

Ferragels: A New Family of Materials For the Remediation of Metal-Contaminated Aqueous Streams

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Intended Applications of Ferragels

- Tank Waste Remediation
- *In situ* Groundwater Remediation
- Separation and Immobilization of Metal Ions
- Degradation of Chlorinated Hydrocarbons
- Technetium Separation and Immobilization
- Vadose Zone Remediation

Ferragels: Nanoscale Zero-Valent Metal(s) Mounted on a Support

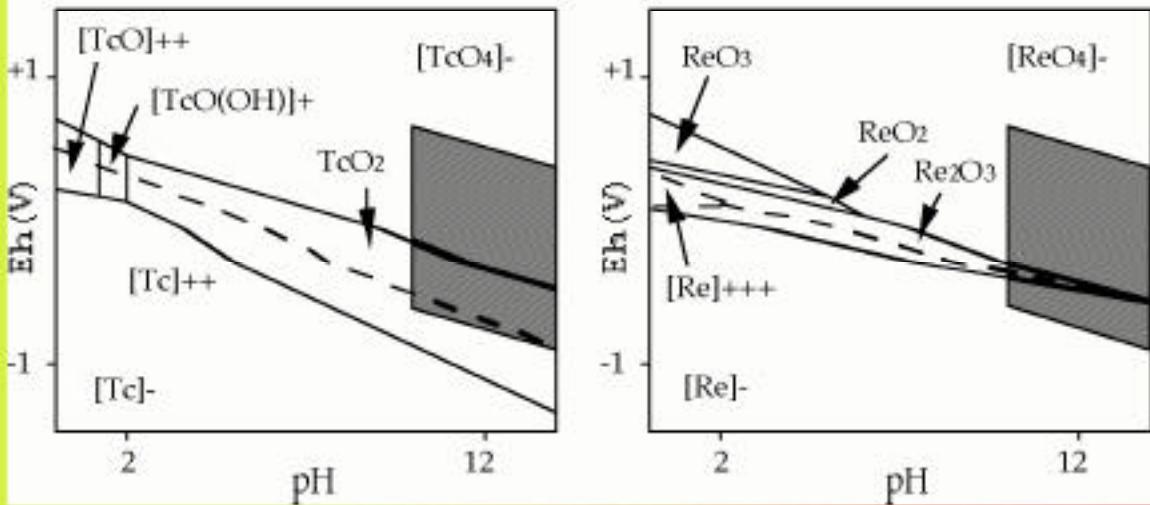
Possible Metals

- Iron
- Tin
- Zinc
- Manganese
- Copper
- Nickel
- Palladium
- Platinum

Possible Support Materials

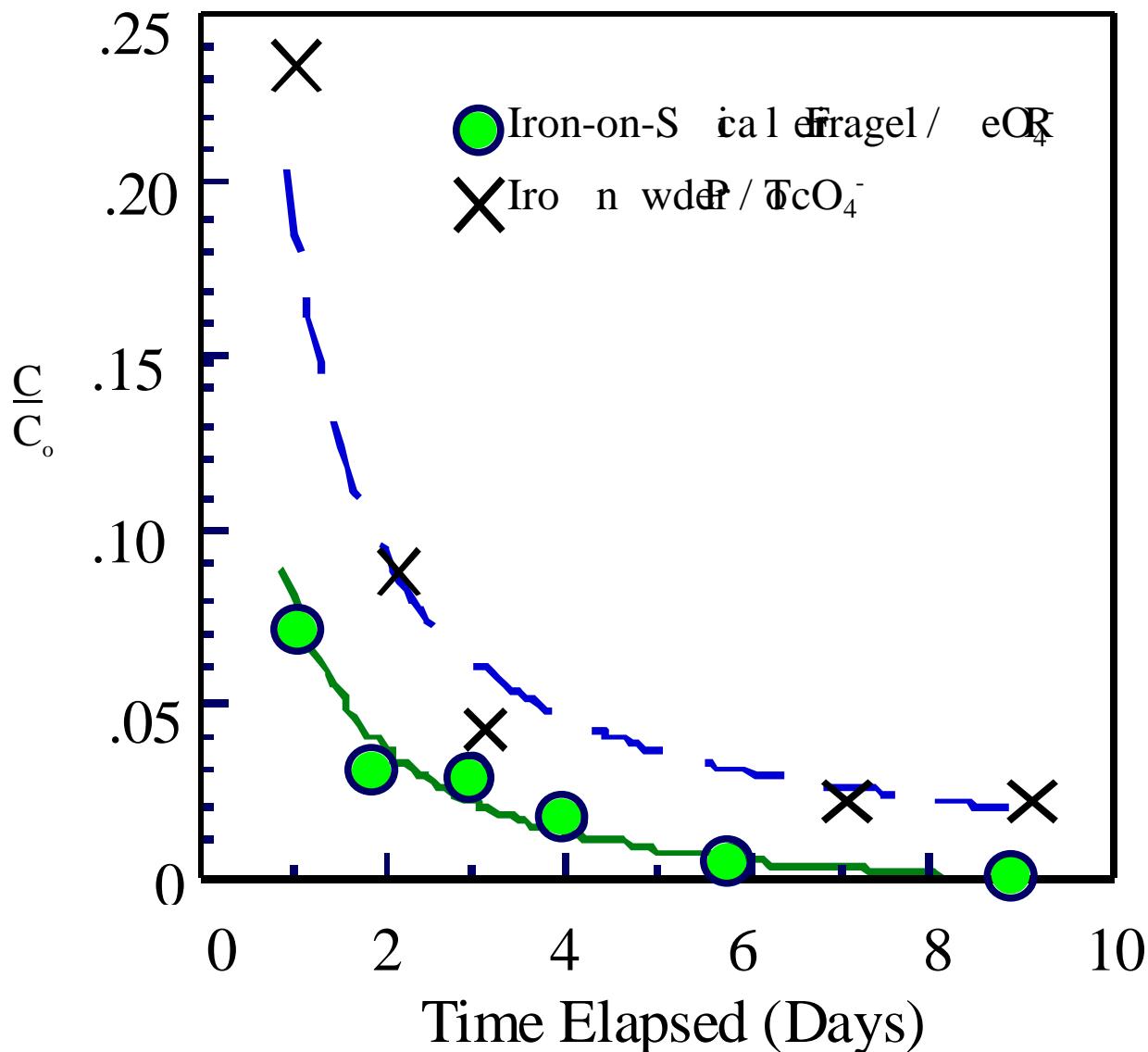
- Polymeric Resin
- Metal oxides
- Silica
- Sand
- Gravel
- Styrofoam

Species Predominance Diagrams For Technetium and Rhenium



J.G. Darab and P.A. Smith, *Chem. Mater.*, 8, (1996) 1004.

