# Sigma Team for Advanced Actinide Recycle FY 2015 Accomplishments and Directions

## Fuel Cycle Research & Development

*Prepared for*
*U.S. Department of Energy*
*Sigma Team for Advanced Actinide Recycle*
***Bruce A. Moyer***
*Oak Ridge National Laboratory*
*September 30, 2015*
**FCRD-MRWFD-2015-000401**

This research was sponsored by the Fuel Cycle Research and Development Program, Office of Nuclear Energy, U. S. Department of Energy.

# SUMMARY

The Sigma Team for Minor Actinide Recycle (STAAR) has made notable progress in FY 2015 toward the overarching goal to develop more efficient separation methods for actinides in support of the United States Department of Energy (USDOE) objective of sustainable fuel cycles. Research in STAAR has been emphasizing the separation of americium and other minor actinides (MAs) to enable closed nuclear fuel recycle options mainly within the paradigm of aqueous reprocessing of used oxide nuclear fuel dissolved in nitric acid. Its major scientific challenge concerns achieving selectivity for trivalent actinides vs lanthanides. Not only is this challenge yielding to research advances, but technology concepts such as ALSEP (Actinide Lanthanide Separation) are maturing toward demonstration readiness. Efforts are organized in five task areas: 1) combining bifunctional neutral extractants with an acidic extractant to form a single process solvent, developing a process flowsheet, and demonstrating it at bench scale; 2) oxidation of Am(III) to Am(VI) and subsequent separation with other multivalent actinides; 3) developing an effective soft-donor solvent system for An(III) selective extraction using mixed N,O-donor or all-N donor extractants such as triazinyl pyridine compounds; 4) testing of inorganic and hybrid-type ion exchange materials for MA separations; and 5) computer-aided molecular design to identify altogether new extractants and complexants and theory-based experimental data interpretation. Within these tasks, two strategies are employed, one involving oxidation of americium to its pentavalent or hexavalent state and one that seeks to selectively complex trivalent americium either in the aqueous phase or the solvent phase. Solvent extraction represents the primary separation method employed, though ion exchange and crystallization play an important role. Highlights of accomplishments include:

- Confirmation of the first-ever electrolytic oxidation of Am(III) in a noncomplexing aqueous solution and submission of this scientific breakthrough as a paper in *Science*;
- The first-ever co-crystallization of Am(VI) with $UO_2(NO_3)_2 \cdot 6H_2O$, opening the door to a new approach for separating hexavalent actinides as a group;
- Results showing that three potentially problematic metals will not present risk in ALSEP;
- Improvement in ALSEP contactor stripping kinetics to acceptable performance;
- A comparison of centrifugal contactors vs mixer-settlers showing the former performs better in ALSEP stripping;
- Synthesis of new mixed N,O-donor extractants with enhanced solubility and strength for selective trivalent actinide extraction;
- Development of computational methods showing promise in prediction of the selectivity of new extractants for trivalent actinides vs lanthanides;
- An order-of-magnitude improvement in aqueous Am/Eu complexation selectivity of an alternative macrocyclic stripping agent for ALSEP, potentially enabling an option for an Am product stream free from both Ln and Cm.
- An alternative aqueous combination of dipicolinate complexant and malonate buffer that may present options for ALSEP and TALSPEAK (Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) type separations.

The ALSEP concept is advancing toward a benchtop flowsheet demonstration planned for FY 2016, and a bench-scale test bed at Idaho National Laboratory (INL) will be employed to demonstrate at least one tandem Am oxidation and separation concept. This report outlines the goals of the STAAR, significance of achieving these goals, STAAR organization around the above aims and questions, recent highlights, and future directions. The report also includes a listing of publications, reports, patents, and dissertations.

# ACRONYMS

| | |
|---|---|
| An | Actinide |
| ALSEP | Actinide-Lanthanide SEParation process |
| ANL | Argonne National Laboratory |
| bp18c6 | *N,N'*-Bis[(6-carboxy-2-pyridyl)methyl]-4,13-diaza-18-crown-6 |
| BTP | Bistriazinylpyridine |
| CDTA | *trans*-1,2-Diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid |
| *D* | Distribution Ratio |
| DFT | Density Functional Theory |
| DIAMEX | Diamide Extraction |
| DTPA | Diethylenetriaminepentaacetic acid, used in TALSPEAK aqueous phase |
| FCRD | Fuel Cycle Research and Development program, DOE sponsor for this work |
| FP | Fission product |
| FY | Fiscal Year |
| GANEX | Group Actinide Extraction |
| HDEHP | Bis(2-ethylhexyl)phosphoric acid |
| HEDTA | Hydroxyethylenediaminetriacetic Acid |
| HEH[EHP] | 2-Ethylhexylphosphonic acid mono-2-ethylhexyl ester |
| INL | Idaho National Laboratory |
| LANL | Los Alamos National Laboratory |
| Ln | Lanthanide |
| MA | Minor Actinide |
| MRWFD | Materials Recovery and Waste Forms Development program |
| NEUP | Nuclear Energy University Programs |
| nITO | Nanoparticles of Tin-doped Indium Oxide |
| OECD | Organization for Economic Cooperation and Development |
| ORNL | Oak Ridge National Laboratory |
| P&T | Partitioning and Transmutation |
| PI | Principal Investigator |
| PNNL | Pacific Northwest National Laboratory |
| PUREX | Plutonium Uranium Redox EXtraction |
| R&D | Research and Development |
| SANEX | Selective ActiNide EXtraction |
| SF | Separation Factor |
| SRNL | Savannah River National Laboratory |
| STAAR | Sigma Team for Advanced Actinide Recycle |
| STMAS | Sigma Team for Minor Actinide Separation (former name of STAAR) |
| T2EHDGA | *N*,*N*,*N*',*N*'-Tetrakis(2-ethylhexyl)diglycolamide |
| TALSPEAK | Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes |
| TALSPEAK-MME | TALSPEAK Mixed Monofunctional Extractants |
| TBP | Tri-*n*-butyl phosphate |

| | |
|---|---|
| TRU | TRansUranic |
| TRUEX | TRansUranic EXtraction |
| UNC-CH | University of North Carolina at Chapel Hill |
| UREX+ | URanium EXtraction plus, a suite of actinide and fission-product separations |
| USDOE | United States Department of Energy |
| WSU | Washington State University |

# SIGMA TEAM FOR ADVANCED ACTINIDE RECYCLE FY 2015 ACCOMPLISHMENTS AND DIRECTIONS

## 1. INTRODUCTION

The overarching goal of the Sigma Team for Advanced Actinide Recycle (STAAR), which prior to mid FY 2015 was named the Sigma Team for Minor Actinide Separation (STMAS), is to develop more efficient separation methods for actinides in support of the USDOE Office of Nuclear Energy objective of sustainable fuel cycles [USDOE, 2010a]. The STMAS was originally formed to bring together a multi-disciplinary team of researchers from across the DOE complex and academia that would work collaboratively to address the difficult technical challenges associated with developing robust processes for the separation of minor actinides (MAs, taken in the present context to mean Am and Cm) from lanthanides [Moyer, 2009, 2010]. The original charter included a secondary objective to devise an efficient separation of Am from Cm, but efforts in this direction have been discontinued. In the past several years, a systems options study in the Materials Recovery and Waste Forms Development (MRWFD) program outlined the merits of full actinide recycle in terms of a future sustainable fuel cycle based on fast reactors with or without thermal reactors [Wigeland et al, 2010, 2014]. A more recent extension of that study examined differences in U/Pu and U/TRU (TRansUranics) recycle schemes, concluding that both are of interest for future development while recognizing the greater development challenge associated with U/TRU recycle [Wigeland et al, 2015; Wigeland, in preparation]. Going forward into FY 2016, the study results have prompted us to broaden the scope of the Sigma Team to include actinide recycle generally vs exclusive focus on recycle of the MAs, and a corresponding change for the Sigma Team name to STAAR has been adopted. Given the research momentum from the past few years in the Sigma Team and the greater technical challenges of MA separation, STAAR will continue its efforts toward a more robust, more efficient actinide/lanthanide (An/Ln) separation process. However, needs for U/TRU recycle are already being considered, with initial venturing toward a group An separation, a theme that will likely expand in future years.

The overall effort within STAAR is carried out within the paradigm of aqueous reprocessing of used oxide nuclear fuel dissolved in nitric acid. The prime question being addressed deals with principles of selectivity through various means including aqueous-phase complexation, use of soft-donor extractants, higher oxidation states of americium, ion exchange, and crystallization/dissolution processes. Closed process cycles employing robust separation agents are sought that function under practical conditions relevant to future technology implementation. While the first years of the STAAR largely entailed the pursuit of science behind germinating technology concepts, the scope of the program has advanced to include the development of functional separations systems, testing, and bench-scale demonstration. Demonstration activities employ simulated feeds using small-scale, continuous prototype equipment. Given that an array of previously matured separation technologies for MA separations had been brought successfully through demonstrations in the context of the UREX+ (Uranium Extraction Plus) suite of processes [Regalbuto, 2011; Gelis, 2009; Laidler, 2008], the overarching question now before us is not the feasibility of separating MAs, but rather the efficiency and economy with which these separations can be achieved toward a manageable and affordable fuel cycle. The magnitude of this problem will require unprecedented simplification and compaction of separations processes, preferably eliminating and combining steps. It is anticipated that this will entail new chemistry and likely altogether new separation agents.

# 2. SIGNIFICANCE

The major long-term benefit of this research is expected to be a significant simplification of aqueous actinide separations, leading to overall better economics, improved reliability, and increased acceptability of nuclear fuel recycle. At the same time, the improved fuel-cycle technology should be safer, produce less waste, and support the purposes of nonproliferation. In fulfilling such needs, this research serves the "Develop Sustainable Nuclear Fuel Cycles" objective of the USDOE Fuel Cycle Research and Development (FCRD) program as described in the Nuclear Energy Roadmap [USDOE, 2010a]. More specifically, the implementation of the roadmap by FCRD relies heavily on a robust research and development (R&D) program to address MA separations as one of two grand challenges in the area of separations [USDOE, 2010b].

In addition to providing for better economics and process performance, improvements in actinide separations technologies resulting from this research will create a broad spectrum of options for crafting future fuel cycles that meet societal needs for clean and safe energy. The time horizon for implementation of a sustainable nuclear fuel cycle in the US and therefore for realization of the impact of this research may be considered to be many decades [Wigeland et al., 2014; Golay, 2015; NNL, 2013]. Over this time period, the fabric of science and society will shift markedly. New science and technology will be imported into the development of new fuel-cycle technologies in unanticipated and powerful ways. Changes in sociopolitical requirements will undoubtedly inspire as well as constrain the course of future fuel-cycle implementation. It is widely thought, as indicated by the theme of the recent Global 2015 conference, that nuclear energy will be part of the solution to reducing future $CO_2$ emissions [Paillere and Kepler, 2015; Van Den Durpel, 2015; Golay, 2015]. In fact, as coal utilization is actually at present the fastest growing component of world electrical energy production, the need for clean energy grows more critical with each passing year, driving a favorable shift in public opinion of nuclear energy. In view of the changing future landscape over many decades with attendant large uncertainties, it is clear that a major objective for R&D on nuclear fuel cycles is the reduction of risk by offering alternatives and making options available [Golay, 2015]. Accordingly, STAAR research is designed to present a broad set of future technology choices.

A recent evaluation of systems options by the USDOE for a sustainable future nuclear fuel cycle [Wigeland et al, 2010, 2014] underscores the need for actinide separations. The evaluation considered a multitude of nuclear fuel-cycle options, narrowing the choices to four best fuel cycles involving continuous recycle of either U/Pu or U/TRU with new natural uranium (no enrichment) in fast critical reactors or in both fast and thermal critical reactors. Any of these four options results in dramatic improvements vs the current once-through system, including more than an order of magnitude decrease in wastes requiring geologic disposal, more than three orders of magnitude reduction in uranium and thorium disposal, and more than two orders of magnitude increase in resource utilization. Similar conclusions have been reached by other investigators, representing an international consensus [Chabert, et al., 2015; Salvatores and Palmiotti, 2011; Kagramanyan, et al., 2015; Poinssot et al., 2015].

While the USDOE systems options study thus recognizes the value of actinide recycle in general, a follow-on study has been raising the question of whether U/TRU recycle offers benefits over U/Pu recycle [Wigeland et al, 2015; Wigeland, in preparation]. In fact, there has been a lively discussion on the need and methods for MA partitioning and transmutation (P&T) for over two decades as shown, for example, in the series of proceedings of the Organization for Economic Cooperation and Development (OECD) Partitioning and Transmutation (P&T) Exchange Meetings [OECD, 2010, 2012]. Relatively minor, though not negligible, benefit in energy utilization is expected from MA recycle. Rather, the international research community has anticipated the benefit of MA recycle as mainly being felt in the back end of a fuel cycle, particularly in reducing the effects of heating on repository performance and in minimizing radiotoxicity [Salvatores and Palmiotti, 2011; Tachimori and Morita, 2010; Hill, 2010, 2011; Boullis, 2008; Arm et al., 2008; Todd and Wigeland, 2006; Nash et al., 2006; Romary and Grygiel, 2015; Poinssot et al., 2015]. The importance of these factors and the extent to which their associated benefits can be realized depends on the design and siting of a repository. As discussed below, criteria for repository selection include technical as well as societal considerations [Carelli, 2011; Poinssot et al., 2015; OECD, 2011; NNL, 2013], which may not lead to coincident preferences [Golay, 2015]. Consent-based siting is in fact a major recommendation of the President's Blue Ribbon Commision [Blue Ribbon Commission, 2012], which injects definite societal input into fuel cycle design.

The benefit of reduced heat generation of nuclear waste due to MA recycle depends on repository design and siting. A significant beneficial increase in waste loading capacity is expected for certain geological characteristics, for example, in the cases of clay, granite, or volcanic tuft formations [OECD, 2011]. With no separations whatsoever, as would be the case with the once-through option, the heat load on a geologic repository out to 2000 years is dominated by $^{241}$Am ($t_{1/2} = 433$ y) after the fission products have decayed sufficiently (75 y) [Wigeland et al., 2006]. Given that heat loading directly determines the storage capacity of a repository, removal of $^{241}$Am alone has clear benefit for increasing storage capacity, reducing repository size, or permitting a lower repository operating temperature. Estimates of such benefits have been given for the case of Yucca Mountain [Wigeland et al., 2006], which can be used as an illustrative example. Accordingly, a 4.3–5.4 fold increase in waste loading would be expected for 90–99.9% removal of Am, assuming equal removal efficiency of Pu. A maximum 225-fold increase in waste loading would be expected upon removal of 99.9% of the Pu, Am, and Cm, along with the fission products Cs and Sr. However, other choices of repository design, such as deep borehole, could possibly reduce or even eliminate the problems associated with heat load [Wigeland et al, 2015; Wigeland, in preparation; Salvatores and Palmiotti, 2011; OECD, 2011].

Without a compelling case for increased repository capacity due to reduced heat generation, is the technical case for U/TRU recycle weakened? If the main advantage of MA recycle is minimized, then the question of the benefit of a U/TRU recycle in the case of such a repository choice would seem to turn on the added cost of R&D and possibly additional implementation costs [Wigeland et al, 2015; Wigeland, in preparation; NNL, 2013]. However, the costs of R&D can be paid back multifold by the future cost reductions in fuel recycle due to that same R&D. Further, game-changing R&D breakthroughs can potentially eliminate implementation costs of MA recycle by transforming the entire actinide separations process. The timeline is long for developing, testing, and implementing a new repository, for adopting and gaining public acceptance for a sustainable fuel cycle, and for transitioning to a sustainable fuel cycle [Passerini et al., 2015; NNL, 2013]. Chances are high that game-changing R&D will occur. The message therefore emerging from the MA separations debate seems to be a resounding research challenge to find new, more efficient actinide separations methods that can create new, attractive options for sociopolitical decision-making.

Repository benefits of MA partitioning and transmutation also include decreased overall repository radiotoxicity and decreased radiotoxicity lifetime, goals that also promote public acceptance of nuclear energy [Carelli, 2011; Poinssot et al., 2015; OECD, 2011]. While decreased radiotoxicity of a repository is itself thought to have limited impact on repository performance, reduction of risk is recognized in terms of disruptive events due, for example, to geologic phenomena and human intrusion [Salvatores, 2011]. Again, such a benefit disappears with certain repository design, such as deep borehole, and use of appropriate barriers, weakening the technical argument for MA separation on the basis of reduced radiotoxicity [Salvatores, 2011; Wigeland et al, 2015; Wigeland, in preparation; NNL, 2013]. Thus, the technical benefits of reduced radiotoxicity are debatable. By contrast, sociopolitical benefits are compelling. Public dialog on the nuclear fuel cycle in Europe and elsewhere has shown that society tends to be most concerned with nuclear safety and waste disposal [Poinssot et al., 2015; Ouzounian and Farin, 2015; Wallard et al., 2012]. With regard to the latter, the longevity of the waste and its radiotoxicity over timescales greater than the history of human civilization give considerable weight to the desirability of reducing the MA content of waste placed in a geologic repository. It therefore makes sense to provide the public with options that accomplish this goal, especially if through R&D it can be accomplished with little or no additional cost.

Specific actinide separation problems of interest include not only separation of MAs from fission products (FPs), but also separation of MAs from lanthanides. Given that an effective chemistry already exists for manipulating Np in contemporary solvent-extraction systems employing tri-*n*-butyl phosphate (TBP), the need for Np separations research therefore seems relatively less urgent than the need for Am and Cm separations research. On the other hand, An/Ln or Am/Cm separations have been especially difficult because the chemistry of their common trivalent oxidation states is very similar. Although we can point to significant progress, a fully satisfactory solution has not yet been found [Hill, 2010, 2011]. An efficient An/Ln separation is important because the lanthanides are strong thermal neutron absorbers and thus cannot be recycled in light-water reactor fuel, though fast-reactor fuel is somewhat more tolerant. The need for a separation of Am from Cm has been debated but appears either doubtful or of limited benefit. On the one hand, it has been argued as a needed process option [Pillon, 2003; Laidler, 2008], as Cm presents difficulties in fuel fabrication due to the greater shielding requirements. On the other hand, this is not a universally agreed upon opinion [Arm, 2008], as Cm will impact repository performance, and its separation would ostensibly entail another separation process, adding overall complexity. As STAAR results show, however, the option of an Am-Cm split would not necessarily add any additional processing steps, regardless of its merits.

