

*Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties.* June 15, 1999

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## RESEARCH OBJECTIVE

The objective of this research is to prepare, characterize, and evaluate new materials for the removal of technetium (Tc) compounds, halogenated organics, and other troublesome metals from DOE waste streams and contaminated areas. This work follows the discovery that a nanoscale form of zero-valent iron, dispersed on high surface area supports, reduces metal ions (Cr, Hg, Pb, Cd) and Re (as a surrogate for Tc) to insoluble forms faster and with higher efficiency than does unsupported iron. Liquid-liquid extraction methods are also being developed for quantitative removal of Cs from tetraphenylborate salt mixtures, which are generated in waste processing at Savannah River, and conversion to vitrifiable inorganic Cs salts.

## RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes progress in the third year of a 3-year collaborative project involving Penn State and Pacific Northwest National Laboratory (PNNL).

Since the last report, mechanistic work has continued on the reactions of supported nanophase iron ("Ferragel") with aqueous metal ions [Cr(VI), Hg(II), Pb(II), Cd(II), and As(V)]. Column tests are currently being conducted to complement the information previously obtained from batch tests and electrochemical corrosion studies. The reductive decomposition of trichloroethylene (TCE) by Ferragels is also being studied in detail. Ni-Fe (4:1) nanoparticles supported on hydrophilic carbon were found to be the most effective remediants for TCE, approximately 15 times faster than unsupported iron filings, and 4-5 times faster than nano-iron on the same support. The increase in activity is ascribed to a bipolar mechanism, in which Ni acts as a catalytic surface and Fe supplies electrons via the conductive carbon. The mechanism is now being studied electrochemically and by monitoring product distributions from different metal/support combinations. Using nano-iron and commercial iron filings, the reduction products cis-dichloroethylene (DCE), 1,1-DCE, and vinyl chloride were observed. When carbon-supported Ni-Fe was used, none of these products were detected. We suspect that ethylene or ethane is formed directly, and are currently improving our techniques to detect these end products.

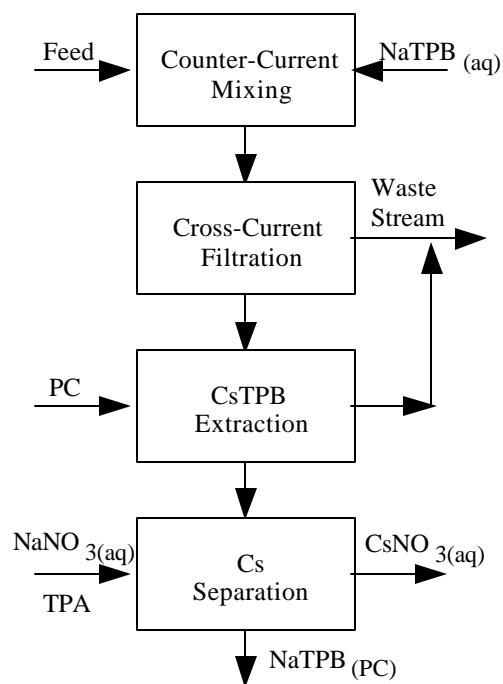
Detailed evaluations were conducted using Ferragel supported on zirconia (ZrO<sub>2</sub>) powders (which can tolerate high pH conditions) for the removal of TcO<sub>4</sub><sup>-</sup> from several simplified low-activity waste (LAW) simulants. The original plan was to use a graded approach to simulant selection, starting with a solution containing NaOH, Na<sub>2</sub>CO<sub>3</sub>, and NaNO<sub>3</sub>, then adding NaNO<sub>2</sub> to the simulant, then other components that influence corrosion behavior such as SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, and Cl<sup>-</sup>, then finally a full DSSF simulant. We had also made arrangements to test Ferragels in actual DSSF waste. In multiple 24-hour batch contact experiments a simulant containing NaOH, NaNO<sub>3</sub>, and NaNO<sub>2</sub> at pH 13 with 0.05 mM TcO<sub>4</sub><sup>-</sup>, >99% of the Tc was removed. Control experiments using silica or zirconia supports alone (no Ferragel) did not result in Tc removal. Ferragels were also tested in simulated eluent that would be generated in removing technetium

from anion-exchange resins. The suggested simulant for this eluent consisted almost entirely of water. Thus, for a first approximation water (deionized, passed through activated carbon to remove organics, and distilled) containing  $0.05 \text{ mM TcO}_4^-$  was used as a simulant to test technetium removal by Ferragel in batch contact experiments. Again, encouraging results were obtained: Ferragel removed  $>99\%$  of the Tc.

