

ANNUAL PROGRESS REPORT

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Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts^(a)

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^(a) This report describes the Pacific Northwest National Laboratory contribution to this project. The ORNL contribution will be described in a separate report.

Summary

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

Research Objectives

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

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

In terms of the science that is needed to discover applicable liquid-liquid separation systems, basic questions that this research addresses include whether it is even possible to remove bulk sodium electrolytes from the waste, what types of chemical systems might be applicable, what functional properties might be obtained, how those functional properties might be understood based on molecular properties, what selectivity might be possible, and how the extraction could be reversed to regenerate the solvent and to recover a usable sodium product stream. In the previous and current funding periods, all of these questions have been in part successfully addressed, with the emergence of some promising systems and associated understanding. Nevertheless, understanding is incomplete, and the overall problem of sodium removal is not

resolved.

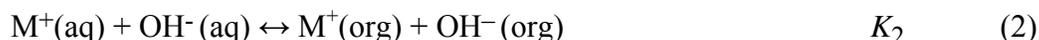
The overall problem is complex in that multiple sodium electrolytes are involved, and generality has not yet been achieved. For example, sodium hydroxide may now be selectively separated from the waste based on our results, an important and useful milestone in itself, but the extraction of the other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

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

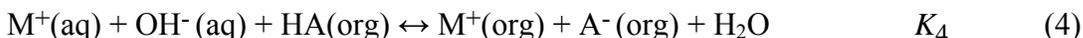
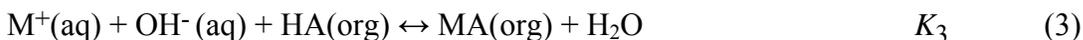
Research Progress and Implications

This annual report covers progress achieved at PNNL in FY 2005. A separate report will be issued reflecting progress to date for work at ORNL. The work conducted at PNNL in FY 2005 focused on developing a pseudohydroxide extraction (PHE) system that utilizes a process-friendly diluent. Pseudohydroxide extraction employs a weak lipophilic organic acid (e.g., a phenol or fluorinated alcohol; represented in this discussion as HA) capable of proton exchange with the aqueous sodium ion at elevated pH. The lipophilic acid is dissolved in a water-immiscible diluent to form the process solvent and is converted to the sodium form upon contact with NaOH solution. Upon subsequent contact with water, the organic-phase sodium salt releases the Na⁺ cation via hydrolysis, thereby producing an aqueous solution of NaOH and regenerating the organic acid. Spectral studies have confirmed that the mechanism of PHE involves the deprotonation of the alcohol to yield the corresponding alkoxide in the organic phase (Maya, Moyer, and Lance 2003).

Cation-exchange processes involving sodium ion are often hindered by the highly positive Gibbs energy of its partitioning into typical water-immiscible solvents (Marcus 1997), and choosing a suitable diluent becomes particularly important. The majority of recently reported investigations of NaOH extraction *via* PHE employed 1-octanol diluent, which exhibits donor-acceptor properties favorable for the stabilization of the deprotonated alkoxide and Na⁺ extraction in comparison with other water-immiscible solvents (Chambliss et al. 2002, Haverlock et al. 2003). In the absence of extractant, partitioning of NaOH into water-saturated 1-octanol has been demonstrated and quantitatively described *via* the proposed ion-pair extraction mechanism described by Reactions 1 and 2 (Kang et al. 2005).



In this investigation, the ion-pair extraction mechanism for the NaOH partitioning was confirmed by vibrational and mass spectroscopic techniques. In PHE, a detailed equilibrium analysis of NaOH extraction into 1-octanol using two model organic acids, 3,5-di-*tert*-butylphenol (35-DTBP), and a fluorinated alcohol in the 0.003 to 0.1 M concentration range has indicated no aggregation behavior, and the cation exchange process mechanism has been described by Reactions 3 and 4.



Although the donor-acceptor properties of 1-octanol are well-suited for PHE, its ability to solubilize appreciable amounts of water and its high viscosity are undesirable in an industrial application. At high sodium loading, expansion of the organic phase volume was observed with 1-octanol as the diluent (Haverlock et al. 2003), and in some cases, gelling of the loaded solvent occurred (Lumetta et al. 2002). Aliphatic diluents are usually preferred for industrial solvent extraction processes. However, they entail trade-offs, such as poor solvation of the ionic species leading to very weak extraction, particularly of the alkali metal ions. Also the solubilities of the lipophilic alcohols in the aliphatic diluents are generally not high enough to yield practical PHE systems. In FY 2005, we investigated the possibility of using a commercially available aliphatic hydrocarbon diluent (Isopar® L) modified with 1-octanol to overcome the limitations of the previously described PHE solvent formulations. The 35-DTBP cation exchanger was used in this work. The moderately high acidity of 35-DTBP (aqueous $pK_a = 9.9$) ensures effective proton/sodium exchange at reasonable aqueous-phase NaOH concentrations and successful regeneration of the phenol by hydrolysis upon contact with water. These properties make 35-DTBP especially suitable for the PHE. Previous comparative studies have demonstrated 35-DTBP to be one of the most efficient sodium extractants in several cation-exchange based extractive systems (Chambliss et al. 2002, Levitskaia et al. 2003). In addition, 3,5-DTBP exhibited improved phase behavior in comparison with other phenols (Haverlock et al. 2003).