The most straightforward scenario for MA separation from lanthanides in STAAR strategy follows a co-decontamination flowsheet such as UREX+ [Regalbuto, 2010] or co-decontamination [Herbst, 2011; Law, 2013] flowsheet in which MA separation must be performed on a highly acidic raffinate stream from which U, Pu, and Np have already been removed. A major advance by itself would be a one-step An/Ln separation [Hill, 2010, 2011; Lumetta et al., 2010a,b]. Two of the most selective solvent-extraction methods were incorporated into the framework of the UREX+ suite in the form of the TRUEX-TALSPEAK (Transuranic Extraction-Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Komplexes) tandem processes or the TRUEX-SANEX (Selective Actinide Extraction) tandem processes using Cyanex® 301 as the SANEX extractant [Regalbuto, 2011]. Demonstrations showed a successful separation of Am and Cm from Ln using either technology. On the other hand, both approaches require two separate processes using disparate solvents and chemistries, and Cyanex® 301 is unstable at practical nitric acid concentrations. Both technologies present major challenges in process control, that is, robustness. These challenges involve narrow processing envelopes, complex chemistry, empirical knowledge bases with limited understanding, reagent stability, voluminous effluent streams, and unknown impacts on downstream processes and waste disposition. Control of pH has been especially problematic for TALSPEAK and related systems employing aqueous-phase buffers and complexants, as distribution ratios are not constant over the expected operating range. Despite these already known challenges, the demonstrations of these technologies confirm the selectivity principles employed, which are outlined further below. Thus, appropriate extractants and aqueous-phase complexants can discriminate between An(III) and Ln(III), and a solution to developing a suitable technology should therefore be within the reach of research that can successfully address the major shortcomings. Given the evident challenge of the task, however, it is also clear that the prior understanding of extraction mechanisms and molecular behavior has been inadequate to generate the needed breakthrough. In the long term, a very attractive though ambitious MA separation meeting both STAAR aims simultaneously would be one in which Am and Cm are separated together in a single stream, thereby simplifying the MA separation overall. Optionally, a co-extraction followed by selective stripping could provide separate Am and Cm streams if desired. Potentially such a process could replace three separate processes with one process, with a high degree of potential flowsheet simplification. If Pu and Np could also be co-extracted with Am and Cm followed by stripping of all, or certain combinations of, these actinides, the landscape of fuel recycle could be even further simplified.

As described above, a clear need to simplify separations in fuel recycle is universally recognized. Although the successful demonstrations of UREX+ [Regalbuto, 2011; Gelis, 2009; Laidler 2008] increased overall confidence in our ability to reprocess used light-water reactor fuel at a commercial scale to meet a variety of potential objectives, the level of complexity and projected cost of deploying multiple process steps was unprecedented. Whether to separate the MAs in the first place and what types of streams the MAs are best suited to fuel fabrication or waste disposal must be a result of a comprehensive fuel-cycle systems analysis. While such guidance is being formulated, a chemical toolbox approach has been undertaken by STAAR under the philosophy that the chemical understanding in the context of potential separation methods will be available for exploitation as systems goals are more clearly defined. At the most fundamental level, the major product of STAAR effort is intended to be a family of chemical principles and corresponding test data enabling the design of efficient Am and Cm separation processes, one or more of which will be demonstrated at the laboratory scale.

# 3. APPROACH

## 3.1 Technical Strategy

As shown in Figure 1, dual strategies for Am separation are being pursued by STAAR based on either complexation or the higher oxidation states of Am [Moyer et al., 2015]. Complexation presents particular challenges in that the trivalent 4f and 5f elements have very similar bonding characteristics, dominated by electrostatics with negligible ligand-field stabilization effects. For Am(III)/Cm(III) separations, the ionic radii differ very slightly, and these fall within the much wider size range of the lanthanides. Regarding the second strategy, the higher oxidation states of Am that can be exploited require aggressively high oxidation potentials and are unstable once formed [Runde, 2011]. Both strategies can be used in either phase of a separation system. For example, by use of the extractant di-2-ethylhexylphosphoric acid (HDEHP), which is slightly selective for Ln(III), and addition of the An(III)-selective complexant diethylenetriaminepentaacetic acid (DTPA) to the aqueous phase, the Ln(III) are rendered significantly more extractable than An(III). This principle can be made to operate in an extraction of Ln(III) away from

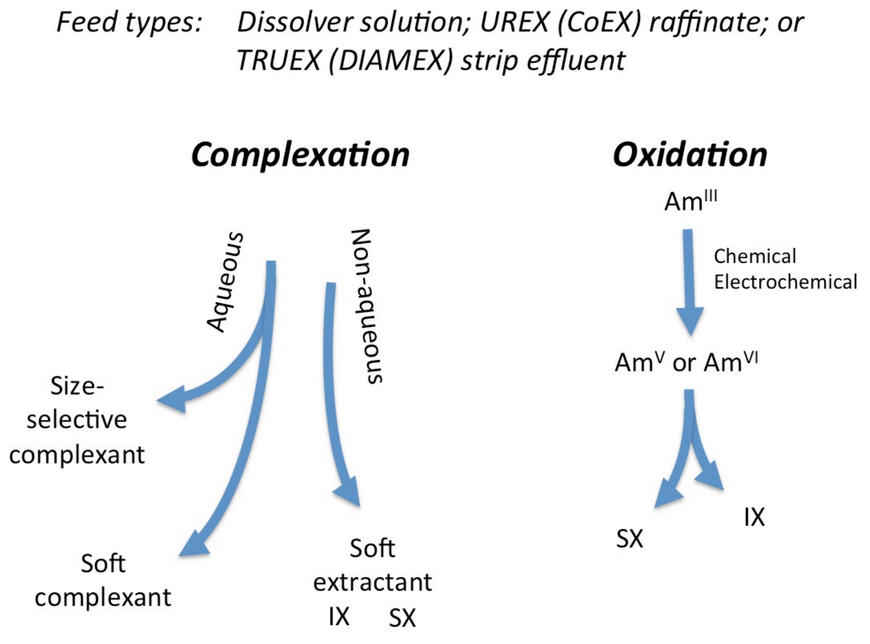


**Figure 1.** Strategies for achieving selectivity in two-phase separation systems.

Am(III) (TALSPEAK) or in stripping Am(III) from extracted Ln(III) (reverse TALSPEAK). Alternatively, the actinide-selective complexant can be the extractant, as is the approach in the SANEX processes. One could employ the same ideas in the use of inorganic ion exchangers. For example, an inorganic exchanger with affinity for both An(III) and Ln(III) is used in the presence of an appropriate aqueous-phase complexant that has an affinity for An(III) vs Ln(III), such that only the Ln(III) are removed from the feed stream. Or the complexant can be added to the eluent after the combined uptake of Am(III) and Ln(III) to selectively desorb the Am(III). Complexation strategies can be sophisticated, taking advantage of subtle effects due to even small differences in ionic radii. Manipulation of the Am oxidation state is in principle a powerful approach for a selective Am separation, either in the context of solvent extraction or ion exchange, but the very high oxidation potentials required for oxidation of Am(III) to Am(V) and Am(VI) [Runde, 2011] present a formidable challenge.

The major questions being pursued within the dual strategy described above naturally sort themselves as follows:

1. Can aqueous complexation provide sufficient discrimination and operational control?
2. Can the higher oxidation states of americium be formed and stabilized for separation?
3. Can soft-donor extractants be made sufficiently robust and effective under desired conditions?
4. Does ion exchange have the selectivity and robustness to operate effectively?

In most cases, research inquiry focuses on obtaining the desired An/Ln selectivity. However, in some cases, selectivity is often not so much in question as such issues as robustness, ability to operate under expected conditions, kinetics, etc. For example, ion-exchange materials have not been strong enough nor stable enough under acidic conditions, and soft-donor extractants like bistriazinylpyridines (BTPs) have presented stability issues of their own.

The scope for STAAR consists of five tasks as follows:

1. ALSEP Development. This task supports the development and testing of a flowsheet that can be demonstrated in FY 2017 for extraction of a simulated high-level raffinate. Scope entails investigations of metal ion interferences, phase phenomena, efficiency of aqueous complexants for stripping, batch extraction of real dissolved fuel, single-stage contactor performance, optimal scrubbing conditions, fission-product partitioning, as well as fundamental aspects.

2. Americium Oxidation. This task serves to advance the understanding of the production, stabilization, and separation of Am(VI) leading to successful testing in FY 2016 of tandem oxidation and extraction in a centrifugal contactor. Oxidation of Am(III) with Ag-catalyzed ozone is being optimized, and alternative oxidants are being investigated, including chemical and electrochemical methods. Extraction tests are performed to determine the efficacy of Am extraction, and alternative extractants, such as butyramides, which appear to not reduce Am as quickly as phosphorus-containing ligands are also investigated. Am(VI) stability and auto-reduction kinetics are being examined, and co-crystallization of Am(VI) with U(VI) and other An(VI) is being tested.

3. Selective Trivalent Actinide Extraction. This task entails development of solvents capable of selective removal of trivalent actinides from high-level raffinate. The major thrust is the synthesis of new mixed-donor extractants that are soluble in aliphatic diluents and testing of their behavior as extractants for Am(III) from trivalent lanthanides. In another thrust, triazinyl-pyridine type extractants are being examined, in particular to characterize their extraction behavior, including selectivity, acid dependence, third-phase formation, and kinetics. A study of dithiophosphinic acid extractants is being closed out.

4. Inorganic Ion Exchange. This task evaluates the performance of actinide separation concepts involving inorganic ion exchangers in conjunction with manipulating the oxidation state of americium to effect selective actinide separations from lanthanides. This activity also supports the testing of new

sorbent materials developed under a Nuclear Energy University Programs (NEUP) project at Texas A&M University.

5. Computational Molecular Design. This task supports the other STAAR tasks with appropriate molecular computations, both to accelerate experimental work and to facilitate correct data interpretation. In turn, experimental results are used to validate the computational models. Specific scope focuses on development of a computational model for predicting Am(III)/Ln(III) selectivity, design of mixed-donor extractants, and investigation of new polyaminocarboxylate complexants for use in ALSEP stripping.

In general, pursuing the above strategy requires a team effort often involving more than one laboratory, bringing together diverse resources and expertise. Administratively, work packages are laboratory-centered but can involve a combination of the five tasks enumerated above. Principal investigators (PIs) from six national laboratories and one university were involved in addressing the above questions in FY 2014, as reported in the corresponding annual reports cited in the Sigma Team Publications and Reports section. The participants are listed in Table 1 together with the questions that their projects are primarily concerned with. It should be noted that each PI leads a team of collaborators, some through subcontract, whose contributions are properly acknowledged in the corresponding annual reports. Questions are crosscutting, as shown in the middle column of Table 1. The composition of the STAAR was selected based on the experience of the PIs in conducting both basic and applied research, having demonstrated success in employing the results of basic research in technology development and in collaborating with engineers in scale-up and implementation. All specialize in separation science and technology, with backgrounds in solvent extraction, resin ion exchange, inorganic ion exchange, crystallization, and dissolution techniques.

**Table 1.** Participating Institutions and PIs in the Sigma Team for Advanced Actinide Separations in FY 2015

| Institution | Tasks | Lead PI |
|---|---|---|
| Argonne National Laboratory (ANL) | #1 | Mark P. Jensen[a] |
| Argonne National Laboratory | #1 | Artem V. Gelis |
| Idaho National Laboratory (INL) | #2 | Bruce J. Mincher |
| Idaho National Laboratory (INL) | #3 | Dean R. Peterman[b] |
| Los Alamos National Laboratory (LANL) | #2 | George S. Goff |
| Oak Ridge National Laboratory (ORNL) | #5 | Vyacheslav Bryantsev |
| Oak Ridge National Laboratory (ORNL) | #3 | Lætitia H. Delmau |
| Pacific Northwest National Laboratory (PNNL) | #1, #2 | Gregg J. Lumetta |
| Savannah River National Laboratory (SRNL) | #2, #4 | David T. Hobbs |
| Washington State University (WSU) | #1, #3 | Kenneth L. Nash[c] |

[a] Now at Colorado School of Mines. Project completed in December 2014; seeking NEUP funding.
[b] Project completed in September 2015.
[c] Project completed in September 2014, continued on carryover till August 2015; seeking NEUP funding.

University subcontracts were not renewed in FY 2015 to accommodate FCRD preference for funding academic investigators through Nuclear Energy University Programs (NEUP). However, the university collaborators were still functioning as performers as project accounts were depleted during the year. At least one university collaborator has succeeded in obtaining funds through the proposal-driven process used by NEUP. Other collaborators have already submitted proposals to, or are in the process of submitting proposals under NEUP. Given that NEUP funding is highly competitive, the transition of all of our academic collaborators to NEUP projects will likely not be completely successful. Potential impact to STAAR scope and planning will be assessed and managed late in FY 2016 as the next NEUP proposal cycle is concluded.

## 3.2 Science-Based Approach

Motivated by the applied goals described above, a hypothesis-driven approach is taken, drawing from fundamental principles to address the most significant questions standing as barriers to progress. As one of its first tasks, the STAAR defined what these questions are, as generalized above [Moyer, 2009, 2010]. Some projects have matured sufficiently to begin to address how the basic principle, now largely substantiated, can be subjected to greater levels of complexity and process requirements. For example, now we know that Am can be oxidized and then separated in batch tests. Can we combine the steps in an integrated test? In FY 2014, we showed the answer is yes. Now, the questions advance to improving upon the oxidation methodology toward practical systems. A conceptual cycle of hypothesis and testing illustrating this iterative process is depicted in Figure 2 [Moyer, 2010]. Based upon the knowledge base available in any given project, the cycle entails formation of hypotheses associated with questions, leading to corresponding experimental thrusts to test the hypotheses. As pertains to the STAAR effort, the input of theory is stressed as playing a key role in each step under the expectation of a significant savings in effort by decreasing empiricism. Subsequent cycles continue to advance toward the maturation of the technology concept, one question after another driving the cycles to a successful technology. After six years of effort, the maturation process in STAAR is clearly evident as will be highlighted below.

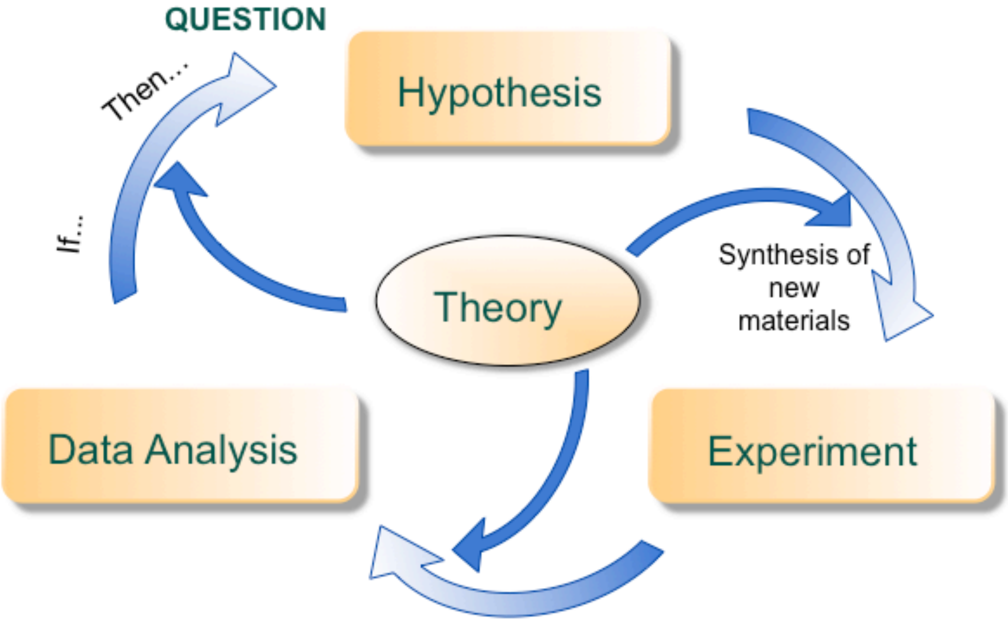


**Figure 2.** Cycle of hypothesis and testing accelerated by theory.

# 4. Highlights OF research progress

Highlights of STAAR accomplishments in FY 2015 are provided in this section as distilled from the annual reports of individual principal investigators of the STAAR. These highlights have been collected in a preliminary report [Moyer, 2015b] for use as input to the annual report on accomplishments of the MRWFD program. See these reports for a more complete account of research progress. A comprehensive listing of Sigma Team publications, reports, patents, and dissertations is given in Section 7.

## 4.1 Electrochemical Oxidation of Americium

C. Dares, and T. J. Meyer (UNC-CH), B. J. Mincher (INL)

We have confirmed our initial results on the electrochemical oxidation of americium reported in FY 2014 [Dares et al., 2014] and have expanded our understanding of this exciting, first ever oxidation of Am(III) at an electrode in a noncomplexing acidic aqueous medium [Dares et al., 2015]. If an electrochemical approach to generating the higher oxidation states of Am in nitric acid media can be made practical, it would enable subsequent americium separations while avoiding the addition of chemical oxidants and corresponding increase in high-level waste mass. Challenges include understanding and controlling the molecular redox processes that occur at the electrode surface and stabilizing the resulting Am(V) and Am(VI) oxidation products to the thermodynamically favorable parasitic oxidation of water.

The electrolysis makes use of a high surface-area, fluoride-doped tin oxide electrode coated with nanoparticles of tin-doped indium oxide (*n*ITO). Experiments were designed to test the hypothesis that binding of Am(III) at the electrode surface facilitates electron transfer to the electrode. Figure 3 illustrates the attachment of an americium-selective terpyridine ligand to the *n*ITO surface. At an anodic potential of 2.25 V vs Ag/AgCl, Am(III) at 84 μM in 0.1 M nitric acid and 0.95 M sodium nitrate oxidizes over 13 h to 36% Am(VI) and 54% Am(V) as observed by electronic spectroscopy (Figure 4). The yield of Am(VI) improves to 53% with 40% Am(V) at 2.7 V and 1.84 mM Am(III) after 7 h, the highest yield observed to date. Control electrolysis at 1.8–2.7 V for *n*ITO without attached ligands gives no oxidation of Am(III); interestingly, the underivatized *n*ITO degrades after an hour of oxidizing conditions, while the derivatized *n*ITO is more robust. In view of the control results, the observed two-electron oxidation of Am(III) is thought to support the hypothesis of facilitated electron transfer by coordination of Am(III) to the surface-bound terpyridine ligand. Systematic investigations will be carried out in the future to understand conditions that lead to electrochemical oxidation of Am(III) to Am(V) or Am(VI) with subsequent separation from a relevant waste composition.

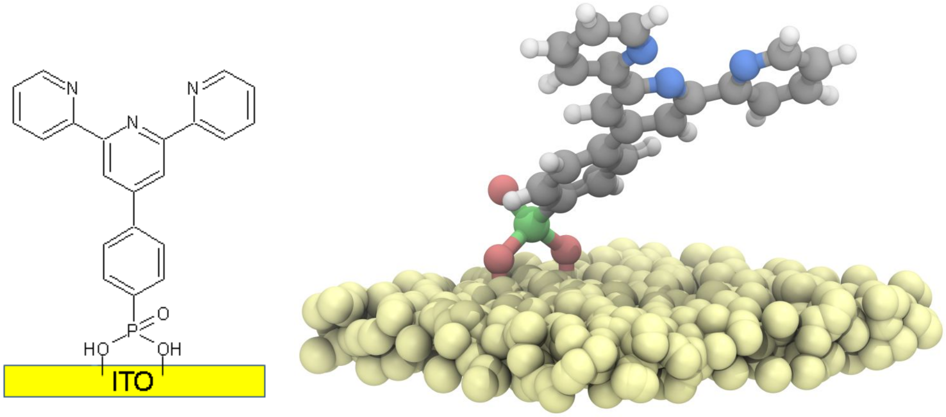


**Figure 3.** A terpyridine ligand bound to an indium tin oxide particle on an electrode surface via a phosphonic acid linker.