Perrhenate Removal With Ferragel versus Iron Powder



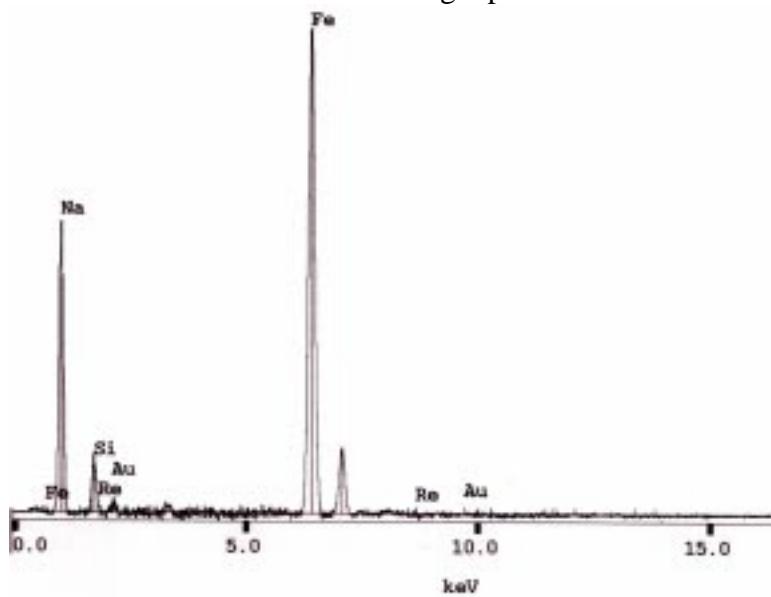
The results of exposing Ferragel to a simulated waste mixture containing ReO_4^- as a surrogate for TcO_4^- (Solid line with circles). For comparison, the removal of TcO_4^- by iron powder is also shown* (Dashed line with crosses).

* Vandergraaf, T.T. *et al.*, in *Geochemical Behavior of Disposed radioactive Waste*, ACS Symp. Ser. 246; Barney, G.S., *et al.*, Eds.; American Chemical Society, Washington, DC, 1984, p. 24.



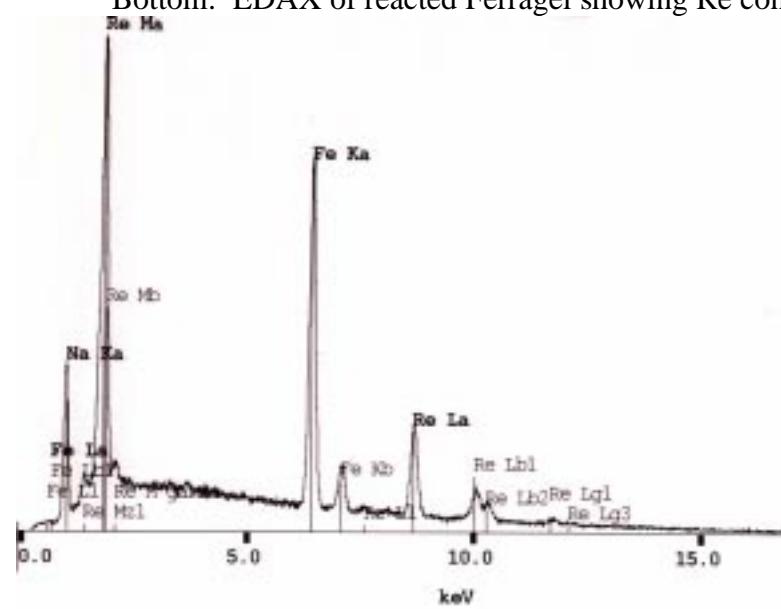
Top: A typical iron-on-silica Ferragel. The silica particle is about 40 microns in diameter.

Bottom: EDAX of this Ferragel prior to reaction.

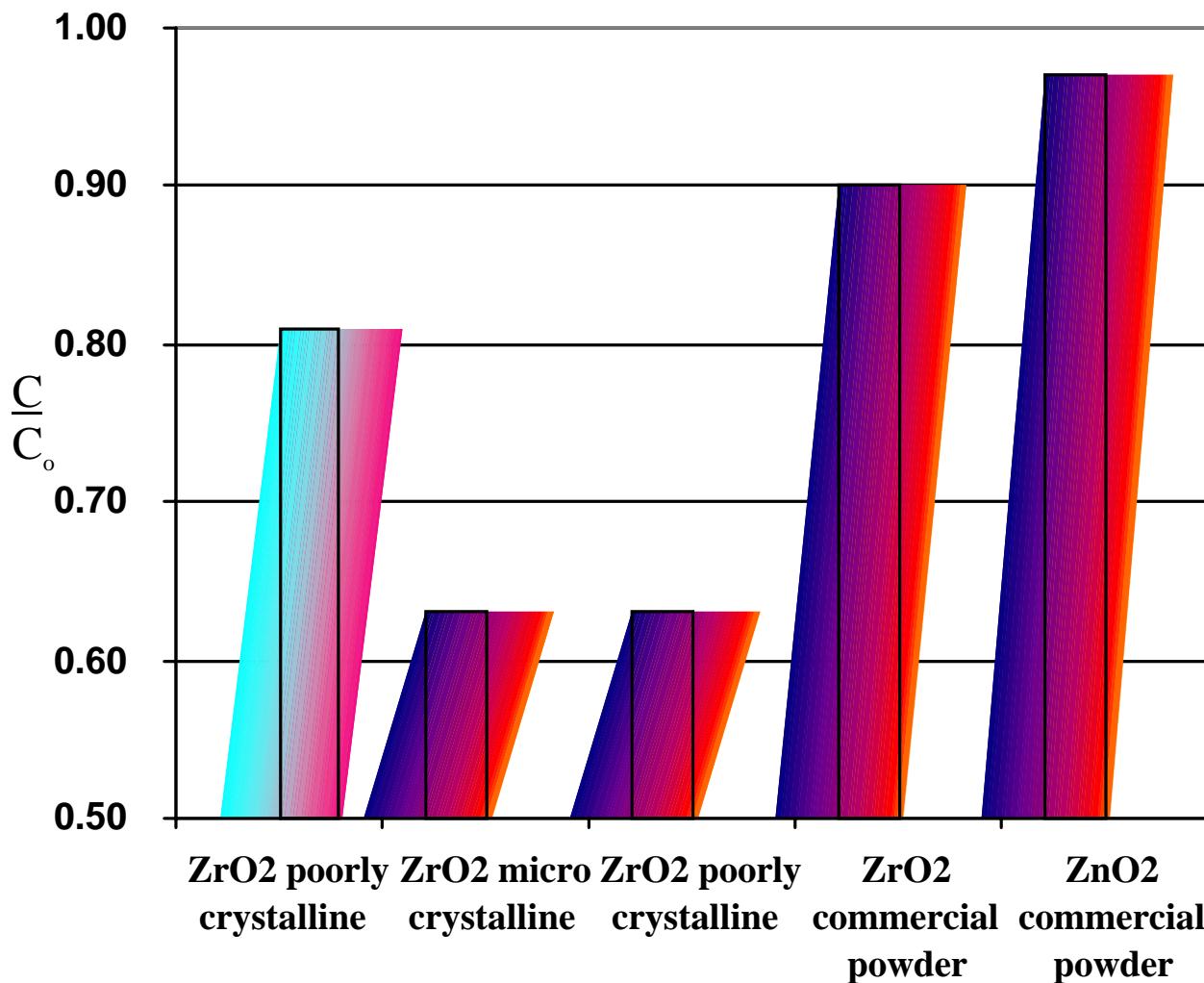


Top: Iron-on-silica Ferragel after reaction with 17 mM K₂ReO₄, 3.8 M NaOH.

Bottom: EDAX of reacted Ferragel showing Re content.



