An Innovative Nanotechnology for In-Situ Mercury Immobilization

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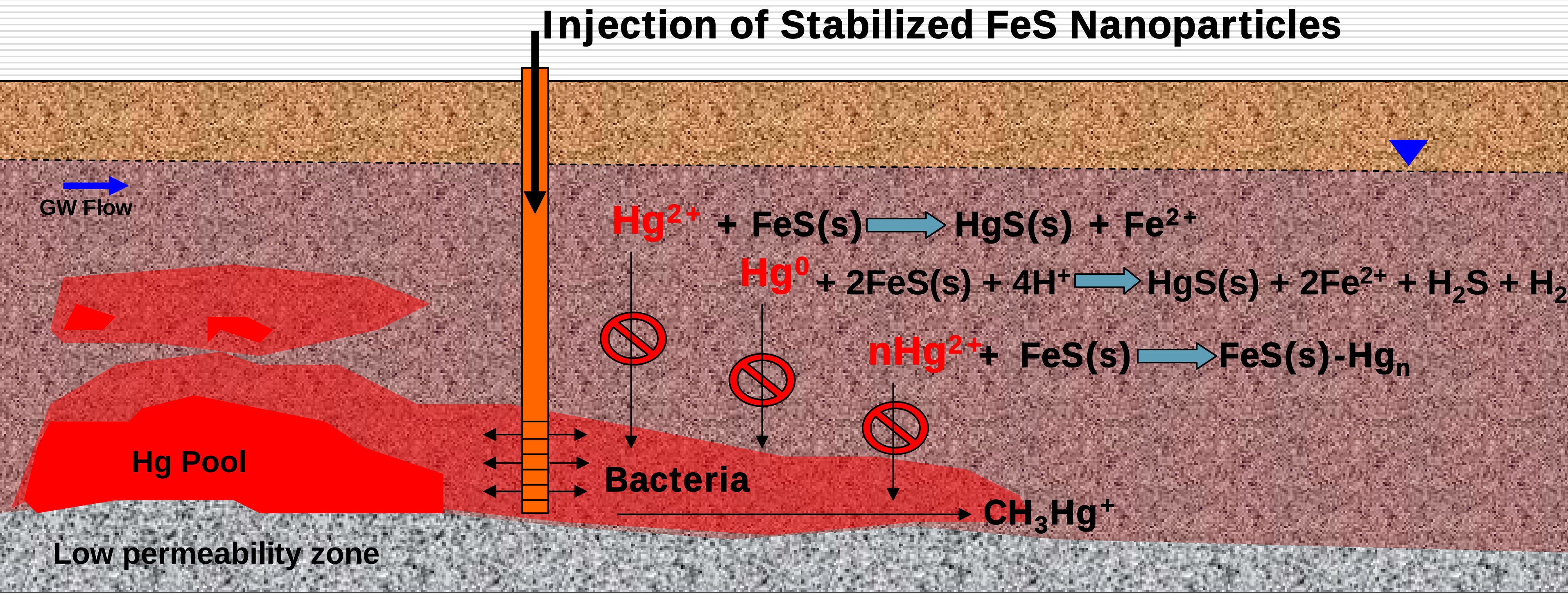
Our Strategy for Mercury Remediation



