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TRIVALENT ACTINIDES/LANTHANIDES SEPARATION USING BIS-TRIAZINYL-PYRIDINES

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ABSTRACT

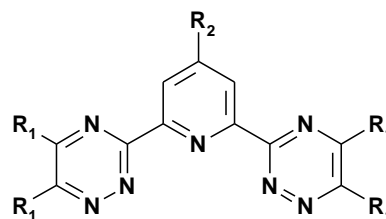
The separation of trivalent minor actinides from trivalent lanthanides is a difficult task. The present paper describes the application of a Bis-Triazinyl-Pyridine in order to separate americium(III) and curium(III) from various lanthanides(III) present in a synthetic aqueous feed solution simulating a stripping solution issued from the DIAMEX process. The performances observed during the counter-current alpha hot test, carried out at CEA Marcoule using two batteries of eight mixer-settlers, are very promising. They remain, up to now, the best An(III)/Ln(III) separation results ever obtained at such a high acidity ($[\text{HNO}_3]_{\text{initial}} = 1 \text{ mol/L}$).

I. INTRODUCTION

In the Partitioning and Transmutation strategy of nuclear spent fuel (P&T), the separation of trivalent minor actinides (americium and curium) from trivalent lanthanides is a very important step. Different systems based on liquid-liquid extraction have been proposed throughout the world to solve this difficult problem. In France, a two steps process is under development. The first step, DIAMEX, allows the co-extraction of trivalent lanthanides and minor actinides from highly active liquid wastes issued from the PUREX process, thanks to a malonamide. The second step, SANEX, is intended to separate trivalent minor actinides (An(III)) from trivalent lanthanides (Ln(III)).

In the past years, many systems based on organic molecules, containing either sulfur or nitrogen atoms (*e.g.*: Cyanex 301, tri-pyridyl-triazines, terpyridines), have been studied at CEA Marcoule for the separation of An(III) from Ln(III). Recently, a new family of extractants, the Bis-Triazinyl-Pyridines (BTPs, see figure 1), has been devel-

oped by Zdenek Kolarik. These BTPs are very efficient extracting agents and remain selective towards An(III) at high acidity ($[\text{HNO}_3] \geq 2 \text{ mol/L}$).¹



with $R_1 = \text{H}$, Methyl, *n*-Propyl, *i*-Pr, *n*-Butyl, *i*-Bu and $R_2 = \text{H}$, *i*-Nonyl

Figure 1: General formula of BTPs

II. SYNTHESIS OF THE *n*Pr-BTP

30 g of *n*-Pr-BTP were synthesized for the alpha hot test, following a published procedure for the synthesis of 1,2,4-triazines substituted in the position 3 by a pyridine ring, by condensing a carboxamhydrazone with α -diketone.²

III. SOLVENT FORMULATION AND PREPARATION OF THE ALPHA HOT TEST

Among the various BTPs available, 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine was chosen to carry out the alpha hot test. The reasons for this choice were the following:

- batch experiments, formerly performed in test tubes with Am(III) and Eu(III) to simulate An(III)/Ln(III) separation, had shown that equilibrium was reached faster than with any other studied BTP,

- *n*Pr-BTP was fairly soluble (≥ 0.05 mol/L) in mixtures of Hydrogenated Tetra-Propylene (TPH) and *n*-octanol, the organic diluent used to prevent precipitate formation,
- *n*Pr-BTP was easy to synthesize on large scale, as required by the implementation of the alpha run.

The extraction properties of *n*Pr-BTP towards nitric acid and different metallic cations, such as lanthanides(III) or palladium(II), were estimated through batch experiments performed in test tubes (0.5 to 5 mL of organic and aqueous phases), using:

- nitric acid solutions ($0.01 \leq [\text{HNO}_3]_{\text{initial}} \leq 1$ mol/L), with palladium(II) at a concentration of 400 mg/L or without,
- molar nitric acid aqueous solutions containing seven lanthanides (*i.e.*: La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III)), and some transition metals such as yttrium, palladium, iron and molybdenum, spiked with alpha and gamma emitters (*i.e.*: ^{59}Fe , ^{103}Ru , ^{152}Eu , ^{241}Am and ^{244}Cm at about 10,000 kBq/L each) to simulate a genuine stripping solution issued from the DIAMEX process,
- synthetic aqueous solutions containing americium(III) in nominal amounts ($[\text{}^{241}\text{Am}] = 120$ mg/L).