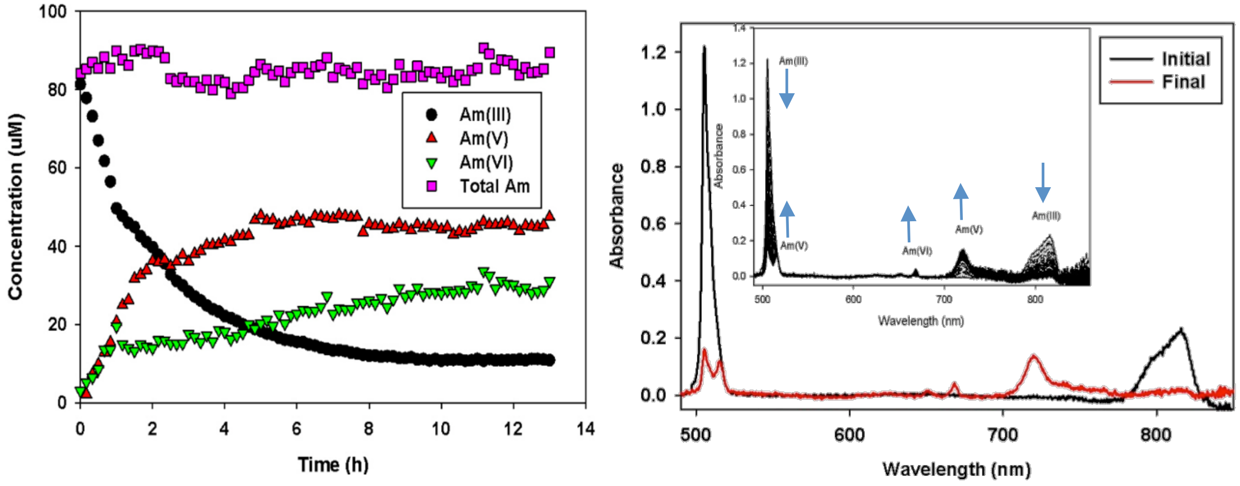


**Figure 4.** Concentration of Am species in solution (left) as measured by visible spectroscopy in a 50 cm waveguide (right) over time during a controlled-potential electrolysis of initially 84 μM Am(III) at 2.25 V vs Ag/AgCl. The working electrode was a ligand-modified high-surface-area *n*ITO, with a Pt foil counter electrode and a Ag/AgCl wire reference electrode. The aqueous electrolyte was 0.1 M nitric acid and 0.95 M sodium nitrate. (Right) Initial and final electronic spectra measured in a 1 cm path-length cuvette and modeled with Gaussian functions.

## 4.2 Co-crystallization of Actinyl Nitrates

J. D. Burns and B. A. Moyer (ORNL)

The first ever co-crystallization of Am(VI) with $UO_2(NO_3)_2{\cdot}6H_2O$ has been achieved. The result opens the door to a new approach of used nuclear fuel recycling where the bulk of the U, Np, Pu, and Am can all be removed from the waste stream together using a single technique without use of organic solvents. The hexavalent dioxo cations of Np, Pu, and Am have all been co-crystallized with $UO_2(NO_3)_2{\cdot}6H_2O$ in near proportion by a simple reduction in temperature, while the tri- and tetravalent states are only slightly removed from solution. In the co-crystallized form, the Am(VI) shows a much greater stability, with no reduction observed after 13 d, while in solution over 50% is reduced after only 10 d.

Americium(VI) proves to be stable in the presence of uranyl nitrate. A sample of Am(VI) was prepared with $NaBiO_3$, and the spectrum was observed for 10 d (see Figure 5). For the first 66 h, no change was observed in the Am(VI) absorption band at 1000 nm. After 10 d roughly 53% of the Am(VI) had become reduced to Am(III). Thus, under simple conditions using bismuthate as oxidant, Am(VI) is expected to persist long enough for subsequent co-crystallization steps.

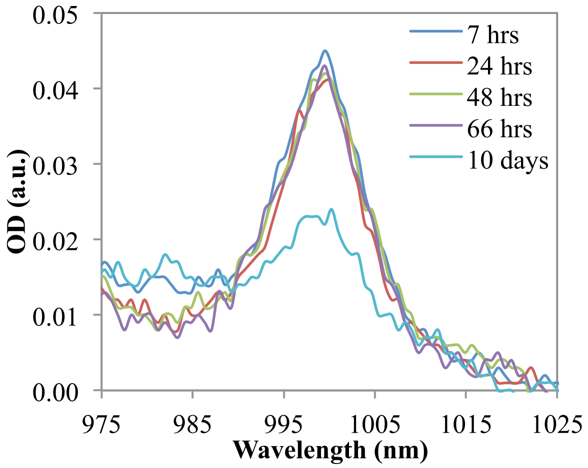


**Figure 5.** Spectra show Am(VI) stability in uranyl nitrate.

Co-crystallization was demonstrated with a freshly prepared Am(VI) sample consisting of 0.84 M [$UO_2^{2+}$] and

0.31 mM [Am(VI)]. Once cooled to 3–4 °C, the mother liquor was separated from the crystals by decantation rather than filtration to avoid any reduction due to the filters; however, it should be noted that decantation does not allow for a separation that is as complete as filtration. The electronic spectrum showed 32.0% of $UO_2^{2+}$ and 31.0% of the Am(VI) had been removed from solution. Gamma spectroscopy showed a similar amount of 34.9% of the $^{243}$Am activity to be in the crystals.

Americium(VI) is stable in the crystals. Upon redissolution of the crystals after 13 d, the spectra revealed 87% Am(VI) with ~13% Am(III), consistent with the known incomplete separation of the crystals from the initial mother liquor. Whereas Am(VI) gradually reduces to Am(III) in the presence of $UO_2(NO_3)_2$, little or no reduction of the Am(VI) occurs in the crystals before dissolution. Crystals from Np(VI) and Pu(VI) co-crystallization experiments were also dissolved and showed similar results as the Am(VI).

Table 2 summarizes the results from separate co-crystallization experiments of U(VI) with with Am(III), Pu(VI), Np(VI), Pu(VI), and Am(VI). For the lower valence ions Am(III) and Pu(VI), the relative amount removed from solution was roughly an order of magnitude lower than that of U(VI), while the An(VI) ions were removed in near proportion to the U(VI). These ratios indicate that the process of removing An(VI) ions from solution is a co-crystallization mechanism rather than just a co-precipitation mechanism, with a strong indication of the An(VI) dioxo cation replacing itself for a $UO_2^{2+}$ in the lattice structure of $UO_2(NO_3)_2{\cdot}6H_2O$.

**Table 2.** Ratios of the percent precipitation of different TRU species with respect to $UO_2^{2+}$

| TRU Species | % Precipitation | | Ratio |
|---|---|---|---|
| | U | TRU | U:TRU |
| Am(III) | 71.5 | 6.4 | 11.2 |
| Pu(IV) | 41.2 | 4.1 | 10.0 |
| Np(VI) | 70.5 | 73.6 | 0.96 |
| | 82.9 | 82.0 | 1.01 |
| Pu(VI) | 29.9 | 28.0 | 1.07 |
| | 79.8 | 73.4 | 1.09 |
| Am(VI) | 32.0 | 31.0 | 1.03 |

## 4.3 ALSEP Process Development for An/Ln Separation

### 4.3.1 General Process Description

G. J. Lumetta (PNNL) and A. V. Gelis (ANL)

The Actinide-Lanthanide SEParation (ALSEP) process concept [Gelis and Lumetta, 2014; Lumetta et al., 2014a] has matured toward a bench-scale test in engineering equipment targeted for FY 2017. ALSEP combines an acidic extractant with a neutral chelating extractant to yield a single hybrid process for recovering the trivalent MA elements Am and Cm from acidic high-level waste raffinate. The raffinate is assumed to be generated by an initial co-decontamination step that removes the bulk of the U, Pu, and Np, as defined in a recent case study [Law et al., 2013]. This single process has the potential to replace two separate processes previously required to achieve this separation, thus significantly simplifying a closed fuel-cycle [Lumetta et al., 2010]. The ALSEP approach involves 1) co-extracting the trivalent actinides (An) and lanthanides (Ln), 2) selectively stripping the actinides from the loaded organic solvent, and 3) stripping the lanthanides and other fission products from the solvent. The neutral extractant serves to co-extract the trivalent An and Ln from nitric acid solutions, while the acidic extractant serves to hold the trivalent Ln in the organic phase while the An are selectively stripped into a carboxylate-buffered solution containing a polyaminocarboxylate complexant (Figure 6). Research has compared the effectiveness of combinations of various candidate extractants, complexants, and buffers [Gelis and Lumetta, 2014;

Lumetta et al., 2014a; Braley et al., 2013; Lumetta et al., 2013; Tkac et al., 2012; Lumetta et al., 2011; Lumetta et al., 2010]. Efforts in FY 2015 dealt with overcoming the unwanted extraction of certain fission products and with improving the kinetics of stripping in the ALSEP process.

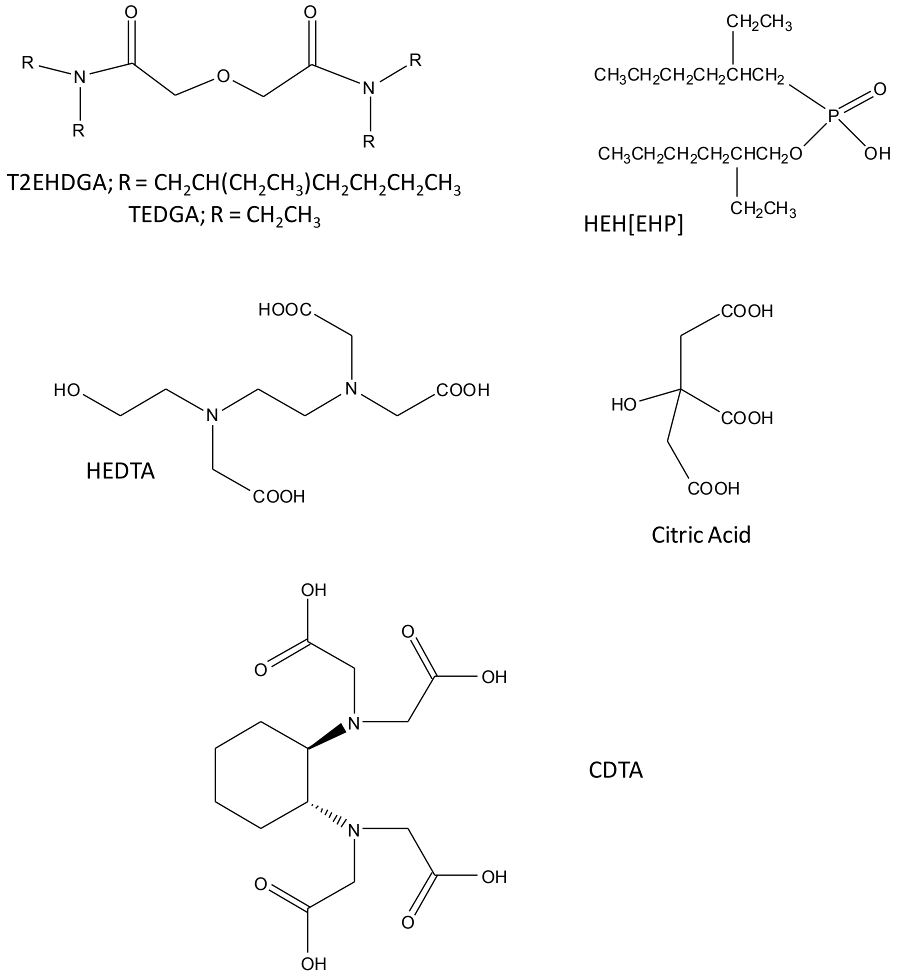


**Figure 6.** Component extractants and aqueous components used in the ALSEP process.

### 4.3.2 Progress in ALSEP Chemical Development

G. J. Lumetta, E. L. Campbell, A. J. Casella, G. Hall, T. G. Levitskaia, F. N. Smith, and G. Carter (PNNL)

Technical risks and uncertainties have been addressed in FY 2015, including: 1) management of zirconium, 2) management of molybdenum, 3) unknown behavior of ruthenium, 4) unknown behavior of iron, and 5) slow stripping of americium from the loaded ALSEP solvent. Efforts have focused on a solvent combination consisting of 0.05 M *N*,*N*,*N*',*N*'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) combined with 0.75 M 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) dissolved in *n*-dodecane.

Problems from three potentially problematic metals can likely be avoided. Zirconium is strongly extracted from nitric acid solutions into the ALSEP solvent. Addition of the complexing agent *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid (CDTA) into the aqueous feed solution completely suppresses the Zr extraction, which can greatly simplify the downstream portions of the ALSEP flowsheet. For this reason, it is recommended that CDTA be added to the ALSEP feed. Ruthenium(III) is not appreciably extracted into the ALSEP solvent, so it is anticipated that Ru will easily be routed to the high-level waste raffinate from the ALSEP process. However, iron(III) is appreciably extracted from nitric acid solutions into the ALSEP solvent. Addition of CDTA reduces the Fe extraction somewhat, but the equilibrium Fe distribution ratios (*D*) are well above 1 at nitric acid concentrations in the extraction operating range for ALSEP (≥2 M $HNO_3$). Fortunately, the Fe extraction is slow. It therefore seems likely that little Fe extraction would occur during the short contact time experienced in a centrifugal contactor. If this proves to be the case, then Fe extraction will not pose a significant problem in implementing ALSEP.

A mixer-settler and a 2-cm centrifugal contactor were directly compared for the Am stripping operation in the ALSEP system. This experiment suggested that, under the conditions examined, there is no advantage to using the mixer-settler rather than the centrifugal contactor. Other solutions to the slow Am stripping are required before an ALSEP demonstration can be achieved.

Certain fundamental aspects of the ALSEP chemistry are being explored. This includes investigating the extraction mechanism through systematic examination of Eu(III) extraction by T2EHDGA, and theoretical calculation of relevant Nd(III) absorption spectra. Measurement of the Eu(III) distribution ratio for extraction from $HNO_3$ solution as a function of the organic-phase T2EHDGA concentration suggests that three T2EHDGA ligands coordinate to Eu(III) in the extracted species. However, the dependence of the Eu(III) distribution ratio on the $HNO_3$ concentration is complex and requires further study. Progress is being made in applying time-dependent density functional theory calculations to interpretation of Nd absorption spectra. Near term, the methodology is being worked out to simulate the electronic absorption spectrum of $Nd^{3+}$ ion in aqueous solution. Once perfected, the method will be extended to calculate the spectra of proposed organic-phase Nd complexes relevant to the ALSEP system.

### 4.3.3 Improving the Stripping Efficiency of ALSEP

A. V. Gelis and M. A. Brown (ANL)

Experiments on the partitioning of the fission products, lanthanides, and americium using a 2-cm ANL centrifugal contactor and a mixer-settler provided valuable information on process dynamics. It has been found that the kinetics of co-extraction of Am and Ln from a PUREX-type simulated raffinate are fast. The Am partitioning compares with batch tests, and no issues with fission products and Ln partitioning have been observed. Molybdenum can be scrubbed from the solvent without any issues.

In contrast, the selective stripping of Am from Ln in the loaded solvent is slow using a buffered solution in a pH range between 2.5 and 3.5 containing either diethylenetriaminepentaacetic acid (DTPA) or hydroxyethylenediaminetriacetic acid (HEDTA) complexing agents. The kinetic behavior results in a loss of stripping selectivity, which improves as the flow rate decreases or temperature increases. HEDTA promotes a faster Am back extraction rate than does DTPA. Stripping efficiency improves further when the extraction is conducted at longer contact time in a modified 2-cm centrifugal contactor with an extended mixing zone. For this work, a newly designed housing was 3D-printed in stainless steel, while the standard 2-cm rotor/motor assembly was used. A minimum separation factor (SF) of 10 for Nd/Am and Pm/Am pairs has been demonstrated numerous times under different chemical conditions at both ambient and elevated temperatures (Figure 7). The SFs for the remaining lanthanides are in the 12 to 90 range. The latest modifications of the contactor housing provided even higher SFs due to the increased residence time in the mixing zone. If HEDTA/citrate buffered solution is used, a SF (Nd/Am) of 16 is achieved. Comparison tests of a mixer-settler and standard 2-cm centrifugal contactors, conducted at PNNL, indicate that due to various reasons none of devices provides sufficient interfacial mass-transfer stage efficiency to accomplish satisfactory Ln/Am separation step.

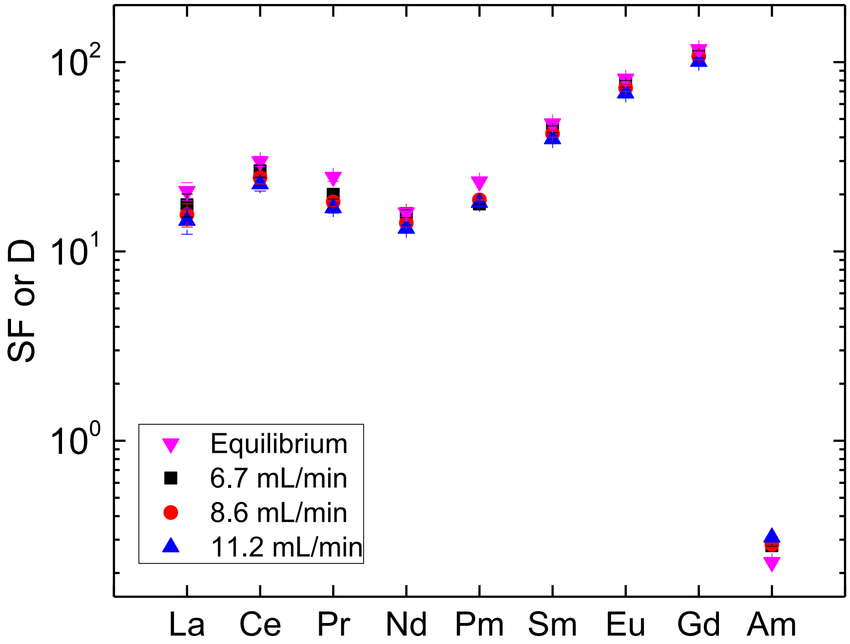


**Figure 7**. Separation factors for Ln(III)/Am(III) and distribution ratios of Am(III) at the Am-strip step using a modified centrifugal contactor with increased mixing residence time. Organic phase: 0.045 M T2EHDGA/0.6 M HEH[EHP]. Aqueous phase: 0.125 M HEDTA/0.2 M citrate, pH 2.81. $T = 21 \pm 2°C$.

