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Project Title: Selective Separation of Trivalent Actinides from Lanthanides by Aqueous Processing with Introduction of Soft Donor Atoms

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Abstract: With increased application of MOX fuels and longer burnup times for conventional fuels, higher concentrations of the transplutonium actinides Am and Cm (and even heavier species like Bk and Cf) will be produced. The half-lives of the Am isotopes (^{241}Am, 433 yrs; ^{243}Am, 7370 yrs) are significantly longer than those of the most important long-lived, high specific activity lanthanides or the most common Cm, Bk and Cf isotopes, thus the greatest concern as regards long-term radiotoxicity. With the removal and transmutation of Am isotopes, radiation levels of high level wastes are reduced to near uranium mineral levels within less than 1000 years as opposed to the 10^4 to 10^5 yr time-frame if they remain in the wastes. Furthermore, an effective separation of Am from Cm and other trans-Am elements will enable fabrication of transmutation targets in glove boxes rather than shielded facilities. As a result there is considerable incentive to isolate Am from Cm and lanthanides. The AFCI advanced aqueous processing capabilities "wish list" includes the means of selectively isolating Am from spent fuel with a separation factor of more than 10^4. Because the chemistries of trivalent lanthanides and actinides under aqueous processing conditions are so similar, satisfying this objective will be extremely challenging. However, among the trivalent transplutonium cations, Am possesses the most accessible higher oxidations states (though each of the oxidized species is a moderately powerful oxidant in its own right). Since trivalent ion-recognition techniques cannot possibly provide an adequate thermodynamic basis for such a separation in an acceptable number of contacts, it is proposed herein to investigate oxidation state adjustment methods to achieve selective partitioning of Am from lanthanides and Cm using otherwise conventional aqueous separations methods and materials. A multifaceted approach has been completed employing both known and unconventional methods and materials. Three separate systems were examined and are described in the attached document: 1) Extraction of lanthanides by trioctylphosphine oxide (TOPO) from NH$_4$SCN media as a means of removing lanthanides while leaving oxidized Am species behind in the aqueous phase, 2) Evaluation of room temperature ionic liquids as a potential means to Am

oxidation to the pentavalent state followed by an unconventional liquid-liquid partitioning scheme, 3) A system based on selective precipitation of lanthanide carbonates or sulfates in the presence of strongly oxidizing media that favors the presence of Am(V/VI). Approaches 1 and 2 were not successful for a variety of reasons. Approach 3 has yielded two potentially viable options for a successful lanthanide/Am(V/VI) separation. In each system, oxidation state analogs were studied in addition to actual oxidized Am species. This research was conducted principally in radiochemistry laboratories at Washington State University. Student internships at the Idaho National Laboratory were also completed to take advantage of the unique facilities and capabilities available existing at the INL. The internships provide the students with a more complete picture of the conduct of research with radioactive materials in a national laboratory environment, while giving INL staff scientists an opportunity to evaluate the performance of the students.

Accomplishments:

In addition to the tangible scientific accomplishments to be discussed below, the following highlights arising from this project can be enumerated:

- A manuscript describing the extraction thermodynamics of lanthanide partitioning from NH_4SCN media into solutions containing trioctyl phosphine oxides (TOPO) is in preparation. Several graduate students have spent portions of their time focusing on this research. A manuscript describing these results is in preparation by graduate student Mr. Derek Brigham, who has completed the final analysis of the work of the other students who have worked on this portion of the project.
- A manuscript describing Am/Ln separations by oxidation of Am and selective precipitation of lanthanides has been submitted for publication at the Actinides 2009 conference. An oral presentation of this work was made at the conference by Mr. Tom Shehee.
- Work describing the application of room temperature ionic liquids for oxidation of Am has been completed by graduate student, John Freiderich. A manuscript is in preparation.
- More detailed manuscripts describing the Am/lanthanide separation from carbonate/bicarbonate and from sulfate media are in preparation as part of the thesis work of Mr. Thomas Shehee. Mr. Shehee is expected to complete his Ph.D. in January, 2010.
- This research has continued for an additional year (to a conclusion) on funding obtained in a subcontract with the Pacific Northwest National Laboratory through the Advanced Fuel Cycle Initiative program (2009).
- A WSU Postdoctoral Associate who worked on this project in its early stages, Dr. Leigh Martin, is now an Assistant Scientist at the Idaho National Laboratory. Dr. Martin has subsequently served as a mentor for Mr. Shehee on internship visits to the INL.
- A WSU Postdoctoral Associate who worked on this project, Dr. Nick Bridges, is now an Assistant Scientist at the Savannah River National Laboratory.

Project Narrative:

   Soft donor extractants like Cyanex 301 have produced Am/lanthanide separation factors as high as 10^4 in laboratory studies, but neither this system nor size–selective separations systems have adequate thermodynamic driving force to accomplish 10^4 separation of Am(III) from Cm(III) in a single contact. It is far more likely that an efficient separation of Am from fission product lanthanides and Cm(III) will be achieved by accessing the higher oxidation states that are uniquely available (among these ions) in Am. In 1.0 M acid solutions, the reduction potentials of Am are E°(III/IV) = +2.62 V, E°(III/V) = +1.72V, E°(III/VI) = +1.68V [1]. Each oxidized Am species is a potent oxidant in aqueous solution, spontaneously returning to the trivalent state in time, whether through the oxidation of water or more rapidly through interactions with any reducing species that might be present. The introduction of complexing agents, whether water soluble or lipophilic, impacts the relative stability of the oxidation states, most significantly stabilizing the species that are most strongly complexed, Am(IV) and Am(VI) [2-12]. We have previously demonstrated that the penta- and hexavalent oxidation states (Am(V/VI)) are considerably stabilized (though still capable of oxidizing water) in strongly basic solutions as well [13]. Am(V) and Am(VI) exist as the linear dioxo cations in conventional aqueous solutions (AmO_2^+ and AmO_2^{2+}) while Am^{3+} and Am^{4+} are spherical hydrated ions. As a result, transitions between the upper oxidation states and lower oxidation states are kinetically hindered in acidic solutions due to the changing coordination environments represented, resulting in kinetic stabilization of thermodynamically unstable species. Previous literature reports indicate that Am(VI) solutions are readily reduced in water ultimately to the trivalent state, in large part facilitated by the inevitable presence of radiolytic H_2O_2. The kinetic barrier to further reduction tends to stabilize Am(V), hence it is arguably the most likely candidate for developing a robust Am/Ln separation based on variation in oxidation states. A number of possible approaches to creating and stabilizing oxidized Am species are known [14].

If Am can be stabilized (even as a transient) in its various upper oxidation states, unique options are available for potential Am/Ln group separations. If we elect to ignore for the moment the strongly oxidizing character of the ions, it is possible to project pathways to successful separations. Am(VI) will preferentially partition into most solvating extractant organic phase to enable its separation from Ln(III) and Cm(III) most strongly. Preadjustment and preoxidation of the contacting extractant phase, or use of a holding oxidant would be required. The separations chemistry could be predicted based on the performance of U(VI) under similar conditions. Am(V) should be most similar overall to Np(V), i.e., it should be poorly extracted by most solvents, hence a Ln/Am(V) separation using solvent extraction methods would have to rely on extractant molecules exhibiting good affinity for Ln(III). Numerous candidates, including TRPO, CMPO's and diamides (malonamides, diglycolamides and even picolinamides) are all potential reagents. It would perhaps be necessary in such a strategy to employ a viable one-electron reductant to take Am(VI) → Am(V). Though Am(V) exhibits some kinetic stability, a water soluble holding oxidant might still be advisable. Am(IV) is the most unstable of oxidized Am species in acidic solutions, hence one demanding the most heroic efforts to stabilize for separations. Russian researchers have previously demonstrated stabilization of Am(IV) by aqueous complexants that either retard [15] or facilitate [2, 8, 16-18] Am(IV) extraction. Amine extractants have been most extensively investigated for selective extraction of Am(IV). No prior information is available in the existing literature on the concept of in situ oxidation of Am(III) in mixed media, though a report of this oxidation in acetonitrile is available [9].

