**RISK*e*Learning**

# Nanotechnology – Applications and Implications for Superfund

March 15, 2007
Session 3:
"Nanotechnology – DNAPL Remediation"
Dr. Matt Hull, Luna Innovations, Inc.
Dr. Peter Vikesland, Virginia Tech
Dr. Greg Lowry, Carnegie Mellon University

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# Magnetite Nanoparticles for Remediation of Contaminated Groundwater

Funded by an EPA SBIR grant
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## Overview

- EPA SBIR Program
- Magnetite Characterization and Reactivity
  - Why Magnetite?
  - Synthesis and Characterization
  - Carbon Tetrachloride
  - Preliminary Results
- Encapsulation of Nanoparticles
- Thoughts on Nanotechnology EHS
- Conclusions

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## EPA SBIR Program

**Goal:** Research, develop, and commercialize high-risk/high-payoff technologies that help solve environmental challenges.

| Phase I | → | Phase II | → | Phase III |
|---|---|---|---|---|
| Demonstrate Technical Feasibility | | Optimization and Scale Up | | Commercialization of Actual Product |

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## Luna/VT EPA SBIR Program (Status: Phase II)

- Develop magnetite nanoparticles for remediation of chlorinated organic compounds (other targets)
- Develop delivery strategies that facilitate particle delivery to subsurface and interaction with target
- Scale-up production of Phase II-optimized magnetite form for commercial application

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# Magnetite Characterization and Reactivity

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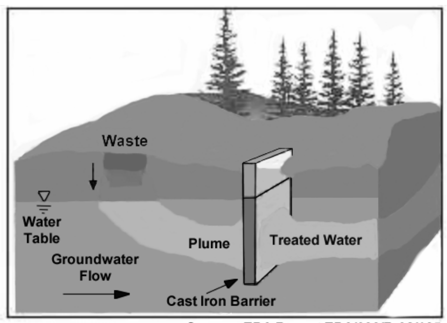
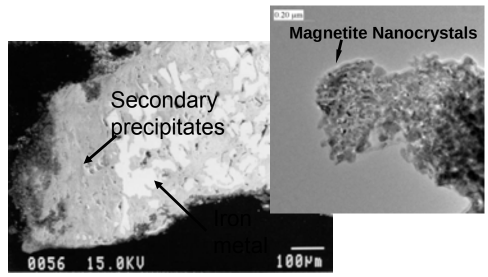
## ZVI Permeable Reactive Barriers Effectively Treat Many Groundwater Contaminants

Fe(0) → Fe(II) → Fe(III)




Source: EPA Report EPA/600/R-98/125

**Nanoscale corrosion products form over time**




(Source: Kohn, Livi, Roberts, and Vikesland, ES&T 2005)

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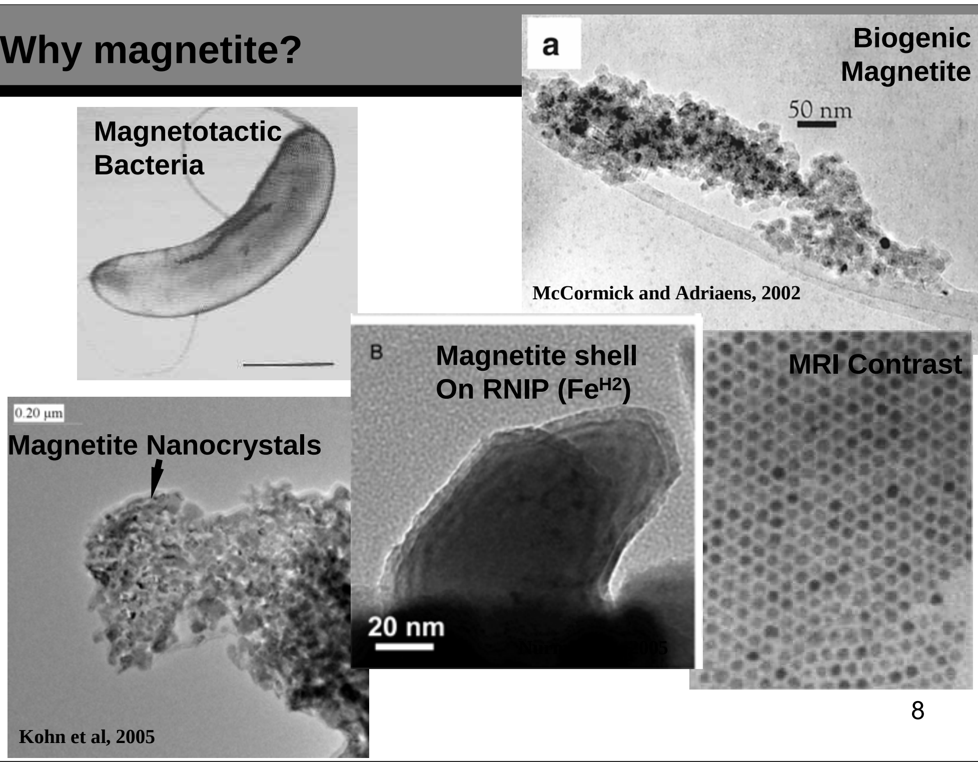
# Why magnetite?

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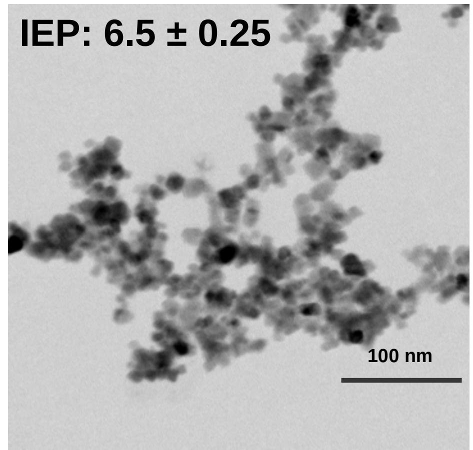
## Magnetite Synthesis and Particle Characterization

- Co-precipitation Method
  - Vayssières et al. J. Coll. Int. Sci. 1998
  - Mixture of $FeCl_3$ and $FeCl_2$ to NaOH
  - Rapid stirring

- Mean Particle Dia. = $9.2 \pm 1.6$ nm




***Synthesis done under conditions of strict oxygen exclusion***

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# Carbon Tetrachloride (CT)

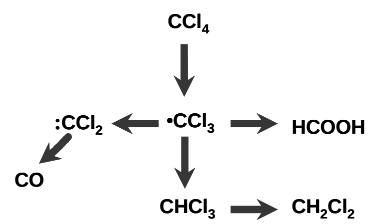
- Manufactured Chemical
  - Refrigeration fluid
  - Propellants for aerosol cans, fire extinguishers
  - Pesticide
  - Cleaning fluid, Degreasing agent

- CT and Human Health
  - Found at 425 of 1,662 EPA NPL sites
  - Exposure via contaminated air, water, soil
  - Damage to liver, kidneys, nervous system.
  - Likely Carcinogenic (DHHS, IARC)
  - EPA limit for drinking water **5 ppb**

- Difficult to Remediate
  - Generates **toxic intermediates**:
    - Chloroform ($CHCl_3$)
    - Dichloromethane ($CH_2Cl_2$)
  - Current methods transfer pollution problem

Source: http://www.exaktaphile.com

CT Breakdown Pathways

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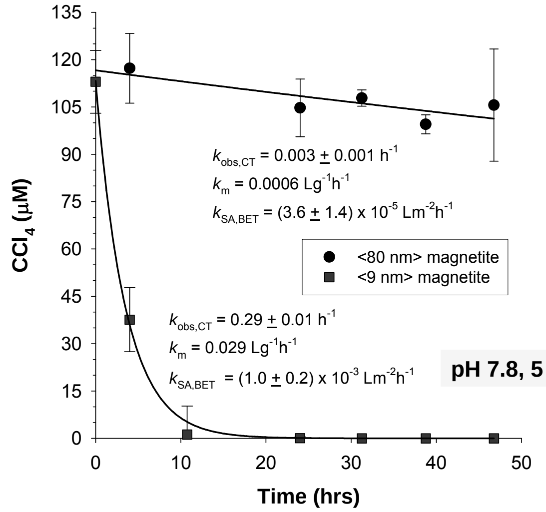
## Carbon Tetrachloride Degradation by Magnetite

- **Reaction rates vary with the size of the particles**




$k_{obs} = k_{SA}[Fe_3O_4\ (m^2/L)]$

$k_m\rho_m = k_{SA}a_S\rho_m$

**pH 7.8, 5 g/L $Fe_3O_4$, 50 mM HEPES, 0.1 M NaCl**

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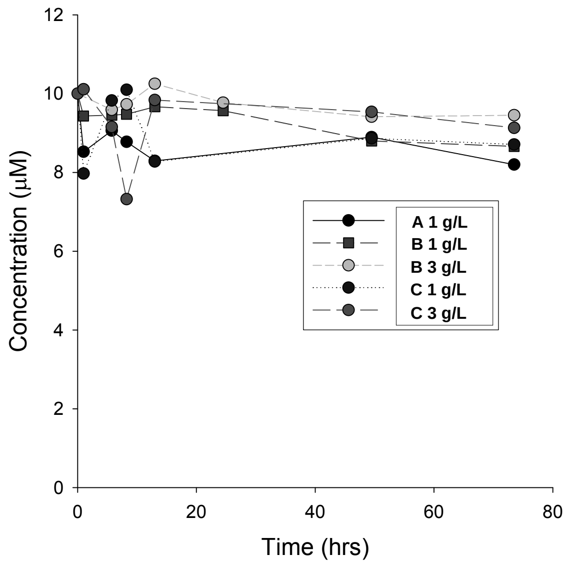
Reporting km values – not ksa; pH range was limited by HEPES buffer…

