

SEPARATION OF MINOR ACTINIDES FROM A GENUINE MA/LN FRACTION

B. Sätmark, O. Courson, R. Malmbeck, G. Pagliosa, K. Römer, J.P. Glatz
European Commission, Joint Research Centre, Institute for Transuranium Elements
Hot Cell Technology, Postfach 2340, 76125 Karlsruhe, Germany

Abstract

Separation of the trivalent Minor Actinides (MA), Am and Cm, has been performed from a genuine MA(III) + Ln(III) solution using BisTriazinePyridine (BTP) as organic extractant. The representative MA/Ln fraction was obtained from a dissolved commercial LWR fuel (45.2 GWd/tM) submitted subsequently to a PUREX process followed by a DIAMEX process. A centrifugal extractor set-up (16-stages), working in a continuous counter-current mode, was used for the liquid-liquid separation.

In the *n*Pr-BTP process, feed decontamination factors for Am and Cm above 96 and 65, respectively were achieved. The back-extraction was more efficient for Am (99.1% recovery) than for Cm (97.5%).

This experiment, using the BisTriazinePyridine molecule is the first successful demonstration of the separation of MA from lanthanides in a genuine MA/Ln fraction with a nitric acid concentration of ca. 1M. It represents an important break through in the difficult field of minor actinide partitioning of high level liquid waste.

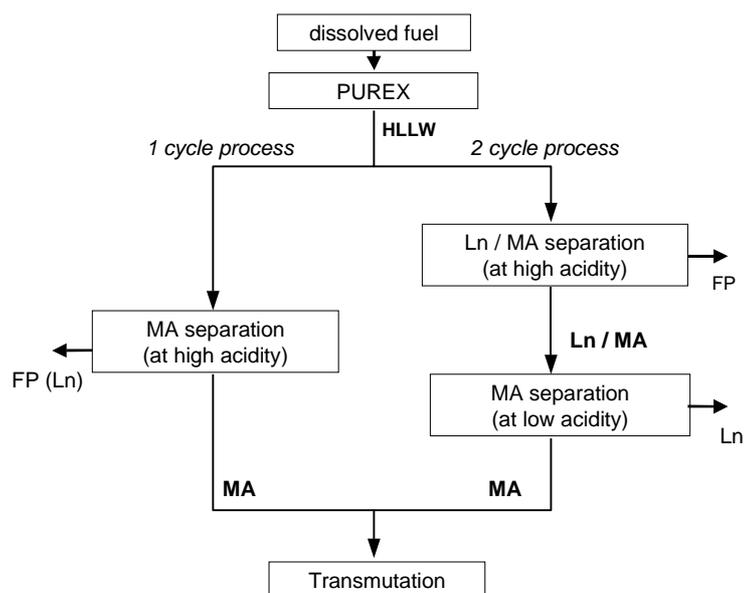
1. Introduction

Radioactive by-products are unavoidably generated during normal reactor operation. Some of these by-products are very long-lived and radiotoxic elements which must be separated from the biosphere for a very long time. The potential harmfulness of the wastes generated by reprocessing are primarily due to the presence of Minor Actinides (MA) and they are of special concern regarding partitioning and transmutation.

Current reprocessing technology is based on the aqueous PUREX process in which uranium and plutonium are recovered. The technique can also be extended for the recovery of neptunium, but americium and curium cannot be separated directly in this process. The partitioning of MA is instead done by advanced reprocessing of High Level Liquid Waste (HLLW) generated by the PUREX process, and different systems based on liquid-liquid extraction have been proposed world-wide.

Due to the difficult separation of trivalent MA from trivalent lanthanides (Ln) especially at high acidities, two step processes are at present considered. In the first step, at high acidity, a group separation of MA and lanthanides is carried out, followed by a separation of MA from lanthanides at lower acidity, see Figure 1.

Figure 1. Main routes for the separation of MA from HLLW



In the French DIAMEX (DIAMide EXtraction) process the minor actinides are directly extracted from the PUREX raffinate together with fission lanthanides using the completely combustible DiMethyl-DiButyl-TetraDecyl MalonAmide (DMDBDMA). The MA(III)+Ln(III) mixture generated after this first step is low-acidic to facilitate the second process, the SANEX process, which concerns the separation of the MA from the lanthanides. This process is based on the BTP, which belongs to a new family of extractants, the Bis-Triazinyl-Pyridine developed by Z. Kolarik et al, and is very efficient for a selective extraction of MA(III) at high acidity [1] and shows good capabilities in centrifugal extractors.

