

Environmental Management Science Program

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Removal of Technetium, Carbon Tetrachloride, and Metals from DOE Properties

Dr. Thomas E. Mallouk
Pennsylvania State University
152 Davey Laboratory
University Park, Pennsylvania 16802
Phone: 814-863-9637
E-mail: tom@chem.psu.edu

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

Sherman M. Ponder
Penn State University
University Park, Pennsylvania 16802
Phone: 814-863-9791
E-mail: ponder@chem.psu.edu

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Research Objective

The objective of the project is to develop and characterize supported reducing agents, and solid waste forms derived from them, which will be effective in the removal of transition metal ions, chlorinated organic molecules, and technetium from aqueous mixed wastes. This work follows the discovery that a nanoscale form of zero-valent iron, dispersed on high surface area supports, reduces metal ions (chromium, mercury, and lead) and rhenium (as a surrogate for technetium) 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 the supported iron aggregates that will optimize their selectivity for the contaminants of interest. The support composition is of particular interest in the case of technetium (Tc) separation and stabilization in the Hanford tank wastes. While it is expected that pertechnetate will be 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 first 8 months of a 3-year collaborative project involving Penn State and Pacific Northwest National Laboratory (PNNL). Aggregates of 10-30 nm diameter iron particles have been prepared by reduction of iron salts onto various supports, including silica, Polyflo resin (a non-porous, high surface area polymer supplied by Puresyn, Inc., Malvern, PA), monoclinic ZrO_2 , and SnO_2 . The kinetics of reduction of aqueous 0.5 mM CrO_3 , PbCl_2 , $\text{Hg}(\text{OAc})_2$, CdSO_4 , and NH_4ReO_4 were studied with these materials ("Ferragels"), and compared to those of unsupported iron. The most easily reduced metals (Cr, Pb, Hg) are removed to levels below the detection limits of atomic absorption spectroscopy, typically 2-20 ppb, and the rates of these reactions are substantially faster than with activated, unsupported iron. A colorimetric test has been developed for studying the corrosion reaction of the particles, and was used to evaluate different monolayer-forming molecules as corrosion inhibitors. These studies are intended to lay the groundwork for design of contaminant-selective monolayer coatings.

The mechanism of metal ion reduction appears to be complex, involving rapid surface adsorption followed by a slower outer-sphere electron transfer step. The reduction processes for Cr, Hg, Pb, and Cr species were first order with respect to amount of supported iron. The rate constants (normalized per gram of supported iron on Polyflo) were 8.9×10^{-2} (Hg), 3.5×10^{-2} (Pb), 1.2×10^{-3} (Cd), and $6.1 \times 10^{-3} \text{ s}^{-1}$ (Cr). The rate increases monotonically with increasing E_0 , the standard potential for the metal ion, except in the case of Cr, where the potential for one-electron reduction to Cr(V) differs considerably from E_0 for the three-electron $\text{Cr}^{6+/3+}$ couple. This trend suggests that outer-sphere electron transfer is the rate-determining step in the reaction. For Cr, which was studied in detail, the reaction is second order in $[\text{Cr}]$, suggesting that the kinetics are further complicated by aggregation of aquo ions. XPS confirms that Cr(VI) is reduced to trivalent insoluble forms, most probably $\text{Cr}(\text{OH})_3$ or Cr_2O_3 . This mechanistic study will be completed in the near term. In this connection, Pb(II)

should be a simpler test system than either Cr(VI) or Hg(II), because it is monomeric and has only one oxidation state in solution.

An interesting variation in reduction rates was found with different high surface area supports. Using Polyflo, a proprietary, non-porous, high-surface-area resin, the rate of Cr(VI) reduction was six times greater than with chromatographic silica under identical conditions. Nitrogen BET analysis shows that iron-on-Polyflo Ferragel (190-200 mg Fe / g) has a surface area of 38 m²/g with little adsorption/desorption hysteresis, compared to iron-on-silica (243 m²/g). Most of the iron in silica Ferragel is deposited in relatively inaccessible mesopores, whereas the non-porous Polyflo resin effectively presents all of the iron nanoparticles to the solution.

Surface modifying layers are being studied as a way of improving the selectivity of the reduction process. One problem with the Hanford tank wastes is that they contain other oxidizing agents, including nitrite (NO₂⁻), as well as various anions (hydroxide, carbonate, nitrate, etc.) at high concentration. Nitrite efficiently oxidizes zero-valent iron in the absence of surface modifiers. Thus, we are looking for a surface modifier that selects TcO₄⁻ and possibly soluble complexes of Tc(IV) from a solution containing anions of higher charge density. Hydrophobic quaternary ammonium ions are selective for hydrophobic anions, but do not adsorb to the iron surface, and so a method of attachment must be found. Towards this end, tetrahexadecylammonium bromide, tridodecylmethylammonium iodide, sodium hexadecylsulfonate, octylphosphonic acid, and phenylphosphonic acid were tested as corrosion inhibitors for iron-on-Polyflo Ferragel. The surfactants were adsorbed from alcohol, then tested in aqueous pH 5.5 solutions of 1,10-phenanthroline (5g/L). These studies show that simple quaternary ammonium salts, alkyl sulfonates, and alkyl/arylphosphonates do not inhibit acid corrosion of iron significantly. Other surfactants containing more aggressive head groups (thiolate, dithiocarbamate, carboxylate, hydroxamate) and polymeric surface modifiers are now being tested.

Planned Activities

Work will continue on the search for an appropriate surface modifier — with a particular emphasis on the Hanford nitrite vs. pertechnetate problem. 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. Similar “tail group” strategies will be applied to selecting for transition metal cations (using ligating groups) and for hydrophobic organic waste components, such as Tc(IV)EDTA and chlorocarbons (using nonpolar tail groups).

As work progresses with surface modification, iron nanoparticles on different support materials will be tested on Tc-containing samples at PNNL. These support materials will include tin oxide, zinc oxide, Polyflo resin, and high surface area cubic zirconia prepared hydrothermally at PNNL. In anticipation of receiving candidate absorbent materials from Penn State for Tc K_d testing, PNNL has made preparations for having Tc isotopes and liquid waste simulants ready. Scoping experiments have been performed on preparing high surface area zirconia-based powders using PNNL's hydrothermal powder production technology, and on pelletizing them into potential supports for iron nanoparticles. PNNL will conduct K_d testing for Tc, and will test the support materials for stability under simulated tank waste conditions.

Addition of another researcher at Penn State in Fall, 1998 allows expansion of the project to aqueous wastes containing halogenated hydrocarbons. Zero valent iron is a demonstrated remediant for these wastes, and the focus of our work with Ferragel will be to control selectivity using appropriate SAMs. Initially, perchlorethylene will be tested as a model contaminant, because the product distribution can provide information on whether hydrolytic dehalogenation or reductive hydrogenation is the operative reaction pathway with supported, SAM-derivatized iron.

Work at PNNL will build on successful reduction of Tc waste simulants by studying the vitrification and subsequent stability of Ferragel supports, as well as actual spent, Tc-containing, Ferragel. If

accessible, testing will progress to actual tank waste. Work on metal remediation with iron-on-Polyflo Ferragel will progress to proof-of-concept studies on actual heavy metal wastes — most likely Pb — at site(s) in Pennsylvania.