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Separation, for analytical purpose, of Np traces from different solutions of fuel reprocessing

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Abstract

Four separation methods were developed for performance control of hydrometallurgical extraction processes as COEX™ or advanced PUREX. These methods used implemented the operations of radionuclides oxidation state adjustment and chromatographic separation using TEVA resin. Concerning FP raffinate, the method consisted in reducing Np traces to the valence IV by a mixture of ferrous sulfamate and ascorbic acid, to fix Np(IV) on “TEVA” resin and to eluate it by a nitrohydrofluoric acid solution. The Np recovery yield is 100%. The decontamination of Np is sufficiently high to allow its analysis by FXL ($Zr/Np < 1$). The study also showed that in presence of Zr and Tc, Pu behaved like Np. The mixture of ferrous sulfamate and ascorbic acid had surprisingly no action on Pu(IV).

Concerning plutonium solution ($[Pu] > 10$ g/L) and uranium solution ($[U] > 100$ g/L), the same method used for Np recovery from FP raffinate led to an eluate containing 100% of the initial Np ($[Np] : 10$ mg/L). The low concentration of U and Pu (< 100 mg/L) allows the determination of Np by FXL. Concerning Pu(III)-U(IV) solution, the method, included 2 redox stages, the first one to oxidize all actinides to oxidation state VI et the second one to reduce Np and Pu respectively to IV and III oxidation state. Then Np(IV) was fixed on TEVA resin. The eluate contains 100% of the initial Np ($[Np] : 10$ mg/L) and a low concentration of U and Pu ($[U] < 20$ mg/L, $[Pu] < 10$ mg/L). The next experiments will consist in consolidating these good results by working with real solutions of fuel reprocessing.

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Keywords : Neptunium; Plutonium; Uranium; Fission products; oxidation state; chromatography extraction; analysis

1. Introduction

Several hydrometallurgical extraction processes as COEX™ or advanced PUREX have been studied and performed in original schemes in Atalante nuclear facility in order to optimize or demonstrate various actinide management options. The behavior of the specific alpha-emitter element neptunium and its distribution into the

fission products (FP) raffinate or uranium and plutonium production is known as one of the key points to assess the separation efficiency. Consequently, the analysis of traces of this element is necessary with a high sensibility whereas the high concentration level of the major elements interferes common analysis methods.

In this work, the method tested implement the operations of radionuclides oxidation state adjustment and separation on chromatographic support to recover quantitatively and selectively Np traces from four different simulated solutions representative of fuel reprocessing flowrates : fission products (FP), plutonium and uranium solutions, Pu(III)-U(IV) solution and finally improve the neptunium detection limit (DL).

2. Experimental

2.1. Principle of the separation

A method, already applied in the past, to recover traces of a radioactive element present in a solution containing one or more macrocomposants is to use a chromatographic support for which the distribution coefficient of the traces and the macrocomposants are respectively very high and very low [1], [2].

Taking into account the redox properties of Np and those of the macrocomposants (U, Pu, FP) [3] and the properties of commercially available extraction chromatographic support [4], were selected :

- the TEVA resin for its great affinity for Np(IV). The distribution coefficient can be higher than 5000 mL/g,
- the mixture composed of ferrous sulfamate and ascorbic acid for the oxidation state ajustement of Np. The reduction of N(V + VI) to Np(IV) is very fast even at room temperature.

Therefore, the principle of the Np recovery consists in stabilize Np to the oxidation state IV and to uptake it on TEVA resin.

2.2. Neptunium in a fission products raffinate

In addition to the quantitative recovery of the neptunium traces, a good decontamination with respect to fission products, especially Zr and Sr, must be achieved. The quantification of Np by X-ray fluorescence is possible if the weight ratios Zr/Np < 100 and Sr/Np < 5 are reached.

At first the distribution coefficient of Np ($k(\text{Np})$) and several PF with respect to TEVA were determined in the range of nitric acidity : 2M-8M (Table 1). The experiments consisted in mixing during 5 mn, 0.2 g of TEVA resin with 2 mL of solution composed of HNO_3 , Fe(II) : 0,05M, $\text{C}_6\text{H}_8\text{O}_6$: 0,05M, Np : 5 mg/L and FP.

Table 1. Distribution coefficient (k) of Np with TEVA resin : influence of nitric acidity

[HNO_3] (M)	$k(\text{Np})$ (mL/g)	$k(\text{Zr})$ (mL/g)	$k(\text{Y})$ (mL/g)	$k(\text{Ru})$ (mL/g)	$k(\text{Sr})$ (mL/g)
2	1400	1.3	1.0	2.9	2.0
5	4119	< 0.1	< 0.1	< 0.1	< 0.1
8	2067	9.5	9.2	0.2	13.7

The results show that the most favorable conditions to separate Np from PF correspond to a nitric acid concentration of 5 mol/L. The separation coefficient $k(\text{Np})/k(\text{PF})$ is greater than 40000.

