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PALADIN: A ONE STEP PROCESS FOR ACTINIDES(III)/ FISSION PRODUCTS SEPARATION

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ABSTRACT

In the frame of the French SPIN program, PALADIN is a one partition cycle process able to separate directly americium and curium from lanthanides(III) and other fission products mixed in concentrated nitric acid (similar to a PUREX raffinate). Batch experiments allowed us to choose and optimize every organic and aqueous reagent. Solvent is composed of a mixture of malonamide and alkylphosphoric acid. Aqueous solutions contain only incinerable reagents (hydroxycarboxylic acids, polyaminocarboxylic acids...).

An inactive mixer-settlers test was carried out in order to study the behavior of some fission products. Hydrodynamics and performances were good for the main steps of the process, in particular very few fission products were found in actinides(III) aqueous outflow solution.

I. INTRODUCTION

As part of SPIN program, the CEA has undertaken research on partitioning of long-lived radionuclides found in a PUREX raffinate. Among them, the more radiotoxic ones are actinides such as americium, curium and neptunium. The last one could be separated with a modified PUREX process. The separation of the others requires specific process which could recover americium and curium from a concentrated nitric medium which contains many fission products such as lanthanides. Since the problem is hard to solve with a one cycle process, the strategy proposed by CEA includes a two partition step cycle. The first one, DIAMEX,¹ using a malonamide, operates a co-extraction of actinides and lanthanides from a PUREX raffinate. The second partition cycle, SANEX,² using extractants with nitrogen such as Bis-Triazinyl-Pyridine, plays on the slight difference between actinides and lantha-

nides to make the separation from a molar nitric acid medium.

A second option studied by CEA consists in operating separation with only one partition cycle, directly from a PUREX raffinate, by selective back-extraction of actinides(III), after their co-extraction with some fission products. PALADIN process is based on that concept. The solvent contains an acidic extractant in addition to the malonamide used in DIAMEX. Selective back-extraction is performed owing to an aqueous system containing polyaminocarboxylic and hydroxycarboxylic acids. Four systems were selected and studied. Among acidic extractant, alkylphosphoric acid gives the better performances.

A flowsheet has been designed thanks to CEA PAREX computing code, with specific objectives for each step of the process. To validate behaviors of extracted fission products in PALADIN and to follow hydrodynamics, an inactive test has been carried out using four batteries of eight mixer-settlers and one battery of sixteen mixer-settlers.

II. PRINCIPLE OF PALADIN PROCESS

PALADIN is the acronym of Partition of Actinides and Lanthanides with Acidic extractant, Diamide and Incinerable complexants. The principle is based on separation by selective back-extraction of actinides(III) in DIAMEX process. Aqueous complexants are generally efficient in low acidic medium, moreover malonamides couldn't extract lanthanides at this acidity. To avoid any addition of nitrate salt, a neat solution is to add an organic acidic extractant to DIAMEX solvent. Thus, this second extractant enhances extractive capacity of the solvent from a low acidic medium.

PALADIN process consists of three main steps:

- Step 1: Co-extraction of actinides(III) and lanthanides(III) (with some other fission products) from PUREX raffinate
- Step 2: Back-extraction of molybdenum, palladium 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.

The great advantage of PALADIN is to separate Am, Cm directly from a highly active liquid waste which contains all fission products in a concentrated nitric acid medium.

II. CHOICE OF REAGENTS

To minimize experiments, we have used results issued from processes called DIAMEX¹ and TALSPEAK³ because the first one could extract actinides(III) from a PUREX raffinate and the second one is based on selective back-extraction of actinides(III) with aqueous reagents.

A. Study of Actinides Extraction

This step is similar to extraction step of DIAMEX process. However, the affinity of HDEHP towards molybdenum and zirconium from high nitric acid medium is so strong that oxalic acid is no more effective to prevent extraction of these elements. This reagent is nevertheless important in PALADIN because, without it, some interphasic precipitation could occurred during 2nd or 3rd step of PALADIN. This phenomenon is certainly linked to the formation of zirconium hydroxide at low acidity.

