

Actinide Lanthanide Separation Process—ALSEP

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ABSTRACT: Separation of the minor actinides (Am, Cm) from the lanthanides at an industrial scale remains a significant technical challenge for closing the nuclear fuel cycle. To increase the safety of used nuclear fuel (UNF) reprocessing, as well as reduce associated costs, a novel solvent extraction process has been developed. The process allows for partitioning minor actinides, lanthanides, and fission products following uranium/plutonium/neptunium removal, minimizing the number of separation steps, flowsheets, chemical consumption, and waste. This new process, actinide lanthanide separation (ALSEP), uses an organic solvent consisting of a neutral diglycolamide extractant, either *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) or *N,N,N',N'*-tetraoctyldiglycolamide (TODGA), and an acidic extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]), dissolved in an aliphatic diluent (e.g., *n*-dodecane). The An/Ln coextraction is conducted from moderate-to-strong nitric acid, while the selective stripping of the minor actinides from the lanthanides is carried out using a polyaminocarboxylic acid/citrate buffered solution at pH anywhere between 3 and 4.5. The extraction and separation of the actinides from the fission products is very effective in a wide range of HNO₃ concentrations, and the minimum separation factors for lanthanide/Am exceed 30 for Nd/Am, reaching >60 for Eu/Am under some conditions. The experimental results presented here demonstrate the great potential for a combined system, consisting of a neutral extractant such as T2EHDGA or TODGA, and an acidic extractant such as HEH[EHP], for separating the minor actinides from the lanthanides.

INTRODUCTION

The recent renewed interest in nuclear power stems from higher petroleum costs and the role of fossil fuels in carbon dioxide emissions.¹ This increase in production, as well as the legacy of light water power generation in the United States means that used nuclear fuel (UNF) will be of concern for the foreseeable future.^{1–3} UNF includes various elements that retain radiotoxicity for hundreds of thousands of years following discharge from a reactor.² One approach to UNF disposal is through vitrification, or solidifying dissolved nuclear fuel in borosilicate glasses, which can be stored in geological repositories until the radioactive elements have decayed sufficiently.^{2,3} Alternatively, more long-lived or toxic elements can be removed by appropriate chemical processes, leaving lower toxicity waste that is easier to dispose. In addition, elements such as the transuranic elements (TRU), which are the major heat contributors to repositories in the thousand to ten thousand year time frame, can be transmuted in nuclear reactors to substantially reduce their decay times.^{2,3}

Of the transuranium elements, the minor actinides (MA) americium (Am) and curium (Cm) have especially high radiotoxicities, making it desirable to remove them from UNF and to deal with them separately.⁴ The separation of the typically trivalent MA from the lanthanides (Ln) is the key step for closing the nuclear fuel cycle, but it is particularly difficult due to the identical oxidation state and similar ionic radii of the two species. Solvent extraction has been the primary technology for large scale UNF separations since the development of the plutonium–uranium extraction (PUREX) process in the 1950s, and a number of MA/Ln partitioning processes have since been developed.^{5,6} Most such separation methods involve multiple intricate chemical stages to achieve effective separations, however, causing them to be too

expensive or unsafe due to the complexity of multiple flowsheets. Therefore, a single process is desired for MA separation from fission products following uranium and plutonium recovery. Our major requirements for organic extractants are that they should be soluble in aliphatic diluents such as *n*-dodecane (considered to be an industry standard due to rather high flash point, 83 °C, and low toxicity⁷), preferably be commercially available, and able to withstand hydrolysis and radiolysis during contacting with spent fuel constituents in the aqueous phase. Furthermore, for a robust process, it is considered necessary to obtain a minimal separation factor (SF) between the minor actinides and the lanthanides of 10.

There is substantial research being conducted in Europe on the development of a universal process using both newly synthesized and commercially available extractants.^{8–13} Over the past several years a number of combinations of neutral and acidic extractants have been investigated. These combined-extractant processes involve extracting MA and Ln from highly acidic media with the neutral extractants, which separates them from other fission products, followed by utilizing the characteristics of the acidic extractant in selectively stripping either the MA or Ln into a buffered aqueous phase.

