

## SANEX-BTP PROCESS DEVELOPMENT STUDIES

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### Abstract

*Bis*-triazinyl-pyridines (BTPs) have been developed at CEA-Marcoule to separate actinides(III) from lanthanides(III). Although high separation performances were observed in the counter-current hot test carried out in 1999 on a highly active effluent, the extraction and back-extraction yields of actinides(III) were lower than expected from calculation. A strong sensitivity of the extractant towards air oxidation and acidic hydrolysis was actually pointed out. Therefore, the hydrolysis of *bis*-triazinyl-pyridines was deeply investigated (qualitative determination of the degradation products) in different experimental conditions. It appeared that the branching of the alkyl groups on the  $\alpha$  position of the triazine rings hindered the hydrolysis of the extractant. The formulation of the solvent was thus optimised and tested again in 2001 on a genuine DIAMEX back-extraction solution in the ATALANTE facility.

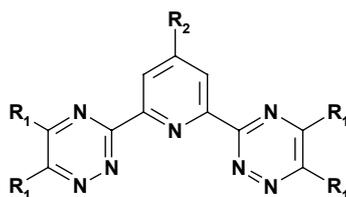
## Introduction

Most of the long term radiotoxicity of the highly active vitrified wastes issuing from the reprocessing of spent nuclear fuels arises from the contained long-lived radionuclides, such as trivalent minor actinides (An(III): Am(III) and Cm(III)). In the partitioning and transmutation strategy, developed to reduce the long term radiotoxicity of the wastes, the separation of An(III) from trivalent lanthanides (Ln(III), accounting for about one third of the total amount of fission products), is a key step named SANEX. However, this separation is very difficult because An(III) and Ln(III) exhibit similar chemical properties.

Several studies in media of low acidity have shown already that hydrophobic nitrogen-containing polydentate ligands (e.g. tri-tertio-butyl-pyridyl-triazine, T<sup>t</sup>BuPTZ), were able to separate An(III) from Ln(III) when mixed with lipophilic anions. [1,2] However, bis-triazinyl-pyridines (BTP, Figure 1), a new family of nitrogen-containing polydentate ligands recently developed by Z. Kolarik *et al.* [3] in the framework of a European contract led by CEA-Marcoule,<sup>1</sup> appeared to be very efficient and selective extracting agents towards An(III), even from very acidic aqueous solutions (e.g. [HNO<sub>3</sub>] ≥ 2 mol/L).

Various BTP molecules bearing different alkyl, aryl or hetaryl groups on the triazines have been synthesised and studied at CEA-Marcoule for “An(III)/Ln(III)” separation. Among them, 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (*n*Pr-BTP) was chosen in December 1999 to perform a counter-current test in the ATALANTE facility on a genuine highly active effluent. The observed decontamination performances were very satisfactory ( $1\ 400 < DF_{Ln(III)}^2 < 450\ 000$ ), but the extraction and back-extraction yields for Am(III) and Cm(III) were lower than predicted by flowsheet modeling. Since experimental concentration profiles of An(III) and Ln(III) in organic and aqueous solutions were better modelled when the initial concentration of the extractant was lowered by 20%, partial degradation of *n*Pr-BTP was assumed to have occurred during the hot test to explain the unexpectedly bad results observed. Therefore, hydrolytic degradation of *n*Pr-BTP under acidic and oxidative conditions was investigated.

Figure 1. General formula of BTPs



with R<sub>1</sub> = H, Methyl, *n*-Propyl, *i*-Propyl, *n*-Butyl, *i*-Butyl and R<sub>2</sub> = H, *i*-Nonyl

## Degradation of *n*Pr-BTP under acidic hydrolysis

Two different methods were used to investigate the stability of *n*Pr-BTP under acidic and oxidative conditions. A qualitative one, consisting in evaluating systematically the extracting properties of the hydrolysed solvent, and a more quantitative one, involving the characterisation of

1. NEWPART: New partitioning techniques for minor actinides. European contract: FI41-CT-96-0010. [4]
2. DF<sub>Ln(III)</sub> lanthanides(III) decontamination factor.