A. Optimization of the composition of the organic solvent

Preliminary tests performed with synthetic aqueous solutions containing 400 mg/L of Pd(II) showed that 30%_{vol} *n*-octanol were at least necessary to prevent Pd complexes from precipitating at the liquid interface. The extraction performances of *n*Pr-BTP towards ^{152}Eu (III) and ^{241}Am (III) were thus studied for two different contents of *n*-octanol in TPH, namely 30%_{vol} and 40%_{vol}. The mixture "TPH (70%_{vol})/*n*-octanol (30%_{vol})" was finally chosen for the alpha hot test, since the extraction performances of *n*Pr-BTP seemed to decrease with the increase of *n*-octanol content in TPH.

In these conditions, the log-log variation of the distribution ratios ($D_{\text{M(III)}}$) of both ^{152}Eu (III) and ^{241}Am (III) with the initial concentration of *n*Pr-BTP in the organic phase (ranging from 0.01 to 0.05 mol/L) seemed to follow a linear relationship with a slope value close to 3, in good agreement with the expected stoichiometry of the extracted complexes.¹ The separation factor remained fairly constant ($\text{SF}_{\text{Am/Eu}} = D_{\text{Am}}/D_{\text{Eu}} \sim 120$) whatever the initial concentration of *n*Pr-BTP in the organic phase.

However, the concentration of *n*Pr-BTP was set at 0.04 mol/L for the alpha hot test, because:

- *n*Pr-BTP seemed to precipitate out from the TPH/*n*-octanol (70/30%_{vol}) mixture, after several weeks at room temperature, when its initial concentration exceeded 0.05 mol/L,

- the distribution ratio of Am(III), D_{Am} , was respectively high enough for $[\text{HNO}_3] = 1$ mol/L ($D_{\text{Am}} \sim 10$), which allowed good extraction in the first extraction stages of the process, and small enough for $[\text{HNO}_3] < 0.06$ mol/L ($D_{\text{Am}} < 0.5$). Higher D_{Am} would indeed disfavor its stripping in the process.

The process flowsheet was elaborated using this concentration (0.04 mol/L).

B. Extraction of nitric acid and palladium(II)

The study of the extraction of nitric acid and palladium(II) revealed that:

- a 1:1 complex was formed in the case of nitric acid,
- a 1:2 complex (*i.e.*: $\text{Pd}(\text{NO}_3)_2\text{L}_2$ with $\text{L} = \textit{nPr-BTP}$) was formed when saturating the organic solution with palladium(II). Considered as a "soft" acid, palladium(II) was undoubtedly well extracted by *n*Pr-BTP.

C. Extraction of An(III), Ln(III) and other metallic cations

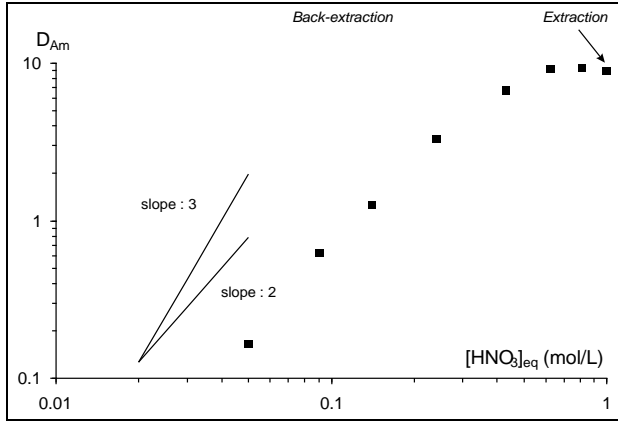
The extraction of ^{59}Fe (III), ^{103}Ru (III), ^{152}Eu (III), ^{241}Am (III) and ^{244}Cm (III) was determined by alpha and gamma spectrometric analyses, both in the presence and absence of palladium(II). As expected, macro amounts of Pd(II) in the aqueous feed solution ($[\text{Pd}]_{\text{initial}} = 400$ mg/L) induced a decrease of the distribution ratios of all other elements.

