Project ID: **54770**

Project Title: **New Anion Exchange Resins for Improved Separations of Nuclear Materials**

DOE Report Number: 99-2910

Lead Principal Investigator:

Dr. Mary E. Barr
NMT-6 Division
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos, New Mexico 87545
Telephone: 505-667-7991
e-mail: mbarr@lanl.gov

Co Principal Investigators:

Dr.Gordon Jarvinen
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos New Mexico 87545

Dr. Eddie Moody
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos New Mexico 87545

Dr. Richard A. Bartsch
Paul Whitfield Horn Professor
Department of Chemistry and Biochemistry
Texas Tech University
Lubbock, Texas 79409 -1061
Telephone: 806-742-3069
e-mail: FRABC@ttacs1.ttu.edu

New Anion-Exchange Resins for Improved Separations of Nuclear Materials

Mid-Year Progress Report

Mary E. Barr*, Gordon Jarvinen, Eddie Moody, Los Alamos National Laboratory
Richard A. Bartsch, Texas Tech University
LANL LAUR #99-2910
June 1, 1999

Goals of Project:

We are developing multi-functional anion-exchange resins that facilitate anion uptake by carefully controlling the structure of the anion receptor site. We are attempting to determine if the precepts of "bite size," "preorganization," and "bidentate" have an appreciable impact upon electrostatic bonding as they do for covalent bonding. If these precepts do have a positive impact, we will develop new ion-exchange resins that interface the rapidly developing field of ion-specific chelating ligands with robust, commercial ion-exchange technology.

The overall objective of our research is to develop a predictive capability that will enable us to design and implement multi-functionalized anion-exchange materials which selectively sorb metal complexes of interest from targeted process, waste, and environmental streams. The following Focus Areas and Crosscutting Programs have described needs that would be favorably impacted by the new materials:

Efficient Separations and Processing - radionuclide removal (Pu, U, Am) from aqueous phases
Plutonium - Pu, Am or total alpha removal to <30 pCi/L before discharge to the environment
Plumes - U and Tc in groundwater; U, Pu, Am, and Tc in soils
Mixed Waste - radionuclide partitioning
High-Level Tank Waste - actinide and Tc removal from supernatants and/or sludges

Technical Description of Work:

We determine actinide-complex speciation in specific media, then develop models for the metal complex/functional site interactions Synthesis of multi-functionalized extractants and ion-exchange materials that implement key features of the optimized binding site, and testing of these materials, provide feedback to the modeling and design activities. To determine optimal binding site characteristics, we have combined empirical testing with theoretical modeling (applied in an iterative mode).

Resin materials that actively facilitate the uptake of actinide complexes from solution should display both improved selectivity and kinetic properties. Our primary 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.

Accomplishments to Date:

Actinide-complex speciation: The primary actinides of interest in nitrate solutions are plutonium (IV) and americium (III). Anion exchange from nitric acid is the most frequently used process used to recover plutonium from a wide variety of residues and wastes in the DOE complex. While Pu(IV) binds strongly to the anion exchange resin at high nitric acid concentrations and can be eluted with lower acid concentrations, the kinetics for sorption and desorption are extremely slow and adversely affect throughput rates. Americium is a primary contaminant in aged plutonium. Am(III), however, is less inclined to form anionic nitrate complexes in high acid media since it competes poorly with H+ . Previous extraction technology for americium has focused on cation-exchange mechanisms, but the presence of large quantities of competing species, such as Fe(III), make this process very non-selective.

Spectroscopic studies of plutonium (IV) in nitric acid sorbed to ion-exchange media eastablish that the 12-coordinate hexanitrato complex is the species sorbed to anion-exchange sites, regardless of the Pu(IV) speciation in solution. Of particular interest is the observation that Pu(IV) sorption onto the resin correlates best with the solution concentration of the uncharged tetranitrato complex, raising the possibility that Pu(IV) sorption occurs concurrently with the acquisition of two nitrato ligands (Figure 1). Individual monocationic sites of conventional anion-exchang resins are not optimally configured to either facilitate this process or to bind the final dianionic complex. Thus, we hypothesized that bifunctional resins could facilitate the uptake process, providing superior binding properties and selectivity for dianionic complexes and exhibiting enhanced kinetics for plutonium uptake from solution.

