In Situ Removal of Heavy Metal Contaminants Using Emulsified Nano- Or Microscale Metal Particles

Kristen M. Milum[1], Cherie L. Geiger[1], Christian A. Clausen[1], Robert DeVor[1], Jacqueline Quinn[2]

[1]Department of Chemistry, UCF

[2]NASA, Kennedy Space Center

Outline

- Heavy Metal Contamination
- Current Remediation Technologies
- Emulsified Zero Valent Metal
- Laboratory Studies
- Summary and Future Efforts

Heavy Metal Contamination

- Coastal/Estuarine sediments: 15-50 mg/kg
- Areas near waste outfalls: may exceed 400 mg/kg
- Lakes in Sudbury Mining District, Canada
  - 250-350 mg/kg in top 10 cm in cores
  - 50 mg/kg below 15 cm in cores

Current Remediation Technologies

- *In situ* technology
  - Biological treatment
  - Chemical treatment
- *Ex situ* technology
  - Treatment of dredged sediments
    - Thermal treatment
    - Stabilization/ Immobilization
    - Extraction technologies
    - Biological treatment

Zero Valent Iron Technology

- Material for permeable reactive barriers
- Used to treat chlorinated organics, nitroaromatics, and heavy metals

$$Fe^{2+} + 2e^{-} \rightarrow Fe^{0} \qquad E_o = -0.447$$

- CrO_4^{2-} reduced to Cr^{3+} with subsequent precipitation as $Cr(OH)_3$ or $Cr_xFe_{1-x}(OH)_3$
- Reduce Cu^{2+}, Ag^{+}, and Hg^{+} to zero valent forms
- Reduce TcO_4^{-}, UO_2^{2+}, MoO_4^{-} to more immobile forms

J. Haz. Mat., 1995, **42**: 201-212.

Emulsion Liquid Membranes

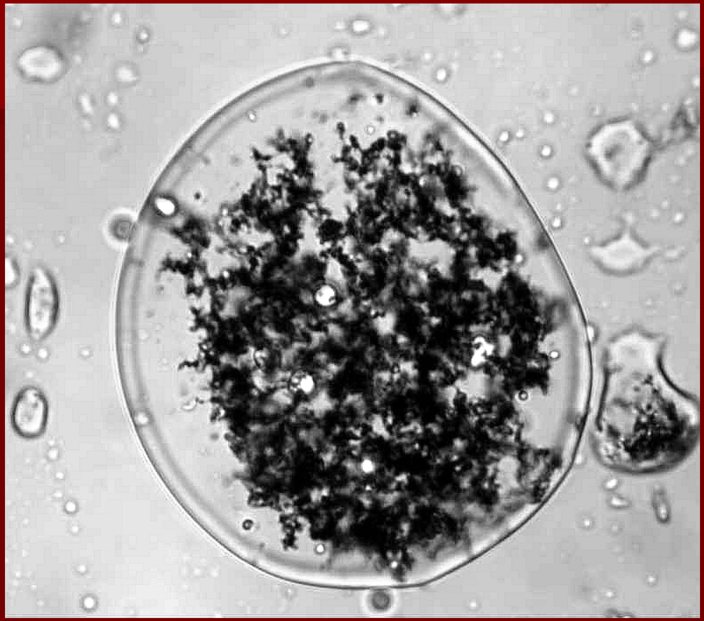
- Liquid membrane system where two mutually miscible phases are separated by an immiscible phase
- Applications for a wide variety of materials
- Facilitation mechanisms also used to enhance removal
  - Type I: reaction on interior of droplet
  - Type II: use of carrier molecules
    - Crown ethers, carboxylic acids, quaternary ammine salts

Patterson, J. W., R. Passino, *et al*. *Metals speciation, separation, and recovery*, 1987.

Emulsified Zero Valent Metal

- Combination of ELM and zero-valent metal
  - Use of iron or magnesium to reduce heavy metal contamination
  - Emulsion droplet provides protective barrier
- Emulsion droplet
  - Organic phase (oil, d-limonene)
  - Water
  - Surfactant (Span 85)
  - Nano- or Microscale metal

