An Advanced TALSPEAK Concept for Separating Minor Actinides. Part 2. Flowsheet Test with Actinide-Spiked Simulant

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RUNNING TITLE

Advanced TALSPEAK Flowsheet Test with Actinide-Spiked Simulant

KEYWORDS

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

ABSTRACT

An Advanced TALSPEAK counter-current flowsheet test was demonstrated using a simulated feed spiked with radionuclides in annular centrifugal contactors. A solvent comprising 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP] or PC88A) in *n*-dodecane was used to extract trivalent lanthanides away from the trivalent actinides Am^{3+} and Cm^{3+}, which were preferentially complexed in a citrate buffered aqueous phase with *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA). In a 24-stages demonstration test the trivalent actinides were efficiently separated from the trivalent lanthanides with decontamination factors >1,000, demonstrating the excellent performance of the chemical system. Clean actinide and lanthanide product fractions and spent solvent with very low contaminations were obtained. The results of the process test are presented and discussed.

INTRODUCTION

Fractionation of used nuclear fuel constituents into different parts based on radiological and chemical considerations is an important research field in view of the nuclear fuel cycle and ultimate waste handling strategy.[1-2] Therefore, a large number of different strategies have been developed worldwide and are still under consideration.[3-7] Recent developments aim at the separation of the minor actinides (MA: Np, Am, Cm) as they are main contributors to the long-term radiotoxicity and repository heat-load.

A partitioning strategy investigated in the United States is based on the separation of the major actinides uranium and plutonium by the PUREX (Plutonium Uranium Reduction Extraction) process, followed by the TRUEX (TRansUranic Extraction)[8-10] and TALSPEAK (Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes) processes.[4, 11] Advanced PUREX processes also aim at the separation of Np, together with U and Pu.[12] The TRUEX process separates the trivalent lanthanides (Ln(III)) together with Am and Cm as a group from the rest of the fission products. Subsequently, Am and Cm are separated from the lanthanides in the TALSPEAK process. This separation of Ln(III) and trivalent actinides (An(III)) is required for the partitioning and transmutation strategy as many lanthanide isotopes have large neutron capture cross-sections and would therefore hinder an efficient re-use of the material. The TALSPEAK process has been investigated since the 1960s and a substantial amount of scientific work has been gathered on this subject.[13-14] However, the chemistry of the original TALSPEAK process is complex and its successful implementation requires tight control of the pH, which has hindered its industrial development. An alternative was sought to overcome these limitations of TALSPEAK.[15-21]

A new chemical system was investigated in-depth based on the use of a combination of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP] or PC88A) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA) in a citrate-buffered system (Figure 1). Optimal process conditions were found for 1.0 mol/L HEH[EHP] in *n*-dodecane as the solvent, and a feed solution containing the metal ions and 0.125 mol/L HEDTA and 0.6 mol/L citrate at pH 2.6.

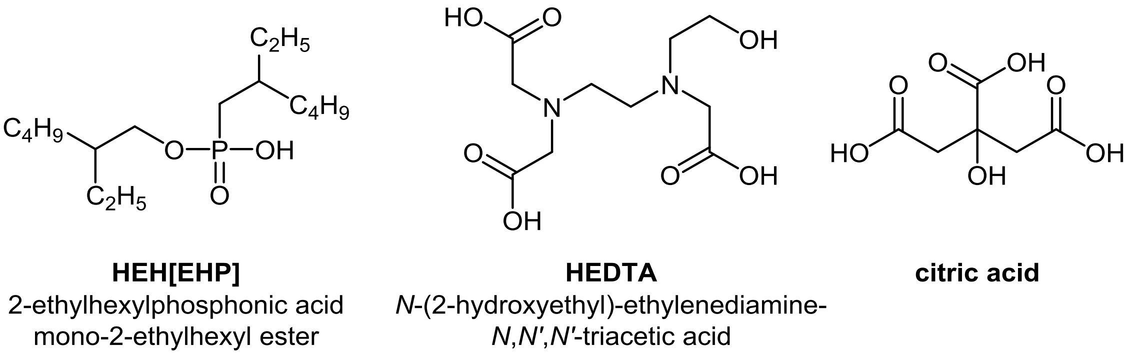

Figure 1. Chemical structures of HEH[EHP] (left), HEDTA (middle), and citric acid (right).

This paper is the second paper of a series describing the development of the Advanced TALSPEAK concept. In the first paper of the series, the optimization of the chemical system and single-stage centrifugal contactor experiments performed to identify the kinetics in the actual devices to be used and to allow the development of a flowsheet for the actual centrifugal contactor demonstration test using computer-code calculations are described.[22] This second paper reports the results of a flowsheet test that was performed with an actinide-spiked simulant solution.

EXPERIMENTAL

Materials

HEH[EHP] (95%) was purchased from BOC Sciences, *n*-dodecane (≥99%, ReagentPlus) was purchased from Sigma-Aldrich, HEDTA (99%) was purchased from Acros Organics, and citric acid (≥99%) and concentrated nitric acid (65%, analytical grade) were purchased from Merck. All chemicals were used as received without further purification. The organic and aqueous solutions were prepared by dissolving weighed quantities of the desired substance in the desired solvent. For aqueous dilutions demineralized water (18.2 MΩcm) was used. The radiotracers ^{241}Am, ^{244}Cm, and ^{152}Eu were purchased from Isotopendienst M. Blaseg GmbH, Waldburg, Germany, Oak Ridge National Laboratory, Oak Ridge, USA, and Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany. Ln nitrate salts were obtained from a variety of commercial sources, and were used as received.