In the present work, the 2,6-Bis(5,6-alkyl-1,2,4-Triazin-3-yl)Pyridine (*n*Pr-BTP) process has been tested in continuous counter-current extraction experiments, using a centrifugal extractor battery

installed in a hot cell. The feed was a genuine MA(III)+Ln(III) mixture obtained from small scale PUREX/DIAMEX reprocessing of commercial LWR fuel (45.2 GWd/tM) [2].

2. Experimental

2.1 Reagents

The *n*Pr-BTP compound was obtained from CEA Marcoule [3]. It was dissolved, using an ultrasonic bath, in Hydrogenated TetraPropene (TPH) and 30vol% of octanol obtained from PANCHIM (France) and MERCK (Germany), respectively. The solvent with a final concentration of 0.04M *n*Pr-BTP was directly used as organic phase in the centrifugal extractor experiment.

All reagents and chemicals were of the analytical reagent grade. MQ grade water (18 MΩ/cm) was used for all dilutions.

2.2 Continuous experiments using a genuine MA/Ln fraction

The centrifugal extractor equipment installed in the hot cells, see Figure 2, is described elsewhere [4,5]. For the *n*Pr-BTP process, 16 extractors were used, with 5 extraction stages, 3 acid scrubbing stages and 8 strip stages. The continuous counter-current centrifugal extraction scheme is shown in Figure 3. This flow-sheet was optimised on the basis of preliminary data obtained from batch tests with spiked solutions [6]. The genuine MA/Ln solution obtained as a product in the DIAMEX process was used as feed solution and adjusted to 1 M HNO₃ with concentrated nitric acid.

Figure 2. **Photograph showing the 16 stage continuous counter-current extractor battery installed in the hot cell**

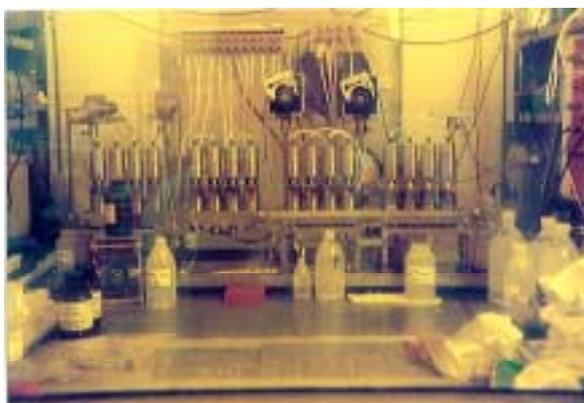
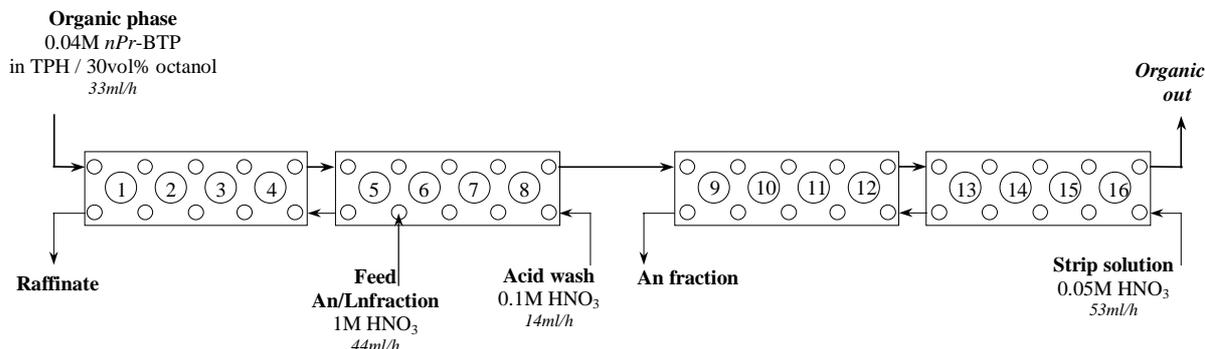


Figure 3. Flowsheet for the hot experiment using the *n*Pr-BTP and centrifugal extractors



