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THE ACTINIDE-LANTHANIDE SEPARATION CONCEPT

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The Actinide-Lanthanide SEparation (ALSEP) concept is described. This concept is based on using an extractant phase consisting of either N,N,N',N'-tetraoctyldiglycolamide (TODGA) or N,N,N',N'-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) combined with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) to separate Am and Cm from lanthanide and other fission and activation products in a single solvent extraction cycle. The neutral TODGA or T2EHDGA serves to co-extract the trivalent actinide and lanthanide ions from nitric acid media. The distribution ratios for Am and the lanthanides increase with increasing nitric acid concentration. TODGA extracts these elements more strongly than T2EHDGA from nitric acid, but the weaker extracting ability of T2EHDGA could allow separation of Am from the light lanthanides during the extraction step. Switching the aqueous phase chemistry to a citrate-buffered diethylenetriaminepentaacetic acid (DTPA) solution at pH 2.5 to 4 results in selective transfer of the actinides to the aqueous phase, thus resulting in separation of these two groups of elements. Separation factors on the order of 20 to 40 can easily be achieved in the ALSEP systems.

Keywords: lanthanide separation, actinide separation, ALSEP, T2EHDGA, TODGA, HEH[EHP], PC88A

INTRODUCTION

In our laboratories we have been exploring the concept of combining a neutral donor extractant with an acidic extractant to form a hybrid solvent system that achieves extraction of trivalent actinide elements from dissolved irradiated nuclear fuel, and separation of these elements from the chemically similar trivalent lanthanides, in a single solvent extraction cycle.^[1–5] This work builds upon other recent investigations of combined solvent systems.^[6–7] The previous research involved combining (1) *N,N,N',N'*-tetrakis(2-methylpyridyl)-ethylenediamine (TPEN) with HDEHP in 1-octanol,^[8] (2) *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy-malonamide (DMDOHEMA) with di-*n*-hexylphosphoric acid (HDHP) or bis-(2-ethylhexyl)phosphoric acid (HDEHP) in an aliphatic diluent,^[9–11] and octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) plus HDEHP.^[12] We refer to the approach taken in our laboratories as the Actinide-Lanthanide SEparation

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(ALSEP) concept.^[13] Successfully developing such a process would constitute a significant advance in closing the nuclear fuel cycle. Isolation of the minor actinide elements (especially Am) would offer the possibility of transmuting them to shorter-lived or stable isotopes. This in turn would reduce the long-term radiotoxicity associated with geological disposition of irradiated nuclear fuel.^[14–15]

The premise of our approach has two aspects. First, the neutral donor extractant is capable of extracting the trivalent actinides and lanthanides from nitric acid solution (up to several mol/L HNO_3). Second, after switching the aqueous chemistry to a carboxylate buffer in the pH range of 3 to 4, a polyaminocarboxylate ligand can be used to selectively strip the trivalent actinides from the lipophilic solvent, while the acidic extractant holds the lanthanides in the organic phase. The co-extraction of actinides and lanthanides from HNO_3 has been established in processes such as the transuranic extraction (TRUEX) process^[16] or the diamide extraction (DIAMEX) process.^[17–18] The higher affinity of polyaminocarboxylate ligands for trivalent actinides compared to the trivalent lanthanides is the basis for the trivalent actinide-lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK) process.^[19] Typically, the minor actinide separation problem is approached using two different processes in tandem. For example, the TRUEX process can be implemented to isolate a mixture of actinides and lanthanides, and then the TALSPEAK process can be used to separate the actinides from the lanthanides.^[20] Combining these two functions into a single solvent extraction cycle would significantly simplify plant design and improve the economics.

Ideally for the approach described above to be effective, the neutral and acidic extractants should work independently, with minimal interaction between the two. Over the past several years a number of combinations of neutral and acidic extractants have been investigated, including

1. CMPO plus HDEHP,^[1–3]
2. CMPO plus 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]),^[4]
3. *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) plus HDEHP,
4. TODGA plus HEH[EHP],
5. *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (T2EHDGA) plus HDEHP,^[21–22] and
6. T2EHDGA plus HEH[EHP].

To some extent, all of these extractant combinations could form the basis of an ALSEP process. But the CMPO/HDEHP combination is complicated by strong interaction between CMPO and HDEHP, and synergic extraction of Am that lowers the lanthanide/actinide separation factor compared to the TALSPEAK process. These effects are reduced in the CMPO/HEH[EHP] combination, but interaction between CMPO and HEH[EHP] does influence the extraction chemistry. Our recent efforts have focused on combining either TODGA or T2EHDGA with HEH[EHP]. These two combinations offer advantages over the other combinations in that the lanthanide and actinide distribution ratios increase with increasing HNO_3 concentration, and the actinide stripping behavior is less sensitive to changes in the pH. The TODGA or T2EHDGA appear to act independently from the HEH[EHP] leading to improved characteristics compared to systems containing CMPO. In this paper we describe the process chemistry for the TODGA/HEH[EHP] and T2EHDGA/HEH[EHP] systems. Figure 1 provides chemical structures for the various compounds relevant to the ALSEP concept.

