

## Modelling and achievement of a SANEX process flowsheet for trivalent actinides/lanthanides separation using BTP extractant (bis-1,2,4-triazinyl-pyridine).

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### Abstract

A test was carried out in the ATALANTE facility at Marcoule using a BisTriazinylPyridine extractant to separate actinides(III) from lanthanides(III) out of a synthetic aqueous feed solution simulating a DIAMEX process stripping solution. This extractant molecule was proposed by Z. Kolarik(2) in the framework of the European contract "NEWPART"(1), coordinated by the CEA. The first CEA studies on BTP in 1998, showed that this extractant was very efficient to separate actinides(III) from a highly concentrated nitric medium.

Preliminary studies allowed to design a first flowsheet with the following sections: an extraction section, a scrubbing section to back-extract the part of lanthanides(III) that follows the actinides(III) in the solvent, a back-extraction section to recover actinides(III) with an organic scrubbing to remove the palladium(II) well extracted by BTP. Preliminary experiments also showed that extraction kinetics were slow, which must be taken into account in the flowsheet design. The PAREX code, with specific models for metal nitrate distribution phenomena and extraction kinetics, was used to elaborate precisely the SANEX/BTP process flowsheet (stage number of each section and flow rates). The test was carried out using 2 batteries of 8 mixers-settlers with a volume of 25 mL for each stage. The radioactive feed solution was a synthetic solution containing every element, at nominal concentration, which could be found in a DIAMEX back extraction solution. This first test showed that the mean objectives have been reached. More than 99.8% of actinides(III) were extracted and 98% of americium(III) and 90% of curium(III) were recovered. Less than 2.3% (in mass) of lanthanides(III) were back extracted along with actinides, in spite of a bad aqueous scrubbing efficiency. Furthermore, only 1% (in mass) of palladium(II) was measured in the actinides(III) stripping solution. Ruthenium was slightly extracted, so the separation of that element is easy by this process. A part of iron has made insoluble complexes with BTP solvent which damages stainless steel.

Experimental concentration profiles of metallic species were correctly reproduced by calculation for extraction sections. The comparison of experimental and calculated concentration profiles led to believe that kinetics are slower for back-extraction than for extraction. This comparison gives an interesting feedback for orientation of future developments.

### INTRODUCTION

The currently retained strategy for the minor actinides separation is based on a process in several steps. The first two steps are the following one: coextraction of actinides(III) and lanthanides(III) from a PUREX raffinate with the DIAMEX process, then selective extraction of actinides(III) from the back-extraction DIAMEX solution. In the framework of the European contract "NEWPART"(1), coordinated by the CEA, Z. Kolarik (2, 3) proposed a new group of extractant molecules, the 2,6-bis-(1,2,4-triazin-3-yl)-pyridines (BTP). The results of the preliminary studies, achieved in Marcoule, confirmed the potential interest of these molecules and the decision was made to establish the scientific feasibility of a separation process based on this kind of extractant. A test with a synthetic radioactive solution was carried out in the C17 laboratory of Atalante in mixers-settlers (MS) batteries. The results of this test was presented at the GLOBAL'99 conference(4), the modelling aspect is particularly developed in the present paper.

### RESULTS ET DISCUSSION

#### Process flowsheet design

The aim of the test was to separate actinides(III) from a solution mostly containing lanthanides(III) and palladium(II). Preliminary experiments showed that actinides are about 100 times more extractable than lanthanides(III) by the 2,6-bis-(5,6-di-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (*nPr*-BTP) extractant chosen for the test. They have also shown that palladium(II) is more extractable than actinides(III) and contributes to saturate the solvent. So the extractant concentration must be optimised and a "palladium scrubbing" section must be included within the back-extraction section. So the process flowsheet includes the following sections: extraction of actinides(III) ; aqueous scrubbing to back-extract the small part of lanthanides(III) extracted in the solvent ; back-extraction of actinides(III) ; organic scrubbing to extract palladium(II) back-extracted with actinides(III). Preliminary experiments to the test showed slow extraction kinetics to be taken into account in the flowsheet design. The PAREX code (5) was used to design precisely the flowsheet, i. e. the stage number of each section (extraction, scrubbing, back-extraction) and the flow rates of liquid (feed, solvent ...). The distribution phenomena of solutes were modelled and included in the code just as the extraction kinetics.

