NIEHS National Institute of Environmental Health Sciences

RISK eLearning

Nanotechnology – Applications and Implications for Superfund

sbrp Superfund Basic Research Program
Balancing Scientific Excellence with Research Relevance

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

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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Magnetite Nanoparticles for Remediation of Contaminated Groundwater

Funded by an EPA SBIR grant
(Contract No. EP-D-06-079)

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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

EPA SBIR Program

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

Phase I
Demonstrate Technical Feasibility

→

Phase II
Optimization and Scale Up

→

Phase III
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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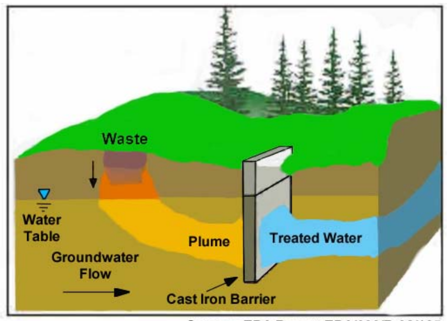
Magnetite Characterization and Reactivity

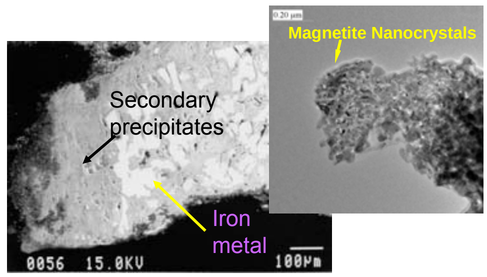
ZVI Permeable Reactive Barriers Effectively Treat Many Groundwater Contaminants

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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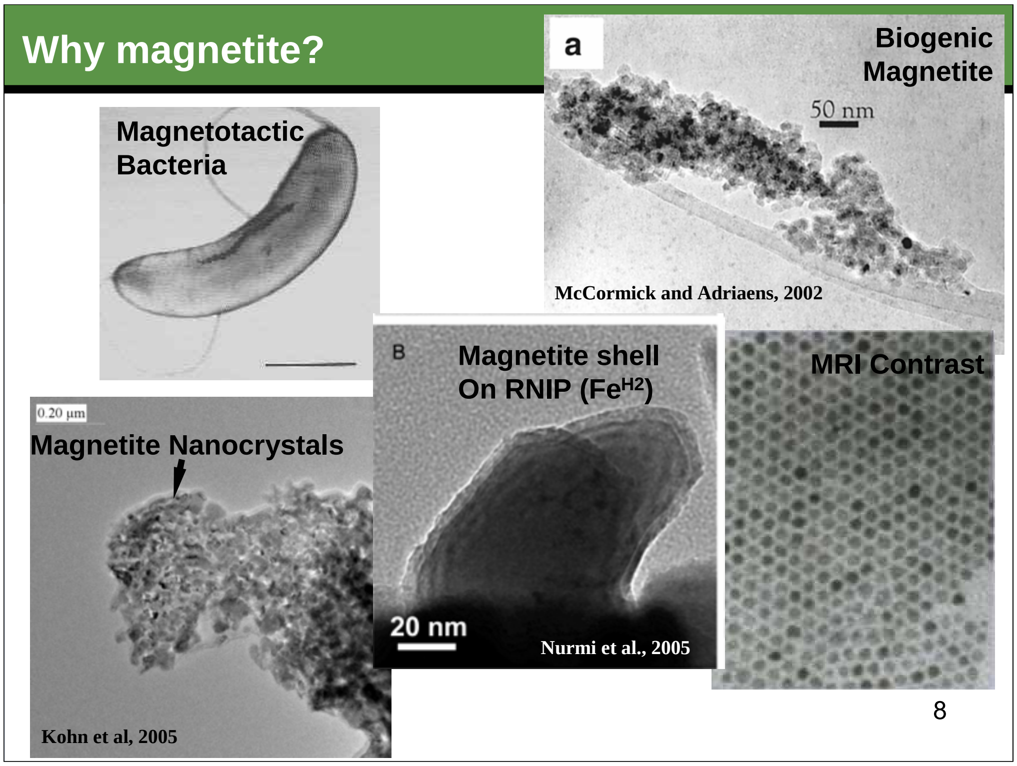
Why magnetite?
Magnetotactic Bacteria
a
Biogenic Magnetite
50 nm
McCormick and Adriaens, 2002
0.20 µm
Magnetite Nanocrystals
Kohn et al, 2005
B
Magnetite shell On RNIP (FeH2)
20 nm
Nurmi et al., 2005
MRI Contrast
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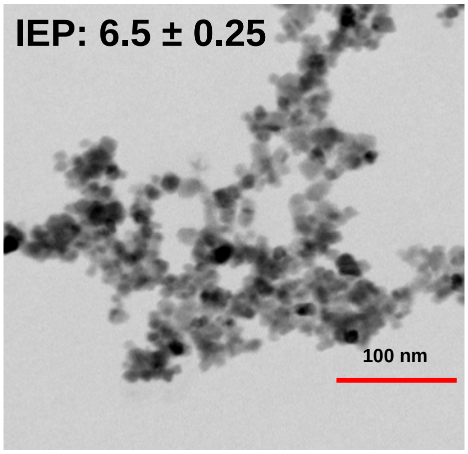
Magnetite Synthesis and Particle Characterization

- 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 ± 1.6 nm



Synthesis done under conditions of strict oxygen exclusion

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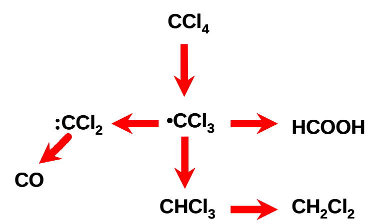
Carbon Tetrachloride (CT)

- 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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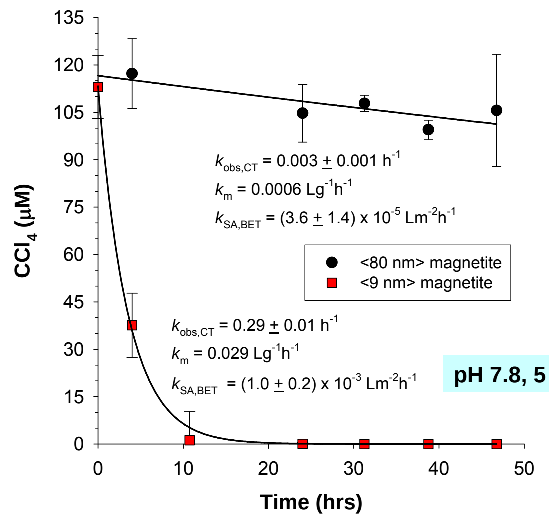
Carbon Tetrachloride Degradation by Magnetite

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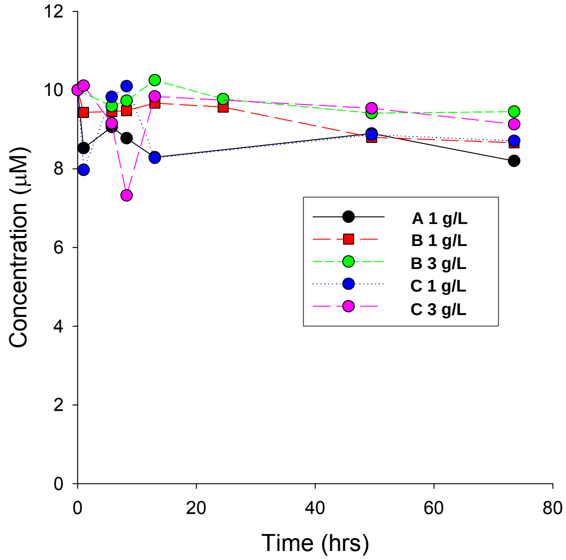
Reporting km values – not ksa; pH range was limited by HEPES buffer…

