An Advanced TALSPEAK Concept for Separating Minor Actinides. Part 1. Process Optimization and Flowsheet Development

Gregg J. Lumetta,[1] Tatiana G. Levitskaia,[1] Andreas Wilden,[2] Amanda J. Casella,[1] Gabriel B. Hall,[1] Leigh Lin,[1,3] Sergey I. Sinkov,[1] Jack Law,[4] Giuseppe Modolo[2]

[1]Pacific Northwest National Laboratory, PO Box 999, MSIN P7-25, Richland, Washington 99352 USA

[2]Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung – Nukleare Entsorgung und Reaktorsicherheit (IEK-6), Jülich, Germany

[3]Current address: Defense Nuclear Facilities Safety Board, Washington, DC, USA

[4]Aqueous Separations and Radiochemistry Department, Idaho National Laboratory, Idaho Falls, Idaho, USA

Corresponding author E-mail: gregg.lumetta@pnnl.gov

An Advanced TALSPEAK Concept for Separating Minor Actinides. Part 1. Process Optimization and Flowsheet Development

ABSTRACT

A solvent extraction system was developed for separating trivalent actinides from lanthanides. This "Advanced TALSPEAK" system uses 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester to extract the lanthanides into an *n*-dodecane-based solvent; the actinides are retained in a citrate-buffered aqueous phase by complexation to a polyaminocarboxylate ligand. Several aqueous phase ligands were investigated, and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid was chosen for further study. Batch distribution measurements indicate that the separation of americium from the light lanthanides increases as the pH increases. However, previous investigations indicated that the extraction rates for the heavier lanthanides decrease with increasing pH. So, a balance between these competing effects is required. An aqueous phase at pH 2.6 was chosen for further process development because this offered optimal separation. Centrifugal contactor single-stage efficiencies were measured to characterize the system's performance under flow conditions, and an Advanced TALSPEAK flowsheet was designed.

KEYWORDS: lanthanide separation, actinide separation, TALSPEAK, HEH[EHP], PC88A

RUNNING HEAD TITLE: Advanced TALSPEAK Concept

INTRODUCTION

The separation of the minor actinide (MA) elements americium (Am) and curium (Cm) from used nuclear fuel has been the subject of extensive study worldwide over the last two decades.[1-3] The primary motivations behind this effort are to 1) lower the heat loading in geological repositories so that space can be optimized and 2) reduce the long-term radiotoxicity of the material disposed in the repositories.[4-6] These goals can be achieved by transmutation of the minor actinides to shorter-lived or stable isotopes in fast neutron reactors. One of the major technical challenges in this regard is separating the trivalent MA elements from the lanthanide (Ln) fission products. Separating these two groups of elements is desirable because of the high neutron capture cross sections of many Ln isotopes. More-efficient utilization of neutrons can be realized in the transmutation of the MA elements by nuclear fission if the Ln elements are not present. However, separating the MA and Ln elements is difficult because they both are predominantly trivalent and have similar ionic radii.[7-9]

Two general approaches have been investigated for separating the MA elements from used nuclear fuel. Both approaches assume an initial separation of uranium, plutonium, and in most cases neptunium, from the HNO_3-dissolved irradiated fuel by extraction with tri-butyl phosphate, resulting in a highly radioactive HNO_3 solution [high activity (HA) raffinate] containing most of the fission products and the MA. One approach involves first separating the MA and Ln elements together from the HA raffinate, and then implementing a second process to separate the MA elements from the Ln elements. The second approach seeks to separate the MA from the HA raffinate (including separation from the Ln elements) in a single process. Although progress has been made regarding the latter approach,[10-15] the two-step approach might be more industrially robust given the current state of the technology.

The most well developed processes for separating the MA and Ln elements as a group are the DIAMide EXtraction (DIAMEX)[16-18] and TRansUranic EXtraction (TRUEX)[19] processes. The Selective ActiNide EXtraction (SANEX) concept has been extensively pursued in Europe for separating the MA elements from the Ln elements.[20] In the SANEX approach, lipophilic ligands containing N- or S-donor ligands[21-22] are used to selectively extract the MA elements from an HNO_3 solution containing the MA/Ln mixture.[23] An alternative approach is the Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes (TALSPEAK) process.[24-26] In this case, the Ln elements are selectively extracted using di-(2-ethylhexyl)phosphoric acid (HDEHP), while the MA are held in the aqueous phase by complexation to a polyaminocarboxylate ligand such as diethylenetriaminepentaacetic acid (DTPA).

More recently, a modification to the TALSPEAK concept has been investigated.[27-28] The primary advantage of the modified process, the Advanced TALSPEAK system, compared to the conventional TALSPEAK process is that it is not highly sensitive to changes in the pH, making it a more attractive option for industrial application. In this Advanced TALSPEAK system, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]; Figure 1) is used as the Ln extractant and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA; Figure 1) is used as the actinide holdback complexant. The aqueous phase is buffered with citrate ion to maintain the proper pH. However, single-stage efficiency tests conducted using a 2-cm centrifugal contactor revealed that low extraction rates for Sm, Eu, and Gd in the previously reported Advanced TALSPEAK system compromise the actinide/lanthanide separation factors achievable in such contactors.[28]

This paper reports on investigations conducted to improve the extraction rates in the Advanced TALSPEAK system to meet the requirements of centrifugal contactor separation systems. Two approaches are considered: (i) optimizing the citrate buffer performance by varying its concentration and the solution pH using HEDTA as the MA holdback complexant, and (ii) replacing HEDTA with an alternative holdback complexant. The former approach produced an optimized Advanced TALSPEAK system that was further tested in single-stage centrifugal contactor experiments. Based on the effective single-stage distribution ratios, an Advanced TALSPEAK flowsheet was developed, which is describe in this paper. Testing of the flowsheet using a simulated dissolved nuclear fuel solution is reported in part 2 of this series of papers.[29]

EXPERIMENTAL

Experimental work was conducted both at the Pacific Northwest National Laboratory (PNNL) and at Forschungszentrum (FZ) Jülich GmbH, Germany. Significant differences in the materials and methods used at these two institutions are indicated in the experimental description below.

Materials

For the batch contact experiments performed to optimize the aqueous phase composition, the HEH[EHP] used was obtained from Yick-Vic Pharmaceuticals Ltd. (Hong Kong) and purified by the method described by Hu et al.[30] The HEH[EHP] used in the batch contact and dynamic flow experiments that used aqueous phases containing mixed lanthanides and Am^{3+} was obtained from BOC Sciences and used as received. Normal dodecane was obtained from Alfa Aesar or from Sigma-Aldrich. HEDTA was purchased from Sigma or Acros Organics, and citric acid was procured from Mallinckrodt or Acros Organics. *N*-(2-hydroxyethyl)iminodiacetic acid (HIDA), nitrilotriacetic acid (NTA), 1,3-diaminopropane-*N,N,N′,N′*-tetraacetic acid (DPTA), and 1,3-diamino-2-hydroxypropane-*N,N,N′,N′*-tetraacetic acid (HDPTA) were purchased from Sigma. Unless otherwise noted, these chemicals were used as received.

The ^{241}Am tracer solution was obtained from Isotope Products Laboratories (Valencia, California) or from Isotopendienst M. Blaseg GmbH, Waldburg, Germany. The ^{152}Eu isotope was supplied by Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany. The ^{244}Cm was purchased from Oak Ridge National Laboratory, USA. The stock lanthanide solutions (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+}) were prepared using corresponding nitrate salts obtained from a number of different commercial sources. All aqueous solutions were prepared with distilled water deionized to ≥15 MΩ-cm with a Barnstead Nanopure or ELGA Purelab Ultra water purification system.

Distribution Measurements

Eu and Am Batch Contact Distribution Measurements

To evaluate the extraction kinetics, equal volumes of aqueous and organic solutions were contacted at room temperature (20 ± 2 °C) using a Fisher Scientific heavy-duty vortex mixer set at 1900 rpm, and sampled at several time points between 2 s and 30 min of agitation. Solution heating during 30-min vortexing was found to be negligible. After mixing, the two phases were separated by centrifugation. This mixing protocol was selected to enable extrapolation of the batch contact distribution data to the conditions of the 2-cm centrifugal contactors. In our previous work, the vortex mixing time that yields extraction performance equivalent to that of the 2-cm contactor was determined to be 20.6 ± 2.4 s.[28] The MA or Ln metal ion (M^{3+}) distribution ratio (D_M) is defined as the organic M^{3+} concentration divided by its aqueous concentration.

In the variable holdback reagent experiments, the Advanced TALSPEAK extraction kinetics was evaluated using aqueous-phase solutions containing 0.125 mol/L complexant (HEDTA, NTA, HIDA, DPTA, or HDPTA), 0.2 mol/L citrate, and 16 mmol/L $Eu(NO_3)_3$ with or without the presence of ^{241}Am tracer at a pH of 3.0–3.25. In these experiments, the organic phase consisted of 1 mol/L HEH[EHP] in *n*-dodecane. The pH of the aqueous solutions was measured using an Orion 525A+ pH meter and Orion 8272BN pH probes. The calibration was done using pH 4.00 and 7.00 buffer solutions, traceable to National Institute of Standards and Technology standards. The ^{241}Am distribution ratios (D_{Am}) were determined as the ratio of the background-corrected relative gamma activities in the organic and aqueous phases measured using an automated gamma counter equipped with a NaI(Tl) detector (Packard Cobra Quantum Model 5003). To determine D_{Eu}, the Eu^{3+} extraction was monitored spectrophotometrically by measuring the relative Eu^{3+} concentration in the aqueous phase using the Eu^{3+} absorbance peak at 394–396 nm using a 400-series charge-coupled-device (CCD) array spectrophotometer (Spectral Instruments, Inc., Tucson, AZ). The organic phase Eu^{3+} concentration was calculated as the difference between the initial and final aqueous-phase concentrations, and assumed no changes in the aqueous or organic phase volumes. The validity of this analytical approach was verified by duplicating the Eu^{3+} distribution measurements using inductively coupled plasma optical emission spectroscopy (ICP-OES) as the analytical technique. Nearly identical results within observed experimental error were obtained for the Eu^{3+} distribution ratios using these two techniques. Even though the spectrophotometric method was limited to measuring Eu^{3+} distribution ratios <100, it offered advantages of simple and rapid analysis without solution pretreatment. So it provided a convenient means to rapidly screen the effects of varying conditions on the Eu^{3+} extraction kinetics.

Mixed Lanthanides and Am Distribution Measurements

Batch distribution measurements were carried out using solutions containing different concentrations of the Ln elements. Experiments with micromolar concentrations of the Ln elements used solutions containing a mixture of La, Ce, Pr, Nd, Sm, Eu, and Gd at 1×10^{-5} mol/L each. Experiments with millimolar concentrations of Ln used a solution of the same lanthanides in concentrations as expected in a feed for the Advanced TALSPEAK process. The concentrations are given in Table 1. HEDTA and citric acid were dissolved in the required Ln solution and the pH was adjusted to the desired value with NaOH. The solutions were then spiked with ^{241}Am, ^{244}Cm, and ^{152}Eu tracers. Following preparation of the aqueous phase, an equal volume of the solvent (1.0 mol/L HEH[EHP] dissolved in *n*-dodecane) was added and the vials were shaken in a temperature-controlled aluminum block (22 °C) using an IKA Vibrax VXR shaking device at maximum speed (2200 rpm) for the desired time period. The vials were centrifuged and the phases were separated manually as quickly as possible. Aliquots of both phases were taken for analysis. For the evaluation of the extraction kinetics, individual contact vials were prepared for each solution condition and time point to be measured (rather than sampling a single contact mixture at different time points). The results indicated that equilibrium was reached after 10 min under these experimental conditions.