#### Distribution ratio model

The model concerns the distribution of the principal species in the processed solution: actinides(III) (americium(III), curium(III)), lanthanides(III) (in particular europium(III), the most extractable by the *nPr*-BTP) and palladium(II). It aims to reproduce, with the available experimental data, the influence of nitrate ions concentration and free *nPr*-BTP concentrations on distribution ratios of species. The usually admitted equilibrium for actinides and lanthanides extraction by BTP is the following one:



The actinides(III) and the lanthanides(III) extraction requires three BTP molecules, and two in the palladium(II) case which is also associated with only two nitrate ions, as shown by the experimental data of change in distribution ratios of

americium(III), europium(III) and palladium(II) with the BTP concentration. The treatment of experimental results led to suggest the following expression to model the distribution ratios of metallic cations:

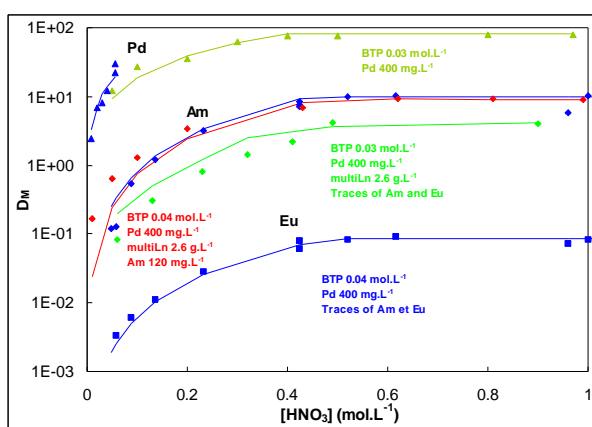
$$D_M = \frac{[M]_{org}}{[M]_{aq}} = k_M \cdot [NO_3^-]^x [BTP_{free}]^y \quad (\text{Eq. 2})$$

Table I presents the parameters of the model for the distribution ratios. The nitric acid concentration that defines two areas for the model, was chosen in order to have continuous distribution ratios when the nitric acid concentration varies.

**Table I: Parameters for distribution ratios ( $D_M$ ) model**

Metallic ion	$[HNO_3] \leq 0.45 \text{ mol.L}^{-1}$			$[HNO_3] > 0.45 \text{ mol.L}^{-1}$		
	$k_M$	$x$	$y$	$k_M$	$x$	$y$
Am(III)	$2.1 \cdot 10^5$	1.8	2.5	$5.3 \cdot 10^4$	0	2.5
Cm(III)	$3.15 \cdot 10^5$	1.8	2.5	$7.95 \cdot 10^4$	0	2.5
Pd(II)	$4.3 \cdot 10^5$	1.1	2	$1.6 \cdot 10^5$	0	2
Eu(III)	1600	1.7	2.5	448	0	2.5

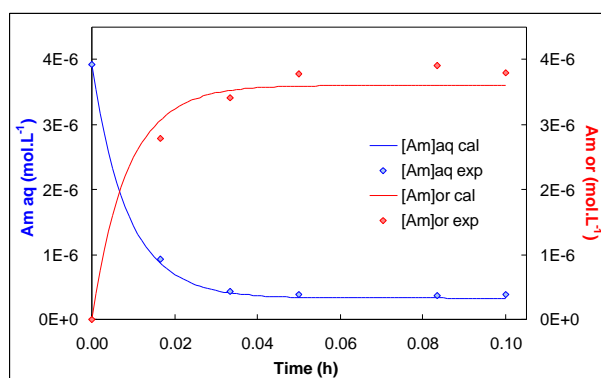
Figure 1 presents the comparison between calculated and experimental distribution ratios in different experimental conditions ( $n$ Pr-BTP concentration, nitric acid concentration).