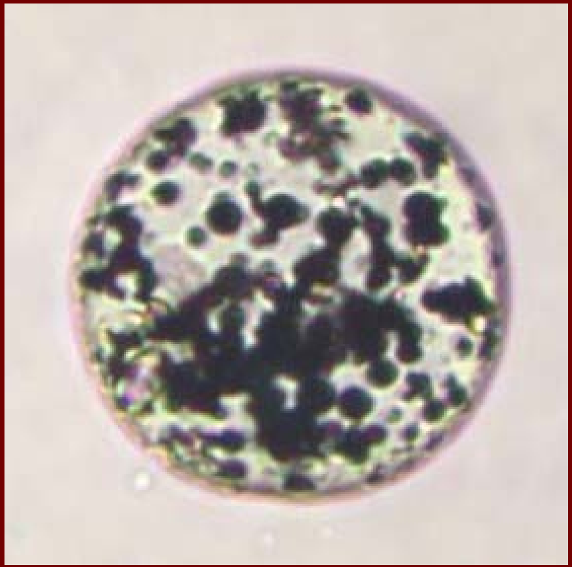
Emulsion Droplets



Nanoscale Iron

Magnesium

Microscale Iron



Demonstration of EZVI

- Field test at Cape Canaveral Air Force Station, Launch Complex 34, interior of ESB
- Emulsion system can degrade DNAPL TCE in both water and soil matrices
- Results of field study show in-situ dehalogenation of DNAPL where emulsion is injected
  - 58% reduction with kriging analysis (80% confidence interval)
  - 86% reduction for total TCE; 84% reduction for TCE DNAPL using contouring software EarthVision® (80% confidence interval)

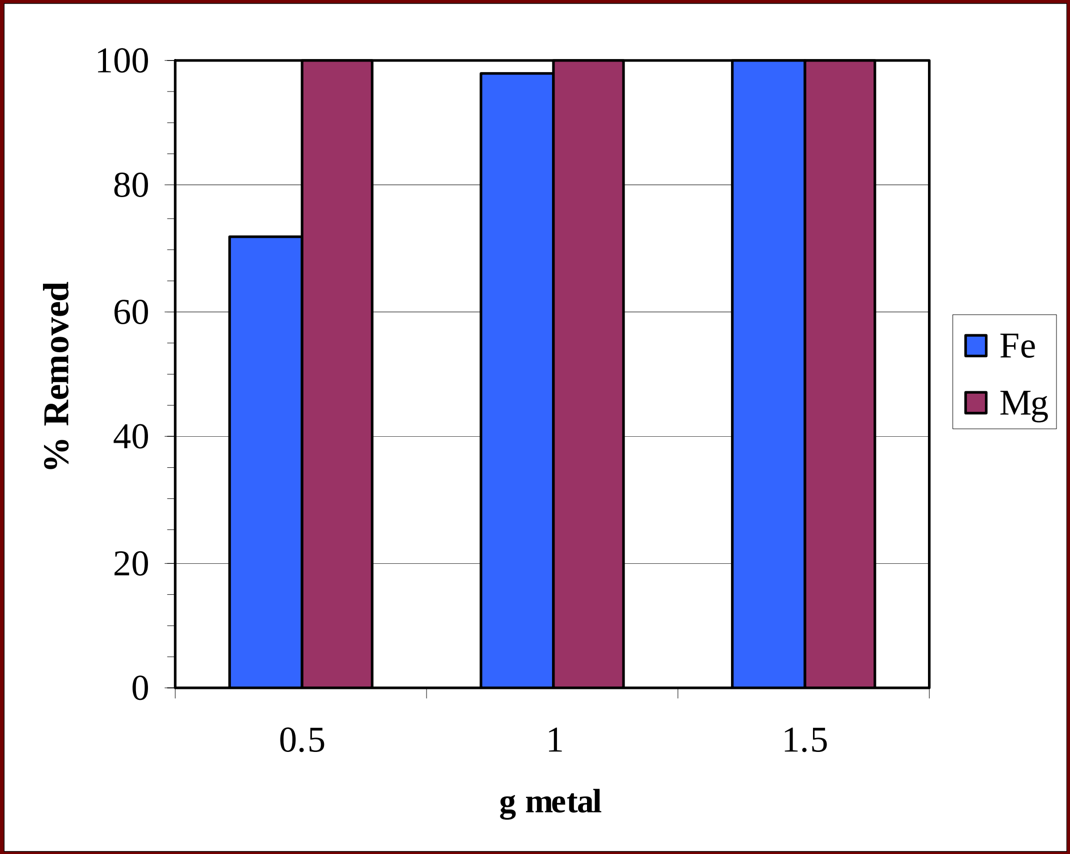
Experimental Objectives

- To demonstrate the removal of metal ions
  - From solution
  - From soil

- To verify the transport of the metal ions into the interior of the emulsion droplet