Besides actinides, the extracted elements in PALADIN are rare earth, molybdenum, zirconium, iron and palladium and, to a lesser extent, ruthenium. The behavior of these elements have to be studied in each step of PALADIN as a preliminary to the mixer-settler test.

B. Study of Actinides(III) Stripping

The malonamide in the organic phase is Dimethyl-dibutyl-tetradecyl-malonamide (DMDBDTMA or C14) or Dimethyl-dioctyl-hexylethoxy-malonamide (C2OC6 or DMDOHEMA). These diamides are the reference extractants of DIAMEX process.

Among acidic extractants tested, only di(2-ethylhexyl)-phosphoric acid (HDEHP) has shown real interest for PALADIN.

For the selective back-extraction of actinides(III), the aqueous phase contains a mixture of a selective reagent and a buffer component at a pH close to 3-4. To follow the incineration principle of aqueous reagents, we have selected only molecules containing C, H, O and N atoms. Among several reagents, four different aqueous systems were chosen.

Selective complexants are:

- N-(2-hydroxyethyl)-ethylenediaminetriacetate (HEDTA),
- diethylenetriaminepentaacetate (DTPA).

For buffering the aqueous solution and also for selectivity, the best reagents are citric or lactic acids. The improving adjustment of acidity is obtained owing to tetramethylammonium hydroxide (Me₄NOH).

Thus, the four optimal aqueous systems are HEDTA/citric, HEDTA/lactic, DTPA/citric, DTPA/lactic. The performances of these systems for actinides(III) stripping were evaluated through batch experiments performed in tubes (0.5 to 10 mL of organic and aqueous phases).

1. Experimental procedure.

To evaluate the performances of the systems, we have used:

- 1) traces of gamma or alpha emitters (¹⁵²Eu, ²⁴¹Am or ²⁴⁴Cm at about 10 MBq/L each),
- 2) europium nitrate added to gamma, alpha tracers,
- 3) a mixture of light lanthanides (La, Ce, Pr, Nd, Sm, Eu and Gd), yttrium, molybdenum, zirconium, iron (spiked with ⁵⁹Fe), ruthenium (spiked with ¹⁰³Ru) and/or palladium, simulating a PUREX raffinate.

Activities or concentrations of elements were checked with gamma-alpha spectrometers, UV-visible spectrophotometer, X-fluorescence or ICP-AES. Solvent was analyzed through titration. Every experiment was thermostated at 22°C or 25°C.

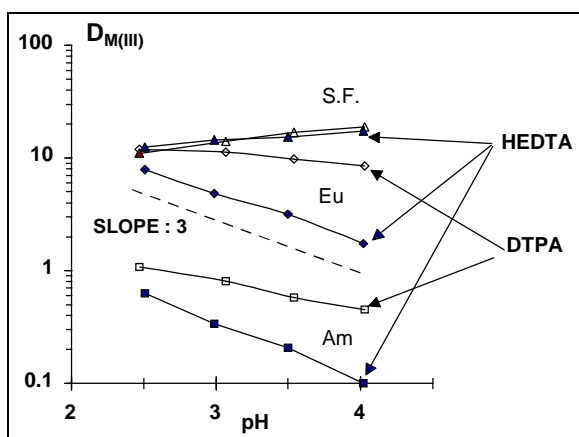
2. Results.

The first organic phase studied is a mixture of HDEHP (0.1-0.3 mol/L) and C14 (0.65 mol/L) in Hydrogenated Tetra-Propylene (TPH).

At a given concentration of citric or lactic acid, the log-log variation of the distribution ratios ($D_{M(III)}$) of ¹⁵²Eu or ²⁴¹Am with the initial concentration of DTPA or HEDTA follows a linear relationship with a slope close to 1. This is in agreement with former studies on aqueous lanthanides-DTPA complexes which have showed that stoichiometry is 1:1.

