

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 a mixture of radionuclides and minor inorganic salts. 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 the separation of 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 and PNNL are investigating the extraction chemistry. PNNL will also test selected extraction systems with Hanford waste. UNT is synthesizing new crown ethers.

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 and in the first eight months of the renewal period. Eight fundamental approaches to hydroxide extraction have been considered.^{5a} The three most promising approaches among them 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. A patent has been issued.⁷ When such cation exchangers are mixed with macrocyclic sodium ion receptors, the second type of system, designated “synergized PHE,” is obtained.⁸ A proposed third type of system, “ditopic PHE,” employs ditopic crown-type sodium ion receptors possessing ionizable groups.

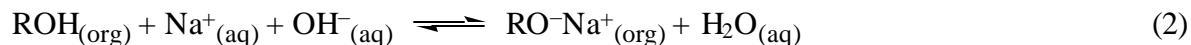
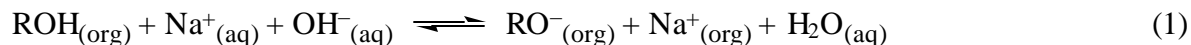
Certain lipophilic phenols and fluorinated alcohols in 1-octanol exhibit selective PHE, converting to their sodium-salt forms when in contact with alkaline salt mixtures.⁵⁻⁷ Quantitative recovery of sodium hydroxide from the loaded solvents by stripping with water was demonstrated, and it was shown that sufficiently lipophilic extractants could be cycled 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. 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 Al(OH)₃ from the hydroxide-depleted aqueous phase. 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.

The first observation of synergized PHE (SPHE) was communicated,⁸ wherein it was shown that enhanced NaOH extraction may be effected by combining fluorinated alcohols with macrocyclic extractants. Prof. Alan Marchand and his group at UNT have carried out the synthesis of novel crown ethers and podands.¹⁰⁻¹³ Synthetic methodology has been devised to produce new cage-annulated oxa-, thia-, and aza-crown ethers that possess varying cavity sizes and shapes and that differ in the number and nature of the donor atoms in the macrocyclic system. Crystal structures have provided 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.^{10,13} Although the macrocycles used alone tend to favor the extraction of salts of large anions, sodium extraction from hydroxide solutions jumps sharply when the macrocycles are combined with certain lipophilic fluorinated alcohols or phenols.⁸ Large synergistic effects have been demonstrated, sufficient to make hydroxide separation competitive with the more abundant nitrate. Results using these successful prototype systems guide continuing efforts.

Results in the Past Year

Pseudo Hydroxide Extraction. This section summarizes work performed during the past year, approximately from the 9th to the 21st months of the three-year renewal period. Considerable insight was gained pertaining to the extraction mechanism of PHE.¹⁵ Spectroscopic experiments were conducted to probe sodium hydroxide extraction from aqueous media by three fluorinated alcohols and a phenol dissolved in 1-octanol. Specifically, it was the aim to use vibrational spectroscopy to identify a signature of the putative alkoxides or phenoxide, which could clarify whether the extraction mechanism involves ion exchange as opposed to extraction of sodium hydroxide as an ion pair, thought to be less likely. 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 authentic alkoxide or phenoxide of each extractant was prepared independently, and its spectrum was 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 or phenol and the corresponding alkoxide or phenoxide. This result thus indicates 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 (or phenoxide) itself, suggesting that the additional sodium hydroxide is extracted as ion-pairs.

In light of the spectroscopic results, investigations are under way to identify the exact chemical equilibria responsible for extraction and to measure the corresponding extraction constants. Confirming simple data interpretation proposed previously,^{6,9} experiments completed to date show that extraction by the weak-acid extractants (HA) in 1-octanol can indeed be quantitatively explained by a basic cation-exchange process in which salts in the solvent formed by the deprotonated weak acids can be ion-paired or dissociated:



Extensive data sets have been collected for one lipophilic phenol and two fluorinated alcohols in 1-octanol as a function of the concentrations of organic-phase extractant and aqueous-phase NaOH. These data have been subjected to rigorous mass-action analysis using the computer program SXLSQI. In the analysis, the extraction of NaOH by 1-octanol alone (no extractants) must be taken into account, as well as activity coefficients. Toward conceptualizing the process in discrete thermochemical steps, it is proposed to relate the obtained equilibrium constants for eqs. 1 and 2 to the acid strengths of the proton-ionizable extractants tested. To assist in this effort, computations of proton affinities for various alcohols are being carried out.¹⁶

