Remediation of Aqueous Metals and Chlorinated Hydrocarbons by Zero Valent Metal Nanocomposites

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Abstract

A powerful composite reductant material can be formed by the borohydride reduction of aqueous metal salts in the presence of a support. The resulting material consists of nanoparticles (10-30 nm) of zero valent metal dispersed on the support. The combination of high surface area, zero valent metal particles, and dispersion of these particles over the bulk support creates a highly active reductant without a concomitant increase in the passive corrosion rate due to exposure to water and dissolved oxygen.

In batch tests on aqueous metal contaminants, resin-supported zero valent iron nanoparticles far outperformed iron filings in terms of initial rates of reduction, atom efficiency of iron, and total contaminant reduced. Yet, the passive corrosion rates of the two materials were comparable. In batch tests on aqueous trichloroethylene, zero valent nickel-iron nanoparticles supported on carbon clearly outperformed iron filings.

The performance of supported zero valent nanoparticles in the reduction of organic and inorganic aqueous contaminants suggests they may be a suitable material for reactive barriers and wastestream remediation.

Concurrent Borohydride Reactions

Borohydride reduction of iron is a complex system in which three reactions run concurrently. As a consequence, iron and boron content, as well as boron valence, are sensitive to pH and the ***rate*** of borohydride addition.

- $BH_4^- + 2\ H_2O \rightarrow BO_2^- + 4\ H_2(g)$
- $BH_4^- + 2\ Fe^{2+} + 2\ H_2O \rightarrow 2\ Fe^0(s) + BO_2^- + 4H^+ + 2\ H_2(g)$
- $BH_4^- + H_2O \rightarrow B(s) + OH^- + 2.5\ H_2(g)$

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

The metal salts and support materials may be used singly or in combination. The support material provides for dispersion of the resulting zero valent metal, as well as hydroconductivity for reactive barriers, but typically does not react with the contaminant.

Possible Metals

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

Possible Support Materials

- Polymeric Resin
- Metal Oxides
- Silica
- Styrofoam
- Carbon
- Sand
- Gravel

Bulk versus Surface Composition of Zero Valent Iron Produced by Borohydride Reduction

Bulk Composition: 22.6% Fe, 4-5% B

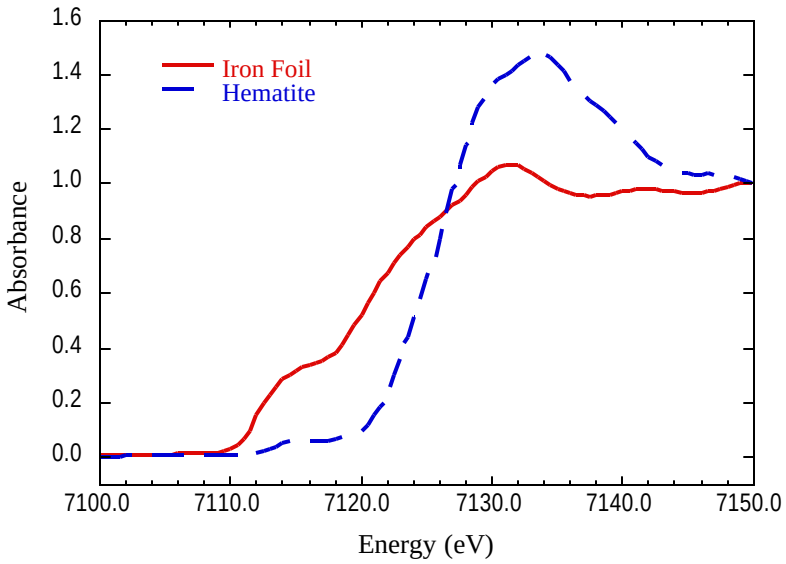
Surface Composition:

	Fe	O	C	B	Na
Iron Filings	9.4	32.0	58.6	0	0
Treated Iron Filings	11.8	55.6	19.6	9.7	3.3
Nano-Iron	15.9	58.7	0	22.5	2.9

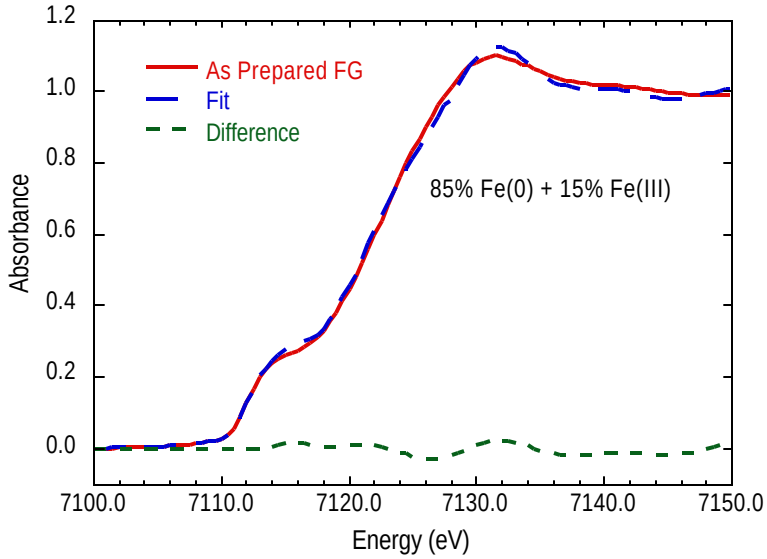
Remediation Steps

- Dissolution of passivating layer, if any, on zero valent metal.
- Adsorption of aqueous contaminant
- Reduction
- Alloy formation (e.g., chromites, $Cr_{(1-x)}Fe_x(OH)_{3(s)}$, where typically x = 0.33)

XANES (X-ray Absorption Near Edge Spectroscopy) of unreacted iron-on-zirconium oxide Ferragel

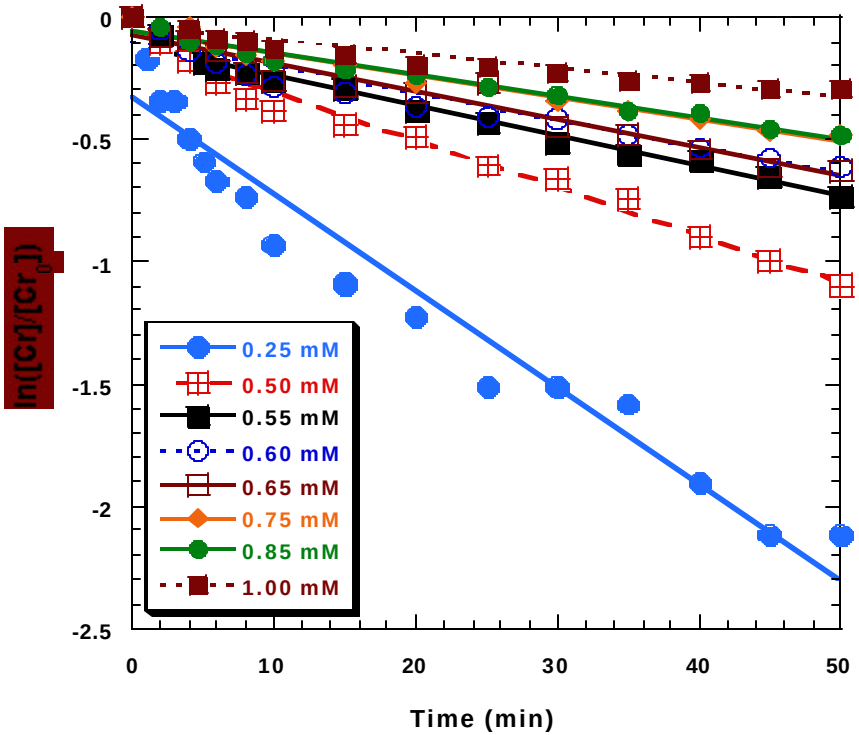


Standards

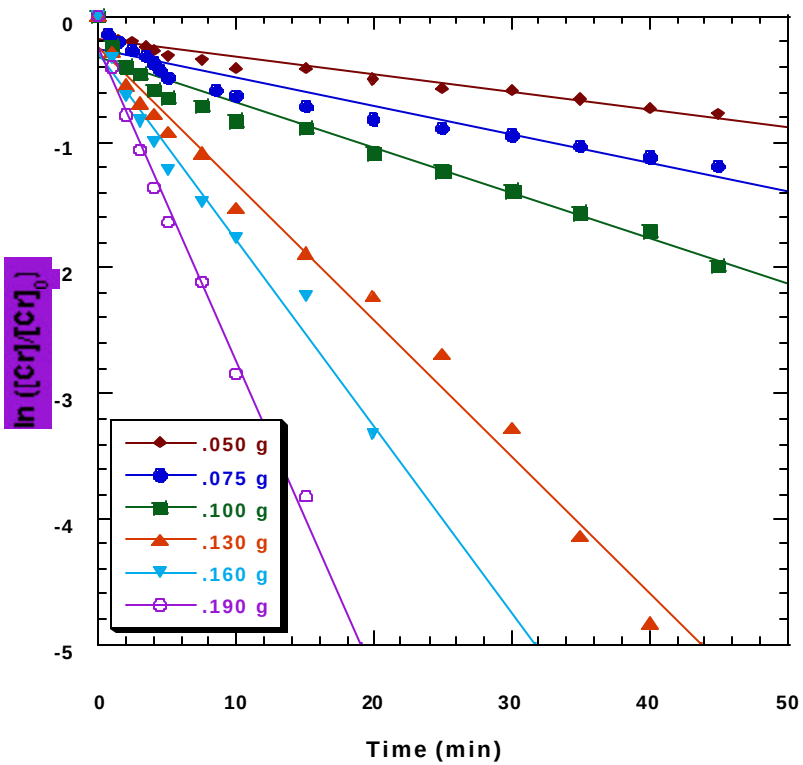


Fit to 85% Fe^0, 15% Fe(III)

Rates of Reduction Dependent on Both Initial Iron Content and Initial Contaminant Concentration.

