

Project ID: **60017**

Project Title: **Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties**

**Lead Principal Investigator:**

Dr. Thomas E. Mallouk  
Professor of Chemistry  
Pennsylvania State University  
152 Davey Laboratory  
University Park, Pennsylvania 16802  
Telephone: 814-863-9637  
e-mail: [tom@chem.psu.edu](mailto:tom@chem.psu.edu)

**Co Principal Investigators:**

Dr. John G. Darab  
Pacific Northwest National Laboratory  
P. O. Box 999  
Richland Washington 99352  
Telephone: 509-375-6608  
e-mail: [jg\\_darab@pnl.gov](mailto:jg_darab@pnl.gov)

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

*Lead PI:* Thomas E. Mallouk, Dept. of Chemistry, Penn State University, University Park, PA 16802. Tel: 814-863-9637. E-mail: tom@chem.psu.edu.

*Co-PI's:* Sherman M. Ponder, Dept. of Chemistry, Penn State University, University Park, PA 16802. Tel: 814-863-9791. E-mail: ponder@chem.psu.edu.

John Darab, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352. Tel: 509-375-6608, E-mail: john.darab@pnl.gov

*Graduate students:* Sherman M. Ponder, Bettina Schrick, Alexandra Amonette

## 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 much faster than does unsupported iron.

The scientific goals of the project are to better understand the mechanism of the reduction process, to develop supports that are compatible with a variety of mixed waste compositions, and to develop surface modifiers for supported iron that will optimize selectivity for the contaminants of interest. The support composition is of particular interest in the case of Tc separation and stabilization in the Hanford tank wastes. While tests with tank waste simulants have shown that pertechnetate is reduced to insoluble  $TcO_2$ , the support material must be compatible with the vitrification process used in the final waste disposition. The surface modifications are also a focal point for Hanford applications because of the complex and variable makeup of the tank wastes.

## RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes progress in the second 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 with aqueous metal ions [Cr(VI), Hg(II), Pb(II), and Cd(II)]. The kinetics of these reactions are complex, involving adsorption, followed by electron transfer and nucleation of the product phase. After the fast initial adsorption reaction, the rate increases monotonically with the ease of reduction of the metal ion, suggesting that electron transfer is the rate determining step. Under equivalent conditions, these reduction reactions are much faster than those of unsupported nanophase iron, or larger zero valent iron particles such as commercial powders or filings. The insoluble products of the reactions have been characterized as  $Cr(OH)_3$ , Hg, Pb, and Cd by XPS and x-ray powder diffraction.

Nanophase iron supported on a variety of base-stable inorganic materials, such as  $ZrO_2$  and ZnO, were studied for removal of pertechnetate ( $TcO_4^-$ ) from simulated aqueous tank wastes. Support materials have included both commercially available products as well as high surface area ( $>200 \text{ m}^2/\text{g}$ ), nano-crystalline ( $<10 \text{ nm}$  crystallite diameter) zirconium oxide. The nanophase iron on  $ZrO_2$  both before and after contact with simulant solutions was characterized using X-ray absorption fine structure (XAFS) spectroscopy. The speciation of the technetium absorbed onto the support after contact was also studied using XAFS. Finally, nanophase iron

supported on  $ZrO_2$  after contact with  $ReO_4^-$  spiked simulants (where Re is being used as surrogate for Tc) was mixed with a glass frit and heat treated to different temperatures to evaluate the potential for encapsulating the loaded absorbant/support material into a waste form.

$TcO_4^-$  removal from a simplified Hanford DSSF (double shell slurry feed) simulant consisting of 7.4 M  $Na^+$ , 3.1 M  $NO_3^-$ , 3.8 M  $OH^-$  and 0.27 M  $CO_3^-$  was studied at pH 13-14. Although we have not yet optimized the materials, we are currently achieving reasonable pertechnetate  $K_d$  values (160 L/kg at a phase ratio of 645 L/kg) in a 24-hour exposure. As a comparison, at a phase ratio of 100 L/kg, the commercial organic ion-exchange resins, Reillex™ HPQ and ABEC-5000, have  $TcO_4^-$   $K_d$  values of 380 and 160 L/kg, respectively. A key difference is that supported iron reduces  $TcO_4^-$  to non-volatile Tc(IV) species, which are compatible with the heating steps used in vitrification. Arrangements are currently being made to test nanoscale iron-on-silica for removal and vitrification of  $TcO_4^-$  from the eluent of a SuperLig separation.