Synergized pseudo hydroxide extraction. In recently published work,¹⁷ SPHE was examined using a series of weak lipophilic hydroxy acids (HA) including fluorinated alcohols and phenols in combination with the crown ether *cis-syn-cis*-dicyclohexano-18-crown-6 in nitrobenzene (NB). Although NB is not a suitable process diluent, its high permittivity favors dissociation of ion-pairs, making it easier to discern separate binding and proton-dissociation processes. The nature of the proton-ionizable extractant was found to have a strong effect, both on extraction strength and selectivity. Sodium extraction by the crown ether used alone was

quantified, and the corresponding equilibrium constants ($\log K_{\text{ex}\pm}$) correlated with the standard Gibbs energy (ΔG_p°) of anion partitioning into NB; extraction was weak and non-selective for the hydroxide ion, in accord with Hofmeister bias. Upon addition of HA into the crown ether solution in NB, sodium extraction was selectively enhanced for hydroxide. The resulting SPHE qualitatively correlates with the $\text{p}K_a$ 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 strongly extracted 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 been focusing on the synthesis of crown ethers¹⁸ and calixarene crown ethers¹⁹ with appended weakly ionizable functionalities for ditopic PHE. Most examples have employed cage substituents on the polyether ring to confer lipophilicity and ring rigidity. The proton-ionizable substituents are essentially the same groups used in the weakly acidic fluorinated alcohols tested for PHE. The ditopic compounds by contrast are expected to lead to a greater degree of control over cation selectivity and possibly enhanced extraction strength. To date, the compounds shown in Figures 1 and 2 have been prepared.

Survey extraction experiments under way entail examining sodium distribution ratios (D_{Na}) for the synthesized weakly acidic crown compounds dissolved in purified NB. The non-ionizable control compounds are run by themselves and also with added control fluorinated alcohols that match the type of ionizable group on the corresponding ditopic extractants. One ionizable control is hexadecafluorononanol, and the other is 4-*n*-octyl- α,α -(trifluoromethyl)benzyl alcohol. Two experiments are being run: a) variation of aqueous [NaCl] and b) variation of aqueous [NaOH] in a constant aqueous concentration of NaCl. The first experiment essentially measures the relative strength of Na^+ binding and extraction without dissociation of the terminal -OH group. The second experiment then measures the total Na^+ binding and extraction as proton-dissociation is "turned on". Preliminary assessment of the data collected thus far reveals expected behavior in terms of the NaCl and NaOH dependences described earlier.¹⁷ Unfortunately, there is as yet no evidence for any of the new ditopic compounds exhibiting enhanced NaOH extraction over and above their corresponding control systems (SPHE systems consisting of crown control plus proton-ionizable control). Further evaluation of the extraction behavior of the ditopic compounds in comparison with their controls is in progress.

Combined Sodium Hydroxide and Sodium Nitrate Extraction. The feasibility of extracting both sodium hydroxide and sodium nitrate, two major sodium components of the tank waste, has been under investigation in the past year at PNNL.²⁰ Building on the concept of PHE, the approach taken was to introduce a neutral receptor capable of binding sodium ion, essentially in the manner of SPHE. The combination of a weak lipophilic cation exchanger (e.g., alkylated phenol) and a neutral sodium receptor (e.g., crown ether) in a suitable organic diluent thus will allow separation of the sodium ion via two mechanisms: ion-exchange (hydroxide driven) and ion-pair extraction (nitrate driven). The resulting greater extraction strength toward NaOH is also expected to allow flexibility in diluent selection, for example, substitution of 1-octanol with a process-compatible aliphatic diluent like Isopar L. Added crown ether is also expected to improve phase behavior in that its binding of sodium ion effectively deaggregates lipophilic sodium salts at high loading.