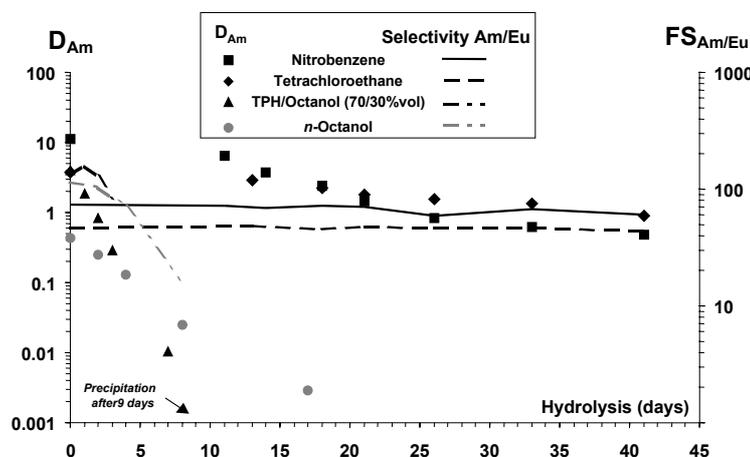
*n*Pr-BTP degradation products by Gas Chromatography coupled with Electronic Impact Ionisation Spectrometry and Electro-spray Ionisation Mass Spectrometry.

### ***Influence of acidic hydrolysis on the extracting properties of nPr-BTP***

As for the hot test of December 1999, *n*Pr-BTP was diluted in a mixture of hydrogenated tetrapropene (TPH) and *n*-octanol (70/30%<sub>vol</sub>), and then contacted with different nitric acid solutions (with or without nitrous acid) for hydrolysis. Organic samples were periodically withdrawn to evaluate the extracting properties of the hydrolysed solvent by measuring the distribution ratios of <sup>241</sup>Am and <sup>152</sup>Eu (used to mimic “An(III)/Ln(III)” group separation). These studies revealed a steady decrease of the extraction properties of *n*Pr-BTP when the atmosphere was rich in oxygen or when [HNO<sub>3</sub>] exceeded 0.5 mol/L. For example, a decrease of 80% of D<sub>Am</sub> was observed after 2 days of hydrolysis, when [HNO<sub>3</sub>]<sub>ini</sub> equaled 1 mol/L. Furthermore, the extracting properties of *n*Pr-BTP quickly decreased when [HNO<sub>2</sub>]<sub>ini</sub> exceeded 0.005 mol/L. For example, a decrease of 50% of D<sub>Am</sub> was observed after only 2 hours of hydrolysis, when [HNO<sub>3</sub>]<sub>ini</sub> equaled 1 mol/L and [HNO<sub>2</sub>]<sub>ini</sub> equaled 0.01 mol/L.

The nature of the organic diluent turned up to influence the stability of *n*Pr-BTP. On the contrary to aliphatic, alcoholic or aromatic diluents, nitrobenzene and chlorinated diluents seemed to prevent *n*Pr-BTP from degrading (Figure 2). However, for safety reasons these organic diluents would not be acceptable in nuclear environments to implement industrial scale separation processes.

Figure 2. **Influence of the nature of the organic diluent on the stability of *n*Pr-BTP under acidic hydrolysis/oxidation**



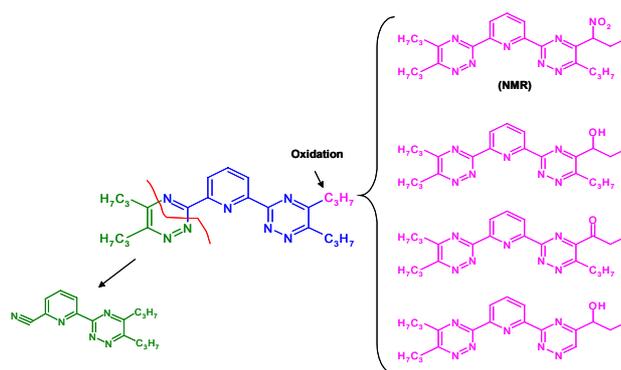
**Hydrolysis cycles at 25°C:** 1 hour mixing followed by 2 hours settling (24 hours/day).  
**Hydrolyzing aqueous solution:** [HNO<sub>3</sub>] = 1 mol/L.  
**Hydrolyzed organic solutions:** [*n*Pr-BTP] = 0.02 mol/L in various organic diluents.  
**Extraction tests at 25°C:** [HNO<sub>3</sub>] = 1 mol/L, spiked with <sup>152</sup>Eu and <sup>241</sup>Am.

