

Project ID: 65409

Title: Electroactive Materials for Anion Separation – Technetium from Nitrate

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Research Objective

Many contaminants of interest to the U.S. Department of Energy (DOE) exist as anions. These include the high-priority pollutants chromate, pertechnetate, and nitrate ions. In addition, there are also industrial and urban applications where the separation of anionic species from aqueous streams is critical. Examples include industrial water recycle and waste water treatment (e.g., chloride ion removal for the pulp and paper industry, borate ion in the chemical and nuclear industries) and drinking water and agricultural waste treatment (e.g., nitrate removal).

In the proposed research, technetium is chosen as the target pollutant. Because of its half-life of 213,000 years, technetium (^{99}Tc) presents a long-term hazard for waste disposal. Much of the ^{99}Tc in the tank wastes is present as pertechnetate (TcO_4^-), accounting for its high solubility and mobility in aqueous systems. Several sorbents are available for removing TcO_4^- from alkaline waste brines, but each has important drawbacks. The use of commercial ion exchange (IX) resins to extract TcO_4^- , e.g., ReillexTM-HPQ (Reilly Industries) and ABEC 5000 (Eichrom Industries), generates significant secondary waste. The elution of TcO_4^- from ReillexTM-HPQ resins requires either concentrated nitric acid or a concentrated caustic solution of ethylene-diamine containing a small amount of tin chloride. This eluant has a short shelf life requiring frequent preparation, and the ^{99}Tc is delivered in a complexed, reduced form. While TcO_4^- can be eluted from ABEC 5000 resins using de-ionized water, the much-reduced capacity of ABEC 5000 resins in comparison to the ReillexTM-HPQ resins leads to a low column capacity. In general, unwanted secondary wastes are generated because 1) the only effective eluant happens to be hazardous and/or 2) the IX material has a low capacity or selectivity for the target ion, resulting in more frequent elution and column replacements.

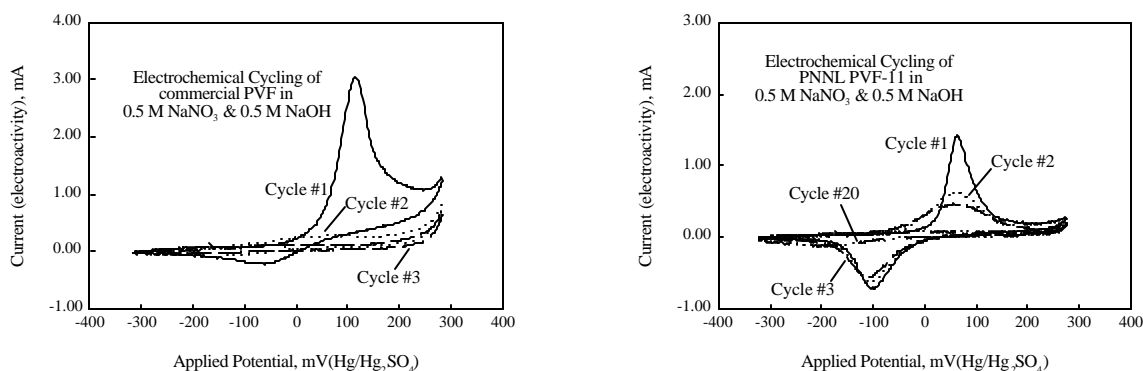
Alternative IX materials that have high capacities, can be regenerated easily, and are highly selective for TcO_4^- would avoid these problems. Electrochemically active IX media meet these criteria. Such an IX system uses electrically induced changes in the media to expel sorbed ions through a charge imbalance rather than requiring chemical eluants to “strip” them. Therefore, this medium eliminates the need to prepare, store, and dispose of many of the process chemicals normally required for IX operations.