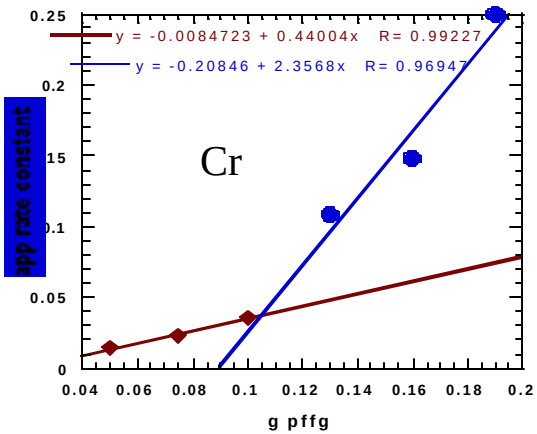


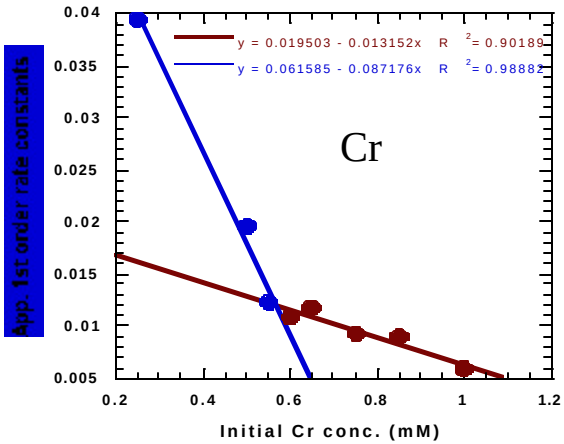
0.100 g iron-on-resin Ferragel,
varied initial [Cr]

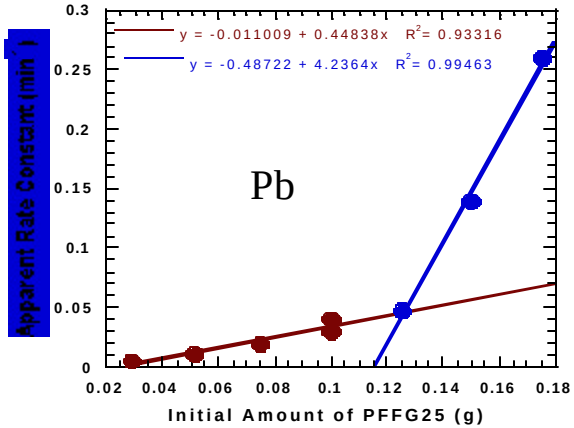


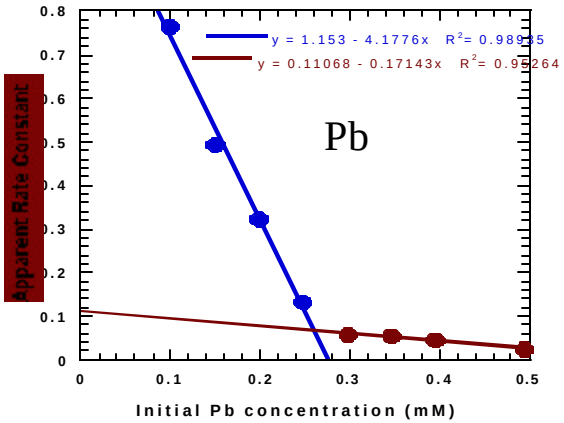
0.50 mM Cr,
varied g iron-on-resin Ferragel

Changes in Apparent First Order Rate Constant





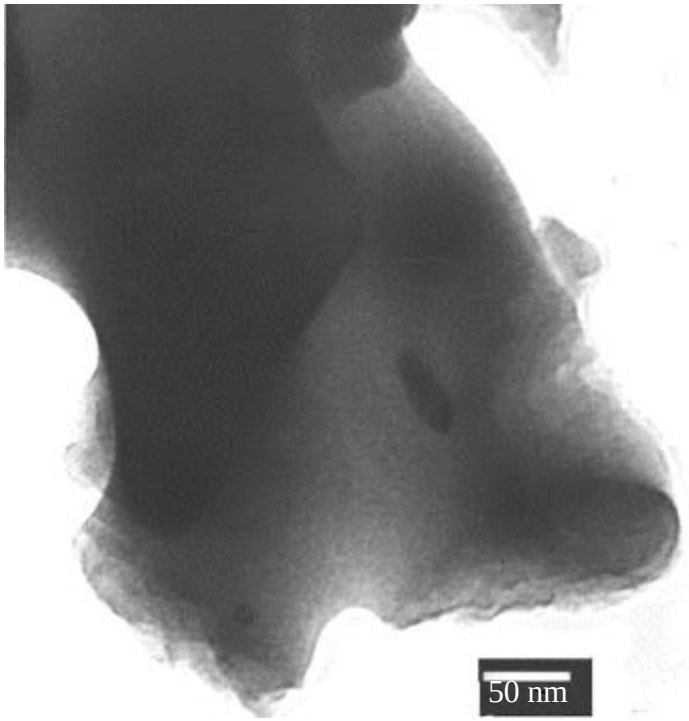




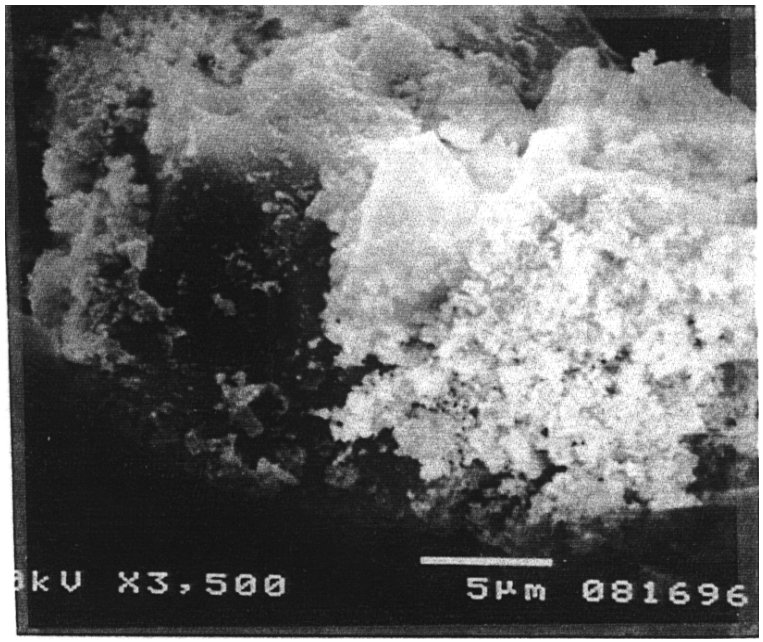
When fit to first order kinetics, the apparent rate constant ($k * A_s$, a factor of iron surface area) increases with increasing iron amounts and decreases with increasing contaminant concentrations--indicating that simple first order kinetics are insufficient to describe the process.

Breakpoints occur when molar iron content is 8-10% of the total moles of contaminant present, indicating that 8-10% of the total iron is located on active sites.

Comparison of iron-on-resin and iron-on-silica gel Ferragels.