In a previous study, the extractive behavior of 35-DTBP in 1-octanol was quantitatively characterized for organic phases with the concentration of phenol not higher than 0.1 M; under these conditions, no aggregation of the free or sodium-loaded extractant was observed (Kang et al. 2005). For an industrial scale PHE process, a much higher concentration of the cation exchanger is needed because high sodium loading is required, and aggregate formation is likely to occur. Our investigation was aimed at elucidating the PHE mechanism under high loading conditions. The speciation and equilibrium behavior of the 35-DTBP was studied using 0.1 to 1 M 35-DTBP concentration in the extraction phase and aqueous phase containing up to 10.5 M NaOH. Water co-extracted with sodium ion was measured for each extraction phase. Sodium distribution results were successfully fit using the SXLSQI modeling program (Baes 1998). Speciation of the sodium-loaded extraction phases was probed by the vibrational spectroscopy and electrospray mass spectrometry. The principle identified species were used as inputs to the SXLSQI model. The survey study of NaOH extraction from mixed inorganic sodium salts solution suggested a small matrix effect on the PHE, the important result for potential industrial applications of this approach. The PHE selectivity for Na^+ in the presence of competing Cs^+ ion

was assessed using aqueous phases containing constant 0.0001 M Cs⁺ and variable 0.01 – 10.5 M Na⁺ concentrations.

The solubility of 35-DTBP in Isopar® L is limited to ~0.15 M, based on experiments performed in our laboratory in which successive portions of 35-DTBP were added to Isopar® L until saturation was reached. For a practical pseudohydroxide extraction system, higher concentrations of 35-DTBP are required. The 1-octanol modifier serves to increase the 35-DTBP solubility in Isopar® L. Sodium extraction from 1.0 M NaOH with 0.1 M 35-DTBP in Isopar® L was determined as a function of 1-octanol concentration, which indicated that the Na distribution coefficient increases steadily with increased 1-octanol concentration, reaching a value at 1.0 M 1-octanol that is approximately half of that observed in 100% 1-octanol diluent. For all subsequent experiments, the Isopar® L diluent was modified with 1.0 M 1-octanol.

The donor-acceptor properties and moderate polarity of 1-octanol permit measurable partitioning of inorganic salts into this solvent. On the other hand, Isopar® L—a kerosene-like solvent containing a mixture of normal and branched alkanes—provides a highly unfavorable environment for solvation of ionic species. Accordingly, a diluent consisting of Isopar® L modified with 1-octanol is expected to exhibit intermediate extraction properties. Sodium distribution behavior with the selected diluent, i.e., 1 M 1-octanol in Isopar® L, was evaluated using 5 to 10.5 M NaOH solutions (Fig. 1). Weak partitioning was observed with corresponding D_{Na} values ranging from 10⁻⁴ to 10⁻³. These values are, as expected, smaller than the D_{Na} value of 7.4 × 10⁻³ observed for 1-octanol diluent using 7 M NaOH aqueous phase (Haverlock et al. 2003).

In the presence of the hydroxide ion, the SXLSQI model accounts for the auto-protolysis of water given by Reaction 5:



where $\log K_w = -14.004$ at 25°C. The program output is expressed by Reactions 6 and 7:

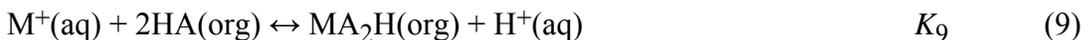


where $\log K_6 = \log K_1 + \log K_w$ and $\log K_7 = \log K_2 + \log K_w$. The logarithmic values of the equilibrium constants $K_6(\text{Na})$ and $K_7(\text{Na})$ were refined by the SXLSQI model to be -19.30 ± 0.05 and -22.82 ± 0.09 (Table 1), respectively. The values of $\log K_1(\text{Na})$ and $\log K_2(\text{Na})$ were calculated to be -5.30 and -8.82 , respectively, and found to be consistently lower than the corresponding values observed for the neat 1-octanol (Kang et al. 2005) because of the effect of Isopar® L. The results of the SXLSQI fit of Na partitioning from NaOH solutions with 1 M 1-octanol in Isopar® L are plotted in Fig. 1.

The extraction behavior of 35-DTBP in Isopar® L modified with 1 M 1-octanol was

characterized by systematic variation of the aqueous-phase NaOH and the organic-phase extractant concentrations. Figure 1 shows the effect of the aqueous Na concentration on the sodium distribution ratio D_{Na} using 1 M 35-DTBP in the modified diluent. The D_{Na} values increase proportionally with Na concentration up to ~ 0.3 M Na, which is indicative of the predominant ion pairing in the diluent. The decline of the D_{Na} values at higher Na concentration can be attributed to increasing loading of the extractant phase.

