

Sigma Team for Minor Actinide Separation: PNNL FY 2010 Status Report

Fuel Cycle Research & Development

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Sigma Team for Minor Actinide
Separation***

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SUMMARY

Work conducted at Pacific Northwest National Laboratory (PNNL) in FY 2010 addressed two lines of inquiry. The two hypotheses put forth were:

1. The extractants from the TRUEX^(a) process (CMPO)^(b) and from the TALSPEAK^(c) process (HDEHP)^(d) can be combined into a single process solvent to separate 1) the lanthanides and actinides from acidic high-level waste and 2) the actinides from the lanthanides in a single solvent extraction process. (Note: This combined process will hereafter be referred to as the TRUSPEAK process.) A series of empirical measurements performed (both at PNNL and Argonne National Laboratory) in FY 2009 supported this hypothesis, but also indicated some nuances to the chemistry. Lanthanide/ameridium separation factors of 12 and higher were obtained with a prototypic TRUSPEAK solvent when extracting the lanthanides from a citrate-buffered DTPA^(e) solution. Although the observed separation factors are sufficiently high to design an actinide/lanthanide separation process, a better understanding of the chemistry is expected to lead to improved solvent formulations and improved process performance. Work in FY 2010 focused on understanding the synergistic extraction behavior observed for Nd(III) and Am(III) when extracted into mixtures of CMPO and HDEHP. The interaction between CMPO and HDEHP in dodecane was investigated by ³¹P NMR spectroscopy, and an adduct of the type CMPO·HDEHP was found to form. The formation of this adduct will reduce the effective extractant concentrations and must be taken into account when modeling metal ion extraction data in this system. Studies were also initiated to determine the Pitzer parameters for Nd(III) in lactate media.
2. Higher oxidation states (e.g., +5 and +6) of Am can be stabilized in solution by complexation with uranophilic ligands, and this chemistry can be exploited to separate Am from Cm. To test this hypothesis, the previously reported stereognostic uranophilic ligands NPB^(f) and EETAC^(e) were investigated. To assess the potential of these ligands to stabilize pentavalent and hexavalent actinides, stability constants were measured for complexation of these ligands to Nd(III), Np(V), and Pu(VI) in a solvent mixture consisting of 80% methanol/20% water. For comparison, an analogous non-stereognostic ligand, NTA,^(f) was also examined. The ligand EETAC showed greater binding affinity for hexavalent Pu versus trivalent Nd by two orders-of-magnitude. Such selectivity was not observed for either NTA or NPB.

(a) TRUEX = transuranic extraction

(b) CMPO = octyl(phenyl)-N,N-diisobutyl-carbamoylphosphine oxide

(c) TALSPEAK = trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes

(d) HDEHP = bis(2-ethylhexyl)phosphoric acid

(e) DTPA = diethylenetriaminepentaacetic acid

(f) NPB = tris(3-(2-carboxy-phenoxy)propyl)amine

(e) EETAC = tris-N,N',N''-[2-(2-carboxy-phenoxy)ethyl]-1,4,7-triazacyclononane

(f) NTA = nitrilotriacetate

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ACRONYMS

CMPO	octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide
DTPA	diethylenetriaminepentaacetic acid
EETAC	tris-N,N',N''-[2-(2-carboxy-phenoxy)ethyl]-1,4,7-triazacyclononane
FCR&D	Fuel Cycle Research and Development
HDEHP	bis(2-ethylhexyl)phosphoric acid
HLW	high-level waste
NPB	tris(3-(2-carboxy-phenoxy)propyl)amine
NTA	nitrilotriacetic acid
OAS	optical absorbance spectroscopy
PNNL	Pacific Northwest National Laboratory
TALSPEAK	trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes
TBP	tributyl phosphate
TRU	transuranic element
TRUEX	transuranic extraction
TRUSPEAK	combined TRUEX and TALSPEAK process
UREX+	uranium extraction plus