Removal of Pertechnetate From a Simulated Hanford DSSF Waste (24-hour Contact)



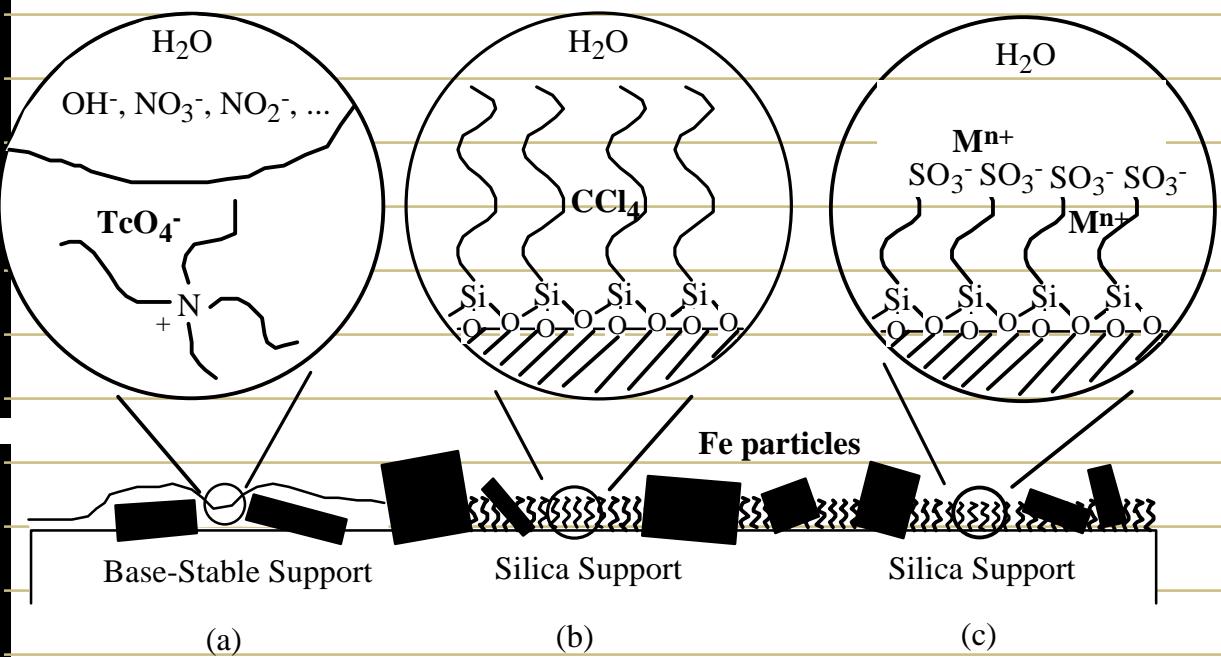
Technetium results. Simulant is 3.8 M OH⁻, 7.4 M Na⁺, 3.1 M NO₃⁻, 0.27 M CO₃²⁻, 8.9 mM TcO₄⁻.

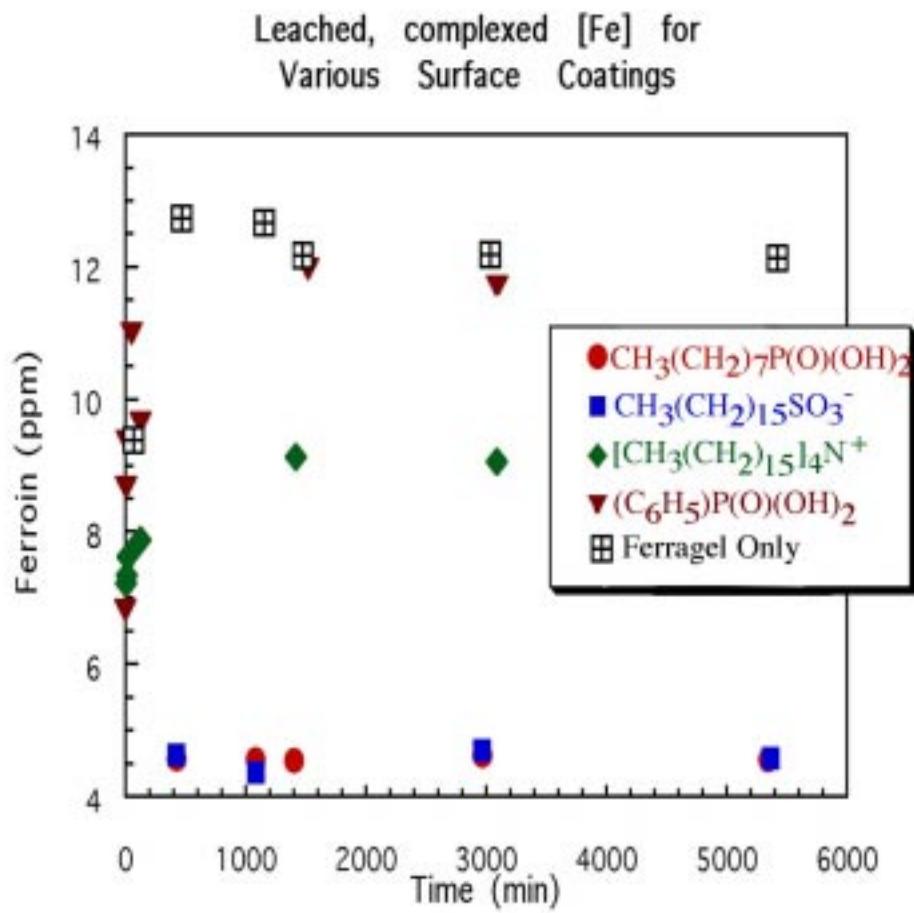
Phase ratio (mL soln/ g adsorbate) was 640 for first column and 150 for all others. K_d, from left to right, was 156, 81, 81, 16, and 6 mL/g, respectively.

Removal of Pertechnetate From a Simulated Hanford DSSF Waste (24-hour Contact)

| | Initial Ratio (mol Tc : mol Fe) | Removal Ratio (mol Tc : mol Fe) |
|---|--|--|
| ZrO₂ poorly crystalline | 1:1 | 1:6 |
| ZrO₂ micro crystalline | 1:5 | 1:12 |
| ZrO₂ poorly crystalline | 1:5 | 1:12 |
| ZrO₂ commercial powder | 1:1.3 | 1:13 |
| ZnO₂ commercial powder | 1:1.3 | 1:45 |