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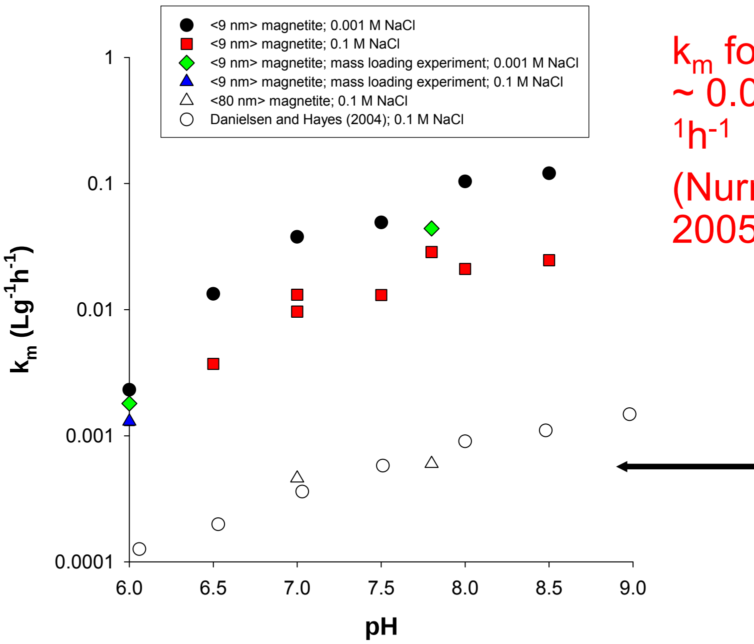
Rxn Rate for CCl_4 Reduction Increases from pH 6.1 to ~ 8



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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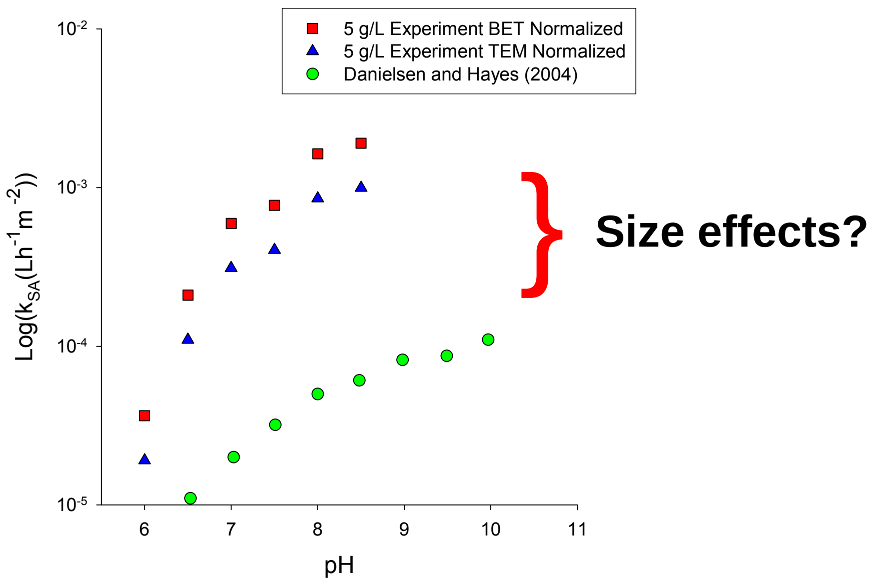
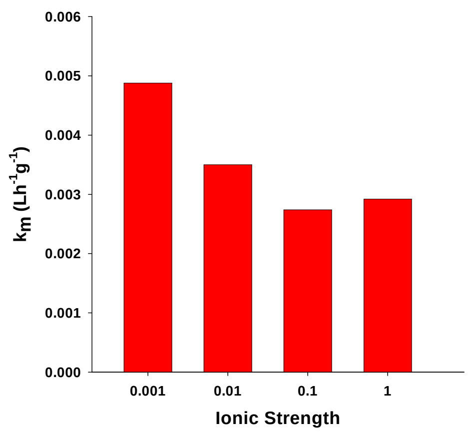
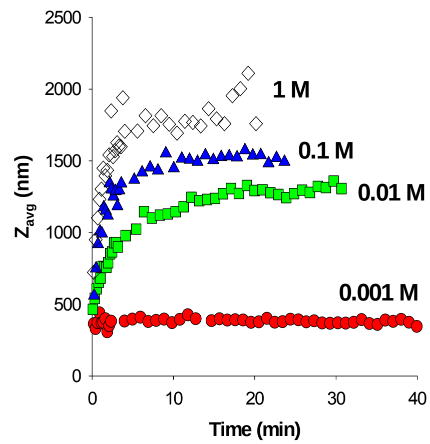
Surface Area Normalized Rate Constants



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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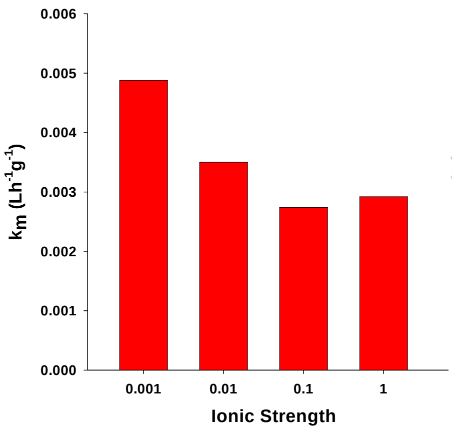
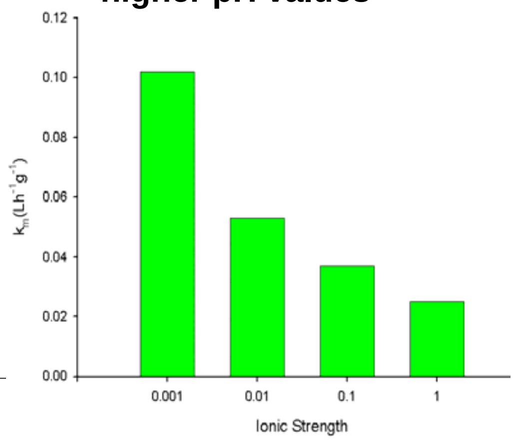
Ionic Strength Affects Reduction of CCl_4

- **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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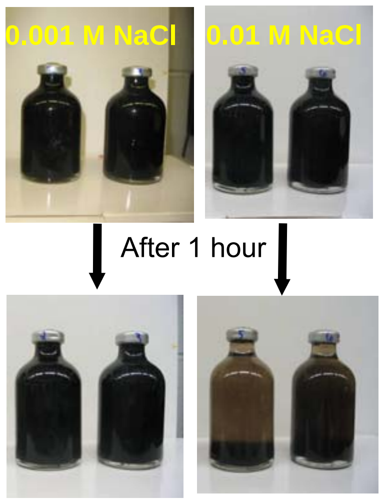
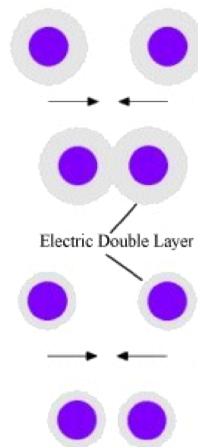
Ionic Strength Effect on Colloidal Stability





Low ionic strengths

As particles approach each other the electric double layers overlap and cause repulsion

High ionic strengths

In increased ionic strength solutions the electric double layers shrink thus allowing the particles to get closer without being repelled

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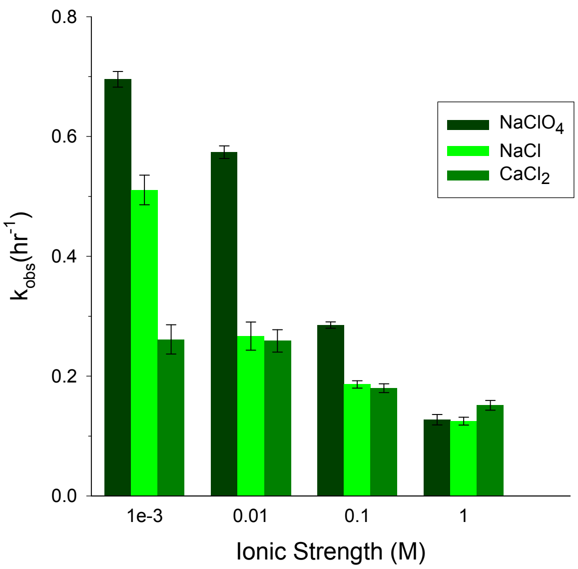
Magnetic forces….