Supported nanophase iron was also tested for the reductive dehalogenation of trichloroethylene (TCE) from water according to EPA method 502.2. Interestingly, unsupported nanophase iron and iron powder were both poor remediants for aqueous TCE. Supporting nano-iron on hydrophilic carbon increased the reaction rate by a factor of 40, and adding a catalytic amount of Ni again increased the rate by a factor of 4-5. With 0.5 g of the bipolar Ni-C-Fe particles, complete removal of TCE from 40 mL of solution was effected in 7 hrs. Under the same conditions, 13 g of iron filings needed 150 hrs to remove TCE from the same volume of solution.

In light of recent events at the Savannah River Site, improved methods for separating  $Cs^+$  from tetraphenylborate ( $TPB^-$ ) ions may have important implications for the process decisions currently being discussed. Benzene formation from the degradation of  $TPB^-$  exposed to radiation has currently halted the waste treatment process. Minimizing  $TPB^-$  exposure time should minimize benzene formation. This has been achieved in a batch process, as described below, and the same method could easily be adapted to a continuous flow process.

$TPB^-$  was separated from  $Cs^+$  and  $NH_4^+$  cations by first separating the solids from the aqueous phase, then dissolving them in acetone. In the case of  $NH_4^+TPB^-$ , the pH is increased by addition of  $NaOH(aq)$ . The resulting solution, containing a much higher concentration of ammonia than the original waste stream, was then distilled to recover both ammonia and acetone. In the case of  $Cs^+TPB^-$ ,  $Cs^+$  was first recovered as solid  $CsCl$  by addition of tripropylamine and  $HCl$ , and the amine and  $TPB^-$  were then recovered by addition of  $NaOH$ . In either case, the regenerated aqueous  $Na^+TPB^-$  can be recycled back into the waste stream. Recovery of cations was quantitative for  $NH_4^+$  and 90% for  $Cs^+$  in batch reactions. Recovery of  $TPB^-$  was quantitative within experimental error.

## PLANNED ACTIVITIES

Work will continue on all aspects of the project described above. Initial results with Tc removal appear quite promising but must be followed up with more detailed experiments that elucidate the kinetics of the reaction, and the compatibility of the resulting solids with waste form processing. Because nitrite is an oxidizer present in the liquid phase of Hanford tank waste, efforts will be made to find an appropriate surface modifying agent with a high selectivity for adsorbing  $TcO_4^-$ . Compounds to be tested include molecules known to form self-assembled monolayers (SAMs), and polymers containing the same surface-active groups. We will measure

equilibrium constants for adsorption of thiolates, dithiocarbamates, carboxylates, and hydroxamates on iron nanoparticles. Polymerized versions of any reversibly-binding monomer that shows significant corrosion resistance should provide a more stable, non-desorbing protective layer. Once the appropriate head group and surfactant structure (monomer or polymer) is selected, compounds containing quaternary ammonium groups will be synthesized and tested for selective binding of pertechnetate. Studies will also continue on the design and characterization of bipolar remediants for chlorinated organics, and on processes for recycling TPB<sup>-</sup> in Cs<sup>+</sup> recovery.

#### INFORMATION ACCESS

Preprints of the following papers will be sent electronically upon request. Contact Tom Mallouk (tom@chem.psu.edu) or Melissa Pressler (scarlett@chem.psu.edu).

S. M. Ponder and T. E. Mallouk, "Recovery of Ammonium and Cesium Ions from Aqueous Waste Streams by Sodium Tetrphenylborate," submitted to *Ind. Eng. Chem. Res.*

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," MRS Symp. Proceedings, *in press*.