Strategies for accomplishing the oxidation state adjustment and demonstration of a successful separation based on the oxidation of Am are the subject of this research. Each of the several options

indicated below builds on previous research while offering new approaches to both the redox and separations chemistry. Significant development efforts on the Am redox approach to aqueous separations have been conducted in France [19,20] and in Russia [2, 21-22]. We have attempted to expand upon both of these efforts, addressing in principal the means to bypass potential bottlenecks to the implementation of this strategy. In this work, a separation process is considered to be potentially viable if a single stage separation factor of 10 is achieved and reasonable extrapolation to four successive contacts (at the same separation factor) can be demonstrated (to reach the targeted 10^4 separation factor). Literature reports identify a number of additional approaches to Am oxidation state adjustment. We have done some work on Am oxidation in alkaline solutions in connection with a previous EMSP project and know that both persulfate and permanganate can accomplish at least partial oxidation of Am(III) to a species more soluble in basic solutions (either Am(V) or Am(VI)) [13]. The oxidized species do exhibit some moderate redox stability in concentrated base. It was considered that this stabilization <u>might</u> require the use of an ammonium salt of nitrate or thiocyanate as a bridge to the alkaline solution contact (to maintain metal ion in the extractant phase) while depleting the organic phase of nitric acid. Two key features that are essential to any separation strategy relying on oxidized Am species are to minimize sitting, contact and phase separation times and to preoxidize impurities in the extractant solutions whenever possible. Each oxidized Am species offers a slightly different avenue to successful isolation of Am from Cm and lanthanides, as follows,

Task 1: Solvent Extraction Processes Based on Ammonium Thiocyanate
Several aqueous processing schemes have been developed to extract trivalent actinides and lanthanides from PUREX process raffinates, including most notably the Diamex, TRUEX, CTH/DIDPA/TALSPEAK and TRPO processes [22]. Diamex has been demonstrated to require [HNO_3] above 3 M for extraction of Am(III) and lanthanides, TRUEX operates most efficiently between 1 and 3 M HNO_3 while both the TRPO and CTH/DIDPA processes are most efficient in the 0.1-0.5 M HNO_3 range. Each of these processes is designed to operate in tandem with the PUREX process, or other suitable methods of removing both uranium and plutonium from the dissolved spent fuel mixture. It is assumed that U, Pu, and Np are removed separately from any raffinate that sees any process involving oxidized Am species. U(VI) and Np(V) are used as oxidation state analogs for more unstable Am species to support predictive evaluation of Am behavior. Because properties of lanthanide ions are known to vary across the series, the lanthanide portions of each investigation has been conducted looking at as many members of the series as is practical. One key feature of this investigation is the need to pay careful attention to those species that might reduce the stability of Am(V/VI). It is important in this context to minimize the presence of potentially oxidizable species in the system. As colleagues at the Idaho National Laboratory chose to examine parallel chemistry using tributyl phosphate as the phase transfer reagent of choice, we elected to focus on the stronger extractant, tri(*n*-octyl) phosphine oxide (TOPO) as our primary phase transfer reagent. Oxidizing anions are the best choice to accommodate the redox stability requirements of Am(V/VI), but we elected to investigate instead partitioning of lanthanide ions from NH_4SCN media, as this reagent is known to be a moderately strong salting agent, i.e., possessed of low phase transfer energy requirements. It is clear that any separation strategy based on oxidized Am will demand rapid phase transfer kinetics due to the transient stability of Am(IV/V/VI). Our concept for the most viable separation approach was to preferentially maintain Am in the poorly extracted pentavalent oxidation state (AmO_2^+). SCN^- also was selected as the anion supporting phase transfer for its expected rapid phase transfer kinetics. In the final analysis, SCN^- proved too reducing to allow

maintaining Am(V), so this portion of the report profiles the interesting behavior of trans-lanthanide extraction from NH₄SCN media into TOPO.

Thiocyanic Acid Extraction

It was discovered in the analysis of these data that thiocyanic acid (HNCS) is moderately extracted by TOPO. Analysis of the data indicated that HNCS forms two extractable species with TOPO, (HNCS)·TOPO and (HNCS)₂·TOPO, the latter probably representing an extractable dimer of HNCS that is known to be present in concentrated aqueous thiocyanate media. In the conduct of these experiments, HCl was used to adjust the acidity of the aqueous phase, as either HNO_3 or $HClO_4$ that might have been used to control acidity would also contribute to lanthanide cation phase transfer. It is known that $LnCl_3$ are only weakly extracted by TOPO. The extraction equilibria defining the partitioning of HNCS are:

$$K_1 = [(HSCN) \cdot TOPO_{org}]/([H^+][SCN^-][TOPO_{org}])$$

$$K_2 = [(HSCN)_2 \cdot TOPO_{org}]/([H^+]^2[SCN^-]^2[TOPO_{org}])$$

The expression is defined in terms of $[H^+]$ and $[SCN^-]$ as the solution being investigated was primarily NH₄SCN with HCl added to control acidity in a region below the hydrolysis field of the lanthanide cations. The mass balance equations for total acid and total TOPO are used to determine $[TOPO]_{free}$

$$[H]_{tot} = [H^+]_f + [(HSCN) \cdot TOPO]_{org} + 2 \cdot [(HSCN)_2 TOPO]_{org}$$

$$[TOPO]_{tot} = [TOPO]_f + [(HSCN) \cdot TOPO]_{org} + [(HSCN)_2 \cdot TOPO]_{org}$$

Values for K_1 and K_2 were determined experimentally and were found to be within reasonable agreement with literature values [23].

[HCl]_{tot}	[HCl]_{free}
0.049 ± 0.083%	0.025 ± 0.80%
0.029 ± 0.75%	0.011 ± 3.4%
0.0099 ± 2.0%	.0024 ± 4.9%

