

# FINAL REPORT

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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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## Executive Summary

The exciting results obtained in the first three years of this project have met the goals set forth in the original proposal submitted in April, 1997. Overall, this research period was intended to provide the scientific foundation upon which the feasibility of liquid-liquid extraction chemistry for bulk reduction of the volume of high-activity tank waste can be evaluated. Primary focus has been on sodium hydroxide separation, with potential Hanford application. Value in sodium hydroxide separation can potentially be found in alternative flowsheets for treatment and disposal of low-activity salt waste. Additional value can be expected in recycle of sodium hydroxide for use in waste retrieval and sludge washing, whereupon additions of fresh sodium hydroxide to the waste can be avoided. Potential savings are large both because of the huge cost of vitrification of the low-activity waste stream and because volume reduction of high-activity wastes could obviate construction of costly new tanks. Toward these ends, the conceptual development begun in the original proposal was extended with the formulation of eight fundamental approaches that could be undertaken for extraction of sodium hydroxide. The eight approaches may be divided into two categories according to whether the underlying mechanism is ion-pair extraction or cation exchange. Four of the eight approaches were examined in detail experimentally. Ion-pair extraction involves transfer of sodium and hydroxide ions to the organic solvent and was found to be weak in the systems examined, even when enhanced with a crown ether. Termed "pseudo hydroxide extraction," the cation-exchange approach employs weak hydroxy acids such as phenols or fluorinated alcohols as extractants. At the elevated pH values characteristic of alkaline tank waste, the hydroxy acids give up their protons in exchange for sodium ions. Contact of the resulting sodium alkoxide- or phenoxide-containing solvent with water results in the water giving up protons in exchange for the organic-phase sodium ions to yield an aqueous sodium hydroxide solution and simultaneous regeneration of the neutral phenol or alcohol in the organic phase. Hence, there is no net consumption of reagent chemicals. Since only hydroxide *equivalents* and not actual hydroxide ions are extracted, the process has been termed pseudo hydroxide extraction. It was found that pseudo hydroxide extraction is chemically viable and economically attractive for process purposes, and a patent has been granted. A series of experiments demonstrated the concept with both selected phenols and novel fluorinated alcohols. It was shown that the separation of sodium hydroxide is efficient and selective in competition with other salts present in alkaline tank waste, and over 90% of the total hydroxide can be extracted. The results were persuasive enough that follow-on funding from the Tanks Focus Area via the Efficient Separations and Processing Crosscutting Program was awarded to carry out applied research toward the development and testing of a process flowsheet on actual tank waste in FY01 and FY02. In collaboration with Prof. Alan P. Marchand, Univ. of N. Texas, crown ethers have been shown to strongly enhance pseudo hydroxide extraction by fluorinated alcohols. Potentially, crown ethers could allow control of cation selectivity, use of weaker hydroxy acids, and greater flexibility in the choice of the organic diluent. Synthetic routes to novel cage-annulated crown ethers have been developed.

In the renewal period, efforts will be extended toward the examination of the question of efficient extraction of sodium nitrate, alone or with sodium hydroxide. Experiments will be carried out to deepen understanding of the mechanism of sodium extraction by hydroxy acids, crown ethers, and their combinations. Synthesis of novel ditopic crown ethers will also be attempted to explore two of the eight approaches to sodium hydroxide extraction that have not yet been examined.

## Research Objectives

This research has focused on new liquid-liquid extraction chemistry applicable to separation of major sodium salts from alkaline tank waste. It was the overall goal to provide the scientific foundation upon which the feasibility of liquid-liquid extraction chemistry for bulk reduction of the volume of tank waste can be evaluated. Sodium hydroxide represented the initial test case and primary focus. It is a primary component of the waste<sup>1</sup> and has the most value for recycle.<sup>2</sup> A full explanation of the relevance of this research to USDOE Environmental Management needs will be given in the Relevance, Impact, and Technology Transfer section below. It should be noted that this effort was predicated on the need for sodium removal primarily from low-activity waste, whereas evolving needs have shifted attention to volume reduction of the high-activity waste. The results of the research to date apply to both applications, though treatment of high-activity wastes raises new questions that will be addressed in the renewal period.

Toward understanding the extractive chemistry of sodium hydroxide and other sodium salts, it was the intent to identify candidate extractants and determine their applicable basic properties regarding selectivity, efficiency, speciation, and structure. A hierarchical strategy was to be employed in which the type of liquid-liquid-extraction system varied in sophistication from simple, single-component solvents to solvents containing designer host molecules.

As an aid in directing this investigation toward addressing the fundamental questions having the most value, a conceptualization of an ideal process was advanced. Accordingly, achieving adequate selectivity for sodium hydroxide represented a primary goal, but this result is worthwhile for waste applications only if certain conditions are met. Based on related alkaline-side solvent-extraction processes recently developed at Oak Ridge and Argonne national laboratories,<sup>3-6</sup> Fig. 1 depicts an idealized extraction cycle, using sodium hydroxide as an example. Waste containing NaOH together with other salts and residual radioactivity is passed through a multi-stage, counter-current contacting device (e.g., mixer-settlers, centrifugal

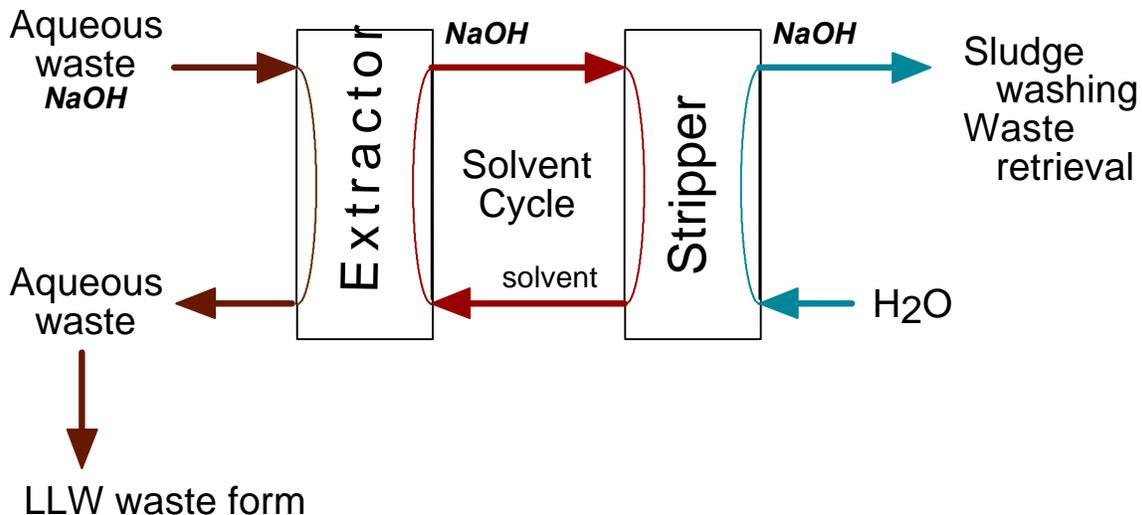


Figure 1. "Ideal" extraction cycle depicting the removal of NaOH from alkaline tank waste.

contactors, or hollow fiber dispersionless contactors) wherein NaOH is transferred to the solvent containing one or more extractants in a water-immiscible diluent. The loaded solvent enters a multi-stage stripping section in which the NaOH is transferred to water, allowing the solvent to be recycled. The treated aqueous waste depleted of NaOH then goes to waste-immobilization processes (current Hanford plan is vitrification). The separated NaOH can then be used for further waste processing. Ideally, the entire process would require no adjustment of the waste stream, consume no chemicals, and add nothing to either the exiting depleted waste or NaOH product streams. Use of water for stripping is highly compatible with such a process, necessitating extractants that release the NaOH upon contact with water. Except for perhaps simple evaporation, no further separation steps would then be needed to put the obtained NaOH product to direct use.

Hence, extractant systems that are particularly attractive have adequate selectivity for NaOH (or other target salt), good loading directly from the waste, and good stripping into water. These criteria were the major ones applied in this research. However, it should be kept in mind that practical extraction systems must ultimately possess other characteristics such as readily available and economical extractants, good phase disengagement, good kinetics, low loss of the extractant to the aqueous phase, resistance to formation of third phases, and stability toward alkaline conditions. Radiation stability would only be an important criterion if the fission product  $^{137}\text{Cs}$  has not been removed in prior steps.

## Methods and Results

### Eight Basic Extractive Approaches to NaOH Separation

Since the chemical literature offers little information on the liquid-liquid extraction of NaOH, we made at the outset no presumption as to the best practical method but rather considered a hierarchy of applicable fundamental chemical processes. These rely on principles of solvation, acid-base reactions, and host-guest chemistry. Table 1 lists eight basic approaches that one might take.<sup>7</sup> The first five approaches entail ion-pair extraction processes in which the extracted cation  $M^+$  and anion  $X^-$  may either be solvated or complexed. The receptor in each case is indicated by a circle without implying any particular topography. The last three approaches entail an acid-base reaction to transfer a hydroxide equivalent to the solvent with or without a receptor for the cation  $M^+$ . The cation exchanger is depicted with an alkyl tail to indicate lipophilicity. As written for all cases except 5 and 8, the product cation and anion species given in each case are dissociated in the solvent, implying ideally little or no influence of the cation and anion upon one another. However, secondary effects such as ion pairing or aggregation can be expected to influence ion selectivity.

The simplest approach in concept entails choice of a water-immiscible solvent that by itself effects the extraction of NaOH from an aqueous mixture of salts (Table 1, Case 1). The solvent molecules must therefore completely accommodate the  $\text{Na}^+$  cation and  $\text{OH}^-$  anion. For  $\text{Na}^+$ , this means supplying electron-pair donor (EPD) groups for coordination.<sup>8</sup> Likewise for  $\text{OH}^-$ , hydrogen-bond donor (HBD) groups are needed.<sup>9</sup> Since the thermochemical radii of both ions

Table 1. Fundamental Approaches Applicable to NaOH Separation using Host-Guest and Liquid-Liquid Extraction Principles

| Case | System                             | Organic-phase species                       |
|------|------------------------------------|---|
| 1    | No receptors                       | $M^+ + X^-$                                 |
| 2    | Cation receptor                    | $\langle M^+ \rangle + X^-$                 |
| 3    | Anion receptor                     | $M^+ + \langle X^- \rangle$                 |
| 4    | Cation receptor + Anion receptor   | $\langle M^+ \rangle + \langle X^- \rangle$ |
| 5    | Ditopic ion-pair receptor          | $\langle M^+ X^- \rangle$                   |
| 6    | Cation exchanger                   | $\sim\sim\sim$                              |
| 7    | Cation exchanger + Cation receptor | $\sim\sim\sim \quad \langle M^+ \rangle$    |
| 8    | Ditopic cation exchanger-receptor  | $\langle M^+ \rangle - A^-$                 |

are small [ $r_{Na^+} = 0.102$  nm and  $r_{OH^-} = 0.133$  nm],<sup>10</sup> the EPD and HBD groups must be significantly stronger than the H<sub>2</sub>O molecules in the source phase for efficient ion partitioning. This is difficult to achieve in a water-immiscible liquid, and indeed, positive standard Gibbs energies of ion transfer<sup>10</sup> lead one to expect weak extraction (Case 1).

Extraction can be enhanced by use of a cation receptor (Case 2), anion receptor (Case 3), both cation and anion receptors in synergistic combination (Case 4), or a ditopic ion-pair receptor (Case 5). For present purposes, a receptor may be defined as a molecule having multiple EPD or HBD groups for partial or complete encapsulation of guest ions. With use of any receptor, the Gibbs energy of complexation augments the Gibbs energy of ion transfer, thereby boosting overall extraction strength.<sup>11</sup> The enhancement can also be made selective. Receptors for Na<sup>+</sup> and other alkali cations are plentiful among crown ethers,<sup>12</sup> cryptands,<sup>13</sup> and calixarenes,<sup>14</sup> for example.<sup>15-17</sup> Receptors for anions are less plentiful, and OH<sup>-</sup> ion has yet to be targeted.<sup>18</sup> Naturally, strong HBD groups directed at the oxygen atom would be favorable, possibly together with an EPD group directed to interact with the hydrogen atom. Ion-pair receptors are still rare, but a few designed examples have been reported.<sup>19</sup>

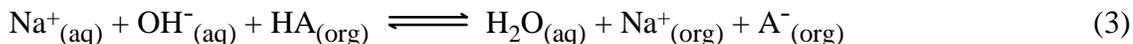
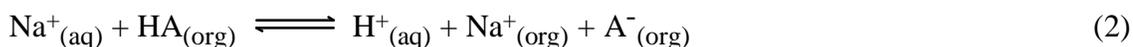
As ion-pair extraction processes, Cases 1 to 5 in Table 1 can be adapted well to cyclic sodium hydroxide extraction and stripping. Taking Case 2 as an example, the aqueous cation (M<sup>+</sup>) and anion (X<sup>-</sup>) are transferred to a solvent phase, where the cation is then complexed with a crown ether:



It may be expected from eq. 1 that high Na<sup>+</sup> concentration drives extraction, and extraction may be subsequently reversed by contacting the solvent with a low-salt aqueous solution, ideally water. Such a cycle is ideal for treatment of high-salt wastes, such as alkaline high-level tank waste, and use of water for stripping introduces no new chemicals or dissolved solids to the process.<sup>3-5</sup>

It is likely that a successful approach employing ion-pair extraction would require use of an anion receptor to obtain sufficient selectivity for OH<sup>-</sup> ion. When the anion is solvated as in Cases 1 and 2 in Table 1, one generally observes Hofmeister-type selectivity.<sup>20</sup> That is, extraction strength is biased in favor of larger, more charge-diffuse anions.<sup>9</sup> Thus, the abundant anion nitrate would be preferentially extracted. In the event that anti-Hofmeister behavior could be demonstrated, fluoride extraction would compete.<sup>9</sup> Although this would be desirable in a scheme to separate nitrate or possibly fluoride salts, a bias-type selectivity would not provide OH<sup>-</sup> selectivity. As mentioned above, a recognition approach would entail building a molecule that directs appropriate HBD and EPD groups in a geometry complementary to OH<sup>-</sup>.