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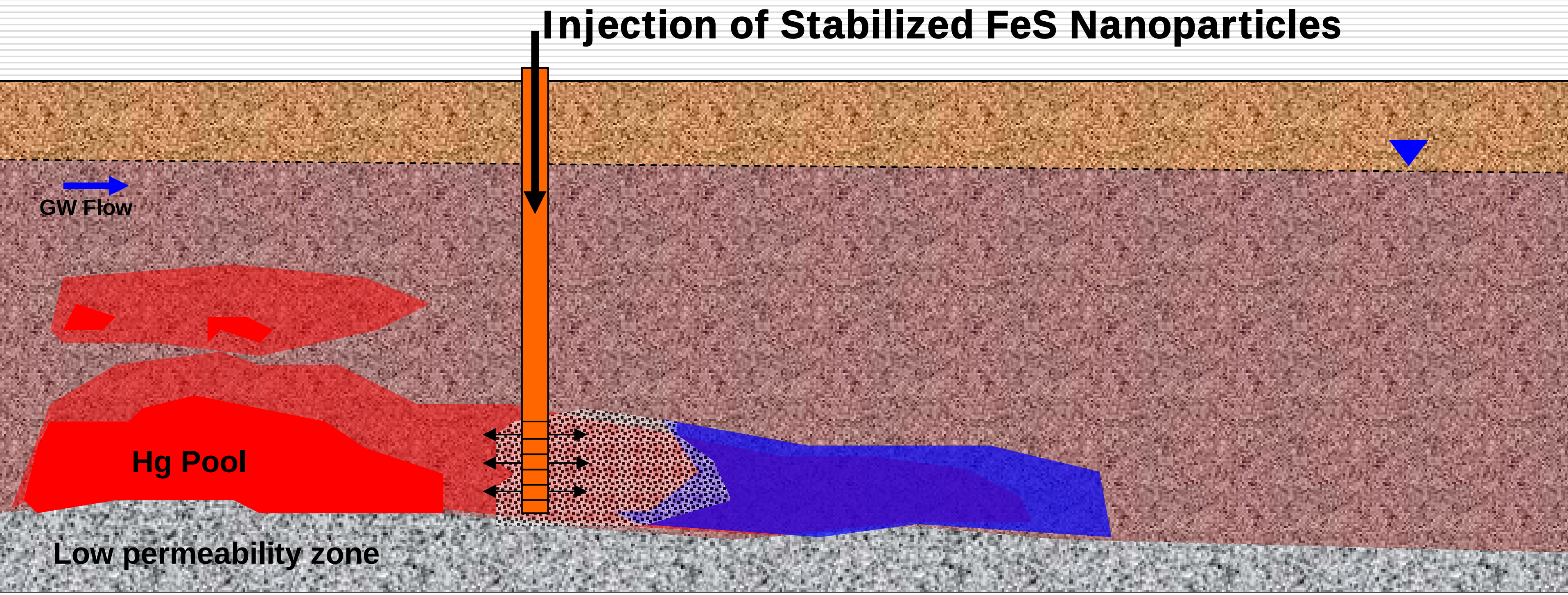

Nanoparticles are delivered to the subsurface; the stabilizer coating biodegrades (days to weeks), and particle agglomerate or absorb to soil/sediment surfaces; over time particles lose mobility but continue to offer prolonged immobilization capacity.

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Nanotechnology (1-100 nm) Advantages

- **Easily delivered (e.g. injected) to near-surface or subsurface where contamination exists**
- **High surface area, highly reactive, and able to diffuse in soil/sediment pores**
- **Can immobilize Hg**
  - **in soil or groundwater**
  - **in a source zone or distal plume**
  - **as a in-situ barrier or cap**
  - **ex situ**

Why FeS?

- Highly stable, i.e. extremely insoluble in water and unavailable to biota; K_{sp} (FeS) = $8x10^{-19}$; innocuous to the environment

- Extremely attractive to Hg:

$$FeS(s) + Hg^{2+} \rightarrow HgS(s) + Fe^{2+}$$

$$FeS(s) + nHg^{2+} \rightarrow FeS\text{-}nHg^{2+}$$

$$2FeS(s) + Hg^{0} + 4H^{+} \rightarrow HgS(s) + 2Fe^{2+} + H_2S + H_2$$

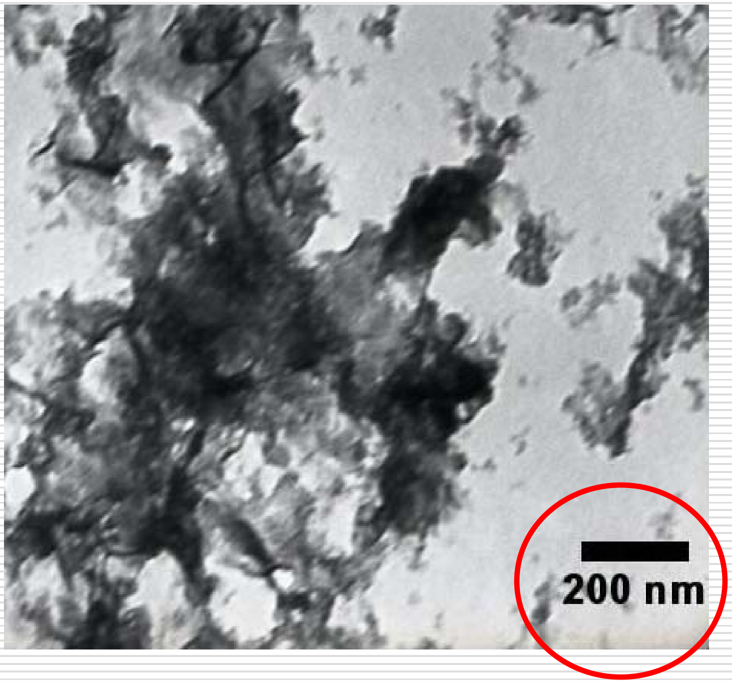
Iron sulfide minerals have been known as excellent dsorbers for Hg^{2+} and Hg^{0} (Brown, et al. ES&T, 1979)