0.5 M NH₄SCN solutions acid concentration before and after contact with 0.03 M TOPO/toluene

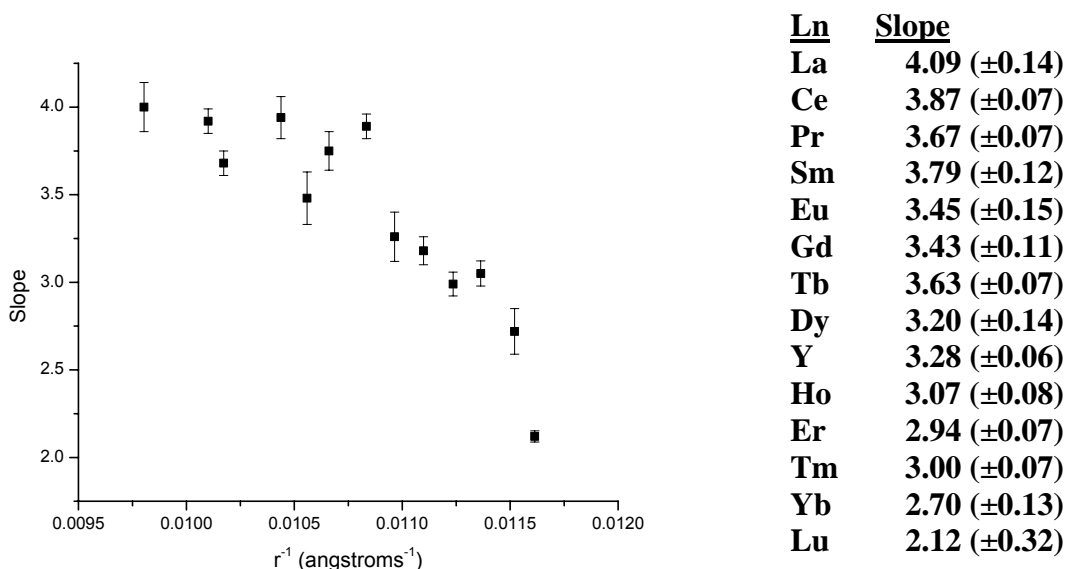log K_1 = 2.48 ± 0.0303
log K_2 = 2.68 ± 0.00146

Lanthanide Extraction

One feature of this system that is of long term value is knowledge of the extraction stoichiometry and how it might change across the lanthanide series. It is well known from previous work that the radius of trivalent lanthanide cations decreases about 20 percent between La^{3+} and Lu^{3+}. As a result of this change, the primary hydration sphere of the lanthanide ions decreases from 9 to 8 near the mid point of the series, In order to perform slope analysis on the extraction data it was necessary to

know the [TOPO]$_{free}$. In the data analysis, [TOPO]$_{free}$ was determined iteratively using the following relationship:

$$[TOPO]_f = ([TOPO]_{tot} - [TOPO]_M) / (1 + K_1[H^+]_f[SCN^-]_f + K_2[H^+]_f[SCN^-]_f)$$

where [TOPO]$_M$ is the concentration of TOPO complexed with the metal. It was assumed there was no competition between the metals and H$^+$ at these concentrations, and that the free acid determined by strong base titration in metal free solutions would be the same as in solutions with metal. Thus the free thiocyanate was total thiocyanate concentration minus the extracted acid (H$^+$) concentration. Lanthanide distribution ratios were determined by ICP-MS, measuring the difference of metal concentration before and after extraction. The distribution ratios are corrected for the presence of Ln(SCN)$^{2+}$ complexes in the aqueous phase. It is assumed that the electroneutral species Ln(SCN)$_3$ is transported to the organic solution. Using the standard technique of slope analysis (and applying appropriate corrections for the extraction of HSCN as indicated above), the dependence of D$_{Ln}$ on [TOPO]$_{free}$ was determined. The general trend is seen to be that of decreasing metal to TOPO ratio as the atomic number increases in the lanthanide series. It is seen that the stoichiometry of the extracted complexes changes steadily across the series, from La(SCN)$_3$(TOPO)$_4$ as the predominant species for the light end of the series to a low of Lu(SCN)$_3$(TOPO)$_2$ at the heavy end of the series. The slopes were determined using error weighted fits at three sigma error in Origin 6.0.

Ln	Slope
La	4.09 (±0.14)
Ce	3.87 (±0.07)
Pr	3.67 (±0.07)
Sm	3.79 (±0.12)
Eu	3.45 (±0.15)
Gd	3.43 (±0.11)
Tb	3.63 (±0.07)
Dy	3.20 (±0.14)
Y	3.28 (±0.06)
Ho	3.07 (±0.08)
Er	2.94 (±0.07)
Tm	3.00 (±0.07)
Yb	2.70 (±0.13)
Lu	2.12 (±0.32)

Ln Extraction

The slope analysis shows a trend of decreasing metal to ligand stoichiometry across the lanthanide series starting at a ratio of 1:4 for lanthanum and decreasing to 1:2 for lutetium. It is clear that across the series more than one discrete Ln(SCN)$_3$ solvate species is present for most of the metal ions. Using data available from the NIST database for the Ln^{3+} SCN$^-$ aqueous complex stability constant, β, to calculate a corrected distribution value D$_0$.

$D_0 = D(1+\beta[SCN^-]_f)$

The corrected distribution value was then used to calculate an extraction constant K_{ex}

$K_{ex} = D_0 / ([SCN^-]^3_f[TOPO]^X)$

where X is TOPO's stochiometric coefficient for the extraction.

Ln	Log(K_{ex})	X
La	8.57 (±0.12)	4
Ce	9.29 (±0.17)	4
Pr	9.40 (±0.14)	4
Sm	9.38 (±0.18)	4
Eu	9.56 (±0.25)	4
Gd	9.74 (±0.26)	4
Tb	9.85 (±0.20)	4
Dy	8.11 (±0.19)	3
Y	7.89 (±0.15)	3
Ho	8.65 (±0.17)	3
Er	9.15 (±0.04)	3
Tm	9.47 (±0.05)	3
Yb	9.88 (±0.14)	3
Lu	8.13 (±0.16)	2

These stoichiometries are generally consistent with those reported in the prior literature for radiotracer concentrations of the lighter lanthanides. The low salvation number for Lu^{3+} in this work suggests one fewer TOPO per metal at macro concentrations than is seen for radiotracer levels.

As the slope analysis gives non-integer values for a majority of the lanthanides and a trend of decreasing values is seen it is proposed that two methods of extraction are possible, defined as K_X and K_{X-1}

$K_X = [Ln(SCN)_3(TOPO)_X] / ([Ln^{3+}]_f[SCN^-]_f[TOPO]^X_f)$

$K_{X-1} = [Ln(SCN)_3(TOPO)_{X-1}] / ([Ln^{3+}]_f[SCN^-]_f[TOPO]^{X-1}_f)$

Values for these equilibrium constants can be resolved using

$D_o = K_X[SCN^-]^3_f[TOPO]^X_f + K_Y[SCN^-]^3_f[TOPO]^{X-1}_f$

A non-physical stoichiometry for the metal ligand ratio of X-0.5 was used in the calculation of $[TOPO]_{free}$ to account for the two different extraction methods. The value of K_X was calculated by using combinations of two sets of data from different TOPO concentrations. K_{X-1} was calculated by using the K_X value. The value of K_{X-1} would be in agreement for both sets of data.

$$K_X = ([SCN^-]^3_{f1}[TOPO]^{X-1}_{f1}D_{02} - [SCN^-]^3_{f2}[TOPO]^{X-1}_{f2}D_{01}) \, /$$
$$([SCN^-]^3_{f1}[SCN^-]^3_{f2}[TOPO]^{X}_{f2}[TOPO]^{X-1}_{f1} - [SCN^-]^3_{f1}[SCN^-]^3_{f2}[TOPO]^{X}_{f1}[TOPO]^{X-1}_{f2})$$

$$K_{X-1} = D_0 - K_X[SCN^-]^3_{f}[TOPO]^{X}_{f} \, / \, ([SCN^-]^3_{f}[TOPO]^{X-1}_{f})$$

Ln	Log(K_x)	Log(K_{x-1})	X	X-1
La	9.89 (±0.45)	8.53 (±0.11)	5	4
Ce	8.86 (±0.76)	6.73 (±0.57)	4	3
Pr	9.11 (±0.34)	6.94 (±0.40)	4	3
Sm	8.99 (±0.30)	7.03 (±0.63)	4	3
Eu	9.08 (±0.40)	7.27 (±0.12)	4	3
Gd	9.39 (±0.33)	7.34 (±0.35)	4	3
Tb	9.61 (±0.31)	7.29 (±0.59)	4	3
Dy	9.81 (±0.05)	7.88 (±0.05)	4	3
Y	9.24 (±0.54)	7.65 (±0.16)	4	3
Ho	9.81 (±0.21)	8.58 (±0.15)	4	3
Er	8.90 (±0.32)	6.51 (±0.90)	3	2
Tm	9.32 (±0.06)	7.14 (±0.36)	3	2
Yb	9.49 (±0.37)	7.65 (±0.55)	3	2
Lu	7.59 (±0.78)	6.24 (±0.40)	2	1

Both sets of extraction constants that have values calculated for different stochiometric value shows a trend of increasing extraction strength as atomic number increases. It is also notable that while there is higher extraction strength for larger stochiometric ratios, larger distribution values are seen for the metals with smaller ratios, i.e. the heavier lanthanides. This can be explained in that while the concentration ratios for metal to ligand stay essentially the same across the series, the concentration of extractable species effectively doubles from lanthanum to lutetium.

