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SEPARATION OF THE MINOR ACTINIDES: THE DIAMEX–SANEX CONCEPT

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ABSTRACT : This paper deals with the recent advances concerning the development of the DIAMEX and SANEX processes for the separation of minor actinides (americium and curium) from the raffinates produced by the PUREX process. The DIAMEX process is at the more advanced stage of development with a reference molecule and reference flowsheet well validated through numerous pilot tests. Concerning the SANEX process, the scientific feasibility of two of the three explored routes is now established and the last one is planned to be demonstrated in 2001 summer. So, by the end of 2001, the CEA will be able to select the best route for the demonstration of the minor actinides separation technological feasibility before 2006.

Keywords : partitioning, minor actinides, lanthanide, liquid-liquid extraction

1- INTRODUCTION

In December 1991 the French parliament passed a law identifying three areas of research concerning long-lived and high-level radioactive waste management. The first of these areas covers processes capable of separating long-lived radionuclides—notably the minor actinides americium and curium—for transmutation [1-2]. The current reference strategy for separating the minor actinides from the high-level liquid waste stream is to develop liquid-liquid extraction processes involving two steps, considering the difficulty of separating the trivalent actinides and lanthanides and the strong acidity of the process solution:

- DIAMEX: coextraction of the actinides and lanthanides from the high-level raffinates produced by the PUREX process.
- SANEX: separation of the actinides from the lanthanides in the flow generated by the DIAMEX process (three variants are currently being investigated).

2- DIAMEX

The first step, the so called DIAMEX process, is currently at a more advanced stage of development. It uses an extractant from the malonamide family that is capable of extracting the actinides (and lanthanides) at their stable oxidation state (III) in a highly acidic medium. The DIAMEX process was tested in 1993 [3] with a diamide extractant on genuine radioactive solutions, demonstrating its scientific feasibility and identifying areas where further improvement was necessary, including:

- optimization of the extractant molecule to enhance the solvent affinity for the extracted species and to increase their solubility;
- elimination of selected fission products coextracted with the actinides and lanthanides, including zirconium, molybdenum and iron.

Following this test, research on the DIAMEX process has focused on the following areas:

- Validation of a new reference extractant molecule: DMDOHEMA (*N,N'*-DiMethyl *N,N'*-DiOctyl HexylEthoxyMalonAmide) [4].
- Implementation of the reference flowsheet on genuine (or surrogate) solutions to validate the oxalic scrubbing step and demonstrate the flexibility of the process, which has been tested in mixer-settlers and in centrifugal extractors at diamide concentrations ranging from 0.5 to 1 mol·L⁻¹ (see Table I) [4 - 5 - 6 - 7].
- Studies to develop a solvent regeneration process [8]: Hydrolytic and radiolytic degradation of the DIAMEX solvent was characterized qualitatively as well as quantitatively. The effects of the main degradation products on the extraction efficiency were assessed, showing that the most detrimental is methyl octyl amine, followed by the carboxylic acids and monoamide. Laboratory studies have shown that acidic scrubbing quantitatively eliminates the amine, which must then be back-extracted during the scrubbing and stripping stages of the DIAMEX cycle. In an other hand, basic contact eliminates about 80% of the carboxylic acids; the principal difficulty lies in implementing these basic scrubbing operations due to the slow settling behavior.

