Environmental Management Science Program
ANNUAL PROGRESS REPORT

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Combined Extraction of Cesium, Strontium, and Actinides from Alkaline Media : An Extension of the Caustic-Side Solvent Extraction (CSSX) Process Technology

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Research Objective

This fundamental research on combined cesium, strontium, and actinide separation from alkaline media by solvent extraction addresses the EM need for more efficient processes for the combined separation of these elements.

The goal of this research is to obtain fundamental information for the development of more efficient processes for the combined separation of cesium, strontium, and transuranic elements from high level waste within the U.S. Department of Energy's (U.S. DOE) complex. These improved processes are targeted primarily for treating the wastes present at the U.S. DOE's Hanford and Savannah River sites. Combined separation of the radionuclides from these wastes would permit disposal of the treated waste as low-level waste, significantly reducing the volume of high level waste. Solvent extraction using the calixarene-based CSSX process has been shown to be a very effective separation method for cesium removal from High Level Waste (HLW) present at the U.S. DOE's Savannah River Site (SRS).

The wastes present at these sites are highly alkaline and accordingly most of the actinides are in the sludge phase. However, enough actinide materials still remain in the supernatant liquid that separation will be required, followed by disposal in a geological repository. The current technologies being considered at Hanford for cesium removal (resins) and at Savannah River for strontium and actinides (monosodium titanate) could be improved, resulting in significant cost savings. Alternatives need to be presented and developed. The principal goal of this work is to extend the solvent extraction technology chosen in October 2001 by U.S. DOE to remove cesium from the SRS high-level waste. It would include removal of strontium and actinides, therefore addressing the need to develop an alternative to MST that would achieve the separation of all radionuclides, possibly in one stage by combining selective ligands in the solvent. The benefits would involve a reduction in the number of operations, in the amount of secondary wastes, and in the footprint of the process. If the actinides were removed along with cesium and strontium, only one stream of HLW would then be generated, and the raffinate could be disposed as Low level Waste. To remove the actinides and strontium present in the waste, new classes of ligands are being developed and tested. Extremely strong chelators capable of binding actinides in alkaline media have been developed in Berkeley based on the demonstrated complexing properties of siderophores. Synthetic analogs of catecholamides or hydroxamic acids proven to be powerful and highly specific actinide(IV) sequestering agents – the 2,3-dihydroxyterephthalamides (TAMs) and the hydroxypyridinones (HOPOs). These ligands bind to actinides with high stability constants that manifest themselves in two important ways: 1) These ligands prevent metal hydrolysis and precipitation at high pH, and, 2) They are capable of sequestering metals that are present in low concentrations. Ultimately, the solvent system developed for the removal of cesium, strontium, and actinides will be tested on actual waste.

Research Progress and Implications

Fundamental research on combined cesium and strontium separation from alkaline media by solvent extraction was conducted. Three classes of ligands have been synthesized and studied as potential extractants for the selective separation of strontium in addition to cesium. Calixarene octaamides have revealed an extraction strength from alkaline media up to a thousand times greater than the reference extractant dicyclohexano18-crown-6, though selectivity over sodium still needs to be improved. This study was started during the last fiscal year and was completed.

Surprisingly, while they were originally designed for actinide separation, terephthalamide derivatives also demonstrated very large strontium distribution ratios regardless of the concentration of sodium. The third class is a combination of a crown ether and a branched long-chain carboxylic acid mixed with the CSSX solvent. This combination yielded very good distribution ratios for strontium while leaving the cesium extraction performance obtained with CSSX untouched, gave very promising results with an alkaline waste simulant and was tested with real waste. The results appear to be in agreement with those obtained with the waste simulants and are still being analyzed at this point.
Fundamental research on uranium, neptunium, and plutonium separation from alkaline media was also developed. Specific extractants for these actinides from alkaline media have been synthesized at UC Berkeley and at ORNL to investigate the feasibility of selective removal of these elements. Two families of extractants have been studied: terephthalamide (Berkeley) and tetra(hydroxybenzyl)ethylene diamine (ORNL) derivatives. Fundamental studies were conducted to characterize their extraction behavior from a wide variety of aqueous conditions. The terephthalamide derivatives exhibit a significant extraction strength along with a discriminatory behavior among the actinides, plutonium being extracted the most strongly. Quantitative extraction of plutonium, moderate extraction of neptunium and uranium was achieved from a simple caustic solution. Addition of the terephthalamide derivative to the CSSX solvent affords the combined extraction of cesiu, strontium, and the actinides of interest from a simple waste simulant. However, their stability to highly caustic solutions still needs to be improved. Tetra(hydroxybenzyl)ethylene diamine derivatives exhibit a very good stability to caustic conditions and are currently being studied.

