

FINAL REPORT

DOE Environmental Management Science Program

**NOVEL FISSION PRODUCT SEPARATION BASED ON
ROOM-TEMPERATURE IONIC LIQUIDS**

9/15/01 to 9/14/05

University of Mississippi Component

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Background

The aqueous high-level waste (HLW) resulting from the reprocessing of civilian nuclear reactor fuel and other nuclear materials contains many long-lived fission products, including $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$. These radionuclides present a serious health risk because they are a major source of radioactivity. In addition, they are significant contributors to the heat that is produced by HLW, which complicates the design of storage facilities. Both $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ have relatively small thermal cross sections and are therefore poor candidates for transmutation. Thus, HLW waste containing these species must be treated by conventional processing methods such as precipitation or ion exchange in order to achieve a reduction in volume and to lower the radioactivity of the waste [1].

The liquid-liquid extraction of long-lived $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ radionuclides from aqueous tank waste into hydrophobic organic solvents, e.g., 1,2-dichloroethane, dichloromethane, toluene, xylene, with various ionophores, such as macrocyclic ligands, has been studied extensively. However, the high vapor pressure and toxicity associated with such solvents are problematic. As a result, hydrophobic room-temperature molten salts or ionic liquids have been investigated as substitutes for the organic solvents normally used in this application [2-6]. These ionic solvents have no detectable vapor pressure at room temperature. Although the toxicity of these solvents is unknown, they are believed to be less toxic than most of the molecular organic solvents listed above.

One class of macrocycles that are promising candidates for the extraction of Cs^+ is the calixarene-crown ethers, especially those based on calix[4]arenes. In a recent investigation, calix[4]arene-bis(*t*-octylbenzo-crown-6) (BOBCalixC6) [7,8] dissolved in 1- C_n -ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (Tf_2N^-) ionic liquids was found to be an extremely effective extraction system for Cs^+ [6]. Likewise, dicyclohexano-18-crown-6 (DCH18C6) was found to be an effective extractant for Sr^{2+} in this same ionic liquid [5]. However, before this extraction system can be used to remove Cs^+ and Sr^{2+} from aqueous tank waste on a practical scale, an economical method for recycling the expensive extraction solvent (macrocyclic ligands + ionic liquid) must be developed.

Project Goals

The overall goal of this research project, which includes investigators at ORNL (Drs. Huimin Luo, Sheng Dai, Peter V. Bonnesen, and A.C. Buchanan, III), the University of Alabama (Professor Robin Rogers), and the University of Mississippi (Professor Charles L. Hussey), is to explore the use of room-temperature ionic liquids as extraction solvents for removing $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ from simulated aqueous tank waste as described above. The specific goals of this project are to (a) synthesize new ionic liquids tailored for the selective extraction of $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$, (b) to select optimum macrocyclic extractants through studies with these fission products, (c) to develop an efficient process for recycling the ionic liquids and ionophores, and (d) to investigate the stabilities of the ionic liquids under extreme conditions, e.g., highly acidic and basic environments and the high-level radiation fields associated with $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$.

At the University of Mississippi, our primary task in this collaborative project was to evaluate the possibility of recovering Cs^+ and Sr^{2+} from the hydrophobic ionic liquid phase after the phase-transfer step was completed. As discussed above, BOBcalixC6 and DCH18C6 were used to extract Cs^+ and Sr^{2+} , respectively. Because it has been established that Cs^+ can be electrochemically reduced from several different organic solvent/electrolyte solutions into mercury electrodes [9], this approach was investigated as a method for recovering the extracted Cs^+ and Sr^{2+} from the ionic liquid/ionophore mixtures described above.

Most of the exploratory work involving the chemical extraction of Cs^+ and Sr^{2+} from aqueous solutions into hydrophobic ionic liquids has been based on dialkylimidazolium cations with anions such as PF_6^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (or Tf_2N^-). Unfortunately, long experience with imidazolium-based ionic liquids in the P.I.'s laboratory has determined that the cathodic electrochemical window of these ionic liquids is insufficient to permit the electrochemical reduction of alkali and alkaline-earth metal ions into mercury electrodes, in spite of the thermodynamic potential advantage associated with amalgam formation. Therefore, very early in this project it became apparent that it would be necessary to identify a new hydrophobic ionic liquid that could be used to extract Cs^+ and Sr^{2+} and would also permit the electrochemical reduction of the coordinated Cs^+ and Sr^{2+} at mercury electrodes. Such an ionic liquid must have a potential window

significantly more negative than those based on dialkylimidazolium cations. Thus, a large portion of the project carried out at The University of Mississippi was devoted to this task.