Samples of the aqueous and organic phases were analyzed by gamma spectroscopy for ^{241}Am and ^{152}Eu using a high-purity Ge-detector system. The samples were also analyzed by alpha spectroscopy for ^{241}Am and ^{244}Cm, after transferring measured aliquots on stainless steel planchets using a method described previously.[31] The concentrations of the nonradioactive Ln elements were determined before and after contact by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer Elan DRC II. For ICP-MS measurements, the aqueous phases were directly measured after appropriate dilution in 1% HNO_3. The organic phases were measured after mixing with the nonionic surfactant Triton-X-100 and dilution into 1% HNO_3 to an appropriate concentration. Details of the equipment, procedure, and analytics are described elsewhere.[14, 32] The distribution ratios (D_M) for the radioisotopes were calculated as the radioactivity of the isotope in the organic phase divided by its radioactivity in the aqueous phase, while the D values for the nonradioactive Ln elements were calculated as the concentration in the organic phase divided by the concentration in the aqueous phase. Distribution ratios between 0.01 and 100 exhibit an uncertainty of ±5%, while lower/higher values exhibit larger uncertainties.

Single-Stage Centrifugal Contactor Runs

The 2-cm centrifugal contactors used in this work at PNNL were manufactured at Argonne National Laboratory.[33] The experiments were conducted at an ambient laboratory temperature of 19.5 °C. The contactor was operated with deionized water and *n*-dodecane for a period of 10 minutes to establish consistent phase separation before changing to the organic (1.0 mol/L HEH[EHP] in *n*-dodecane) and aqueous (Table 1, PNNL solution) feeds. The organic and aqueous feeds were run through the single-stage 2-cm centrifugal contactor for 20 minutes in order to establish a chemically steady state prior to sample collection. Five samples were collected into pre-tared vials for a period of 1 minute each over a period of 16 minutes. The net mass of each sample collected was determined and the average flow rates were calculated to be 12.4 ± 0.2 mL/min for the aqueous phase and 10.4 ± 0.3 mL/min for the organic phase.

The effective distribution ratios obtained in the 2-cm contactor for ^{241}Am were determined by sampling equal volumes of both phases and gamma counting on a NaI detector. The distribution ratios for the Ln elements were determined by analyzing the initial aqueous feed solution and the aqueous raffinate from the contactor by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer ICP-OES Optima

7300DV. The organic phase Ln concentrations were determined by the difference between the starting and ending aqueous phase concentrations. Parallel batch contacts were performed by mixing the organic and aqueous phases in high density polyethylene vials on a wrist action shaker for a period of 24 hours at ambient laboratory temperature.

The 1-cm annular miniature centrifugal contactor used in this work was manufactured by the Institute of Nuclear Energy Technology, Tsinghua University, Beijing, China.[34] The rotor was made of titanium, while the stator housing was made of stainless steel. Typically, the centrifugal contactors come as blocks of four contactors each. A modified version of one of those contactor housings to separate only one stage, i.e., one stator block, was cut and tube connectors were welded to the inlet and outlet where necessary. The rotation speed of the contactor was set to 4500 rpm using a stroboscope light and the speed was checked regularly during the experiment. The organic and aqueous phases were delivered using syringe pumps that supplied highly accurate flow rates.

In the single-stage centrifugal contactor experiments, the extraction section of a foreseen Advanced TALSPEAK flowsheet was simulated using conditions optimized in this work. A solvent containing 1.0 mol/L HEH[EHP] in *n*-dodecane was used. In the extraction section of a process, typically the aqueous feed stream is mixed with the scrub stream; this was simulated here by mixing the feed (FZ Jülich composition given in Table 1) with an equal volume of scrub solution. The scrub solution consisted of 0.6 mol/L citric acid and 0.125 mol/L HEDTA with the pH set to 2.6.

Two different flow rates were tested, first a higher flow rate of 20 + 40 mL/h (organic + aqueous) and then a lower flow rate of 10 + 20 mL/h (organic + aqueous). Samples from the aqueous and organic outlets of the single centrifugal contactor were taken regularly and were immediately measured by gamma spectroscopy for ^{241}Am and ^{152}Eu to monitor the evolution of a steady state. After the steady state was reached at the higher flow rate, the flow rates were reduced. After reaching the new steady state, the contactor and pumps were stopped and the content of the mixing chamber was transferred to a test tube. The test tube was shaken for 15 min to reach chemical equilibrium, and then centrifuged. Samples from both phases were taken for analysis. All samples were subjected to ICP-MS and alpha and gamma spectroscopies.

RESULTS AND DISCUSSION

Optimization of the Aqueous-Phase Composition to Improve Extraction Kinetics

In our previously reported work, the aqueous feed solution for the Advanced TALSPEAK system consisted of a solution of the Ln and An, along with 0.125 mol/L HEDTA plus 0.2 mol/L citrate buffer at pH 3.1.[28] Because this system displayed slow extraction rates for Sm^{3+}, Eu^{3+}, and Gd^{3+}, alternative aqueous phase formulations were considered. Two factors that can be hypothesized to influence the extraction rate are (a) the formation of metal complexes with neutral charge that can be expected to be more interfacially active than charged complexes, and (b) the rate of decomplexation of the metal ion from the aqueous-phase complexant. Related to the latter point is the amount of uncomplexed, hydrated M^{3+} ion in the aqueous phase. The uncomplexed ion should be rapidly extracted since decomplexation from citrate or the aminocarboxylate is not necessary. Some indication regarding the former factor can be gleaned from examining the M^{3+} (where M = Eu or Am) speciation diagrams corresponding to the aqueous solutions containing citrate buffer and HEDTA, or the potential alternative ligands HIDA, NTA, or DPTA. HIDA and NTA represent aminocarboxylate ligands with reduced denticity compared to HEDTA, while DPTA represents an aminocarboxylate ligand that contains the same number and type of donor groups as HEDTA, but with an extra carbon atom in the ligand backbone (Figure 1). HDPTA was another ligand in the latter class that was considered in this work, but reliable Eu and Am complexation data could not be found in the literature for this ligand, so its speciation diagrams could not be generated. Also, it should be noted that a self-consistent set of complexation data for HIDA at 25 °C could not be found in the literature. The protonation constants used in this case were measured at 35 °C rather than 25 °C, so the HIDA speciation diagrams shown in

Figure 2 should be viewed as approximate.

Figure 2 presents the relevant speciation diagrams that were calculated using the computer program Hyperquad Simulation and Speciation (HySS) version 4.0.31.[35] For each aqueous aminocarboxylate/citrate system, the input file contained the speciation model that included (1) protonation constants for citrate, (2) protonation constants for the aminocarboxylate, and (3) the complex formation constants for M^{3+} with citrate and the aminocarboxylate. The formation of the mixed-ligand ternary aqueous complexes was not taken into consideration because of the lack of reported relevant thermodynamic data. For each system, the speciation model and the corresponding literature sources[36-46] are summarized in the tables in

Figure 2. Extraction equilibria were not considered in this analysis. The concentrations of the aqueous components specified in the input files were 16 mmol/L Eu^{3+} corresponding to the test conditions applied in this work or 0.585 mmol/L Am^{3+} corresponding to the Am^{3+} concentration in the URanium EXtraction (UREX) raffinate,[47] 0.2 mol/L citrate buffer, and 0.125 mol/L aminocarboxylate.

Figure 2 compares the distribution of M^{3+} species in the presence of HEDTA, NTA, HIDA, and DPTA as a function of pH. To consider the hypothesis that the presence of electrically neutral metal ion complexes or the uncomplexed hydrated metal ion will result in more rapid extraction, Table 2 lists the fraction of Eu and Am in the form of free metal ion or neutrally charged complexes in 0.2 mol/L citrate buffer at the previously investigated pH condition of 3.1, and at one-half of a pH unit lower (pH 2.6). Based on this simple argument, it can be predicted that the extraction rates would follow the order DPTA > HIDA > NTA ~ HEDPA. At both pH conditions, a large fraction (>80%) of the metal ions exist in either the uncomplexed form, or as the neutral citrate complex when DPTA is used as the actinide holdback ligand. HIDA results in approximately 30 to 60% of the metal ions being present in neutral or uncomplexed form. HEDTA and NTA display very little uncharged or uncomplexed form at pH 3.1, but approximately 10 to 20% at pH 2.6. The latter observation points to another prediction that can be made from these data; that is, the extraction rates should increase with decreasing pH because of the increase in uncharged metal ion complexes or uncomplexed metal ions.

Figure 3a presents the time-dependent distribution ratios for extraction of Eu^{3+} from 0.125 mol/L HEDTA, HIDA, NTA, DPTA, or HDPTA in 0.2 mol/L citrate buffer at pH 3.1. In a previous study, the distribution ratios obtained at 21 s of vortex mixing time under these conditions were correlated to the distribution ratios expected in a 2-cm centrifugal contactor.[28] This 21-s time point is indicated by the vertical dashed lines in Figure 3. As predicted from the above considerations, Eu^{3+} was efficiently and rapidly extracted from the solution containing HIDA and DPTA; HDPTA also resulted in rapid Eu^{3+} extraction. In these cases, the Eu^{3+} concentration in the aqueous phase was below the detection limit for the spectrophotometric technique after 20 s of vortex mixing. Also as predicted from the above considerations, the Eu^{3+} extraction was relatively slow in the presence of NTA and HEDTA.

Another series of extraction experiments was performed to explore the behavior of Am^{3+} aqueous solutions containing 0.125 mol/L HIDA or NTA, 16 mmol/L Eu^{3+}, and 0.2 mol/L citrate buffer at a pH of 3. These contacts were done in a manner identical to that above except that the aqueous phases were spiked with ^{241}Am. The results obtained are presented in Figure 3b. Although the speciation plots (

Figure 2) are similar for Eu^{3+} and Am^{3+}, the Am^{3+} extraction kinetics behavior was different from that for Eu^{3+}. In particular, D_{Am} reached equilibrium values very rapidly (within 10 s) with NTA as the aqueous-phase holdback complexant. The differences in the Eu^{3+} and Am^{3+} extraction kinetics in the NTA system might be associated with the other factor stated above, namely, differences in the rates of dissociation of the metal-NTA complexes. However, no information could be located in the literature regarding the relative dissociation rates of the Eu-NTA and Am-NTA complexes.