Metal Removal from Solution

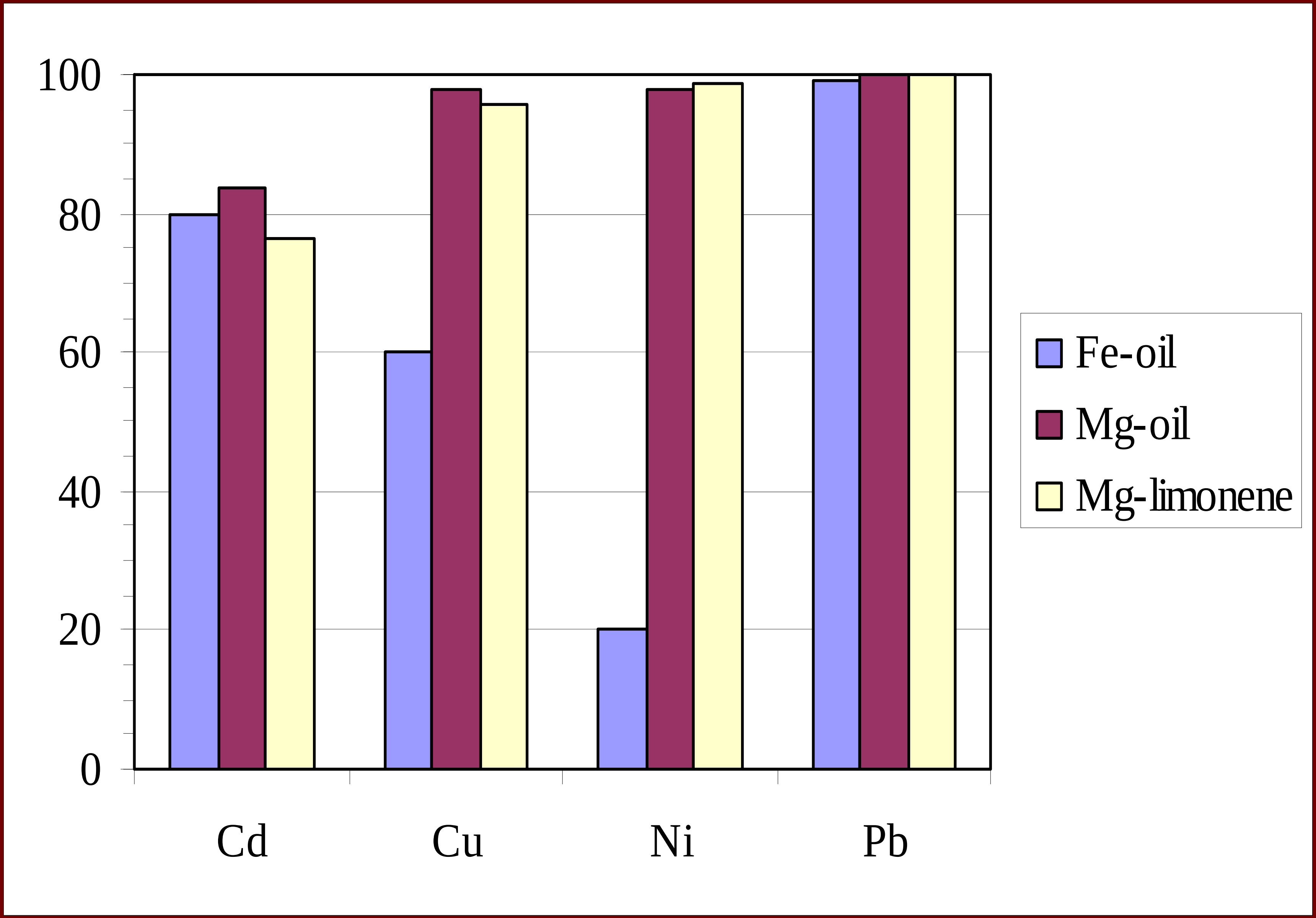
- Vial Study
  – Variable weight neat <10 μm Fe, 1-3 μm Mg
  – 20 mL of 500 ppm Pb solution
- Solution analyzed after 2 days by FAAS