Ironically, cation exchange provides an alternative approach for an effective extraction of OH<sup>-</sup> ion.<sup>7,21</sup> Possessing exchangeable acidic protons, such extractants (HA) have many variants, but all function according to a common exchange process, which (neglecting complications due to aggregation and ion pairing) may be written most simply as eq 2 or its equivalent in terms of OH<sup>-</sup> (eq 3):

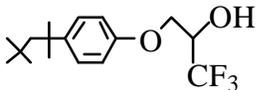
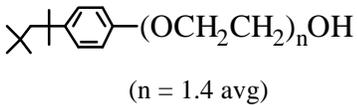
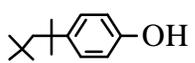
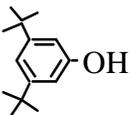
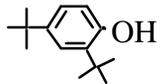
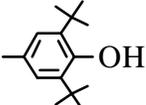
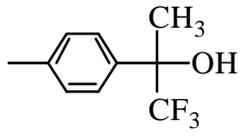
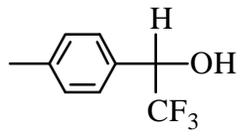
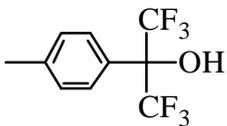


The reverse reaction affords recovery of sodium hydroxide upon stripping with water, whereby HA returns to its protonated form in the organic phase. When used in tandem, the forward and reverse steps constitute a cyclic process affording the transfer of alkali metal hydroxide from an aqueous mixture into water. To function efficiently for hydroxide recovery, HA must possess weak acidity ( $pK_a$  ca. 9-14) so that contact of the loaded solvent with water readily regenerates the protonated form of the extractant. Surprisingly, a single study involving phenols represents the only citation of such a process in the literature.<sup>22,23</sup> As before, a cation receptor may be added to the solvent as a synergist<sup>24</sup> for the cation exchanger (Case 7), and one may envision that the cation receptor could also contain the cation-exchange functionality in the same molecule (Case 8). Whereas the desired extraction-stripping cycle is again possible using water for stripping, the major advantage of any of the cation-exchange approaches is the potentially high selectivity for OH<sup>-</sup> ion. Only highly basic anions can undergo the acid-base process given in eq. 3.

### Pseudo Hydroxide Extraction Approach to NaOH Separation

Pseudo hydroxide extraction, Case 6 in Table 1, was examined early in the project and indeed found to be a highly promising approach to NaOH separation from alkaline salt solutions.<sup>7,21</sup> Not only was the principle shown to be sound, but the reagents are very economical for process use. Table 2 lists the fluorinated alcohols and alkylated phenols used as extractants in the study. In the first set of experiments, equal volumes of an organic phase consisting of 0.2 M extractant dissolved in 1-octanol and an aqueous phase containing varying concentrations of sodium nitrate or sodium hydroxide and ca. 10<sup>-9</sup> M <sup>22</sup>Na tracer were

Table 2. Compound Key for Hydroxy-Acid Extractants

| Compound  | Structure   |
|---|---|
| 1H,1H,9H-hexadecafluorononanol ( <b>1a</b> )                              | $\text{HF}_2\text{C}(\text{CF}_2)_7\text{CH}_2\text{OH}$  |
| 1H,1H-perfluorononanol ( <b>1b</b> )                                      | $\text{F}_3\text{C}(\text{CF}_2)_7\text{CH}_2\text{OH}$   |
| 3-(perfluorohexyl)propanol ( <b>1c</b> )                                  | $\text{F}_3\text{C}(\text{CF}_2)_5(\text{CH}_2)_3\text{OH}$   |
| 1,1,1-trifluoro-3-(4- <i>tert</i> -octylphenoxy)-2-propanol ( <b>2a</b> ) |                  |
| Triton <sup>®</sup> X-15 surfactant ( <b>2b</b> )                         | <br>(n = 1.4 avg) |
| 4- <i>tert</i> -octylphenol ( <b>3a</b> )                                 |                  |
| 3,5-di- <i>tert</i> -butylphenol ( <b>3b</b> )                            |                 |
| 2,4-di- <i>tert</i> -butylphenol ( <b>3c</b> )                            |                |
| 2,6-di- <i>tert</i> -butyl-4-methylphenol ( <b>3d</b> )                   |                |
| 1,1,1-trifluoro-2-(4-methylphenyl)-2-propanol ( <b>4a</b> )               |                |
| 4-methyl- $\alpha$ -(trifluoromethyl) benzyl alcohol ( <b>4b</b> )        |                |
| 1,1,1,3,3,3-hexafluoro-2-(4-methylphenyl)-2-propanol ( <b>4c</b> )        |                |

equilibrated as described earlier.<sup>7,21</sup> A well-studied water-immiscible alcohol, 1-octanol, was chosen as the diluent to provide a suitable solvation environment for organic-phase sodium salts, as few alternative non-alcohol diluents compare in ability to solvate both cations and anions.<sup>8</sup> Plots of the equilibrium concentration of sodium in the organic phase vs. the equilibrium concentration of NaOH or NaNO<sub>3</sub> in the aqueous phase are shown in Fig. 2.

A salient feature of these data is the markedly different behavior observed for extraction of sodium from aqueous NaOH solutions as opposed to extraction from aqueous NaNO<sub>3</sub> solutions. As shown in Fig. 2, most of the tested hydroxy acids significantly enhanced the extraction of sodium from aqueous NaOH over that which is extracted by 1-octanol alone. In contrast, little or no enhancement of sodium extraction from aqueous NaNO<sub>3</sub> solution by the same compounds may be seen, an encouraging demonstration of the specificity of the tested hydroxy compounds toward hydroxide, albeit under non-competitive conditions. Discussion of the nature of the curves with respect to underlying equilibria and speciation will be given further below.

Comparative data for the efficacy of the various hydroxy acids in extraction of NaOH together with data demonstrating the recovery of NaOH are given in Table 3. In the experiments, equal volumes of an organic solution containing 0.2 M hydroxy acid in 1-octanol and an aqueous solution containing 7.0 M NaOH and ca. 10<sup>-9</sup> M <sup>22</sup>Na tracer were equilibrated at 25 °C. Following extraction, the loaded solvents were stripped with an equal volume of pure water. Parallel experiments were performed with 7.0 M NaOH that did not contain <sup>22</sup>Na tracer, and the total concentration of base in the aqueous strip solution was determined by titration. This concentration corresponds to the concentration of OH<sup>-</sup> in the strip solution, provided that partitioning of sodium alkoxide or phenoxide salts to the strip phase is negligible, which will be shown is true below. The data collectively demonstrate near-quantitative recovery of sodium hydroxide into water for all solvents tested, as evidenced by the near-unity values of the ratio

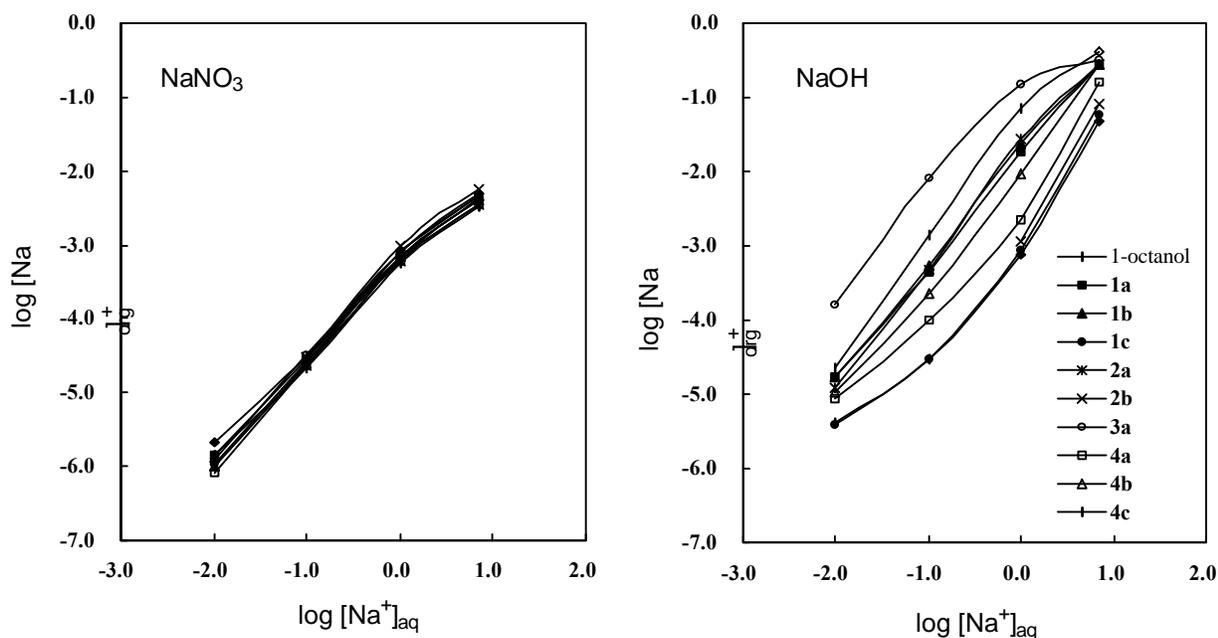


Figure 2. Equilibrium isotherms for the extraction of sodium salts by hydroxy acids.

Table 3. Extraction and Stripping of Hydroxide Ion from Aqueous 7.0 M NaOH<sup>a</sup>

| Compound  | [Na] <sub>extr</sub> <sup>b</sup><br>(M) | [Na] <sub>strip</sub> <sup>c</sup><br>(M) | % strip | [Base] <sub>strip</sub> <sup>d</sup><br>(M) | [Base] <sub>strip</sub> /[Na] <sub>strip</sub> |
|-----------|--|---|---------|---|--|
| <b>1a</b> | 0.29                                     | 0.29                                      | 100%    | 0.30  | 1.0  |
| <b>1b</b> | 0.29                                     | 0.28                                      | 97%     | 0.30  | 1.1  |
| <b>1c</b> | 0.058                                    | 0.058                                     | 100%    | 0.056                                       | 0.97   |
| <b>2a</b> | 0.28                                     | 0.28                                      | 100%    | 0.30  | 1.1  |
| <b>2b</b> | 0.087                                    | 0.087                                     | 100%    | 0.087                                       | 1.0  |
| <b>3a</b> | 0.31                                     | 0.26                                      | 82%     | 0.26  | 1.0  |
| <b>3b</b> | 0.29                                     | 0.26                                      | 91%     | ND  | ND   |
| <b>3c</b> | 0.22                                     | 0.22                                      | 100%    | ND  | ND   |
| <b>3d</b> | 0.049                                    | 0.048                                     | 98%     | 0.056                                       | 1.2  |
| <b>4a</b> | 0.18                                     | 0.18                                      | 100%    | 0.19  | 1.1  |
| <b>4b</b> | 0.29                                     | 0.29                                      | 100%    | 0.28  | 0.97   |
| <b>4c</b> | 0.40                                     | 0.39                                      | 96%     | 0.36  | 0.92   |
| 1-octanol | 0.050                                    | 0.050                                     | 100%    | 0.056                                       | 1.1  |

<sup>a</sup>See text for experimental details. <sup>b</sup>The equilibrium concentration of sodium in the organic phase following extraction. The concentration of fluorinated alcohol or alkylated phenol in 1-octanol was 0.2 M. <sup>c</sup>The equilibrium concentration of sodium in the aqueous strip phase. <sup>d</sup>The equilibrium concentration of titratable base in the aqueous strip phase. ND = Not determined.