As hypothesized previously, increasing the amount of uncharged metal ion complexes or uncomplexed metal ions would be expected to increase the metal ion extraction rates. One approach considered to achieve this was to alter the citrate concentration and/or the pH in the aqueous phase, while maintaining the HEDTA concentration at the original value of 0.125 mol/L. The influence of the citrate concentration on the Eu^{3+} extraction rate was investigated by determining the D_{Eu} values as a function of time for extraction into 1.0 mol/L HEH[EHP] from aqueous solutions containing 0.125 mol/L HEDTA and varying citrate concentrations at pH = 3.1 (Figure 4a). Generally, the D_{Eu} values decreased with increasing citrate concentration, likely due to increased participation of citrate in the complexation of Eu^{3+} ions in the aqueous phase, especially the negatively charged $[Eu(citrate)_2]^{3-}$ complex. This is especially evident under the equilibrium conditions achieved after 5 min of mixing. The data also suggest that in the 0.4 to 0.6 mol/L citrate range, the D_{Eu} values are near or slightly above 1 at 21 s of mixing, which was an improvement over the D_{Eu} value (~0.7) previously observed for the 0.2 mol/L citrate system.[28] For this reason, the 0.6 mol/L citrate condition was explored further.

The extraction of Eu^{3+} from 0.6 mol/L citrate + 0.125 mol/L HEDTA into 1.0 mol/L HEH[EHP] in *n*-dodecane was investigated at several different pH conditions (Figure 4b). The extraction rates tended to decrease as the pH was increased. Again, this is likely because of increased binding of Eu^{3+} by HEDTA and citrate, as the carboxylate groups on these ligands become increasingly deprotonated with increasing pH. Interpolation of the data in

Figure 4b suggests the effective D_{Eu} value in a 2-cm centrifugal contactor (i.e., at 21 s of contact with the vortex mixer) would be approximately 5 at pH 2.6. Based on this promising result, another test was performed under these conditions with additional lanthanides present.

A mixed-lanthanide solution containing 0.125 mol/L HEDTA in a 0.6 mol/L citrate buffer at pH 2.6 was prepared and contacted with 1.0 mol/L HEH[EHP] dissolved in *n*-dodecane. The lanthanide distribution ratios were measured at incremental time points up to 5 min of mixing time. Figure 5a presents the kinetic data obtained for extraction of the trivalent La, Ce, Pr, Nd, Sm, Eu, and Gd ions, and Figure 5b compares the same data for Sm, Eu, and Gd to analogous data obtained in previous work[28] using an aqueous phase of 0.125 mol/L HEDTA in a 0.2 mol/L citrate buffer at pH 3.1. The total initial lanthanide concentration in this experiment was 15 mmol/L. The lanthanide extraction rates are significantly improved in the 0.6 mol/L citrate/pH 2.6 system compared to the 0.2 mol/L citrate/pH 3.1 system, although the equilibrium D values for the lighter lanthanides are somewhat lower at the higher citrate concentration compared to those measured at 0.2 mol/L citrate. Despite the lower D values, it should be possible to operate the Advanced TALSPEAK system in centrifugal contactors with an aqueous phase consisting of 0.125 mol/L HEDTA + 0.6 mol/L citrate buffer at pH 2.6, since the Ln^{3+} D values are all projected to be >2 in the contactor system (based on the 20-s vortex mixing data).

The results presented in Figure 3 suggest that NTA holds some promise for significantly improving the rate of Eu extraction in the Advanced TALSPEAK system, but the NTA system exhibited an unsatisfactorily high distribution value for Am^{3+} under the specific conditions examined. Additional optimization of the NTA system is required for this to be a practical option. Suggested future experiments to optimize the NTA system include lowering the HEH[EHP] concentration in the organic phase or increasing the citrate concentration in the aqueous phase. The aqueous system consisting of 0.125 mol/L HEDTA + 0.6 mol/L citrate buffer at pH 2.6 was chosen for further process development.

Batch Extraction of Americium and Selected Ln Elements

Using the 0.125 mol/L HEDTA + 0.6 mol/L citrate buffer system, the extractions of Am and the Ln elements were examined under two different loading conditions. Under one condition, each Ln element concentration was on the order of 10^{-5} mol/L, and in the other condition, each Ln element concentration was on the order of 10^{-3} mol/L (Table 1; data from FZ Jülich). In both cases, ^{241}Am was at tracer concentration (3.1 MBq/L; 9.7×10^{-8} mol/L). The distribution ratios are plotted versus the pH in Figure 6. The D values increase with increasing pH for the lighter Ln elements (La, Ce, and Pr). The D_{Nd} values are essentially flat across the pH region examined, and the heavier Ln elements (Sm, Eu, and Gd) and Am show decreasing D values as the pH increases. A similar trend was seen in early investigations of the Advanced TALSPEAK system.[28] One consequence of this is that the minimum separation factor (SF = the D value for the Ln element divided by the D value for Am) increases with increasing pH (Figure 6). For example, for the case in which millimolar concentrations of the Ln elements were present (Figure 6b), the minimum SF increases from 2.5 at pH 2.0 (defined by the La/Am couple up to pH ~2.6) to 13.4 at pH 3.0 (defined by the Nd/Am couple at pH > 2.8). However, as indicated by the data in Figure 4b, the extraction rates slow with increasing pH, so a balance must be struck between these two competing phenomena. That is why an operating pH of 2.6 was chosen for further testing.

The batch *D* values obtained with millimolar concentrations of the Ln elements were less than those obtained with micromolar concentrations of the Ln elements present. This can be attributed to higher loading of the solvent, effectively lowering the free HEH[EHP] concentration, although the total loading of HEH[EHP] with the Ln elements in the millimolar range can only be up to about 10% (assuming a stoichiometry of six HEH[EHP] molecules involved in the complexation of one Ln ion[26]). The effect is particularly pronounced for Gd. With micromolar concentrations of Ln elements present, Gd is the most strongly extracted Ln element. However, with millimolar concentrations of the Ln elements, the D_{Gd} values are less than those of both Sm and Eu (Figure 6b). In this regard, the behavior of Gd appears to be anomalous. Based on the distribution ratios measured at micromolar concentrations of the Ln elements, the loading impacts would be expected to be greatest for the lighter lanthanides (since they have lower affinity for HEH[EHP]), and become progressively less with increasing atomic number of the Ln. This trend is true up to Gd. Factors other than simple loading effects may be significant for Gd.

The batch distribution ratios for extraction of Am and the Ln elements from 0.125 mol/L HEDTA + 0.6 mol/L citrate (pH 2.5–2.6) were measured both at FZ Jülich in Germany and at PNNL in the United States. It was of interest to compare the results of these separate measurements since (1) different sources of the Ln elements, HEDTA, and citric acid were used, (2) slightly different procedures were used, and (3) different personnel performed the measurements. The HEH[EHP] used at both laboratories was labeled as being from the same lot. The initial aqueous phases used are compared in Table 1. Figure 7 presents a direct comparison of the distribution ratios measured at FZ Jülich to those measured at PNNL. Good agreement was obtained between the two laboratories, except for Gd, for which the value obtained at PNNL was about twice as high as that obtained at FZ Jülich. The values obtained at PNNL tended to be slightly higher than those measured at FZ Jülich. For the light Ln elements, this might be attributable to the slightly lower pH at which the PNNL measurements were made compared to the FZ Jülich measurements. Lower pH would be expected to lead to higher distribution ratios for La, Ce, and Pr per Figure 6.

Single-Stage Centrifugal Contactor Experiments

To aid in the design of the Advanced TALSPEAK flowsheet,[29] a single-stage extraction experiment was performed using a 2-cm centrifugal contactor. The composition of the aqueous solution used in this experiment was the same as that indicated in Table 1 (PNNL composition), and the organic solvent was 1.0 mol/L HEH[EHP] in *n*-dodecane. For this experiment, the target flow rates for the organic and aqueous phases were both 10 mL/min; the measured flow rates were 10.4 and 12.4 mL/min, respectively.

Table 3 presents the average steady-state distribution ratios obtained in the 2-cm centrifugal contactor for Am and the Ln elements examined, along with the calculated stage efficiencies. The stage efficiency in the 2-cm contactor was ~75% for most of the Ln elements examined. Europium and Gd displayed lower stage efficiencies, consistent with the previous reports of slow extraction rates for these elements.[28] The Am distribution ratio measured in the 2-cm contactor was within 7% of the batch equilibrium value. Based on these results, the minimum separation factor expected for implementing the Advanced TALSPEAK system with 2-cm centrifugal contactors would be 9.0, defined by the La/Am couple.

The steady-state distribution ratios for the 2-cm centrifugal contactor reported in Table 3 were used to design an Advanced TALSPEAK flowsheet.[29] However, testing of the flowsheet was to be performed using 1-cm centrifugal contactors. An additional set of single-stage measurements was performed using a 1-cm centrifugal contactor to determine the stage efficiencies under these conditions. The FZ Jülich aqueous feed solution described in Table 1 was used for these tests, except that it was diluted with an equal volume of 0.125 mol/L HEDTA + 0.6 mol/L citrate (pH 2.6) solution to simulate the dilution that would occur by mixing with a scrub stream. Again, the organic solvent was 1.0 mol/L HEH[EHP] in *n*-dodecane. Two different flow regimes were examined: a low flow of 10 mL/h of organic and 20 mL/h of aqueous phase, and a high flow of 20 mL/h of organic and 40 mL/h of aqueous phase. Table 3 presents the results of these measurements.

The stage efficiencies for La, Ce, and Pr achieved in the 1-cm centrifugal contactor at the low flow rate were approximately 20 to 30% higher than those obtained in the 2-cm centrifugal contactor. Under these conditions, the stage efficiency for Nd was also about 10% higher in the 1-cm contactor than in the 2-cm contactor. This trend was consistent with the much longer residence times achieved in the 1-cm contactor (~12 minutes at the lower flow rate) compared to the 2-cm contactor (~10 seconds). In the 2-cm centrifugal contactor, the stage efficiencies were substantially lower for the heavier Ln elements (Sm, Eu, and Gd), but this effect was more pronounced in the 1-cm centrifugal contactor. More rapid initial loading of the light Ln elements in the 1-cm contactor might explain the more pronounced depression of the stage efficiency in that case. A substantial drop in performance in the 1-cm contactor occurred when the flow rates were doubled, as expected based on the decrease of the residence time by a factor of 2. The stage efficiencies for Sm, Eu, and Gd were particularly low at the higher flow rates.

Further insight into the contactor behavior can be obtained by examining the relative stage efficiencies normalized to those measured for La (Figure 8). In the 2-cm centrifugal contactor, the relative stage efficiencies stay nearly constant up through Sm, but the efficiencies progressively drop as atomic number, Z, increases to those of Eu and Gd. In the 1-cm centrifugal contactor, the stage efficiencies decline across the Ln series from Ce to Eu. As might be expected, this trend is more pronounced at the higher flow rate. The greater relative stage efficiency for Gd compared to Eu in the 1-cm contactor is somewhat surprising, and is unexplained at this point. Americium also showed relatively lower stage efficiencies in the 1-cm contactor. The stage efficiency for Am in the 2-cm contactor relative to La was 1.34, whereas that in the 1-cm contactor was 0.84 at the lower flow rate and 0.89 at the higher flow rate.

From this comparison of stage efficiencies, it can be concluded that testing in the 1-cm centrifugal contactor should provide a conservative assessment of the Advanced TALSPEAK flowsheet performance, and that better separation factors can be expected for operation in 2-cm contactors.

