

Demonstration of the LUCA process for the separation of americium(III) from curium(III), californium(III), and lanthanides(III) in acidic solution using a synergistic mixture of bis(chlorophenyl)dithiophosphinic acid and tris(2-ethylhexyl)phosphate

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Summary. The LUCA process was developed at Forschungszentrum Jülich for the selective separation of Am(III) from an acidic solution containing the trivalent actinides Am(III), Cm(III), and Cf(III) as well as lanthanides. A mixture of 0.4 mol/L bis(chlorophenyl)dithiophosphinic acid and 0.15 mol/L tris(2-ethylhexyl)phosphate dissolved in 20% isooctane/80% *tert*-butyl benzene was used as the extractant. The process was carried out in centrifugal contactors using an optimized flowsheet involving 7 stages for extraction, 9 stages for scrubbing and 8 stages for back-extraction. Very encouraging results were obtained. A high feed decontamination factor was obtained for Am(III) (> 1000), and recovery in the product after stripping was higher than 99.8%. The Am(III) product was contaminated with 0.47% Cm(III). More than 99.9% Cf(III), Eu(III) and > 99.5% Cm(III) inventories were directed to the raffinate and the contamination with Am(III) (< 0.08%) was low. The experimental results were in good agreement with the predictions of a computer code.

1. Introduction

Plutonium and the minor actinides (MA) Np, Am and Cm are mainly responsible for the long-term radiotoxicity of the waste generated from nuclear power production. If these radionuclides are removed from the waste (partitioning) and converted by neutron fission (transmutation) into shorter-lived or stable elements, the remaining waste loses most of its long-term radiotoxicity. Thus, partitioning and transmutation are considered attractive options for reducing the burden on geological disposals. This is important both in the case of a nuclear phase-out, as well in the case of the continuous use of nuclear power as part of a sustainable energy supply [1]. Today, Pu and uranium are industrially separated

from spent fuel using the well-established PUREX process, which can also be adapted for partitioning Np [2]. There is no potential for recovering Am or Cm using the PUREX process because the tri-*n*-butylphosphate (TBP) extractant shows a very low affinity for trivalent actinides. During the last decade a large amount of research has been conducted in several countries on the separation and recovery of Am and Cm from the high-level liquid waste (HLLW) fraction of the PUREX process. A comprehensive survey on actinide separation science and technology is given by Nash *et al.* [3]. Most partitioning strategies rely on the following separation processes.

1. Separation of uranium and/or plutonium from spent fuel dissolution liquors (*e.g.* PUREX, UREX).
2. Co-extraction of the trivalent actinides and lanthanides (*e.g.* TRUEX, DIAMEX, TRPO, TODGA).
3. Separation of trivalent actinides from lanthanides (*e.g.* TALSPEAK, SANEX).

The last step is important because it is essential to separate americium and curium from trivalent lanthanides to avoid the strong absorption of thermalized neutrons by the lanthanides, particularly if the trivalent actinides are to be recycled as fuel (or targets for transmutation) in a current generation reactor. Due to similarities in the chemical properties and behaviour of trivalent actinides and lanthanides extractants or complexing agents containing soft donor atoms such as N, S, Cl, *etc.* are required for reliable group separations [4–8]. After the An(III)/Ln(III) separation process, the product fraction contains approx. 0.35 to 0.45 g/L Am and Cm (*e.g.* after a BTBP process [9]).

In principal, both elements could be transmuted together in a fast reactor or ADS system. However, because of the high heat decay and neutron emission of curium, any dry or wet fabrication process will require remote handling and continuous cooling in hot cells behind thick concrete shielding. The development of a simple, compact and robust fabrication process appears to be a great challenge [10]. One option involves the interim storage of curium for about

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100 years, after which the relatively short-lived curium isotopes (^{242}Cm , ^{243}Cm , and ^{244}Cm) decay to form plutonium isotopes which can then be easily separated from americium. Therefore, an effective method for separating Am from Cm prior to re-fabrication is a major prerequisite for the discussion of further fuel cycle scenarios [1].

The separation of adjacent trivalent actinides represents an even more challenging task than the An(III)/Ln(III) separation. It is known that the separation of americium from curium is a very difficult operation, due to the very similar properties of these elements [3]. The development of solid ion-exchange materials, which are capable of capturing and reversibly releasing the metal ions back into the contacting solution, represents a big step forward in separating elements with similar properties. These separations depend more on differences in the complexing power of the eluants towards the metal ions than on the selectivity of the resin. According to this method, Am/Cm separation is carried out by selective elution of Am(III) and Cm(III), and the quality of separation is a function of the nature of the eluant. Promising results for transplutonium separations were obtained on a DOWEX 50 cation exchanger using α -hydroxy-isobutyric acid as an eluant [11]. The α -hydroxy-isobutyric acid provides average separation factors for adjacent lanthanides or trivalent actinides of about 1.3–1.5.