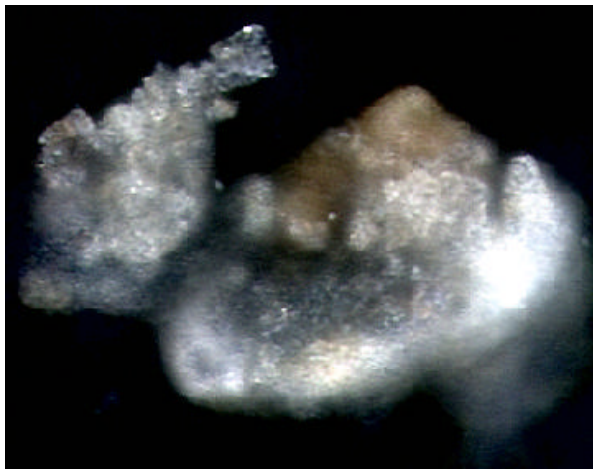
TEM of iron-on-resin Ferragel



SEM of iron-on-silica gel Ferragel

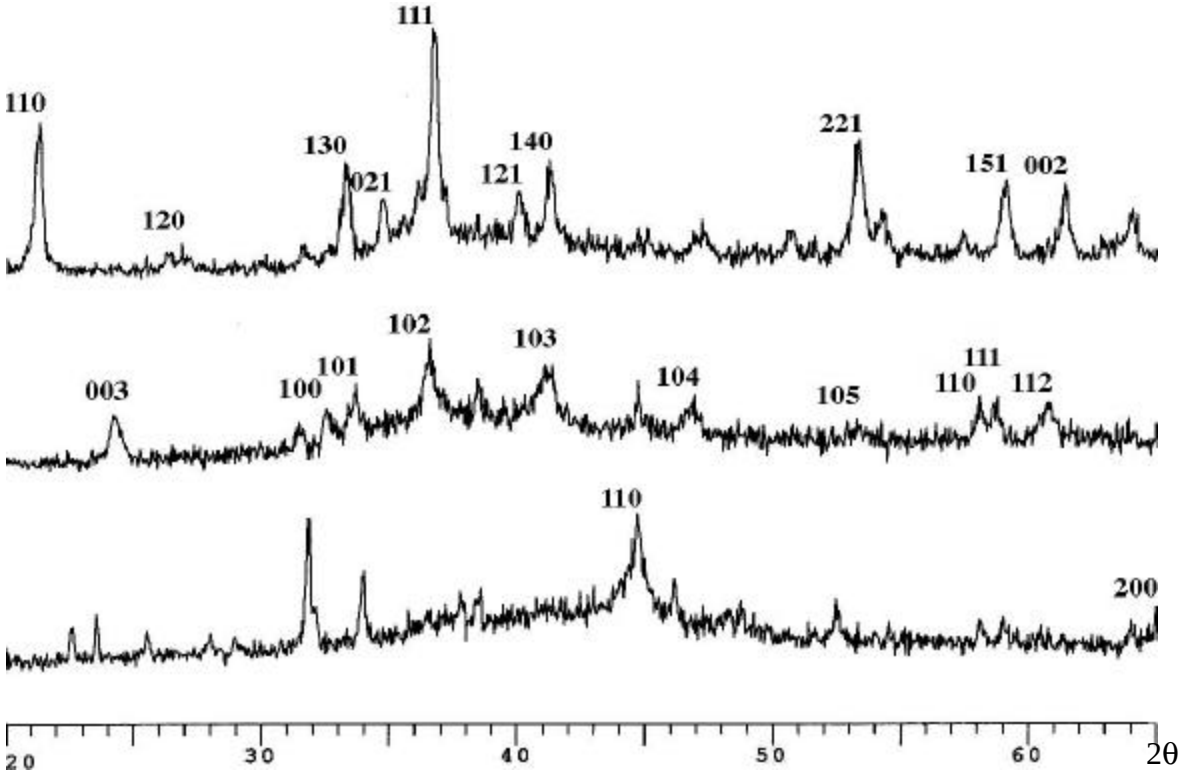
Synthesis of Iron-on-Resin Ferragel

Top: Optical micrograph of PolyFlo® resin particles, 20-30 μm in diameter prior to borohydride reduction.



Bottom: Optical micrograph of the finished iron-on-resin Ferragel.

Evolution of Goethite (α-FeOOH) as iron-on-resin Ferragel corrodes in water.

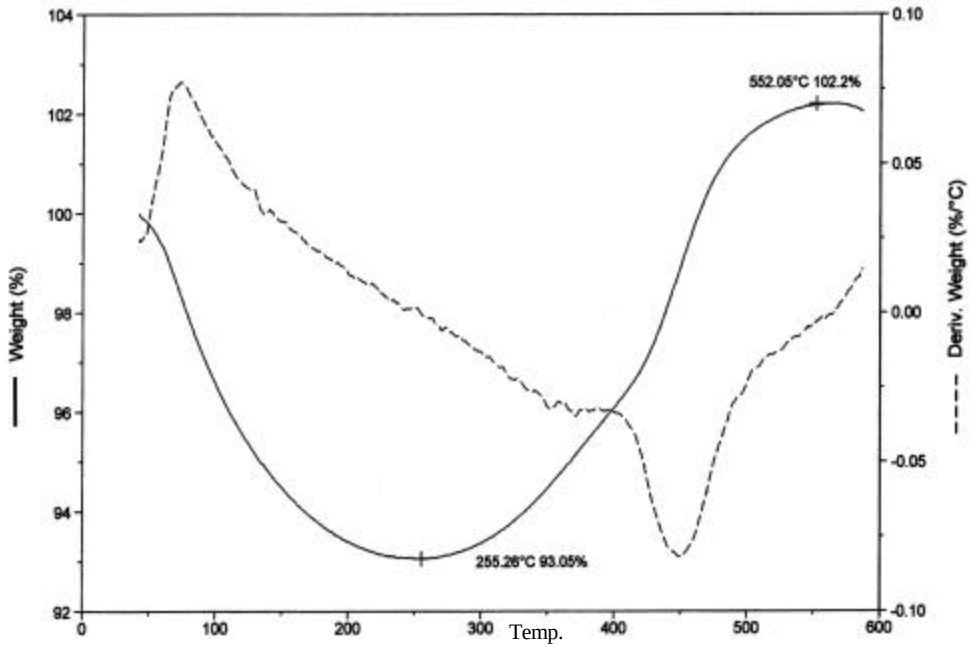


X-ray diffraction patterns. Bottom: zero valent iron in iron-on-resin Ferragel. Middle: green rust formation in damp Ferragel. Top: goethite formation in iron-on-resin Ferragel after 2 weeks exposure to air and water.

Thermogravimetric analysis: Unsupported iron nanoparticles significantly more hydrated than iron filings

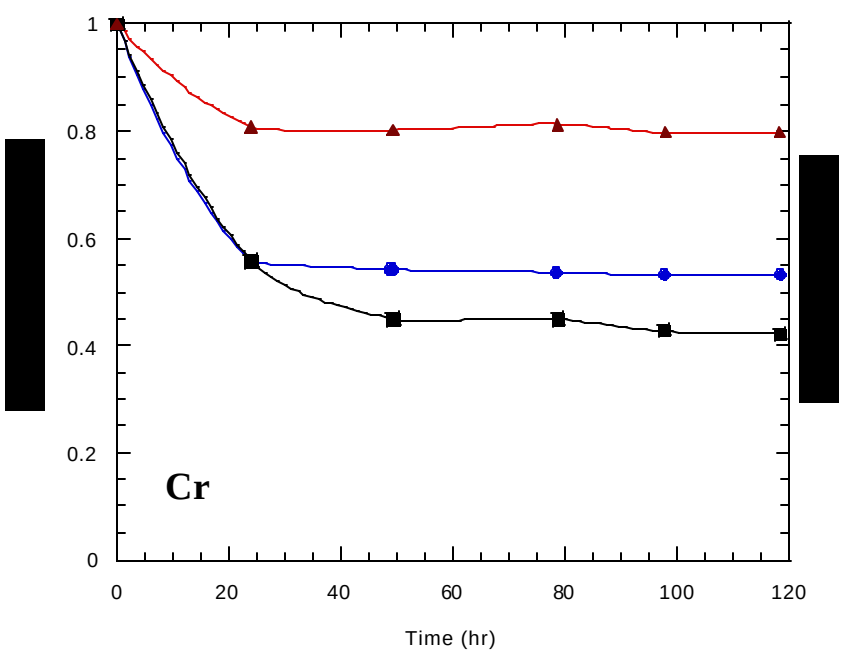
Weight loss below 100º C. equals 1.4 water molecules / surface-exposed Fe. Total weight loss shows 2.7 water molecules present per surface Fe.

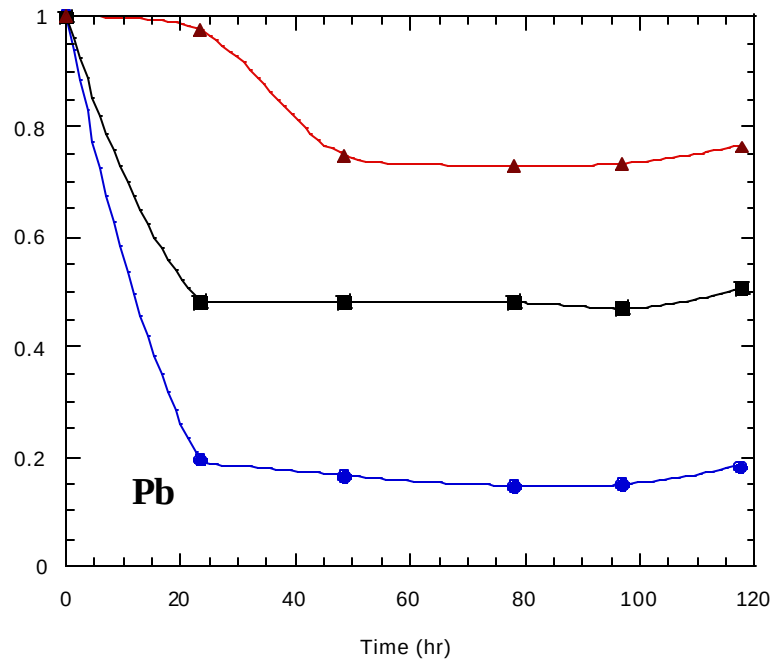
Subsequent weight gain is consistent with 1.2 - 1.5 oxygen atoms / zero valent Fe atom to form hematite (α-Fe_2O_3). Heating unsupported nano-iron at 600º C. for 2 hours produces hematite.



Maximum water loss for unsupported nano-iron was 6.95% and percent weight gain was 9.15% between 255º and 552º C. In contrast, the maximum water loss for iron filings was 0.14% at 386º C. and percent weight gain was 0.155% between 386º and 629º C.

