

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

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ANNUAL PROGRESS REPORT

U.S. Department of Energy

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

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Number of undergraduate students: 0

Number of graduate students: 6

Number of postdocs: 1

Summary

The purpose of this research involving collaboration between Oak Ridge National Laboratory (ORNL) and Pacific Northwest National Laboratory (PNNL) is to explore new approaches to the separation of sodium hydroxide, sodium nitrate, and other sodium salts from high-level alkaline tank waste. The principal potential benefit is a major reduction in disposed waste volume, obviating the building of expensive new waste tanks and reducing the costs of vitrification. Principles of ion recognition are being researched toward discovery of liquid-liquid extraction systems that selectively separate sodium hydroxide and sodium nitrate from other waste components. The successful concept of pseudo hydroxide extraction using fluorinated alcohols and phenols is being developed at ORNL and PNNL toward a greater understanding of the controlling equilibria, role of solvation, and of synergistic effects involving crown ethers. Synthesis efforts are being directed toward enhanced sodium binding by crown ethers, both neutral and proton-ionizable. Studies with real tank waste at PNNL will provide feedback toward solvent compositions that have promising properties.

Research Objectives

Purpose. The primary purpose of this project is to gain new fundamental knowledge that can ultimately point to practical approaches to the reduction of the volume of radioactive tank waste that must be vitrified, especially in large centralized processing plants such as the Hanford Waste Treatment Plant. The overall goal is to provide the scientific foundation upon which the feasibility of liquid-liquid extraction chemistry can be evaluated for separation of sodium hydroxide, sodium nitrate, and other sodium salts (e.g., nitrite and sulfate) from alkaline tank waste. Toward this end, a collaboration between ORNL (B. A. Moyer and P. V. Bonnesen) and PNNL (T. G. Levitskaia and G. J. Lumetta) combines expertise and special facilities in organic synthesis (ORNL), solvent extraction (ORNL and PNNL), and radioactive waste processing (PNNL). Our approach aims to gain insights at the molecular level and challenge these insights as far as simple experiments on actual waste.

As explained in more detail in the following section, this work aims for a principal potential benefit in terms of a major reduction in vitrified waste volume by removal of soluble sodium electrolytes, which constitute most of the mass of the tank-wastes. As such, sodium has a direct bearing on the amount of waste that must be vitrified, and some anions of its salts play special roles in waste treatment. For example, nitrate leaching from waste forms such as grout limit their performance and acceptability; sulfate has a low solubility in borosilicate glass melts; and hydroxide has potential value for recycle (e.g., in retrieval).

In terms of the science that is needed to discover applicable liquid-liquid separation systems, basic questions that this research addresses include whether it is even possible to remove bulk sodium electrolytes from the waste, what types of chemical systems might be applicable, what functional properties might be obtained, how those functional properties might be understood based on molecular properties, what selectivity might be possible, and how the extraction could be reversed to regenerate the solvent and to recover a usable sodium product stream. In the previous and current funding periods, all of these questions have been in part successfully addressed, with the emergence of some promising systems and associated understanding. Nevertheless, understanding is incomplete, and the overall problem of sodium

removal is not resolved.

The overall problem is complex in that multiple sodium electrolytes are involved, and generality has not yet been achieved. For example, sodium hydroxide may now be selectively separated from the waste based on our results, an important and useful milestone in itself, but the extraction of the other bulk sodium electrolytes in the waste, such as sodium nitrate, nitrite, and sulfate, has not yet been satisfactorily explored and remains impractically weak. In addition, there are outstanding issues regarding sodium hydroxide extraction that must be addressed for closure in this area, including a successful proof-of-principle demonstration in a simple real-waste test for facilitating technology transfer to potential users.

This project addresses the OBER long-term environmental-remediation goal "Develop science-based solutions for cleanup and long-term monitoring of Department of Energy (DOE) contaminated sites." It is clearly aimed toward development of a science-based solution to tank-waste cleanup, with potentially large cost savings.

EM needs benefited by this research. Toward basic research having the most value to the US Department of Energy (USDOE) Office of Environmental Management (EM), site needs are here considered toward a defensible separations-technology concept based on solvent extraction (SX). Although actual development of such technology will be left for follow-on applied research, efforts herein are directed toward generating the key fundamental information needed for assessing feasibility and possibly contributing to prototype design. Research is aimed primarily at two technology options for sodium separation from tank waste. The first, often referred to as caustic recycle, proposes the recovery and recycle of sodium hydroxide for use in waste treatment and waste retrieval. The second is a clean removal of bulk sodium. Applicable processes that one could envision include sodium hydroxide separation, sodium nitrate separation, or a combined separation of the major sodium components.

This research addresses the general need recently articulated by the National Research Council for "high-efficiency, high-throughput separation methods that would reduce high-level waste program costs over the next few decades including: a. High-efficiency separation, and b. Minimization of the volume of secondary waste" (URL <http://www.nap.edu/catalog/9992.html>). Needs have been expressed at the Hanford Site regarding minimizing glass production through identification of supplemental treatment technologies. Technology options toward this end were reviewed at the Mission Acceleration Initiative Technology Demonstration Workshop, held in Richland, WA, Apr. 2–3, 2002. Pseudo hydroxide extraction (PHE), a technology invented at ORNL under this project (Moyer, et. al., 2001) as described below, was considered within the scope of possible options and judged as meriting further development.

