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Redox-Based Separation of Americium from Lanthanides in Sulfate Media

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In the development of advanced nuclear fuel cycles, a primary motivation is the reduction of the long-term radiotoxicity of the wastes. From a few decades to several thousand years after removal of the fuel from the reactor, americium (Am) dominates the radiotoxicity of used fuel, thus its transmutation represents an attractive option for improved management of the residues. However, every viable scenario for transmutation of Am demands some degree of separation of Am from fission product lanthanides. Partitioning of Am from curium further simplifies the transmutation process. The mutual separation of these elements is very challenging due to their similar chemistry. The focus of this work is on the utilization of the upper oxidation states of americium (Am(V/VI)) to facilitate a more efficient separation of Am from fission product lanthanides and curium. A minimum 90% efficient separation of americium from the lanthanides and curium has been achieved in the laboratory by selectively oxidizing trivalent Am to the hexavalent state using $Na_2S_2O_8$. At equilibrium, lanthanides are precipitated as sodium lanthanide sulfate double salts, while oxidized Am species remain predominantly in the supernatant phase. Trivalent curium is readily coprecipitated with the $NaLn(SO_4)_2$ solid. Parallel studies of oxidized uranium, neptunium, and plutonium solutions support the conclusion that Am(VI) has sufficient stability to allow the separation to be completed in a reasonable time frame. A particular advantage of this approach is the absence of readily oxidized species that can quickly reverse the oxidation of Am and thus negate the separation. A variety of chemical and physical characterization techniques have been applied to profile the performance of the system.

Keywords americium; lanthanides; persulfate; solid-liquid separation

INTRODUCTION

Dissolved used nuclear fuel mixtures contain U, Np, Pu, Am, Cm, lanthanides and other fission products, a chemically diverse mixture representing about 1/3 of the elements in the periodic table. Americium, being a long-lived α-emitter (and growing in concentration in used fuel in storage as a result of decay of ^{241}Pu), is the greatest contributor to the radiotoxicity of the byproducts of fission between about 50 and 3000 years after removal from the reactor for intact used fuel, 100–7000 years for high level wastes from PUREX reprocessing. The fraction of Am isotopes in used fuel increases with the utilization of mixed-oxide (MOX) fuels and with longer burn-up cycles. On this basis, Am is an attractive target for transmutation. Unfortunately, the lanthanides, representing about 40% of the mass of fission products, compete with Am for neutrons that would be used in any advanced transmutation process. Thus the mutual separation of Am from chemically similar lanthanides remains a significant obstacle to the implementation of advanced closed-loop nuclear fuel cycles that include Am transmutation. A separation of Am from Cm would greatly simplify Am transmutation target preparation.

Most of the important methods for separating americium from the lanthanides (at either the analytical scale or in proposed industrial applications) rely on the slightly greater strength of interaction of trivalent actinides with ligand donor atoms softer than oxygen. The TALSPEAK process, based on the application of diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid (DTPA) and developed during the 1960s at Oak Ridge National Laboratory (1) is currently considered the best option for the transmutation-enabling separation of trivalent Am and Cm from fission product lanthanides in the U.S. advanced fuel cycle research effort. Advanced separations processes and specialized polyaza complexants are at the core of lanthanide/trivalent actinide separation by advanced nuclear fuel processing in the European research program (2). Thiophosphinic acids have also been advanced as possible reagents for separating trivalent actinides from fission product lanthanides (3–5). Average Am/Ln separation factors of 10–100 have been reported in laboratory research. Unfortunately, each approach has been plagued by ligand instability and/or extraction/complexation kinetics complications.

A separation method based on oxidized Am species would accrue the added advantage of allowing Cm to remain with the lanthanide fraction. It is widely noted that

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in a given oxidation state, actinides and lanthanides behave similarly, hence in a process that maintains trivalent Cm while Am is oxidized, it should be expected that Cm will accompany the lanthanides. A Cm/Ln waste stream would only require a few hundred years of decay before the greatest contributor to radiotoxicity was abated. Furthermore, the main curium isotope in used fuel (^{244}Cm) with its high specific activity would make the creation of Am transmutation targets more difficult. With Cm present the targets would have to be made within a hot cell; without the Cm, the targets could probably be produced in a glove box.

Unfortunately, oxidized Am species (Am^{4+}, AmO_2^+, AmO_2^{2+}) are each potent oxidizing agents in acidic aqueous media, hence their persistence in solution is limited. The oxidizing nature of these ions makes the application of solvent extraction separation procedures problematic. Among others, Belova and coworkers (6) report that the radiolysis products of TBP would reduce the oxidized americium and consume the HNO_3 present within the system. For such a solvent extraction-based process to be viable, a holding oxidant capable of maintaining oxidized Am species that does not simultaneously destroy the phase transfer ability of the extractant phase would be required. Mincher et al. (7) have reported preliminary results investigating the application potential of $NaBiO_3$ for such applications. Given the apparent limitations of separating oxidized Am species from lanthanides and Cm by solvent extraction and the evident advantages of isolating Am from Cm, developing separations based on oxidized Am still has significant appeal.

