Developing Functional Fe^0-based Nanoparticles for In Situ Degradation of DNAPL Chlorinated Organic Solvents

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Carnegie Mellon University

1. Civil & Env. Eng. 2. Chemistry 3. Physics 4. Chemical Eng.

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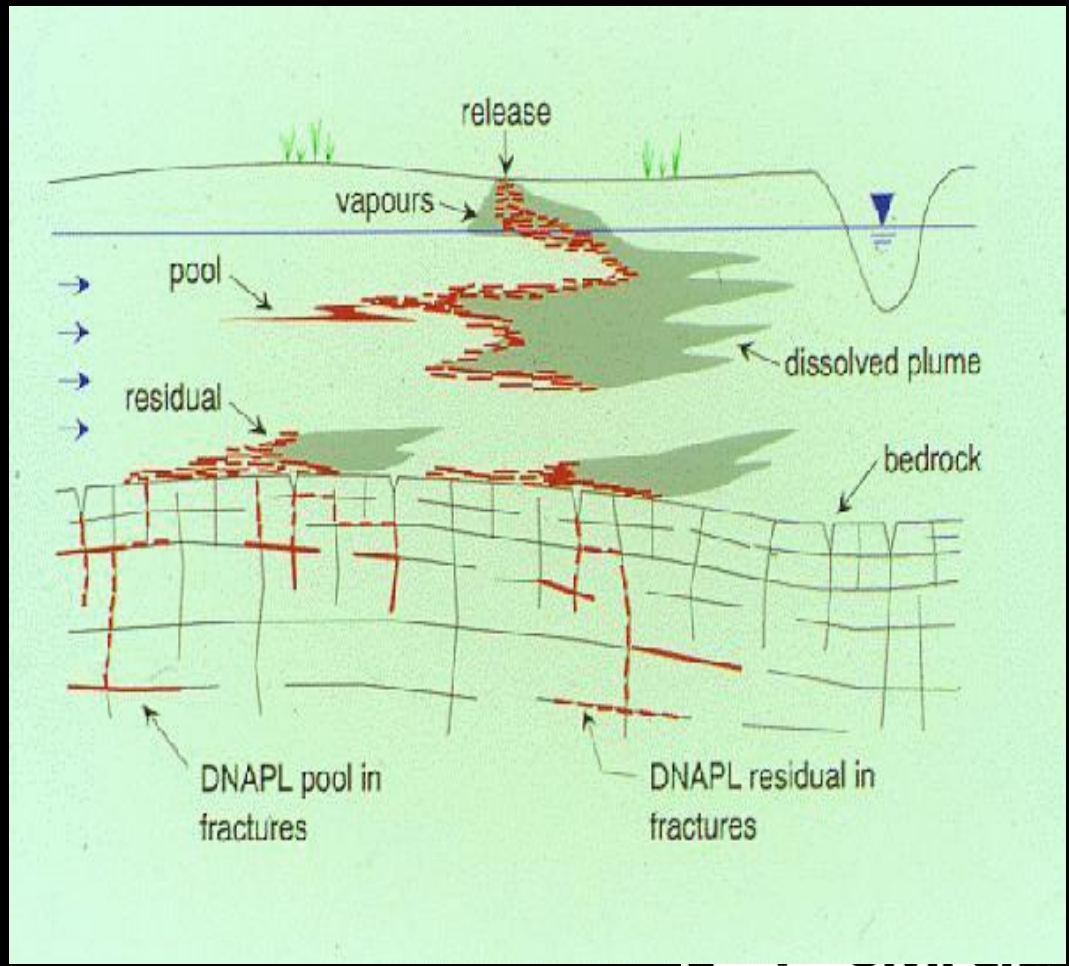
Background

- DNAPL Contamination
  - Long-term source
  - Source area removal can expedite remediation
  - Lower stewardship cost
- Reactive Nanoparticles
  - Fe^0 and bimetallics proven remedial agents
  - Effective delivery to source area is limiting factor