Possible Surface Modifications to Ferragels



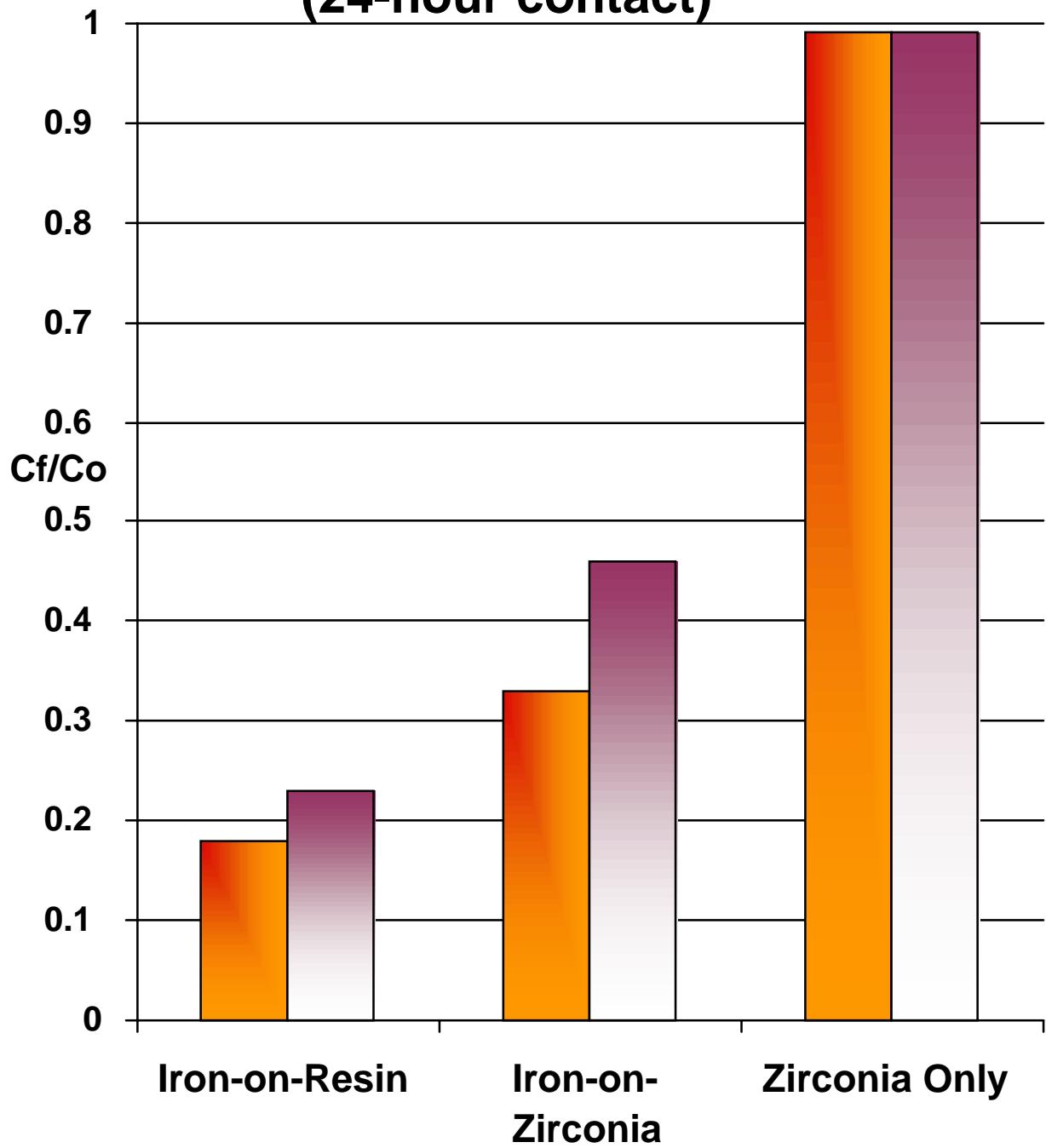


Results of surface modifications to Ferragel.

1,10-phenanthroline was used to oxidize Fe^0 and complex Fe^{2+} . $\text{Fe}(\text{III})$ formation prevented by hydroxylamine. Total complexed iron was followed colorimetrically.

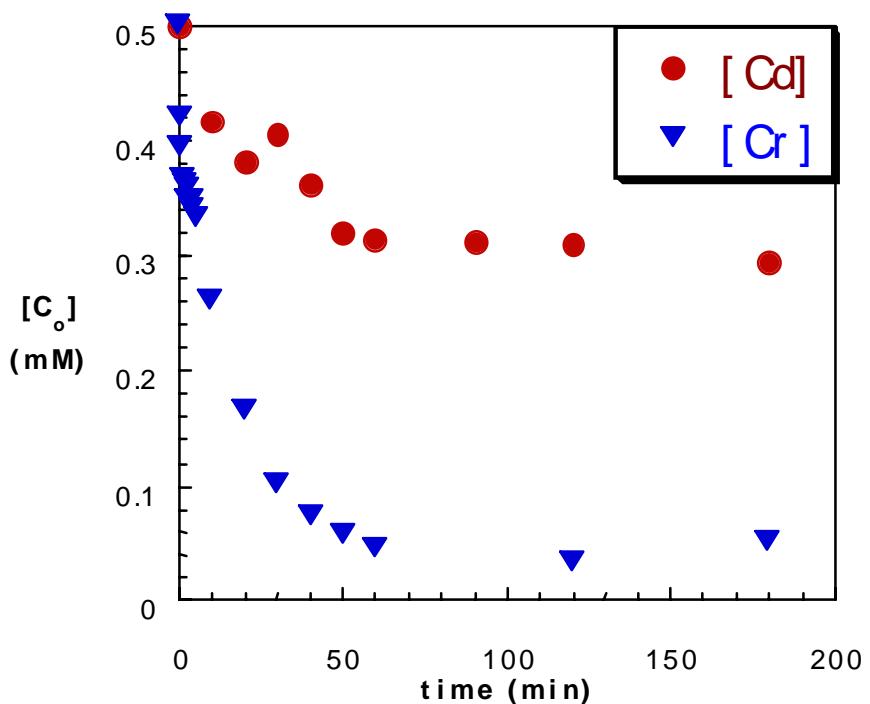
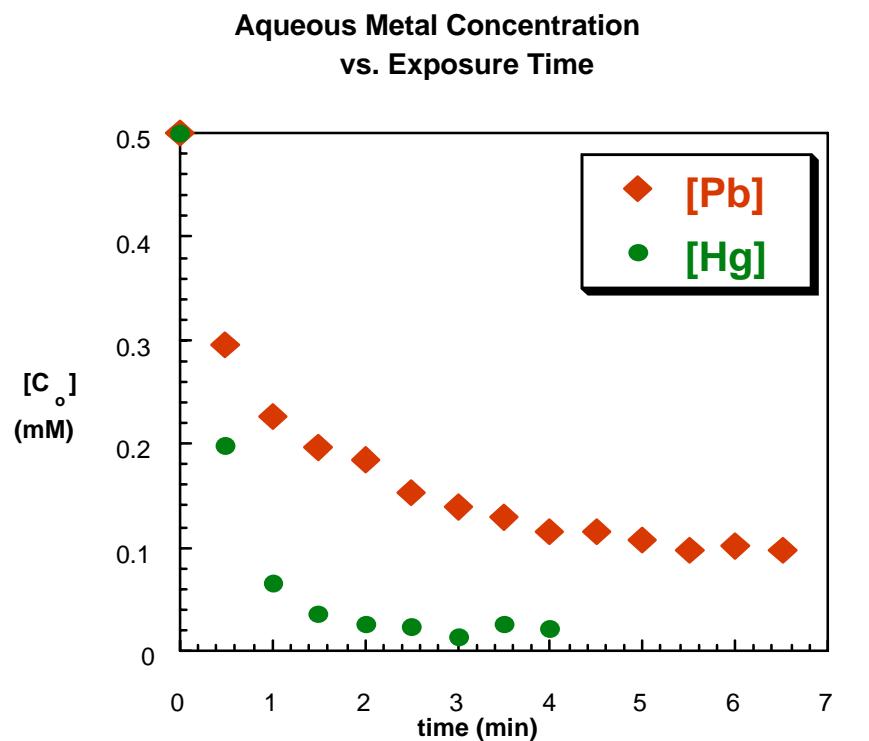
Phenylphosphonic acid does not self-assemble. The alkylsulfonate and octylphosphonic acid self-assemble, but inhibit the oxidation reaction. Tetrahexadecyl ammonium appears to limit access to the iron without inhibiting the reaction.