Task 2: Room temperature ionic liquids (RTILs) as media for Am oxidation state adjustment

Room temperature ionic liquids (RTIL's) are organic compounds, actually salts of (most commonly) lipophilic ammonium, phosphonium or imidazolium cations in association with appropriate classes of large, generally hydrophobic, anions [24-26]. The anions are of either organic or inorganic composition. The combined salts have widely tunable physical properties, in many cases a wide electrochemical window for conducting redox chemistry, and an almost completely unknown ability to interact with f-element cations, their inorganic salts and chelate complexes. Results in the literature to date indicate that substitution of RTIL's for conventional diluents in liquid-liquid extraction is unlikely to prove satisfactory due to instability of the RTIL formulations, their high viscosities, and low volatility that makes their purification/cleanup moderately challenging [27-30]. Lipophilic variants have also demonstrated little ability to dissolve salts of polyvalent metal ions like trivalent lanthanides or actinides [31]. Studies of solvent substitution reactions have relied on conventional solvent extraction reagents as the vehicle for providing appropriate partitioning of the metal ion into the RTIL phase. In this application, RTIL formulations tested to date have proven inadequate, as they tend to lose components irreversibly into the contacting aqueous solution [29-31].

However, RTILs also can be created in water-miscible formulations [26]. The solvation properties of such species for large polyvalent cations like the lanthanides and actinides are unknown. Such solutions bear some similarity to concentrated salt solutions or alcoholic acid

solutions that have been investigated as media for accomplishing actinide separations [33-36]. The use of water-miscible RTIL's in combination with conventional organic solvents [37-39] might provide some unique opportunities to accomplish unusual separations. Both the potential unique solvation properties of RTILs and the wide electrochemical window for oxidation state adjustment are attractive features of these materials to the challenging separation of Am from Cm and fission product lanthanides. This latter feature may sidestep one of the primary obstacles to fully aqueous separations, the difficulty of maintaining oxidized Am species due to their ability to oxidize water. This portion of the research program is highly speculative; but, because so little is truly understood about the performance of RTIL's in liquid-liquid extraction, it is worth some consideration in this investigation. We propose to investigate this chemistry as follows:

1. The most promising approach would appear to be introduction of water-miscible ionic liquids as the medium into which the Am is stripped from the loaded organic phase. We would conduct a conventional forward extraction of trivalent lanthanides, Am and Cm into any of the several extraction systems that have been described in Task 1. Conduct of electrochemical operations (either with electrodes and an applied potential or the dissolution of oxidants like permanganate or persulfate) in the contacting RTIL phase could be used to alter the redox conditions and selectively convert Am to the less extractable pentavalent oxidation state. No prior work has been reported on the reduction potentials of Am in RTIL media, but it is reasonable to anticipate that Am(V) would be the most stable oxidized Am species, thus most readily created and stripped from the loaded organic solution.

2. A water immiscible ionic liquid might be used as a substitute solvent in the solvent extraction. Though this approach has suffered in previous studies from irreversible phase transfer reactions, the opportunity to do in-situ redox chemistry (that is, within the organic RTIL phase) could create Am species that would be readily stripped into a suitable aqueous solution. The application of the RTIL organic solution as the solvent could enable the use of a number of aqueous media that might be otherwise unacceptable for conventional solvent extraction media, including facilitating use of alkaline processing options that have been previously demonstrated by Russian researchers.

Though research on the applications of RTIL's in solvent extraction to date have exposed problems along with promise, too little is known about the possible applicability of these reagents to liquid-liquid separations to reject their potential without some investigation. This portion of the program explored some opportunities for conducting unique actinide and separations chemistry while avoiding the pitfalls that have already been exposed in careful examination of the properties of the system.

In previous investigations, room temperature ionic liquids (RTILs) have been used to extract metal ions from an aqueous phase. Distribution ratios for these systems are large. Previous IL/aqueous systems have focused on historical RTILs which have undergone extensive investigation such as $bmimPF_6$ and $bmimBF_4$. Ligands used in these systems have been neutral oxo-donors (TBP) and β-diketones (HTTA). Many investigators have determined that during a metal extraction from the aqueous phase to the RTIL phase that the RTIL can undergo cation or anion exchange. While this phenomenon may be fundamentally interesting, it does not sanction RTILs as satisfactory solvents for use on an industrial scale.

To make RTILs into viable industrial solvents they must be more robust in a solvent extraction context. This work has been aimed with the goal of demonstrating a solvent extraction process which

will mitigate a cation or anion exchange mechanism of metal ion transfer and also allow for the extraction of macroscopic quantities of metals. To accomplish this, the aqueous phase and the RTIL phase must not come into mutual contact. In essence, a solvent in between the aqueous and RTIL will facilitate the creation of a neutral complex and then transfer it to the RTIL. A common problem which has occurred in this research has been to find proper solvents and complexing ligands which will behave in the desired manner. The current mind set is to find a solvent which is lipophilic enough in nature to form an immiscible phase with an aqueous phase and the RTIL. In addition, the ligand must transport the metal ion from the aqueous to the lipophilic phase and then preferentially partition to the RTIL once the lipophilic phase is contacted with the RTIL.
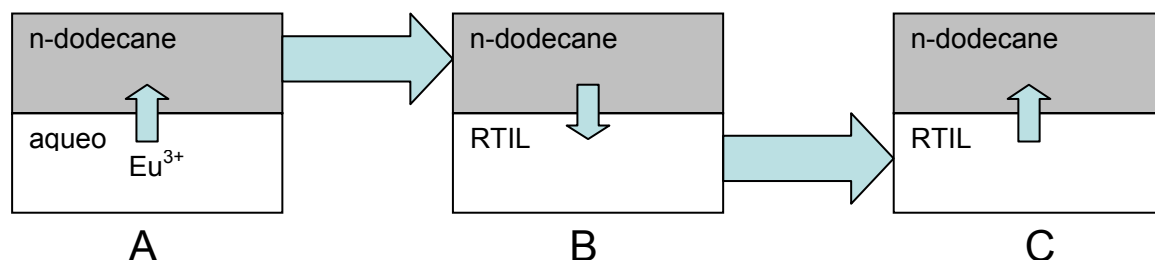