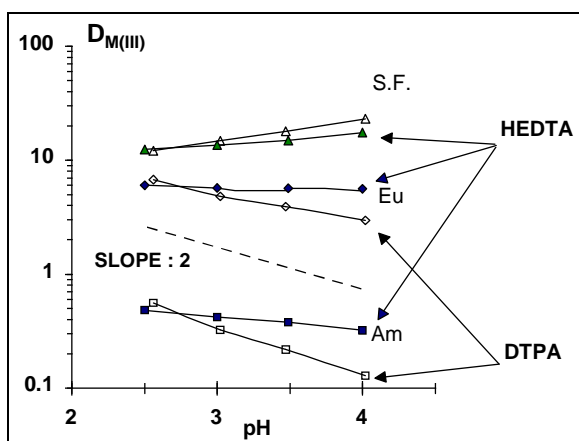
Thanks to these extraction experiments on gamma emitters, we have selected aqueous compositions which

allow good extraction of Eu(III) ($D_{Eu(III)} > 1$) and good selectivity ($SF_{Eu/Am} = D_{Eu}/D_{Am} > 10$). We noticed that the buffer solution could change extraction performances of the system towards Eu and Am. In the case of citric acid systems (Figure 1), D_M are less sensitive towards acidity for DTPA (slope close to 0) than HEDTA (slope 3). It is exactly the contrary in the case of lactic acid systems (slopes 2 for DTPA and close to 0 for HEDTA, see Figure 2). This last point is not crucial for PALADIN process since aqueous solution for the An(III) stripping step is buffered.



Organic solution: ^{241}Am , ^{152}Eu ,
HDEHP 0.2 mol/L, DMDBTDMA 0.65 mol/L, TPH
Aqueous solutions: [citric acid] = 1 mol/L, $T=22^\circ\text{C}$
[DTPA]=0.001 mol/L or [HEDTA]=0.1 mol/L

Figure 1: Influence of acidity on Am and Eu extraction (citric systems)



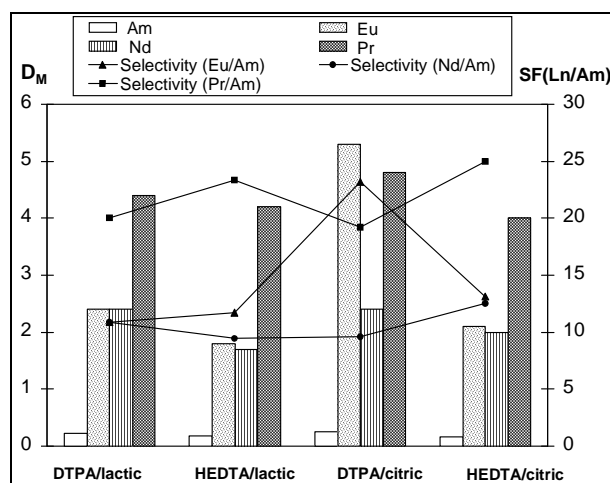
Organic solution: ^{241}Am , ^{152}Eu ,
HDEHP 0.2 mol/L, DMDBTDMA 0.65 mol/L, TPH
Aqueous solutions: [lactic acid] = 1 mol/L, $T=22^\circ\text{C}$
[DTPA]=0.005 mol/L or [HEDTA]=0.3 mol/L

Figure 2: Influence of acidity on Am and Eu extraction (lactic systems)

With 0.2 mol/L of HDEHP in the solvent, optimal compositions are these aqueous solutions at pH 3:

- [DTPA]=0.01 mol/L, [lactic acid]=1 mol/L, (DTPA/lactic),
- [HEDTA]=0.3 mol/L, [lactic acid]=1 mol/L, (HEDTA/lactic),
- [DTPA]=0.003 mol/L, [citric acid]=0.5 mol/L, (DTPA/citric),
- [HEDTA]=0.1 mol/L, [citric acid]=0.5 mol/L (HEDTA/citric).

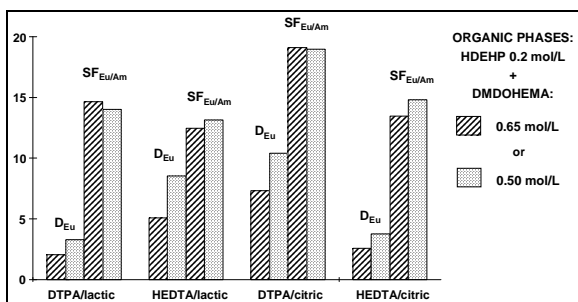
The four aqueous systems led to satisfactory performances for a process. With a feed solution containing light lanthanides at nominal concentrations, we have obtained in each case, $SF(\text{Ln}/\text{Am}) > 10$ and $D_{Ln} > 1$ (Figure 3). For the mixer-settlers test, we have chosen HEDTA/citric system owing to an easier waste treatment with these reagents.