MINOR ACTINIDE SEPARATION SIGMA TEAM PACIFIC NORTHWEST NATIONAL LABORATORY

1. INTRODUCTION

Advanced concepts for closing the nuclear fuel cycle typically include separating the minor actinides (i.e., Am and Cm) from other fuel components. The reason for separating these elements stems from their long-term impacts on the performance of geologic repositories for irradiated fuel. Separating these elements from the material going to the repository and subsequently converting them (e.g., by fission with fast neutrons) to stable or short-lived nuclides would greatly reduce the long-term risks associated with nuclear power. Separating Cm also has near-term benefits for the repository by reducing the heat load. Recent efforts in the United States have considered separating the transuranic (TRU) elements (Np, Pu, Am, Cm) from irradiated nuclear fuel as a single group. Including the minor actinides with the Pu makes the Pu less desirable for weapons production and thus improves the proliferation resistance of the fuel cycle compared to conventional fuel recycling schemes (which separate pure Pu) (Todd and Wigeland 2006).

One of the critical challenges in this regard is separating the TRU elements (especially Am and Cm) from the lanthanide fission products. The lanthanides are generally neutron poisons and thus reduce the efficiency of destruction processes for the TRU elements. Although there are active programs worldwide investigating the separation of TRU elements from the lanthanides, recent work in the United States has focused on the uranium extraction plus (UREX+) suite of separation processes. One of the disadvantages of this approach is the process complexity. For example, in the “UREX+1a” concept for irradiated fuel recycling, a series of four solvent extraction processes are proposed to partition the fuel into useful products and fission product waste (Mincher et al. 2009). The Minor Actinide Separation Sigma Team was established within the Fuel Cycle Research and Development (FCR&D) Program to discover and develop new more efficient methods for separating the TRU elements from the lanthanide elements and for separating americium from curium. This report summarizes work conducted at Pacific Northwest National Laboratory (PNNL) in FY 2010 as part of the Minor Actinide Separation Sigma Team.

Work conducted at PNNL in FY 2010 addressed two lines of inquiry. The two hypotheses put forth were:

1. The extractants from the transuranic extraction (TRUEX) process and from the trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK) process can be combined into a single process solvent to separate 1) the lanthanides and actinides from acidic high-level waste (HLW) and 2) the actinides from the lanthanides in a single solvent extraction process. In this report, we refer to this conceptual combined process as the “TRUSPEAK” process.
2. Higher oxidation states (e.g., +5 and +6) of Am can be stabilized in solution by complexation with uranophilic ligands, and this chemistry can be exploited to separate Am from Cm.

Experiments summarized in this report were performed to test each of these hypotheses.

2. SIGNIFICANCE

2.1 TRUSPEAK Task

Developing a single process that combines the attributes of the TRUEX and TALSPEAK processes would benefit the development of advanced closed fuel cycles by reducing the complexity of operations required to recover the minor actinides. Converting the transuranic elements to short-lived or stable nuclides requires separation from the lanthanide elements, which are generally neutron poisons and thus reduce the efficiency of fissioning processes. As previously mentioned, the “UREX+” suite of separation processes recently developed and investigated in the U.S. suffers the disadvantage of process complexity because of the number of different solvent extraction steps required. Combining two of these solvent extraction steps into a single process to reduce the complexity of materials handling has significant potential value in reducing the process complexity and thereby improving the economics of advanced fuel cycle recycle technology. Two processes that might be suited to “blending” are the TRUEX and the TALSPEAK processes. Section 3 presents the background material concerning these two processes.

2.2 Stabilization of Am(V)/Am(VI)

Stabilizing either Am(V) or Am(VI) by complexing with ligands selective for linear actinyl ions would provide opportunities to separate Am from Cm (e.g., by precipitation or solvent extraction). It is a significant challenge, however, to manage Cm in a closed nuclear fuel cycle, especially with regards to handling this element in fabricating fuels or targets for burning the TRU elements in fast reactors. One option is to separate the Cm from the other TRU elements and store it for decay. However, separating americium from curium is a significant technical challenge because of the very similar chemistries of Am^{3+} and Cm^{3+} . One key distinction between Am and Cm is that Am can be oxidized to Am(V) and Am(VI) in aqueous media. The accessibility of the higher Am oxidation states can be exploited to separate Am from Cm, but the higher Am oxidation states are difficult to maintain. That is why we have undertaken a study to determine if ligands that are known to strongly bind to uranyl ion (the so-called uranophiles) can be used to stabilize Am(V) or Am(VI) in aqueous solution.

