

Research Objective

Collaborative research by the Idaho National Engineering and Environmental Laboratory and the Khlopin Radium Institute (St. Petersburg, Russia) has already developed and validated the concept of a Universal Extraction (UNEX) solvent for simultaneously removing radioactive strontium, cesium, and transuranics from acidic aqueous waste streams in a single unit operation. These development efforts focused on the application of the process, where extractants were simply evaluated for extraction efficiency. No fundamental data exist on the chemistry of the UNEX solvent or its molecular interactions with extracted metal ions. The objective of this project is to conduct research that experimentally combines classical chemical techniques with advanced instrumental methods to elucidate the mechanisms of simultaneous metal extraction, along with subsequent deployment of Extended X-Ray Absorption Fine Structure (EXAFS) experiments to identify and explain the coordination geometries of extracted metal ions. This project will develop a fundamental understanding of the complicated, synergistic extraction chemistry of the multi-component UNEX extractant. The results will facilitate enhancements to the process chemistry—increasing the efficiency of the UNEX process, minimizing primary and secondary waste streams, and enhancing compatibility of the product streams with the final waste forms—with the global objective of implementing the UNEX process at the industrial scale.

Research Progress and Implications

This report summarizes work after 7 months of a 3-year project.

A subcontract was established between the INEEL and KRI to develop an experimental plan and begin execution of the experimental program. A detailed list of 28 potential diluents (all but 4 are commercially available from Aldrich and/or Lancaster) to evaluate the effects and interactions of organic phase water was developed. It is anticipated that KRI will synthesize experimental quantities of the potential diluents that are not commercially available. Both institutions have ordered samples of the commercially available diluents for the experimental work. Additionally, a freshly prepared batch of chlorinated cobalt dicarbollide (CCD, as the cesium salt) was synthesized by and procured from KatChem (Czech Republic). The CCD was synthesized as a single batch and aliquots were shipped to both the INEEL and KRI in order that all experimental work conducted independently at both institutions would utilize the same CCD material.

Preliminary evaluation of the interactive effects of the UNEX solvent using IR spectroscopy is in progress at KRI. The results of this work indicate the nature of water on the synergistic extraction of Sr from CCD and mixtures of crown ethers or polyethylene glycols. The extraction of the Sr^{+2} cation by a combination of CCD (acid form) with several different polyethylene glycols (PEG), and two crown ethers (15C5 and 18C6) from a 1,2 dichloroethane (DCE) diluent was studied. These data indicate that in the absence of polyethers, the protonated form of CCD is strongly hydrated and the extraction of Sr^{+2} is poor due to formation of strongly hydrated species of the type $[\text{Sr}^{+2} \cdot 8\text{H}_2\text{O}] \cdot m\text{H}_2\text{O}$ with a low m number (coordinated waters in the second or outer coordination sphere). In the presence of PEG compounds, the readily extractable hydrophobic compound $[\text{Sr}^{+2} \cdot \text{PEG}]$ is formed, with PEG-400 (which contains 9 $\text{CH}_2\text{CH}_2\text{O}$ groups) being the

most suitable for filling the first coordination sphere of Sr^{+2} and resulting in a higher Sr extraction efficiency than the other PEG compounds studied. Evaluation of the hydration of Sr complexes formed by mixtures of CCD and 15C6 or 18C6 were used to explain the extremely high Sr extraction by CCD with 15C5 relative to the CCD + 18C6 mixture. These results were presented at a poster session at the 14th Radiochemical Conference in the Czech Republic (see Information Access section below).

The initial experimental plan requires the determination of organic phase water content in saturated diluents to establish a set of potential diluents containing a discernable range of entrained water. The subsequent work will use this defined set of diluents to evaluate water effects via the batch contact (wet chemistry), NMR, IR, and eventually EXAFS experiments. The Karl Fischer titration apparatus at the INEEL is antiquated and currently unusable. It is anticipated that a new coulometric Karl Fischer titration instrument will be procured and set up through a sub-contract with Dr. Sue Clark at Washington State University, who is a Co-PI and collaborator on this EMSP project. The subcontract will be placed in June 2002 and the work largely completed in September 2002.

Planned Activities

Procure a coulometric Karl Fischer titrator and develop the necessary analytical procedure (including error analysis) to determine water content in a number of water saturated organic phases. Develop a set of diluent systems containing a broad range of water content to evaluate the effects of water on the extraction mechanism. Nitrobenzene, 1,2-dichloroethane, and phenyl trifluoromethyl sulfone will be included in the list of "baseline" diluent systems, as these diluents have been used extensively in previous studies with CCD extraction systems.

Continue wet chemistry (evaluation of distribution coefficients) and spectroscopic (primarily NMR and IR) evaluations at both the INEEL and KRI for the various diluents (i.e., differing water content) identified above. Examples of the anticipated data include plots of D_{metal} (where metal = Cs and/or Sr) as a function of organic phase water content, which allows development of the functionality of organic phase water to extraction efficiency. NMR spectra will be obtained for the pure diluents and the diluents with various permutations of PEG and/or CCD concentrations. NMR spectra will also be obtained for these systems in the presence of Sr or Cs at varying concentrations. IR spectra on similar systems will be obtained to discern between the different types of water (inner or outer coordination sphere) present in the system.

The above information obtained regarding the extraction mechanism and stoichiometry will be used to develop the necessary EXAFS experiments to verify the initial hypotheses.

Information Access

Smirnov, I. V.; Stoyanov, E. S.; Vorob'eva, T. P.; "Nature of Strontium Extraction by Synergistic Mixtures of Chlorinated Cobalt Dicarbollyde and Polyethers" Poster Presentation at the 14th Radiochemical Conference, Sponsored by the Czech Technical University in Prague, April 14 – 19, 2002, Marianske Lazne, Czech Republic.