## 4.4 Aqueous Complexes for Size-Based Actinide Separation

M. P. Jensen and R. Chiarizia (ANL)

Separating Cm from other minor actinides (MAs) may be desirable for advanced nuclear fuel cycles involving actinide partitioning and transmutation because the reduced radiation would simplify fuel fabrication and reduce the buildup of transcurium actinides in subsequent transmutation cycles [Pillon, 2003]. Separating Am from Cm was de-emphasized as a Sigma Team goal in FY 2015, but studies of approaches to increase the An(III)-Ln(III) selectively of our sterically constrained complexants for Am/Cm separation continued until December 2015. In FY 2014, we reported a method to selectively strip Am from Cm in a modified ALSEP system using the aqueous ligand bp18c6 (Figure 8). This approach offers the major advantage that a separate unit operation does not need to be devoted to an Am-Cm separation; rather, ALSEP chemistry can be modified to deliver a Cm-free Am product. As described in a recent publication, Am stripping kinetics with bp18c6 are favorable, and the necessary discrimination between Am and the light lanthanides can be achieved in the ALSEP loading stages [Jensen et al., 2015].

In FY 2015 we greatly enhanced the Am/lanthanide selectivity of the base bp18c6 ligand in a modified ALSEP process. Prior quantum chemical studies of An and Ln complexes of bp18c6 [Jensen et al. 2014] revealed different roles for the two types of nitrogen donor atoms in bp18c6. On one hand, the tertiary nitrogen atoms in the crown ether ring are central to the size-selectivity of the ligand. On the other hand, the pyridine nitrogen atoms in the picolinic acid arms are central to the An(III)/Ln(III) selectivity observed for bp18c6 because they form notably more covalent bonds with An(III) cations. Based on this knowledge, two bp18c6 derivatives we expected to possess improved actinide/lanthanide selectivity (Figure 6) were designed, synthesized, and screened for both Am/Cm selectivity and An/Ln selectivity. Our hypothesis was correct. Substitution of hydroxy or methoxy groups on the pyridine rings substantially improved the Eu/Am selectivity under conditions representing the Am stripping stages. In particular, methoxy substitution increased selectivity by more than an order of magnitude over the base bp18c6 ligand without significantly altering the size-based Am/Cm selectivity (Table 3). This implies potential for tuning the bonding in the bp18c6 framework to further simplify selective Am recovery in the ALSEP framework.

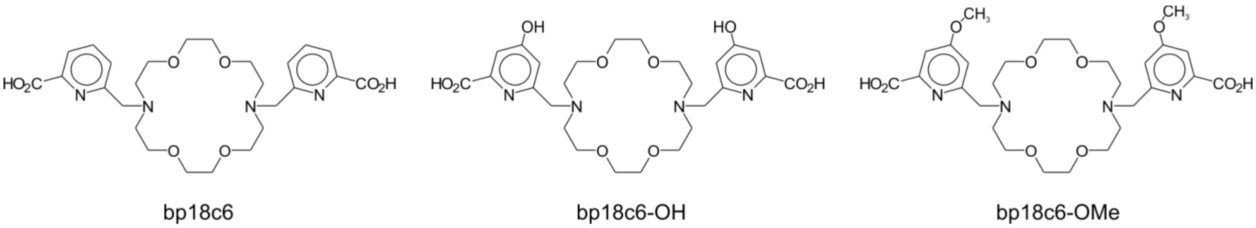


**Figure 8.** Structures of sterically constrained macrocyclic ligands under study: *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-4,13-diaza-18-crown-6 (bp18c6) and two new derivatives tested in FY 2015.

**Table 3.** Separation factors of bp18c6 derivatives as Am stripping agents for a modified ALSEP process

| | $SF_{Eu/Am} = D_{Eu}/D_{Am}$ | $SF_{Cm/Am} = D_{Cm}/D_{Am}$ |
|---|---|---|
| bp18c6 | 460 | 5.5 |
| bp18c6-OH | 1400 | 6.0 |
| bp18c6-OMe | $1.1 \times 10^4$ | 6.0 |

## 4.5 Fundamental Chemistry of TALSPEAK-Based Systems

K. L. Nash (WSU)

In a 1974 review of trivalent Ln-An separations, Boyd Weaver (developer of the TALSPEAK process) articulated the philosophy of his approach to accomplishing this challenging separation with the observation that (after years of seeking actinide-selective extractants) "…the separation was only accomplished by drastically altering the aqueous phase…" Broadly considered, most An(III)/Ln(III) solvent extraction/ion exchange based separations under investigation globally (e.g., GANEX, DIAMEX-SANEX, TRUSPEAK, ALSEP) are based on this approach and the application of pH-buffered actinide-selective N-donor stripping agents. This investigation has focused from the beginning on advancing the fundamental science that underpins TALSPEAK-like separations of the MAs from fission-product lanthanides. The increased understanding that has been gained regarding TALSPEAK-based separations [Nash, 2015] has effectively enabled the development of Advanced TALSPEAK and ALSEP systems.

TALSPEAK-like separations are those systems based on the use of actinide-selective aqueous polyaminopolycarboxylate complexants like DTPA. As recently reviewed [Nash, 2015], it has been demonstrated that conventional TALSPEAK (based on lactate buffers, HDEHP/diisopropylbenzene, and DTPA) is characterized by complex interactions that reduce predictability of system performance. These interactions give rise to the impractical steep pH dependence that defines conventional TALSPEAK separations. Insights developed in the WSU investigations have led to the Advanced TALSPEAK system based on the phosphonate (HEH[EHP]) analog to the TALSPEAK extractant HDEHP matched to a weaker holdback reagent and potentially a different buffer. The combination dramatically reduces the need for a concentrated buffer, improves predictability of TALSPEAK separations, and almost completely eliminates the pH dependence. The Advanced TALSPEAK concept and the introduction of HEH[EHP] led to the ALSEP combined process concept (see above).

Current research has focused on 1) alternative buffers (specifically malonate) for Advanced TALSPEAK, 2) dipicolinate derivatives as alternatives to conventional polyaminopolycarboxylate holdback reagents, and 3) a mixed-extractant system based on equimolar mixtures of the commercially available extractants Cyanex 923 and HEH[EHP] (commercially available as PC-88A, Ionquest 801) combined with a glycine buffer and various actinide selective holdback reagents. The latter system, TALSPEAK-MME (Mixed Monofunctional Extractants), enables efficient and rapid extraction of $Ln(NO_3)_3/An(NO_3)_3$ from 1 M $HNO_3$ media, conditioning to pH 2.5 using a glycine buffer, and selective removal of $Am^{3+}$ with a glycine-buffered HEDTA or triethylenetetraminehexacetic acid solution with a (not fully optimized) group SF of 10. An example of a new dipicolinate derivative applied as an actinide-selective stripping agent in the TALSPEAK-MME system is shown in Figure 9.

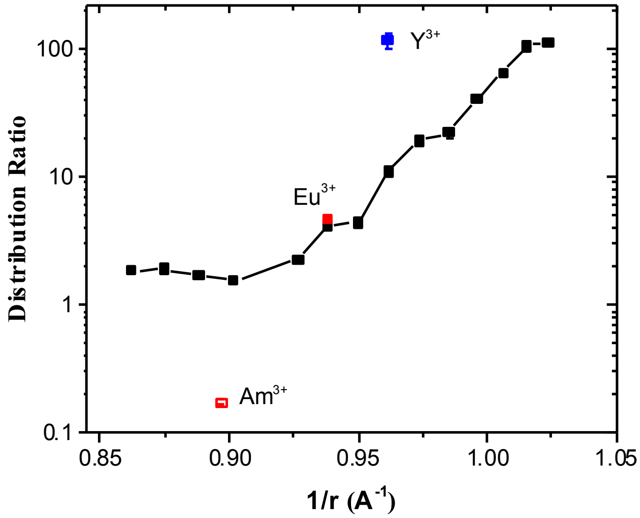


**Figure 9.** Application of actinide stripping agent in TALSPEAK-MME Ln/Am separation system. Aqueous phase: 7.01 mM *N*-methylpiperidine dipicolinic acid, 0.1 M glycine, pH 2.55. Organic phase: 0.4 M (HEH)EHP and 0.4 M Cyanex 923 in *n*-dodecane.

A recent advance was the demonstration that an alternative buffer, malonate, was applicable in TALSPEAK-like systems. An investigation of the basic extraction chemistry of the malonate/HEDTA/HEH[EHP]-dodecane system has established the potential to produce acceptable Ln/Am SFs at pH 2.5 with rapid extraction kinetics and a flat separation vs. pH profile. Toward a more thermodynamic understanding, spectrophotometric investigations conducted at PNNL (Figure 10) revealed the formation of mixed Ln(Mal)(HEDTA) complexes in the aqueous phase of a malonate-based Advanced TALSPEAK system. The principal issue with this system is that $La^{3+}$ is relatively poorly extracted, possibly resulting in some La contamination of the Am product (also observed in ALSEP separations). Separation of Am from strongly neutron absorbing Nd, Sm, Eu, and Gd is significantly better.

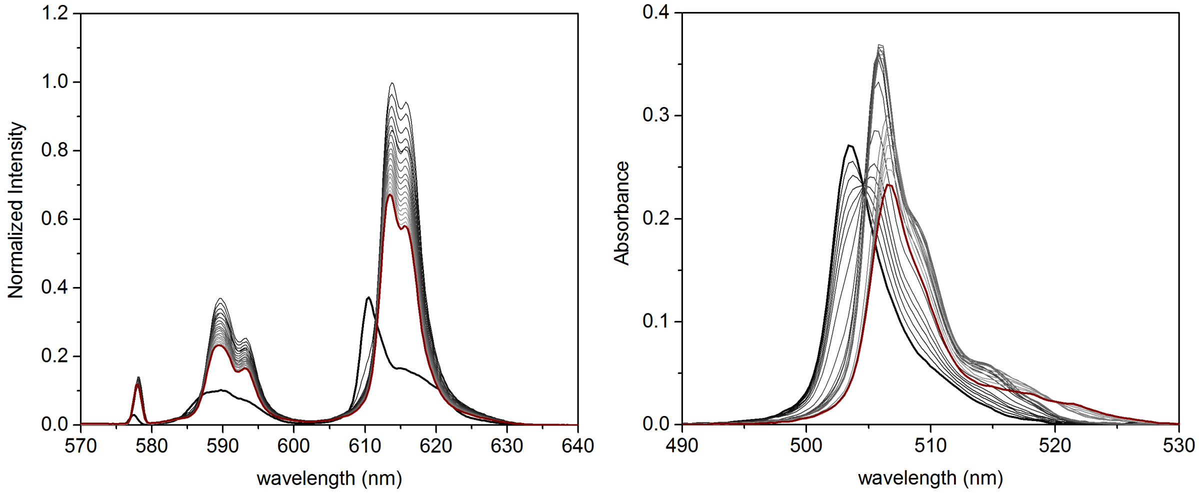


**Figure 10.** Luminescence ($Eu^{3+}$) and absorption ($Am^{3+}$) spectroscopy determination of thermodynamic parameters confirming the existence of mixed $M(Mal)(HEDTA)^{2-}$ complexes in malonate buffered Advanced TALSPEAK. Left: 99.8 mM HEDTA titrated into 1.98 mM $Eu^{3+}$, 0.500 M malonate. Right: 25.0 mM HEDTA titrated into 0.818 mM $Am^{3+}$, 0.600 M malonate.

## 4.6 Mixed-Donor Extractants

S. Jansone-Popova, V. Bryantsev, F. V. Sloop, Jr., R. Custelcean, and B. A. Moyer (ORNL)

Two new classes of mixed N,O-donor ligands have been identified for effective An(III)/Ln(III) separation (Figure 11, A). Bidentate ligand **6** and tetradentate ligand **7** possess N-heterocycle (triazole, phenanthroline) linked with δ-lactam unit(s). Both ligands are highly preorganized (rigid cyclic amide vs acyclic amide), leading to stronger binding of trivalent Ln and An ions.

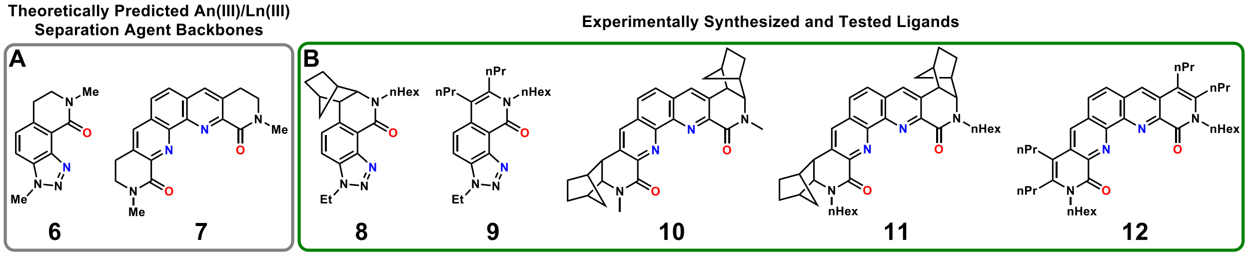


**Figure 11.** New bidentate and tetradentate mixed N,O-donor ligands.

Judicious selection of synthetic manipulations allows for introduction of long aliphatic substituents around the backbones in **6** and **7** that improve the solubility of the ligands in nonpolar solvents. Multi-step syntheses were used to prepare ligands **8** through **12** with good overall yields (Figure 11, B). We have established through experiment that the unsaturated ligands **9** and **12** are more soluble in nonpolar solvents (*n*-dodecane) than their corresponding saturated counterparts (**8**, **10**, and **11**). Additionally, tests employing 3 M $HNO_3$ revealed much higher stability of saturated series (ligands **8**, **10**, and **11** proved to be quite robust) compared to the unsaturated ones; this is mainly attributed to the absence of easily oxidizable benzylic C–H bonds in former case.

Next, all new ligands were tested as extracting agents for the selective separation of An(III) from Ln(III) ions. The small quantities of the compounds available limited the experiments to a single set of conditions, and thus, the influence of kinetics, nitric acid concentration, etc. cannot be fully appreciated at this early stage. Nevertheless, the initial results are encouraging overall. Representative preliminary extraction results are combined in Table 4. Bidentate ligands **8** and **9** were found to be very poor extractants in 1,2-dichloroethane and nitrobenzene under both high acidity and low acidity/high ionic strength conditions. Conversely, saturated tetradentate phenanthroline–based ligands **10** and **11** proved to be very strong extractants of both Am(III) and Eu(III) ions when tested at 1 mM concentrations under both high acidity and low acidity/high ionic strength conditions using 1,2-dichloroethane and nitrobenzene as the solvent. However, the SFs were quite low. Relatively high solubility of the unsaturated tetradentate phenanthroline–based ligand **12** permitted use of *n*-dodecane as an organic solvent. Ligand **12** exhibited excellent SFs in all solvents under high acidity/low ionic strength conditions with the highest SF of An(III) over Ln(III) of 65.

**Table 4**. Preliminary distribution ratios and SFs of Am(III)/Eu(III) using ligands **10**, **11**, and **12**

| **Ligand, (1mM)** | **Solvent** | **Aqueous Phase** | $D_{Am}$ | $D_{Eu}$ | **SF** |
|---|---|---|---|---|---|
| **10** | Nitrobenzene | 1 M $HNO_3$ | 9333 | 2909 | 3.2 |
| **11** | Nitrobenzene | 0.1 mM $HNO_3$ + 7 M $LiNO_3$ | 581 | 479 | 1.2 |
| **12** | 1,2-Dichloroethane | 1 M $HNO_3$ | 2.5 | 0.06 | 42 |
| | Nitrobenzene | 1 M $HNO_3$ | 0.83 | 0.01 | 59 |
| | *n*-Dodecane | 1 M $HNO_3$ | 0.05 | <0.01 | 65 |

The crystal structure of **11** complexed with $Eu(NO_3)_3$ was obtained (Figure 12). The ligand binds $Eu^{3+}$ ion via two phenanthroline N-atoms and two amide O-atoms, and three bidentate nitrate anions complete the coordination sphere, yielding a charge-neutral complex [Eu(**11**)$(NO_3)_3$)]. UV-vis titration experiments performed in methanol confirmed the formation of a 1:1 complex between ligand **11** and $Eu(NO_3)_3$.

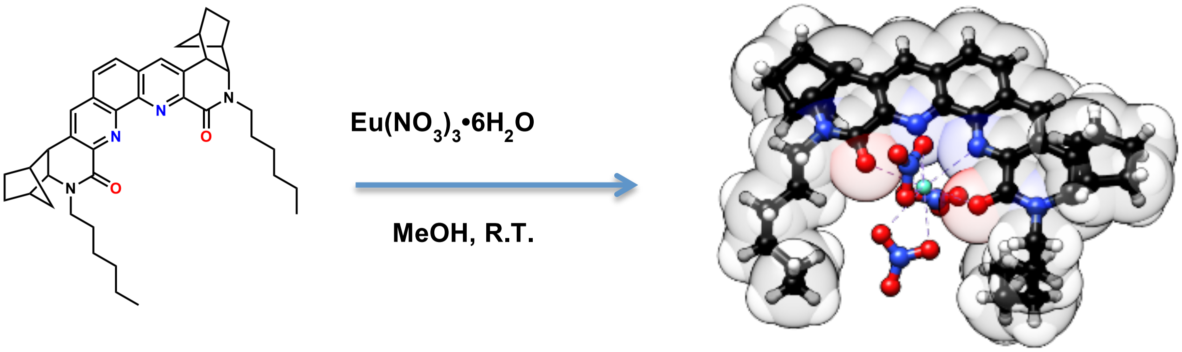


**Figure 12.** Crystal structure of extractant **11** with $Eu(NO_3)_3$.

## 4.7 Theoretical prediction of Am(III)/Eu(III) selectivity

V. S. Bryantsev and B. P. Hay (ORNL)

Establishing a reliable computational protocol for predicting the thermodynamics of binding An(III) and Ln(III) can provide valuable insights into their solution chemistry and open up new opportunities for the use of theory to guide design of novel ligands for An(III)/Ln(III) separation. To address this question, we examined the ability of several density functional theory (DFT) methods to predict Am(III)/Eu(III) selectivity with six oxygen, mixed oxygen-nitrogen, and sulfur donor ligands, as observed in liquid-liquid extraction and aqueous-phase selective complexation studies. Am(III)/Eu(III) selectivities were calculated as the differences in complexation energies between the extractants and metal ions:

$$\mathrm{Am}[(\mathrm{H_2O})_9]^{3+}{}_{(\mathrm{aq})} + \mathrm{Eu}(\mathrm{L})_n(\mathrm{NO_3})_{3(\mathrm{org})} \rightleftharpoons \mathrm{Am}(\mathrm{L})_n(\mathrm{NO_3})_{3(\mathrm{org})} + \mathrm{Eu}[(\mathrm{H_2O})]_9{}^{3+}{}_{(\mathrm{aq})},\ \ \Delta\Delta G_{\mathrm{ext}}(\mathrm{Am/Eu}) \tag{1a}$$

$$\Delta\Delta G_{\mathrm{ext}}(\mathrm{Am/Eu}) = \Delta G_{\mathrm{ext}}(\mathrm{Am}) - \Delta G_{\mathrm{ext}}(\mathrm{Eu}) \tag{1b}$$

The results established that certain diffuse density functionals are capable of correctly predicting the selectivity differences among several ligands. The composition of the extracted species used in the calculations is consistent with the proposed stoichiometry of the organic-phase complexes. Selectivities estimated as $\Delta\Delta G_{\mathrm{ext}}$(Am/Eu) values were obtained by combining our best estimates of the gas-phase free energies with implicit solvent corrections for both the aqueous and organic phase included. Table 5 shows that our computational protocol is able to reproduce higher affinity of the mixed N,O-donor and S-donor ligands for Am(III) over Eu(III) and rank-order their separation ability.