The following test was carried out from the solution composed of HNO_3 : 5M, Np : 10 mg/L, Pu : 10 mg/L, U : 10 mg/L, Tc : 200 mg/L, Mo : 1 g/L, Zr : 1 g/L, Ru : 1 g/L according to the schematic diagram of the figure 1.

The eluate composition (table 2) showed :

- . a quantitative recovery of Np and Pu,
- . a weak residual concentration of Zr ($[Zr] < 2 \text{ mg/L}$).

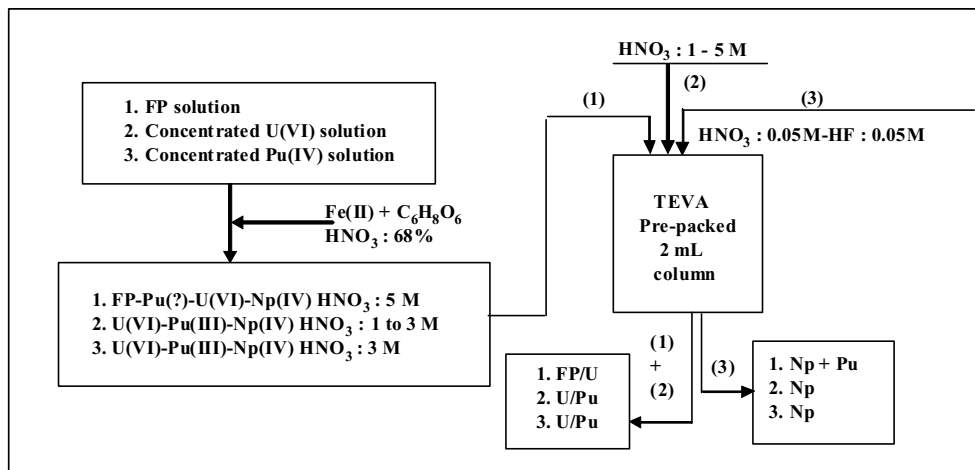


Figure 1 : Schematic diagram of operating procedure used for separation of Np from a FP or U or Pu solution

To understand the behavior of Pu, for which the mixture $\text{Fe(II)} + \text{C}_6\text{H}_8\text{O}_6$ had surprisingly no effect, leading to the fixation of Pu(IV) on TEVA resin, some additional tests, which differ from the fission product composition of the initial solution, were performed according to the same schematic diagram (Fig. 1).

The eluate composition (table 2) showed that in the absence of Tc or Zr, the recovery yield of Pu in the eluate which contains Np was less than 25% (table 2). Tc and Zr affect the behavior of Pu and have no effect on Np. This phenomenon is not explained to date.

Table 2. Influence of FP on the behavior of Pu during the separation Np/FP on TEVA resin

		Eluate							
PF in Initial solution	[Np] (mg/L)	[Np]/[Np] _{init} (%)	[Pu] (mg/L)	[Pu]/[Pu] _{init} (%)	[U] (mg/L)	[U]/[U] _{init} (%)	[Zr] (mg/L)	[Zr]/[Zr] _{init}	
Mo, Ru, Zr, Tc	9.6	100	9.6	100	2	11	1.9	0.2	
Zr, Tc, Ru no Ru	9.3	100	9.4	100	< 0.5 (DL)	5	0.4	0.04	
Mo, Zr, Ru no Tc	10.1	100	9.85	100	< 0.5 (DL)		1	0.1	
Mo, Zr, Ru no Tc	9.5	100	< 0.5 (DL)		< 0.5 (DL)		1.3	0.15	
Mo, Tc, Ru no Zr	9.8	100	2.3	25	< 0.5 (DL)				

The method comprising a step of reduction by a mixture of ferrous sulfamate and ascorbic acid and a step of chromatographic separation using the resin TEVA is effective to recover quantitatively Np traces in a simulated solution of FP.

The influence of Zr and Tc on the behavior of Pu is shown but further study is needed to understand their role.

2.3. Neptunium in a solution of concentrated uranium(VI)

In addition to the quantitative recovery of the neptunium traces in a concentrated uranium solution ($[U] > 50$ g/L) a good decontamination with respect to uranium must be achieved. The quantification of Np by X-ray fluorescence is possible if the weight ratios $U/Np < 20$.