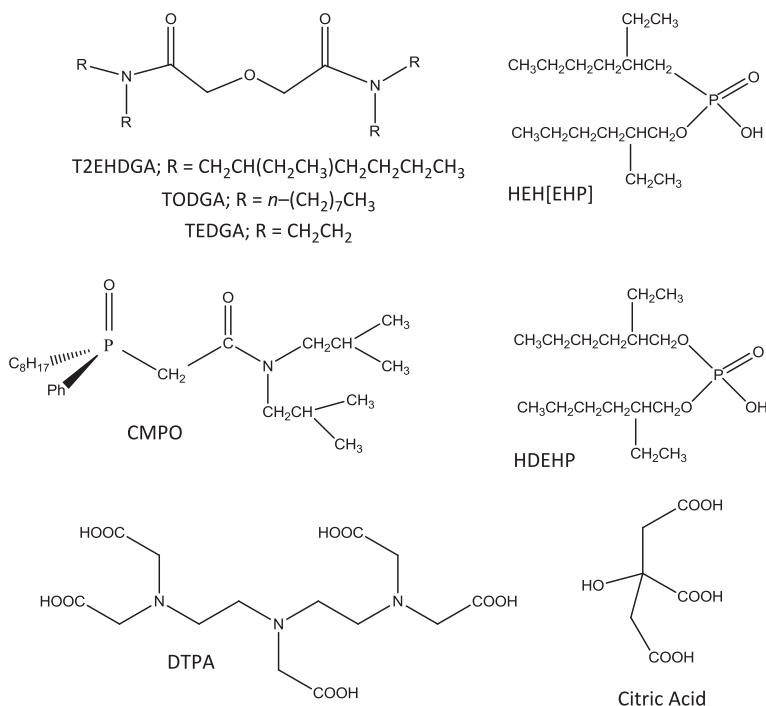


Figure 1 Chemical structures of the compounds used in this study.

EXPERIMENTAL

Materials

TODGA and T2EHDGA were procured from Eichrom Technologies (Lisle, Illinois); they were used as received. HEH[EHP] was obtained from Yick-Vic Pharmaceuticals Ltd (Hong Kong) and was purified by the method described by Hu et al.^[23] Normal dodecane was obtained from Alfa Aesar (Ward Hill, Massachusetts), diethylenetriaminepentaacetic acid (DTPA) was purchased from Alfa Products (Danvers, Massachusetts), citric acid was procured from Mallinckrodt (St. Louis, Missouri), and *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) was obtained from Technochem Ltd (Falkland, Scotland, UK). The latter four compounds were used as received. The ²⁴¹Am tracer solution was obtained from Isotope Products Laboratories (Valencia, California).

Distribution Measurements

The starting aqueous solutions used for the extraction experiments typically contained between 0.1 and 5 mmol/L of each element, except for Fe, which typically was 0.02 to 0.06 mmol/L (Fe was included at lower concentrations reflecting what might be expected in a dissolved nuclear fuel solution). Equal volumes of aqueous and organic phases were mixed with either a vortex mixer or with a combination of a vortex mixer followed by a wrist-action shaker. The experiments were performed at ambient temperature (nominally 21 to 23°C). Extended mixing times (3 h) were shown to result in only minor

($\sim 0.5^{\circ}\text{C}$) increases in temperature. The specific mixing conditions used for each data set are given in the respective figure captions. Except for the extraction kinetics data presented, all distribution ratios reported were determined at equilibrium conditions. For the kinetics experiment, the aqueous and organic phases were mixed using a vortex mixer set at 1900 rpm. Aliquots of the aqueous phase were taken for inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis at cumulative mixing times of 1, 5, 15, and 30 min. Corresponding proportions of the organic phase were also removed during the sampling events to keep the organic-to-aqueous phase ratio equal to 1. After 30 min of mixing, the aqueous phase was analyzed by potentiometric titration with NaOH to determine the HNO_3 concentration. Parallel measurements were made under identical conditions, but with the solutions spiked with the ^{241}Am tracer solution. In the latter case, aliquots of both phases were taken for analysis by gamma spectroscopy at cumulative mixing times of 1, 15, and 30 min. After mixing, the two phases were separated by centrifugation. The Am distribution ratios were determined by sampling both the aqueous and organic phases and measuring the relative activity in each phase using an automated gamma counter equipped with a NaI(Tl) detector. The Am distribution ratio was calculated as the gamma activity in the organic phase divided by that in the aqueous phase. To determine the distribution ratios for nonradioactive elements, the aqueous phase was sampled before and after contacting. The aqueous phase aliquots were diluted into a HCl matrix and analyzed by ICP-OES using a Perkin Elmer ICP-OES Optima 7300DV operated with WinLab32 software. The detection limits were estimated to be in the range of 0.001 to 0.04 mmol/L, depending on the dilution factor used and the element in question. The organic-phase concentration for each element was calculated as the difference between the initial and final aqueous phase concentrations. Unless otherwise noted, distribution measurements were made for multiple elements simultaneously by using solutions containing a mixture of elements (typically La, Ce, Pr, Nd, Sm, Eu, Gd, Y, Zr, Mo, Ru, and Fe; and in some cases Pd).