Advanced TALSPEAK Flowsheet

The batch contact distribution ratio data measured by PNNL and distribution ratio data from FZ Jülich using a single 1-cm centrifugal contactor under the low-flow scenario (Table 3) were used in conjunction with the Argonne Model for Universal Solvent Extraction (AMUSE) code[48] to develop an Advanced TALSPEAK flowsheet for testing at FZ Jülich. It should be noted that minor differences in temperatures were likely between batch distribution measurements and the single-stage measurements; however, these temperature differences are not expected to significantly affect the flowsheet design. A separate investigation of Nd extraction in the Advanced TALSPEAK system showed the D_{Nd} values varied less than 15% over the temperature range of 6 to 35 °C, with the extraction reaction being endothermic.[49] The flowsheet was designed for 24 contactor stages, although only 16 stages are available in Jülich. Therefore, the actual test was done in two consecutive parts.[29] The goal was to achieve greater than 99% recovery of the Am with less than 0.1% contamination of the Am product by the Ln fission products. The process variables considered in the flowsheet design included the number of extraction, scrub, and strip stages, relative flow rates of the aqueous and organic solutions in each of these sections, and steady-state distribution ratios for each stage (based upon experimental data). Distribution ratios were assumed to be constant for each component within a given section of the flowsheet. Scrub distribution ratios were assumed to be the same as extraction distribution ratios. Conservative distribution ratios of 0.1 were assumed for the Ln elements and Am in the stripping section of the flowsheet. This conservative assumption was supported by batch distribution measurements for extraction of these elements from 4 mol/L HNO_3 into 1.0 mol/L HEH[HEP], which indicated D values <0.05 under these conditions.

The resulting flowsheet is presented in Figure 9. The recovery percentages of the lanthanides and Am predicted by the AMUSE code using the distribution ratio data from FZ Jülich with a single 1-cm centrifugal contactor under the low-flow scenario are presented in Table 4. These predicted results meet the goals of >99% recovery of the lanthanides and <0.1% loss of Am with the Ln product. The flowsheet presented in Figure 9 was tested with an active simulant, and the results from that test are presented in Part 2 of this series of papers.[29]

CONCLUSION

Measurements of distribution ratios for Am and the Ln elements both in batch mode and in single-stage 1- or 2-cm centrifugal contactors indicate the Advanced TALSPEAK system is a promising option for separating the trivalent An elements from the Ln elements. The centrifugal contactor stage efficiencies decline with increasing Z of the Ln, but this is compensated to some extent by the higher *D* values for Sm, Eu, and Gd. At a flow rate of about 10 mL/min for each phase, a minimum single-stage separation factor of 9 can be expected using a 2-cm centrifugal contactor, defined by the La/Am couple. In the case of the 1-cm contactor at flow rates of 10 mL/h organic and 20 mL/h aqueous, a minimum single-stage separation factor of 10 can be expected, defined by the Nd/Am couple. This study laid the groundwork for design of an Advanced TALSPEAK flowsheet. The testing of that flowsheet will be reported in Part 2 of this series of papers.

ACKNOWLEDGMENT

This work was funded by the U.S. Department of Energy, Office of Nuclear Energy, through the Fuel Cycle Research and Development Program. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RL01830. Financial support was further provided by the European Commission (project SACSESS – Contract No. FP7-Fission-2012-323-282).

REFERENCES

1. Mathur, J. N.; Murali, M. S.; Nash, K. L. Actinide Partitioning--A Review. Solvent Extr. Ion Exch. 2001, *19* (3), 357-390.

2. Modolo, G.; Geist, A.; Miguirditchian, M. Minor Actinide Separations in the Reprocessing of Spent Nuclear Fuels: Recent Advances in Europe. In *Reprocessing and Recycling of Spent Nuclear Fuel*; Taylor, R., Ed. Woodhead Publishing: Cambridge, 2015; pp 245-287.

3. Moyer, B. A.; Lumetta, G. J.; Mincher, B. J. Minor Actinide Separation in the Reprocessing of Spent Nuclear Fuels: Recent Advances in the United States. In *Reprocessing and Recycling of Spent Nuclear Fuel*; Taylor, R., Ed. Woodhead Publishing: Cambridge, 2015; pp 289-312.

4. Todd, T. A.; Wigeland, R. A. Advanced Separation Technologies for Processing Spent Nuclear Fuel and the Potential Benefits to a Geologic Repository. In *Separations for the Nuclear Fuel Cycle in the 21st Century*; Lumetta, G. J.; Nash, K. L.; Clark, S. B.; Friese, J. I., Eds; American Chemical Society: Washington, DC, 2006; pp 41-55.

5. Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. Use of Soft Heterocyclic N‑Donor Ligands to Separate Actinides and Lanthanides. Inorg. Chem. 2013, *52*, 3414-3428.

6. Poinssot, C.; Boullis, B.; Bourg, S. Role of Recycling in Advanced Nuclear Fuel Cycles. In *Reprocessing and Recycling of Spent Nuclear Fuel*; Taylor, R., Ed. Woodhead Publishing: Cambridge, 2015; pp 27-48.

7. Nash, K. L. A Review of the Basic Chemistry and Recent Developments in Trivalent f-Elements Separations. Solvent Extr. Ion Exch. 1993, *11* (4), 729-768.

8. Geist, A.; Hill, C.; Modolo, G.; Foreman, M. R. S. J.; Weigl, M.; Gompper, K.; Hudson, M. J.; Madic, C. 6,6-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2]bipyridine, an effective extracting agent for the separation of americium(III) and curium(III) from the lanthanides. Solvent Extr. Ion Exch. 2006, *24* (4), 463-483.

9. Modolo, G.; Nabet, S. Thermodynamic study on the synergistic mixture of bis(chlorophenyl) dithiophosphinic acid and tris(2-ethylhexyl) phosphate for separation of actinides(III) from lanthanides(III). Solvent Extr. Ion Exch. 2005, *23* (3), 359-373.

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

11. Lumetta, G. J.; Gelis, A. V.; Carter, J. C.; Niver, C. M.; Smoot, M. R. The Actinide-Lanthanide Separation Concept. Solvent Extr. Ion Exch. 2014, *32*, 333-347.

12. Carrott, M.; Bell, K.; Brown, J.; Geist, A.; Gregson, C.; Hères, X.; Maher, C.; Malmbeck, R.; Mason, C.; Modolo, G.; Müllich, U.; Sarsfield, M.; Wilden, A.; Taylor, R. Development of a New Flowsheet for CoSeparating the Transuranic Actinides: The "EURO-GANEX" Process. Solvent Extr. Ion Exch. 2014, *32*, 447-467.

13. Miguirditchian, M.; Roussel, H.; Chareyre, L.; Baron, P.; Espinoux, D.; Calor, J.-N.; Viallesoubranne, C.; Lorrain, B.; Masson, M. HA demonstration in the Atalante facility of the Ganex 2nd cycle for the grouped TRU extraction. Global 2009: The Nuclear Fuel Cycle: Sustainable Options & Industrial Perspectives, Paris, France, French Nuclear Energy Society: Paris, France, 2009; p Paper 9378.

14. Wilden, A.; Modolo, G.; Schreinemachers, C.; Sadowski, F.; Lange, s.; Sypula, M.; Magnusson, D.; Geist, A.; Lewis, F. W.; Harwood, L. M.; Hudson, M. J. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of $CyMe_4BTBP$ and TODGA as 1-cycle SANEX Solvent Part III: Demonstration of a Laboratory-scale

Counter-Current Centrifugal Contactor Process. Solvent Extr. Ion Exch. 2013, *31* (5), 519-537.

15. Hill, C. Overview of Recent Advances in An(III)/Ln(III) Separation by Solvent Extraction. In *Ion Exchange and Solvent Extraction: A Series of Advances*; Moyer, B. A., Ed. CRC Press: Boca Raton, 2010; Vol. 19, pp 119-193.

16. Courson, O.; Lebrun, M.; Malmbeck, R.; Pagliosa, G.; Römer, K.; Sätmark, B.; Glatz, J.-P. Partitioning of minor actinides from HLLW using the DIAMEX process. Part 1 – Demonstration of extraction performanes and hydraulic behavior of the solvent in a continous process. Radiochim. Acta 2000, *88* (12), 857-863.

17. Malmbeck, R.; Courson, O.; Pagliosa, G.; Römer, K.; Sätmark, B.; Glatz, J.-P.; Baron, P. Partitioning of minor actinides from HLLW using the DIAMEX process. Part 2 – "Hot" continuous counter-current experiment. Radiochim. Acta 2000, *88* (12), 865-871.

18. Modolo, G.; Vijgen, H.; Derrano-Purroy, D.; Christiansen, B.; Malmbeck, R.; Sorel, C.; Baron, P. DIAMEX Counter-Current Extraction Process for Recovery of Trivalent Actinides from Simulated High Active Concentrate. Sep. Sci. Technol. 2007, *42* (3), 439-452.

19. Horwitz, E. P.; Kalina, D. G.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. The TRUEX Process – A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent. Solvent Extr. Ion Exch. 1985, *3*, 75-109.

20. Modolo, G.; Wilden, A.; Geist, A.; Magnusson, D.; Malmbeck, R. A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate. Radiochim. Acta 2012, *100*, 715-725.

21. Panak, P. J.; Geist, A. Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N-Donor Ligands. Chem. Rev. 2013, *113* (2), 1199-1236.

22. Geist, A.; Modolo, G.; Weigl, M. SANEX-IV process development studies: Di(chlorophenyl)dithiophosphinic acid as selective extractant for actinides(III). International Workshop on P&T and ADS Development, Mol, Belgium, SCK-CEN: Mol, Belgium, 2003.

23. Ekberg, C.; Fermvik, A.; Retegan, T.; Skarnemark, G.; Foreman, M. R. S.; Hudson, M. J.; Englund, S.; Nilsson, M. An overview and historical look back at the solvent extraction using nitrogen donor ligands to extract and separate An(III) from Ln(III). Radiochim. Acta 2008, *96*, 225-233.

24. Weaver, B.; Kappelmann, F. A. Preferential Extraction of Lanthanides Over Trivalent Actinides by Monoacidic Organophosphates from Carboxylic Acids and From Mixtures of Carboxylic Acids and Aminopolyacetic Acids. J. Inorg. Nucl. Chem. 1968, *30*, 263-272.

25. Nilsson, M., Nash, K.L. Review Article: A Review of the Development and Operational Characteristics of the TALSPEAK Process. Solvent Extr. Ion Exch. 2007, *25*, 665-701.

26. Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. Solvent Extr. Ion Exch. 2015, *33*, 1-55.

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

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

29. Wilden, A.; Lumetta, G. J.; Sadowski, F.; Schmidt, H.; Schneider, D.; Gerdes, M.; Law, J. D.; Geist, A.; Bosbach, D.; Modolo, G. An Advanced TALSPEAK Concept for

Separating Minor Actinides. Part 2. Flowsheet Test with Actinide-Spiked Simulant. Solvent Extr. Ion Exch. 2017, To be submitted.