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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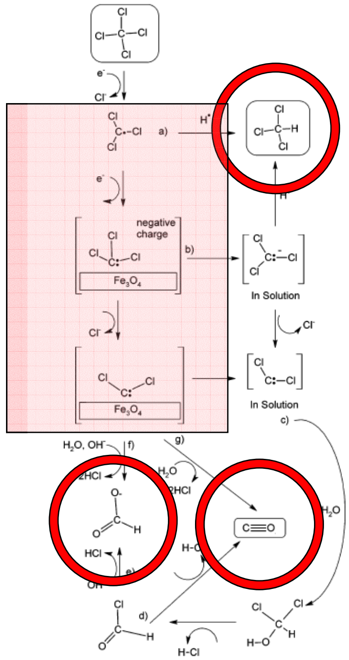
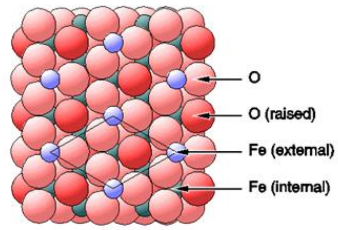
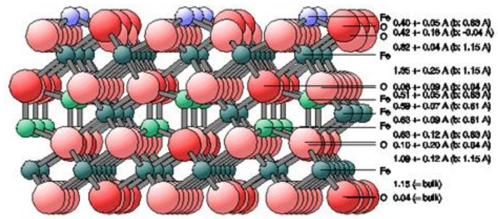
Magnetite Reactivity







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

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

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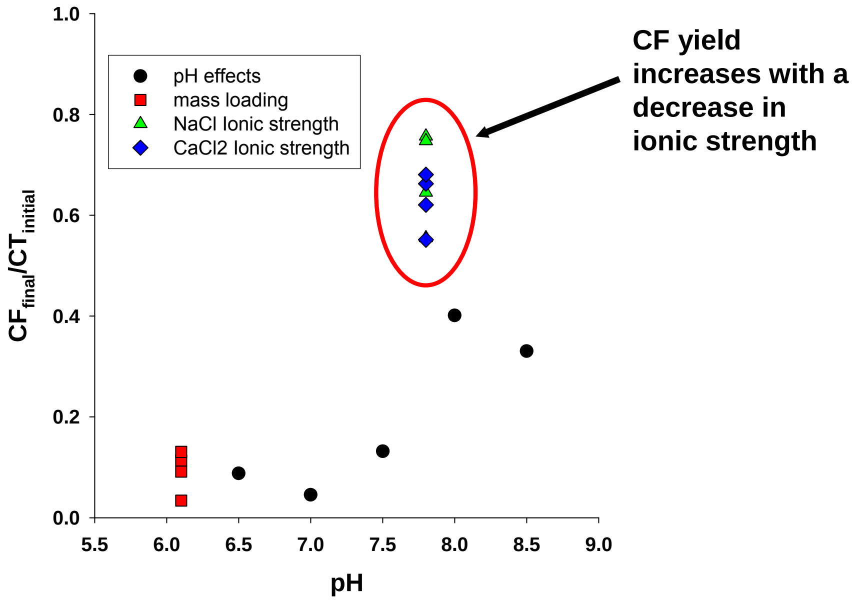
Reactivity may be attributed to octahedral layer in its inverse spinel crystal structure

Chloroform Yields Increase with pH



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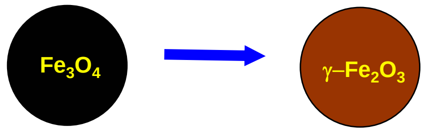
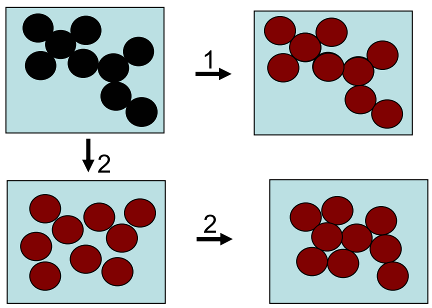
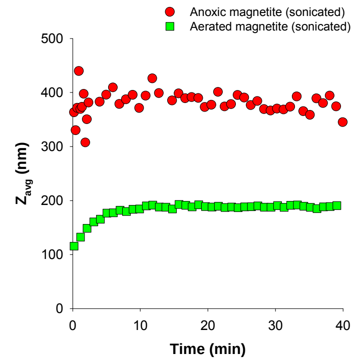
Magnetite is Topotactically Converted to Maghemite







Aggregate restructuring may occur during oxidation

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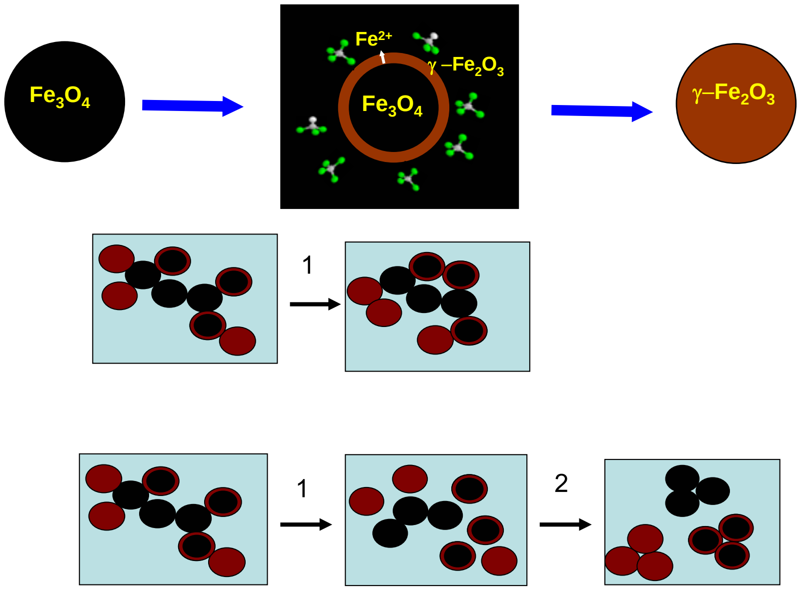
Aggregation Behavior may be Affected by Oxidation



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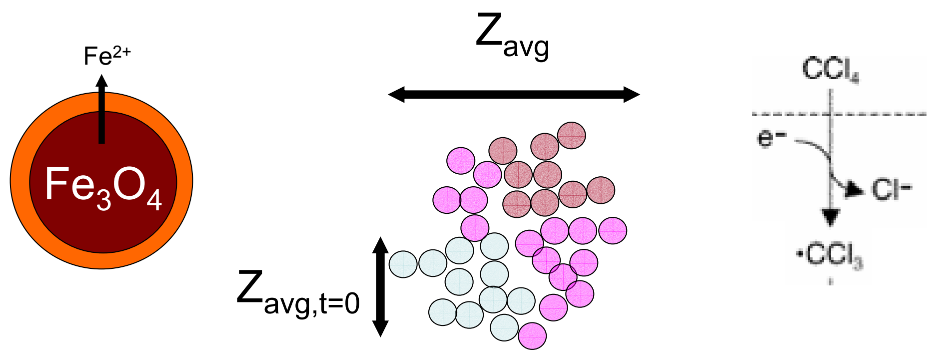
Thoughts on CCl_4 Reactivity