[Base]/[Na<sup>+</sup>]<sub>strip</sub>. Consistent with previous results on phenols,<sup>22,23,25</sup> Fig. 2 and Table 3 show that the strength of sodium extraction from NaOH solutions correlates directly with acidity or hydrogen-bond donor strength of the tested hydroxy acids, as perturbed by steric effects. By reference to Fig. 2, relative differences in extraction efficiency for these compounds appear to become more pronounced at hydroxide concentrations less than 1 M, owing to the saturation seen for some compounds and steepened extraction by 1-octanol alone at higher hydroxide concentrations. Appreciable extraction of sodium from 7.0 M NaOH is observed for solvents containing compounds **1a**, **1b**, **2a**, **3a-c**, and **4a-c**, whereas extraction for solvents containing **1c**, **2b**, and **3d** is on the order of that observed for 1-octanol alone. Weak extraction by **1c** and **2b** presumably reflect the absence of electron-withdrawing groups in proximity to their hydroxy protons. The p*K*<sub>a</sub> of **3d** (2,6-di-*tert*-butyl-4-methylphenol) can be estimated to be about 2.5-3 p*K*<sub>a</sub> units higher than that of **3a**,<sup>25</sup> attributable to severe steric inhibition of solvation of the phenoxide by the two *tert*-butyl groups.<sup>25b</sup> The less sterically-congested 3,5-di-*tert*-butyl phenol (**3b**) and 2,4-di-*tert*-butyl phenol (**3c**) are predicted to have p*K*<sub>a</sub> values higher than **3a** but lower than **3d**, and extraction of sodium from 7.0 M NaOH does in fact reveal the expected trend of **3a** > **3b** > **3c** > **3d**.<sup>25a</sup>

Comparison of the data for compounds **4a-c** illustrates “fine tuning” of acidity within a single class of hydroxy acids by variation of the electron-withdrawing ability of a substituent attached to a particular position. In compounds **4a-c**, the substituent -X in the core molecule *para*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C(CF<sub>3</sub>)(X)-OH was respectively varied as -CH<sub>3</sub>, -H, and -CF<sub>3</sub>. The electron-withdrawing effect increases in the order -CH<sub>3</sub> < -H < -CF<sub>3</sub>, and accordingly, the resultant acidity of the

alcohol as reflected by the amount of sodium extracted into the solvent phase ( $[\text{Na}]_{\text{org}}$ , Table 3) increases in that order ( $0.18 < 0.29 < 0.40$ ). Not surprisingly, the stripping efficiency for these compounds (and also phenols **3a-d**) follows the opposite trend of the extraction efficiency. In that the extraction efficiency of **4b** and **4c** is impressive, they are considered promising for practical applications, though the methyl group attached to the 4-position of the aromatic ring should probably be replaced by more bulky alkyl groups for increased lipophilicity.

Additional extractant design principles may be deduced by comparing the observed extraction efficiencies for linear and aryether alcohol extractants. For example, the importance of the proximity of electron-withdrawing fluorine atoms in relation to the hydroxy proton in the structure of linear alcohol extractants can be evaluated by comparing data for fluorononanol **1a-c**. For this series, where only one methylene group separates the fluoroalkyl and hydroxyl moieties, sodium extraction from 7 M NaOH is essentially the same (0.29 M). This observation suggests that substitution of hydrogen for fluorine at the terminal carbon atom (i.e.,  $\text{HF}_2\text{C-}$  vs.  $\text{F}_3\text{C-}$ ) has negligible effect on the extraction behavior of this class of compounds. In contrast, fluorononanol **1c**, with three methylene groups separating the fluoroalkyl and hydroxyl moieties, displays greatly reduced sodium extraction strength (0.058 M sodium in the organic phase).

Similarly, the necessity of a strongly electron-withdrawing  $-\text{CF}_3$  group attached to the alpha carbon (with respect to the  $-\text{OH}$  group) of aryether alcohol extractants is realized by comparing extraction data for compounds **2a** and **2b**. Not surprisingly, the structurally similar compound **2b**, which does not contain a  $-\text{CF}_3$  group, was not very effective. The extraction strength of **2a** is similar to that observed for compounds **1a** and **1b** above, suggesting that the effect of an ether linkage and a single  $-\text{CF}_3$  group in proximity to the  $-\text{OH}$  functionality is comparable to that of multiple fluorination starting at the beta carbon on linear fluorinated alcohols.

The data presented for compound **3a** may be used to compare the new fluorinated extractant **2a** with a structurally similar phenol. While solvents containing **3a** are impressive with respect to sodium extraction, only 82% of the extracted sodium is recovered as the hydroxide salt in a single contact, indicating that the overall efficiency for hydroxide recovery is somewhat diminished compared to tested fluorinated extractants. It may therefore be concluded that **3a** is approaching an upper limit of acidity in terms of efficient recovery of sodium hydroxide. As was demonstrated with phenols **3b-d**, the effective acidity of **3a** could be decreased by moving the bulky alkyl substituents on the aromatic ring closer to the hydroxyl group.<sup>26</sup> However, none of the phenolic species investigated possessed as good a combined extraction and stripping performance as the better-performing fluoroalcohols **1a**, **1b**, **2a**, and **4a-c**.

In order to evaluate extraction selectivity for hydroxide under competitive conditions, the extractants **1a**, **2a** and **3a** at 0.2 M in 1-octanol were equilibrated with aqueous solutions containing high concentrations of competitive anions. Experiments employed solutions containing 1.75 M NaOH (typical of alkaline tank waste) plus either 3.5 M NaCl or 3.5 M  $\text{NaNO}_3$ . A third aqueous solution was a simulant of Hanford tank AW-101 Double-Shell Slurry Feed (DSSF-7).<sup>26</sup> As shown in Table 4, the selectivity for hydroxide separation was very good over other anions. Extraction from the DSSF-7 waste simulant gave very high selectivities over  $\text{Al}(\text{OH})_4^-$  ion with selectivity factors ranging from 280 (**1a**) to 650 (**2a**). Selectivity factors exceeded 20 for the key anion  $\text{NO}_3^-$ . Since Fig. 2 shows that the nitrate extraction is largely due to the background salt extraction by 1-octanol, it may be expected that anion selectivities will improve with use of higher, more practical concentrations of extractant.

Table 4. Equilibrium Organic-Phase Concentrations of Extracted Ions and Hydroxide Selectivity Factors<sup>a</sup>**Aqueous phase: 1.75 M NaOH/3.5 M NaCl**

| Compound  | [Na <sup>+</sup> ] <sub>org</sub> <sup>b</sup> (M) | [OH <sup>-</sup> ] <sub>org, eff</sub> <sup>c</sup> (M) | [Cl <sup>-</sup> ] <sub>org</sub> <sup>d</sup> (M) | a <sub>OH<sup>-</sup>/Cl<sup>-</sup></sub> <sup>e</sup> |
|-----------|--|---|--|---|
| <b>1a</b> | 8.3 × 10 <sup>-2</sup>                             | 8.6 × 10 <sup>-2</sup>                                  | 6.4 × 10 <sup>-3</sup>                             | 28  |
| <b>2a</b> | 9.9 × 10 <sup>-2</sup>                             | 1.2 × 10 <sup>-1</sup>                                  | 6.9 × 10 <sup>-3</sup>                             | 36  |
| <b>3a</b> | 1.8 × 10 <sup>-1</sup>                             | 2.0 × 10 <sup>-1</sup>                                  | 1.2 × 10 <sup>-2</sup>                             | 37  |

**Aqueous phase: 1.75 M NaOH/3.5 M NaNO<sub>3</sub>**

| Compound  | [Na <sup>+</sup> ] <sub>org</sub> <sup>b</sup> (M) | [OH <sup>-</sup> ] <sub>org, eff</sub> <sup>c</sup> (M) | [NO <sub>3</sub> <sup>-</sup> ] <sub>org</sub> <sup>d</sup> (M) | a <sub>OH<sup>-</sup>/NO<sub>3</sub><sup>-</sup></sub> <sup>e</sup> |
|-----------|--|---|---|---|
| <b>1a</b> | 8.6 × 10 <sup>-2</sup>                             | 9.0 × 10 <sup>-2</sup>                                  | 8.5 × 10 <sup>-3</sup>  | 22  |
| <b>2a</b> | 1.1 × 10 <sup>-1</sup>                             | 1.0 × 10 <sup>-1</sup>                                  | 9.3 × 10 <sup>-3</sup>  | 24  |
| <b>3a</b> | 1.8 × 10 <sup>-1</sup>                             | 1.9 × 10 <sup>-1</sup>                                  | 1.6 × 10 <sup>-2</sup>  | 26  |

**Aqueous phase: DSSF-7 simulant**

| Compound (M) | [Na <sup>+</sup> ] <sub>org</sub> <sup>b</sup> (M)     | [K <sup>+</sup> ] <sub>org</sub> <sup>b</sup> (M)                       | [Al <sup>3+</sup> ] <sub>org</sub> <sup>b</sup> (M)     | [OH <sup>-</sup> ] <sub>org, eff</sub> <sup>c</sup> (M)             | [Cl <sup>-</sup> ] <sub>org</sub> <sup>d</sup> (M) | [NO <sub>3</sub> <sup>-</sup> ] <sub>org</sub> <sup>d</sup> (M) |
|--------------|--|---|---|---|--|---|
| <b>1a</b>    | 1.2 × 10 <sup>-1</sup>                                 | 4.6 × 10 <sup>-3</sup>  | 2.0 × 10 <sup>-4</sup>                                  | 1.3 × 10 <sup>-1</sup>  | 3.0 × 10 <sup>-3</sup>                             | 7.8 × 10 <sup>-3</sup>  |
| <b>2a</b>    | 1.5 × 10 <sup>-1</sup>                                 | 6.3 × 10 <sup>-3</sup>  | 1.0 × 10 <sup>-4</sup>                                  | 1.5 × 10 <sup>-1</sup>  | 3.0 × 10 <sup>-3</sup>                             | 7.5 × 10 <sup>-3</sup>  |
| <b>3a</b>    | 1.7 × 10 <sup>-1</sup>                                 | 7.1 × 10 <sup>-3</sup>  | 2.0 × 10 <sup>-4</sup>                                  | 2.0 × 10 <sup>-1</sup>  | 4.2 × 10 <sup>-3</sup>                             | 1.2 × 10 <sup>-2</sup>  |
|              | a <sub>Na<sup>+</sup>/K<sup>+</sup></sub> <sup>e</sup> | a <sub>OH<sup>-</sup>/Al(OH)<sub>4</sub><sup>-</sup></sub> <sup>e</sup> | a <sub>OH<sup>-</sup>/Cl<sup>-</sup></sub> <sup>e</sup> | a <sub>OH<sup>-</sup>/NO<sub>3</sub><sup>-</sup></sub> <sup>e</sup> |  |   |
| <b>1a</b>    | 3.5  | 280   | 2.5   | 35  |  |   |
| <b>2a</b>    | 3.2  | 650   | 3.0   | 42  |  |   |
| <b>3a</b>    | 3.3  | 460   | 2.9   | 38  |  |   |

<sup>a</sup>See text for experimental details. <sup>b</sup>Determined by ICAP-AES. <sup>c</sup>Determined by titration with standardized HCl. These values represent effective hydroxide equivalents extracted and are not meant to imply actual extraction of hydroxide ion into the organic phase. <sup>d</sup>Determined by ion chromatography. <sup>e</sup>The selectivity factor, defined as the ratio of distribution ratios for two ions (e.g.,  $\alpha(\text{OH}^-/\text{Cl}^-) = D(\text{OH}^-)/D(\text{Cl}^-)$ ); again, OH<sup>-</sup> refers to hydroxide equivalents.

In order to demonstrate recyclability of the extractants, experiments were performed using compounds **1a** and **3a** at 0.2 M in 1-octanol and equilibrated with the DSSF-7 waste simulant containing  $^{22}\text{Na}$  tracer. Table 5 shows that both solvent systems perform consistently through four cycles, although recovery of the hydroxide from the phenol (**3a**) required a second strip that was not needed with **1a**. The constancy of the sodium distribution ratio implies complete regeneration of the solvent in the stripping steps. It also implies negligible loss of these hydroxy acids to the aqueous phases. In this regard, we note that preliminary results have shown that **4c** is not completely recyclable, which may be related to insufficient lipophilicity. Further work on the lipophilicity issue is in progress.

Table 5. Results for Multiple Cycles Using DSSF-7 Simulant

Solvent: Compound **1a** at 0.2 M in 1-octanol

| Cycle | $D(\text{Na})$ | $[\text{Na}]_{\text{extr}}$ (M) | $[\text{Na}]_{\text{strip1}}$ (M) |
|-------|----------------|---------------------------------|-----------------------------------|
| 1     | 0.018          | 0.12                            | 0.12                              |
| 2     | 0.018          | 0.12                            | 0.12                              |
| 3     | 0.018          | 0.12                            | 0.12                              |
| 4     | 0.018          | 0.12                            | 0.12                              |

Solvent: Compound **3a** at 0.2 M in 1-octanol

| Cycle | $D(\text{Na})$ | $[\text{Na}]_{\text{extr}}$ (M) | $[\text{Na}]_{\text{strip1}}$ (M) | $[\text{Na}]_{\text{strip2}}$ (M) |
|-------|----------------|---------------------------------|-----------------------------------|-----------------------------------|
| 1     | 0.031          | 0.21                            | 0.16                              | 0.051                             |
| 2     | 0.031          | 0.21                            | 0.16                              | 0.052                             |
| 3     | 0.032          | 0.21                            | 0.16                              | 0.047                             |
| 4     | 0.030          | 0.21                            | 0.16                              | 0.038                             |

Although a detailed examination of the equilibria and organic-phase speciation is beyond the scope of this report, the data obtained support an interpretation based on cation exchange (Eq. 3). 1-Octanol alone extracts alkali metal salts by simple ion-solvation principles,<sup>8,27,28</sup> as may be seen from Fig. 2 for sodium nitrate. Salt extraction by pure organic solvents has been reviewed,<sup>8</sup> and equilibrium behavior is generally understood in terms of the solvated cation and anion in the organic phase, either completely dissociated or ion-paired according to the dielectric constant of the solvent and the ionic strength. The question arises as to whether the added hydroxy acids simply enhance this mechanism for sodium hydroxide extraction, since the greater acidity of these extractants would provide greater ability to solvate small anions.<sup>8,9,29</sup> To explain the selectivity for hydroxide over nitrate, one must therefore postulate an anti-Hofmeister selectivity,<sup>9,20</sup> that is, one that becomes increasing favorable with increasing anion charge density. However, the data in Table 3 clearly show that nitrate is preferred over chloride, implying a normal Hofmeister-type selectivity. Thus, the apparent selectivity for hydroxide is best interpreted as arising from cation exchange, a process that is pH driven and thus uniquely applicable to strongly basic anions.