Dependence of the Na extraction on the 35-DTBP concentration in the diluent was studied at three different initial NaOH concentrations to assess the extractant behavior under variable loading conditions (Fig. 2). Sodium extraction increases nearly linearly with the 35-DTBP concentration in the diluent, the slopes predicted by SXLSQI for the log-log plots being 1.58, 1.43, and 1.23 for the 0.1, 1.04, and 2.63 M NaOH initial solutions, respectively. The slope values greater than unity are indicative of the formation of the 1:1 and 1:2 sodium-to-extractant species. This result was supported by our electrospray ionization mass spectrometry (ESI-MS) data collected in the anion mode, which demonstrated presence of the two principle species A^- and A_2H^- in the sodium extraction phases, corresponding to the distribution experiment depicted in Fig. 1. These observations prompted us to use Reactions 8 and 9 in the SXLSQI fitting.



This simple model adequately described the Na extraction. The data points corresponding to the Na extraction from the aqueous 10.5 M NaOH solution were not included in the input data set because of the formation of the multiple sodium-phenol aggregates in the extraction phases highly loaded with Na as determined by ESI-MS analyses. The values of $\log K_8(\text{Na})$ and $\log K_9(\text{Na})$ were refined by SXLSQI fitting to be -14.31 ± 0.07 and -13.46 ± 0.04 (Table 1), respectively. Reactions 8 and 9 can be written as Equations 3 and 10, respectively, when expressed in terms of hydroxide solution:



where $\log K_3 = \log K_8 - \log K_w$ and $\log K_{10} = \log K_9 - \log K_w$. The values of $\log K_3(\text{Na})$ and $\log K_{10}(\text{Na})$ were calculated to be -0.31 and 0.54 , respectively. The former value can be compared with the corresponding value of 0.47 reported for the neat 1-octanol diluent (Kang et al. 2005); that is, $K_3(\text{Na})$ is ~ 6 -fold lower because of the effect of Isopar® L. Another difference between 1-octanol and Isopar® L modified with 1 M 1-octanol diluents is the ion pairing behavior in the extraction phase. In 1-octanol, appreciable dissociation of the NaA ion pairs was found and quantitatively described. In this investigation, reasonable computer fitting (Fig. 1 and 2) was obtained assuming complete ion pairing in the extraction phase, which is consistent with the non-polar nature of the alkane Isopar® L diluent. The combined sodium model is summarized in Table 1. Another assumption applied in the SXLSQI modeling was the absence of 35-DTBP

self-association in the Isopar® L modified with 1-octanol diluent. The validity of this assumption was supported through vibrational spectroscopy and ESI-MS. The ESI-MS data indicated the presence of a small amount of the 35-DTBP dimer, with the monomer-to-dimer ratio of 10:1. The relatively minor self-aggregation of the 35-DTBP can be attributed to its effective solvation by 1-octanol.

It is of interest to compare sodium extraction isotherms for the 1-octanol and Isopar® L modified with 1 M 1-octanol. Figure 3 presents the sodium distribution experiment depicted in Fig. 1 in terms of the extraction isotherm and the analogous isotherm for 1.0 M 35-DTBP in 1-octanol (Haverlock et al. 2003). Interestingly, the extraction isotherm for 1.0 M 35-DTBP plus 1.0 M 1-octanol in Isopar® L is nearly the same as that observed when 1-octanol was the diluent. This result indicates that formulations of the PHE solvent are possible that retain the bulk properties of the aliphatic Isopar® diluent and yet retain the extraction performance of 1-octanol.

To determine the Na extraction isotherm under conditions relevant to recycling NaOH from solutions generated from leaching high-level radioactive tank waste, a series of simple simulants were prepared with compositions: 0.7 M NaAlO₂, 0.5 M NaNO₃, 0.05 M Na₂CO₃, and 1, 2, 3, 4, or 5 M NaOH. Figure 1 shows the Na extraction behavior for these simple sludge leaching simulants using 1 M 35-DTBP in the modified Isopar® L diluent and Fig. 3 shows the corresponding extraction isotherm. The purpose of this experiment was to preliminarily assess the process performance upon contact of the simulants with the PHE solvent, including the effectiveness of the sodium extraction, phase disengagement behavior, precipitate formation in the extraction phase, etc. It should be emphasized that for the complex simulant aqueous matrix consisting of the caustic and neutral sodium salts, two different extraction mechanisms, namely PHE and ion pair extraction, are expected to be valid, with PHE being the predominant mechanism. As it was noted previously, both 1-octanol and 35-DTBP extract neutral sodium salts *via* the ion-pair extraction mechanism. Specific interaction between an anion and hydroxy acid *via* hydrogen bonding drives ion pair extraction. The more acidic 35-DTBP ($pK_a = 9.9$) possesses enhanced proton donicity and is thus a more efficient extractant than 1-octanol ($pK_a = 20$). The ²²Na analysis used in this study measures bulk Na extracted and does not allow differentiation between the two mechanisms. Nevertheless, the observed overall Na distribution ratios are very similar to those obtained for the NaOH aqueous phases (in which only the PHE extraction mechanism is operable) despite the fact that the corresponding simulant aqueous solutions are less caustic. No precipitation, gelation, or third-phase formation was observed in the simulant contact phases. The aqueous solutions were stable for a period of at least 76 days. The phase disengagement was complete after centrifuging for 1 min. A previous PHE solvent formulation using 4-*t*-octylphenol in 1-octanol was plagued with the formation of gels at ambient temperature (Lumetta et al. 2002). The current formulation is superior in this respect as no gel formation was indicated.