Numerous other techniques, including high-pressure ion exchange, extraction chromatography, and solvent extraction using *e.g.* di(2-ethylhexyl)phosphoric acid (HDEHP) have also been used for Am(III)/Cm(III) separation and purification [12–15]. However, the Am/Cm separation factors were low and do not exceed 3, necessitating a large number of stages in order to obtain a pure product. The TALSPEAK process can be adapted for liquid membrane separations [16]. The authors report on the use of a “supported liquid membrane” impregnated with HDEHP for the separation of Am(III) and Cm(III) using DTPA, citric acid, and the potassium salt of a heteropolyacid, potassium phosphotungstate ($\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$), as aqueous complexants. The optimum separation factors reported are $\text{SF}_{\text{Am(III)/Cm(III)}} \approx 5.0$.

The best separation of transplutonium elements has been obtained using methods based on the various oxidation states of the separated elements. Contrary to Cm, Am can be oxidized in aqueous solutions to oxidation states higher than III, *i.e.* IV, V and VI. Nevertheless, these Am oxidation states are thermodynamically unstable in acidic aqueous solutions [17]. The solvent extraction of hexavalent Am has been studied by several authors [18, 19]. In the SESAME process, developed at CEA (France), an electrochemical method was used to oxidize the americium to IV and VI in the presence of heteropolyanions, such as phosphotungstate $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$. The Am(VI) generated in this manner can be separated from Cm(III) by extraction, for example with TBP. In-depth experience has been gained at CEA over the last 20 years, and several SESAME tests have been carried out in Marcoule, France [20]. Although the results of the tests were encouraging, the process was nevertheless not sufficiently robust for further industrialisation.

The CEA is now considering the development of a novel option for Am/Cm separation based on the difference of the affinity of the DIAMEX extractant (DMDOHEMA) for Am(III) and Cm(III) [21]. Since the Am(III)/Cm(III) sep-

aration factor of 1.6 is low, this process requires a large number of stages. Nevertheless, a flowsheet comprising 24 extraction, 24 scrubbing and 8 stripping stages was successfully tested in 2002 using surrogate solutions without significant difficulties. The performance of this test was good, as was predicted by calculations: more than 99.9% of each actinide was recovered. 0.6% Am was found within the Cm product solution, 0.7% Cm within Am product solution, and only 0.02% Am and 0.01% Cm remained in the stripped solvent.

Recently, Myasoedov *et al.* [22] reported on Am(III)/Cm(III) separation by counter-current chromatography (CCC) using the DIAMEX solvent. The application of CCC, a multistage extraction technique, makes it possible to separate the elements within 100 min: the Cm fraction contains 99.5% Cm(III) and 0.6% Am(III) inventories and the Am fraction contains 99.4% Am(III) and 0.5% Cm. However, CCC can only be applied to analytical and radiochemical separations on a laboratory scale, whereas solvent extraction processes are predominantly proposed for use on an industrial scale.

The synergistic mixture (Fig. 1) composed of bis(chlorophenyl)dithiophosphinic acid [(CIPh) $_2$ PSSH] and tris(2-ethylhexyl)phosphate (TEHP) showed a very high affinity for actinides(III) over lanthanides(III). Am(III)/Eu(III) separation factors were over 2000. Surprisingly high Am(III)/Cm(III) separation factors of 6–10 were also reported by Modolo *et al.* [23]. Using $^1\text{H-NMR}$, the aggregation of (CIPh) $_2$ PSSH has been determined, and its effect on the extraction has been considered. Treatment of distribution data by slope analysis suggests that the extracted An(III) and Ln(III) complexes have the composition of $\text{ML}_3(\text{Syn})_{\text{xorg}}$, where $\text{HL} = (\text{CIPh})_2\text{PSSH}$ and $\text{Syn} = \text{neutral synergist TEHP}$. Furthermore, the thermodynamic parameters ΔH^0 , ΔS^0 , and ΔG^0 of the extraction have been determined in the temperature range between 10 and 45 °C.

Based on the extraordinary extraction properties of the above synergistic mixture, the LUCA process [24] was invented. LUCA is the acronym for Lanthaniden Und Curium Americium Trennung. The present paper relates to the development and demonstration of a continuous LUCA process for the selective recovery of Am(III) from an aqueous nitric acid solution ($\approx 0.1 \text{ mol/L HNO}_3$) containing trivalent actinides (*i.e.* Am(III), Cm(III) and Cf(III)) and trivalent lanthanides.

A detailed stability study of the (CIPh) $_2$ PSSH used in the LUCA process was carried out previously [25]. The experimental investigations revealed that aromatic dithiophos-

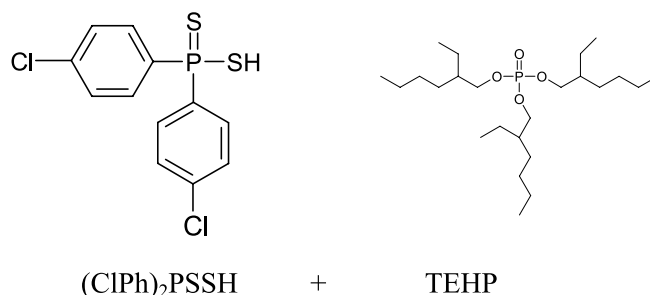


Fig. 1. Synergistic mixture of bis(chlorophenyl)dithiophosphinic acid and tris(2-ethylhexyl)phosphate used in the LUCA process.

phinic acids are more stable to hydrolysis and radiolysis than aliphatic dithiophosphinic acids (Cyanex 301). The aromatic dithiophosphinic acids dissolved in an aromatic solvent such as toluene do not degrade in contact with 3 mol/L HCl, degrade only slightly with 3 mol/L H₂SO₄ but completely in contact with > 2 mol/L HNO₃ during 100 d of contact. With the aid of the HNO₂ scavengers amidosulfuric acid, hydrazine or urea it was possible to also stabilize the extractants in contact with 2 M HNO₃ against hydrolysis.