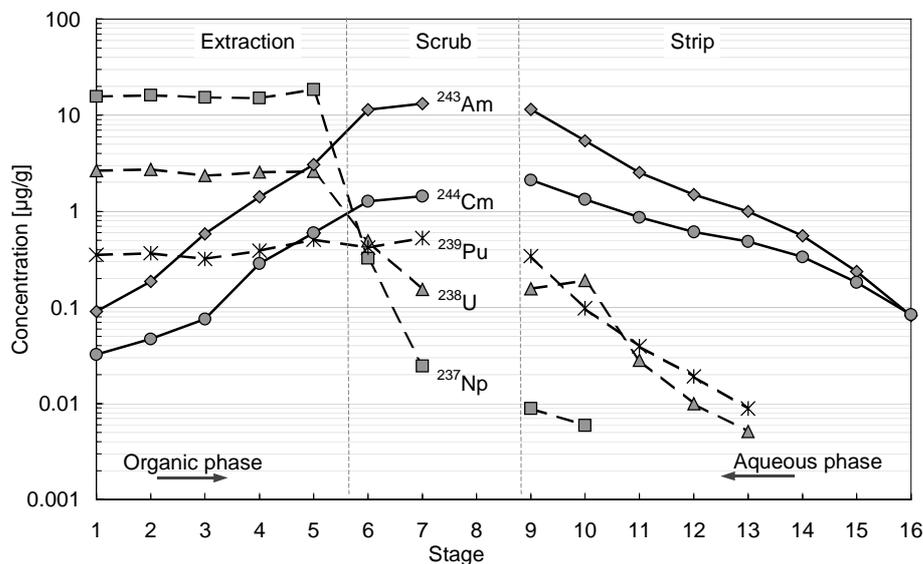
After the system reached steady-state conditions (ca. 3 h), the outgoing fractions were collected for about 30 min. At the end of the experiment the centrifuges and the pumps were switched off simultaneously and samples were taken from mixing chambers (well sampling) of each centrifuge.

All concentrations in the aqueous samples were determined using a quadrupole ICP-MS (Perkin-Elmer, ELAN250).

3. Results and discussion

The aqueous concentration profiles of actinides (Np, U, Pu, Am and Cm) in μg of isotope per g of solution are shown in Figure 4.

Figure 4. Aqueous profiles of actinides in the wells

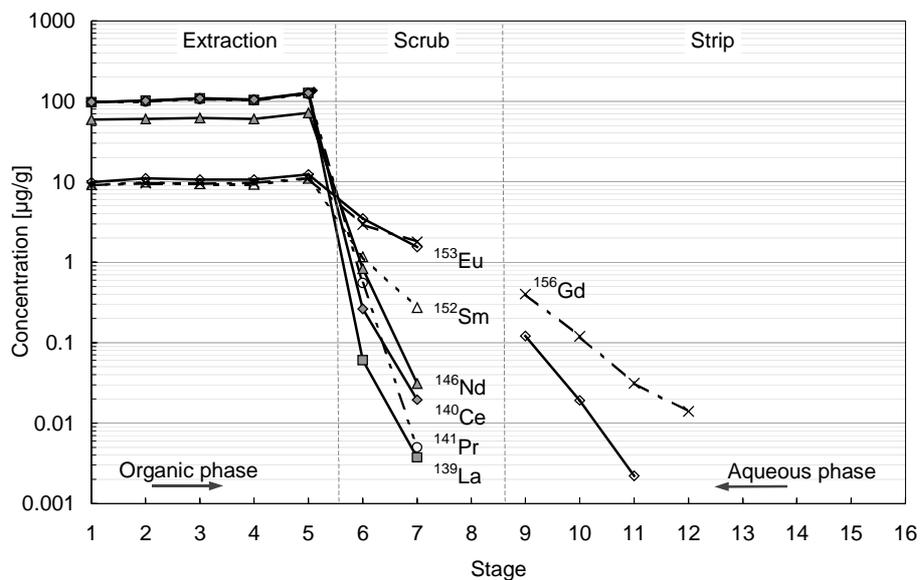


Similar extraction behaviour of Am and Cm is observed and the concentrations of those elements decrease by several orders of magnitude. Np and U are efficiently washed out in the scrubbing section but Pu is co-extracted. In the strip section all actinides are back-extracted. It should be mentioned that

the concentrations of U, Pu and Np in a MA/Ln feed originating from optimised PUREX/DIAMEX process schemes will be insignificant.

In Figure 5 the aqueous concentration profiles of lanthanides are shown.

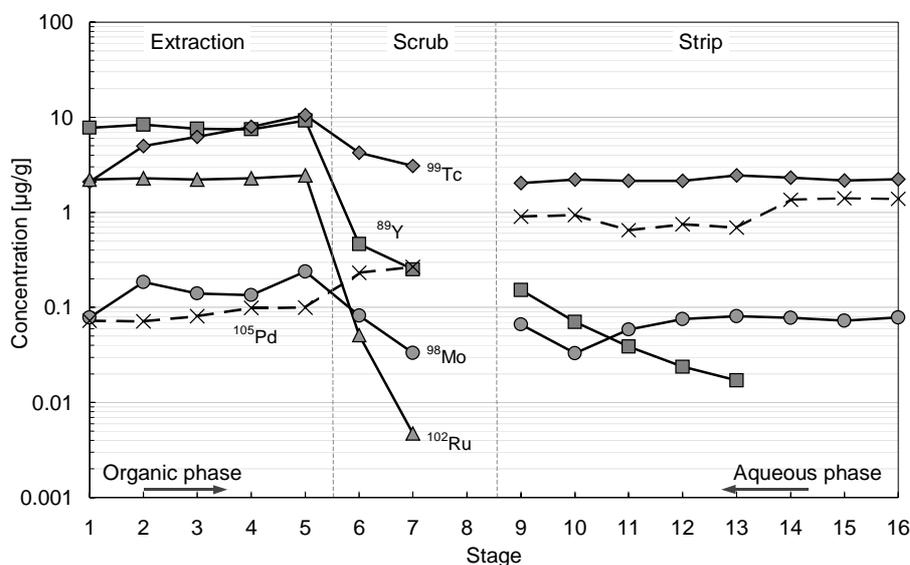
Figure 5. Aqueous profiles of lanthanides in the wells