K_{sp} (HgS) = $2x10^{-53}$ (black) or $2x10^{-54}$ (red)

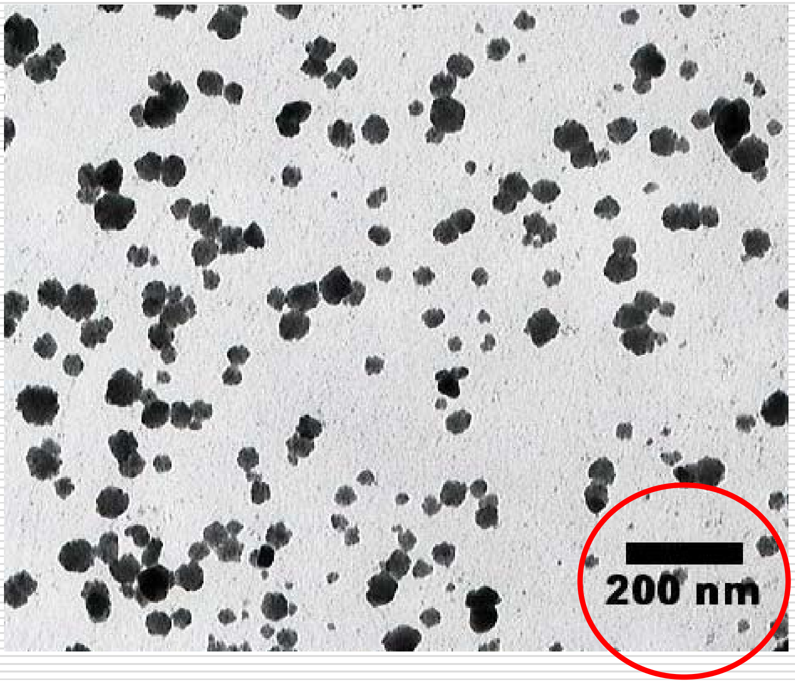
Why Stabilizers are Needed for the Nanoparticles?

- Control size (prevent agglomeration) and soil/sediment mobility of the nanoparticles
- Enhance Hg immobilization due to smaller particle size, greater surface area
- Stabilizers are polysaccharides (water-soluble starch or cellulose)
- Low cost, environmentally friendly "green" product

Transmission Electron Microscope (TEM) Images of FeS Particles



(a) Fresh 0.5 g/L FeS without a stabilizer



(b) Fresh 0.5 g/L FeS with 0.2% (w/w) CMC

D = 38.5 ± 5.4 nm

Xiong, Z.; He, F.; Zhao, D.; Barnett, M.O. **Water Research, 2009**
Zhao, D.; Xiong, Z.; Liu, R.; He, F.; Barnett, M.O.; Harper, W.F., **2009, U.S. Patent, US 7,581,902 B2.**

