EFFECTIVE ACTINIDE(III)-LANTHANIDE(III) SEPARATION IN MINIATURE HOLLOW FIBRE MODULES

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Abstract

Miniature hollow fibre modules were fabricated as phase contactors for liquid-liquid extraction. They were tested for americium(III)-lanthanide separation, using 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine or a synergistic mixture of di(chlorophenyl)dithiophosphinic acid and tri-n-octyl phosphine oxide as extractants. Americium could be removed from the feed phase to 99.95% using the former extractant, and to 99.996% with the synergistic mixture. These miniature hollow fibre modules require feed volumes as low as several ten millilitres to run a test. This is their main advantage over commercially available hollow fibre modules which were used in our previous work.

Introduction

Within the Partitioning & Transmutation strategy, [1] the separation of trivalent actinides from the fission lanthanides is a key step. Due to the chemical similarity of the two groups it presents a major challenge. Liquid-liquid extraction is one of the most suitable technologies for this task: From the PUREX process, there is experience in handling liquid-liquid extraction in a highly active environment and on an industrial scale. However, suitable extractants for actinide(III)-lanthanide separation were not available until a few years ago.

This has changed with the development of alkyl-substituted di-triazinyl pyridines, e.g., 2,6-di (5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (n-Pr-BTP), [2] and aromatic dithiophosphinic acids. [3] These extractants are able to selectively extract trivalent actinides over fission lanthanides from up to 1 M nitric acid. The former, acting as a solvating extractant, separates trivalent actinide nitrates from 1-2 M nitric acid with an americium(III)-europium(III) separation factor, $SF_{\mathrm{Am/Eu}}$, of approx. 130. [4] Di(chlorophenyl)dithiophosphinic acid ($(\mathrm{ClPh})_2\mathrm{PSSH}$) selectively extracts americium(III) over europium(III) with a separation factor of 30 from 0.5 M nitric acid when used in a synergistic mixture with tri-n-octyl phosphine oxide (TOPO). [4]

The requirements for an actinide(III) separation process are that the product contains more than 99.9% of actinides(III) and approx. 0.2% of the lanthanide inventory. These requirements can only be met in a multi-stage process. Mixer-settler or centrifugal contactor cascades, or columns are the common equipment to perform such a liquid-liquid extraction separation process. Hollow fibre modules are a promising alternative to conventional liquid-liquid extraction process equipment. [5] Their major advantage is the forced flow through and around a bundle of porous hollow fibres: The process is not subject to hydrodynamic restrictions.

To shed some light on the usability of the above extractants in a HFM, we have already performed several actinide(III)-lanthanide(III) separation tests in commercially available hollow fibre modules. [6-9] However, feed volumes in the range of several litres were required. This is inconvenient considering the extractants used are not commercially available.

To overcome this drawback, miniature hollow fibre modules were successfully manufactured. They consist of 55 or 100 polypropylene hollow fibres, as opposed to 10,000 in the modules used previously. [6-9] Hence, the mini modules require significantly less feed volumes: Some 10 mL are sufficient for an extraction test.

With these modules, once-through, single-module counter-current tests were performed. A first test, using n-Pr-BTP as extractant, was very promising: Americium was extracted to 99.95%. The mass fraction of co-extracted lanthanides was only approx. 1%. [10]

Two more single-module separation tests have been performed lately, using n-Pr-BTP and $(\mathrm{ClPh})_2\mathrm{PSSH}$+TOPO as extractants. Finally, the mini-module set-up was expanded to a micro-plant consisting of three coupled modules. This set-up is capable of performing continuous separation processes with extraction, lanthanides scrubbing and back extraction. It has so far been tested on an inactive praseodymium-europium separation experiment with di(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant.

Experimental

Materials

n-Pr-BTP was synthesised according to [2]. $(ClPh)_2PSSH$ was synthesised by an external laboratory according to [3]. D2EHPA (>97%), TOPO (>97%), tert.-butyl benzene (>99%), 1-octanol (>99.5%), kerosene, and TPH (a French kerosene-type diluent) were used as received. Lanthanide nitrates and nitric acid were of analytical grade. Americium-241 tracer was from laboratory stock.

