

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. The global objective is implementing the UNEX process at the industrial scale.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project.

Structure of the Sr:PEG:CCD complex

We have continued the evaluation of the interaction of the Sr^{+2} cation with polyethylene glycol (PEG) and chlorinated cobalt dicarbollide (CCD) in the organic phase using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic methods. The objective of these studies were to determine the stoichiometry of the Sr:PEG-400:CCD complex. Using IR spectroscopy on the organic phase requires the use of an “optically transparent” diluent that has no absorption bands in the IR regions of interest. 1,2-Dichloroethane (DCE) was selected for this purpose since CCD is sufficiently soluble in this diluent. Using Sr^{+2} saturated organic solution containing 0.05 M CCD in DCE (w/o PEG), the complex formed is $[\text{Sr}^{+2} \cdot 8\text{H}_2\text{O}] \text{CCD}_2$. For an organic phase containing Sr^{+2} saturated solution of 0.05 M CCD & 0.05 M PEG-400 in DCE, the complex formed is $[\text{Sr}^{+2} \cdot \text{PEG}] \text{CCD}_2$, indicating the formation of the 1:1 Sr:PEG complex. Apparently, the etherial oxygens of PEG displace the 8 H_2O molecules from the 1st coordination sphere of Sr. 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 size for filling the first coordination sphere of Sr^{+2} and resulting in a higher Sr extraction efficiency than the other PEG compounds studied. Thus, these results are consistent with Sr^{+2} extraction data vs. PEG size, where PEG size is related to the general formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n \text{H}$:

	Ave. n	D_{Sr}
PEG-300	6-7	4.0
PEG-400	9	4.1
PEG-1500	33-34	0.6

The ramifications of establishing the stoichiometry of the Sr:PEG:CCD complex is that the relative concentrations of PEG and CCD in the organic phase can be estimated for a given concentration of Cs and Sr in the aqueous stream to be treated by the extraction process. This information has already been used in determining organic phase concentrations of CCD and PEG for treatment of dissolved spent nuclear fuel streams. For that particular application, the extraction process is based on CCD and PEG to remove the radioactive fission products of ^{137}Cs and ^{90}Sr in the Advanced Fuel Cycle Initiative (AFCI), sponsored under the auspices of the US DOE Office of Nuclear Energy. For the AFCI application, CMPO is not used in the organic phase extractant since actinide recovery will be accomplished by other methods. The composition of the spent fuel solution is dramatically different than that of tank wastes previously

studied and contains substantially higher concentrations of ^{137}Cs and ^{90}Sr than in legacy tank wastes. The AFCI program intends to run experimental demonstrations with this system later in FY-03, and success of these tests will in part, be associated with the fundamental understanding of the chemistry developed in this EMSP project.

Diluent Effects

Our observations have indicated that the diluent used in the UNEX system plays a dramatic role in the extraction of the target radionuclides from aqueous waste streams. The choice of a suitable diluent has been largely a trial and error process to this point. Understanding the role of the diluent in the extraction behavior and fundamental chemistry of the system is of particular importance. Physical properties of over 25 different organic diluents have been evaluated thus far to discern the role of the diluent used during extraction on the properties of the extraction system. Simple correlations between D_{Cs} and diluent physical properties have not been observed. Collection of additional diluent data and evaluation of multi-parameter correlations are planned.

Diphenyl CMPO Complexes

We have initiated an evaluation of the behavior and interactions of diphenyl-*N,N*-di-*n*-butyl-carbamoylmethylphosphine oxide (CMPO, the active actinide extractant) in the extraction mixture. Experimental work to date has focused on NMR and IR evaluations of an organic phase containing CMPO in several different diluents – in the absence of CCD or PEG. We have determined that strong acids, such as HClO_4 or HCCD (relative to HNO_3) form new complexes with CMPO by protonation of the nitrogen nuclei. The ^{13}C NMR spectra for 0.2 M CMPO in DCE exhibit significant downfield chemical shifts and a decrease in the diastereotopic nature of the carbon nuclei resonance in the butyl groups adjacent to the nitrogen when contacted with aqueous HClO_4 of increasing concentration:

	d CH ₂ (ppm)	?d (ppm)
“wet”	48.6, 45.9	2.7
6M HClO_4	49.9, 47.8	2.1
8M HClO_4	50.7, 49.0	1.7
11M HClO_4	51.9, 50.5	1.4