Fourier-transform infrared (FTIR) and Raman spectra were recorded for the extracts obtained by contacting 1.0 M 35-DTBP in 1.0 M 1-octanol/Isopar® L with NaOH solutions (initial NaOH concentrations of 0.1, 0.5, 1.04, 2.63, 7.89, and 10.52 M). Spectra were also obtained for water-saturated 1.0 M 1-octanol in Isopar® L and for water-saturated 1.0 M 35-DTBP plus 1.0 M 1-octanol in Isopar® L. Following baseline correction, the contribution due to 1-octanol and Isopar® L was subtracted from the spectra of the extracts to reveal the spectral features of those species involving the phenol or phenolate. Figure 4 shows the FTIR spectrum of the organic

phase with increasing Na loading in the range 830 to 1005 cm^{-1} . Maya et al. (2003) previously reported this region to be diagnostic in the conversion of 35-DTBP to the corresponding alkoxide $[\text{Na}^+35\text{-DTBP}^-]$ in the 1-octanol modified Isopar® L solvent. The changes observed here confirm the formation of the alkoxide $[\text{Na}^+35\text{-DTBP}^-]$ in the 1-octanol modified Isopar® L solvent. The transformation from the phenol to the sodium alkoxide is evidenced by the collapsing of the band at 859 cm^{-1} and the corresponding splitting of this band into bands at 849 and 865 cm^{-1} . Similarly, the band at 959 cm^{-1} due to 35-DTBP shifts to 966 cm^{-1} upon loading of the solvent with Na^+ . The corresponding band positions in 1-octanol diluent are 859 and 961 cm^{-1} for 35-DTBP and 845, 865, and 965 cm^{-1} for $[\text{Na}^+35\text{-DTBP}^-]$.⁵ The $[\text{Na}^+35\text{-DTBP}^-]$ prepared by an independent route (treatment of 35-DTBP with NaH), exhibited essentially identical FTIR spectra of $[\text{Na}^+35\text{-DTBP}^-]$ and the Na-loaded extract confirms the formation of the sodium alkoxide in the PHE system. Analogous spectral changes upon solvent loading were also observed in the Raman spectra.

Table 1. Extractive Equilibrium Constants Obtained via SXLSQI Computer Modeling for Isopar® L Modified with 1 M 1-Octanol Diluent.

Equilibrium Reaction	log K values				Method of Calculation
	1 M 1-Octanol/IsoparL		35-DTBP in 1 M 1-Octanol/IsoparL		
	Na Extraction $\sigma = 1.87^a$	Cs Extraction $\sigma = 1.44^b$	Na Extraction $\sigma = 3.71^c$	Cs Extraction $\sigma = 2.24^d$	
1	-5.30	-5.07			$\log K_1 = \log K_6 - \log K_w$
2	-8.82	-9.17			$\log K_2 = \log K_7 - \log K_w$
6	-19.30 ± 0.05	-19.07 ± 0.03			Computer Fit
7	-22.82 ± 0.09	-23.17 ± 0.07			Computer Fit
3			-0.31	0.49	$\log K_3 = \log K_8 - \log K_w$
8			-14.31 ± 0.07	-13.51 ± 0.05	Computer Fit
9			-13.46 ± 0.04	-12.37 ± 0.04	Computer Fit
10			0.54	1.63	$\log K_{10} = \log K_9 - \log K_w$

^a Applied model: $\log K_6(\text{Na})$ and $\log K_7(\text{Na})$ are refined. OH^- is defined as the reference ion.¹²

^b Applied model: $\log K_6(\text{Na})$ and $\log K_7(\text{Na})$ are fixed; $\log K_6(\text{Cs})$ and $\log K_7(\text{Cs})$ are refined. OH^- is defined as the reference ion.¹²

^c Applied model: $\log K_6(\text{Na})$ and $\log K_7(\text{Na})$ are fixed; $\log K_8(\text{Na})$ and $\log K_9(\text{Na})$ are refined. OH^- is defined as the reference ion.¹²

^d Applied model: $\log K_6(\text{Na})$, $\log K_7(\text{Na})$, $\log K_8(\text{Na})$, $\log K_6(\text{Cs})$, and $\log K_7(\text{Cs})$ are fixed; $\log K_8(\text{Cs})$, $\log K_9(\text{Cs})$, and $\log K_9(\text{Na})$ are refined. OH^- is defined as the reference ion.¹² In this fit, the $\log K_9(\text{Na})$ value was obtained to be -12.47 ± 0.07 .