A feed solution with the same Ln in concentrations as expected in a feed for the Advanced TALSPEAK process was used, which was spiked with the radiotracers ^{241}Am, ^{244}Cm, and ^{152}Eu. The feed solution was prepared by dissolving Ln nitrates, citric acid and HEDTA in water. Then, the pH was set to the desired pH value using a 10 mol/L NaOH solution in water and finally adding the radiotracers. The final concentrations and the pH value of the feed solution are given in Table 1.

Table 1. Composition of the Advanced TALSPEAK feed solution.

Component	Concentration	Component	Concentration	Component	Concentration
La	260.0 mg/L	Eu	39.5 mg/L	citrate	0.6 mol/L
Ce	570.2 mg/L	Gd	98.4 mg/L	HEDTA	0.125 mol/L
Pr	213.5 mg/L	^{241}Am	3.6 MBq/L	pH	2.6
Nd	1029 mg/L	^{244}Cm	3.6 MBq/L		
Sm	171.4 mg/L	^{152}Eu	10.2 MBq/L		

Procedures and analytical methods of the process demonstration

The demonstration of the process was carried out using 1 cm annular miniature centrifugal contactors produced by Institute of Nuclear Energy Technology, Tsinghua University, Beijing, China, with the rotors made of titanium and the stator housings made of stainless steel.[23-24] The process was run in counter-current mode with a rotator speed of 4,500 rpm and the speed was checked with a stroboscope tachometer regularly during the experiment. The contactor battery setup consists of four batteries with four stages each, resulting in a total available number of 16 stages. As the calculated flowsheet comprises 24 stages, the test was split into two parts as described below. Calibrated syringe pumps were used to deliver the different organic and aqueous flows.

The following analyses were carried out on all samples collected from all stages (aqueous and organic), including the samples taken to determine the steady-state: γ-spectroscopy for ^{241}Am and ^{152}Eu using a high-purity Ge-detector system, α-spectroscopy for ^{241}Am and ^{244}Cm, and ICP-MS for all inactive elements. The aqueous phases were directly measured after appropriate dilution. The organic phases were also directly measured after mixture with the non-ionic surfactant TRITON-X-100 and dilution to an appropriate concentration. The acidity profiles were determined for the aqueous phase by potentiometric titration with NaOH or pH measurement using a Metrohm 691 pH Meter. Details of the equipment, procedure, and analytics are described elsewhere.[25-27]

Distribution ratios were calculated as the radioactivity or concentration of the metal ion in the organic phase divided by the respective radioactivity or concentration in the aqueous phase. Distribution ratios between 0.01 and 100 exhibit an uncertainty of ±5%, while lower/higher values exhibit larger uncertainties.

The process decontamination factor $DF_{\text{feed/An product}}$ was calculated according to Equation 1, where Q is the volumetric flow rate and C is the metal ion concentration. The An/Ln decontamination factors were calculated according to Equation 2.

Equation 1.

$$DF_{\text{feed/An product}} = \frac{Q_{\text{feed}} \cdot C_{\text{feed}}}{Q_{\text{raffinate}} \cdot C_{\text{An product}}}$$

Equation 2.

$$DF_{\text{An/Ln}} = \frac{Q_{\text{feed}} \cdot C(\text{Ln})_{\text{feed}} \cdot C(\text{An})_{\text{prod}}}{Q_{\text{prod}} \cdot C(\text{Ln})_{\text{prod}} \cdot C(\text{An})_{\text{feed}}}$$

RESULTS AND DISCUSSION

This paper describes a laboratory-scale spiked demonstration of the Advanced TALSPEAK process. Part 1 of this series of publications describes the optimization of the chemical system which found a combination of 1.0 mol/L HEH[EHP] in *n*-dodecane and 0.125 mol/L HEDTA in an citric acid (0.6 mol/L) buffered aqueous phase at pH 2.6 to be most effective for the desired separation of An(III) from Ln(III). Further batch distribution measurements and single-stage kinetics tests using different types of centrifugal contactors are presented.[22] Based on these findings a flowsheet was designed and simulated using the Argonne Model for Universal Solvent Extraction (AMUSE) Code[28], which is shown in Figure 2. The flowsheet consists of three parts: extraction, scrubbing and stripping. In the extraction section Ln(III) are extracted into the organic phase. An aqueous to organic phase ratio of 2:1 is used. In the scrubbing section a 1:1 phase ratio is applied. The scrubbing section is used to back-extract An(III), which are co-extracted in minor amounts. The stripping section is used to strip Ln(III) back into an aqueous phase and again a 2:1 phase ratio is used. The organic solvent could then be recycled. The average residence time of the phases in the mixing chamber of the centrifugal contactors for each part of the flowsheet is given in Table 2. The residence time is relatively long compared to other processes run in these centrifugal contactors, e.g. for An(III)/Ln(III) co-extraction,[25] but comparable to processes for the selective separation of An(III) from Ln(III).[26, 29]

Due to the limitation of the available number of 16 centrifugal contactors, it was not possible to run the complete process in a single run. Therefore, the extraction + scrubbing part was tested first and enough loaded solvent was collected and stored overnight to be used on the consecutive day for the stripping part.