Removal of Tc From BNFL (MAC) Simulant (24-hour contact)

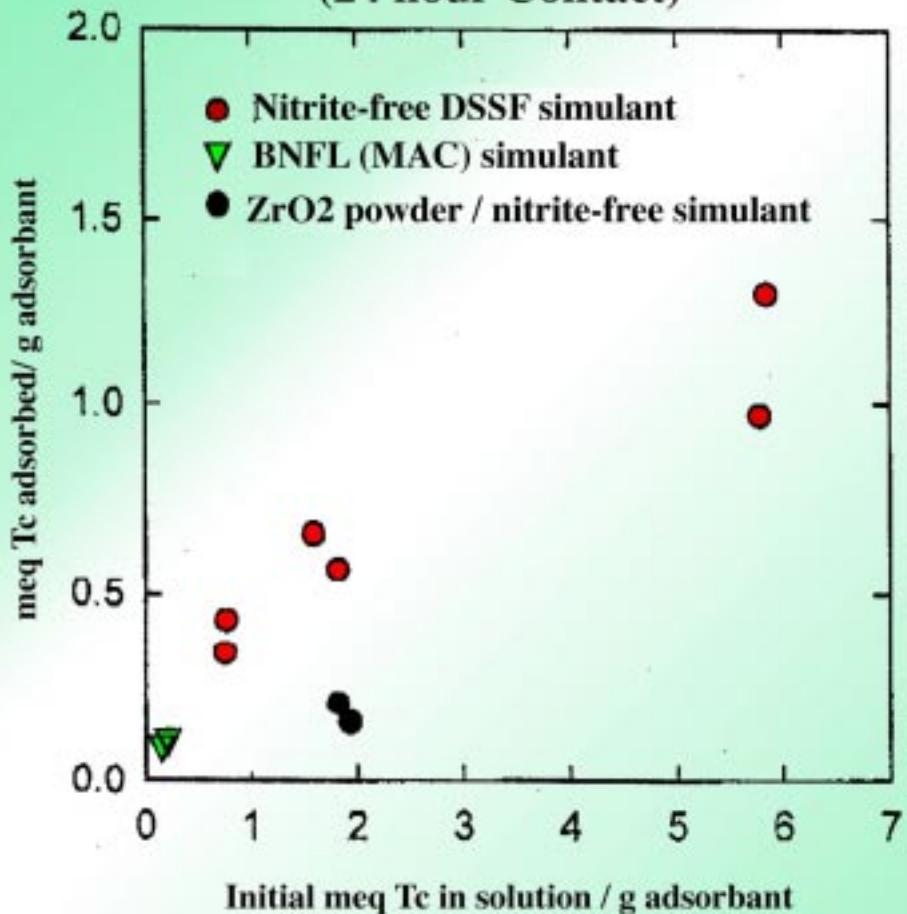


Removal of Aqueous Metal Ions from Solution Using Ferragel

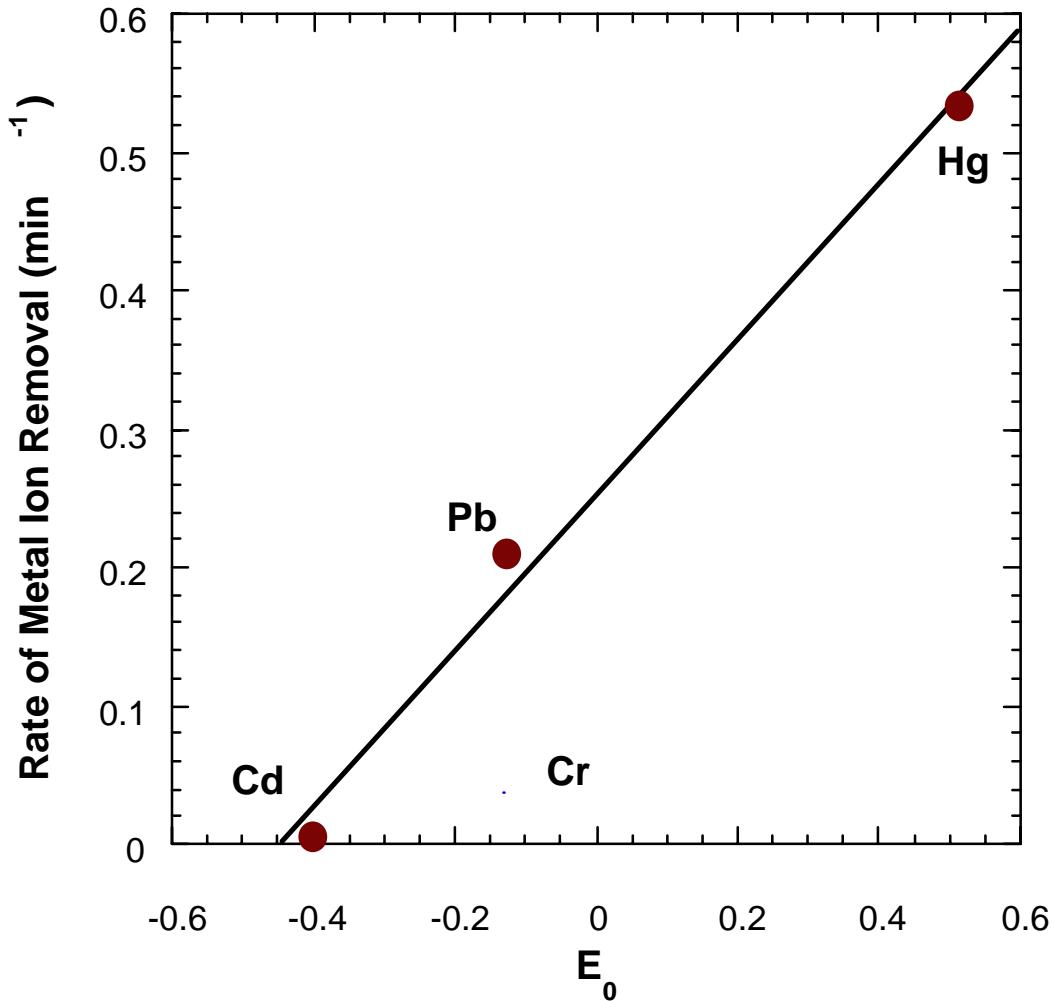
Shown are aqueous concentrations of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, HgCl_2 , CrO_3 , CdSO_4 . In each case, 100 mL of 0.5 mM solution was mixed with 0.100 g of iron-on-resin Ferragel.