**Table 5**. Calculated and measured selectivities in the solvent extraction of $\mathrm{Am}^{3+}$ and $\mathrm{Eu}^{3+}$ (kcal/mol)[a]

| Complex | Calc | Expt |
|---|---|---|
| $\mathrm{M(H_2O)_4(NO_3)_3}$ | 0.861 | ~0 |
| $\mathrm{M(\mathbf{1})_2(NO_3)_3}$ | –2.23 | –1.53 |
| $\mathrm{M(\mathbf{2})_3}$ | –3.97 | –6.82 |

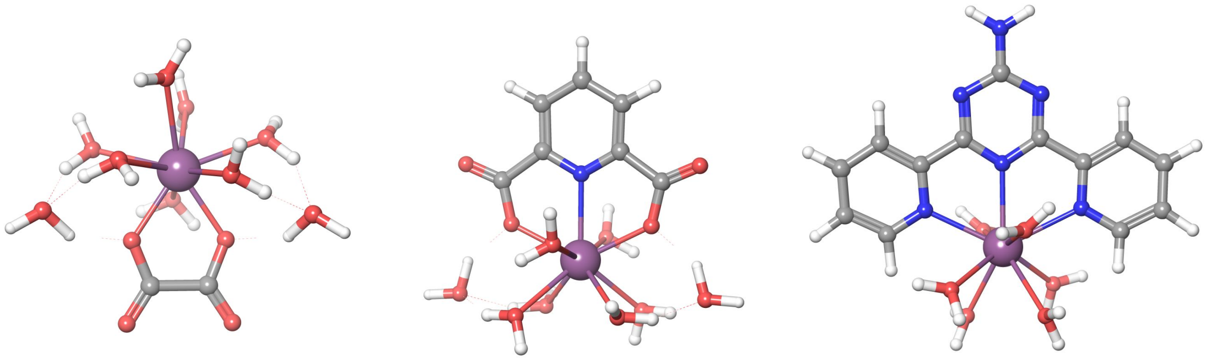
[a]Computed selectivities are obtained as the changes in the free energies for reaction 1a ($\Delta\Delta G_{\mathrm{ext}}$(Am/Eu)). **1** is 7-methyl-8-hydroxyquinolinol, and **2** is bis(*o*-trifluoromethylphenyl)dithiophosphinic acid.

Further validation of our theoretical model was carried out by comparison of the predicted and measured relative complexation energies of $\mathrm{Am}^{3+}$ and $\mathrm{Eu}^{3+}$ in the aqueous phase. Ligands with O- (oxalate), mixed N,O- (dipicolinate), and N-donor (ADPTZ) atoms were included (Figure 13). A competitive complexation of $\mathrm{Am}^{3+}$ and $\mathrm{Eu}^{3+}$ ions with these ligands was modeled according to reaction (2):

$$[\mathrm{Am(H_2O)_9}]^{3+} + [\mathrm{Eu(ligand)(H_2O)}_n]^{m+} = [\mathrm{Am(ligand)(H_2O)}_n]^{m+} + [\mathrm{Eu(H_2O)_9}]^{3+} \tag{2a}$$

$$\Delta\Delta G_{\mathrm{compl}}(\mathrm{Am/Eu}) = \Delta G_{\mathrm{compl}}(\mathrm{Am}) - \Delta G_{\mathrm{compl}}(\mathrm{Eu}) \tag{2b}$$

Several initial geometries were built by substituting two and three water molecules in $[\mathrm{M(H_2O)_9}]^{3+}$ by the corresponding bidentate and tridentate ligands, respectively. Adding two additional water molecules to solvate dianionic ligands was deemed necessary to stabilize each cluster in the nine-coordinate geometry. With these considerations, the results shown in Table 6 demonstrate that our theoretical prediction of aqueous complexation agrees closely with experimental measurements, reproducing the selectivity of 'hard' O-donor ligands for $\mathrm{Eu}^{3+}$ and 'softer' polyazine ligands for $\mathrm{Am}^{3+}$.



$[Am(oxalate)(H_2O)_9]^+$ $[Am(dipicolinate)(H_2O)_8]^+$ $[Am(ADPTZ)(H_2O)_5]^+$

**Figure 13.** Optimized structures for aqueous 1:1 metal ion-ligand complexes stabilized in the nine-coordinate geometry

**Table 6**. Predicted and experimental differences in complexation free energies of O- and N-donor ligands with $Am^{3+}$ and $Eu^{3+}$ ions in aqueous solution (kcal/mol)[a]

| Complex | Calc | Expt |
|---|---|---|
| Oxalate | 1.60 | 0.20 |
| Dipicolinate | 0.89 | 0.0 |
| ADPTZ | –1.91 | –1.72 |

[a] Computed selectivities are obtained as the changes in the free energies for reaction 2a ($\Delta\Delta G_{\mathrm{compl}}$(Am/Eu)).

Building upon the results obtained in FY 2015, in the next research cycle we will further examine several types of models for their ability to reproduce An(III)/Ln(III) selectivities for a larger set of ligands, including heterocyclic N-donor and mixed N,O-donor ligand. The most accurate computational scheme will be applied to estimate the selectivity of novel mixed oxygen-nitrogen donor ligands formed by covalently linking a heterocycle with an amide group (see above).

# 5. FUTURE PROGRESS

In the coming two years, the Sigma Team will likely move towards a laboratory-scale demonstrations of americium separation. While it remains to define the requirements of the test, it is anticipated that it will likely entail a demonstration flowsheet of Am separation with simulated feed using prototype small-scale engineering equipment in FY 2017. Based on the progress to date, ALSEP is the most mature technology concept, and planning is moving ahead to finalize an ALSEP flowsheet and design a demonstration. Problems to be first solved in FY 2016 include mainly improving the kinetics of stripping.

Promising technology concepts will be further matured in FY 2016. Systems of interest overall will include mainly acidic media, especially >1 M $HNO_3$. Testing of Am oxidation followed by extraction in a tandem centrifugal contactor will continue with candidate oxidation and extraction systems. Two possible tests include a second cycle of Am oxidation and extraction with sodium bismuthate and possibly the effectiveness of Cu(III) periodate as an oxidant; a decision point will move forward one of the candidates. Developing the catalyzed ozone oxidation followed by extraction will be a priority. Soft-donor extractants will be further developed and matured, including mixed N,O-donor extractants and bistriazinyl type extractants. Issues to be tackled include synthesis, stability to chemical degradation, solubility, kinetics, selectivity, and closing the extract/scrub/strip solvent cycle.

Even as efforts become more applied in some projects, the Sigma Team will maintain its science-based approach overall, as we seek understanding of the underlying chemical principles in hypothesis-driven inquiry. An understanding of the chemical and radiolytic stability of extractants and complexants will be sought, along with identifying conditions for extraction from molar nitric acid. Radiolytic stability of the higher oxidation states of Am will be characterized, and various chemical and electrochemical methods for Am oxidation will be investigated. The kinetics of oxidation Am(V) and Am(VI) will be elucidated along with pathways and rates of reduction. Speciation of extraction will be characterized more fully for TALSPEAK-like systems including ALSEP and soft-donor extractants. A dedicated effort to computationally design and test a new family of mixed-donor extractants for An/Ln separation will entail new ligand design, synthesis of candidate compounds, and experimental testing. Computations will also be directed at understanding actinide selectivity in soft-donor extractants and complexants.

In summary, it is clear that STAAR has established a world-class research effort with novel results of lasting scientific value and significant potential technological impact. A total of 87 open-literature publications have been issued, together with 10 graduate-student dissertations, 1 patent, and 3 patent applications. In the future, the Sigma Team will continue its efforts to conceive, develop, and mature new concepts for the selective separation of MA from lanthanides, employing science-based inquiry to strengthen and accelerate research.

## 6. Acknowledgments

The Sigma Team for Advanced Actinide Recycle is funded by the Fuel Cycle Research and Development program of the Office of Nuclear Energy, US Department of Energy. The author wishes to thank especially Dr. Terry Todd for his guidance and support as National Technology Director for the Materials Recycle and Waste Forms Development Campaign. Many thanks must also be accorded to the Sigma Team and its network of collaborators for their dedication and hard work that has made the reported results possible. Frederick V. Sloop is also thanked for his suggestions in improving this report.

# 7. CITED REFERENCES

Arm, S. T.; Phillips, C.; Dobson, A. Industrial Application of GNEP Solvent-Extraction Processes. In *Solvent Extraction: Fundamentals to Industrial Applications. Proceedings of ISEC 2008 International Solvent Extraction Conference*; Tucson, AZ, Sept. 15–19, 2008; Moyer, B. A., Ed.; The Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, 2008; Vol. 1, pp 709–714, 2008.

Blue Ribbon Commission, *Blue Ribbon Commission on Americ's Nuclear Future.* Report to the Secretary of Energy, January 2012.

Braley, J. C.; Lumetta, G. J.; Carter, J. C. Combining CMPO and HEH[EHP] for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2013**, *31* (6), 567–577.

Boullis, B. Future Nuclear Fuel Cycles: Prospects and Challenges. In *Solvent Extraction: Fundamentals to Industrial Applications. Proceedings of ISEC 2008 International Solvent Extraction Conference*; Tucson, AZ, Sept. 15–19, 2008; Moyer, B. A., Ed.; The Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, 2008; Vol. 1, pp 29–41.

Carelli, M.; Franceschini, F.; Lahoda, E.; Petrovic, B. In proceedings of the *WM2011 Conference*; American Nuclear Society: Phoenix, AZ, 2011, Paper 11452.

Chabert, C.; Tiphine, M.; Krivtchik, G.; Allou, A.; Saturnin, A.; Girotto, J.-L.; Sarrat, P.; Hancok, H.; Mathonnière, G.; Gabriel, S.; Baschwitz, A.; Fillastre, E.; Giffard, F. X.; Jasserand, F.; Boullis, B.; Leudet, A.; Caron-Charles, M.; Senentz, G.; Carlier, B.; Van Den Durpel, L.; Grosman, R.; Van Der Werf, J.; Laugier, F.; Settimo, D.; Garzenne, C. Considerations on Industrial Feasibility of Scenarios with the Progressive Deployment of Pu Mulitrecycling in SFRs in the French Nuclear Power Fleet. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5351, pp 296–305.

Dares, C.; Meyer, T. J. *Strategic Plan for Am Oxidation*, FCR&D-SWF-2014-000422, Idaho National Laboratory, Idaho Falls, ID, August 25, 2014.

Dares, C. J.; Lapides, A. M.; Mincher, B. J.; Meyer, T. J. Electrochemical Oxidation of $^{243}$Am(III) in Nitric acid by a Terpyridyl-Derivatized Electrode. Submitted to *Science*, June 2015.

Gelis, A. V.; Lumetta, G. J. Actinide Lanthanide Separation Process—ALSEP. *Ind. Eng. Chem. Res.* **2014**, *53*, 1624–1631.

Gelis, A. V.; Vandegrift, G. F.; Bakel, A.; Bowers, D. L.; Hebden, A. S.; Pereira, C.; Regalbuto, M. Extraction Behaviour of Actinides and Lanthanides in TALSPEAK, TRUEX and NPEX Processes of UREX+. *Radiochim. Acta* **2009**, *97*, 231–232.

Golay, M. Developing Timely, Desirable Future Low-Carbon Energy Economies. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5474, pp 150–152.

Herbst, R. S.; Baron, P.; Nilsson, M. Standard and Advanced Separation: PUREX Processes for Nuclear Fuel Reprocessing. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing: Oxford, 2011, pp 141–175.

Hill, C. Overview of Recent Advances in An(III)/Ln(III) Separation by Solvent Extraction. In *Ion Exchange and Solvent Extraction*; Vol. 19; Moyer, B. A., Ed.; Taylor and Francis: Philadelphia, 2010; Chap. 3.

Hill, C. Development of Highly Selective Compounds for Solvent Extraction Processes: Partitioning and Transmutations of Long-Lived Radionuclides from Spent Nuclear Fuels. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing: Oxford, 2011, pp 311–362.

Jensen, M. P.; Chiarizia, R.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M. M.; Roca-Sabio, A.; de Blas, A.; Rodríguez-Blas, T. Solvent Extraction Separation of Trivalent Americium from Curium and the Lanthanides. *Solvent Extr. Ion Exch.* **2015**, *33(4)*, 329–345.

Jensen, M. P.; Chiarizia, R.; Shkrob, I. A.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M.; Roca-Sabio, A.; Platas-Iglesias, C.; de Blas, A.; Rodríguez-Blas, T. Aqueous Complexes for Efficient Size-based Separation of Americium from Curium. *Inorg. Chem.* **2014**, *53*, 6003–6012.

Kagramanyan, V.; Usanov, V.; Kalashnikov, A.; Kvyatkovskii, S. Medium-Term Nuclear Industry Prospects Associated with Synergistic LWR/SFR System and Related Closed Nuclear Fuel Cycle. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5115, pp 15–22.

Laidler, J. J. An Overview of Spent-Fuel Processing in the Global Nuclear-Energy Partnership. In *Solvent Extraction: Fundamentals to Industrial Applications. Proceedings of ISEC 2008 International Solvent Extraction Conference*; Tucson, AZ, Sept. 15–19, 2008; Moyer, B. A., Ed.; The Canadian Institute of Mining, Metallurgy and Petroleum: Montreal, 2008; Vol. 1, pp. 695–701.

Law, J.; Soelberg, N.; Todd, T. A.; Tripp, J.; Pereira, C.; Williamson, M.; Ebert, W.; Jubin, R. T.; Moyer, B. A.; Vienna, J.; Lumetta, G. J.; Crum, J. V.; Rudisill, T.; Bresee, J.; Phillips, C.; Willis, B.; Murray, P.; Bader, S. *Separation and Waste Form Campaign Full Recycle Case Study*. FCRD-SWF-2013-000380 (Limited Distribution), Idaho National Laboratory: Idaho Falls, ID, 2013.

Lumetta, G. J.; Carter, J. C.; Gelis, A. V.; Vandegrift, G. F. Combining Octyl(phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine Oxide and Bis(2-ethylhexyl)phosphoric Acid Extractants for Recovering Transuranic Elements from Irradiated Nuclear Fuel. In *Nuclear Energy and the Environment*; Wai, C. M, Mincher, B. J., Eds.; ACS Symposium Series 1046; American Chemical Society: Washington, DC, 2010a; pp 107–118.

Lumetta, G. J.; Gelis, A. V.; Vandegrift, G. F. Review: Solvent Systems Combining Neutral and Acidic Extractants for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2010b**, *28*(3), 287–312.

Lumetta, G. J.; Gelis, A. V.; Carter, J. C.; Niver, C. M.; Smoot, M. R. The Actinide-Lanthanide Separation Process. *Solvent Extr. Ion Exch.* **2014a**, *32(4)*, 333–347.

Lumetta, G. J.; Gelis, A. V.; Braley, J. C.; Carter, J. C.; Pittman, J. W.; Warner, M. G.; Vandegrift, G. F. The TRUSPEAK Concept: Combining CMPO and HDEHP for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2013**, *31(3)*, 223–236.

Lumetta G. J.; Neiner, D.; Sinkov, S. I.; Carter, J. C.; Braley, J. C.; Latesky, S. L.; Gelis, A. V.; Tkac, P.; Vandegrift, G. F. Combining Neutral and Acidic Extractants for Recovering Transuranic Elements from Nuclear fuel. Proceedings of the 19th International Solvent Extraction Conference; L. Valenzuela, F; Moyer, B. A., Eds.; Gecamin Ltd: Santiago, Chile; Paper No. 68, 2011.

Moyer, B. A. *Sigma Team for Minor Actinide Separation Annual Report*. AFCI-SEPA-PMO-MI-DV-2009-000180, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2009.

Moyer, B. A. *Sigma Team for Minor Actinide Separation FY2010 Annual Report*. FCRD-SEPA-2010-000125, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2010.

Moyer, B. A.; Lumetta, G. L.; Mincher, B. J. Minor Actinide Separation in the Reprocessing of Spent Nuclear Fuels: Recent Advances in the United States. In *Reprocessing and Recycling of Spent Nuclear Fuels*, Woodhead Publishing, Waltham, MA, 2015; Chap. 11, pp 289–312.

Moyer, B. A. *Sigma Team for Advanced Actinide Recycle FY2015 Highlights*. FCRD-MRWFD-2015-000399, Oak Ridge National Laboratory: Oak Ridge, TN, September 15, 2015.

Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extr. Ion Exch.* **2015**, *33*(1) 1–57. DOI 10.1080/07366299.2014.985912

Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. Actinide Separation Science and Technology. In *The Chemistry of the Actinide and Transactinide Elements.* 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Katz, J. J., Eds.; Springer: Dordrecht, 2006; Vol. 4, Ch. 22, pp 2622–2798.

NNL, Minor Actinide Position Paper, National Nuclear Laboratory, Warrington, United Kingdom, 2013; downloaded September 2015 from http://www.nnl.co.uk/media/1053/minor_actinide_transmutation_-_position_paper_-_final_for_web1.pdf.

OECD Nuclear Energy Agency, *Actinide and Fission Product Partitioning and Transmutation, Tenth Information Exchange Meeting*; Mito Japan, October 6–10, 2008; NEA No. 6420, ISBN 978-92-64-99097-5; Organisation for Economic Cooperation and Development: Paris, France, 2010.

OECD Nuclear Energy Agency, *Actinide and Fission Product Partitioning and Transmutation, Eleventh Information Exchange Meeting*; San Francisco, CA, USA, November 1–4, 2010; NEA No. 6996, ISBN 978-92-64-99174-3; Organisation for Economic Cooperation and Development: Paris, France, 2012.

OECD Nuclear Energy Agency, *Potential Benefits and Impacts of Advanced Nuclear Fuel Cycles with Actinide Partitioning and Transmutation*, NEA No. 6894, Organisation for Economic Cooperation and Development: Paris, France, 2011.

Ouzounian, G.; Farin, S. The French Radioactive Waste Disposal System: Communication and Dialogue. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5052, pp 1826–1832.

Paillére, H.; Kepler, J.-H. Realising the Full Contribution of Nuclear Power to Combat Climate Change. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5409, pp 47–54.

Passerini, S.; Feng, B.; Fei, T.; Kim, T. K.; Taiwo, T. A.; Brown, N. R.; Cuadra, A. Analysis of Transition to Fuel Cycle System with Continuous Recycling in Fast and Thermal Reactors. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5060, pp 275–285.

Pillon, S.; Somers, J.; Grandjean, S.; Lacquement, J. Aspects of fabrication of curium-based fuels and targets*. J. Nucl. Mat.* **2003**, *320*, 36–43.