The slope behavior observed for NaOH extraction in Fig. 2 is consistent with the postulated process shown in Eq. 3. Since the aqueous sodium and hydroxide concentrations are equal, the expression for the equilibrium constant may be expanded as follows:

$$\log[\text{Na}^+]_{\text{org}} = 2 \log[\text{Na}^+]_{\text{aq}} + \log[\text{HL}]_{\text{org}} + \log K + \log \zeta \quad (4)$$

where  $K$  is the equilibrium constant and  $\zeta$  is the ratio of molar activity coefficients  $g_{\text{HL}}(g_{\text{NaOH}\pm})^2/g_{\text{NaL}}$ . The expression predicts a slope of 2 for a condition far from saturation of the extractant. For compounds **3a** and **4c**, the slopes indeed tend to 1.9 at the lowest concentrations after a minor (7%) correction for aqueous activity coefficients.<sup>30</sup> For the other, weaker extractants, the background extraction of 1-octanol becomes important, and the slopes lie between 2 and 1 (the corresponding slope for 1-octanol alone). Also, as the organic-phase ionic strength decreases, the ion pairs shown in eq. 2 may dissociate, in which case the expansion of the equilibrium expression predicts a unit slope. It should be pointed out that, although the agreement of the model with the data is encouraging, it is equally consistent with an ion-pair extraction model. As discussed above, the evidence for cation exchange lies in the selectivity for hydroxide.

Reference to Fig. 2 and Table 3 reveals a saturation effect, but one that is superstoichiometric. Namely, Table 3 shows that the organic-phase concentration of sodium upon extraction from NaOH solutions reaches concentrations greater than what can be accounted for by a 1:1 extraction of sodium (Eq. 3) and the background extraction of 1-octanol (0.050 M). The origin of this apparent synergism is presently unknown and is under continuing investigation. It may be due to polarization of 1-octanol or organic-phase water molecules by extracted  $\text{Na}^+$  ions, the same mechanism thought to account for the decreased auto-ionization constant for water in the presence of sodium salts.<sup>30</sup> The synergism appears to be somewhat higher for the fluoroalcohols, as **1a,b** performed similarly on extraction to **3b**, yet phenol **3b** is expected to be 1.5-2  $\text{p}K_{\text{a}}$  units more acidic.<sup>22,23,25</sup>

Although the initial results described above employed at most 0.2 M, it has been shown in as yet unpublished work that 1H,1H-perfluorononanol (**1b** in Table 1) and 3,5-di-tert-butylphenol (**3b** in Table 1) can be employed up to 1 M, leading to solvent loading of sodium exceeding 1 M. However, viscosity increases significantly at high sodium loading with any of the hydroxy acid extractants at 25 °C, and even gel formation was observed. This problem was readily alleviated with warming, and isotherms were determined at 60 °C for 1 M solutions of selected hydroxy acids [**1b**, **2a**, **3a**, **3b**, and a relative of **2a**, 1-trifluoromethyl-2-(3,5-di-tert-butylphenoxy)-ethanol] in 1-octanol. Sodium hydroxide was released from these loaded solvents on contact with water. In this manner, it was demonstrated with **3a** that over 90% of the total hydroxide content of the DSSF simulant and over 40% of its sodium content can be removed on successive extraction contacts. In this test, bayerite (a form of aluminum trihydroxide) precipitated in the simulant, releasing one additional recoverable mole of hydroxide for each Al(III) precipitated. Applied research under the Efficient Separations and Processing Crosscutting Program, USDOE Office of Environmental Management has been commissioned to develop and demonstrate a process flowsheet.

In summary, fluoroalcohols can be used effectively for the selective separation of NaOH from a variety of caustic matrices. Factors influencing the efficiency of extraction and stripping include electron-withdrawing effects of fluorine-containing substituents and steric effects of

alkyl groups. Despite their higher cost, the fluoroalcohols may offer increased alkaline stability, as alkylphenols can degrade, most commonly by oxidation, when in prolonged contact with caustic solutions.<sup>31</sup> Further work to investigate the underlying extraction mechanism is in progress and also constitutes part of the goals of the renewal period. Results have been successfully transferred to an applied task to develop a practical process for the recovery of hydroxide from caustic media is in progress.

## Synthesis of Novel Cage-Functionalized Hosts

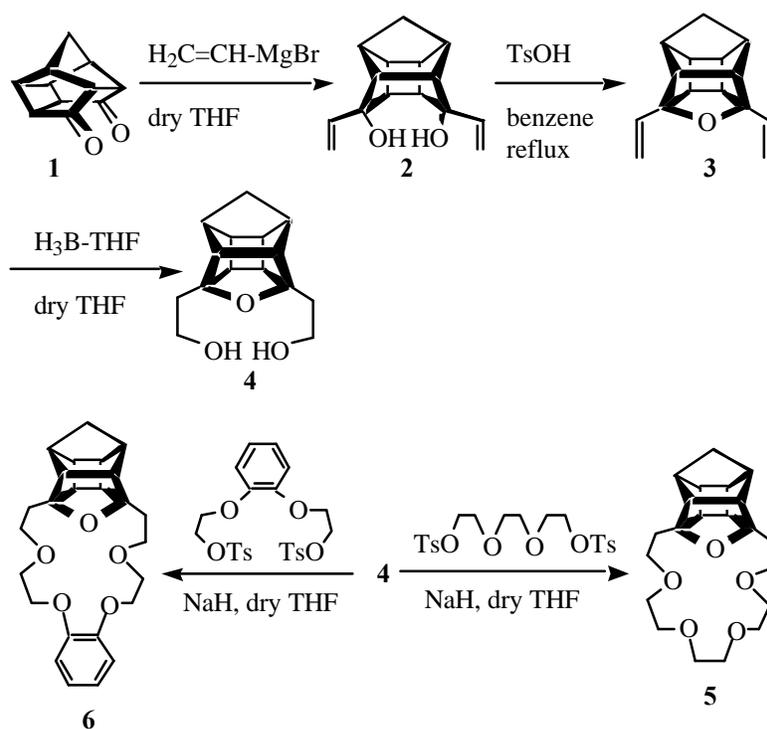
In relation to the problem of separating sodium salts from high-salt wastes, the structure of macrocyclic cation receptors allows control of the cation selectivity and flexibility in selection of a suitable diluent. Initial work by Prof. Marchand and his group at the University of North Texas focused upon the synthesis of novel, cage-annulated crown ethers,<sup>32</sup> cryptands,<sup>33</sup> and molecular clefts.<sup>34</sup> In each case, the ability of these unusual host systems to function as selective metal cation complexants and to selectively transport alkali metal cations was evaluated via a series of alkali metal picrate extraction experiments.<sup>35</sup> More recently, these efforts have been directed toward the design of specific hosts for selective NaOH complexation and transport.

Several cage-functionalized crown ethers and related aza-crown systems, each of which contains a 4-oxahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecane moiety, have been synthesized. In several instances, incorporation of this cage unit into these systems has produced a dramatic effect upon their ability to function as ionophores. Here, the cage unit functions as a lipophilic "spacer" that also serves to increase the rigidity of the crown system in the resulting macrocycle relative to the corresponding non-cage-containing analog, thereby influencing the overall conformational mobility of the host. Incorporation of the cage unit also affects the shape and size of the cavity in the host system. In addition, the *furano* oxygen atom in the 4-oxahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecane cage moiety potentially can participate along with the remaining Lewis base atoms in the macrocycle during formation of an eventual host-guest complex.

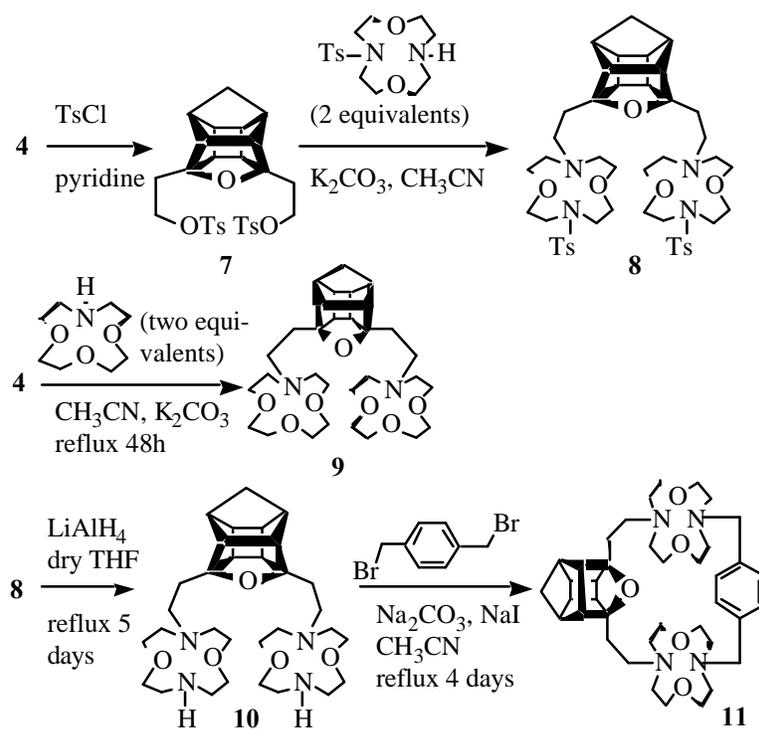
Our first attempts to incorporate the 4-oxahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecane cage moiety into crown ethers resulted in the synthesis of two novel host systems, **5** and **6** in Scheme 1, which summarizes the methodology that was employed successfully for this purpose.<sup>32a</sup> Thus, reaction of pentacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane-8,11-dione ("PCU-8,11-dione", **1**) with excess vinylmagnesium bromide afforded the corresponding diol, **2**, in 60% yield. Dehydration of diol **2** produced 3,5- divinyl-4-oxahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]dodecane, **3** (77% yield). Subsequent hydroboration-oxidation of the carbon-carbon double bonds in **3** afforded the corresponding cage diol, **4**, in 85% yield. Diol **4** proved to be a key starting material for the preparation of several of the new cage-functionalized crown ethers and cryptands reported herein.

In an effort to probe the importance of proximity effects (i.e., "host preorganization") on host-guest complexation properties, a series of 3,5-difunctionalized 4-oxahexacyclo[5.4.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecanes has been prepared. These compounds serve as templates to develop a series of novel complexing agents that can be used for metal ion separation and transport. Thus, for example, 1-aza(12-crown-4) (i.e., 1,4,7-trioxa-10-azacyclododecane) and several substituted 1,4-diaza(12-crown-4) derivatives have been prepared, and these species subsequently have been affixed as pendant "arms" to the polycyclic template by using the synthetic strategy shown in Scheme 2.<sup>32b</sup>

### Scheme 1



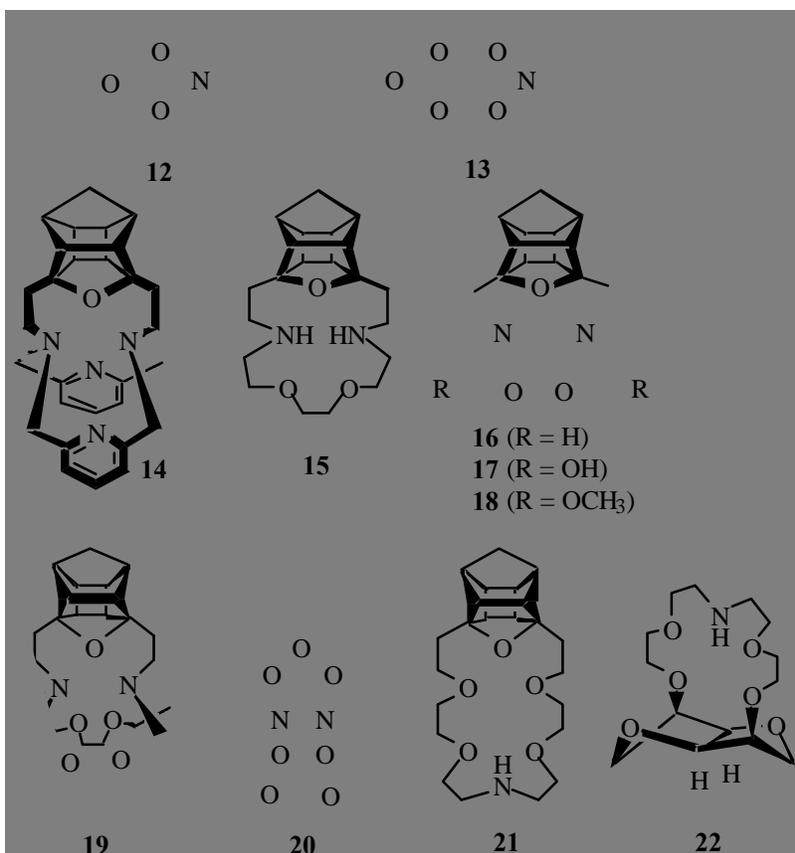
### Scheme 2



Whereas the pendant (12-crown-4) moieties in **8**, **9**, and **10** are conformationally mobile, the situation is quite different in **11**. Thus, in **11**, the use of a *p*-xylyl unit as a covalent linking agent results in the formation of a "molecular box"<sup>36</sup> with concomitant "forced cooperativity" between the otherwise distant 1,4-diaza(12-crown-4) moieties. Thus, it was of interest to determine how the anticipated increase in host preorganization brought about through "forced proximity" between the opposing 1,4-diaza(12-crown-4) moieties might influence the avidity and/or selectivity of **11** *vis-à-vis* **8-10** toward, for example, complexation of alkali metal picrates.