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



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

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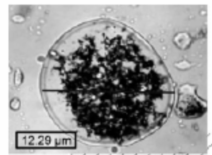
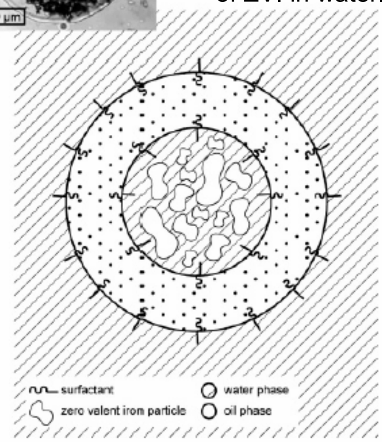
Precedent: NASA EZVI (Quinn et al., 2005)

- 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)

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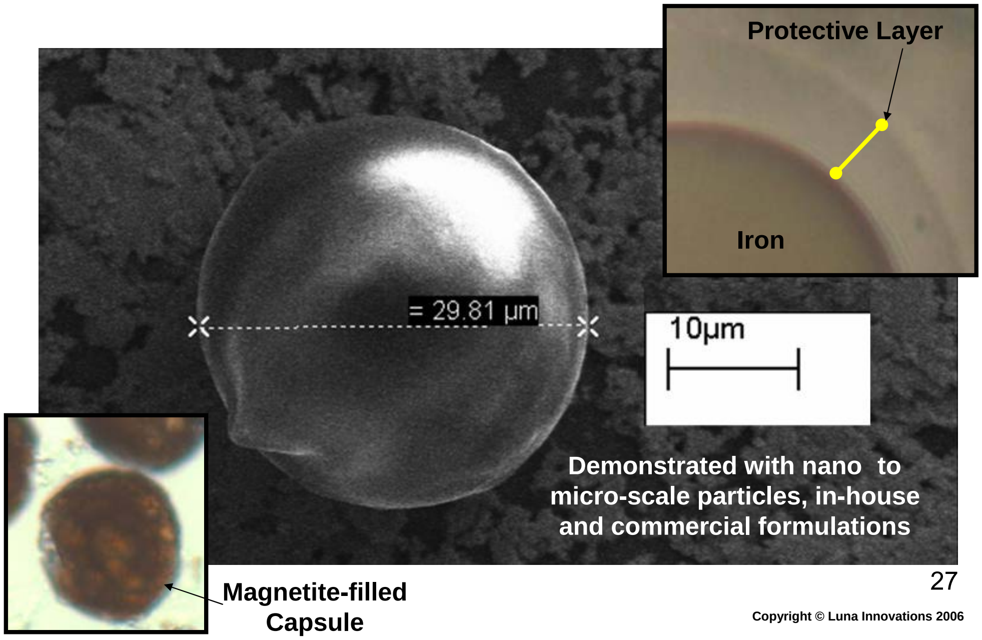
Encapsulation



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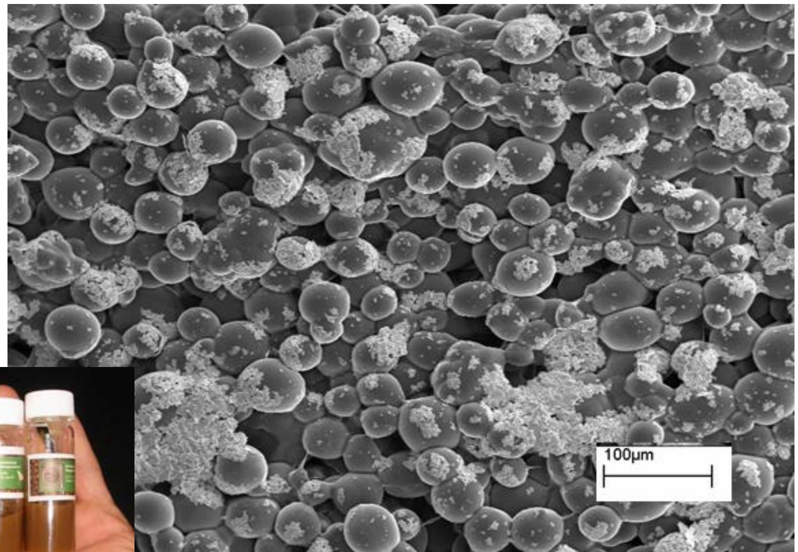
Encapsulated Magnetite Nanoparticles



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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?

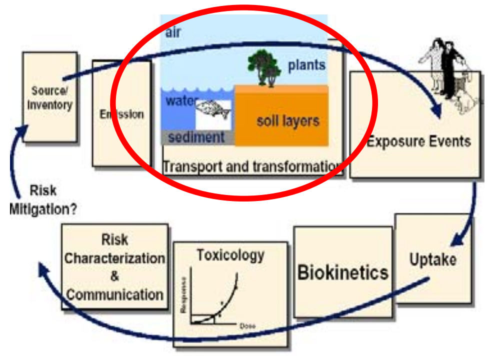
How much DNAPL does it take to get to the center of the iron-filled capsules?

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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- Funding
  - US EPA SBIR Program
  - NSF (Dr. Vikesland's Lab)
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  - Advanced Materials Group
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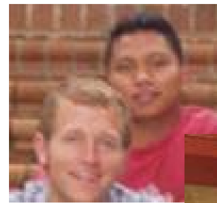

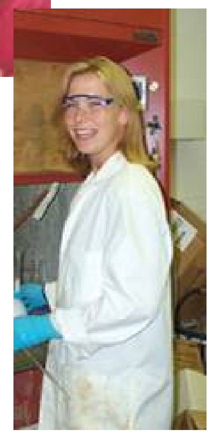

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Contact Information

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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

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Students and Collaborators

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  - 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



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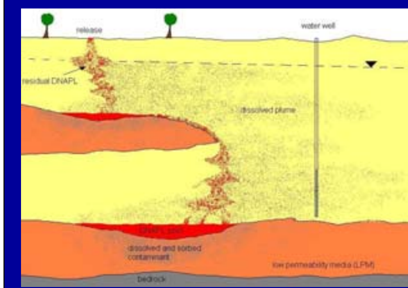
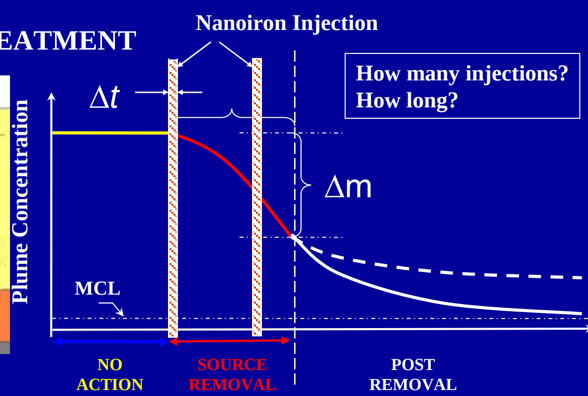
DNAPL Contamination