Poinssot, C.; Boullis, B.; Bourg, S. Role of Recycling in Advanced Nuclear Fuel Cycles. In *Reprocessing and Recycling of Spent Nuclear Fuels*, Woodhead Publishing, Waltham, MA, 2015; Chap. 2, pp 27–48.

Regalbuto, M. Alternative Separation and Extraction: UREX+ Processes for Actinide and Targeted Fission Product Recovery. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing: Oxford, 2011, pp 176–200.

Romary, J.-M.; Grygiel, J.-M. Ambitioning a Zero Radioactive Waste Future for Nuclear Energy. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5343, pp 1849–1858.

Runde, W. H.; Mincher, B. J. The higher oxidation states of americium: preparation, characterization and use for separations. Chem. Rev. **2011**, *111*(9), 5723–5741; dx.doi.org/10.1021/cr100181f.

Salvatores, M.; Palmiotti, G. Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges. *Progr. Part. Nucl. Phys.* **2011**, *66*, 144–166.

Tachimori, S.; Morita, Y. Overview of Solvent Extraction Chemistry for Reprocessing. In *Ion Exchange and Solvent Extraction*; Vol. 19; Moyer, B. A., Ed.; Taylor and Francis: Philadelphia, 2010; Chap. 1.

Tkac, P.; Vandegrift, G. F.; Lumetta, G. J.; Gelis, A. V. Study of the Interaction between HDEHP and CMPO and its Effect on the Extraction of Selected Lanthanides. *Ind. Eng. Chem. Res.* **2012**, *51*(31), 10433–10444.

Todd, T. A.; Wigeland, R. A. 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*; Lumetta, G. J., Nash, K. L., Clark, S. B., Friese, J. I., Eds.; American Chemical Society: Washington DC, 2006; Vol. 933, pp 41–55.

USDOE, *Nuclear Energy Research and Development Roadmap, Report to Congress*. US Dept. of Energy, Office of Nuclear Energy: Washington, DC, April 2010a.

USDOE, *Research Objective 3 Implementation Plan: Developing Sustainable Fuel Cycle Options*. FCRD-TIO-2011-000025, DOE Office of Nuclear Energy: Washington, DC, December 2010b.

Van Den Durpel, L. Globally Sustainable Nuclear Energy System with Regional Competitiveness. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5503, pp 306–310.

Wallard, H.; Duffy, B.; Cornick, P. *After Fukushima, Global Opinion on Energy Policy.* Ipsos Social Research Institute, Paris, France, March 2012.

Wigeland, R.; Taiwo, T.; Ludewig, H.; Todosow, M.; Halsey, W.; Gehin, J.; Jubin, R.; Buelt, J.; Stockinger, S.; Jenni, K.; Oakley B. *Nuclear Fuel Cycle Evaluation and Screening—Final Report.* FCRD-FCO-2014-000106, Idaho National Laboratory, Idaho Falls, ID, October 8, 2014.

Wigeland, R. A.; Taiwo, T.; Todosow, M. Investigation of Benefits from U/TRU Recycle - Quantification and Comparison to U/Pu Recycle. In *Proceedings of Global 2015*, Sept. 20–24, 2015, Paris, France; Paper 5238, pp 329–335.

Wigeland, R. A.; FCRD-MRWFD-2015, report in preparation.

Wigeland, R. A.; Bauer, T. H.; Fanning, T. H.; Morris, E. E. Separations and transmutation criteria to improve utilization of a geologic repository. *Nucl. Technol.* **2006**, *154*, 95–106.

Wigeland, R.; Taiwo, T.; Todosow, M.; Halsey, W.; Gehin, J. Nuclear Fuel Cycle Options. In *Proceedings of International Congress on Advances in Nuclear Power Plants ICAPP 2010*. San Diego, CA, June 13–17, 2010.

# 8. SIGMA TEAM PUBLICATIONS AND REPORTS

## 8.1 Publications

### 8.1.1 Publications in 2015

Bryantsev, V. S.; Hay, B. P. Theoretical prediction of Am(III)/Eu(III) Selectivity to Aid the Design of Actinide-Lanthanide Separation Agents. *Dalton Trans.* **2015**, *44*, 7935–7942.

Dares, C. J.; Lapides, A. M.; Mincher, B. J.; Meyer, T. J. Electrochemical Oxidation of $^{243}$Am(III) in Nitric acid by a Terpyridyl-Derivatized Electrode. Submitted to *Science*, June 2015.

Hay, B. P.; Panagopoulos, A. M.; Delmau, L. H.; Custelcean, R.; Moyer, B. A.; Watson, L.A., Ligand Preorganization Leads to $10^8$-fold Increase in Extraction Efficiency of Trivalent f-block Metal Ions by Lipophilic Picolinamides. Submitted to *Inorg. Chem.*, Sept. 2015.

Jensen, M. P.; Chiarizia, R.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M. M.; Roca-Sabio, A.; de Blas, A.; Rodríguez-Blas, T. Solvent Extraction Separation of Trivalent Americium from Curium and the Lanthanides. *Solvent Extr. Ion Exch.* **2015**, *33(4)*, 329–345.

Johnson, A. T.; Nash, K. L. Mixed Monofunctional Extractants for Trivalent Actinide/Lanthanide Separations: TALSPEAK MME. *Solvent Extr. Ion Exch.* **2015**, *33*, in press; DOI 10.1080/07366299.2015.1085225

Krahn, E. O.; Nash. K. L. Insights in Lanthanide-HEH[EHP] Exchange Dynamics in Advanced TALSPEAK Systems. Proceedings of Global 2015, September 20–24, 2015, Paris (France); Paper 5360.

Lapka, J. L.; Nash, K. L. Advanced TALSPEAK Separations Using a Malonate Buffer System. *Solvent Extr. Ion Exch.*, 2015, **33**, in press; DOI 10.1080/07366299.2015.1012878

Lumetta, G. J.; Casella, A. J.; Rapko, B. M.; Levitskaia, T. G.; Pence, N. K.; Carter, J. C.; Niver, C. M.; Smoot, M. R. An Advanced TALSPEAK Concept Using 2-Ethylhexylphosphonic Acid Mono-2-ethylhexyl Ester as the Extractant. *Solvent Extr. Ion Exch.* **2015**, *33*, 211–223.

Mincher, B. J.; Schmitt, N. C.; Schuetz, B. K.; Shehee T. C.; Hobbs, D. T. Recent Advances in *f*-Element Separations Based on a New Method for the Production of Pentavalent Americium in Acidic Solution. *RSC Advances* **2015**, *5*, 27205–27210.

Mincher, B. J.; Tillotson, R. D.; Law, J. D.; Garn, T.; Rutledge, V.; Schmitt, N. C. 2015. The Solvent Extraction of Am(VI) Using Centrifugal Contactors. Submitted to *J Radioanal Nucl Chem*, June 2015.

Moyer, B. A.; Lumetta, G. L.; Mincher, B. J. Minor Actinide Separation in the Reprocessing of Spent Nuclear Fuels: Recent Advances in the United States. In *Reprocessing and Recycling of Spent Nuclear Fuels*, Woodhead Publishing, Waltham, MA, 2015; Chap. 11, pp 289–312.

Nash, K. L.; Lapka, J. L.; Wahu, S.; Ferru, G.; Heathman, C. R.; Johnson A. T. Improving TALSPEAK Separations: New Knowledge Leading to Alternate Extractants, Holdback Reagents, and Buffers. Proceedings of Global 2015, September 20–24, 2015, Paris (France); Paper 5128.

Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extr. Ion Exch.* **2015**, *33*(1) 1–57. DOI 10.1080/07366299.2014.985912

Shehee, T. C.; Hobbs, D. T. Oxidation of Metal Ions by Peroxydisulfate in Dilute Nitric Acid. Submitted to *Radiochimica Acta*.

Sinkov, S. I.; Lumetta, G. J. Americium(III) Oxidation by Copper(III) Periodate in Nitric Acid Solution as Compared with the Action of Bi(V) Compounds of Sodium, Lithium, and Potassium. *Radiochim. Acta* **2015**, *103*, 541–552.

Tai, S.; Marchi, S. V.; Carrick, J. D. Efficient Preparation of Pyridinyl-1,2,4-triazines via Telescoped Condensation with Diversely Functionalized 1,2-Dicarbonyls. *J. Heterocyclic Chem.* **2015**, DOI: 10.1002/jhet.2374.

Tai, S.; Marchi, S. V.; Dover, E. J.; Carrick, J. D. Pd-Catalyzed Diamination of Dibromo-1,2,4-triazinyl Complexant Scaffolds. *J. Org. Chem.* **2015**, DOI: 10.2021/acs.joc.5b00710.

Tai, S.; Williams, N. J.; Carrick, J. D. Synthesis of *bis*-1,2,4-Triazines via Telescoped Condensation of [1,10]-Phenanthroline-2,9-dicarbonitrile with Aromatic 1,2-Dicarbonyls. *J. Heterocyclic Chem.* **2015**, DOI: 10.1002/jhet.2295.

Tevepaugh, K. N.; Carrick, J. D.; Tai, S.; Coonce, J. G.; Delmau, L. H.; Ensor, D. D. Separation of Americium from Europium using Camphor-BisTriazinyl Pyridine, A Fundamental Study. *Solvent Extr. Ion Exch.* (accepted).

Todd, T. A.; Moyer, B. A.; Mincher, B. J.; Law, J.; Goff, G.; Sinkov, S.; Lumetta, G. J. Oxidation and Extraction of Americiium(VI) from Lanthanides. In Nuclear Fuel Cycle for a Low-Carbon Future, Global 2015, Paris, France, September 20–24, 2015.

### 8.1.2 Publications in 2014

Brown, M. A.; Kropf, A. J.; Paulenova, A.; Gelis. A. V. Aqueous Complexation of Citrate with Neodymium(III) and Americium(III): A Study by Potentiometry, Absorption Spectrophotometry, Microcalorimetry, and XAFS. *Dalton Trans.* **2014**, *43*, 6446–6454.

Gelis, A.V.; Lumetta, G. J. Actinide Lanthanide Separation Process—ALSEP. *Ind. Eng. Chem. Res.* **2014**, *53*, 1624–1631.

Grimes, T. S.; Nash, K. L. Acid Dissociation Constants and Rare Earth Stability Constants for DTPA. *J. Solution Chem.* **2014**, *43 (2)*, 298–313.

Jensen, M. P.; Chiarizia, R.; Shkrob, I. A.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M.; Roca-Sabio, A.; Platas-Iglesias, C.; de Blas, A.; Rodríguez-Blas, T. Aqueous Complexes for Efficient Size-based Separation of Americium from Curium. *Inorg. Chem.* **2014**, *53 (12)*, 6003–6012.

Law, J.; Mincher, B.; Garn, T.; Greenhalgh, M.; Schmitt, N.; Rutledge, V. Development and Testing of an Americium/Lanthanide Separation Flowsheet Using Sodium Bismuthate. In *Proceedings of ICAPP*, Charlotte, NC, Apr. 4–6, 2014; American Nuclear Society, La Grange Park, IL, 2014; Paper 14040.

Lumetta, G. J.; Gelis, A. V.; Carter, J. C.; Niver, C. M.; Smoot, M. R. The Actinide-Lanthanide Separation Process. *Solvent Extr. Ion Exch.* **2014**, *32 (4)*, 333–347. DOI:10.1080/07366299.2014.895638.

Lumetta, G. J.; Levitskia, T. G.; Rapko, B. M.; Carter, J. C.; Niver, C. M.; Gelis, A. V. Development of the Actinide-Lanthanide Separation (ALSEP) Process. In *Proceedings of the 20th International Solvent Extraction Conference*, Würzburg, Germany, Sept. 7–11, 2014; DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V., Frankfurt am Main, Germany, 2014; Paper No. 8709, pp. 557–562.

Marie, C.; Krahn, E. O.; Nash, K. L. Probing Ligand Exchange Kinetics in Actinide/Lanthanide Solvent Extraction Systems using NMR Spectrometry. In *Proceedings of the 20th International Solvent Extraction Conference*, Würzburg, Germany, Sept. 7–11, 2014; DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V., Frankfurt am Main, Germany, 2014; Paper No. 4850.

Mincher, B. J.; Schmitt, N. C.; Tillotson, R. D.; Elias, G.; White, B. M.; Law, J. D. Characterizing Diamylamylphophonate (DAAP) as an Americium Ligand for Nuclear Fuel Cycle Applications. *Solvent Extr. Ion Exch.* **2014** *32*, 153–166.

Nash, K. L.; Heathman, C. New Dipicolinic Acid Derivatives for Actinide-Lanthanide Separations. In *Proceedings of the 20th International Solvent Extraction Conference*, Würzburg, Germany, Sept. 7–11, 2014; DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V., Frankfurt am Main, Germany, 2014; Paper No. 8947.

### 8.1.3 Publications in 2013

Braley, J. C.; Lumetta, G. J.; Carter, J. C. Combining CMPO and HEH[EHP] for Separating Trivalent Lanthanides from the Transuranic Elements, *Solvent Extr. Ion Exch.* **2013**, *31* (6), 567–577. DOI:10.1080/07366299.2013.785912.

Braley, J. C.; McAlister, D.; Horwitz, E. P.; Nash, K. L. Explorations of TALSPEAK Chemistry in Extraction Chromatography: Comparisons of TTHA with DTPA and HDEHP with HEH[EHP]. *Solvent Extr. Ion Exch.* **2013** *31(2)*, 107–121.

De Sahb, C.; Watson, L. A.; Nadas, J.; Hay, B. P. Design Criteria for Polyazine Extractants to Separate An(III) from Ln(III). *Inorg. Chem.* **2013**, *52 (18)*, 10632–10642.

Freiderich, M. E.; Peterman, D. R.; Klaehn, J. R.; Marc, P. Delmau, L. H. Chemical Degradation Studies on a Series of Dithiophosphinic Acids (DPAHs). *Ind. Eng. Chem. Res.* **2014**, *53 (9)*, 3606–3611.

Johnson, A. T.; Nash, K. L. A Combined Cyanex-923/HEH[EHP]/Dodecane Solvent for Recovery of Transuranic Elements from Used Nuclear Fuel. Paper 8247, Global 2013, Salt Lake City, Utah, 9/29–10/3, 2013.

Leggett, C. J.; Jensen, M. P. Studies of Size-Based Selectivity in Aqueous Ternary Complexes of Americium(III) or Lanthanide(III) Cations. *J. Solution Chem.*, **2013**, *42 (11)*, 2119–2136.

Lumetta, G. J.; Gelis, A. V.; Braley, J. C.; Carter, J. C.; Pittman, J. W.; Warner, M. G.; Vandegrift, G. F. The TRUSPEAK Concept: Combining CMPO and HDEHP for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.*, **2013**, *31 (3)*, 223–236.

Lumetta, G. J.; Carter, J. C.; Niver, C. M.; Gelis, A. V. Zirconium and Fission Product Management in the ALSEP Process. In *Proceedings of Global 2013*, Salt Lake City, UT, September 29–October 3, 2013; American Nuclear Society, La Grange Park, Illinois.

Nash, K. L; Lumetta, G. J.; Vienna, J. D. Irradiated Nuclear Fuel Management: Resource Versus Waste. In *Radioactive Waste Management and Contaminated Site Clean-up*; W. E. Lee, M. I. Ojovan, C. M. Jantzen, Eds.; Woodhead Publishing, Oxford, 2013; Chap. 5, pp 145–170.

Nash, K. L. Advancing the Scientific Basis of Trivalent Actinide-Lanthanide Separations. Paper 8246, Global 2013, Salt Lake City, Utah, 9/29–10/3, 2013.

Zalupski, P. R.; Ensor, D. E.; Riddle, C. L.; Peterman, D. R. Complete Recovery of Actinides from UREX-like Raffinates using a Combination of Hard and Soft Donor Ligands. *Solvent Extr. Ion Exch.* **2013**, *31*, 430–441.

### 8.1.4 Publications in 2012

Braley, J. C.; Carter, J. C.; Sinkov, S. I.; Nash, K. L.; Lumetta, G. J. The Role of Carboxylic Acids in TALSQuEAK Separations. *J. Coord. Chem.* **2012**, *65*, 2862–2876.

Braley, J. C.; Grimes, T. S.; Nash, K. L. Alternatives to HDEHP and DTPA for Simplified TALSPEAK Separations. *Ind. Eng. Chem. Res.* **2012**, *51*, 629–638.

Brown, M. A; Paulenova, A; Gelis, A.V. Aqueous Complexation of Thorium(IV), Uranium(IV), Neptunium(IV), Plutonium(III/IV), and Cerium(III/IV) with DTPA. *Inorg. Chem*. **2012**, *51(*14), 7741–7748.

Burns, J. D.; Borkowski, M.; Clearfield, A.; Reed, D. T. Separation of oxidized americium from lanthanides by use of pillared metal(IV) phosphate-phosphonate hybrid materials. *Radiochim. Acta* **2012**, *100*, 381–387.

Burns, J. D.; Clearfied, A.; Shehee, T. C.; Hobbs, D. T. Separation of Americium from Curium by Oxidation and Ion Exchange. *Anal. Chem.* **2012,** *84*(16), 6930–6932.

Daly, S. R.; Klaehn, J. R.; Boland, K. S.; Kozimor, S. A.; MacInnes, M. M.; Peterman, D. R.; Scott, B. L. NMR Spectroscopy and Structural Characterization of Dithiophosphinate Ligands Relevant to Minor Actinide Extraction Processes. *Dalton Trans.* **2012**, *41*(7), 2163–2175.

DeVore, M. A., II, Gorden, A. E. V. Copper and Uranyl Extraction from Aqueous Solutions Using Bis-dithiophosphinate Ligands Have Been Characterized. *Polyhedron* **2012**, *42*(1), 271–275.

Elvington, M. C.; Shehee, T. C.; Rudisill T. S.; Hobbs, D. T. Separation of Americium and Lanthanides Using Titanium-Based Materials. *Solvent Extr. Ion Exch.*, **2012**, *30*(7), 669–682.

Grimes, T. S.; Jensen, M. P.; Debeer-Schmidt, L.; Littrell, K.; Nash, K. L. Small Angle Neutron Scattering (SANS) Study of Organic Phase Aggregation in the TALSPEAK Process. *J. Phys. Chem. B* **2012**, *116*(46) 13722–13730.

Grimes, T. S.; Tian, G.; Rao, L.; Nash, K. L. Optical Spectroscopy Study Of Lanthanide Organic Phase Complexes in the TALSPEAK Separations Process. *Inorg. Chem.* **2012**, *51*(11), 6299–6307.

Groenewold, G.S.; Peterman, D.R.; Klaehn, J.R.; Delmau, L. H.; Marc, P.; Custelcean, R. Oxidative Degradation of Bis(2,4,4-trimethylpentyl)dithiophosphinic Acid in Nitric Acid Studied by Electrospray Ionization Mass Spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 2195–2203.

Heathman, C. R.; Nash, K. L. Characterization of Europium and Americium Dipicolinate Complexes. *Sep. Sci. Technol*. **2012**, *47*, 2029–2037.