At the time our investigations began, the transuranic extraction (TRUEX)¹⁴ and trivalent actinide–lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK)¹⁵ processes were considered in the United States to be the most robust processes available for Ln and An extraction and mutual separation. Our studies started

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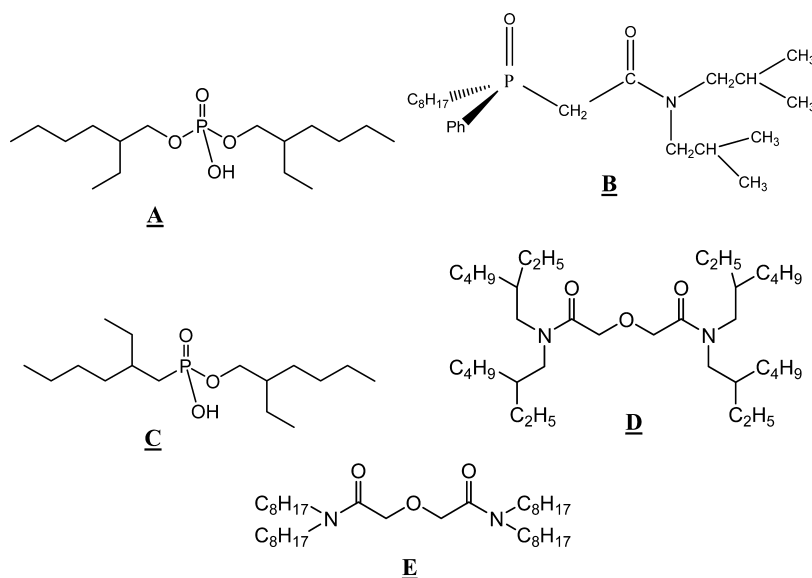


Figure 1. Structures of the extractants used in this study: (A) HDEHP, (B) CMPO, (C) HEH[EHP], (D) T2EHDGA, and (E) TODGA.

with combining the neutral and acidic extractants used in these two solvents but then were extended to include other major commercial extractants. Investigated mixtures include the following: (1) octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO, Figure 1B) and bis(2-ethylhexyl)-phosphoric acid (HDEHP, Figure 1A); (2) CMPO plus 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH-[EHP], Figure 1C);^{16,17} and mixtures involving diglycolamides (DGA), such as 3) *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, Figure 1E) plus HDEHP, (4) TODGA plus HEH[EHP], (5) *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA, Figure 1D) plus HDEHP, and (6) T2EHDGA plus HEH[EHP], briefly reported in the ALSEP patent.¹⁸

The ALSEP process has resulted from a joint project between Argonne National Laboratory (ANL) and the Pacific Northwest National Laboratory (PNNL). This is the first paper on ALSEP and describes some of the major accomplishments that have been achieved as a result of this joint project.

EXPERIMENTAL SECTION

Materials. All of the chemicals were purchased from Sigma-Aldrich, A.C.S. reagent grade, unless specified otherwise. All aqueous solutions were prepared using Milli-Q (18.1 MΩ cm) deionized (DI) water. Lanthanide and fission product simulant stock solutions were prepared from the corresponding nitrate salts except for Mo, Ru, and Zr (Na_2MoO_4 , $\text{RuO}(\text{NO}_3)_3$, and $\text{ZrO}(\text{NO}_3)_2$ were used). The ^{241}Am stock solution in 1 M HNO_3 was used for spiking the aqueous phase without additional purification. Ln radiotracers were purchased from Eckert & Ziegler Isotope Products. TODGA and T2EHDGA (>99% pure) were purchased from Eichrom and used as received. Anhydrous dodecane (99+%) was used for the preparation of the organic phases. Bis(2-ethylhexyl) phosphoric acid (HDEHP) was received from Alfa-Aesar and purified using a Cu salt precipitation method;¹⁹ HEH[EHP] was obtained from Yick-Vick Chemicals and was purified using a literature procedure.²⁰

The purity of both acidic extractants was determined by titrating in a methanol–water mixture (7:3 ratio) using a Metrohm automated titrator, Titrando 836. Solutions were maintained at 25.0 ± 0.1 °C using a circulating water-jacketed

titration cup that had been calibrated using a National Institute of Standards and Technology (NIST) traceable thermometer. The analyte solution was purged with N_2 gas in each set of experiments. The titrant was prepared by dilution of the carbonate-free 50% NaOH with boiled DI water. The concentration of NaOH was determined by titrating two acidic volumetric standards, 0.1 M HCl and 0.1 M HNO_3 (Fluka). The purity of both extractants was found to be at least 99%.