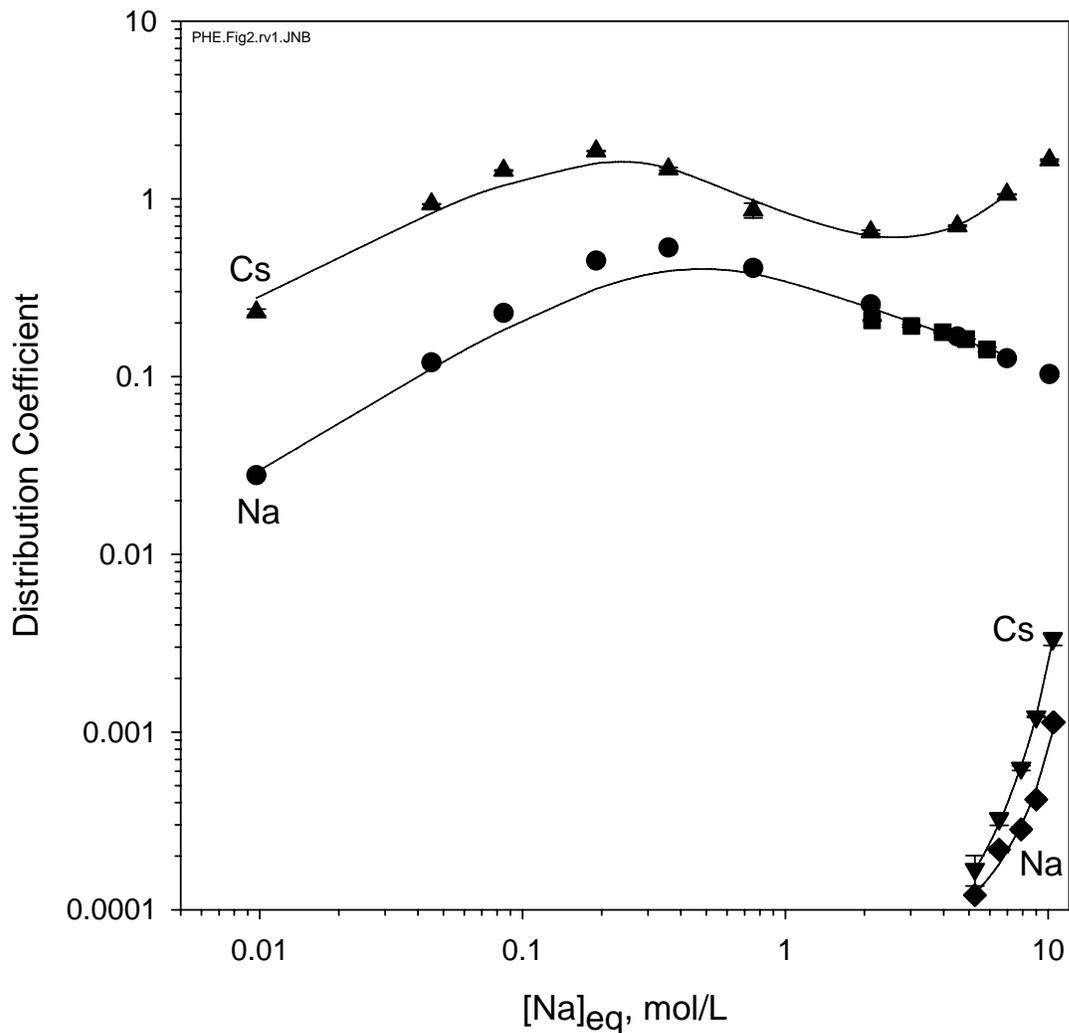


Figure 1. Dependence of sodium and cesium extraction aqueous into 1.0 M 1-octanol/Isopar® L upon equilibrium Na^+ concentration at 25 °C. The symbol notations are as following: inverted triangles and diamonds represent NaOH and CsOH partitioning, respectively, with no 35-DTBP present in the solvent phase; circles and squares represent Na^+ extraction from pure NaOH solutions and simple caustic sludge leaching simulant, respectively; triangles represent Cs^+ extraction from pure NaOH solutions. The plotted lines represent the calculated values based on the SXLSQI modeling described in the text and Table 1. Note: The error bars representing the standard deviation between duplicate measurements are small enough that they are typically covered by the symbols in the plot.