## Commercially Available Magnetite Not Reactive




- Three commercially available magnetite products
- Variable loading 1 g/L vs. 3 g/L
- Essentially no reactivity observed

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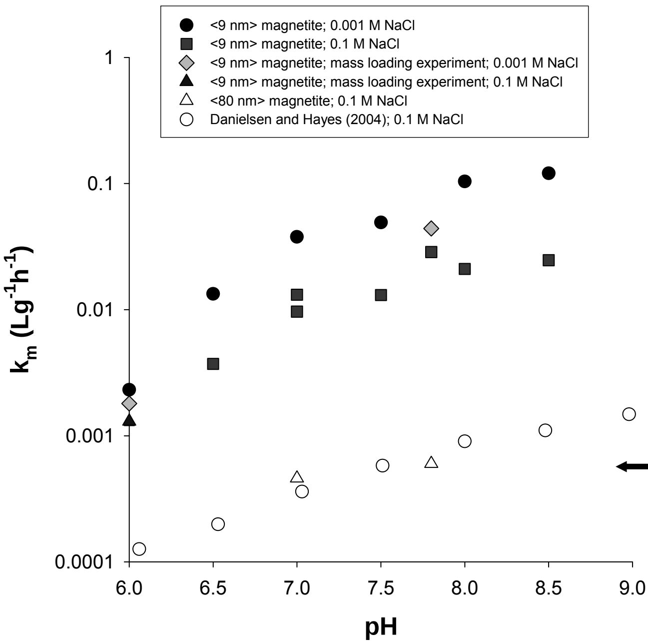
## Rxn Rate for $CCl_4$ Reduction Increases from pH 6.1 to ~ 8




$k_m$ for NZVI ~ 0.007 – 0.2 $Lg^{-1}h^{-1}$ (Nurmi et al. 2005)

**$k_m$ for bulk magnetite is consistent with previous study**

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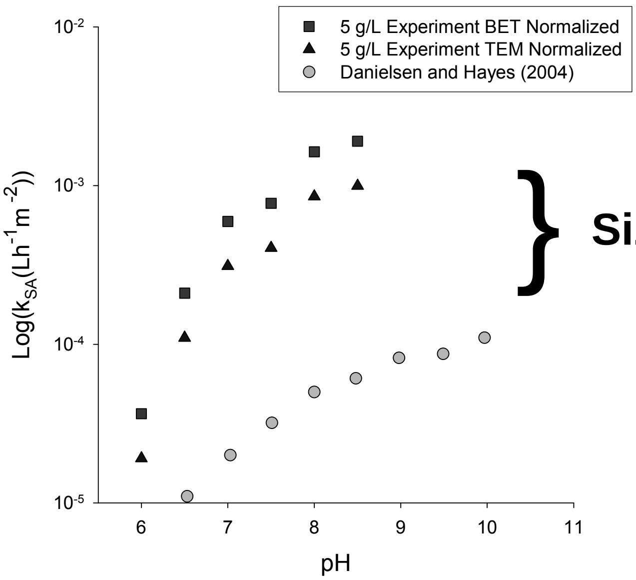
## Surface Area Normalized Rate Constants




**Size effects?**

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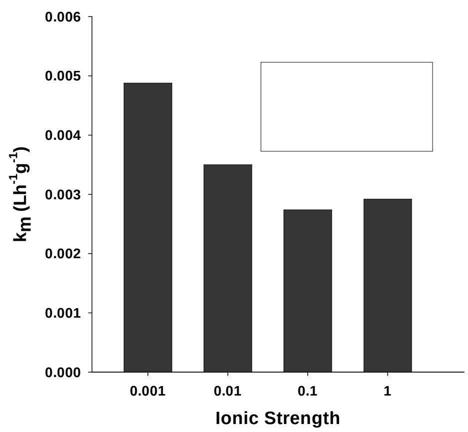
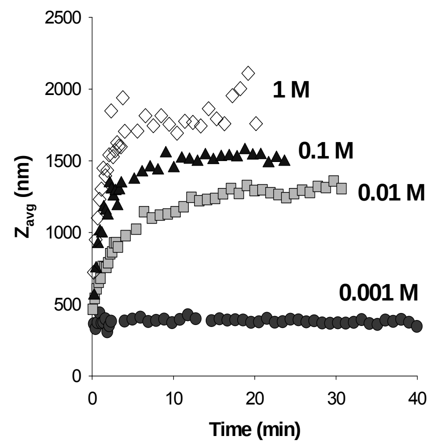
## Ionic Strength Affects Reduction of $CCl_4$

- **CT degrades faster at lower ionic strength**




**pH 7, 50 mM HEPES, $[CT]_0$ = 100 μM, 5 g/L magnetite**

**Stable aggregate size measured using Dynamic Light Scattering**

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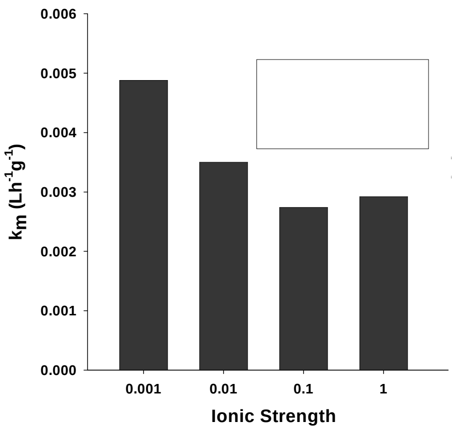
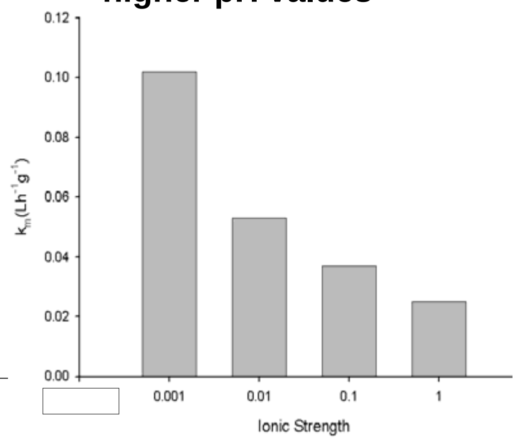
## Ionic Strength Affects Reduction of $CCl_4$

- **CT degrades faster at lower ionic strength**




**pH 7, 50 mM HEPES, $[CT]_0$ = 100 μM, 5 g/L magnetite**

- **Effect is magnified at higher pH values**




**pH 7.8 , 50 mM HEPES, $[CT]_0$ = 100 μM, 5 g/L magnetite**

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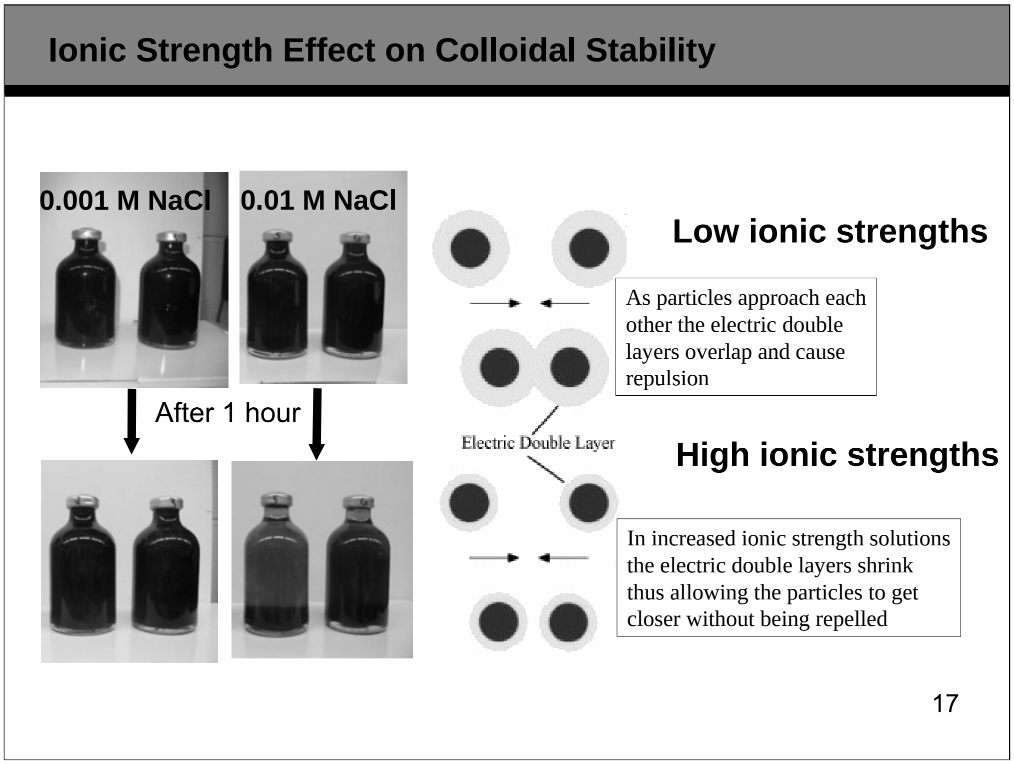
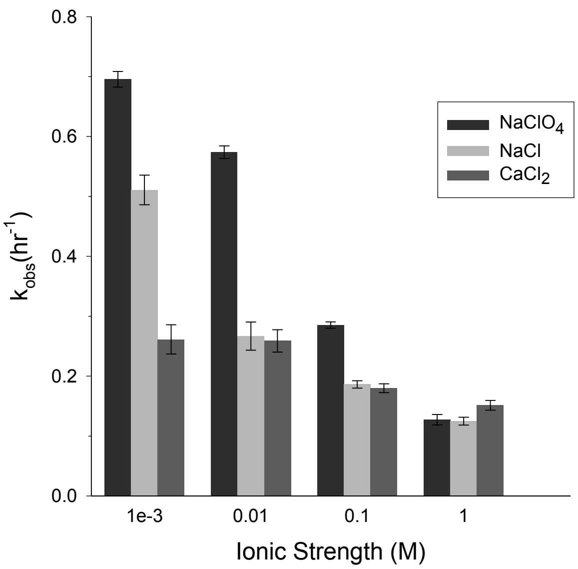