Though it was ultimately replaced by the far cleaner (and more efficient) option of solvent extraction, the first isolation of actinides either at the laboratory or industrial scale was accomplished using solid-liquid partitioning schemes. The $BiPO_4$ process (9) was scaled up from the microgram to the kilogram scale (a factor of 10^9) in the Manhattan Project to enable the creation of kilogram quantities of plutonium. Lanthanide fluoride co-precipitation processes were (and remain today) important analytical procedures supporting the isolation of the first samples of transuranium elements in the laboratory (8). Though separation processes based on solid-liquid separation have a number of limitations, in the case of Am partitioning from Cm and lanthanides, accomplishing this task by other means has proven a formidable task.

There are a number of known approaches to lanthanide/actinide partitioning that involve (at an analytical scale) solid-liquid separations. Most are based on the observation that oxidized actinides stay in solutions while lanthanides (or reduced actinides) can be precipitated. A fractional precipitation of americium and lanthanum oxalates has been shown to provide a highly enriched americium precipitate and about 50% of the lanthanum being rejected at each stage (10). Separation of americium from curium by oxidizing americium to the hexavalent state with peroxydisulfate followed by a precipitation of CmF_3 has been reported (11). Separation of Am (VI) from large quantities of the lanthanides also has been demonstrated through precipitation of the lanthanide trifluorides (12). These fluoride precipitations can achieve >90% separation; both employ 3–4 M HF as the precipitating agent.

In this work the separation of Am from fission product lanthanides and curium from sulfate media begins with the selective adjustment of the oxidation state of Am to the accessible upper oxidation states, primarily the hexavalent oxidation state. Neither Cm nor the lanthanides are comparably transformed, i.e., they remain trivalent. In the following, the results of an investigation of the oxidation of Am (III) by persulfate ($S_2O_8^=$) and the concomitant precipitation of lanthanide and curium ions from sulfate media is demonstrated.

EXPERIMENTAL

Reagents

The oxidizing agents Oxone $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Sigma Aldrich) or $Na_2S_2O_8$ 98 + % (Acros) were used as received. Europium used in these experiments was diluted to 0.1 M from a 0.488 M $Eu(ClO_4)_3$ stock solution that had been prepared previously from 99.999% Eu_2O_3 (Arris International Corp.). That stock had been standardized using ICP-OES. A 0.5 M silver nitrate solution was made from ACS grade 99.0% $AgNO_3$ (EM Science).

Radioisotopes

Progress of the precipitation reaction was monitored radiometrically using $^{152/154}$Eu (as a representative fission product lanthanides) and actinide (^{233}U, ^{237}Np, ^{238}Pu, and ^{241}Am) radiotracers. The use of a radioactive tracer allowed for accurate tracking of the lanthanide and actinide concentrations during the multi-step precipitation separation process. The isotope $^{152/154}$Eu has been made by neutron irradiation of 99.999% Eu_2O_3 from Arris International Corp. at the Washington State University Nuclear Radiation Center's 1 MW TRIGA reactor. Actinide radiotracers were obtained from standardized stocks of the WSU and INL inventories. Experiments done at macroscopic concentrations of Am were completed at the Idaho National Lab (as described in the following) using ^{243}Am. Curium experiments (also conducted at INL) employed radiotracer ^{244}Cm.

Procedures

Both single and dual label experiments have been performed in this work. Studies conducted at the radiotracer level were primarily carried out at the Harold Dodgen Research Center at Washington State University. Samples

containing ^{241}Am and $^{152/154}$Eu were analyzed using a Packard Cobra II Auto-gamma counter. Experiments were also performed using ^{233}U, ^{237}Np and ^{238}Pu radiotracers and quantified using a Beckman LS 6500 Multi-Purpose Scintillation Counter using National Diagnostics "Ecoscint" scintillation fluid. Studies performed at the Idaho National Lab were either single or dual label for ^{244}Cm or ^{243}Am and ^{154}Eu respectively. Quantification of ^{244}Cm activity (5.81 MeV α) was done by liquid scintillation. Curium samples produced at the INL were placed in 20 mL glass scintillation vials with 20 mL of Ultima Gold LLT scintillation fluid and counted on a Tri-Carb 3170TR/SL liquid scintillation counter. All americium samples produced at the INL were counted using an ORTEC Digital Gamma Ray Spectrometer, DSPEC Jr. 2.0. The counter has been optimized for 1 mL of solution in a 20 mL scintillation vial. Each sample was diluted to 1 mL to match this optimized geometry.

In single label experiments, 5 μL of the desired radiotracer was added to 250 μL of a 0.1 M $Eu(ClO_4)_3$ solution. To this homogeneous aqueous solution, 300 μL of 0.5 M $Na_2S_2O_8$ or 0.4 M Oxone and 25 μL of 0.5 M $AgNO_3$ were mixed in a 12×75 mm capped polypropylene tube. The tubes were then heated to above 90°C in a water bath for 15 minutes with periodic shaking to help facilitate the oxidation of the Am tracer (13). A solid precipitate appeared during this equilibration period. After the fifteen minute heating period, the tubes were removed from the water bath, capped, and centrifuged for 5 minutes to firmly pack the solid in the base of the round bottom tube. Separation was achieved by decanting the supernatant into a second gamma tube. In the americium and europium studies, a 300 μL aliquot of the supernatant was removed and counted with the Cobra system to determine the percent of the tracer retained in the solution. During the heating period it has been noted that an average 10% loss in solution volume occurred during the experiment. Taking into account the 10% loss, the initial reaction volume and aliquot size, the percent radiotracer can be determined through a comparison with an average of counts from a 5 μL spike from the respective radiotracer. Studies using ^{233}U, ^{237}Np, and ^{239}Pu were performed in the same manner as the americium and europium studies with the only change coming in the sample prep for counting purposes. In these experiments, a 200 μl aliquot was removed from the supernatant and placed in a 7 ml glass scintillation vial in 7 ml scintillation fluid for alpha assay via liquid scintillation.