It has been found that the hydrolytic and radiolytic degradation by oxidation of the dithiophosphinic acids produces the corresponding monothioderivatives and also the dioxophosphinic acids which appear to have no significant influence on extraction. The distribution ratio D_{Am} and, consequently, the *e.g.* Am/Eu separation factors decrease with increasing degradation but this decrease can be explained by the reduction in extractant concentration. The possible radiolytic degradation of TEHP and the effect on extraction has so far not been investigated and taken into account within the framework of this study. However, it can be supposed that TEHP shows similar stability as for TBP. For the required regeneration, however, methods still have to be developed to separate the oxidation products formed during hydrolysis and radiolysis. This will be the subject of future investigations.

Within the present study optimisation studies were carried out to define the best conditions for extraction, scrubbing and stripping. In addition to the batch extraction studies, a single-stage extraction experiment was conducted to obtain more data on the system kinetics, and to generate data required for the flowsheet calculations. After the data was collected, a 24-stage flowsheet was designed, and the final assessment was performed in a counter-current test using miniature centrifugal contactors.

2. Experimental

2.1 Reagents

(CIPh)₂PSSH was synthesized in our own laboratories according to the method [8] previously described, and purified by recrystallization (twice from isopropyl alcohol). TEHP (Aldrich, 97%) was used as received without further purification. *Tert*-butyl benzene (Merck, p. a.) and isooctane (Merck, p. a.) were used as the organic diluent. The organic solution was prepared by dissolving 0.4 mol/L (CIPh)₂PSSH and 0.15 mol/L TEHP in a *tert*-butyl benzene/isooctane (80/20) mixture. This solvent composition was elaborated according to the published data in reference [23] and further unpublished optimisation studies. Addition of 20% isooctane increases slightly the actinides(III) distribution ratios, whereas Am(III)/Cm(III) separation factor was not affected.

All other reagents and chemicals were of analytical reagent grade. Nitric acid solutions were prepared by diluting concentrated nitric acid (Merck, p. a.) with ultrapure water. The radiotracers ²⁴¹Am, ²⁴⁴Cm, ²⁵²Cf, and ¹⁵²Eu were supplied by Isotopendienst M. Blaseg GmbH, Waldburg, Germany. The composition of the LUCA feed used for the single-centrifuge and full counter-current test is shown in Table 1.

2.2 Analysis

Activity measurements of the γ -ray emitters ²⁴¹Am and ¹⁵²Eu were performed with a HPGe γ -ray spectrometer, EG-G Ortec, Munich, Germany. The nuclides ²⁴⁴Cm, ²⁴¹Am and ²⁵²Cf were measured by means of α -spectrometry, EG-G Ortec. The acidity of aqueous solutions was determined by potentiometric titration, using a Metrohm 798 MPT Titrimo device and a [NaOH] = 0.1 mol/L or 0.01 mol/L solution.

2.3 Equipment and procedure

2.3.1 Batch extraction tests

The batch extraction experiments were performed in 2 mL glass vials. 500 μ L organic and aqueous phases were spiked with 10 μ L radioactive tracer solution and equilibrated for 15 min by vigorous shaking in a vortex mixer. This contact time was sufficient to attain the distribution equilibrium. After phase separation by centrifugation, 200 μ L aliquots of each phase were withdrawn for radio analysis.

2.3.2 Single-centrifuge experiments

The experiments were performed in a single-stage centrifugal contactor setup, comprising a single 1 cm stainless steel centrifugal contactor (produced by INET, China) and a contactor house, which was a self-produced Plexiglas copy of the original. Two syringe pumps were connected to the contactor and used to precisely pump the organic and aqueous solutions after prior calibration. The experimental conditions for the determination of the centrifuge efficiency during extraction, scrubbing and stripping are summarized in Table 2.

First, the extraction performance was tested. Attainment of the steady state (after \approx 30 min operation) was checked by γ -spectrometry of ²⁴¹Am and ¹⁵²Eu. After extraction, the collected organic solution was used for scrubbing with 0.23 mol/L HNO₃ + 0.5 mol/L NaNO₃. Stripping was carried out with 0.7 mol/L HNO₃ using the collected organic solution after scrubbing. After each step, distribution ratios were also determined using the solutions taken from the wells after the contactor was completely emptied. Additional batch tests were performed in glass vials to achieve the equilibrium data: 3 mL solvent were contacted for 15 min with 3 mL feed (*cf.* Table 1). Phases were separated by centrifugation and samples were taken for analysis. 1 mL loaded organic phase from the extraction was used for scrubbing (15 min) with 0.23 mol/L HNO₃ + 0.5 mol/L NaNO₃.

