

ANNUAL PROGRESS REPORT

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Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts

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Research Objectives

The overall goal of this research conducted under the auspices of the USDOE Environmental Management Science Program (EMSP) 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. Disposal of high-level nuclear waste is horrendously expensive, in large part because the actual radioactive matter in the tanks has been diluted over 10,000-fold by ordinary inorganic chemicals.¹ Quite simply, if the radioactive matter and bulk inorganic chemicals could be separated into separate streams, large cost savings would accrue, because the latter stream is much cheaper to dispose of. In principle, one could remove the radionuclides from the waste, leaving behind the bulk of the waste; or one could remove certain bulk chemicals from the waste, leaving behind the radionuclides. The preponderance of effort over the past two decades has focused on the former approach, which produces a high-level stream for vitrification and a low-activity stream for either vitrification (Hanford) or grout (Savannah River). At Hanford, a particular concern arises in that vitrification of a large volume of low-activity waste will be unacceptably expensive. To make matters worse, a projected future deficit of tank space may necessitate construction of expensive new tanks. These problems have raised questions as to whether a solution could be devised based on separation of sodium from the waste, resulting in the reduction of the total volume of waste that must be vitrified.²

The research reported herein focuses on fundamental chemistry that could support development of methods for separation of sodium hydroxide and sodium salts from alkaline tank wastes. In particular, sodium hydroxide is an attractive target, because it is a bulk waste constituent that can be recycled, and it is also compatible with grout, possibly enhancing the regulatory acceptability of this economical waste form. 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, the addition of fresh sodium hydroxide could be avoided, ultimately reducing the final waste volume and associated disposal costs.³ Although the percent volume reduction is rather modest, perhaps 15%, the savings is possibly still significant and may be enough to avoid construction of new tanks. Even more tantalizing, if nitrate and nitrite anions in the waste could be reduced to nitrogen gas and hydroxide (e.g., electrochemically), the bulk of the sodium in the waste could then be separated as a single component, sodium hydroxide.

Based on the above considerations, the major objective of this project since FY 1998 has been to explore new solvent-extraction approaches to the selective separation of sodium hydroxide from alkaline tank wastes. In the renewal period beginning in FY 2002, attention is also being given to separating salts of the other abundant anions, especially nitrate. A comprehensive approach toward understanding the extractive chemistry of sodium salts is envisioned, involving systems of varying complexity, from use of simple solvents to new bifunctional host molecules for sodium cation exchange. Ideal extractants will 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.

This research is being carried out in a collaboration involving Oak Ridge National Laboratory (ORNL), Pacific Northwest Laboratory (PNNL), and the University of North Texas (UNT). ORNL is developing and probing the extraction chemistry. Having joined the project in FY 2001, PNNL is engaged in testing candidate extraction systems with actual Hanford waste. UNT has been synthesizing new crown ethers for the project.

Research Progress and Implications

Summary of Prior Results

This section outlines progress in the first three years of this project, for which a detailed progress report has been issued.⁴ Eight fundamental approaches to hydroxide extraction have been considered.⁵ Three have proven most promising and have received focused attention. All three 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. Contact of the solvent phase with water then regenerates the neutral alcohol by hydrolysis, releasing sodium hydroxide into the water. Since hydroxide ion is not actually extracted, this type of system has been designated “pseudo hydroxide extraction” or PHE.⁵⁻⁷ Based on this principle, the first type of system employs alkylated phenols or fluorinated alcohols. When such cation exchangers are mixed with macrocyclic sodium ion receptors, the second type of system, designated “synergized PHE,” is obtained.⁸ A third type of system, “ditopic PHE,” employs ditopic crown-type sodium ion receptors possessing ionizable groups.

Using 1-octanol as a diluent, certain fluorinated alcohols and lipophilic phenols were shown to exhibit selective PHE, converting to their sodium-salt forms when in contact with alkaline salt mixtures.⁵⁻⁷ 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 at least several times in the laboratory without loss of performance. Efforts also began to address several issues pertaining to solvent capacity.⁹ It was found that good loading of the solvent exceeding 1 M sodium can be achieved, but high solvent viscosity or even gelation occurs at 25 °C. This may be overcome by performing extraction and stripping at 60 °C, and isotherms have been obtained for several candidate extractants. It was shown that greater than 90% of the free hydroxide in a simple tank-waste simulant may be recovered. At least two extractants for PHE appear to be viable for process use in terms of efficacy and cost. Caustic-recycle applications may also extend to certain industrial processes.