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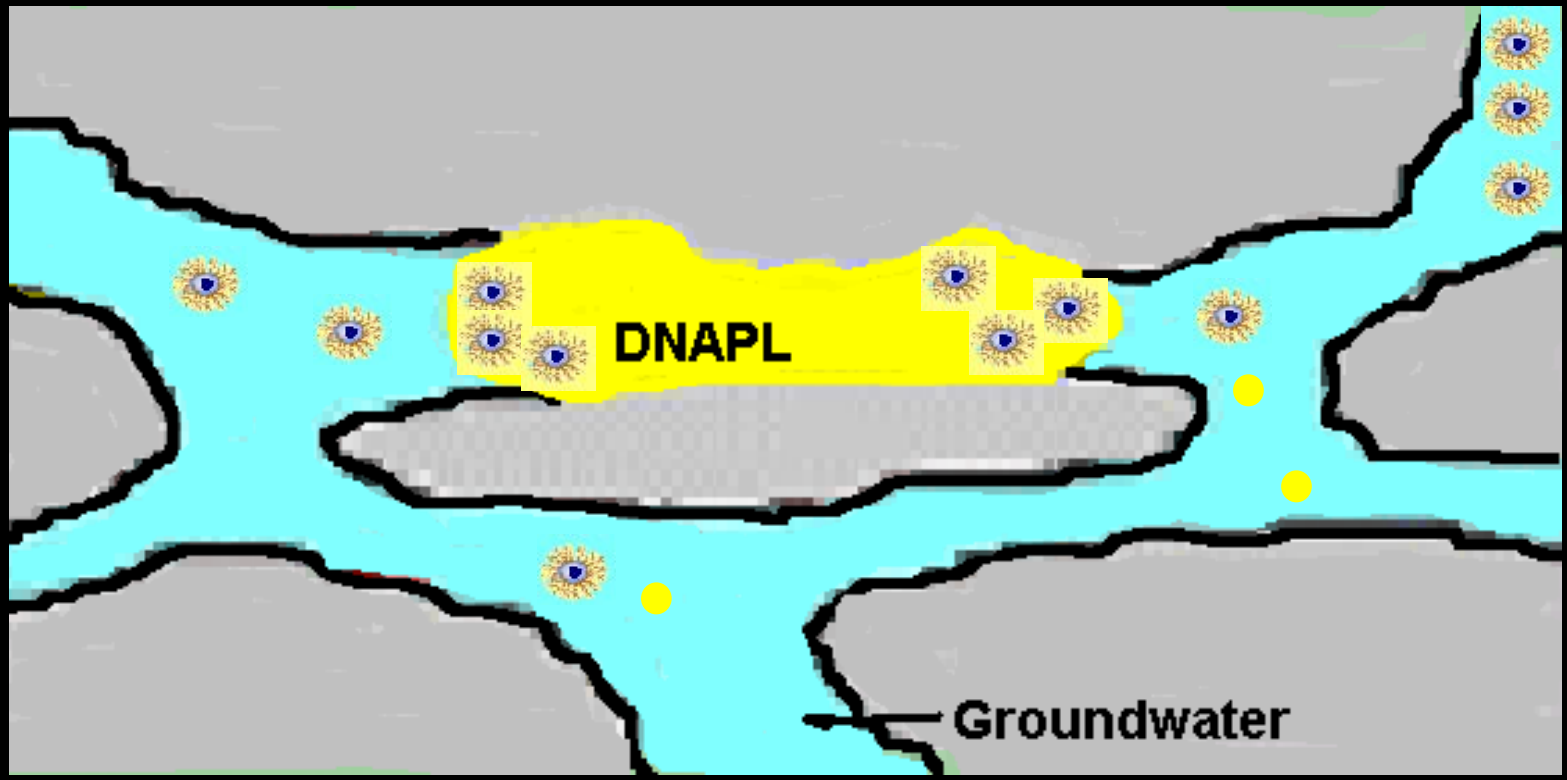
Conceptual Model



: surface-modified, reactive nanoparticles

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Goal/Approach

Project Goal

Synthesize surface modified Fe^0-based nanoparticles that can transport in a saturated porous matrix, preferentially localize at the NAPL-water interface, and degrade NAPL to non-toxic products.

Approach

- Understand the factors controlling reactivity/lifetime of Fe^0 nanoparticles
  - Compare effectiveness of two particle types
- Identify block co-polymers that provide desired transport and targeting behavior
  - Polymer selection
  - Synthesizing polymer coated particles
- Characterize polymer/particles
  - Size, NAPL-water partitioning, transport

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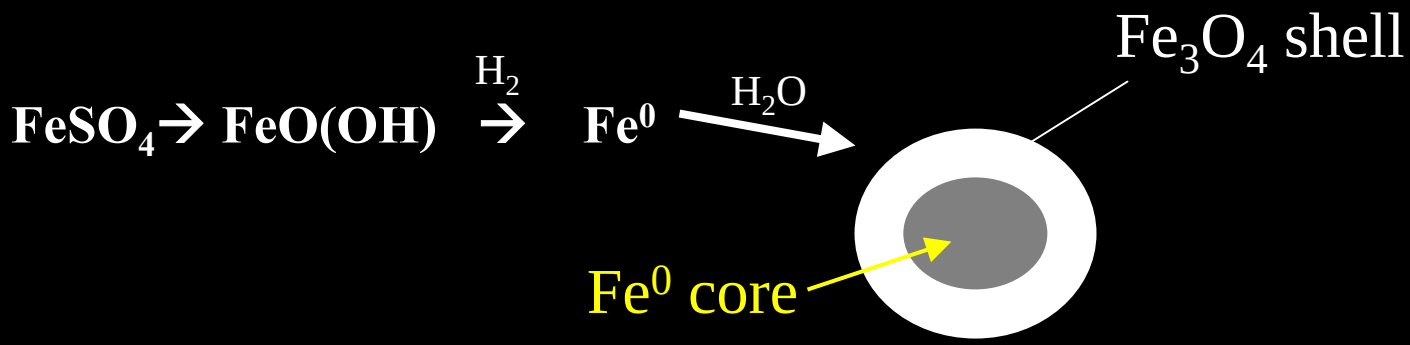
Fe Nanoparticles Evaluated

- Borohydride reduction[1]

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

- Gas phase reduction by H_2[2]