More Than 90% of Total Contaminant Reduction Occurs in First 48 Hours of Exposure

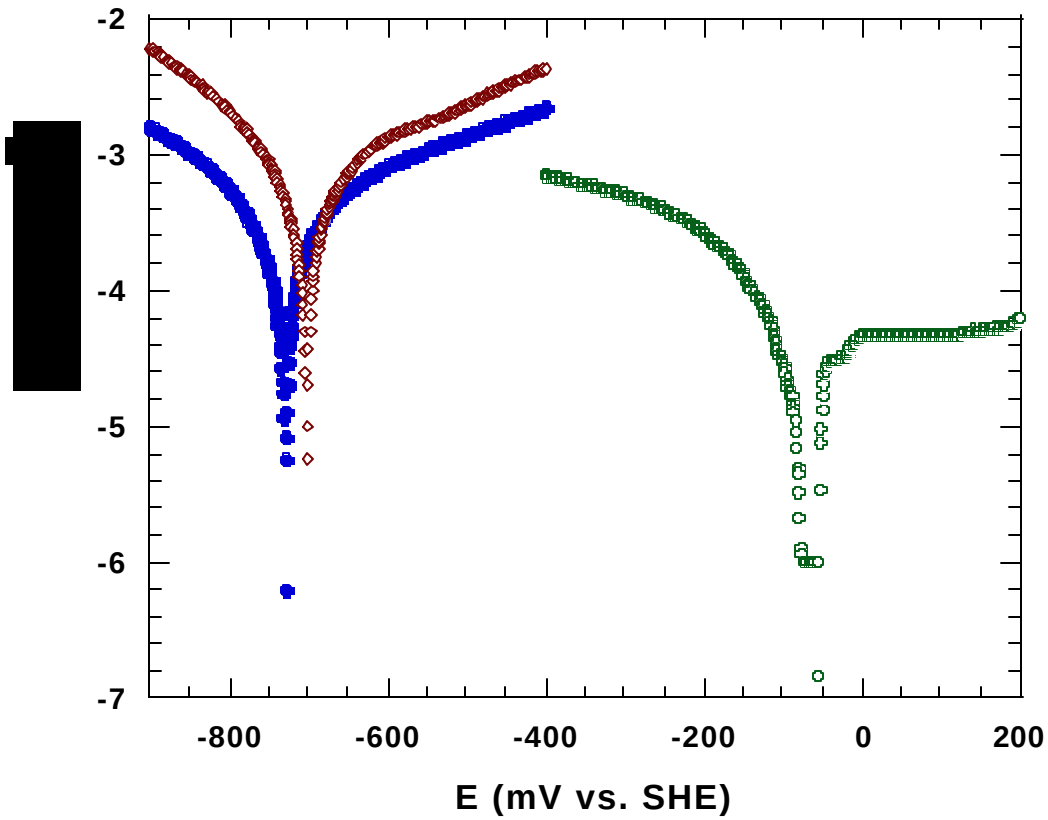


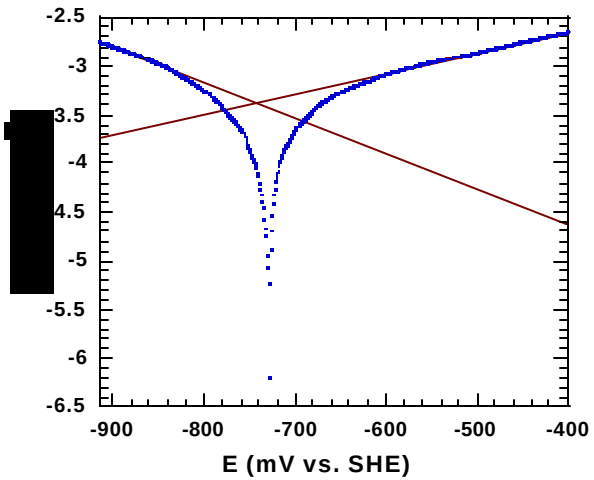


Batch studies of reduction of 1.500 mmol of contaminant in 1.000 L water. Each iron bearing material contained a total of 1.414 mmol of Fe. Red = commercial iron filings (0.100 g). Blue = iron-on-resin Ferragel (0.465 g). Black = unsupported nano-iron (0.239 g).

Passive Corrosion of Iron-Bearing Materials

Dynamic voltammetry, 8-12 hr equilibration in 0.1 M $KClO_4$



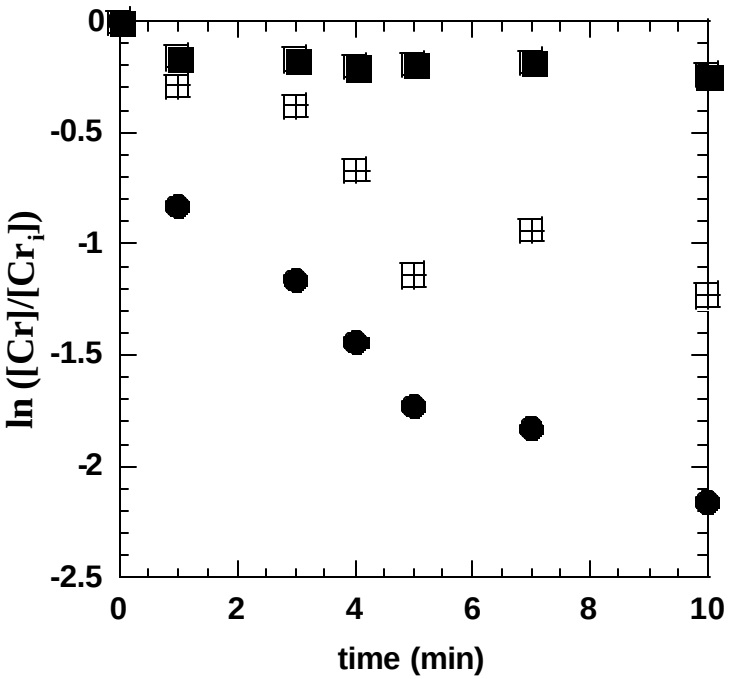


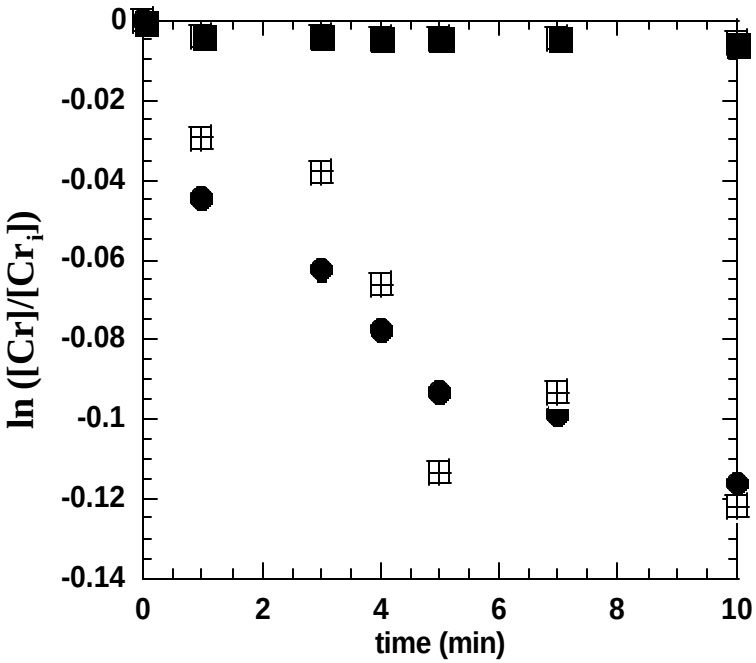
Left: Anodically controlled passive corrosion of iron filings, unsupported nano-iron, iron-on-resin Ferragel.

Above: Off-center (from E_{corr}) intersection of Tafel plots for iron-on-resin Ferragel indicates complex system with competing or concurrent dynamics.

Atom Efficiency

Nanoparticles Show Greater Use of Zero Valent Iron



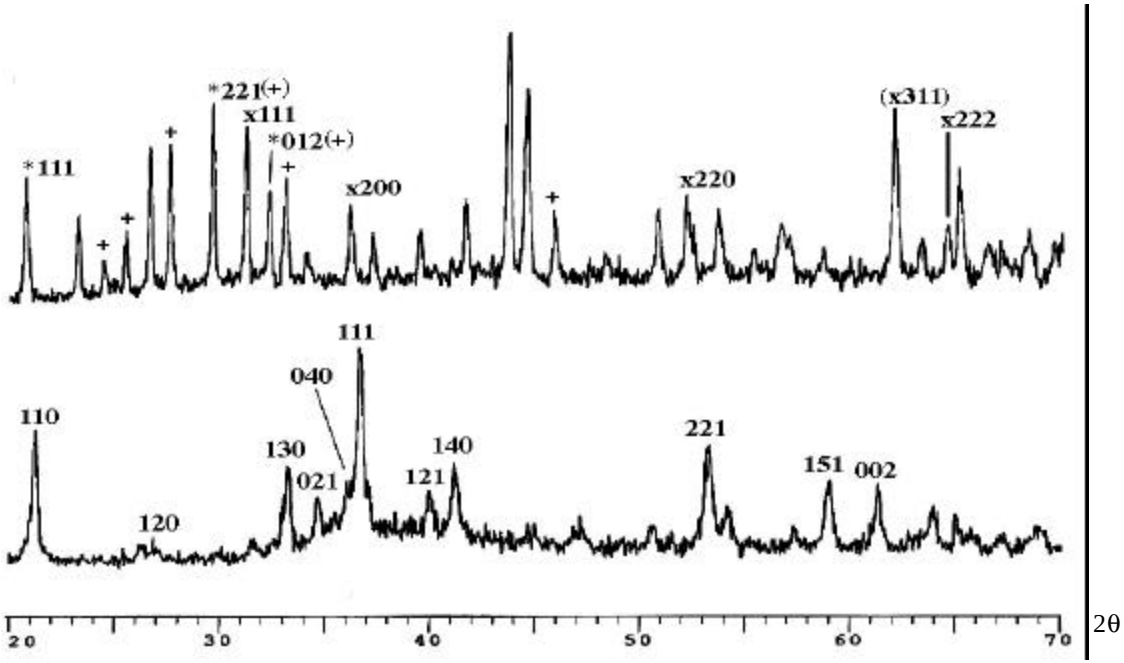


Left: Removal of Cr(VI) from 100 mL of 0.50 mM solution by 0.100 g of supported nano-iron (‹,Ferragel), unsupported nano-iron (1), and iron powder (4,-325 mesh, Baker).

Right: The same data normalized per mole of iron present.

