues

Marty Spitzer

House Committee on Science

U.S. House of Representatives

Marty Spitzer, who works with Chairman Boehlert of the House Committee on Science (Science Committee), said the Science Committee provides national oversight and coordination of nanotechnology. Spitzer is involved mainly with environmental issues.

In 2003, the Science Committee wrote and held hearings on the 21st Century National Nanotechnology Research and Development Act, which it now oversees and coordinates. This Act authorizes 3.7 billion dollars for nanotechnology research through FY 2008 for NSF, DOE, NIST, EPA, and NASA. The Act established the NNI, oversight and coordinating mechanisms, interagency committees, the National Nanotechnology Advisory Board, and annual progress reports to Congress. It encourages the growth of research and educational programs and partnerships between academia and industry. The Act recognizes the importance of societal concerns, which encompass environmental issues related to nanotechnology. While the Science Committee focuses mostly on the commercialization of nanotechnology as an economic engine, it has begun promoting the environmental implications and applications issues.

Funding for NNI has increased from 460 million dollars in 2001 to 1.1 billion dollars in 2004. In comparison, the private sector spent about 2 billion dollars in 2004 on nanotechnology. Most of those funds were slated for research, development, and venture capitalism to start up small companies. The states have spent about 400 million dollars mostly for infrastructure and research at public universities. Japan and Europe collectively spent about 2.8 billion dollars in 2004, and businesses outside North America spend about 2 billion dollars a year.

According to the Nanotechnology Advisory Panel, the United States still remains the world's leader in nanotechnology based on spending and number of patents and publications in high-impact journals. However, many other nations are catching up by increasing their investments or focusing on specific technology areas where they can excel and compete.

Nanotechnology, which is poised to impact nearly every aspect of our lives, is expected to continue this rapid growth rate. Lux Research, Inc., an independent research firm, says that in 2004, 13 billion dollars worth of products containing nanomaterials were on the market, globally. By 2014, 2.6 trillion dollars worth of nanotechnology products are expected to be on the market, representing a startling 15% of the world's manufacturing output. An estimated 10 million nano-related jobs are projected by 2014, representing 11% of manufacturing jobs.

The president requested over 80 million dollars for nanotechnology research in FY 2006 for societal implications. Of that amount, 38.5 million dollars will be directed toward environmental health and safety research. The rest is slated to address workforce, educational, and ethical issues. This funding does not include private sector money. Societal implications of nanotechnology represent about 8% of the federal investment in nanotechnology and 4% of that is for environmental concerns.

Alarmingly, very little is known about the implications of nanomaterials, including their risks and how those risks can be managed. The implications research will address real as well as perceived risks. While it may turn out that many, or even most nanomaterials will be proven safe, early evidence indicates that some of them are potentially harmful to human health and the environment.

When faced with a lack of information on the risks, studies show that members of the public get suspicious and fill the information gaps with their imaginations, which are influenced by their past experiences with failed technologies. However, when members of the public are taught about nanotechnology, evidence shows that 80% either favor it or are neutral toward it. The public wants to be informed, are suspicious of voluntary programs to deal with risk issues, and are suspicious of industry in general. This evidence suggests that if the real and perceived risks from nanotechnology are not addressed, commercialization of nanotechnology could be seriously hindered. The lesson is that we still have time to shape public opinion and perceptions and ensure a reasonable regulatory framework.

Not only does the public want a reasonable regulatory framework, so does business. Without regulatory protections and favorable public opinion, nanotechnology could cause reactions similar to those that have plagued genetically modified organisms in Europe.

The common ground among environmentalists, business leaders, researchers, and developers is the realization that a reasonable and stable regulatory framework and high quality information for the public are needed. However, the scientific building blocks are not in place for creating regulations. The basic nomenclature, for instance, is lacking. Regulators need an appropriate way to define and characterize nanomaterials in terms of surface area and other key parameters. Tools for toxicity screening and risk characterization of nanomaterials are largely nonexistent and may take several years to develop. After developing regulatory tools, they will have to be applied in life cycle terms, such as cradle to grave or cradle to cradle.

While the recognition is growing that with some adaptations, some of our existing regulatory programs may be able to address nanomaterials, disagreements have begun over how much adaptation is needed. Federal regulators will have to give special consideration to the many small businesses that are developing nanomaterials because most of them have only minimal experience dealing with the regulatory environment.

It has become increasingly clear that a comprehensive short-term and long-term research strategy with adequate funding is needed to support regulatory protections. Such a strategy should expand the focus of research to anticipate products in the pipeline of development. Most of the current focus has been on materials currently in the marketplace, largely ignoring products that will be introduced in 5-10 years.

Although consensus is lacking on some of the most important environmental research concerns, the Nanotechnology Advisory Panel's first report pointed to workplace exposure, disposal, reuse, and recycling as a key issue. Another key concern has to do with what the U.S. policy should be on dispersive uses.

In November, the Science Committee will hold its first hearing on the environmental implications of nanotechnology as part of its oversight of the nanotechnology field.