Name /Date	CYRANO 1993 [3]	Oxalic scrubbing /FAR 1995 [4]	Oxalic scrubbing /MAR 1997 [5]	ITU (oxalic scrubbing) 1998 [6]	ENEA/FZJ (oxalic scrubbing) 1998 [7]	C11-C12 (oxalic scrubbing) 1999
Type of test	HA	inactive	inactive	HA	Spiked solution	HA
Duration	16 h	22 h	18 h	4 h	11 h	45 h
Contactor	M - S	M - S	M - S	C - C	M - S	M - S
Solvent	DMDBTDMA 0.5 M	DMDBTDMA 0.5 M	DMDOHEMA 0.65 M	DMDBTDMA 0.5 M	DMDBTDMA 1 M	DMDOHEMA 0.65 M
Feed	MOX [HNO ₃]=4 M	MOX type [HNO ₃]=3.5 M	Uox2 type [HNO ₃]=2.9 M	Uox2 [HNO ₃]=3.5 M	Uox2 type [HNO ₃]=4 M	MOX [HNO ₃] = 3 M
Product	>99.9 % Am ~ 99.9 % Cm	>99.8 % Nd >99.8 % Ce 99 % Eu 73 % Fe	>99.8 % Nd >99.8 % Ce >98.5 % Eu 3.4 % Ru 0.5 % Fe	>99 % An ~ 85 % Pd ~ 9 % Ru ~ 18 % Y	98.9 % Am 98.2 % Eu 1 % Ru	~ 99.9 % An ~ 60 % Pd ~ 10 % Ru Zr, Mo < d.l.*
Raffinate	~ 50 % Ru ~ 13 % Fe (>99.99 % Zr if KMA scrubbing)	>99.9 % Zr 95 % Mo 27 % Fe	>99.7 % Zr >99.7 % Mo >98.1 % Fe > 79 % Ru	>99.9 % Zr >99.9 % Mo >75 % Ru ~ 5 % Pd ~ 13 % Y	99.9 % Mo 99.9 % Zr 73 % Ru	~ 75 % Ru

* d.l. detection limit

Table I : DIAMEX flowsheets tested

The DIAMEX tests performed in 1998 in ITU and in 1999 in ATALANTE C11-C12 hot cells with HARs showed that part of palladium contained in HAR followed the actinides and lanthanides during the stripping operation of the DIAMEX process (Table I). So the recent DIAMEX flowsheet studies concerned the behaviour of palladium and the possible way to get rid of this element at the extraction-scrubbing section of the process.

Laboratory studies showed the advantages and the efficiency of HEDTA as complexing agent in order to prevent the extraction of palladium with diamide extractant. The palladium distribution ratios obtained during these studies were then integrated in the PAREX code. Using this simulation code a new DIAMEX flowsheet was designed and a test of this flowsheet was carried out in the ATALANTE C11/C12 hot cells using the new ECLHA centrifugal contactor test loop developed by the CEA.

As no degradation of the DIAMEX solvent was noticed during the previous HA run in 1999, it was decided to reuse the latter spent solvent for this new run without any preliminary treatment.

The flowsheet tested and the main results are presented in Figure 1, and can be summarised as followed :

- the hydrodynamic behaviour of the ECLHA centrifugal contactors was excellent all along the run (~37 hours),
- during the first part of the run (14h30), the solvent issuing the stripping section was directly recycled at the stage 1 of the extraction section without any treatment. Taking into account the hold up of solvent used, the solvent has been recycled about 6 times during the hot test without any noticeable degradation of its performances (hydrodynamic and chemical),
- good recovery yield of actinides (and lanthanides): the concentrations of Am, Cm and Ln are under the limits of detection in the raffinate,
- high An-Ln product decontamination factor for Mo, Zr and **Pd** (concentrations of Mo, Zr and Pd under the limits of detection in An-Ln stripped solution).

The short-term research objectives are to propose a solvent regeneration flowsheet and test its feasibility, and to select and design a liquid-liquid extractor suitable for industrial use. It will then be possible to obtain an initial performance assessment of the process for industrial operation.

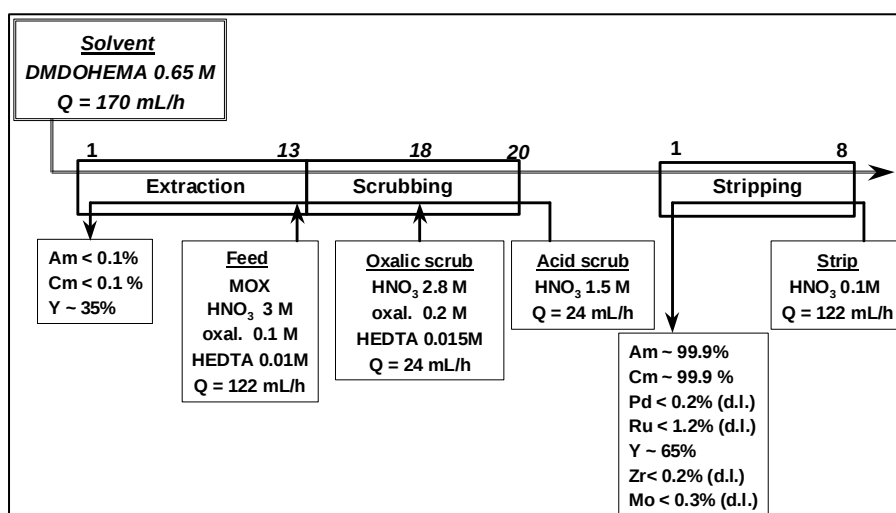


Figure 1 : hot test flowsheet of DIAMEX process in small centrifugal extractors

3- SANEX

The second step addresses the difficult issue of separating the trivalent actinides from the trivalent lanthanides (Selective ActiNide EXtraction concept). Three approaches are being investigated concurrently:

- The basic reference strategy seeks to separate the actinides from the lanthanides following the DIAMEX process by selective extraction of the trivalent actinides without any intermediate acidity adjustment (i.e. in $0.5\text{--}1\text{ mol}\cdot\text{L}^{-1}$ nitric acid). The extractant molecules likely to provide such selectivity must include “soft” donors (nitrogen or sulfur atoms). The principal systems investigated comply with the CHON principle (i.e. solvent made exclusively of C, H, O and N atoms) and thus do not raise any serious new waste management obstacles. These studies are carried out with nitrogenous ligands.
- Variant 1 is based on the same criteria as the reference strategy, but includes adjustment of the acidity by adding a buffer reagent (numerous An(III)/Ln(III) separation systems are effective at $\text{pH} > 2$).
- Variant 2 is based on an appreciably different concept: selective stripping of the trivalent actinides in the second step of the DIAMEX process; this approach allows the trivalent actinides and lanthanides to be coextracted and separated in a **single liquid-liquid extraction cycle**.

3.1- SANEX – The basic reference strategy

In the frame of the European contract NEWPART (4th PCRD), the discovery by Z. KOLARIK and col. [9] of a new family of nitrogenous ligands, the 2,6-di(5,6-dialkyl-1,2,4-triazine-3-yl)pyridines, has allowed the design of flowsheets which had been tested using surrogate solutions in mixer settlers (ATALANTE [10]), then using genuine DIAMEX solution in centrifugal contactors at ITU [11].

Even if the results of these tests with the 2,6-bis-(*n*-propyl-1,2,4-triazin-3-yl)-pyridine (*n*Pr-BTP) seemed to be very encouraging, the global performances in term of recovery yield of actinides were lower than the target value of 99.9 %. In particular, the recovery yield of Cm was only 95 % (2.5 % left in the raffinate and 2.5 % left in the stripped solvent). As the metal ion concentration profiles seemed to indicate that an increase of the number of stages may solve this problem, a new test was implemented in the ATALANTE C11/C12 hot cell using genuine DIAMEX solution in mixer-settlers with a double number of stages (32 instead of 16 for the firsts run, Figure 2).

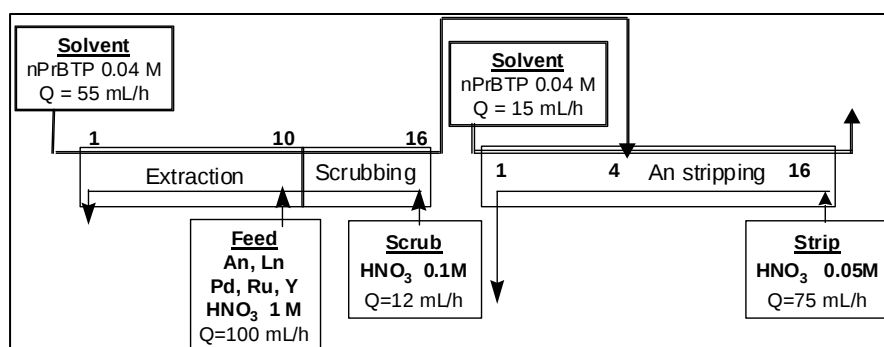


Figure 2: SANEX-nPr-BTP flowsheet for the second hot test.

The main results of this run can be summarized as follows:

- high An/Ln decontamination factors (DF) were obtained (even higher than expected: DF_{Eu} calculated ~ 9000 , observed ~ 18000),
- lower performances than expected for the recovery yields of An (2.5 % of Am and Cm left in the raffinate and 1.4 % of Cm left in the stripped solvent).