Evaluation of the effect of added silver on the precipitation of the lanthanides (after oxidation of the americium) followed the same procedure as described in the single label experiment above. In these experiments, the solid precipitate was used for γ-counting after decanting the supernatant. The solids were left in the original 12×75 mm tube and analyzed using the Packard Cobra II Auto-gamma counter. Since the total solid was used for counting, the net count rate compared with the amount added initially could be used to determine the percent radiotracer found in the solid phase. It was assumed that there were no absorption losses in the solid samples.

Macro-americium studies were performed at the Idaho National Laboratory. All work was completed in accordance with the necessary Radiological Work Permit (RWP) and Lab Instructions (LI). To conform to restrictions imposed by the RWP and LI, slight modifications to the previously described procedure were required. Changes included use of 1.5 mL screw cap micro-centrifuge tubes instead of the 12×75 mm gamma tubes, the use of two radioactive isotopes simultaneously for experiments looking at the separation of americium from a europium-containing solution, and radiation detection using a high purity germanium detector. In the dual label experiments, 5 μL samples of both ^{243}Am and ^{154}Eu were added to 250 μL of a (non-radioactive) 0.1 M $Eu(ClO_4)_3$ solution. To this homogeneous aqueous solution, 300 μL of 0.5 M $Na_2S_2O_8$ or 0.4 M Oxone and 25 μL of 0.5 M $AgNO_3$ were added to the screw cap micro-centrifuge tube. These experiments were also performed in the absence of silver. A ^{244}Cm single label experiment had 5 μL of the radiotracer added to 250 μL of a 0.1 M $Eu(ClO_4)_3$ solution using the same experimental procedure as was used in the dual label experiments. After the 15 minutes of equilibration in the water bath ay 95°C and centrifugation, a 350 μL aliquot of the supernatant was removed for radiometric assay. The sample was diluted to 1 mL to match the optimized counting geometry of the detector. Data analysis was as described previously.

Spectrophotometric analysis of the supernatant solution was performed with a Cary 50 spectrophotometer using a Cary 50 fiber optic coupler (allowing the cell holder and samples to remain in the fume hood). The progress of the americium oxidation using sodium persulfate ($Na_2S_2O_8$) was monitored using the Am (III) characteristic peaks at 503 and 811 nm and the Am (VI) characteristic peaks at 666 and 996 nm. A 100 μL aliquot of the 1 mM americium working stock was placed in a Hellma Quartz Suprasil Type# 105.253 – QS 1 cm cell along with 50 μL of 1 M $Na_2S_2O_8$ and the spectra recorded. This solution was allowed to sit for 1 hour at room temperature and the spectrum recorded again after 1 hour. The americium solution was removed from the cell, placed in a 1.5 mL screw cap micro-centrifuge tube, then placed in a 98°C water bath for 5 minutes. The solution was returned to the 1 cm cell for analysis. The sample was then returned to the water bath and heated for another 5 minutes. This sequence was repeated at 5 minute intervals to provide spectra of the solution from 0–25 minutes. After final heating the solution was allowed to cool for 1 hour and a final spectrum was recorded.

X-ray powder diffraction was performed on a sample of the dried solid precipitate. The powder was held in place on a 2″ square glass plate using petroleum jelly spread in an oval shape $\sim 1 \times 1.5''$. X-ray powder diffraction was performed using 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: 0.02 d/min; 2θ range: 5–55. The diffractograms were produced using supporting MDI Data Scan 4 and Jade 8 software packages. The raw pattern was compared to powder patterns in the ICSD (International Crystal Structure Database) to identify the material in the solid phase. Radiometric analysis of the supernatant was also completed to determine the amount of each isotope remaining in the supernatant phase.

RESULTS

Tracer Studies

The separation was monitored radiometrically using lanthanide ($^{152/154}$Eu) and actinide (^{233}U, ^{237}Np, ^{238}Pu, ^{244}Cm, and ^{241}Am) radiotracers. The ^{233}U, ^{237}Np, and ^{239}Pu experiments have been done to demonstrate that the separation of oxidized actinides from trivalent lanthanides and actinides is a universal feature of this chemistry. Using the concept of oxidation state analogs and the more favorable redox chemistry of U, Np, and Pu, these experiments also serve to support the concept that Am is oxidized to the hexavalent (or retained in the pentavalent) oxidation state in the treatment regimen. Under the conditions of these experiments, uranium will remain hexavalent throughout. The initial oxidation states of the radiotracer neptunium and plutonium were the V and IV states, respectively. In contact with $S_2O_8^{=}$, each is believed to have been relatively quickly oxidized to the VI state. Europium radiotracer, $^{152/154}$Eu, was used as a representative of the trivalent lanthanides; it is expected (though not verified in this study) that the fission product lanthanides (La through Gd plus Y) will behave similarly to Eu. The results of these radiotracer experiments are shown in Table 1.