Liquid scintillation counting (LSC) was performed with α/β discrimination using a PerkinElmer Tri-Carb 3100TR. γ counting was performed with a Ge(Li) well detector operated by ORTEC software, and inductively coupled plasma mass spectrometry (ICP-MS) was performed using PerkinElmer SCIEX ELAN DRC II for the analysis. The radioactivity of ^{241}Am was measured using either γ counting (59.5 keV) or by α counting using LSC in the case in which there were no other radioactive elements present. The radioactivity of ^{152}Eu was measured by γ counting using the 344 keV peak. The radioactivities of ^{147}Pm and ^{151}Sm were determined by β counting using LSC when only a single radionuclide was present in the solution. The ^{141}Ce radioactivity was determined by γ counting at 144.9 keV. The concentrations of stable Ln and FP in the aqueous phase were determined using ICP-MS before and after the extraction. The pH of the aqueous solutions was measured using an Orion 525A+ pH meter and Orion 8272BN pH probes. The calibration was done using 4.01 and 7.00 buffer solutions, traceable to NIST standards. The electrode was used only if the correlation coefficient for the measured slope exceeded 58 mV/(pH unit), close to the theoretical value of 59.15 mV/pH. The nitric acid concentration was determined following the extraction by titration with standard NaOH. Culture tubes containing organic and aqueous phases were shaken on a Genie-2 Vortex mixer at the maximum intensity (3200 rpm). The volume ratio of the phase was 1:1 unless otherwise stated. Control experiments established that 50–60 s of contact was sufficient to attain equilibrium in the Am extraction from nitric acid. The experiments on the back-extraction kinetics were conducted using the following procedure: several milliliters of the organic phase were contacted with a nitric acid solution spiked with ^{241}Am and ^{152}Eu , and then 1 mL of f-element containing

organic phase was mixed with 1 mL of DTPA/citrate solution on a Vortex mixer for a certain period of time, after which the mixture was centrifuged and the organic and aqueous phases analyzed by γ counting.

The pH of the aqueous phases was measured after the extraction. All of the extraction experiments were carried out at 22 ± 1 °C. The samples were analyzed in at least duplicate, and the counting results were used if the deviation did not exceed 1%. However, the analytical methods utilized in the study as ICP-MS possess larger systematic error; therefore the estimated standard deviations were determined to be 10%, 3%, and 1% for ICP-MS, γ counting, and LSC analysis, respectively. The distribution ratio for a given element is defined as the ratio of the concentration of the element in the organic phase to its concentration in the aqueous phase. The separation factor is defined as the ratio of the distribution ratios of the corresponding radionuclides.

RESULTS AND DISCUSSION

Extraction from Nitric Acid Media. The completeness of MA extraction over a wide range of nitric acid concentrations is one of the key requirements for an effective combined Ln/MA separation process. The extraction of Ln, on the other hand, is not critical as they may be directed to the raffinate with the other fission products. The extraction behavior of $^{241}\text{Am(III)}$ from nitric acid by the various extractants tested is shown in Figure 2.

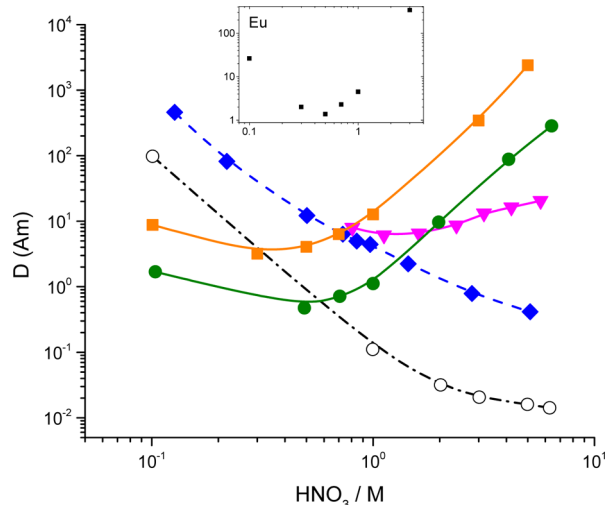


Figure 2. ^{241}Am distribution ratios from HNO_3 with (open black circles) 1 M HDEHP, (filled blue diamonds) 0.1 M CMPO/(1 M HDEHP), (filled pink triangles) 20 mM T2EHDGA/(1 M HDEHP), (filled green circles) 50 mM T2EHDGA/(0.75 M HEH[EHP]), and (filled orange squares) 50 mM TODGA/(0.75 M HEH[EHP]) all in *n*-dodecane with an organic/aqueous ratio of 0.5. Inset: ^{152}Eu extraction from HNO_3 by 50 mM T2EHDGA/(0.75 M HEH[EHP]).

The data presented in Figure 2 show that the Am extraction from nitric acid of moderate (1–5 M) concentration can be drastically improved if T2EHDGA or TODGA are used as a neutral extractant instead of CMPO. Even at low T2EHDGA concentration (20 mM) in a mixture with 1 M HDEHP, $D(\text{Am})$ exceeds 10 at acidities greater than 2 M, whereas 0.1 M CMPO/(1 M HDEHP) mixture shows a decrease in $D(\text{Am})$ with increasing acidity. For 50 mM T2EHDGA/(0.75 M HEH[EHP]), the Am and Eu (the inset in Figure 2)

partitioning goes through a minimum at about 0.5 M HNO_3 . The Am and Ln partitioning in ALSEP from weak nitric acid can be improved by increasing the concentrations of both HEH[EHP] and T2EHDGA (e.g., 75 mM T2EHDGA/(1 M HEH[EHP])) or by using TODGA instead of T2EHDGA as 0.05 M TODGA/(0.75 M HEH[EHP]) demonstrates rather high extraction affinity toward Am (Figure 2).