Table 1. Composition of the synthetic An(III)/Ln(III) feed used for the single-centrifuge tests and the full counter-current test.

Solute	Concentration
²⁴¹ Am	2.89 MBq/L
²⁴⁴ Cm	2.79 MBq/L
²⁵² Cf	1.75 MBq/L
¹⁵² Eu	5.20 MBq/L
HNO ₃	0.13 or 0.084 mol/L
NaNO ₃	0.5 mol/L
Eu	100 mg/L

Table 2. Conditions for the determination of the extraction, scrubbing and stripping efficiency of a single centrifuge.

Conditions	Organic phase	Aqueous phase	A/O ratio
Extraction	0.4 mol/L (CIPh) ₂ PSSH + 0.15 mol/L TEHP in 20% isooctane/80% <i>tert</i> - butyl benzene	<i>cf.</i> Table 1 0.13 mol/L HNO ₃	35 mL/h / 25 mL/h
			50 mL/h / 35 mL/h
			70 mL/h / 50 mL/h
Scrubbing	Loaded organic phase collected from extraction	0.23 mol/L HNO ₃ + 0.5 mol/L NaNO ₃	10 mL/h / 25 mL/h
			15 mL/h / 35 mL/h
			20 mL/h / 50 mL/h
Stripping	Loaded organic phase collected from scrubbing	0.7 mol/L HNO ₃	25 mL/h / 25 mL/h
			35 mL/h / 35 mL/h
			50 mL/h / 50 mL/h

Stripping with 0.7 mol/L HNO₃ was also performed with the loaded organic solution from extraction. Phase separation and analysis were performed as described above.

2.4 Flowsheet design

The flowsheet proposed for the separation test is shown in Fig. 2. It was calculated as described in the following. To calculate a flowsheet, a computer code similar to codes used for mass transfer calculations in hollow fibre modules [26, 27] was established, however using discrete stages representing the centrifugal contactors used in the experimental setup. The code uses the equilibrium data shown in Fig. 3. A mean Am(III)/Cm(III) separation factor of 7 was used. Furthermore the code only takes into account diffusive mass transfer resistance, as mass transfer kinetics for a similar extraction system is controlled by diffusion [28].

To calculate fluxes in an extraction system controlled by diffusion, knowledge of the specific interfacial area (*i.e.*,

droplet size and holdup) and of mass transfer coefficients is required. As these are not easily accessible for a centrifugal contactor, we assumed reasonable individual mass transfer coefficients for all species involved, and used the drop size as fitting parameter: To describe the efficiency of the centrifuges under extraction, scrubbing and stripping conditions, a single-stage computer code was used, and drop sizes were adjusted to give the non-equilibrium distribution ratios found for the conditions of the experimental single-stage runs (see Table 2). The fit drop sizes were not varied with flow rate (work performed by Leonard, *e.g.* [29], indicates that this is a realistic assumption). The fit drop sizes were the same for the scrubbing and stripping sections; the fit drop size in the extraction section was 35% of that used in the scrubbing and stripping sections. However, these drop sizes used in the calculations do not necessarily represent the actual conditions in the mixing zone of the centrifugal contactors (the single-stage calculations could also be fit by using constant drop sizes throughout and varying the mass transfer coefficients).

The fit drop sizes were then used in the multi-stage counter-current code to calculate a flowsheet. The calculations aimed achieving $\approx 0.1\%$ Am(III) in the raffinate and $\approx 2\%$ Cm(III) in the product (of course, the product is even better decontaminated from metal ions less-extracted than Cm(III), *i.e.* Cf(III) and Eu(III), which is the reason why they were not included in the calculations). The major constraint was that 16 stages were available for extraction and scrubbing. Of the 16 stages available, seven stages were dedicated to extraction and nine stages to scrubbing. Eight stages were used for stripping. After the test was performed, the flowsheet was re-calculated with the flow rates and nitric acid concentrations that were actually measured.

2.4.1 Counter-current test in miniature centrifugal contactor battery

The continuous extraction/scrubbing and stripping tests with an actinide(III)/lanthanide(III) surrogate were carried out using Chinese 1 cm miniature centrifugal extractors in a counter-current mode. Details of the contactor setup can be found elsewhere [30]. The proposed flow rates (*cf.* Fig. 2) were adjusted before the tests were started using