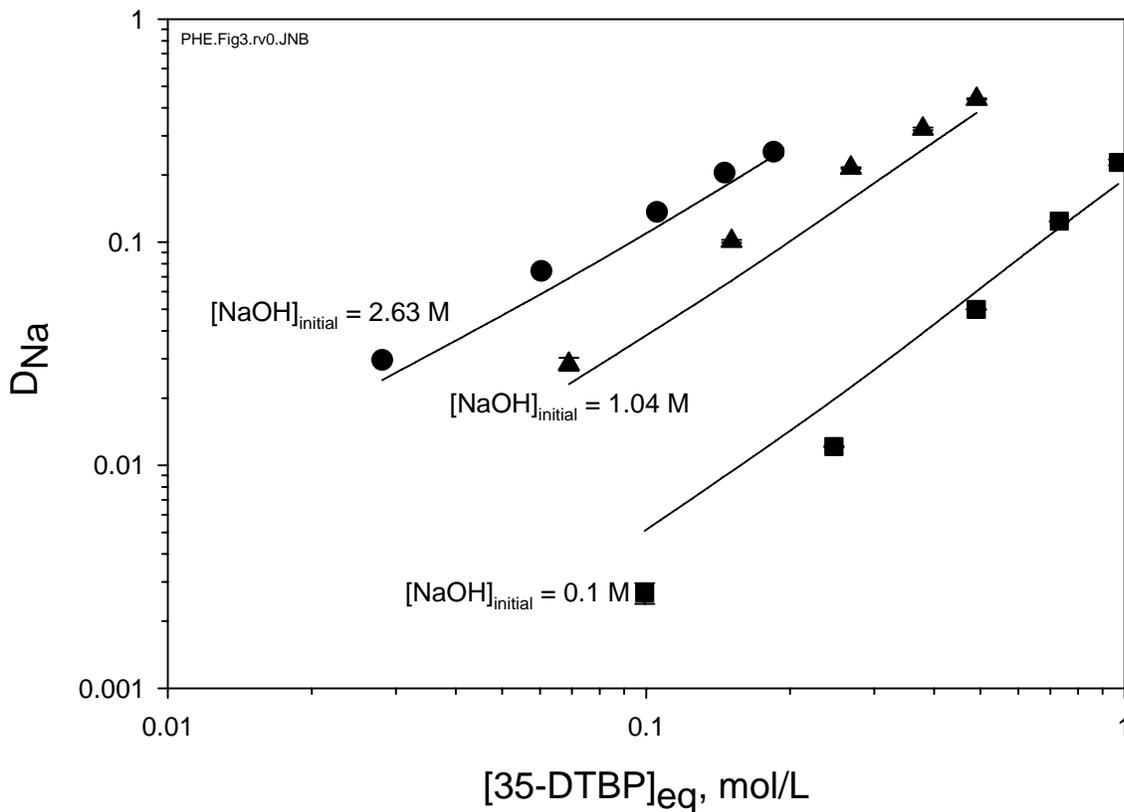


Figure 2. Dependence of sodium extraction upon 35-DTBP concentration in 1.0 M 1-octanol/Isopar® L at 25 °C using aqueous NaOH solutions of 0.10, 1.04, and 2.63 initial molarity. The plotted lines represent the calculated values based on the SXLSQI modeling described in the text and Table 1. Error bars on the D_{Na} data points indicate the standard deviation between duplicate measurements.

