

STATUS OF CEA EXPERIENCE
ON THE MINOR **ACTINIDES** SEPARATIONS

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I - CHRONOLOGY OF THE PROGRAMS, STATUS OF THE KNOW-HOW

1.2. Chronology of the programs

A great part of the CEA experience relative to the separation chemistry of neptunium and transplutonium elements has been acquired in the achievement of productions programs of transuranium elements.

Their chronology could be resumed as follows :

- 1970-1978:* Production program of ^{238}Pu by irradiation and chemical treatment of irradiated targets ^{237}Np (NpAl or NpO_2/MgO), which has requested the supply of large amounts of neptunium 237 accomplished with specific campaigns in UP 1 and UP2 plants ;
- 1974-1985:* Production program of ^{243}Am and ^{244}Cm at the scale of ten grams per year ; which has been fulfilled by treatment of irradiated targets of ^{239}Pu or ^{242}Pu ;
- 1981 to nowadays:* Production program of ^{241}Am at the scale of several hundred grams per year, which is performed by chemical treatment of effluents or aged PuO_2 stocks ;
- 1970-1983:* Study program for the knowledge of the behavior and control of neptunium during the U and Pu purification cycles throughout the PWR fuels reprocessing ;
- 1975:* Beginning of the study program relative to the alpha emitters extraction from fission products solutions ;
- 1979-1981:* CEA/EURATOM/ISPRA program concerning the validation of flowsheets for the alpha emitters separation on real high activity solutions ;
- 1981 up to now :* Study programs on the trivalent actinides extraction from acid solutions and on selective extraction of tetravalent or hexavalent actinides.

1.2. Know-how on the neptunium management

1.2.1. Nowadays predicted management of neptunium in UP3

The figure 1 exhibits the repartition of ^{237}Np in the different flux of the PUREX process in UP3 plant. With a neptunium feed at 434 g.t^{-1} :

around 2.3 % of the initial neptunium is carried along with the refined products uranium : 3 g/t and plutonium : 7 g/t ;

- the balance 97.7 % is held or injected in the high activity effluent which will be concentrated and finally vitrified.

In fact, the neptunium is confined in by two flux :

- raffinate of the first extraction U + Pu cycle (17%) ;

acid recovery n° 2 (352 g/l) corresponding to the neptunium which has followed uranium (66.8 % of Np) and plutonium (17 % of Np) after the first extraction cycle.

Other ways of neptunium management are envisageable for its recovery during the full reprocessing.

1.2.2. Other possible neptunium managements

First mode : separate management of neptunium

- Neptunium recovery from the concentrate of the acid recovery n° 2.
This operation taking into account only 80 % of the neptunium formed in the fuel, requires the modification of UP3 treatment diagram.
- Neptunium extraction from concentrates of acid recovery 1 and 2.
This operation will take in account 97 % of the neptunium present in the fuel. This management mode does not require the modification of the UP3 treatment but requests the construction of a special high activity unit in regard to the presence of fission products.

Second mode : management of both neptunium and plutonium

It is possible to lead 80 % of the neptunium initially present in the fuel, in the plutonium flux and to send it toward the transmutation step through the plutonium recycling. Two different procedures are to be considered :

neptunium "send back" to the second Pu cycle feeding. The neptunium present in the acid recovery n° 2 is added to the feed of the second Pu cycle ;

neptunium separation with the plutonium at the first cycle,

The neptunium coextracted with U and Pu at the first cycle could be kept in the Pu flux by

using a pardoning reactant less powerful than U(IV) to avoid the partial reduction of Np(V) on Np(IV) and its carrying away in the uranium flux.

1.2.3. Conclusions on the neptunium management

CEA disposes of most of the chemical data to install a improved management of neptunium in the fuel reprocessing plant.

Nevertheless, even in the scenario of a quantitative neptunium recovery in the HLLW, the benefit in terms of storage of glass blocks is modest. Indeed, ^{241}Am and ^{241}Pu still present in the effluents build up by total decrease around 220 g/t(H.M) of ^{237}Np corresponding to 50 % of ^{237}Np present in the fuel at the reprocessing time.

1.3. Know-how of the **transplutonium** elements

1.3.1. Production of **transplutonium** elements

The routine production of the isotopes ^{243}Am , ^{244}Cm then ^{241}Am at the respective amount of around : 10, 10 and 500 g/y has been performed in CEN/FAR with improved techniques. Thus, the chemical treatment of the irradiated ^{239}Pu or ^{242}Pu targets includes the recovery of the residual plutonium and the separation of trivalent actinides (Am, Cm) from the F.P. and trivalent lanthanides. These separations are performed with chromatographic extraction.