**Fig. 1: Change in distribution ratios of metallic species with nitric acid concentration**

#### Transfer efficiency

An extraction kinetic study was performed in test tube using the same blade propeller as those used in the mixers-settlers. Considering that diffusional resistance is negligible in the mixer, transfer resistance to metal nitrate extraction was attributed to interfacial reactions. The change in concentration with time was reproduced (Figure 2) fitting interfacial transfer coefficient (Table II) for each species.



**Fig. 2: Modelling of americium(III) extraction kinetic (dots: experience, lines: calculation)**

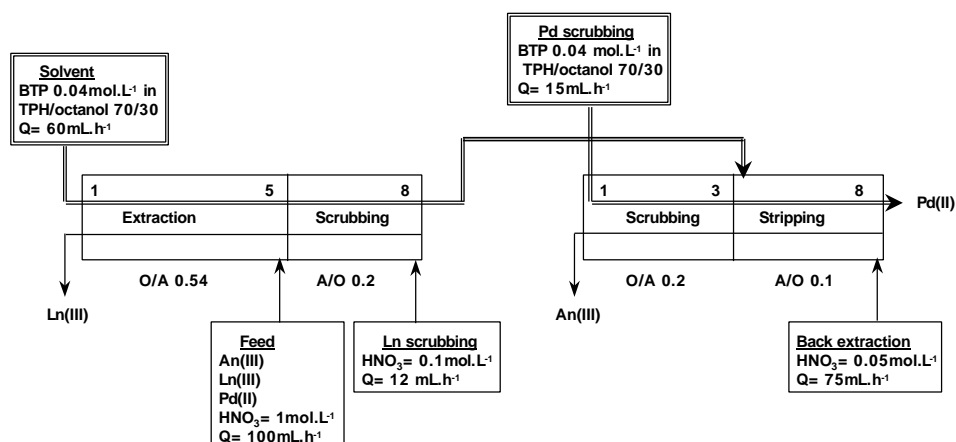
**Table II: Interfacial transfer coefficients ( $k_e$ )**

Metallic ion	$k_e \text{ (m.s}^{-1}\text{)}$
Am	$1.5 \cdot 10^{-6}$
Eu	$9 \cdot 10^{-8}$
Pd	$3 \cdot 10^{-6}$

During this test, change in palladium concentration with time was not measured, however, it appeared that to represent correctly the extraction kinetic of europium(III) it is necessary to model a sufficiently quick transfer of palladium(II).

### Final process flowsheet design

The feed to process simulates a DIAMEX production flow from an UOX fuel (irradiated to 45GWj/t) HLLW treatment. The specified performances were to recover more than 99.9% of actinides(III) with less than 5% of lanthanides(III) (in mass) and less than 1% of palladium(II) (in mass). The selected solvent is composed of *n*Pr-BTP 0.04 mol.L<sup>-1</sup> in TPH/octanol 70/30%<sub>vol</sub>. The highest possible extractant concentration was chosen to increase extraction performances and to limit the necessary organic volume, respecting the extractant solubility with a reasonable margin. The process flowsheet, presented on the Figure 3, was designed using the PAREX code.



**Fig. 3: Flowsheet of the BTP test**

In the first battery of mixers-settlers, the extraction-scrubbing section, five stages are devoted to actinides(III) extraction. Then, lanthanides(III), (slightly) extracted, are back-extracted on three stages ("lanthanides scrubbing" section). The second battery is used to back-extract actinides(III) on five stages. This battery also contains a "palladium scrubbing" section of three stages. According to the calculation, with these operating conditions, the expected recovery rate of actinides is equal to 99.5% with a residual contamination of 0.02% in mass of lanthanides(III) and 1% in mass of palladium(II).

### Starting conditions optimisation of the test

The PAREX code also allows to make transient calculations and then to estimate the needed time to achieve equilibrium. For this test, initial conditions were optimised to reduce this time, which permitted to minimise the amount of extractant and effluent. The choice of the starting aqueous composition in the extraction and scrubbing stages allows to reduce the needed time to achieve equilibrium from 14 hours to 10 hours.

### Sequence of the test

All elements that might be in a production flow to process, were introduced in the synthetic feed prepared for the test (Table III). Concentrations are nominal, even a bit higher than the reality to simulate an extreme case (case of palladium and ruthenium).