The former EM Tanks Focus Area (TFA) and the Hanford Site Contractor (CHG) previously identified a critical need (former URL <http://www.pnl.gov/tfa/emsp/needs.stm#rlwt088>, 2001) to establish more tank space in the Hanford tank farms. This additional tank capacity is needed to safely manage the tank wastes and to properly stage materials to be fed to the Hanford Waste Treatment Plant. To avoid building new double-shell tanks at \$75M apiece, it would be desirable to process the tank-waste liquids to remove much of the bulk nonradioactive materials (i.e., the sodium salts) so that they could be disposed of as incidental waste.

One approach to decreasing the cost of the low-activity waste (LAW) vitrification involves separation of the major forms of bulk sodium from the waste. The sodium could then be recycled as hydroxide, disposed more cheaply as incidental waste, or possibly returned to the US chemical economy (subject to change of *de minimus* regulations). As an example of recycling, sodium

hydroxide could immediately be reused for such purposes as sludge washing, corrosion inhibition, or waste retrieval within the Hanford tank pretreatment flowsheet itself. It is estimated that 32% of the sodium in the Hanford tanks could be recovered as sodium hydroxide, half of which is needed for recycling. On the other hand, sodium nitrate is not readily recyclable without employing a salt-splitting or calcination process, but if the 145,000 metric tons of sodium nitrate in the Hanford tanks could be cleanly recovered, it would potentially reduce the final vitrified LAW volume by 90%.

Approach. Our overall strategy entails three major thrusts:

a) Elucidation of PHE is being deepened by showing how extraction strength relates to the inherent acidity of proton-ionizable extractants. We will derive pK_a values from the extraction data and correlate these values with obtained results. Structure-function correlations with calculated quantities such as proton affinities and with experimental ones such as solvatochromic shifts will then permit the prediction of extraction strength for untested extractants.

b) Greater emphasis is being placed on our previous objective to examine sodium salt extraction, especially that of sodium nitrate, using crown ethers. Depending on the choice of conditions, it is likely that this approach could lead to either a sodium nitrate selective system or a combined extraction of sodium hydroxide and salts. Stronger crown ethers than we have hitherto tested must be employed. The most promising candidates from the literature or design are being synthesized or purchased if commercially available, and extraction experiments will be conducted as the compounds are acquired.

c) Using the same crown ethers tested above, we will examine the potential of SPHE for a combined extraction of sodium hydroxide and sodium salts. In this case, the crown ether does double duty by synergizing PHE and also extracting sodium salts. Again, we will conduct extraction experiments both for survey purposes and detailed understanding.

In that 1-octanol has proven to be a good model diluent for our studies, it continues to be the diluent of choice for much of our work. Since a large number of useful extraction constants for various proton-ionizable extractants into this diluent have already been obtained, we will add to this set new equilibrium constants corresponding to systems containing various crown ethers. In principle, the total set of constants and derived structure-function relationships will allow the prediction of behavior in many untested systems. It is of interest to understand diluent systems other than 1-octanol, and we will devote some effort to addressing the question of the role of the diluent.

Precise extraction data collected for equilibrium-constant determination are being subjected to equilibrium analysis with our own software developed by Baes, SXLSQI and SXFIT. These programs are the most sophisticated extraction-modeling programs in existence and allow the deduction of the stoichiometry of extraction species and their corresponding equilibrium constants from precise distribution data.

Although PHE has proven to be selective with regard to hydroxide separation vs other anions, the question of radionuclide selectivity in PHE has not received due attention, and we intend to redress this issue in this work. In that selectivity with regard to radionuclides is desirable to varying degrees, appropriate survey extraction experiments are being conducted for

PHE, as well as for SPHE and ion-pair extraction systems. Distribution of the key contaminants (Cs, Sr, and Tc) will be determined for selected proton-ionizable extractants and crown ethers under uniform conditions.

For deeper understanding of structure, bonding, and solvation, we will conduct spectroscopic (e.g., FTIR and NMR) experiments where needed. Recent results using vibrational spectroscopy have helped in establishing the PHE mechanism. Additionally, crystals of crown ethers and/or their complexes may be obtained for X-ray structural analysis at ORNL.

Finally, real-waste tests will be conducted on the most promising systems. Isotherm data on PHE will be collected and used to design a meaningful batch real-waste test, which will be conducted at PNNL as a proof of principle of this type of system. It will also be desirable to test the most promising system for combined sodium hydroxide and sodium salt extraction, either by simple ion-pair extraction or by an SPHE system.

Research Progress and Implications

This annual report covers progress in the period corresponding approximately to FY 2004. Because the convention has herein been adopted to use the most recent Field Work Proposal (ERKP607, submitted in March 2005) as the basis for this annual report, the results shown below partly overlap with those reported in the previous annual report.