Metal Removal from Solution

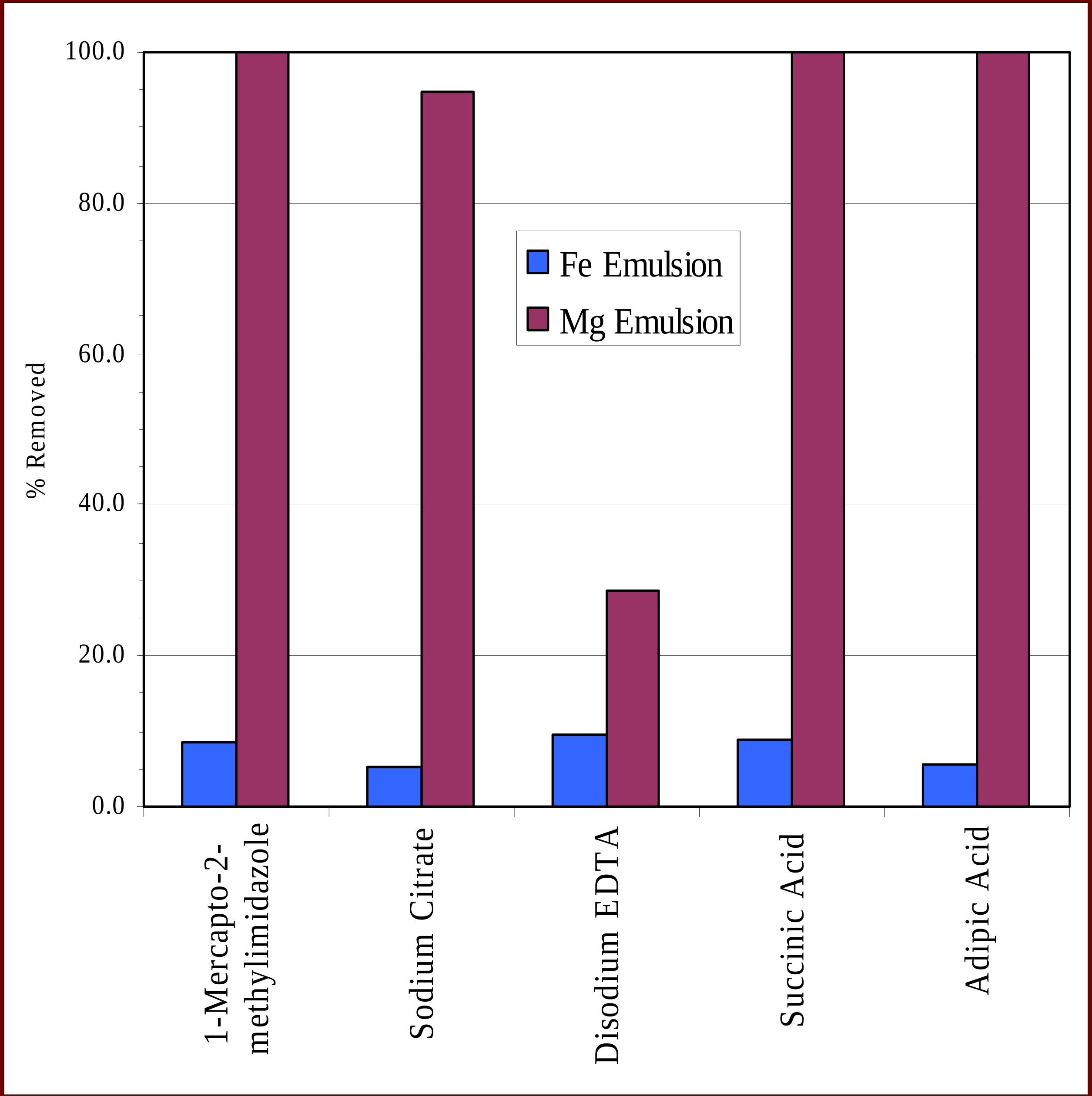
- Vial study
  - 5 g emulsion
  - 10 mL, 100 ppm metal solution
- Solution analyzed after 5 days
  - Flame atomic absorption spectroscopy

Metal Removal from Solution



Matrix Effects on Removal Efficiency

- 5 g emulsion
- Modification of lead solution, 100 ppm Pb & 10 mM organic
  - 2-Mercapto-1-methylimidazole
  - Sodium citrate
  - Succinic acid
  - Adipic acid
  - Disodium EDTA