**Magnetic forces….**

## Degradation Rate Affected by Electrolyte Identity




**The rate of loss of $CCl_4$ in presence of $CaCl_2$ was much lower than in presence of NaCl or $NaClO_4$**

**The effect of electrolyte identity becomes less important at higher salt concentration**

**The rate of loss of $CCl_4$ in 0.001 M $NaClO_4$ was faster compared to NaCl**

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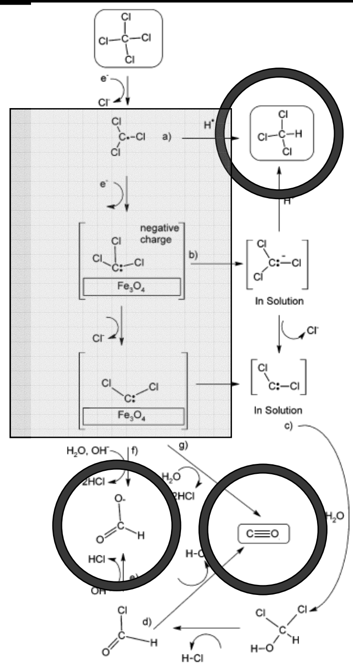
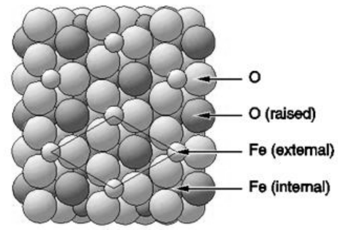
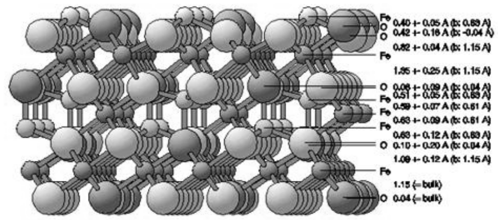
## Magnetite Reactivity



www.sitp.lbl.gov/graphs/figures/fe3o4.html

**Overlapping 3d electrons 'hop' between adjacent octahedral iron atoms**

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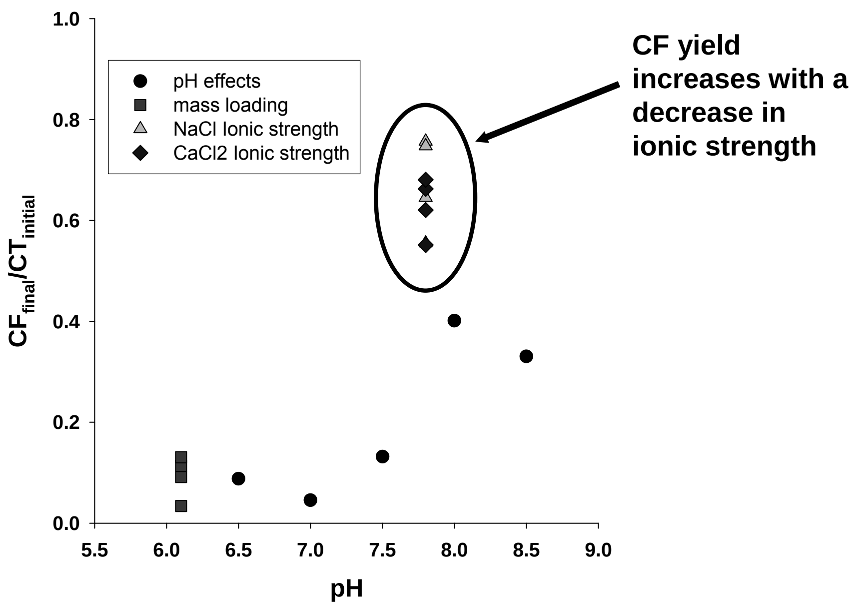
**Reactivity may be attributed to octahedral layer in its inverse spinel crystal structure**

## Chloroform Yields Increase with pH

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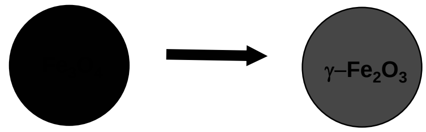
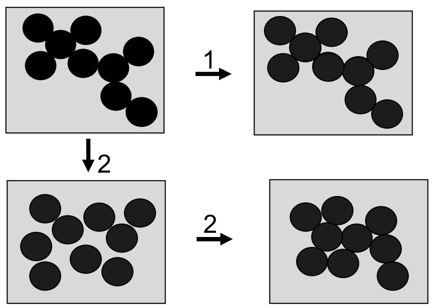
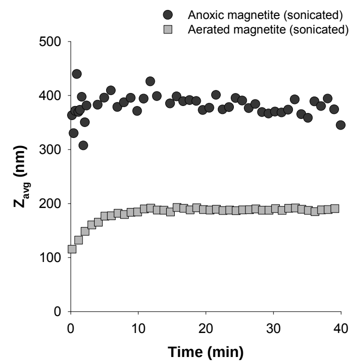
## Magnetite is Topotactically Converted to Maghemite




**Aggregate restructuring may occur during oxidation**

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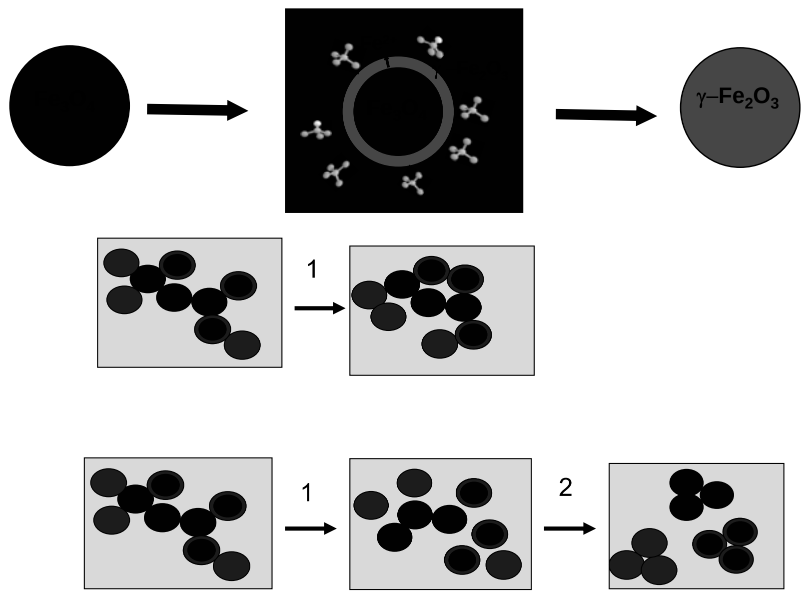
## Aggregation Behavior may be Affected by Oxidation

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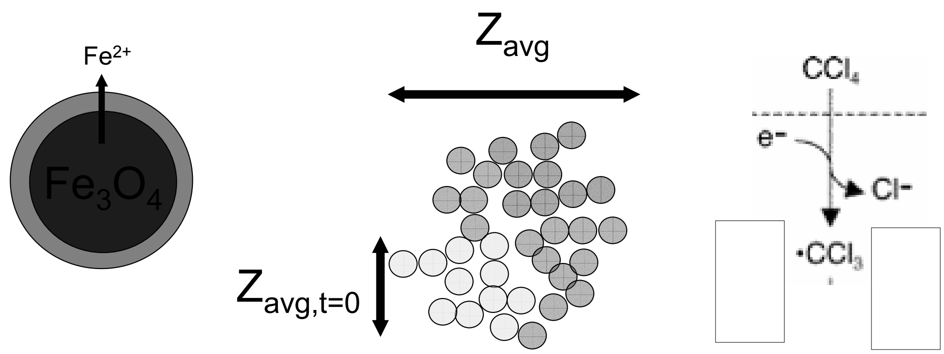
## Thoughts on $CCl_4$ Reactivity

$$Fe_3O_4 + CCl_4 \rightarrow \gamma\text{-}Fe_2O_3 + Fe^{2+} + CHCl_3$$




**Possible rate modifying effects:**

1. Diffusion of $Fe^{2+}$ within a magnetite particle
2. Diffusion of $CCl_4$ to a reactive site within aggregate or on surface of aggregate
3. Electron transfer

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# Encapsulation of Nanoparticles for Environmental and Biological Applications

## Concept and Advantages

- Maintain anaerobic micro-environment
- Microvessels for addition of rate-enhancing reactants, remediation cocktails (Quinn et al., 2005)
- Functionalize surface for enhanced suspension properties
- May facilitate long-term storage under ambient conditions
- Add control over reaction chemistry, kinetics

'Trojan Horse' Concept

**Source:** http://911review.com/disinfo/

Encapsulation affords an added layer of engineering control over reaction chemistry and timing

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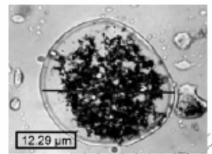
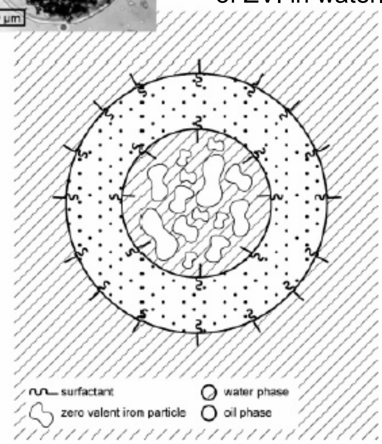
# Precedent: NASA EZVI (Quinn et al., 2005)