Proof-of-Principle Experiment

To prove the principle, an experiment was conducted using an ALSEP solvent formulation of 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] in *n*-dodecane, and a simulated acidic high-level waste (HLW) solution (Table 1). A series of batch contacts were performed to represent the following ALSEP steps: extraction, nitric acid scrubbing, citrate scrubbing to remove Mo from the solvent, minor actinide stripping, lanthanide stripping, and Zr stripping (Table 2). For the extraction step, 48 mL of 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] in *n*-dodecane was contacted with 48 mL of the aqueous feed by vortex mixing for 1 min followed by shaking on an orbital shaker at 300 rpm for 15 min. After centrifuging to separate the phases, 26 mL of the loaded organic phase was subjected to the series of batch contacts listed in Table 2. The 0.25 mol/L TEDGA/1.0 mol/L HNO_3 solution was used within 1 day of its initial preparation to minimize any acidic decomposition of the TEDGA. Another 14-mL portion of the loaded organic phase was spiked with ^{241}Am and subjected to a parallel series of batch contacts with organic-to-aqueous phase ratios the same as those listed in Table 2. For the extraction contact, the distribution ratios for the nonradioactive components were determined by measuring the component concentration in the aqueous phase before and after contact. The organic phase concentration was calculated as the difference between the concentrations before and after contact. For the subsequent contacts, the distribution ratios were determined using the organic phase

Table 1 Composition of the feed solution for the ALSEP proof-of-principle experiment.

Component	Conc. (mmol/L)
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 , M	2.56

concentrations calculated from the previous contact and the analysis of the aqueous phase; again, the equilibrium organic phase concentration was deduced by assuming a 100% mass balance. A separate small portion of the feed solution was spiked with ²⁴¹Am and contacted with an equal volume of 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] in *n*-dodecane to determine the Am distribution ratio for the extraction step. The Am distribution ratios were calculated as the relative activity in the organic phase divided by that in the aqueous phase.

RESULTS AND DISCUSSION

Kinetics of Extraction from Nitric Acid

To establish the experimental conditions necessary to attain equilibrium in the extraction contacts, a series of experiments was performed in which HNO₃ solutions containing La, Ce, Pr, Nd, Sm, Eu, Gd, Y, Zr, Mo, and Fe (Table 3) were contacted with 0.05 mol/L T2EHDGA + 1.0 mol/L HEH[EHP] dissolved in *n*-dodecane, and the distribution ratios were determined as a function of time. Figure 2 presents the results obtained for when the aqueous phase contained 3.5 mol/L HNO₃. Similar trends were observed at 1.4 and 5.2 mol/L HNO₃. Equilibrium was reached within 5 min of vortex mixing for the trivalent lanthanides and Am. Yttrium(III) behaved similarly. The extraction kinetics for Mo(VI) and Fe(III) were noticeably slower. Shorter residence times could be used to improve the separation of these elements from Am. The DGA-type extractants are not known to strongly extract Mo(VI),^[24] so it can be surmised that HEH[EHP] is mainly responsible for the strong extraction of Mo(VI) in the ALSEP solvent system. The Zr(IV) extraction kinetics could not be fully characterized because this element is extracted so strongly that it could not be detected in the aqueous phase after the 5-min contact point; the distribution ratio for Zr(IV) is greater than 3700 under these conditions. On the other hand, the Ru(III) distribution ratios were too low to be accurately determined by the ICP-OES technique used (the final measured Ru concentration values in the aqueous phase were actually slightly higher than those measured before the contact was performed).

Table 2 Contacts performed during the ALSEP proof-of-principle experiment*.