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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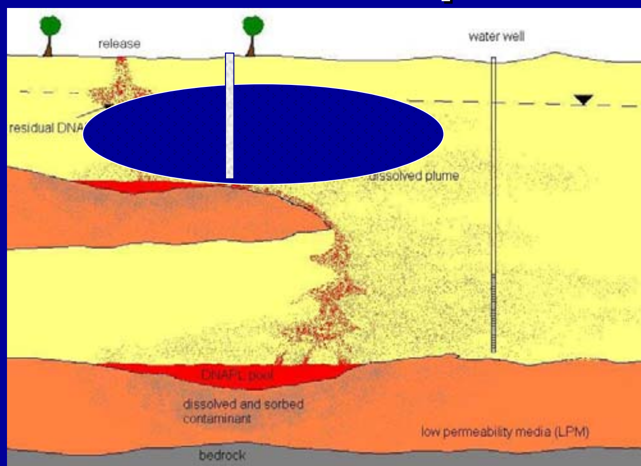
Treatment with Reactive Nanoparticles



Effective Treatment Requires

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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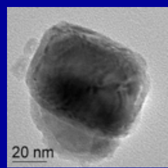
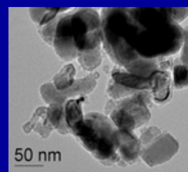
Functionalized Reactive Nanoiron (NZVI)

Nanoiron (RNIP)





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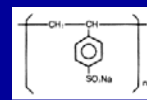
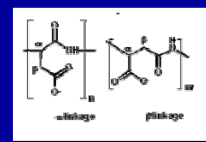
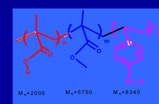
Surface modifiers



PSS



PAP

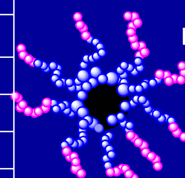


PMAA-PMMA-PSS

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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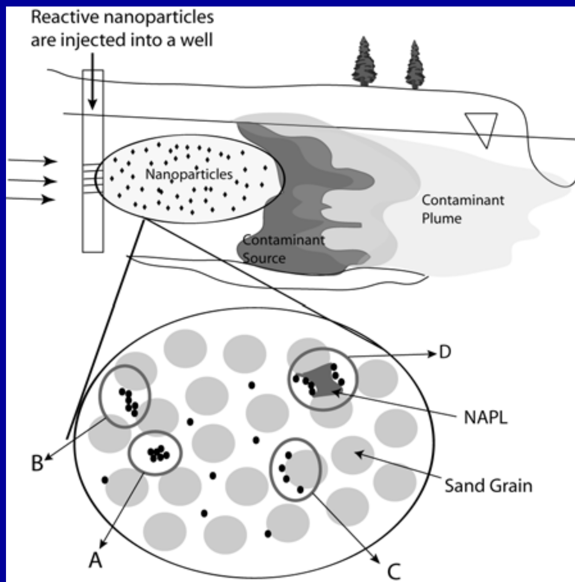
Nanomaterial Mobility in Porous Media



- 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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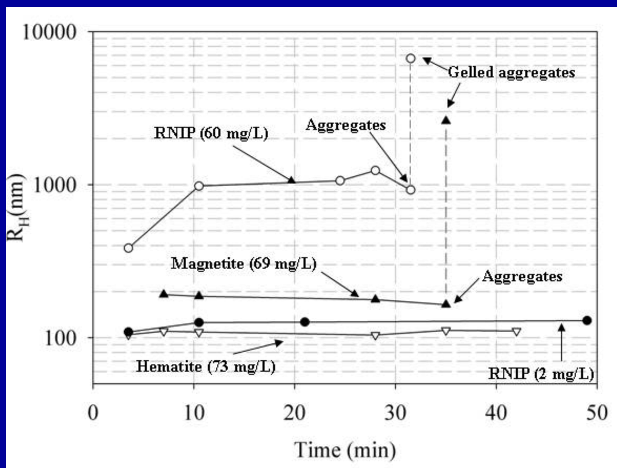
How Long is Bare NZVI Nano?



- 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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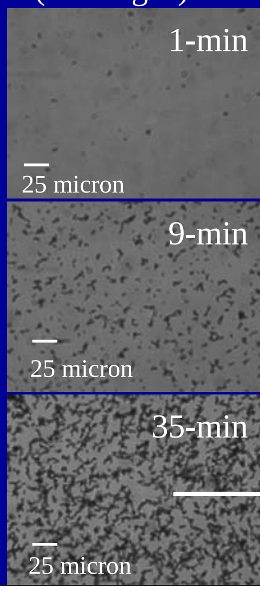
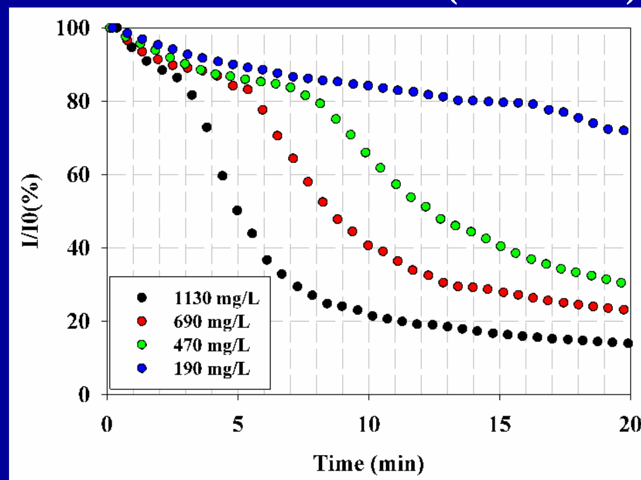
NZVI Aggregation & Sedimentation

$\Phi=10^{-5}$
(~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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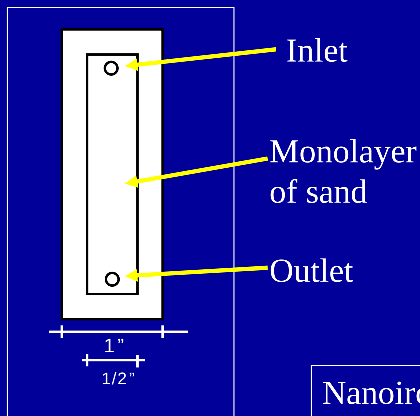
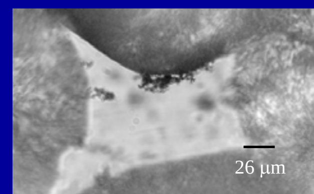
Attachment Limits Mobility



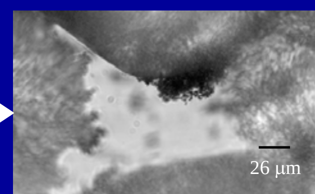
Micro-fluidic PDMS cell

Time=1 min



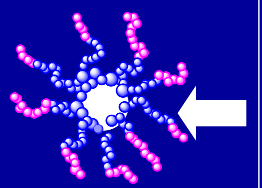
Time=10 min

Nanoiron aggregates are filtered



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

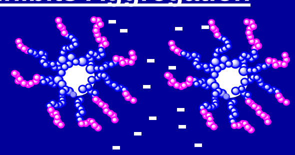
Surface Modifiers Inhibit Aggregation and Attachment and Increase Mobility



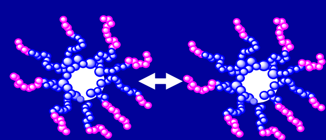
Common Surface Coatings

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

Inhibits Aggregation

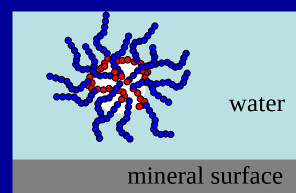


Charge Stabilization



Steric Stabilization

Inhibits Particle-Media Interactions



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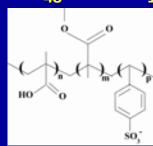
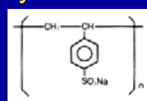
Different Modifiers

Copolymer (MW=125k)

