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Futuristic back-end of the nuclear fuel cycle with the partitioning of minor actinides

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Abstract

For future back-end of the nuclear fuel cycle, the partitioning of minor actinides: Np, Am and Cm, followed by their transmutation will minimize importantly the radiotoxicity of nuclear glass waste. In this paper, the research done in France and in Europe will be presented: (i) partitioning of Np by modified PUREX process, (ii) partitioning of Am and Cm by the DIAMEX and SANEX hydrometallurgical processes.

Keyword: Actinide alloys and compounds

1. Introduction

The reprocessing of nuclear spent fuels is industrially carried out in several countries in the world. The most important reprocessing facility is situated in France at La Hague (Aréva-Cogéma Company). At La Hague, two reprocessing plants are working: (1) UP3 to reprocess spent fuels from other countries that France, (2) UP2-800 for reprocessing EdF spent fuels (France).

Today, the aims of the reprocessing are:

(i) to recover the elements U and Pu, by the hydrometallurgical PUREX process, which have large potentiality to produce more energy and which can be recycled as new fuels (for example MOX fuel for the recycled Pu),
(ii) to condition the nuclear wastes into solid matrices. Most of the radionuclides from the wastes are conditioned in glass.

The glasses contain most of the Fission Products (FPs) and the minor actinides (MAs): Np, Am and Cm. These glass wastes will be in the future disposed of into deep geological repositories. Fig. 1 presents the radiotoxicity of an UOX spent fuel with a burn-up of 45 GWd/t.

After three centuries, the radiotoxicity is mainly due to the presence of the MAs in these glass wastes. So, a new strategy is under consideration in numerous nuclear countries: elimination of the MAs from the glass wastes. After their partitioning, the MAs can be considered as destructible by nuclear facilities, such as the accelerator driven systems (ADSs). So, in France,

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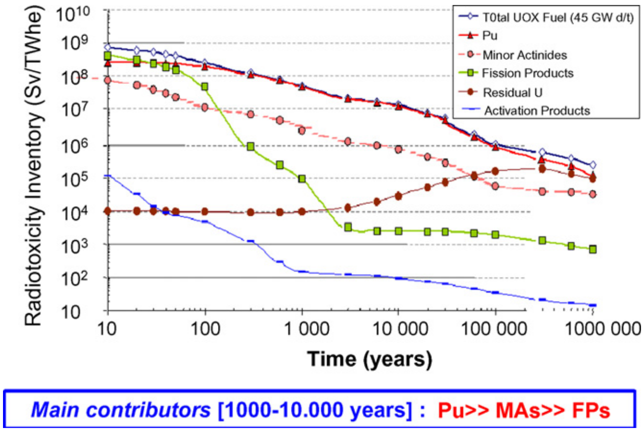

Fig. 1. Radiotoxic inventory of an UOX spent fuel (45 GWd/t).

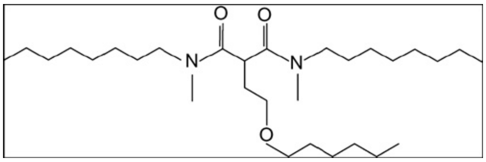

Fig. 2. The malonamide DMDOHEMA.

in Europe, and in numerous countries in the world, important research for MAs partitioning is done. Most of the work done was in the domain of hydrometallurgy, but pyrometallurgy is also considered as an efficient research domain for MAs partitioning [1]. The nuclear energy agency (NEA) of the OECD organised every 2 years a Conference on “Partitioning and Transmutation. The last Conference was held at Las Vegas, USA [2] in 2004 and the next one will be in Nîmes, in France, in September 2006. The most important results obtained recently in Europe during the framework programs (FP): (1) FP3 [4], (2) FP4 (NEWPART, Ref. [5]), (3) FP5 (PARTNEW, Ref. [6]) in the domain of MAs partitioning using hydrometallurgy processes will be presented briefly in this paper.