Summary of Accomplishments

The goals of the project as defined above for the work that was to be conducted at The University of Mississippi were fully realized. The effective extraction of Cs^+ and Sr^{2+} into a relatively new and heretofore untested hydrophobic ionic liquid, tri-*n*-butylmethylammonium bis[(trifluoromethyl)sulfonyl]imide was demonstrated with calix[4]arene-bis(*tert*-octylbenzo-crown-6) and dicyclohexano-18-crown-6, respectively. The coordinated Cs^+ and Sr^{2+} were subsequently removed from the ionic liquid extraction solvent by an electrochemical reduction process carried out at mercury electrodes. This process is non-destructive, permitting the ionic liquid and ionophores to be recycled. Although the process is based on mercury electrodes, this is a benefit rather than a detriment because the liquid mercury containing the Cs and Sr can be easily transported to another electrochemical cell where the Cs and Sr could be electrochemically recovered from the mercury amalgam and concentrated into a minimum volume of water or some other inexpensive solvent. This should facilitate the development of a suitable waste form for the extracted Cs^+ and Sr^{2+} . Thus, the feasibility of the proposed ionic liquid-based extraction cycle for the removal of $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ from simulated aqueous tank waste was demonstrated.

Results of the Project

*I. Preparation, physical properties, and electrochemical potential window of the tri-*n*-butylmethylammonium bis[(trifluoromethyl)sulfonyl]imide ($\text{Bu}_3\text{MeN}^+\text{Tf}_2\text{N}^-$) ionic liquid.* - As described above, it became apparent early in this project that the negative potential limit of the dialkylimidazolium-based Tf_2N^- ionic liquid was insufficient to permit the reduction of alkali or alkaline-earth metal ions at mercury electrodes. Thus, we set about identifying another type of ionic liquid that might be more suitable for the proposed electrochemical extraction/recycling process. A search of the literature indicated that tetraalkylammonium (onium)-based ionic liquids have electrochemical windows with much more negative cathodic limits than the corre-

sponding dialkylimidazolium salts [10-12]. However, in order to achieve the desired low-melting behavior needed to produce a room-temperature ionic liquid, a highly unsymmetrical cation is needed. These characteristics were satisfied by Bu_3MeN^+ [12].

An effective method for the synthesis of this ionic liquid was as follows. A commercial aqueous solution of tributylmethylammonium chloride ($\text{Bu}_3\text{MeN}^+\text{Cl}^-$) was distilled under reduced pressure at ~ 353 K in order to remove most of the water. The flask was then evacuated at 10^{-4} torr for at least 2 days while being heated to 383 K. A white crystalline solid was obtained when the flask was cooled to room temperature. The solid material was transferred to Schlenk flasks and recrystallized from acetonitrile-ethyl acetate mixtures using the same procedure described for the purification of $\text{EtMeIm}^+\text{Cl}^-$ [13]. The $\text{Bu}_3\text{MeN}^+\text{Tf}_2\text{N}^-$ room-temperature molten salt was prepared by mixing an exactly equal number of moles of $\text{Bu}_3\text{MeN}^+\text{Cl}^-$ and *N*-lithiotrifluoromethane-sulfonimide ($\text{Li}^+\text{Tf}_2\text{N}^-$), also known by the common name, lithium bis((trifluoromethyl)sulfonyl)imide in dry acetonitrile (MeCN). This solution was stirred and refluxed at about 353 K for at least 3 days. As the reaction proceeded, fine white particles of LiCl precipitated from the solution. At the end of the reaction period, the solution was filtered with a fritted glass filter to remove the precipitate and then evacuated to 10^{-4} torr at 373 K in order to remove all traces of MeCN. After most of the MeCN was removed, the temperature was increased gradually to about 393 K and evacuation was continued until bubble formation ceased. As the MeCN was removed, additional LiCl precipitated from the ionic liquid, and this was removed by again filtering the ionic liquid through a glass frit. The resulting hydrophobic ionic liquid was washed repeatedly with water to remove any unreacted starting materials and again evacuated to 10^{-4} torr for several days to remove all traces of water. As a final purification step, the ionic liquid was electrolyzed at $E_{\text{appl}} = -2.8$ V vs. Ag at a Hg pool electrode until cyclic voltammetry at a Pt-disk electrode indicated that no significant amounts of any electroactive impurities remained in the liquid. This final step is the key to obtaining a high quality ionic solvent for electrochemistry.