30. Hu, Z.; Pan, Y.; Ma, W.; Fu, X. Purification of organophosphorus acid extractants. Solvent Extr. Ion Exch. 1995, *13,* 965-976.

31. Kaufholz, P.; Modolo, G.; Wilden, A.; Sadowski, F.; Bosbach, D.; Wagner, C.; Geist, A.; Panak, P. J.; Lewis, F. W.; Harwood, L. M. Solvent Extraction and Fluorescence Spectroscopic Investigation of the Selective Am(III) Complexation with TS-BTPhen. Solvent Extr. Ion Exch. 2016, *34* (2), 126-140.

32. Modolo, G.; Asp, H.; Vijgen, H.; Malmbeck, R.; Magnusson, D.; Sorel, C. Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from a Simulated PUREX Raffinate, Part II: Centrifugal Contactor Runs. Solvent Extr. Ion Exch. 2008, *26* (1), 62-76.

33. Leonard, R. A.; Bernstein, G. J.; Ziegler, A. A.; Pelto, R. H. Annular Centrifugal Contactors for Solvent Extraction. Sep. Sci. Technol. 1980, *15*, 925-943.

34. Duan, W.; Zhao, M.; Wang, C.; Cao, S. Advances in the Development and Application of Annular Centrifugal Contactors in the Nuclear Industry. Solvent Extr. Ion Exch. 2014, *32* (1), 1-26.

35. Alderighi, L.; Gans, P.; Ienco, A.; Peters, D.; Sabatini, A.; Vacca, A. Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species. Coord. Chem. Rev. 1999, *184*, 311-318.

36. Martell, A. E.; Smith, R. M. *Critical Stability Constants*. Plenum Press: New York, 1974.

37. Choppin, G. R.; Muscatello, A. C. The Complexation of Trivalent Actinides by TMDTA. Inorg. Chim. Acta 1985, *109*, 67-70.

38. Powell, J. E.; Ling, D. R.; Tse, P.-K. Complexes of Rare-Earth Elements with 1,3-Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid. Inorg. Chem. 1986, *25*, 585-586.

39. Arena, G.; Cali, R.; Grasso, M.; Musumeci, S.; Sammartano, S.; Rigano, C. The Formation of Proton and Alkali-metal Complexes with Ligands of Biological Interest in Aqueous Solution. Part 1. Potentiometric and Calorimetric Investigations of H^+ and Na^+ Complexes with Citrate, Tartrate and Malate. Thermochim. Acta 1980, *36*, 329-342.

40. Rabindra Reddy, P.; Shamanthakamani, J.; Khan, M.; Taqui Khan, M. M. Formation, Hydrolysis, and Olation of Hafnium(IV) Chelates. J. Inorg. Nucl. Chem. 1978, *40*, 1673-1675.

41. Thompson, L. C.; Loraas, J. A. Complexes of the Rare Earths. VI. N-Hydroxyethyliminodiacetic Acid. Inorg. Chem. 1963, *2*, 594-597.

42. Moeller, T.; Ferrus, R. Observation on the Rare Earths. LXXIV. The Enthalpy and Entropy of Formation of the 1:1 and 1:2 Chelates of Nitrilotriacetic Acid with Tripositive Cations. Inorg. Chem. 1962, *1*, 49-55.

43. Clegg, S. L.; Zalupski, P. R.; Dutech, G. Ion Interaction Models and Measurements of Eu^{3+} Complexation: HEDTA in Aqeuous Solutions at 25 °C Containing 1:1 Na^+ Salts and Citrate pH Buffer. Ind. Eng. Chem. Res. 2016, *55*, 2083-2096.

44. Gatez, J. M.; Merciny, E.; Duyckaerts, G. Étude thermodynamique de la complexation des lanthanides trivalents avec l'acide hydroxyethyl-ethylenediaminetriacetique et d'autres acides aminoacetiques: III. Détermination des Constantes de Formation des Complexes Mixtes par Titrage Potentiométrique. Anal. Chim. Acta 1977, *94*, 91-110.

45. Choppin, G. R.; Thakur, P.; Mathur, J. N. Complexation thermodynamics and structural aspects of actinide-aminopolycarboxylates. Coord. Chem. Rev. 2006, *250*, 936-947.

46. Thakur, P.; Xiong, Y.; Borkobski, M.; Choppin, G. R. Thermodynamic modeling of trivalent Am, Cm, and Eu-citrate complexation in concentrated $NaClO_4$ media. Radiochim. Acta 2012, *100*, 165-172.

47. Pereira, C. personal communication. 2016.

48. Frey, K.; Krebs, J. F.; Pereira, C. Time-Dependent Implementation of Argonne's Model for Universal Solvent Extraction. Ind. Eng. Chem. Res. 2012, *51*, 13219-13226.

49. Heller, F. D. Phase Transfer Kinetics and Mechanisms of Advanced TALSPEAK Solvent Extraction Systems. Washington State University, Pullman, Washington, 2017.

Figure Captions

Figure 1. Chemical structures of the organic extractant HEH[EHP], aqueous complexants, and buffers relevant to the Advanced TALSPEAK concept.

Figure 2. Speciation plots for Eu^{3+} (16 mmol/L) and Am^{3+} (0.585 mmol/L) in a solution of HEDTA, HIDA, NTA, or DPTA (0.125 mol/L; represented by L) buffered with citrate (0.2 mol/L; represented by Cit) as a function of pH. Citrate pK_a values and binding constants for Eu^{3+} and Am^{3+} are taken from the literature at 25 °C and ionic strength $I = 0.1$ mol/L, with $\log\beta$ values of CitH = 5.8, $CitH_2$ = 10.1, $CitH_3$ = 13.1, EuCit = 7.4, $EuCit_2$ = 11.1, AmCit = 7.64, $AmCit_2$ = 11.89.

Figure 3. Time dependence of Eu^{3+} (a) and Am^{3+} (b) extraction from aqueous solutions containing 0.125 mol/L of different aminocarboxylate complexants in 0.2 mol/L citrate buffer into 1 mol/L HEH[EHP] in *n*-dodecane at room temperature. For the data in both (a) and (b), the initial aqueous phase contained 16 mmol/L Eu^{3+}; the data in (a) were obtained with no ^{241}Am present, while the data in (b) were obtained by spiking the initial aqueous phase with tracer-level ^{241}Am. The initial pH values of the aqueous phase were 3.04, 3.17, 3.23, 3.10, and 3.10 for HIDA, NTA, DPTA, HDPTA, and HEDTA, respectively. Distribution data for Am^{3+} using the previously[28] reported HEDTA system correspond to an aqueous feed containing mixed lanthanides at a total concentration of 18.5 mmol/L but under otherwise identical conditions. The dashed vertical lines represent the elapsed time at which the D values would be expected to be approximately the same as in a 2-cm centrifugal contactor.[28]

Figure 4. Time dependence of Eu^{3+} extraction from an aqueous solution containing 16 mmol/L Eu^{3+} and 0.125 mol/L HEDTA into 1 mol/L HEH[EHP] in *n*-dodecane as a function of (a) citrate concentration at initial pH 3.1, or (b) the initial pH at 0.6 mol/L citrate buffer. The dashed vertical lines represent the elapsed time at which the D values would be expected to be approximately the same as in a 2-cm centrifugal contactor.[28]

Figure 5. (a) Time dependence of Ln^{3+} extraction from an aqueous solution containing 0.6 mol/L citrate, 0.125 mol/L HEDTA, 1.82 mmol/L La^{3+}, 3.37 mmol/L Ce^{3+}, 1.59 mmol/L Pr^{3+}, 6.44 mmol/L Nd^{3+}, 0.97 mmol/L Sm^{3+}, 0.21 mmol/L Eu^{3+}, and 0.47 mmol/L Gd^{3+} at a pH of 2.6 into 1.0 mol/L HEH[EHP]/*n*-dodecane. (b) Comparison of the Sm^{3+}, Eu^{3+}, and Gd^{3+} extraction data for a system of 0.125 mol/L HEDTA in 0.6 mol/L citrate at pH = 2.6 to those for a system of 0.125 mol/L HEDTA in 0.2 mol/L citrate at pH = 3.1 taken from ref [28]. The dashed vertical lines represent the elapsed time at which the *D* values would be expected to be approximately the same as in a 2-cm centrifugal contactor.[28]

Figure 6. Minimum separation factors (*SF*) and batch distribution ratios for Am and the Ln elements in the Advanced TALSPEAK system at (a) micromolar concentrations and (b) millimolar concentrations of the Ln elements. Organic phase: 1.0 mol/L HEH[EHP] in *n*-dodecane; aqueous phase: 0.125 mol/L HEDTA + 0.6 mol/L citrate at variable pH.

Figure 7. Comparison of batch distribution ratios measured at two different research institutions. Organic phase: 1.0 mol/L HEH[EHP] in *n*-dodecane; aqueous phase: millimolar Ln concentrations (Table 1) plus 0.125 mol/L HEDTA plus 0.6 mol/L citrate at pH 2.6 (FZ Jülich) or 2.5 (PNNL).

Figure 8. Comparison of the relative stage efficiencies for extraction of the Ln elements, normalized to the La stage efficiency, for 1-cm and 2-cm centrifugal contactors. The flow rates used are indicated in Table 3. Organic phase: 1.0 mol/L HEH[EHP] in *n*-dodecane; aqueous phase: 0.125 mol/L HEDTA + 0.6 mol/L citrate at pH 2.6 (1-cm contactor) or 2.5 (2-cm contactor).

Figure 9. Advanced TALSPEAK Flowsheet recommended for testing in 1-cm centrifugal contactors. The numbers shown represent the relative flowrates of each solution entering the process.