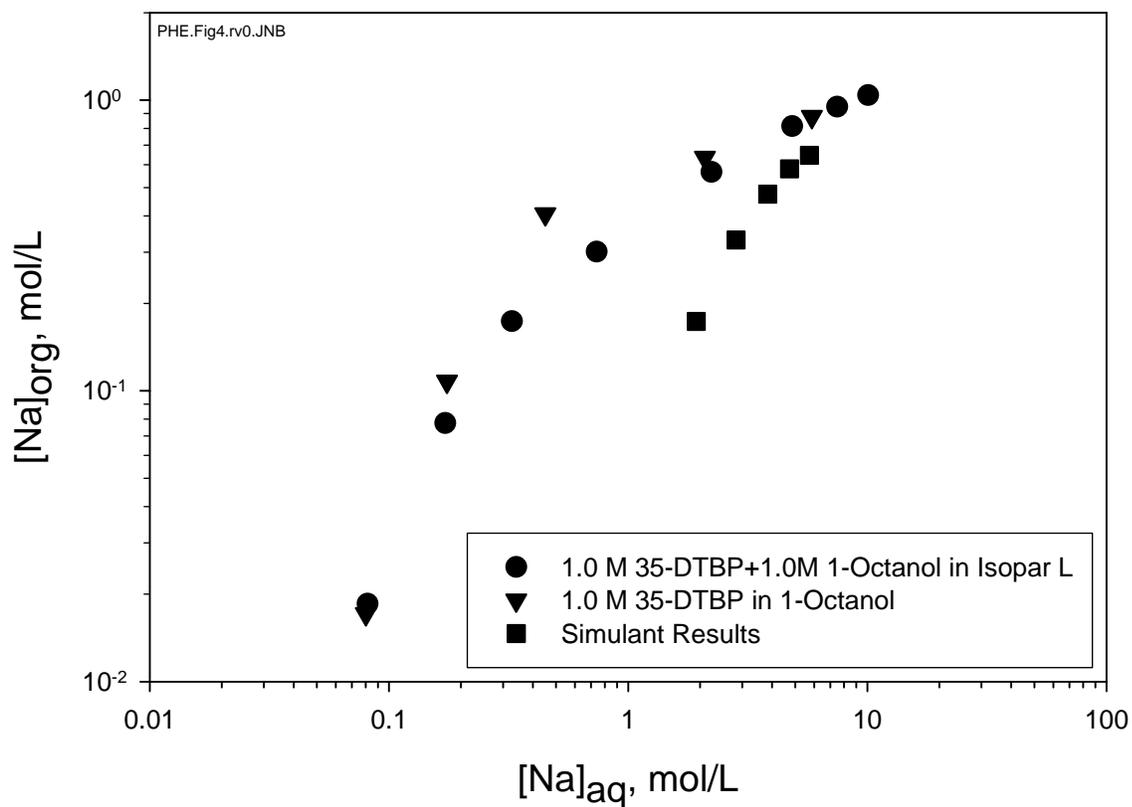


Figure 3. Comparison of the sodium extraction isotherms for 1.0 M 35-DTBP in 1.0 M 1-octanol/Isopar® L (this work) and 1.0 M 35-DTBP in 1-octanol (Haverlock et al. 2003) obtained using single NaOH solutions at 25 °C. Also shown is the extraction isotherm from simple sludge leaching simulant solutions with 1.0 M 35-DTBP in 1.0 M 1-octanol/Isopar® L at 25 °C.

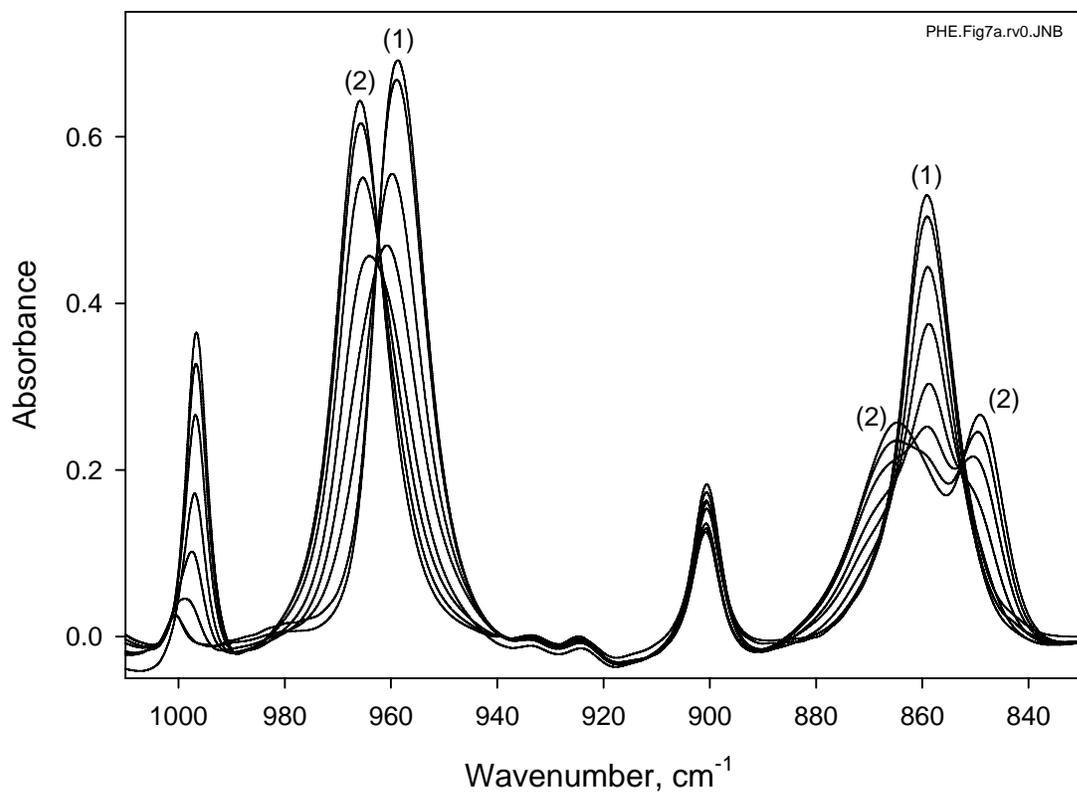


Figure 4. FTIR spectra for 1.0 M 35-DTBP in 1.0 M 1-octanol/Isopar® L with increasing Na loading. Bands marked with (1) are due to 35-DTBP; those marked with (2) are due to the Na-loaded solvent.

Planned Activities

Pseudo Hydroxide Extraction. Studies of the fundamental chemistry of PHE in modified aliphatic diluents (i.e., Isopar® L) will be continued. Included in these studies will be investigations into the effects of using alternative solvent modifiers. The diluent dependence of PHE will also be investigated in the context of the extractant structure. The resulting structure-function relationship will potentially allow prediction of the behavior of untested diluent modifiers and cation exchangers. The selectivity investigation of the selected PHE solvent systems will be continued, particularly in relation to rejection of ^{137}Cs and other radionuclides. Based on the PHE system described above (1 M 35-DTBP/1 M 1-octanol in Isopar® L), or one which is identified with alternative modifiers, experiments will be performed with simulated tank waste caustic leaching solutions as a prelude to experiments with actual tank waste. These experiments will be designed to determine the hydroxide recovery achieved based on conceptual flowsheets such as that shown in Figure 5. The behavior of other waste components will also be determined. Provided appropriate tank waste samples are made available, experiments on actual waste will be performed to confirm that the expected chemical behavior of sodium separation systems extends accurately to real-world solutions. Resulting data represent valuable feedback that the principles employed are sound, laying the intellectual foundation for future applied efforts to develop working separation systems.