Module fabrication and HFM set-up

Mini HFM were fabricated by potting an appropriate number of hollow fibres into a glass shell tube, using an epoxy resin. Hollow fibres were Celgard X-30 polypropylene fibres. Inner and outer fibre diameters are 0.24 mm and 0.30 mm, respectively. Nominal pore size and porosity are 20 nm and 40%. Two types of modules were fabricated, see Table 1.

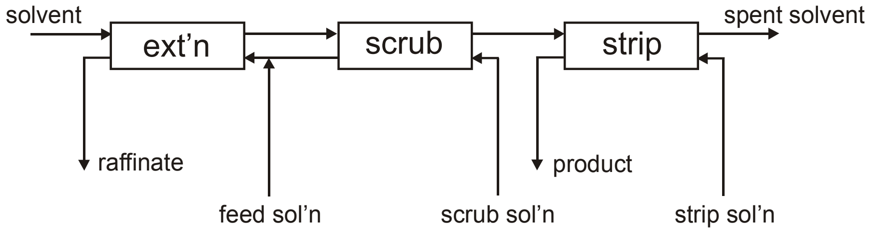
With these modules, a single-module set-up similar to the one used earlier [6-9] was built. However, feed pumps were peristaltic pumps. Flow rates were determined by weighing feed tanks and effluent samples. This set-up was expanded to a HFM micro-plant consisting of three modules. These modules were connected in a way to represent the extraction, scrubbing and stripping sections in a conventional extraction set-up, cf. Figure 1.

In any case, aqueous phase was led inside the hollow fibres for extraction, and shell-side for scrubbing and stripping. [9] Aqueous pressure was kept approx. 0.5 bar higher than organic pressure to prevent solvent from leaking through the membrane pores.

Table 1. **Mini modules fabricated**

No. of hollow fibres	Shell tube I.D.	Active length
55	3 mm	0.20 m
100-105	4 mm	0.20 m

Figure 1. **Schematic HFM micro-plant set-up**



Americium(III)-Lanthanide separation using n-Pr-BTP

The Am(III)-Ln separation test presented in [10] was reproduced. A module consisting of 100 fibres was used (a module with 105 fibres was used in [10], and not 100 fibres as stated then). Feed was a solution of lanthanides (La-Gd+Y) traced with Am-241 in 1 M nitric acid, cf. Table 2. Organic phase was 0.04 M (16.2 g/L) n-Pr-BTP in TPH/1-octanol (7:3 by volume). Aqueous phase was led inside the fibres. Flow rates were varied, 0.70 mL/h and 0.92 mL/h, with $Q_{org} \approx Q_{aq}$. Samples were taken from both aqueous (raffinate) and organic (loaded solvent) effluents.

Table 2. **Composition of aqueous feed solutions for the Am(III)-Ln(III) single-module separation tests**

Compound	n-Pr-BTP	$(ClPh)_2PSSH$+TOPO
^{241}Am	3.7 MBq/L	19 MBq/L
Y	87 mg/L	224 mg/L
La	298 mg/L	788 mg/L
Ce	559 mg/L	1 547 mg/L
Pr	276 mg/L	716 mg/L
Nd	1 005 mg/L	2 548 mg/L
Sm	191 mg/L	491 mg/L
Eu	38 mg/L	89 mg/L
Gd	48 mg/L	97 mg/L
total Ln	2 502 mg/L	6 500 mg/L
HNO_3	1.0 M	0.5 M

Americium(III)-Lanthanide separation using $(ClPh)_2PSSH$+TOPO

A single-module americium(III)-lanthanides separation test was performed in a module consisting of 100 fibres. Aqueous phase was led inside the fibres. Aqueous flow rate was varied between 2.9 mL/h and 6.8 mL/h. Organic flow rate was kept constant at 3 mL/h. Feed was a solution of lanthanides (La-Gd+Y) traced with Am-241 in 0.5 M nitric acid, cf. Table 2. Organic phase was 0.5 M $(ClPh)_2PSSH$+0.25 M TOPO in tert.-butylbenzene.