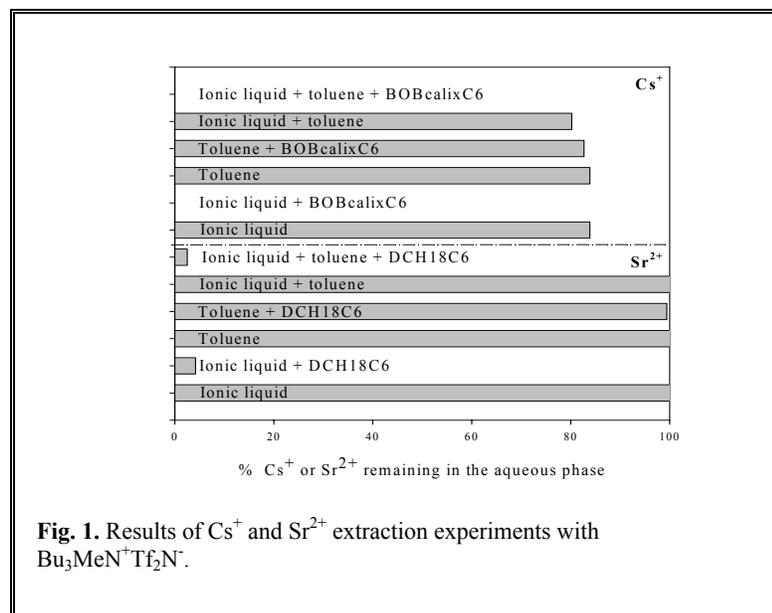
The physical properties of the $\text{Bu}_3\text{MeN}^+\text{Tf}_2\text{N}^-$ ionic liquid are compared to some other ionic liquids in Table I. Also shown for comparison are the physical properties of a 0.01 molal aqueous solution of KCl. Overall, this ionic liquid is more viscous and less conductive than many of the common ionic liquids that are under exploration today such as $\text{EtMeIm}^+\text{BF}_4^-$.

Although the primary focus of this research is electrochemistry, it is necessary to know if this ionic liquid is suitable for use as an extraction solvent when paired with the appropriate

Table I. Comparison of the physical and transport properties of ionic liquids

Composition	m.p. (K)	ρ (g cm ⁻³)	η (cP)	η (S m ⁻¹)
Bu ₃ MeN ⁺ Tf ₂ N ⁻	—	1.253(303K)	386(303K)	0.041(303K)
HeEt ₃ N ⁺ Tf ₂ N ⁻	293	1.270(293K)	167(298K)	0.067(298K)
0.01 m aq. KCl	—	~1.00(298K)	~1.00(298K)	0.141(298K)
EtMeIm ⁺ BF ₄ ⁻	~286	1.240(295K)	37.7(295K)	1.30(298K)
EtMeIm ⁺ Tf ₂ N ⁻	270	1.520(293K)	34.0(293K)	0.880(293K)
BuMeIm ⁺ BF ₄ ⁻	~192	1.170(303K)	233(303K)	0.173(298K)
BuMeIm ⁺ PF ₆ ⁻	212	1.370(303K)	312(303K)	0.146(298K)
BuMeIm ⁺ Tf ₂ N ⁻	269	1.429(292K)	52.0(293K)	0.390(293K)
EtMeIm ⁺ AlCl ₄ ⁻	280	1.294(298K)	17.8(298K)	2.29(298K)