Tc Adsorbed Onto ZrO₂-Supported Ferragel (24 hour Contact)

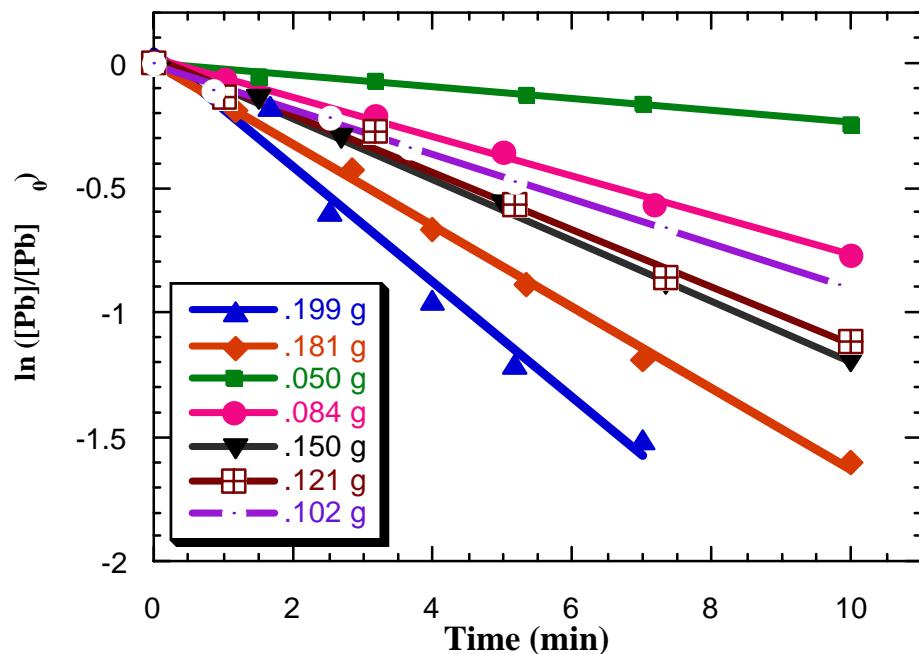


Rates of Reaction Versus E_0

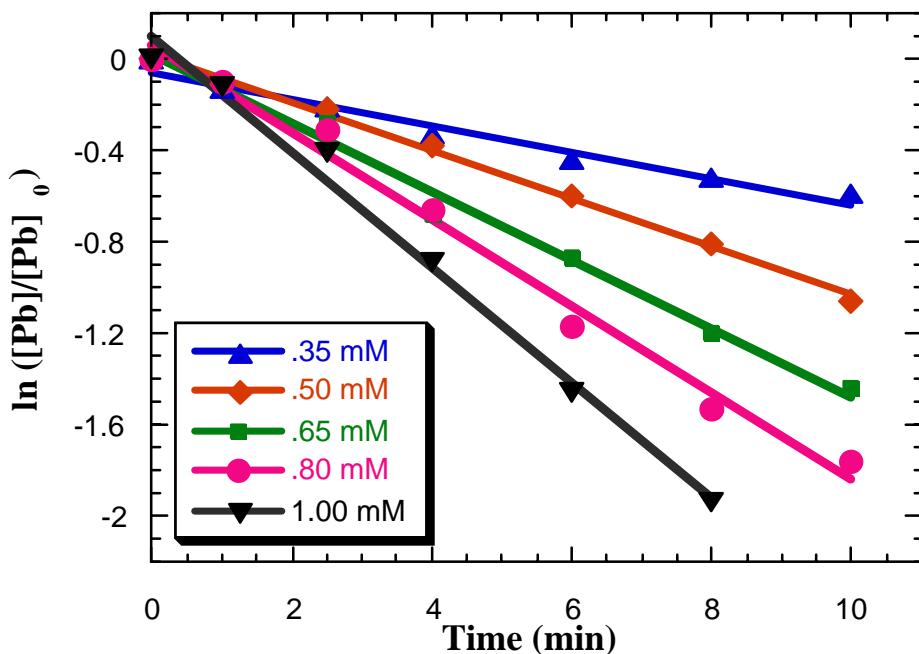


For each reaction, 0.100 g of iron-on-resin Ferragel was mixed with 100 mL of 0.5 mM of Pb(II), Cd(II), Hg(II) or Cr(VI).

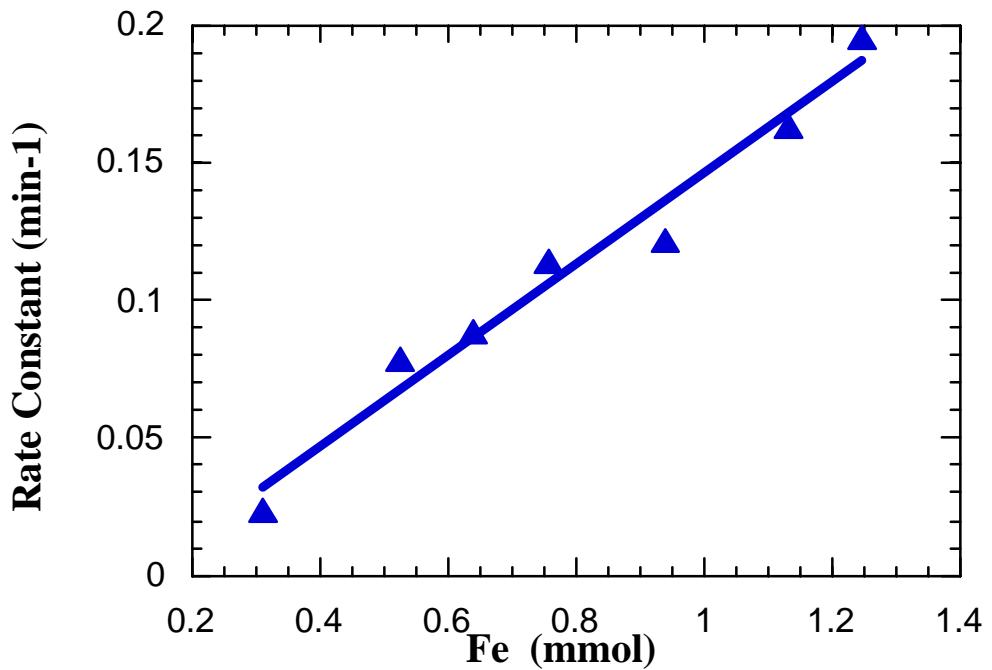
Effect of Amount of Ferragel on Pb Removal
(100 mL of 102.5 ppm $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$)



