

MINOR ACTINIDE SEPARATION

RECENT ADVANCES AT THE CEA

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ABSTRACT

In the frame of the french SPIN programme, R&D work has been undertaken at the CEA in order to develop minor actinides separation. The main route concerns solvent extraction processes, and in particular :

- PUREX process adjustment for Np selective recovery;
- DIAMEX process development for Am and Cm extraction from PUREX raffinate.

Important advances have been recently achieved, especially in the field of Am and Cm separation : optimization of diamide formula, flowsheet improvement to prevent FP extraction, progress in An(III)/Ln(III) separation using new extractants.

Main R&D results are presented and discussed.

1. INTRODUCTION

In December 1991, the French Parliament passed a law on research into radioactive waste management. One of its Articles required the "finding of solutions for the separation and transmutation of long-lived radionuclides present in high-level long-lived wastes". The law set a time limit of fifteen years.

This request is connected with the chemical separation of certain elements and radionuclides of spent fuels to transmute some of their long-lived radioactive isotopes liable to incur long-term hazards. The target elements of this strategy are primarily the so-called minor actinides (neptunium, americium and curium), due to their large contribution to the waste radiotoxic inventory after 1000 years.

Given the large amounts of irradiated fuels to be reprocessed, any valid separation process must be industrial, implying processes as reliable as possible, and always striving to minimize the doses to the personnel and the production of effluents and secondary wastes.

The field is hence limited by these restrictions. The CEA accordingly decided to develop original processes, by relying on considerable basic research conducted for a better understanding of the separation mechanisms. This paper reviews the methods selected and sheds light on recent developments.

2. PROBLEMATICS OF THE SEPARATION OF MINOR ACTINIDES

Irradiated fuel reprocessing by the PUREX process generates a high-level effluent containing all the soluble fission products and minor actinides. This effluent is concentrated today, and then, after interim storage of about one year, the elements it contains are encapsulated in a glass matrix which guarantees high-quality conditioning.

Table 1 lists the quantities of minor actinides contained in one ton of reference UOX fuel, irradiated to 33 GWd/t and cooled for three years.

element	isotope	half-life (years)	mass (g/t)
Np	237	2.1×10^6	430
Am	241	430	220
	243	7400	100
Cm	243	28	0.3
	244	18	24
	245	8500	1

Table 1 : Minor actinides contained in reference UOX fuel

It is important to develop separation processes whose feasibility can be proved before 2006, the deadline set by the law. It was decided to assign priority to developing liquid/liquid extraction processes, which are extremely efficient and could be integrated with the present PUREX process.

The separation of minor actinides raises two very different technical problems according to the element concerned.

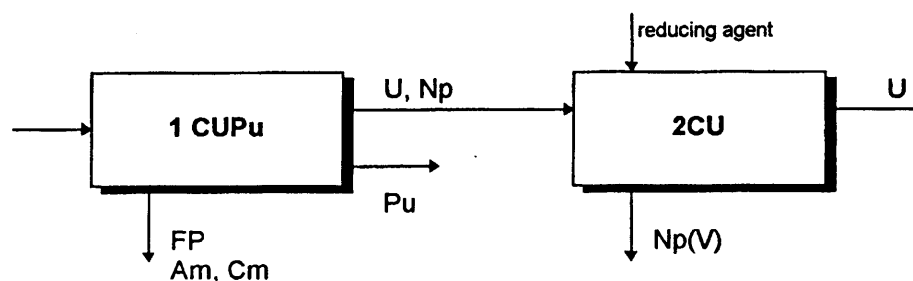
- In some conditions, neptunium can be extracted in tri-n-butylphosphate (TBP), the solvent used in the PUREX process. In the operating conditions of the standard PUREX process, it is estimated that about 3/4 of the neptunium is extracted by the TBP in the first extraction cycle, and then separated in the second uranium purification cycle. To guarantee more complete separation of this element, the PUREX process conditions must therefore be adjusted to achieve the desired performance.