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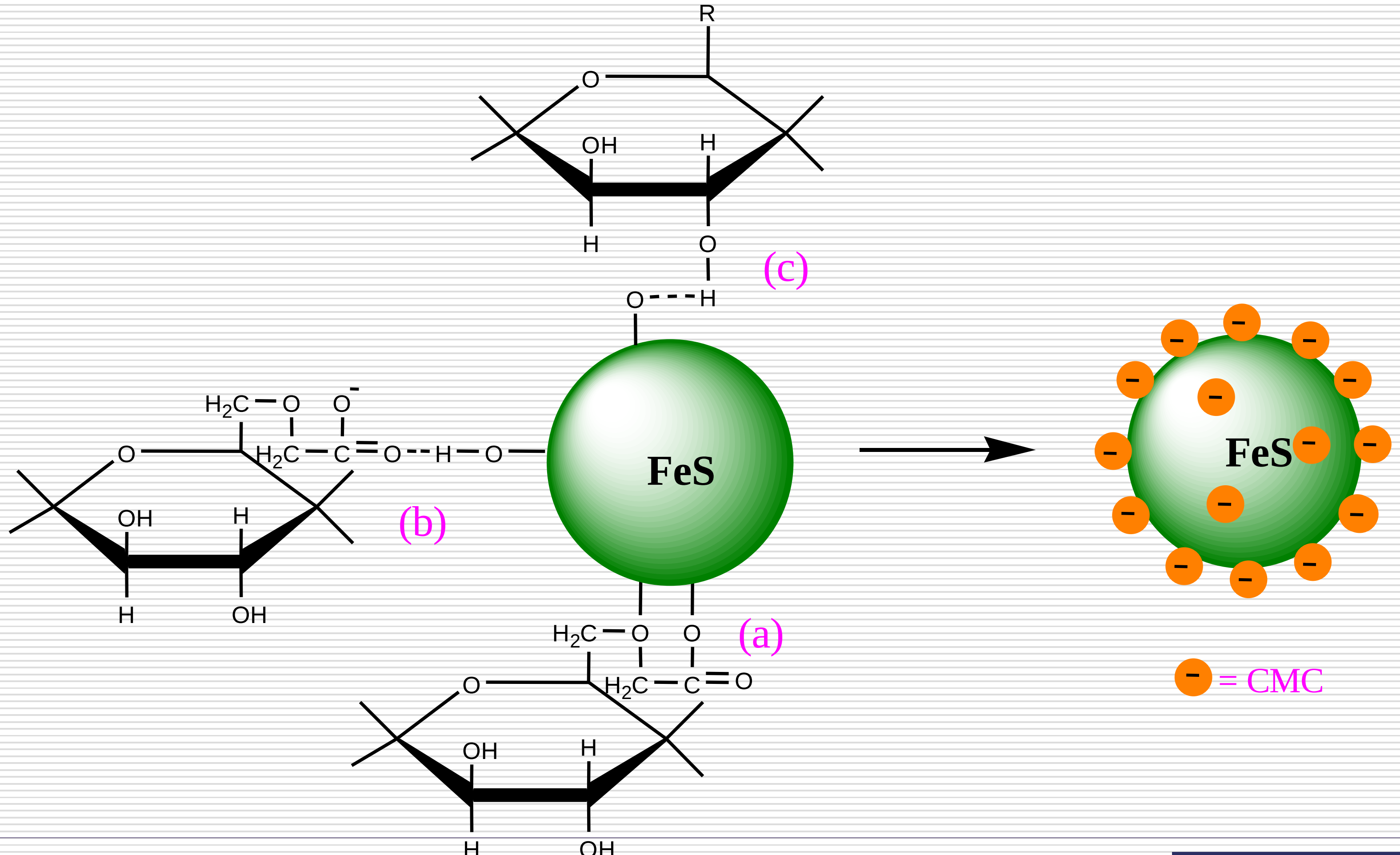
Comparison of FeS Nanoparticles w/ and w/o a Stabilizer

(a) w/o a stabilizer (b) with 0.1% (by wt.) of NaCMC

When kept in sealed vials, the capped nanoparticles remain fully suspended for weeks; When exposed to air, the particles are oxidized in days.

Stabilization Mechanism



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FeS Nanoparticles can be Prepared On-site to Maximize Performance

Step 1. Prepare CMC and Fe^{2+} stock solutions containing 0~0.5% (w/w) of CMC and 0.1-1 M Fe^{2+}.

↓

Step 2. Vary the stabilizer-to-Fe molar ratio and mix CMC-Fe^{2+} solution under purified N_2 gas.

↓ ← **System under vacuum and mixing**

Step 3. Add stoichiometric amount of Na_2S solution into the above mixture and allow for reaction under vacuum and at room temperature.