Pseudo Hydroxide Extraction. Considerable insight was gained pertaining to the extraction mechanism of pseudo-hydroxide extraction (PHE) of sodium. So-called pseudo-hydroxide extraction has been proposed as a method for separating alkali metal hydroxide from alkaline salt solutions by use of weak-acid cation exchangers such as lipophilic phenols or fluorinated alcohols. Under extraction conditions, these lipophilic weak acids (HAs) are converted to their salt forms when dissolved in a suitable water-immiscible polar diluent like 1-octanol. Upon contact with water, the loaded solvents release alkali metal hydroxide to the aqueous phase by hydrolysis, thereby regenerating the extractant. This type of cycle has been demonstrated in previous work, wherein it was shown that bulk concentrations of sodium hydroxide could be selectively separated from alkaline high-level waste simulants (e.g., Haverlock, et al., 2003; Chambliss, et al., 2002). In the present work (see, for example, Kang, et al., in press), it has been our aim to identify the controlling equilibria and predominant species involved in the extraction process within the framework of a thermochemical model. Lipophilic weak acids under investigation are shown in **Fig. 1**. Using 1-octanol as the diluent, distribution ratios for sodium (D_{Na}) extraction were measured as a function of organic-phase HA and aqueous-phase NaOH molarity at 25 °C. The tested weak acids, 3,5-di-*tert*-butylphenol (**1b**) and 1-trifluoromethyl-2-(3,5-di-*tert*-butylphenoxy)ethanol (**3**), significantly enhanced the extraction of NaOH over the minor amount that is extracted by 1-octanol alone, **1b** being approximately 10-fold more efficient than **3**. By use of the equilibrium modeling program SXLSQI, it was shown that a simple model is sufficient to quantitatively explain the observed extraction behavior based upon a) ion-pair extraction to give Na^+OH^- ion pairs and corresponding free ions in 1-octanol and b) cation exchange by monomeric HA molecules to form monomeric organic-phase Na^+A^- ion pairs and corresponding free organic-phase ions.

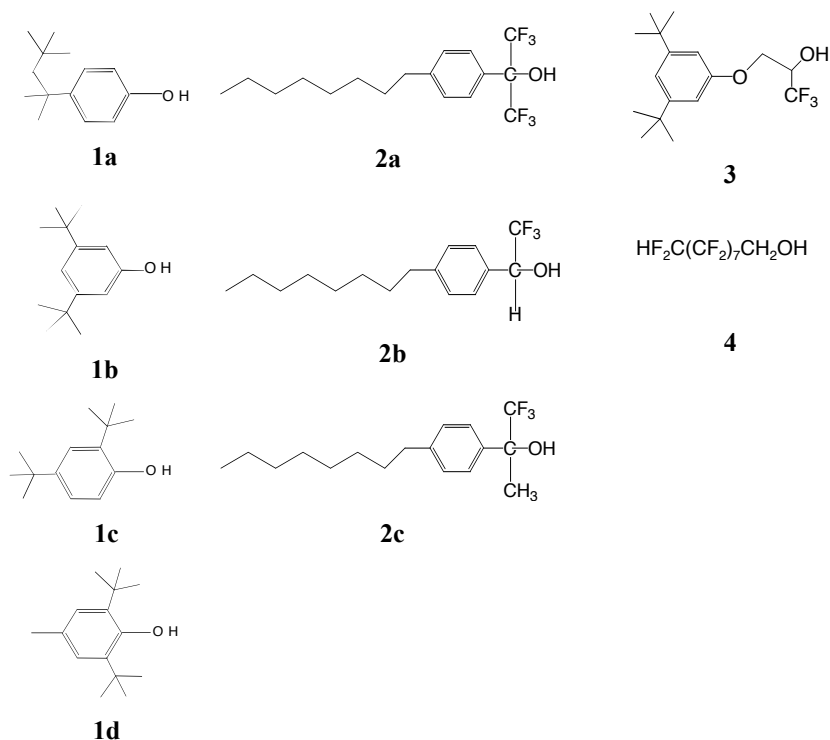


Figure 1. Compounds investigated for pseudo hydroxide extraction (PHE).

Ditopic pseudo hydroxide extraction. Previous synthesis efforts by Prof. A. P. Marchand (former collaborator on this project, now retired from the Univ. of N. Texas) focused on crown ethers and calixarene crown ethers with appended weakly ionizable functionalities for ditopic PHE. Most examples 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. Overall, 14 compounds were prepared, and survey extraction experiments have been completed. Two experiments were 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". The collected data are currently being evaluated. Unfortunately, there is as yet little or 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).

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. 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 synergized PHE (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, such as in substitution of 1-octanol with an aliphatic diluent. 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.

An initial study focused on evaluating the cooperative performance of a simple crown ether and cation exchanger in an aliphatic diluent (Isopar L) towards Na^+ extraction via combined pseudo-hydroxide and ion-pair extraction mechanisms. A crown ether representing the 18-crown-6 family, namely 4,4'(5')-di-*tert*-butylcyclohexano-18-crown-6 and two cation exchangers of different acidity, **3** ($\text{p}K_a = 12.5$) and **1b** ($\text{p}K_a = 9.9$) (**Fig. 2**), were tested using three kinds of aqueous phases: NaOH, NaNO_3 , and their combination. These experiments revealed strong SPHE at high alkalinity and moderate ion-pair extraction of sodium nitrate under neutral conditions. Effect of the HA acidity on SPHE and ion-pair extraction was pronounced, phenol **1b** being stronger than fluorinated alcohol **3**. As expected, reverse efficiency order was observed for stripping. Combined extraction of sodium hydroxide and nitrate was demonstrated. The contribution of the NaNO_3 ion-pair extraction to the overall Na^+ extraction was found to be dependent upon HA acidity and concentration in the diluent and was significantly higher for the less acidic **3**. It was shown to be possible to strip the extracted sodium with water. Although the results are promising, the following needs were identified: a) increased solubility of neutral and proton-ionizable extractants, b) higher sodium loading, and c) higher sodium nitrate extraction efficiency.