- Americium and curium are not extractable by TBP and remain in the aqueous phase produced by the PUREX process. The separation of these elements will require finding new classes of extractants, or the development of different separation techniques. It goes without saying that the latter problem is far more complex than the former.

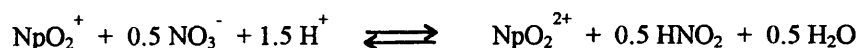
3. SEPARATION OF NEPTUNIUM

Neptunium, whose stable oxidation state in nitric medium is (V), is relatively inextractable as this species by TBP. However, the dissolution liquors fed to the first extraction cycle of the PUREX process contains significant amounts of nitrous acid, which oxidizes a portion of the Np(V) to Np(VI), a form in which neptunium can be extracted in the organic phase.

Once the neptunium is extracted by the TBP, it follows the uranium stream, and can be separated easily from this stream in the second uranium purification cycle, by changing its oxidation state.



The basic principle of intensive neptunium separation consists in privileging its oxidation to the hexavalent state by the following reaction:



This reaction is reversible and catalysed by the nitrous acid produced by the reaction.

To develop this process, two types of investigation were conducted :

- Consolidation of the PAREX code used to predict the behavior of neptunium in the PUREX process. Backup laboratory tests were also performed to consolidate know-how on the redox mechanisms of the Np(V)/Np(VI) system in the presence of the pair HNO₃/HNO₂.
- Comparison of the results of the model with experiments performed in a laboratory-scale installation of α pulsed columns.

These studies revealed that relatively simple changes to the standard PUREX process should significantly improve the neptunium extraction yield. The overall target is a yield of 99.9% (99% in the PUREX process and complementary 0.9% in the DIAMEX process).

If the separation performance is insufficient in terms of the objective assigned, the oxidation of neptunium would have to be intensified by using a specific oxidant of the element, such as vanadium (V). This method has not undergone any development at the CEA for the time being.

4. SEPARATION OF AMERICIUM AND CURIUM

The high-level raffinate from the first extraction cycle of the PUREX process contains the whole americium and curium inventory, and most of the fission products from the irradiated fuel. The CEA is developing two types of process to extract and separate these minor actinides from the fission products. The first is based on extracting the actinides at their stable degree of oxidation in nitric medium, An(III), and the second process chiefly relies on the selective oxidation of americium in degree (IV) or (VI), followed by its selective separation by extraction or nanofiltration. This process, named *SESAME*, is not dealt with here.

In developing the extraction process for actinides in oxidation degree (III), two requirements were decided from the outset.

- To perform the extraction of An(III) without adjusting the nitric acidity of the high-level raffinate, to eliminate any risk of undesirable precipitation of fission products.
- To minimize the production of secondary wastes by only using totally degradable organic compounds (extractants or reagents). This principle was named *the CHON principle*, by reference to the substances used, which exclusively contain the atoms C, H, O and N.

The diamide extractants and especially those of the malonamide family (in which the two amide functions are separated by a single carbon atom) can extract An(III) while meeting the above two requirements. This process was named *DIAMEX* (DIAMide EXtraction).

Like the other compounds developed to extract An(III), diamide extractants display no selectivity for all trivalent elements. In particular, the elements of the lanthanide family which have external electron structures and dimensions comparable to those of Am³⁺ and Cm³⁺ ions, are extracted jointly. This entails the need for a supplementary step to separate the two families.

In brief, the separation process for americium and curium is a two-step process:

- An(III)-Ln(III) co-extraction by the *DIAMEX* process,
- An(III)/Ln(III) partition.

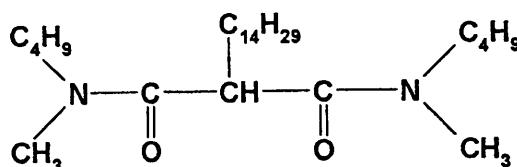
A detailed description of this process is given below.