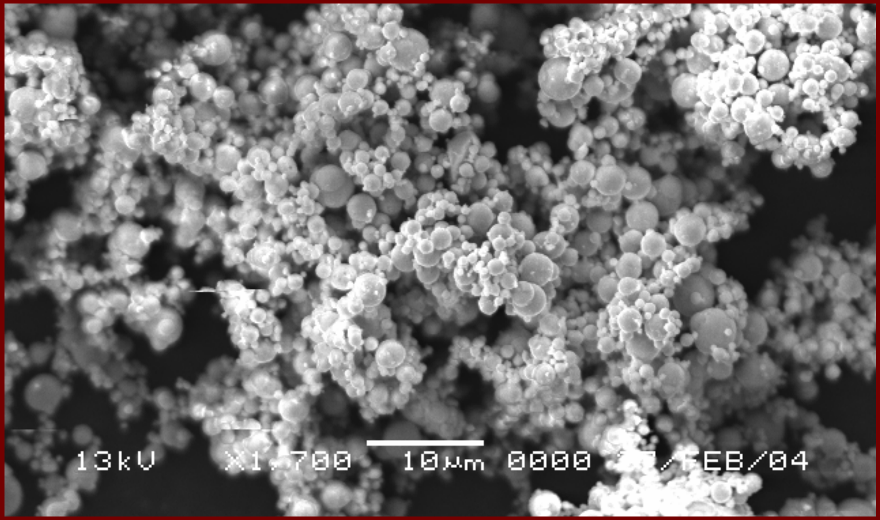
Lead in Organic Phase

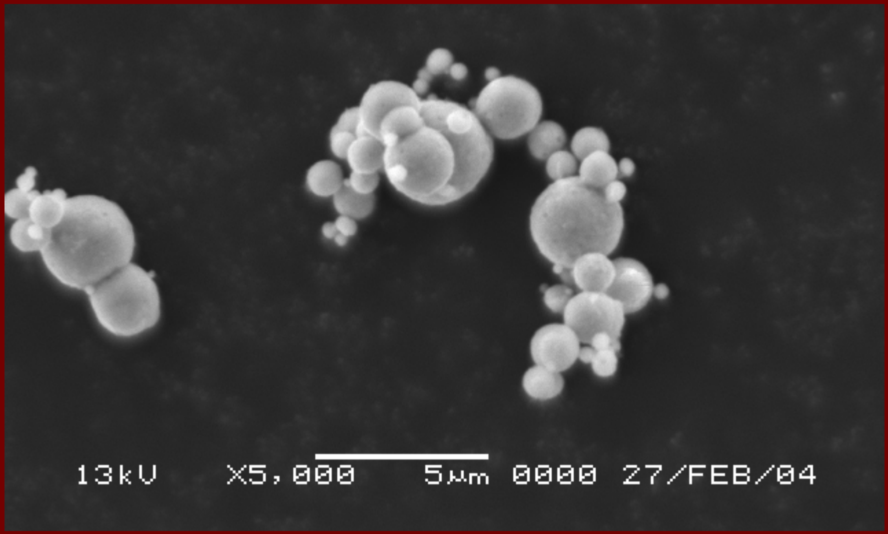
- Vial study
  - 10 mL corn oil or d-limonene
  - 10 mL, 10 ppm lead solution
- Additional studies
  - Surfactant in oil/d-limonene
  - EDTA in oil