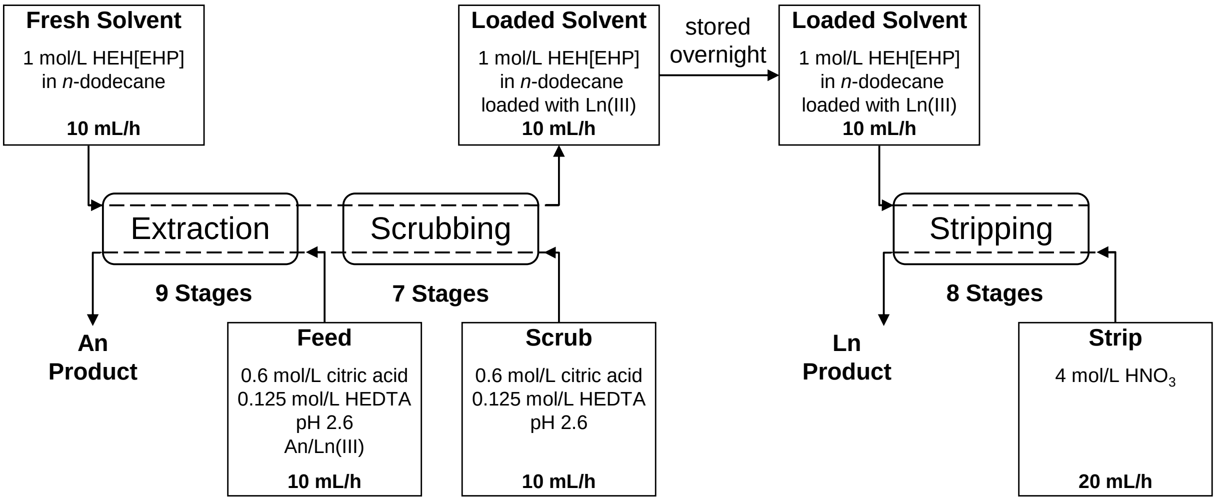

Figure 2. Flowsheet of the Advanced TALSPEAK process demonstration test.

Table 2. Average residence time of the phases in the mixing chambers of the centrifugal contactors (approx. 6 mL volume) for each part of the flow-sheet (see Figure 2)

Section	Total flow rate (org. + aq.) [mL/h]	Residence time [min]
Extraction	30	12
Scrubbing	20	18
Stripping	30	12

For the actual process test, the centrifugal contactors were first filled with scrub solution through the inlets for scrub and feed, as it had an identical composition as the feed except for metal ions. After the first drops of aqueous phase left the contactor rig through the aqueous outlet, the solvent was fed into the rig until the first organic phase left the rig through the organic outlet, with the aqueous flows set in the correct ratios to the organic flow. After the centrifugal contactors were completely filled with both phases, the active feed was introduced and the process test was started using the flow-rates given in Figure 2. During the process test, samples of the organic and aqueous effluents were taken to follow the evolution of the steady-state. Gamma spectroscopy was used to monitor the ^{241}Am and ^{152}Eu concentrations in the effluents at run time, while alpha spectroscopy and ICP-MS measurements were performed later. Figure 3 shows the concentrations of all metal ions in the organic phase outlet and those of the radioactive tracers in the aqueous phase outlet as a function of the experiment run-time.

The organic profiles show that steady-state was reached after 3 hours, as the ^{152}Eu concentration reached a plateau. This result from gamma spectroscopy was confirmed by ICP-MS measurements. Europium and the other Ln metal ions were routed to the organic phase outlet and the steady-state was reached in the same time for all Ln. The Ln concentrations in the aqueous phase outlet were very low (close to or below the detection limits) and therefore only the results from ^{152}Eu are shown here. Am and Cm were routed to the aqueous phase outlet. The ^{241}Am and ^{244}Cm concentrations however increased slower and it took 10 hours to reach the steady-state. The selectivity of the Advanced TALSPEAK system for An/Ln separation was very good, as concentrations of Am and Cm close to or below the detection limits were found in the loaded organic phase and similarly low concentrations of Ln were found in the aqueous An product phase.

All organic samples collected after 240 minutes were combined and stored overnight. The concentrations of ^{241}Am and ^{244}Cm in the loaded solvent were close or below the detection limits. The Ln were quantitatively extracted, which is also confirmed by the Ln concentration profiles (Figure 5 and Figure 6) and the fact that the concentrations of Ln in the An product fraction were extremely low (Table 3). The Ln-loaded solvent was clear and free of precipitates or phase entrainment and was directly used the next day.