3. APPROACH

3.1 TRUSPEAK Task

3.1.1 TRUSPEAK: Background

The TRUEX process extracts the TRU elements (Np, Pu, Am, Cm) and the lanthanide fission products from the other fission products from 1 to 3 M HNO_3 . This is achieved by extracting the TRU elements with octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO, Figure 3.1a) into an aliphatic hydrocarbon diluent. Tributyl phosphate (TBP) is added to the TRUEX solvent as a modifier to prevent third phase formation at high solvent loading (Horwitz et al. 1985). The TALSPEAK process uses bis(2-ethylhexyl)phosphoric acid (HDEHP, Figure 3.1b) as the extractant (Nilsson and Nash 2007). In this case, an aqueous-soluble complexant, diethylenetriaminepentaacetic acid (DTPA), is used to complex the actinide ions and prevent their extraction into the organic phase (or to strip the actinides from the organic phase in the so-called “reverse TALSPEAK” method). Because DTPA binds the lanthanide ions less strongly than the actinide ions, the lanthanides are extracted by HDEHP in the presence of DTPA, thereby achieving a separation of the lanthanides from the actinides.

macro quantities of the metal ion would be required. Because of the relatively high Nd/Am separation factor observed in TRUSPEAK (Lumetta et al., in press) compared to the TALSPEAK process, it was hypothesized that CMPO synergizes the extraction of Nd(III) much in the same way as it does for Am(III). Experiments were performed to test this hypothesis and this was shown to be the case (*vide infra*). So, Nd(III) was chosen to be used as a surrogate for Am(III) in the TRUSPEAK equilibria studies. Although previous results have suggested better lanthanide/actinide separation factors are obtained when citrate is used as a buffer, we have chosen to use lactate as buffer, primarily because it has only one protonation reaction to consider, but also because most related studies reported in the literature have been carried out using lactate buffer. The following key lines of inquiry were pursued in FY 2010:

1. Investigate the interaction between CMPO and HDEHP in *n*-dodecane
2. Determine Pitzer parameters for Nd(III) ion in high lactate media
3. Measure Nd(III) distribution ratios as a function of CMPO mole fraction, HDEHP concentration, and CMPO concentration
4. Perform equilibrium modeling of the Nd extraction using the computer program SXFIT.

3.2 Stabilization of Am(V)/Am(VI)

3.2.1 Stabilization of Am(V)/Am(VI): Background

A variety of solvent extraction and ion exchange methods have been reported for separating trivalent Am and Cm (Lumetta et al. 2006), but these methods typically require the use of very high salt solutions, so they are not attractive for large-scale use in processing commercial irradiated fuel. Americium was separated from Cm at the Savannah River Site by oxidizing Am(III) to Am(V) in K_2CO_3 solution, causing the double salt $K_5AmO_2(CO_3)_3$ to precipitate at 85°C (Groh et al. 1965). But again, this method uses significant quantities of salt, which would require disposal, and it is unproven at the industrial scale required to support advanced fuel cycles for commercial irradiated fuel. Thus, new methods to separate Cm from Am are needed that work efficiently at industrial scale and that do not lead to the creation of large amounts of secondary TRU waste.

One key distinction between Am and Cm is that Am can be oxidized to Am(V) and Am(VI) in aqueous media, forming the trans-dioxo cations AmO_2^+ and AmO_2^{2+} , respectively. The accessibility of the higher Am oxidation states can be exploited to separate Am from Cm, but the higher Am oxidation states are difficult to maintain. In this work, we have undertaken a study to determine if ligands that are known to strongly bind to uranyl ion (the so-called uranophiles) can be used to stabilize Am(V) or Am(VI) in aqueous solution. In the 1990s, Raymond and co-workers proposed that enhanced selectivity for *trans*-dioxo cations could be obtained by designing ligands that simultaneously form coordinate bonds to the equatorial region of the metal center and N-H hydrogen bonds to the axial oxygen atoms (Franczyk et al. 1992). This has been referred to as stereognostic ligand design and as is conceptually illustrated in Figure 3.2. In this work, we are investigating *tris*(3-(2-carboxy-phenoxy)propyl)amine (NPB; Figure 3.3) and *tris*-N,N',N''-[2-(2-carboxy-4-ethyl-phenoxy)ethyl]-1,4,7-triazacyclononane (EETAC; Figure 3.3) as potential Am(V)- or Am(VI)-stabilizing ligands. These ligands were prepared according to the literature methods (Franczyk et al. 1992, Walton and Raymond 1995, respectively) and were isolated as the hydrochloride salts for use in this work.