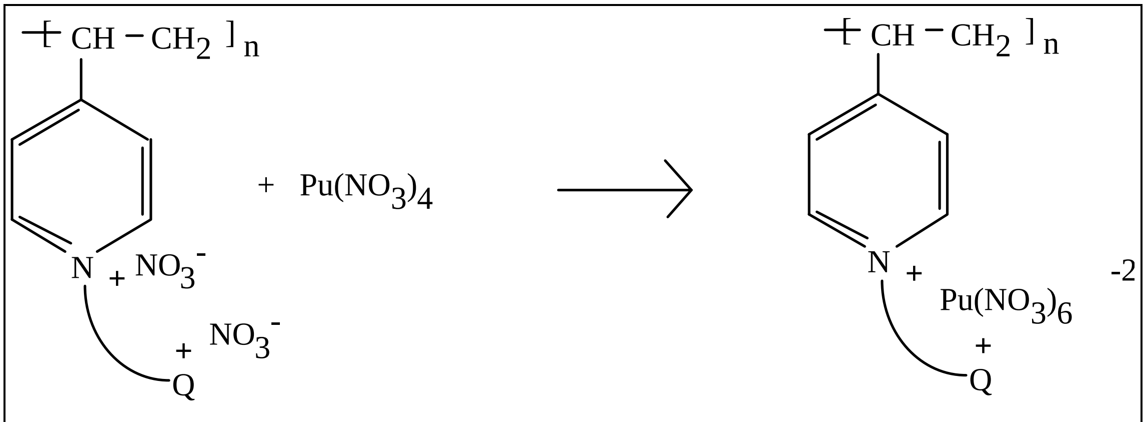


Figure 1. Concept drawing of 'facilitated uptake' of Pu onto new resins

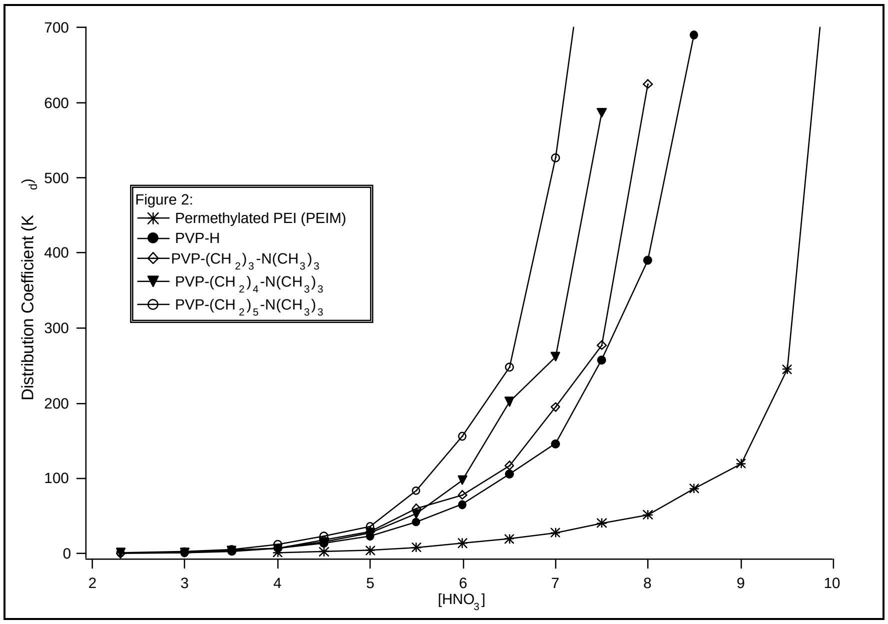
Evaluation of multi-functionalized anion-exchange materials: We have synthesized and determined Pu(IV) distribution (K_d) onto several 'systematic series' of mono- and bifunctional resins to examine the effects of varying the following conditions:

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 plutonium uptake.
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%.

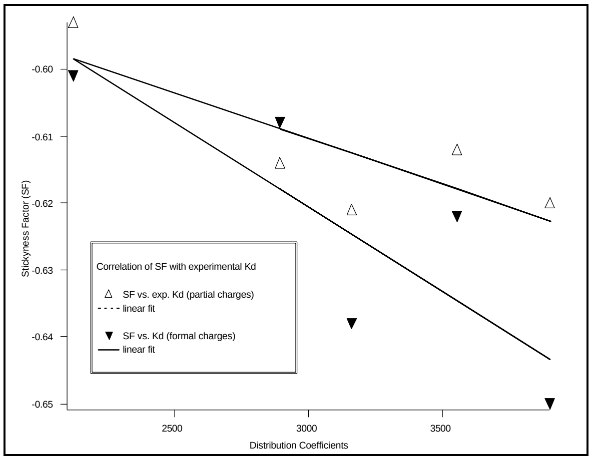
K_d values determined for in #1 and #2 above are used in the development of molecular models for the electrostatic interactions between the $Pu(NO_3)_6^{2-}$ dianion and the dicationic sites.