In addition, several new cage-functionalized crown ethers and cryptands have been prepared as part of this study (see Scheme 3). Thus, compounds **12-14** contain one or more 2,6-pyridiyl moieties in addition to the 4-oxahexacyclo[5.4.1-.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecane cage.<sup>36</sup> Another series of novel host molecules, **15-20**, is comprised of cage-functionalized diaza(17-crown) ethers.<sup>32c,33a,33b</sup> Finally, two additional cage-functionalized host systems, **21**<sup>37</sup> and **22**,<sup>38</sup> have been synthesized. Based upon literature precedent,<sup>39</sup> it was anticipated that cage-functionalized cryptands might display enhanced avidity and/or selectivity toward complex formation with alkali metal cations due to the increased preorganization inherent in their structural frameworks.

Scheme 3



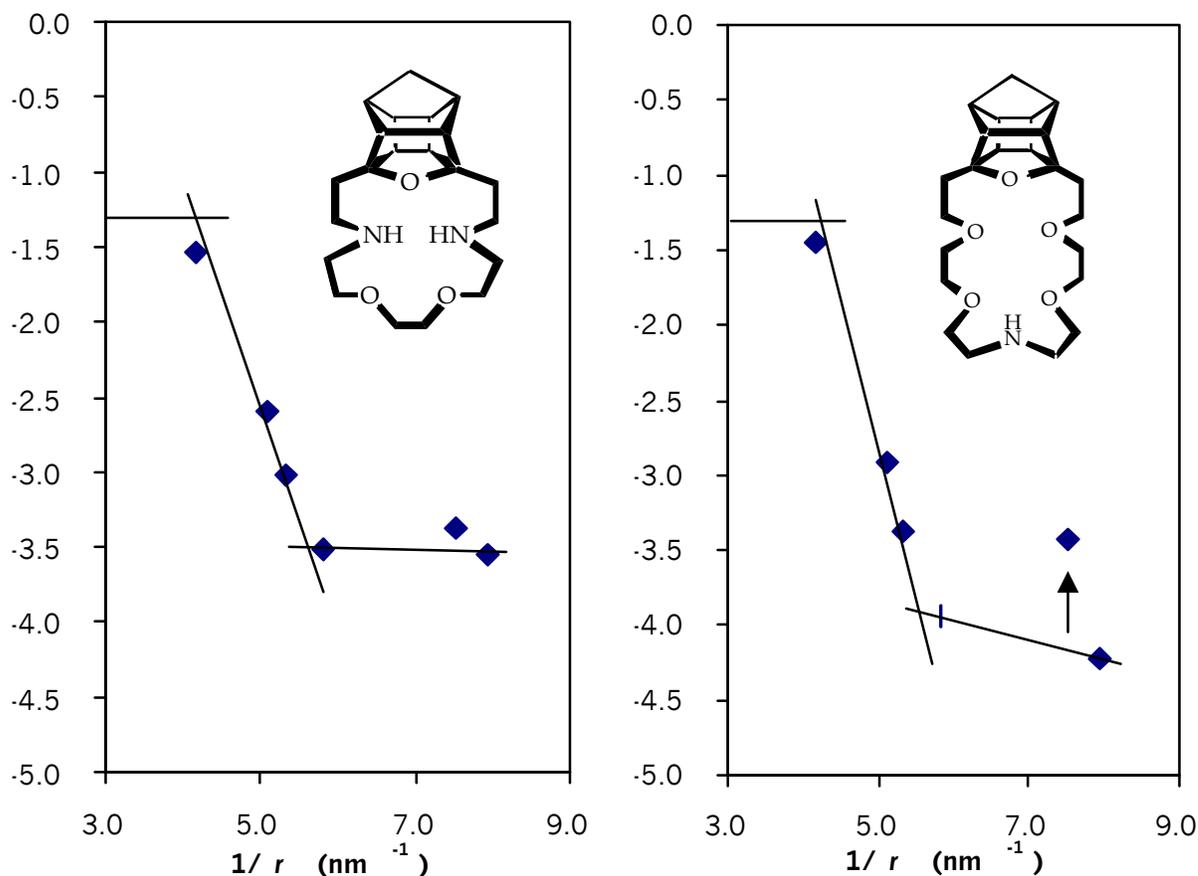


Figure 3. Plots of the logarithm of sodium distribution ratios vs. reciprocal thermochemical anion radii for two aza macrocycles. Conditions: 0.05 M macrocycle in nitrobenzene, 1 M aqueous sodium salt, 1:1 phase ratio, and 25 °C.

### Ion-Pair Extraction Using Cage-Functionalized Hosts

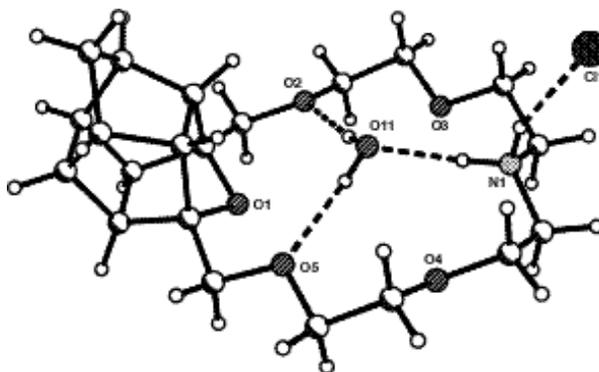
For the three nitrogen-containing macrocycles **15**, **21**, and **22** (Scheme 3), a series of non-competitive extraction studies of Na<sup>+</sup>X<sup>-</sup> salts was performed by personnel in the Chemical and Analytical Sciences Division, Oak Ridge National Laboratory.<sup>7</sup> Interestingly, plots of the logarithm of Na<sup>+</sup> distribution vs. the reciprocal of thermochemical anion radii for extraction of Na<sup>+</sup>X<sup>-</sup> by the three azamacrocycles into nitrobenzene revealed that all three hosts display significantly higher avidity toward extraction of NaOH than would be expected simply on the basis of ionic radii considerations (Fig. 3). Each plot exhibits three regions indicated by the straight line segments. The top-most horizontal segment simply indicates saturation level of the macrocycle by Na<sup>+</sup> cation, whence a maximum in the distribution ratio  $D_{\text{Na}}$  (i.e., 0.05) is expected if a 1:1 macrocycle:metal stoichiometry is obtained. The steeply descending straight line segment indicates the natural bias<sup>9</sup> expected for extraction of large anions, which may be termed the Hofmeister effect.<sup>20</sup> Roughly linear dependence on  $1/r$  with negative slope is expected based on the form of expressions for Gibbs energy of ion transfer derived from the Born charging equation.<sup>9</sup> Hence, such a plot provides a convenient and qualitatively meaningful

vehicle for presenting the data on the basis of ion size. Perchlorate is strongly extracted and exhibits significant saturation in each case. Since perchlorate is large and practically unhydrated in the organic phase, it is most likely to conform to the ideal ion-pair model given by eq. 1 (Table 1, Case 2), in which the macrocycle binds the cation and the anion is solvated. On this basis, the inherent macrocycle extraction strength toward  $\text{Na}^+$  ion may be given as  $\mathbf{21} > \mathbf{15} > \mathbf{22}$  (not shown). Although this ordering seems readily defensible, it persists for none of the other anions. Thus, anion selectivity appears to depend upon the structure of the macrocycle, and the mechanism (eq. 1) cannot be generalized to the other anions.

Although extrapolation of the electrostatic arguments based on the radii of bare ions would predict that extraction of NaOH and NaF by macrocycles **15**, **21**, and **22** would be exceedingly low, Fig. 3 shows that the  $D_{\text{Na}}$  values for these anions do not continue to follow the steeply decreasing trend. Indicated arbitrarily by a straight line segment joining the points for  $\text{Cl}^-$  and  $\text{F}^-$ , the third region of the plots in fact exhibits no obvious dependence upon ion radius. A straightforward explanation under investigation lies in the fact that the small anions are highly hydrated in organic solvents equilibrated with water. For example, the ions  $\text{Br}^-$  and  $\text{Cl}^-$  have respectively an average of 1.8 and 3.3 water molecules per ion in water-saturated nitrobenzene at 23 °C.<sup>40</sup> Although data are lacking,  $\text{OH}^-$  and  $\text{F}^-$  ions would be expected to have even greater hydration. The effect of ion hydration in the organic phase is to make the Gibbs energy of ion partitioning more favorable,<sup>9</sup> compensating for the decreased ion radius. One could say simply that the highly hydrated anions behave as if they have effectively comparable solvation in the organic phase. Further investigation into the reasons for this behavior is needed.

### Structural Results on Cage-Functionalized Hosts

X-ray crystal structures have proven informative in cases where it has been possible so far to grow crystals.<sup>33d,41</sup> The structure of crown **21** was determined<sup>33d</sup> and is illustrated here. It clearly demonstrates how this crown might interact with both halves of an ion-pair with  $[\text{H}_3\text{O}][\text{Cl}]^-$  serving as a model. The amine group has been protonated, forming an ammonium ion, which donates hydrogen bonds to water (inside the cavity), and to chloride. The water molecule also donates two hydrogen bonds to ether oxygen atoms. It is not too difficult to imagine  $\text{Na}^+$  and  $\text{OH}^-$  replacing the observed  $[\text{H}_3\text{O}][\text{Cl}]^-$  ion-pair.



### Synergistic Pseudo Hydroxide Extraction

A novel extraction approach has been demonstrated for the separation of sodium hydroxide from other sodium salts based on the cooperative effect of a weakly acidic proton-ionizable fluorinated alcohol and cage-annulated crown ethers.<sup>42</sup> Liquid-liquid extraction experiments were carried out using six different sodium salts (Fig. 4). Distribution results revealed that addition of the fluorinated alcohol to a nitrobenzene phase containing any of the cage-

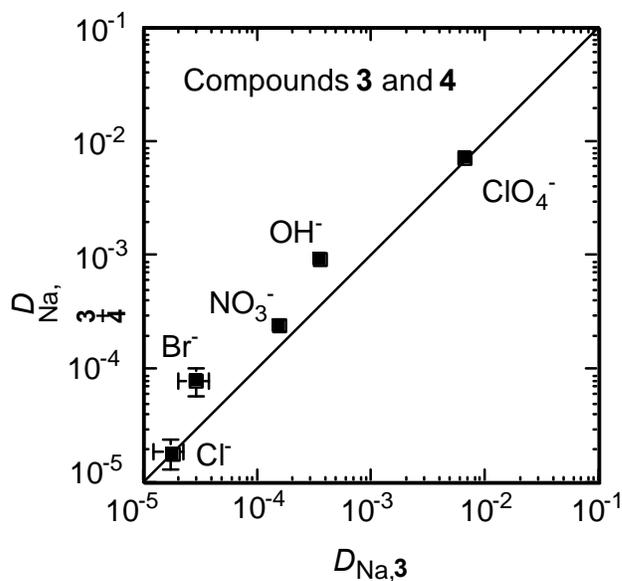
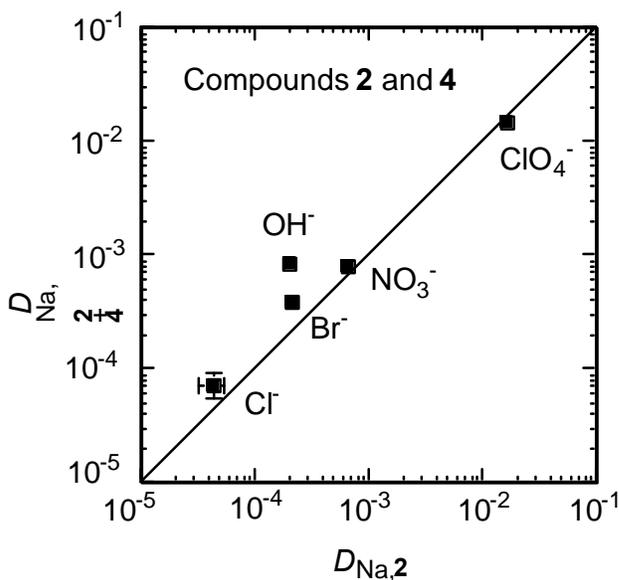
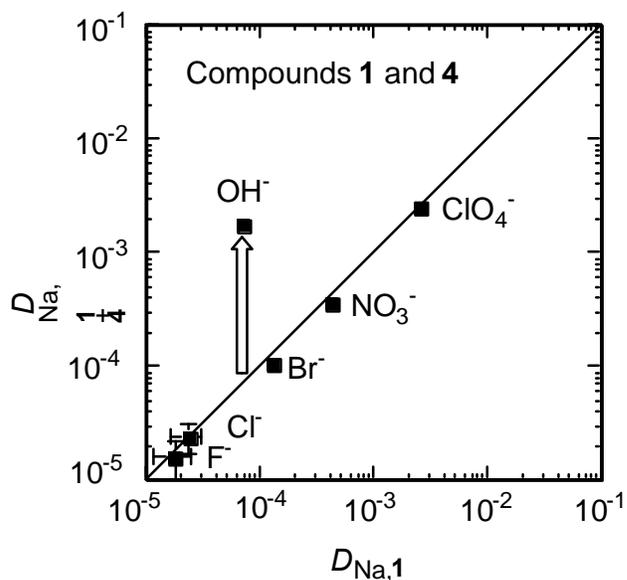


Figure 4.  $Na^+$  ion distribution results obtained using crown ethers **1**, **2** and **3** with and without fluorinated alcohol **4** at 25 °C (see Table 6 for compound key). Values of  $D_{Na,CE+4}$  and  $D_{Na,CE}$  for  $ClO_4^-$  and  $OH^-$  ions were corrected for the  $Na^+$  ion partitioning between water and NB and/or  $Na^+$  ion extraction by **4** alone in NB. Aqueous phase: 1 M  $NaX$  ( $X = ClO_4^-, NO_3^-, Br^-, Cl^-, F^-,$  or  $OH^-$ ). Organic phase: 22 mM **1**, **2** or **3** in NB; 22 mM **1**, **2** or **3** + 44 mM **4** in NB. Experimental uncertainty is approximately  $\pm 5\%$  unless otherwise indicated by error bars.

functionalized aza-crown ethers synergistically enhanced extraction of NaOH. Little or no enhancement of extraction of the other salts was observed, and one system in particular separated sodium hydroxide nearly as effectively as sodium perchlorate (Fig. 4). The demonstration of the principle of synergized pseudo hydroxide extraction is significant for sodium salt separation systems proposed in section 4 for high rejection of radioactive contaminants such as  $^{137}\text{Cs}$ .