It is important to note that both TODGA and T2EHDGA based processes have been successfully demonstrated for Am separation from fission products on a laboratory scale using centrifugal contactors^{21–23} and an extraction system containing TODGA for the Am/Ln separation.^{24,25} These solvents utilize a phase modifier (octanol, isodecanol, tributyl phosphate (TBP), or *N,N*-dihexyloctanamide (DHOA)) to prevent third phase formation at high metal and nitric acid loading. The concentrations of the DGA's in the reported processes are in the 0.05–0.2 M range in the case of TODGA and 0.1–0.2 M in the case of T2EHDGA. In ALSEP, the polar acidic extractant serves as a phase modifier, so no third phase was observed under the experimental conditions including the tests carried out at concentrated HNO_3 and high loadings of stable Ln.

Figure 3 shows that lanthanum is the least extractable lanthanide in the system studied. Since lanthanum can be

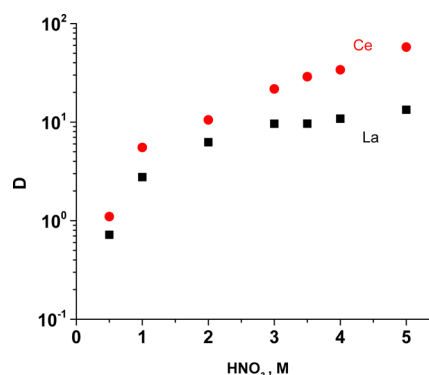


Figure 3. Extraction of stable La and Ce from nitric acid by 0.05 M TODGA/(0.75 M HEH[EHP]).

responsible for up to 30% of the lanthanides' mass in the spent fuel,³ its extraction behavior defines the efficiency of the process with regard to Ln recovery. $D(\text{La})$ are above 6 if $[\text{HNO}_3]$ is over 2 M for an ALSEP solvent consisting of 0.05 M TODGA + 0.75 M HEH[EHP], which is sufficient for the complete removal of La given that the nitric acid concentration of the raffinate stream after U, Np, and Pu coextraction, which is the aqueous feed to the process, is around 3 M. As shown below, the distribution ratios can be increased further if higher TODGA or T2EHDGA concentrations are utilized.

However, depending on the reprocessing goals, it may be desirable to direct the light lanthanides to the raffinate with the remaining fission products. In this case the extraction and the scrubbing can be conducted at lower acidity as the D values drop below 1 for La in 0.5 M HNO_3 .

The dependence of Am extraction from 3 M HNO_3 on the TODGA concentration is shown in Figure 4. In the TODGA concentration range from 3 to 100 mM in *n*-dodecane, there is a second order dependence for 1 M HDEHP/TODGA solvent. The order increases up to a fractional 2.4 if TODGA is mixed with 1 M HEH[EHP] (the order is 2.56 if the range of TODGA concentration is limited to 10–100 mM). There is a nearly second order dependence on T2EHDGA concentration

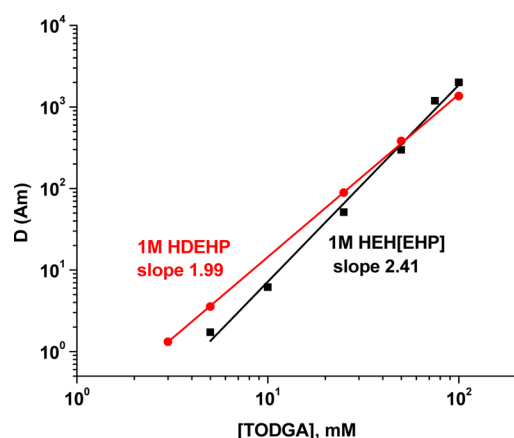
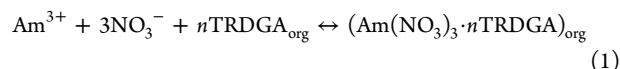


Figure 4. Am extraction by 1 M HDEHP/TODGA and 1 M HEH[EHP]/TODGA as a function of TODGA concentration from 3 M nitric acid.

under similar conditions in 1 M HDEHP (not shown). It should be noted that if the extraction is carried out from 1 M HNO_3 solutions in 1 M HDEHP/DGA systems, a less than second order dependence (~ 1.35) is observed for both T2EHDGA and TODGA, thus indicating a stronger interaction of HDEHP with the cations at lower acidities. In the absence of the acidic extractants, it has been proposed that Ln^{3+} or Am^{3+} are extracted from HNO_3 in accordance with eq 1, where $n = 3$ for T2EHDGA, and $n \geq 3$ for TODGA.^{26,27}



Based on these data, it is apparent that in HEH[EHP]–DGA mixtures the DGA molecules play a leading role in the extraction of trivalent cations from solutions of moderate nitric acid concentrations, but the role of HEH[EHP], if any, is not clear at this stage. For the HDEHP–DGA mixtures, HDEHP is involved in the interaction with cations forming perhaps ternary M–HDEHP–DGA complexes with possible coordination of nitrate ions. Such mixed complexes have been proposed for HDEHP–CMPO extraction systems.²⁸ Further study on the lanthanide speciation in ALSEP solvent is in progress.