Although iron(III) and ruthenium seemed to be slowly extracted as compared to europium(III), americium(III) and curium(III), the affinity of *n*Pr-BTP towards iron(III) was fairly high at equilibrium (which required more than one hour to be reached). Besides, curium(III) was always better extracted than americium(III), by a factor of 1.5.

The extraction of all seven lanthanides(III) was checked by ICP-AES analysis. Along the 4*f* family, elements of the middle of the series, such as europium(III) or gadolinium(III), were better extracted than lighter ones.

Kinetics of extraction and back-extraction of macro amounts of americium(III) seemed similar: less than 5 minutes were required in test tubes (vortex agitation), whatever the initial concentration of lanthanides(III) in the aqueous phase. Figure 2 shows the variation of the distribution ratio of americium(III) with nitric acid concentration for an initial concentration of *n*Pr-BTP equal to 0.04 mol/L in TPH/*n*-octanol (70/30%_{vol}).

All these thermodynamic data were computed in order to elaborate and design the proper flowsheet to be applied during the alpha hot test.



Aqueous feed solution: synthetic solution simulating a DIAMEX stripping solution, $[Am^{241}]_{initial} = 120 \text{ mg/L}$
Organic solution: $[nPr\text{-}BTP]_{initial} = 0.04 \text{ mol/L}$ in TPH/ *n*-octanol (70/30%_{vol})
Aqueous back-extraction solution: diluted nitric acid temperature = $22 \pm 0.5^\circ\text{C}$

Figure 2: Extraction and back-extraction of macro amounts of americium(III) by *nPr*-BTP

D. Hydrodynamic studies

A single-stage extraction test, aimed to estimate the actual extraction efficiency of the mixer-settlers and to measure the time required to reach the equilibrium state, was carried out in a plastic tube of 1.3 cm internal diameter (volume of aqueous and organic phases = 2.5 mL) equipped with a blade propeller, stirred at 3200 rpm. This test showed that 3 minutes were at least necessary to reach the equilibrium, thus indicating that the efficiency of the mixer-settlers would not be optimal (residence time < 2 minutes).

The hydrodynamic behavior of the organic solvent (*nPr*-BTP in "TPH/octanol") was also checked during four counter current cold tests using a battery of eight mixer-settlers (two stages for extraction, two stages for scrubbing and four stages for stripping):

Test n°1: nitric acid (1 mol/L) vs TPH/*n*-octanol (70/30%_{vol}).

Test n°2: nitric acid (1 mol/L) vs *nPr*-BTP : 0.04 mol/L in TPH/*n*-octanol (70/30%_{vol}).

Test n°3: europium(III) (0.02 mol/L in molar nitric acid) vs *nPr*-BTP : 0.04 mol/L in TPH/*n*-octanol (70/30%_{vol}).

Test n°4: europium(III) (0.02 mol/L) and palladium(II) (0.004 mol/L in molar nitric acid) vs *nPr*-BTP (0.04 mol/L) in TPH/*n*-octanol (70/30%_{vol}). In the latter run however, a small black colloid was observed in the settler of the feed input stage (introduction of the feed solution).

These counter-current cold tests allowed all parameters required by the alpha hot test (*i.e.* : stirring speed of the mixers, level of the interfaces in the settlers, flows) to be properly adjusted.

IV. ALPHA HOT TEST SETTING UP

The composition of the synthetic aqueous feed solution used in the alpha hot test is recalled in Table 1. The unexpected high concentration of yttrium(III) was due to a printing mistake on the sticker of the commercialized flask of lanthanum(III) nitrate salt (the chemicals supplier unfortunately provided yttrium(III) nitrate instead of lanthanum(III) nitrate). All other elements were correctly concentrated except gadolinium(III) (twice more).