HFM micro-plant: Praseodymium-Europium separation process using D2EHPA

As a first test of the new HFM micro-plant, a Pr-Eu separation process using D2EHPA as extractant was performed. Feed was 92.5 mg/L Pr and 96.4 mg/L Eu in 0.1 M nitric acid. Scrubbing solution was 0.2 M nitric acid, stripping solution was 1.0 M nitric acid. Solvent was 0.05 M D2EHPA (dimeric concentration) in kerosene. Extraction and scrubbing modules consisted of 55 fibres, the stripping module consisted of 60 fibres. Aqeous phases were led inside the fibres (extraction module) and shell-side (scrubbing and stripping modules). Flow rates were 1.92 mL/h (feed), 1.39 mL/h (scrubbing solution), 1.92 mL/h (stripping solution), and 2.59 mL/h (solvent). The test was run for six hours. Samples were taken from the raffinate, product and spent solvent.

Analytics

Am-241 was counted on a gamma counter (Packard Cobra Auto-Gamma). Lanthanides were measured by ICP-MS, with the organic phases previously being stripped into nitric acid of adequate concentration.

Calculations

Mass transfer calculations are basically as described before. [11,8,9] However, by scaling down these calculations, the experimental results regarding the miniature HFM could not be modelled adequately. Possibly, the shell-side mass transfer correlation used [12] would not correctly describe the shell-side mass transfer characteristics of the miniature HFM. An appropriate shell-side mass transfer correlation is currently being established, and is not yet available. As a quick fix, we found that using in the calculations a membrane porosity of 25-30% (instead of the nominal 40%) quite well described experimental results.

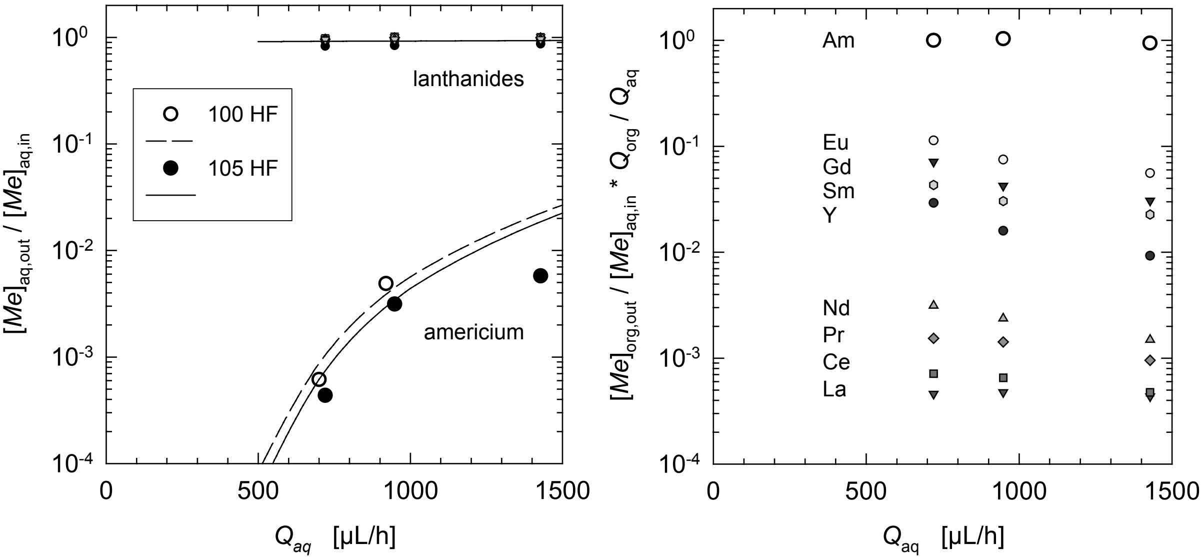
Next, a code was written to calculate the micro-plant experiment. Extraction, scrubbing and stripping sections were coupled. Since this code which is used to calculate transient effluent concentrations does not yet account for dead volumes, the time scale from the calculation was spread by a factor of 2.5.