Minor Actinide Stripping. The Am stripping is carried out using a buffered DTPA solution of low concentration. If $[\text{DTPA}] = 0.025 \text{ M}$, Am and Eu appear to attain equilibrium for the back-extraction within 100 s (Figure 5). The forward extraction rates of these cations were found to be about the same as their back-extraction rates at the same DTPA and citrate concentrations. However, to ensure equilibrium conditions the forward extraction tests from buffered DTPA solutions were conducted with 3 min of mixing.

The dependence of the Eu/Am separation factor, defined as the ratio of $D(\text{Eu})$ over $D(\text{Am})$, as a function of TODGA concentration is shown in Figure 6, while the pH dependence is given in Figure 7. The radioactivity of both ^{241}Am and ^{152}Eu was determined simultaneously. The separation factor decreases gradually as the TODGA concentration increases, but it remains rather high at TODGA concentrations under 0.1 M. The SF increases from approximately 50 to 90 as the pH increases from 3.3 to 4.1 (Figure 7), primarily due to a decrease in the Am partitioning values. This pH profiles resemble the nearly flat pH profile reported for a modified TALSPEAK process using HEH[EHP] as the acidic extractant.²⁹ At the Am stripping step, the T2EHDGA–HEH[EHP] mixture shows

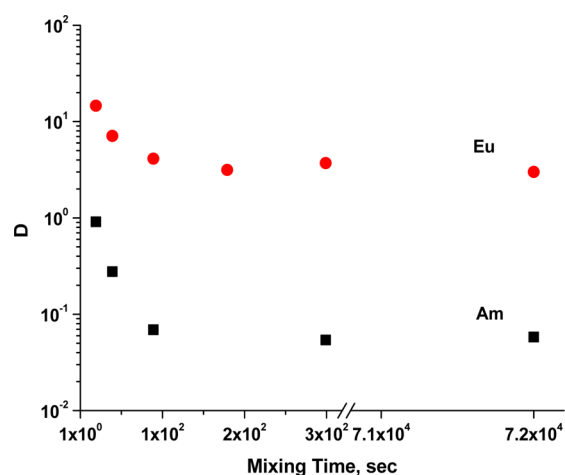


Figure 5. Kinetics of Am/Eu stripping from 0.05 M TODGA/(0.75 M HEH[EHP]) in 0.025 M DTPA/(0.5 M $(\text{H}/\text{NH}_4)_3$ citrate) at $\text{pH}_{\text{eq}} 3.5$.

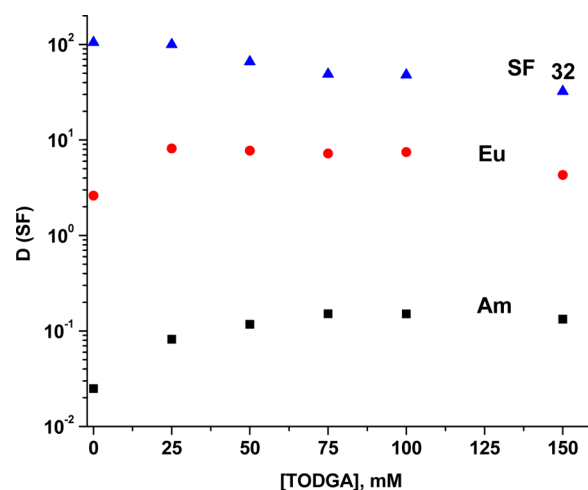


Figure 6. Eu and Am stripping and Eu/Am separation factors: organic phase, 1 M HEH[EHP]/TODGA in *n*-dodecane; aqueous phase, 0.025 M DTPA/(0.5 M $(\text{H}/\text{NH}_4)_3$ citrate), $\text{pH} = 3.5 \pm 0.05$.