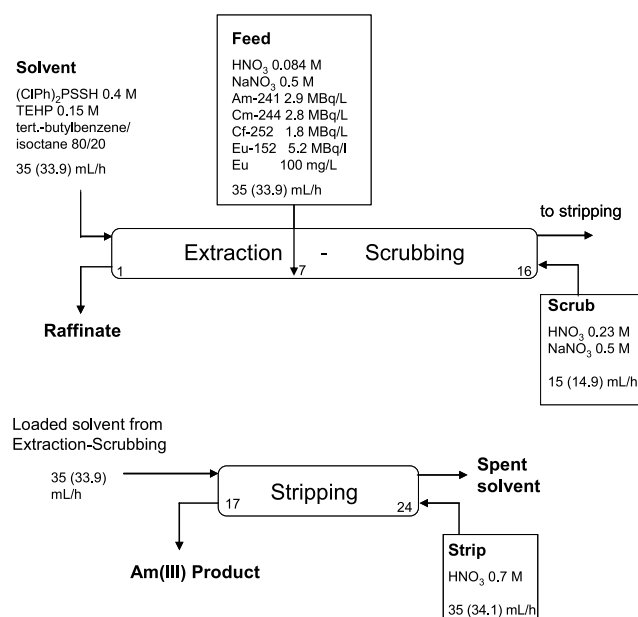


Fig. 2. Flowsheet for the LUCA process with proposed and actually measured (in brackets) flow rates.

calibrated metering pumps with associated controllers. During the tests, the actual volumetric flow rates were recorded by a mass balance. Since only 16 stages were available, stripping was performed on the second day. The solvent loaded with Am(III) (coming from stage 16) was collected in two batches for this purpose and the steady-state fraction was used for stripping. The attainment of the steady state was checked using gamma spectrometric measurements of ^{241}Am and ^{152}Eu and by alpha spectrometry of ^{241}Am and ^{244}Cm at the outlets of raffinate, collected solvent (at stage 16), Am(III) product (at stage 17) and stripped solvent. At the end of the experiments, the motors and pumps were switched off and the individual stages were drained. Subsequently, the organic phases were separated from the aqueous phases by centrifuging, and aliquots from both phases were used for the analyses. The following analyses were carried out on all samples collected from all stages (aqueous and organic), including the samples taken to determine the transient state: γ -spectroscopy for ^{241}Am , ^{152}Eu and α -spectroscopy for ^{241}Am , ^{244}Cm and ^{252}Cf . The acidity profile was determined for the aqueous phase by titration with NaOH.

3. Results and discussion

3.1 Optimisation studies for Am(III)/Cm(III) separation

The primary aim of the present studies was to determine the conditions for continuous Am(III)/Cm(III) separation with the aid of centrifugal extractors. Batch studies with HNO_3 solutions spiked with ^{241}Am and ^{244}Cm (≈ 1000 Bq/mL each) showed, however, that the aqueous phase emulsified after extraction at HNO_3 concentrations < 0.2 mol/L. This was not caused by degradation of the solvent and was not observed with feeds containing macro amounts of lanthanides. In further investigations, we found that this problem did not occur when the aqueous feed phase contained a salt load (*e.g.* lanthanide nitrates, sodium nitrate, or $\text{HNO}_3 >$

0.2 mol/L). For the optimisation studies, we therefore used nitric acid solutions (0.01–0.5 mol/L) containing variable NaNO_3 concentrations (0.25, 0.5 and 1.0 mol/L) in order to improve the hydrodynamic properties. Fig. 3 shows the results of Am(III) and Cm(III) extractions (both present in the same vial) from 0.05 to 0.5 mol/L HNO_3 for varied NaNO_3 concentrations. We observed a faster phase separation with rising NaNO_3 concentrations, while Am(III) and Cm(III) distribution ratios decreased slightly for constant HNO_3 concentration. Am(III) and Cm(III) distribution ratios determined by various methods (γ -spectroscopy for ^{241}Am ; α -spectroscopy for ^{241}Am and ^{244}Cm ; LSC for ^{244}Cm alone) showed good agreement.

3.2 Single-centrifuge experiments

Equilibrium batch extraction data are generally used to design flowsheets. To get an idea of how efficient each step (extraction, scrubbing and stripping) is, a series of single-centrifuge experiments was also carried out. The results from single-centrifuge experiments at the flow rates proposed for the counter-current test, and the comparison with the computer code calculations and experimental batch equilibrium data are shown in Table 3. The flow rates used allow a residence time in the mixer of the centrifuges which is not sufficient to attain equilibrium: single-stage distribution ratios are lower (extraction) or higher (scrubbing and stripping) than the respective equilibrium distribution ratios.

The single-stage calculations were fit to the experimental data to agree with Am(III) distribution ratios for extraction and stripping and with Cm(III) distribution ratio for scrubbing. The reason for doing so is as follows: in the flowsheet calculations, only the Am(III) extraction section concentration profiles and the Cm(III) scrubbing section concentration profiles are sensitive to the drop size in the respective sections (the Cm(III) extraction section and Am(III) scrubbing section profiles are not sensitive). With regard to the stripping section, Cm(III) is stripped better than Am(III). Fitting