Results and discussion

Single-HFM tests: Americium(III)-Lanthanide separation using n-Pr-BTP

In the first n-Pr-BTP test, [10] using a module consisting of 105 fibres, aqueous flow rates were varied, 0.72 mL/h, 0.95 mL/h, 1.43 mL/h, with aqueous and organic flow rates being approximately equal. The test ran 16 h. Throughout this time, both effluent phases were clear, showing no signs of phase entrainment. Steady state has been achieved for each flow rate.

Figure 2. **Am(III)-Ln(III) separation with n-Pr-BTP in a HFM**



Aqueous phase: in HF 3.7 MBq/L Am-241+2.5 g/L Ln in 1.0 M HNO_3.
Organic phase: shell-side, 0.04 M n-Pr-BTP in TPH/1-octanol (70:30 vol.). $Q_{org} = Q_{aq}$.
Left: relative aqueous effluent concentrations over flow rate (symbols: experiments, lines: calculations).
Right: relative organic effluent concentrations over flow rate.

Aqueous metal outlet concentrations, $[Me]_{aq,out}$, normalised to aqueous inlet concentrations, $[Me]_{aq,in}$, over aqueous flow rate, Q_{aq}, are shown in Figure 2 (left). Extraction efficiency is dependent on residence time and hence, flow rate. At an aqueous flow rate of 0.72 mL/h, 99.95% americium could be separated. This corresponds to an americium decontamination factor of DF_{Am} = 2 000 (cf. Table 3). Only approx. 1% of the lanthanide inventory was co-extracted. The relative amounts of lanthanides in the organic effluent are shown in Figure 2 (right): The lighter lanthanides are less extracted than the heavier ones, which is in agreement with respective distribution data. [4] A total lanthanides concentration of 21.5 mg/L was found in the organic phase at an aqueous flow rate of 0.72 mL/h. With the corresponding organic flow rate being 0.76 mL/h, this corresponds to a lanthanide decontamination factor of DF_{Ln} = 110 (cf. Table 3). This good value has been achieved even without lanthanide scrubbing, and is due to n-Pr-BTP's high americium-lanhanide separation factors. [4]

This test was reproduced, using a 100-fibre module. As shown in Figure 2 (left), the results agree well with the first test (data for lanthanides are not shown as they do not differ within experimental error).

The calculations are in good agreement with the experiments. As indicated by the calculations, the slightly better americium separation efficiency in the first test might be attributed to the difference in numbers of hollow fibres (100 vs. 105).

Single-HFM test: Americium(III)-Lanthanide separation using $(ClPh)_2$PSSH+TOPO

The performance of a mini HFM has also been tested using the $(ClPh)_2$PSSH+TOPO synergistic mixture. Total operating duration of this separation test was 18 hours. Both aqueous and organic effluents were clear throughout the test.

In this test, too, americium extraction efficiency is strongly dependent on flow rate, cf. Figure 3. At an aqueous flow rate of 2.9 mL/h, 99.996% of americium could be removed from the organic phase, corresponding to an americium decontamination factor of DF_{Am} = 27,000 (cf. Table 3). Americium decontamination comparable to the n-Pr-BTP test, i.e., DF_{Am} = 2,000, would be achieved at an aqueous flow rate of approx. 3.5 mL/h, as compared to approx. 0.7 mL/h with n-Pr-BTP (cf. Figures 2 and 3). This can be ascribed to the faster mass transfer kinetics of the $(ClPh)_2$PSSH+TOPO system as compared to the n-Pr-BTP system. [10]

A total of 4 875 mg/L lanthanides was left in the raffinate at an aqueous flow rate of 2.9 mL/h. With the total lanthanides concentration being 6 500 mg/L in the feed, this corresponds to a lanthanide decontamination factor of DF_{Ln} = 4.0, without lanthanide scrubbing (cf. Table 3).

As with the n-Pr-BTP tests, the calculations are in good agreement with experimental results.