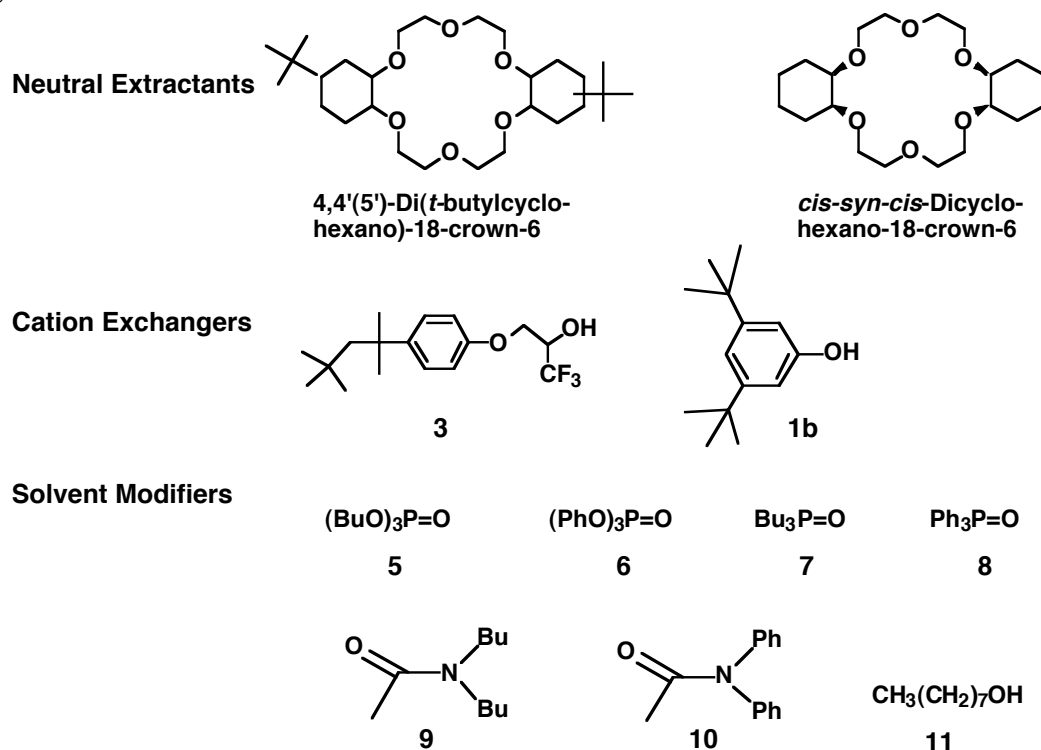


Figure 2. Crown ethers, cation exchangers, and EPD modifiers employed.

Effect of EPD modifiers on NaNO₃ ion-pair extraction. Under neutral conditions, our results with crown ethers demonstrated that certain lipophilic alcohols mildly enhance NaX extraction by anion solvation. Further enhancement of sodium nitrate extraction is desirable, and we proposed the use of modifiers with electron-pair donor (EPD) groups to lower the sodium ion partitioning energy. Detailed investigation of such modifiers was conducted at PNNL. Again, *csc*-DC18C6 (**Fig. 2**) served as a model lipophilic sodium extractant. As documented by numerous crystal structures, encapsulation of Na⁺ into the crown ether cavity often does not saturate its inner coordination sphere, and as a result, Na⁺ readily coordinates additional ligands such as water or organic solvent molecules, oxygen donor anions, or another crown ether molecule to form a sandwich complex. To this end, it seems feasible to exploit this effect by introducing EPD solvating agents into the solvent. A series of EPD modifiers with strong H-bond acceptor abilities was investigated, including tri-*n*-butyl- and triphenylphosphate, tri-*n*-butyl- and triphenylphosphine oxide, *N,N*-di-*n*-butyl- and *N,N*-di-phenylacetamide, and 1-octanol (**Fig. 2**). The extraction behavior of *cis-syn-cis*-di-*tert*-butylcyclohexano-18-crown-6 (*csc*-DC18C6) was characterized by systematic variation of the aqueous-phase sodium nitrate concentration at fixed composition of the organic phases containing 0.2 M EPD modifier and 0.05 M *csc*-DC18C6 in nitrobenzene (NB) (**Fig. 3**). Comparison of the extraction isotherms obtained with and without EPD modifiers in the NB phase indicates that the EPD modifiers moderately increase NaNO₃ extraction by *csc*-DC18C6. 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 found to correlate linearly with the EPD strength of the added modifiers described by the Kamlet-Taft π solvatochromic parameter (**Fig. 4-a**). These results provide the means for the quantitative prediction of the extraction performance of the modified diluent. In the presence of the phenol, the EPD solvating agents slightly lowered NaNO₃ extraction by *csc*-DC18C6 and phenol, which, however, remained higher than NaNO₃ extraction by *csc*-DC18C6 alone. This slight reduction in extraction strength was attributed to the competitive interaction between phenol and EPD modifier.

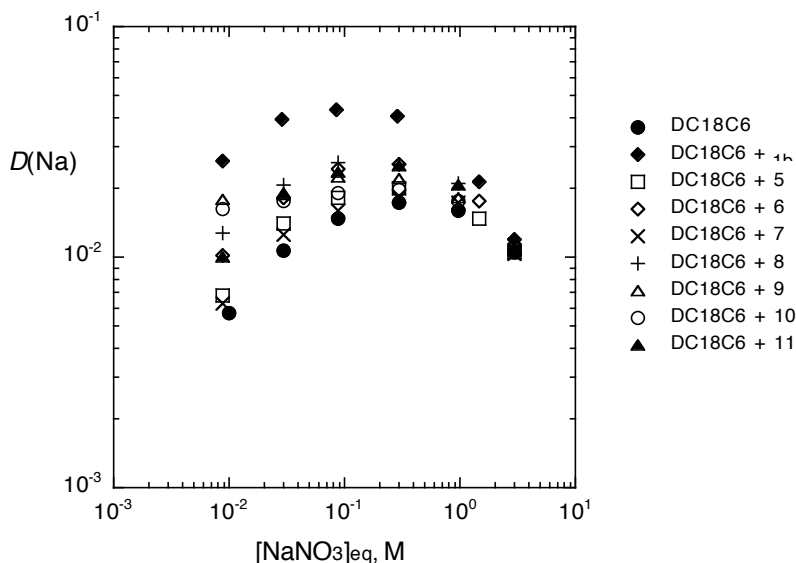


Figure 3. Dependence of NaNO₃ extraction on the aqueous NaNO₃ concentration by *csc*-DC18C6 in NB with and without solvent modifier.