4.1. DIAMEX process

The extraction of trivalent cations from strongly acidic nitric medium is a difficult operation due to the weak extraction ability of An(III) nitrates and the strong competition which occurs between the extraction of nitric acid and that of the An(III) nitrates.

Diamides, which have two donor oxygen atoms, react with the metallic ion to form a six-apex chelation ring, which is extremely stable. This property considerably increases the affinity of the extractant for trivalent cations.

A first compound was selected in 1991 for the development of the *DIAMEX* process, dimethyl-dibutyltetradecylmalonamide (DMDBTDMA), with the following semi-developed formula :



This substance was used for the first tests performed on real active solutions in 1993. These tests confirmed the possibility of quantitatively extracting americium and curium (a yield in excess of 99.5% was obtained with only six extraction stages), and then to strip them using a weakly acidic aqueous solution.

However, many flaws were identified at the time:

- a very limited operating range due to a low threshold of third phase appearance,
- undesirable extraction of some fission products, such as Zr, Mo and Ru.

Two research directions were pursued in parallel to solve these problems:

- optimization of the formula of the diamide extractant to improve its properties related to third-phase formation,
- the development of a flowsheet designed to increase the extraction selectivity.

Extractant optimization

The properties of diamide extractants can be adjusted by selecting the types of radical carried by the nitrogen atoms of the amide functions and by the central methylene bridge.

Third-phase formation in an extraction process is due to exceeding the solubility of the ligand/cation complex in the organic phase, and results in separation of the organic phase into two phases.

Increasing the length of the alkyl groups helps to increase the lipophilic property of the extractant and of its solvates, increasing the solubility of these products in the organic phase. However, this elongation may have two harmful effects :

- it increases the size of the molecule and, in some situations, decreases the accessibility of the amide functions, to the detriment of the extractive properties,
- it increases the risk of the formation of long-chain degradation products, which may have undesirable surfactant properties, and are difficult to remove from the degraded solvent by aqueous washing because of their insolubility in water.

Hence, optimization of the extractant involves finding the best compromise between the foregoing antagonistic effects. A new compound is currently being identified. It will be synthesized and tested to check that the improvements anticipated are effectively achieved.

Increasing extraction selectivity

The alternatives considered to minimize the undesirable extraction of Zr and Mo are based on the formation of inextractable complexes. Several processes have been envisaged, including :

- a separate complexation of the two elements (ketomalonic acid for Zr and hydrogen peroxide for Mo), which necessarily demands two distinct steps because these two compounds interact with each other,
- a combined complexation of both elements by oxalic acid.

It is also necessary to control the behavior and extraction of ruthenium. This is a much more difficult problem, because this fission product has an extremely complex and still virtually unknown chemistry within the *DIAMEX* process conditions.

4.2 Actinide(III)/lanthanide(III) partition

When they leave the *DIAMEX* process, the actinides(III) are in dilute nitric acid solution, mixed with lanthanides(III). The latter are much more abundant because the molar ratio $R = \text{number of moles Ln}/\text{number}$

of moles An is close to 50 for standard UOX fuel. It was decided to assign priority to developing processes for the extractive selection of An(III), leaving the most abundant elements in the initial aqueous solution. This helps to limit the solvent inventory and the size of the extraction units.

Actinide(III)/lanthanide(III) partition is certainly the most difficult step to design in a separation process for minor actinides. This is because very selective compounds have to be found, capable of recognizing elements with very similar properties, and which also have sufficient extraction properties.

All known processes for the separation of the actinide/lanthanide group in oxidation state (III) use the selective properties of ligands containing 'soft' donor atoms. These form stronger complexes with An(III) than with Ln(III).

The most common explanation for this is the existence of a stronger degree of covalence in bonds with actinides, due to a larger spatial extension of the 5f orbitals (actinides) in comparison with the 4f orbitals (lanthanides).