1.3.2. Studies on the alpha emitters/F.P. separations

In the framework of contract between CEA and EURATOM/ISPRA, two diagrams for the separation of alpha emitters from fission products has been tested on real solutions provided by a fuel reprocessing issued of BORSSELE reactor (PWR) [1].

The two flow diagrams were based on the use of:

or one extractant molecule HDEHP (di-2-ethylhexylphosphoric acid)

either two extractants molecules TBP and HDEHP in two successive steps.

The obtained results on real solutions suited, for the main part, to the previsions.

II - SCHEMES OF ALPHA EMITTERS SEPARATIONS FOR **H.A. LIQUID** WASTE

IV.1. Already studied processes

All the processes already defined for the alpha emitters separation of from H.A. effluents and tested at laboratory scale, arise the problem of the trivalent elements extraction An(III) (Am and Cm) then the separation of An(III) from trivalent lanthanides around (10 kg.t⁻¹) coextracted with actinides. These processes are based on :

Either the coextraction of trivalent actinides and lanthanides from acid solutions with **extractants** such as :
carbamoylmethylene phosphonate : CMP, or carbamoylmethylphosphine oxide : CMPO (TRUEX process) followed by successive back-extractions and ending

"inexorably" by the TALSPEAK process using HDEHP and DTPA as completing agent of An(III) in aqueous phase.

Or: the use of TBP, HDEHP for An(III) + Ln(III) coextraction which requires for the TBP employment of concentrated saline solutions and for HDEHP an increase of the organic solution and a delicate pH adjustment of the aqueous phase.

Both processes request also the final Am(III) + Cm(III)/Ln(III) separation.

The figure 2 resumes the different steps of these two processes mostly related in different manners.

11.2. Directions in the future

In respect to the extreme complexity of the above processes, other methods for minor actinides/FP separation have to be imagined. In the terms of radiotoxicity in the scale of 300 years, no substantial benefit could be taken in account if the curium is kept out from the H.A. effluents. So, an another strategy could be built if recovery of U, Np, Pu and Am was performed with 99 % yield from the waste.

This possible way consists in prospecting for separation methods allowing the selective extraction An(III) from acid solutions.

III - RECENT ADVANCEMENTS IN THE R & D WORKS

III.1. Coextraction of actinides at higher oxidation states IV or VI

On the contrary to the lanthanides which mostly exhibit the valence III, the actinides U, Np, Pu, Am may exist at higher valences IV or VI in nitric acid. So a new way is possible for separation of minor actinides from lanthanides [2] :

1. oxidation of actinides to higher valence states IV or VI ;
2. selective extraction of actinides

When working in this field we must take into account the problems arising from particular elements contained in HLW solution in considerable amounts. Ru and Ce can occur in higher oxidation state and therefore will interact with the proposed separation process.

a/ Elimination of ruthenium : To avoid any interference of ruthenium in the process, "the electrovolatilization" was selected for Ru elimination from the HLW solution as RuO₄. In an electrochemical cell, RuO₄ is formed, then volatilized and trapped in NaOH solution.

The parameters governing this volatilization (temperature, potential, effect of mediator) have been examined and the feasibility of the quantitative elimination of Ru has been demonstrated on HLLW coming from MOX fuels reprocessing (figure 3).

b/ Electrooxidation and extraction of americium : The second step is to oxidize the actinides to higher oxidation states in order to design a system for selective separation of these from the rare earths.

As the main difficulty is to oxidize Am at oxidation state 4 or 6 which are thermodynamically unstable, most of the efforts has been done to determine the conditions of oxidizing and stabilization of Am(IV) or Am(VI) species in nitric acid.

At the present time, the laboratory studies have been only conducted on electrochemical oxidation of An(III) in An(IV) in presence of the phosphotungstate ligand ($K_{102}P_{17}O_{61}$, P. W.) in nitric acid (figure 4). In nitric media containing phosphotungstate the really observed valence states are : Am(IV), Pu(IV), Np(IV), Np(VI), U(VI).

Additionally extractions using dioctylamine in order to separate trivalent from tetravalent metal ions are under progress at laboratory scale.