- Two components:
  - ZVI for reductive dechlorination
  - Veg oil for enhacement of microbes
- Unclear whether reactivity with TCE due to ZVI or microbial enhancement
- Injection methods can damage EZVI droplets

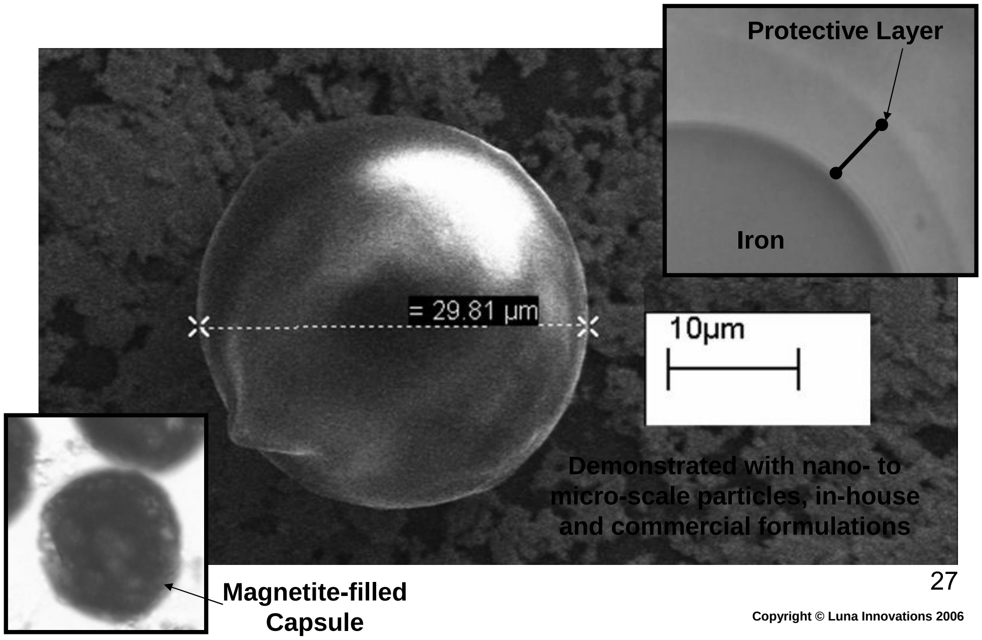



**EZVI droplet:**
Oil-liquid membrane surrounding particles of ZVI in water.




**(Source: Quinn et al, ES&T 2005)** 26

# Encapsulation

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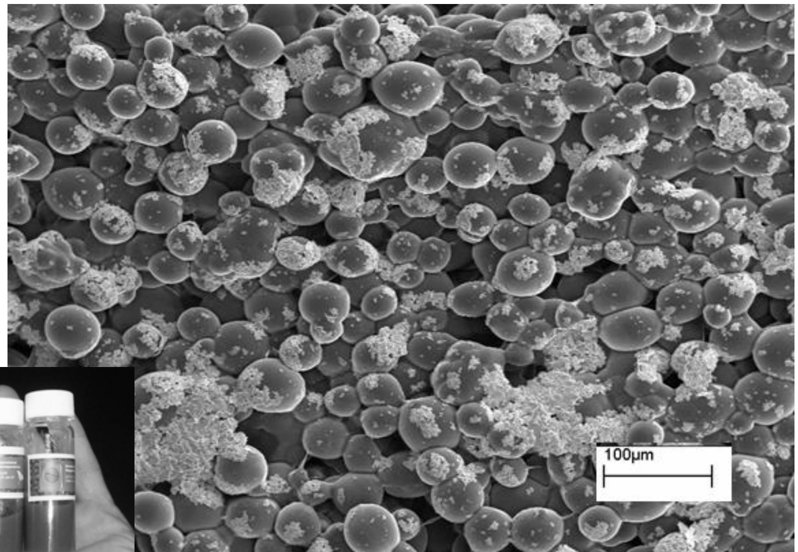
## Encapsulated Magnetite Nanoparticles

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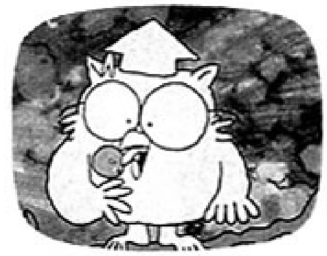
Beta Testers, Product Development Partners Welcomed

## Burning Questions

- Reactivity of encapsulated magnetite nanoparticles?
- Control/tunability of the capsule/particle composite?
- Preservation of particle reactivity in the capsule?
- Breakdown and particle release process?



***How much DNAPL does it take to get to the center of the iron-filled capsules?***

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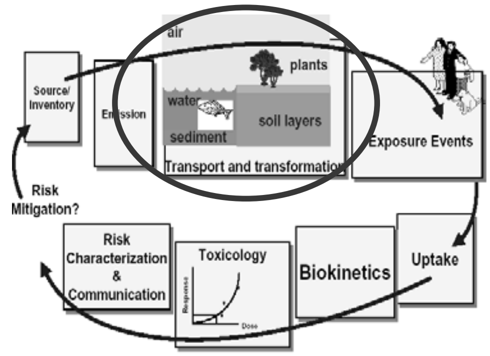
## Thoughts about Nanotech EHS

- Realize societal benefits of nanotechnology responsibly
  - Unique reactivity
  - Possible unintended effects
- **Luna NanoSafe™:** Started in 2003 to address EHS concerns proactively
- **Q2 2007:** Begin third party ecotox testing of various nano iron species and composites




**Adapted From Mark Alper, DOE Molecular Foundary—LBNL**

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## Conclusions

- Magnetite prepared under strict anaerobic conditions can degrade CT without adding $Fe^{II}$.
- On a mass basis, CT loss rates are enhanced in the presence of nanoparticulate magnetite.
- Chloroform yields are affected by both solution pH and ionic strength.
- Surface normalization of the reactivity of nanoparticle suspensions may be unwise.
- Encapsulation may offer additional engineering control over interaction of particles with remediation target.
- Must determine EHS issues with nano iron

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  - US EPA SBIR Program
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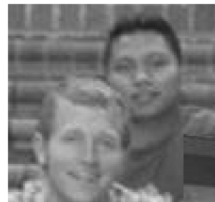
    - Natasha Belcher
  - Advanced Materials Group
    - Kristen Selde
    - Bryan Koene

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## Contact Information

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# Functionalized Reactive Nanoscale $Fe^0$ (NZVI) for in situ DNAPL Remediation: Opportunities and Challenges


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NIEHS Webinar Series on Nanotechnology
March 15, 2007




NSF
CNXT
SERDP Strategic Environmental Research and Development Program
A Partnership to Improve the Environment
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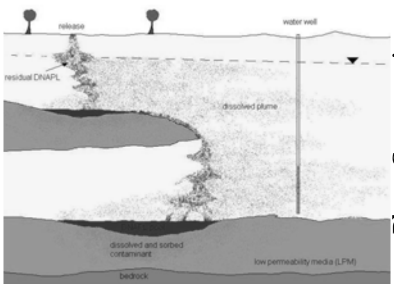
Civil and Environmental Engineering
Carnegie Mellon

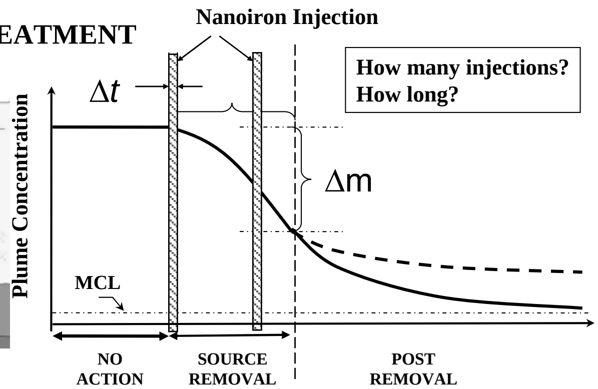
# Students and Collaborators

- Faculty
  - – Robert Tilton (Chem Eng)
  - – Krzystzof Matyjaszewski (Chemistry)
- Post Docs and Students
  - – Dr. Abdulwahab Almusallam, Dr. Bruno Dufour, Dr. Jeongbin Ok, Dr. Traian Sarbu
  - – Dr. Yueqiang Liu, Tanapon Phenrat, Navid Saleh, Kevin Sirk, Hye-Jin Kim
  - – Dan Schoenfelder

# DNAPL Contamination

**DNAPL SOURCE ZONE TREATMENT**




- ➢**Mass emission is a function of the total DNAPL mass and architecture.**
- ➢**Reducing the source mass (Δ*m*) decreases mass emission and downgradient loading.**
- ➢**Cost-effectiveness relies on effective placement of nanoiron.**

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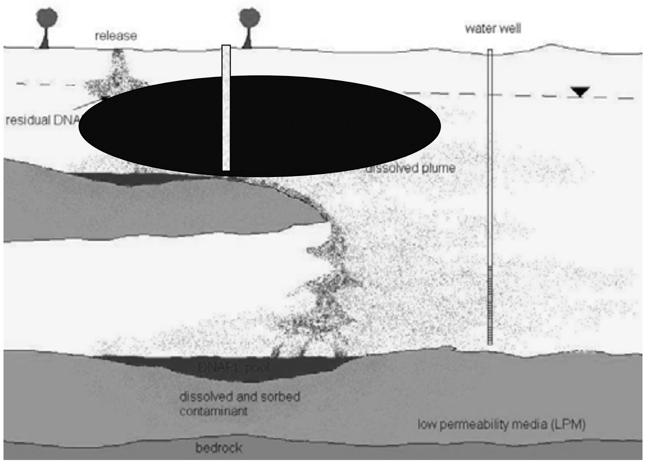
# Treatment with Reactive Nanoparticles