Figure 1. This displays the extraction behavior of Eu(III), Nd(III) and Am(III) through this three contact system. Contact A shows the extraction of the Eu(PMBP)$_3$TBP species to n-dodecane. Contact B shows the stripping of this Eu-complex to neat RTIL. Contact C shows the extraction of Eu-complex to a fresh n-dodecane phase by TOPO.
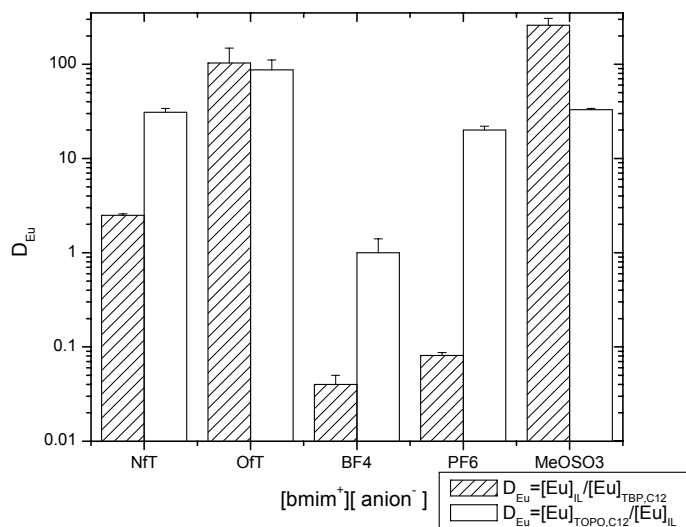

Figure 2. Various bmimX RTILs screened with a Eu-PMBP-TBP complex. The stripping of the Eu-complex into the RTIL (dashed bars) and the extraction into fresh dodecane solvent (clear bars) is shown.

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In an attempt to understand the complex stoichiometry of the extracted and stripped metal species, the ligand concentration was varied in each phase and the partitioning of Eu was described using [152,154]Eu radiotracer. All solvents were pre-equilibrated with appropriate counter-phases prior to introduction of the metal ion into the system. The log D_{Eu} vs. log [HPMBP] and log D_{Eu} vs. log [TBP] yielded slopes of 2.79($\pm$0.12) and 1.08($\pm$0.12) respectively, for the traditional dodecane/aqueous system (contact A). This follows the expected result predicted by equation (1.1).

$$Ln^{3+}_{(aq)} + 3\overline{HPMBP} + \overline{TBP} \rightleftharpoons \overline{Ln(PMBP)_3 TBP} + 3H^+_{(aq)} \qquad (0.1)$$
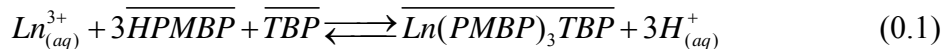
The slope analysis for contact B yielded varying results. Upon contact and allowing equilibration to occur the slope of a log D_{Eu} vs log [HPMBP]$_{sys}$ was found to be 0.94($\pm$0.02).

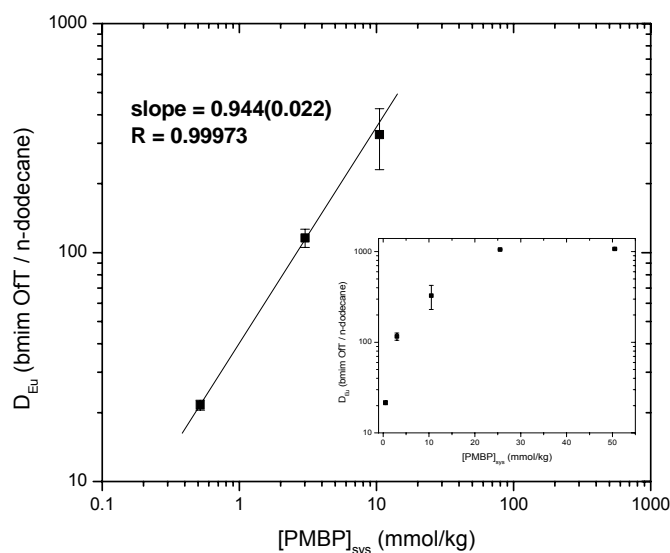**Figure 3. Slope analysis for contact B with a dependence of HPMBP.**

In addition, the [H$^+$] was varied. This yielded a slope of -0.81(0.02). However, this dependency was only observed from [H$^+$] = 0.001M to 0.1M. So the observed trends in the data from figures 2 and 3 may suggest the following equilibria (eqn. 1.2 and/or 1.3) are relevant for describing this system.
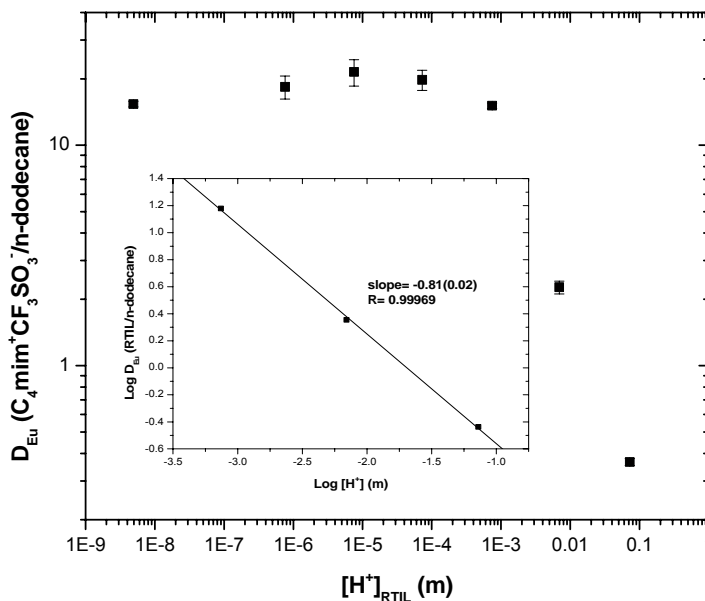
Figure 4. H$^+$ dependency by spiking a bmimOfT phase with 1M HOfT in bmimOfT.

$$\overline{Ln(PNMBP)_3 TBP} + HPMBP_{il} \leftrightarrow [Ln(PMBP)_4 TBP]_{il}^- + H_{il}^+ \qquad (0.2)$$

$$\overline{Ln(PNMBP)_3 TBP} + HPMBP_{il} \leftrightarrow [Ln(PMBP)_4 TBP]_{il}^- + H_{il}^+ + TBP_{ilordodecane} \qquad (0.3)$$

No dependence could be observed for the TBP when Eu was stripped from the *n*-dodecane to RTIL. However, in the presence of different solvating ligands like tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO) and tri-butyl phosphine oxide (TBPO), a dependency on the adduct ligand is noticeable. Eu strips efficiently to the RTIL, with short butyl alkyl chains of TBP and TBPO, D >200. When the Eu(PMBP)$_3$TOPO complex is present in the *n*-dodecane no stripping occurs to the RTIL, D = 0.03. This suggests that the metal complex does not dissociate when it partitions to the RTIL. Finally, slope analysis for contact C suggests a change in the extraction mechanism as the slope is initially at 1 and then becomes 4 for a TOPO dependency.