The $^{152/154}$Eu radiotracer results demonstrated that (under the conditions of these experiments) about 8% of the lanthanide remains in solution after the precipitation has occurred. Neither longer times in the water bath nor higher concentrations of $S_2O_8^{=}$ increased the completeness of the precipitation of Eu^{3+}. On average, 93% of ^{233}U remained in the solution phase after precipitation of the

TABLE 1
Results of radiotracer and macro separation studies

	Conditions	% Radiotracer (aq)	$SF_{An/Eu}$ (aq)
Radiotracer experiment using silver catalyst			
$^{152/154}$Eu		8.2 ± 0.8	
^{233}U	25 µL 0.5 M	93 ± 1	11 ± 1
^{237}Np	$AgNO_3 + 300$	86 ± 2	10 ± 1
^{238}Pu	µL $Na_2S_2O_8$	94 ± 2	11 ± 1
^{241}Am (2×10^{-8} M)		93.6 ± 0.3	11 ± 1

	Conditions	% Radiotracer (aq)	$SF_{Am/Eu}$ (aq)	$SF_{Am/Cm}$ (aq)
Macro Am experiment using silver catalyst				
^{243}Am (2×10^{-5} M)	$Na_2S_2O_8$	95 ± 7	4 ± 1	10 ± 3
	Oxone	18.9 ± 0.8	0.9 ± 0.3	1.2 ± 0.1
^{154}Eu (aq)	$Na_2S_2O_8$	23 ± 6		
	Oxone	20 ± 6		
^{244}Cm (aq)	$Na_2S_2O_8$	10 ± 3		
	Oxone	16 ± 1		

	Conditions	% Radiotracer (aq)	$SF_{Am/Eu}$ (aq)
Macro Am experiment without silver catalyst			
^{243}Am (2×10^{-5} M)	$Na_2S_2O_8$	100 ± 5	3.7 ± 0.2
	Oxone	20 ± 6	1.5 ± 0.8
^{154}Eu (aq)	$Na_2S_2O_8$	27 ± 1	
	Oxone	13 ± 5	

lanthanide sulfate solid. This value is considered to represent the essential separation capacity of the system. As no sulfate-based solubility limiting species for U(VI) are known, the 7% lost to the solid is attributed to entrained ^{233}U radiotracer in the solid phase; attempts to "wash" the solid gave no significant improvements in U-Eu separation. Similar results were obtained for Np (86%) and Pu. (94%). The slightly lower solubility of Np is statistically significant and may indicate the presence of some residual Np(V).

Americium retention in the supernatant phase is more consistent with the U and Pu results than those for Np, implying (based on analogy with Np) that Am is predominantly in the hexavalent oxidation state under these conditions. The average actinide/europium separation factor $SF_{An/Eu}$ ($SF = (\%Am_{aq})/(\%Eu_{aq})$) is about 11. As noted above, an average of 6% of the actinide is lost to the solid phase in a single contact. After some initial tests, it was determined that washing of the solid with various fluids led to unacceptable levels of redissolution of the $NaEu(SO_4)_{2(s)}$.

Through radiotracer studies, the effect of silver nitrate concentration has also been evaluated over a silver concentration range of 0.004–0.04 M (Fig. 1). Lower [$AgNO_3$] yields the lowest percent of Eu^{3+} in the solid phase, providing the worst overall separation efficiency. At 0.02 M [$AgNO_3$], the percent Eu^{3+} in the precipitate has achieved a maximum that does not change with further addition of silver to the system over the range of silver concentrations studied in this work. The concentration of silver present in the system had at best only negligible effects on the oxidation of americium and therefore on the percent of americium being found in the precipitate. At $\pm 1\sigma$ error the percent americium in the precipitate is equivalent across the silver concentration range investigated.

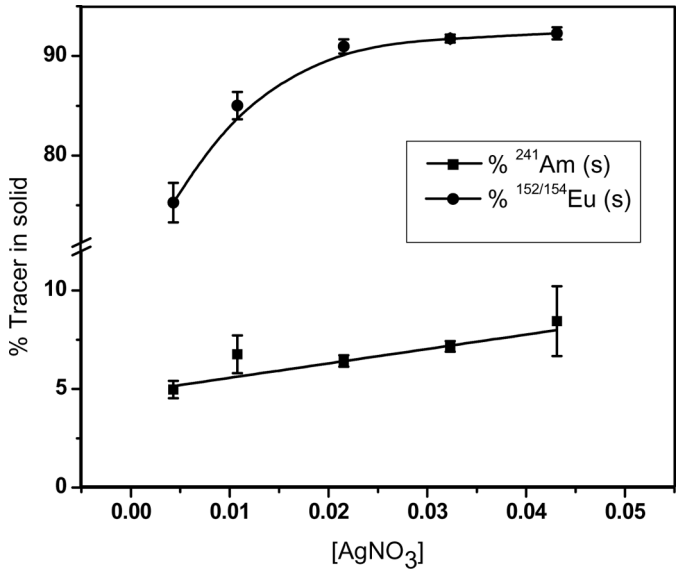

FIG. 1. The effects of [Ag^+] on Am/Eu partitioning at constant [Eu^{3+}] and [$S_2O_8^{=}$]. Uncertainties are presented at the $\pm 1\sigma$ level.