The simplest example of the so-called pseudo hydroxide extraction has already been demonstrated<sup>7,21</sup> and was discussed at length above (Case 6, Table 1). This approach employs a weak lipophilic organic acid (e.g., phenol or fluorinated alcohol) dissolved in a water-immiscible diluent to exchange its proton for an alkali cation at elevated pH. Given that cation-exchange processes involving alkali metal cations are hindered by poor cation solvation in typical water-immiscible diluents, we proposed that this solvation barrier could be overcome by employing an appropriate cation host molecule (Case 7, Table 1).<sup>7</sup> An effective host lowers the net barrier to extraction via complexation of the cation synergistically enhancing the alkali metal extraction at a given pH. An added benefit of the host molecule entails control over the cation selectivity, which would be key for rejection of cesium in the systems proposed in the renewal period. We report for the first time a remarkable synergistic effect in the pseudo hydroxide extraction by novel cage-annulated crown ethers **1** – **3** in combination with an activated fluorinated alcohol **4** in nitrobenzene (Fig. 5).<sup>41</sup> The key for the compounds discussed in section 3.4.6 is given in Fig. 5 below; note that compound **2** is the same as **21** in Scheme 3, and compound **4** is a relative of **2a** in Table 2).

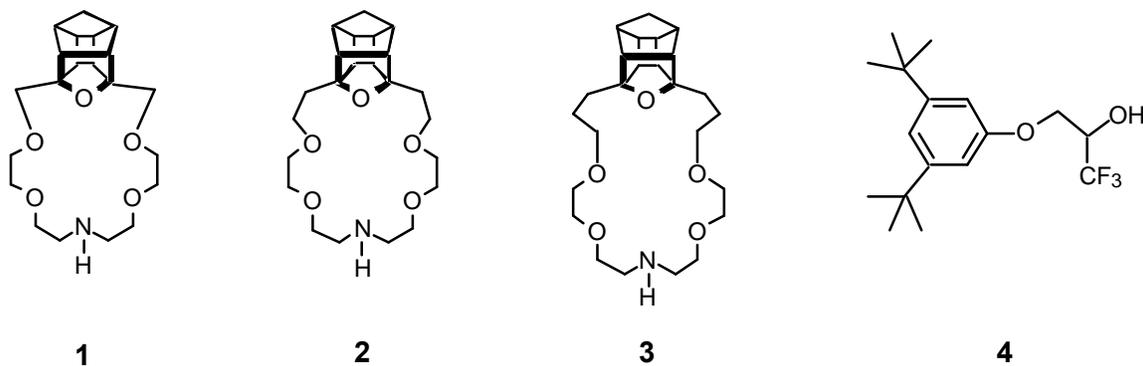


Figure 5. Compound Key for Synergistic Pseudo Hydroxide Extraction (Fig. 4).

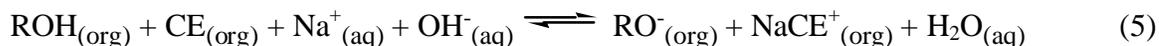
In crowns **1** – **3**, cage-annulation provides both lipophilicity and ring-rigidification, and the amine functionalities serve as potential pivot points for eventual sidearm substitution. They also presumably promote hydrogen-bonding interactions with the alcohol. Organic phases contained 22 mM CE or 22 mM CE plus 44 mM **4** in nitrobenzene (NB). Application of NB as a model diluent possessing a high dielectric constant ( $\epsilon = 34.8$ )<sup>43</sup> minimizes ion-pairing effects in the organic phase. In addition, this solvent is nearly ideal for the examination of the anion selectivity, since it lacks hydrogen-bond donicity<sup>43</sup> and thus minimizes any effect of specific interactions with aprotic anions. Nitrobenzene is not, however, a potential process diluent, because of its toxicity, and 1-octanol will be proposed in follow-on research. In view of published standard Gibbs energies of anion transfer,<sup>10</sup> the effect of NB also exhibits a strong

Hofmeister bias, increasing the challenge of selective hydroxide separation. To evaluate the expected synergistic effect toward NaOH, distribution experiments were performed by contacting aqueous phases containing 1 M NaX (where  $X^- = \text{ClO}_4^-, \text{NO}_3^-, \text{Br}^-, \text{Cl}^-, \text{F}^-$ , or  $\text{OH}^-$ ) with each of the six organic phases. Upon equilibration at 25 °C, sodium distribution ratios ( $D_{\text{Na}} = [\text{Na}^+]_{\text{org}}/[\text{Na}^+]_{\text{aq}}$ ) were determined by  $^{22}\text{Na}$  radio-tracer techniques for each experiment. In control experiments,  $\text{Na}^+$  extraction by **4** used alone in NB was found to be negligible, and  $\text{Na}^+$  ion partitioning between water and NB was found to be negligible.

Figure 4 compares the distribution behavior of  $\text{Na}^+$  ion observed using each combination of CE and **4** with that of the corresponding behavior for the CE alone. A datum point falls on the diagonal line when  $D_{\text{Na}}$  values are the same with and without cation exchanger in the NB phase. This condition is met or nearly so for all anions other than hydroxide. Considering the fact that  $\text{Na}^+$  extraction was negligible in the control experiments using **4** alone in NB, one may conclude that **4** has little or no effect on the extraction of tested sodium salts by the crown ethers. That is, the combination of **4** and any of the crowns does not function as a dual-host ion-pair recognition system (Case 4, Table 1). Data points above the diagonal line indicate synergistic enhancement of the sodium extraction by the cooperative effect of the cation exchanger and crown ether. As it may be seen in Fig. 4, combined application of cage-functionalized crown ethers with **4** in the NB phase yields enhanced extraction of NaOH. Synergistic factors ( $S = D_{\text{Na,CE+4}}/(D_{\text{Na,CE}} + D_{\text{Na,4}})$ ) for NaOH were 24.5, 3.5, and 3.4 using **1**, **2** and **3**, respectively.  $\text{Na}^+$  ion extraction with anions other than  $\text{OH}^-$  ion gave negligible if any enhancement upon addition of **4** into the extraction system.

The lack of synergism in extraction of all salts other than NaOH supports the hypothesized cation-exchange process for NaOH. Some synergism might be expected based upon a hydrogen-bond interaction between **4** and the various anions (dual-host mechanism, Case 4, Table 1). That the synergism is weak except for the case of hydroxide implies that such a solvation-based enhancement must be weak for all anions down to the smallest tested,  $\text{F}^-$  ion. Hence, the selective response for  $\text{OH}^-$  ion must be an acid-base reaction.

It may be noted for combination of **1** and **4** that the enhancement with  $\text{OH}^-$  ion puts the pseudo hydroxide extraction nearly on par with perchlorate extraction. Interestingly, the synergistic enhancements were not all the same, as would be expected by the simplest possible hypothetical model reaction:



This model predicts that the synergistic enhancement depends only on the properties of the ion exchanger and thus is expected to be the same for hosts **1**, **2**, and **3**. (Note that a stronger host molecule only moves the point up the diagonal line. It is the effective acidity of the hydroxy acid that moves the point above the diagonal.) Thus, the simple model reaction (eq. 1) does not describe the NaOH extractive process in full, and additional interactions which depend on the structure of the host molecule must occur. Although an argument has been advanced that these interactions entail ion-pairing, there is clearly a need for further investigation.

In conclusion, distribution studies demonstrated that extraction of NaOH is synergistically enhanced by the cooperative effect of cage-annulated crown ethers and a proton-ionizable fluorinated alcohol **4**. This novel approach based on the simultaneous utilization of ion-exchange and recognition processes can be successively used for pseudo extraction of the  $\text{OH}^-$  ion from alkaline media with near parity with anions as hydrophobic as the  $\text{ClO}_4^-$  ion.

## Relevance, Impact, and Technology Transfer

### General Relevance to USDOE Cleanup Mission

This research has addressed 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.”<sup>44</sup> In so doing, this research also directly meets the relevance criteria recently outlined in the FY01 call for proposals under the Environmental Management Science Program (EMSP).<sup>45</sup> Experiments were conceived that would have the most value to the USDOE Office of Environmental Management (EM), and specific site needs were considered toward a defensible separations-technology concept based on solvent extraction. Although actual development of such technology should be left for subsequent applied R&D, the research results obtained here provide key fundamental information that could form the basis for assessing the feasibility of technology development and possibly contributing to its design.

### Potential Impact on Cost Reduction and Mission Acceleration

**General technology concept.** As pointed out in the preceding section, the chief accomplishment of this effort toward foreseeable application has been the demonstration of a promising new concept for sodium hydroxide separation, dubbed “pseudo hydroxide extraction.” Data supporting the feasibility of a solvent-extraction process much as envisioned in Fig. 1 have been presented above. In an integrated flowsheet application, sodium hydroxide separation would likely follow radionuclide separation, although this assumption is being examined in the renewal period. The sodium hydroxide is then either recycled, or if sufficiently clean, it could be grouted. Sodium hydroxide is an excellent feed for an inexpensive grout waste form and would avoid problematic nitrate leaching. If nitrate is destroyed in a unit operation prior to hydroxide separation, the quantity of sodium as hydroxide that can be separated increases greatly.

By reference to the hydrometallurgical industry, solvent extraction is generally recognized as providing economical, selective, energy-efficient, low-footprint, high-throughput methodology and is widely practiced for a variety of metal separations.<sup>46</sup> By extension, a proposed liquid-liquid extraction process for separating sodium hydroxide from alkaline tank waste is expected to offer these same potential advantages. The expected 33,000 L/day (6 gal/min) throughput needed to process the contents of one tank in a year would normally be accommodated by compact centrifugal contactors; a well-studied design for a 25-cm contactor has a nominal total throughput of 170,000 L/day.<sup>47</sup> Experience with employing solvent extraction in the nuclear industry has also been extensive, productive, mature, and widely accepted.<sup>48,49</sup> Indeed, solvent extraction as a large-scale industrial technique for metal separation probably owes its birth to the needs of the nuclear industry. The use of solvent extraction for nuclear applications has lain overwhelmingly on the acid side, while applications for alkaline-side separations have only been recently considered.<sup>3-6</sup> Nevertheless, in the case of technetium separation from alkaline tank waste, recent work has set the precedent that efficient, cost-effective processes are not only feasible and demonstrable by solvent extraction, but also highly selective.<sup>3</sup> This expectation has been borne out even more recently with the development and current testing of the caustic-side solvent extraction (CSSX) process for removal of cesium from the alkaline tank waste as the Savannah River Site.<sup>4-6</sup>

The potential value of removing sodium hydroxide is several-fold: a) reducing the volume of vitrified low-activity waste (LAW), b) increasing the available space in storage tanks at Hanford and thereby avoiding the construction of new tanks, and c) accelerating the cleanup at Hanford through an alternative flowsheet and thereby avoiding construction of another Waste Treatment Plant (WTP) at Hanford. These possibilities have implications for both cost savings and schedule acceleration and are discussed individually below.