### ***Characterisation of nPr-BTP degradation products***

The main degradation products of *n*Pr-BTP were qualified by Gas Chromatography Mass Spectrometry and Electro-spray Ionisation Mass Spectrometry. Whatever the initial experimental conditions (presence or absence of an acidic aqueous phase in contact with *n*Pr-BTP), the degradation products of *n*Pr-BTP were always almost the same only their proportions varied.

A degradation pathway was proposed for *n*Pr-BTP, the first step of which being the attack of one CH<sub>2</sub> group on the α position of the triazinyl rings to form a nitro compound observed by <sup>15</sup>N NMR (Figure 3). In a second step, the compound would degrade into an alcohol (which was also the main degradation product observed in the absence of acidic aqueous phase) or into a ketone (which was the main degradation product observed after the hydrolysis of *n*Pr-BTP by molar nitric acid). Besides, a second CH<sub>2</sub> group would also be attacked, resulting in the formation of doubly functionalised compounds (dialcohols and diketones in Figure 3). The alcohol compounds would also lose one propyl chain. Side and minor reactions would consist in breaking triazinyl rings leading to cyano compounds.

Figure 3. Hypothetical degradation pathway of *n*Pr-BTP under acidic hydrolysis/oxidation



### Optimisation of the formulation of the new BTP solvent tested in June 2001

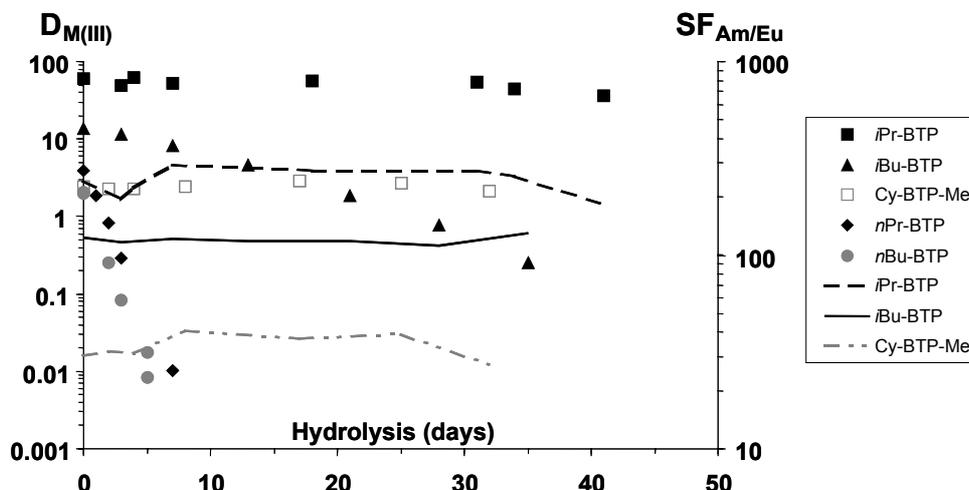
Since *n*Pr-BTP showed up to be unstable under acidic hydrolysis, chemical stability of the BTPs was chosen as the most relevant criterion when selecting an other BTP candidate for the optimisation of the new solvent formulation. Therefore, all available BTP molecules have been submitted to acidic hydrolysis and their resistance compared in order to select the best BTP to be used in an active counter-current hot test in June 2001.

The second important criterion for the process set-up in short time phase contactors (e.g. centrifugal contactors or mixer settlers) was the kinetics of extraction (forward and backward) of the new system developed.