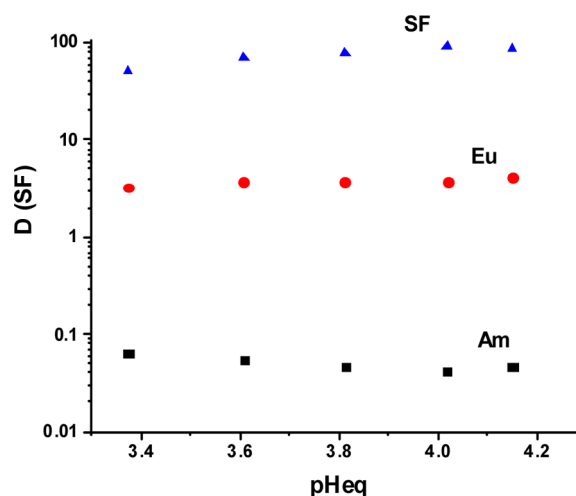


Figure 7. pH profile for Eu and Am stripping and Eu/Am separation factors from 0.05 M TODGA/(0.75 M HEH[EHP]) in *n*-dodecane into a solution containing 0.025 M DTPA/(0.25 M $(\text{H}/\text{NH}_4)_3$ citrate).

similar Ln/Am separation efficiency and extraction rates similar to those of the TODGA–HEH[EHP] system.

In order to determine the limiting An/Ln pair for separations, the full range of lanthanides and americium were stripped from a typical proposed ALSEP organic phase into a buffered aqueous phase containing 0.025 M DTPA. The distribution ratios and separation factors of the individual lanthanides to americium are shown in Figure 8. The lowest

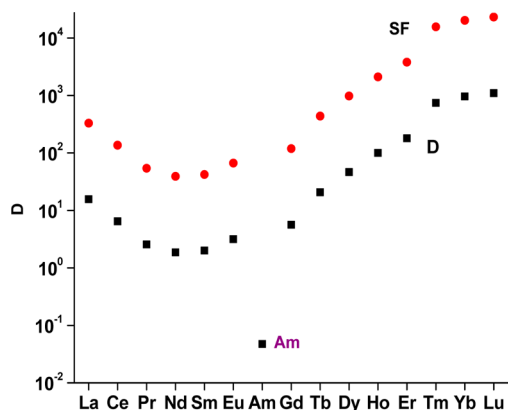


Figure 8. Distribution ratios and Ln/²⁴¹Am separation factors for stripping from 0.05 M TODGA/(0.75 M HEH[EHP]) organic phase into a pH 4.15 solution containing 0.025 M DTPA/(0.25 M (H/NH₄)₃ citrate).

Ln/Am separation factor is 39 (Nd/Am), while the separation factors for lanthanum and cerium are over 100 (since the concentration of the stable Ln was determined by ICP-MS, 10% uncertainty should be taken into account when considering the values of the separation factors). This rather high SF displays the effectiveness of the ALSEP solvent formulation for Ln/Am separations in large scale UNF reprocessing.

In contrast to HEH[EHP], HDEHP, if mixed with T2EHDGA, does not show a flat pH profile nor are the SF's as high. The pH profile for stripping select lanthanides and americium from 1 M HDEHP/(0.04 M T2EHDGA) solvent resembles one reported for TALSPEAK (Figure 9).¹⁵ The

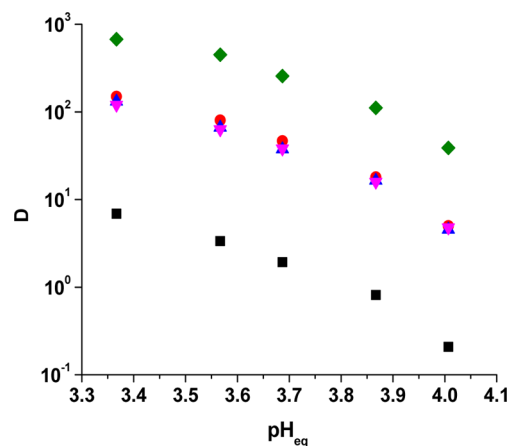


Figure 9. The pH profile for ¹⁴¹Ce (filled green diamonds), ¹⁵²Eu (filled red circles), ¹⁴⁷Pm (filled blue up-triangles), ¹⁵¹Sm (filled pink down-triangles), and ²⁴¹Am (filled black squares) stripping from 0.04 M TEHDGA/(1.0 M HDEHP) in *n*-dodecane into a nitric acid solution containing 0.05 M DTPA/(0.5 M (H/NH₄)₃ citrate).

lowest separation factors are about 20 for Pm/Am and Sm/Am. These SF's are sufficient for an effective process, although this steep pH dependence may present a challenge in the case of unexpected process feed transients.

We also found that the TODGA-HDEHP mixture does not exhibit as robust Ln/Am selectivity, as the SF drops to ~9 for 25 mM TODGA/(1 M HDEHP)/*n*-dodecane solvent indicating perhaps stronger interaction between the extractants, resulting in a Ln/Am selectivity similar to that observed in the CMPO–HDEHP system.