The origin of these low performances seems to be a "saturation" phenomenon of the solvent (lack of capacity of the solvent towards extractable elements). In fact, the shape of the concentration profiles of Am and Cm in the extraction section is typical of this phenomenon.

The most credible hypothesis for these "poor" results is an apparent decrease of the solvent affinity for An(III) ions equivalent to a decrease of 20 % of *n*Pr-BTP concentration in the solvent (remaining *n*Pr-BTP equal to 0.032 mol/L instead of 0.04 mol/L as expected). Figure 3 shows the comparison between calculated and experimental Am concentration profiles based on this hypothesis.

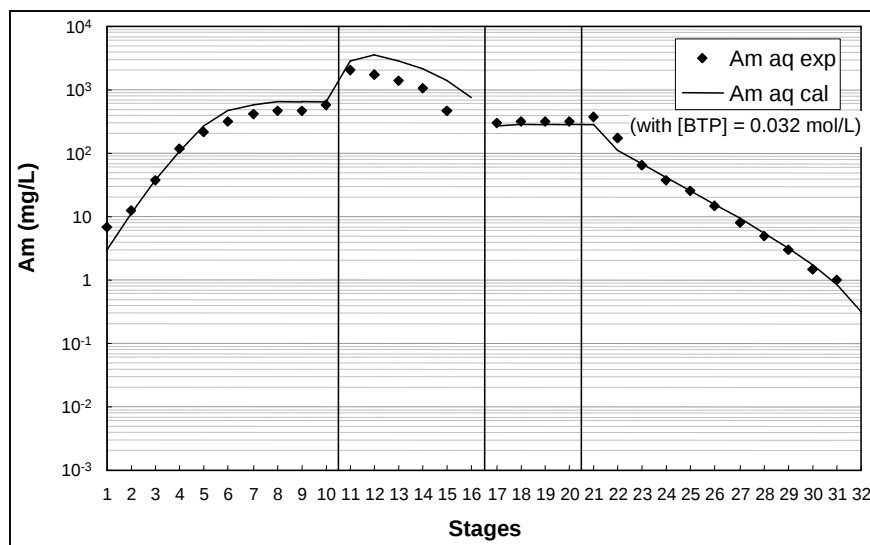


Figure 3: SANEX-*n*Pr-BTP hot test. Comparison between experimental and calculated Am concentration profiles (the deficit in *n*Pr-BTP concentration is proved).

So the recent studies have been devoted to:

- the understanding of the instability of *n*Pr-BTP under hydrolysis/oxidation in acidic conditions,
- the development of a new formulation of the SANEX-BTP organic solvent.

A systematic measurement of the extraction properties of *n*Pr-BTP towards Am(III) and Eu(III), after hydrolysis by nitric acid (with or without the presence of nitrous acid), showed up that *n*Pr-BTP degraded steadily when the atmosphere was rich in oxygen and when $[HNO_3]$ exceeded 0.5 mol/L (D_{Am} decreases of 80% after 2 days of hydrolysis by $[HNO_3] = 1$ mol/L), and rather quickly when $[HNO_2]$ exceeded 0.005 mol/L (D_{Am} decreases of 50% after 2 hours of hydrolysis by $[HNO_2] = 0.01$ mol/L).

Other substituted BTP molecules, especially those bearing branched groups on the α position of the triazine rings, such as Cy-BTP-Me and *i*Pr-BTP, proved to be more stable than *n*Pr-BTP in acidic conditions. Although these molecules were not chosen in 1999 for the implementation of counter-current hot tests, because of several practical reasons (*i.e.*: tedious synthesis, low solubility in organic diluent, slow kinetics of extraction), they actually showed a favourable stability over 30 days of hydrolysis/oxidation in acidic conditions.

A compromise had been found between high trivalent actinide extraction performances and good stability for the BTP extractant : the best choice today appears to be *i*Pr-BTP in a mixture of "*n*-octanol/diamide".

This system will be tested in 2001 summer on a genuine highly active DIAMEX back-extraction solution.

3.2- SANEX - VARIANT 1

The selected extraction system comprises a solvent with a substituted bis-pyridinetriazine (TMHADPTZ) acting synergistically with octanoic acid, and glycolic acid as a buffer for the aqueous phase.