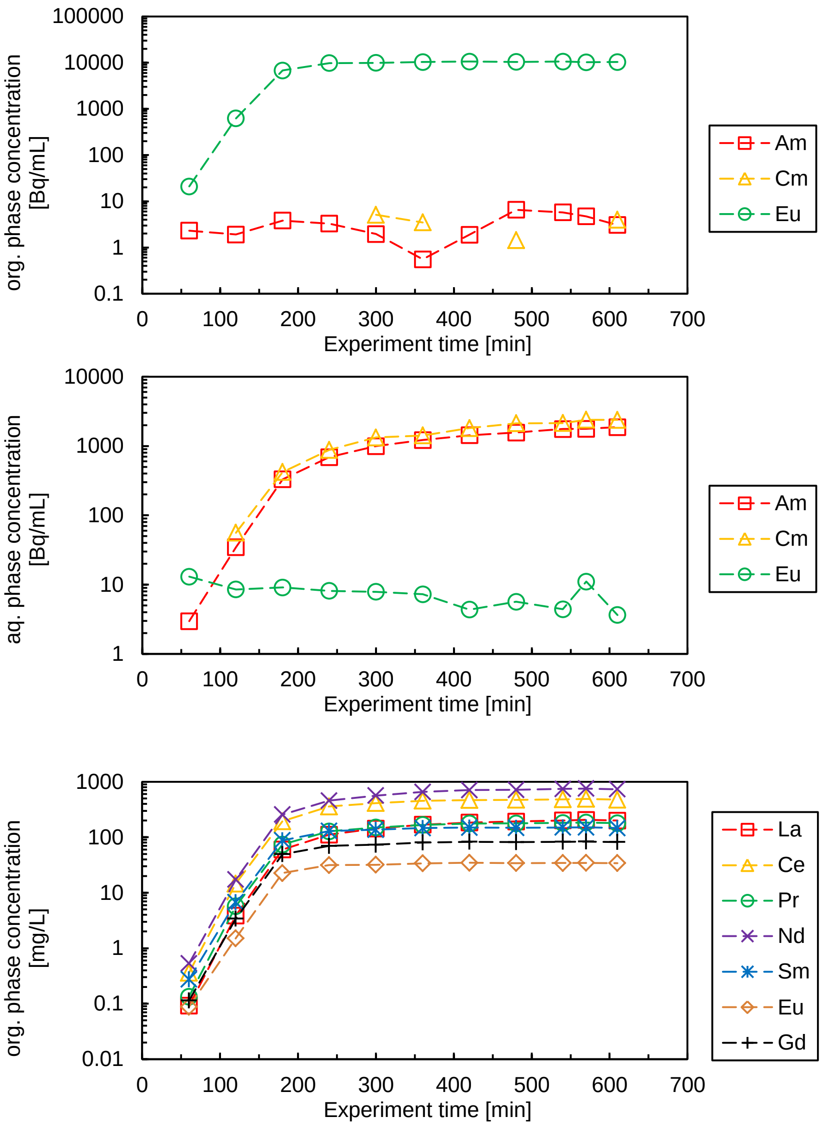

Figure 3. ^{241}Am, ^{244}Cm and ^{152}Eu concentrations in the organic (top) and aqueous (middle) outlets and the other Ln metal ions in the organic outlet (bottom) of the centrifugal contactor battery as a function of the experiment run-time of the extraction/scrubbing part of the test. ^{241}Am and ^{152}Eu data points show results from gamma-spectroscopy, ^{244}Cm data points show results from alpha-spectroscopy. The Ln metal ion concentrations were determined by ICP-MS. Missing data points were below the detection limit.

On the next day, the stripping part of the flow-sheet was tested with eight centrifugal contactors. The contactors used in stages 9 – 16 were used after flushing with 4 mol/L HNO_3 and *n*-dodecane in counter-current mode. For the stripping test the contactors were prepared using 4 mol/L HNO_3 and fresh solvent. Then, the organic phase was switched to the loaded organic phase of the first day and the test was run for just under six hours.

Figure 4 shows the ^{152}Eu concentrations measured by gamma spectroscopy and the concentrations of all Ln measured by ICP-MS in the aqueous and organic outlets as a function of the stripping test run-time. Again, a plateau was reached very fast indicating a quick evolution of the steady-state. All Ln metal ions were stripped efficiently and routed to the aqueous Ln product stream. Am and Cm results are not shown in Figure 4 as the concentrations determined by alpha and gamma spectroscopy were below or close to the detection limits.

The mass balances, recoveries and decontamination factors obtained during the Advanced TALSPEAK test are shown Table 3. The mass balances of the Ln elements measured by ICP-MS in the aqueous Ln product were between 97 – 115%. This large uncertainty is due to the accumulation of uncertainties in the ICP-MS measurements and the process flow-rates. The concentrations of Ln in the other process streams (An product and spent solvent) were extremely low and <0.1% of the feed concentrations, Therefore, nearly quantitative recovery of Ln in the aqueous Ln product is assumed and the mass balances were given as >99.9% in the table. The decontamination factors were calculated according to Equation 1 and Equation 2 and were found to be excellent with the lowest process DF-value of 800 found for ^{152}Eu. The An/Ln decontamination factors were all >1000, proving the high selectivity of the Advanced TALSPEAK system.