In answer to a question, Spitzer said that the Department of Defense is spending a substantial amount of money on nanotechnology. However, the Science Committee does not have jurisdiction over the military or health applications of nanotechnology. A participant asked if the Congress would be interested in doing a demonstration of nanotechnology on one of the many contaminated military sites in the District of Columbia to promote the technology to Congress. Spitzer said that although the Science Committee funds many demonstrations through its research and development program, it cannot do anything on military sites. In answer to a question about how the regulatory process will come about, he predicted it will be incremental, slow, and not as systematic as most people would like.

Nanoparticle Transport in Porous Media

Mark Wiesner
Rice University

Mark Wiesner thanked his research team and collaborators who are studying the transport, fate, potential impact, and control of the mobility of nanomaterials in the environment to ensure that they arrive when and where they are needed. Before releasing nanomaterials for site remediation, an understanding of their potential movements and impacts at each location is important because transport and fate affect efficacy and the potential for harm. Predicting toxicity, which involves fate and transport processes, is largely speculation at this point. Even nanomaterials with desirable properties, such as those that can enter cells and deliver medications, could carry unanticipated substances, like bacteria, in with them in Trojan horse fashion. They also might enter the food chain with the potential for toxicity and bioaccumulation at great distances from the installation point.

Toxicity studies have focused primarily on the fullerenes. Some of the early studies suggest that colloidal aggregates of one of the nC60 fullerenes (buckyballs) apparently are very toxic. The mechanism underlying the increased toxicity appears to be the production of reactive oxygen species that damaged lipid membranes. However, this interpretation of toxicity may have to be fine tuned. Wiesner's team has identified other possible mechanisms. More recent studies of the same material have shown decreased respiration rates in bacteria and an associated inhibition of colony growth. All of this suggests that it is not possible to talk about nanomaterials in monolithic terms.

The methods for making colloidal aggregates have been available for about ten years. The process involves adding and later removing solvents, which raises questions about the impacts of the solvents. Wiesner's team is studying the transport, potential for aggregation, and the interactions with surfaces and other contaminants and natural materials that could significantly alter nanomaterial function, stability, and reactivity. Risk from a media standpoint, has focused on toxic effects; however, risk involves hazard and exposure as well. While it is obvious that

mobility, and therefore risk, differs with different nanomaterials, the public may not be aware of this.

The nC_{60} molecules are relatively immobile in homogeneous porous media, but there is a high potential for these materials to destabilize and form colloidal aggregates. When put in water with no ionic strength, the molecules are stable for long periods. However, adding just a little salt causes them to aggregate quickly and settle out. Many spontaneously form aggregates in water, and they can vary in size, morphology, and mobility in porous media.

In studies to determine how to make nanomaterials mobile enough to reach their receptors, Wiesner has found that contrary to most predictions, the higher the velocity, the less mobile these particles are in porous media. This effect is probably linked to high Van der Waals attraction, a characteristic of the fullerenes. Surface chemistry changes mobility. The greater the affinity for water, the less sticky are the tested nanomaterials. Both transport mechanisms, which are dependent on the particle size distribution, and surface chemistry can be modeled.

Thus, just because materials are nanometer in size does not mean they are mobile. They have unique transport properties, and Wiesner's team is finding there are different mechanisms of toxicity as well.

Nanoiron in the Subsurface: How Far Will It Go and How Does It Change?

Greg Lowry
Environmental Engineering
Carnegie Mellon University

Greg Lowry explained that nanoiron has the potential for in situ treatment of groundwater (source or plume), particularly water contaminated with chlorinated organics and heavy metals, but they have to move over some distance because the treatment is injected into wells. Therefore, an understanding of the transport and fate of nanoiron in the subsurface is essential to optimize treatment and minimize unwanted exposures and risks.

For risk to occur, the receptor must be exposed, which raises several questions: What will the receptor be exposed to? How much nanoiron will reach the receptor? What conditions contribute to toxicity? Lowry's team has studied two types of nanoiron: Fe(B), which is an amorphous type made from borohydride reduction of dissolved Fe(III), and Toda RNIP (reactive nano-scale iron particle), which is a crystalline type of nanoiron made from gas phase reduction of FeOOH.

After reaction with TCE in water over several months, the ZVI is largely depleted from RNIP, but the result resembles the particle at the beginning of the process. The Fe(B) ends up resembling hexagonal-type crystals, probably due to oxygenated dissolution and re-precipitation. By putting the particles in water and measuring hydrogen evolution over time, they could track the amount of ZVI left in these particles and predict their lifetime. They found that different particle types have different lifetimes. For instance, at pH 8-9 (the equilibrium pH for these particles), almost all of the ZVI was oxidized to hydrogen in the Fe(B) within about 2 weeks; whereas, it took about a year for almost all of the ZVI to oxidize to hydrogen in the RNIP material. However, when the pH is reduced to 6.5, the RNIP iron particles last about 2 weeks. Therefore, the hydrochemistry plays a major role in the lifetime of these particles.