### Comparison of the chemical stability of substituted BTP molecules under acidic hydrolysis

Molecules bearing branched alkyl groups on the α position of the triazinyl rings, such as Cy-BTP-Me and *i*Pr-BTP, appeared to be much more stable than *n*Pr-BTP or *n*Bu-BTP, bearing linear alkyl groups. Cy-BTP-Me and *i*Pr-BTP had not been chosen previously when preparing the hot test of 1999 because of several practical reasons: tedious synthesis, low solubility in organic diluents, slow kinetics of extraction. However, they showed good stability over 30 days under acidic hydrolysis (Figure 4).

Figure 4. Comparison of the stability of different BTPs under acidic hydrolysis



**Hydrolysis cycles at 25°C:** 1 hour mixing followed by 2 hours settling (24 hours/day).

Hydrolyzing aqueous solution:  $[\text{HNO}_3] = 1 \text{ mol/L}$ .

Hydrolyzed organic solutions:  $[\text{BTP}] = 0.005 \text{ or } 0.01 \text{ mol/L}$  in *n*-octanol or “*n*-octanol /TPH”.

**Extraction tests at 25°C:**  $[\text{HNO}_3] = 1 \text{ mol/L}$ , spiked with  $^{152}\text{Eu}$  and  $^{241}\text{Am}$ .

### Comparison of the kinetics of extraction of substituted BTP molecules

The major drawback of Cy-BTP-Me and *iPr*-BTP was their too slow kinetics of extraction of An(III) for the implementation of a counter current hot test in mixer-settlers or centrifugal contactors. Several attempts were made to accelerate their kinetics by using other co-extractants, such as TBP or malonamides. In some cases, the latter modifiers fastened the kinetics of extraction of An(III), in other cases they enhanced the extraction performances of the BTPs or their stability under acidic hydrolysis, but on the contrary, they also lowered their selectivity towards An(III).

The case of *iPr*-BTP was rather peculiar. When aqueous solutions were spiked with  $^{241}\text{Am}$  and  $^{152}\text{Eu}$  at traces level and *iPr*-BTP was diluted in a mixture of TPH and *n*-octanol (as for *nPr*-BTP in the hot test of 1999), the kinetics of extraction of Am(III) was fast (less than 5 minutes to reach the equilibrium), whereas that of Eu(III) was very slow (more than an hour required to reach the equilibrium). Unexpectedly, a precipitate occurred when a synthetic aqueous solution was used simulating a genuine DIAMEX<sup>3</sup> back-extraction effluent containing almost 18 mmol/L of Ln(III).

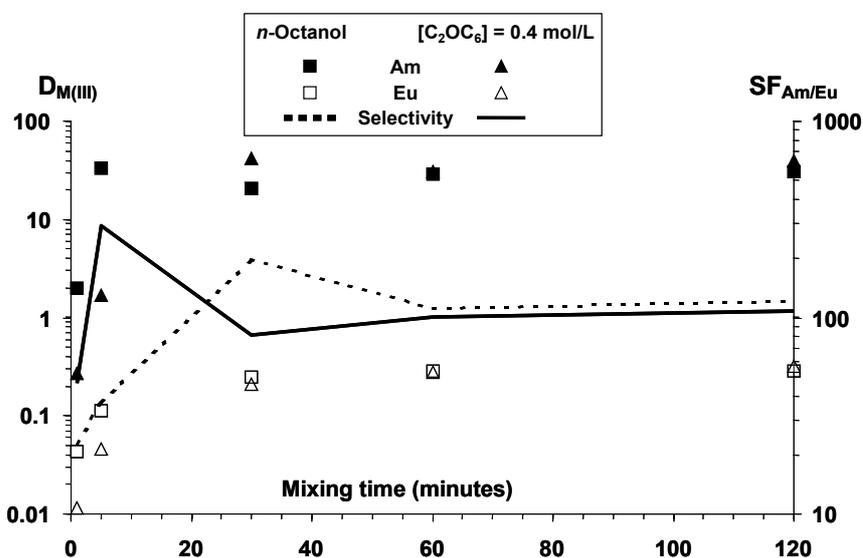
However, no precipitation occurred with this feed solution when *iPr*-BTP was dissolved in more polar diluents, such as pure *n*-octanol, tetrachloroethane or nitrobenzene; but the kinetics of extraction of Am(III) and Eu(III) both became very slow (more than an hour required to reach the equilibrium as shown on Figure 5 for *n*-octanol). Tetrachloroethane and nitrobenzene being unacceptable for further industrial process development, *n*-octanol was finally chosen for the demonstration hot test of June 2001.