The concept has been validated by carrying out a hot test, in mixer settlers, with surrogate solution containing nominal amount of americium (140 mg/L) and lanthanides (0.018 mol/L). Few curium (0.4 mg/L) were also added to follow behavior of this element by alpha spectrometry.

Figure 4 gives the flowsheet of this hot test. Since separation factors between actinides(III) and lanthanides(III) were not very high (about 4-8), it was necessary to apply two scrubbing. The first one contained large amount of glycolic acid in order to diminish distribution ratios of lanthanides and to buffer well aqueous solution since most elements are back extracted in this part of process. The splitting of flows in first scrubbing allowed a better spreading of buffer effect. The second scrubbing, with less glycolic acid, was necessary to back extract traces of lanthanides while actinides remained in solvent.

The flowsheet has been implemented on 4 days with a stop of 8 hours during the night and the solvent issuing the stripping section was directly recycled at the stage 1 of the extraction section without any treatment.

During the test, pH has been measured and a spectrophotometer has given concentration values of americium and neodyme, continuously, at stages 1, 17 and 25.

Figure 5 show the good correlation between experimental and calculated concentrations profiles of actinides, except for actinides in the stripping section due perhaps to slow kinetics of back-extraction. Since solvent was not completely discharged at outflow, few actinides were reintroduced in first stages. This explains why there are slightly more americium and curium than expected in stages 1-7 on Figure 5.

The performances of this hot test were very satisfactory (see Figure 4). More than 99.9% of americium and about 99.9% of curium were recovered with less than 5% in mass of lanthanides.

This test shows that a flowsheet could be elaborated despite small separation factors between actinides and lanthanides. Moreover, the recycling of Variant 1 solvent has demonstrated its stability towards alpha irradiation.

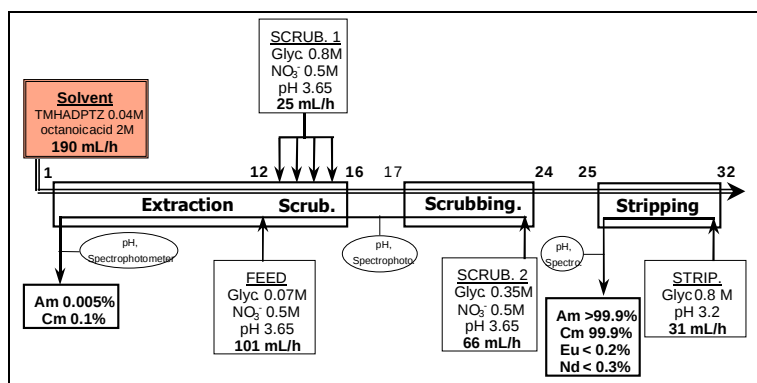


Figure 4 : hot test flowsheet of Variant 1 process in small mixer settlers

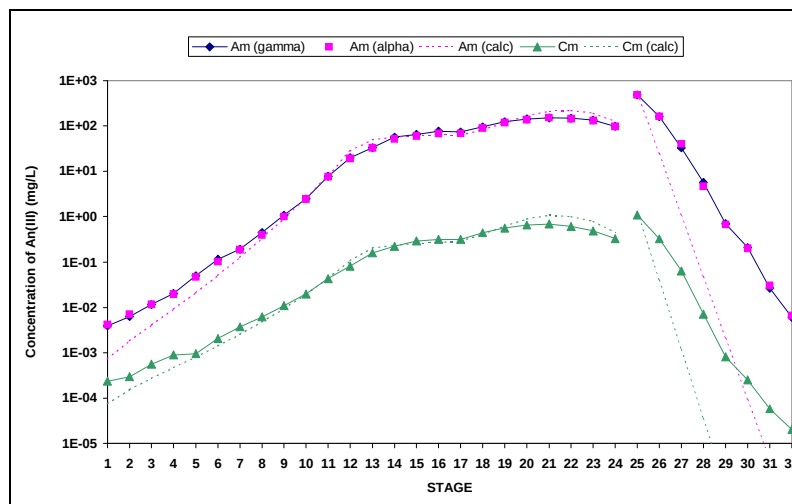


Figure 5 : aqueous profiles of actinides(III) in the extraction-scrubbing and stripping sections

3.3- SANEX - VARIANT 2

The solvent of Variant 2 is similar to DIAMEX one supplemented by the diethyl-hexyl-phosphoric acid (HDEHP). This latter ensure effective extraction at $\text{pH} > 2$. The aqueous mixture of polyaminocarboxylate complexing agent (HEDTA) buffered at pH 3 by citric acid was selected for selective stripping of actinides(III).