Zirconium and Lanthanide Extraction Behavior: Initial Proof-of-Principle.

A number of the complexing agents were tested in order to decrease Zr extraction from nitric acid solutions, because without such complexants, the *D*_{Zr} values are greater than 100 for all of the extraction systems tested in the study. Only 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA) and oxalic acid were found to effectively mask Zr extraction.³⁰ Thus, at 0.096 M CDTA in 3 M HNO₃, the Zr distribution ratios, as determined by ICP-MS, were 0.010 and 0.016 for 0.05 M TODGA/(0.75 M HEH[EHP]) and 0.05 M T2EHDGA/(0.75 M HEH[EHP]), respectively. These data are consistent with the observations reported for the 0.1 M T2EHDGA/(0.25 M HDEHP) solvent.³¹ Oxalic acid is a very effective masking agent for Zr. However, if used there is a possibility of forming insoluble lanthanide oxalates in the feed. If introducing CDTA into the feed solution is not desirable, Zr can be completely extracted by either of the two solvent formulations, and, after stripping of the An and Ln, Zr could be quantitatively stripped by 0.5 M oxalic acid in three stages, as the distribution ratio under these conditions is below 0.05.³²

A scoping test with a Ln- and fission-product-containing (FP) simulant feed solution was conducted to determine the separation of Am from Ln and major fission products. The organic phase used for this study was 0.05 M T2EHDGA/(0.75 M HEH[EHP]) in *n*-dodecane, and the composition of the aqueous feed in 3 M HNO₃ is shown in Table 1. HEDTA and

Table 1. Composition of the Feed Solution

component	concn, mM
La	1.36
Ce	2.61
Pr	0.69
Nd	3.67
Sm	0.92
Eu	0.21
Gd	0.24
Y	0.68
Zr	1.04
Mo	0.91
Ru	3.54
Pd	1.42
Fe	0.11
HNO ₃ , mol/L	3

citrate scrubbing were introduced to remove transition metals such as Mo from the organic phase.²¹ Also, a citrate scrub at pH 3.4 should wash out any nitric acid extracted at the loading step. The mixing time in these tests was limited to 50 s for the extraction, HNO₃/HEDTA, and citrate wash steps, and 100 s for the Am strip step. The distribution ratios of the major FP are presented in Table 2. Overall, their extraction behavior

Table 2. Distribution Ratios for Am, Ln, and FP in 0.05 M T2EHDGA/(0.75 M HEH[EHP])/n-Dodecane (FP, Fission Product; ND, Not Detectable)

process step FP	extraction 3 M HNO ₃	2 M HNO ₃ /(0.3 M HEDTA) wash	0.4 M citrate wash, pH 3.4	Am strip 0.025 M DTPA/(0.25 M citrate), pH 3.85	SF (FP/Am) at stripping
La	1.2	6.6×10^{-1}	1.2×10	2.2	1.2×10^2
Ce	3.1	1.3	3.1×10	1.6	8.6×10
Pr	5.7	2.0	3.2×10	8.4×10^{-1}	4.5×10
Nd	1.1×10	3.3	3.6×10	6.8×10^{-1}	3.6×10
Sm	3.9×10	1.0×10	2.3×10^2	1.5	8.0×10
Eu	5.9×10	1.5×10	3.6×10^2	2.9	1.5×10^2
Gd	3.6×10	1.3×10	4.9×10^2	5.1	2.7×10^2
Y	1.3×10^2	2.6×10	9.3×10^3	6.7×10^2	3.6×10^4
Zr	1.4×10^2	6.9×10	1.2×10^2	1.0×10^2	5.6×10^3
Mo	6.4×10^2	4.2×10^2	1.8	8.0×10^{-1}	4.3×10
Ru	6.0×10^{-3}	ND			
Pd	2.7×10^{-1}	7.7×10^{-1}	3.7×10	2.1×10	1.1×10^3
Fe	3.5×10^{-1}	ND	ND	ND	
Am	1.5×10	3.9	1.2×10	1.9×10^{-2}	

seems to be favorable. The only fission products of concern are Zr, Fe, and Mo. Although Fe partitioning at the extraction was minor ($D = 0.35$), we found that it was difficult to scrub extracted iron from the organic phase. Studies are on the way to find optimal conditions for Fe handling. Regarding Mo, one contact with the citrate buffer did not provide sufficient removal. It has been demonstrated that at least three scrub stages of citric acid at pH ~ 3 are required to decrease its D value below 1, and consequently to effectively remove Mo from the organic phase.³²

The obtained SF for Nd/Am, 36, is consistent with the value obtained for the TODGA/HEH[EHP] system within the experimental error (Table 2 and Figure 8). The SF for Gd/Am seems to be excessively high (Table 2). This could be due to the fact that 100 s of contact time from MA stripping was not sufficient for achieving equilibrium with the heavier Ln. Hence, a relatively short extraction time favors heavy Ln/Am separation.