In order to fasten the kinetics of extraction of *iPr*-BTP in *n*-octanol, phase transfer catalysts such as malonamides were tried. Figure 5 shows the influence of dimethyl-dioctyl-hexylethoxy-

3. DIAMEX: First step consisting in co-extracting An(III) and Ln(III) from PUREX raffinates.

malonamide ( $C_2OC_6$ ; the reference molecule in the DIAMEX process) in *n*-octanol. Phase equilibrium was reached within 5 minutes for Am(III), and selectivity was higher than that observed in pure *n*-octanol.

Figure 5. Influence of  $C_2OC_6$  on the kinetics of extraction of *iPr*-BTP in *n*-octanol



Aqueous solution: synthetic solution simulating a DIAMEX back-extraction effluent ( $[Ln(III)]_{tot, ini.} \sim 18$  mmol/L,  $[HNO_3]_{ini} = 1$  mol/L), spiked with  $^{152}Eu$  and  $^{241}Am$ .

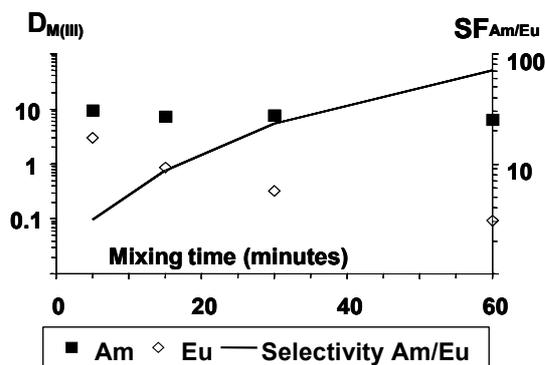
Organic solution:  $[iPr-BTP] = 0.01$  mol/L in various diluents;  $\theta = 25^\circ C$ .

Preliminary to the design of the process flowsheet tested in June 2001 on highly active wastes, numerous series of experiments have been carried out on synthetic aqueous solutions simulating DIAMEX back-extraction solutions issuing from the reprocessing of Uox 2 type or Mox type spent fuels by PUREX process. The influence of different parameters, such as the concentration of *iPr*-BTP or  $C_2OC_6$  in *n*-octanol and that of  $HNO_3$ , Ln(III), An(III) and Pd(II) in the aqueous solution, was evaluated on the extraction yields and extraction kinetics of Ln(III) and An(III). The process flowsheet was finally designed on the basis of the following solvent formulation:  $[iPr-BTP]_{ini} = 0.01$  mol/L +  $[C_2OC_6]_{ini} = 0.5$  mol/L in *n*-octanol.

### Kinetics of back-extraction of M(III) with *iPr*-BTP

As a contrary to *nPr*-BTP, in the case of *iPr*-BTP, the back-extraction of Am(III) and Eu(III) appeared to be too slow in diluted nitric acid to allow the implementation of short time contactors. Figure 6 shows that phase equilibrium requires more than 1 hour of mixing in 0.1 molar nitric acid. That is why, hydrophilic complexing agents, such as citric acid or glycolic acid, were tried to favour and fasten the back-extraction of Am(III) and Eu(III) within at least 3 minutes of mixing.

Figure 6. Kinetics of back-extraction of Am(III) and Eu(III) in nitric acid



Organic solution: [iPr-BTP] = 0.01 mol/L + [C<sub>2</sub>OC<sub>6</sub>] = 0.5 mol/L in n-octanol, contacted with a synthetic solution simulating a DIAMEX back-extraction effluent ([Ln(III)]<sub>tot, ini.</sub> ~9 mmol/L, [HNO<sub>3</sub>]<sub>ini</sub> = 0.5 mol/L), spiked with <sup>152</sup>Eu and <sup>241</sup>Am.