Figures

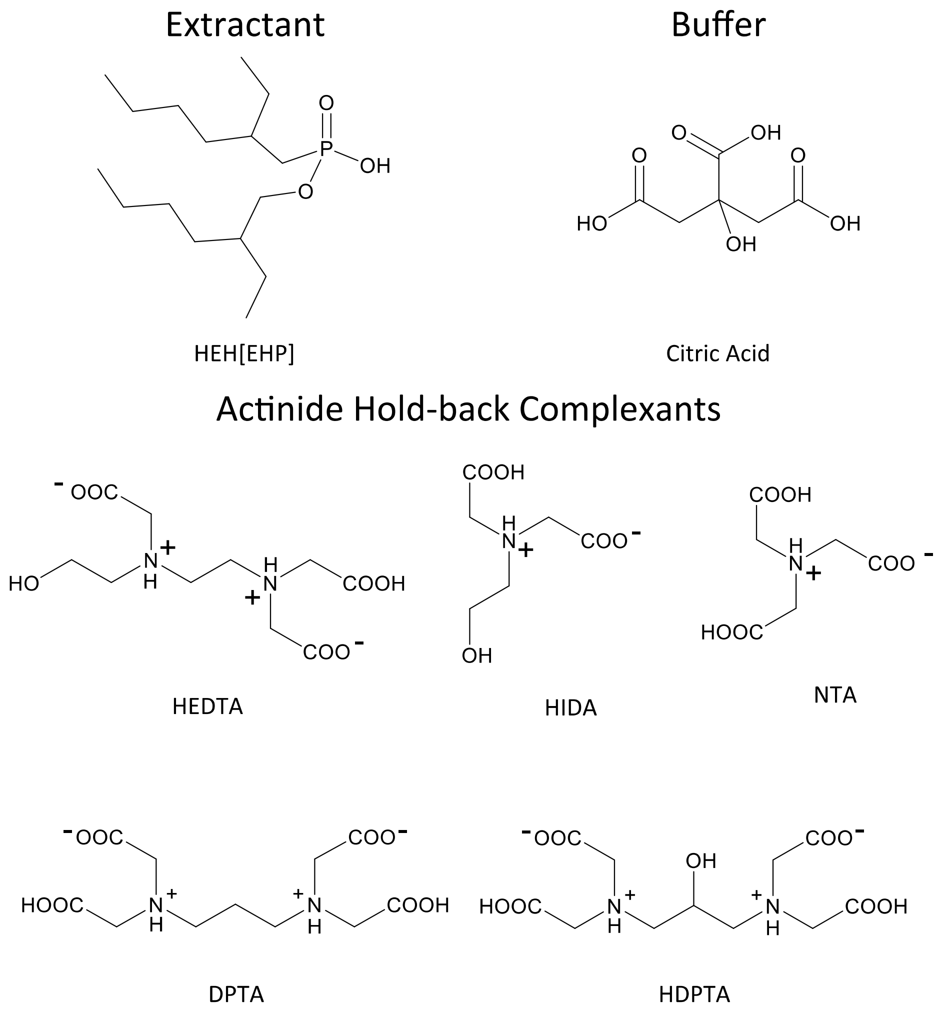
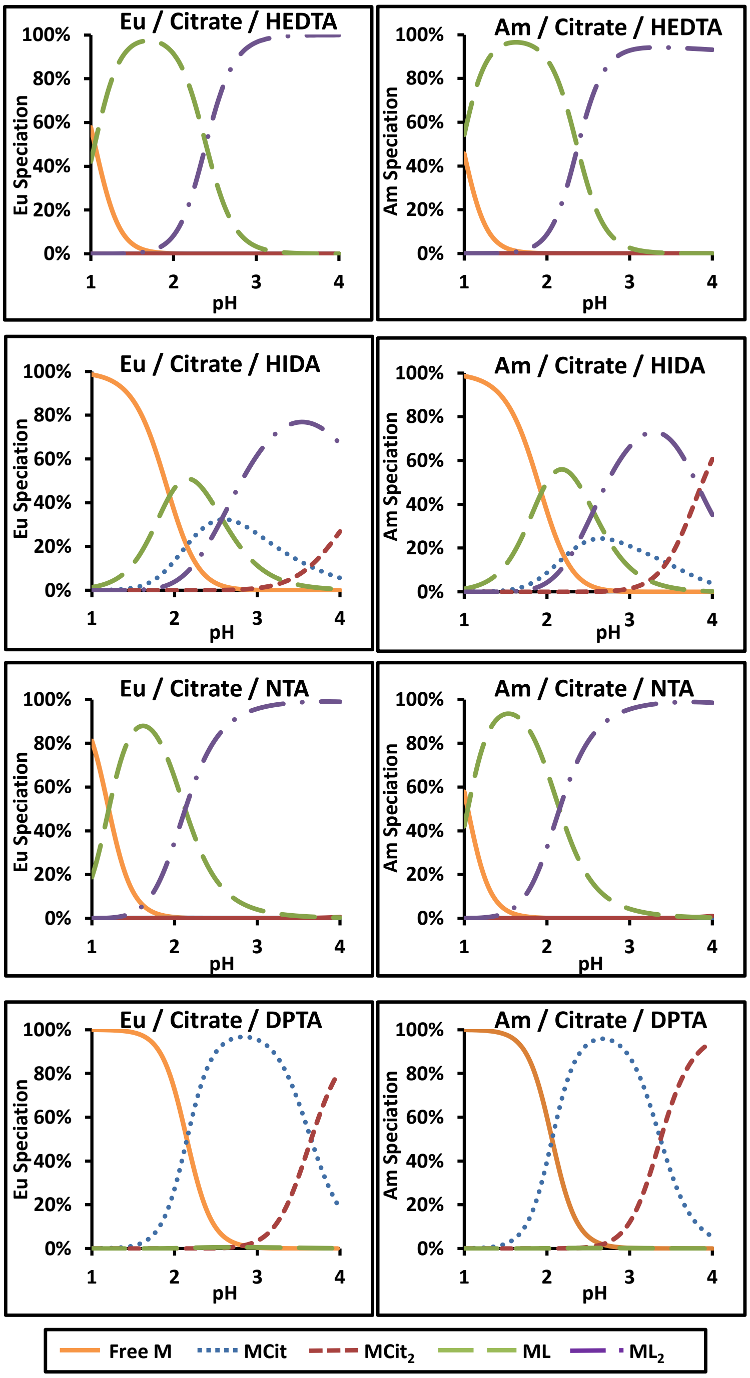


Figure 1



Species	log β	log *K*, 25◦C, I = 0.1	Ref.
HEDTAH	9.7	9.7	38
HEDTAH$_2$	15.1	5.4	38
HEDTAH$_3$	17.7	2.6	38
EuHEDTA	15.5	15.5	38
EuHEDTA$_2$	27.2	11.7	39
AmHEDTA	15.7	15.7	40
AmHEDTA$_2$	27.4	11.7	40

Species	log β	log *K*, 25-35 ◦C, I = 0.1	Ref.
HIDAH	8.8	8.8	35
HIDAH$_2$	12.0	3.3	35
EuHIDA	9.1	9.1	36
EuHIDA$_2$	17.0	7.9	36
AmHIDA	9.1	9.1	31
AmHIDA$_2$	17.0	7.9	31

Species	log β	log *K*, 25 ◦C, I = 0.1	Ref.
NTAH	9.7	9.7	31
NTAH$_2$	12.2	2.5	31
NTAH$_3$	14.0	1.8	31
NTAH$_4$	14.8	0.8	31
EuNTA	11.5	11.5	37
EuNTA$_2$	20.7	9.2	37
AmNTA	12.0	12.0	40
AmNTA$_2$	21.1	9.1	40

Species	log β	log *K*, 25 ◦C, I = 0.1	Ref.
DPTAH	10.5	10.5	31
DPTAH$_2$	18.5	8.0	31
DPTAH$_3$	21.1	2.6	31
DPTAH$_4$	22.9	1.9	31
EuDPTA	13.5	13.5	32
AmDPTA	13.5	13.5	32

Figure 2

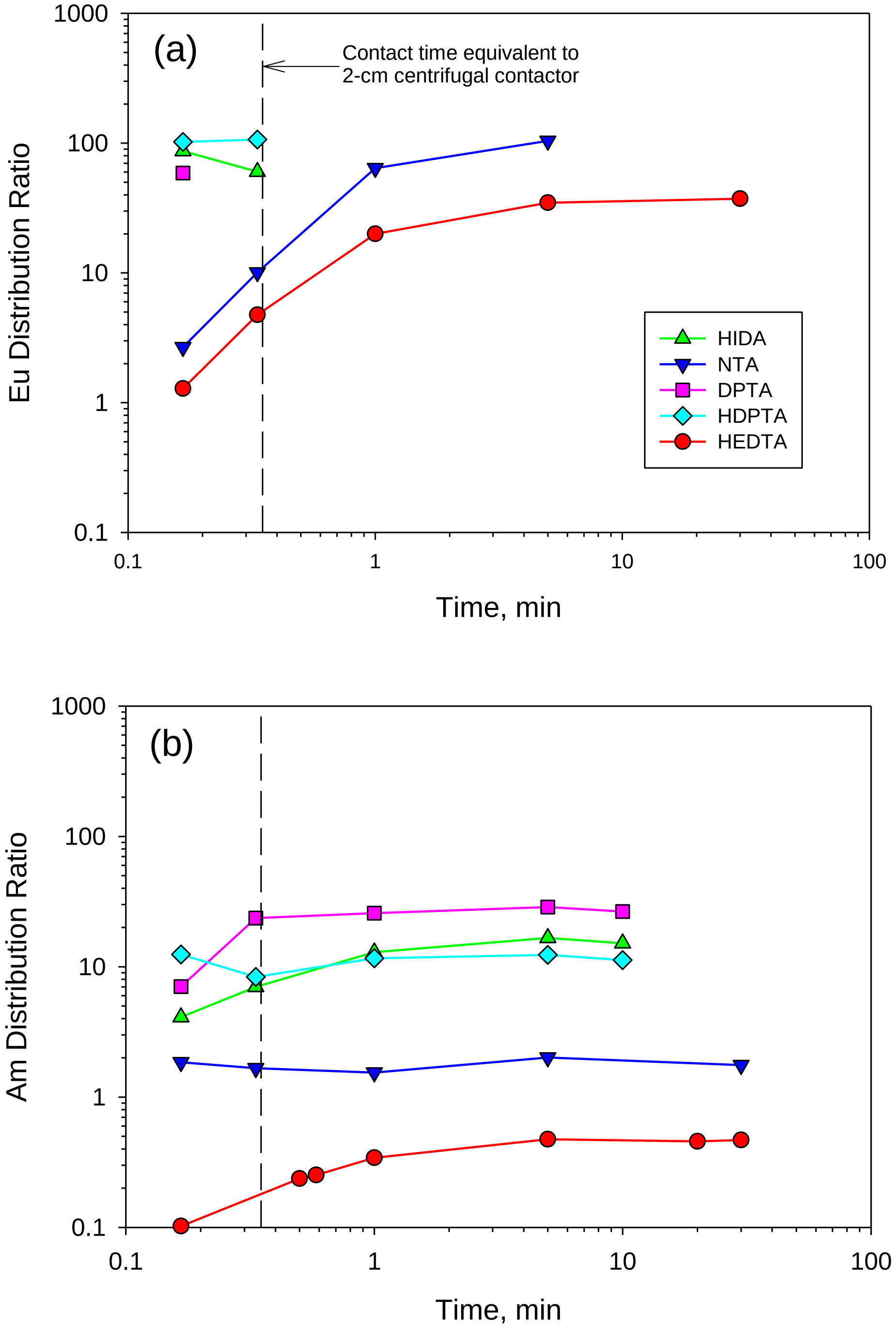

(a)
Contact time equivalent to
2-cm centrifugal contactor
Eu Distribution Ratio
1000
100
10
1
0.1
0.1
1
10
100
Time, min
HIDA
NTA
DPTA
HDPTA
HEDTA
(b)
Am Distribution Ratio
1000
100
10
1
0.1
0.1
1
10
100
Time, min