As a first demonstration of synergized PHE, synergistic effects in sodium hydroxide separation have been discovered by combining fluorinated alcohols with macrocyclic extractants.⁸ Prof. Alan Marchand and his group at UNT are carrying out synthesis of novel crown ethers and podands.¹⁰⁻¹³ The UNT group has devised workable synthetic methodology to produce a series of novel cage-annulated oxa- and aza-crown ethers that possess varying cavity sizes and shapes and that differ in the number and nature of the donor atoms contained in the macrocyclic system. Crystal structures of selected compounds have been determined, providing valuable information on the macrocycles’ preferred conformations.¹⁴ 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.¹⁰ 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.⁸ Large synergistic effects have been recorded, sufficient to make hydroxide separation competitive with the more abundant nitrate. These successful prototype systems have provided valuable information that is guiding continuing efforts to design more effective host species. One such direction entails ditopic pseudo hydroxide extractants, and a first example was successfully synthesized and delivered to ORNL.

Results in FY 2002

Pseudo Hydroxide Extraction. This section summarizes work performed during the first eight months of the three-year renewal period. Significant progress has been made toward attracting users and ultimately transferring the technology concepts that have emerged in this work. A patent was issued, detailing the chemistry of PHE, examples of extractants, and how they may be used.⁷ Recent progress was presented at the EMSP High-Level Waste Workshop, PNNL, Richland, Washington, Nov. 7–9, 2001, where information was exchanged with Hanford site representatives as well as EMSP and TFA (Tanks Focus Area) managers. A presentation was also made at the Mission Acceleration Initiative Technology Demonstration Workshop, PNNL, Richland, WA, Apr. 2–3, 2002. Feedback from this workshop was positive, supporting further R&D on sodium solvent extraction for possible Hanford applications to waste-volume reduction.^{2a} A spin-off project in the EM-50 Efficient Separations and Processing Crosscutting Program funded in FY 2001 will be completed in FY 2002 to adapt this technology to a Hanford application. Feedback from the Principal Investigators (G. M. Brown at ORNL and G. J. Lumetta at PNNL) confirms that the concept basically functions as expected from results with simulants, and hydroxide may be separated from actual Hanford waste.

Considerable insight was gained pertaining to the extraction mechanism of PHE.¹⁵ A series of experiments was conducted to probe sodium hydroxide extraction from aqueous media by hydroxylic extractants, including three fluorinated alcohols and a phenol, dissolved in 1-octanol. The main thrust of this effort was the use of vibrational spectroscopy to identify a signature of the corresponding alkoxide, which could clarify whether the extraction mechanism involves ion exchange as opposed to extraction of sodium hydroxide as an ion pair. Infrared and Raman spectra were collected from the pure extractants dissolved in 1-octanol as well as extracts after contact with aqueous sodium hydroxide solutions. The alkoxide of each extractant was prepared independently and its spectrum obtained to assist in the assignment of the bands observed in the extracts. In all cases, the extracts contained only two discernable species, that of the starting alcohol and the corresponding alkoxide. This result is consistent with an ion-exchange mechanism in the extraction of sodium hydroxide up to a stoichiometric equivalent with respect to the extractant. In the case of superloading of the extractant, the extractant does not form any identifiable species other than the alkoxide itself, suggesting that the additional sodium hydroxide is extracted as ion-pairs.

Given that the mechanism PHE is consistent with cation exchange, investigations have been initiated to relate the extraction strength to the acidity of the hydroxy acid extractants. Computations of proton affinities for various alcohols were initiated. Preliminary results on aliphatic alcohols suggest that this computational method produces results consistent with experimentally derived values, but good agreement has not yet been obtained for the phenols.¹⁶

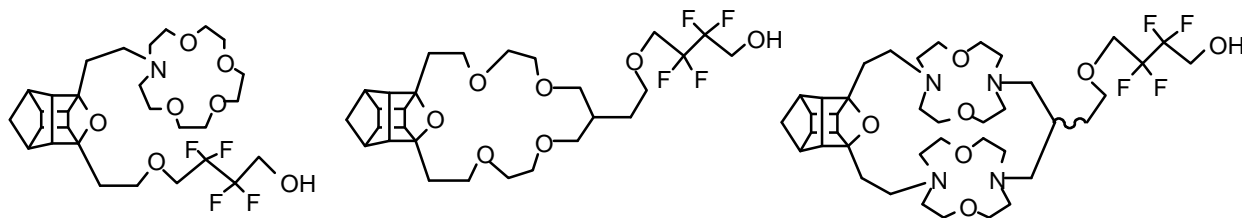
A study on the extraction behavior of a series of lipophilic weak hydroxy acids, including alkyl phenols and fluorinated alcohols, in 1-octanol was completed.⁹ Extraction was characterized as a function of temperature (10–60 °C), extractant concentration (up to 1 M), and aqueous NaOH concentration (up to 7 M). High loading may be achieved, and the slope of the isotherms at low loading has the expected value close to 2. Extraction strength increases qualitatively with hydroxy acid acidity, being strongest with two alkyl phenols and 4-*n*-octyl- α,α -bis(trifluoromethyl)benzyl alcohol. Complete and selective removal of free hydroxide from a solution containing sodium hydroxide, nitrate, and aluminate was accomplished using 1 M 4-*tert*-octylphenol at 60 °C. Aluminum precipitates as $\text{Al}(\text{OH})_3$. Quantitative stripping with

water was demonstrated.