Table 3. **Americium and lanthanides decontamination factors achieved in the single-HFM tests**

	n-Pr-BTP	**$(ClPh)_2$PSSH+TOPO**
Q_{aq}	0.7 mL/h	2.9 mL/h
DF_{Am}	2 000*	27 000*
DF_{Ln}	110**	4.0***

Note that these tests do not include lanthanide scrubbing.

* $DF_{\mathrm{Am}} = [Am]_{\mathrm{aq,in}}/[Am]_{\mathrm{aq,out}}$

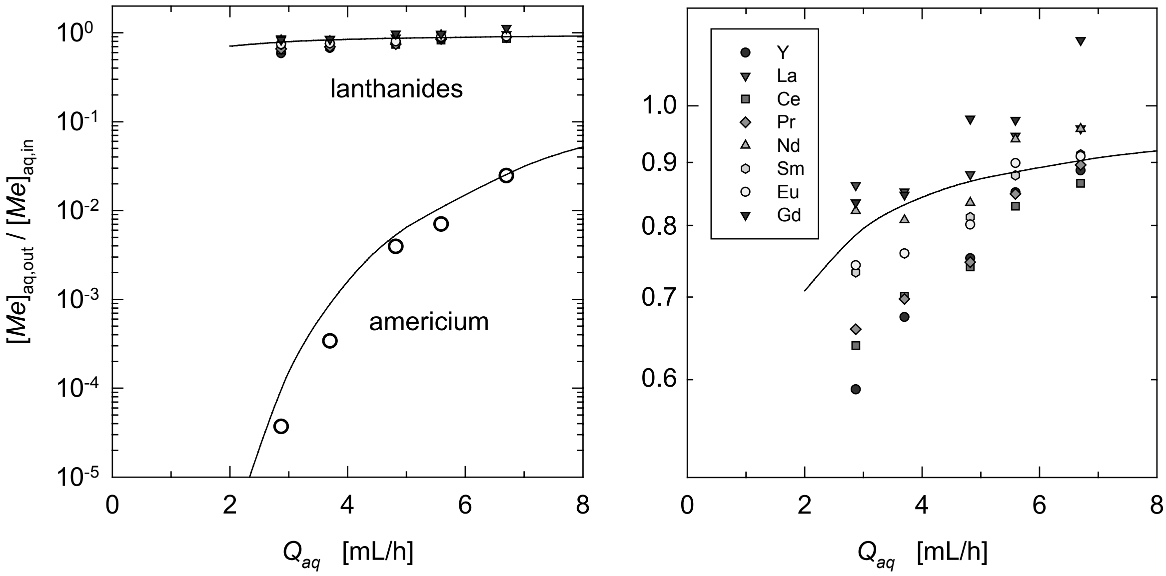
** $DF_{\mathrm{Ln}} = ([Ln]_{\mathrm{aq,in}} \cdot Q_{\mathrm{aq}}) / ([Ln]_{\mathrm{org,out}} \cdot Q_{\mathrm{org}})$

*** $DF_{\mathrm{Ln}} = ([Ln]_{\mathrm{aq,in}}) / ([Ln]_{\mathrm{aq,in}} - [Ln]_{\mathrm{aq,out}})$

HFM micro-plant: Pr-Eu separation process using D2EHPA

In this test, europium, which is better extractable into D2EHPA, should go to the product, whereas praseodymium should stay in the raffinate. The relative amounts of europium and praseodymium in all effluents (i.e., spent solvent, raffinate, product) are given in Table 4. Obviously, stripping was not very effective: 14.5% of europium were still found in the spent solvent. Furthermore, the decontamination factors were not too good. The raffinate decontamination factor regarding europium, DF_{Eu}, was 54, the product decontamination factor regarding praseodymium, DF_{Pr}, was 30.

Figure 3. **Am(III)-Ln(III) separation with (ClPh)2PSSH+TOPO in a HFM**



Aqueous phase:	in HF, 19 MBq/L Am-241+6.5 g/L Ln in 0.5 M HNO_3.
Organic phase:	shell-side, 0.5 M (ClPh)2PSSH+0.25 M TOPO in tert.-butyl benzene. Q_{org} = 3 mL/h.
Left:	relative aqueous effluent concentrations over flow rate (symbols: experiments, lines: calculations).
Right:	lanthanides zoomed in.

