Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate

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Bruce A. Moyer, Oak Ridge National Laboratory

Prof. Alan P. Marchand, University of North Texas

Research Objective

The major objective of this research is to explore new liquid-liquid extraction approaches to the selective separation of sodium hydroxide from alkaline high-level wastes stored in underground tanks at the Hanford and Savannah River sites. Secondary priority is given to separating potassium and abundant anions, including nitrate, nitrite, aluminate, and carbonate. Salts of these ions represent possible additional value for recycle, alternative disposal, or even use as commodity chemicals.

A comprehensive approach toward understanding the extractive chemistry of these salts is envisioned, involving systems of varying complexity, from use of simple solvents to new bifunctional host molecules for ion-pair recognition. These extractants will ideally require no adjustment of the waste composition and will release the extracted salt into water, thereby consuming no additional chemicals and producing no additional waste volume. The overall goal of this research is to provide a scientific foundation upon which the feasibility of new liquid-liquid extraction chemistry applicable to the bulk reduction of the volume of tank waste can be evaluated.

Research Progress and Implications

This report summarizes work performed during the first eighteen months of a three-year project. Initial experiments have focused on identifying candidate extraction systems possessing appreciable loading, effective stripping with water, and adequate selectivity for hydroxide. An exciting new class of readily available and potentially economical extractants has been identified and tested in a water-immiscible process-suitable diluent. The actual composition of the solvent is presently proprietary and is consequently not disclosed in this report. A patent application has been filed as a first step toward attracting users and ultimately transferring the technology. Selective extraction of sodium hydroxide was demonstrated in several systems involving simple aqueous phases and complex waste simulants. Quantitative recovery of sodium hydroxide by stripping with water was demonstrated, and it was shown that certain solvents could be cycled several times without loss of performance. Selectivity for hydroxide over nitrate transfer exceeds 20:1. Caustic recycle applications include recycle of sodium hydroxide at several DOE sites as well as in certain industrial processes.

Synthesis of novel cage-functionalized crown ethers and podands is being carried out by Prof. Alan Marchand and his group at the University of North Texas (UNT). These cation receptors offer the potential to enhance sodium hydroxide separation efficiency and selectivity, and indeed this has been shown to be the case among several nitrogen-containing macrocycles that have been prepared and tested. These successful initial investigations have provided valuable information that is guiding continuing efforts to design more effective host species.

Planned Activities

During the remainder of the project, we plan to probe the properties and underlying chemistry of the selective separation of NaOH from aqueous mixtures using the compound classes identified in the

past eighteen months. Toward attracting the interest of the EM Tanks Focus Area and potential users, experiments are being conducted to boost the extraction efficiency so that 90% of the sodium hydroxide can be removed from the tank waste. Recent results show promise at higher temperatures, where it is possible to operate with up to 1 M extractant and where precipitation of aluminum hydroxide can be avoided. However, the results point to the need to increase the organic-phase solubility of the extraction complexes, either through synthesis of more soluble extractant derivatives or through use of alternative diluents. It is hoped that the 90% separation goal can be reached by the conclusion of the fiscal year. In FY 2001, work will focus on gaining a firmer understanding of candidate systems and exploring other properties, such as stability, needed for development of a robust process. Synthesis of both simple compounds and macrocycles will be continued, and these efforts will be guided both by results of crystal structures that provide detailed information on conformation and coordination and by extraction experiments that illuminate extraction behavior and thermodynamics..

Information Access and Selected Publications

See www home page of the ORNL Chemical Separations Group: http://www.ornl.gov/csg

B. A. Moyer, C. K. Chambliss, P. V. Bonnesen, and T. J. Keever, "Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures," Patent Application Ser. No. 09/404,104, Sept. 23, 1999.

B. A. Moyer, P. V. Bonnesen, C. K. Chambliss, T. J. Haverlock, A. P. Marchand, H-S. Chong, A. S. McKim, K. Krishnudu, K. S. Ravikumar, V. S. Kumar, and M. Takhi, "Use of Cage-Functionalized Macrocycles and Fluorinated Alcohols in the Liquid-Liquid Extraction of NaOH and other Sodium Salts," ACS Symposium Series, American Chemical Society, Washington, DC (Submitted).

A. P. Marchand, and H.-S. Chong, "Synthesis and Alkali Metal Picrate Extraction Capabilities of Novel, Cage-Functionalized Diaza(17-crown-5) Ethers", *Tetrahedron* **1999**, *55*, 9697-9706.