1.Shen, J., Li, Z., Yan. Q., Chen. Y., *J. Phys. Chem.*, **1993**, *97*, 8504-8511
Wang and Zhang, 1997 ES&T, *31*, 2154-2146.
2. U.S.Patent Application, US2003/0217974A1

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Fe Nanoparticle Properties

	Size[1] (nm)	Surface Area (m^2/g)	Elem. Comp. (%)	Morph.
Fe/B	30-40	36	Fe-92 **B-4** O-4	Core-shell
Fe/Fe_3O_4	40-60	23	Fe-88 O-11	Core-shell

1. Primary Particle Size

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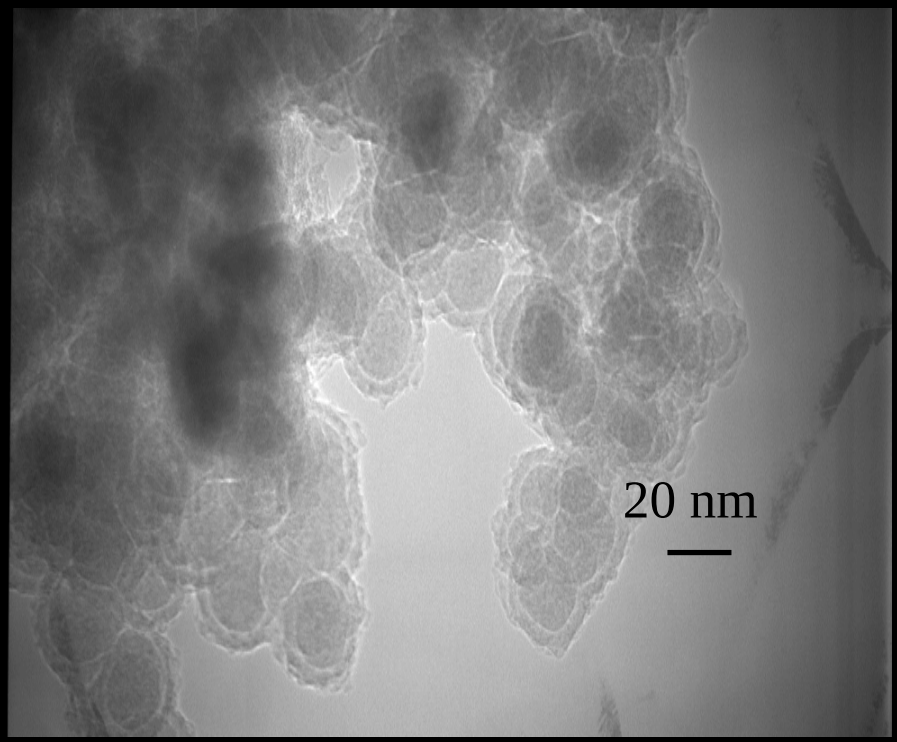
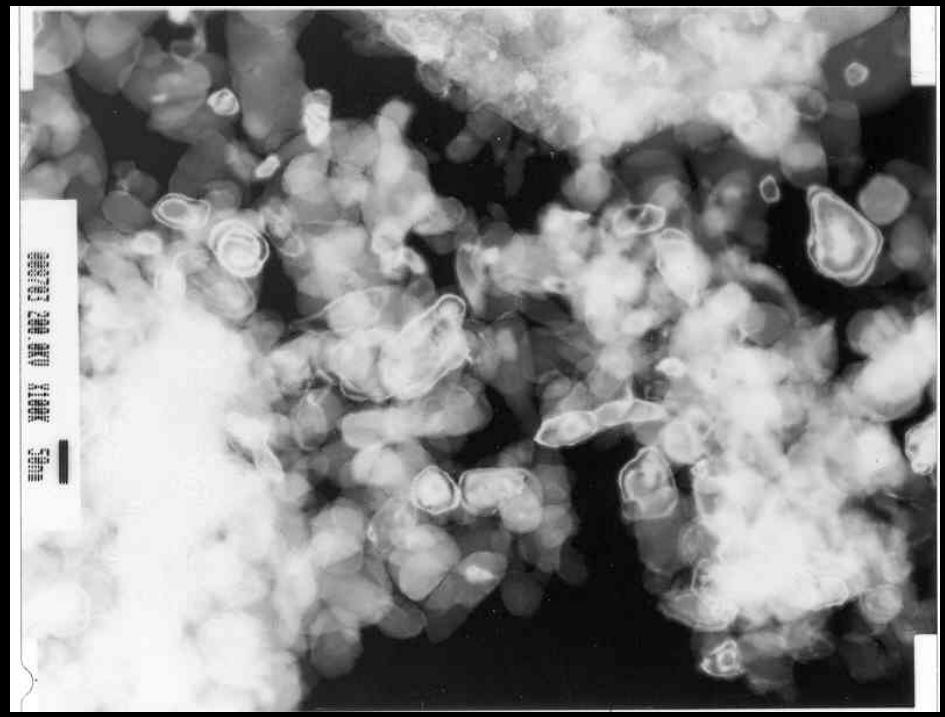
Iron Core-Shell Morphology