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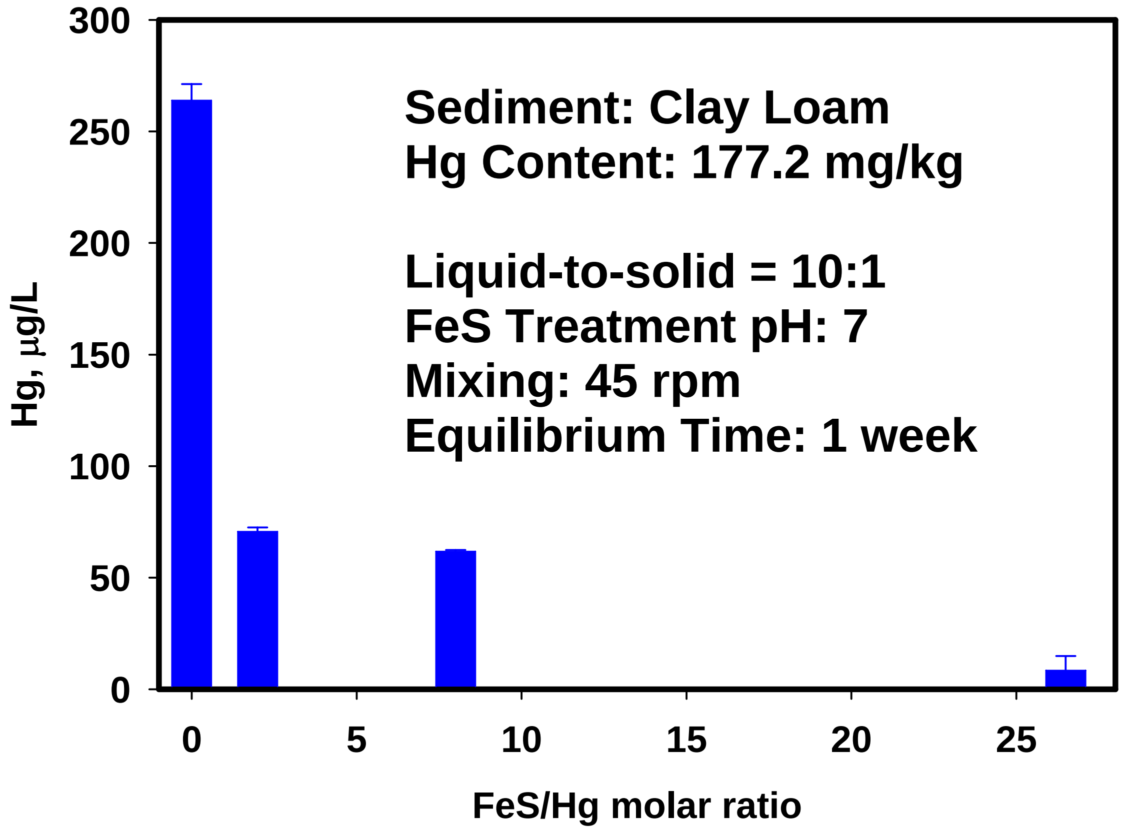
Batch Test: Hg-Laden Sediment Treatment with FeS Nanoparticles



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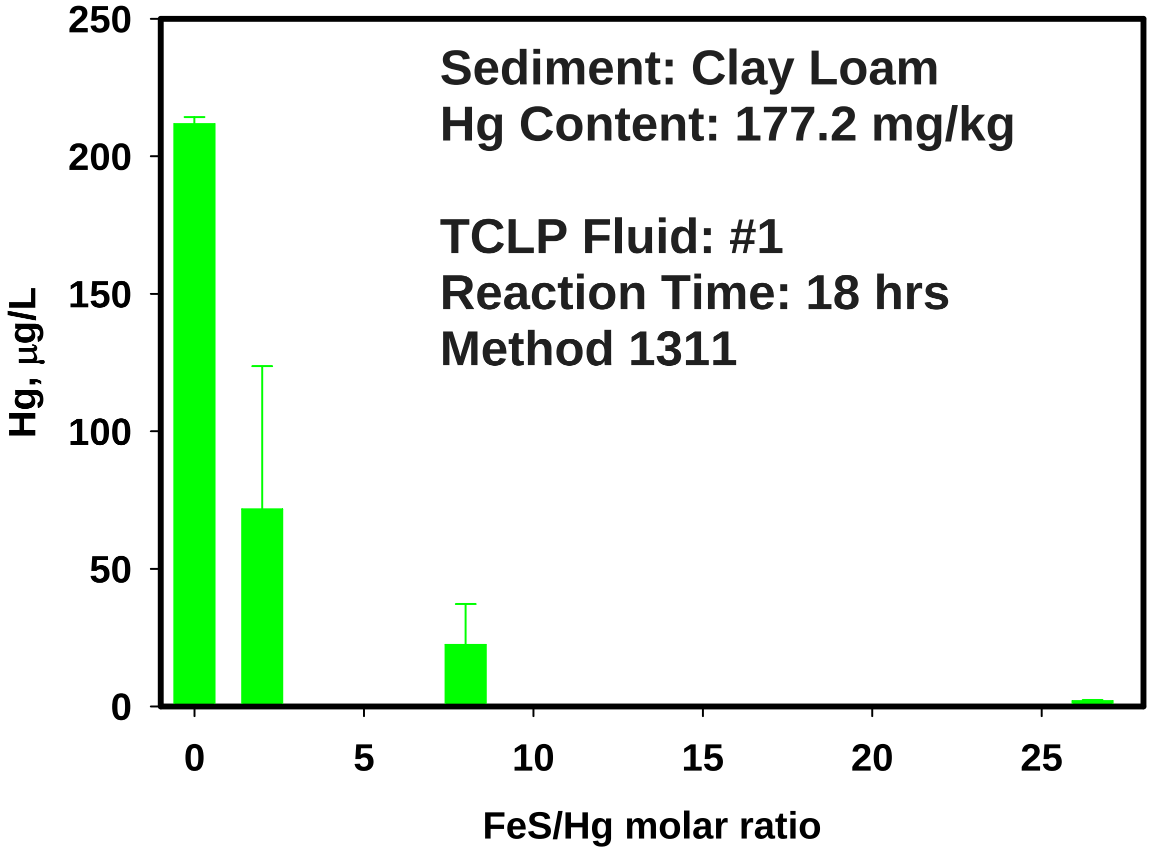
Toxicity Characteristic Leaching Procedure (TCLP) Tests