As expected, the lanthanides are not extracted and the acid scrubbing efficiently reduces the co-extraction. However, the scrubbing efficiency significantly decreases with the increase of the element number. Higher lanthanides (Eu, Gd) are to some extent transported to the organic phase and efficiently back-extracted together with the MA. This co-extraction can be prevented by addition of more scrubbing stages.

The aqueous concentration profiles of some lighter fission products are shown in Figure 6.

Figure 6. Aqueous profiles of fission products in the wells



Extraction can be seen for Tc, Pd and Mo. The acid scrubbing efficiently removes Ru and Y from the organic phase, especially Ru is almost completely washed-out. For Tc the number of scrubbing steps is not enough, and Pd is even extracted in the scrubbing section. In the strip section only Y is well back-extracted. The other elements Tc, Mo and Pd are accumulated in the organic phase.

In Table 1 the process decontamination factors, DF, is shown. They were calculated according to Equation 1, where **C** and **V** are aqueous component mass concentration ($\mu\text{g/g}$) and total volume (mL), respectively.

$$DF = \frac{C_{\text{feed}} \cdot V_{\text{feed}}}{C_{\text{raff}} \cdot V_{\text{raff}}} \quad (1)$$

Table 1. Decontamination factors of the feed (in $\mu\text{g/g}$)

	DF		DF		DF		DF
^{89}Y	1.02	^{105}Pd	300	^{144}Nd	1.00	^{237}Np	1.00
^{98}Mo	13	^{139}La	1.00	^{152}Sm	1.00	^{243}Am	122
^{99}Tc	11	^{140}Ce	1.00	^{153}Eu	1.01	^{244}Cm	64
^{101}Ru	1.00	^{141}Pr	1.00	^{156}Gd	1.04		

In spite of the high acidity of the process (1M HNO_3) high decontamination factor is achieved for the MA elements. Lanthanides are not extracted except for Eu and Gd showing DF of 1.01 and 1.04, respectively. In parallel the DF of Eu, Cm and Am were also determined by α and γ spectrometry to be 1.01, 151 and 112 respectively.

Table 2 shows the recovery in the raffinate and in the MA fraction obtained after 3.5 hours of experiment. The small amounts of co-extracted lanthanides are efficiently back-extracted in the scrubbing section, as can be seen in Figures 5 and 6. To decrease the amount of co-separated higher lanthanides the number of scrubbing stages has to be increased. This is also the case for some lighter fission products such as Y, Mo and Tc.

Table 2. Recovery (% feed)

	Raffinate	MA fraction		Raffinate	MA fraction		Raffinate	MA fraction
Y	98.2	1.8	Ce	>99.99	–	Np	99.9	0.05
Mo	7.5	6.0	Pr	>99.99	–	Pu	52	48
Tc	9.2	8.5	Nd	>99.9	–	Am	0.8	99.1
Ru	99.8	0.2	Sm	99.9	0.1	Cm	1.6	97.5
Pd	0.3	3.9	Eu	99.9	0.1			
La	>99.99	–	Gd	96	4			

4. Conclusion

The process reported, using the BisTriazinePyridine molecule, is the first successful demonstration of MA separation from lanthanides in a genuine MA/Ln fraction with a nitric acid concentration ~1 M. In the experiment, carried out in a centrifugal continuous counter-current set-up, a MA fraction almost free of lanthanides was obtained. Due to an efficient MA extraction and back-extraction a reasonably good recovery of Am was achieved. However, the process scheme has to be improved to increase the recovery of Cm, to decrease the co-extraction of lanthanides, and to prevent the Pd accumulation in the organic phase. Nevertheless, this result represents an important break through in the difficult field of minor actinide partitioning of high level liquid waste.

Acknowledgements

This work was partially funded by the European Commission in the framework of its R&D programme “Nuclear Fission Safety (1994-1998)”, Project: “NEWPART: New partitioning techniques”, contract FI4I-CT96-0010.

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