2. Partitioning of minor actinides

2.1. *Separation of neptunium (Np)*

It is considered that the neptunium can be co-extracted with U and Pu in the PUREX process, by changing slightly the experimental conditions. The CEA proposed a new PUREX scheme, presented at the Las Vegas NEA P&T Meeting in November 2004 [3]. This new scheme was successfully tested in 2005 in the hot-cell CBP in ATALANTE facility at CEA-Marcoule using 14 kg of spent UOX fuel.

2.2. *Separation of americium (Am) and curium (Cm)*

As Am and Cm exist in the spent fuel aqueous dissolution liquor as trivalent actinide ions (An):Am(III) and Cm(III), it was necessary to design new extractant able to co-extract An(III) from the nitric acid raffinate issuing the PUREX process. Moreover, as about a third of the FPs is composed of trivalent lanthanides ions (Ln(III)), the co-extraction of An(III) + Ln(III) is obtained. So, after the co-extraction of An(III) + Ln(III) a separation An(III)/Ln(III) should be done.

2.2.1. *DIAMEX process for An(III) + Ln(III) co-extraction*

For the co-extraction of An(III) + Ln(III) nitrates from high active wastes, a lot of work has been done to select a new extracting agent. The family of malonamide molecules was chosen by C. Musikas from CEA [7–9]. The main interests using malonamide extractants are: (i) An(III) and Ln(III) can be extracted efficiently from nitric acid aqueous solution, (ii)

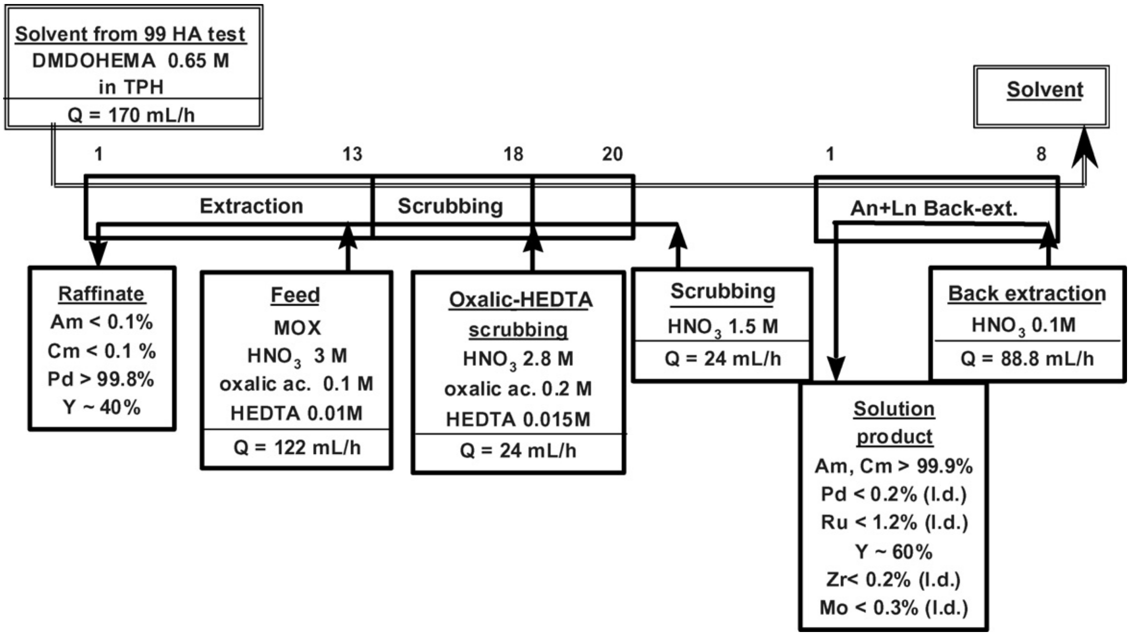

Fig. 3. DIAMEX flowsheet tested in ATALANTE and main results.

