Research Objective

Through collaborative research by the Idaho National Engineering and Environmental Laboratory and the Khlopin Radium Institute (St. Petersburg, Russia) the concept of a Universal Extraction (UNEX) solvent for simultaneously removing radioactive strontium, cesium, lanthanides, and transuranics from acidic aqueous waste streams in a single unit operation was developed and validated. These development efforts focused on the application of the process, where extractants were simply evaluated for extraction efficiency. The objective of this project is to conduct research that combines classical chemical techniques with advanced instrumental methods to elucidate the mechanisms of simultaneous metal extraction and study further the coordination geometries of extracted metal ions. This project is developing a fundamental understanding of the complicated, synergistic extraction chemistry of the multi-component UNEX solvent system. 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. The global objective is implementing the UNEX process at the industrial scale.

Research Progress and Implications

This report summarizes work through 2.5 years of a 3-year project. Prominent recent results from this annual reporting period are presented below.

Effects of the Diluent and Water

Water markedly affects the extraction process. We have obtained data on the state of water in CCD-based extraction systems from interpretation of NMR spectra. The presence of water in two different states in the organic phase is a special feature of these extraction systems. The first state involves the water dissolved in the solvent and not bonded to or coordinated in the metal complexes. This water exchanges rapidly upon treatment with heavy water (D_2O). The second state of water involves that bound in the CCD complexes. The chemical shift of this water in the NMR spectrum is about $\delta = 5$ ppm and upon saturation of the organic phase with D_2O, the exchange process proceeds much more slowly (complete exchange within 24 h). Our data indicate that the role of water in CCD-based systems is more complicated than with neutral extractants.

The concentration of water dissolved in the organic diluent has a marked effect on the measured distribution coefficients. Water contents were determined for select diluents, both alone and for solutions of CCD and PEG-400 dissolved in the diluents. In all cases the organic solutions were equilibrated with various concentrations of nitric acid, ranging from 0 to 5 M HNO_3. In general, the concentration of water present in the various organic solutions showed little dependence upon the aqueous nitric acid concentration. The equilibrium concentrations of water dissolved in the organic diluents with and without CCD/PEG-400 are presented in Figure 1. The addition of CCD and PEG-400 resulted in a significant increase in the equilibrium concentration of water dissolved in the organic solvents.

The ^{137}Cs and ^{85}Sr distribution coefficients were determined for solutions containing 0.06 M CCD and 0.03 M PEG-400 dissolved in the various organic diluents. The distribution coefficients from 0.5 M HNO_3 are plotted versus the concentration of dissolved water in Figure 2. No simple correlation between the magnitude of the ^{137}Cs and ^{85}Sr distribution coefficients and the concentration of dissolved water is observed. The lack of a simple correlation points to the fact that simple hydration effects alone cannot explain the interaction of dissolved water and cationic species in the UNEX process. Other factors such as solvent polarity need to be considered, and multiple parameter statistical correlations are currently being investigated.

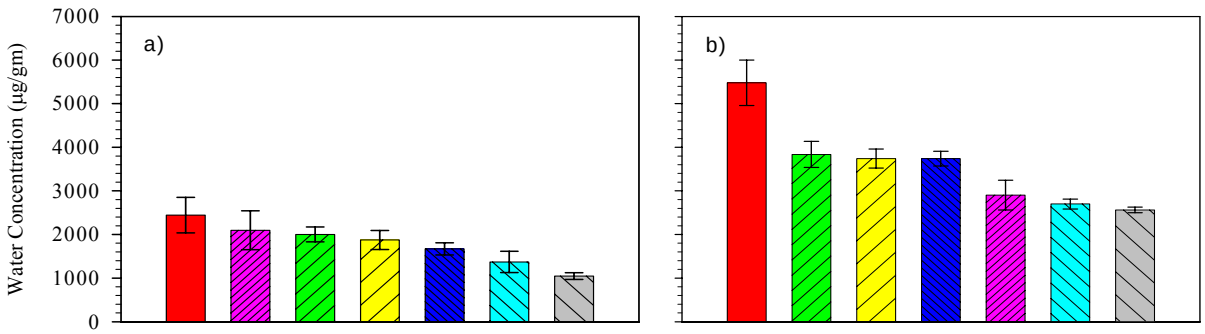

Figure 1. Concentration of water dissolved in (a) organic diluents without CCD/PEG-400 and (b) organic diluents containing 0.06 M CCD and 0.03 M PEG-400.