Fresh Fe/B particles



Fresh Fe/Fe_3O_4 particles

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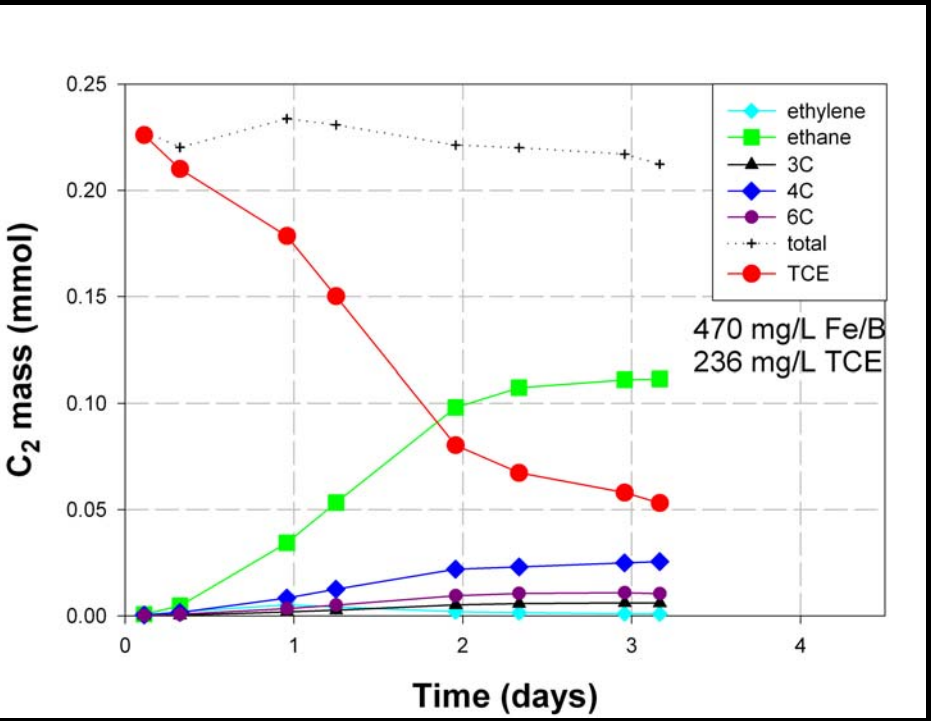
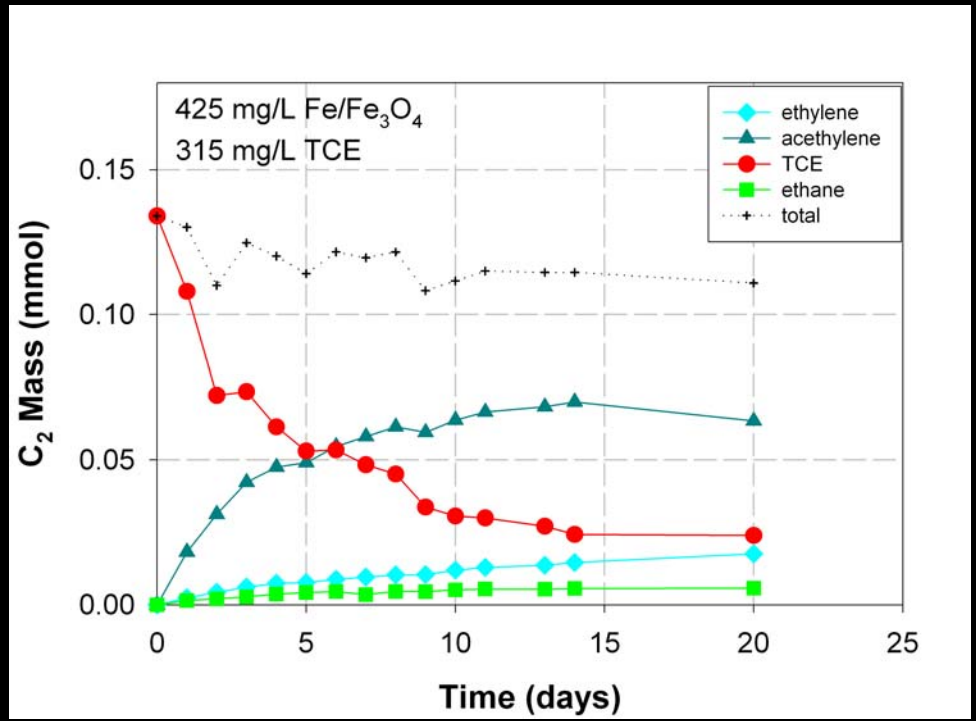
TCE Reactivity Trends





