

Project Summary

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

April 24, 2000

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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.

DOE Problems Addressed by Project:

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.

Research Objective:

The objective of this project is to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction (SCDE) 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 the work performed during the first 1.3 years of a 3-year program. Because our planned studies of metal complexation and the development of techniques for actinide removal from solids are dependent on the availability of suitable ligands, our efforts to date have focused primarily on the synthesis of selected alkyl- or silicon-containing diphosphonic acids. Our principal targets have been derivatives in which the silicon-containing groups either serve as the ester function or are attached to the anchor carbon of the diphosphonic acid. Because methylenediphosphonic acid (MDPA) is commercially available and because its esterification with simple alcohols to yield symmetrical diesters is well-established, our initial studies have focused on this ligand and its reactions with silyl alcohols.

Success has been achieved in the reaction of MDPA and its ethylene, propylene, and butylene analogs with 3-(trimethylsilyl)-1-propanol. Using a procedure similar to that previously employed for the synthesis of C-8 dialkylmethylenediphosphonic acids, this series of alkylenediphosphonic acids has been esterified in good yield (ca. 60%) to the symmetrically-substituted diesters. Vapor phase osmometric and cryoscopic studies of these compounds in toluene and 1-decanol, respectively, indicate that their aggregation properties closely parallel those of the dialkyl-substituted alkylenediphosphonic acids, specifically, the P,P'-bis(2-ethylhexyl) alkylenediphosphonic acids, H₂DEH[ADP]. Infrared spectroscopy and molecular mechanics methods have been employed to obtain information about the structures of the dimers of P,P'-di-[3-(trimethylsilyl)-1-propylene] methylenediphosphonic acid, H₂TMSP[MDP], and its propylene analog. Infrared spectroscopy has also been employed to provide qualitative information on the binding of various metal ions by H₂TMSP[MDP]. The metal complexation properties of this ligand have been found to be similar to those of di-(2-ethylhexyl)methylenediphosphonic acid, examined previously. Studies of the extraction of various cations (*e.g.*, Fe(III), Th (IV), Am(III)) by H₂TMSP[MDP] and its ethylene analog in conventional organic diluents (*e.g.*, *o*-xylene) indicate that the extraction behavior of the silyl-derivatized diphosphonic acids closely mimics that of conventional alkylenediphosphonic acids. Thus, derivatization has no adverse impact on the complexation or extraction properties of the diphosphonic acids.

Planned activities:

Because our initial studies of the silyl-derivatized diphosphonic acids indicate that these compounds may lack sufficient SC-CO₂ solubility for the anticipated application, for the remainder of the current fiscal year, the synthesis and characterization of additional alkyl- and silicon-based diphosphonic acid derivatives will be carried out. In addition, we will investigate the use of modifiers as a means of improving the compatibility of the silyl derivatives with SC-CO₂. We expect that shortly, conditions suitable for the solubilization of adequate concentrations of diphosphonic acids in SC-CO₂ will be identified. Work to examine their metal complexation chemistry in SC-CO₂ will then be performed, along with the design and testing of procedures for the removal of actinides from porous solids.