<u>Effective Treatment Requires</u>

1. Mobility
2. Target specificity
3. High reactivity and long lifetime
4. Minimal risk of nanoparticle migration to sensitive receptors (low concentration)

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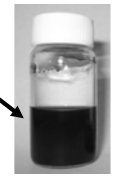
# Optimizing Two Scenarios

- High concentration of Nanoparticles
  - At injection site
  - Need to maximize mobility to be able to "deliver" the materials
  - Optimize remediation performance



- Low concentration of Nanoparticles
  - After dilution in aquifer
  - Need to minimize mobility to ensure that nanoparticles remain in place
  - Minimize risks

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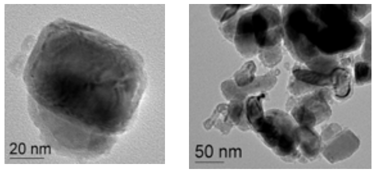
# Functionalized Reactive Nanoiron (NZVI)

**Nanoiron (RNIP)**

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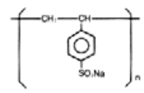
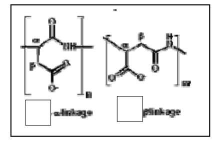
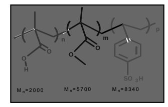
**Surface modifiers**



**PSS**



**PAP**

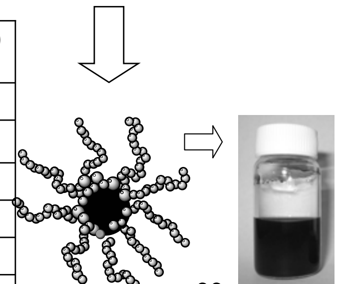


**PMAA-PMMA-PSS**

**TCE + $Fe^0$ → HC Products + $Cl^-$ + $Fe^{2+}/Fe^{3+}$**

Liu, Y., Lowry, G.V. et al, (2005) *ES&T 39, 1338*
Liu and Lowry (2006) *ES&T* 40, 6085

| RNIP Modifier | ζ potential (mV) | Average Dia (nm) |
|---|---|---|
| RNIP (none) | -29.6±2.8 | 146±4 |
| $PMAA_{48}$-$PMMA_{17}$-$PSS_{650}$ | -42.3±1.5 | 212±21 |
| SDBS | -38.25±0.9 | 190±15 |
| MRNIP (PAP MW=2.5k) | -37.6±1.1 | 66±3 |
| PAP (MW=2.5k) | -51.7±0.4 | 32.6±18.6 |
| PSS (MW=70k) | -48.9±1.5 | 31.1±16.6 |



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# Outline

- Getting particles to DNAPL (NP mobility)
  – Aggregation
  – Attachment/filtration
  – Coatings to minimize filtration
- DNAPL degradation rates (Reactivity and Lifetime)
  – Effect of groundwater geochemistry and surface coatings
  – Fate of particles and coatings
- DNAPL Targeting
  – Approaches for in situ targeting

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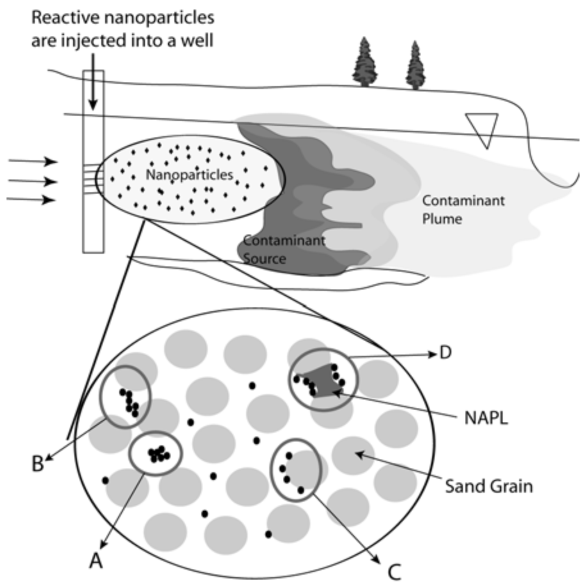
# Nanomaterial Mobility in Porous Media




- A---Aggregation
- B---Straining
- C---Attachment
- D---NAPL
  Targeting

Factors affecting mobility

Chemical
  pH, I, surface chemistry

Physical
  flow velocity,
  particle/aggregate size,
  heterogeneity

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Lowry, in *Env. Nanotech*. (in press).

# Nanoparticle Aggregation

- Nanoparticles aggregate in water:
  - High Hamaker constant-i.e. attractive van der Waals forces
  - Chemical bonding
  - Hydrophobicity
  - Magnetic attraction ($Fe^0$)
- Nanoparticles have high diffusion coefficients and many particle collisions

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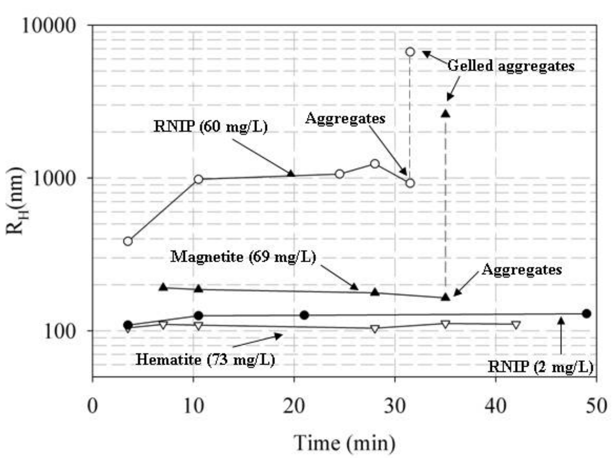
# How Long is Bare NZVI Nano?




- Aggregate size depends on
  - Particle concentration
  - Time
  - Magnetic properties

$M_{s\ RNIP} > M_{s\ Magentite} > M_{s\ Hematite}$

Phenrat T. , Lowry G.V., et al., (2007) *ES&T* 41, 284.

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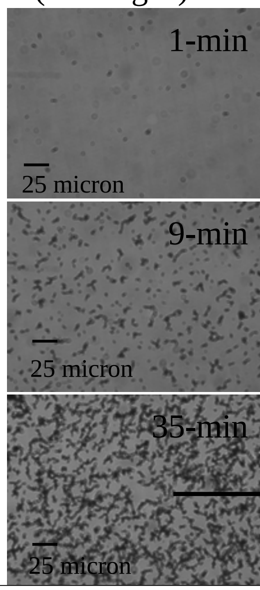
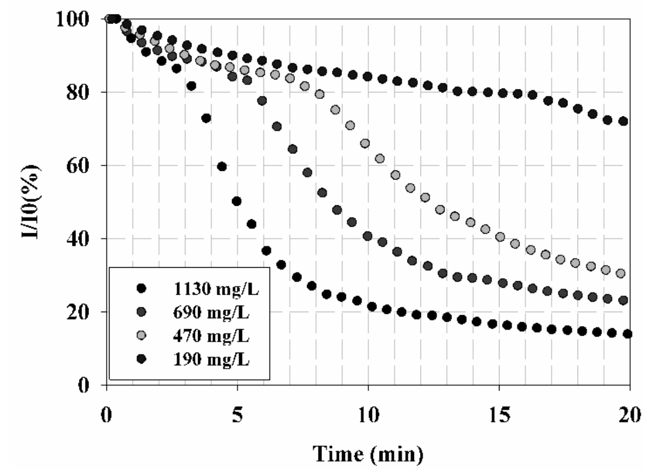
# NZVI Aggregation & Sedimentation

$\Phi = 10^{-5}$
(~80 mg/L)




**Nanoiron sedimentation curves (1 mM NaCl)**




~40-140 micron diameter ($D_F$=1.8)

44

Phenrat T. , Lowry G.V., et al., (2007) *ES&T* 41, 284.

## Attachment to Surfaces

- Attachment is an important fate process
  - Limits mobility in porous media
  - May limit bioavailability/transformation/degradation
- Attachment is a function of the particle and coating type
  - Differences between NPs and coatings

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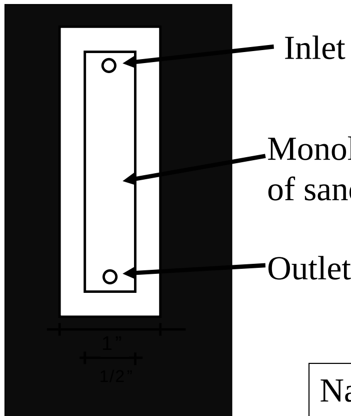
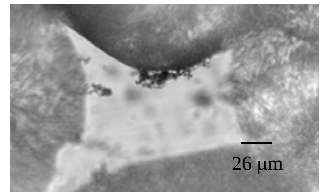
# Attachment Limits Mobility



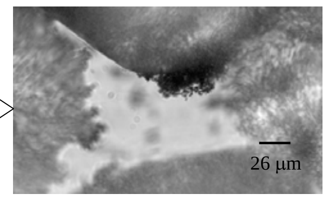

Micro-fluidic PDMS cell

Time=1 min



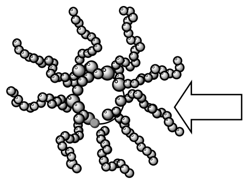

Time=10 min

Nanoiron aggregates are filtered




Saleh, N. Lowry, G.V. et al. *Environ. Eng. Sci.* 24 (1) 2007 p.45-57.