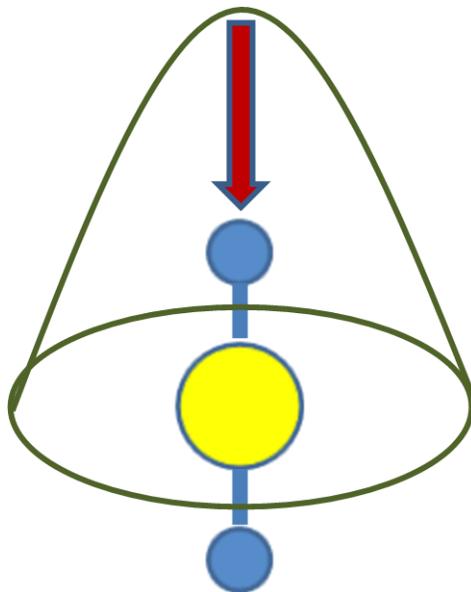


Figure 3.2. Conceptual Illustration of the Stereognostic Ligand Design Concept in Which a Ligand Binds an Actinyl Ion in the Equatorial Plane, but the Complex Is Also Stabilized Through Hydrogen Bonding (depicted by the arrow) to an Axial Oxygen Atom

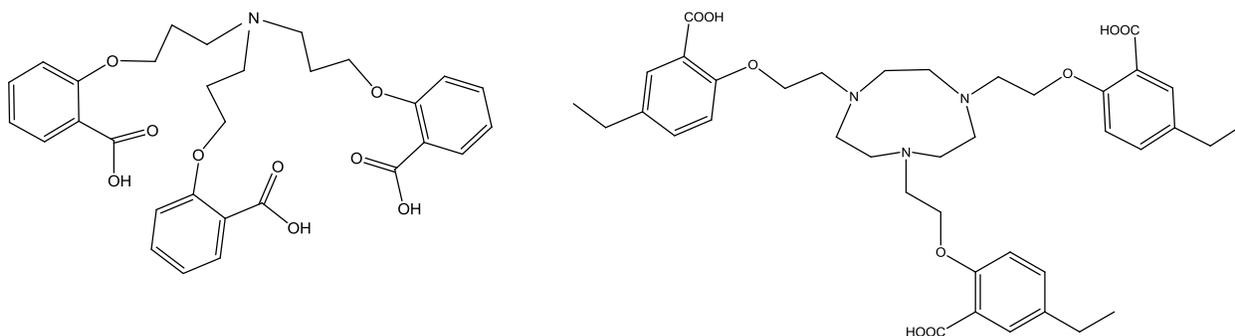


Figure 3.3. Structure of the Uranophilic Ligands NPB (left) and EETAC (right)

3.2.2 Stabilization of Am(V)/Am(VI): Approach

To assess the potential applicability of the stereognostic ligands in stabilizing higher oxidation states of Am, we began by measuring the binding constants for these ligands with more readily available Am analogs. Specifically, we investigated complexation to Nd(III), Np(V), and Pu(VI), representing the +3, +5, and +6 oxidation states of Am. Optical absorbance spectroscopy (OAS) was used for probing the Nd(III), Np(V), and Pu(VI) complexation by NPB and EETAC. For comparison, analogous complexation constants were measured for nitrilotriacetic acid (NTA), which represents a stereognostically “blind” reference ligand. The solvent system used was 80% methanol/20% water. This solvent was suitable for maintaining homogeneous solutions under all conditions investigated.

The major experiments performed to date include:

- Determination of protonation constants for NPB, EETAC, and NTA in the chosen solvent system
- Determination of binding constants for the three ligands with Nd(III), Np(V), and Pu(VI).