Fe/B
Faster Reaction
Saturated Products
k_{1sa}=0.02 L/m²d

Fe/Fe_3O_4
Slower reaction
Unsaturated Products
k_{1sa}=0.006 L/m²d

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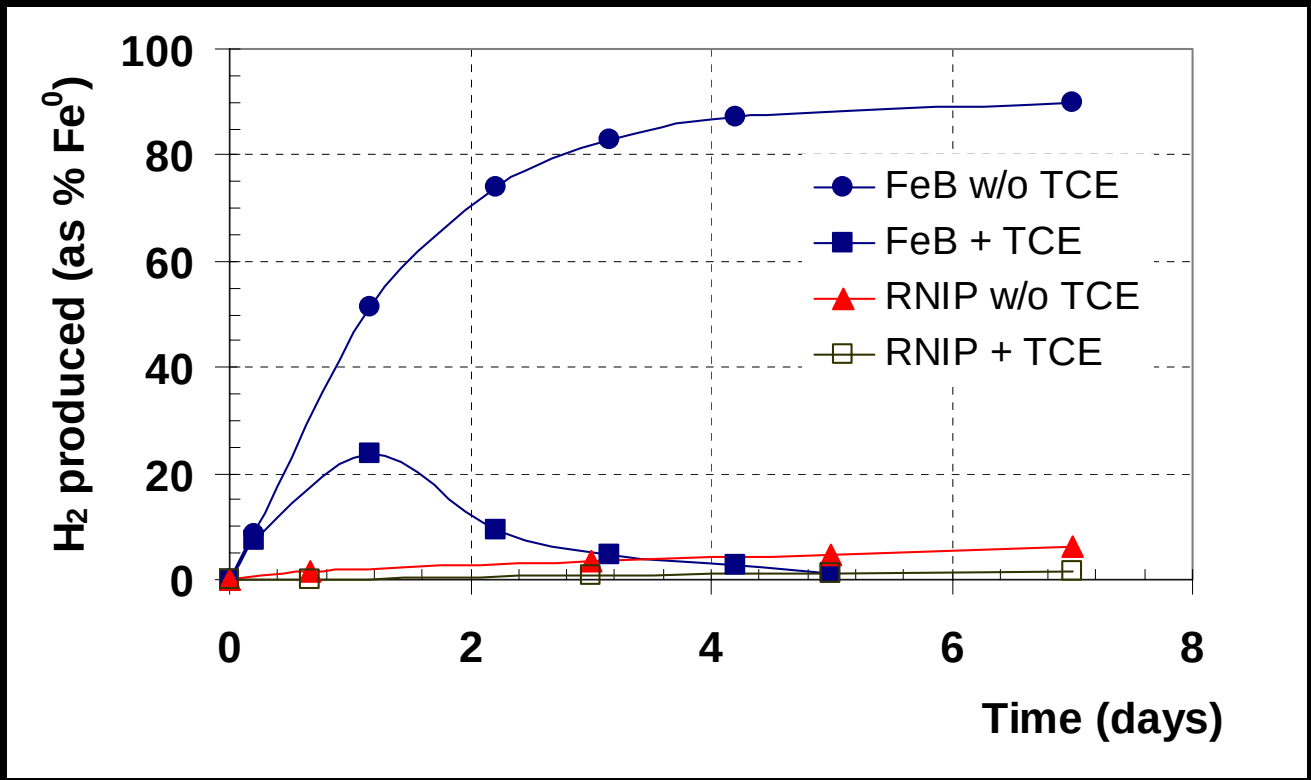
Longevity

- Competing processes
  - $Fe^0 + TCE \rightarrow Fe^{2+} + HC\ products + Cl^-$ (desired)
  - $Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$ (undesired)



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Polymer & Particle/polymer Development