III.2. Selective extraction of trivalent actinides from acid solutions

Two research paths have been followed :

1. in the short term to look for two kinds of extractants : extractants of Am(III,IV,VI) and some extractants for the La(III)/An(III) groups separations ;
2. for the longer term research, to look for an extractant for only actinides.

Good candidates for the first extractant are the diamides studied by C. MUSIKAS et al [3]. Bench-scale tests with diamides were performed to check the quality of the solvent and the possibility of using it for waste treatment.

The flow sheet and the conditions for extraction are shown in figure 5. The results are compared with those from TRUEX process.

Concerning the choice of extractants for the separation of actinides and lanthanides groups, important results have been obtained by employment of extractants with S or N donor atoms (soft complexants).

Systems containing extractants such as TPTZ-HDNNS or TPTZ-a-bromocapric acid has been tested with success to the separation of Am(III) from Ce(III) and Eu(III).

Both systems has been tested on a bench scale with mixer-settlers (for TPTZ-HDNNS) or in chromatographic extraction for TPTZ-a-bromocapric acid) figure 6.

IV. CONCLUSIONS

Although modest, the studies achieved in the CEA, these last years, have given interesting results. On the selective extraction of hexavalent or tetravalent actinides and selective extraction of trivalent actinides from acid solutions.

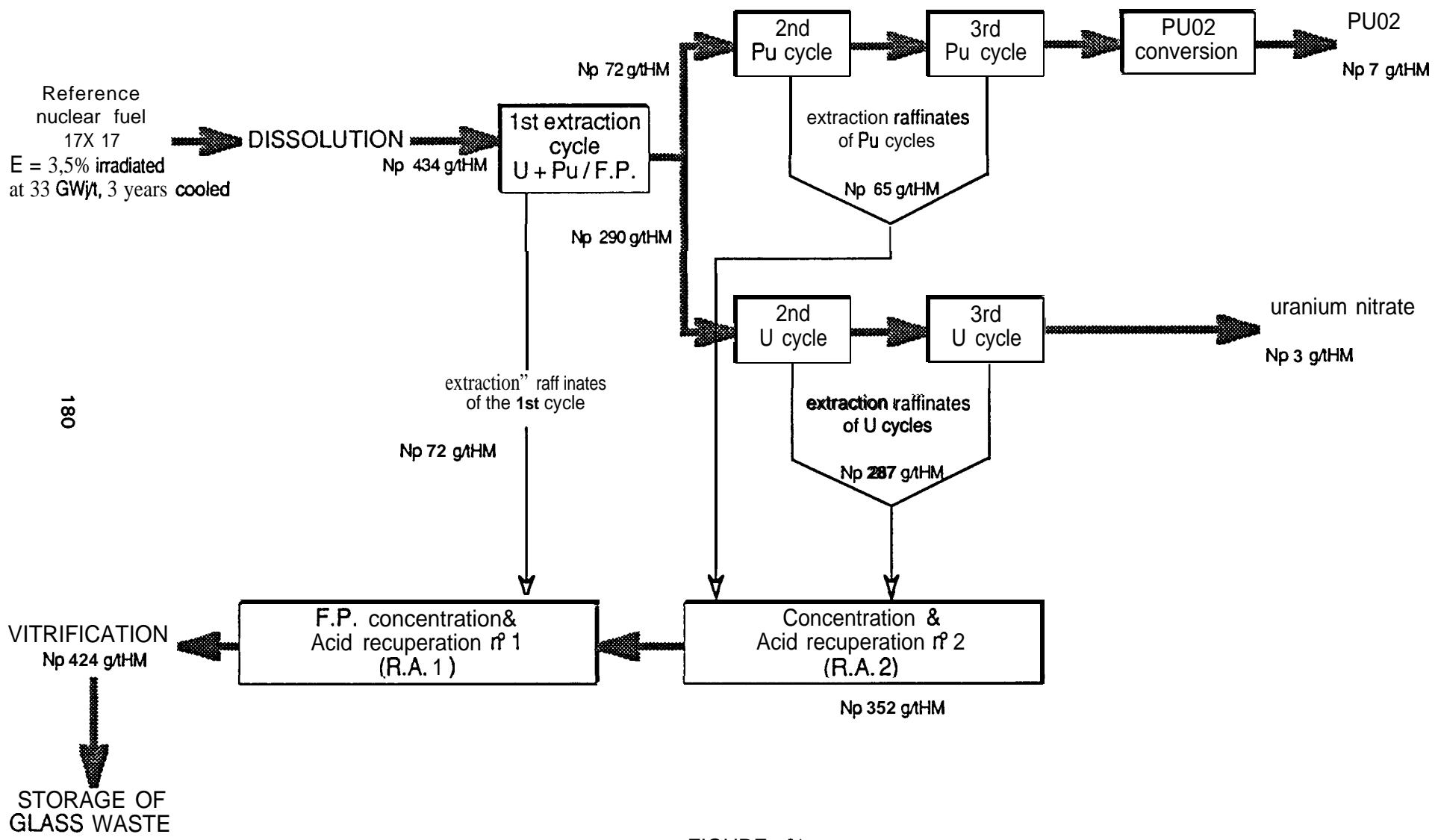
Nevertheless important R & D effort must be pursued to define new processes based on these concepts.