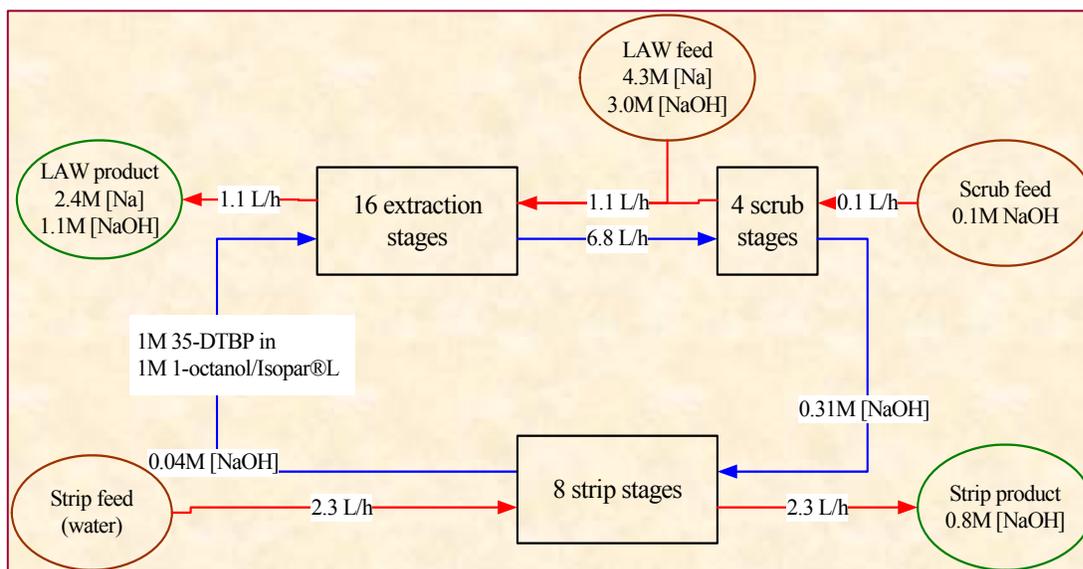


Figure 5. Conceptual PHE flowsheet for recovering sodium hydroxide from Hanford tank sludge leaching solutions.

Synergized Pseudo Hydroxide Extraction (SPHE). Simultaneous application of neutral and proton-ionizable extractants within one extraction system offers the benefit of the extraction enhancement explained via unique synergistic equilibrium reaction. In this synergistic process, neutral macrocyclic extractant effectively binds sodium ion, increases the extraction power of the cation-exchanger, provides controlled sodium extraction selectivity, and improves the phase

behavior reducing viscosity and water extraction. For the weak caustic solutions containing other sodium salts (e.g. nitrate, nitrite, sulfate, etc.), a neutral receptor can remove bulk salt components from the waste via ion-pair extraction mechanism, which is in turn expected to be enhanced by the favorable hydrogen bond interaction between protonated cation exchanger and anion co-transported with Na. Feasibility of NaNO_3 extraction will be established. Design and synthesis of the new sodium macrocyclic receptors is being conducted at ORNL. The newly obtained compounds will be examined for the sodium affinity and the most promising candidates will be selected for the systematic investigation of SPHE combined with the bulk sodium salts extraction to elucidate the speciation and transport mechanism. This will lead to the development of the comprehensive thermodynamic extractive models allowing prediction of the sodium transport in the organic solvent under wide concentration range. Spectroscopic studies will be used probe such equilibrium processes as aggregation of the organic acid and its interaction with the donor atoms of the neutral sodium receptor and with anions via H-bonding. Spectral results will be correlated with independently determined extraction results. Diluent effect on SPHE efficacy and selectivity will be investigated and selected solvent formulations will be subjected to the tests with simulated and real tank waste.

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

In FY 2006, experiments with actual Hanford tank waste will be initiated. The primary focus of these experiments will be to confirm the ability of the formulated solvent to extract sodium hydroxide from the actual waste and to be appropriately stripped within the test parameters. The behavior of minor, but significant, anions will be evaluated, including chromate, phosphate, and sulfate, which can have significant adverse effects on vitrification processes. The key analytes to be followed will include Na, NO_3^- , NO_2^- , PO_4^{3-} , SO_4^{2-} , CrO_4^- , Al, ^{137}Cs , and alpha emitters. In selected experiments, the solutions will be analyzed for ^{99}Tc and ^{90}Sr .

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

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FY2003 – FY2004 other publications

Levitskaia, T. G., G. J. Lumetta, and B. A. Moyer, "Combined Utilization of Cation Exchanger and Neutral Receptor to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts," 227th American Chemical Society National Meeting, Anaheim, CA, March 28–April 1, 2004.

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