Figure 3

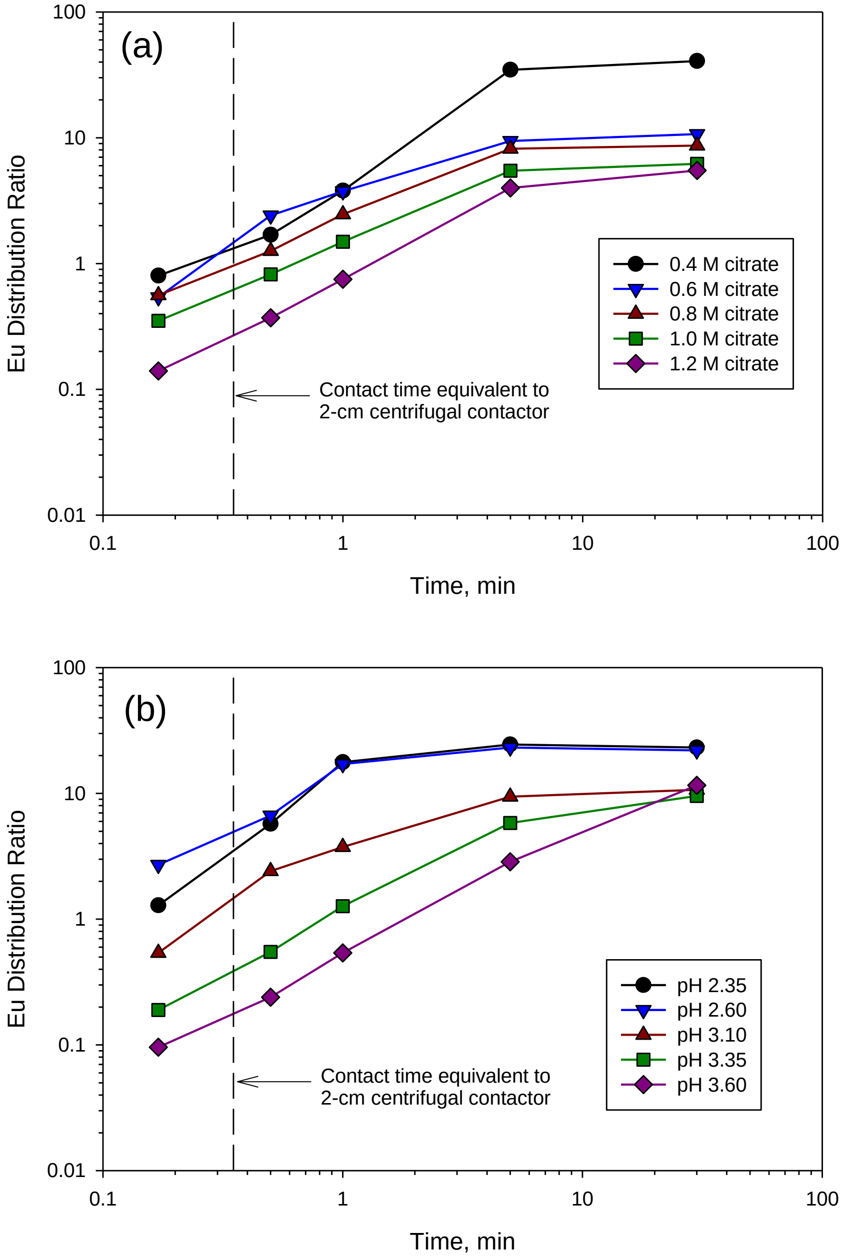

(a)
Eu Distribution Ratio
100
10
1
0.1
0.01
0.1
1
10
100
Time, min
0.4 M citrate
0.6 M citrate
0.8 M citrate
1.0 M citrate
1.2 M citrate
Contact time equivalent to
2-cm centrifugal contactor
(b)
Eu Distribution Ratio
100
10
1
0.1
0.01
0.1
1
10
100
Time, min
pH 2.35
pH 2.60
pH 3.10
pH 3.35
pH 3.60
Contact time equivalent to
2-cm centrifugal contactor

Figure 4

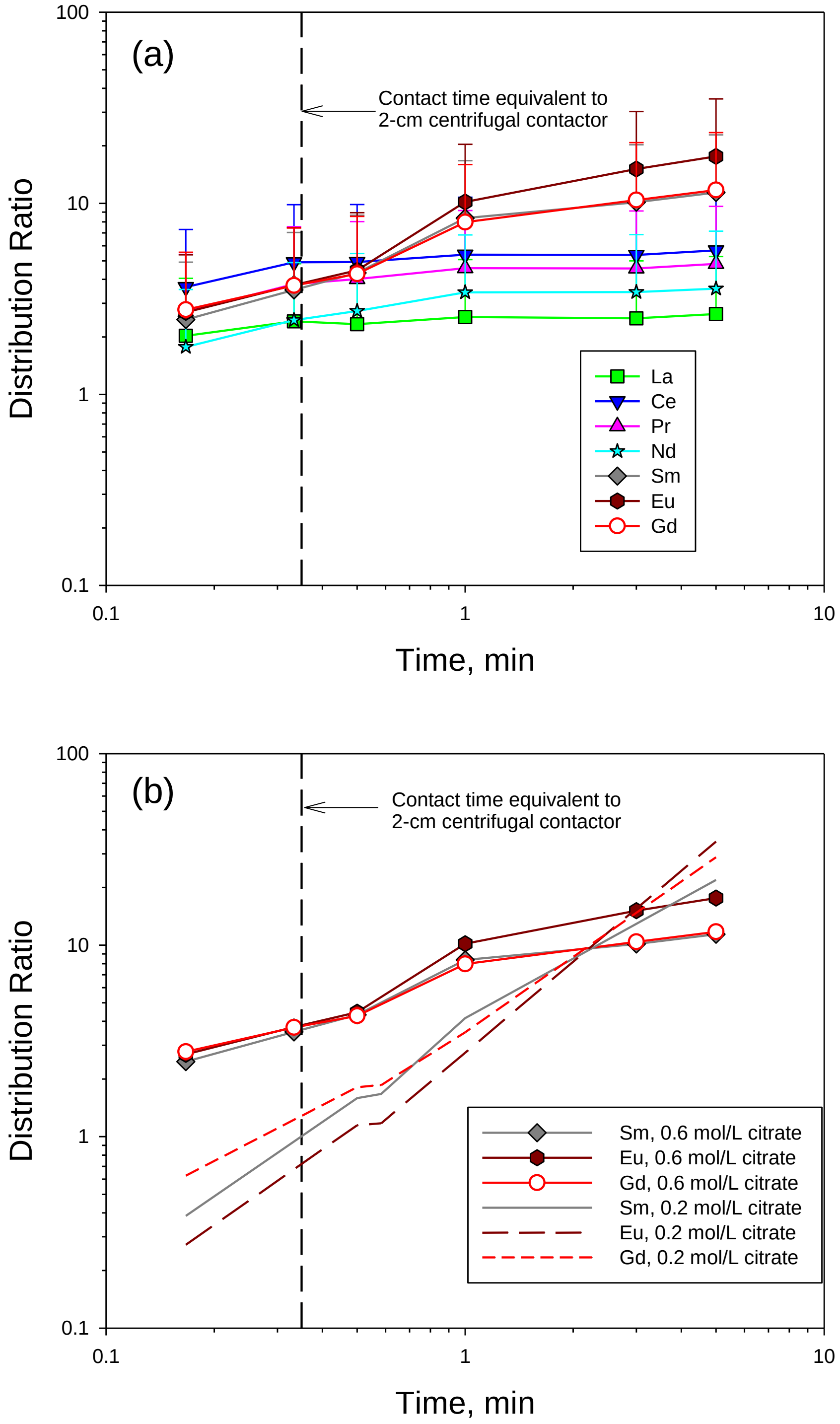

(a)
Contact time equivalent to
2-cm centrifugal contactor
Distribution Ratio
100
10
1
0.1
0.1
1
10
Time, min
La
Ce
Pr
Nd
Sm
Eu
Gd
(b)
Contact time equivalent to
2-cm centrifugal contactor
Distribution Ratio
100
10
1
0.1
0.1
1
10
Time, min
Sm, 0.6 mol/L citrate
Eu, 0.6 mol/L citrate
Gd, 0.6 mol/L citrate
Sm, 0.2 mol/L citrate
Eu, 0.2 mol/L citrate
Gd, 0.2 mol/L citrate

Figure 5

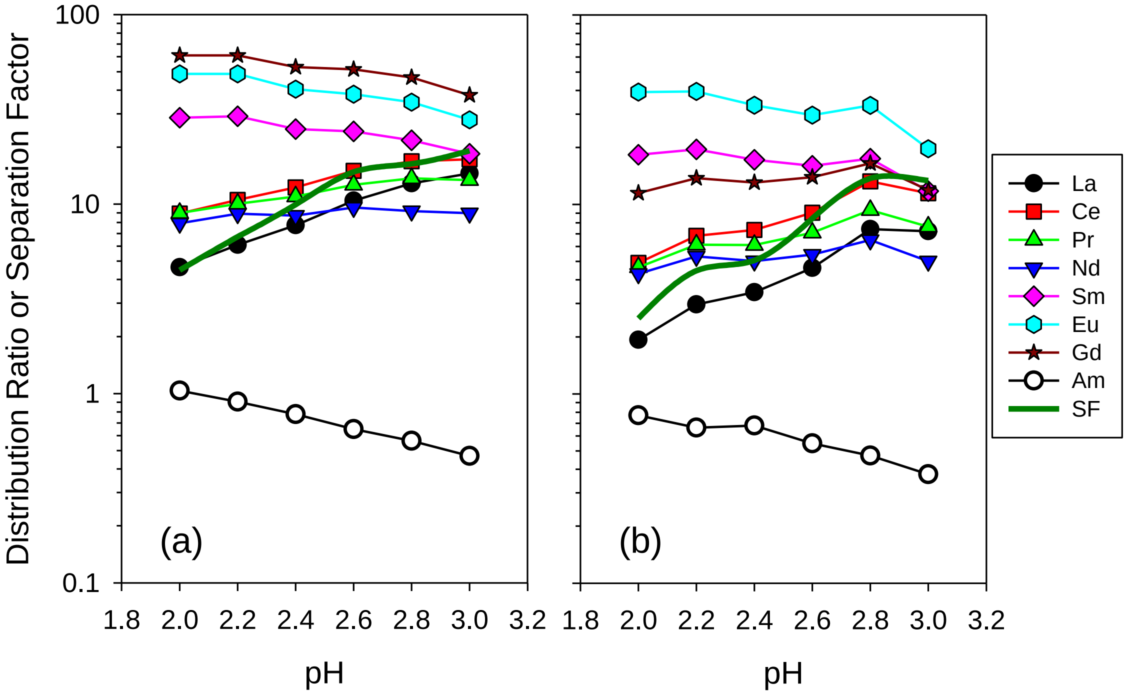

Distribution Ratio or Separation Factor
100
10
1
0.1
(a)
(b)
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
pH
La
Ce
Pr
Nd
Sm
Eu
Gd
Am
SF