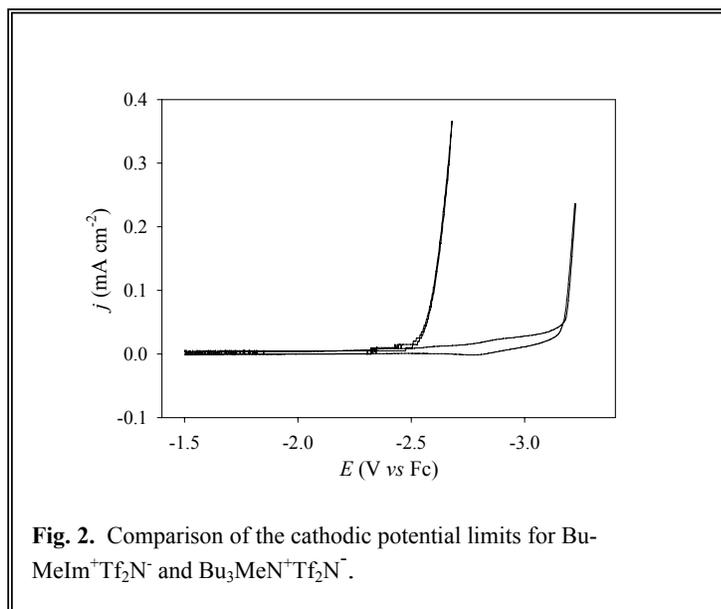
ionophore. Figure 1 shows the concentrations of Cs⁺ and Sr²⁺ remaining in the aqueous layer after extraction experiments with BOBcalixC6 and DCH18C6, respectively. All concentrations were determined with flame emission spectroscopy by using standard methods. The concentrations of Cs⁺ and Sr²⁺ remaining in the aqueous layer after one extraction cycle are shown in each case. The text in each bar of this graph indicates the composition



of the solvent used for the particular extraction experiment. This figure reveals that the Bu₃MeN⁺Tf₂N⁻ ionic liquid alone or mixed with a small amount of an organic solvent such as toluene has an extraordinary ability for extracting Cs⁺ and Sr²⁺ from aqueous solutions when paired with a suitable ionophore. The results for Cs⁺ extraction are particularly noteworthy.

The electrochemical cathodic limits measured at a platinum electrode in 1-butyl-3-methylimidazolium triflate (BuMeIm⁺Tf₂N⁻) and Bu₃MeN⁺Tf₂N⁻ are illustrated in Fig. 2. This

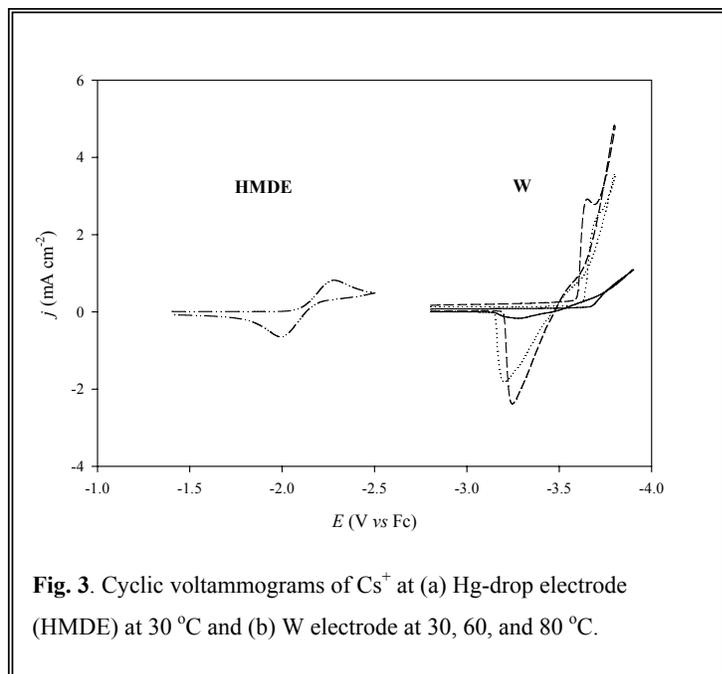
figure shows that the cathodic limit of the electrochemical window obtained in $\text{Bu}_3\text{MeN}^+\text{Tf}_2\text{N}^-$ is



0.6 V more negative than that of $\text{Bu-MeIm}^+\text{Tf}_2\text{N}^-$. This extraordinarily negative electrochemical window makes it possible to electrochemically reduce ionophore-coordinated Cs^+ and Sr^{2+} to the respective metal in this ionic liquid at a Hg-film electrode. Thus, the electrochemical advantages of this ionic liquid more than offset the less than desirable physical and transport properties of $\text{Bu}_3\text{MeN}^+\text{Tf}_2\text{N}^-$.