Nanorion is not particularly stable as a function of time. Dynamic light scattering data show that at very low concentrations (about 2 mg/L) the plot starts at about 100 nm. After 2-3 minutes, the size increases as these particles aggregate for several reasons. The final size after about 15 minutes is about 400 nm. At high concentrations (about 80 mg/L), most of the particles are at a micron, after 1-2 minutes, and after about 15 minutes, most of the particles are about 5 microns, demonstrating rapid aggregation.

Are aggregates of nanoparticles nano? The objective when treating DNAPLs is to minimize attachments to sand grains and flocculation. Thus, to increase transportability, the researchers have tried surface coating the particles with, for instance polyelectrolyte, surfactants, and cellulose/polysaccharides. The coatings enhance transport and provide an affinity for NAPLs. It is possible to select the distance one would like the particles to move based on the surface coating. Breakthrough curves for polymer modified RNIP at pH 7.6 show that at low ionic strength, transportability is much better than at high ionic strength. These findings indicate that transportability is a strong function of site hydrogeochemistry.

ZVI causes oxidative stress, a predictor of toxicity, because it forms charged particles that tend to penetrate brain cells. Also, there are reactive oxygen species on the iron. Mammalian brain macrophages (microglia) were studied because of the brain's relative importance to survival and because the brain is sensitive to oxidative stress. When the macrophages were exposed to iron particles, they took up the iron, which appeared to affect the mitochondria. Both ZVI and magnetite appear to cause oxidative stress at high iron concentrations.

In conclusion, the potential for toxicity warrants careful evaluation. ZVI fairly rapidly oxidizes to iron oxides. The transport of unmodified nanoiron in porous media is limited. Particle surface chemistry strongly influences transportability, which is a function of the type of modifier and the geochemical conditions of the aquifer. Matching surface modifications to site geochemistry offers the potential for well controlled placement.

Health Risk Assessment of Manufactured Nanomaterials: More than Just Size

Kevin Dreher

National Health and Environmental Effects Research Laboratory

U.S. Environmental Protection Agency

Kevin Dreher's research focuses on the pulmonary and cardiovascular toxicity associated with ambient air particulate matter (PM) and leaking sources, particularly ultra-fine particles in the same size range as nanoparticles.

The factors that regulate particle toxicity involve more than just size, and nanomaterials tend to have unique toxicities. Photo-catalytic nanometals are being used in cement, paint, and self-cleaning glass surfaces. The European Union is using photocatalytic innovative coverings for depollution assessment NOx reduction. However, questions about their environmental interactions, transformations, fate, and potential health effects have not been answered.

Companies in Europe are using cerium oxide nanoparticles (10 nm) in on-road and off-road diesel/gas additives, thereby increasing fuel economy by 12-20% while reducing emissions. Soon, these additives will be used in New Zealand and Asia as well. Studies of cerium additives confirm

that they reduce NO_x levels, increase carbon dioxide, and decrease PAHs. However, the diesel exhaust also showed a 50% increase in each of the following: benzene, 1,3-butadiene, and acetaldehyde, which are air toxics.

Numerous reports on the uncertainties in nanotechnology risk assessment were published worldwide in 2004, and many published papers stemmed from those reports. The uncertainties of the risk of nanotechnology can be characterized in terms of health, ecological, and environmental effects; and the toxicity metric (hazard identification), which is the property of the nanomaterial that correlates best with the toxic effect and is important for monitoring and setting standards. Other areas of uncertainty include nomenclature; exposure/detection; fate, transport, and transformation; waste generated; and production volume.

Thousands of publications related to air toxics have been published between 1982 and 2004, according to a query of PubMed's particle toxicology database, but only a few of them are about nanomaterials. So while very little information is available on the toxicity of nanomaterials, some information can be gleaned from the existing database.

Nanoparticle size is very important in terms of deposition, translocation, and fate in biological systems. For instance, one patient inhaled carbon black in the 5-10 nm range during pulmonary imaging. The particles were found later in the lung but also in the head, neck, heart, kidney, liver, and gastrointestinal track. This has been verified in an animal model system and appears to be a common effect among humans and other animals. Therefore, systemic as well as local health effects can be expected following nanoparticle exposure depending on the point of exposure. Also, the granulomas observed in the pulmonary tissue formed without evidence of inflammation, which suggests a new type of mechanism may be involved.

The effects of carbon-based nanomaterials on alveolar macrophages exhibit different dose-response curves. Studies show that single-wall carbon nanotubes are more toxic than multi-wall carbon nanotubes. This study demonstrates unique toxicities among the same carbon-based nanomaterials on a single cell type. Thus, categorizing nanomaterials for extrapolation may not be possible.

A study of the pulmonary toxicity of intact carbon nanotubes versus ground carbon nanotubes that may be created during use shows that the ground carbon nanotubes at the same mass basis cause a greater response on LDH activity and on the number of neutrophils, eosinophils, and total protein compared to intact nanotubes.

At concentrations as low as 60 micrograms per milliliter, single wall carbon nanotubes cause cellular toxicity in epidermal keratinocytes. They also generate hydroxyl radicals, possibly due to the iron in the nanotubes.