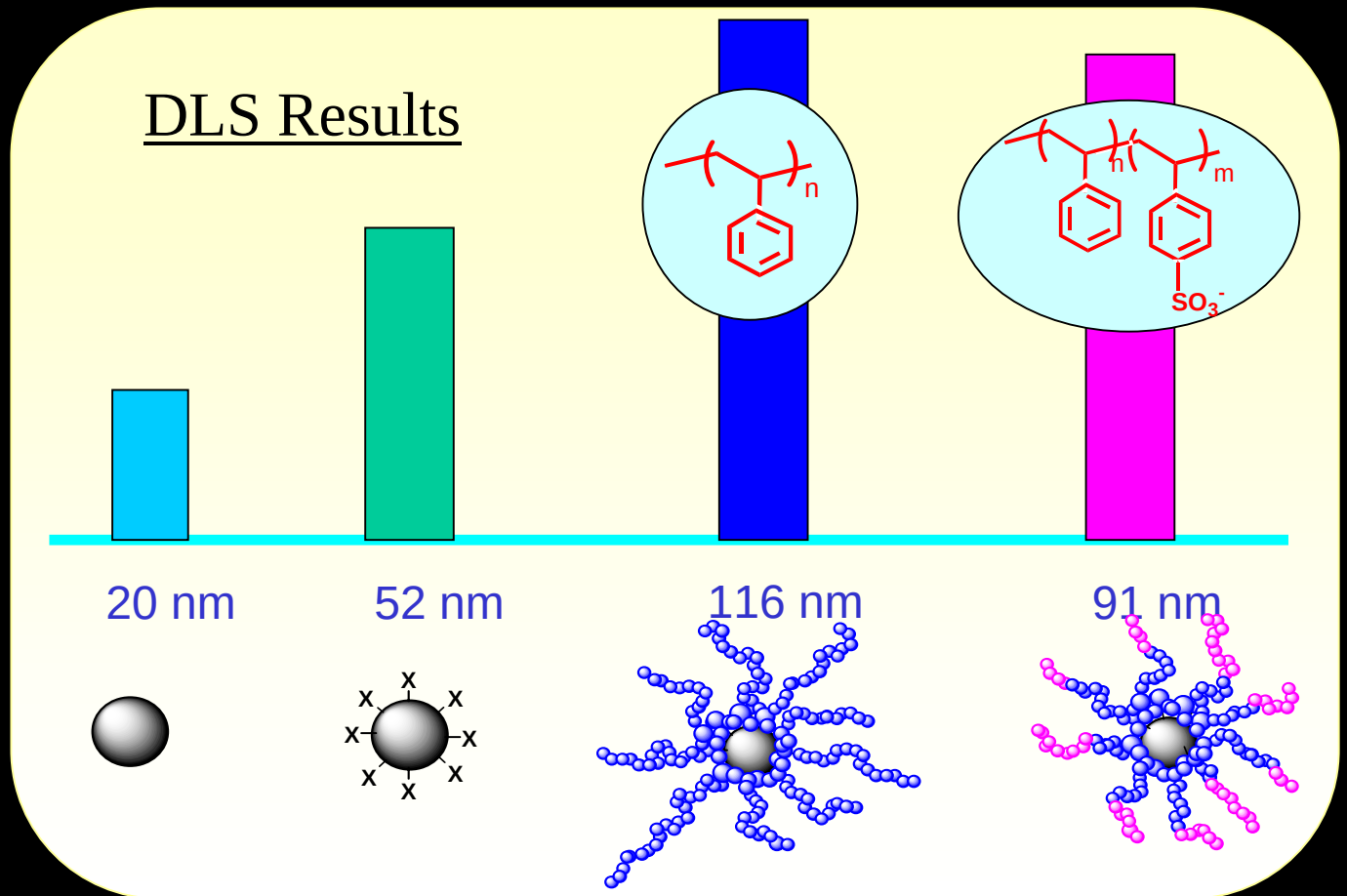
Which polymers?

<u>Requirements</u>
Stable Suspensions

Repulsion from aquifer grains

NAPL-water Partitioning

Inexpensive



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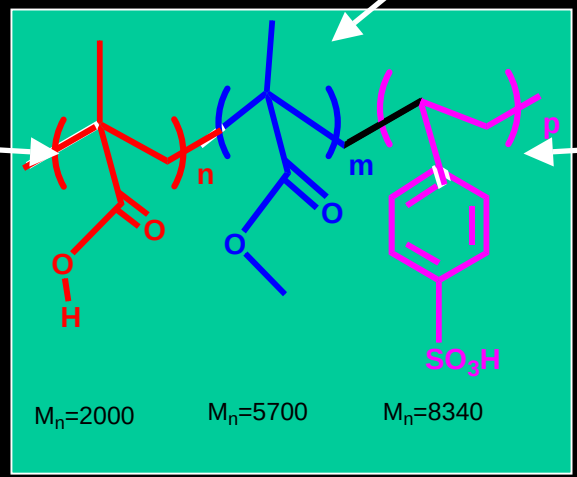
Good Candidate Polymers

- Hydrophobic Blocks
  - Polystyrene
  - poly methyl (or butyl) methacrylate
- Hydrophilic blocks
  - Sulfonated polystyrene

Hydrophobic Block (PMMA or PBMA)

Fe Attachment (PAA)

Hydrophilic Block (PSS)