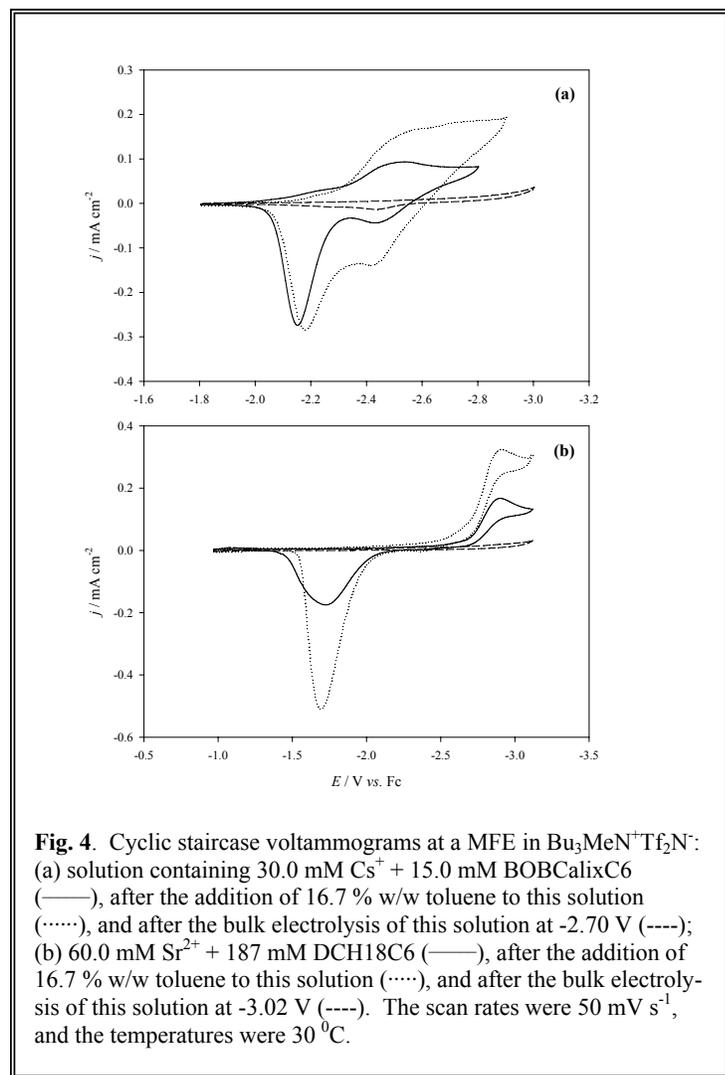
II. The electrochemical behavior of uncomplexed Cs^+ and ionophore coordinated Cs^+ and Sr^{2+} .

- Cyclic voltammograms recorded for Cs^+ at Hg and W electrodes are shown in Fig. 3, and they show reduction and oxidation waves due to the deposition and stripping of Cs. These results verify that it is possible to reduce Cs^+ to the metal in this melt; however, the reduction of Cs^+ at a W electrode occurs so close to the cathodic limit of the ionic liquid that W cannot be used as an effective substrate in the treatment of aqueous tank waste. Therefore, Hg is the electrode of choice because of the large positive potential shift arising from alloy (amalgam) formation (Fig. 3).



Although Cs^+ can be reduced in this ionic liquid at Hg, it is more important to know if ionophore coordinated- Cs^+ and $-\text{Sr}^{2+}$ can also be reduced because these are the solvated forms of

these metal ions that will exist during the treatment of tank waste. Figure 4 indicates that both of

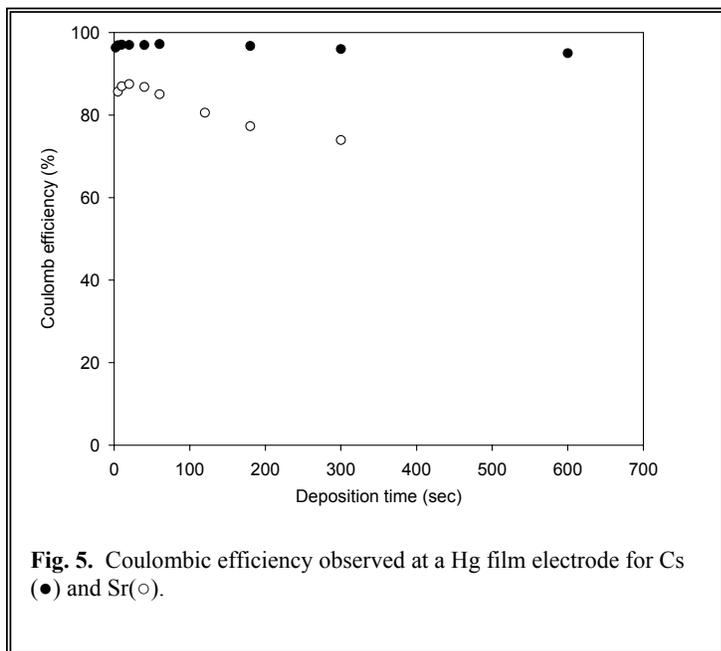


these coordinated species can be reduced at a Hg film electrode to produce the corresponding amalgam within the potential window of the ionic liquid. Furthermore, the potentials at which ionophore coordinated- Cs^+ and $-\text{Sr}^{2+}$ are reduced are sufficiently different to permit the individual electrochemical separation of Cs and Sr from the ionic liquid solvent, if necessary.