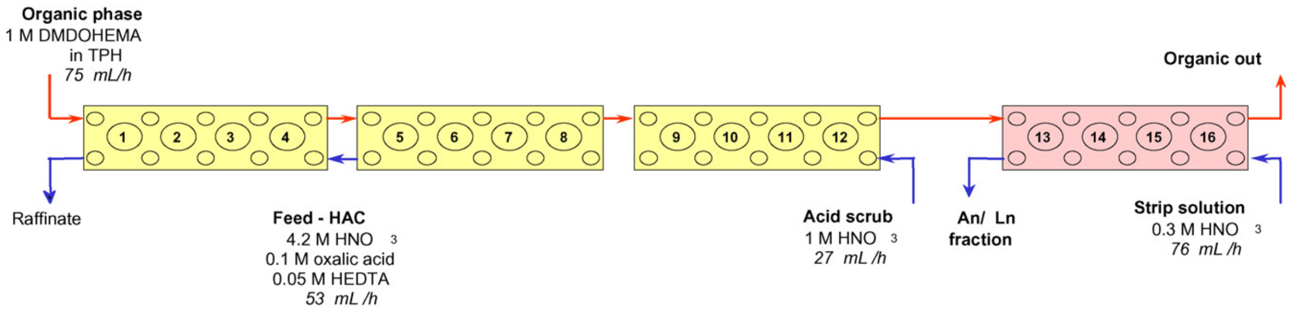

Fig. 4. DIAMEX flowsheet tested at the ITU on genuine HAC.

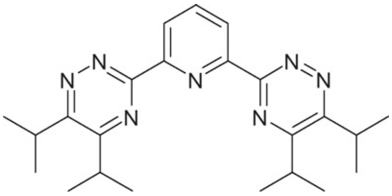

Fig. 5. Formula of the *iPr*-BTP.

the malonamide extractants are made of, C, H, O, N atoms, so secondary wastes are not generated, which is an important factor if we compared with the phosphate wastes generated by the PUREX process. The first malonamide selected was the dimethyldibutyltetradecylmalonamide (DMDBTDMA) and a DIAMEX process was designed and tested successfully on real high active raffinate. Moreover, in order to improve the DIAMEX process numerous malonamide ligands were tested, and it was found that the dimethyldioctylhexylethoxymalonamide (DMDOHEMA, see Fig. 2) is the best ligand for a futuristic industrial DIAMEX process. This new malonamide is more efficient to extract An(III) and Ln(III) from aqueous nitric acid solutions. The DIAMEX process was successfully tested on high active raffinate (HAR) both at CEA-Marcoule and at the ITU (Karlsruhe, Germany).

The flow-sheet of the DIAMEX process tested in a hot-cell using a set of centrifugal contactors at the ATALANTE facility in CEA-Marcoule is presented on Fig. 3.

In the feed and in the scrubbing solutions, two complexing agents were added to prevent the co-extraction of some fission products: (i) Zr(IV) and Mo(VI) are not extracted due to the presence of oxalic acid, (ii) Pd(II) is not extracted owing to the presence of *n*-(2-hydroxyethyl)-ethylenediaminotriacetic acid (HEDTA). On Fig. 3 it was mentioned that more than 99.9% of Am and Cm are found in the solution product, with the Ln.

Moreover, at the ITU, the DIAMEX process was also tested using high active concentrate (HAC with a concentration factor versus HAR of 10). The process scheme is shown on Fig. 4.

The fuel was a MOX fuel (1.4 kg) with a burn-up of 30 GWd/t. The spent fuel was dissolved in a 7 M HNO_3 aqueous solution, then U and Pu were extracted by a PUREX process. The High Active Raffinate (HAR) produced has a 4.064 L volume, then the HAR was concentrated and denitrated to generate the high active concentrate (HAC) of 0.442 L of volume which was used for the active DIAMEX test. The results obtained were excellent: 99.9% of An(III) and Ln(III) were recovered in this test [10].