Reaction Products

Contaminants Reduced to Insoluble Forms, Iron Oxidized to Geothite



Powder XRD patterns and Miller indices of spent Ferragels

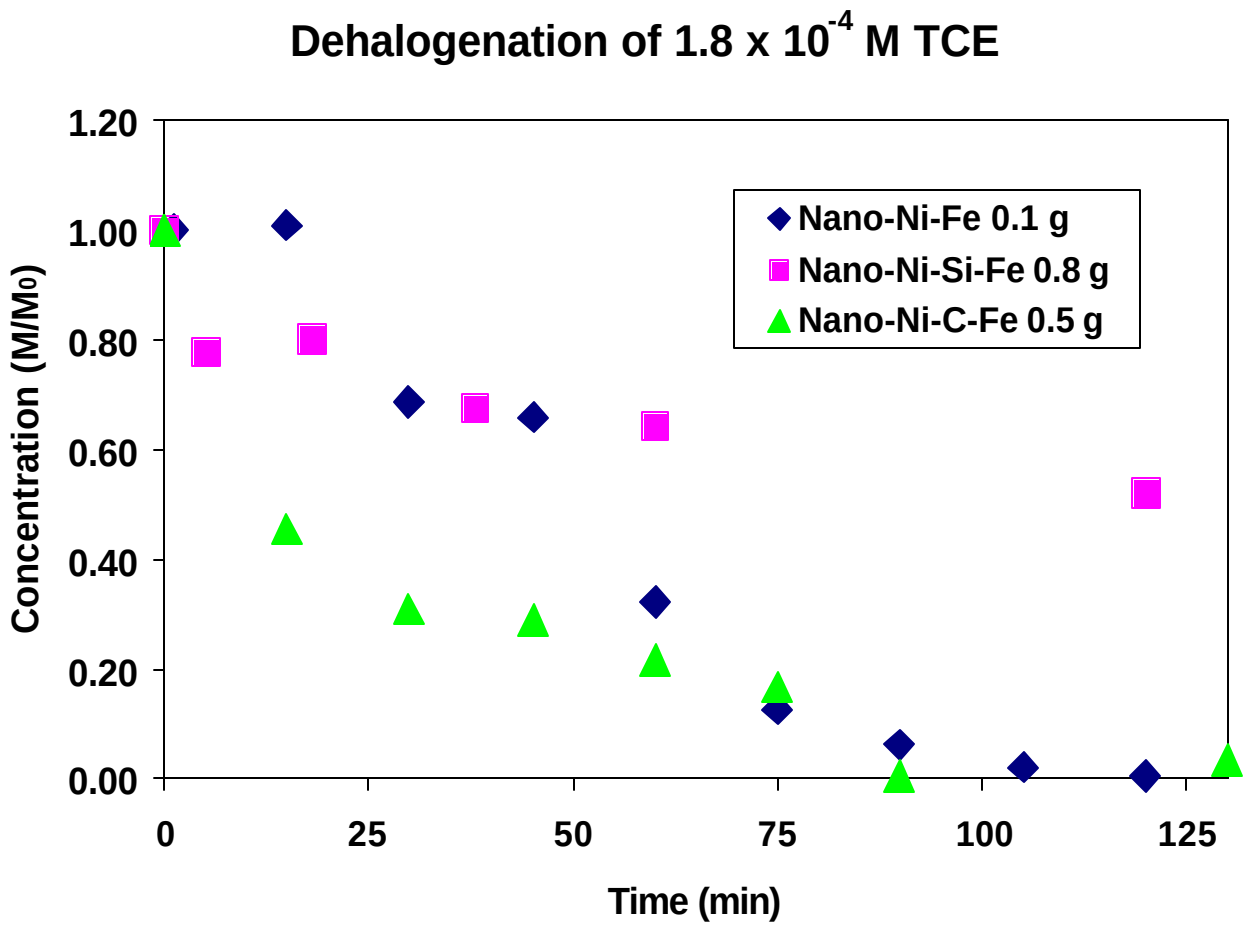
Top: After exposure to Pb(II) solution. **x** =Pb(0), ***** =PbO•xH_2O (tentative), and + =$Pb(OH)_2$ (tentative, no indexing available).

Bottom: After exposure to Cr(VI) solution. Indexed peaks are for goethite (α-FeOOH). Reduced Cr is amorphous, but determined to be Cr(III) by XPS.

Dehalogenation of Chlorinated Hydrocarbons using Nano-Ni-Fe Particles

- Use high surface area nanometals for the reductive dehalogenation of halogenated organics (TCE, PCE etc.) from ground and waster water streams
  - Employ borohydride reduction with ratio of Fe:Ni 4:1
  - Characterize by XPS, XRD, BET, ICP, microscopy
- Halogenated organics are dissolved in ground water (15 mg/l), and are carcinogens, $t_{1/2}$= 9 months
- EPA maximum allowed water concentration is $5x10^{-4}$ mg/l – current but inefficient remediation method: pump & treat
- Mount Nano-Ni-Fe particles onto high surface area supports, such as silica and carbon

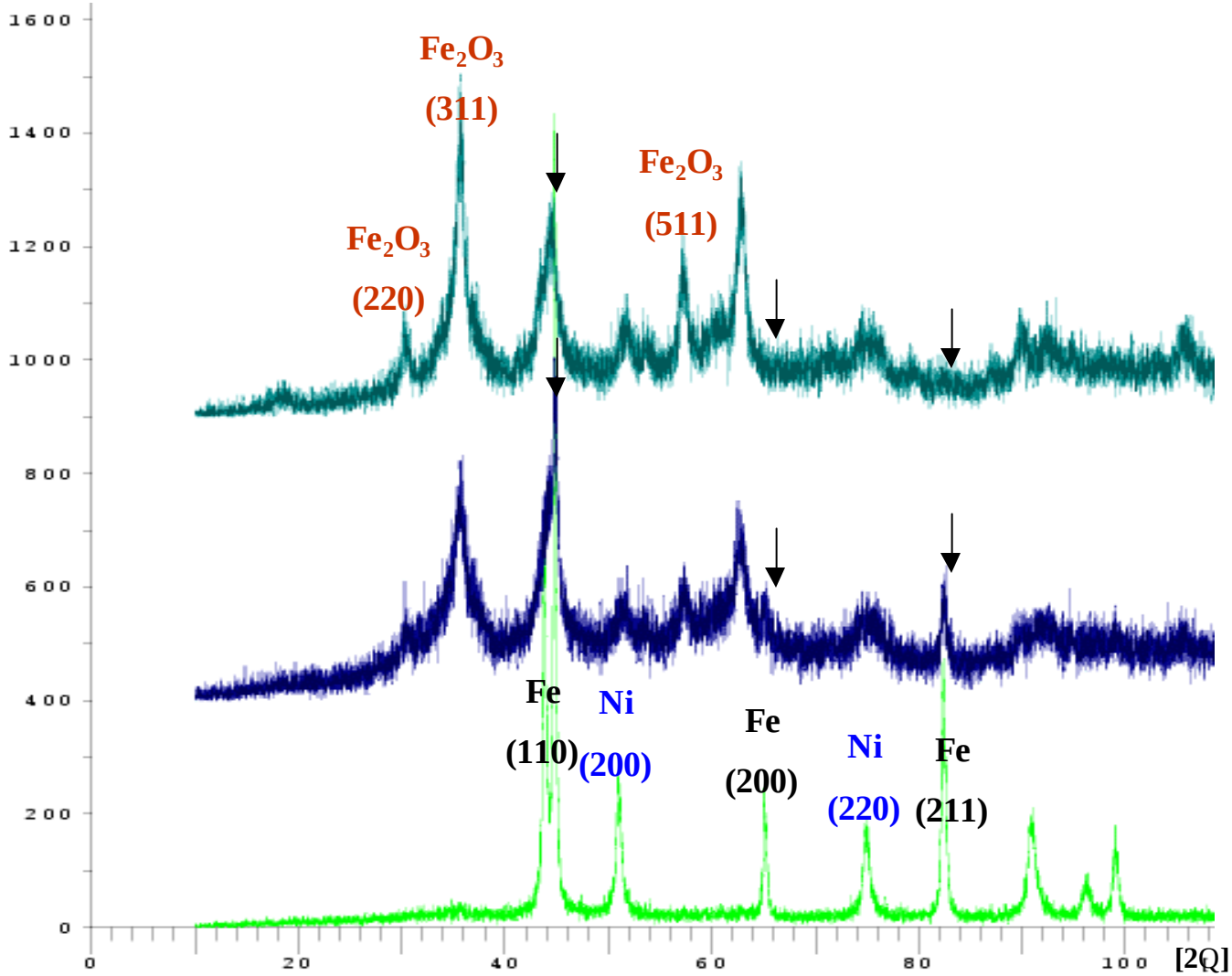
Nano-Ni-Fe Supported on Hydrophilic Carbon Dehalogenate TCE at the Fastest Rate



Dehalogenation of TCE using unsupported Ni-Fe, and supported on hydrophilic carbon and silica gel.

Ni-Fe supported on Carbon reduces TCE at fastest rate, by preconcentrating the TCE and by being conductive which completes a circuit with Nickel as the cathode.