Organic solutions: ^{241}Am , ^{152}Eu and Nd, Pr, Eu (0.01 mol/L each)
HDEHP 0.2 mol/L, DMDBTDMA 0.65 mol/L, TPH
Aqueous solutions: see text for compositions

Figure 3: lanthanides(III)/actinides(III) separation with optimal systems

After optimization of the aqueous phase, the two malonamides were tested in order to choose the best organic phase. There was no effect of the type of diamide on extraction performances. However, Figure 4 shows that the decrease of diamide concentration increases the distribution ratios of elements without changing separation factor.



Organic solutions: ^{241}Am , ^{152}Eu , HDEHP, DMDOHEMA, TPH
Aqueous solutions: see text for compositions

Figure 4: Effect of diamide concentration on extraction of Am, Eu with optimal systems

From these results, we decided to choose the new reference malonamide of DIAMEX *i.e.* DMDOHEMA (0.5 mol/L). Moreover, this molecule has better extractive performances and higher third phase limitation than DMDBTDMA in the first step of PALADIN.

In order to prevent organic phase from any saturation at low acidity with a concentrated feed, we have decided to use an organic phase containing also 0.3 mol/L of HDEHP.

Batch experiments with a feed solution containing, among others, zirconium(IV), molybdenum(VI) and yttrium(III) showed that Zr and Y had a same behavior similar than lanthanides during step 3. On the other hand, Mo(VI) was back-extracted with actinides(III). That is the reason why step 2 is necessary, to back-extracted molybdenum before the actinides(III).

C. Study of Molybdenum Stripping

Molybdenum ionic form is modified with the acidity of the medium. It is a cation in high nitric acid and becomes a anion when acidity diminishes. Therefore, we have chosen a moderate acidic medium ($\text{pH} > 3$) to back-extract selectively Mo. Thus, since HDEHP extracts only cations from moderate acidic medium, molybdenum is no more extracted unlike actinides.

To perform back-extraction at pH from 3 to 4, we have selected buffer solutions containing carboxylic acid with a pK_a close to 3.

Several batch tests were performed to evaluate performances and to avoid any potential precipitation. The best aqueous solution was a mixture of citric acid and tetramethylammonium hydroxide. Tartaric acid or ammonium hydroxide induced either precipitation or bad performances.

At pH 3-4, nitric acid which is in the solvent after the first step of PALADIN (about 0.4-0.5 mol/L), is quantita-

tively back-extracted. Since buffer solution is not enough powerful, it is necessary to add Me_4NOH in order to neutralize this acidity. This base has also the great advantage to increase distribution ratios of actinides(III) and to reduce potential precipitation in case of too loaded solvent. Indeed, extractions have been performed with solvent containing nitric acid (or not) and Eu, Am, contacted with a mixture of citric buffer and Me_4NOH (or not). Without Me_4NOH , distribution ratios were 1.5 times lower than in the first case. Moreover, if europium concentration was increased, precipitation appeared all the more quickly in the second case since there was less citric acid.

According to these results, we have chosen citric acid (0.5 mol/L) at pH 3-4 adjusted by Me_4NOH as aqueous phase for the molybdenum stripping step.