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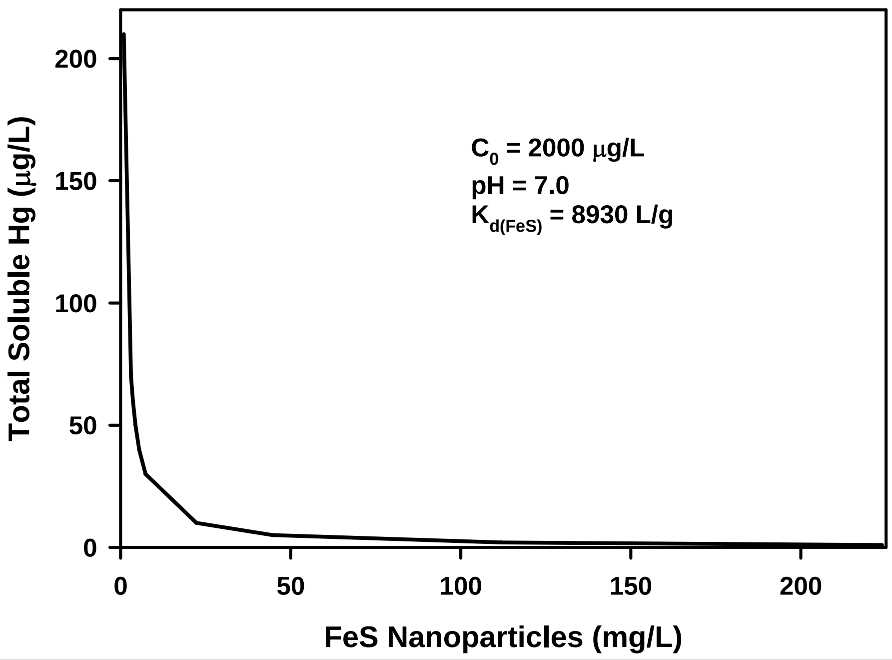