XANES results confirm that the Tc sorbed onto nano-iron/silica as well as the unsupported nanophase iron (in both simulants) was in a reduced form, most likely Tc(IV). EXAFS results on these same systems were similar, revealing that the Tc has 6 oxygen neighbors at  $2.02 \text{ \AA}$  and approximately 3 Fe neighbors at  $3.2 \text{ \AA}$ , i.e., that it exists in a mixed oxide phase. Using  $\text{ReO}_4^-$  as a non-radioactive surrogate for  $\text{TcO}_4^-$ , larger-scale batch contact operations were conducted on Ferragel supported on either zirconia or silica. These materials are currently being studied using thermal gravimetric analysis (TGA) and associated techniques to understand any potential off gas ( $\text{NO}_x$ , CO, etc.) and batch expansion issues. The ultimate goal with this part of the work is to encapsulate the loaded Ferragel into an alkali boro-aluminosilicate waste form by mixing Ferragel

with glass frit and sintering the below  $800^\circ\text{C}$ . We have used this approach to prepare a solid waste form pellet with Re-loaded Ferragel, although the process and final glass properties have not been optimized.

Improved methods for separating  $\text{Cs}^+$  from tetraphenylborate ( $\text{TPB}^-$ ) are needed for Savannah River Site (SRS) operations, where current and proposed in-tank processing methods cannot avoid formation of benzene by radiolysis and base hydrolysis of TPB. The flow chart in Fig. 1 summarizes the process we are developing, using propylene carbonate (PC) to extract CsTPB from the slurry collected by cross-current filtration. PC removes Cs below our current detection limits (by AES), using a realistic SRS simulant, and TPB is below detection limits in the aqueous phase returned to the waste stream by H-NMR. We are currently developing the last step of the process, in which Cs is isolated as a mixture (with Na and K) of nitrate salts and the TPB ion is recycled as NaTPB.



**Figure 1.** Process scheme currently in development for separation of  $^{137}\text{Cs}$  from SRS waste streams. TPA = tri(n-propyl)amine.

## PLANNED ACTIVITIES

We continue to optimize metal/support combinations for remediation of waste streams containing metals, chlorinated organics, and Tc. Once the processing parameters pertaining to the encapsulation of Tc-loaded Ferragel materials are understood, actual encapsulation work will continue. Relevant thermodynamic quantities (partition coefficients and ion-pairing equilibria) are also being studied in an effort to optimize the Cs remediation process.

## INFORMATION ACCESS

The following papers will be sent electronically upon request (tom@chem.psu.edu):

1. S. M. Ponder, J. G. Darab, J. Bucher, D. Caulder, I. Craig, L. Davis, N. Edelstein, W. Lukens, H. Nitsche, L. Rao, D. K. Shuh, and T. E. Mallouk, "Surface Chemistry and Electrochemistry of Supported Zero Valent Iron Nanoparticles in the Remediation of Aqueous Metal Contaminants," submitted to Chem. Mater.
2. S. M. Ponder, J. G. Darab, and T. E. Mallouk, "Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported, Nanoscale Zero Valent Iron," Environ. Sci. Technol., 34, 2564-2569 (2000).
3. S. M. Ponder and T. E. Mallouk, "Recovery of Ammonium and Cesium Ions from Aqueous Waste Streams by Sodium Tetrphenylborate," Ind. Eng. Chem. Res., 38, 4007-10 (1999).
4. S. M. Ponder, J. R. Ford, J. G. Darab, and T. E. Mallouk, "Ferragels: A New Family of Materials for Remediation of Aqueous Metal Ion Solutions," Mater. Res. Soc. Symp. Proc., 556(Scientific Basis for Nuclear Waste Management XXII), 1269-1276 (1999).