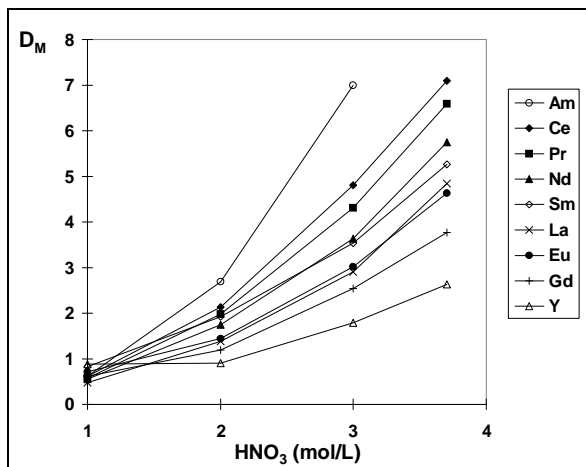
D. Study of Zirconium, iron and Rare Earth Stripping

Zirconium and iron are elements which are difficult to back-extracted from PALADIN solvent. Picolinic acid proved to be effective but its aromatic cycle is a drawback towards waste management (explosive by-products).

A better solution is to carry out two steps for stripping rare earth elements at first and then back-extracting Zr and Fe. Thus, it is possible to use oxalic acid to complex zirconium and iron without risk of lanthanide oxalates precipitation. Back-extraction of lanthanides is performed thanks to molar nitric acid. At this acidity, HDEHP and DMDOHEMA are bad rare earth extractants. However, since there is a synergism between HDEHP and DMDOHEMA, distribution ratios of lanthanides and yttrium are close to 1 (see Figure 5). Therefore, quantitative stripping of these elements is difficult in only 8 stages (as imposed in our test).

Thus, to avoid any risk of oxalate precipitation, we have chosen the following aqueous stripping solutions:

- 1) molar nitric acid for rare earth elements back extraction,
- 2) molar nitric acid and 0.1 mol/L of oxalic acid for zirconium and iron back-extraction.



Organic solutions: HDEHP 0.2 mol/L, DMDOHEMA 0.5 mol/L, TPH
Aqueous solutions: ^{241}Am , ^{152}Eu , HNO_3

Figure 5: Influence of nitric acid on extraction of americium and rare earth elements

III. DESIGN OF A PALADIN FLOWSHEET

The design of flowsheet is based on interpolation of batch experiments, and consists in choice of flows, number of stages, acidity and concentration of reagents. Optimization of flowsheet is important to spent as little solvent as possible (cost of DMDOHEMA). We have used CEA PAREX computing code, with specific objectives for each step of the process.

- Step 1: Quantitative extraction of lanthanides (simulating actinides)
 $\%(\text{Am and Cm extracted}) > 99.9\%$
- Step 2: Quantitative molybdenum and nitric acid back-extractions without lanthanides (simulating actinides)
- Step 3: $\%(\text{Am, Cm back-extracted}) > 99.9\%$ and $\text{DF}(\text{Ln}/\text{Am}) < 5\%$ (in mass).
- Step 4: Quantitative lanthanides and other fission products stripping

Since there were no actinide in this mixer-settlers test, the objective was centered on europium for the first step because this lanthanide is less extracted than the both actinides(III). For the second step, no lanthanide should be mixed with molybdenum (same behavior between actinides and neodymium, cerium at this step).

For the code, experimental distribution ratios have been interpolated as exponential or logarithmic law, in order to simulate stage performances for each element in the feed solution.

The flowsheet included 6 stages for the first step, 8 stages for second, the fourth and the fifth step, and 16 stages for the third step. According to computation, the equilibrium was expected to be reached within 15 hours.

III. SEQUENCE OF PALADIN COLD RUN

The cold test was conducted in five batteries of mixer-settlers: 8 stages for each battery A, B, D, E (step1, 2 and 4), 16 stages for battery C (step 3). Each stage consisted of 6 mL mixer chamber and a 17 mL settler chamber. The rotation speed of the mixer blade propellers was around 3000 rpm. Figure 6 shows the flowsheet and the corresponding measured flow rates during the run.

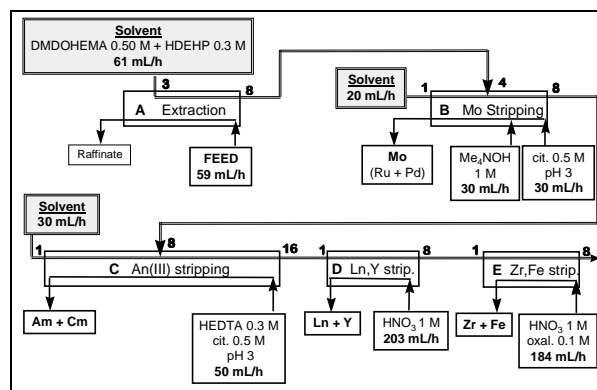


Figure 6: Flowsheet of the run with the measured flows

For the feeding of solvent and aqueous phases of batteries A, B and C, we used double syringe displacement pumps. For batteries D and E, we used gear pumps, controlled by weighing.