**Reducing vitrified LAW volume.** As argued in our original proposal in FY98, it is highly desirable to remove sodium salts from the LAW stream that would otherwise have to be vitrified after removal of the major radionuclides.<sup>2,50</sup> The long-term implications are easily understood. For example, if the estimated  $6.8 \times 10^7$  kg of total sodium inventory<sup>1b</sup> of the Hanford tanks is vitrified in the LAW borosilicate glass, each glass canister having a mass of 1650 kg and containing 15% sodium, then one expects a production of 280,000 LAW glass canisters, neglecting other glass-limiting components like sulfate. If the cost per canister is \$0.5M, then the LAW vitrification will alone cost a staggering \$140B. A technical approach to decreasing the cost of the LAW vitrification would be to cleanly separate the major sodium salts from the waste.<sup>2,50</sup> The sodium salts could then be recycled, 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.<sup>2</sup> 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.<sup>2a</sup> 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%.<sup>50</sup>

**Increasing available tank space.** In the time since this work began in late FY98, the urgency for methods to remove sodium salts from the Hanford waste has increased as related to avoidance of construction of expensive new storage tanks. This and related needs were discussed intensively at the Mission Acceleration Initiative Technology Demonstration Workshop held at Pacific Northwest National Laboratory, Richland, WA, Apr. 2-3, 2002.<sup>52</sup> The Tanks Focus Area (TFA) and the Hanford Site Contractor (CHG) have identified a critical need (<http://www.pnl.gov/tfa/emsp/needs.stm#rlwt088>) 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 (WTP). One option for establishing additional working tank space is to build new double-shell tanks. However, at an estimated cost of \$75M per tank, this is not a desirable option (see also need statement <http://www.pnl.gov/stcg/fy01needs/tanks/index.stm>). An alternative strategy would be to process the tank-waste liquids to remove much of the bulk nonradioactive materials (i.e., the sodium salts) so that they can be disposed of as incidental waste. This would free up significant tank space and eliminate the need to construct new tanks. For this strategy to succeed, the salts removed from the tank wastes would need to be sufficiently free of radionuclides such that they can be managed as incidental waste. Currently, there are no firm requirements regarding the radionuclide levels in incidental waste. If a stringent target of less than 10% of the NRC Class A low-level waste limits<sup>1cd,51</sup> is assumed, we estimate that a <sup>137</sup>Cs decontamination factor of ca. 50,000 would be needed. As a working assumption, then, we assume that a radionuclide removal step will be needed prior to sodium removal. Although a sodium hydroxide separation on such a stream would possibly offer significant savings, the bulk of the sodium would remain

in the waste. Thus, it is also expected that nitrate and nitrite must be destroyed so that subsequent sodium hydroxide separation would remove most of the sodium from the salt waste.

**Mission acceleration.** Considerable savings are expected if the treatment of high-level tank wastes can be accelerated. Recent discussion at the Mission Acceleration Initiative Technology Demonstration Workshop<sup>52</sup> focused on primarily treating the salt cakes in close proximity to the tanks, avoiding processing through large facilities. In much the same way as shown above for increasing tank space, a sodium hydroxide separation may well be able to play a role in mission acceleration by facilitating sodium removal from the waste.

### **Bridging the Fundamental–Applied Gap**

This research has laid a foundation of fundamental information from which to proceed with addressing further fundamental questions and potential applications. Questions related to sodium binding and extraction by novel cation-exchange reagents directly point to specific methods by which bulk levels of sodium could be removed from alkaline nuclear waste. A concept for doing so has been presented above. It should be stressed that at present, the results have so far produced a concept only, and a technology has yet to be developed. Synthesis data have provided information on preparative routes to desired families of new compounds that could be employed in such a technology application. Distribution data that have value for thermodynamic understanding also can be used for flowsheet design. Applied R&D will now be needed to make use of these data to find the optimum solvent components and conditions for practical use.

### **Site-Specific Impact**

The concept developed over the past three years has been targeted primarily at a Hanford application in tank-waste cleanup. Contacts with the Hanford site and Tanks Focus Area have been significant and encouraging in this regard, as enumerated in the Interaction section below. Results have been communicated to these personnel and used by them in planning strategies for Mission Acceleration and related needs. An outcome of the Mission Acceleration Initiative Technology Demonstration Workshop<sup>52</sup> was recognition of the merit of sodium hydroxide recovery by solvent extraction. It was recommended that research continue on this topic toward a higher level of maturity. Applied efforts are therefore warranted to perform batch tests on actual waste as well as to design and test candidate flowsheets for counter-current separations.

Follow-on funding from the Tanks Focus Area via the Efficient Separations and Processing Crosscutting Program was awarded to carry out applied research toward the development and testing of a process flowsheet on actual tank waste. Submitted in early FY 2001, the proposal was in response to the call “Sludge Washing, Task 1: Leaching of Hanford Tank Sludge.” The project title is “Liquid-Liquid Extraction of NaOH for Caustic Recycle in Augmented Sludge Washing,” Technical Task Plan No. 3TMK OR01C322 (EW4010000). Gilbert M. Brown is the Principal Investigator; David J. Wesolowski of ORNL and Gregg J. Lumetta of PNNL are co-investigators. Collaborators include Peter V. Bonnesen and Bruce A. Moyer of ORNL. The premise of the project states that efficient leaching of aluminum from tank sludge may be afforded by higher concentrations of sodium hydroxide obtained by separation and recycle from the tank waste. Efforts by Wesolowski involve examination of the question of mineral solubilities, and Gregg Lumetta has examined the efficiency of sludge leaching on real tank sludge. Brown and co-workers have been conducting batch extraction studies.

## Project Productivity

Significant accomplishments were made in every area of this project as described above. Specific achievements include the following:

- Eight fundamental approaches to the separation of sodium hydroxide from aqueous salts were conceptualized, and one novel approach was termed “pseudo hydroxide extraction.”
- A series of novel fluorinated alcohol extractants was prepared and characterized.
- Fluorinated alcohol extractants and alkyl phenols in 1-octanol were shown to efficiently and selectively separate sodium hydroxide from aqueous salts into a second aqueous solution.
- The behavior of the fluorinated alcohol extractants and alkyl phenols was shown to be consistent with the pseudo hydroxide extraction mechanism based on cation exchange.
- A patent application was filed covering the novel fluorinated alcohols and their use.
- A follow-on proposal was prepared and was funded to perform applied development.
- New cage-annulated aza crown ethers were prepared, and they were shown to be effective alkali metal extractants in survey extraction experiments.
- The cage-annulated aza crown ethers enhance sodium hydroxide extraction by fluorinated alcohol extractants, termed synergized pseudo hydroxide extraction.
- Seventeen papers were published in the peer-reviewed literature.
- Thirty five technical presentations were given.
- Two Ph.D. degrees and one M.S. degree were awarded.

The project proceeded on schedule, and project objectives were achieved in a timely manner. In general, the work plan proceeded as proposed, though early success with sodium hydroxide separation by fluorinated alcohols and alkyl phenols led to more extensive project resources being focused on this approach, as it was clear that the development of an economical process was a distinct potentiality. In fact, follow-on funding was obtained to pursue applied research (see above). Owing to this shift in priorities, less attention was paid to extraction of other sodium salts, and certain extractants (e.g., boron-containing compounds) were not pursued.

## Personnel Supported

At Oak Ridge National Laboratory, various staff from the Chemical Separations Group (see Table 6 below) participated in the project at the level of 0.4–0.5 Full Time Equivalents per year. In any given year, the project also involved 0.5–1 postdoctoral research associates. A leased chemist also worked several months on organic synthesis in the first year of the project.

At the University of North Texas, the project supported four postdoctoral research associates throughout the first year of the project. During the third year of the project, three postdocs (12 months), and one Visiting Professor (3 summer months) received salary support. During all three project years, three graduate student research projects were supported via purchase of expendable equipment and supplies; graduate student salaries were paid from other sources (UNT Chemistry Department teaching assistantships). Professor Alan Marchand directed the research and was supported half-time during 1.5 summer months (year 1) and 1 summer month (year 2). A Grant Supplement to the Univ. of N. Texas in the amount of \$10,000 was used to

support the Visiting Professor, Dr. Kata Mlinaric-Majerski, during three Summer months, 2000. Three graduate degrees have been awarded (see Table 6).

Table 6. Project Personnel

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|   |                                 |
|---|---------------------------------|
| Bruce A. Moyer, Group Leader, PI        | Chemical Separations Group      |
| Peter V. Bonnesen, Research Staff       | Chemical Sciences Division      |
| Jeffrey C. Bryan, Research Staff        | Oak Ridge National Laboratory   |
| Gilbert M. Brown, Research Staff        | Oak Ridge, Tennessee 37831-6119 |
| Tamara J. Haverlock, Jr. Research Staff |                                 |
| Nancy L. Engle, Leased Chemist          |                                 |
| C. Kevin Chambliss, Postdoc             |                                 |
| Tatiana G. Levitskaia, Postdoc          |                                 |

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|--|-----------------------------|
| Alan P. Marchand, Co-PI                    | Department of Chemistry     |
| Bishwajit Ganguly, Postdoc                 | University of North Texas   |
| I. N. N. Namboothiri, Postdoc              | NT Station, P.O. Box 305070 |
| K. S. Ravikumar, Postdoc                   | Denton, TX 76203-5070       |
| Hendrik G. Kruger, Postdoc                 |                             |
| Trevor D. Power, Postdoc                   |                             |
| Bo-Liang Deng, Postdoc                     |                             |
| Kata Mlinaric-Majerski, Visiting Professor |                             |
| Artie S. McKim, Ph. D., May, 1999          |                             |
| Hyun-Soon Chong, Ph. D., Aug., 1999        |                             |
| Anna Hazlewood, M. S., Aug., 2001          |                             |

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## Publications

### Peer-Reviewed articles

- S. M. Blair, J. S. Brodbelt, A. P. Marchand, H.-S. Chong, and S. Alihodzic, "Evaluation of Alkali Metal Binding Selectivities of Caged Aza-Crown Ether Ligands by Electrospray Ionization Quadrupole Ion Trap Mass Spectrometry," *J. Am. Soc. Mass Spectrom.*, **11**, 884-891 (2000).
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- J. C. Bryan, K. Mlinaric-Majerski, G. Kragol, and A. P. Marchand, "Crystal Structure of 1,3-Hydroxymethyl-2-oxaadmantane, C<sub>11</sub>H<sub>18</sub>O<sub>3</sub>," *Z. Kristallogr.* **216**, 277-279 (2001). Joint sponsorship with the Robert A. Welch Foundation, the Texas Advanced Technology Program, and the Ministry of Science and Technology of the Republic of Croatia.
- J. C. Bryan, T. G. Levitskaia, C. Giacomazzo, G. Cascarano, A. P. Marchand, Z. Huang, V. S. Kumar, and T. D. Power, "Synthesis, Alkali Metal Picrate Extraction Properties, and X-ray Crystal Structure of a Novel, Cage-Annulated 18-Crown-6 Host," *Struct. Chem.* **12**, 313-322 (2001).
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- A. T. Macias, K. A. Kumar, A. P. Marchand, and J. D. Evanseck, "Synthesis and Inclusion Complexation Studies of a Novel and Selective Molecular Receptor for 1,4-Disubstituted Benzenes and 4,4'-Disubstituted Biphenyls," *J. Org. Chem.*, **65**, 2083-2089 (2000).
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- A. P. Marchand, H.-S. Chong, M. Takhi, W. H. Watson, and S. G. Bodige, "Synthesis and Extraction Studies of an Unusual Cage-Functionalized Cryptand," *Heterocycles*, **54**, 151-158 (2001).
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B. A. Moyer, G. M. Brown, J. C. Bryan, C. K. Chambliss, T. J. Haverlock, T. G. Levitskaia, and A. P. Marchand, "Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate," FY 2001 EMSP Annual Report, Aug., 2001; available on the EMSP web site <http://emsp.em.doe.gov/>.

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## Interactions

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A. P. Marchand, T. D. Power, B. A. Moyer, T. G. Levitskaia, P. V. Bonnesen, and J. C. Bryan, "Ion-Pair Extraction by Using Cage-Functionalized Hosts: Strategy for Selective Extraction of NaOH from Wastes," ACS National Meeting, Chicago, IL, Aug. 26-30, 2001 (CONTRIBUTED - ORAL PRESENTATION).

B. A. Moyer, P. V. Bonnesen,, G. M. Brown, J. C. Bryan, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, and F. J. Sloop, "Liquid-Liquid Extraction Approaches to the Treatment of Alkaline High-Level Waste," ACS National Meeting, Chicago, IL, Aug. 26-30, 2001 (INVITED - KEYNOTE LECTURE).

A. P. Marchand, "Evaluation of Binding Selectivities of Cage-Annulated Crown Ligands Toward Alkali Metal and Heavy Metal Cations by Electrospray Ionization/Quadrupole Ion Trap Mass Spectrometry," Rudjer Boskovic Institute, Zagreb, Croatia, June 20, 2001 (Colloquium -INVITED).

A. P. Marchand, "From Cage Compounds to Molecular Clefts. Novel Cage-Annulated Crown Ethers, Cryptands, and Molecular Boxes: A New Class of Ionophores for Selective Ion Complexation," Department of Chemistry, Rutgers University, Newark, NJ, April 27, 2001 (Departmental seminar speaker - INVITED).

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P. V. Bonnesen, L. H. Delmau, N. L. Engle, T. J. Haverlock, T. G. Levitskaia, B. A. Moyer, "Application of Fluorinated Alcohols in Metal Ion Solvent Extraction Processes for Nuclear Waste Disposal and Environmental Remediation," 221<sup>st</sup> Meeting of the ACS, San Diego, CA, Apr. 1-5, 2001 (CONTRIBUTED - ORAL PRESENTATION).

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Alan P. Marchand, "Synthesis and Chemistry of Unnatural Products: From Cage Compounds to Molecular Clefts. Novel Cage-Annulated Crown Ethers, Cryptands, and Molecular Boxes: A New Class of Ionophores for Selective Ion Complexation," Department of Chemistry, University of Texas at San Antonio (UTSA), San Antonio, TX, November 3, 2000 (INVITED - Departmental seminar speaker).