Lumetta, G. J.; Levitskaia, T. G.; Latesky, S. L.; Henderson, R. V.; Edwards, E. A.; Braley, J. C.; Sinkov, S. I. Lipophilic Ternary Complexes in Liquid-Liquid Extraction of Trivalent Lanthanides. *J. Coord. Chem.* **2012**, *65*, 741–753.

Marc, P.; Custelcean, R.; Groenewold, G. S.; Klaehn, J. R.; Peterman, D. R.; Delmau, L. H. Degradation of CYANEX® 301 in Contact with Nitric Acid Media. *Ind. Eng. Chem. Res.* **2012**, *51*(40), 13238–13244. http://pubs.acs.org/doi/abs/10.1021/ie300757r (August 16, 2012).

Marie, C.; Hiscox, B.; Nash, K. L. Characterization of HDEHP-Lanthanide Complexes Formed in a Non-Polar Organic Phase Using $^{31}$P NMR and ESI-MS. *Dalton Trans.* **2012**, *41*(3), 1054–1064.

Mincher, B. J.; Martin, L. R.; Schmitt, N. C. Diamylamylphophonate Solvent Extraction of Am(VI) from Nuclear Fuel Raffinate Simulant Solution. *Solvent Ext. Ion Exch.* **2012**, *30*, 445–456. http://dx.doi.org/10.1080/07366299.2012.671108

Mincher, M. E.; Quach, D. L.; Liao, Y. J.; Mincher, B. J.; Wai, C. M. The Partitioning of Americium and the Lanthanides Using Tetrabutyldiglycolamide (TBDGA) in Octanol and in Ionic Liquid Solution. *Solvent Extr. Ion Exch.* **2012**, *30*, 735–747.

Sinkov, S. I.; Lumetta G. J.; Warner, M. G.; Pittman, J. W. Binding of Stereognostically Designed Ligands to Trivalent, Pentavalent, and Hexavalent f-Block Elements. *Radiochim. Acta.* **2012**, *100*, 349–357.

Taylor-Pashow, K. M. L.; Shehee, T. C.; Hobbs, D. T. Advances in Inorganic and Hybrid Ion-exchangers. *Solvent Extr. Ion Exch.* **2013**, *31*, 122–170.

Tkac, P.; Vandegrift, G. F.; Lumetta, G. J.; Gelis, A. V. Study of the Interaction between HDEHP and CMPO and its Effect on the Extraction of Selected Lanthanides. *Ind. Eng. Chem. Res.* **2012**, *51*(31), 10433–10444.

### 8.1.5 Publications in 2011

Casely, I. J.; Ziller, J. W.; Mincher, B. J.; Evans, W. J. Bismuth Coordination Chemistry with Allyl, Alkoxide, Aryloxide, and Tetraphenylborate Ligands Attached to the $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}^{1+}$ Cation. *Inorg. Chem.* **2011**, *50*, 1513–1520.

Klaehn, J. R.; Peterman, D. R.; Harrup, M. K.; Luther, T. A.; Daniels, L. M. Bis(o-trifluoromethylphenyl) dithiophosphinic Methyl Ester. *Inorg. Chim. Acta.* **2011**, *370*, 519–522.

Lumetta G. J.; Neiner, D.; Sinkov, S. I.; Carter, J. C.; Braley, J. C.; Latesky, S. L.; Gelis, A. V.; Tkac, P.; Vandegrift, G. F. Combining Neutral and Acidic Extractants for Recovering Transuranic Elements from Nuclear fuel. Proceedings of the 19th International Solvent Extraction Conference; L. Valenzuela, F; Moyer, B. A., Eds.; Gecamin Ltda: Santiago, Chile; Paper No. 68, 2011.

Mincher, B. J.; Schmitt, N. C.; Case, M. E. A TRUEX-Based Americium/Lanthanide Separation. *Solvent Extr. Ion Exch.* **2011**, *29*, 247–259.

Nash, K. L.; Braley, J. C. Chemistry of Radioactive Materials in the Nuclear Fuel Cycle. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing Series in Energy, Number 2; Woodhead Publishing: Cambridge, 2011; pp 3–22.

Nash, K. L.; Marie, C.; Ogden, M. D.; Brigham, D. Soft-Donor Extractants vs. Aqueous Complexants in Trivalent Lanthanide/Actinide Separations. Proceedings of the 19th International Solvent Extraction Conference; L. Valenzuela, F., Moyer, B. A., Eds.; Gecamin Ltda: Santiago, Chile.

Nash, K. L.; Nilsson, M.; Grimes, T.; Braley, J.; Uruga, K.; Marie, C. Complex Interactions in Solvent Extraction—Biphasic Speciation in the TALSPEAK Process. Proceedings of the 19th International Solvent Extraction Conference; L. Valenzuela, F., Moyer, B. A., Eds.; Gecamin Ltda: Santiago, Chile.

Nash, K. L.; Lumetta, G. J. Eds. *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Woodhead Publishing Series in Energy, Number 2; Woodhead Publishing: Cambridge, 2011; p 492.

Runde, W. H.; Mincher, B. J. The Higher Oxidation States of Americium: Preparation, Characterization and Use for Separations. *Chem. Rev.* **2011**, *111*(9), 5723–5741.

Tranter, T. J. Solid Phase Extraction Technology for Actinide and Lanthanide Separations. In *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment*; Nash, K. L., Lumetta, G. J., Eds.; Woodhead Publishing Series in Energy, Number 2; Woodhead Publishing: Cambridge, 2011; pp 377–413.

Watson, L. A.; Hay, B. P. Role of the Uranyl Oxo Group as a Hydrogen Bond Acceptor. *Inorg. Chem.* **2011**, *50*, 2599–2605.

### 8.1.6 Publications in 2010

Goff, G. S.; Cisneros, M. R.; Kluk, C.; Williamson, K.; Scott, B.; Reilly, S.; Runde, W. Synthesis and Structural Characterization of Molecular Dy(III) and Er(III) Tetra-carbonates. *Inorg. Chem.* **2010**, *49*, 6558–6564.

Grimes, T. S.; Nilsson, M. A.; Nash, K. L. Lactic Acid Partitioning in TALSPEAK Extraction Systems. *Sep. Sci. Technol.* **2010**, *45*(12–13), 1725–1732.

Leggett, C. J.; Liu, G. K.; Jensen, M. P. Do Aqueous Ternary Complexes Influence the TALSPEAK Process? *Solvent Extr. Ion Exch.* **2010**, *28*(3), 313–333.

Lumetta, G. J.; Carter, J. C.; Gelis, A. V.; Vandegrift, G. F. Combining Octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine Oxide and Bis(2-ethylhexyl)phosphoric Acid Extractants for Recovering Transuranic Elements from Irradiated Nuclear Fuel. In *Nuclear Energy and the Environment*; Wai, C. M, Mincher, B. J., Eds.; ACS Symposium Series 1046; American Chemical Society: Washington, DC, 2010; pp 107–118.

Lumetta, G. J.; Gelis, A. V.; Vandegrift, G. F. Review: Solvent Systems Combining Neutral and Acidic Extractants for Separating Trivalent Lanthanides from the Transuranic Elements. *Solvent Extr. Ion Exch.* **2010**, *28*(3), 287–312.

Nash, K. L.; Braley, J. C. Challenges for Actinide Separations in Advanced Nuclear Fuel Cycles. In *Nuclear Energy and the Environment*; ACS Symposium Series 1046; American Chemical Society: Washington, DC, 2010; pp 19–38.

Shehee T. C.; Martin L. R.; Zalupski P. J.; Nash K. L. Redox-based Separation of Americium from Lanthanides in Sulfate Media. *Sep. Sci. Technol.* **2010**, *45*(12,13), 1743–1752.

Zalupski, P. R.; Nash, K. L.; Nakamura, Y.; Yamamoto, M.; Martin, L. R. Toward Understanding the Thermodynamics of TALSPEAK Process. Medium Effects on Actinide Complexation. In *IOP Conference Series: Materials Science and Engineering* (2010); Proceedings of the Actinides 2009 Conference, San Francisco, CA, July 2009; 9, 012076/1–012076/8.

### 8.1.7 Publications in 2009

Gelis, A. V.; Vandegrift, G. F.; Bakel, A.; Bowers, D. L.; Hebden, A. S.; Pereira, C.; Regalbuto, M. Extraction Behaviour of Atinides and Lanthanides in TALSPEAK, TRUEX and NPEX Processes of UREX+. *Radiochim. Acta* **2009**, *97*, 231–232.

Martin, L. R.; Mincher, B. J.; Schmitt, N. C. Extraction of Am(VI) with a Neutral Organophosphorous Ligand. *J. Radioanal. Nucl. Chem.* **2009**, *282*, 523–526.

Nash, K. L.; Grimes, T. S.; Nilsson, M. Trivalent Actinide–Lanthanide Separations Using TALSPEAK: Explorations of the Basic Chemistry. Proceedings of Actinides 2009 Conference, San Francisco, CA, July 12–17, 2009.

Nash, K. L.; Grimes, T. S.; Nilsson M. Fundamental Studies of TALSPEAK Chemistry for Trivalent Actinide–Lanthanide Separations; Proceedings of the Advanced Nuclear Fuel Cycles in Global 2009 Conference, September 6–11, 2009, Paris, France, pp 1099–1106.

Nilsson, M.; Nash, K. L. Trans-Lanthanide Extraction Studies in the TALSPEAK System: Investigating the Effect of Acidity and Temperature. *Solvent Extr. Ion Exch.* **2009,** *27*, 354–377.

Zalupski, P. R.; Nash, K. L.; Nakamura, Y.; Yamamoto, M.; Martin, L. R. Toward Understanding the Thermodynamics of TALSPEAK Process. Medium Effects on Actinide Complexation. In *IOP Conference Series: Materials Science and Engineering* (2010), Conference Proceedings of Actinides 2009 Conference, San Francisco, CA, July 2009; 9, 012076/1–012076/8.

### 8.1.8 Publications in 2008

Mincher, B. J.; Martin, L. R.; Schmitt, N. C. Tributylphosphate Extraction Behavior of Bismuthate-Oxidized Americium. *Inorg. Chem.* **2008**, *47*, 6984–6989.

## 8.2 Sigma Team Patents and Patent Applications

Gelis, A. V.; Brown, M. A. *Transition metal recovery from nitric acid*. Patent application submitted.

Dares, C. J.; Lapides, A. M.; Mincher, B. J.; Meyer, T. J. Electrochemical Treatment of Nuclear Waste Streams. Patent pending.

Gelis A.V. Actinide and Lanthanide Separation Process (ALSEP). United States Patent 8354085, January 15, 2013.

Goff, G. S.; Seaman, L. S.; Runde, W.; Jarvinen, G. D. Oxidation of Americium in Acidic Solution. Patent Pending.

## 8.3 Dissertations

Tevepaugh, K. New Nitrogen-Based Extractants for Separation of Minor Actinides from Lanthanides. M.S. Dissertation, Tennessee Technological University, Cookeville, TN, July 2014.

Johnson, A. T. A Combined Cyanex-923 and HEH[EHP] Process for Partitioning Used Nuclear Fuels: Characterizing Complex Interactions. Ph.D. Dissertation, Washington State University, Pullman, WA, May 2014.

Heathman, C. Functionalization Characterization and Evaluation of Dipicolinate Derivatives with f-Element Complexes. Ph.D. Dissertation, Washington State University: Pullman, WA, September 2013.

Brigham, D. Lanthanide-Polyaminopolycarboxylate Complexation Kinetics in High Lactate Media: Investigating the Aqueous Phase of TALSPEAK. Ph.D. Dissertation, Washington State University, May, 2013.

Johnson G. E., Studies of the Thermodynamics of DTPA Complexation Of The Rare Earth Elements At High Ionic Strength: Applications to the TALSPEAK Process. MS Thesis: December 2012.

Burns, J. D. Development of Pillared M(IV) Phosphate Phosphonate Hybrid Ion Exchange Materials for Applications in Separations Found in the Nuclear Fuel Cycle. Ph.D. Dissertation, Texas A&M University: College Station, TX, December, 2012.

Leggett, C. J. Thermodynamic Investigations of Aqueous Ternary Complexes for Am/Cm Separation. Ph.D. Dissertation, University of California Berkeley, 2012.

Dunne, J. Study of Synergistic Mixtures of Bis(O-Fluoromethylphenyl)-Dithiophosphinic Acid And Neutral Oxygen Donor Ligands. M.S. Dissertation, Tennessee Technological University, Cookeville, TN, December 2011.

Grimes, T. S. Coordination Chemistry of f-Elements in the TALSPEAK Process. Ph.D. Dissertation, Washington State University, Pullman, WA, 2011.

Braley, J. C. The Use of Organophosphorus Extractants in f-Element Separations. Ph.D. Dissertation, Washington State University, Pullman, WA, 2010.

## 8.4 Sigma Team Reports

### 8.4.1 Reports in 2015

Boland, K. S.; Dry, D. E.; Gallegos, M. J.; Goff, Seaman, L.; Runde, W. *Sigma Team for Minor Actinide Separations: Spectroscopic Determination of Americium(III) in Nitric Acid Solutions*. FCRD-MRWFD-2015-000595, Los Alamos National Laboratory: Los Alamos, NM, March 31, 2015.

Bryantsev, V. S.; Jansone-Popova, S.; Sloop, F. V., Jr.; Custelcean, R.; Moyer, B. A. *First-Principles Prediction of An(III)/ Ln(III) Selectivity and Synthesis of Actinide Sequestering Agents*, FCRD-MRWFD-2015-000404, Oak Ridge National Laboratory, Oak Ridge, TN, August 2015.

Burns, J. D.; Moyer, B. A. *Co-crystallization of Actinyl Complexes: FY15 Final Report*, FCRD-MRWFD-2015-000406, Oak Ridge National Laboratory, Oak Ridge, TN, August 2015.

Delmau, L. H.; Hill, T. G.; Tevepaugh, K. N.; Richards, K.; Carrick, J.; Ensor, D. D. Trivalent Actinide – Lanthanide Separation using Bis Triazinyl Pyridine Derivatives, FCRD-MRWFD-2015-000405, Oak Ridge National Laboratory, Oak Ridge, TN, August 2015.

Gelis, A. V.; Brown, M. A. *ALSEP Year-End Report*, FCRD-MRWFD-2015-000544, Argonne National Laboratory, Argonne, IL, September 2015.

Gelis, A. V.; Brown, M. A.; Lumetta, G. J.; Casella, A. J. *Recommendation on the ALSEP lab-scale flowsheet readiness*, FCRD-MRWFD-2015-000005, Argonne National Laboratory, Argonne IL and Pacific Northwest National Laboratory, Richland, Washington, June 2015.

Goff, G. S.; Boland, K. S.; Jarvinen, G. D.; McCurdy, N. B.; Runde, W.; Seaman, L.; Wolfsberg, L. *Silver Catalyzed Ozonation of Americium(III) in Nitric Acid Media*. FCRD-MRWFD-2015-000072, Los Alamos National Laboratory: Los Alamos, NM, July 31, 2015.

D. T. Hobbs, T. C. Shehee, *Experimental Findings on Actinide Recovery Utilizing Oxidation by Peroxydisulfate Followed by Ion Exchange*, FCRD-MRWFD-2015-000798, Savannah River National Laboratory, Aiken SC, September 2015.

G. J. Lumetta, T.G. Levitskaia, E.L. Campbell, and J.C. Carter. 2015. *Characterization of the Zirconium, Ruthenium, and Iron Behavior in the Actinide-Lanthanide Separation (ALSEP) System*, FCRD-MRWFD-2015-000112 (PNNL-24489; client distribution only), Pacific Northwest National Laboratory: Richland, Washington, July 2015.

G. J. Lumetta, E. L. Campbell, A. J. Casella, G. Hall, T. G. Levitskaia, F. N. Smith, and G. Carter *Sigma Team for Advanced Actinide Recovery: PNNL FY 2015 Summary Report*, FCRD-MRWFD-2015-000471, Pacific Northwest National Laboratory: Richland, Washington, August 2015.

Grimes, T. S.; Mincher, B. J.; Schmidt, N. C. *Reduction Rates for Higher Americium Oxidation States in Nitric Acid.* FCRD-MRWFD-2015-000045, Idaho National Laboratory, Idaho Fall, ID, September 24, 2015.

Mincher, B. J. *Higher Oxidation States of Americium-FY15 Final report*, FCRD-MRWFD-2015-00244, Idaho National Laboratory, Idaho Fall, ID, September 2015.

Moyer, B. A. *Sigma Team for Advanced Actinide Recycle FY2015 Highlights*. FCRD-MRWFD-2015-000399, Oak Ridge National Laboratory: Oak Ridge, TN, September 15, 2015.

Moyer, B. A. *Sigma Team for Advanced Actinide Recycle FY2015 Accomplishments and Directions*. FCRD-MRWFD-2015-000401, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2015.

T. C. Shehee and D. T. Hobbs, *Oxidation of Metal Ions by Peroxydisulfate in Dilute Nitric Acid*, FCRD-MRWFD-2015-000525, Savannah River National Laboratory, Aiken SC, August 2015.

T. C. Shehee and D. T. Hobbs, M3FT-15SR0303071 *Perform batch contact tests on two ion-exchange flowsheet concepts,* FCRD-MRWFD-2015-000524, Savannah River National Laboratory, Aiken SC, September 2015.

### 8.4.2 Reports in 2014

Dares, C.; Meyer, T. J. *Strategic Plan for Am Oxidation*. FCR&D-SWF-2014-000422, Idaho National Laboratory: Idaho Falls, ID, August 25, 2014.

Delmau, L. H.; Tevepaugh, K. N.; Richards, K,; Carrick, J.; Ensor, D. D. *Trivalent Actinide – Lanthanide Separation using Bis Triazinyl Pyridine Derivatives*. FCRD-SWF-2014-000225, Oak Ridge National Laboratory: Oak Ridge, TN, August 2014.

Gelis, A. V.; Brown, M. A. *ALSEP Year-End Report*. FCRD-SWF-2014-000216, Argonne National Laboratory: Argonne, IL, September 2014.

Gelis, A. V.; Pereira, C.; Lumetta, G. J. *AMUSE Model of a Conceptual Actinide-Lanthanide Separation (ALSEP) Flowsheet*. FCRD-SWF-2014-000027 (Limited Distribution); Pacific Northwest National Laboratory: Richland, WA, 2014.

Goff, G. S.; Seaman, L.; Jarvinen, G. D.; Runde, W. *Sigma Team for Minor Actinide Separations: LANL FY2014 Annual Report*. FCRD-SWR-2014-000221, Los Alamos National Laboratory: Los Alamos, NM, September 19, 2014.

Hay, B. P.; Bryantsev, V. *Molecular Modeling and Synthesis of Sequestering Agents for An(III)/Ln(III) Partitioning*. FCRD-SWF-2014-000228, Oak Ridge National Laboratory: Oak Ridge, TN, August 2014.

Hobbs, D. T.; Shehee, T. C. *Experimental Findings on Minor Actinide and Lanthanide Separations Using Ion Exchange*. FCRD-SWF-2014-000230 (SRNL-STI-2014-00398), Savannah River National Laboratory: Aiken, SC, September 12, 2014.