BIBLIOGRAPHY

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- [2] J.M. ADNET and C. MADIC
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Results and prospects for some extractants in minor actinide partitioning
Workshop on partitioning and transmutation of minor actinides
KARLSRUHE 16-18 October 1989



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FIGURE n°1

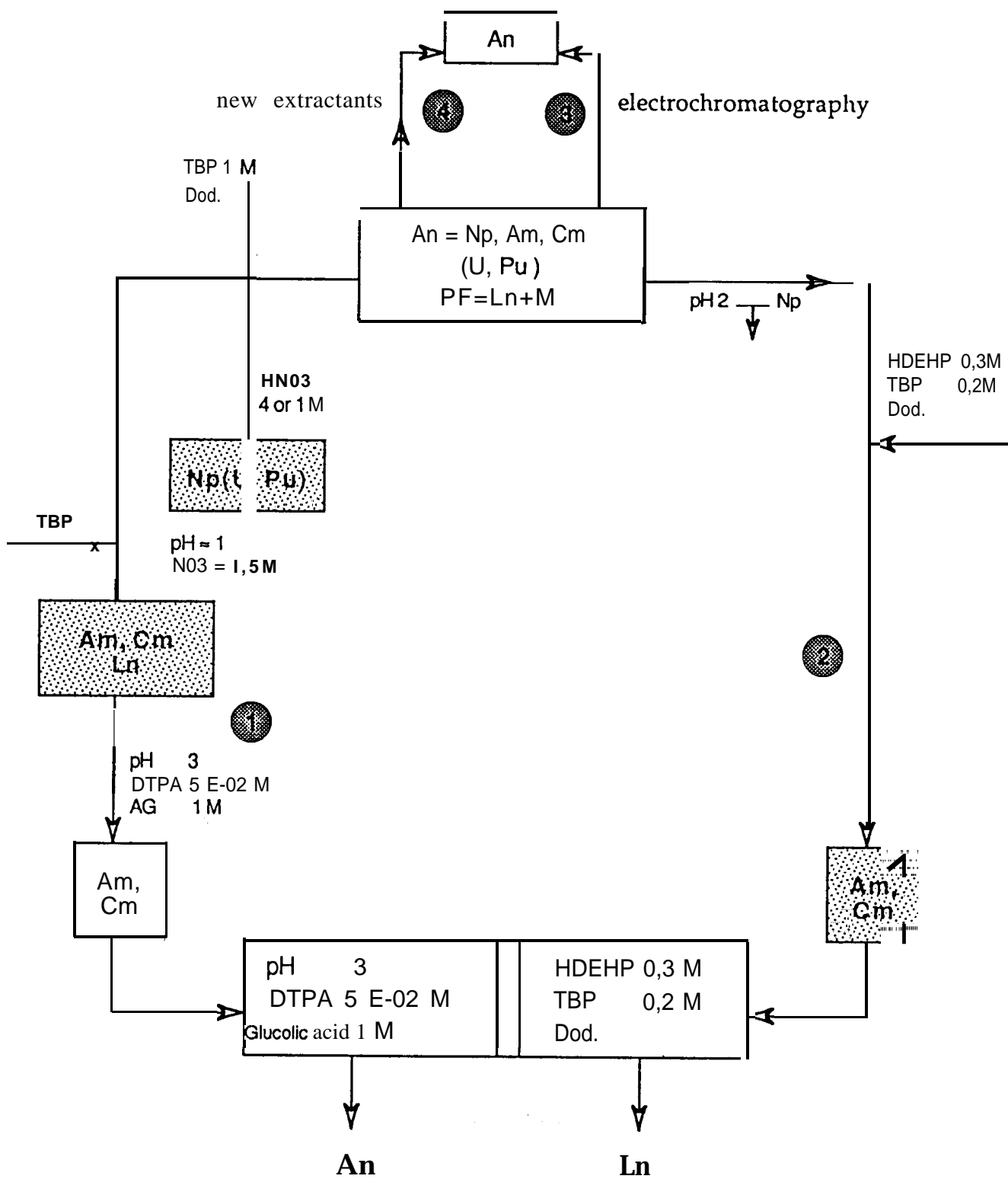


FIGURE n°2

SPECIES	[H ⁺]	3.0 N
	[PI-I]	8.4 mg.l ⁻¹