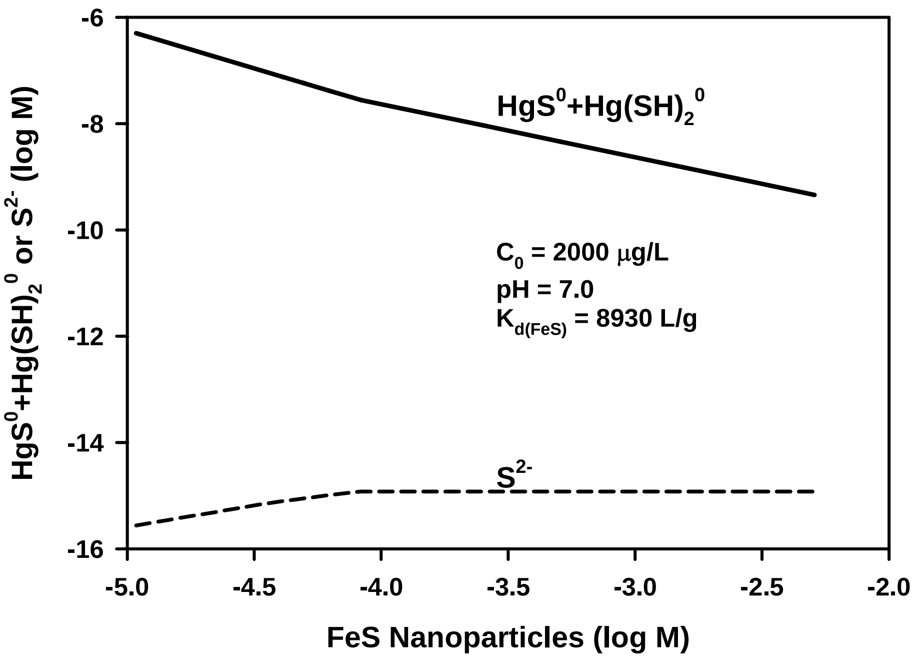
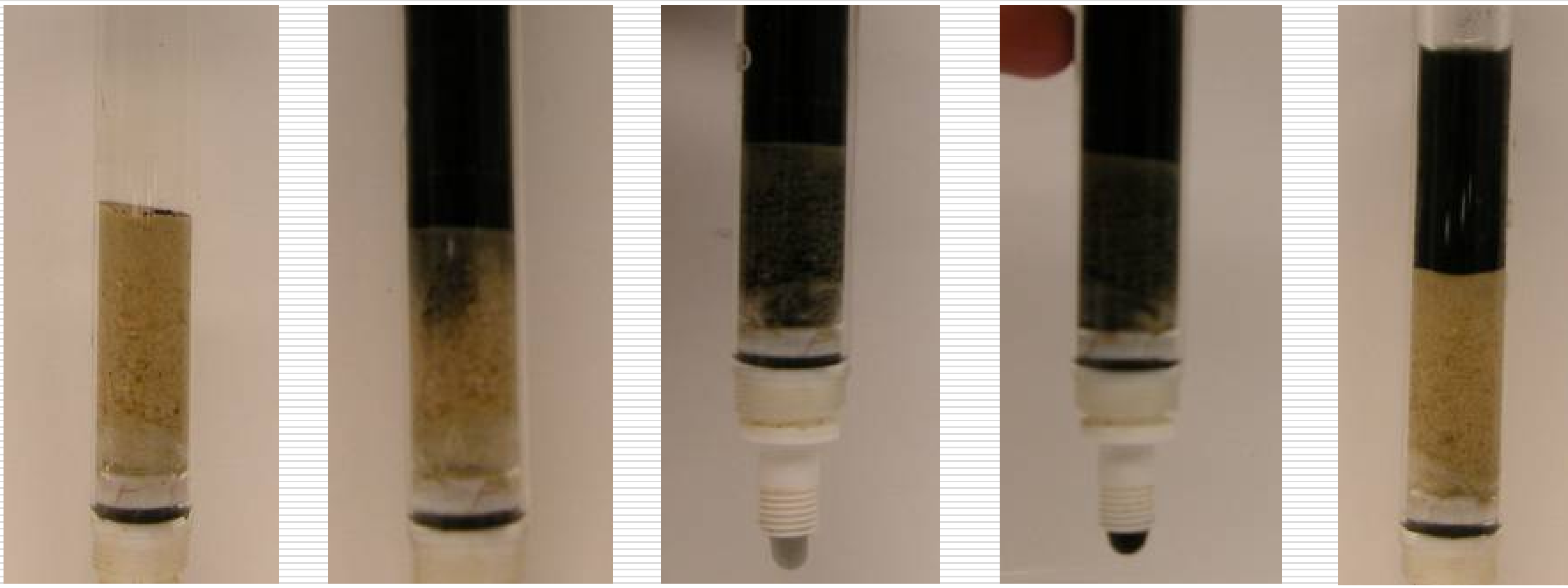
Hg Speciation Study Using MINTEQ