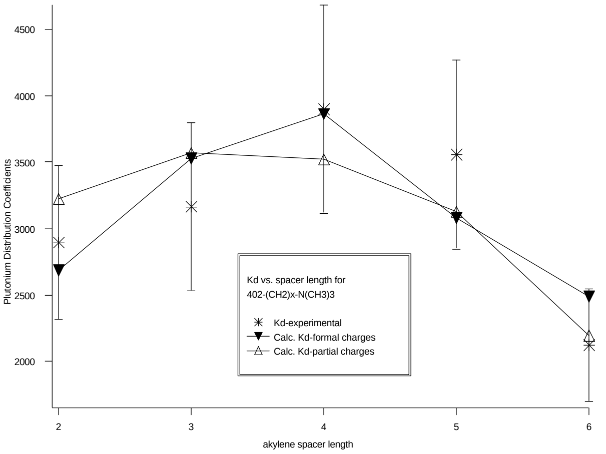
We have also synthesized a number of soluble anion-exchange polymers based on linear poly(4-vinylpyridine) and developed spectroscopic methods to determine plutonium distribution coefficients. These evolution of these materials was motivated by our desire to decouple the effects of solution-to-solid phase-transition energies and kinetics from the much weaker forces of electrostatic attraction. Our models (discussed below) focus on the *differences* in electrostatic attraction observed for the $Pu(NO_3)_6^{2-}$ anion within a series of resins with variable 'spacer' lengths between the two cationic sides. Without specific values for the energy of phase-transfer, we are forced to assume that this energy term is constant within a series (i.e. $\Delta E_{PT} = 0$). While this assumption is not unreasonable, it is quite risky in that the energies of phase-transfer from solution to solid are significantly greater than the energies of electrostatic attraction. Thus, even small variations in ΔE_{PT} could bias our calculations.

Normally, this type of information would be derived from liquid extraction studies, but initial development of appropriate dicationic extractants was problematic (we now have several promising candidates for future work). In the interim, though, we have determined that overall plutonium affinity for the anion-exchange sites in the soluble polymers is much lower than for comparable solid resins (as expected for the lower ΔE_{PT}), but the K_d values exhibit the very similar trends in that bifunctionalized materials are superior to monofunctionalized and a five-atom 'spacer' between the two cationic sites is superior to shorter spacers (Figure 2). Thus, we are more confident that the experimental data from Pu(IV) sorption onto solid-phase resins are appropriate to use to evaluate our electrostatic models.



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 hexanitrato dianions was problematic because of the exceptionally high orbital degeneracy of the complex. We developed a 'theoretical model' compound, the $Pu(NO_3)$ triradical, for which partial charges could be determined using *ab initio* calculations. Via calculation of the electrostatic interactions (called 'stickyness factor' or SF) between the Pu-hexanitrato dianion and the dicationic "resin site", we have correlated SF with experimental K_ds for three series of resins. Correlation is good using both formal charge and partial charge models.





Planned Activities: We have extended this work to other selected actinide complexes (chloro-, carbonato-) and to non-actinide complex anions, but need to pursue these avenues further, particularly with respect to commercialization and LANL plutonium-facility utilization. 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 (this summer) and determination of K_d values for extractants and soluble polymeric forms. We have promising results on direct correlation of SF with *ab-initio* -determined energy terms that need to be refined. Since EMSP funding for this project is officially ending in FY99, we will also send much of the remaining time collating data into manuscripts (see **Additional Information** below). Essentially, we plan to publish much of the 'raw' data as LANL internal reports and pick selected areas of more general interest for peer-reviewed journals. Working on the manuscripts alone will take an estimated 3 months, so experimental work will be ending soon.

Significant Project Accomplishments (to date):

1) Patent has been obtained for materials developed.
2) Licensing agreement with Reilly Industries for the commercialization of the new anion-exchange materials has been completed. May apply for R&D 100 award with Reilly Industries.
3) Experimental resins proven effective at removal of Am(III) from high salt/ high acid evaporator waste at LANL to meet regulatory disposal requirements. Selected as one of DOE-AL "success-stories" of the year (FY98).
4) Have firmly established link between molecular mechanics-determined parameters, *ab-initio* -determined energy terms and experimentally-determined distribution coefficients. This link effectively allows us to pre-determine optimally-arranged anion-exchange site.
5) The basis research/ applied systems approach for this project has been featured in LANL's Actinide Quarterly magazine and in several division-wide technical reviews.
6) New materials show promise for small-scale, rapid-throughput processing of Pu-238 scrap.