	[U]	138.4 mg.l ⁻¹
	[Mo]	639 mg.l ⁻¹
	[Zr]	695 mg.l ⁻¹
	[Fe]	840 mg.l ⁻¹
$\beta \gamma$ Activities in Cl.l ⁻¹ (25/08/1988)	¹⁴⁴ Ce + ¹⁴⁴ Pr	13.96
	¹²⁵ Sb	0.50
	¹⁰⁶ Ru + ¹⁰⁶ Ru	11.22
	¹³⁴ Cs	7.40
	¹³⁷ Cs	18.61
	¹⁵⁴ Eu	1.24

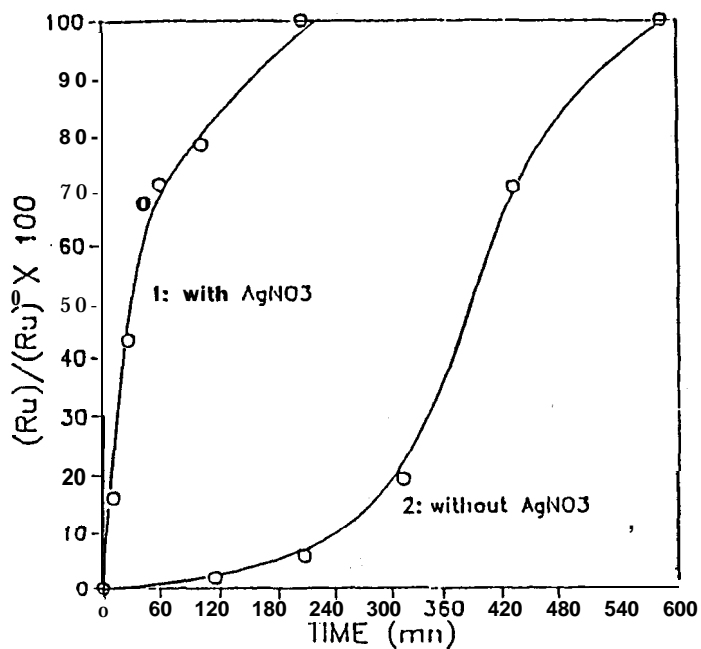
$$\Sigma (\beta \gamma \text{ activities}) = 52.95 \text{ Cl.l}^{-1}$$

$$\Sigma (\beta \gamma \alpha \text{ activities}) = 0.67 \text{ W. l-i}$$

COMPOSITION OF THE F.P. SOLUTION

(concentration factor : 5300 l/l)