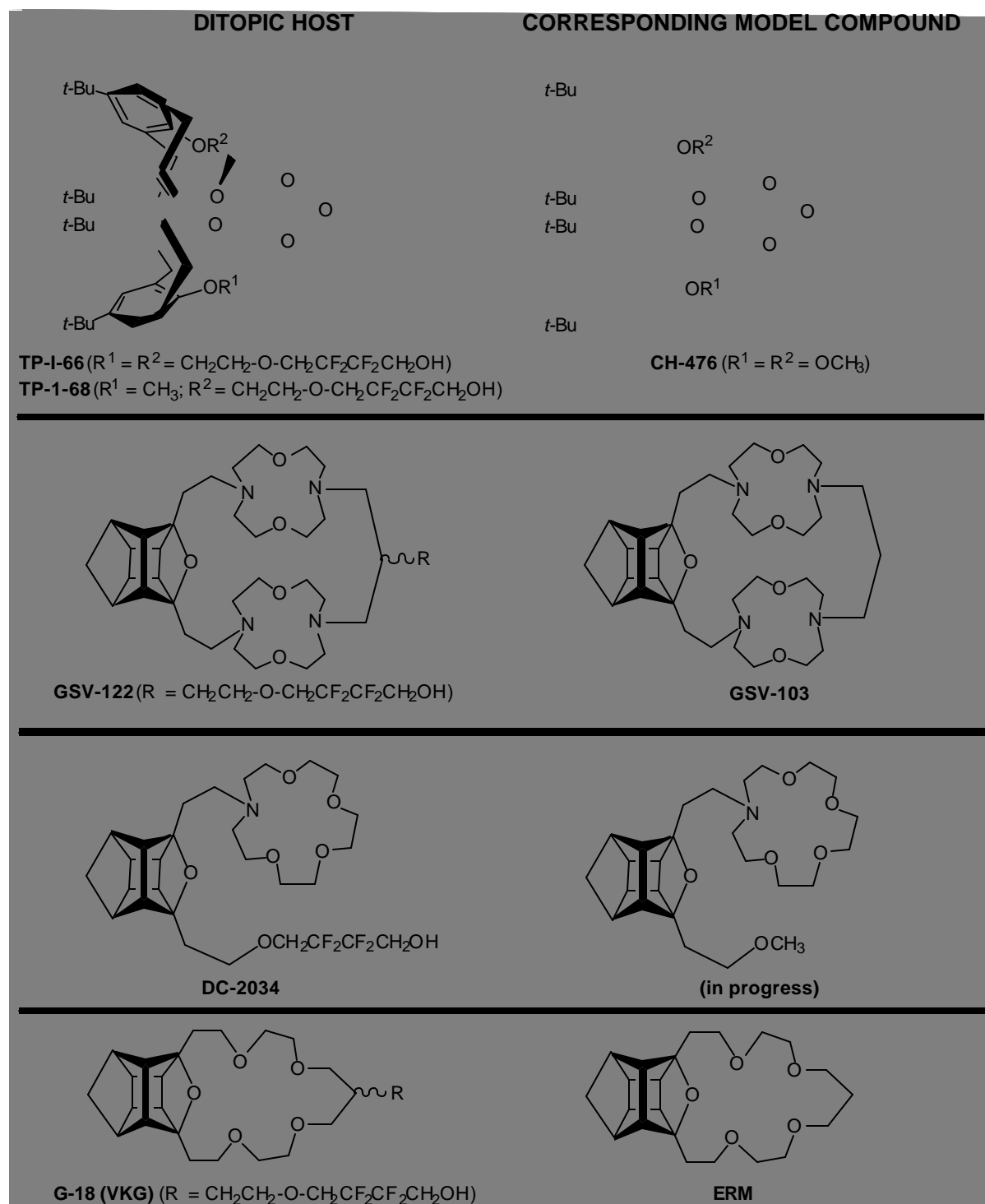


Figure 1. Synthesized weakly acidic proton-ionizable crown ethers and calixarene crown ethers for ditopic pseudo hydroxide extraction.