Fullerenes of the same size exhibit different degrees of toxicity on different cell types, and while they may be insoluble, they have a fair degree of toxicity, including developmental toxicity in *in vivo* studies.

In vitro intestinal toxicity testing of dendrimers suggests that their surface charge is more important than their size, with the cationic dendrimers having more toxicity than the anionic dendrimers, and the cationic dendrimers integrate more quickly into organs than the anionic

dendrimers. Cationic dendrimers impact some tissues, such as the lungs, spleen, brain, and liver, more than other tissues.

Studies of nano-titanium dioxide in rats suggest that while surface area may be more important than particle size, size and surface area characteristics do not regulate the pulmonary toxicity. Hydroxyl radicals also play a role.

Nanotoxicology for risk assessment is critical to ensure responsible development of the beneficial applications of nanotechnology. It is clear that nanotoxicology research will require a multidisciplinary and coordinated approach. For instance, toxicologists will have to work with material scientists to relate toxic effects to particle properties. Particle toxicity is multi-factorial, involving more than just particle size factors. Analyses of health effects need to include systemic toxicity, which may be more adverse than local toxicity. Nanomaterials have unique toxicities, which mean they cannot be grouped for extrapolation. Attention must be given to finding all of the unique properties of the nanomaterials that may regulate toxicity. Photocatalytic properties are important. Effective technologies are needed to detect nanomaterials in environmental and biological systems for exposure assessments. Work has not even begun on the health effects associated with the interactions of nanomaterials or nanotechnology applications with co-pollutants in environmental media.

Nano and the Public: Duh, Yuck, and Wow!

Julia Moore

Project on Emerging Nanotechnologies

Woodrow Wilson International Center for Scholars

Julia Moore explained that the “duh” term in the title of her presentation represents the fact that the public knows virtually nothing about nanotechnology. Often what they do know frightens them, which reflects the “yuck” term. However, when told that nanotechnology drugs will be able to treat cancer, they say, “wow.” These three factors represent important variables that nanotechnology scientists will have to deal with continuously in the years to come.

The Project on Emerging Nanotechnologies, sponsored by the Woodrow Wilson International Center for Scholars (which is part of the Smithsonian Institute) and The Pew Charitable Trusts, was born when it became apparent that nanotechnology had become part of the popular culture mostly in a negative way. Nanotechnology has spawned over 20 science fiction novels written since 1982, a variety of feature films, console video games, messages imbedded in ads, and public protests.

The commercialization of nanotechnology is growing rapidly. An NSF-funded study by *Small Times* magazine identified 475 products being produced by 215 of the over 875 nanotechnology companies. Similarly, an internal EPA survey identified over 270 firms with nano-products on the market. These products offer only marginal improvements over existing products, ranging from cosmetics and tennis rackets to underwear, self cleaning windows, and car paint.

The NSF reported on a study by researchers at North Carolina State University that says while over 80% of the public knows little or nothing about nanotechnology, it tends to see more benefits than risks, particularly in medicine. However, over 90% of those surveyed have little or

no trust in either government or industry to manage any risks associated with technology, including nanotechnology. People with higher educational levels reported the lowest trust levels.

The public knows that any technology will have benefits and risks. The nanotechnology- related areas that most frequently worry the public involve military uses, evil doers, weapons of mass destruction; long-term health effects; environmental impacts; loss of freedom and privacy; rush to market; and the insulation of scientists and regulators from those issues that most concern the public.

A study in the United Kingdom last year suggested similar results. About 29% of the UK's public claimed to have heard of nanotechnology, but only 19% of those surveyed could offer any kind of definition of the term. Of those who offered a definition, 68% said it would make life easier. The most frequent concerns they raised had to do with the loss of privacy, taxpayer development costs, and scientists trying to "play God." This last theme reflects the publicized view of Prince Charles who is inherently suspicious of technology and occasionally accuses scientists of trying to play God.

Nanotechnology's most important benefits perceived by the U.S. public include new and better ways to detect and treat disease (57%) and to clean up the environment (16%); increased national security and defense (12%); improvements in physical and mental abilities (11%); and cheaper, longer-lasting consumer products (4%).

A Royal Academy of Engineering Report (www.nanotec.org.uk/finalReport.htm) from the Royal Society released last year recommended that until more is known, nanoparticles and nanotubes should be kept out of the environment. Specifically, the report recommends that the use of free (not fixed in a matrix) manufactured nanoparticles in environmental applications, such as remediation, be prohibited until appropriate research can demonstrate that the potential outweighs the risks. This report is important because it is considered the gold standard for how to manage the risks and benefits of nanotechnology in Europe. The European Commission is looking to the UK and to a lesser extent Germany to lead Europe's management of nanotechnology, and U.S. environmental organizations would like the U.S. Government to hold to the Royal Society's recommendations.

Moore advanced a few recommendations of her own that she called Moore's Laws: (1) make your case (by obtaining third-party validation of your product's safety); (2) make friends (by reaching out to environmental organizations as Dupont has done recently with Environmental Defense and take every opportunity to educate people about nanotechnology to build public support); (3) make what you do transparent and make your top priority responding to public concerns; and (4) make sense (the public is not dumb; it knows when government and industry are not playing straight or are bending rules, and it will bite back).