Process Step	Aqueous Phase	Aqueous Phase Vol. (mL)	Organic Phase	Organic Phase Vol. (mL)
Extraction	Feed (Table 1)	48	0.075 mol/L TODGA/1.0 mol/L HEH[EHP]	48
Nitric acid scrub (1)	2.5 mol/L HNO ₃	13	Organic from extraction	26
Nitric acid scrub (2)	2.5 mol/L HNO ₃	12	Organic from nitric acid scrub (1)	24
Citrate scrub (1)	0.2 mol/L citrate, pH 3	11	Organic from nitric acid scrub (2)	22
Citrate scrub (2)	0.2 mol/L citrate, pH 3	10	Organic from citrate scrub (1)	20
Minor actinide strip (1)	0.02 mol/L DTPA+0.2 mol/L citrate at pH 3	9	Organic from citrate scrub (2)	9
Minor actinide strip (2)	0.02 mol/L DTPA+0.2 mol/L citrate at pH 3	8	Organic from minor actinide strip (1)	8
Minor actinide strip (3)	0.02 mol/L DTPA+0.2 mol/L citrate at pH 3	7	Organic from minor actinide strip (2)	7
Lanthanide strip (1)	0.25 mol/L TEDGA+1.0 mol/L HNO ₃	6	Organic from minor actinide strip (3)	6
Lanthanide strip (2)	0.25 mol/L TEDGA+1.0 mol/L HNO ₃	5	Organic from lanthanide strip (1)	5
Lanthanide strip (3)	0.25 mol/L TEDGA+1.0 mol/L HNO ₃	4	Organic from lanthanide strip (2)	4
Zirconium strip (1)	0.5 mol/L H ₂ C ₂ O ₄	3	Organic from lanthanide strip (3)	3
Zirconium strip (2)	0.5 mol/L H ₂ C ₂ O ₄	2	Organic from zirconium strip (1)	2
Zirconium strip (3)	0.5 mol/L H ₂ C ₂ O ₄	1	Organic from zirconium strip (2)	1

*This table describes the nonradioactive contacts that were performed. A parallel set of contacts was performed in which 14 mL of the organic phase from the extraction contact was spiked with ²⁴¹Am and then subjected to the various scrubbing and stripping steps.

Table 3 Average composition of the initial aqueous phase in the extraction contacts performed to determine the extraction kinetics for the 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP]*n*-dodecane ALSEP solvent.

Component	Conc. (mmol/L)	Component	Conc. (mmol/L)
La	3.58	Gd	0.77
Ce	4.49	Y	2.33
Pr	1.17	Zr	2.02
Nd	5.70	Mo	1.41
Sm	2.58	Ru	4.63
Eu	0.55	Fe	0.04

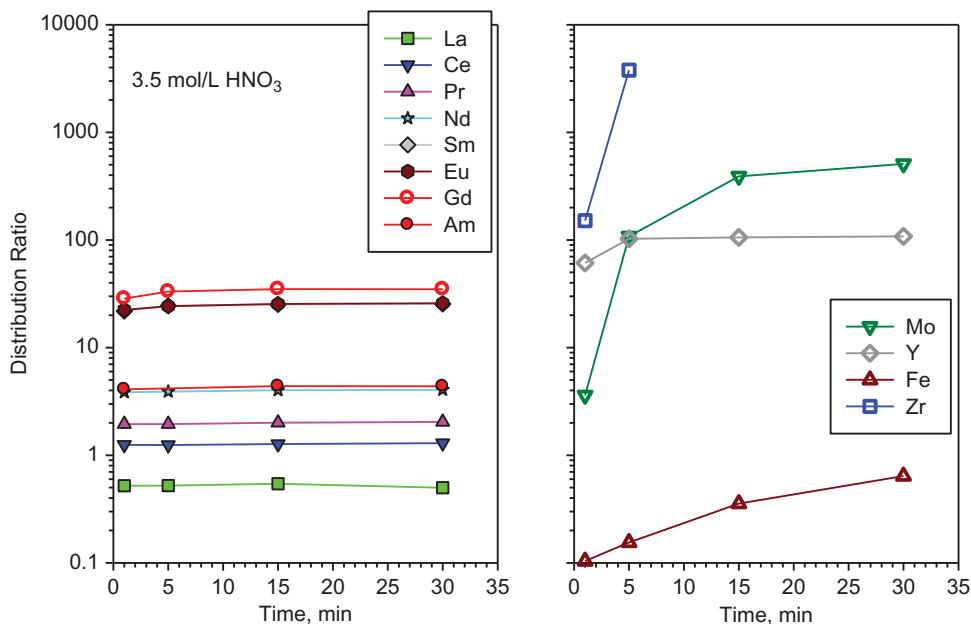


Figure 2 Distribution ratios as a function of time for the extraction of various elements from 3.5 mol/L HNO₃ (or 3.8 mol/L HNO₃ for the Am data) by 0.05 mol/L T2EHDGA + 1.0 mol/L HEH[EHP] in *n*-dodecane; contacting method: vortex mixing.