Spectrophotometric data suggests that the metal complex exists as a charged species in the RTIL and a neutral species in *n*-dodecane.
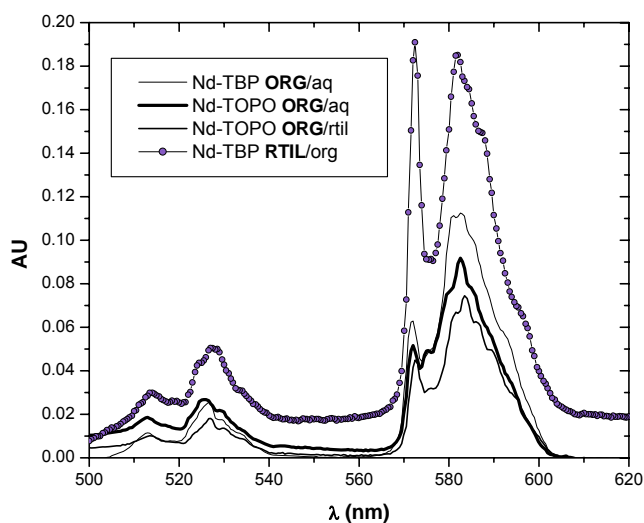
13

Figure 4. The lower absorbance spectra show the Nd-PMBP-L (L=TBP or TOPO) complex as it exists after extraction from an aqueous or RTIL phase. The Nd-complex in the RTIL shows strong hypersensitive bands at 575nm and 583nm.

Attempts to recreate the complexing environment for Nd in bmimOfT were done. $Nd(OfT)_3$ was dissolved in bmimOfT. HPMBP and TBP ligands were added to the solution and spectra were obtained. No characteristic charged Nd-complex bands were observed. It was thought that the solvation environment of the Nd was compromised by waters of hydration. Karl-Fischer titrations showed that the water content of the RTIL with the added $Nd(OfT)_3$ was statistically equivalent to that of neat RTIL.

ESI-MS data was also collected to determine the extent, if any, of cation or anion exchange between the RTIL and the *n*-dodecane phase during a metal-complex portioning. This was conducted with bmimOfT as the RTIL. The results concluded that the ratio of the anion/cation which exists in the *n*-dodecane with and without metal-complex partitioning is 4.45(9%) and 4.43(13%). In addition, the concentration of the RTIL in the *n*-dodecane phase was three orders of magnitude lower than the quantity of Eu metal that partitioned across the interface.

The compilation of radiometric, spectrophotometric, and mass spectrometry results suggest several conclusions about RTILs as solvents in metal ion extraction. The first of these is that RTILs can indeed be used in the manner presented. The ESI-MS data suggests that the partitioning of the RTIL to n-dodecane, as a metal-ligand complex partitions across the interface, is negligible and does not support the existence of cation or anion exchange. However, the spectrophotometric data suggests the existence of a charged species. The presence of a charged species in the RTIL phase is perplexing when one considers that it was previously a neutral species in n-dodecane. The driving force for the partitioning of $Eu(PMBP)_3TBP$ to RTIL must be the solubility of the complex in different solvents. The coordination environment of the Nd-PMBP-TBP complex in bmimOfT could not be reproduced and as a result the identity of the complex and its mechanism of extraction remain unclear at this time. Additional problems arise from the observation that equivalent experiments

would sometime yield very different results. For example, the dependence of the HPMBP on the stripping of the Eu from the *n*-dodecane to the RTIL would sometimes show no dependence. Although not stated above, the extraction behavior of Eu into RTILs quickly decay after the first several contacts. This suggests that the RTILs cannot be reused over and over again. In the absence of Eu, HPMBP will partition in what seem to be nearly unpredictable ways. Several measurements (acid-base titration, spectrophotometric) of contact B suggest that the K_d for HPMBP can range from 3 to 22. Where

$$K_d = \frac{[HPMBP]_{RTIL}}{[HPMBP]_{ORG}} \tag{0.4}$$

This result does not seem to be consistent with the extractability of metal ions into the RTIL as the distribution ratio is orders of magnitude above these values.

The complex nature of RTILs as heterogeneous solvents leads to many difficulties in understanding their fundamental interactions. The solvent extraction process developed and examined in this research may have many benefits over previous literature RTIL solvent extraction systems. However, these benefits can not be realized if the system does not behave in a predictable and reproducible manner. An assessment of the potential of RTILs in solvent extraction of actinides and lanthanides remains elusive.

Task 3. Am/Ln Separation with Oxidation State Adjustment and Precipitation of Lanthanides

It was determined early on that initial plans to oxidize Am(III)-Am(IV) and stabilize in polyoxometallate media was a less attractive option to the simpler option of oxidizing Am to the pentavalent or hexavalent oxidation state and taking advantage of the relatively lower solubility of lanthanides in selected media. Three options were identified as potentially workable: 1) Fluoride precipitation of lanthanides (well known as an analytical procedure and used as a purification step – though not for Am/Ln separations – in the $BiPO_4$ Pu production process in the Manhattan Project) – oxidized Am would remain in the supernatant phase, 2) Carbonate precipitation of lanthanides (both $Ln_2(CO_3)_3$ and $Ln(OH)CO_3$ are known crystalline species) – oxidized Am(VI) would preferentially remain soluble as the triscarbonato complex anion ($AmO_2(CO_3)_3^{4-}$ or possibly $AmO_2(CO_3)_3^{5-}$), 3) Sulfates of lanthanide ions ($Ln_2(SO_4)_3$) are precipitated while $AmO_2^{+/2+}$ remains soluble, probably as sulfate complexes. There are known examples of double salts that can assist or interfere with these processes. In principle, quite high separation efficiencies are attainable using any of these approaches. Because the fluoride process has received significant previous attention, the carbonate and sulfate systems became the primary focus of this portion of the investigation.

The mutual separation of Am(III) from chemically similar Ln(III)/Cm(III) remains one of the most challenging impediments to the implementation of any nuclear fuel cycle in which Am is to be transmuted. Good single-stage separation efficiency should be observed if americium was oxidized to the AmO_2^+ of AmO_2^{2+} oxidation states potentially available; however, the instability of these oxidation states makes any separations process utilizing them inherently challenging. In acidic solutions, the relative order of stability of Am ions is Am(III) >> Am(V) > Am(VI) >> Am(IV). Literature has shown in 1 M carbonate media, the four accessible oxidation states of Am are of comparable stability.[39] The improvement in stability of the upper oxidation states is invaluable in

developing a procedure for the selective removal of Am from Cm and the lanthanides. Complexing ligands such as O^{2-}, OH^-, or CO_3^{2-} can form strong complexes with the actinides in the order $An^{4+} > AnO_2^{2+} \geq An^{3+} > AnO_2^+$. In carbonate solutions, Am(VI) can oxidize Am(III) by means of the equilibrium:

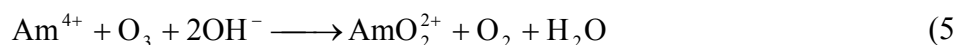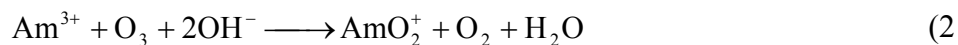$$Am(III) + Am(VI) \leftrightarrow Am(IV) + Am(V) \tag{1}$$
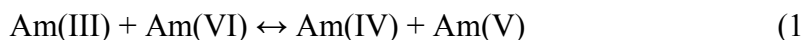
This electron transfer along with the complexation by carbonate allows for four valence forms to be present in aqueous solutions. The observation can be explained through an inspection of the reduction potentials tabulated by Newton and Sullivan and reproduced partially here in Table 1.[39] Of note is the considerably lower potential for the VI/V and IV/III couples when in carbonate media. These lower potentials mean that the americium will be easier to oxidize in the carbonate solutions chosen for this research as opposed to the attempted oxidation under acidic conditions.

Table 1. Americium reduction potentials. V vs. S.H.E. at 25°C.