Triblock copolymer

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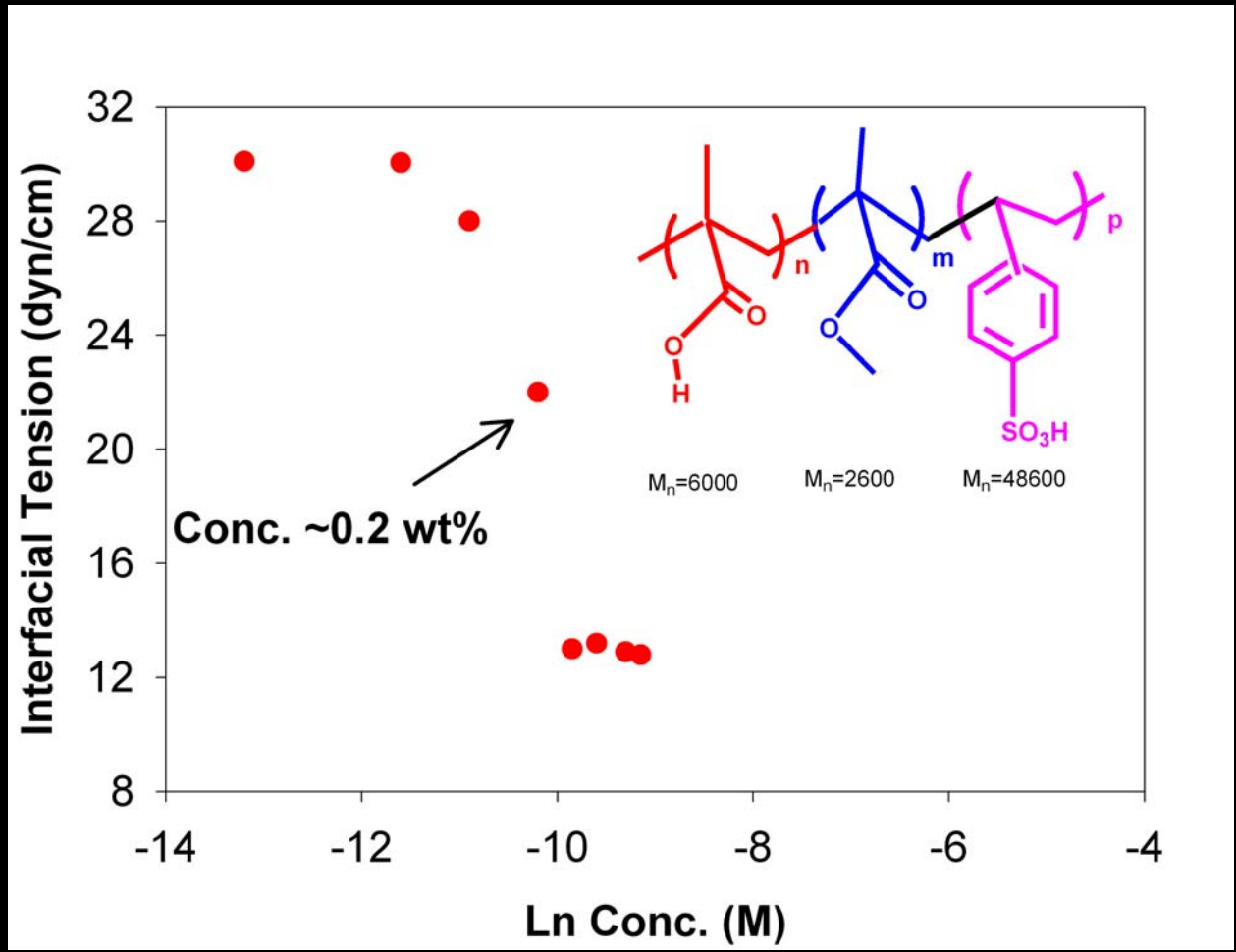
TCE-Water Partitioning

- Du-Nouy ring
- Polymer/Particle partitioning similar
- Demonstrates desired interfacial behavior
- Screening tool
  - block length
  - Block type



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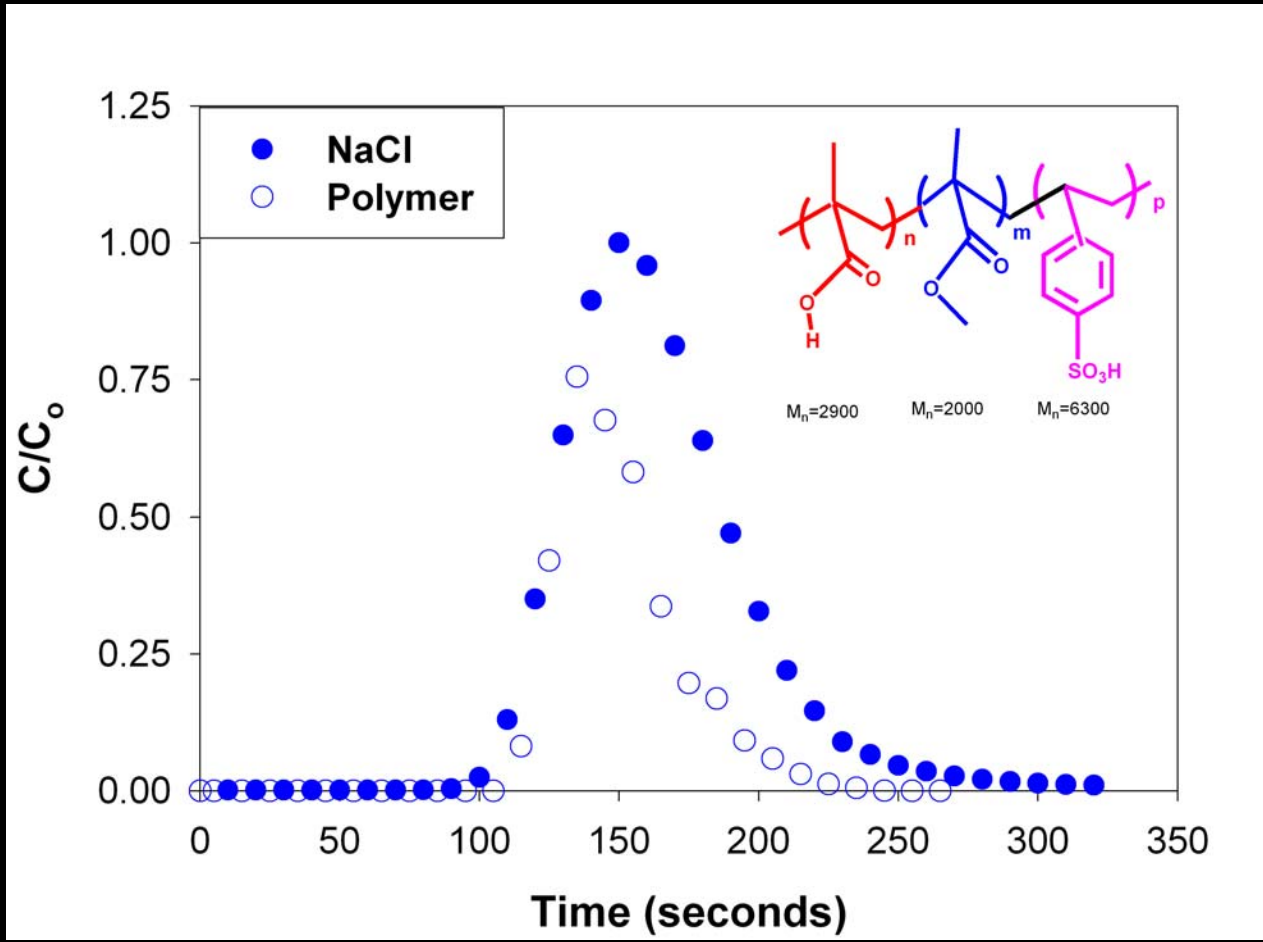
Transport