Extraction as a Function of HNO₃ Concentration

Figure 3 shows the distribution ratios for Am and the lanthanides, along with Y and Pd, as a function of the HNO₃ concentration for extraction into 0.075 mol/L T2EHDGA + 1.0 mol/L HEH[EHP] and 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP]. The data indicate that T2EHDGA is a somewhat weaker extractant than TODGA. For both solvent formulations, the Am and the lanthanide distribution ratios increase with increasing HNO₃ concentration. This trend is consistent with previous studies of trivalent actinides and lanthanides extraction with TODGA.^[16–17] Maintaining high distribution ratios at several molar HNO₃ is a desirable feature of the T2EHDGA and TODGA extractants. Previous ALSEP formulations using CMPO as the neutral extractant showed decreased Am and lanthanide distribution ratios with increasing nitric acid concentration, which limited the useful HNO₃ concentration range in which these solvents are effective.^[1–4]

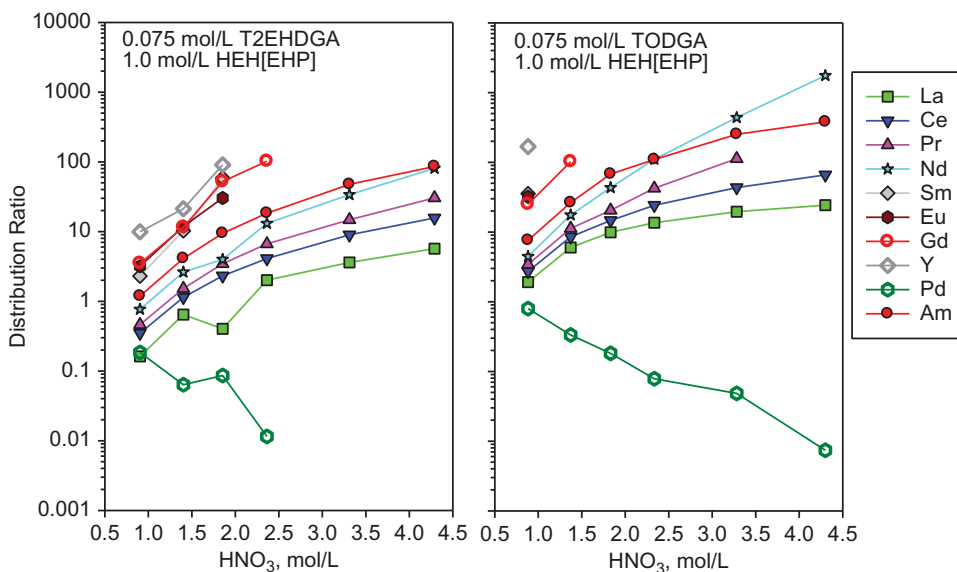


Figure 3 Distribution ratios as a function of HNO₃ concentration for the extraction of various elements by 0.075 mol/L T2EHDGA (left) or 0.075 mol/L TODGA (right) + 1.0 mol/L HEH[EHP] in *n*-dodecane; contacting method: 1-min vortex mixing followed by 60-min mixing on a wrist-action shaker.

Zirconium(IV) and Mo(VI) were quantitatively extracted into the 0.075 mol/L T2EHDGA + 1.0 mol/L HEH[EHP] and 0.075 mol/L TODGA + 1.0 mol/L HEH[EHP] solvents. Molybdenum(VI) can be removed from the solvent by scrubbing with a citrate buffer before implementing the minor actinide stripping step. For example, when a loaded ALSEP solvent consisting of 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in *n*-dodecane is contacted with 0.2 mol/L citrate solution, the Mo distribution ratios are ~ 0.2 in the range pH 3.3 to 4.0. As previously described, Zr(IV) can be removed from the solvent after the minor actinide stripping step by first contacting the solvent with an acidic solution of TEDGA to remove the lanthanides, and then contacting with oxalic acid to remove the Zr.^[25] As was previously observed, the Ru(III) distribution ratios were too low to be accurately determined. Figure 3 indicates that Pd(II) is weakly extracted at 1.0 mol/L HNO₃ and the distribution ratio for this element decreases with increasing HNO₃ concentration. Therefore, scrubbing of Ru(III) and Pd(II) from the ALSEP solvent should be feasible.

The solvent formulations used to collect the data in Figs. 2 and 3 were not necessarily optimized. Based on examinations with various extractant concentrations, we have chosen 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in *n*-dodecane as the reference ALSEP solvent formulation for further process development. Figure 4 shows the dependency of the distribution ratios for Am, Y, and selected lanthanide elements on the HNO₃ concentration. Again, the distribution ratios increase with increasing HNO₃ concentration for this formulation of the ALSEP solvent. A particularly interesting feature of this system is that the lanthanum distribution ratio is less than 1 over most of the HNO₃ concentration range examined. This offers the possibility of separating La from Am in the extraction step. Substantial separation of Am from Ce and Pr might also be achieved in this manner. As expected based on the previous experiment, Zr(IV) and Mo(VI) were strongly extracted into 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] at all nitric acid concentrations

