

Annual Progress Report

Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids (EMSP Project Number 64965)

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Graduate student/postdoctorate involvement:

Four graduate students, two at the University of Notre Dame and two at Loyola University Chicago (both of whom hold joint appointments with Argonne), are performing research under this program. In addition, one postdoctoral research associate is devoting a portion of her effort at Argonne to this work. Finally, a postdoctoral fellow working under a sub-contract to Dr. Amadhu Gopalan (NMSU) is partly supported by this program.

Research Objective:

Numerous types of actinide-bearing waste materials are found throughout the DOE complex. Most of these wastes consist of large volumes of non-hazardous materials contaminated with relatively small quantities of actinide elements. Separation of these wastes into their inert and radioactive components would dramatically reduce the costs of stabilization and disposal. For example, the DOE is responsible for decontaminating concrete within 7000 surplus contaminated buildings. The best technology now available for removing surface contamination from concrete involves removing the surface layer by grit blasting, which produces a large volume of blasting residue containing a small amount of radioactive material. Disposal of this residue is expensive because of its large volume and fine particulate nature. Considerable cost savings would result from separation of the radioactive constituents and stabilization of the concrete dust. Similarly, gas diffusion plants for uranium enrichment contain valuable high-purity nickel in the form of diffusion

barriers. Decontamination is complicated by the extremely fine pores in these barriers, which are not readily accessible by most cleaning techniques. A cost-effective method for the removal of radioactive contaminants would release this valuable material for salvage.

The objective of this project is to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction of actinide ions from solid wastes. Specifically, selected diphosphonic acids, which are known to form extremely stable complexes with actinides in aqueous and organic solution, are to be rendered carbon dioxide-soluble by the introduction of appropriate alkyl- or silicon-containing substituents. The metal complexation chemistry of these new ligands in SC-CO₂ will then be investigated and techniques for their use in actinide extraction from porous solids developed.

Research Progress and Implications:

This report summarizes work performed during the first 2.6 years of a 3-year program. Because the development of supercritical carbon dioxide (SC-CO₂)-based methods for the removal of actinides from solids is dependent on the availability of suitable ligands, a substantial portion of our efforts to date have focused on the synthesis of various diphosphonic acids (DPAs). Because our early work suggested that DPAs bearing only alkyl groups were unlikely to exhibit a solubility in SC-CO₂ sufficient to render them useful in actinide recovery, the preparation of various silicon-functionalized compounds in which the silicon-containing moieties either serve as the ester functionality or are attached to the anchor carbon of the diphosphonic acid has been undertaken. By employing an approach similar to that used previously for the synthesis of dialkylmethylenediphosphonic acids, a series of alkylenediphosphonic acids (e.g., methylenediphosphonic acid) have been esterified with 3-(trimethylsilyl)-1-propanol in good yield to the symmetrically-substituted diesters. Extensive characterization of these trimethylsilyl-derivatized DPAs (TMS-DPAs) via cryoscopic and vapor-pressure osmometric methods, infrared spectroscopy, P-31 NMR, and solvent extraction has demonstrated that this derivatization has no adverse impact on either the complexation or extraction properties of the DPAs. Unfortunately, our initial vapor/liquid equilibrium (VLE) measurements for these compounds indicate that, like their underivatized analogs, the TMS-DPAs do not exhibit significant solubility in SC-CO₂ under our experimental conditions.

In addition to ligand synthesis and characterization, we have devoted considerable effort to the development of methods to accurately model the solubility of a metal complex in SC-CO₂ containing an excess of an extractant/ligand, conditions resembling those expected in "real world" applications involving removal of metal contaminants by a SC-CO₂ solution of the ligand.

Planned activities:

Successful application of an extractant to the removal of actinides from solid materials requires not just that the extractant itself be sufficiently CO₂-philic, but that the solubility of the metal complexes it forms also be adequate. Having identified several promising

extractants, we will now investigate the solubility of their metal complexes. In conjunction with this work, scale-up of the synthesis of these extractants, most of which are currently available only in milligram quantities, will be undertaken. At the same time, we will continue our ongoing investigations of the use of various phase modifiers as a means of improving the compatibility of both the ligands and their metal complexes with SC-CO₂. Once appropriate conditions have been identified, work to design and test procedures for the removal of actinides from porous solids will be performed. Additional details concerning the activities planned under this program are provided in the EMSP Field Work Proposal entitled "Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids" (1998).

Information access:

Publications and submissions

1. D. R. McAlister, M. L. Dietz, R. Chiarizia, P. R. Zalupski, A. W. Herlinger, "Metal ion extraction by silyl-substituted diphosphonic acids. Part 2. Effect of alkylene bridge length on aggregation and metal ion extraction behavior", *Sep. Sci. Technol.*, submitted (2001).
2. D. R. McAlister, M. L. Dietz, R. Chiarizia, A. W. Herlinger, "Aggregation and metal ion extraction properties of novel, silicon-substituted alkylenediphosphonic acids", *Proceedings of the International Solvent Extraction Conference (ISEC 2002)*, submitted (2001).
3. D. R. McAlister, M. L. Dietz, R. Chiarizia, A. W. Herlinger, "Metal ion extraction by silyl-substituted diphosphonic acids. Part 1. P,P'-di-[3-(trimethylsilyl)-1-propylene] methylene- and ethylene- diphosphonic acids", *Sep. Sci. Technol.*, in press (2001).
4. E. Roggeman, A. M. Scurto, J. F. Brennecke, "Spectroscopy, solubility, and modeling of cosolvent effects on metal chelate complexes in supercritical carbon dioxide solutions", *Ind. Eng. Chem. Res.* **40**, 980-989 (2001).
5. J. A. Griffith-Dzielawa, R. E. Barrans, Jr., D. R. McAlister, M. L. Dietz, A. W. Herlinger, "Synthesis and characterization of di-[3-(trimethylsilyl)-1-propylene] alkylenediphosphonic acids", *Synth. Commun.* **30**, 2121-2132 (2000).