4. SUMMARY OF RESULTS

4.1 TRUSPEAK Results

Interaction of CMPO and HDEHP in n-Dodecane. The interaction between CMPO and HDEHP in *n*-dodecane was investigated using $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The chemical shift of the CMPO phosphoryl group in 0.1 M CMPO solution was measured as the amount of HDEHP in solution was varied from 0 to 1 M. The change in the position of this resonance can be related to the fraction of bound and unbound CMPO in the mixture, which in turn can be related to the equilibrium constant for the formation of the CMPO-HDEHP adduct. Figure 4.1 shows the best fit to the experimental data, which suggests the formation of an adduct of the form CMPO·HDEHP with $\log K = 3.06$ for its formation. A value of $\log K_{dim} = 4.43$ was used for the HDEHP dimerization constant in *n*-dodecane (Gen and Wang 1982). The formation of the CMPO·HDEHP adduct will reduce the effective extractant concentrations and must be taken into account when modeling metal ion extraction data in this system. For example, in the prototypic TRUSPEAK solvent of 0.1 M CMPO + 1 M HDEHP in *n*-dodecane, the concentrations of (HDEHP)₂, HDEHP, CMPO·HDEHP, and CMPO are 0.456, 0.004, 0.083, and 0.017 M, respectively.

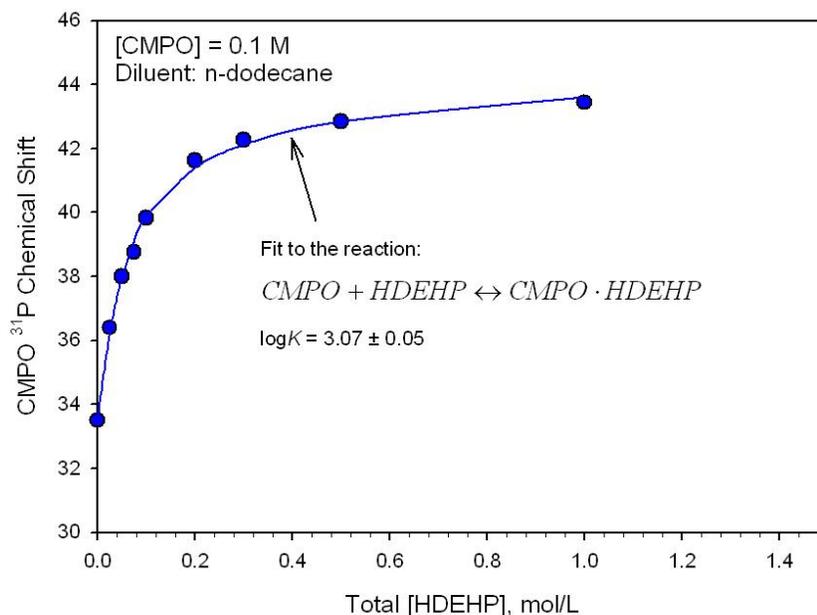


Figure 4.1. Position of the ^{31}P Resonance for the CMPO Phosphoryl Group as a Function of HDHEP Concentration; Comparison of Experimental and Calculated Values

Progress on Determining Pitzer Parameters for High Lactate Media

To model the equilibria involved in solvent extraction systems such as TRUSPEAK, it is necessary to have the means to calculate the solution activities for the key species present in solution. For modeling the behavior of Nd in lactate media, we are employing the ion-interaction model of Pitzer (1991). Pitzer parameters characterize the interactions amongst ions and solvent. The parameters may be determined by measuring osmotic coefficients. Isopiestic measurements were initiated to determine relevant Pitzer parameters for high lactate media.

Work conducted in FY 2010 has focused on establishing the capability to perform the isopiestic measurements and validating the methods used by measuring known chemical systems. Two experimental setups are currently under consideration and testing. One consists of a stainless steel alloy autoclave with a Ti/Pd alloy block and high density vitreous carbon crucibles. The other experimental is a Plexiglas rectangular box, with an aluminum block inside and metal crucibles. Two well established chemical systems are currently under investigation to validate our methodology: a 1:1 electrolyte and standard NaCl and a 1:2 electrolyte used as a sample system, CaCl₂.