To reduce the time needed to achieve equilibrium, the stages of the mixers-settlers batteries were filled with solutions containing either americium(III) and curium(III) or lanthanides(III) or nitric acid.

**Table III: Composition of the synthetic aqueous feed used for the SANEX/BTP process test**

Element	Nuclides	Concentration (mg.L <sup>-1</sup> )	Activity (MBq.L <sup>-1</sup> )
Am	<sup>241</sup> Am	126	1.6 10 <sup>4</sup>
Cm	<sup>244</sup> Cm	0.98	2.9 10 <sup>3</sup>
Y	natural	280	—
La	natural	315	—
Ce	natural	598	—
Pr	natural	285	—
Nd	natural	980	—
Sm	natural	190	—
Eu	natural	42	—
Eu	<sup>152</sup> Eu		94
Gd	natural	56	—
Ru	natural	62	—
Ru	<sup>103</sup> Ru		9
Pd	natural	392	—
Fe	<sup>59</sup> Fe		6

During the test the flow rates were measured by weighing. At the end of the test, balances of outflow solutions volumes allow to confirm flow rates (except for the aqueous scrubbing). Hydrodynamic behaviour of the system was

satisfactory. No mixing of organic and aqueous phases in settling chambers have been noticed. After about six hours, some little solid particles were observed in the extraction section of the first battery. This phenomenon did not modify the hydrodynamics. Regularly sampling the outlets allowed to check the attainment of the steady state (Figure 4). Analyses of Am, Cm, Eu, Ru and Fe were carried out thanks to gamma spectrometry ( $^{152}\text{Eu}$ ,  $^{103}\text{Ru}$ ,  $^{59}\text{Fe}$  and  $^{241}\text{Am}$ ), alpha counting ( $^{244}\text{Cm}$  +  $^{241}\text{Am}$ ), alpha spectrometry ( $^{244}\text{Cm}$  and  $^{241}\text{Am}$ ) and ICP-MS for lanthanides, palladium and ruthenium. Since solvent could not be analysed by the last method, organic phases were contacted with a solution containing citric acid  $1 \text{ mol.L}^{-1}$ , at pH 3 to back-extract in aqueous phase the elements to be analysed. Table IV summarises the results obtained for the outflows (including radioactive and ICP-MS analyses).

**Table IV: Mass balance and decontamination factors**

Element	Mass balance	% in raffinate	% in An stripping	% in solvent	Decontamination factor (strip/feed)
Am	99.4%	0.11%	<b>97.6%</b>	1.7%	
Cm	97.6%	0.15%	<b>89.4%</b>	8.1%	
Y	114%	112%	1.8%	< 0.11%	56
La	114%	114%	< 0.05%	< 0.10%	> 2100
Ce	114%	114%	< 0.03%	< 0.05%	> 4000
Pr	114%	114%	< 0.05%	< 0.11%	> 1900
Nd	114%	114%	< 0.02%	< 0.03%	> 6500
Sm	113%	113%	0.4%	< 0.16%	248
Eu	111%	109%	2.3%	< 0.7%	43
$^{152}\text{Eu}$	119%	117%	2.4%	0%	41
Gd	108%	105%	3.0%	< 0.55%	33
Ru	95%	94%	0.7%	< 8.3%	152
$^{103}\text{Ru}$	113%	112%		0.63%	> 2400
Pd	74%	0.09%	1.0%	72%	102
$^{59}\text{Fe}$	70%	6.3%	< 1.3%	62%	> 79

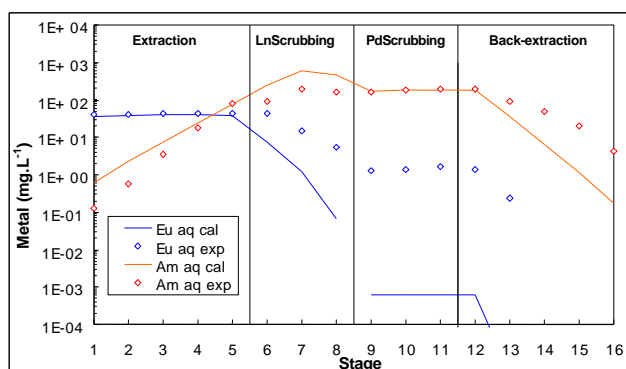
The principal result of this test is that the major aims were more or less reached, in particular:

- More than 99.8% of americium and curium are extracted in 5 stages,
- 98% of americium and 90% of curium are recovered (objective 99.9%) despite a back-extraction in 5 stages, not so much efficient,
- Contamination of actinides by lanthanides is less than 2.3% in mass (objective <5%), despite a very bad efficiency of the 3 scrubbing stages (due to very slow transfer kinetic, perhaps exacerbated by a default of scrubbing flow rate still not explained),
- Despite their coextraction in the first section, palladium and iron are well separated from actinides,
- Ruthenium proved to be very little extractable by this solvent, unlike by extractants containing pyridinic motif.

Even though they proved to be lower than those expected, the decontamination factors are very high. This shows that this solvent thanks to its good performances can reach the defined objectives. However, the actinides back-extraction proved to be not quantitative, probably because of slow kinetics. Moreover, the analysis of the particles that appeared during the test, exhibits a high iron content probably resulting from the damage of stainless steel of the batteries by the BTP extractant.

### Comparison between experimental and calculated concentration profiles

Figure 4 presents experimental and calculated (PAREX code) concentration profiles and transient-state americium(III) concentration in the stripping solution.



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**Fig. 4: Results of the test: concentration profiles of americium(III) and europium(III) / transient-state americium(III) concentration in the stripping solution (dots: experience, lines: calculation)**

Experimental concentration profiles of metallic species in the extraction sections are correctly reproduced by the calculation. Comparison between experimental and calculated profiles led us to think that back-extraction kinetics were slower than extraction kinetics. Results of this test and the comparison between experimental and calculated profiles allow to direct the coming research. In particular, it would be desirable to study chemistry of extraction reaction to explain and to model the kinetic differences observed during the extraction and the back-extraction. Concerning the distribution of metallic species, additional data of distribution ratios at low nitric acid concentration could be performed if we want to favour back-extraction operating at lower acidity.

## CONCLUSION

This test of a SANEX/BTP process allowed to confirm the validity of the americium(III) and curium(III) selective extraction by a solvent containing a BisTriazinylPyridine extractant, although the molecule used for his test proved to be not so much stable. Research will be necessary to find a more stable molecule. Several phenomena exhibit the necessity to improve the knowledge of the system, in particular concerning the back-extraction kinetics of actinides(III). At each phase

of the flowsheet development, the PAREX code proved to be a very useful tool including results of experimental data in test tube (distribution ratios, kinetics extraction) and allowing to design the flowsheet and to optimise starting conditions of the test.

1. Z. Kolarik, U. Müllich, Extraction of Am(III) and Eu(III) Nitrates by 2,6-Di-(5,6-Dialkyl-1,2,4-Triazin-3-yl) Pyridines, Poster, 5<sup>th</sup> International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation, Mol, Belgique, 25-27 November (1998)
2. Z. Kolarik, U. Müllich, F. Gassner, Selective Extraction of Am(III) over Eu(III) Nitrates by 2,6-Ditriazolyl- and 2,6-Ditriazinylpyridines, Solvent Extraction and Ion Exchange, 17, 1, 23-32, (1999)
3. Z. Kolarik, U. Müllich, F. Gassner, Extraction of Am(III) and Eu(III) Nitrates by 2,6-Di-(5,6-Dipropyl-1,2,4-triazin-3-yl)pyridines, Solvent Extraction and Ion Exchange, 17, 1, 1155-1170, (1999)
4. C. Hill, X. Hérès, J.-N. Calor, D. Guillaneux, P. Rivalier, B. Rat, Trivalent Actinides/Lanthanides Separation using Bistriazinylpyridines, GLOBAL'99, International Conference on Future Nuclear Systems, Snow King Resort, Jackson Hole, Wyoming, (30/08/1999-02/09/1999)
5. B. Dinh, P. Baron, Modélisation des opérations de retraitement, Rapport scientifique DCC, (1997)