# Surface Modifiers Inhibit Aggregation and Attachment and Increase Mobility



**Common Surface Coatings**

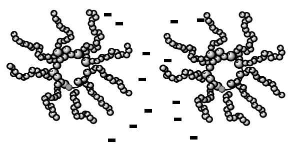
**Polymers/Polyelectrolyte**

- ✓**Triblock copolymers (electrosteric)**
- ✓**Polyaspartic acid (electrostatic)**
- ✓**Cellulose/polysaccharides (steric)**
- ✓**PEG (steric)**

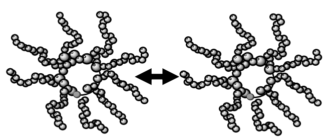
**Surfactants**

- ✓**SDBS (electrostatic)**

**Inhibits Aggregation**

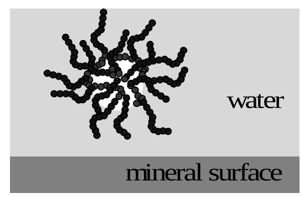


Charge Stabilization



Steric Stabilization

**Inhibits Particle-Media Interactions**

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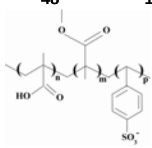
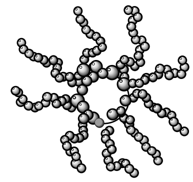
# Different Modifiers

Copolymer (MW=125k)

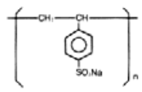
**$PMAA_{48}$-$PMMA_{17}$-$PSS_{650}$**



Increasing MW

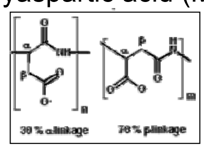


Polystyrene sulfonate (MW=70k)



**Polyelectrolytes**

Polyaspartic acid (MW=3k and 10k)



SDBS (MW=350)

$C_{12}H_{25}(C_6H_4)SO_3^-$

**Surfactant**

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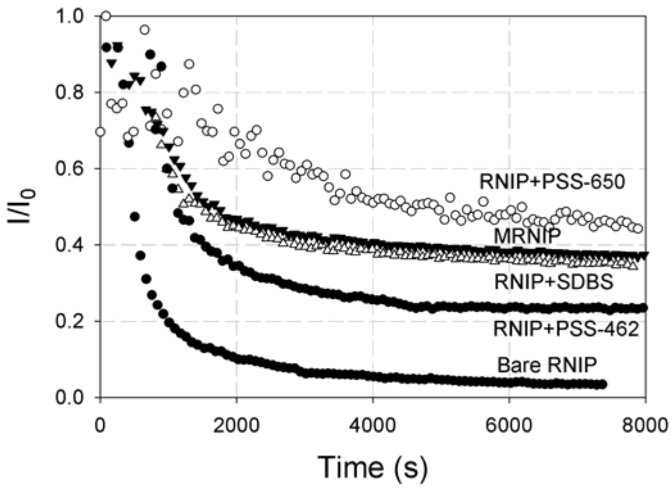
# Modifiers Inhibit Agg/Sed




**Largest Polymer**
**Least aggregation**

**No Polymer**
**Most aggregation**

Saleh, N., Lowry, G. V., et al. **(2005).** "*Nano Lett.* 5 (12) 2489-2494.
Saleh, N., Lowry, G. V., et al. *Environ. Eng. Sci.* 24 (1) 2007 p.45-57.

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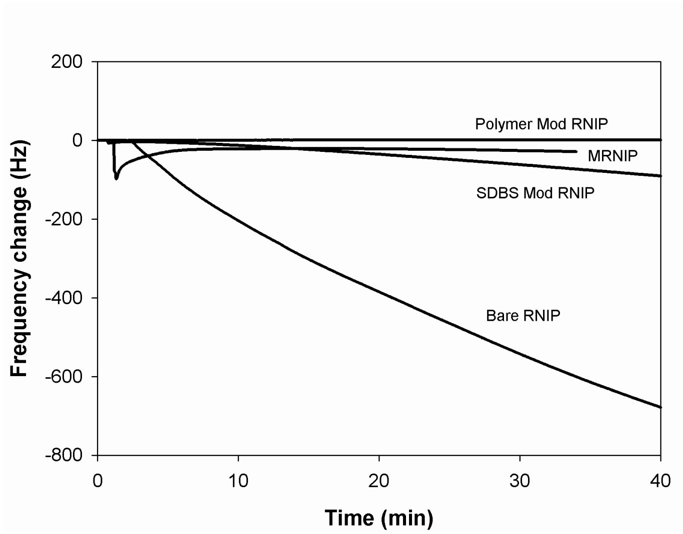
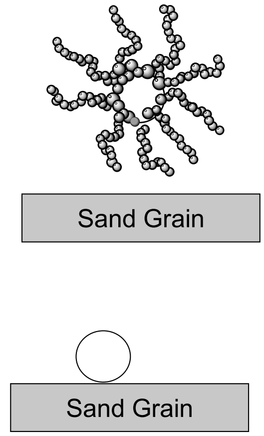
# Modifiers Decrease Attachment to $SiO_2$ Surfaces




QCM is a good predictor of mobility!

Saleh et al. *Environ. Eng. Sci.* 24 (1) 2007 p.45-57.

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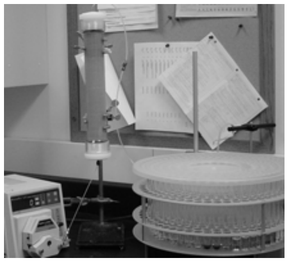
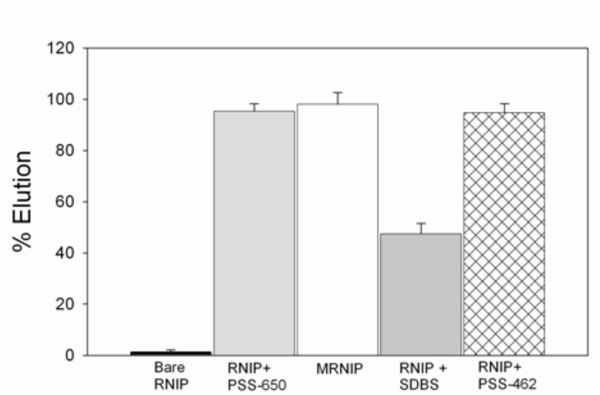
# Modifiers Enhance RNIP Mobility






L=12.5-cm silica sand column with porosity of 0.33. Particle concentration is 3 g/L and I=1mM. Modifying agents were added at 2g/L concentration in each case. MRNIP was supplied by Toda Kogyo, Inc. The approach velocity was 93 m/d.

- ✓ **All modifiers enhance mobility relative to bare RNIP**
- ✓ **Variation between polymers and surfactants implies potential to select a transport distance**

**Saleh et al., 2007 EES 24(1) 45-57.**

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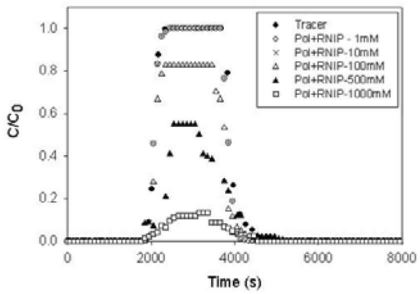
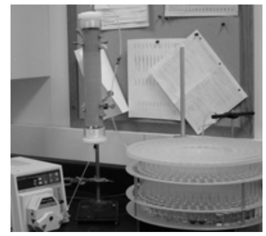
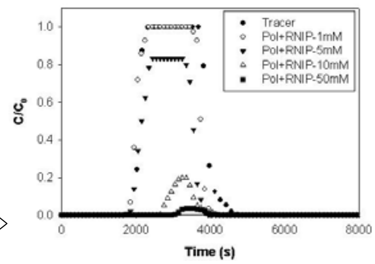
# Mobility Depends on Ionic Strength and Composition




$Na^+$ inhibits mobility



$Ca^{2+}$ inhibits mobility more than $Na^+$




**Sand**
**L=61 cm**
**porosity=0.33**
**Velocity $3.2 \times 10^{-2}$ cm/s**
**I=1-1000 mM**
**$Na^+$ or $Ca^{2+}$**
**<u>30 mg/L</u> particles**

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Saleh, N. et al. ES&T (in prep)

# Mobility depends on Site Geochemistry

**Applying a simple filtration model yields the predicted transport distance needed for 99% removal**

| **Modifier** | **$Na^+$ (mM)** | **Log α (--)** | **Dist. (m)** | **$Ca^{2+}$ (mM)** | **Log α (--)** | **Dist. (m)** |
|---|---|---|---|---|---|---|
| **Polymer** | 10 | -- | -- | 0.5 | -- | -- |
| (MW=125k) | 100 | -2 | 33 | 5 | -1.89 | 25 |
| **Aspartate** | 10 | -2.5 | 45 | 0.5 | -1.77 | 8 |
| (MW=3k) | 100 | -0.96 | 1.2 | 1 | -0.96 | 1.2 |
| **SDBS** | 10 | -2.7 | 150 | 0.5 | -1.33 | 6.6 |
| (MW=350) | 100 | -0.6 | 1.2 | 1 | -0.89 | 2.4 |

| Site | **$K^+ + Na^+$ mM** | **$Ca^{2+} + Mg^{2+}$ mM** |
|---|---|---|
| Alameda Point, CA | **197** | **2.4** |
| Paris Island, SC | **6.1** | **1.3** |
| Mancelona, MI | **0.14** | **1.9** |

"Typical" concentrations of monovalent and divalent cations

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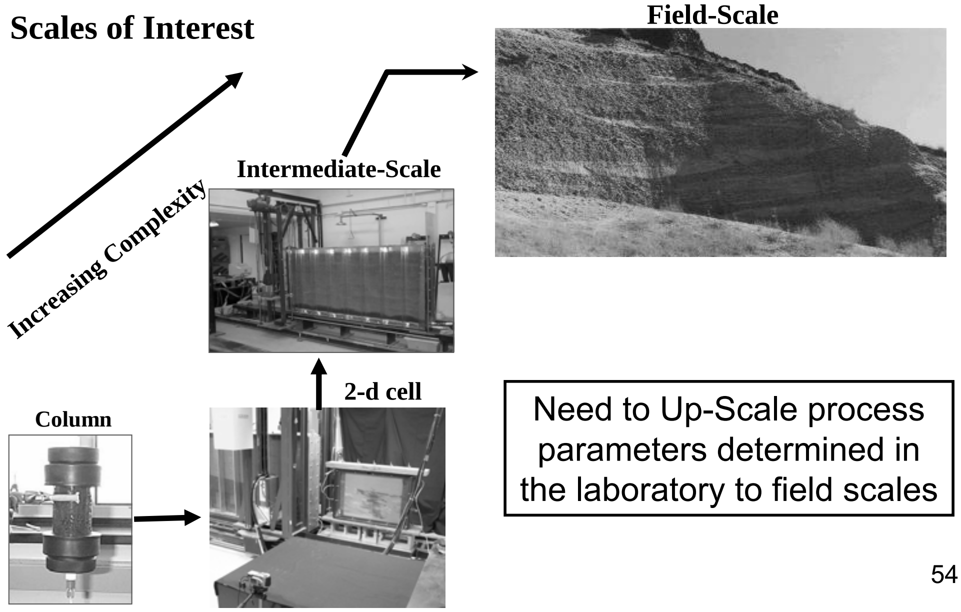
# Real Sites are NOT Sand columns!