BREAKOUT SESSIONS REPORTS—DAY 2

On day 2 of the workshop, five simultaneous breakout groups discussed public perception and communication; technology transfer and validation; and legal, regulatory, and policy issues and reported their findings to the plenary.

Red Group

David Carrillo

U.S. Air Force

1. Public Perception and Communication

Risk communication is needed to deal with public perception and requires a review of the:

- Definition of Nanotechnology

- Past use (history) under different names, such as

 - Paint pigments

 - Whiteners

 - Dyes

 - Cosmetics

- Processes used for years (+10 yrs)

- Understanding risks

 - Obtain knowledge from those, such as manufacturers, OSHA, NIOSH, NIH, and

 - European Union (EU) who have been using nanotechnology

- Need risk communication experts to lead multi-day session

2. Regulation

- Who is regulating now (OSHA, NIH, FDA, EPA, EU)?

- What are the current regulations on Nanotechnology?

- Future regulations on nanotechnology

 - Need funding

 - Need scientific base

 - Need R&D (yesterday discussions)

- Who leads (who will be the honest broker)?

- What needs to be regulated?

 - Exposure

 - Effects

- Drivers for regulations

 - Health and environmental pathways

 - Measurement issues

 - Health effects (example asbestos)

3. Technology Transfer

Because people are already using ZVI, public barriers for this technology may not be relevant at this point, but for other nanomaterials, the barriers and how to overcome them (needs) are listed here:

- Barriers

 - Nomenclature (names used)

 - Definitions

 - Unknowns

 - All of the above lead to negative public perceptions

- Needs

 - Research and development

 - Partnerships involving

 - Regulators

 - Universities

 - Manufacturers

Users
Public, including Congress (especially for funding and to keep informed)
Leads back to public perception and yesterday's discussions

Green Group

Don Lentzen
Department of Energy

1. Technology Transfer

The main concern is the reluctance to use the technology because of health and safety, effectiveness, peer review, cost-effectiveness concerns
Need more case studies that are peer-reviewed
Research to "tweak" it for use in the field to get the desired results

2. Validation

SITE (Superfund Innovative Technology Evaluation) program may be ending. It involved getting a company and funds in place to do a cleanup.
DoD ESTCP (Environmental Security Technology Certification Program) is a field demonstration program to ready technologies for use at DoD sites (internal program but maybe partnerships could be developed)
Environmental Technology Verification (ERT) program (EPA)
Recommend that all sites using nZVI should involve do [?] validation, health and safety testing, and publicize "success stories"

3. Intellectual Property: Potential Hindrance

Private companies may not be willing to share as much as they could
Will this technology become like emerging technology in pharmaceuticals?
Are there ways to deal with this in academia, federal agencies, and public companies? (c.g., NASA has developed a technology that can be licensed)

4. Public Perception

Validation of technologies will improve public perception
Engage environmental groups early on
Need more information to be able to assure the public
Temple University, PA, has an effective program to teach high school teachers about nanotechnology. More is needed to get nano into the educational system, and much care should be given to developing educational programs because so little is known about nanotechnology at this point
When educating the public, tell them the benefits, the risks, and the uncertainties.

5. Partnerships

Can we get the occupational health people together with those who are using the technology in the field?
Some consultants and other companies are taking first steps to look at the risks of the technology. For instance, there is a consortium forming in the UK (championed by Golder UK) to push the technology forward against a serious legal barrier that exists there. It is incumbent on companies to produce the material for a specific use to ensure that it can be

used safely. Part of the process of developing technologies must address health and safety issues

NASA and similar government sites may be good test sites, because they are somewhat enclosed, fenced, and government controlled

Yellow Group

David Blockstein

National Council for Science and the Environment

1. Needs Related to Information and Communication

Information products, e.g., fact sheets

Synthesized information, such as comparison chart of costs and benefits. Decisionmakers need to know when to apply nanotechnologies for remediation

Training courses

A coordinating office (one-stop shop) within EPA with responsibilities for everything from validation and testing to communication and public education

Programmatic focus with one-stop shopping on the EPA web site

Create a formal federal advisory committee to create public dialogue

Direct outreach to the states because they are regulators

Engage the public, but many key issues people need to know are not understood at this time, so

Basic understanding of nanotechnology for site remediation at a local scale and generally

2. Needs Related to Lack of Scientific Understanding

Funding for research, focusing on the understanding of transport, fate, and impacts of nanoparticles both on a local scale and generally

3. Needs Related to Connecting Research with Applications

Simplified information to compare technologies using costs/benefits

Increase SITE, ETV, DOE, etc. program budgets for technology transfer

Increase joint solicitations

4. Needs Related to Leadership

EPA programmatic element with a tie-in to coordination office

Coordination office because of the lack of communication among offices

Fact sheets to all agencies to inform them of nanotechnology

Basic training courses

Blue Group

Jon Josephs

Office of Research and Development

U.S. Environmental Protection Agency

The Blue Group selected the following as the highest priorities:²

Validation:

- Validation by third party important

² More detailed notes from the Blue Group on Day 2 can be found in Appendix B. Meeting Summary EPA Workshop on Nanotechnology for Site Remediation

Funding:

- Federal government needs to have a role in funding site demos (presumably at federal sites)
- Greater emphasis on applied research and field implementation in grants

Information:

- Website as site for all information on fate & transport, modeling and predictive tools, etc. (online proceedings from this workshop may be a start for this; also IRIS database, ETOP, CLU-IN)
- Ensure researchers understand needs of end users and address them in technology transfer plans
- Appropriate sites for innovative technologies should be identified, giving technology developers and vendors the opportunity to learn the needs of site managers before submitting proposals

Orange Group

Madeleine Nawar

Office of Air and Radiation

U.S. Environmental Protection Agency

1. Public Participation

How to establish trust?

Transparency (tell them what you know and do not know, and what you hope to know)

Increase meetings

Education/outreach

Make technology understandable using clear nomenclature

Determine how to disseminate information (consider media, fact sheets, libraries)

Demonstrate benefits

Remove the nano-label issue (explain as emerging technology not necessarily in nano-terms)

Focus on specific issues related to specific technologies

Communicate real and perceived risks and how they will be managed

Organize information types for different public audiences

Adapt current community relations protocol for nanotechnology

Need a process to evaluate risk

Funding for community relations and education (train the trainers so messages are consistent)

Funding for basic research on risk assessment and management

Program to fund help startup companies that make nanotechnologies to evaluate risk (e.g., Small Business Innovative Research Grants)

Develop inexpensive protocols to evaluate risk

2. Legal/Regulatory/Policy

Need to establish legacy standards for nanotechnology treated sites

Describe risks at the site

BUT we do not know the risks

Incentives for developers to contribute to risk understanding

Incentives for green manufacturing

APPENDIX A – DETAILED NOTES RED GROUP BREAKOUT SESSION – DAY 1

Red Group Breakout Session Notes on Research Needs/Data Gaps

Group participants included: Jon Josephs, EPA (Group Leader); Chris Clausen, University of Central Florida; Kathy Brooks, University of Central Florida; Suzanne Davis, California EPA; Tim Sivalec, General Electric; Cathy Davis, EPA and Keith Henn, Tetra Tech.

After discussions described below, the Red Group selected the following research needs as the highest priorities:

- Research on the fate and transport of nanoparticles and nanoparticle-sequestered contaminants
- Research on toxicity (to humans and biota) of nanomaterials and derivatives formed after their release to the environment
- Research on the best delivery methods for different nanomaterials/site conditions
- Research to lower the cost of nano remediation (although this research should be conducted/funded chiefly by the private sector, rather than the government)
- Research to develop nanomaterials with appropriate reactivity and mobility for different site conditions and contaminants
- Research to extend nano remediation to other media (e.g., unsaturated soil and sediments)
- Research to develop a tool or methodology for determining whether the use of nanotechnology is appropriate given site conditions

Notes from Breakout Group Discussions:

Group Leader Jon Josephs posed the following question: What are the research needs for nanoscale zero valent iron?

Chris Clausen: When the University of Central Florida (UCF) began its research on emulsified nZVI, sufficient quantities of nZVI were commercially available only from Japan and the material was too expensive. As a result, UCF manufactured its own nZVI. Although the material is now available from a number of commercial sources, it is still very expensive. Research to lower the cost of producing nZVI is needed.

In addition, delivery of emulsified nZVI was difficult and research was undertaken on delivering the material to the subsurface contaminants. Additional research is needed to find the best technologies for delivery of nanoscale or nanostructured materials to the subsurface, with the appropriate technologies depending on the nature of the nanomaterials and the subsurface conditions.

Also, cost-effective means of tracking the location of the nZVI in the subsurface are needed. Perhaps a remote tracking method based on the magnetic properties of ZVI can be developed.

Kathy Brooks: Research to extend the nZVI technology to unsaturated soils and contaminated sediments is also needed, as is research to extend the technology to other contaminants (e.g., PCBs). (UCF is currently performing research using microscale zero-valent magnesium to treat PCBs.)

Tim Sivalec: Raised the issue about the safety of injecting bimetallic particles into aquifers. The group agreed that further research is needed to ensure that the technology does not present unacceptable adverse effects on human health and the environment. This need is applicable to all nanoparticles, not just those based on nZVI.

Tim also said that research was needed to distinguish between the abiotic and biotic affects of nZVI.

(At this point, the discussions focused less on nZVI, and became more general.)

Suzanne Davis: Said that research is needed to better understand the fate and transport of nanomaterials, as is research on methods to monitor fate and transport of nanomaterials.

Jon Josephs: Said that nanomaterials are not equally reactive. Development of more highly reactive nanoparticles is needed.

Suzanne: Emphasized the need for more information about human and environmental effects. Toxicity studies need to be performed on the nanomaterials being used, as well as the materials remaining after use.