- Triblock micelles transport through saturated sand columns
  - Little retardation
  - Good efficiency
  - Needs optimization



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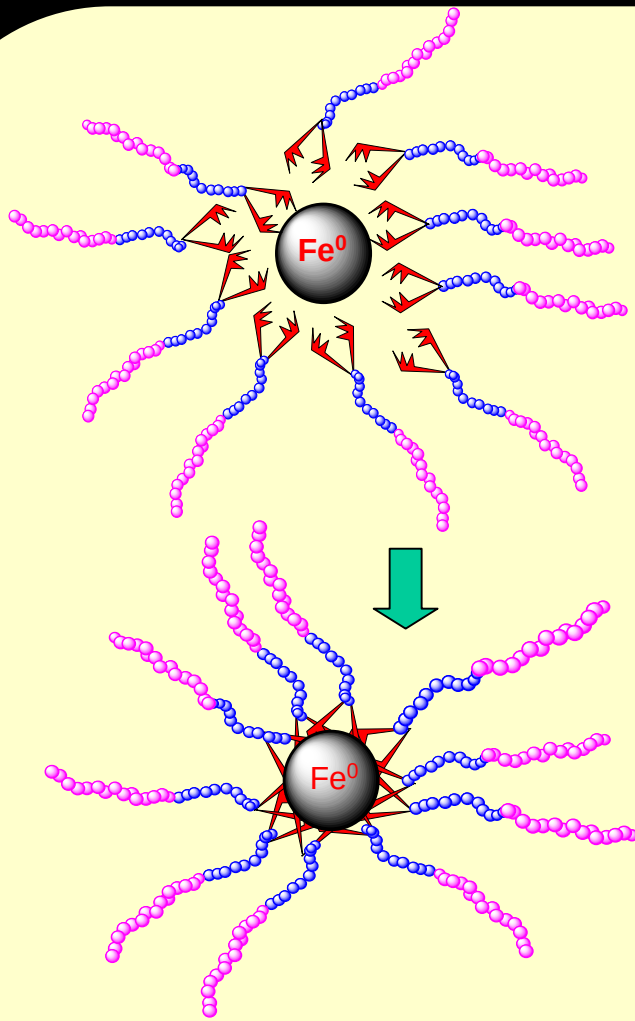
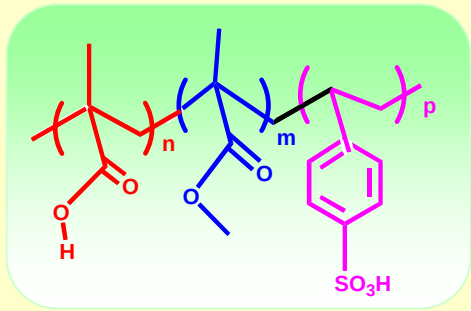
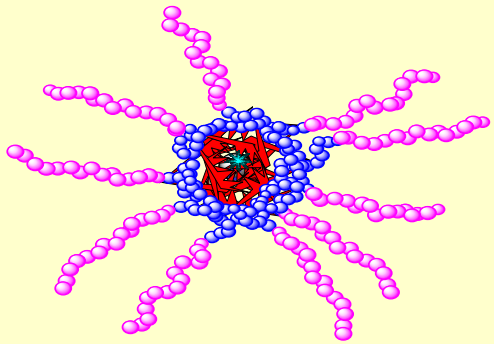
Fe^0 Core-Shell Nanoparticles





Poly (MAA)-b-poly(MMA)-b-poly(STS)



Triblock copolymers anchor Fe nanoparticles via poly(AA) groups

The hydrophobic blocks form a protective shell around the Fe nanoparticle

Summary

- Fe^0 nanoparticles are highly reactive, fully utilized, and very efficient in TCE-water systems
- Polymer-particle hybrid particles have been synthesized
  - Nano sizes (~100 nm)
  - Good NAPL-water partitioning
  - Good transportability
- PAA-PMMA-PSS triblock copolymers provide desired transport and NAPL-water partitioning
- Polymer coated Fe0 particles synthesized but not yet optimized

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