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# NZVI Reactivity and Lifetime

- Fundamental Questions
  - What are the reaction rates and products?
  - How long do the particles remain reactive?
  - What geochemical factors affect their reactivity and lifetime?
  - How do surface modifiers affect reactivity?

Liu et al, (2005) *ES&T 39,* 1338
Liu and Lowry, (2006) *ES&T, 40 (19)* 6085
Liu, Phenrat, and Lowry, (2007) *ES&T, (in prep)*

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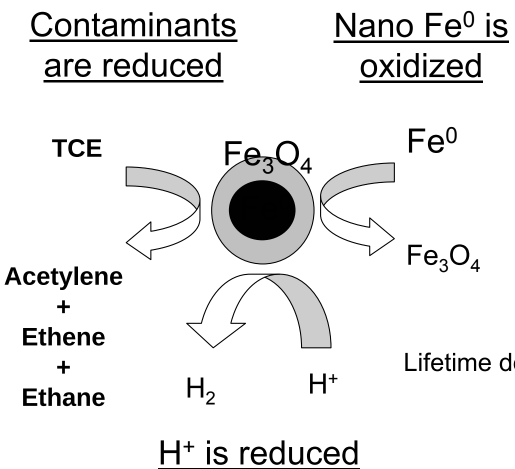
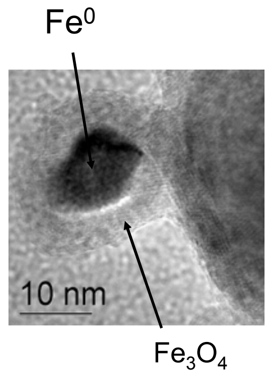
# Reactive $Fe^0$ Nanoparticles




Lifetime depends on Oxidant loading and pH

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Liu et al, (2005) *ES&T 39*, 1338

Liu and Lowry, (2006) *ES&T, 40 (19)* 6085

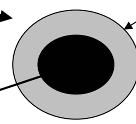
# Types of Nanoiron

- Borohydride reduction[1,2]

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 \downarrow + B(OH)_3 + 2H_2 + 3H^+$$

- Gas phase reduction by $H_2$[1]
  – Toda Kogyo (RNIP)

$$FeSO_4 \rightarrow FeO(OH) \xrightarrow{H_2} Fe^0 \xrightarrow{H_2O}$$




~5000 ppm S (reduced)

1 Liu, et al., *Environ. Sci. & Technol.* **2005,** *39*, 1338-1345

2 Liu et al., *Chem Mater*. **2005**, 21 5315-5322

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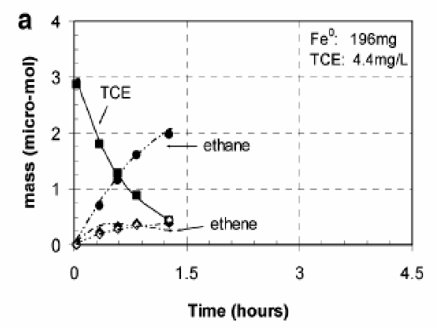
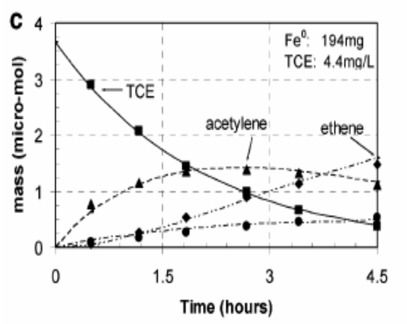
# Differences in Reactivity

<u>Fe(B)</u>




Faster Reaction
k=1.4 X $10^{-2}$ L $hr^{-1}$ $m^{-2}$
<u>Saturated Products</u>
TCE $t_{1/2}$=~ 2 hr (@2g/L)

<u>RNIP</u>




Slower reaction
k=3 X $10^{-3}$ L $hr^{-1}$ $m^{-2}$
<u>Unsaturated Products</u>
TCE $t_{1/2}$=~ 8 hr (@2g/L)

*Iron Filings
k=$10^{-3}$ to $10^{-4}$ L $hr^{-1}$ $m^{-2}$

1 Liu, et al., *Environ. Sci. & Technol.* **2005,** *39*, 1338-1345

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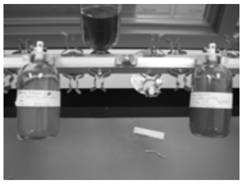
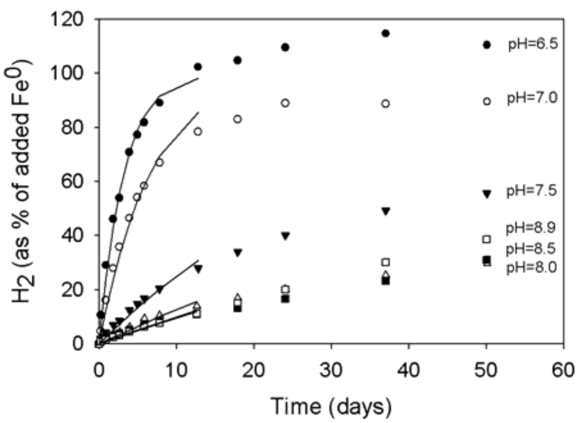


# NZVI Lifetime Depends on pH

$$\mathrm{Fe}^0 + 2\mathrm{H}^+ \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}_2 \uparrow$$




Liu and Lowry, (2006) *Environ. Sci. Technol., 40 (19) 6085*

~2 weeks
pH=6.5

~9 months
pH≥8.0

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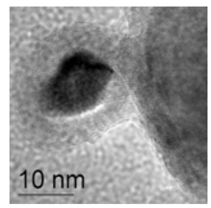
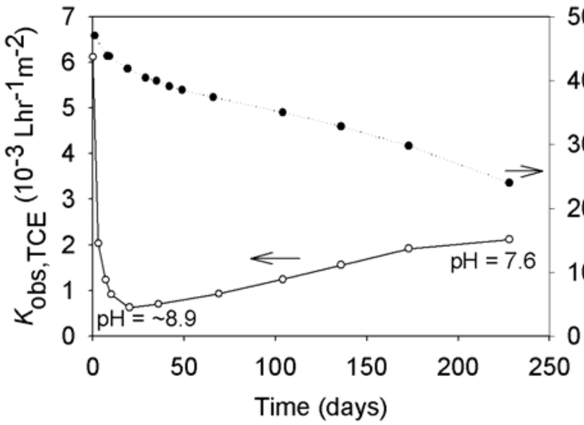
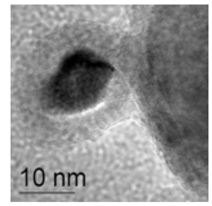


# TCE Dechlorination Over Particle Lifetime




$k_{obs,TCE}$ is relatively constant as particles age

Liu and Lowry, (2006) *Environ. Sci. Technol., 40 (19) 6085*

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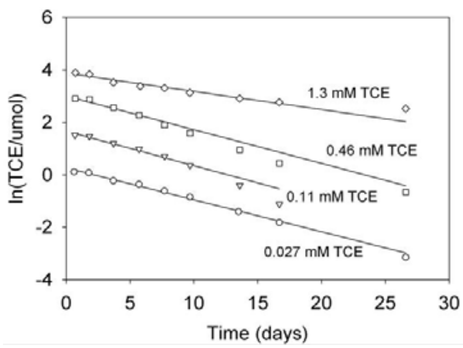
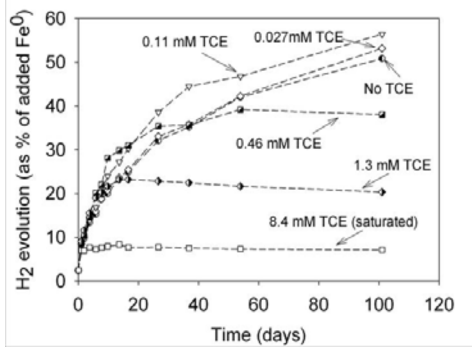
# Effect of TCE Concentration on $Fe^0$ Utilization