The process includes 4 steps :

- Step 1: Co-extraction of An(III) and Ln(III) (with some other fission products) from PUREX raffinate
- Step 2: Back-extraction of molybdenum, palladium, ruthenium and nitric acid.
- Step 3: Selective back-extraction of actinides(III), thanks to aqueous selective reagents, at low acidity (pH>2)
- Step 4: Stripping of elements remaining in solvent (Ln, Zr, Fe)

Tests with inactive solutions, then with surrogate solutions in mixer-settler banks provided a preliminary demonstration of process feasibility [12]. A test was therefore undertaken with a genuine solution in a centrifugal extractor bank (see Figure 6).

Since only 32 stages of centrifugal extractors were available, the test was implemented in two parts : first steps 1, 2 and 3; secondly step 4. Duration for each part was about 6 hours.

During the test, located in outflows of step 2 (Mo, Pd stripping) and step 3 (An(III) stripping), a UV-visible spectrophotometer has measured continuously the concentration of americium and pH has been estimated by electrodes. Temperatures in centrifugal extractors have been also measured in these 3 banks and was closed to 40°C.

Aqueous concentration profiles of extraction bank (step 1) are given on Figure 7. Actinides(III) and europium are well extracted, profiles decreased straightly from stage 8 (feed introduction) to stage 1. Nevertheless, computed profiles of europium are better than experimental ones. This could be explained by the temperature inside centrifugal extractors. Flowsheet was elaborated with extraction data at room temperature, and the malonamide extraction strength is lower at high temperature.

Figure 8 gives aqueous concentration profiles of An(III) and Eu(III) in stripping bank (step 3). Stages 9-16 show a very good stripping of americium and curium, whereas europium remains in solvent (flat profile). For the organic scrubbing part (stages 1-8), europium is well scrubbed (with a good correlation between experimental and calculated profiles (no influence of temperature).

The main results of this run can be summarized as follows:

- high recovery yields of An : more than 99.9% of Am(III) and 99.7% of Cm(III),
- good An/Ln decontamination factors DF were obtained : less than 2% of lanthanides in mass with actinides(III),
- and also good An/FP decontamination factors were observed : only 0.5% of Pd and less than 0.01% of Ru remained with actinides(III).

This hot test shows SANEX Variant 2 process could recover selectively actinides(III) with only one partition cycle, directly from a PUREX raffinate. The main objectives have been reached except 0.2% of curium in the raffinate, but 2 additional stages in extraction section should be sufficient to enhance performances for that element.

These promising first results allow the CEA to continue the process development of SANEX Variant 2 in order to propose a complete integrated process in the future. The next step of development is the process simplification to minimize number of steps necessary to recover actinides(III) with the good performances and to minimize the volume of effluents.

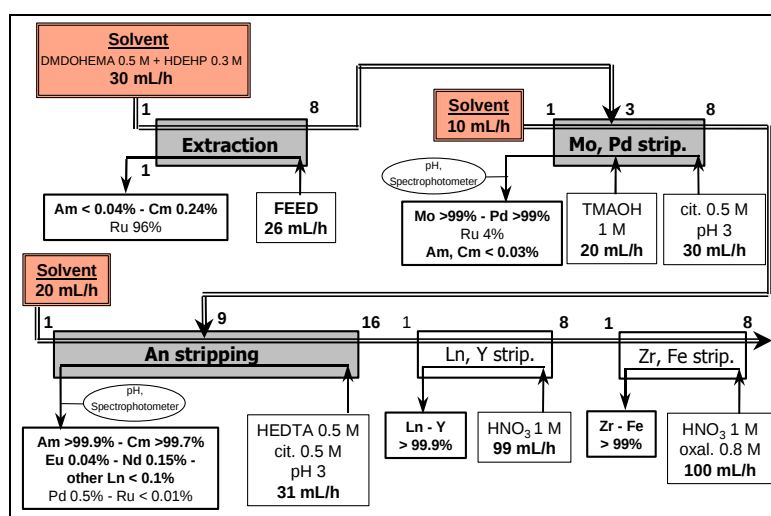


Figure 6 : hot test flowsheet of Variant 2 process in small centrifugal extractors (ECLHA)