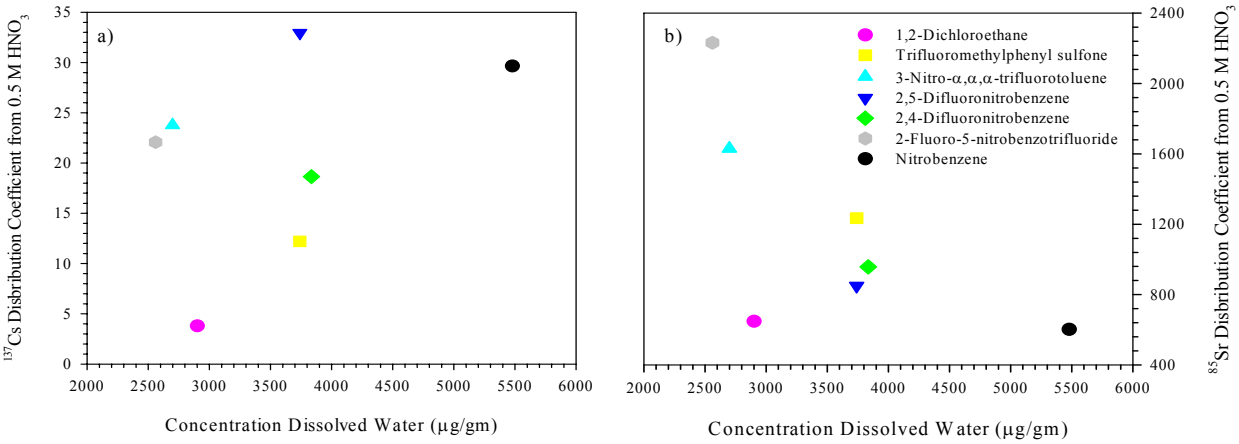

Figure 2. Cs-137 (a) and Sr-85 (b) distribution coefficients for solutions containing 0.06 M CCD and 0.03 M PEG-400 dissolved in various organic solvents plotted versus concentration of dissolved water.

Actinide Complexes

To elucidate the fundamental chemical interactions involved with the selective extraction of actinides and lanthanides in the UNEX solvent, several related extractants were investigated. A series of diphosphine dioxide (DO) extractants with the general formula $R_2P(O)(CH_2)_nP(O)R_2$ where R = phenyl (Ph) and/or butyl (Bu), n = 1 or 2, as well as two carbamoylmethylphosphine oxides (CMPOs), octylphenyl-*N*,*N*-diisobutylCMPO (OPhCMPO) and diphenyl-*N*,*N*-di-*n*-butylCMPO (DiPhCMPO) have been evaluated experimentally. It is a well-known fact that the relative basicity of the oxygen atoms in the C=O and/or P=O moieties is a measure of the extraction ability for the actinide and lanthanide elements in the coordinated metal complexes: the more basic the oxygens, the stronger the extractant.