Product Formation during the Dehalogenation Reaction



- Fe_2O_3 (Magnetite) forms as Iron corrodes; Nickel remains zero-valent
- Fe-Ni particles are not alloyed
- Form chloride ions in the course of the reaction

Ni-Fe unsupported after 135 min of 1.8 x 10^{-4} M TCE exposure

Ni-Fe unsupported after 5 min of 1.8 x 10^{-4} M TCE exposure

Ni-Fe unsupported no TCE exposure

Comparison of Dehalogenation Rates using various Iron-Based Materials

Material used	hr^{-1}
Iron filings (BH_4^- treated) 5g	0.092
Fe unsupported 5g	0.0042
Fe on hydrophilic Carbon 0.5 g	0.17
Ni-Fe on hydrophilic Carbon 0.5 g	1.58
Ni-Fe on silica gel 0.8 g	0.34

•Using just Nanonickel and sintered commerical Ni:Fe (50:50 wt. ratio, Alfa Aesar) did not show any significant dehalogenation

The surface area of unsupported Ni-Fe is ~ 56 m^2/g. Nickel is located on the outer surface of the particles relative to iron. Nickel enhances dehalogenation rate by :

(a) acting as hydrogenation catalyst (compare to Pd)

(b) resisting corrosion, thereby allowing continued electron transfer at the surface as Fe corrodes

(c) participating in a bipolar process: Ni is cathode where TCE is reduced, Fe is anode where iron corrodes

Comparison of Volumes and Surfaces

Right: Comparison of free-flowing and compressed volumes of resin-supported Ferragel versus iron filings. ➔

Type of Material	Density (g / cc)	Surface Area (sq.m / g)
resin	--	3
nano-iron on resin	1.1	24
unsupported nano-iron	--	22
silica gel	--	440
nano-iron on silica gel	1.3	240
unsupported nano-Ni-Fe	--	56
iron filings (~40 mesh)	6.7	2

	Ferragel (mL/g)	Iron filings (mL/g)	Ratio (Ferragel/ filings)
dry, uncompressed	1.60	0.32	5.0
water displacement, uncompressed	0.90	0.15	6.0
water displacement, compressed to 1 ton pressure (600 psi)	.72	.15	4.8
water displacement, compressed to 4.4 ton pressure (2900 psi)	.72	.17	4.2

🡐 Left: Comparison of densities, and surface areas as determined by nitrogen BET.

Comparison of Reductive Capacities and Rates

Right: Comparison of fraction of total contaminant removed in batch tests over 60 days. ➔

Type of Iron	Cr(VI)	Pb(II)
Commercial Iron Filings	0.10	0.15
Unsupported Nano-Iron	0.45	0.65
Resin-supported Nano-Iron	0.40	>0.99

Type of Iron	mmol Fe /g	Apparent rate constant for Cr(VI) (hr^{-1})	Apparent rate constant for Pb(II) (hr^{-1})
Resin-supported Ferragel	4.05	1.18	1.44
Iron filings, ~40 mesh	14.1	0.22	0.09
Iron powder, -325 mesh	14	0.24	0.05
"Activated" iron powder, -325 mesh	----	0.28	0.33
High purity iron chunks, 10-30 mesh	18	0.22	0.08
Unsupported nano-iron	5.96	1.16	-----

🡐 Left: Comparison of apparent rate constants for various iron-bearing materials. (100 mL of 0.50 mM solutions, 0.100 g of iron-bearing material.)

Conclusion

- Initial Rates for aqueous Cr(VI) and Pb(II) remediation by resin-supported Ferragels are 3-5 times faster than filings on a weight basis, and 12-20 times faster than filings on a (Fe)molar basis. Ni-Fe composites are >50 times faster than iron filings in reducing TCE (weight basis).
- Total remediation is 4.8 times greater for Ferragels (Cr^{6+}, 2-3 months) on a weight basis, when compared to iron filings, and 21 times greater on a molar (Fe) basis. The greater atom efficiency of Fe overrides the inherent volume increase entailed in using a support, and points to the possibility of thinner reactive barriers and lower excavation costs.
- While active reduction is greatly increased, passive corrosion by water and oxygen are equal to or less than that of iron filings.
- Based on batch tests, supported nanoparticles are clearly a superior remediant over iron filings. However, the effects of a continual fresh supply of water and contaminant remain to be studied in column and field testing.

Acknowledgements

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- Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by the Battelle Memorial Institute under contract DE-AC06-76RLO 1830.
- PolyFlo® is a registered trademark of Puresyn, Inc., Malvern, PA.
- 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.
- Fe synchrotron work performed at Brookhaven National Laboratory.

Separation and Immobilization of Aqueous Cesium

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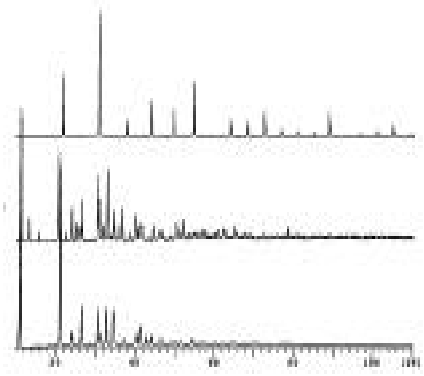
Introduction

Separation of ^{137}Cs from an aqueous feedstream by precipitation with sodium tetraphenylborate has caused difficulties at SRS. The problem may be simply stated in that radiolysis of tetraphenylborate anion (TPB) by the ^{137}Cs creates benzene, which then coalesces in the aqueous medium, and rises to the surface and volatizes. The simplest solution, without changing the process, is to reduce the exposure time of TPB to ^{137}Cs by employing a continuous-flow separation process rather than a million gallon batch process. As a corollary, the ^{137}Cs would optimally be rendered into a vitrifiable form at the end of the separation process.

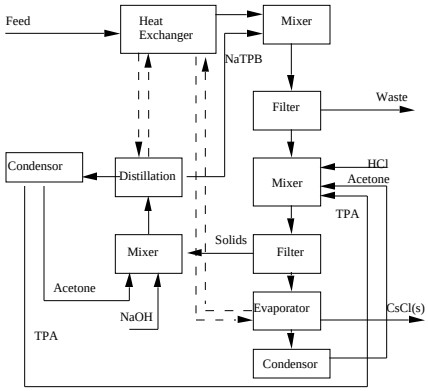
Two possible processes are examined which utilize a continuous-feed stream to a plate-and-frame press filter. The recovered CsTPB is solvated and the Cs recovered as an inorganic salt. Total exposure time of TPB to Cs is reduced to about 15 minutes.

Tracking Cs in the Solids



Bottom: NaTPB; Middle: CsTPB; Top: CsCl.

Proposed Continuous-Flow Process with Acetone Solvent



Scheme for Remediation of $^{137}Cs^{+}_{(aq)}$ Using Acetone as the Solvent

- $Cs^{+}_{(aq)} + NaTPB_{(aq)} \xrightarrow{H_2O} CsTPB_{(s)}$
- $CsTPB_{(s)} + TPA \xrightarrow{\text{acetone, HCl (or } HNO_3)} Cs^{+}_{(aq)} + TPA^{+}TPB^{-}_{(s)}$
- $Cs^{+}_{(aq)} + Cl^{-}_{(aq)} \xrightarrow{-H_2O} CsCl_{(s)}$ (or $CsNO_3$)
- $TPA^{+}TPB^{-} + NaOH_{(aq)} \xrightarrow{\text{-acetone, -TPA}} NaTPB_{(aq)}$

TPB=tetraphenylborate anion

TPA=tripropyl amine

Overview of Recovery Process Using Acetone Solvent

Disadvantages

- Acetone is SARA listed and has a low flash point.
- Chloride is corrosive to steels used in plant.
- Recycling of TPB does not provide cost benefit when supply is pre-contracted.

Advantages

- Exposure time of TPB to ^{137}Cs is reduced to approximately 15 minutes.
- ^{137}Cs is recovered as a readily vitrifiable inorganic salt.
- All materials, including heat, are recycled–except for small quantities of NaOH and acid.
- HNO_3 may be used in place of HCl, and ^{137}Cs recovered as $^{137}CsNO_3$.

Scheme for Remediation of $^{137}Cs^{+}_{(aq)}$ Using Propylene Carbonate as the Solvent

- $Cs^{+}_{(aq)} + NaTPB_{(aq)} \xrightarrow{H2O} CsTPB_{(s)}$
- $CsTPB_{(s)} + C_4O_3H_6 + TPA + NaNO_{3(aq)} \longrightarrow Cs^{+}_{(aq)} + NaTPB_{(PC)} + TPA$
- $Cs^{+}_{(aq)} + NO_3^{-}{}_{(aq)} \xrightarrow{-H2O} CsNO_{3(s)}$

TPB=tetraphenylborate anion
TPA=tripropyl amine
PC=propylene carbonate

Filtration

Using Plate- and-Frame Press Filter

- A pre-coat and filter aid are used to prevent blinding by CsTPB. Celite 521 in water at 1.0% (w/w) was used for both. Slurry content has not yet been optimized (between 0.2% and 1.0 w/w) for a 1.5 mM CsTPB (200 ppm Cs) aqueous stream.
- Fill time ~ 3 seconds.
- Pump provides 8 psi, resulting in a flow of 1.5 L / min. No CsTPB is found in the effluent (Cs detection limit 0.1 ppm)
- Air blowdown at 30 psi until pressure drop increases from 20 psi to 25 psi (about 2 min) yields cake with 35% solids.

Komline-Sanderson Model 177 Laboratory Filter Specs

- Max. filtration pressure 100 psi
- Room on filter rack for total of 4 chambers. Each chamber 7”x7”x1.25”.
- Each filter chamber: area 34.25 sq.in.; volume 21.4 cu.in.

Filtration Timeline

- 0-2 min: Pre-coat with 3 L 1.0% w/w Celite 521
- 2-9 min: Filter feed slurry of 1.0% w/w Celite 521 and 0.685% CsTPB at 1.5 L/min. (9 psig)
- 9-11 min: Air blowdown at 30 psi
- 11-13 min: Cake removal.

Estimated Scale-Up to 5 gal/min Feedstream

Filter feed needed:

5 gal/min feedstream x 13 min total time / 7 min filtration time= 9.3 gal/min.

Filter Volume Required (cu.ft.) =

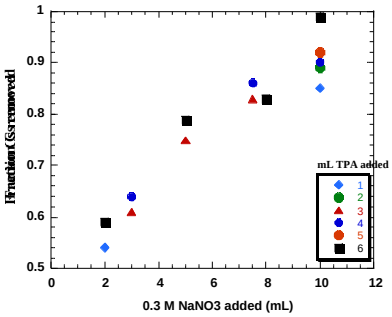
$$\frac{\text{65 gal x 8.34 lbs/gal x 1.01 est. sp.gr.x 1.6\% wght solids in feed}}{\text{35\% solids in cakes x 54.4 lbs/cu.ft. cake density}}$$

= 0.46 cu.ft.