What is more important, the agreement of experimental values and transient calculations is very good (Figure 4). The only larger discrepancy regards the concentration of europium in the raffinate, which is off by a factor of approx. three.

Taking a look at the transient effluent concentrations it is evident that the test has not reached steady state within six hours. However, this and the not-so-good decontamination factors are not a problem of HFM performance: When the experiment was planned, the respective computer code was not yet available, and sub-optimal experimental conditions were selected.

Table 4. **3-HFM Pr-Eu separation process using D2EHPA,**
relative fractions of Pr and Eu in the effluents (experimental data after 5.5 hours)

	Solvent	**Raffinate**	**Product**	**Sum**	**DF**
Praseodymium	0.33%	103.8%	3.28%	107.4%	30*
Europium	14.5%	1.84%	84.4%	100.7%	54**

* $DF_{Pr} = ([Pr]_{feed} \cdot Q_{feed}) / ([Pr]_{prod} \cdot Q_{prod})$, with $Q_{prod} = Q_{strip}$

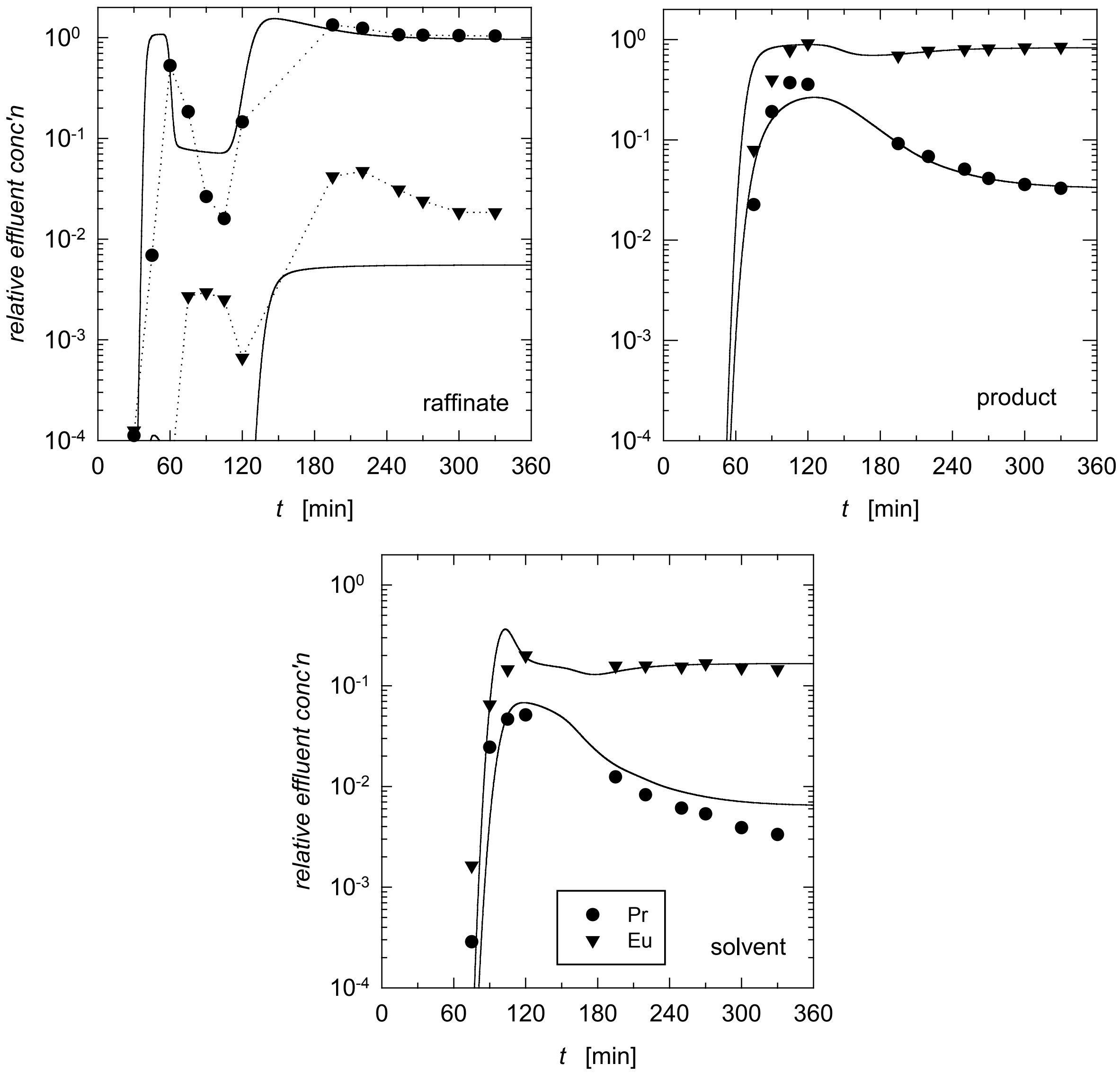
** $DF_{Eu} = ([Eu]_{feed} \cdot Q_{feed}) / ([Eu]_{raff} \cdot Q_{raff})$, with $Q_{raff} = Q_{feed} + Q_{scrub}$