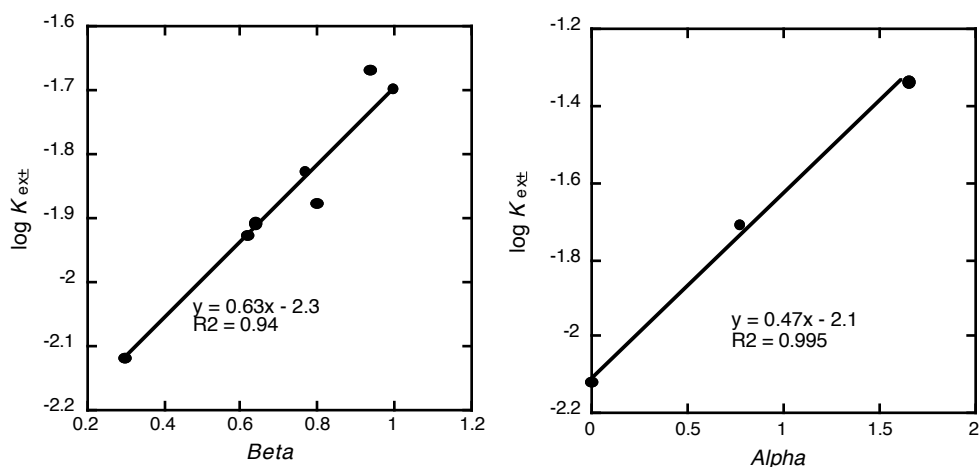


Figure 4. Dependence of NaNO_3 extraction by *csc-DC18C6* in NB on a) basicity of the EPD solvent modifier or b) hydrogen-bond donicity of the HBD solvent modifier.

Investigation of hydrogen bonding in ion-pair extraction. Addition of a weak organic acid to an organic phase lowers the anion-partitioning energy barrier based upon an H-bond interaction between the organic acid and the anion. As demonstrated previously, the stability of the anionic solvate formed in the NB phase depends on the $\text{p}K_{\text{a}}$ of the organic acid. Quantitative assessment of this effect on the NaNO_3 extraction was conducted employing solvating agents **1b** and **11** possessing different abilities to donate an H-bond as given by the solvatochromic parameter π . 1-Octanol **11** also exhibits EPD properties similar to those of EPD modifiers discussed above, and phenol **1b** is a weak EPD similar to that of NB by itself. The extraction behavior of *csc-DC18C6* was characterized by systematic variation of the aqueous-phase sodium nitrate concentration at fixed composition of the NB phases containing 0.2 M **1b** or **11** and 0.05 M *csc-DC18C6*. 1-Octanol **11** exhibited only marginal enhancement of NaNO_3 extraction, on par with the EPD modifiers tested. Significant extraction enhancement was observed with the phenol **1b**, which surpassed the performance of the EPD solvating agents. The distribution data were fit using the SXLSQI modeling program. Values of $\log K_{\text{ext}}$ exhibited a linear dependence on π (Fig. 4-b).

Understanding the effect of an HBD modifier on ion-pair extraction involves assessment of many different processes such as H-bonding with the anion, aggregation, and solvation of the free extractant and its cationic complex. While EPD properties of the solvent modifier are important in solvation of the complex cation, solvation of the free crown ether is based upon specific H-bond interactions with the HBD groups of the modifier. Known examples of similar solvation phenomena include: hydration of crown ethers; formation of phenol-crown ether H-bond-based aggregates in the solid state, influencing the conformation of the macrocycle; and the reverse-phase HPLC separation of phenol and its derivatives, in which the addition of 18-crown-6 to the mobile phase led to a decrease in retention time via complexation between the hydroxy compounds and the crown ether. This H-bonding of the HBD modifier to the oxygen donor atoms of the crown ether could potentially compete with metal ion interaction and partially suppress the gain in extraction due to favorable anion solvation by HBD modifier.

To probe H-bonding interactions in the NB extraction phase, an IR investigation of the O–H bonds of phenol and water in NB in the presence of free or Na⁺-loaded crown ether *csc*-DC18C6 is under way. A series of FTIR spectra of the water-washed solutions of phenol **1b** in the 0.05–0.8 M concentration range were acquired. Phenol **1b** exhibited no self-aggregation in NB, as no signal broadening, position shift, or appearance of new bands was found for the narrow band of its O–H group. In agreement with literature reports, the free crown ether *csc*-DC18C6 in NB without phenol was found to exist in the hydrated form. The broad water O–H band in the 3200–3700 cm⁻¹ region has three maxima corresponding presumably to a crown-water adduct in which the water molecule is coordinated to the crown ether in mono- and bidentate fashion (**Fig. 5**). Loading of the crown ether with Na⁺ ion slightly shifts, and increases the relative intensity of, the high-energy water O–H band at 3665 cm⁻¹. Addition of the phenol to the Na⁺-loaded crown ether causes the appearance of the new band at 3250 cm⁻¹ due to the H-bonding of the phenolic O–H group to the NO₃⁻ anion. This phenol-nitrate interaction lowers the energy barrier of the nitrate partitioning into NB and boosts the ion-pair sodium extraction.