Species	Isotopes	Concentration (mg/L)	Activity (MBq/L)
HNO ₃		63 10 ³	
Am	²⁴¹ Am	126	1.6 10 ⁴
Cm	²⁴⁴ Cm	0.98	2.9 10 ³
Y	natural	280	
La	natural	315	
Ce	natural	598	
Pr	natural	285	
Nd	natural	980	
Sm	natural	190	
Eu	natural	42	
Eu	¹⁵² Eu		94
Gd	natural	56	
Ru	natural	72	
Ru	¹⁰³ Ru		9
Pd	Pd	392	
Fe	⁵⁹ Fe		6

Table 1: Composition of the synthetic aqueous feed solution used for the hot test

For the flowsheet implementation, two batteries of eight mixer settlers were used. Each stage consisted of a 6 mL mixer chamber and a 17 mL settler chamber. The rotation speed of the mixer blades was set at 3000 rpm approximately. The pumps used in the hot test were rotary piston pumps, able to produce small flows, controlled by weighing. The temperature was measured in the back-extraction stages and ranged from 24°C (at the beginning of the run) to 31°C (at the end of the run). The tested process flowsheet and the corresponding measured flowrates are shown in Figure 3.

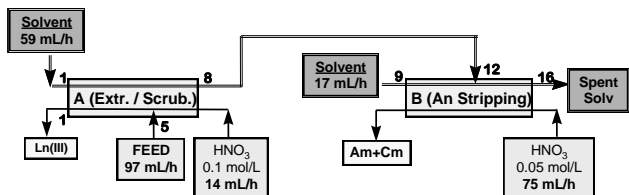


Figure 3: Flowsheet of the hot test with the measured flows

V. SEQUENCE OF THE ALPHA HOT TEST

According to the computed flowsheet, the equilibrium was expected to be reached within 10 hours. In order to eventually reduce this delay, the following aqueous phases were prepared and poured into the 16 stages of the batteries, before the starting of the hot test:

- stages 1 to 4, solution S_1 : $[\text{HNO}_3] = 1 \text{ mol/L}$ and rare earth at concentrations given in table 1,
- stages 6 to 8, solution S_2 : ^{241}Am at 350 mg/L and ^{244}Cm at 3mg/L in $[\text{HNO}_3] = 0.15 \text{ mol/L}$,
- stage 5, half solution S_1 and half solution S_2 ,
- stages 9 to 16, $[\text{HNO}_3] = 0.05 \text{ mol/L}$.

The hydrodynamic behavior was very satisfactory. No emulsion of organic and aqueous phases were noticed during the run in the settling chambers. After about 6 hours of functioning, small solid particles were observed in the extraction part of the first battery (A), especially in the feed introduction stage. However, this phenomenon did not alter the hydrodynamics of the system.

The achievement of the steady state was followed by regular samplings of the outlets. $^{152}\text{Eu(III)}$, $^{103}\text{Ru(III)}$, $^{59}\text{Fe(III)}$ and $^{241}\text{Am(III)}$ were analyzed by gamma spectrometry; $^{241}\text{Am(III)}$ and $^{244}\text{Cm(III)}$, both by alpha counting and alpha spectrometry.

After 10 hours and 30 minutes, all pumps and engines were stopped. Every stage was emptied and the organic phases were separated from the aqueous phases. A thin deposition of black particles was noticed on some blades propellers of the first battery. Besides, some black particles also appeared in the raffinate solution, the day after the hot test.

VI. RESULTS OF THE ALPHA HOT TEST

Since it was not possible to analyze any organic phase by ICP-MS, the latter were stripped twice with molar citric acid solutions (pH was adjusted to 3 with NaOH), using organic to aqueous volume ratios of 0.5. This allowed complete back-extraction of the rare earth elements and palladium(II).

A. Separation performances of the alpha hot test

Table 2 summarizes the performances of the alpha hot test (based on α and γ analyses or ICP-MS analyses). Main conclusions are:

- americium(III) and curium(III) were quantitatively extracted ($> 99.85\%$),
- more than 98% of americium(III) and more than 91% of curium(III) were recovered in the back-extraction solution,
- decontamination factors of Am(III) and Cm(III) for La(III), Ce(III), Pr(III), Nd(III) and Sm(III) were high,
- only 0.97% of palladium(II) were mixed with actinides(III) in the stripping solution,
- ruthenium(III) was not much extracted (only 0.7% in the solvent and almost 100% in the raffinate),
- iron(III) was extracted at 70% in the solvent and 7% followed the raffinate.