For the same system, the ^1H NMR spectra indicate the water content in the organic phase increases (based on integration) with increasing acid strength:

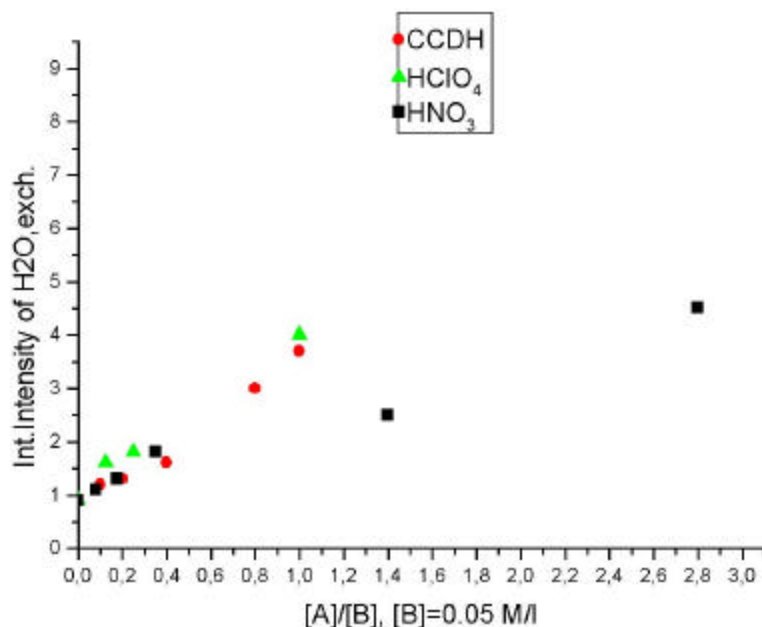
	d (ppm)	Intensity
“wet”	2.35	2.05
6M HClO_4	9.10	2.62
8M HClO_4	10.65	2.61
11M HClO_4	11.58	3.99

In conjunction with ^{31}P NMR data, it appears that HNO_3 protonates CMPO in this system primarily through the P=O and the C=O oxygens. With stronger acids, HCCD and HClO_4 , additional protonation occurs at the N atom in CMPO after the phosphoryl and carbonyl oxygens are fully protonated or saturated.

In fact, comparing the spectral intensities of the exchanged water peak in the ^1H NMR as a function of acid and acid concentration for the system 0.05 M CMPO in 1,2-DCE, the organic phase water content decreases in the order:



The effects are more pronounced at higher acid concentrations. This is an excellent indication of the relative acid strength in the organic phase and the ability to pull water into the organic phase.



Dependence of water intensity in H^+A – CMPO systems versus concentration of acid. In all cases the concentration of CMPO is constant at 0.05 M in 3-nitrobenzotrifluoride.

Planned Activities

Evaluation of organic phase structures via wet chemistry techniques.

Initiate wet chemistry (evaluation of distribution coefficients) and continue spectroscopic (NMR and IR) evaluations at both the INEEL and KRI further verify the structure of the Sr:PEG:CCD complex. Examples of the anticipated data include plots of D_{metal} (where metal = Cs and/or Sr) as a function of CCD or PEG concentration in the organic phase, which allows development of the organic phase stoichiometry by classical slope analysis techniques.

Continue efforts to correlate extraction distributions to physical properties of the diluent.

Additional physical properties of various diluent will continued to be developed and the ability to correlate diluent properties to extraction efficiency will be pursued using multi-parameter correlations.

Ultimately verify structures using EXAFS.

The above information obtained regarding the extraction mechanism and stoichiometry will be used to develop the necessary EXAFS experiments to verify the initial hypotheses of the stiochiometry of the complexes formed in the organic phase.

Information Access

Invited presentation for the EMSP symposium on Nuclear Waste Management, 226th National Meeting of the American Chemical Society, New York, New York, September 2003.

Presentation at the American Nuclear Society/European Nuclear Society International Winter Meeting, *Global 2003*, New Orleans, Louisiana, November 2003.