Figure 6

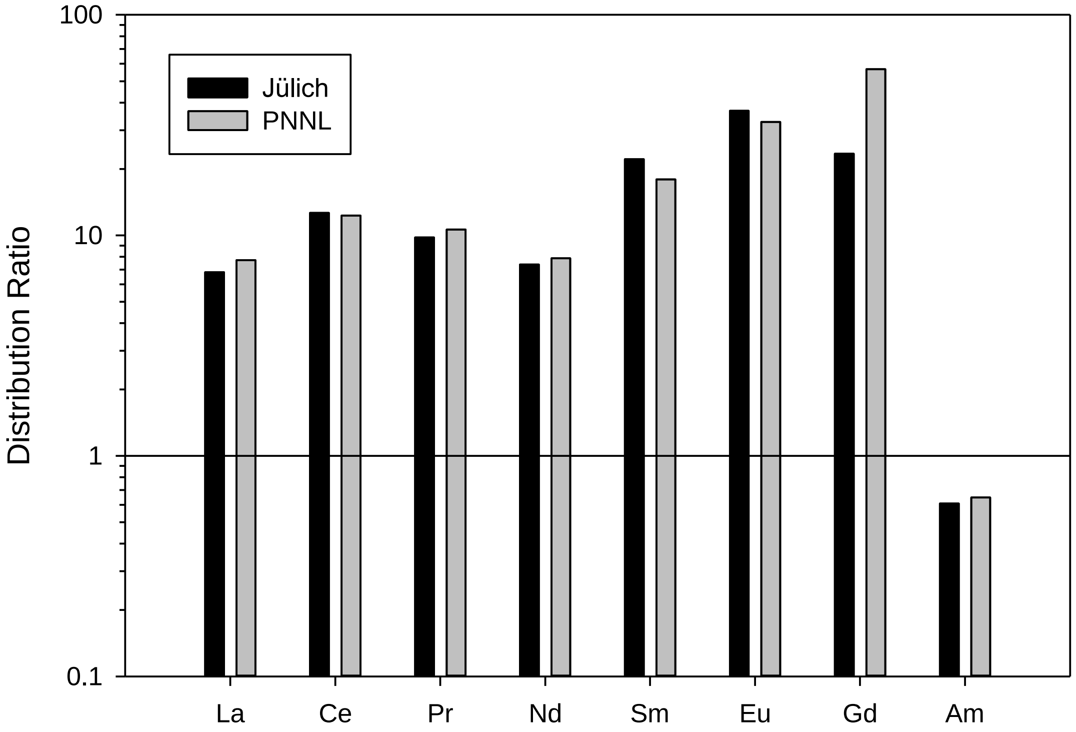

100
10
1
0.1
Distribution Ratio
Jülich
PNNL
La
Ce
Pr
Nd
Sm
Eu
Gd
Am

Figure 7

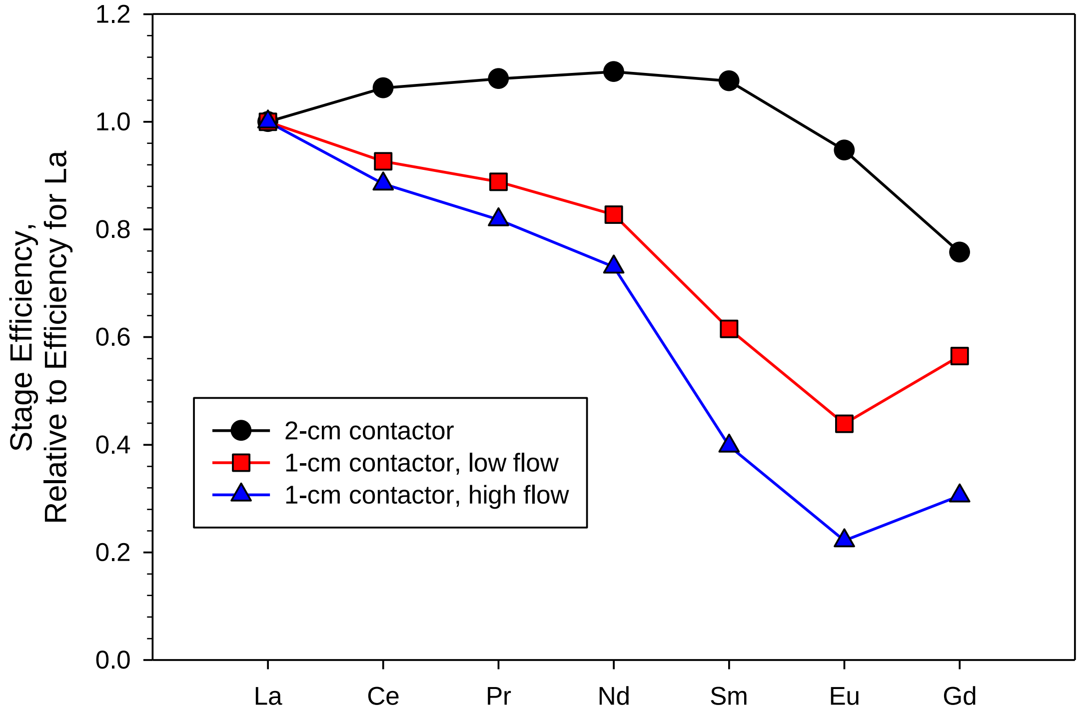

Stage Efficiency,
Relative to Efficiency for La
1.2
1.0
0.8
0.6
0.4
0.2
0.0
La
Ce
Pr
Nd
Sm
Eu
Gd
2-cm contactor
1-cm contactor, low flow
1-cm contactor, high flow

Figure 8

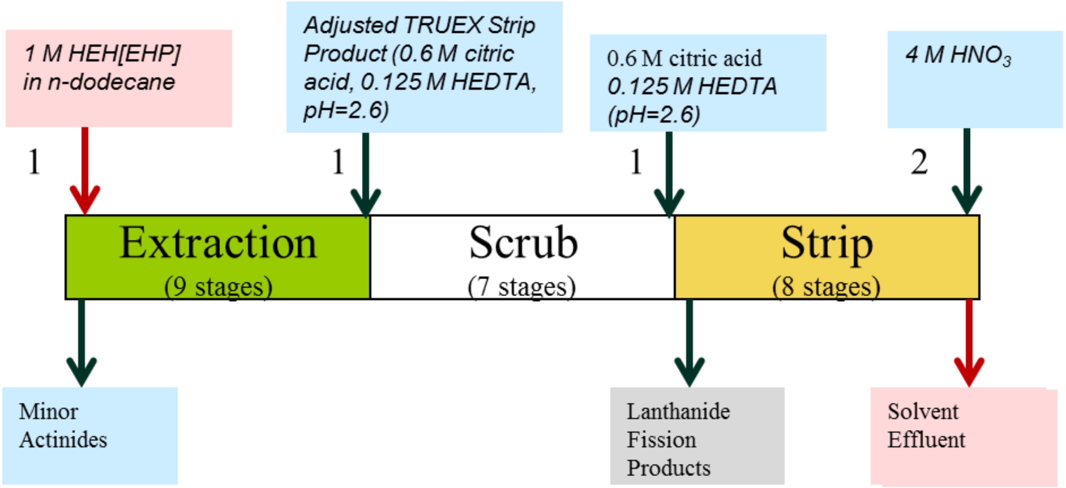

1 M HEH[EHP] in n-dodecane
Adjusted TRUEX Strip Product (0.6 M citric acid, 0.125 M HEDTA, pH=2.6)
0.6 M citric acid 0.125 M HEDTA (pH=2.6)
4 M HNO3
1
1
1
2
Extraction (9 stages)
Scrub (7 stages)
Strip (8 stages)
Minor Actinides
Lanthanide Fission Products
Solvent Effluent

Figure 9

Tables

Table 1. Initial aqueous solution composition for the high-loading-condition batch Advanced TALSPEAK measurements.

	Concentration, mmol/L	
Component	PNNL	FZ Jülich
La	1.65	1.97
Ce	3.10	3.98
Pr	2.07	1.56
Nd	5.45	6.01
Sm	1.11	1.12
Eu	0.21	0.25
Gd	0.35	0.59
	Concentration, mol/L	
Citrate	0.6	0.6
HEDTA	0.125	0.125
pH	2.5	2.6

Table 2. Fraction of Eu and Am in the form of free metal ion or neutrally charged complexes in 0.2 mol/L citrate buffer at pH 2.6 or 3.1; corresponding to the plots in

Figure 2.

	Percentage of Metal in the Complex at pH 2.6					
Ligand(L)	***Am^{3+} (free)***	***Am(Cit)***	***AmL***	***Eu^{3+} (free)***	***Eu(Cit)***	***EuL***
HEDTA	0	0	18	0	0	23
NTA	0	0	13	0	0	13
HIDA	0	24	34	2	32	32
DPTA	0	95	1	6	93	1
	Percentage of Metal in the Complex at pH 3.1					
HEDTA	0	0	2	0	0	2
NTA	0	0	3	0	0	3
HIDA	0	19	8	0	23	8
DPTA	3	80	0	0	93	1

Table 3. Steady-state and equilibrium distribution ratios and stage efficiencies(a) for the Advanced TALSPEAK system. Initial aqueous phase compositions as indicated in Table 1; organic phase 1.0 mol/L HEH[EHP] dissolved in *n*-dodecane. O/A = organic/aqueous. Estimated residence times were 10 seconds for the 2-cm contactor test, 12 minutes for the low-flow 1-cm contactor test, and 6 minutes for the high flow 1-cm contactor test.

2-cm centrifugal contactor (PNNL)

	Distribution Ratio		
Component	Equilibrium	10.4/12.4 mL/min (O/A)	Stage Efficiency, %
Am (γ)	0.64	0.60	93.8
La	7.72	5.41	70.1
Ce	12.3	9.16	74.5
Pr	10.6	8.02	75.7
Nd	7.88	6.04	76.6
Sm	17.9	13.5	75.4
Eu	32.7	21.7	66.4
Gd	56.7	30.1	53.1
Min $SF_{\mathrm{La/Am}}$	12.0	9.0	--

1-cm centrifugal contactor (FZ Jülich)

	Distribution Ratio			Stage Efficiency, %	
Component	Equilibrium	10/20 mL/h (O/A)	20/40 mL/h (O/A)	10/20 mL/h (O/A)	20/40 mL/h (O/A)
Am (γ)	0.54	0.48	0.41	88.1	75.3
Am (α)	0.55	0.44	0.39	79.2	70.5
Cm (α)	0.56	0.44	0.36	79.4	63.9
La	4.81	5.05	4.05	100	84.2
Ce	9.62	9.37	7.17	97.3	74.5
Pr	7.45	7.45	5.13	93.3	68.9
Nd	5.76	5.01	3.55	86.9	61.5
Sm	16.3	10.5	5.44	64.6	33.5
Eu (ICP-MS)	29.3	13.5	5.49	46.1	18.7
Eu (γ)	26.4	14.1	6.77	53.6	25.7
Gd	16.1	9.57	4.61	59.3	25.7

Min $SF_{\mathrm{La/Am}}$	11.2	10.5	9.9	--	--

[a] The stage efficiency is defined as the ratio of the effective distribution ratio measured in the centrifugal contactor to the batch equilibrium value, expressed as a percentage.

Table 4. Predicted Recovery in the raffinate and lanthanide product streams for the Advanced TALSPEAK flowsheet depicted in Figure 9.

Component	Raffinate	Lanthanide Product
Am	99.94%	0.06%
La	0.12%	99.88%
Ce	0.05%	99.95%
Pr	0.07%	99.93%
Nd	0.12%	99.88%
Sm	0.05%	99.95%
Eu	0.04%	99.96%