Nanoparticle Delivery by Gravity



Soil type: sandy soil

1 min | 15 min | 20 min

0.5 g/L FeS stabilized with 0.2% CMC

Non-stabilized 0.5 g/L FeS (30 min)

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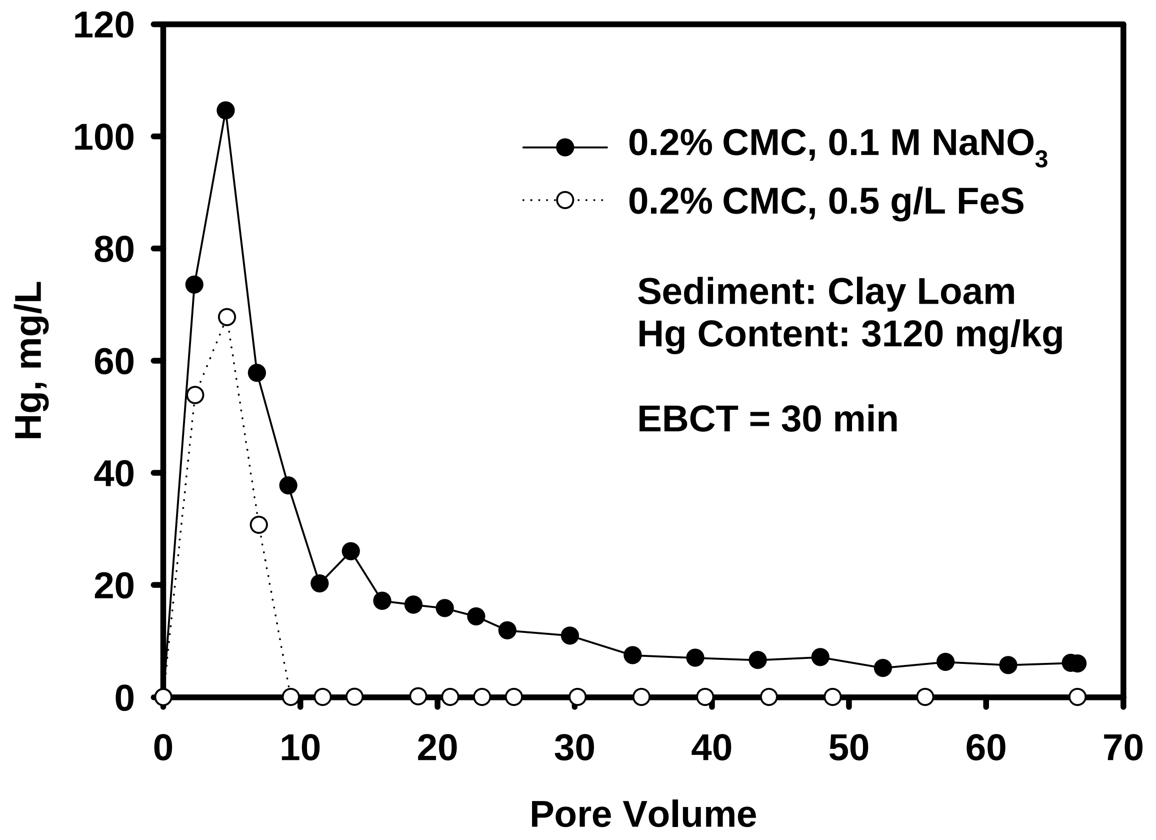
Column Test: Hg-Laden Sediment Treatment with FeS Nanoparticles



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Chemical Cost of FeS Nanoparticle

Chemicals	lb needed/lb-FeS	Unit industrial price, $/lb	Sub-total, $	Total, $
$FeSO_4 \cdot 7H_2O$	3.16	0.0795	0.251	1.12
$Na_2S \cdot 9H_2O$	2.72	0.186	0.506	
Starch	2	0.18	0.36	

Chemical Cost for Remediation: $1.12/yd³
Assumption: 1 lb FeS treats ~1 yd³ contaminated soil/sediment

Funding History of This Technology

- US EPA STAR (GR832373), USGS-AWRRI (Alabama Water Resource Research Institute), Alabama Agricultural Initiative to Auburn University
- DOE Small Business Innovative Research (SBIR) awarded to AMEC Geomatrix in March 2008, but grant couldn’t be placed in June 2008 because we lost small business status due to AMEC acquisition
- AMEC Research & Development program recently provided funding to further develop this technology

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Our Experience

- **Auburn University: Lab testing of FeS nanoparticles, development of patented nanotechnologies**
- **AMEC Geomatrix has extensive experience implementing innovative methods for site remediation**

Iron nanoparticles injection in CA

Iron nanoparticles injection in AL

First PRB in the US in 1994

Summary

- The stabilized FeS nanoparticles are highly dispersive and can be easily injected into Hg-contaminated sediment.
- Mercury in soil or sediment can be immobilized effectively by FeS nanoparticles.
- Estimated costs for FeS nanoparticle in remediation of Hg in groundwater show that it can be a cost-effective approach

Questions?