The separation Np-U consists in retain Np(IV) on a of TEVA resin, whereas U(VI) which doesn't change of oxidation state in presence of $Fe(II) + C_6H_8O_6$ passes through the column.

Several experiments were done according to the schematic diagram of the figure 1. The influence of the nitric acid concentration of the chromatographic cycle feed solution and the influence of the volume of the washing solution on the eluate composition ($[Np]$, $[Pu]$, $[U]$) were studied.

Whatever the experimental conditions tested, the recovery yield of Np is equal to 100 % (Table 3).

By increasing the volume of the washing solution from 15 to 20 mL, the U content of the eluate decrease slightly without affecting the performance of Np. The decontamination factor of Np with respect to U (1) is greater than 1000.

$$(1) DF(Np/U) = (mNp_{initial}/mNp_{eluate}).(mU_{initial}/mU_{eluate})$$

Table 3. Influence of the nitric acid concentration of the chromatographic cycle feed solution and influence of the volume of the washing solution on the eluate composition ($[Np]$, $[U]$, $[Pu]$)

U(VI) initial solution	Chromatographic cycle feeding solution			Eluate		
	$[HNO_3]$ (M)	$[Np]$ (mg/L)	$[Np]/[Np]_{init}$ (%)	$[Pu]$ (mg/L)	$[U]$ (mg/L)	$[U]/[U]_{init}$ (%)
$[U(VI)] : 50$ g/L $[Np] : 30$ mg/L $[Pu] : 10$ mg/L	1	27	100	< 1 (DL)	42	0.1
	3	25	100	< 1 (DL)	32	0.1
	Washing solution volume (mL)					
$[U(VI)] : 120$ g/L $[Np] : 10$ mg/L $[Pu] : 10$ mg/L $[HNO_3] : 3M$	15	10	100	< 1 (DL)	82	0.1
	20	10	100	< 1 (DL)	56	0.06

The method comprising a step of reduction by a mixture of ferrous sulfamate and ascorbic acid and a step of chromatographic separation using the resin TEVA is effective to recover quantitatively Np traces from a highly concentrated uranium solution.

Uranium contamination of the "purified" neptunium solution is sufficiently small ($[U]/[Np] < 20$) to quantify Np by X-ray fluorescence.

2.4. Neptunium in a solution of concentrated plutonium(IV)

In addition to the quantitative recovery of the neptunium traces in a concentrated plutonium solution ($[Pu] > 6$ g/L) a good decontamination with respect to plutonium must be achieved. The quantification of Np by X-ray fluorescence is possible if the weight ratios $Pu/Np < 20$.

The separation Np-U consists in retain Np(IV) on a of TEVA resin, whereas Pu(IV) reduced to the oxidation state III in presence of $Fe(II) + C_6H_8O_6$ passes through the column.

Several experiments were done according to the schematic diagram of the figure 1. The influence of the initial plutonium concentration and the influence of the volume of the washing solution on the eluate composition

([Np], [Pu]) were studied.

Each experiment led to a recovery yield of Np equal to 100 % (Table 4).

By increasing the volume of the washing solution from 15 to 20 mL, the Pu content of the eluate doesn't change ([Pu] ~ 100 mg/L).

By increasing the initial plutonium concentration from 6 to 10 g/L, the Pu content of the eluate doesn't change ([Pu] ~ 100 mg/L). The decontamination factor of Np with respect to Pu is greater than 50.

Table 4. Influence of the [Pu] initial solution and influence of the volume of the chromatographic cycle washing solution on the eluate composition ([Np], [Pu], [U])

Pu(IV) initial solution	washing solution volume (mL)	Eluate					
		[Np] (mg/L)	[Np]/[Np] _{initial} (%)	[Pu] (mg/L)	[Pu]/[Pu] _{initial} (%)	[U] (mg/L)	[U]/[U] _{initial} (%)
[Pu(IV)] : 6g/L	15	10	100	102	1.7	< 0,5	
[Np] : 10 mg/L	20	10	100	123	2.0	0.5	2.5
[U(VI)] : 20 mg/L							
[Pu(IV)] : 10 g/L	15	10	100	119	1.2	2	10
[Np] : 10 mg/L							
[U(VI)] : 20 mg/L							

The method comprising a step of reduction by a mixture of ferrous sulfamate and ascorbic acid and a step of chromatographic separation using the resin TEVA is effective to recover quantitatively Np traces from a concentrated plutonium solution.

Plutonium contamination of the "purified" neptunium solution is sufficiently small ([Pu]/[Np] < 20) to quantify Np by X-ray fluorescence.