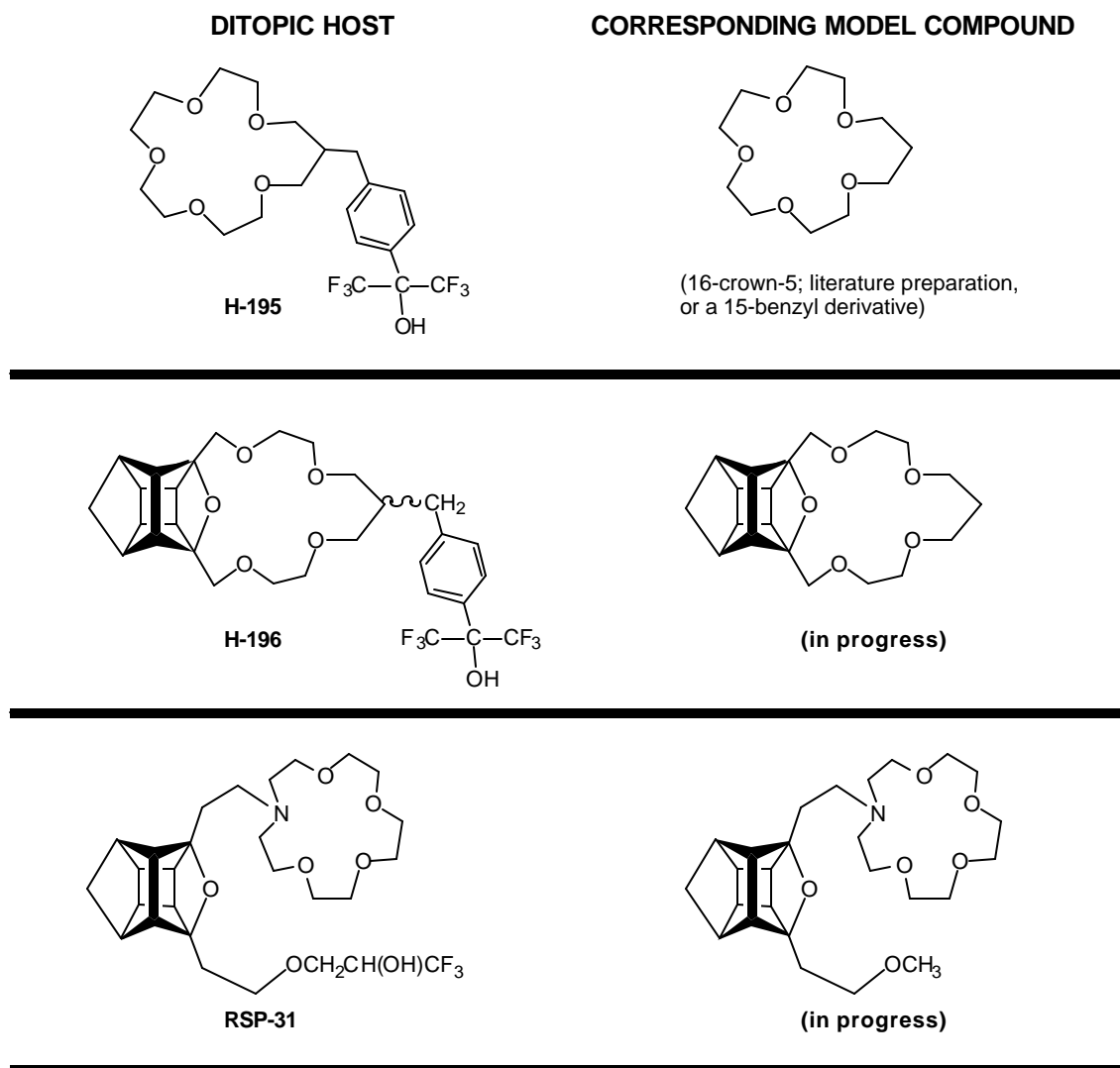


Figure 2. Additional synthesized weakly acidic proton-ionizable crown ethers and calixarene crown ethers for ditopic pseudo hydroxide extraction.

An initial study focused on evaluating the cooperative performance of a simple crown ether and cation exchanger in the Isopar L diluent towards Na^+ extraction via combined pseudo-hydroxide and ion-pair extraction mechanisms. A crown ether representing the well-known 18-crown-6 family and two organic acids, 1,1,1-trifluoro-3-(3,5-di-*t*-butylphenoxy)-2-propanol or 3,5-di-*t*-butylphenol, were chosen for this study. Experiments conducted with 4',4''(5'')-bis(*t*-butylcyclohexano)-18-crown-6 at 0.5 M with either the phenol or fluorinated alcohol at 0.5–1 M revealed strong SPHE at high alkalinity and moderate ion-pair extraction of sodium nitrate under neutral conditions. Combined extraction of sodium hydroxide and nitrate was demonstrated. It was shown to be possible to strip the extracted sodium with water. Although the results are promising, the following improvements will be needed toward a more practical system: a)

increased solubility of crown and proton-ionizable extractant, b) higher sodium loading, and c) higher sodium nitrate extraction efficiency.

A series of experiments were conducted using NB as the diluent for purposes of identifying the extraction equilibria more precisely and also assessing the effect of added electron-pair-donor solvating agents (tri-*n*-butyl- and tri-phenylphosphate, tri-*n*-butyl- and tri-phenylphosphine oxide, and *N,N*-di-*n*-butyl- and *N,N*-di-phenyl acetamide). The co-extractants chosen included *cis-syn-cis*-dicyclohexano-18-crown-6 and 3,5-di-*t*-butylphenol. Distribution results for the crown ether used alone or with the solvating agents were successfully fit using the SXLSQI modeling program, whereupon the obtained extraction constants were shown to correlate linearly with the electron-pair donicity of the added modifiers (Kamlet-Taft β solvatochromic parameter). In the presence of the phenol, the solvating agents slightly lowered NaNO₃ extraction by the crown ether and phenol, which, however, remained higher than NaNO₃ extraction by the crown ether used alone.

Planned Activities

In the coming year, the current series of extraction and mass-action modeling experiments to understand the underlying properties of the controlling equilibria in PHE will be completed using 1-octanol as the diluent. Additional fluorinated alcohols and phenols that function by cation exchange at elevated pH values will be tested. 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 SPHE, especially with a view toward increasing sodium nitrate extraction efficiency and thereby boosting the total fraction of sodium that may be extracted from the waste (PNNL). Additional new ionizable lariat ethers will be synthesized as representatives of the class of ditopic PHE materials (UNT). The primary goal of extraction experiments using these compounds will be to demonstrate that PHE is operating and to determine whether the ditopic receptors offer advantages over the simpler synergized PHE systems. Experiments intended to explore combinatorial concepts for more rapid identification of effective materials are being considered at UNT. Studies with real tank waste at PNNL will be initiated.

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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. 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>.