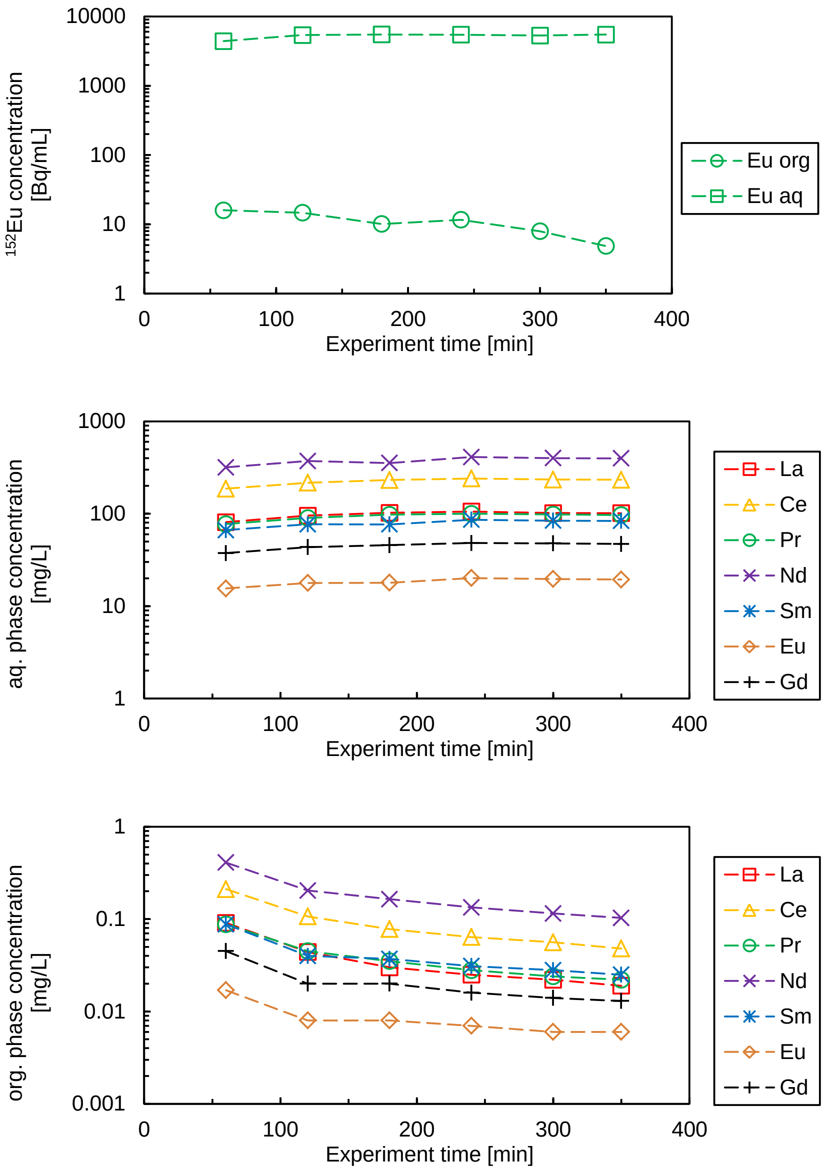

Figure 4. ^{152}Eu concentrations in the organic and aqueous outlets (top) and the other Ln metal ions in the aqueous (middle) and organic outlet (bottom) of the centrifugal contactor battery as a function of the experiment run-time of the stripping part of the test. ^{152}Eu data points show results from gamma-spectroscopy, ^{241}Am and ^{244}Cm data is not shown as the measured concentrations were very low and close or below the detection limits. The Ln metal ion concentrations were determined by ICP-MS.

Table 3. Mass balances, recoveries, process and An/Ln decontamination factors obtained during the Advanced TALSPEAK test.

Element	% in An product	% in loaded solvent	% in Ln product	% in spent solvent	$DF_{feed/An\ product}$	$DF_{An/Ln}$
^{241}Am	99.9	0.1	0.1	<0.1	1	-
^{244}Cm	>99.9	<0.1	<0.1	<0.1	1	-
La	0.002	>99.9	>99.9	0.017	3.0E+04	1.5E+04
Ce	<0.001	>99.9	>99.9	0.020	1.2E+05	6.2E+04
Pr	<0.001	>99.9	>99.9	0.023	1.1E+05	5.4E+04
Nd	0.003	>99.9	>99.9	0.023	1.6E+04	8.2E+03
Sm	<0.001	>99.9	>99.9	0.033	>1.0E+04*	>1.0E+04*
^{152}Eu	0.1	99.9	99.9	<0.1	8.0E+02*	>1.0E+03*
Eu	0.001	>99.9	>99.9	0.032	5.9E+04	3.0E+04
Gd	0.001	>99.9	>99.9	0.029	4.9E+04	2.5E+04

*The concentration in the An product was close to or below the detection limit

The concentration profiles were determined by sampling the content of the contactor mixing chambers after steady-state was reached and the process was stopped. Samples taken from each mixing chamber were analyzed using alpha and gamma spectroscopy as well as ICP-MS. The ^{241}Am, ^{244}Cm and ^{152}Eu profiles are shown in Figure 5 and the profiles of the other Ln elements is shown in Figure 6. The Am and Cm profile clearly show the routing of those two elements to the aqueous raffinate and a steep profile in the scrubbing section. Distribution ratios of 0.6 and 0.4 were measured for both Am and Cm in the extraction and scrubbing sections, respectively (Table 4); these values were consistent with previously measure batch distribution ratios.[22] Only low concentrations have been measured in the stripping section. However, in stages 19 and 20 increased concentrations were observed. They were presumably caused by impurities of Am and Cm left over from insufficient rinsing of the contactors when set up for the stripping test. The contactors used here as stages 19 and 20 have been used as stages 11 and 12 on the first day, where high concentrations of An(III) were still present in the stages.

