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

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

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Research Objective

The objective of this research is to explore new liquid-liquid extraction approaches to the selective separation of major sodium salts from alkaline high-level wastes stored in underground tanks at Hanford, Savannah River, and Oak Ridge sites. Disposal of high-level waste is horrendously expensive, in large part because the actual radioactive matter in the tanks has been diluted over 1000-fold by ordinary inorganic chemicals. Since the residual bulk chemicals must still undergo expensive treatment and disposal after most of the hazardous radionuclides have been removed, large cost savings will result from processes that reduce the overall waste volume. It is proposed that major cost savings can be expected if sodium hydroxide needed for sludge washing can be obtained from the waste itself, thus avoiding the addition of yet another bulk chemical to the waste and still further increase of the waste volume and disposal cost. 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 eight 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. In fact, 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. An invention disclosure has been drafted as a first step toward evaluating patentability and technology transfer. Extraction strength was found to vary with the initial composition and pH of the aqueous phase and the nature of the extractant. Appreciable loading was identified in several systems for extraction from simple aqueous phases containing two major constituents of tank waste (1.75 M NaOH, 5.25 M NaNO₃). Quantitative recovery of sodium hydroxide by

stripping with water was demonstrated by Na-22 tracer counting and acid-base titration. Selectivity for hydroxide over nitrate transfer exceeds 20:1. It was also found that effective extractant systems can be designed to accommodate a variety of aqueous-phase compositions by strategic placement of functional groups within the same class of extractant compounds. This study represents the first example of a liquid-liquid extraction process allowing for the selective transfer of NaOH from an aqueous mixture of ions to water and affords the opportunity to consider a number of caustic recycle applications. Such applications include recycle of sodium hydroxide at several DOE sites as well as in certain industrial processes.

As part of a continuing collaboration with Prof. Alan Marchand at the University of North Texas (UNT), we have received several novel cage-functionalized crown ethers and podands and have begun investigations of their recognition properties for sodium and hydroxide ions. Three nitrogen-containing macrocycles have been identified as effective extractants, whose extraction strength compares to that of lipophilic 18-crown-6 ethers, suggesting that they may be useful for the extraction of sodium salts from aqueous mixtures. Preliminary investigations have provided valuable information that is guiding continuing efforts to design monofunctional and ditopic host species capable of recognizing sodium and hydroxide ions either separately or as an ion pair.

Planned Activities

During the next year, we plan to probe the properties and underlying chemistry of the selective transfer of NaOH from aqueous mixtures to water using the compound classes identified in the past eight months. These tests will allow the hydroxide selectivity to be evaluated in the presence of a number of competing anions. Planned experiments also include an assessment of cation selectivity. It will be interesting to investigate the effect of including macrocycles in the solvent phase as effective hosts for sodium ions. In this regard, synthetic efforts are currently underway at UNT to prepare bifunctional host macrocycles capable of selectively binding sodium and affording the selective transfer of hydroxide in a single molecule. Efforts to accurately characterize the extraction chemistry of the new liquid-liquid process and the speciation of organic-phase extraction products will include modeling studies of distribution data using the program SXLSQI and spectroscopic investigations.

We recently received several new cage-functionalized crown ethers from UNT that will be tested for dual recognition of sodium and hydroxide ions. Molecular modeling studies performed at UNT suggest that one of the macrocycles possesses an ideal geometry for dual recognition. Efforts will be initiated at Oak Ridge National Laboratory to isolate crystals with both sodium and hydroxide ions incorporated in the solid state structure of this and related macrocyclic hosts. Solution characterization of the recognition properties of these new macrocycles will also be investigated.

Limited process testing using a simulant of Hanford Double-Shell Slurry Feed will be conducted to the extent needed to attract follow-on funding from EM-50 focus or crosscut programs. These funding sources and private industry will be contacted, and information transfer will be initiated. In addition, when proprietary issues are resolved, publications describing results will be forthcoming.