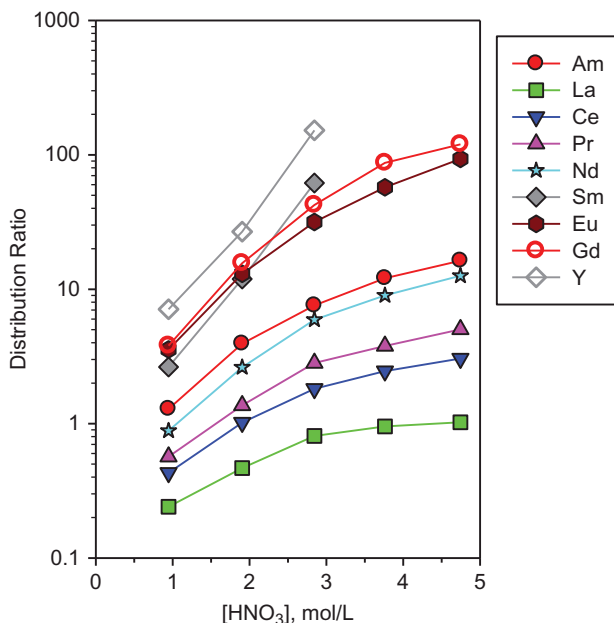


Figure 4 Distribution ratios as a function of HNO_3 concentration for the extraction of various elements by 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] in *n*-dodecane; contacting method: 15-min vortex mixing.

examined, but no extraction of Ru(III) was observed. The Fe(III) distribution ratios were less than 1 except for $[\text{HNO}_3] = 2.85$, at which $D_{\text{Fe}} = 5.4$, and $[\text{HNO}_3] = 3.76$, at which $D_{\text{Fe}} = 1.05$. There is significant uncertainty in the Fe distribution ratios resulting from the low initial concentrations for this element in these experiments. Further investigation of the behavior of Fe(III) in the ALSEP solvent system is required to develop appropriate strategies to prevent this element from contaminating the minor actinide product.

Lanthanide/Americium Separation

The selective stripping of Am from the lanthanide- and Am-loaded 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP]/*n*-dodecane ALSEP solvent was investigated using 0.015 mol/L DTPA + 0.2 mol/L citrate as the stripping solution. Figure 5a presents the measured distribution ratios as a function of the aqueous solution pH at equilibrium. Except for La, the lanthanide distribution ratios decrease as the pH increases from 1.7 to 2.9. Above pH 2.9, the lanthanide distribution ratios tend to increase slightly. Lanthanum behaves differently in that the La distribution ratio increases with increasing pH throughout the pH range examined. This is perhaps due to increased competition of the higher lanthanides for DTPA as the pH increases, leaving La(III) more prone to extraction by HEH[EHP]. The Am distribution ratios decrease with increasing pH until a minimum at approximately pH 3.4, then the Am distribution ratios increase slightly with increasing pH. The minimum lanthanide/amerium separation factor achieved does not vary much above pH 2.9, with the separation factor being on the order of 30 (Fig. 5a).

Around pH = 3, the Nd distribution ratios were only slightly greater than 1 when 0.015 mol/L DTPA + 0.2 mol/L citrate was the stripping solution. To increase the D_{Nd}

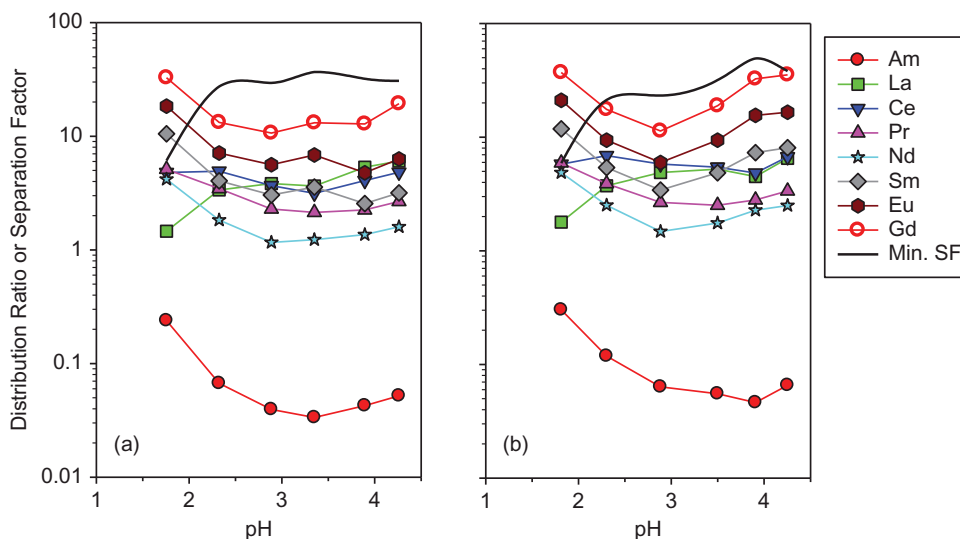


Figure 5 Distribution ratios as a function of pH for the back-extraction of various elements from an *n*-dodecane solution of 0.05 mol/L T2EHDGA + 0.75 mol/L HEH[EHP] into aqueous a) 0.015 mol/L DTPA + 0.2 mol/L citrate and b) 0.010 mol/L DTPA + 0.2 mol/L citrate; contacting method: 30-min vortex mixing.

values in the minor actinide-stripping step, the DTPA concentration in the aqueous phase was decreased to 0.010 mol/L (Fig. 5b). This resulted in higher Nd distribution ratios, especially in the pH 3.5 to 4.3 range. The Nd/Am separation factors were also slightly improved in this pH range when the DTPA concentration was decreased to 0.010 mol/L.