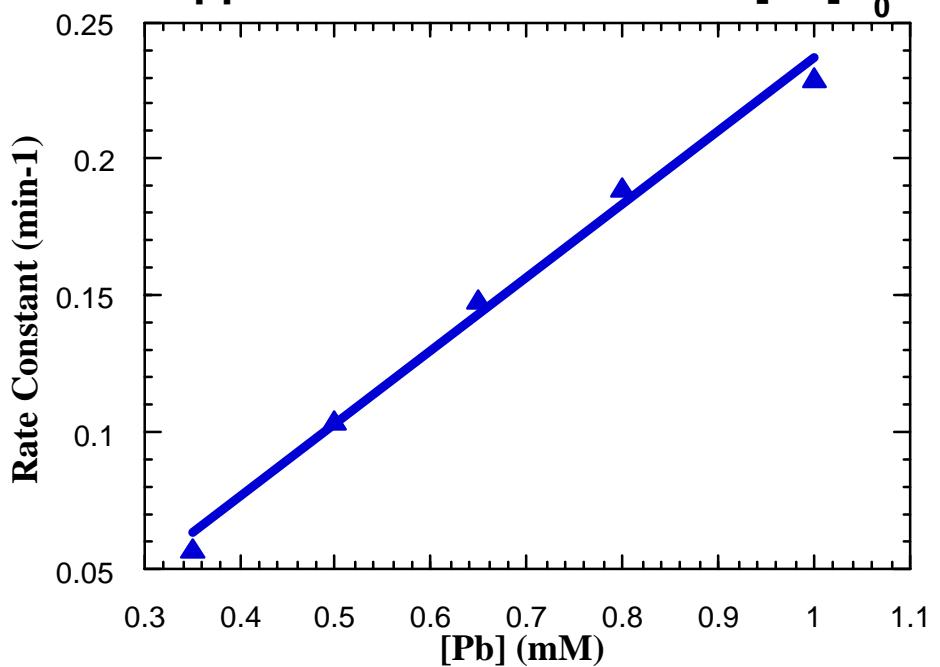
Effect of $[\text{Pb}]_0$ on Pb Removal
(0.100 g Ferragel in 100 mL soln)



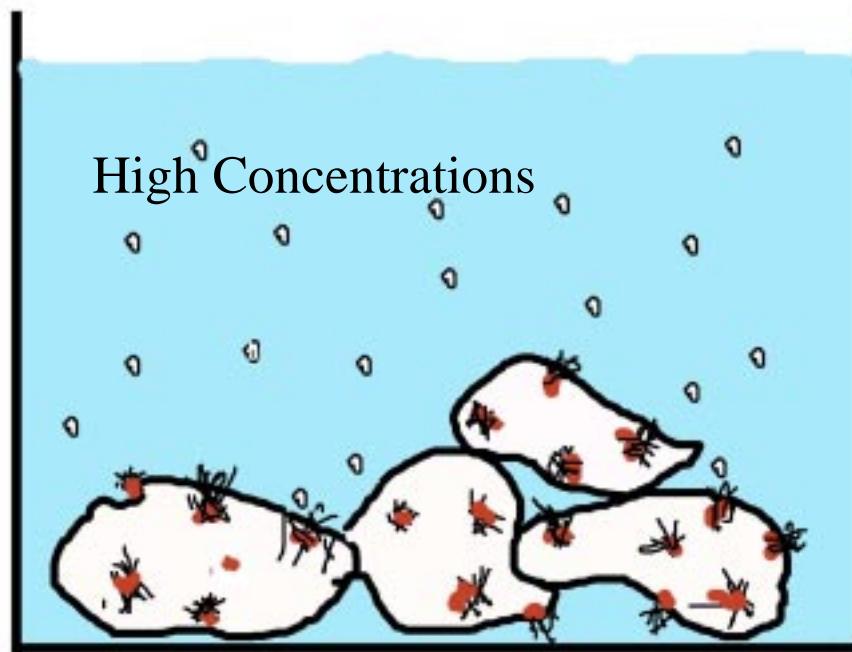
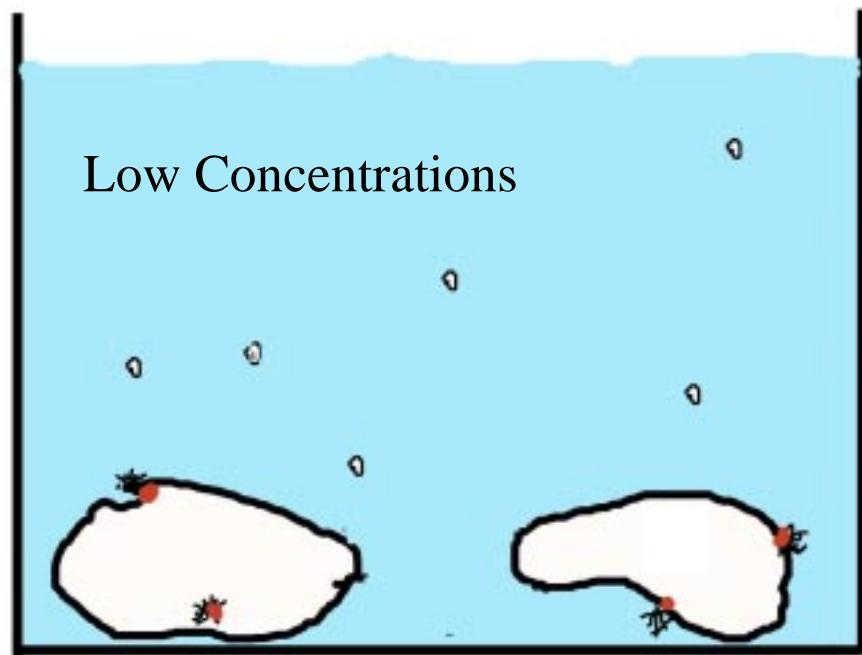
Apparent Rate Constant vs. Total Fe (mmol)