Identification of Predominant Solid Species

Powder XRD has been used to identify solids formed in both the Oxone and $Na_2S_2O_8$ oxidation/precipitation separations. The precipitation was performed on a cold (sample containing no radiotracer) sample of $Eu(ClO_4)_3$ following the same procedure as before. The pattern gave a best match for the double sulfate salt of the lanthanide, $Gd_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$ (14). The double sulfates of sodium and the lanthanides have been reported for the complete series of the lanthanides (15). Solids formed with Oxone or $Na_2S_2O_8$, providing K^+ or Na^+ respectively for the co-precipitation, both matched the XRD pattern for the Gd analogue closely. The double sulfates of the lanthanides are isostructural and show a steady decrease in the cell volume across the lanthanide series as would be expected with the lanthanide contraction (16). These solids are reported to be insoluble in alcohol, ether, and acetone, sparingly soluble in water, and readily soluble in dilute hydrochloric and nitric acids (15). These solids are stable to ~350°C at which temperature the loss of water from the crystal is observed. At ~747°C, the anhydrous salt has been observed to dissociate into its component parts $Ln_2(SO_4)_3$ and M_2SO_4. Upon heating to 1100°C, XRD of the resulting solid shows only the structure of lanthanum oxide sulfate (17).

Macro Americium Studies

In experiments performed at the Idaho National Laboratory the overall concentration of americium in solution was increased from 2×10^{-8} M (in the radiotracer experiments) to 2×10^{-5} M. This study was performed both in the presence and absence of silver. Parallel radiotracer studies were also completed at this time to profile the partitioning of ^{244}Cm. Dual label experiments using ^{243}Am and ^{154}Eu, evaluated the differences in oxidation ability of Oxone and $Na_2S_2O_8$. When $Na_2S_2O_8$ was used to oxidize americium, 95% of americium and 23% of the europium remained in the supernatant after separation. Oxidation with Oxone provided only 19% of americium and 20% of the europium in the supernatant phase. These experiments were then repeated without the addition of silver. For both oxidation by $Na_2S_2O_8$ and Oxone, the results without the silver are within $\pm 1\sigma$ error of the results with the silver included.

As this procedure is designed to separate americium from curium and the lanthanides, the $Na_2S_2O_8$ separation was tested using ^{244}Cm in a single label experiment. The $Na_2S_2O_8$ system was chosen exclusively as it provides a better separation than Oxone. Results of these experiments can be seen in Table 1. It can be seen that 10% of the

curium tracer remained in the supernatant phase after treatment of the sample following the same procedure as was used for both americium and europium (i.e., $NaEu(SO_4)_2$ formed the bulk of the solid phase). This result is in good agreement with the europium results. All reported uncertainties are at the $\pm 1\sigma$ level. The results clearly establish the viability of the separation of Am from both Cm and lanthanides by this selective oxidation and precipitation of sulfate solids.

Spectrophotometric Studies of Oxidation of Am by $S_2O_8^{=}$

The spectrophotometric demonstration of the oxidation of americium by $Na_2S_2O_8$ is seen in Fig. 2. The disappearance of the Am^{3+} characteristic peaks at 503 and 811 nm is accompanied by the appearance of the characteristic peaks of Am(VI) at 666 and 996 nm. The characteristic Am(III) peak was observed in the solution even after 5 minutes in contact with 0.5 M $S_2O_8^{=}$ at room temperature. After the reaction vessel had been placed in a boiling water bath for 5 minutes, the Am(III) peak at 503 nm was greatly diminished and the peak at 811 nm had completely disappeared. There is no spectrophotometric evidence for any intermediate species having been created, implying a comparatively rapid process in which three electrons are lost by Am^{3+} and the linear dioxocation AmO_2^{2+} is rapidly formed. The resulting solution takes on an amber-orange coloration. The final solution was left in the cuvette at room temperature for 1 hour with no change in the absorbance of the Am(VI) and no reappearance of the Am(III) or peaks characteristic of Am(V). While excess $S_2O_8^{=}$ persists, Am(VI) remains in the solution. When the holding oxidant is consumed, Am(VI) reduction proceeds. As has been described in the prior literature, Am(VI) is reduced by oxidation of H_2O and H_2O_2 (a product of α–radiolysis of water) ultimately returning to Am^{3+} following a one step reduction to AmO_2^{+} and subsequent disproportionation.

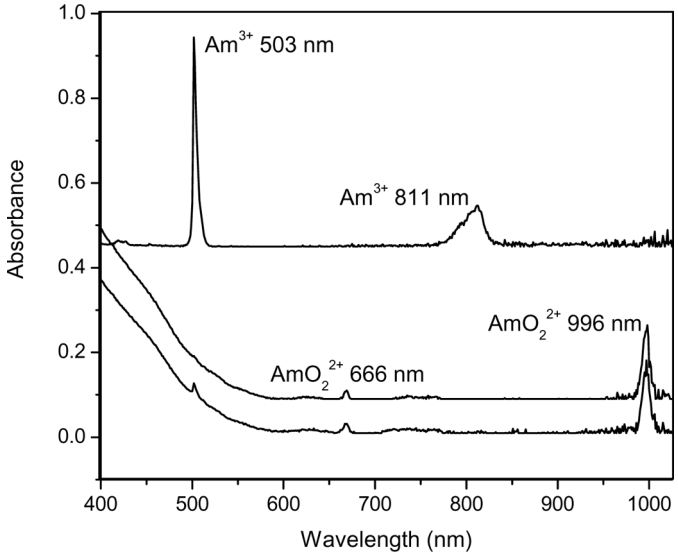

FIG. 2. Spectra of 1 mM americium in 0.1 M H_2SO_4. The spectra shown include T = 0 (no time in the water bath), T = 5 min and T = 10 min equilibration at 95°C for the upper, lower and middle spectra respectively. In the T = 0 sample, $Na_2S_2O_8$ has been added without heating the solution.