ALSEP Proof-of-Principle Experiment

Table 4 presents the distribution ratios of each element for each process step in the ALSEP proof-of-principle experiment. Efficient extraction of all the lanthanides was achieved, and the distribution ratios exceeded 20. The distribution ratios for the lanthanides generally increased with increasing atomic number, as would be expected based on the increase in the charge-to-size ratios for these ions. Like the lanthanides, Am was efficiently extracted, with $D_{Am} \sim 200$. These results were consistent with the distribution data shown in Fig. 3. Also, as expected based on the results described above, Zr and Mo were extracted into the TODGA/HEH[EHP] solvent, and the distribution ratios exceeded 1000. Distribution ratios for Fe, Ru, and Pd were all less than 1 in the extraction contact, but they increased in the scrubbing and stripping steps, which will need to be considered during flowsheet design. The Pd result is particularly puzzling given the decline in Pd distribution ratios with increasing HNO_3 concentration for extraction by the ALSEP solvents (Fig. 3). The observed trend suggests there might be extractable chemical forms of Fe, Ru, and Pd that become dominant as the non-extractable forms are removed from the solvent by nitric acid scrubbing.

The lanthanide distribution ratios remained well above 1 throughout the nitric acid scrubbing, citrate scrubbing, and minor actinide stripping steps. The Am distribution ratio was ~ 0.6 in the first minor actinide stripping contact, but dropped to 0.2 for the second and third minor actinide stripping contacts. The minimum separation factor that was achieved

Table 4 Component distribution ratios.*

Process Step	La	Ce	Pr	Nd	Sm	Eu	Gd	Y	Zr	Mo	Ru	Pd	Fe	Am
Extraction	21.2	41.5	72.0	179	Large	1609	Large	Large	1794	1257	0.22	0.23	0.61	203
Nitric acid scrub (1)	14.8	28.5	43.7	119	669	1910	1032	Large	21287	922	45.8	4.46	53.3	59.7
Nitric acid scrub (2)	17.7	33.9	52.5	145	723	2307	1821	Large	Large	1440	239	16.1	98.3	114
Citrate scrub (1)	5.35	9.96	11.1	13.5	32.4	59.9	82.4	Large	Large	13.2	848	71.8	448	11.0
Citrate scrub (2)	1299	1524	1231	1563	5502	7121	1408	Large	1551	0.26	1304	92.0	1178	144
Minor actinide strip (1)	87.0	36.2	15.6	5.61	6.51	9.97	18.1	Large	Large	Small	1064	14.0	69.8	0.59
Minor actinide strip (2)	62.5	28.1	12.4	4.70	5.51	8.51	15.6	Large	Large	NA	1723	31.6	69.2	0.22
Minor actinide strip (3)	102	39.8	17.1	6.87	10.4	18.7	37.2	Large	100.2	NA	9137	32.0	61.6	0.22
Lanthanide strip (1)	Small	Small	Small	Small	Small	Small	Small	Small	143.4	NA	1260	5.25	74.0	Small
Lanthanide strip (2)	NA	NA	NA	270	NA	NA	NA	NA	105.9	NA	2579	68.5	405	NA
Lanthanide strip (3)	NA	NA	NA	Large?	NA	NA	NA	NA	687189	NA	9412	59.5	997	NA
Zirconium strip (1)	NA	NA	NA	84	NA	NA	NA	NA	0.022	NA	Large	142	0.38	NA
Zirconium strip (2)	NA	NA	NA	3751	NA	NA	NA	NA	1.93	NA	6674	54.6	4.02	NA
Zirconium strip (3)	NA	NA	NA	Large?	NA	NA	NA	NA	9.29	NA	1876	77.4	3.54	NA

**"Large" indicates that the concentration in the aqueous phase was below the analytical detection limit. "Small" indicates that the component was essentially completely distributed to the aqueous phase. Fields marked as NA are not applicable because the component was completely removed from the solvent in a previous step.

in the first minor actinide stripping contact was for Nd, with the Nd/Am separation factor equal to 9.5. The Nd/Am separation factor increased to 22 and 31 in the second and third minor actinide stripping contacts, respectively.

The lanthanides were essentially quantitatively stripped in one contact with 0.25 mol/L TEDGA in 1.0 mol/L nitric acid, consistent with our previous observations.^[25] The Nd distribution ratios appeared to increase in subsequent stripping contacts, but this was probably an artifact of experimental uncertainty resulting from the low residual Nd concentration, rather than a real phenomenon. Zirconium was efficiently stripped in a single contact with 0.5 mol/L $\text{H}_2\text{C}_2\text{O}_4$. Like Nd during lanthanide stripping, the Zr distribution ratios appeared to increase with subsequent oxalic acid stripping steps, but again, this is can probably be attributed to experimental uncertainty.