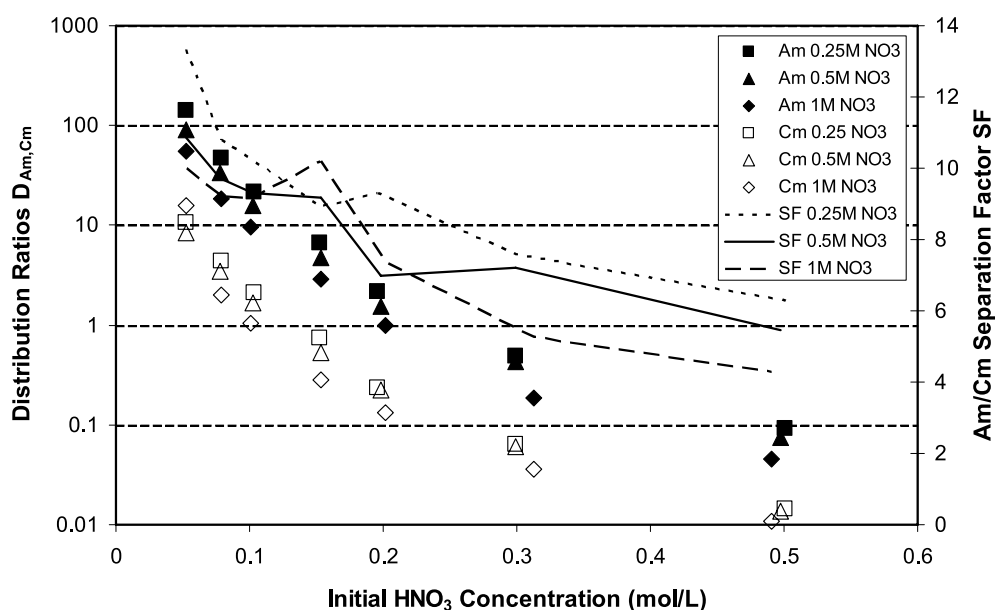


Fig. 3. Influence of NaNO_3 on the extraction of Am(III) and Cm(III) from HNO_3 . Organic phase, 0.4 mol/L $(\text{CIPh})_2\text{PSSH} + 0.15$ mol/L TEHP in 20% iso-octane/*tert*-butyl benzene. Aqueous phase, variable $\text{HNO}_3 +$ variable NaNO_3 (0.25, 0.5 and 1 mol/L), trace amounts of ^{241}Am , ^{244}Cm .

Table 3. Results of the experimental single centrifugal contactor tests and the comparison with single-stage calculations and batch extraction tests.

Single centrifuge	A/O ratio	$D_{Am,\gamma}$	$D_{Eu,\gamma}$	$D_{Am,\alpha}$	$D_{Cm,\alpha}$	$D_{Cf,\alpha}$	SF _{Am/Cm,α}	SF _{Am/Eu,γ}
Extraction	50/35	3.44	0.007	3.73	0.86	0.57	4.3	460
Calculation		3.48		3.48	0.72		4.8	
Batch/well	15/35	4.26	0.008	4.28	0.77	0.65	5.5	520
Scrubbing		2.66	0.063	3.08	0.60	0.58	5.1	42
Calculation		1.76		1.76	0.57		3.1	
Batch/well	35/35	0.84	0.015	1.17	0.22	0.30	5.4	54
Stripping		0.58	0.081	0.66	0.22	0.20	3.0	7
Calculation		0.56		0.56	0.52		1.1	
Batch/well		0.038	0.004	0.04	0.022	0.025	1.8	10
Batch tests	Mixing	$D_{Am,\gamma}$	$D_{Eu,\gamma}$	$D_{Am,\alpha}$	$D_{Cm,\alpha}$	$D_{Cf,\alpha}$	SF _{Am/Cm,α}	SF _{Am/Eu,γ}
Extraction	15 min	4.64	0.007	4.60	0.63	0.52	7.3	637
Scrubbing	15 min	1.09	0.32	1.24	0.22	0.34	5.7	3
Stripping	15 min	0.045	–	0.047	0.020	0.016	2.4	–

to the Am(III) non-equilibrium distribution ratio is therefore more important.

3.3 Counter-current test in miniature centrifugal contactor battery

The first objective of the LUCA test was to separate Am(III) from Cm(III) owing to the relatively large Am(III)/Cm(III) separation factor of 6–10. The feed used for this test was an acidic feed containing trace amounts of the trivalent actinides Am(III), Cm(III) and Cf(III) (*cf.* Table 1). Europium was also added as a representative for the lanthanides in order to obtain information as to whether this process is also suitable for the selective extraction of Am(III) from a SANEX-type solution, leaving Cm (possibly also Cf) in the lanthanide fraction.

The experimental conditions of the test run are described in the experimental section and the main results are summarized in Table 4. No hydrodynamic problems occurred during the test. The material balance was quite satisfactory and between 99% (*e.g.* ²⁴¹Am) and 112% (*e.g.* ²⁵²Cf) of the elements were recovered. Yields above 100% are explainable by the sum of analytical errors ($\pm 5\%$) and the error of the flow rate determinations ($\pm 5\%$), which amounts up to 10% of material balance uncertainties. Small recovery rates, such as the yield of 0.077% of ²⁴¹Am in the raffinate have an error up to 20%. All phases collected were clear

Table 4. Main results of the LUCA process.