Jon: For nanomaterials that sequester contaminants rather than destroy them, he suggested that there may be a need for research to recover sequestered contaminants/nanomaterials and remove them from the environment.

Tim and Kathy: Agreed on the need for research on the long-term fate of nanomaterial-sequestered contaminants.

Jon: Commented that the use of nZVI as a catalyst for oxidation reactions (as described during one of the plenary presentations) doesn't seem especially promising, given the status of established chemical oxidation technologies.

Suzanne: Research is needed to make future decisions such as: Should nano be used for source reduction, plume mitigation or both? At what types of sites will it be effective? What are the criteria for determining whether its use is appropriate?

Tim: Research is needed to determine cost-effectiveness.

Chris: A research need is to develop a tool or methodology for determining when nanotechnology is an appropriate remedy.

Keith: Not all nano iron is created equal. We need information to pick the type of nano iron best suited for site conditions and contaminants (e.g., the nanoparticle reactivity and mobility appropriate for a given site).

APPENDIX B – DETAILED NOTES BLUE GROUP BREAKOUT SESSION – DAY 2

The participants included: Jon Josephs, EPA (Group Leader); Mitch Lasat, EPA; Lorraine Edmond, EPA; Robbie Hedeon, EPA; Nora Savage, EPA; Richard Mach, U.S. Navy; Krishna Reddy, University of Illinois; Emma Hayes, Environment Agency-England, UK; Cathy Davis, EPA; Christian Clausen, University of Central Florida; Harch Gill, PARS Environmental, Inc.; Scott Walsh, Environmental Defense (Notetaker); Chris Koerner, CDM; Paul Wolf, M & E; Dora Chiang, Earth Tech; Wei-xian Zhang, Lehigh University; Tom Nicholson, Nuclear Regulatory Commission; Richard Raetz, GRT, Inc.

Moderator's Summary – Blue Breakout Group

Tech Transfer:

Validation:

- Validation by third party important

Funding:

- Fed gov't needs to have a role in funding site demos
- Greater emphasis on applied research and field implementation in grants

Information:

- Website as site for all information on fate & transport, modeling & predictive tools, etc. (proceedings from this may be a start for this; also IRIS database, ETOP, CLU-IN)
- Ensure researchers understand needs of end users and incorporate them into tech transfer plans
- Solicitors should solicit appropriate sites for demonstration, giving proposers chance to talk to site managers before submitting proposal

Public Communication:

- Exposure can be limited to limit risk
- Nano iron less risky than contaminated material being remediated
- Data needed on exposure and toxicity to assure public
- Funding for communication will be needed
- Citizen's Guide to Nano Remediation would be helpful

Notes from Breakout Group Discussions

Tech Transfer/Validation:

Chris Clausen began the discussion by describing the successful tech transfer process for remediation with emulsified nanoscale ZVI from idea at University of Central Florida to field testing with support from NASA and an EPA SITE (Superfund Innovative Technology Evaluation) Program evaluation. Government support and field testing with independent agency evaluation were critical in commercializing this technology, which has been licensed to vendors. As an aside, a rumor that the SITE Program funding is being cut was confirmed by Navy and EPA representatives.

Recommendations:

A program for independent objective evaluation of what the nanotechnology is actually accomplishing is very important.

Government financial support is also important as the cost of developing and demonstrating remedial technologies can be greater than that which is affordable by private parties.

Richard Mach pointed out that there is a lack of agreement on what "tech transfer" includes. Different tech transfer mechanisms are applicable depending on the definition.

Group Leader, Jon Josephs said that the broadest definition of tech transfer will be used for the breakout discussions, so that the group recommendations will not be limited to certain aspects of tech transfer.

Krishna Reddy: Need a way to evaluate the readiness of technologies for field demonstrations.

Richard Mach: Moving technologies from researchers to use in field is essential. However, researchers don't always understand the needs of the project managers, which is detrimental to the tech transfer process. Researchers often don't have tech transfer or end user needs in mind when conducting research. Their goal is often to satisfy publishers, not technology users (e.g., project managers).

Recommendation:

Researchers must be required to demonstrate in their grant applications how the research and tech transfer plan will be implemented to meet the needs of technology end users, not research for the sake of research. Grant awards should be contingent on the applicants demonstrating that they have consulted with the end users and understand their needs.

Clausen pointed out that not all research findings need technology transfer. The research must first demonstrate the potential for the technology to be effective and capable of successfully completing in the remedial technology marketplace.

Mitch Lasat, EPA: Someone needs to put research results in context, to make the most promising technologies attractive for further research and funding.

Clausen: Many universities create incubator companies to commercialize their technologies. A big barrier is getting field tests, which requires regulatory agency approval.

Dora Chiang, EarthTech: The lack of information about nano-remediation presents difficulties for consultants evaluating the technology. She has a client asking if their site is appropriate for nano-remediation who wants to know: How ready is the technology? What kind of risk? What kind of effectiveness? How ready is the Agency to approve? State agency? It's difficult to find funding from government, easier to find funding from commercial clients like Lockheed.

