Environmental Management Science Program

Project ID Number 54770

New Anion-Exchange Resins for Improved Separations of Nuclear Materials

Dr. Mary E. Barr
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos, New Mexico 87545
Phone: 505-667-7991
E-mail: mbarr@lanl.gov

Dr. Richard A. Bartsch
Texas Tech University
Lubbock, Texas 79409
Phone: 806-742-3069
E-mail: FRABC@ttacs1.ttu.edu

June 1, 1998

New Anion-Exchange Resins for Improved Separations of Nuclear Materials

Dr. Mary E. Barr, Los Alamos National Laboratory

Dr. Richard A. Bartsch, Texas Tech University

Research Objective

The overall objective of our research is to develop a predictive capability which allows the facile design and implementation of multi-functionalized anion-exchange materials which selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. The basic scientific issues addressed are actinide complex speciation along with modeling of the metal complex/functional-site interactions in order to determine optimal binding-site characteristics. Our new ion-exchange resins interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology. Various Focus Areas and Crosscutting Programs have described needs that would be favorably impacted by the new materials: Efficient Separations and Processing; Plutonium; Plumes; Mixed Waste; High-Level Tank Waste. Sites within the DOE complex which would benefit from the improved anion-exchange technology include Hanford, INEL, Los Alamos, Oak Ridge, and Savannah River.

Research Progress and Implications

As of April 1998, this report summarizes work after 1.6 years of a 3-year project. Our technical approach combines empirical testing with theoretical modeling (applied in an iterative mode) in order to determine optimal binding-site characteristics. We determine actinide-complex speciation in specific media, then develop models for the metal complex/functional-site interactions. Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials that implement key features of the optimized binding site provide feedback to the modeling and design activities. Resin materials which actively facilitate the uptake of actinide complexes from solution should display both improved selectivity and kinetic properties. Our implementation of the bifunctionality concept involves N-derivatization of pyridinium units from a base poly(4-vinylpyridine) resin with a second cationic site such that the two anion-exchange sites are linked by 'spacer' arms of varying length and flexibility.

Actinide-complex speciation: The primary actinides of interest in nitrate solutions are plutonium (IV) and americium (III). We have refined plutonium mono- and di-nitrato formation complexes. As expected, in higher ionic strength media, the formation of the tetranitrato complex shifts to lower acid concentrations than in pure nitric acid. Addition of a water-soluble anion-exchange polymer to solutions of plutonium in nitric acid also shifts the solution equilibrium to favor the dianionic hexanitrato complex, but with K_d values orders of magnitude lower than for the solid resins. Even americium(III), which does not form anionic nitrato complexes in pure nitric acid media, binds to the anion-exchange resins in solutions with excess nitrate. X-ray fluorescence experiments on Eu(III) (an Am surrogate) show that addition of excess nitrate results in the removal of one to two waters of hydration, but we have not been able to determine the exact anionic species. We have, however, begun pilot-scale evaluation of one new resin for the removal of Pu(IV) and Am(III) from process waste solutions.

Synthesis and evaluation of multi-functionalized extractants and ion-exchange materials: We have synthesized and tested a 'systematic series' of bifunctional resins that examines the effects of varying the following conditions:

- 1) The chemical structure of the second cationic site: pyridium > trimethylphosphonium > trimethylammonium.

- 2) The length and chemical structure of the spacer between the two cationic sites: generally a 4-5 atom spacer is optimal for plutonium uptake. A shorter spacer appears better for americium.
- 3) The percent crosslinking of the substrate: decreasing the crosslinking from 25% to 18% yields a ca. 50-100% increase in K_d with little impact upon resin stability.
- 4) The percent derivatization: performance increases with greater derivatization up to 100%. Most bifunctional resins, however, cannot be derivatized above 75%.

Two manuscripts (published, in press) and several presentations cover much of this work to date. We have synthesized and evaluated the first tri-functional (polystyrene-based) resin for plutonium/americium uptake. Preliminary tests of this particular material were disappointing in that, despite the higher cationic charge density, it did not display the Am(III) affinity that we had hoped for. We have completed synthesis, but not evaluation, of bifunctional extractants. We were able to achieve desired the organic miscibility for the dicationic material by adding two dodecyl groups to the pyridine functionality in the meta positions.

Modeling and design activities: We have developed partial charge and MM2 parameters for Pu, U, Th and Np (IV) nitrate systems. Using these parameters, we can very accurately model the nitrate-actinide interactions. Determination of the charge distribution of the hexanitrate dianions was problematic because of the exceptionally high orbital degeneracy of the complex. We developed a 'theoretical model' compound, the $\text{Pu}(\text{NO}_3)_3$ triradical, for which partial charges could be determined using ab initio calculations. Via calculation of the electrostatic interactions between the Pu-hexanitrate dianion and the dicationic "resin site", we have correlated the 'stickyness factor' with experimental K_d s for three series of resins. Correlation is good using both formal charge and partial charge models. Two manuscripts (submitted, in preparation) cover this work to date. The models show that the butylene spacer for the trimethylammonium derivative of polyvinylpyridine changes from an 'anti' configuration in its free state to a 'syn' configuration in the docked state. This observation has led to the hypothesis that a cis-butene spacer may exhibit improved sorption kinetics. We have synthesized, but not yet evaluated, a resin based on this functionality.

Planned Activities

Most of the baseline work was conducted on resins unsuitable for column applications, so we need to correlate those results with the new 21% cross-linked materials. We have begun extending this work to other actinide complexes (chloro-, carbonato-) and to non-actinide complex anions. Extension of the modeling activities to obtain predictive capabilities will require determination of the major energy terms which factor into the final K_d value. We hope to obtain this information via calorimetry and determination of K_d values for extractants and soluble polymeric forms. We would also like to extend our models to include the polymeric matrices and solvent effects. We anticipate completing the preliminary work in all these areas by the end of FY98/early FY99 and using the final year (FY99) to refine the work and develop applications.