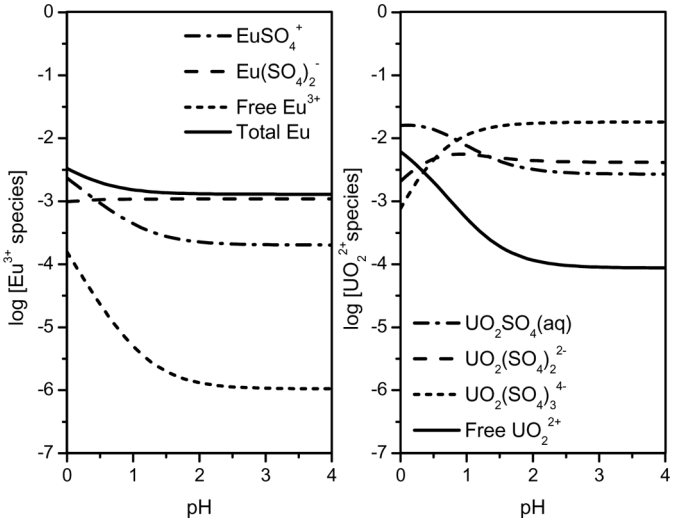

FIG. 3. Speciation diagrams for Eu^{3+} and UO_2^{2+} ions in sulfate containing solution. Concentrations $[M^{m+}] = 0.025$ M metal ion in both to match the $[Ln^{3+}]$ and 0.5 M $SO_4^{=}$, pH = 1 at 25°C. Equilibrium constants employed in the calculations are found in Table 2.

DISCUSSION

The separation of americium from curium and the lanthanides using the method described here requires the oxidation of Am to its pentavalent or hexavalent oxidation state. Standard reduction potentials (1.0 M $HClO_4$) for the Am (VI/V), (V/IV) and (IV/III) couples are 1.60, 0.83, and 2.60 V respectively (18). Despite the large IV/III couple, quantitative oxidation of americium to the hexavalent oxidation state has been achieved in acidic solutions through the use of ozone (19) and $S_2O_8^{=}$ (13). Persulfate has been chosen in this work due to its ability to completely oxidize americium and for its stability in acid solution. The byproduct of its reduction ($SO_4^{=}$) serves as the primary source for the sulfate that precipitates the lanthanides.

A study of the speciation of the hexavalent and pentavalent actinides vs. the trivalent lanthanides gives an indication of the thermodynamic basis for the separation by $S_2O_8^{=}$ oxidation and sulfate precipitation. The hexavalent actinide and trivalent species have been represented here by UO_2^{2+} and Eu^{3+} respectively. The speciation of Eu^{3+} in sulfate is assumed to represent the probable speciation

TABLE 2
Equilibrium constants for speciation plots

	log β		log β
$UO_2(OH)^+$	−6.2	$EuOH^{2+}$	−8.07
$UO_2(OH)_2$ (aq)	−11.3	$Eu_2(OH)_2^{4+}$	−14.34
$(UO_2)_2(OH)_2^{2+}$	−6.60	$Eu(OH)_3$ (s)	−16.81
UO_2SO_4 (aq)	1.85	$EuSO_4^+$	2.63
$UO_2(SO_4)_2^{2-}$	2.4	$Eu(SO_4)_2^-$	3.71
$UO_2(SO_4)_3^{4-}$	3.4	$NaEu(SO_4)_2$ (s)	−5.8
$H(SO_4)^-$	1.08	$H(SO_4)^-$	1.08

[1]All values $\mu = 1$ and $t = 25°C$ except $NaEu(SO_4)_2$ (s).
[2]$NaEu(SO_4)_2$(s) – value extrapolated from literature data (22,23) – μ = unknown and $t = 20°C$.
[3]Stability constants for UO_2^{2+} are found in Chemical Thermodynamics of Uranium (24).
[4]Stability constants for Eu^{3+} are found in the Martell and Smith Database (25).
[5]Eu hydrolysis products $- xEu^{3+} + yH_2O \Leftrightarrow Eu_x(OH)_y^{3x-y} + yH^+$.
[6]UO_2^{2+} hydrolysis products $- xUO_2^{2+} + yH_2O \Leftrightarrow (UO_2)_x(OH)_y^{2x-y} + yH^+$.
[7]Eu sulfate complexes $- xEu^{3+} + ySO_4^{2-} \Leftrightarrow Eu_x(SO_4)_y^{3x-2y}$.
[8]UO_2^{2+} sulfate complexes $- xUO_2^{2+} + ySO_4^{2-} \Leftrightarrow (UO_2)_x(SO_4)_y^{2x-2y}$.
[9]Solubility product $NaEu(SO_4)_{2(s)}$: $NaEu(SO_4)_2(s) \Leftrightarrow Na^+ + Eu^{3+} + 2\ SO_4^=$.