Table 5 presents the mass balance for the nonradioactive components in the simulated HLW solution. Mass recoveries were generally excellent, especially for the lanthanides and Zr. This table also illustrates that the various components were directed to the desired process stream. For example, most of the mass of the lanthanide elements appeared in the aqueous phase from the first lanthanide stripping step and most of the Zr appeared in the aqueous phase from the first Zr stripping step. An exception is Mo, which was not efficiently removed from the solvent in the first citrate scrub step, as was desired. Molybdenum was distributed mostly between the second citrate scrub and the first minor actinides stripping step. This situation can be corrected by increasing the initial pH of the citrate scrubbing solution so that there is sufficient buffering capacity to neutralize nitric acid in the loaded solvent.

This experiment demonstrates the feasibility of the ALSEP concept. It shows that (1) the minor actinides and the lanthanides can be co-extracted from nitric acid media, (2) the minor actinides can be separated from the lanthanides by selective stripping with a polyaminocarboxylate ligand, (3) the lanthanides can be stripped from the solvent with TEDGA and nitric acid, and (4) Zr can be stripped with oxalic acid. Some optimization is still needed. For example, the scrubbing steps will need to be optimized to make sure that Mo does not contaminate the minor actinide product. However, these adjustments to the process chemistry should be relatively minor.

CONCLUSION

The basic aspects of the ALSEP concept have been described. The trivalent lanthanides and actinides can be co-extracted from HNO_3 solution, primarily through the action of the diglycolamide extractant (T2EHDGA or TODGA). The actinides can be selectively stripped into a citrate-buffered DTPA solution, and the acidic HEH[EHP] extractant keeps the lanthanides in organic phase. The solvent can be regenerated by first contacting with an acidic TEDGA solution to remove the lanthanides, then by contacting with oxalic acid to remove the Zr. This approach offers a one-cycle means of separating and recovering Am and Cm from acidic HLW solutions.

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Table 5 Nonradioactive component mass balance.

Process Step	Relative Mass of Each Component in the Aqueous Phase													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Y	Zr	Mo	Ru	Pd	Fe	
Extraction	In	189.18	365.22	97.72	529.96	138.74	32.34	37.78	60.65	94.57	87.29	357.62	151.25	5.96
	Out	8.50	8.60	1.34	2.95	0.00	0.02	0.00	0.00	0.05	0.07	293.82	122.90	3.71
Nitric acid scrub (1)	Out	5.90	6.15	1.09	2.20	0.11	0.01	0.02	0.00	0.00	0.05	0.69	2.86	0.02
Nitric acid scrub (2)	Out	4.81	5.09	0.90	1.80	0.10	0.01	0.01	0.00	0.00	0.03	0.13	0.77	0.01
Citrate scrub (1)	Out	14.53	17.33	4.23	19.32	2.26	0.27	0.23	0.00	0.00	2.00	0.04	0.17	0.00
Citrate scrub (2)	Out	0.06	0.11	0.04	0.17	0.01	0.00	0.01	0.00	0.03	34.66	0.02	0.13	0.00
Minor actinide strip (1)	Out	1.77	9.28	5.69	79.09	19.48	2.95	1.98	0.00	0.00	33.72	0.06	1.63	0.03
Minor actinide strip (2)	Out	2.42	11.55	6.61	77.77	19.48	3.09	2.15	0.00	0.00	8.64	0.04	0.70	0.03
Minor actinide strip (3)	Out	1.46	7.96	4.53	46.46	9.37	1.33	0.88	0.00	0.93	1.21	0.01	0.67	0.03
Lanthanide strip (1)	Out	163.06	324.62	79.38	307.69	103.50	26.05	34.62	67.78	0.65	0.28	0.05	3.43	0.03
Lanthanide strip (2)	Out	0.09	0.08	0.02	0.04	0.01	0.00	0.03	0.01	0.87	0.01	0.02	0.26	0.01
Lanthanide strip (3)	Out	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03	0.01	0.29	0.00
Zirconium strip (1)	Out	0.00	0.07	0.00	0.14	0.00	0.01	0.00	0.03	90.15	1.06	0.00	0.12	1.51
Zirconium strip (2)	Out	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.68	0.19	0.01	0.31	0.11
Zirconium strip (3)	Out	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03	0.13	0.11	0.03	0.22	0.10
Total Out		202.60	390.84	103.82	537.63	154.34	33.74	39.95	67.87	93.49	82.05	294.92	134.46	5.60
Mass Recovery		107%	107%	106%	101%	111%	104%	106%	112%	98.9%	94.0%	82.5%	88.9%	94.0%

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