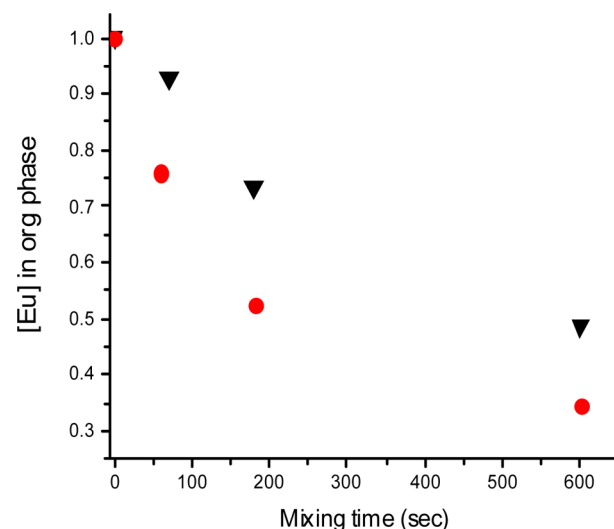
The distribution ratios for Nd and Pr are below 1, thus contaminating the Am stream. This issue can be easily overcome by increasing the volume ratio of the organic to the aqueous stream up to 3:1 or higher. The resulting extraction factor, E , for a single stage could be calculated as follows in eq 2:³³

$$E = RD \quad (2)$$

where D is the distribution ratio at equilibrium and R is the ratio of the flow rates of the organic and the aqueous phases.

In a separate set of experiments, we have tested concentrated solutions of DTPA for stripping Ln from the 0.05 M T2EHDGA/(0.75 M HEH[EHP]) organic phase. The lanthanides of the first tetrad (Ln through Nd) were stripped within 3 min of mixing time; their D values did not exceed 0.1. Europium has shown a much slower back-extraction rate, as can be seen in Figure 10.

Based on these preliminary results (Figure 10), it is interesting to note that at higher pH the concentration of free DTPA⁵⁻, responsible for Eu³⁺ complexation in the aqueous phase, is significantly higher than at pH 3.1; however, the Eu back-extraction is slower. The concentration of fully protonated citric acid, on the other hand, is higher at pH 3.1 than at pH 4.25 as its pK_{a1} is around 3.1.^{34,35} Therefore, one may conclude that the back-extraction rate depends on the concentration of citric acid as it probably facilitates Eu³⁺ transfer through the

**Figure 10.** Eu back-extraction kinetics: organic phase, 0.05 M T2EHDGA/(0.75 M HEH[EHP]); aqueous phase, (filled black down-triangles) pH 4.25, 0.24 M DTPA, 1.0 M citrate and (filled red circles) pH 3.1, 0.2 M DTPA, 0.8 M citrate.

interface. A similar role was proposed for lactic acid in the lactic acid/DTPA aqueous phase in TALSPEAK.³

CONCLUSION

In this work we describe the results of feasibility studies on the combined actinide–lanthanide separation process (ALSEP). We demonstrate that if the acidic extractant, HEH[EHP], is combined with either of the neutral extractants TODGA or T2EHDGA, an efficient extraction of minor actinides from the fission product stream can be achieved. Depending on the neutral extractant used, either complete or partial recovery of Ln can be accomplished in the step, as the T2EHDGA-containing solvent does not extract light Ln as efficiently as TODGA. Selective Am stripping with buffered DTPA solutions allows for a separation of the MA from the lanthanides with only several stages in a counter-count extraction process, with separation factors exceeding 30 for Nd/Am. Besides HEH[EHP], T2EHDGA can be combined with HDEHP, with Ln/Am separation factors of nearly 20 achievable. The only drawback of the latter system is that it demonstrates a steep pH

profile for Am stripping, similar to the one reported for TALSPEAK.

We also found that the TODGA–HDEHP solvent system does not possess sufficient selectivity for the Ln/Am separation at $[TODGA] = 0.025\text{ M}$ and $[HDEHP] = 1\text{ M}$ in *n*-dodecane.

No significant issues separating MA from the fission products have been observed so far. Zr extraction can be prevented by adding CDTA; otherwise it can be stripped from the organic phase by oxalic acid.

The radiation stability of ALSEP organic phase (either containing TODGA or T2EHDGA) and the effect of hydrolysis are to be determined in a separate study. Reports describing studies on the fission products' behavior and the cation organic speciation in ALSEP are to follow. Selection of an optimal ALSEP solvent formulation will be made after completion of all of these studies.

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Notes

The authors declare no competing financial interest.

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