2.2.2. An(III)/Ln(III) separation: SANEX processes

For the separation of An(III) versus Ln(III) issuing the DIAMEX process, it was necessary to define very specific extractants able to selectively extract the An(III). In this very difficult domain, several processes were designed including:

(i) SANEX process based on the tridentate N-ligand *iPr*-BTP, and

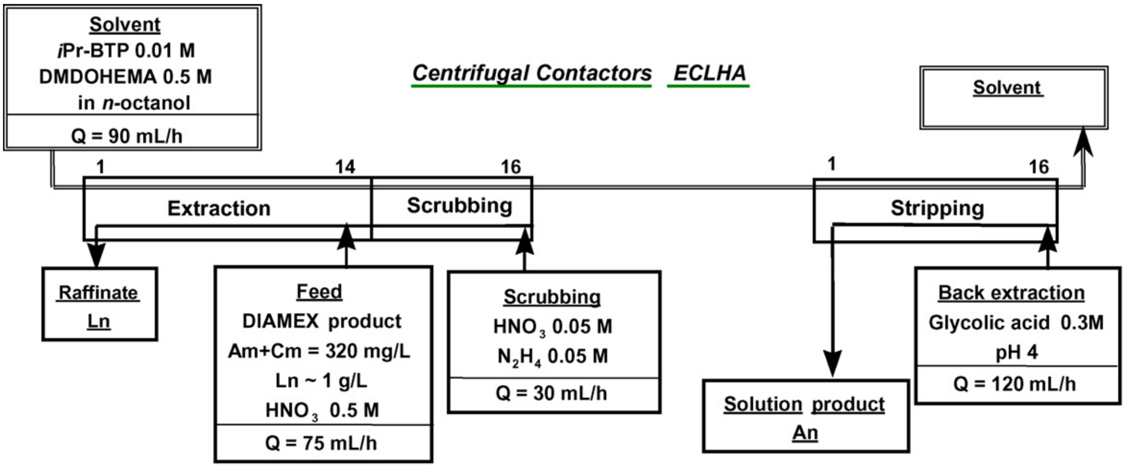

Fig. 6. Flow-sheet of the SANEX-*i*PrBTP process hot test carried out in June 2001.

(ii) SANEX process using synergistic mixture of bis-chlorophenyl-*di*-thiophosphinic acid ($(ClPh)_2PSSH$) + TOPO.

Hot tests of the SANEX process using BTP ligands were done at CEA-Marcoule and at the ITU.

The bis-substituted-1,2,4-triazinyl-pyridines (BTPs) were created by Z. Kolarik and co-workers at INE-FZK (Germany) in the frame of the NEWPART European MAs partitioning programme [11,12]. The initial best BTP extractant was the *iPr*-BTP which formula is presented on Fig. 5.

A SANEX process was designed, based on the use of the *iPr*-BTP and was successfully tested on An(III) + Ln(III) active solutions issued from the DIAMEX process at the CEA-Marcoule and at the ITU. The scheme of the process tested at CEA-Marcoule is presented on Fig. 6.

If the results obtained were good, unfortunately, it was demonstrated that the radiolysis of the solvent destructed the *i*Pr-BTP. So, new research were done to design more robust BTPs. Among the best one, the $CyMe_4$-BTP was selected (see Fig. 7). Possibly in the near future a SANEX flowsheet based on this new BTP extractant will be designed and hot tested.

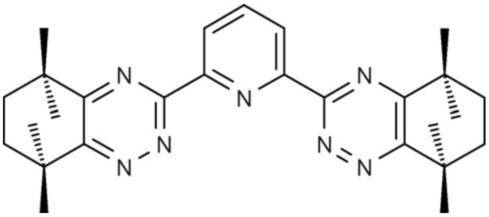

Fig. 7. Formula of the $CyMe_4$-BTP.

The SANEX process based on $(ClPh)_2PSSH$ + TOPO mixture, named SANEX-ALINA process, was successfully tested on synthetic spiked solutions at FZ-Jülich (Germany) on a solution spiked with traces of Am and Cm nuclides. The test was performed using a bank of 24 centrifugal contactors (CCs). The process scheme is presented on Fig. 8.

The main results obtained are presented in Table 1.