Jensen, M. P.; Chiarizia, R. *Feasibility of Americium-Curium Separation by Sterically Constrained Complexes*. FCRD-SWF-2014-000213, Argonne National Laboratory: Argonne, IL, September 30, 2014.

Lumetta, G. J.; Levitskaia, T. G.; Rapko, B. M.; Sinkov, S. I.; Niver, C. M.; Smoot, M. R. *Sigma Team for Minor Actinide Separation: PNNL FY 2014 Summary Report*. FCRD-SWF-2014-000229, Pacific Northwest National Laboratory: Richland, WA, September 2014.

Mincher, B. J.; Tillotson, R.; Law, J. D.; Garn, T.; Schmitt, N. *Sodium Bismuthate Process: Oxidation Test Bed Setup and Hot Testing*. FCR&D-SWF-2014-000218, Idaho National Laboratory: Idaho Falls, ID, September 30, 2014.

Mincher, B. J. *Am(VI) Partitioning Studies: FY14 Final Report*. FCR&D-SWF-2014-000630, Idaho National Laboratory: Idaho Falls, ID, September 30, 2014.

Moyer, B. A. *Sigma Team for Minor Actinide Separations FY2014 Accomplishments and Directions*. FCRD-SWF-2014-000223, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2014.

Nash, K. L. *Fundamental Studies for Improving TALSPEAK-Type Separations*. FCRD-SWF-2014-00224, Washington State University: Pullman, WA, August 26, 2014.

Peterman, D. R.; Zalupski, P. R.; Klaehn, J. R.; McDowell, R. G.; Law, J. D. *FY-2014 Summary Report—Minor Actinide Separations Using INL DPAH Extractants*. FCRD-SWF-2014-000615, Idaho National Laboratory: Idaho Falls, ID, September 29, 2014.

Peterman, D. R. *Identification of Process Suitable Diluent*. FCRD-SWF-2014-00423, Idaho National Laboratory: Idaho Falls, ID, January 16, 2014.

Peterman, D. R.; Zalupski, P. R.; Klaehn, J. R. *Minor Actinide Separation Using INL DPAH and Synergist*. FCRD-SWF-2014-000219, Idaho National Laboratory: Idaho Falls, ID, August 1, 2014.

Peterman, D. R.; Zalupksi, P. R.; Klaehn, J. R.; Law, J. D. *Flowsheet for Minor Actinide Separation Using INL DPAH Extractants – OUO*. FCRD-SWF-2014-000220, Idaho National Laboratory: Idaho Falls, ID, August 28, 2014.

Zalupski, P.; McDowell, R.; Peterman, D. *Distribution Behavior of Soft Metal in INL DPAH Solvent*. FCRD-SWF-2014-00424, Idaho National Laboratory: Idaho Falls, ID, July 21, 2014.

### 8.4.3 Reports in 2013

Alsobrook, A. N.; Hobbs, D. T. *Ion Exchange Performance of Titanosilicates, Germanates and Carbon Nanotubes*. FCRD-SWF-2013-000147 (SRNL-STI-2013-00234), Savannah River National Laboratory: Aiken, SC, April 24, 2013.

Delmau, L. H.; Tevepaugh, K. N.; Freiderich, M. E. *Trivalent Actinide-Lanthanide Separation Using Bis-Dithio Phosphinic Acids and Bis Triazinyl Pyridine Derivatives*. FCRD-SWF-2013-000274, Oak Ridge National Laboratory: Oak Ridge, TN, August 30, 2013.

Garn, T. G.; Law, J. D.; Mincher, B. J.; Greenhalgh, M.; Rutledge, V. *Ce oxidation, Filtration and Distribution in 0.25 M Diamylamylphosphonate*. FCRD-SWF-2013-000365, Idaho National Laboratory: Idaho Falls, ID, 2013.

Gelis, A. V. *ALSEP Annual Report*. FCRD-SWF-2013-000364, Argonne National Laboratory: Argonne, IL, September 2013.

Gelis, A. V. *Actinide-Lanthanide Separation—ALSEP—Process Zr Suppression*. FCRD-SWF-2013-000091, Argonne National Laboratory: Argonne, IL, January 30, 2013.

Goff, G. S.; Seaman, L.; Jarvinen, G. D.; Runde, W. *Sigma Team for Minor Actinide Separations: Determination of the Feasibility of Oxidation of Americium by Ozone in Nitric Acid*. FCRD-SWR-2013-000209, Los Alamos National Laboratory: Los Alamos, NM, June 28, 2013.

Goff, G. S.; Seaman, L.; Jarvinen, G. D.; Runde, W. *Sigma Team for Minor Actinide Separations: LANL FY2013 Annual Report*. FCRD-SWR-2013-000367, Los Alamos National Laboratory: Los Alamos, NM, September 20, 2013.

Guelis, A. V.; Lumetta G. J. *Recommendation Regarding the Reference ALSEP Solvent Formulation*. FCRD-SWF-2013-000097, Argonne National Laboratory: Argonne, IL and Pacific Northwest National Laboratory: Richland, WA, March 2013.

Hay, B. P.; Delmau, L. H.; Moyer, B. A. *Sigma Team for Minor Actinide Separations: Data on Computation, Synthesis, and Testing*. FCRD-SWF-2013-000253, Oak Ridge National Laboratory: Oak Ridge, TN, August 30, 2013.

Hobbs, D. T.; Shehee, T. C.; Clearfield, A. *Experimental Findings on Minor Actinide and Lanthanide Separations Using Ion Exchange*. FCRD-SWF-2013-000276 (SRNL-STI-2013-00524), Savannah River National Laboratory: Aiken, SC, September 19, 2013.

Jensen, M. P.; Chiarizia, R. *Constrained Complexes for Americium-Curium Separation*. FCRD-SWF-2013-000333, Argonne National Laboratory: Argonne, IL, September 13, 2013.

Lumetta, G. J.; Carter, J. C.; Niver, C. M.; Gelis, A. V. 2013. *Recommendation Regarding Stripping Zirconium from ALSEP Solvents*. FCRD-SWF-2013-000038, Pacific Northwest National Laboratory: Richland, WA, January 2013.

Lumetta, G. J.; Carter, J. C.; Niver, C. M.; Smoot, M. R. *Actinide-Lanthanide Separation (ALSEP) Process Development: PNNL Results for FY 2013*. FCRD-SWF-2013-000210, Pacific Northwest National Laboratory: Richland, WA, August 2013.

Meyer, T. J.; Dares, C. *Electrochemical Oxidation of Actinides*. Report to INL, University of North Carolina: Chapel Hill, NC, August 19, 2013.

Mincher, B. J.; Schmitt N. C.; Law, J. D. *A Refined Bismuthate Flowsheet Concept*. FCR&D-SWF-2013-000361, Idaho National Laboratory: Idaho Falls, ID, September 27, 2013.

Moyer, B. A. *Sigma Team for Minor Actinide Separations FY2013 Accomplishments and Directions*. FCRD-SWF-2013-000389, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2013.

Nash, K. L. *Fundamental Studies for Improving TALSPEAK-Type Separations*. FCRD-SWF-2013-00323, Washington State University: Pullman, WA, September 18, 2013.

Peterman, D. R.; Zalupski, P. R.; Riddle, C. L.; Klaehn, J. R.; Law, J. D. *Flowsheet Concept for the Separation of Minor Actinides Using INL DPAH Extractants*. FCRD-SWF-2013-000334, Idaho National Laboratory: Idaho Falls, ID, September 20, 2013.

Shehee, T. C.; Alsobrook, A. N.; Burns, J. D.; Silbernagel, R.; Clearfield A.; Hobbs D. T. *2013 Actinide Separation Conference Presentations on Minor Actinide Separations by SRNL Participants*. FCRD-SWF-2013-000187 (SRNL-L3100-2013-000107), Savannah River National Laboratory: Aiken, SC, June 17, 2013.

Shehee, T. C.; Hobbs D. T. *Status of Testing at the Savannah River National Laboratory Investigating the Oxidation and Ion Exchange of Americium*. FCRD-SWF-2013-00192 (SRNL-L3100-2013-00103), Savannah River National Laboratory: Aiken, SC, June 18, 2013.

### 8.4.4 Reports in 2012

Delmau, L. H.; Freiderich, M. E. *Trivalent Actinide-Lanthanide Separation Using Bis-dithiophosphinic Acids*. FCRD-SWF-2012-0071, Oak Ridge National Laboratory: Oak Ridge, TN, February 29, 2012.

Delmau, L. H.; Freiderich, M. E. *Trivalent Actinide-Lanthanide Separation Using Dithiophosphinic Acids*. FCRD-SWF-2012-0307, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2012.

Goff, G. S.; Jarvinen, G. D.; Runde, W. *Sigma Team for Minor Actinide Separations: LANL FY2012 Annual Report*. FCRD-SWF-2012-000353, Los Alamos National Laboratory: Los Alamos, NM, September 14, 2012.

Hay, B. P. *M4FT-12OR0303042: Sigma Team for Minor Actinide Separations: Design of New Dithiophophinic Acids Status Report*. ORNL/LTR-2012/173, Oak Ridge National Laboratory: Oak Ridge, TN, April 2012.

Hay, B. P. *Sigma Team for Minor Actinide Separations: Molecular Modeling of Americium Extractants.* FCRD-SWF-2012-000300, Oak Ridge National Laboratory: Oak Ridge, TN, September 18, 2012.

Hay, B. P., Moyer, B. A. *Sigma Team for Minor Actinide Separations: Mixed-Donor Extractant Synthesis.* FCRD-SWF-2012-000299, Oak Ridge National Laboratory: Oak Ridge, TN, September 18, 2012.

Hobbs, D. T., Shehee, T. C., Clearfield, A. *Minor Actinide Separations Using Ion Exchange*. FCRD-SWF-2012-000242, Savannah River National Laboratory: Aiken, SC, September 13, 2012.

Jensen, M. P., Chiarizia, R. *Aqueous Complexes for Americium-Curium Separation*, FCRD-SWF-2012-000277, Argonne National Laboratory: Argonne, IL, September 14, 2012.

Lumetta, G. J.; Braley, J.C.; Sinkov, S.I.; Carter, J.C. *Separating the Minor Actinides Through Advances in Selective Coordination Chemistry*. FCRD-SWF-2012-000174 (PNNL-21642), Pacific Northwest National Laboratory: Richland, WA, August 2012.

Mincher, B. J.; Uhnak, N.; Wurth, L. *Electrochemical preparation of high valent americium*. FCRD-SWF-2012-000126, Idaho National Laboratory: Idaho Falls, ID, 2012.

Mincher, B. J.; Schmitt, N. C. *Fission Product Behavior in DAAP AmVI Extraction*, FCRD-SWF-2012-000171, Idaho National Laboratory: Idaho Falls, ID, June 27, 2012.

Mincher, B. J. *Americium Separations Based on Higher Oxidation States*: *FY12 Year End Report*, FCRD-SWF-2012-000285, Idaho National Laboratory: Idaho Falls, ID, September 1, 2012.

Moyer, B. A. *Sigma Team for Minor Actinide Separations FY2012 Accomplishments and Directions*, FCRD-SWF-2012-000302, Oak Ridge National Laboratory: Oak Ridge, TN, September 28, 2012.

Nash, K. L. *Fundamental Studies for Improving TALSPEAK-type Separations*, FCRD-SWF-2012-000301, Washington State University, Pullman, WA, September 19, 2012.

Peterman, D. R., Groenewold, G. S.; Klaehn, J. R.; McDowell, R. G. *Evaluation of the Hydrolytic Stability of Dithiophosphinic Acid*. FCRD-SWF-2012-000076, Idaho National Laboratory: Idaho Falls, ID, March 30, 2012.

Peterman, D. R., Groenewold, G. S.; Klaehn, J. R.; McDowell, R. G. *Stability of Dithiophosphinic Acid Extractants: INL 2012 Status Report*. FCRD-SWF-2012-000267, Idaho National Laboratory: Idaho Falls, ID, September 1, 2012.

### 8.4.5 Reports in 2011

Delmau, L.; Marc, P. *Trivalent Actinide-Lanthanide Separation Using Bis-dithiophosphinic Acids*. FCRD-SWF-2011-000274, Oak Ridge National Laboratory: Oak Ridge, TN 37831, August 30, 2011.

Gelis, A. V. *Combining TRUEX and TALSPEAK in One Process*. FCRD-SWF-2011-000282, Argonne National Laboratory: Argonne, IL, August 30, 2011.

Hay, B. P. *Sigma Team for Minor Actinide Separations: Reagent Modeling and Design FY11 Status Report*. FCRD-SWF-2011-000275, Oak Ridge National Laboratory: Oak Ridge, TN, August 2011.

Hobbs, D. T.; Clearfield, A.; Visser, A. E.; Bridges, N. J. *Minor Actinide Separations Using Ion Exchangers or Ionic Liquids*. FCRD-SWF-2011-000276, Savannah River National Laboratory: Aiken SC, September 20, 2011.

Jensen, M. P.; Chiarizia, R. *Sterically Constrained Complexes for Americium-Curium Separation*. FCRD-SWF-2011-000277, Argonne National Laboratory: Argonne, IL, September 9, 2011.

Lumetta, G. J.; Braley, J. C.; Sinkov, S. I.; Levitskaia, T.; Carter, J. C.; Warner, M. G.; Pittman, J. W. *Sigma Team for Minor Actinide Separation: PNNL FY 2011 Status Report*. FCRD-SWF-2011-000261, Pacific Northwest National Laboratory: Richland, WA, August 2011.

Mincher, B. J. *Americium Separations Based on Higher Oxidation States*. FCRD-SWF-2011-000278, Idaho National Laboratory: Idaho Falls, ID, August 11, 2011.

Moyer, B. A. *Sigma Team for Minor Actinide Separation FY 2011 Annual Report*. FCRD-SWF-2011-000273, Oak Ridge National Laboratory: Oak Ridge, TN, September 29, 2011.

Moyer, B. A. *Sigma Team for Minor Actinide Separation Peer Review*. FCRD-SWF-2011-000107, Oak Ridge National Laboratory: Oak Ridge, TN, May 31, 2011.

Nash, K. L. *Fundamental Studies for Improving TALSPEAK-type Separations*. FCRD-SWF-2011-000279, Washington State University, Pullman, WA, September 30, 2011.

Peterman, D. R.; Klaehn, J. R.; McDowell, R. G.; Snow M. S. *Stability of Dithiophosphinic Acid Extractants: INL 2011 Status Report*. FCRD-SWF-2011-000280, Idaho National Laboratory: Idaho Falls, ID, August 30, 2011.

### 8.4.6 Reports in 2010

Delmau, L.; Sloop, F. V., Jr.; Gorden A. E.V. *Trivalent Actinide-Lanthanide Separation Using Bis-dithiophosphinic Acids*. FCRD-SEPA-2010-000000, Oak Ridge National Laboratory: Oak Ridge, TN, December 29, 2010.

Goff, G. S.; Jarvinen, G.; Runde, W. *Am/Cm Separations in Alkaline Solutions;* FCRD-SEPA-2010-000119, Los Alamos National Laboratory: Los Alamos, NM, September 30, 2010.

Guelis, A. V.; Vandegrift, G. F. *Combining TRUEX and TALSPEAK in One Process;* FCRD-SEPA-2010-000124, Argonne National Laboratory: Argonne, IL, September 14, 2010.

Hobbs, D. T.; Clearfield, A.; Visser, A. E.; Bridges, N. J. *Minor Actinide Separations Using Ion Exchangers or Ionic Liquids;* FCRD-SEPA-2010-000118, Savannah River National Laboratory: Aiken, SC, September 2010.

Jensen, M. P.; Chiarizia, R. *Ternary Complexes for Americium-Curium Separation;* FCRD-SEPA-2010-000120, Argonne National Laboratory: Argonne, IL, August 13, 2010.

Lumetta, G. J.; Sinkov, L. I.; Neiner, D.; Levitskaia, T. G.; Braley, J. C.; Carter, J. C.; Warner, M. G.; Pittman, J. W.; Rapko, B. M. *Sigma Team for Minor Actinide Separation: PNNL FY 2010 Status Report;* FCRD-SEPA-2010-000121, PNNL-19655, Pacific Northwest National Laboratory: Richland, WA, September 2010.

Mincher, B. J. *Americium Separation from Nuclear Fuel Dissolution Using Higher Oxidation States;* FCRD-SEPA-2010-000122, Idaho National Laboratory: Idaho Falls, ID, September 2010.

Moyer, B. A. *Sigma Team for Minor Actinide Separation FY2010 Annual Report*. FCRD-SEPA-2010-000125, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2010.

Nash, K. L. *Basic Investigations of Current and Future Options for TALSPEAK;* FCRD-SEPA-2010-000123, Washington State University, WA, September 2010.

### 8.4.7 Reports in 2009

Delmau, L. H.; Hay, B. P.; Sloop, F. V.; Gorden, A. E. V. *Trivalent Actinide-Lanthanide Separation Using Bis-di-thiophosphinic Acids*. AFCI-SEPA-PMO-MI-DV-2009-00214, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2009.

Gelis, A. V.; Vandegrift, G. F. *Combining TRUEX and TALSPEAK in One Process*. AFCI-SEPA-AQUE-MI-DV-2009-00220, Argonne National Laboratory: Argonne, IL, September 2009.

Goff, G. S.; Jarvinen, G.; Runde, W. *Am/Cm Separations in Alkaline Solutions*. AFCI-SEPA-AQUE-MI-DV-2009-000374, Los Alamos National Laboratory: Los Alamos, NM, September 2009.

Jensen, M. P.; Chiarizia, R. *Initial Studies of Ternary Complexes for Am/Cm Separation*. AFCI-SEPA-PMO-MI-DV-2009-00182, Argonne National Laboratory: Argonne, IL, September 3, 2009.

Hobbs, D. T.; Visser, A. E.; Bridges, N. J. *Minor Actinide Separations Using Ion Exchangers or Ionic Liquids*. AFCI-SEPA-PMO-MI-DV-2009-00202, Savannah River National Laboratory: Aiken, SC, September 2009.

Lumetta, G. J.; Sinkov, L. I.; Carter, J. C.; Warner, M. G.; Pittman, J. W. *Sigma Team for Minor Actinide Separation: PNNL FY 2009 Status Report*. AFCI-SEPA-AQUE-MI-DV-2009-00136, PNNL-18674, Pacific Northwest National Laboratory: Richland, WA, September 2009.

Mincher, B. *Americium Separation from Nuclear Fuel Dissolution Using Higher Oxidation States*. AFCI-SEPA-PMO-MI-DV-2009-00197, Idaho National Laboratory: Idaho Falls, ID, September 8, 2009.

Moyer, B. A. *Sigma Team for Minor Actinide Separation Annual Report*. AFCI-SEPA-PMO-MI-DV-2009-000180, Oak Ridge National Laboratory: Oak Ridge, TN, September 30, 2009.

Nash, K. L. *Thermodynamics and Kinetics of the TALSPEAK Process*. AFCI-SEPA-PMO-MI-DV-2009-000218, Washington State University: Pullman, WA, September 2009.