Elem ^t	% in raffinate	% in An stripping	% in solvent	Mass bal. (%)	DF strip/feed
Am	0.11	98.3	1.71	100.2	
Cm	0.15	93.9	8.07	102.1	
Y	114	1.8	< 0.06	115.8	54
La	119	< 0.05	< 0.05	119.0	> 2000
Ce	118	< 0.03	< 0.03	118.0	> 3800
Pr	120	< 0.05	< 0.05	120.0	> 1800
Nd	119	< 0.02	< 0.02	119.0	> 6300
Sm	114	0.4	< 0.08	114.4	246
Eu	112	2.3	< 0.37	114.3	43
^{152}Eu	116	2.4	< 0.01	118.4	41
Gd	108	3.1	< 0.28	111.1	32
Ru	96	0.7		96.7	143
^{103}Ru	112	< 1	0.66	112.7	
Pd	0.09	0.97	75.5	76.6	103
^{59}Fe	6.8	< 2	73.4	80.2	

Table 2 : Mass balance and decontamination factors of the different elements of the feed

The mass balances were good for Am(III) and Cm(III). There was a little excess for elements which were not much extracted such as lanthanides(III) and ruthenium(III) (actually, measured concentrations in the raffinate were higher than those in the feed solution).

There was a lack of 23% in the mass balance of palladium(II) and 20% in that of iron(III). However, this discrepancy could easily be explained by the occurrence of the black precipitate. Indeed, the ICP-MS analysis of the dissolution liquor of the precipitate revealed a high content

of Pd(II) and Fe(III). The unexpected presence of macro concentrations of Fe(III), which was only introduced at trace level in the feed solution, could arise from the corrosive effect of the solvent on the steel devices (blades and pipes).

The decontamination factors of lanthanides(III) increased with the decrease of atomic number, in agreement with the results obtained in batch experiments. Unexpectedly, the decontamination factor of yttrium(III) was close to that of europium(III), in disagreement with former extraction results. However, in genuine irradiated fuels, the major rare earth elements are usually the lightest ones (*i.e.*: La(III), Ce(III), Pr(III), Nd(III) and Sm(III)), whereas europium(III), gadolinium(III) and yttrium(III) should be much less concentrated.

B. Aqueous and organic concentration profiles

The acidity profile (acid concentration was determined in each stage, by duplicated NaOH titration analyses) showed that a little amount of nitric acid had been back-extracted in the second battery (B). Actually, the acidity increased from 0.05 mol/L (stages 12 to 16) to 0.07 mol/L (stages 9 to 11), indicating that the scrubbing of the acidity was not totally efficient in the first battery (A). The computed acidity values for stages 6 to 8 were much lower than the measured ones.

The profiles of the aqueous and organic concentrations of each element have been determined after analyzing both organic and aqueous phases of each stage of the two batteries (extraction-scrubbing (A) and stripping (B)), either by ICP-MS or by gamma and alpha spectrometry. These profiles are described on Figures 4 to 7. The distribution ratios were then calculated and compared to computed values.

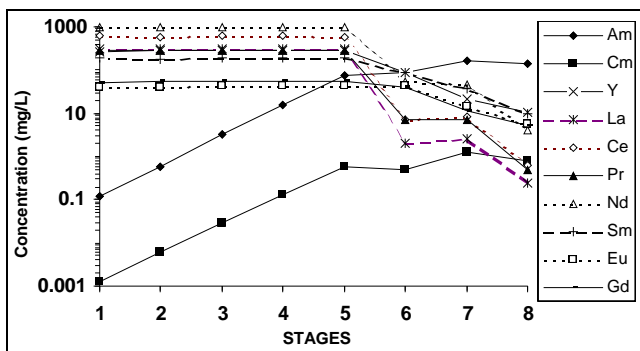


Figure 4: Aqueous concentration profiles of trivalent actinides and rare earth elements in the first extraction-scrubbing battery (A)