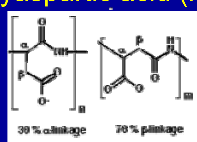
$PMAA_{48}$-$PMMA_{17}$-PSS_{650}



Polystyrene sulfonate (MW=70k)



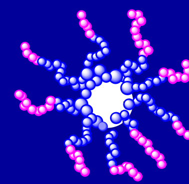
Polyaspartic acid (MW=3k and 10k)



SDBS (MW=350)

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

Increasing MW



Polyelectrolytes

Surfactant

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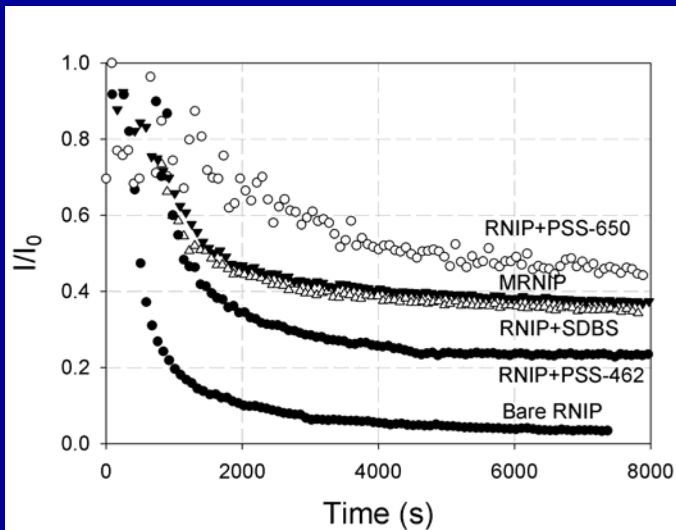
Modifiers Inhibit Agg/Sed



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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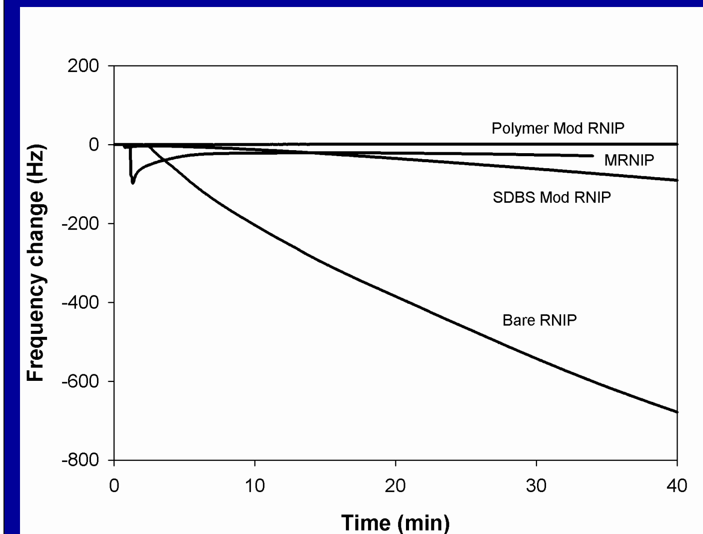
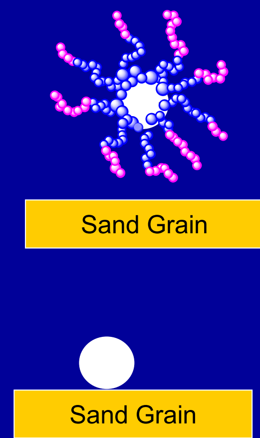
Modifiers Decrease Attachment to SiO_2 Surfaces





QCM is a good predictor of mobility!

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

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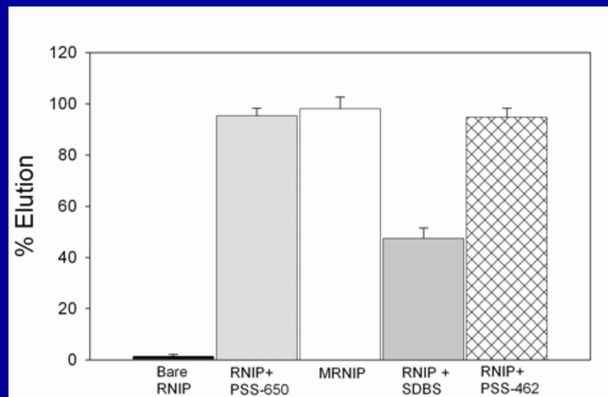
Modifiers Enhance RNIP Mobility



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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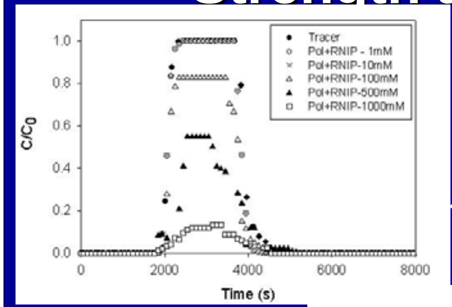
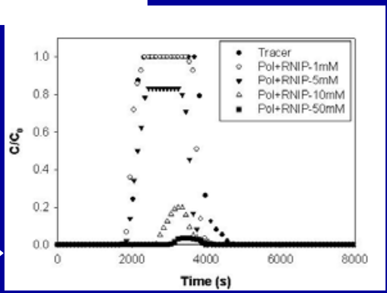
Mobility Depends on Ionic Strength and Composition



Na^+ inhibits mobility

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



Sand
L=61 cm
porosity=0.33
Velocity $3.2x10^{-2}$ 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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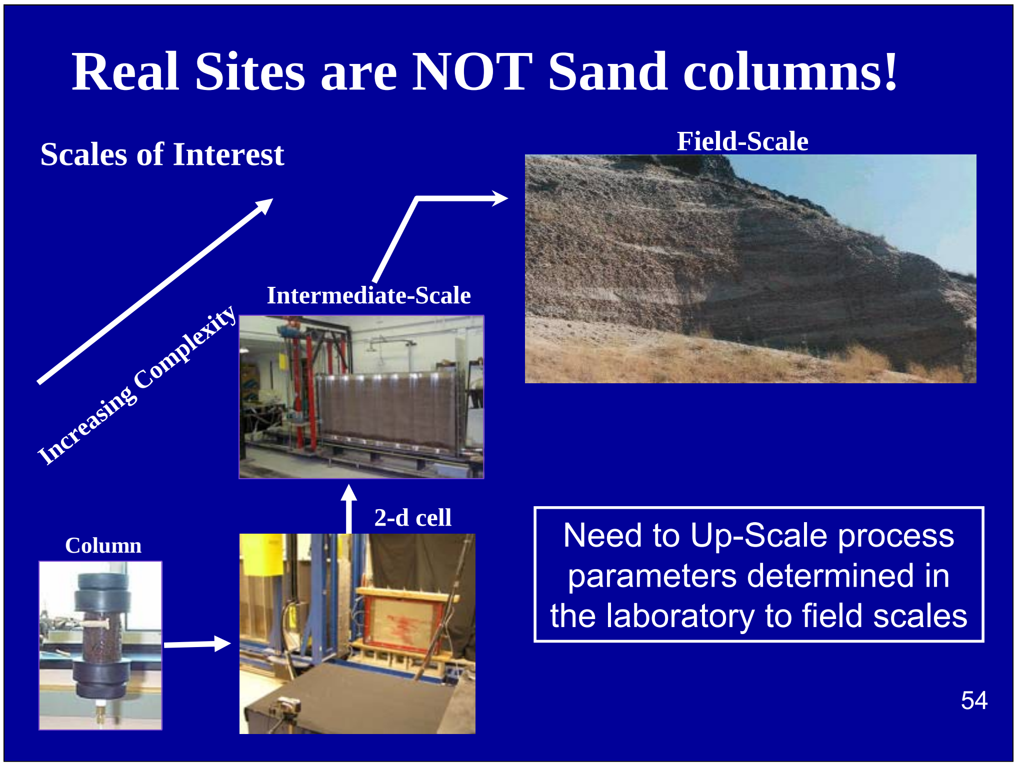
Real Sites are NOT Sand columns!
Scales of Interest
Field-Scale
Intermediate-Scale
Increasing Complexity
2-d cell
Column
Need to Up-Scale process parameters determined in the laboratory to field scales
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NZVI Reactivity and Lifetime