Small effect of TCE concentration on reactivity

Use in source zone increases $Fe^0$ efficiency

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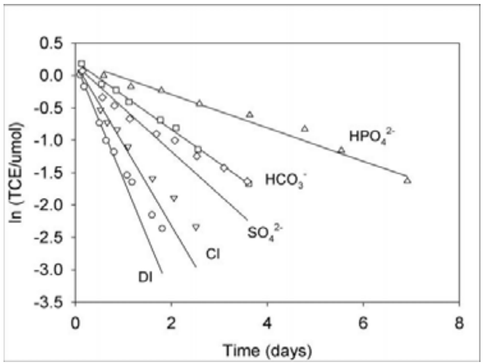
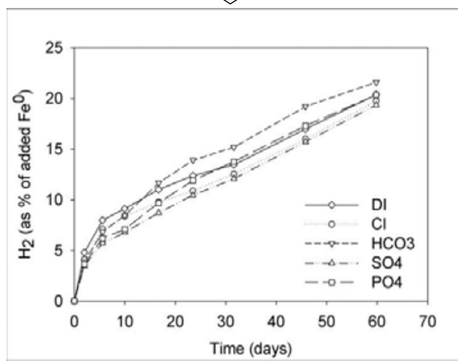
Liu, Phenrat, and Lowry, *Environ. Sci. Technol., (in prep)*

# Effect of Groundwater Solutes on Reactivity with TCE




Dissolved solutes had no effect on $H_2$ evolution




Dissolved solutes lower reactivity by a factor of 2 to 7 depending on the solute

Effect follows expected trend of solute strength of complexation with HFO

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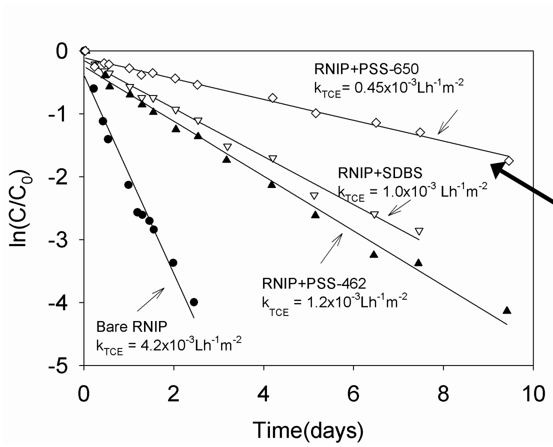
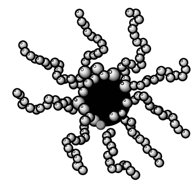
Liu, Phenrat, and Lowry, *Environ. Sci. Technol., (in prep)*

# Effect of Modifiers on RNIP Reactivity with TCE




$PMAA_{48}$-$PMMA_{17}$-$PSS_{650}$ modified RNIP: <u>10 times less reactive</u> then unmodified RNIP, but still reactive enough

TCE $t_{1/2} \approx$ 6 days (at 2 g/L) for the lowest activity modified particles



Saleh, G. V. Lowry, et al. *Environ. Eng. Sci.* 24 (1) 2007 p.45-57.

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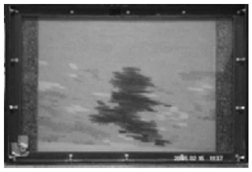
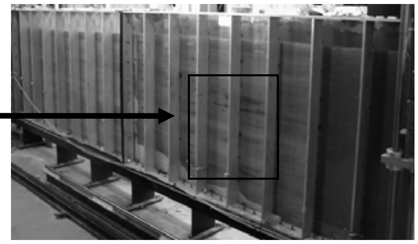
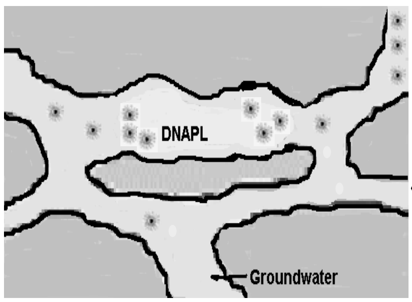
# Contaminant Source Zone Targeting



Contaminant Source Zone



Without Targeting Nanoparticles can flow past source zone




**Nanoparticle surface coatings can provide an affinity for DNAPL**

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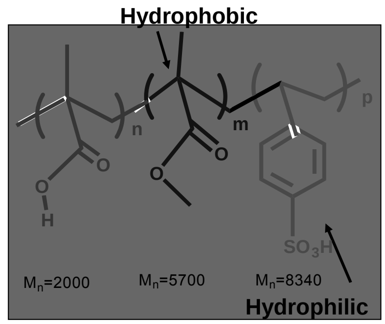
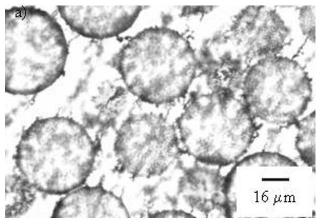
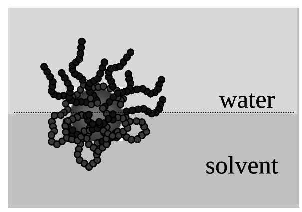
# Potential Strategies for Targeting

- Interfacial targeting
- Destabilization Targeting
- Controlled placement




Particles Attach to the
NAPL/water interface

Saleh, N., Lowry, G. V., et al. **(2005)**. "*Nano Lett.* 5 (12) 2489-2494.

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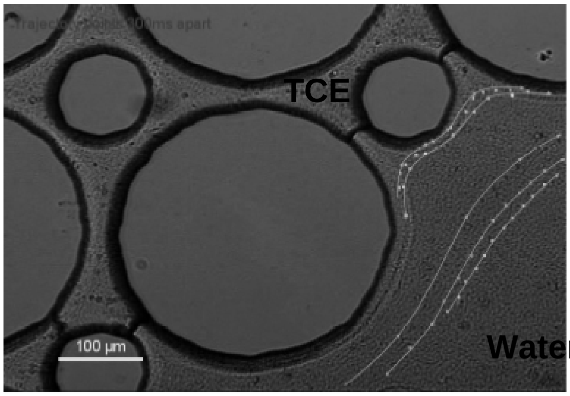
# Interfacial Targeting Challenges




**Nanoiron Trajectory at different porewater velocities**

- Flow velocities: 30-150 µm/s (2.6-13m/day)
- Residence time: 1-10 s

Baumann, T., Keller, A. A., Auset-Vallejo, M., Lowry, G V. (2005).
AGU Fall Meeting, San Francisco, CA, December 5-9, 2005.

# Destabilization Targeting

**Polymer adsorption to RNIP is strong and effectively irreversible**

**Higher MW=stronger sorption**

**Mitigates concern of NAPL mobilization**

| | | **Percent Remaining Adsorbed** | | |
|---|---|---|---|---|
| **Modifier** | **Initial Adsorbed mass ($mg/m^2$)** | **2weeks** | **4weeks** | **8weeks** |
| PAP 2.5K | 0.85±0.23 | 91 ± 3 | 86 ± 4.7 | 82 ± 5.5 |
| PAP 10K | 1.47±0.14 | 94 ± 4.1 | 91 ± 2.5 | 90 ± 2 |
| | | **2weeks** | **5weeks** | **8weeks** |
| PSS 70K | 2.89±0.59 | 94 ± 0.5 | 93 ± 0.6 | 93 ± 0.6 |
| PSS 1M | 2.55±0.45 | 96 ± 4.1 | 95 ± 4.7 | 95 ± 4.7 |
| | | **2weeks** | **6weeks** | **8weeks** |
| CMC 90K | 2.09±0.02 | 88 ± 2.1 | 83 ± 2.9 | 81 ± 3.1 |
| CMC 700K | 3.71±0.43 | 94 ± 0.4 | 91 ± 0.8 | 90 ± 0.9 |

Kim, H-J., Lowry, G.V. et al., (in prep)

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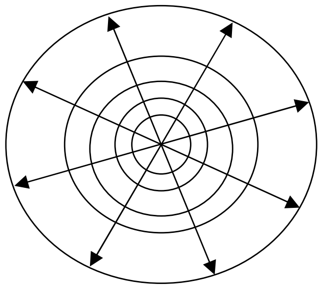
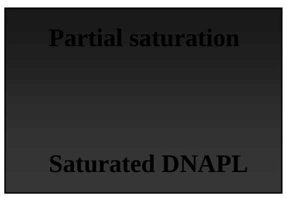
# Strategies for Controlled Placement of Nanoiron



- Geochemical conditions change from the injection well down gradient due to dilution.
- Potential geochemical changes that can afford targeting include:
  - Ionic strength variation (from low to high)
  - Velocity variation (from high to low)




- DNAPL saturation varies from saturated at a pool surface to just a few percent at the fringe. DNAPL architecture may afford targeting opportunities
  - Hydrodynamic trapping
  - Co-solvency effects

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# Conclusions

- Aggregation and attachment limits bare $Fe^0$ NPs mobility in aquifers
- Surface modification increases mobility
  - GW geochemistry ($Ca^{2+}$ and $Mg^{2+}$) controls mobility
  - Mobility of 10's of meters possible with appropriate coatings at typical GW ionic composition
- NZVI is highly reactive with TCE under environmental conditions
  - Lifetime depends of geochemistry and oxidant loading
  - Use in NAPL source zone maximizes $Fe^0$ utilization
- In situ targeting of entrapped NAPL requires optimization of the coatings
  - Matching modifier and GW geochemistry offers potential for controlled placement

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# Nano vs. Micro

- Greater surface area of nano (15-30 $m^2/g$) provides higher reactivity than micro (~0.1 $m^2/g$)
  - nanoiron → 0.5 to 1.5 $lb/yd^3$;
  - microiron → > 20 $lb/yd^3$
- Delivery to source
  - Nanoiron-direct push wells
  - Micoiron-high pressure injection and greater cost
- Total cost includes
  - Management/engineering
  - Injection services
  - Materials (~15% at pilot scale)

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# Field Validation Needed

- Assessment of the effect of treatment on the DNAPL mass and mass emission from the source is needed
- Pilot-scale field demonstration WITH substantial characterization before, during, and after treatment is needed
- Better understanding of the between NZVI and the microbial communities at a site are needed

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# Thank You

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