Nd(III) Distribution Ratios

In FY 2009, it was shown that CMPO and HDEHP act synergistically in the extraction of Am(III) from lactate-buffered DTPA solution. Under the same conditions, only a very weak synergism is observed in the extraction of Eu(III) (Lumetta et al., in press). In FY 2010, analogous extraction experiments were performed for Nd(III). Figure 4.2 compares the Nd(III) extraction data to that for Am(III). The behavior of Nd(III) is similar to that of Am(III) in that there is a strong synergistic effect between HDEHP and CMPO. This result indicates that Nd(III) should serve as a good surrogate for Am(III) in investigating the fundamental extraction equilibria involved in the TRUSPEAK solvent extraction system.

Data on the extraction of Nd(III) from 1.5 M lactic acid solution at pH 1 were collected as a function of HDHEP concentration and as a function of CMPO concentration. In the latter case, it was necessary to have some HDEHP present to obtain measurable values of the distribution ratio. Full interpretation of the data from these measurements must await the results of the SXFIT equilibrium modeling, which is planned for FY 2011.

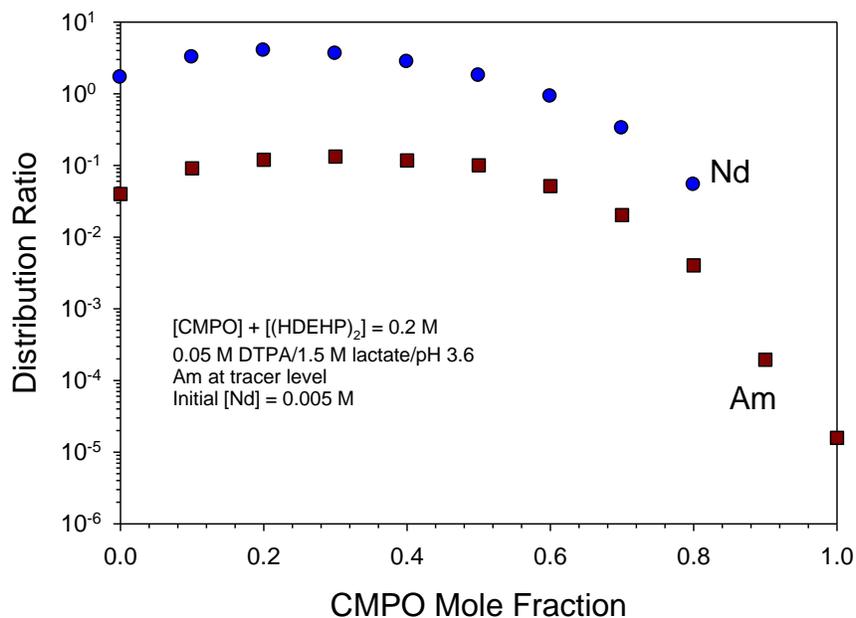


Figure 4.2. Extraction of Nd(III) and Am(III) from 0.05 M DTPA/1.5 M Lactate Solutions at pH 3.6 with HDEHP/CMPO Mixtures (*n*-dodecane diluent) as a Function of the CMPO Mole Fraction

4.2 Stabilization of Am(V)/Am(VI) Results

Spectrophotometry was used to determine a) the stepwise protonation constants for NTA, NPB, and EETAC in 80% CH₃OH - 20% H₂O medium at $I = 0.5$ M (NaClO₄) and b) formation constants for complexation of these ligands with Nd(III), Np(V), and Pu(VI). All the formation constants found in the course of testing of stereognostically active ligands are summarized in Table 4.1. NTA data are included in the same table for comparison and quantification of the magnitude of the stereognostic effect for +5 and +6 oxidation states.

Table 4.1. Formation Constants of NTA, NPB, and EETAC with Metal Cations in Oxidation States +3, +5, and +6

Metal Cation	Formation Constants [nM + mH ⁺ + pL = M _n H _m L _p (logβ format)]			
	NTA	NPB	EETAC	
Nd ³⁺	ML: 14.63 (0.07)	MHL: 18.37 (0.03)	MHL: 17.01 (0.01)	
	ML ₂ : 27.13 (0.07)	MH ₂ L ₂ : 35.62 (0.06)	MH ₂ L ₂ : 30.98 (0.09)	
NpO ₂ ⁺	ML: 12.78 (0.02)	MHL: 15.09 (0.01)	MHL: 14.56 (0.01)	
PuO ₂ ²⁺	ML: 14.33 (0.05)	MHL: 18.96 (0.02)	MHL: 19.41 (0.21)	