2.2.3. DIAMEX-SANEX process

Since some years, the CEA decided to regroup the DIAMEX and SANEX processes. On HAR first the DIAMEX process is implemented. Then the SANEX (An(III)/Ln(IIII)) separation is done in the following way: (i) addition to the loaded solvent of a new extractant, the di-2-ethylhexylphosphoric acid (HDEHP), (ii) An(III) stripping by contacting the solvent with an aqueous solution containing An(III) complexants: HEDTA and citric acid, (iii) Ln(III) stripping by contacting the solvent with moderately acidic aqueous solution. The DIAMEX-SANEX process

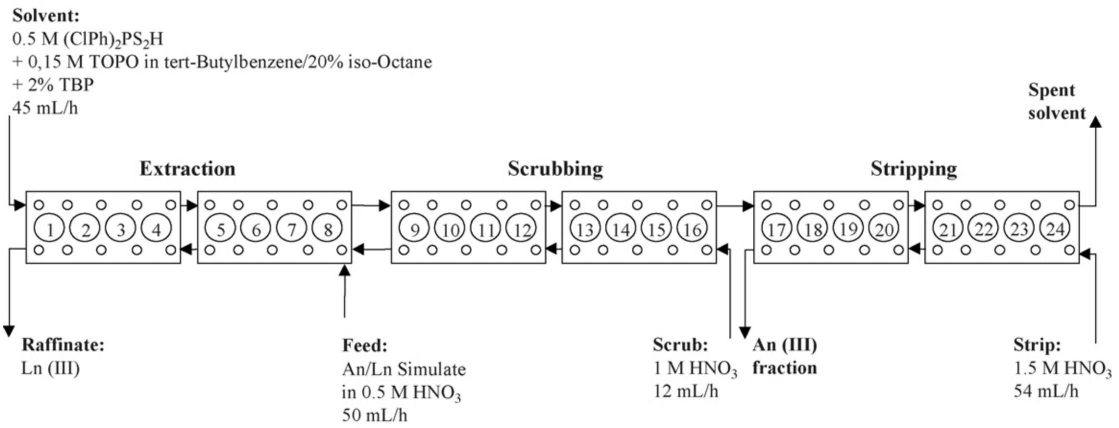

Fig. 8. Flow-sheet of the SANEX-ALINA process tested with a bank of 24 CCs.

Table 1
Main results of the SANEX-ALINA spiked test

Isotope	% in solvent stage 24	% in solvent stage 16	% in raffinate stage 1	Mass balance ext.-scrub. in % stages 1–16	$DF_{Am/Ln}$	$DF_{raf/feed}$
Am-241	0.025	108.4	0.095	108.5		1058.081
Cm-244	0.025	74.2	22.5	96.7		4.445
Ce-139	–	2.5	102.4	104.9	48.4	0.976
Ce-140	0.011	3.2	103.4	106.6	38.4	0.967
Eu-152	–	1.4	102.2	103.6	88.3	0.978
Eu-153	0.0194	1.8	105.5	107.4	65.9	0.948
Gd-153	–	1.2	101.9	103.2	101.4	0.981
Gd-158	0.0226	1.5	104.8	106.3	82.1	0.954
Y-89	0.09	3.7	100.6	104.2	33.5	0.994
La-139	0.0039	0.7	105.5	106.2	178.4	0.947
Pr-141	0.055	2.9	105.6	108.6	41.5	0.947
Nd-142	0.006	0.9	96.9	97.9	126.1	1.032
Sm-152	0.011	1.7	106.0	107.8	71.2	0.943

was successfully tested at CEA-Marcoule in the CBP hot-cell (ATALANTE) in December 2005 on the raffinate (HAR) which was generated by the treatment of the 14 kg of spent fuel by the PUREX process. The good results were presented at the Conference Global-2005, Japan [13].

2.2.4. *Cm/Am separation*

As it will be difficult to destroy Cm nuclides, it was considered necessary to define an Am(III)/Cm(III) separation process. As the malonamide DMDOHEMA possesses a slight higher affinity for Am(III) versus Cm(III) ($SF_{Am/Cm} = 1.6$), a DIAMEX-2 process was defined and successfully tested at CEA-Marcoule with real hot feed.

3. Future work

Most of the successful work on the partitioning of MAs described herein was done within the NEWPART IP of FP-4 [5] and PARTNEW IP of FP-5 [6]. Now, since 2004, the research continues in Europe within the IP EUROPART (FP-6), which incorporates not only MAs partitioning work in hydrometallurgy, but also work in pyrometallurgy [14].

Acknowledgements

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