- All vials showed no lead removal from water by organic phase alone

Plating Study

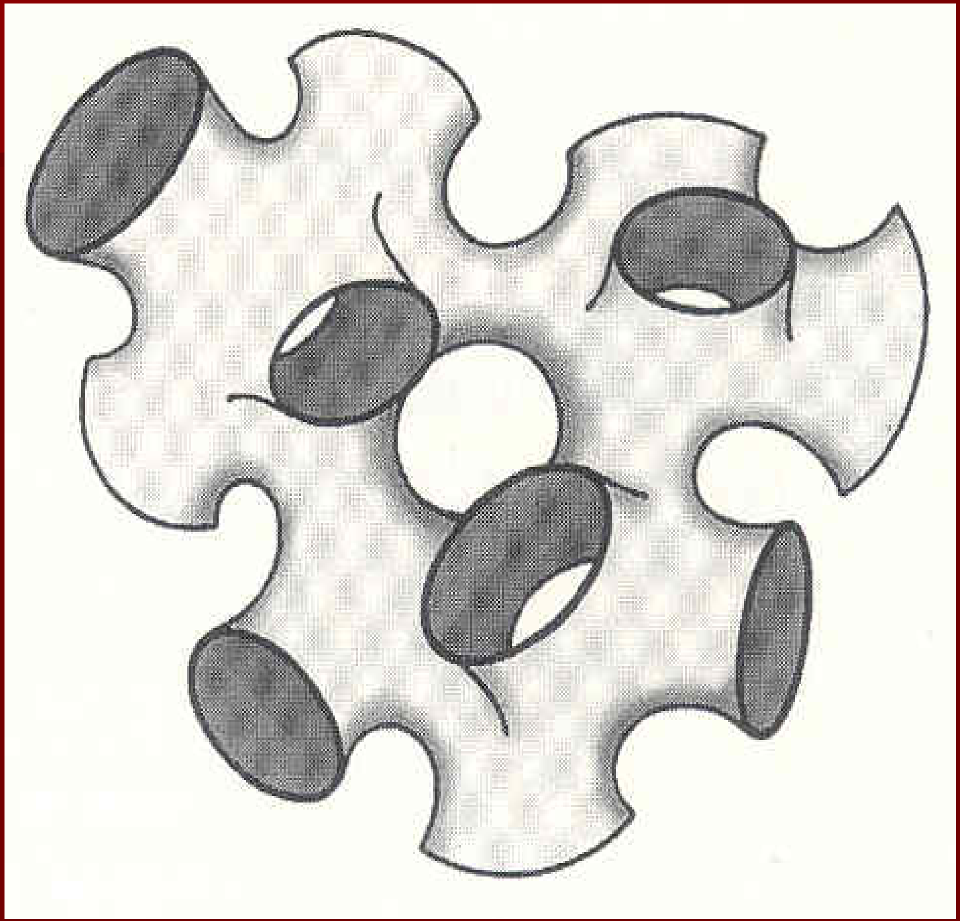
- Metal recovered from emulsion
  - Acidified
  - Analyzed by FAAS
- Fe-oil emulsion
  - 40-60% Pb recovered
- Mg-oil emulsion
  - 45-65% Pb recovered
- Mg-limonene emulsion
  - 60-75% Pb recovered
- XPS confirmed presence of Pb