Josephs: Agreed that the client would be taking a risk to use an innovative technology. However, more information is becoming available on nano-remediation, such as the workshop proceedings which will be posted on the Internet. In addition, EPA has a policy to encourage innovation, sometimes agreeing to share the risk if the technology should fail.

Mach: The risk of failure can be minimized by starting with benchscale testing of several promising technologies, followed by pilot-scale testing.

Nora Savage, EPA: While bench-and pilot-tests may answer questions about technology performance, answers are still needed to questions about the toxicity of nano-materials.

Lasat: Typical hesitancy from companies because none of us can answer their concerns about risk, effectiveness, legal problems they might face.

Recommendation:

Need to have a reliable, accessible source of information about the technology (a virtual center)

Josephs: EPA's online web site, the Environmental Technology Opportunities Portal (ETOP), is intended to be a one-stop shop for information on environmental technologies. It could be helpful in distributing the best available information about nano-remediation.

Lasat: Research proposals for field work get bad grades because field work because it is so hard to control the many variables. Therefore, universities usually have a preference for applied research than for field work.

Mach: Remediation market is smaller than most other markets.

Wei-xian Zhang, Lehigh University: Bottom line is money, a well documented test site demonstration takes a lot of money. Private entities are usually not in position to fund this; it should be the role of federal government.

Harch Gill, PARS Environmental: In working with most PARS clients, the first step, bench scale test for proof of concept, then a pilot test, applying info from lab to the field. Then full scale application. My clients usually have no interest in research or theory, but are interested chiefly in getting ppm below regulated concentration levels. PARS does obtain funding from clients other than Govt. However, DoD has been a prime mover in advancing this technology.

Mach: The Navy invites vendors to submit documentation about technologies which need sites where they can be applied. Other DOD Departments are doing the same and attempts are being made to consolidate these efforts. The submitted information is distributed to project managers who match the technology documentation with site-specific needs. This approach applies to all remedial technologies submitted, not just nano.

Zhang: That's a great way to do it, but it shouldn't be limited to DOD.

Mach: We're trying to spread the idea

Gill: In one case, the site managers did not have the money to buy enough nano-iron to do the job right. Presently, nano iron is best suited for hot-spot applications, use other techniques for other areas to control costs. The cost of nano iron will come down, and then it can be applied over larger areas.

Group Leader's List of Highlights:

Validation:

- Validation by third party important

Funding:

- Fed gov't needs to have a role in funding site demos (presumably at federal sites)
- Greater emphasis on applied research and field implementation in grants
- Information:
 - Website as site for all information on fate & transport, modeling & predictive tools, etc. (online proceedings from this workshop may be a start for this; also IRIS database, ETOP, CLU-IN)
- Ensure researchers understand needs of end users and address them in tech transfer plans
- Appropriate sites for innovative technologies should be identified, giving technology developers and vendors the opportunity to learn the needs of site managers before submitting proposals

Public Perception:

Josephs: The Royal Society report suggests there is the potential for large public backlash.

Gill: The public's concern is that injecting nano-iron into site could lead to transport far downstream. My concern is usually that it will travel far enough to reach the contaminants. Nano iron generally moves only tens of feet.

Clausen: Society doesn't understand that nano materials are all around us. Nanoparticles for remediation should not be treated any differently than any other substances, in that their toxicities should be individually evaluated. Discussions of toxicity need to be specific to the specific nanomaterials.

Cathy Davis, EPA: We need to keep in mind that nanoparticles are different than their larger scale counterparts; that carbon nanotubes are not the same as graphite. They don't have the same properties.

Josephs: Should EPA and vendors inform the public that there's a lot we don't know about this technology? How do we get the public to accept some degree of uncertainty?

Davis: The major part of the public perception problem is they only have a small amount of information. What scares the public is "free" nanomaterials, rather than fixed nanomaterials. There is also a public reaction to "releasing" something to the environment, rather than using it in a contained setting.

Mach: Fate and transport is key for public understanding; if it's not going to go anywhere and doesn't reach receptors, it doesn't matter whether it's toxic.

Lasat: We also need to think about ecological toxicity

Emma Hayes, UK EPA: We also need to consider how the press will react and affect public perceptions.

Josephs: How much outreach has anyone done with nano remediation?

Mach: We let the neighbors know. They usually don't worry about it; usually it's only the activists who worry about it.

Josephs: But it's important to generate data to demonstrate safety.

Scott Walsh, Environmental Defense: The public we talk to are worried, despite our efforts to provide a balanced message. Data are needed to assure public.

Josephs: Listed the following highlights:

- The public should be told that the remedy can be designed to limit exposure to nanoparticles, thereby controlling risk
- With nanoparticles typically being injected only in contaminant source areas, it is unlikely that they will migrate beyond the contaminated area
- Nano iron is less toxic, less mobile and less persistent than most hazardous substances being remediated
- Data is still needed on toxicity to assure public
- Funding for communication is important
- Information geared to the layman's level (e.g., A Citizen's Guide to Nano Remediation) would be helpful

Due to time constraints (the group had already run over into the lunch hour), the topic of Legal and Regulatory Issues was not discussed.