III. The electrochemical removal of coordinated- Cs^+ and $-\text{Sr}^{2+}$ and the stability of the resulting amalgam.- Cyclic voltammograms recorded before and after the electrochemical reduction of Cs^+ and Sr^{2+} into a mercury pool electrode are also presented in Fig. 4. There are no obvious reduction waves in this figure

after electrolytic processing was completed. This result suggests that within the detection limit of the cyclic voltammetric technique, all Cs^+ and Sr^{2+} seems to have been removed from the respective ionic liquid/ionophore mixture. Figure 5 shows the coulombic efficiency for the removal of Cs^+ and Sr^{2+} from the ionic liquid/ionophore mixture. The coulombic efficiency is defined as the ratio of the stripping charge to the reduction charge during the electrolysis experiment, and it can be viewed as the index of stability of the amalgam produced after reducing the corresponding cations. The coulombic efficiency is close to 100 % for Cs, but is somewhat smaller for Sr. In fact, in the latter case, the coulombic efficiency drops to $\sim 70\%$ 5 min. after the deposition process has been completed. It is not clear if the Sr amalgam reacts with impurities in

the ionic liquid, such as trace water, or whether it reacts with ionic liquid itself. Furthermore, the products of this reaction have not yet been determined. However, these investigations will continue.



Summary and Conclusions

During this project, the effective extraction of Cs^+ and Sr^{2+} from simulated aqueous tank waste was demonstrated in the hydrophobic ionic liquid, tri-n-butylmethylammonium bis[(trifluoromethyl)sulfonyl]imide containing the ionophores calix[4]arene-bis(*tert*-octylbenzo-crown-6) and dicyclohexano-18-crown-6, respectively. A simple electrochemical reduction process utilizing a mercury electrode was used to remove the Cs^+ and Sr^{2+} from the extraction solvent without damaging the ionic liquid or the ionophores. The use of a mercury electrode in the recycling process is an advantage because the liquid Hg can be easily transported to a stripping cell, where the Cs^+ and Sr^{2+} can be removed from the amalgam and concentrated in another solvent such as water. It is envisioned that this solvent can be absorbed with a zeolite and converted into a solid waste form for disposal in a repository.

Although we have demonstrated the feasibility of this overall process for treating aqueous tank waste, more work is needed to fully understand and improve the process. For example, the coulombic efficiency of the electrolytic processes must be improved. In addition, the studies reported above were carried out under inert atmosphere conditions, i.e., in the absence of H₂O and O₂. We must assess the electrochemical recovery process in an air atmosphere containing various amounts of water and oxygen in order to learn the limitations of the treatment process. This work is ongoing in the P.I.'s laboratory.

Information Access

Publications resulting from this project:

1. P.-Y. Chen and C. L. Hussey, "Electrodeposition of Cesium at Mercury Electrodes in the Tri-1-butylmethylammonium Bis((trifluoromethyl)sulfonyl)imide Room-Temperature Ionic Liquid," *Electrochim. Acta*, **49**, 5125 (2004).
2. P.-Y. Chen and C. L. Hussey, "Electrochemistry of Ionophore-Coordinated Cs and Sr Ions in the Tri-1-butylmethylammonium Bis((trifluoromethyl)sulfonyl)imide Ionic Liquid," *Electrochim. Acta*, **50**, 2533 (2005).

Conference presentations resulting from this project:

1. "Electrodeposition of Cs and Sr Ions from the Tri-*n*-butylmethylammonium Triflate Ionic Liquid, 204th Meeting of the Electrochemical Society, Orlando, Florida, October 12-16, 2003 (invited).
2. "Application of the Tri-1-butylmethylammonium Bis((trifluoromethyl)sulfonyl)imide Ionic Liquid to the Removal of Cs⁺ and Sr²⁺ from Nuclear Waste," 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 3-8, 2004 (invited).

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