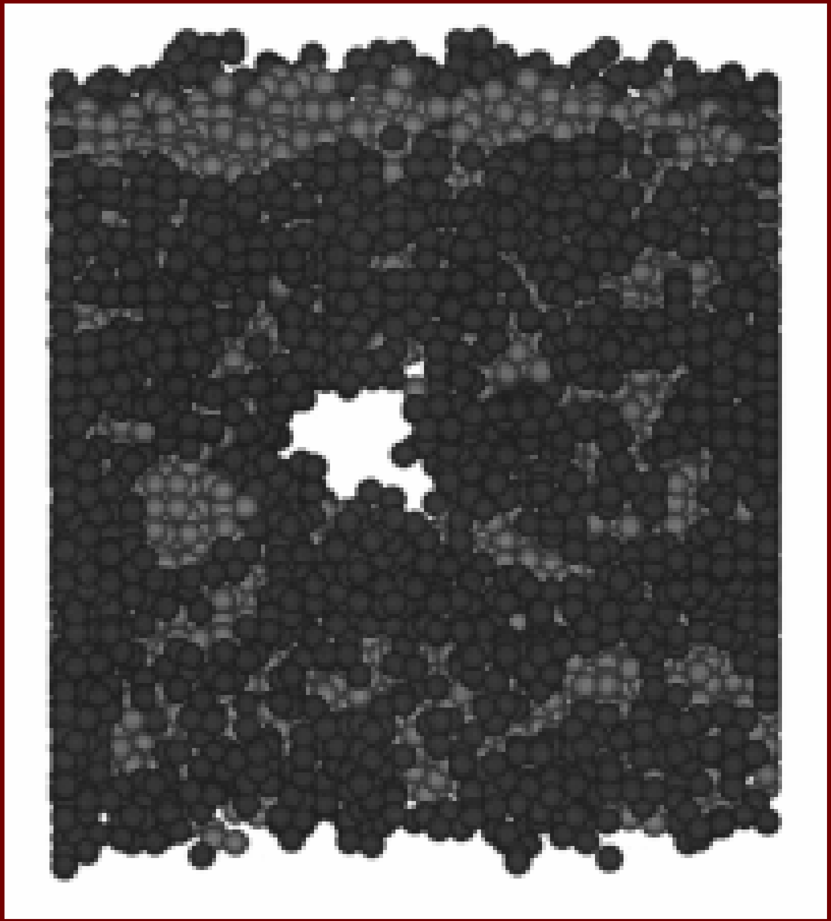




SEM of recovered iron

Possible Transport Mechanisms





- Channel formation with amphiphilic molecules

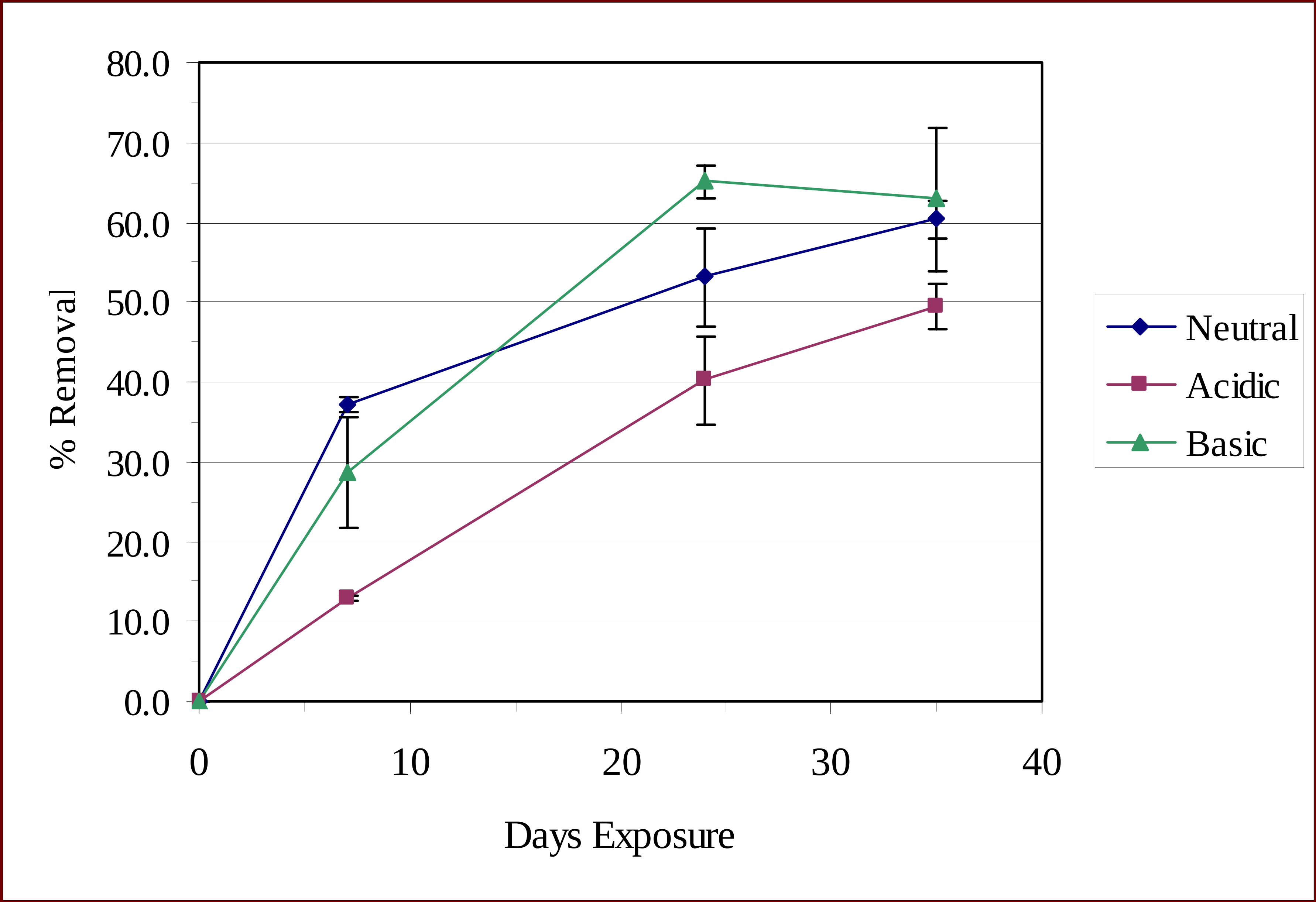
K. R. Lange, *Surfactants*, 1999 *J. Chem. Phys.*, 1996, 105(18), 8282-8292