for trivalent lanthanide ions and curium. Setting the concentrations of the metal at 0.025 M and the ligand ($SO_4^=$) at 0.5 M, representative of the conditions in the experimental procedure, the speciation has been predicted using equilibrium constants shown in Table 2. The log β values selected for these calculations are reported for an ionic strength of 1 M, approximating the experimental conditions (I = 1.5 M). The results of the calculations indicate that at the experimental pH = 1 $UO_2(SO_4)_3^{4-}$ is the dominant species, though $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)$ represent respectively 18 and 12 percent of the total uranium in solution. The uncharged UO_2SO_4 complex is thought to become increasingly important at higher temperatures (20). Secoy found that the solubility of this species continued to increase up to 180°C (21). In the presence of excess sulfate ion, as in this system, it is likely that the anionic complexes $AnO_2(SO_4)_2^=$ and $AnO_2(SO_4)_3^{4-}$ will dominate the actinide speciation over the entire range of temperatures employed. The major species present below pH 9 in the europium simulation is the $NaEu(SO_4)_2$(s) double salt. At higher pH, the thermodynamic data predicts $Eu(OH)_{3\ (S)}$ to control the solubility of Eu^{3+}.

Americium Oxidation by Persulfate

The results shown in Fig. 2 demonstrate the successful oxidation of americium by $S_2O_8^=$ at temperatures above 90°C. The americium (III) characteristic peaks at 503 and 811 nm disappear while peaks characteristic of Am(VI) at 666 and 996 nm simultaneously appear. The initial americium solution (upper spectrum) included $Na_2S_2O_8$, but had not been heated in the water bath. The spectrum remained unchanged; showing only Am(III) peaks remaining while monitoring for one hour. Persulfate is well known to be a slow oxidant at room temperature. Oxidation with persulfate often exhibits an induction period prior to oxidation of any substrate, a period often attributed to the time required for the formation of the more facile persulfate radical ion $SO_4^{-\cdot}$. This spectrum is representative of that of the Am^{3+} aquo cation, implying that under these conditions there is no spectrophotometric evidence for the existence of an $Am^{3+} - S_2O_8^=$ complex.

The oxidizing power of $S_2O_8^=$ at elevated temperatures is demonstrated by the rapid disappearance of Am^{3+} after only five minutes of heating at the boiling point of water. By 10 minutes thermal treatment Am^{3+} is fully oxidized to AmO_2^{2+}. Of note in the spectra from 5 and 10 minutes of heating (Fig. 2) is the broad feature in the 400–600 nm range. This feature only appears upon heating, during which time americium is being oxidized. This feature may be associated with the formation of an americium (VI) sulfate species in solution. After 10 minutes of heating, the absorptivity is more intense at 400 nm than is seen at 5 minutes, coincident with the disappearance of the final traces of Am(III) at 503 nm. To test whether this absorption band might be replicated in uranyl-sulfate solutions, a spectrum was taken of uranyl sulfate; no change in the spectrum was seen upon heating the system. Upon adding ethanol to reduce americium, the feature from 400–600 nm began to disappear as characteristic peaks for Am(V) appeared. The precise origin of this change in color is not clear, though it is almost certainly associated with the presence of Am(VI).

The oxidation of americium is thought to occur by two possible reaction paths. The first proposed path involves

the Ag^{+} being oxidized by $S_2O_8^{=}$, which then splits the $S_2O_8^{=}$ into two sulfate radicals. The radical is thought to be at least partially responsible for the oxidation of the Am (III) to Am (VI). Following oxidation of the americium, the sulfate binds with the lanthanide thus precipitating the sodium lanthanide salt. The second proposed path involves the oxidation of Ag^{+} to Ag^{2+}. Americium present as Am (III) is then oxidized by the divalent silver. It is known from the prior literature that $S_2O_8^{=}$ oxidations (absent a catalyst) often proceed after a substantial induction period. The standard reduction potentials of Ag^{2+} and $S_2O_8^{=}$ are:

$$Ag^{2+} + e^{-} \Leftrightarrow Ag^{+} \qquad E^{\circ} = 1.989V$$
$$S_2O_8^{=} + 2e^{-} \Leftrightarrow 2SO_4^{=} \qquad E^{\circ} = 2.01V.$$

Both the Ag^{2+} and $S_2O_8^{=}$ are sufficiently strong oxidants to oxidize the Am (III) to the hexavalent oxidation state. It is probable that both Ag^{2+} and $SO_4^{-}\cdot$ contribute to Am oxidation when silver is present. A possible complication arises in the decomposition of $S_2O_8^{=}$ under acidic conditions. At acid concentrations $\geq 0.5\,M$, the peroxydisulfate is decomposed by a first order, acid-catalyzed path giving peroxy-mono-sulfuric acid which forms hydrogen peroxide (26). H_2O_2 is known to reduce Am (VI). This should not be a concern within this system, as the $S_2O_8^{=}$ should be stable under these conditions toward this possibly detrimental decomposition path. Silver nitrate has been used in all of the tracer studies given that the majority of the literature has used it in the oxidation of Am (13,27). Penneman and Keenan have suggested that the use of silver nitrate as a catalyst is not necessary (28).