Americium and europium distribution coefficients for the different extractants were experimentally determined under identical conditions of extractant concentration in the organic phase and 3 M HNO_3 in

the aqueous phase. Additionally, the acidity of the methylene protons was probed by using NMR (^1H) investigations to examine the rate of deuterium substitution for hydrogen into the bridging methylene positions of the various extractants. Finally, preliminary IR data indicate that a hydrated proton (probably as $H_3O^+ \cdot 4H_2O$) forms a bidentate complex with the extractants, the stability of which provides a relative measure of the oxygen's basicity. We have evaluated the extraction of acid and performed additional NMR studies to verify bidentate coordination of acid with the various extractants. Data from these independent studies suggests several qualitative measures of extractant basicity and indicates the relative strength the different extractants, which increases in the order:

$Bu_4EtDO < Ph_2Bu_2EtDO < Bu_4MeDO < Ph_4EtDO < OPhCMPO < DiPhCMPO < Ph_2Bu_2MeDO < Ph_4MeDO$

The reversal in relative basicity and extraction efficiency for Am and Eu (Bu_4EtDO is the most basic extractant, yet has the lowest metal distribution coefficients) is explained by competition between the hydrated proton and metal cation with the more basic extractants at the higher acidity used in these tests (3 M HNO_3). At this acid concentration the proton out-competes the metal ion for the extractant by shear mass action effects.

Planned Activities

With the remaining time and funding, limited experimental work will be completed to fill gaps in existing data and prepare scientific publications on the results of this project. Four journal articles relating to the results are currently in preparation. Note that a proposal for renewal for this project was submitted in April 2004, continued experimental efforts would depend on the results of that competition.

Information Access

Herbst, R.S., D.R. Peterman, T.A. Luther, V.A. Babain, I.V. Smirnov, and E.S. Stoyanov, "Fundamental Chemistry of the Universal Extractant (UNEX) for the Simultaneous Separation of Major Radionuclides (Cesium, Strontium, Actinides, and Lanthanides) from Radioactive Wastes," Environmental Management Science Program (EMSP) Symposium on Nuclear Waste Management, Division of Nuclear Chemistry and Technology, American Chemical Society 226th ACS National Meeting, New York, NY, September 7-11, 2003, *in press*.

Babain, V.A., I.V. Smirnov, N.G. Antonov, T.A. Luther, R.S. Herbst, and D.R. Peterman, 2003, "Synergistic Mixtures of Chlorinated Cobalt Dicarbollide and Bidentate Organophosphorus Compounds for High-Level Waste Reprocessing," Proceedings of Int. Conf. GLOBAL'03, New Orleans, USA, Nov. 16-22, pp. 732-735.

Peterman, D. R., R.S. Herbst, T.A. Luther, R.D Tillotson, T.G. Garn, V.A Babain, I.V. Smirnov, E.S. Stoyanov, "Fundamental Chemistry of the Universal Extractant (UNEX) for the Simultaneous Separation of Major Radionuclides (Cesium, Strontium, Actinides, and Lanthanides) from Radioactive Wastes," Environmental Management Science Program (EMSP) Symposium on Nuclear Waste Management, 227th National Meeting of the American Chemical Society, Anaheim, California, March 2004.

Smirnov, I.V., V. A. Babain, A. Yu. Shadrin, T. I. Efremova, N.A. Bondarenko, R. S. Herbst, D.R. Peterman, T.A. Todd, "Extraction Of Americium And Europium By Diphosphine Dioxides And Their Mixtures With Chlorinated Cobalt Dicarbollide," *submitted to Solvent Extraction and Ion Exchange, March 2004.*

Luther, T. A., R.S. Herbst, D.R Peterman, R.D. Tillotson, T.G. Garn, V.A. Babain, I.V. Smirnov, E.S. Stoyanov, "Examination of the Fundamental Chemistry of the Universal Extractant (UNEX) for the Simultaneous Separation of Major Radionuclides (Cesium, Strontium, Actinides, and Lanthanides) from Radioactive Wastes," American Chemical Society 59th Northwest/18th Rocky Mountain Regional Meeting, Logan, Utah, June 2004.

Herbst, R. S., D.R. Peterman, T.A. Luther, T. A. Todd, I.V. Smirnov, V.A. Babain, E.S. Stoyanov, N.G. Antonov, "Fundamental Aspects of Actinide and Lanthanide Extraction with Functionalized Diphosphine Dioxides and Carbamoylmethyl Phosphine Oxides," 28th Annual Actinide Separations Conference, Asheville, North Carolina, June 7 – 10, 2004.