The Ln showed a steep profile in the extraction and stripping sections and were routed first to the loaded solvent and then to the aqueous Ln product. In the scrubbing section of the flowsheet a parallel profile was obtained, indicating constant distribution ratios and no recycling of any of the elements. Stripping with 4 mol/L HNO_3 was very efficient; the Ln were stripped efficiently in the first two stripping stages (stages 17 – 18). The distribution ratios of all metal ions were low (Table 4) at the stripping conditions, resulting in steep concentration profiles. However, the relatively high concentrations of Ln measured in stages 20-24 were presumably also caused by insufficient rinsing of the contactors when set up for the stripping test as described above.

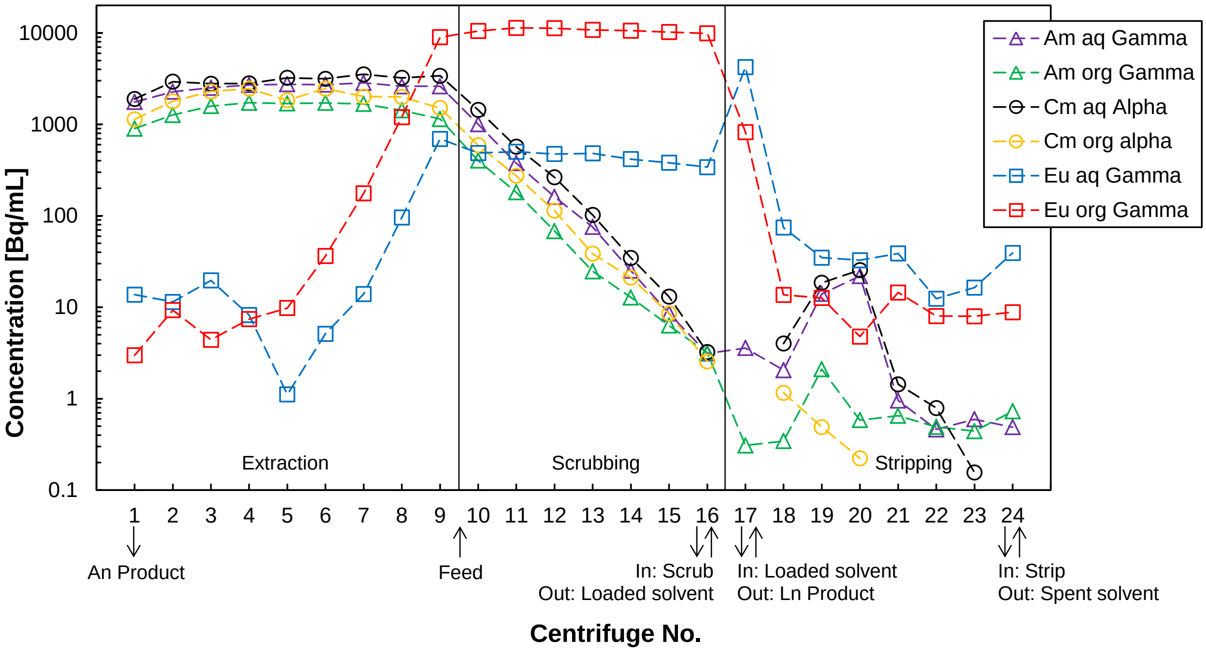

Figure 5. Experimental aqueous and organic concentration profiles of ^{241}Am, ^{244}Cm and ^{152}Eu for the whole test. Stage numbering and section labeling is given according to the flowsheet given in Figure 2.