Aqueous stripping solution: [HNO<sub>3</sub>]<sub>eq</sub> = 0.11 mol/L; θ = 25°C.

Glycolic acid was chosen ([glycolic acid]<sub>ini</sub> = 0.3 mol/L, neutralised at pH 4 by NaOH) because of its easy destruction by heat and/or oxidation before further waste management (e.g. An(III) intra-group separation for transmutation or glass storage).

#### Counter-current tests performed on genuine high level wastes using new BTP solvent

In order to reduce the potential hydrolysis of iPr-BTP by nitrous acidic, hydrazinium nitrate was added to the scrubbing solution (it had been shown previously that hydrazine prevented BTP molecules from acidic hydrolysis).

A once through process flowsheet was firstly run for 8 hours in small scale centrifugal contactors and gave far better recovery yields of An(III) than the hot test performed in 1999 using nPr-BTP. Actually, more than 99.9% of Am(III) and more than 99.8% of Cm(III) were recovered from the genuine feed. Losses of An(III) in the raffinate solution and in the spent solvent, respectively, reached 180 and 13 µg/L for Am(III) and 23 and 1 µg/L for Cm(III). A mean decontamination factor of 150 was estimated for An(III) vs Ln(III); but higher values were calculated for lighter Ln(III), which were also the major components initially present in the feed (Table 1). Ln(III) amount in mass of An(III) product solution was lower than 2.5%.

Table 1. Results of the once-through hot test (June 2001)

Element	La(III)	Ce(III)	Pr(III)	Nd(III)	Sm(III)	Eu(III)	Gd(III)
Feed (mg/L)	130	232	115	376	105	21	28
Product (mg/L)	<0.25	<0.25	<0.25	1.2	0.55	0.90	1.2
DF <sub>Ln(III)/An(III)</sub> <sup>4</sup>	>350	>625	>300	210	110	15	13

4. Taking into account the flow-rates of the process flowsheet.

Analyses of all aqueous and organic phases at equilibrium are still under progress, but available analytical results already show that Am(III) and Ln(III) aqueous and organic profiles are in fairly good agreement with the models, especially for the extraction and acid scrubbing sections (Figures 7 and 8). The stripping section is apparently worse modelled, and further analyses are still needed.

Figure 7. Aqueous and organic profiles of Am(III) (dots: experimental points; lines: model)

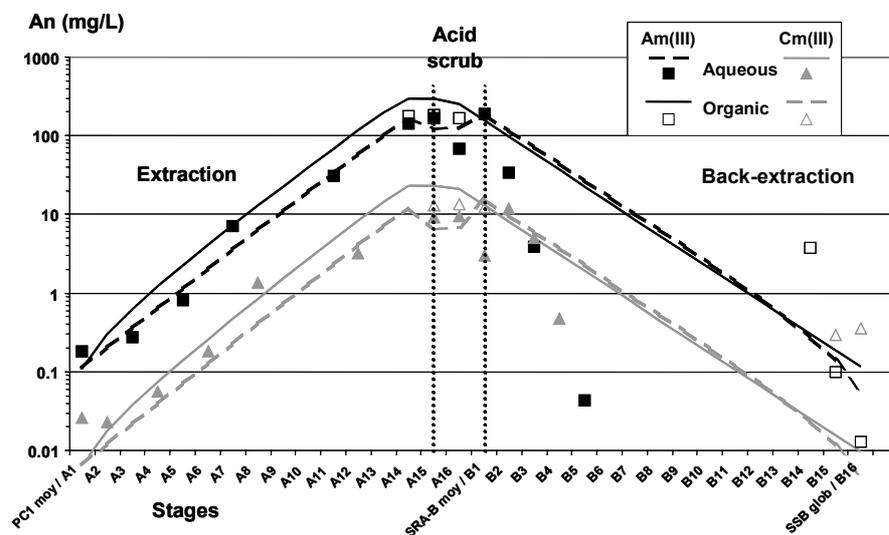
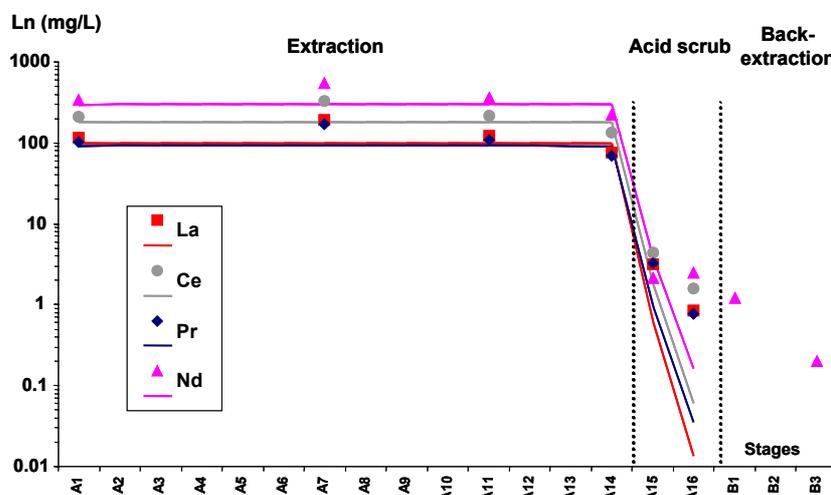