Element	% in raffinate (1 aq)	% in product (17 aq)	% in solvent (24 org)	DF feed/raff	DF Am/M(III)
¹⁵² Eu (γ)	106.7	d.l.	d.l.	0.9	7693
²⁴¹ Am (γ)	0.077	103.3	0.089	1306	–
²⁴¹ Am (α)	d.l.	98.9	d.l.	>1000	–
²⁴⁴ Cm (α)	108.8	0.469	d.l.	0.92	214
²⁵² Cf (α)	112.0	0.057	d.l.	0.89	1744
Am calc'd	0.17	99.8	0.03	573	–
Cm calc'd	98.7	1.3	0.0004	–	77

d.l. = below detection limit.

and free of entrainment. In total, the test took 12 h (9 h for extraction/scrubbing and 3 h for stripping).

The process decontamination factors DF_{Am/M(III)} and DF_{feed/raff} were calculated according to the following Eqs. (1) and (2), where Q is the flow rate in mL/h and C is the concentration of the element in MBq/L:

$$DF_{Am/M(III)} = \frac{Q_{feed} C_{M(III) feed} C_{Am organic product (stage16)}}{Q_{organic phase} C_{Am feed} C_{M(III) organic product (stage16)}} \quad (1)$$

$$DF_{feed/raff} = \frac{Q_{feed} C_{feed}}{Q_{raff} C_{raff}} \quad (2)$$

A high decontamination factor of over 1000 was obtained for americium between the feed and raffinate. As expected, only Am(III) was quantitatively extracted and around 99.8% Am(III) was back-extracted using 0.7 mol/L HNO₃. A small amount of 0.09% Am(III) remained in the spent solvent.

The raffinate contained the complete Cm(III) (> 99.5%), Cf(III) (> 99.9%) and Eu(III) (> 99.9%) inventory and the contamination of Am(III) (< 0.08%) was low. On the other hand, the Am(III) product after back-extraction was contaminated with only 0.47% Cm(III), which resulted in a high DF_{Am/Cm} of 214. A higher decontamination factor of 1744 was measured between Am(III) and Cf(III). As expected from the high Am/Eu separation factors obtained during the batch extraction tests, very good decontamination (DF_{Am/Eu} = 7693) was achieved between Am(III) and Eu(III).

The aqueous acidity profile was in agreement with the acidities originating from the feed solutions. This is obvious as the LUCA solvent does not co-extract nitric acid.

Organic and aqueous steady-state Am(III) and Cm(III) concentration profiles (see Fig. 4) and effluent concentrations (see Table 4) re-calculated with the flow rates and nitric acid concentrations that were actually measured are in good agreement with the experimental results. For comparison, results from the initial calculation are: Am(III) in raffinate, 0.13%; Cm(III) in product, 2.0%; Am(III) in solvent, 0.03%.

In the extraction section, the calculations describe the experiment very well. Only the Am(III) raffinate concentration was slightly over-estimated by the calculation (0.17% calculated vs. 0.077% measured). The Cm(III) profile in the scrubbing section is described well for stages 8–13 but

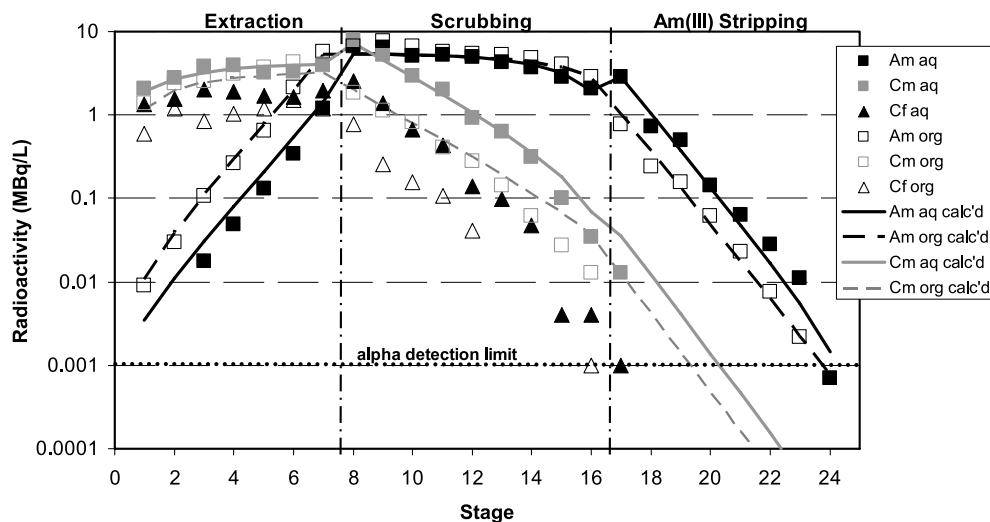


Fig. 4. Experimental (alpha measurements) and calculated steady-state concentration profiles from the counter-current test.