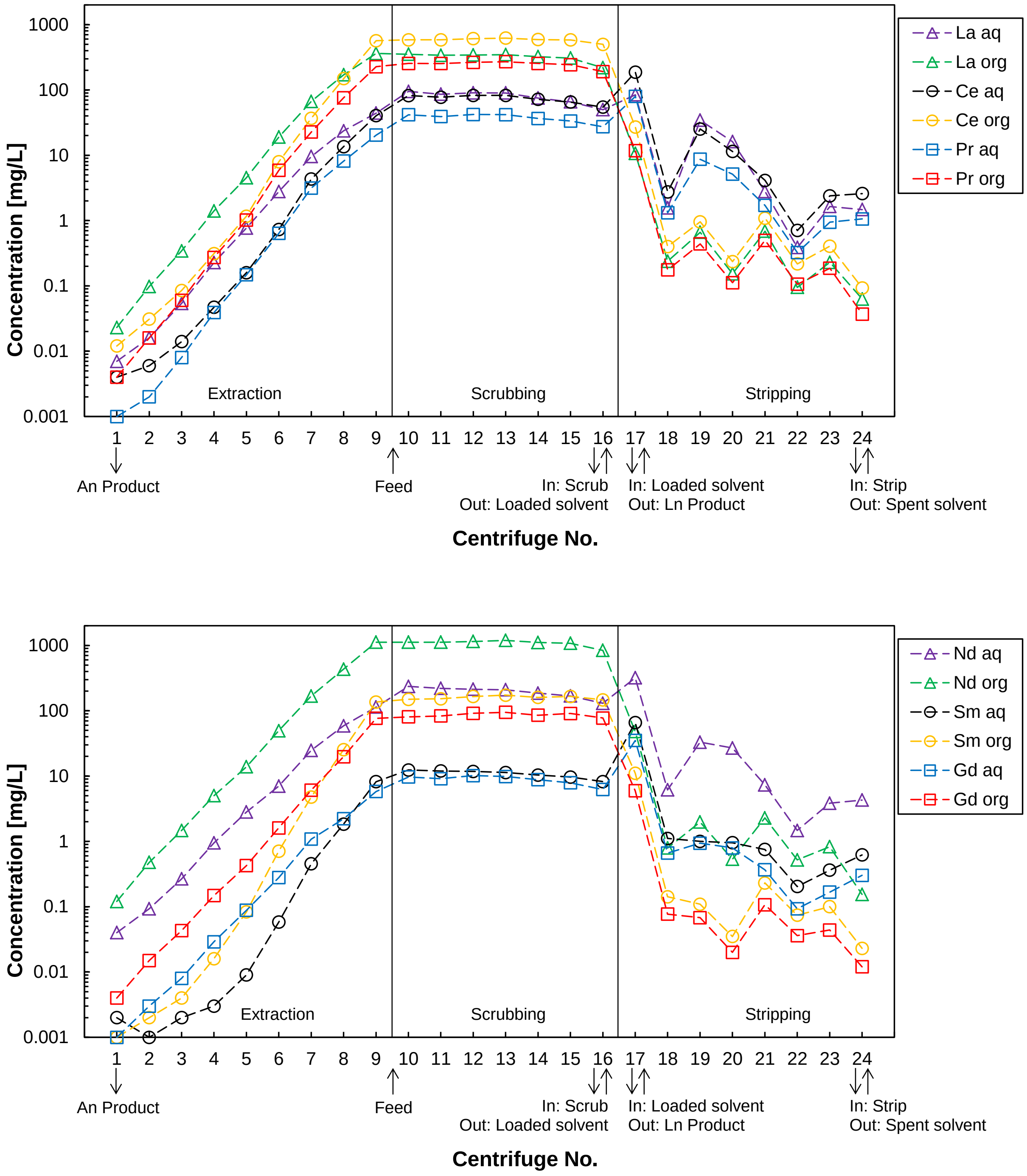

Figure 6. Experimental aqueous and organic concentration profiles of the Ln elements for the whole test. Eu profiles are not shown here, as they are comparable to those shown for ^{152}Eu in Figure 5. Stage numbering and section labeling is given according to the flowsheet given in Figure 2.

Table 4. Distribution ratios in the different process sections at steady state.

Element	Extraction Stage 7	Scrubbing Stage 12	Stripping Stage 17
^{241}Am	0.6	0.4	0.1
^{244}Cm	0.6	0.4	D.L.*
La	7.0	3.8	0.1
Ce	8.5	7.4	0.1
Pr	7.2	6.3	0.2
Nd	6.8	5.4	0.2
Sm	10.5	14.1	0.2
^{152}Eu	12.7	23.7	0.2
Eu	17.2	21.7	0.2
Gd	5.6	9.0	0.2

*D.L.: at least one measured concentration below the detection limit

The concentration profiles were calculated using a computer-code model using batch extraction and single stage centrifugal contactor kinetics data.[22, 30-31]

Figure 7 shows the experimental and calculated concentration profiles for ^{241}Am and ^{152}Eu using distribution data as reported in in Part 1[22] of this series of papers. Since the single stage centrifugal contactor kinetics data had been measured only for the experimental conditions prevailing in the extraction section of the flowsheet, assumptions had to be made for the scrubbing and stripping sections: Equilibrium distribution ratios were used in the scrubbing section, and distribution ratios of 0.1 were arbitrarily used in the stripping section. Agreement between experimental and calculated concentration profiles was relatively good in the extraction section, but deviations were observed especially for Am(III) in the scrubbing section. This is presumably due to the assumptions made for the scrubbing section and the lack of experimental single-stage data for this section. Small deviations of the pH or unknown species, which were co-extracted in the extraction section and facilitate the back-extraction of Am in the scrubbing section, could be other explanations.

Therefore, the Am stage efficiency for the scrubbing section was adjusted to fit the experimental profiles by using a distribution ratio of 0.4 (cf. Table 4). As shown in Figure 8, this results in good agreement also for the scrubbing section. The discrepancy in the Am concentrations in stage 17 may be due to contamination, as discussed above.