The stability of $S_2O_8^{=}$ under the conditions of these experiments must be examined to probe the chemical and radiological robustness of this separations process. Persulfate in solutions will decompose by three different reaction pathways dependent on the conditions of the system. In the dilute acid solutions observed in this separation, the decomposition proceeds through the acid catalyzed first order reaction (26).

$$S_2O_8^{=} + H_2O \rightarrow 2HSO_4^{-} + \frac{1}{2}\,O_2$$

Also, there is considerable evidence that sulfate free radicals ($SO_4^{-}\cdot$) are created by the thermal decomposition of $S_2O_8^{=}$ in neutral and alkaline solutions (29). The mechanisms proposed for the thermal decomposition of $S_2O_8^{=}$ in aqueous solutions are shown below.

A: Un-catalyzed reaction $S_2O_8^{=} \rightarrow 2SO_4^{-}\cdot$

$$2SO_4^{-}\cdot + 2H_2O \rightarrow 2HSO_4^{-} + 2HO\cdot$$
$$2HO\cdot \rightarrow H_2O + \frac{1}{2}\,O_2$$

B: Hydrogen-ion catalyzed reaction $S_2O_8^{=} + H^{+}$

$$\rightarrow HS_2O_8^{-} \rightarrow SO_4 \quad + HSO_4^{-}SO_4 \rightarrow SO_3 + \frac{1}{2}\,O_2$$

These reactions are independent and occur simultaneously in aqueous solutions. The studies that proposed the above mechanisms, noted that in dilute acid solutions ozone was present as detected by the odor of the gas and by action of the gas on starch iodide paper (26). Notice also the production of the hydroxyl radical in the un-catalyzed reaction. The formation of this radical could also contribute to the oxidation of americium in this system. The hydroxyl radical is a strong oxidizing agent with a standard potential of $\sim$2.7 V (30,31). From this information, the decomposition rates of $S_2O_8^{=}$ and the reaction completion rate observed in this study it can be concluded that during the time scale of this separation the decomposition of the $S_2O_8^{=}$ will not be a detriment to the process.

Tracer Study

With >90% U, Pu, Am and 86% Np remaining in the solution phase after the precipitation, it is clear that oxidized actinides can be partitioned away from Cm and Ln(III) from acidic sulfate systems. The americium is being oxidized to its hexavalent state as demonstrated in Fig. 2. It also appears likely to be soluble in a sulfate-containing solution, as was demonstrated with uranyl in the speciation calculations. Silver was added in these experiments as a catalyst as per previous literature; however, as observed in Fig. 1 the addition of silver provided little advantage in the oxidation of americium. Over the silver concentration range studied, the percent americium found in the solid appears to increase slightly however, upon inspection of the $\pm 1\sigma$ errors at each concentration, the effect has been determined to not be statistically significant. The addition of silver does produce a statistically significant increase in the percent europium found in the precipitate. This increase could result from the formation of a silver lanthanide salt that has been reported (32). The increased partitioning of Eu^{3+} to the solid phase suggests that $AgEu(SO_4)_2$ may be either less soluble than $NaEu(SO_4)_{2\,(S)}$ or that Eu^{3+} is more efficiently incorporated into the resulting solid.

Macro Study

At macro americium concentrations, the percentages of the americium and europium in solution are in very good agreement with results observed in radiotracer studies. The results of both sets are found in Table 1. The similarity in these percentages indicates that oxidized americium species are indeed soluble in a sulfate containing solution. This study was repeated without silver present. This experiment indicated that Ag^{+} was not needed to achieve

separation of Am from the Ln and Cm at macro concentrations of Am. The spectrum of americium was recorded to directly observe the oxidation state of americium in this system. The results of these spectra clearly establish that Am(VI) is (as expected) the terminal oxidized americium species under these conditions, that Ag^{+} need not be present for the oxidation to occur, and that Am(VI) persists at least for some time in this medium. The spectra indicate that Am(VI) was stable towards reduction to Am(V) for at least 1 hour which should provide adequate time to complete the separation of the solid and supernatant phases. It is likely that this condition would persist for an extended period of time as long as excess $S_2O_8^{=}$ remained in the solution. To implement an industrial-scale procedure based on these results, it is clear that an excess of $S_2O_8^{=}$ and elevated temperatures would be necessary.

CONCLUSION

A successful separation of oxidized americium from europium and curium has been demonstrated. The optimized method has resulted in the retention of 86, 90, and 94% of the actinide in the solution for ^{237}Np, ^{241}Am, and ^{238}Pu respectively. The analog studies are consistent with the presence of oxidized Am species in these experiments. Addition of more $Na_2S_2O_8$ does not appreciably increase the percent actinide found in solution giving results that were within $\pm 1\sigma$ of the results for ^{241}Am studies. As was expected, curium precipitated along with the europium during this separation. These retention percentages give an Am-Eu/Cm separation factor of $\sim$11 in a single contact. On average, about 7% of the Am is lost to the solid phase.

In the context of advanced fuel cycle processing schemes, a solid-liquid separation based on acidic $S_2O_8^{=}$ media could be envisioned to follow the application of a TRUEX (or DIAMEX or TODGA) separation of lanthanides and actinides from fission products. The dilute acid conditions of a TRUEX strip would appear to be ideally suited to the application of $S_2O_8^{=}$ oxidation and precipitation of Ln/Cm double sulfate salts. Subsequent manipulation of the supernatant phase to again reduce the Am to the trivalent oxidation state would enable transmutation target fabrication; in fact, the reduction would occur spontaneously as a result of radiolysis and interaction of Am(VI/V) with radiolytically-produced H_2O_2.

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