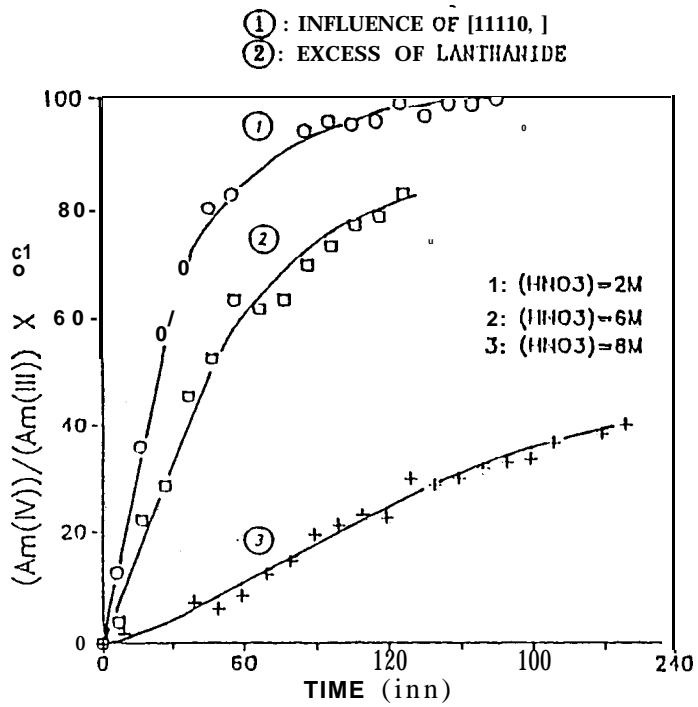
ELECTROVOLATILIZATION OF RUTHENIUM ON REAL F.P. SOLUTIONS



CONDITIONS

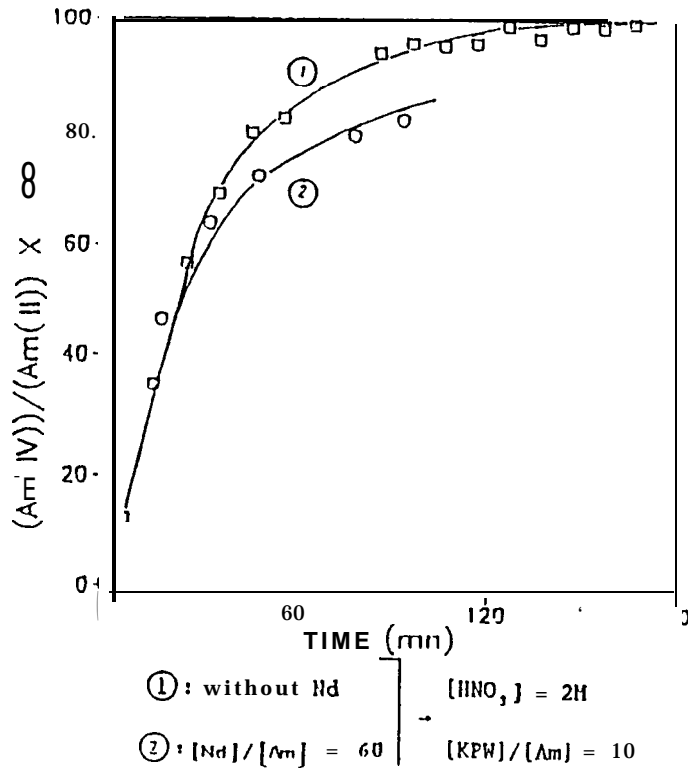
[HNO₃] = 3M ; T = 60°C ;
I = 0.45A ; S = 17.6 cm² ;
dH₂ = 40 l h⁻¹ ;
[Ag⁺]/[Ru] = 1.0

FIGURE 3
ELECTROVOLATILIZATION OF RUTHENIUM



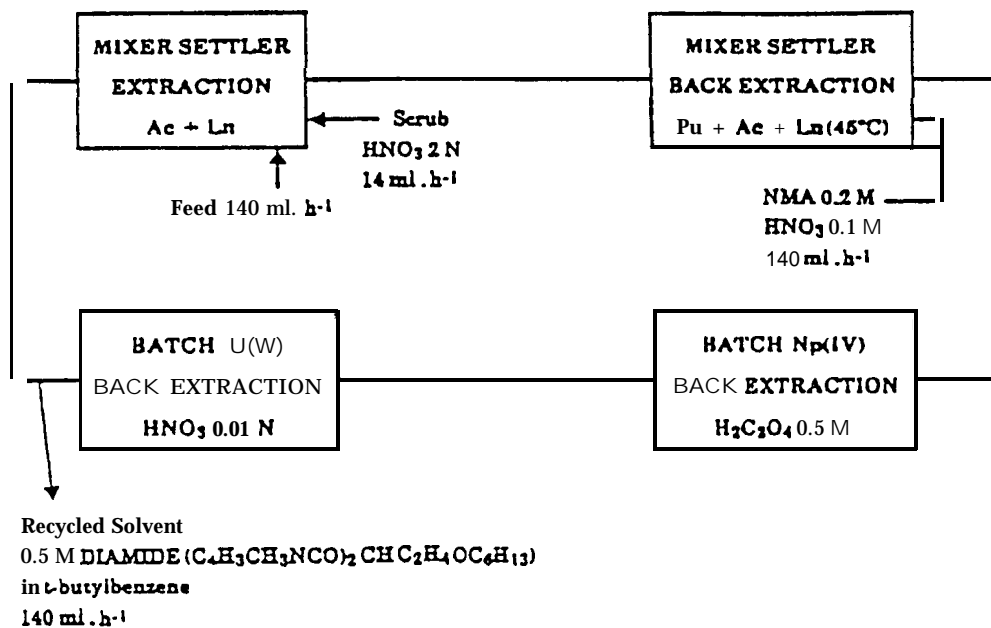
①

CONDITIONS
 T = 25° C ; I = 50 mA ; S = 6.3 cm² ; V = 20 ml ;
 [Am] = 10⁻³M ; [FW]/[Am] = 10