The composition of the feed solution is summarized in Table 1. It simulates the raffinate of a PUREX process performed on a UOX2 spent fuel (except Eu, Y, Sn which are at least twice more concentrated to ease analytical detection).

Species	Concentration (mg/L)
HNO ₃	198 10 ³
oxalic acid	12,6 10 ³
La	322
Ce	618
Pr	279
Nd	934
Sm	243
Eu	124
Y	99
Zr	762
Mo	926
Pd	299
Fe	111
Ru	224

Table 1: Composition of the synthetic feed solution

IV. RESULTS OF THE COLD RUN

A. Performances of the test

Hydrodynamic behavior of the solvent was satisfying for every battery. Though, a black precipitate (probably RuO₂) occurred at the feed introduction stage. Nevertheless, this precipitate didn't disturb the hydrodynamics.

Table 2 summarizes the performances of the test. Aqueous phases were analyzed by ICP-AES. For iron, solvent was stripped twice with oxalic solution (oxalic 0,5 mol/L, HNO₃ 1 mol/L), using organic to aqueous volume ratio of 0.5. Otherwise, organic phase was analysed directly by X-fluorescence.

% in Outflow	batte. A	batte. B	batte. C	batte. D	batte. E	solvent
La	< 0.31	< 0.31	< 0.26	97.8	<0.96	< 0.26
Ce	< 0.16	< 0.16	< 0.14	98.1	2.4	< 0.14
Pr	< 0.36	< 0.36	< 0.30	100.6	4.0	< 0.36
Nd	< 0.10	< 0.10	< 0.09	99.7	3.1	< 0.10
Sm	< 0.41	< 0.41	< 0.35	94.4	5.6	< 0.35
Eu	< 0.81	< 0.81	< 0.68	99.4	5.2	< 0.68
Y	< 1.0	< 1.0	< 0.85	60.9	28.4	< 10
Zr	< 0.13	0.64	0.31	< 0.45	27.1	75
Mo	< 0.11	101.2	0.29	< 0.37	<0.33	< 0.33
Pd	7.9	75.3	9.9	1.5	<1.0	<1.0
Fe	2.8	< 0.91	8.6	< 3.1	45.0	49
Ru	83.5	6.4	0.60	< 1.5	<1.4	5.8

Table 2: distribution of elements in every aqueous outflow

The mass balances were comprised between 99% and 104% for every element. The aimed performances were achieved except for the battery D.

- Battery A (step 1): extraction of more than 99% of lanthanides.
- Battery B (step 2): back-extraction of more than 99.7% of Mo and more than 81% of Pd from solvent.
- Battery C (step 3): back-extraction of less than 0.7% of lanthanides.
- Battery D and E (step 4): Almost 100% of rare earth back-extracted, only 50% of Fe and 25% of Zr stripped.

B. Aqueous concentration profiles

There were steady acidic profiles in each battery, *e.g.* A: 3,2 mol/L; B and C: 10⁻³ mol/L; D: 0.98 mol/L; E: 1.2 mol/L..

For batteries A-D, aqueous concentration profiles are in good agreement with the expected ones unlike for battery E. Figure 7 shows the good extraction of lanthanides. Molybdenum was efficiently selectively back-extracted and palladium was also well stripped (Figure 8). Figure 9 shows that no lanthanide was back-extracted and that the remaining palladium was here completely back-extracted.

Back-extraction of palladium could be improved owing to a better optimization of step 2. Since no lanthanide was detected in stage 1 (battery B), more stages of back-extraction could be added with less organic scrubbing.

A solution to improve the stripping of zirconium and iron is to increase concentration of oxalic acid in the aqueous phase of battery E. This is possible since lanthanides were quantitatively back-extracted in battery D. Batch experiments showed that it was possible without any precipitate.