Flammability and Volatility

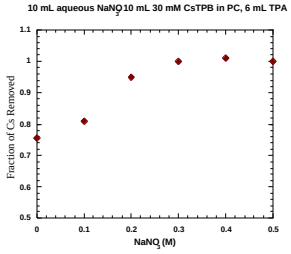
Solvent	Flash Point (ºC.)	Boil Point (ºC.)
Acetone	-20	56
Tripropylamine	33	156
Propylene Carbonate	132	240
Benzene	-11	80
Water	--	100

TPA has Minor but Measurable Effect on Cs Separation



Although its chemical action in this system is yet poorly understood, tripropylamine (TPA) does increase overall extraction percentages. TPA also aids in separation of the aqueous phase.

Optimizing $Na^{+}_{(aq)}$ Content and Reagent Effects on pH

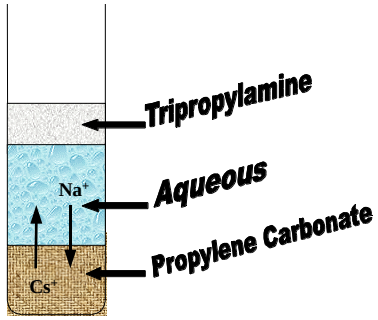


Optimal NaNO3 molarity for the aqueous phase is 0.35 M, when TPA is present in the system.

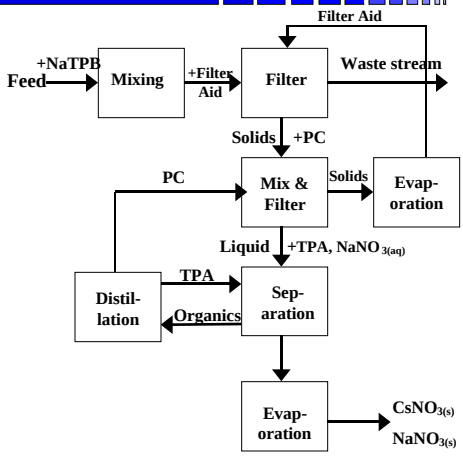
mL H_2O	mol PC	mol TPA	mol $NaNO_3$	mol CsTPB	pH
10.0					6.53
10.0	1.16E-01				6.57
10.0		3.20E-02			10.68
10.0			5.00E-03		5.83
10.0	1.16E-01	3.20E-02			8.53
10.0	1.16E-01		5.00E-03		6.91
10.0	1.16E-01	3.20E-02	5.00E-03		8.10
10.0	1.16e-01	3.20E-02		3.20E-04	7.76
10.0	1.16E-01	3.20E-02	5.00E-03	3.20E-04	7.94
10.0	1.16E-01		5.00E-03	3.20E-04	6.79

TPA raises pH, $NaNO_3$ lowers pH, PC buffers both TPA and $NaNO_3$, indicating hydrolysis of PC.

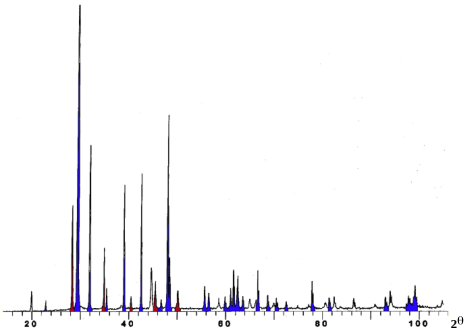
Tri-phase Cesium Exchange



Simplified Scheme for Cs Separation with Propylene Carbonate Solvent



Final Recovery Form of Cs by PC Method is $CsNO_3$



XRD pattern of solids from evaporated aqueous phase of extraction from CsTPB in propylene carbonate by 0.5 M $NaNO_3$ and TPA. Blue indicates peaks assigned to (rhombohedral) $NaNO_3$. Red indicates peaks assigned to (cubic) $CsNO_3$.

Overview of Recovery Process Using Propylene Carbonate Solvent

Disadvantages

- TPA complicates system, its actions are as yet poorly understood, and it has the lowest flash point of any component.
- Celite 521 is not easily wet by propylene carbonate in the presence of water (as in filter cake).
- TPB anion not recycled, destroyed in organic phase.

Advantages

- Exposure time of TPB to ^{137}Cs is reduced to approximately 15 minutes.
- ^{137}Cs is recovered as a readily vitrifiable inorganic salt.
- No SARA listed chemicals used.
- Minimal footprint for entire process.
- Organics and filter aid can be recovered and recycled.
- All aromatics separated to and recoverable from organic phase.

Future Work Planned for Propylene Carbonate Method

- Investigation of role of TPA--or replace TPA entirely with higher concentration of $NaNO_3$. Preliminary results show that aqueous $NaNO_3$ solutions of 0.5 M or higher will phase separate and extract Cs without the presence of TPA. The drawback is an increase in salts to be vitrified.
- Replace Celite 521 with a filter aid that is easily wetted by both water and PC. Since the filter aid is intended to be recycled, even a highly specialized material may be acceptable, as long as filtration specifications are met.
- Replace the current underpowered (8-10 psig) filter feed pump with a pump that can generate up to 100 psig.
- Test PC method with radioisotopic Cs.

Acknowledgement

This work was supported by a grant from the U.S. Department of Energy, DE-FG07-97ER14822

Material for the Immobilization and Stabilization of Technetium

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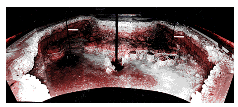
ABSTRACT

Supported nano-scale zero valent iron ("Ferragel") is a powerful reductant for aqueous metal ions. These materials consist of particles of iron, 10-30 nm in diameter, immobilized on a support material via borohydride reduction of an aqueous iron salt. Typically, Ferragels contain about 20-25% iron by weight, 85% of which is in the zero-valent state, and about 15% of which is oxidized to trivalent iron oxides/oxyhydroxides. Ferragels are relatively stable in air, once dried, but are highly active reductants when wet. They can be made with a wide variety of support materials, including polymer resins, zirconia, and silica. One of our goals is to use appropriately supported Ferragels to reduce and remove TcO_4^- from waste streams and to subsequently stabilize the Tc-loaded material. Ferragels on base-stable supports have been tested and shown to be effective for the removal of TcO_4^- directly from highly alkaline tank-waste simulants. While it is not stable in strong base, silica Ferragel is effective in removing TcO_4^- from neutral or mildly basic solutions. Ferragels are also, therefore, a reasonable candidate for the subsequent reduction of TcO_4^- that is eluted from commercial ion exchange resins which are currently planned to process the original alkaline tank waste. Thus, a simple "pour-through" of the exchange resin eluent into a silica Ferragel column should provide an insoluble and non-volatile solid technetium-containing product that can be stabilized directly by vitrification. Both near-edge and extended fine-structure X-ray absorption spectra (XANES and EXAFS) of the product after exposure of silica Ferragels to aqueous TcO_4^- show that the Tc is removed from the aqueous solution and reduced to an insoluble product. XANES features of the immobilized Tc are consistent with a reduced Tc species - perhaps Tc(IV). Initial EXAFS analysis shows 6 Tc-O bonds and one close Tc-Tc contact, consistent with rutile-type TcO_2 or a related product. The second nearest neighbor shell also contains Fe, which suggests that the immobilized product is in intimate contact with the iron oxide product of the reaction. Finally, the use of an inorganic support material gives the additional advantage of readily converting the Tc-Ferragel to a vitrified form, and glasses have already been made from the product (with Re as a surrogate for Tc) using an alkali borosilicate frit.

BACKGROUND

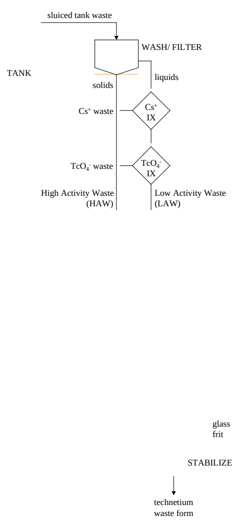
The Hanford Site



B The Hanford Site in Southeast Washington State contains 177 underground storage tanks that hold approximately 60 million gallons of radioactive aqueous waste that varies in chemical complexity and physical consistency.

B The current plan is to pre-treat the waste and vitrify it into immobilized high and low activity waste glass.

Removal of Technetium (^{99}Tc) from Waste Streams



B Required to meet low activity waste (LAW) glass requirements and, furthermore, to alleviate volatility problems during vitrification.

