Nanoiron in the Subsurface:
How far will it go and how does it change?

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Nanoiron treatment of source or plume is possible

$\text{TCE} + \text{Fe}^0 \rightarrow \text{HC Products} + \text{Cl}^- + \text{Fe}^{2+}/\text{Fe}^{3+}$
Conceptual Model

Potential human exposure

Goal: Maximize treatment, and minimize unwanted exposures

Need to understand transport and fate of nanoiron to optimize treatment and understand potential risks
Does Nanoiron Pose a Risk?

• Exposure
  – What are we potentially exposed to?
    • What Fe phases and nanoparticle sizes?
    • Does nanoiron change over time?
    • How quickly does it change?
  – How much are we exposed to?
    • Nanoiron transport distance?
    • What hydrogeochemical factors control it?

• Toxicity
  – Is there toxicity or ecotoxicity?
    • What conditions lead to toxicity?
Types of Nanoiron

**RNIP**
- Fe\(^0\) core
- Fe\(_3\)O\(_4\) shell
- FeOOH \(\rightarrow\) Fe\(^0\) \(\rightarrow\) Fe\(^0\)/Fe\(_3\)O\(_4\)

**Fe(B)**
- Fe\(^0\) core
- Borate shell
- Fe\(^{2+}\) + BH\(_4^-\) \(\rightarrow\) Fe\(^0\)/FeB\(_x\)/Na\(_2\)B\(_4\)O\(_7\)

Nanoiron After Reaction with TCE in Water

RNIP + TCE/H₂O

Fe(B) + TCE/H₂O
**Fe⁰ Corrosion Rate (pH=8-9)**

**RNIP**

Fe⁰/Fe₃O₄ + H₂O → Fe₃O₄ + H₂

**Fe(B)**

Fe⁰/FeBₓ/Na₂B₄O₇ + H₂O → Fe-oxide + H₂ + B₄O₇²⁻

~1 year

~1-2 weeks
Fe⁰ Corrosion Rate Depends on pH

RNIP

~2 weeks
pH=6.5

~1 year
pH=8.9
How long is Nanoiron Nano?

Concentration=1.9 mg/L
Stable size=~400 nm
Time=15 minutes

Concentration=79 mg/L
Stable size=~5000 nm
Time=10 minutes
Nanoiron Transport is a Filtration Problem

Flocculation and straining (cake filtration)

Particle-DNAPL Interactions (Attachment)

Particle-Media Interactions (Attachment)

**Uniqueness** - High particle concentration and flow velocity
Nanoiron Aggregation Affects the Ability to Transport

Nanoparticles are aggregated and filtered through a monolayer of sand in a micro-fluidic PDMS cell.

Time=1 min

Time=10 min

Micro-fluidic PDMS cell

Nanoiron aggregates are filtered
Surface Modifiers Increase Transportability

1. Potential Surface Coatings
   - Polyelectrolyte
   - Surfactants
   - Cellulose/polysaccharides

2. Enhanced transport
   Charge and steric stabilization minimize particle-particle and particle-media interactions

3. Affinity for DNAPL
   Surface coatings provide affinity for NAPL
Effect of Different Modifiers

\([\text{Fe}^0] = 3 \text{ g/L}\)

Potential to select transport distance
Hydrogeochemical Effects on Nanoiron Transport

Transportability is a strong function of site hydrogeochemistry.

Systematic evaluation of hydrogeochemical effects is needed.
Nanoiron Toxicity?

Why suspect that ZVI causes OS?
• Surface chemistry
• Reactive oxygen species
• Literature-daphne, fish ….. glutathione depletion

Why the brain?
• Serious consequences from damage
• Target of OS-lipid content…high energy use
Nanoiron Toxicity

Mammalian brain macrophage (microglia)

✓ Fe⁰ and modified-Fe⁰ (1-30 ppm)
✓ Whole-cell and genomic responses
  ✓ OS-specific endpoints
  ✓ TEM, confocal microscopy
Fe$^0$-induced Oxidative Stress in CNS Cells

Response of Microglia (BV2) and Mesencephalic Neurons (N27) to Iron Nanoparticles (1-30 ppm)

Future Studies: Apo E Mice and Medaka Fish
Conclusions

• Potential toxicity risk warrants careful evaluation

• Fe$^0$ fairly rapidly oxidizes to Fe-oxides
  – Fe$^0$ lifetime ranges from weeks to a year
  – Lifetime depends on nanoiron properties and geochemical conditions (e.g. pH)
  – Unmodified nanoiron rapidly aggregates, size is concentration dependent
Conclusions

• Transport of unmodified nanoiron in porous media is limited.

• Particle surface chemistry strongly influences transportability
  – function of modifier type and geochemical conditions
  – May be predictable from filtration/colloid transport theory
  – Matching surface modifications to site geochemistry offers the potential for well-controlled placement
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