Synthesis of a new fluorinated alcohol was completed to address the insufficient lipophilicity encountered with the most powerful of the fluorinated alcohols examined to date for PHE.⁹ Accordingly, 4-*n*-octyl- α,α -bis(trifluoromethyl)benzyl alcohol was synthesized from phenyloctane and hexafluoroacetone, using Friedel-Crafts type conditions. This fluorinated alcohol was successfully employed in the PHE studies described above.

Synergized pseudo hydroxide extraction. The first observation of synergized PHE was communicated.⁸ In this example, synergistic PHE involved the cooperative effect of a proton-ionizable fluorinated alcohol and a series of cage-annulated crown ethers in nitrobenzene (NB). Although it is not a suitable process diluent, NB was selected for this study, because it has a high polarity, facilitating fundamental understanding of the extraction behavior. Synergism was selective for hydroxide compared with normally more extractable inorganic anions. Unexpectedly, the crowns gave unequal synergistic effects, and the strongest sodium salt extraction did not correspond to the strongest synergism. The nature of hydroxy acid also has a strong effect, both on extraction strength and selectivity.¹⁷ A series of weak lipophilic hydroxy acids (HA) including fluorinated alcohols and phenols was tested together with the crown ether *cis-syn-cis*-dicyclohexano-18-crown-6 in NB. Sodium extraction by the crown ether used alone correlated with the standard Gibbs energy (ΔG_p°) of anion partitioning into NB and was weak and non-selective for the hydroxide ion, in accord with Hofmeister bias. Upon addition of a hydroxy acid into the crown ether solution in NB, sodium extraction was selectively enhanced for hydroxide. The resulting synergistic PHE correlates with the pK_a of the employed HA; the most acidic cation exchangers provide the greatest synergism. The synergistic factor obtained using a fluorinated alcohol was as high as 256. One particularly effective synergistic combination preferentially extracted NaOH over all other sodium salts, including the normally preferred nitrate and perchlorate salts. Quantitative recovery of NaOH from the NB phase was demonstrated upon a single contact of the loaded solvent with water.

Ditopic pseudo hydroxide extraction. Synthesis efforts at UNT have continued to focus on crown ethers with appended hydroxy acid functionalities for ditopic PHE. Such compounds are expected to lead to a greater degree of control over cation selectivity and possibly enhanced extraction strength. To date, three compounds have been prepared:



Characterization of these compounds is in progress.

Tests with actual Hanford waste. Thus far in FY 2001, several actual Hanford tank waste samples that can be used in Na extraction tests have been identified. Salt cakes from single-shell tanks are most appropriate, as these represent the bulk of the sodium problem in the Hanford wastes and are accordingly the major concern in the Mission Acceleration Initiative.^{2a} An available 30-g sample of salt cake from tank S-102 was selected and shipped to PNNL. Based on previous analytical data on S-102, a simulant recipe was developed for preliminary testing.

Planned Activities

In the coming two years, further efforts to understand the underlying properties of the controlling equilibria in PHE will be pursued, employing fluorinated alcohols and phenols that function by cation exchange at elevated pH values. Studies on vibrational spectroscopy will be completed, and equilibria in candidate PHE systems will be examined with the aid of computer modeling. An attempt will be made to quantitatively relate the acidity of hydroxy acids with their extraction strength in PHE. Crown ethers designed for sodium binding will be examined as potential synergists for synergized PHE. Experiments will be directed toward gaining a greater understanding of such systems toward increasing the total fraction of sodium that may be extracted from the waste. New ionizable lariat ethers will be synthesized as representatives of the class of ditopic PHE materials (UNT). The primary goal will be to demonstrate that PHE is operating and to determine whether the ditopic receptors offer advantages over the simpler synergized PHE systems. Studies with real tank waste at PNNL will be initiated. The first of these will attempt to show how a dissolved salt cake can be subjected to cesium extraction, nitrate destruction, and PHE for net removal of the majority of sodium in the waste sample.

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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. This list is divided into two files corresponding to the initial three-year period and to the present renewal period. A final report for the first three years of the project provides detailed information on the accomplishments of the first three years of this project.⁴ See also the www home page of the ORNL Chemical Separations Group: <http://www.ornl.gov/csg>.

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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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Patent Status

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