The effect of preferential binding of NPB and EETAC toward transdioxo-cations of Np(V) and Pu(VI) can be rationalized by analyzing the differences in the values of formation constants between the spherically symmetric metal cation Nd(III) and selected dioxocations Np(V) or Pu(VI) for all three ligands. For example, in the case of Np(V), the difference in the values of formation constants between the Np(V)-NTA complex and the Nd(III)-NTA complex is $12.78 - 14.63 = -1.85$, and this should be compared with the respective difference between the Np(V)-HNPB and Nd(III)-HNPB complexes: $15.09 - 18.37 = -3.28$. The more negative difference in the latter case compared with the former case indicates that NPB does not show any preferential complexation toward Np(V) compared with NTA. The similar calculation for EETAC ($14.56 - 17.01 = -2.45$) also indicates that EETAC does not exhibit any preferential binding of Np(V) compared with stereognostically inactive NTA.

The Pu(VI) case is quite different from Np(V). In this case, the Pu(VI)-NTA and Nd(III)-NTA difference is slightly negative ($14.33 - 14.63 = -0.30$), whereas the Pu(VI)-HNPB and Nd(III)-HNPB difference is positive ($18.96 - 18.37 = +0.59$). This means that the overall stereognostic effect for NPB and Pu(VI) is $0.59 - (-0.30) = +0.89$ in log scale or, in other words, NPB is a $10^{0.89} = 8$ times more efficient binder for Pu(VI) than NTA.

EETAC interaction with Pu(VI) shows a much more pronounced effect of stereognostic amplification of binding strength. Indeed the Pu(VI)-HEETAC and Nd(III)-HEETAC difference is substantially more positive ($19.41 - 17.01 = +2.40$) than the number calculated above for HNPB (+0.59). This finding is consistent with the Walton and Raymond (1995) assumption that the EETAC-based family of ligands might show an enhanced stereognostic effect because these ligands are 1) fully predisposed to interact with the oxo- group of the metal cation, 2) structurally arranged so as to preclude hydrogen bonding to an external solvent molecule, and 3) more preorganized for binding with the triazacyclononane cavity compared to the NPB-family of ligands.

5. REFERENCES

- Franczyk TS, KR Czerwinski, and KN Raymond. 1992. Stereognostic Coordination Chemistry. 1. The Design and Synthesis of Chelators for Uranyl Ion, *J. Am. Chem. Soc.* **114**:8138-8146.
- Gen P and X Wang. 1982. Determination of some basic constants of HDEHP and equilibrium constants for extraction of trivalent light rare earth ions, *Beijing Daxue Xuebao, Ziran Kexueban*, **5**:59-69.

- Groh HJ, RT Huntoon, CS Schlea, JA Smith, and FH Springer. 1965. ^{244}Cm Production and Separation—Status of the Pilot Production Program at Savannah River, *Nucl. Appl.*, **1**:327-336
- Horwitz EP, DG Kalina, H Diamond, GF Vandegrift, and WW Schulz. 1985. The TRUEX Process – A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent, *Solvent Extr. Ion Exch.*, **3**:75-109.
- Lumetta GJ, JC Carter, AV Gelis, and GF Vandegrift. In press. “Combining octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel,” *Nuclear Energy and the Environment Symposium*, ACS Symposium Series, Washington, DC.
- Lumetta GJ, SI Sinkov, JC Carter, MG Warner, and JW Pittman. 2009. *Sigma Team for Minor Actinide Separation: PNNL FY 2009 Status Report*, PNNL-18674, Pacific Northwest National Laboratory, Richland, Washington.
- Lumetta GJ, MC Thompson, RA Penneman, and PG Eller. 2006. Curium, Ch. 9 in *The Chemistry of the Actinide and Transactinide Elements*, 3rd Ed., LR Morss, NM Edelstein, J Fuger, eds., Springer, Dordrecht; pp. 1397–1443.
- Mincher BJ, G Modolo, and SP Mezyk. 2009. Review Article: The Effects of Radiation Chemistry on Solvent Extraction: 1. Conditions in Acidic Solution and a Review of TBP Radiolysis, *Solvent Extr. Ion Exch.*, **27**:1–25.
- Nilsson M and KL Nash. 2007. Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process, *Solvent Extr. Ion Exch.* **25**:665–701.
- Pitzer KS. 1991. *Activity Coefficients in Electrolyte Solutions: 2nd Edition*, CRC Press, Boca Raton, FL.
- Todd TA and RA Wigeland. 2006. “Advanced Separation Technologies for Processing Spent Nuclear Fuel and the Potential Benefits to a Geologic Repository.” In: *Separations for the Nuclear Fuel Cycle in the 21st Century*, ACS Symposium Series 933, American Chemical Society, Washington, DC; pp. 41–55.
- Walton PH and KN Raymond. 1995. “Stereognostic coordination chemistry 4 The design and synthesis of a selective uranyl ion complexant.” *Inorg. Chim. Acta* **240**:593–601.