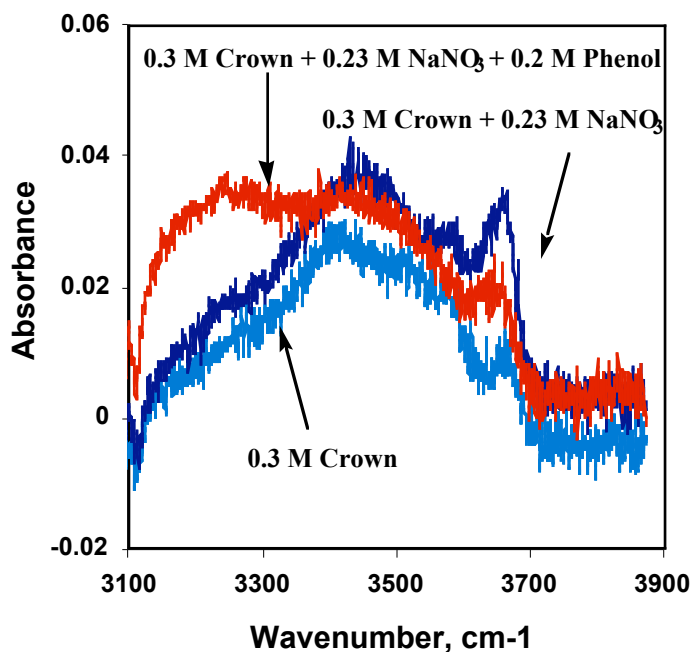


Figure 5. IR spectra of the O–H bond of phenol and water in NB in the presence of *csc*-DC18C6 and/or NaNO₃.

Planned Activities

Pseudo Hydroxide Extraction. In the renewal three-year funding period, principles of ion recognition will continue to be researched toward discovery of liquid-liquid extraction systems that selectively and efficiently separate sodium hydroxide, sodium nitrate, and other bulk salts from the waste. Successful approaches to sodium hydroxide separation that were previously discovered in this project will be expanded by further efforts to understand underlying features of

the controlling equilibria and to investigate alternative extractants. The future work will employ the novel concept of PHE by very weakly acidic proton-ionizable organic acids that function by cation exchange at elevated pH values. Such compounds include fluorinated alcohols and phenols. Measurements of the actual acidity of the -OH exchange groups are in progress through analysis of extraction data so as to establish a clear relationship with extraction strength. Preliminary results have shown that such a relationship exists, and future work will entail completing this study as further enhanced by inclusion of proton-affinity calculations. The resulting structure-function relationship will potentially allow prediction of the behavior of untested cation exchangers. An understanding of the factors governing the selectivity of PHE will also be sought, particularly in relation to rejection of ^{137}Cs and other radionuclides.

During previously performed PHE experiments using 1-octanol as diluent, changes in the relative organic-to-aqueous (o/a) phase ratio were observed, especially at ROH concentrations that would be required for industrial applications. This phenomenon is presumed to be due to transfer of significant amounts of water into the organic phase. Such changes in the o/a ratio would be highly undesirable in practical applications of PHE. In the coming year, experiments will be performed to examine the PHE chemistry in aliphatic hydrocarbon diluents. Typically, the solubility of PHE reagents such as 3,5-di-*tert*-butylphenol in aliphatic hydrocarbons is relatively low. However, preliminary results indicate the solubility can be significantly increased by adding 1-octanol as a solvent modifier. Other suitable modifiers may also be considered. Our strategy will be to add sufficient modifier (e.g., 1-octanol) to achieve the desired solubility of the PHE extractant, while otherwise maintaining the bulk properties of the unmodified hydrocarbon diluent. In this way it is anticipated that water extraction will be suppressed due to the hydrophobic nature of the aliphatic hydrocarbon diluent, which in turn will greatly reduce the tendency for changes in the o/a phase ratio. Experiments will be designed to test this hypothesis.

The diluent dependence of PHE will also be investigated in the context of the extractant structure. Although the donor-acceptor properties of 1-octanol are well-suited for PHE, its ability to solubilize an appreciable concentration of water and its high viscosity are undesirable. In this investigation, several extractants, examples of which are found in **Fig. 2**, will be examined. Their solubility in different diluents will be surveyed and preliminary PHE tests conducted to assess the achievable loading. The selected extractant-diluent candidates will be subjected to distribution analysis and evaluation of selectivity over Cs^+ and TcO_4^- . The distribution behavior will be correlated with the predictive values of the extractants, such as $\text{p}K_a$ obtained in 1-octanol. Such nonpolar diluents as 1,3-diisopropylbenzene, *o*-xylene, and *n*-dodecane, will be examined.

Synthesis of substituted crown ethers for sodium binding. For both synergized pseudo hydroxide extraction and ion-pair extraction systems, crown ethers with stronger sodium ion binding strength than the currently examined DtBuC18C6 and *csc*-DC18C6 will need to be examined. Some of the additional issues that will need to be addressed are adequate solubility and lipophilicity, and sufficient sodium selectivity to minimize the co-extraction of potassium and especially cesium.