②

FIGURE 4
 ELECTROOXIDATION OF AMERICIUM



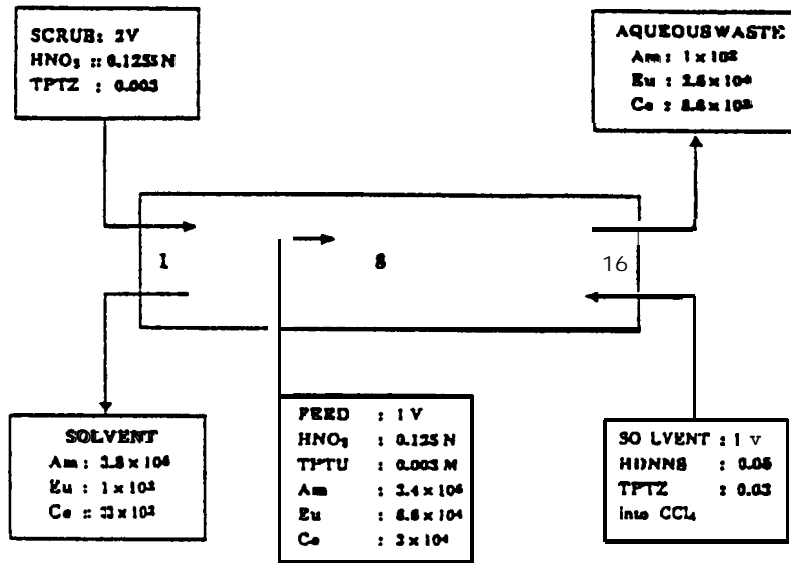
Flow sheet used for the bench scale extraction

Decontamination factors for the bench scale separation of the actinides using DIAMIDE - Comparison with the TRUEX process

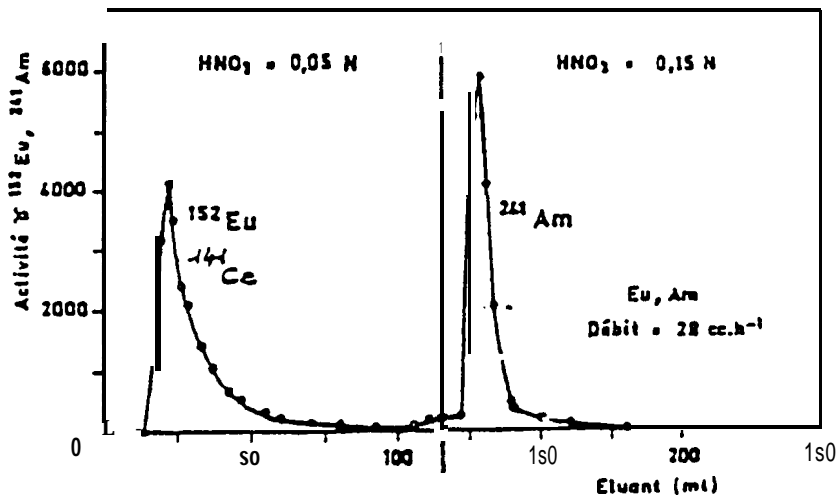
Element	TRUEX	DIAMIDE
UO ₂ ²⁺	>105	>105
Pu ⁴⁺	> 105	>105
Am ³⁺	5X10 ⁴	L 2 x 10 ⁴
Eu ³⁺ +(Cm ³⁺)		6.7x10 ³
Np	6	144

DIAMIDE 0.51 in t- butylbenzene
 (C₄H₉CH₃NCO)₂ CHC₄H₉OC₆H₁₃

FIGURE 5



*Actinide-Lanthanide mixer-settler separation
Solvent: HDNNS + TPTZ into CCl₄*



Elution curve of a mixture ²⁴¹Am - ¹⁵²Eu from a column of XAD4 resin loaded with 30% C₉H₁₉BrCOOH, 1.8% TPTZ

FIGURE 6