Nanoparticles in Environmental Engineering: Implications Ranging from Molecular-Scale Processes to Public Policy

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http://www.ebs.ogi.edu/tratnyek/
http://cgr.ebs.ogi.edu/iron/
1. Natural NPs
2. Anthropogenic NPs
3. Engineered NPs
4. Remediation with NPs
5. nZVI PRBs
6. Science issues
7. Risk
8. Policy

Nano-Technology
Devices with (Supra)molecular Scale Engineering

Environmental Chemistry
Fate and Effects of Chemicals (Natural and Anthropogenic)

Green Chemistry
Sustainable Chemical Production and Products
Nanoparticles—Earth Science Perspective

- Sources
- Thermodynamics
- Kinetics
- Nucleation
- Growth
- Aggregation
- Structure
- Phase Transitions
- Magnetism
- Characterization
- Modeling
- Fate
- Effects
Environmental Nanoparticles—Natural

Aquatic and Atmospheric

Fig 1 (McCormick et al. 2002); Fig 2 (Finnlayson-Pitts and Pitts, 2000)
Environmental Nanoparticles—Contaminant

Uraninite and Fullerenes in Atmospheric Particles

Environmental Nanoparticles—Manufactured

Characteristics:
- Fugitive vs. purposeful release
- Detection vs. remediation
- Absorbants, reactants, or catalysts
- Supported vs. unsupported

Examples:
1. Fullerenes
2. Carbon nanotubes
3. Titanium dioxide
4. Dendrimers
5. SAMMs
6. Iron oxides
7. Iron “metal”

Self-Assembled Monolayers on Mesoporous Supports (SAMMS)

- Absorbs large quantities of metals without creating secondary waste, and is disposable as nonhazardous waste.

- Advantages:
  - Macrocations (Ca, Mg, Na, K) and macroanions (Cl, CN, HCO$_3$, CO$_3$, SO$_4$) do not affect adsorption.
  - High loading (40 - 600 mg/g)
  - Fast Adsorption kinetics
  - High Selectivity Coefficient
  - Highly stable waste form
Nanotechnology for Environmental Remediation—2

'Nanorust' cleans arsenic from drinking water

Tiny tech promises 'no-energy' solution for global problem

HOUSTON, Nov. 9, 2006 -- The discovery of unexpected magnetic interactions between ultrasmall specks of rust is leading scientists at Rice University's Center for Biological and Environmental Nanotechnology (CBEN) to develop a revolutionary, low-cost technology for cleaning arsenic from drinking water. The technology holds promise for millions of people in India, Bangladesh and other developing countries where thousands of cases of arsenic poisoning each year are linked to poisoned wells.

The new technique is described in the Nov. 10 issue of Science magazine.

"Arsenic contamination in drinking water is a global problem, and while there are ways to remove arsenic, they require extensive hardware and high-pressure pumps that run on electricity," said center director and lead author Vicki Colvin. "Our approach is simple and requires no electricity. While the nanoparticles used in the publication are expensive, we are working on new approaches to their production that use rust and olive oil, and require no more facilities than a kitchen with a gas cooktop."

CBEN's technology is based on a newly discovered magnetic interaction that takes place between particles of rust that are smaller than viruses.

"Magnetic particles this small were thought to only interact with a strong magnetic field," Colvin said. "Because we had just figured out how to make these particles in different sizes, we decided to study just how big of magnetic field we needed to pull the particles out of suspension. We were surprised to find that we didn't need large electromagnets to move our nanoparticles, and that in some cases hand-held magnets could do the trick."

Three approaches to application of iron particles for groundwater remediation: (A) a conventional "permeable reactive barrier" made with millimeter-sized construction-grade granular iron; (B) a "reactive treatment zone" formed by sequential injection of nanosized iron to form overlapping zones of particles adsorbed to the grains of native aquifer material; and (C) treatment of non-aqueous phase liquid (DNAPL) contamination by injection of mobile nanoparticles. In B and C, nanoparticles of iron are represented by black dots and zones that are affected by nanoparticles are represented as pink plumes. In B, the nanoparticles are assumed to have little mobility in the porous medium; whereas in C, nanoparticles modified to impart significant mobility are necessary. Note that reaction will only occur when contaminant—either dissolved in the groundwater or as DNAPL—comes into contact with the iron surfaces.
First Pilot Demonstration—Trenton, NJ

# Commercial nZVI for Remediation

<table>
<thead>
<tr>
<th>Iron Product</th>
<th>Supplier</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Catalyzed” BNP (dry NZVI)</td>
<td>PARS environmental</td>
<td>$31-$66/lb, depending on type</td>
</tr>
<tr>
<td>“Catalyzed” Zloy</td>
<td>OnMaterials, Inc.</td>
<td>$23/lb</td>
</tr>
<tr>
<td>“Catalyzed” PolyMetallix™</td>
<td>Crane Company</td>
<td>$72-$77/lb, depending on quantity</td>
</tr>
<tr>
<td>“Catalyzed” RNIP</td>
<td>Toda America</td>
<td>$26-$34/lb, depending on quantity</td>
</tr>
<tr>
<td>Microscale ZVI</td>
<td>ARS Technologies</td>
<td>$1-$1.70/lb</td>
</tr>
<tr>
<td>Granular Iron</td>
<td>Peerless Metal Products, Master Builders</td>
<td>$0.40/lb</td>
</tr>
</tbody>
</table>

Table: Nancy Ruiz (NFESC, Port Hueneme, CA)
Environmental Fate and Effects of NPs

Fate = $f$ [Transport, Transformation]
Transport of NPs

Filtration Model:
- Collisions due to Brownian motion, interception, and gravitational settling.
- Sticking coefficient depends on particle and solution properties.