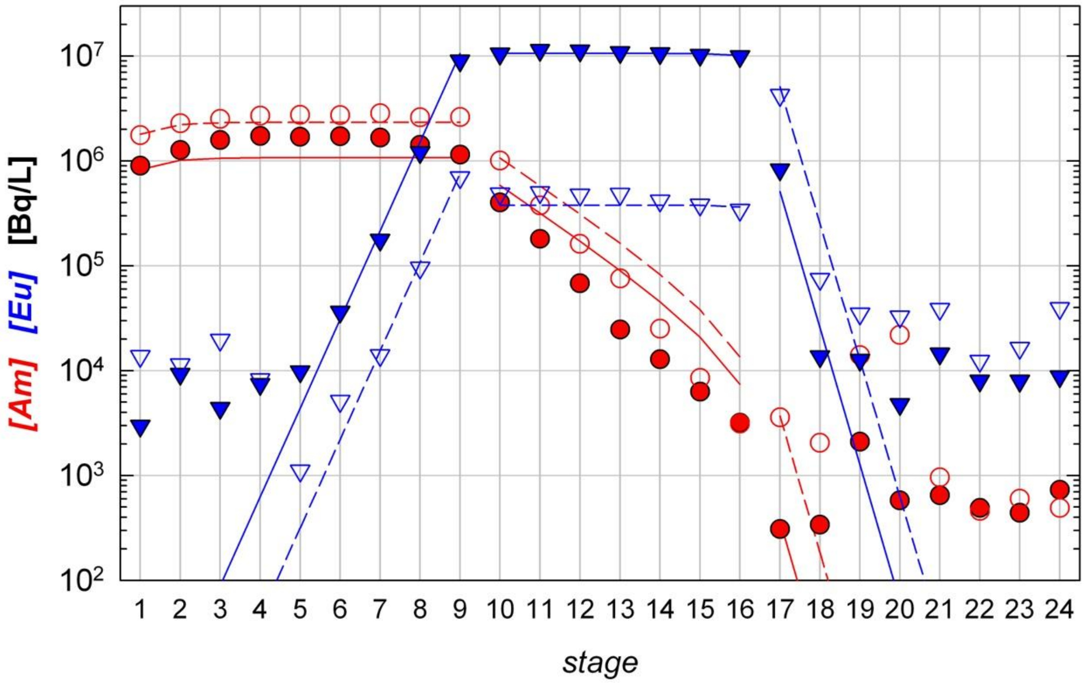

Figure 7. Experimental (data points) and calculated (lines) concentration profiles for ^{241}Am (circles) and ^{152}Eu (triangles) using the stage efficiencies determined from single stage centrifugal contactor experiments.[22] Organic phase: filled symbols, solid lines. Aqueous phase: open symbols, dashed lines.

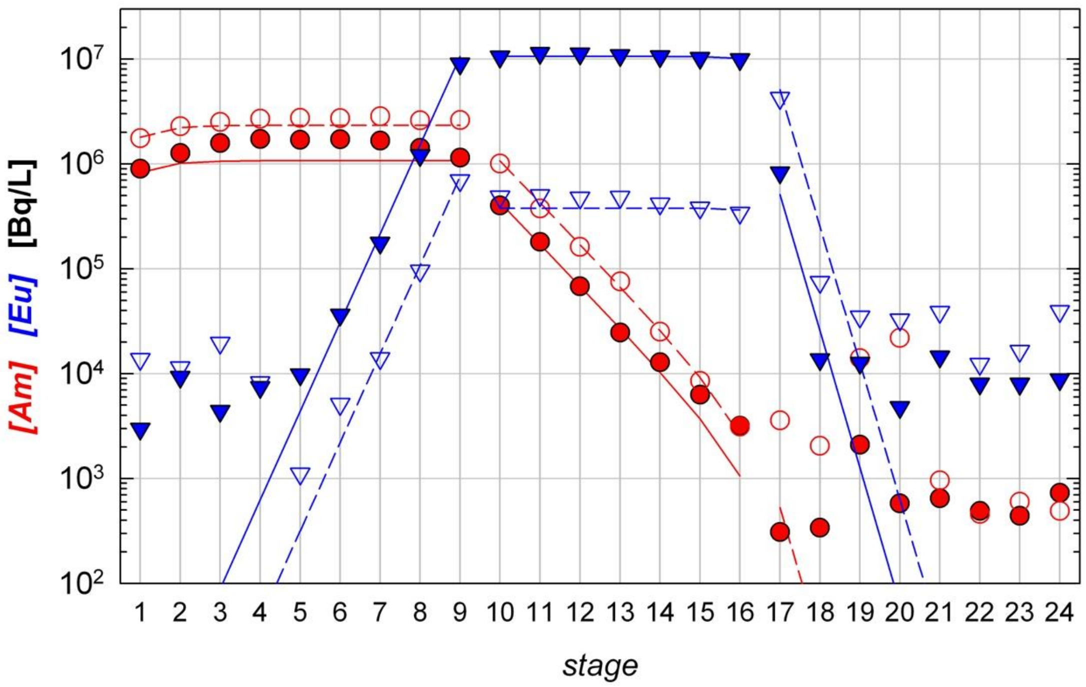

Figure 8. Experimental (data points) and calculated (lines) concentration profiles for ^{241}Am (circles) and ^{152}Eu (triangles) using the stage efficiencies determined from single stage centrifugal contactor experiments[22] *except for Am in the scrubbing section*. Organic phase: filled symbols, solid lines. Aqueous phase: open symbols, dashed lines.

CONCLUSIONS

The presented Advanced TALSPEAK process is based on a chemical system using HEH[EHP] in *n*-dodecane to extract the trivalent lanthanides away from the trivalent actinides Am^{3+} and Cm^{3+}. The An(III) elements are kept in the aqueous phase by preferential complexation with HEDTA in a citrate buffered solution at pH 2.6. A 24-stages flow-sheet was tested in counter-current mode using 1 cm centrifugal contactors. An excellent performance was observed, as clean An(III) and Ln(III) product fractions were obtained with high decontamination factors (>1000). The spent solvent was also very clean enabling an easy recycling of the solvent. No hydrodynamic problems were observed during the test. The measured metal ion concentration profiles were described very well by a slightly modified computer-code model. The small adjustment of the Am stage efficiency in the scrubbing stages was needed as experimental data were only available for the extraction section of the flowsheet. In summary, the process performance was better than expected based on the initial

AMUSE simulation; i.e., a reduced number of stages could be used in further process development. The presented Advanced TALSPEAK process would be an excellent choice following a TRUEX process by separating the An(III) from Ln(III).

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