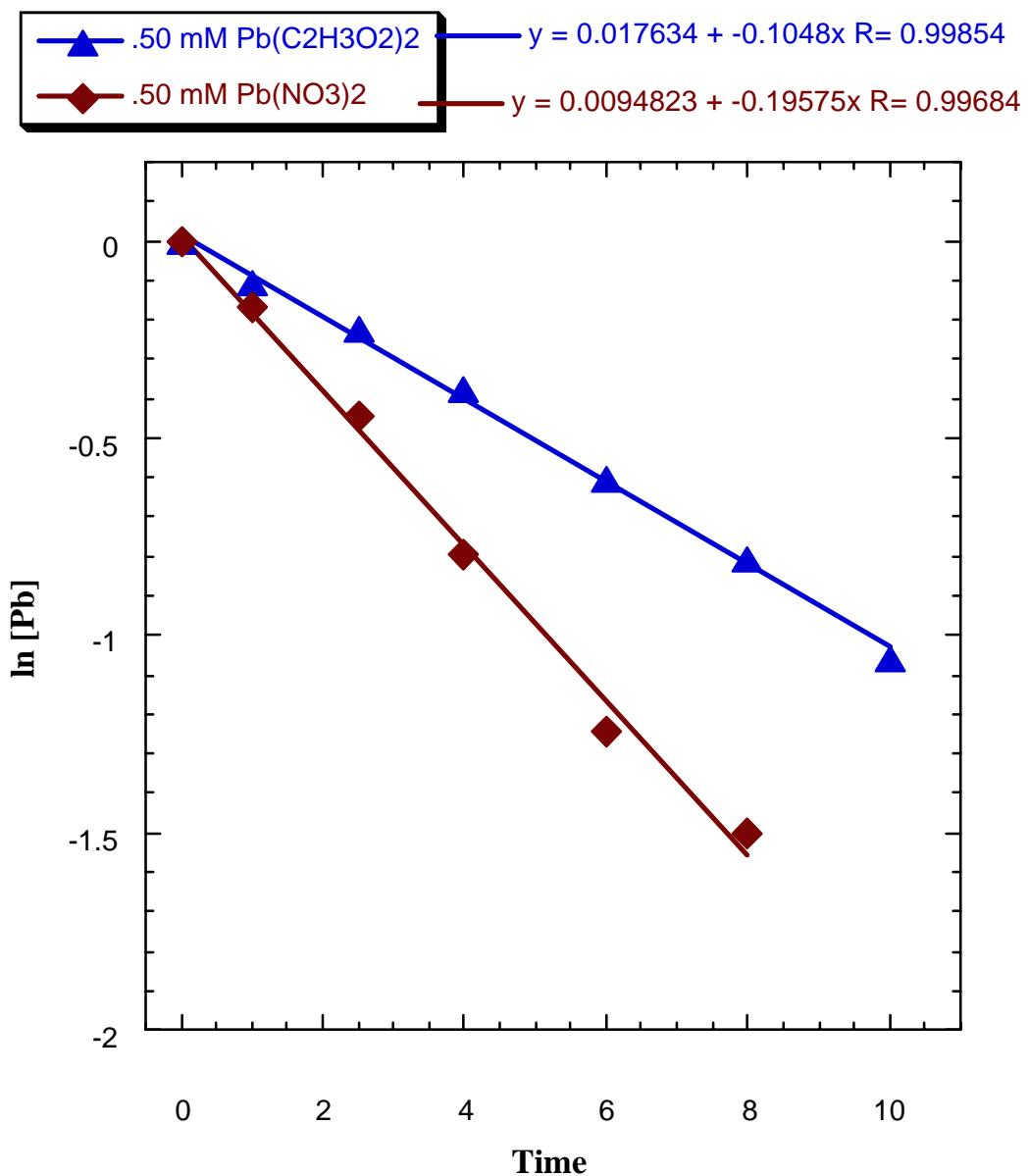


Apparent Rate Constant vs [Pb]

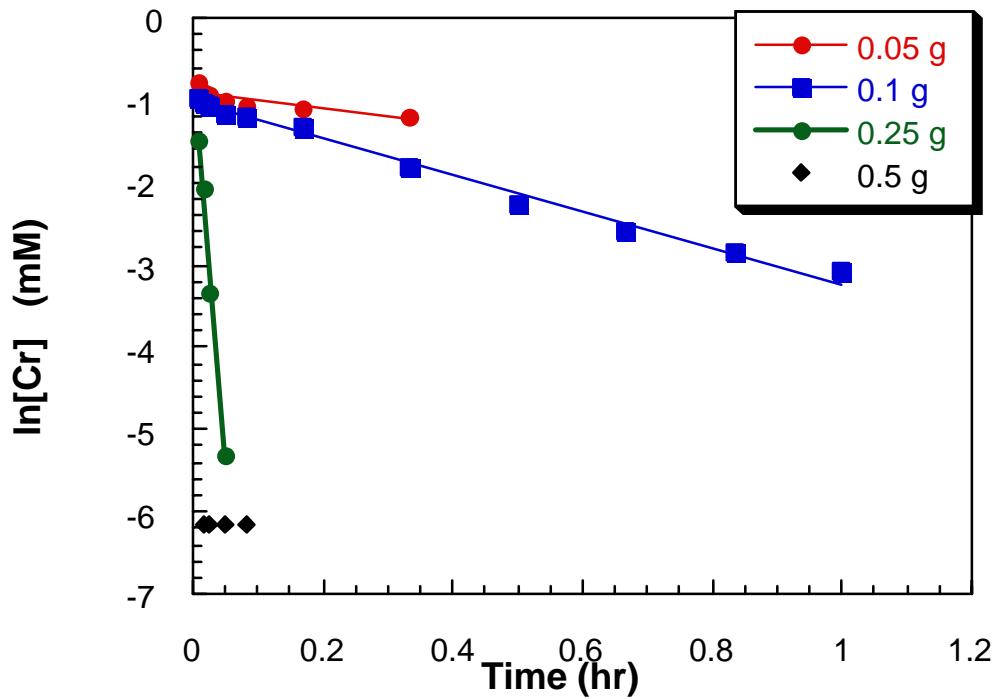


Possible Mechanism / Nucleation

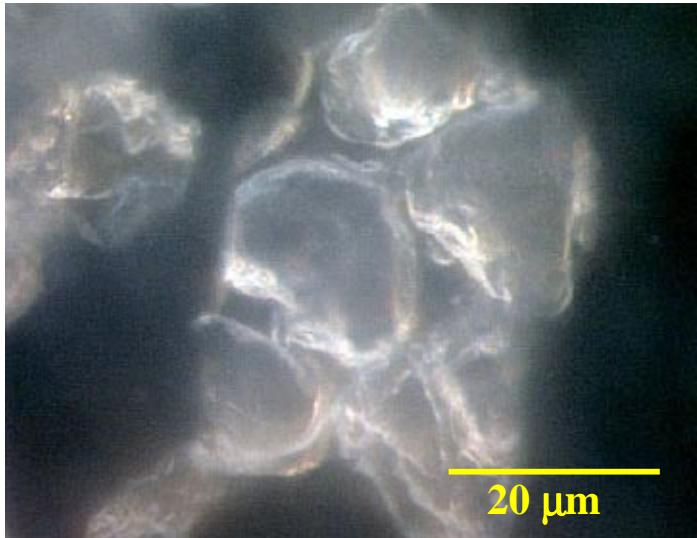




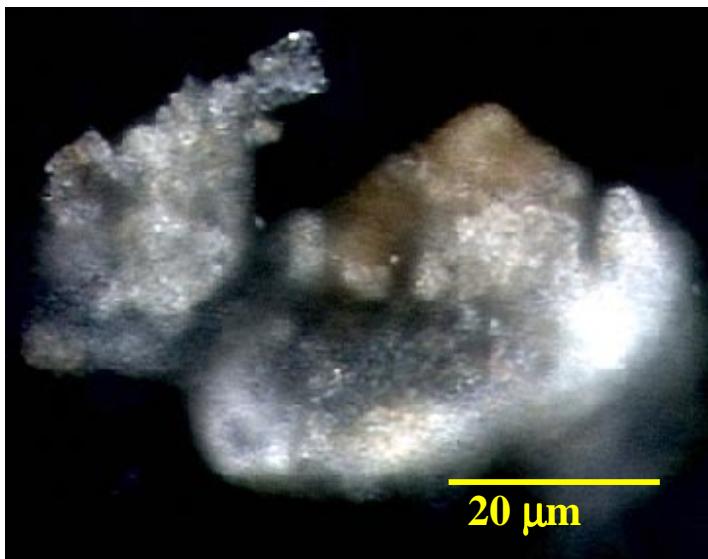
Cr Removal as a Function of Weight of PFFG Used



Synthesis of Ferragel



Top: PolyFlo®
resin prior to addition
of zero valent metal.



Bottom: Finished
iron-on-resin
Ferragel.

*PolyFlo® is a registered
trademark of Puresyn, Inc.,
Malvern, PA.*

Acknowledgements

- This work was supported by a grant from the U.S. Department of Energy, DE-FG07-97ER14822
-
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- Electron microscopy and X-ray microanalysis performed at the Electron Microscope Facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University.

Conclusion

- TcO_4^- removed from complex alkaline mixtures, including BNFL (MAC) simulant, by reduction onto Ferragel.
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- Reducible metal ions (Cr(VI) , Pb(II) , Hg(II) , Cd(II)) reduced to levels of < 1 ppm.
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- Kinetics controlled by electron transfer and nucleation.
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- Preliminary experiments show surface modification is feasible, and may be used to increase selectivity.