Metal Removal from Soil

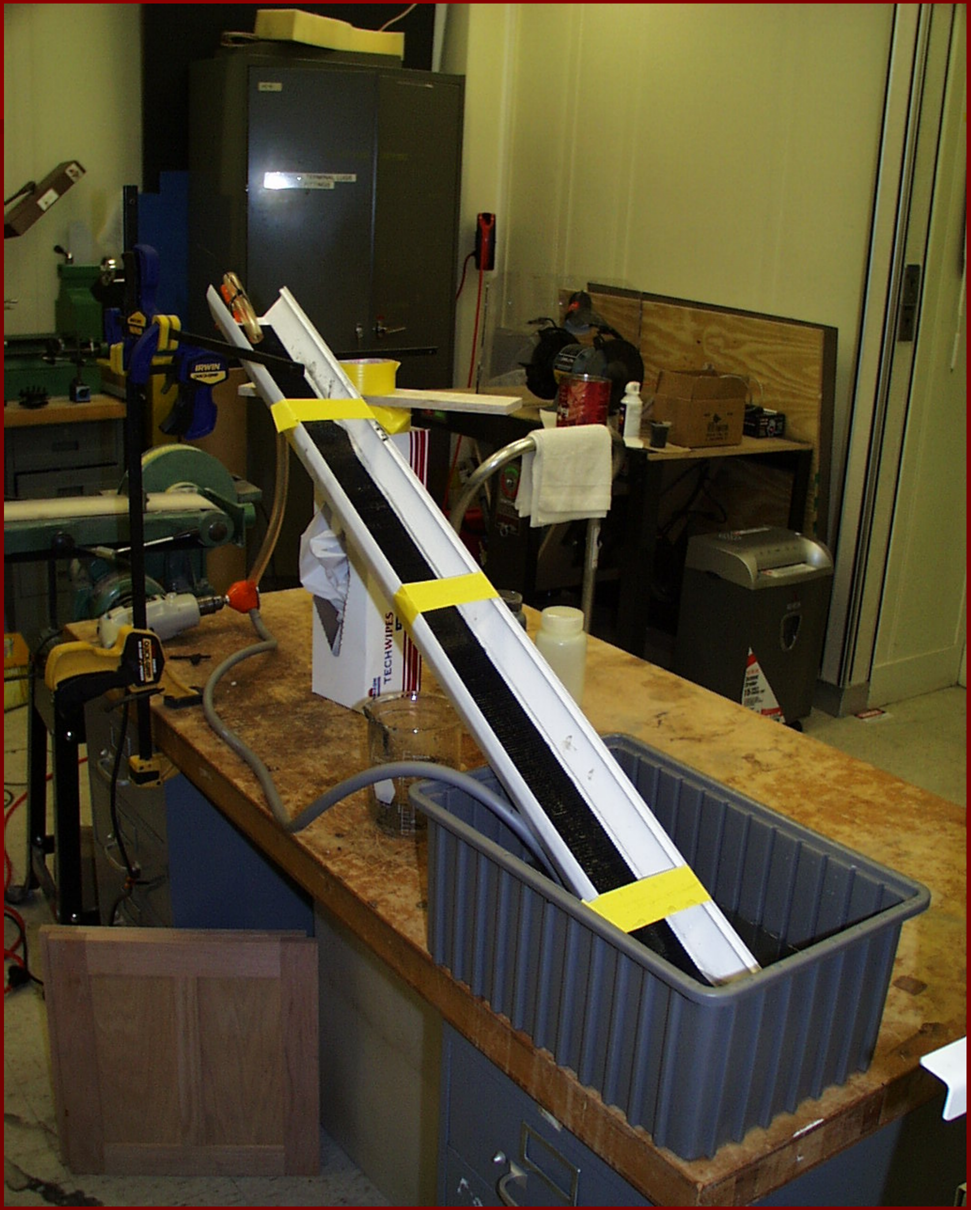
- Vial study
  - 20 g lead-spiked soil
    - 100 mg Pb/kg soil
  - 3 mL of iron emulsion
  - 5 mL water beyond incipient wetness

- Analyzed using a variation of EPA Method 3050b

Metal Removal from Soil



Larger Scale Emulsion Recovery



Summary

- Demonstrated removal of metal ions from a variety of different solutions
- Presence of lead on iron recovered from the interior of the emulsion droplets
- Capability of emulsion for the removal of metal ions from soil

Current and Future Efforts

- Investigation into the fate of the metal in the interior of the emulsion droplet
- Simulation of more complex environments
- Small-scale field test to demonstrate applicability of this technique

Acknowledgements

- NASA,
  Kennedy Space Center

- Dr. Julia Fulghum,
  University of New Mexico