Couple	Element	1 M CO_3^{2-}	1 M $HClO_4$	Difference
Am(VI)/(V)	Am	0.964	1.600	0.636
		0.91		0.69
Am(V)/(IV)	Am	1.1	0.83	-0.27
Am(IV)/(III)	Am	0.92	2.60	1.68

Oxidations of americium reported in the literature have established that pure americium samples have achieved a degree of oxidation as high as 98-99% using the oxidants employed in this study. Americium (VI) was quantitatively produced in 0.1M $NaHCO_3$ containing a suspension of $Am(OH)_3$ when 5% ozone was passed through for one hour. If a solution of 2 M Na_2CO_3 is used, Am(III) is oxidized with ozone to Am(VI) at room and lower temperatures with an accumulation of Am(V) occurring at higher temperatures. [40-41] In 0.03-0.1M $KHCO_3$, Am(V) precipitates as the salt $KAmO_2CO_3$. Without a consideration of the possible complexes that can be formed with americium, the oxidation of Am(III) could be described by the following equations.

$$Am^{3+} + O_3 + 2OH^- \longrightarrow AmO_2^+ + O_2 + H_2O \tag{2}$$

$$AmO_2^+ + O_3 \longrightarrow AmO_2^{2+} + O_3^{-\bullet} \tag{3}$$

$$Am^{3+} + O_3^{-\bullet} \longrightarrow Am^{4+} + O_2 \tag{4}$$

$$Am^{4+} + O_3 + 2OH^- \longrightarrow AmO_2^{2+} + O_2 + H_2O \tag{5}$$

Experiments with 5 M K_2CO_3 verified the reaction mechanism seen in Equation 2 where the oxidation with ozone is accompanied by a replacement of the water molecule in the coordination sphere of the Am(III), however this experiment also demonstrated that an increased concentration of

carbonate can sterically hinder the insertion of ozone resulting in an outer sphere process to form Am(IV). [42] Am(VI) has been produced in aqueous 2 M carbonate solutions as well through the oxidation of Am(III), Am(IV), or Am(V) with ozone giving an intensely red-brown Am(VI) carbonate complex. [40]

Basic carbonate solutions form strong complexes with hexavalent actinide ions. [43] The terminal complex, $AnO_2(CO_3)_3^{4-}$ ion, has been observed in U, Pu and Np and is the dominate species at relatively low carbonate concentrations between pH ≈ 7-11. [44,45] Reports have claimed the limiting species for Am(VI) in carbonate containing solution is $AmO_2(CO_3)_3^{4-}$. [46,47] At higher pH values, mixed hydroxycarbonates have been reported. To add to the complexity of this system, a soluble tetrahydroxide species has been identified as the dominant species at pH 12-14. [48-50]

Curium has a barely accessible tetravalent oxidation state, but does not appear in the penta- or hexavalent oxidation states in aqueous solutions.[51] Likewise only a very small number of the lanthanides can be oxidized to the tetravalent oxidation state; all Ln(IV) are strong oxidants. Carbonate and sulfate retain AnO_2^{2+}, AnO_2^{+} and An^{4+} species in solution and precipitate trivalent species. This principle has been manipulated for the separation of Am from the trivalent lanthanides and curium. This work focuses on the utilization of the upper oxidation states of Am (IV, V, VI) in carbonate/bicarbonate and sulfate media to facilitate a more efficient separation from fission product lanthanides utilizing solid-liquid separation methods that have been proven feasible. [52-53]

All materials were reagent grade and used as received. Sodium carbonate, bicarbonate and persulfate solids were Fisher, J.T. Baker and Acros, resepectively. Oxone was obtained from Sigma Aldrich and used as received. Silver nitrate was of 99% purity from EM Science. Solids were diluted volumetrically. Experiments done using $^{152/154}$Eu(NO$_3$)$_3$, ^{237}Np(NO$_3$), ^{233}UO$_2$(NO$_3$)$_2$, ^{238}Pu(NO$_3$)$_4$ and ^{241}Am(NO$_3$)$_3$ were prepared by dilution of standardized stocks from the Washington State University (WSU) inventory. Radioactive $^{152/154}$ Eu was created by neutron activation of 99.999% Eu$_2$O$_3$ (Arris International) using a Teaching, Research, Isotopes General Atomics (TRIGA) reactor with a neutron flux of 5×10^{12} n/cm^2·sec at the Nuclear Radiation Center at WSU. . Ozone oxidation was achieved through the use of an Azco Industries LTD model CDO-8000S ozone generator. Ozone was produced by an Ozone Solutions laboratory ozone generator model OS-8C capable of producing up to 8 grams of ozone per hour. The ozone flow rate was maintained through use of an AALBORG 20-250mL/min flow rate meter. Powder XRD was performed with a Siemens Kristalloflex D500 diffractometer with the following parameters: Copper source (Kα; 1.5406 Å); 35 keV, 30 mA, Kβ filter: Ni; scintillation counter detector; Continuous mode: 0.02d/min; 2θ range: 5-55. The diffractograms were produced using supporting MDI Data Scan 4 and Jade 8 software packages. Radiotracer experiments using $^{152/154}$Eu were analyzed on a NaI(Tl) solid scintillation counter, a Packard Cobra-II auto gamma, for gross gamma counting. Radiotracer experiments using ^{233}U, ^{237}Np and ^{238}Pu were analyzed using a Beckman LS6000 liquid scintillation counter for alpha detection and 5 mL of EcoScint® scintillation fluid.

2.1 Ozone oxidation and separation

In each precipitation, 5μL of the radiotracer was added to 250μL of a 0.1M lanthanide solution followed by the precipitation of the lanthanide hydroxide through the addition of 1.0M NaOH in a 12x75mm gamma tube. The tube was centrifuged for 2 minutes then the supernate was decanted.

To the hydroxide precipitate, 500µL of either 1M Na_2CO_3 or $NaHCO_3$ was added to slurry the solid. Ozone was then bubbled through the solution at a rate of 40 mL/min (providing $4.7\pm0.2 \times 10^{-4}$ g O_3/hr). A 1mL pipette tip was used to deliver the ozone to the reaction vessel. After bubbling the ozone through the solution for the desired time period, the sample was centrifuged for 10 minutes followed by decanting the supernate. The solid was washed once using 500µL of the respective 1M carbonate followed by a final centrifugation/separation step.

2.2 Persulfate oxidation and separation

The precipitation procedure made use of 5µL of the desired radiotracer added to 250µL of a 0.1M $Eu(ClO_4)_3$ followed by the addition of 300µL of 0.5M $Na_2S_2O_8$ or 0.4M Oxone and 25µL of 0.5M $AgNO_3$ in a 12x75mm gamma tube. The tubes were then heated to 90-93ºC in a water bath for 15 minutes with periodic shaking to help facilitate the oxidation of the Am tracer. The tubes were allowed to cool for 30 minutes before being centrifuged for 10 minutes. Separation was achieved by decanting the supernatant into a second gamma tube.