With regard to increasing overall binding strength, crown ethers possessing the decalino substituent will be synthesized. Kobirot et al. have demonstrated the use of the decalino group (**Fig. 6**) to gain an order-of-magnitude increase in both sodium and potassium ion binding strength. The rigidity and steric bulk of the decalino groups are believed to impart a cylindrical shape to the crowns, which in turn is believed to increase the selectivity for the metal ion that the crown cavity size is best matched with. Thus, potassium binding strength and selectivity increases in the order TD18C6 > DD18C6 > DC18C6. With smaller ring-size crowns such as the

16-crown-5 family, the bulk and rigidity provided by the didecalino subunit groups will be synthesized toward improved selectivity *for sodium* over potassium and cesium by blocking complex formation with these larger ions.

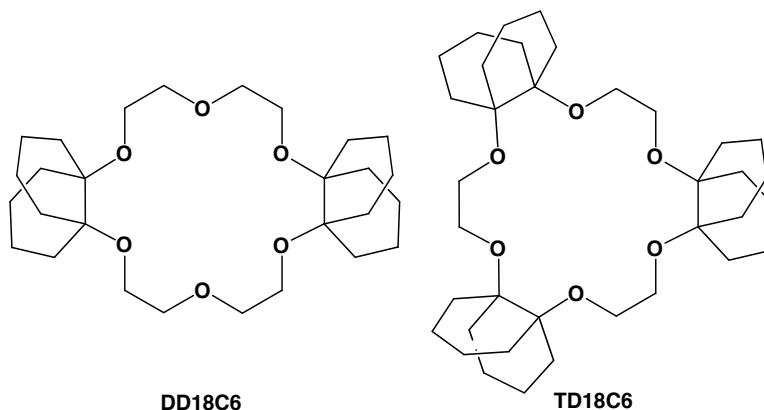


Figure 6. Didecalino- and tridecalino-18-crown-6 ethers.

Another promising candidate 16-crown-5 for investigation is one that possesses the tetramethylethoxy moiety (derived from pinacol) that can additionally be substituted with alkyl chains for greater lipophilicity, as is shown in the structure for R,R'-DTM16C5B (**Fig. 7**). Members of this family where R' = H, and R = H, or $n\text{-C}_{14}\text{H}_{29}$, have been previously prepared and shown to have good sodium/potassium selectivity and should also possess good Na binding strength. The di-tetramethylethoxy crowns (such as R,R'-DTM16C5B) have the advantage over the didecalino crowns that the precursor diol, pinacol, is relatively inexpensive (<50 cents per gram in bulk), and procedures for crown syntheses using pinacol are well established.

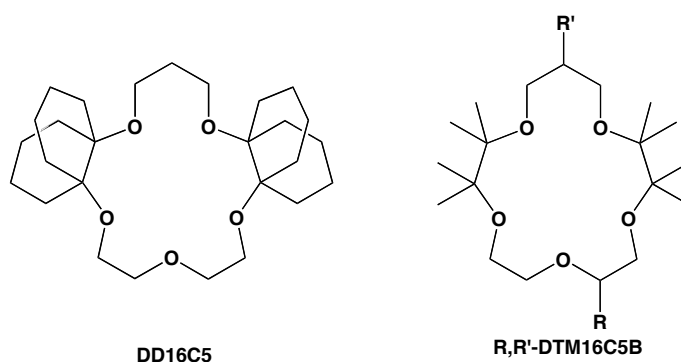


Figure 7. Sodium-selective crowns that will be investigated.

Synthesis and evaluation of proton-ionizable sodium receptors. With the retirement of Professor Marchand from UNT in late 2003, the design and synthesis proton-ionizable sodium receptors will be undertaken at ORNL. Phenols that project an ionizable -OH group into the

binding cavity are obvious candidates. Other possibilities include 16-crown-5 ethers such as those substituted with both a hydroxyl and an electron-withdrawing trifluoromethyl group at the central carbon of the propoxy linkage (see **Fig. 8**). These crowns would be accessible by cyclizing with methallyl chloride to afford the methyleno crown, converting the methyleno group to a ketone via ozonolysis, and reacting the ketone with trifluoromethyl(trimethyl)silane to afford the trifluoromethyl-substituted alcohol. An alternative route could involve a cyclization reaction between the diol precursor and 1-chloro-2,3-epoxy-2-trifluoromethylpropane.

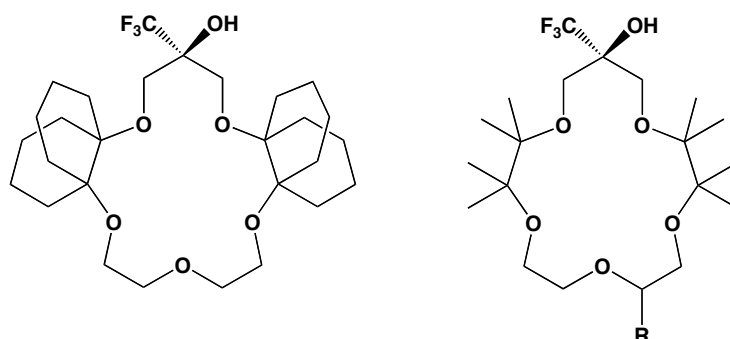


Figure 8. Proton-ionizable 16-crown-5 ethers.

