

Project ID: 54770

Project Title: New Anion-Exchange Resins for Improved Separations of Nuclear Material

Publication Date: March 1, 2000

Lead Principal Investigator: Dr. Mary E. Barr, Los Alamos National Laboratory, NMT-6, Los Alamos, NM 87545; phone - (505) 667-7991; e-mail - Mbarr@lanl.gov

Co-Investigators: Dr. Richard A. Bartsch, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409; phone - (806) 742-3069; e-mail - rabartsch@ttu.edu

Dr. Gordon D. Jarvinen, Los Alamos National Laboratory, NMT-11, Los Alamos, NM 87545; phone: (505) 665-0822; e-mail - gjarvinen@lanl.gov

Number of Graduate Students Actively Involved in Project: 2

Research Objective:

We are developing bifunctional anion-exchange resins that facilitate anion uptake by carefully controlling the structure of the anion receptor site. Our new ion-exchange resins interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology. 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. Resin materials that 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 (PVP) with a second cationic site, such that the two anion-exchange sites are linked by 'spacer' arms of varying length and flexibility.

The overall objective of our research is to develop a predictive capability that allows the facile design and implementation of multi-functionalized anion-exchange materials to selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. Various *Focus Areas and Crosscutting Programs* have described needs that would be favorably impacted by the new materials: *Tanks, Plutonium; Subsurface Contaminants; Mixed Waste; and Efficient Separations*. Sites within the DOE complex which would benefit from the improved anion-exchange technology include Hanford, Idaho, Los Alamos, Oak Ridge, and Savannah River.

Research Progress and Implications:

As of March 2000, this report summarizes work near the end of our highly successful 3-year project. Our technical approach has combined 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 interaction at the metal complex/functional-site. *Synthesis and evaluation* of bifunctionalized extractants and ion-exchange materials that implement key features of the optimized binding site provide feedback to the *modeling and design activities*.

Actinide-complex speciation: The primary actinides of interest in nitrate solutions have been plutonium (IV) and americium (III). We have refined plutonium mono- and di-nitrate formation complexes. We find that addition of water-soluble anion-exchange polymers to solutions of plutonium in nitric acid shifts the solution equilibrium to favor the dianionic hexanitrate complex, but with K_d values orders of magnitude lower than for sorption onto solid resins. Even Am(III), which does not form anionic nitrate complexes in pure nitric acid media, binds to the anion-exchange resins in solutions with excess nitrate. We are awaiting EXAFS data analysis (on Nd(III) surrogates) to determine the exact anionic species in solution and sorbed to the resin. We have conducted promising 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 systematic series of bifunctional resins that examine 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 both americium and plutonium uptake from nitrate solutions. Soluble polymers based on linear PVP display similar trends.
- 3) The percent crosslinking of the substrate: Decreasing the crosslinking from 25% to 18% yields an *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%.

We synthesized and evaluated a tri-functional (polystyrene-based) resin for plutonium and americium uptake. Despite the higher cationic charge density, it did not display enhanced Am(III) uptake. We have completed the synthesis, but not the 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 successfully demonstrated that our simple molecular mechanics-based model is sufficient to predict which 'spacer' length is optimal for electrostatic binding of the Pu-hexanitrate dianion with the dicationic 'resin site' (modeled as a free pyridinium species). Thus, we have established that even diffuse and non-directional ionic bonding interactions are determined by many of the same forces as strong, directional covalent interactions (*i.e.*, the 'chelate' effect on entropy, optimized 'bite' size, *etc.* We have also confirmed our molecular-mechanics models with *ab initio* calculations and have used these calculations to help determine the overall enthalpic and entropic contributions to the ΔG of sorption from solution onto the solid exchangers. Correlation with experimental data is good using both formal charge and partial charge models. Models show that a 1,4-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, leading to the hypothesis that a 1,4-*cis*-2-butene spacer may exhibit improved sorption kinetics. This hypothesis was supported by experimental results, although the effect was not as significant as we had hoped. Subsequent modeling of diffusion properties show that bulk diffusion rates of solution into the solid matrix are rate-determining. Studies using analogous soluble polymers, based on linear PVP, are not complicated by diffusion or phase-change energy terms, and thus provide clear support for the assumption in our model that these terms are essentially constant for a given series of resins.

Future Work and Application:

These new anion-exchange materials are still being evaluated for use at LANL for plutonium process improvement, ^{238}Pu recovery and Am removal from pre-cementation wastes. We hope to capitalize on our licensing agreement with Reilly Industries to continue development of this new class of resins for large-scale commercial applications, as well as for select EM needs.

Patent and Licensing Agreement:

US Patent #5,670,550 (Sept. 23, 1997) - "Ion-Exchange Polymers for Anion Separations"

Materials and applications licensing agreement - Reilly Industries, Indianapolis, Indiana - May 1999.

Publications and Presentations:

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, SF; Jarvinen, GD; Bartsch, RA; *Reactive Polymers* **1997**, 35, 75-80.

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, SF; Jarvinen, GD; Bartsch, RA; Nam, J.; Barr, ME; *J. Radioanal. Nucl. Chem.* , **1998**, 235, 37-40.

"Development of Anion-Exchange Resins for Separations of Actinides" Barr, ME; Jarvinen, GD; Marsh, SF; Bartsch, RA, Abstracts ACS, v. 213(pt. 2) p. 73-IEC Apr. 13, **1997**.

"Sorption of Pu(IV) by Soluble Anion-Exchange Polymers" Barr, ME; Jarvinen, GD, Moody EW, Vaughn, RB; Abstracts ACS, v.216(pt.2) pp. 88-NUCL AUG 23, **1998**, and v.216(pt.1) pp. 5-TECH AUG 23, **1998**.

"Americium Separations from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; Abstracts ACS, v. 217 pp. 019-IEC MAR 21, **1999**.

"Sorption of Pu(IV) from Nitric Acid by Bifunctional Anion-Exchange Resins" Bartsch, RA, Zhang ZY, Elshani S, Zhao W, Jarvinen GD, Barr ME, Marsh SF, Chamberlin RM; Abstracts ACS, v. 217 pp. 125-IEC MAR 21, **1999**.

"QSAR of distribution coefficients for actinide hexanitrate complexes" Moody EW, Barr ME, Jarvinen GD; Abstracts ACS, v. 217(pt.2) pp. 170-NUCL MAR 21, **1999**.