Projections:

We anticipate near-completion of the FY97-99 scope by the end of September with *some modification*. A brief summary of the status of the original project milestones is given.

Year 1 (FY 97)

- Complete actinide speciation analysis for actinides in nitrate solutions - *completed*
- Complete synthesis of a systematic series of bifunctional poly(4-vinylpyridine) polymers, complete testing of the radionuclide sorption properties of these materials - *completed*
- Synthesize a partial set of the multifunctional extractants for structural and speciation studies - *completed*
- Develop molecular modeling parameters for relevant actinide complexes - *completed*

Year 2 (FY98)

- Perform actinide speciation analyses for actinides in chloride and carbonate solutions - *completed*
- Complete synthesis of a systematic series of bifunctional polystyrene polymers, complete testing of the radionuclide sorption properties of these materials - *completed*
- Synthesize and evaluate a partial set of the multifunctional extractants - *dropped*
- Refine molecular modeling parameters for radionuclide/functional site interactions - *completed*

Year 3 (FY99)

- Complete speciation analyses for actinides in chloride and carbonate solutions, examine other relevant media - *incomplete*
- Complete synthesis and evaluation of the multifunctional resins - *dropped*
- Complete synthesis and evaluation of the multifunctional extractants - *dropped*
- Prepare final molecular modeling parameters for radionuclide/functional site interactions - *in progress*
- Decision point for implementation plan for facilitate uptake methodology - *in progress*
- Work with industrial partners in commercialization plan for new materials - *in progress*

Additional Information:

Publications

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment" Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A. *Reactive Polymers* 1997, *35*, 75-80.

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment-II" Marsh, S. F.; Jarvinen, G. D.; Bartsch, R. A.; Nam, J.; Barr, M. E. *J. Radioanal. Nucl. Chem.* , 1998, *235*, 37-40.

Planned Publications

"Extension of Molecular Mechanics to High-Coordinate Actinide Complexes: Prediction of the Structures of Pu(IV), U(IV), Np(IV) and Th(IV) Hexanitrato Complexes" Moody, E. W.; Barr, M. E.; Jarvinen, G. D.; submitted to *Journal of Computational Chemistry*.

"QSAR of Distribution Coefficients for $Pu(NO_3)_6^{2-}$ Complexes using Molecular Mechanics" Moody EW, Barr ME, Jarvinen, GD; to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"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; in preparation, to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"Plutonium (IV) Sorption by Soluble Anion-Exchange Polymers" Barr ME, Jarvinen GD, Moody EW, Vaughn RB, Bartsch RA; in preparation, to be submitted to *Separation Science and Technology: Solvent Extraction and Ion Exchange*.

"Trivalent Lanthinide and Actinide Sorption from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; in preparation.

Presentations

"Americium Separations from Complex Mixtures using Anion Exchange" Barr ME, Jarvinen GD, Schulte LD, Stark PC, Chamberlin, RM; Abstracts of Papers of the American Chemical Society, 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 of Papers of the American Chemical Society, v. 217 pp. 125-IEC MAR 21, 1999.

"QSAR of distribution coefficients for actinide hexanitrato complexes" Moody EW, Barr ME, Jarvinen GD; Abstracts of Papers of the American Chemical Society, v. 217(pt.2) pp. 170-NUCL MAR 21, 1999.

"Sorption of Pu(IV) by Soluble Anion-Exchange Polymers", Barr ME, Jarvinen GD, Moody EW, Vaughn RB; Abstracts of Papers of the American Chemical Society,V. 216(PT.2) PP. 88-NUCL AUG 23, 1998, and v. 216(pt.1) pp. 5-TECH AUG 23, 1998

"Development of Anion-Exchange Resins for Separations of Actinides", Barr ME, Jarvinen GD, Marsh SF, Bartsch RA; Abstracts of Papers of the American Chemical Society, v. 213(pt.2) pp. 73-IEC APR 13, 1997

"New Bifunctional Anion-Exchange Resins for Nuclear Waste Treatment", Marsh SF, Jarvinen GD, Bartsch RA, Nam J, Barr ME; Marc IV conference on Radioanalytical Chemistry, Kona, HI, April 1997