1.1. Ozone oxidation in carbonate media

The separation scheme presented is heavily dependent on the pH of the system during the oxidation step. The pH throughout the separation for both sodium carbonate and sodium bicarbonate changes as follows:

1. 0.1M $Eu(ClO_4)_3$ pH = 3.4
2. After NaOH precipitation   pH = 12.0
3. Slurry with $NaHCO_3$ pH = 9.2 / Na_2CO_3 pH = 11.7
4. After 2 hours under ozone $NaHCO_3$ pH = 9.5 / Na_2CO_3 pH = 10.3

These pH changes become significant in the quality of the separation when using sodium carbonate vs. bicarbonate. Speciation plots of europium in the carbonate/bicarbonate system show that the solid europium species $Eu_2(CO3)_3$, $Eu(OH)CO_3$ and $Eu(OH)_3$ dominate in the pH range of 0-7, 7-12 and 12-14 respectively. The literature has shown that Am is oxidized under the conditions shown above as long as the temperature is maintained at or below 25ºC for Na_2CO_3 and from $0 – 90$ºC in $NaHCO_3$. [43]

The ^{241}Am radiotracer shows that $3 \pm 2\%$ and $85 \pm 3\%$ americium can be found in the solution phase after the 2 hr ozone oxidation for Na_2CO_3 and $NaHCO_3$ respectively. Addition of a wash step using the 1M Na_2CO_3 and $NaHCO_3$ removes another $15 \pm 2\%$ and $10 \pm 2\%$ americium respectively from the solid precipitate after the 2 hr oxidation. This data combined with the $^{152/154}$Eu tracer data, Table 2, provides an aqueous separation factor ($SF_{Am/Eu}$) of 1.6 ± 0.8 vs. 47 ± 2 respectively for the 1M Na_2CO_3 and $NaHCO_3$ systems. The lower amount of lanthanide in the solid when using the 1M Na_2CO_3 could be explained through the formation of soluble 1:4 hydrolysis product such as currently found in the literature for neodymium, $Nd(OH)_4^-$.[NIST] The large portion of americium in the solid could come from the greater tendency of Am(VI) toward hydrolysis and polymerization than observed in U(VI) in the presence of the carbonate ion. [43]

Table 2. Results of the ozone oxidation of an Am-241 tracer in 250µL of 0.1M $Eu(ClO_4)_3$ when slurried in either Na_2CO_3 or $NaHCO_3$ with a comparison to the use of Eu-152/154 tracer to verify the percent lanthanide that has been precipitated in the form of a carbonate.

		Percent tracer retained in the supernate/wash			Percent tracer retained in the solid			SF$_{aq}$ (Am/Eu)			SF$_{solid}$ (Eu/Am)		
Na$_2$CO$_3$	^{241}Am	19	±	2	81	±	2	1.6	±	0.8	1.10	±	0.03
	$^{152/154}$Eu	12	±	5	87	±	1						
NaHCO$_3$	^{241}Am	95	±	4	5	±	1	47	±	2	20	±	5
	$^{152/154}$Eu	2.02	±	0.04	96.93	±	0.06						

1.2. Persulfate oxidation and separation

The effect of silver nitrate concentration has been evaluated over a concentration range of 0.004-0.04M. The dependency shows the distribution of Eu to the solid phase was steeply impacted by changes in the Ag(NO$_3$) concentration up to 0.02 M. After 0.02 M silver nitrate, the changes in the concentration of Ag(NO$_3$) had a minimal impact. The Am distribution to the solid phase seemed largely independent of the concentration of silver. This supports the suggestion in the literature that the use of silver nitrate as a catalyst is not necessary in the oxidation of americium. [56]

Heating the system at temperatures higher than 90ºC would probably serve the same function yet the reaction kinetics would most likely be slower than with the addition of silver. The silver is thought to split the persulfate into two sulfate radicals. The radical is responsible for the oxidation of the Am(III) to Am(VI). If the sulfate radical was the sole oxidizing agent then the removal of silver would drastically reduce the oxidation of Am(III) to Am(VI). Complete removal was not possible in these experiments as the only way to gauge the oxidation of americium was in the percent of the americium that was in the supernate after separation. The observation was made that after 15 minutes in the water bath with no silver present, no solid was formed. A silver lanthanide double sulfate salt has been shown to be capable of forming. The precipitation of AgEu(SO$_4$)$_2$ increases the likelihood of the trivalent species to be found in the solid phase and could have been a major contributor in the solid produced.
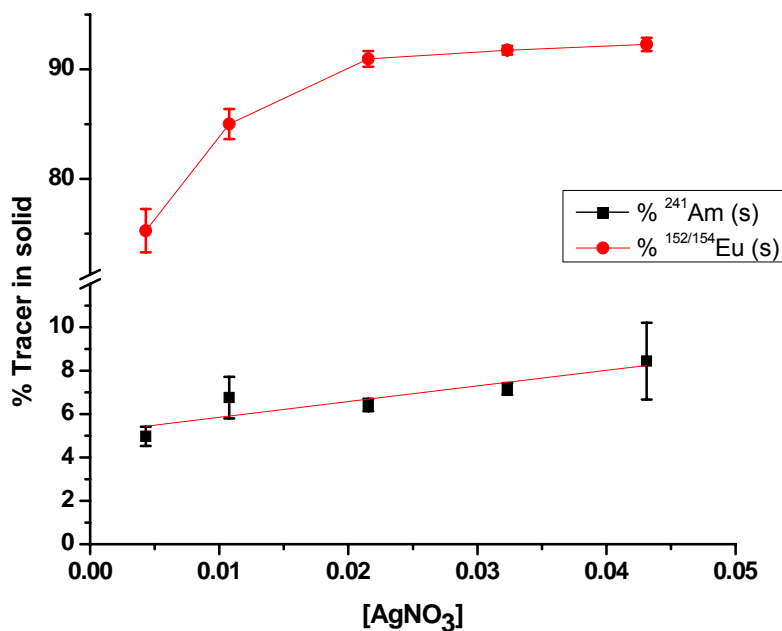
Figure 1. Effect of the concentration of Ag$^+$ on the percent Am-241 or Eu-152/154 retained in the precipitate.

Powder XRD has been used to identify solids formed in both the Oxone and sodium persulfate oxidation/precipitation separations. The pattern gave a best match for the double sulfate salt of the lanthanide, $Eu_2(SO_4)_3 \cdot M_2SO_4 \cdot 2H_2O$, where M = K or Na for the Oxone or sodium persulfate respectively. The double sulfates of sodium and the lanthanides have been prepared for the complete series of the lanthanides. [53] A minor product observed in the pattern but unable to be identified is most likely the previously mentioned $AgEu(SO_4)_2$.

When the 0.02M $AgNO_3$ is used, the best separation factor is achieved in the supernate. Table 3 shows a comparison of four actinide tracers under the conditions where $[Ag^+]$ = 0.02 M. With all of the tracers, a separation factor of 11 ± 1 has been observed.

Table 3. Comparison of the actinide tracers using 25µL 0.5M AgNO$_3$ + 300µL Na$_2$S$_2$O$_8$

	Percent tracer retained in the supernate	Percent Tracer retained in the solid	SF $_{Am/Eu}$
$^{152/154}$Eu	8.2 ± 0.8	91.8 ± 0.8	
^{233}U	92 ± 1	7 ± 1	11 ± 1
^{237}Np	86 ± 2	14 ± 2	11 ± 1
^{238}Pu	94 ± 1	5 ± 1	11 ± 1
^{241}Am	89.6 ± 0.6	10.4± 0.6	11 ± 1

Conclusions

Two successful separation schemes have been presented at the tracer level. The ozone oxidation of americium hydroxide slurried in a 1M sodium bicarbonate proved best with separation factors of 47.0 and 20.4 for the aqueous and solid phases respectively. Separation using sodium persulfate was good with separation factors >10 for U, Np, Pu and Am. This scheme had the advantage of simplicity with fewer steps but is complicated by the heat required for the separation.

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