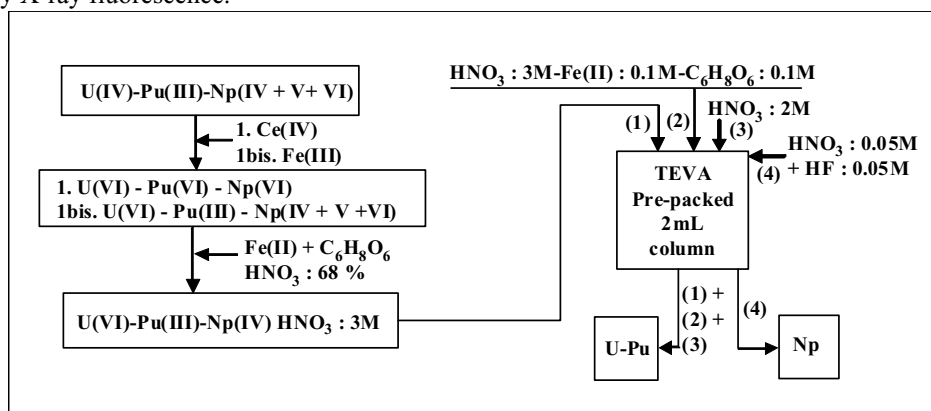


Figure 2 : Schematic diagram of operating procedure used for separation of Np from a U(IV)-Pu(III) solution

2.5. Neptunium in a solution of concentrated plutonium(III)/Uranium(IV)

The objective is to obtain quantitative separation of the neptunium traces from a solution of Pu(III)/U(IV) ([Pu(III)] : 15g/L, [U(IV)] : 4 g/L). A good decontamination of Np with respect to plutonium and uranium must be achieved to avoid interferences with uranium for the quantification of neptunium by X-ray fluorescence ([Pu]/[Np] < 20, [U]/[Np] < 20).

Unlike the previous situations, the separation Np/(U(IV) + Pu(III)) includes two oxydo-reduction stages and a chromatographic cycle on a TEVA resin (Fig. 2).

The experiments consisted to test two systems of oxydo-reduction (table 5).

For each oxydo-reduction system tested, the recovery yield of Np is equal to 100% and the U and Pu content is low ($[U] < 20$ mg/L, $[Pu] < 10$ mg/L).

Table 5. Influence of the oxido-reduction systems on the chromatographic cycle eluate composition ($[Np]$, $[Pu]$, $[U]$)

Pu(III)/U(IV) initial solution	Oxydation reduction stages	Eluate					
		[U] (mg/L)	$[U]/[U]_{init}$ (%)	[Pu] (mg/L)	$[Pu]/[Pu]_{init}$ (%)	[Np] (mg/L)	$[Np]/[Np]_{init}$ (%)
[U] : 4g/L [Pu] : 15 g/L [Np] : 10 mg/L	Ce(IV) Fe(II) + C ₆ H ₈ O ₆	3	0.2	< 0.5 (DL)		5.5	100
[U] : 4 g/L [Pu] : 15 g/L [Np] : 100 mg/L	Fe(III) Fe(II) + C ₆ H ₈ O ₆	18	2	6	0.2	46	100

The method comprising a step of oxidation (Ce(IV) or Fe(III)) followed by a step of reduction (Fe(II) + C₆H₈O₆) and a step of chromatographic separation using the resin TEVA is effective to recover quantitatively Np traces from a solution of Pu(III)-U(IV).

Plutonium contamination of the “purified” neptunium solution is sufficiently small ($[Pu]/[Np] < 20$, $[U]/[Pu] < 20$) to quantify Np by X-ray fluorescence.

3. Conclusion

Experimental conditions leading to a total recovery of neptunium traces initially present in solutions simulating a fission products raffinate, a concentrated U(VI) or Pu(IV) solution and a U(IV)-Pu(III) solution are determined.

For each solution, recovery of the Np comprises one or two redox stages consisting in the addition of oxidizing (Ce(IV)) or reducing reagents (Fe(II) + C₆H₈O₆) then a chromatographic separation using the TEVA resin.

The performances achieved are very good :

- . The neptunium recovery yield is 100%,
- . The dilution factor is less than 2,
- . The contamination of the “purified” Np solution is weak ($[Zr]/[Np] < 1$, $[U]/[Pu] < 20$, $[Pu]/[Np] < 20$).

From these studies will result protocols which must be validated with real samples of fuel reprocessing.

A special effort has to be done to understand the similar behaviour of Np and Pu in the separation with respect to PF. Initial tests have shown the influence of Zr and Tc.

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