Synergized Pseudo Hydroxide Extraction. Crown ethers will be examined as synergists for PHE, giving rise to SPHE. The crowns boost the extraction power of the cation-exchanger compounds, provide cation selectivity, and reduce viscosity and water extraction. Accordingly, SPHE systems may be a useful variant of the PHE concept for sodium hydroxide separation. Additionally, we propose that a single SPHE system could remove sodium hydroxide together with bulk salt components in the waste. This is a particularly challenging and important question, not only for tank-waste cleanup, but for other industrial or analytical uses, as many applications could emerge from a method to cleanly desalt solutions without removing other components. Involving a combination of a crown ether and a weakly proton-ionizable organic acid, SPHE will be systematically related to equilibrium constants already obtained. Based on recent experiments, this approach will require a more strongly binding crown ether for sodium ion, and synthesized crown ethers (e.g., see **Fig. 7**) will be examined in extraction studies in comparison with commercially available crowns such as DC18C6 and DtBuCH18C6. Particular attention will be paid to maximizing the solubility of the crown ether and the sodium complexes formed during extraction, as it would be desirable to attain 1 M sodium concentration in the solvent phase. The effective acidity of HA will be tuned to have a proper balance of extraction and stripping for the diluent system employed. Study of the speciation of the selected organic acids as cation exchangers and solvating agents in the solvent phase will be undertaken using FTIR, Raman, and NMR spectroscopic techniques. These spectroscopic studies will probe such equilibrium processes as aggregation of the organic acid and its interaction with the donor atoms of the neutral sodium receptor and with anions via H-bonding. Spectral results will be correlated with independently determined extraction results.

Ditopic Pseudo Hydroxide Extraction. As new ionizable lariat ethers (e.g., **Fig. 8**) become available through synthesis, extraction studies in FY 2006 will focus on their separation properties. The primary goal of these extraction experiments will be to demonstrate that PHE is operating and to determine whether the ditopic receptors offer advantages over the simpler SPHE

systems. The approach used will entail measuring the sodium distribution ratio as a function of aqueous alkalinity and comparing the observed behavior to that of control systems composed of analogous pairs of neutral crown ether and lipophilic weak acid.

Ion-Pair Extraction of Sodium Using Crown Ethers. Major emphasis will be devoted to the question of separating sodium nitrate and other bulk salts from the waste via ion-pair extraction using crown ethers. We propose that means may be found to remove either pure salts such as sodium nitrate or to effect a bulk removal of the major forms of sodium. The most promising crown ethers have so far been commercially available ones, which is helpful, but these still do not possess sufficient sodium binding strength, making that a key issue for future synthesis efforts. Thus, experiments will be carried out using non-ionizable crown ethers such as shown in **Fig. 7**. Solubility, viscosity, and molar-volume properties of crown ethers represent other salient issues for study, as well as the change in selectivity as high loading of sodium salts is achieved. Anion selectivity will be of critical importance, as it will be the object to level the selectivity so that a range of the major sodium salts in the waste can be extracted with approximately equal effectiveness. Fundamental approaches to manipulating anion selectivity include a) varying bias by using an alcohol diluent or alcohol diluent modifier that has strong HBD strength, b) designing the crown ether so that an incompletely encapsulated sodium ion can still form contact ion pairs, and c) adding an anion receptor to the solvent. Experiments will be conducted over a range of crown ether concentrations extending to its maximum, subject to viscosity and solubility limitations at 25 °C. In all of the experiments, NaX (X = OH⁻, NO₃⁻, NO₂⁻, etc.) extraction isotherms will be determined and rejection of TcO₄⁻ ion evaluated according to the usual separation factor D_{Na}/D_{Tc} . The bias of the solvent system toward anions will be modulated by addition of selected fluorinated alcohols, either as diluent modifiers or (depending on viscosity) as pure diluents, and the separation factor D_{Na}/D_{Tc} will be related to the apparent acidity of the hydroxy modifiers. If promising selectivity is obtained, more detailed studies including computer modeling will be carried out.

Tests with Tank Waste. Experiments on actual waste will seek to confirm that the expected chemical behavior of sodium separation systems extends accurately to real-world solutions. Resulting data represent valuable feedback that the principles employed are sound, laying the intellectual foundation for future applied efforts to develop working separation systems. Specific tank-waste samples to be used in testing sodium recovery via PHE methodology will be identified. Archived samples at the Hanford 222-S Laboratory and at PNNL's Radiochemical Processing Laboratory (RPL) will be assessed for suitability in the testing effort. Samples from double-shell tanks that have large sodium inventories would be desirable. Details such as permissions and shipping will be addressed. Upon obtaining a suitable candidate waste sample of known composition, a batch contacting test will be planned. The test will be designed both to provide a confirmation of the scientific principle of PHE under realistic conditions and to evaluate performance for purposes of transitioning data to engineering users. PHE isotherms at 25 °C for sodium and other important ions will be obtained for appropriate extraction and stripping conditions. McCabe-Thiele diagrams will be constructed as an aid in defining the conditions of the test, especially the O/A phase ratios.

In FY 2006, experiments with actual Hanford tank waste will be initiated. The primary focus of these experiments will be to confirm the ability of the formulated solvent to extract sodium hydroxide from the actual waste and to be appropriately stripped within the test parameters. The behavior of minor, but significant, anions will be evaluated, including chromate, phosphate, and sulfate, which can have significant adverse effects on vitrification processes. The

key analytes to be followed will include Na, NO_3^- , NO_2^- , PO_4^{3-} , SO_4^{2-} , CrO_4^- , Al, ^{137}Cs -137, and alpha emitters. In selected experiments, the solutions will be analyzed for ^{99}Tc and ^{90}Sr .

In FY 2007, a real waste test at PNNL will encompass assessment of the performance of the sodium ion-pair and SPHE extraction as corresponding solvent systems will be developed based on newly prepared neutral extractants.

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Information Access

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