The focus of the project is to develop a fundamental understanding of how the physical and chemical properties of electroactive ion exchange (EaIX) materials control their efficiency when used as mass separation agents. Specifically, the desirable characteristics of EaIX materials for separation applications are 1) high reversibility, 2) high selectivity, 3) acceptable physical and chemical stability, 4) rapid intercalation and de-intercalation rates, and 5) high capacity. Because of these requirements, EaIX materials share many properties in common with conventional ion exchangers and electroactive polymers. For example, EaIX materials require the selectivity typically found in ion exchangers; they also require the redox reversibility of electroactive polymers. The results of this work will allow the rational design of new materials and processes tailored for the separation of specific anions.

Research Progress and Implications

This report summarizes work completed in the first 17 months of a 3-year project. The two components of the project are (1) synthesis and (2) characterization of EaIX materials. The monomer constituents of the electroactive polymer ultimately control the desirable characteristics described earlier. We have, therefore, focussed our efforts in the synthesis monomers with the appropriate functional groups. From our discussions with the Tank Focus Area's

Technology Integration Manager for Pretreatment, Phil McGinnis, synthesis of materials that are stable under highly alkaline conditions has been one of our priorities. We have recently synthesized new ferrocene-containing polymers that, under alkaline conditions, exhibit more stability than commercially available polyvinylferrocene (PVF). The figure below compares the characteristics of PNNL-synthesized and commercially available PVF polymers; the



commercial PVF is deactivated in less than 2 cycles. Although PNNL PVF-11 is mainly deactivated after 20 cycles, our study where we are systematically modifying the basic ferrocene units to make the resulting polymer more stable in alkaline conditions is not completed, and therefore, we are very hopeful that we will successfully synthesize alkaline-stable electroactive polymers. We have successfully synthesized vinyl-ether ferrocene monomers; these monomers will allow us to systematically study the effects of charge site mobility and molecular weight on characteristics listed earlier (mainly #3 and #4). Initial attempts of using phase-inversion techniques with commercial PVF for making high-capacity electrodes (#5 above) have failed; this has been attributed to the inability to make highly concentrated solutions. In addition, variabilities in commercially available PVF have made systematic studies of the process conditions difficult. PNNL is currently synthesizing polymers to overcome both of these difficulties. Studies on the application of phase-inversion techniques for making high capacity electrodes are continuing using model polyaniline polymers.

The methods for obtaining in situ x-ray absorption spectroscopy (XAS) on PVF electrodes in perrhenate (ReO₄⁻) electrolytes have been refined and improved. Most of the problems in collecting spectra at the Fe K edge accrue from the large background from the ReO₄⁻ ions, which has been resolved by reconfiguring the electrodes in the spectroelectrochemical cell. It was necessary to optimize the x-ray optics in two separate x-ray scans to obtain good near edge (XANES) and extended fine structure (EXAFS) spectra. Spectra have also been obtained ex situ at the Fe K edge on several electrodes prepared from polymer materials synthesized at PNNL. XAS and electrochemical studies were also done on ferrocenium perrhenate, dimethylferrocenium perrhenate and ferrocenium nitrate, that were synthesized at BNL. The electrochemical studies indicated a stronger interaction of the perrhenate anion with the ferrocenium cation than that seen with the nitrate anion.

Planned Activities

We plan to have alkaline-stable electroactive polymers by June 2000. We plan to prepare polymers ready for further phase-inversion studies by October 2000. Recently obtained XAS results mentioned above are currently being analyzed.

Information Access

Hubler, T.L., G.M. Anderson, J.H. Sukamto, M.A. Lilga, and S.D. Rassat. "Polyvinylferrocene (PVF) polymers as electroactive ion-exchange materials for separation of pertechnetate ion from high nitrate ion containing wastes: Issues and synthetic strategies." Poster presented at the 218th ACS National Meeting, August 22-26, 1999, New Orleans.

Gronda, A.M. and W.H. Smyrl. "High capacity electroactive polymers for radioactive waste removal." Oral presentation at the 196th Electrochemical Society Meeting, October 17-22, 1999, Honolulu.

Sukamto, J.H., S.D. Rassat, R.J. Orth, and M.A. Lilga, "Electrochemical Ion Exchange." To appear in the *Encyclopedia of Separation Science*, Academic Press.