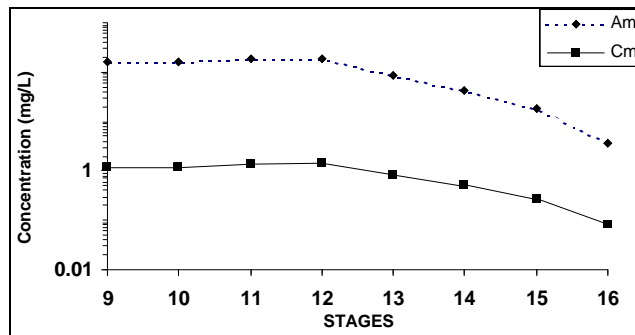


Figure 5: Aqueous concentration profiles of trivalent actinides in the stripping battery (B)

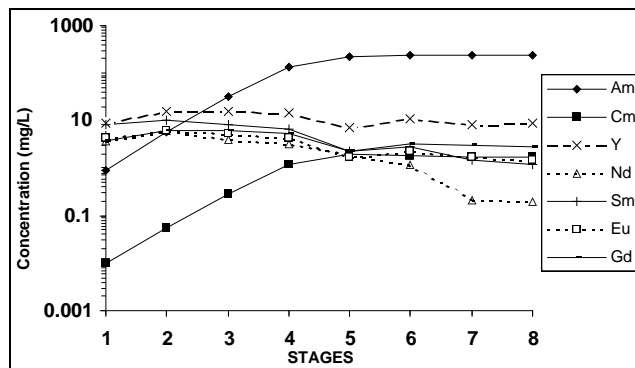


Figure 6: Organic concentration profiles of trivalent actinides and rare earth element in the first extraction-scrubbing battery (A)

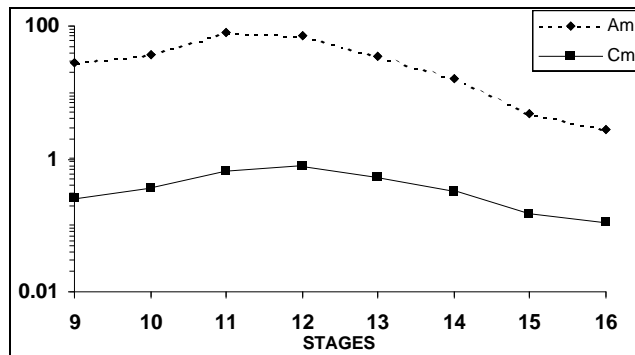


Figure 7: Organic concentration profiles of trivalent actinides in the stripping battery (B)

In the particular case of the distribution ratios of europium(III), a good agreement was observed for stages 1 to 5 between experimental and computed values. However, for the scrubbing stages, experimental distribution ratios were ten times higher than the computed ones. This could be explained by a too low exchange efficiency owing to a too high flow ratio.

Concerning the stripping battery (stages 9 to 16), the distribution ratios of curium(III) were higher than expected (by a factor of 2). The fact that about 23% of palladium(II) were missing could not fully explain this discrepancy. The equilibrium was probably not reached in every stage, due to a too short contact time in the mixer chambers.

VII. CONCLUSION

The objective of the partitioning strategy is to recover actinides(III) with less than 5% (in mass) of rare earth elements vs actinides(III). The results of this alpha hot test exhibited a mass ratio of rare earth elements in the actinides(III) back-extraction solution of 7%. However, taking into account the exceeding concentration of yttrium(III) in the synthetic aqueous feed solution (there was 6 times more yttrium(III) nitrate than expected from a genuine spent fuel), only 3.9 % of rare earth elements would be present in the actinides(III) stripping solution (which is consistent with the objective).

Although 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)pyridine may not be the best candidate (among the BTPs family) to be used in an alpha hot test (because of the partial dissolution of the extractant in the aqueous raffinate and its rather low radiolysis stability), the performances observed at CEA Marcoule for the treatment of a synthetic aqueous feed solution, simulating a DIAMEX stripping solution, are very promising. They remain, up to now, the best An(III)/Ln(III) separation results ever obtained in a counter current test performed at such a high acidity.

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