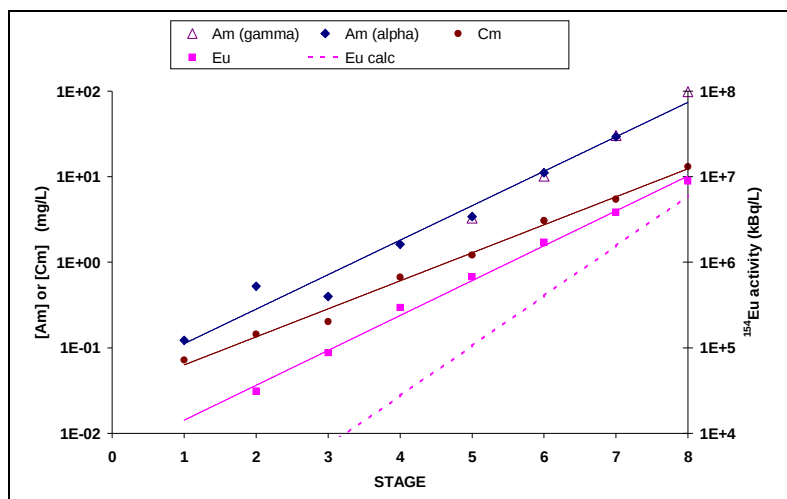


Figure 7 : aqueous profiles of actinides(III) and ^{154}Eu in the extraction section (step 1)

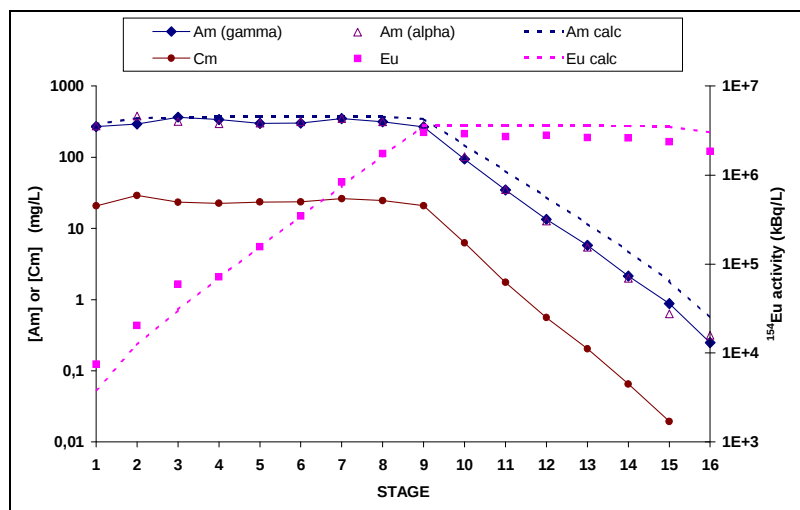


Figure 8 : aqueous profiles of actinides(III) and ^{154}Eu in the An stripping section (step 3)

4- CONCLUSION

In conclusion the recent advance and the perspectives for minor actinides separation can be resume as follows :

- Concerning the DIAMEX process, we have now a reference flowsheet with a new reference molecule, globally well validated through numerous cold and hot pilot runs. Solvent regeneration and industrial scaling studies are now under progress.
- For the SANEX - basic reference strategy (selective extraction of actinide from DIAMEX product) : the BTP's family is well suited for An/Ln separation, but the tested molecule nPr-BTP present insufficient stability characteristics, so new formulation of the solvent is proposed in order to realise a new HA test in 2001 summer.
- Concerning the SANEX - Variant 1 (idem reference strategy with feed acidity adjustment) : a successful pilot test on surrogate solution has been realised. The drawback of this route, beside the need of a pH adjustment of the feed with a buffer, is the high sensitivity of the flowsheet to flow rates due to the limited separation factor procured by the selected extraction system.
- For the SANEX –Variant 2 (selective An stripping in DIAMEX process) : A good extraction yield of An and good DF An/Ln has been achieved in a surrogate and a HA tests. However, further optimisation of this process is needed regarding effluent volumes and number of steps necessary to recover actinides(III).

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