Using the transient code, conditions were sought to achieve both DF_{Eu} and DF_{Pr} >1 000. The following flow rates were selected in the calculations: Feed and stripping solution, 2 mL/h, scrubbing solution, 0.4 mL/h, solvent, 0.5 mL/h. Scrubbing solution acidity was changed to 0.15 M. All other conditions remained unchanged. Calculated steady-state results are compiled in Table 5. The calculations suggest that the test would require approx. 15 hours to reach steady state.

Table 5. **Calculated efficiency of a 3-HFM Pr-Eu separation process using D2EHPA with optimised parameters**

	Solvent	Raffinate	Product	DF
Praseodymium	10^{-5}%	99.95%	0.05%	2 000
Europium	0.02%	0.05%	99.95%	2 000

Figure 4. **Praseodymium-europium separation in the HFM micro-plant, transient relative effluent concentrations in raffinate, product and spent solvent**



Modules: 55 HF (extraction and scrubbing) and 60 HF (stripping).
Flow rates: 1.92 mL/h (feed), 1.39 mL/h (scrubbing solution), 1.92 mL/h (stripping solution), and 2.59 mL/h (solvent).
Feed: 92.5 mg/L Pr+96.4 mg/L Eu in 0.1 M nitric acid.
Scrubbing solution: 0.2 M nitric acid.
Stripping solution: 1.0 M nitric acid.
Solvent: 0.05 M D2EHPA (dimeric concentration) in kerosene.
Symbols: experiment.
Lines: transient calculations.

Conclusions

To make P&T a success, an actinide separation efficiency of 99.9% has to be achieved. This implies that each process step has to be >99.9% efficient. An americium extraction efficiency of >99.9% was demonstrated by our experiments using two extraction systems in a single miniature HFM.

The next step to a complete separation process was made by coupling three modules to continuously perform extraction, scrubbing and stripping. Although a first test did not show high decontamination factors, the viability of a HFM micro-plant working in the mL/h flow rate range was demonstrated. Furthermore, a transient computer code was established which is useful in planning such experiments.

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Nomenclature

$(ClPh)_2PSSH$	di(chlorophenyl)dithiophosphinic acid
D2EHPA	di(2-ethylhexyl)phosphoric acid
DF	decontamination factor
HF	hollow fibre
HFM	hollow fibre module
I.D.	inner diameter
n-Pr-BTP	2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine
PUREX	Plutonium and Uranium Recovery by Extraction
Q	flow rate
SF	separation factor
TOPO	tri-n-octyl phospine oxide
TPH	tetrapropylhydrogène
[ ]	concentration
aq	regarding aqueous phase
feed	regarding feed solution
in	regarding inlet (feed)
org	regarding organic phase
out	regarding outlet (effluent)
prod	regarding product solution
raff	regarding raffinate solution
scrub	regarding scrubbing solution
strip	regarding stripping solution

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