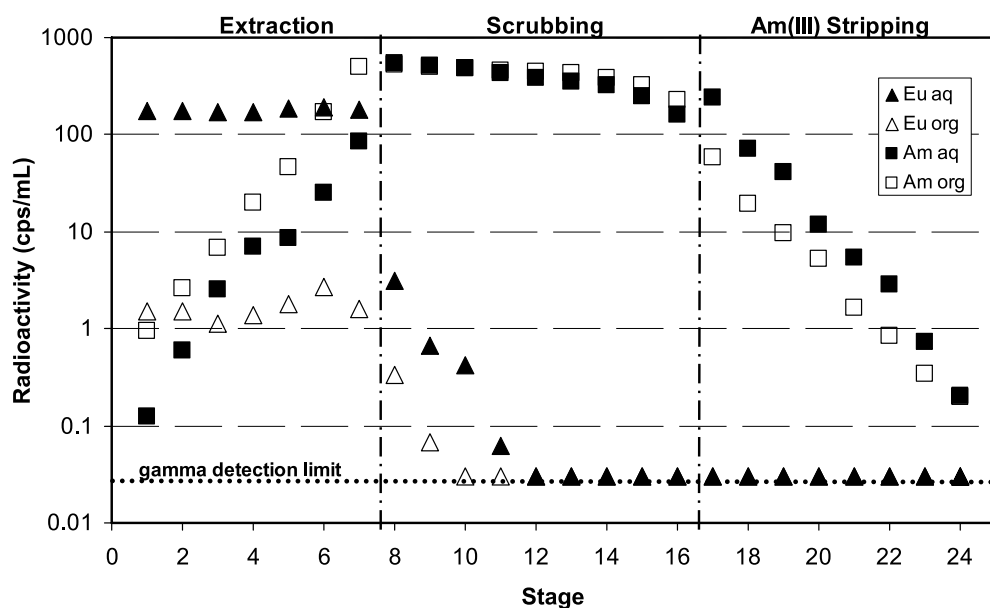


Fig. 5. Experimental steady-state concentration profiles of Am(III) and Eu(III) from the counter-current test (gamma measurements).

slightly underestimated for stages 14–16. This deviation naturally leads to an overestimation of the Cm(III) product concentration (1.3% calculated *vs.* 0.47% measured). The kind of calculation performed cannot predict the increasing slope of the Cm(III) profiles towards the end of the scrubbing section, as constant hydrodynamic parameters were used throughout a section. The deviation of the Am(III) concentration profiles in the first stages of the scrubbing section (stages 8–10) must be understood in the same manner. As for the stripping section, the Am(III) concentration profiles are described well; the spent-solvent Am(III) concentration was slightly underestimated (0.03% calculated *vs.* 0.089% measured). No experimental data are available for Cm(III) in the stripping section. Taking into account the simplicity of the computer code used and the fact that real “predictive modelling” was performed, the results agree quite well with those of the experiment.

The concentration profiles of californium are shown also in Fig. 4. As expected, the behaviour of Cf(III) is similar to that of Cm(III). Cf(III) is not extracted and the scrubbing efficiently reduces the co-extraction. Only 0.045% of

the initial amount was found in the Am(III) product fraction (Table 4). Fig. 5 shows the concentration profiles of Am(III) and Eu(III), which were measured by gamma spectroscopy of ^{241}Am and ^{152}Eu , respectively. The extraction of Eu(III) is very low and scrubbing with 0.23 mol/L HNO_3 decreased the concentration of Eu(III) after just 4 stages to below the detection limit. The behaviour of the other lanthanides was not studied within this test run. From our batch extraction data [23], we assume a similar behaviour for Pr, Nd, Sm and Gd. The lighter lanthanides La and Ce, however, have considerably higher distribution data, although the Am/La and Am/Ce separation factors are still high (> 40). Here we expect that more than 4 scrubbing stages are necessary for efficient decontamination.

4. Conclusions

In this paper we showed that the difficult recovery of Am(III) is possible from an acidic solution containing a mixture of trivalent actinides (Am(III), Cm(III) and Cf(III)) and

Eu(III) as a lanthanide representative. A successful LUCA demonstration was carried out in a centrifugal continuous counter-current setup using 24 stages. The main goals of the process, which were optimized by a simple computer model, were achieved: namely high recovery yields for Am(III) and good decontamination of Cm(III), Cf(III) and Eu(III).

The LUCA process can be used after a co-extraction process (e.g. after DIAMEX) for the selective extraction of Am(III), leaving Cm(III) together with the lanthanides in the raffinate fraction. Alternatively, the process can also be run after a SANEX process (e.g. BTBP) for mutual Am/Cm separation. In the future, we plan to optimize the formulation of the extractant composition, i.e. by changing the diluent. Initial experiments showed that up to 60% of the diluent can be replaced by the aliphatic TPH [30], which is the diluent used in the La Hague reprocessing plant. The promising results obtained here with a surrogate solution should also allow a hot demonstration to be performed in the near future with a genuine process solution. We are confident, that the aromatic dithiophosphinic acids under real process conditions (0.1–0.3 mol/L HNO₃, total doses up to 0.5 MGy) are sufficiently stable within the LUCA process. However, at higher acidities (> 0.5 mol/L HNO₃, e.g. during stripping) considerable degradation (by oxidation) of the (ClPh)₂PSSH was observed in a former study. Oxidation of the ligand can be suppressed by adding HNO₂ scavengers or using hydrochloric acid as stripping media. The results obtained represent an important breakthrough in the difficult field of actinide partitioning.

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