B Current approach uses commercially available organic ion-exchange resins (e.g., Reillex™).
- works well for removing pertechnetate, TcO_4^-
- generates large volumes of resin eluate waste containing TcO_4^-, which needs to be treated
- current plans are to add the eluate waste to the HAW melter feed
- problems associated with Tc(VII) volatility during HAW vitrification will still need to be addressed

B A different approach is to use an inorganic ion-exchange material or an inorganic adsorbent
- technetium species ion-exchange with or are sorbed to the inorganic material
- ideally, elution of the technetium from the material will not be required as the technetium-loaded material can be stabilized directly through encapsulation in glass or other waste form
- material and process can be designed to reduce the Tc(VII) volatility problem during stabilization

B Specifically, we propose the use of ultra-fine metals (e.g., Fe^0) dispersed on inorganic supports (Ferragels®) to reduce and contain the technetium
- involves electrochemical reactions:
  $3Fe (s) + 2TcO_4^- (aq) + 2H_3O^+ (aq) \longrightarrow 3Fe(OH)_2 (s) + 2TcO_2 (s)$
  TcO_2 (s) trapped in pores of support material
- stabilize technetium-loaded material through encapsulation in glass
- requires high surface area, base-stable (pH 7- 13) support materials amenable to stabilization

B Ferragel® (FG)
- novel method of preparing ultra-fine Fe^0 or other metallic particulates and loading them onto support materials
- developed by S. Ponder and T. Mallouk at *The Pennsylvania State University* (PSU)

REMOVAL OF PERTECHNETATE FROM SIMULATED LOW-ACTIVITY WASTE

Experimental

B A variety of inorganic particulate materials were employed as supports for the ultra-fine Fe^0.
- commercially available particulates
  e.g., SnO_2, ZnO, ZrO_2, SiO_2
- nano-crystalline particulates produced by PNNL's RTDS (Rapid Thermal Decomposition of Solutes) system
  e.g., c-ZrO_2 (≈200 m²/g surface area), m-ZrO_2 (≈50 m²/g)

B Application of the ultra-fine Fe^0 to the support materials to form Ferragel (FG) sorbents was performed at The Pennsylvania State University using a borohydride reduction of an aqueous iron salt:

Sample	Description	mg Fe^0/ g sample
FG SnO_2	FG on commercial tin oxide	20
FG ZnO_2	FG on commercial zinc oxide	20
FG ZrO_2	FG on commercial zirconia	20
FG RTDS-10	FG on PNNL RTDS monoclinic zirconia	80
FG RTDS-6	FG on PNNL RTDS cubic zirconia	80
RTDS-6	PNNL RTDS cubic zirconia (no FG)	0

FG = Ferragel

B Several different waste simulants were used to study how well the FG sorbents remove pertechnetate under different chemical conditions:

Component	DSSF	S1	S2	S3	Eluent
Al^{3+}	1.0		0.0003		
B^{3+}					0.0010
Ca^{2+}	0.0010		0.0018		
Cr^{3+}	0.0087		0.0026		
CrO_4^{2-}			0.0002		
Fe^{3+}	0.0008		0.014		
K^+	0.50		0.0003		
Mg^{2+}	0.0010		0.0006		
Mn^{2+}	0.0004		0.0002		
MoO_4^-	0.017		0.0001		
Na^+	10.	7.4	3.7	7.7	0.0046
Ni^{2+}					
Si					0.0008
Zn^{2+}					
CO_3^{2-}	0.27	0.27			
Cl^-	0.16				0.0004
F^-	0.25				
NO_3^-	3.1	3.1	0.057	2.7	0.0003
NO_2^-	1.7			1.9	0.0002
OH^-	3.8	3.8	3.7	3.1	
PO_4^{3-}	0.043				
SO_4^{2-}	0.043		0.0009		
TOC[a]	1.4				
Cs^+	0.017				
IO_3^{3-}	0.017				
Sr^{2+}	0.017				
TOC					
pH	13-14	13-14	11	13-14	7
density	1.42	1.31	1.19	nm	1.00

[a] Total Organic Carbon (TOC) from EDTA.

B Procedure for batch contact experiments
- simulants were spiked with $Na^{99}TcO_4$ to the appropriate concentration
- ~0.03 g of each of the adsorbent materials were weighed and placed in pre-weighed centrifuge tubes
- to each centrifuge tube, an aliquot of technetium-spiked simulant was added using a plastic syringe
- a blank spike and a blank were also analyzed
- centrifuge tubes were placed on an Orbit® shaker operating at 100 rpm for 24 hours then centrifuged at 1500 rpm for 10 minutes
- an aliquot of each sample, filtered through a 0.2 µm filter, was placed in a pre-weighed glass scintillation vial
- to each vial was added ~15 mL of Optifluor® liquid scintillation cocktail (LSC) and shaken by hand
- the starting and final concentrations of pertechnetate in solution, $[TcO_4^-]_0$ and $[TcO_4^-]_f$, were determined both by liquid scintillation using a Wallac 1415 LSC instrument as well as by detection of Bremsstrahlung secondary photon emission using a Autogamma Wallac 1411 instrument
- knowing the volume of solution, Vsol, in contact with the mass of adsorbent, m_{ads}, the distribution coefficient, K_d, was determined: $K_d = \{([TcO_4^-]_0 - [TcO_4^-]_f)/ [TcO_4^-]_f\} \{V_{sol}/m_{ads}\}$

* Current affiliation: Washington State University—Tri-Cities, Richland, WA, 99352.

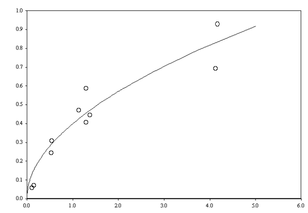
** Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by the Battelle Memorial Institute.

Results

B Reasonable K_d values for the removal of pertechnetate using supported Ferragels have been demonstrated. Note that the RTDS-6 without iron does not remove pertechnetate. :

Sample	simulant	$[TcO_4^-]_0$ (mM)	phase ratio (L/kg)	K_d (L/kg sample)	K'_d (L/kg Fe^0)
FG RTDS-6	S2	0.51	360	370±30	4600±400
FG RTDS-6	S1	9.0	640	160±30	2000±400
FG RTDS-6	S1	9.7	80	85±26	1100±300
FG RTDS-6	S1	12	140	80±17	1000±200
RTDS-6	S1	9.7	160	2±1	NA
FG ZrO_2	S1	12	150	16±4	800±200
FG SnO_2	S1	9.0	640	17±9	850±450

B A more detailed analysis of the data yields additional information.
- determine the normalized concentrations of technetium (eq Tc/eq Fe on the support) sorbed, S, and in the starting solution, C'
- model results based on corrosion theory:
  For a constant base simulant composition, the corrosion potential will depend on the concentration of pertechnetate in solution. During active corrosion, the potential for FG in contact with pertechnetate-containing simulant is proportional to the log of the corrosion current and is thus proportional to the log of the pertechnetate reduction rate.
- expanding on the rudiments listed above, a good fit (solid line in the graph at right) to the data (open circles) obtained from FG RTDS-6 and FG ZrO_2 sorbent materials is obtained:



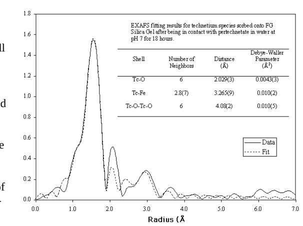
ADDITIONAL STUDIES

B Although these results are quite encouraging, in the event that commercially available organic ion-exchange resins are selected as the technology for removing pertechnetate from LAW, Ferragels could still be used to treat the large volumes of technetium-containing eluate from these ion-exchange resins.

B Experiments on removing pertechnetate from ion-exchanger eluate involved XANES and EXAFS (extended X-ray absorption fine structure) spectroscopic studies at the Stanford Synchrotron Radiation Laboratory (SSRL) with collaborators at the Lawrence Berkeley National Laboratory (LBNL).

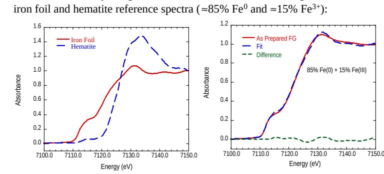
B Various Ferragel sorbents were contacted with pertechnetate-containing simulants for ≈18 hours. XANES results confirmed that the technetium on the FG Silica Gel as well as on the unsupported nano-crystalline iron occurred in a reduced form, most likely Tc(IV). EXAFS results on these same systems are similar, and are consistent with the formation of an insoluble Tc(IV)-Fe(III) oxide.

ample	Simulant used for Contact Experiments	Energy Shift from TcO_4^- (eV)	% TcO_4^- Removed during Contact
cO₄⁻ (aq)	-	0.0	-
echnetium on Reillex	water	-0.2	nm
echnetium on nano-crystalline iron	water	-4.2	>99
echnetium on FG Silica Gel	water	-4.4	>99
echnetium on nano-crystalline iron	S3	-3.2	>99
cO₂ (s)	-	-4.3	-



CHARACTERIZATION OF AS-PREPARED FERRAGEL SORBENT MATERIAL

X-ray Absorption Near Edge Structure (XANES) spectroscopy was performed on the as-prepared FG RTDS-6 sorbent material as well as reference materials at the National Synchrotron Light Source (beam line X-19A) at Brookhaven National Laboratory. A good fit to the data was obtained using a mixture of iron foil and hematite reference spectra (≈85% Fe^0 and ≈15% Fe^{3+}):



STABILIZATION OF LOADED FERRAGEL

B Encapsulate by sintering glass frit around loaded Ferragel particulates at low temperature (<800°C)

[frit used was the "NBS" alkali borosilicate based glass composition developed by Vienna et. al. at PNNL for the low temperature (<800°C) encapsulation of Rocky Flats ash

[preliminary work has involved Re-loaded FGRTDS-10 as a surrogate for Tc-loaded materials to first determine the optimal processing conditions

B A mechanically stable glass waste form containing the loaded Ferragel sorbent material has been prepared by sintering a mixture of 20wt% Re-loaded FGRTDS-10 and 80wt% NBS frit at 700°C:

SUMMARY

Taken together, these results show definitively that Ferragels, supported on appropriate materials, can efficiently remove pertechnetate from high pH, high ionic strength solutions containing nitrates and nitrites, as well as from neutral pH solutions. The XANES results indicate another important aspect of the Ferragel technology: the technetium species sorbed to Ferragels is in a reduced state, most likely Tc(IV). This reduced form of technetium should provide for a more efficient means of incorporating it into a waste form during vitrification or encapsulation, as the lower oxidation states of technetium allow for lower volatilities. EXAFS results indicate that there are Tc-Fe interactions, suggesting the formation of an insoluble Tc(IV)-Fe(III) oxide compound on the Ferragels. Finally, the loaded Ferragel sorbents can readily be stabilized into a waste form by encapsulation with alkali borosilicate glass frit at temperatures below 800°C.