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Z. Chen and A. P. Marchand, "Synthesis and Alkali Metal Picrate Extraction Capabilities of Cage-annulated Crown- and Azacrown Ethers. Part I.," 33rd Annual ACS-DFW Meeting-in-Miniature, University of North Texas, Denton, TX, April 15, 2000, Graduate Section; Paper No. G-03 (CONTRIBUTED - ORAL PRESENTATION).

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## **Collaborations**

Bruce A. Moyer directed the project, offering technical guidance on the experiments to be performed and on interpretation of results, integrating the collaborative research efforts, and providing administrative support for appropriate staffing and reporting of results. Peter V. Bonnesen was responsible for the organic synthesis at ORNL, as related to novel fluorinated alcohols and phenols. Jeffrey C. Bryan performed X-ray crystal structures and addressed structural questions.

Prof. Alan P. Marchand and his group at the University of North Texas (UNT) carried 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. As initially planned, these compounds were shared with the ORNL group for liquid-liquid extraction studies and crystal-structure determinations. A number of joint publications have resulted from this collaboration (see above listing), and a fruitful understanding of the properties of the UNT compounds has been obtained. One of these publications reported for the first time the observation of the phenomenon of synergized pseudo hydroxide extraction.

Gilbert M. Brown of ORNL acted as a consultant on NaOH recycle questions. He was supported under the related project "Sludge Washing: Leaching of Hanford Tank Sludge," Efficient Separations and Processing Crosscutting Program, Office of Science and Technology, USDOE Office of Environmental Management

## **Transitions**

The Tanks Focus Area was routinely informed of progress in this project. The primary contact was the Technical Integration Manager for Pretreatment, Dr. C. Phil McGinnis. Feedback from Tanks Focus Area was important in directing some experimental effort toward the investigation of the questions of extraction efficiency and capacity. The results from these experiments were promising, leading to key participation in Hanford workshops in FY 2002. Information on sodium hydroxide extraction was also provided to Mr. Michael Johnson, CH2MHill Hanford Group, Richland, Washington and to Dr. Gregg J. Lumetta, Pacific Northwest Laboratories. Interaction with Dr. Lumetta has resulted in his contribution to the renewal proposal for this project as co-PI.

## **Patent**

B. A. Moyer, C. K. Chambliss, P. V. Bonnesen, and T. J. Keever, "Solvent and Process for Recovery of Hydroxide from Aqueous Mixtures," U. S. Patent 6,322,702, Nov. 27, 2001.

## Future Work

In the renewal 3-year period, a collaborative project involving Oak Ridge National Laboratory, Pacific Northwest National Laboratory (G. J. Lumetta), and the University of North Texas (Prof. A. P. Marchand) will be undertaken to explore new approaches to the separation of sodium hydroxide, sodium nitrate, and other sodium salts from high-level alkaline tank waste. Again, the principal potential benefit of this research will be a major reduction in the volume of the high-activity waste stream, obviating the building of expensive new waste tanks and reducing the costs of vitrification. Principles of ion recognition will be researched toward discovery of liquid-liquid extraction systems that selectively separate sodium hydroxide and nitrate from waste-like matrices. Successful approaches to sodium hydroxide separation that were discovered in the prior three years will be enhanced by further efforts to understand the controlling equilibria, selectivity, and capacity. This work will employ the novel concept of pseudo hydroxide extraction by fluorinated alcohols and phenols that function by cation exchange at elevated pH values. Crown ethers designed for sodium binding will be examined as possible synergists, and new ionizable lariat ethers will be synthesized as a new class of pseudo hydroxide extractants (UNT). A new thrust will be initiated to specifically target sodium nitrate. Applicable principles to be understood include solvation effects that promote efficient sodium nitrate extraction and appropriate crown ether design for efficient sodium binding and rejection of cesium. A proposed approach to the combined removal of sodium salts will be examined. Studies with real tank waste at PNNL will provide feedback toward solvent designs that have desirable properties.

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## Feedback

Fruitful interactions have taken place with the Tanks Focus Area (TFA), the PI receiving welcome advice on technology needs and contacts at the Hanford site. Both the TFA managers and EMSP program managers have been accessible and have greatly facilitated contacts of the PI with Hanford site personnel. This facilitation was productive and greatly appreciated. Workshops held in FY 2002 were very well done and provided a unique forum for discussion between PIs and Hanford problem holders. These worthwhile discussion forums should be continued on a periodic basis. With the Office of Environmental Management in transition during FY 2002, care should be taken to maintain the integration function that the TFA has been providing for EMSP PIs. Communication channels with the sites are invaluable, and the success of the EMSP in having impact on site needs will depend on how well communications continue.

## Appendices: Biographical Sketches of Senior Investigators

### ***Bruce A. Moyer***

Group Leader, Chemical Separations  
Chemical Sciences Division  
Oak Ridge National Laboratory

Bruce A. Moyer leads the Chemical Separations Group of ORNL's Chemical and Analytical Sciences Division and has over 100 career publications, 6 patents, 3 pending patent applications, and 3 review book chapters, primarily in the area of separation chemistry and chemical recognition by liquid-liquid extraction and ion exchange. He graduated *summa cum laude* from Duke University in 1974 with a B.S. degree in chemistry with honors and from the University of North Carolina at Chapel Hill in 1979 with a Ph.D. in inorganic chemistry (T. J. Meyer, Advisor). Memberships in honorary societies include Phi Beta Kappa, Phi Eta Sigma, and Phi Lambda Upsilon. He has been a research chemist at Oak Ridge National Laboratory since 1979 and has held the positions of Group Leader, Chemical Separations Group, since 1987, and Group Leader, Transuranium Research Laboratory, 1990-1991. He has been a member of the American Chemical Society since 1979, serving in the elected positions of Secretary-Treasurer (1992,1993) and Vice Chair-Elect through Past Chair (1994-1997) of the Separation Science and Technology Subdivision of the I&EC Division. For the journal *Solvent Extraction and Ion Exchange*, he has served as Editorial Board member (1988-1993), Assoc. Editor (1993-2000), and Co-Editor (2000-). He also serves on the Editorial Board of the journal *Hydrometallurgy* (1994-). He served on the Advisory Committee of the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory (1995-1999), chairing the Research Environments User Sub-Committee (1997-1999). Dr. Moyer received three ORNL Chemical and Analytical Sciences Division Technical Awards in the period 1996-1999. In 1999, he received three Lockheed Martin Research Corporation Achievement awards: Leadership Award for leadership in research; Development Award for contribution to the development of a novel bifunctional anion exchange resin; and Development Award for achievement in the invention, development, and testing of a novel process for cesium separation from waste. In 2000, he received a UT-Battelle Technical Achievement Award for contributions to the development of novel resin regeneration methods. He has given 15 invited lectures in the past 3 years, including 4 lectures as Visiting Scientist at the Japan Atomic Energy Research Institute, a tutorial lecture on environmental aspects of inorganic chemistry at the 1999 Fall ACS National Meeting, and 4 university departmental seminars; he has also been invited to lecture at the upcoming Gordon Conference on inorganic chemistry and will be a plenary speaker at the EMSP Symposium at the Fall ACS meeting.

## ***Peter V. Bonnesen***

### **EDUCATION**

**Ph.D. in Inorganic Chemistry**, March, 1989, University of California, Los Angeles.  
**B.S. (ACS certified) in Chemistry**, May, 1983, Lafayette College, Easton, PA.

### **EXPERIENCE**

Research Staff, Chemical and Analytical Sciences Division (CASD),  
Oak Ridge National Laboratory, 1993-present  
Postdoctoral Research Associate, University of California, Berkeley, 1991-1993.  
Research Scientist, Rohm and Haas Company, Spring House, PA, 1989-1991.

### **INTERESTS AND EXPERTISE:**

Research interests include both basic and applied aspects of separation science and technology based upon chemical recognition principles. This includes the design and synthesis of ligands and extractants used in separations science. Other interests include radiochemistry, environmental chemistry, and sensor technology.

### **AWARDS**

UT Battelle ORNL Technical Achievement Award for Development Accomplishment (2000)  
Lockheed Martin Energy Research Corporation Valuable Invention Award (1999)  
Lockheed Martin Research Corporation Development Awards (two in 1999)  
ORNL CASD Technical Achievement Development Awards (1998, 1999)  
ORNL CASD Technical Achievement Invention Award (1996)  
Martin Marietta Energy Systems Technology Transfer Award (1994)

## **Jeffrey C. Bryan**

### **EDUCATION**

University of Washington, Seattle  
Chemistry, Ph.D., September 1988

University of California, Berkeley  
Chemistry, A.B., March 1982

American River College, Sacramento, California

### **PROFESSIONAL EXPERIENCE**

Oak Ridge National Laboratory, Oak Ridge, Tennessee 10/94-present  
Research Staff Member. Research in structure and design of novel reagents for molecular recognition. Responsible for operation of X-ray diffraction laboratory, structure determination and design of new solvent extraction agents, with application to environmental problems at Department of Energy sites, and program development to maintain current funded areas as well as initiating new areas of research. System administrator for UNIX workstation and network of Apple computers.

Pellissippi State Technical Community College, Knoxville, Tennessee 1/96-12/98  
Adjunct Faculty, Department of Natural Sciences. Responsible for lecture portion of an evening general chemistry course. Taught four semesters.

Los Alamos National Laboratory, Los Alamos, New Mexico 9/89-10/94  
Postdoctoral Fellow and Staff Member. Initiated and developed new research programs investigating fundamental technetium ( $^{99}\text{Tc}$ ) and rhenium chemistry with applications to environmental fate, waste processing, and development of new radiopharmaceuticals. Responsible for technical execution including operation of X-ray diffraction laboratory, promotion of technical accomplishments, obtaining funding, developing effective collaborations, recruiting and supervising students, and developing and implementing new safety and waste disposal procedures including organization and maintenance of new radiological laboratories.

University of Auckland, New Zealand 10/88-8/89  
Postdoctoral Research Associate with Professor Warren R. Roper. Research in organometallic and organic chemistry; directed towards synthesis, characterization and reactivity of iridium-carbon triple bonds.

International Christian Youth Exchange, New York, New York 4/82-7/84  
Director for Overseas Program, U.S. Committee. Responsible for placement of 95-100 foreign exchange students around the U.S. Coordinated a national network of volunteers. Worked with two other staff implementing new educational materials, programs and policies, and grant writing resulting in 35% expansion of participation. Networked with similar organizations and potential funding sources.

## ***Alan P. Marchand***

Dept. of Chemistry  
University of North Texas  
Denton, Texas

Professional Experience: Alan P. Marchand is Regents' Professor of Chemistry at the University of North Texas and has approximately 300 career publications, including six books, fifteen review articles, and one U. S. patent. Dr. Marchand received his B. S. degree in Chemistry (with honors) from Case Institute of Technology (1961) and his Ph. D. degree at the University of Chicago in 1965. After a postdoctoral year at the University of California, Berkeley (1965-1966), he joined the faculty at the University of Oklahoma, Norman, OK as Assistant Professor of Chemistry. He was promoted to Associate Professor in 1970 and then to Professor of Chemistry in 1976. In that year, he received the Sigma Xi faculty research award at the University of Oklahoma. Dr. Marchand was appointed Adjunct Professor of Pharmacy at the University of Oklahoma's College of Pharmacy in 1979, a position which he held until 1982. In that year, he moved to the Department of Chemistry, University of North Texas, where he presently holds the position of Regents' Professor of Chemistry. Dr. Marchand was the 1989 Regents' Faculty Lecturer at the University of North Texas. He received the Wilfred T. Doherty Award of the Dallas-Fort Worth Section of the American Chemical Society in April, 1991. He was appointed Erskine Fellow in the Department of Chemistry, University of Canterbury, Christchurch, New Zealand during May-August, 1992. He was appointed Visiting Scientist at the University of Tokyo by the Japanese Ministry of Education during December, 1992 and January, 1993. Later in 1993, he was named Robert B. Toulouse Scholar at the University of North Texas. He presented the 1993 Henry Lardy Lecture at South Dakota State University in April, 1993. He was Visiting Scientist in the Chemical and Analytical Sciences Division at Oak Ridge National Laboratory, Oak Ridge, TN during the Summer, 1994. He was appointed Decker Scholar at the University of North Texas (1999-2001). Dr. Marchand edits a monograph series, "*Methods in Stereochemical Analysis*", that has been published continuously by VCH Publishers (now by Wiley-VCH: New York) since 1982. He was appointed to the Editorial Boards of the *Journal of Energetic Materials* and *Structural Chemistry*, and he is also a member of the Editorial Advisory Board of "*Structure, Energy, and Reactivity in Chemistry*", a monograph series edited by Joel F. Liebman and Arthur Greenberg and published by Chapman & Hall: New York. In 2001, he was appointed to membership on the International Advisory Board of *Kemija u industriji* (Croatian Chemical and Biochemical Engineering Quarterly) and to the Editorial Advisory Board of "*Advances in Heterocyclic Chemistry*" (term of service 2001-2005).

Interest and Expertise: Studies of inclusion phenomena and molecular recognition; metal ion separation and transport; applications of advanced theoretical methods to problems in structural and mechanistic organic chemistry; synthesis of polycarbocyclic "cage" compounds and novel energetic materials.