Planned Activities

This is the last year of the project, and therefore remaining activities will cover only the last few months of the fiscal year. Further investigations on the tetra(hydroxybenzyl)ethylene diamine derivatives will be carried out to obtain results that will enable us to model the extraction system. Improvement of the cesium/strontium extraction system will be carried out to obtain the optimized extraction, scrub, and strip values. Experiments involving the combination of the CSSX solvent with terephthalamide derivatives will be repeated to demonstrate the feasibility to achieve a combined extraction of cesium, strontium, and the actinides in more complex simulantss.

Information Access

Publications

Gramer, C. J.; Raymond, K. N.; Jarvinen, G. D.; Schroeder, N. C.; Robison, T. W.; Smith, B. F. "The Removal of Dilute Concentrations of Pu(IV) from Waste Streams Using 2,3-Dihydroxyterephthalamide-Functionalized PEI and Polymer Filtration," *Sep. Sci. and Technol.* **2003**, *39*, 321 - 339.

Gorden, A. E. V.; Xu, J.; Raymond, K. N.; Durbin, P. W., "The Rational Design of Sequestrating Agents for Plutonium and other Actinide Elements," *Chem. Rev.* **2003**, *103*, 4207 – 4282.

Gramer, C. J.; Raymond, K. N. "Characterization of 2,3-Dihydroxyterephthalamides as M(IV) Chelators." *submitted to Inorg. Chem.*

Gramer, C.; O'Sullivan, B.; Van Horn, J. D.; Wieland, N. S.; Raymond, K. N. "3,4-Dihydroxysulfonamides: Comparison of Neutral Catechol Ligands to Tiron"*in preparation for submission to Inorg. Chem.*

Delmau, L. H.; Bonnesen, P. V.; Engle, N. L.; Haverlock, T. J.; Sloop, F. V.; Moyer, B. A. "Combined Extraction of Cesium and Strontium from Alkaline Nitrate Solutions," *in preparation for submission to Solvent Extr. Ion Exch.*

Delmau, L. H.; Haverlock, T. J.; Casnati, A.; Ungaro, R.; "Extraction of Strontium From Alkaline and Nitrate Solutions Using Calix[8]arene Octaamides, *in preparation for submission to Radiochimica Acta.*

Xu, J.; Gorden, A. E. V.; Raymond, K. N.; "Octadentate Ligands Containing 2,3-Dihydroxybenzamide and 2,3-Dihydroxyterephthalamide Coordinating Subunits on a Tetrapodal Amine Backbone for Chelation of Actinides**,"** *Eur. J. Org. Chem., in press*.

Veeck, A. C.; White, D. J.; Whisenhunt Jr., D. W.; Xu, J.; Gorden, A. E. V; Romanovski, V.; Hoffman, D.C.; Raymond, K. N.; "Hydroxypyridone Extraction Agents for Pu(IV),"*submitted to Solv. Extr. Ion Exch.*

Presentations

Delmau, L. H.; Haverlock, T. J.; Bostick, D. A.; Casnati, A.; Ungaro, R.; Raymond, K. N.; Moyer, B. A. "Extraction of Strontium and Actinides from Caustic Media: Fundamental Studies Towards the Extension of the CSSX Process," 27th Actinide Separations Conference, Chicago, IL, June 9–12, 2003.

Delmau L. H., Bonnesen, P. V. Engle, N. L. Raymond, K. N. Xu, J. "Extraction of Uranium, Neptunium, and Plutonium from Caustic Media," 227th ACS Meeting, Anaheim, CA, March 28-April 1, 2004

Delmau, L. H.; Bonnesen, P. V.; Haverlock, T. J.; Sloop, F. V.; Casnati, A.; Ungaro, R.; Raymond, K. N.; Xu, J. "Combined Extraction of Cesium and Strontium from Caustic Media," 227th ACS Meeting, Anaheim, CA, March 28- April 1, 2004

Delmau, L. H.; Bonnesen, P. V.; Engle, N. L., Haverlock, T. J.; Sloop, F. V.; Raymond, K. N.; Xu, J. "Combined Extraction of Cesium and Strontium from Caustic Media," 28th Actinide Separations Conference, Asheville, NC, June 8–11, 2004.

List of publications or presentations relevant to this project are posted on the www home page of the ORNL Chemical Separations Group: http://www.ornl.gov/csg.