Figure: Calculated distance of 99% removal for 3 sticking coefficients. Assumes subsurface porosity = 0.36, GW velocity = 0.1 m/d, soil particle diameter = 0.3 mm, nanoparticle density = 6.7 g/m³.
Transport of NPs—Enhancement

Coating effects:
• Less particle-particle attraction
• Less particle-media attraction
• More particle-contaminant attraction

Coating materials:
1. Surfactants
2. Polysaccharides
3. Polyelectrolytes

Cartoon: Lowry (CMU), Photos: Schrick and Mallouk (PSU)
Reaction of NPs—Effects of Particle Size

\[ k_{\text{obs}} = k_{\text{sa}} a_s \rho_m \]

1) Specific Surface Area

2) “Intrinsic” site reactivity

![Graph showing specific surface area vs. particle diameter](image)

- <10 nm →
- >100 nm ↓
Reaction of NPs—Effects of Particle Size on Rate

Contaminant/Probe:
- \( \text{CCl}_4 \)

Conclusions:
- \( k_M \) (Nano > Micro)
- \( k_{SA} \) (Nano \( \approx \) Micro)

Also:
- \( k_M \) (Pure \( \approx \) Impure)
- \( k_{SA} \) (Pure > Impure)

Caveat:
- \( a_s \) (effect of oxides)

Tratnyek and Johnson (2006) NanoToday; 1:44; Sarathy and Tratnyek (in prep.)
Reaction of NPs—Effects of Particle Size on Products

\[ k_{CT} = k_m \rho_m = k_{sa} a_s \rho_m \]

\[ Y_{CF} = \frac{k_{CF}}{k_{CF} + k_{unk}} \]
Reaction of NPs—Aging

Aggregation, coagulation, dissolution, (re)precipitation, ripening, autoreduction, diagenesis, cementation, etc.

(Dry) Fe\(^{H2}\) exposed to DI water: Top = 2 hr, Bottom = 145 hr

TEMs from Don Baer (PNNL)
Reaction of NPs—Effects of Aging

Bimetallic nZVI
- Pd, Ni, provide catalysis
- Faster rates, other products
- Cost/benefit
- Poisoning

Emulsified nZVI (EZVI)
- nZVI in micelle of food-grade, biodegradable vegetable oil.
- Hydrophobic exterior miscible with NAPL.
  Direct treatment of DNAPL?
- Abiotic reduction inside micelle, biodegradation simulated outside.

Membrane Immobilized nZVI
Policy Implications—European Perspective

Precautionary Approach:
“We recommend that the use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications such as remediation be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risks.”

Nanoscience and Nanotechnologies: Opportunities and Uncertainties
Royal Society & Royal Academy of Engineering
July 2004 (http://www.nanotec.org.uk)
Policy Implications—U.S. EPA Perspective

Not-so Precautionary Approach:

• … Lead research on the fate of nanomaterials, such as zero-valent iron, used in the remediation of chemically contaminated sites.
• … Address impacts on the fate of other contaminants at remediation sites.
• … Collaborate with state environmental programs and academia on this research.
• … This could be conducted within a few years.
Policy Implications—EPA R&D Initiatives

**EPA (NCER) Nanotechnology Activities**

**2001/2002 RFAs**
- Environmentally Benign Manufacturing and Processing;
- Remediation/Treatment;
- Sensors;
- Environmental Implications of Nanotechnology (LCA)

**Applications and Implications**

**Building a Green Nanotech Community**

**EPA NanoMeeters**
- Dec. 2003 Societal Implications II
- Wilson Center Meetings
- SPC White Paper
- 2004, 2005 GRO

**SBIR Nanomaterials and Clean Technologies**
- ACS Symposia-2003, 04, 05
- Gordon Conference- 2006?
- Grand Challenges Workshop
- Interagency Environmental Conference
- Edited journals
- NanoRemediation workshop

Barbara Karn (US EPA, ORD)
Summary and Credits

Summary:
“nZVI and the related materials used for in situ remediation applications are not as small, reactive, persistent, or mobile as most of the materials for which specific evidence is available suggesting the potential for human or ecological risk.”


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  - Y. Qiang, A. Sharma, J. Antony (U. Idaho)
  - Rick Johnson, Jack McCarthy (OHSU)

- **Samples**
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  - W.-X. Zhang (Lehigh Univ.)
  - Clint Bickmore (OnMaterials, LLC)
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