Figure 8. Aqueous profiles of Ln(III) (dots: experimental points; lines: model)



After this opened-cycle hot test, a solvent recycling process flowsheet was run for 54 hours to treat 3.85 litres of a DIAMEX back-extraction effluent. This second hot test, which allowed 6.5 litres of “Am(III) + Cm(III)” product to be generated, also pointed out partial degradation of *i*Pr-BTP, probably because of alpha/gamma radiolysis. For instance, a 40% decrease of the extraction performances of the solvent was observed after two cycles (much less indeed than previous *n*Pr-BTP, the performances of which had decreased by more than 50% after only one cycle). Analyses of aqueous and organic samples of this hot test are also under progress.

## Radiochemical stability of *iPr*-BTP

In order to investigate the radiochemical stability of *iPr*-BTP, several samples of SANEX-BTP solvent have been irradiated using a cobalt source, in the presence or absence of nitric acid (dose absorbed: 0.1 MGy). The main degradation products of *iPr*-BTP, qualified by Atmospheric Pressure Chemical Ionisation Mass Spectrometry, appeared to differ from those issuing from acidic hydrolysis. Heavier compounds than *iPr*-BTP (M.M. = 405.5 g/mol) were formed, probably resulting from the addition of one or two octanol moieties on the starting molecule, thus rendering the degradation compounds more lipophilic and more difficult to eliminate.

## Conclusion

The hot test carried out at CEA-Marcoule in 1999 with 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine pointed out the strong sensitivity of this extractant towards air oxidation and acidic hydrolysis. Qualitative determination of the degradation compounds of *nPr*-BTP allowed a better understanding of its degradation mechanism: *nPr*-BTP mainly degraded into alcoholic derivatives through the oxidation of its substituting propyl groups. Therefore, many efforts were put forward to strengthen the stability of BTPs under hydrolysis and to optimise the formulation of the new BTP solvent.

A mixture of 2,6-bis(5,6-*iso*-propyl-1,2,4-triazin-3-yl)-pyridine (*iPr*-BTP) and dimethyl-dioctyl-hexylethoxy-malonamide (C<sub>2</sub>OC<sub>6</sub>) in *n*-octanol was chosen to carry out two hot tests on genuine DIAMEX back-extraction solutions in June 2001. During these hot tests, *iPr*-BTP turned out to be sensitive to alpha/gamma-radiolysis and the spent solvent unsuitable to recycling. However, the once-through process hot test has demonstrated that *iPr*-BTP was able to separate An(III) from Ln(III) with sufficiently high recovery yields and selectivity.

Further researches will be devoted to the strengthening of *iPr*-BTP towards alpha-radiolysis.

## Acknowledgements

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