6. INDICATORS OF PROJECT QUALITY AND PRODUCTIVITY

Publications

- Lumetta GJ, AV Gelis, and GF Vandegrift. 2010. “Solvent Systems Combining Neutral and Acidic Extractants for Separating Trivalent Lanthanides from the Transuranic Elements.” *Solvent Extr. Ion Exch.* **28**:287–312.
- Lumetta GJ, JC Carter, AV Gelis, and GF Vandegrift. “Combining octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel.” *Nuclear Energy and the Environment Symposium*, in press.

Presentations

- Lumetta GJ et al. 2010. “TRUSPEAK Combined Solvent Extraction System for Recovering Transuranic Elements from Irradiated Nuclear Fuel.” In: *34th Actinide Separations Conference*, May 20, 2010, Argonne, Illinois.

Sinkov SI et al. 2010. "Complexation of Nd(III), Pu(IV), Np(V), and Pu(VI) with ligands designed for enhanced binding of U(VI)." In: *34th Actinide Separations Conference*, May 20, 2010, Argonne, Illinois.

Rapko BM et al. 2010. "Stereognostically Optimized Ligands as Selective Complexants for Trans-Dioxo Actinide Cations." In: *239th National Meeting of the American Chemical Society*, March 24, 2010, San Francisco, California.

Gelis AV et al. 2010. "Actinide and Lanthanide Separation in TALSPEAK and combined TRUEX-TALSPEAK processes." In: *239th National Meeting of the American Chemical Society*, March 22, 2010, San Francisco, California.

Lumetta GJ et al. 2009. "TRUSPEAK Development: Combining CMPO and HDEHP into a Single Process Solvent for Recovering Transuranic Elements." In: *Sixteenth Symposium on Separation Science and Technology for Energy Applications*, Gatlinburg, Tennessee, October 21, 2009.

Lumetta GJ et al. 2009. "Combining octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and bis-(2-ethylhexyl)phosphoric acid extractants for recovering transuranic elements from irradiated nuclear fuel." In: *238th National Meeting of the American Chemical Society*, August 18, 2009, Washington, DC.

Sinkov SI et al. 2009. "TALSPEAK Chemistry in the Absence of DTPA: Nd(III) Speciation in Organic Phase Helps to Identify One More Previously Unaccounted for Player in the Process." In: *33rd Actinide Separations Conference*, May 20, 2009, Tahoe City, California.

7. COLLABORATORS AND PARTICIPANTS

The key researchers involved in this work are:

- Gregg Lumetta, Principal Investigator, responsible for overall project technical content and design and execution of TRUSPEAK experiments
- Sergey Sinkov, Senior Research Scientist, responsible for design and execution of Am oxidation/complexation experiments
- Tatiana Levitskaia, Senior Research Scientist, responsible for equilibrium modeling of solvent extraction data
- Doinita Neiner, Research Scientist, responsible for measuring activity coefficients and performing NMR measurements
- Jenifer Braley, Research Scientist, responsible for design and execution of solvent extraction and other experiments
- Jennifer Carter, Technician, responsible for execution of experiments as directed by the project scientists
- Marvin Warner, Senior Research Scientist, responsible for leading ligand synthesis
- Jonathan Pittman, Masters Intern, responsible for ligand synthesis
- Stan Latesky, visiting scientist from the University of the Virgin Islands; leads a faculty and student team (two students each summer) working on various aspects of Nd extraction chemistry