- 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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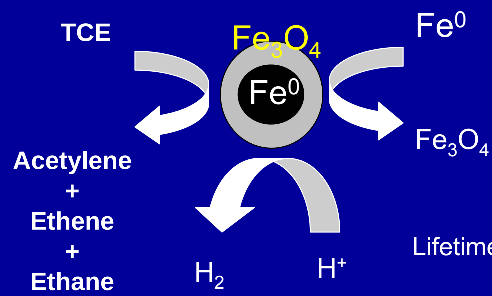
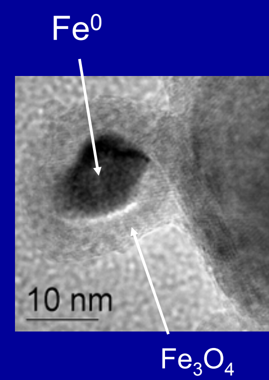
Reactive Fe^0 Nanoparticles

Contaminants are reduced

Nano Fe^0 is oxidized



H^+ is reduced



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

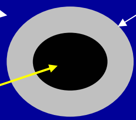
Types of Nanoiron

- 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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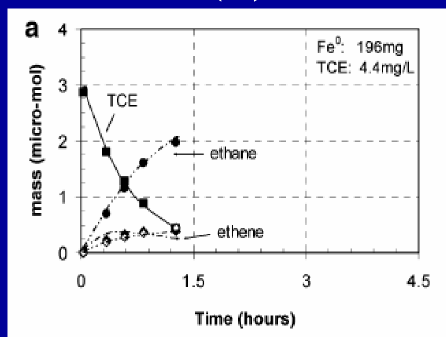
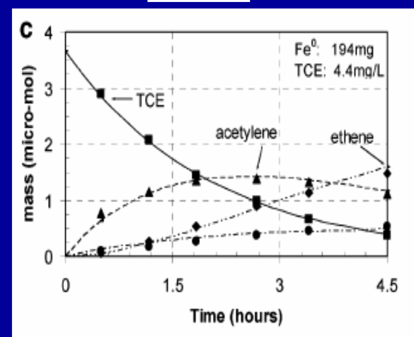
Differences in Reactivity





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

Slower reaction
$k=3 \times 10^{-3}$ L hr^{-1} m^{-2}
Unsaturated Products
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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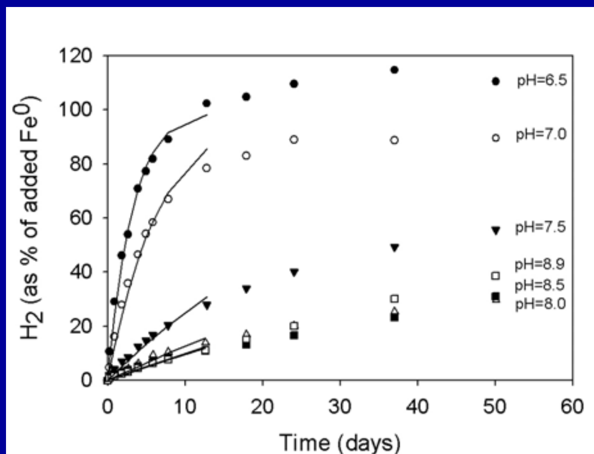
NZVI Lifetime Depends on pH

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$$



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

~2 weeks
pH=6.5

~9 months
pH≥8.0

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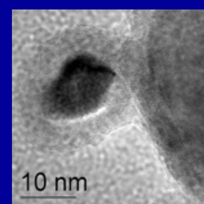
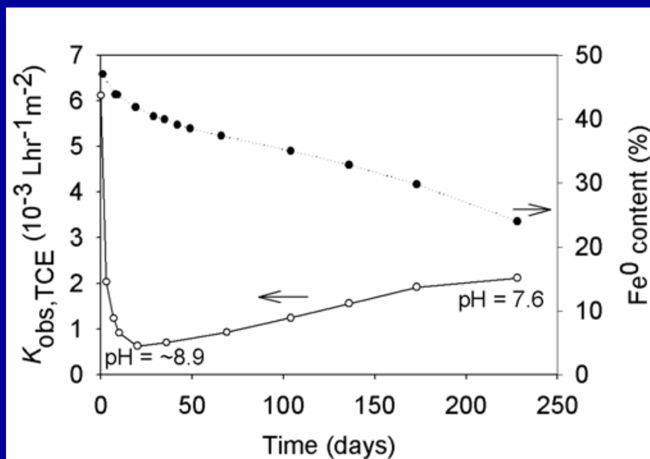
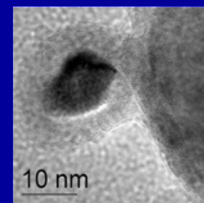
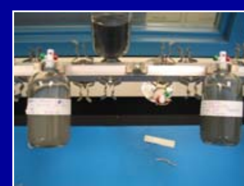


TCE Dechlorination Over Particle Lifetime





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



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

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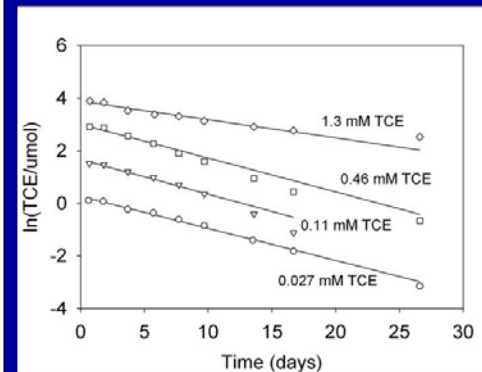
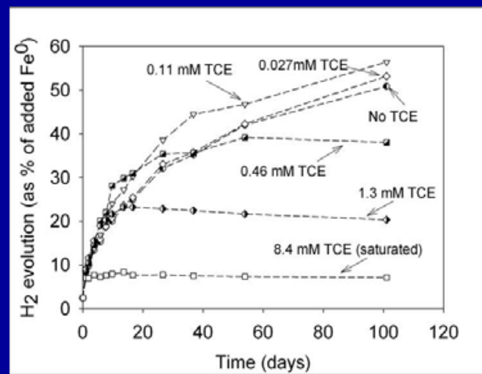
Effect of TCE Concentration on Fe^0 Utilization





Small effect of TCE concentration on reactivity

Use in source zone increases Fe^0 efficiency

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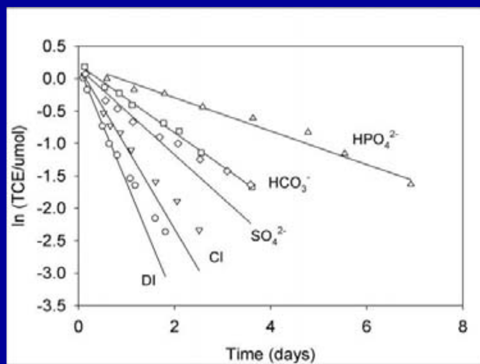
Liu, Phenrat, and Lowry, *Environ. Sci. Technol., (in prep)*