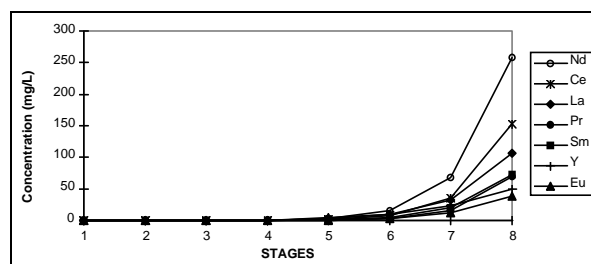


Figure 7: Aqueous profiles of rare earth elements in the battery A (step 1)

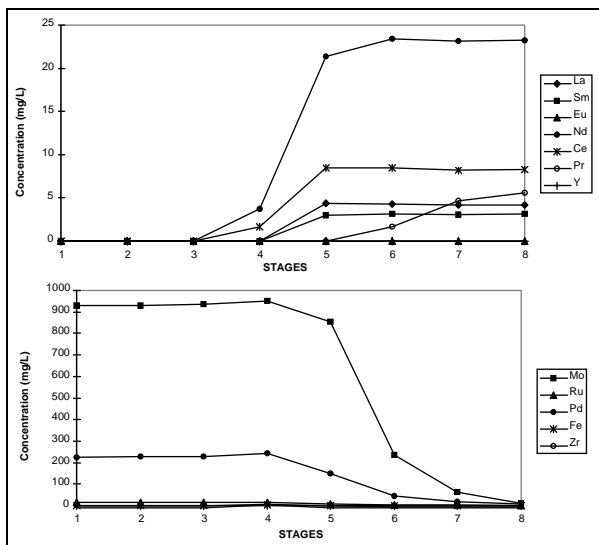


Figure 8: Aqueous profiles in the battery B (step 2)

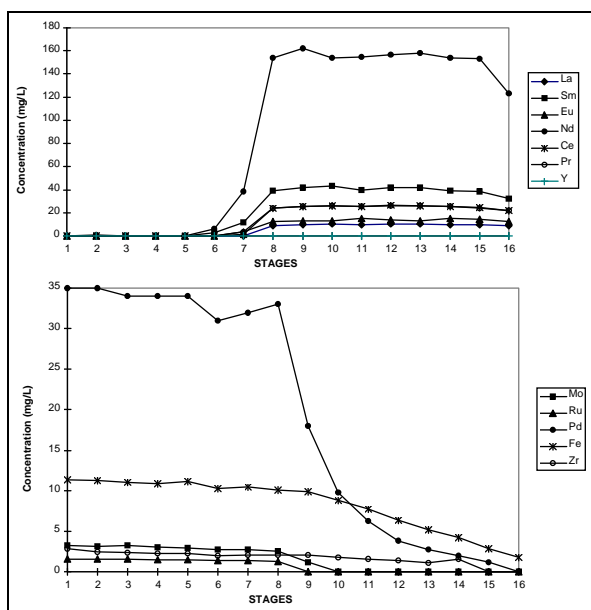


Figure 9: Aqueous profiles in the battery C (step 3)

V. CONCLUSION

The inactive run of PALADIN showed that this process could treat a feed solution with many fission products mixed in concentrated nitric acid medium (as expected from a genuine spent fuel solution). Hydrodynamic behavior was correct. Main extraction performances were achieved:

- lanthanides extraction was quantitative (step 1),
- molybdenum and palladium back extraction was good without any mixing of lanthanides (step 2),
- no lanthanide and very few other fission products in the actinides(III) stripping solution (step 3),
- lanthanides were finally quantitatively back-extracted (step 4).

Improvement of the step 2 and 4 will be done in the future to minimize palladium quantity in step 3 and to recover a cleaner solvent.

Batch experiments showed that this process could separate actinides from rare earth elements (separation factor better than 10). A hot test will be carried out in 1999 to validate feasibility of PALADIN process, which could recover actinides(III) directly from a PUREX raffinate, in one partition cycle.

ACKNOWLEDGMENTS

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