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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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Number of graduate students: 2

Number of postdocs: 7

Research Objective

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. Treatment processes themselves can exacerbate the problem by adding further volume to the waste. Waste retrieval and sludge washing, for example, will require copious amounts of sodium hydroxide. If the needed sodium hydroxide could be separated from the waste and recycled, however, the addition of fresh sodium hydroxide could be avoided, ultimately reducing the final waste volume and associated disposal costs.

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. Consideration is also 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 21 months of a three-year project. Experiments have focused on identifying candidate extraction systems possessing appreciable loading, effective stripping with water, and adequate selectivity for hydroxide. Eight fundamental approaches to developing extractants for this task have been proposed. Three of the approaches employ a cation-exchange principle in which a very weakly acidic reagent exchanges a proton for sodium ion at elevated pH values characteristic of alkaline tank waste. Based on this principle, an exciting new class of readily available and potentially economical extractants has been identified and tested in a water-immiscible process-suitable diluent. As an example, the fluorinated alcohol 1H,1H,9H-hexadecafluorononanol (HDFN) in 1-octanol has sufficient acidity to be converted to its sodium salt when contacted with highly alkaline aqueous solutions. Using 1-octanol as a diluent, a series of fluorinated alcohols of varying structure has been tested together with selected lipophilic phenols. Certain phenols and the more activated fluorinated alcohols exhibited selective extraction of sodium over a range of temperatures and extractant concentrations. Simple aqueous phases, such as sodium nitrate and sodium hydroxide mixtures, as well as complex waste simulants were successfully treated. Quantitative recovery of sodium hydroxide from the loaded solvents by stripping with water was demonstrated, and it was shown that sufficiently lipophilic extractants could be cycled several times without loss of performance. Selectivity for hydroxide over nitrate transfer exceeds 20:1. Good loading of the solvent with sodium, exceeding 1 M, can be achieved. Caustic recycle applications include recycle of sodium hydroxide at several DOE sites as well as in certain industrial processes. A patent application

has been filed as a first step toward attracting users and ultimately transferring the technology.

Exciting synergistic effects in sodium hydroxide separation have been discovered by combining fluorinated alcohols with macrocyclic extractants. Prof. Alan Marchand and his group at the University of North Texas are carrying out synthesis of novel crown ethers and podands. The UNT group has devised workable synthetic methodology to produce a series of novel cage-annulated oxa- and aza-crown ethers (a) that possess varying cavity sizes and shapes and (b) that differ in the number and nature of the donor atoms contained in the macrocyclic system. A crystal structure of one of the aza macrocycles, as an HCl salt, has been determined, providing valuable information on the macrocycle's preferred conformation. By appropriate variation of macrocycle structure, the strength and selectivity of extraction of alkali metal cations may be controlled, as shown in standard picrate extraction surveys. Although the macrocycles used alone tend to favor the extraction of sodium salts of large anions, sodium extraction from hydroxide solutions jumps sharply when the macrocycles are added to active fluorinated alcohols. Large synergistic effects have been recorded, sufficient to make hydroxide separation competitive with the more abundant nitrate. 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 earlier. 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. For example, questions will be addressed regarding the mechanism of extraction and structure of extraction complexes. Synthesis of novel macrocycles, fluorinated alcohols, and phenols will be continued, as 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. Properties such as stability will also be pursued as needed to support the development of a robust process in potential applied follow-on tasks that are being sought.

Information Access

A complete list of publications, patent application, and presentations for this project is also available as optional additional information associated with this annual report. See also www home page of the ORNL Chemical Separations Group: <http://www.ornl.gov/csg>.