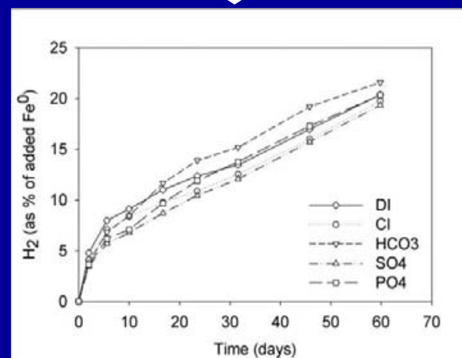
Effect of Groundwater Solutes on Reactivity with TCE



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

Effect follows expected trend of solute strength of complexation with HFO

Dissolved solutes had no effect on H_2 evolution



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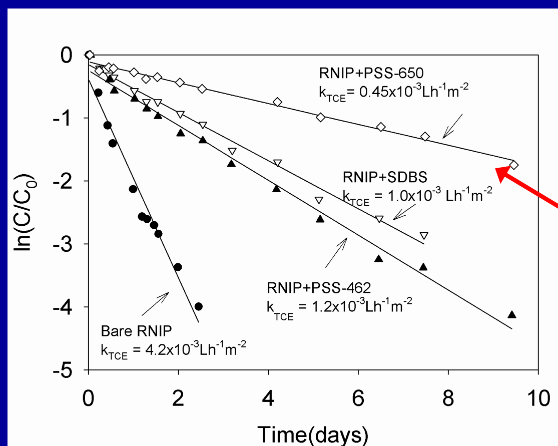
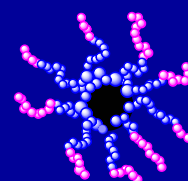
Liu, Phenrat, and Lowry, *Environ. Sci. Technol., (in prep)*

Effect of Modifiers on RNIP Reactivity with TCE



$PMAA_{48}$-$PMMA_{17}$-PSS_{650} modified RNIP: 10 times less reactive 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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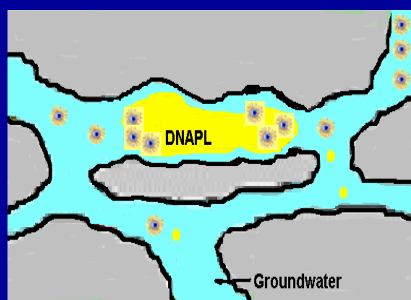
Contaminant Source Zone Targeting

Contaminant Source Zone

Without Targeting Nanoparticles can flow past source zone



Nanoparticle surface coatings can provide an affinity for DNAPL

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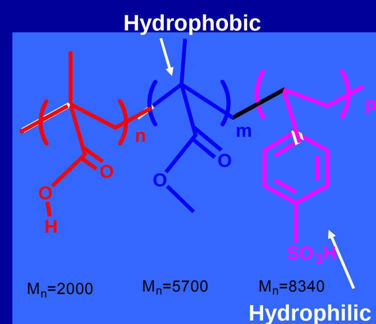
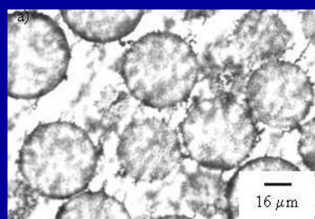
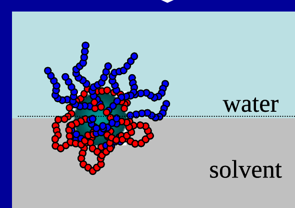
Potential Strategies for Targeting

- Interfacial targeting
- Destabilization Targeting
- Controlled placement





Particles Attach to the NAPL/water interface



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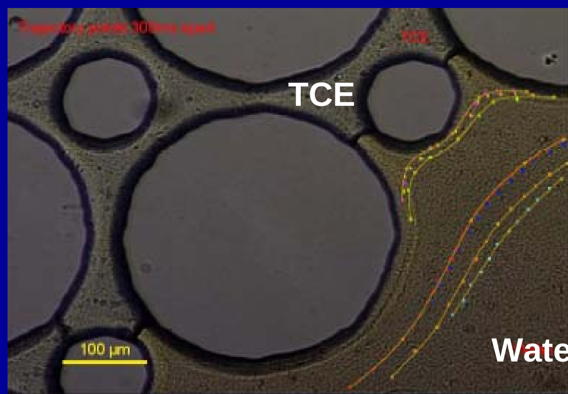
Saleh, N., Lowry, G. V., et al. **(2005)**. "*Nano Lett.* 5 (12) 2489-2494.

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.

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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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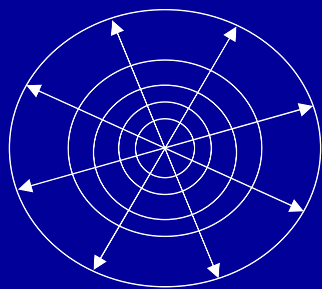
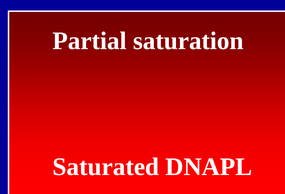
Strategies for Controlled Placement of Nanoiron





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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Acknowledgement

- Toda Koygo Corp.
- U.S. EPA-STAR (R830898)
- US DOE EMSP Program (DE-FG07-02ER63507)
- US DoD (SERDP) (W912HQ-06-C-0038)
- US NSF (CBET-0608646)

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R830898

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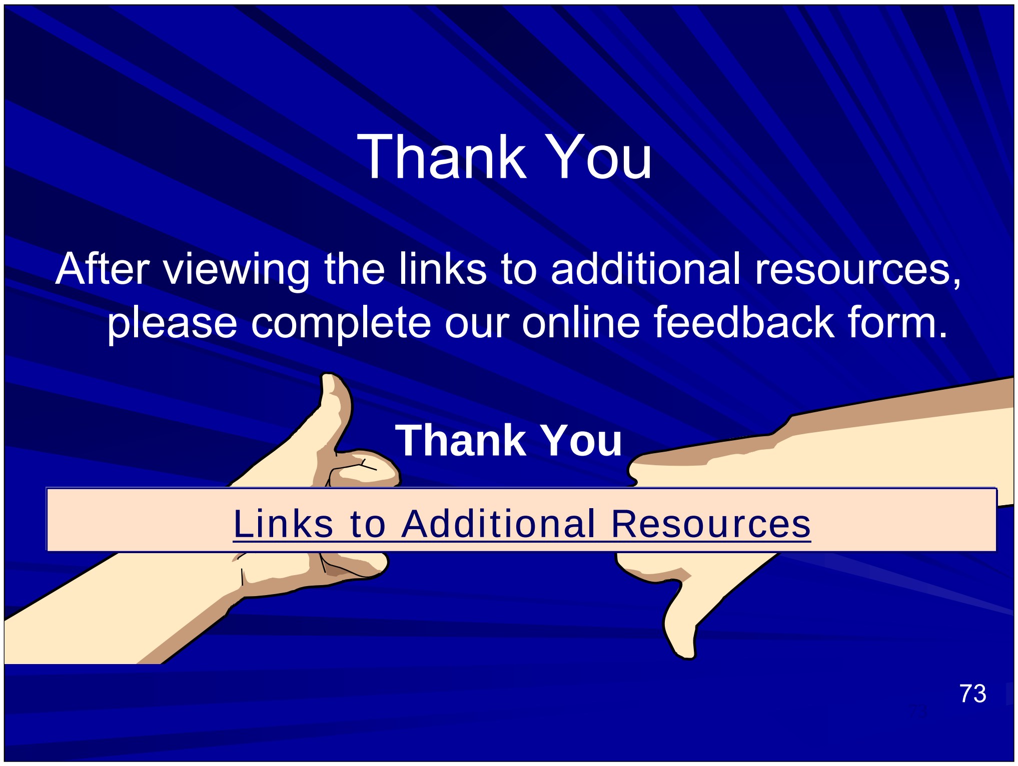

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