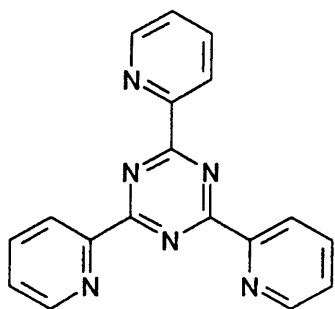
Since trivalent actinides and lanthanides are 'hard' cations in the HSAB (Hard Soft Acid Base) classification, the bonds with 'hard' ligands, such as those which have oxygen donor atoms, are essentially electrostatic, and this partial covalence can only occur with less electro-negative donor atoms than oxygen, i.e. nitrogen or sulfur.

The CEA pursues the following basic objective :

- Selective extraction of An(III) which account for the minority portion of the elements present, by developing an extractant compound which has 'soft' donor atoms.
- Use of an extractant which raises no new problems in waste management and preferably complies with the CHON principle. This limitation reduces the choice to nitrogen molecules and excludes the use of sulfur atoms.
- Direct operation on the aqueous solutions produced by the DIAMEX process, without intermediate acidity adjustment. This implies the presence of an extractant system which operates at relatively high acidity (0.5 to 1 mol/L).

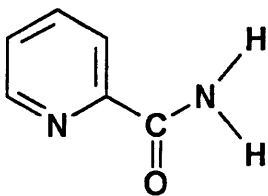
The approach adopted is to design an extractant compound based on a selective complexant for the actinides, made lipophilic by the addition of organic groups.

Two nitrogen complexants were selected :



TPTZ (tripyridyltriazine)

This compound has a coordination site with three nitrogen atoms, which favors good selectivity for An(III) versus Ln(III).



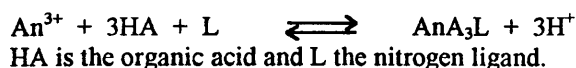
Pyridine 2 carboxamide (picolinamide)

also capable of selective complexation of the actinides, probably via the nitrogen/oxygen site.

Nevertheless, this type of ligand forms weaker bonds with metallic cations than those obtained with oxygenated ligands. This factor underlies the chief difficulty in the application of the processes : competition with oxygenated ligands (e.g. molecules of solvation water), during the extraction process, in which the total or partial dehydration of the metallic ion is required.

The grafting of alkyl groups on these complexing molecules has not made it possible so far to guarantee the intrinsic lipophilic property of the complex to obtain its extraction in the organic phase in the desired acidity range.

This problem is being dealt with by examining the possibility of associating a more lipophilic anion with the extraction process than the nitrate anion, such as the conjugate base of an organic acid:



The nitrogen complexant/acid exchanger pair forms a synergistic mixture whose extraction efficiency is increased in comparison with that of the two constituents considered separately. The nitrogen complexant cannot extract the actinide nitrates from the aqueous solution by itself, because of the insufficient lipophilic property of the complex formed. Conversely, the acid exchanger cannot distinguish the actinides from the lanthanides because it only has 'hard' donor atoms.

To be effective in relatively acidic medium, the organic acid must be sufficiently strong to ensure the lability of the H^+ proton in this medium. Synergistic systems including α -bromodecanoic acid and TPTZ or TtBPTZ (tri-tertbutylpyridyltriazine) were studied.

The following results were obtained :

- americium is extracted better than europium with a separation factor of around 10,
- TtBPTZ offers better metal ions distribution coefficients than TPTZ, demonstrating the influence of the lipophilic property of the nitrogen agent on the extracting power of the synergistic mixture.

The entire challenge of this approach is thus contingent on finding strong organic acids, which comply with *the CHON principle*. Investigations so far have focused on carboxylic acids with an electron attractor group in the α position, such as -CN and -OH.

5. CONCLUSIONS

Major breakthroughs have been achieved in research under way at the CEA on the development of separation processes for the minor actinides.

The intensive separation of neptunium appears feasible if a limited change is made to the PUREX extraction flowsheet. This theory will have to be corroborated in a perfectly representative situation.

The development of actinide(III)/lanthanide(III) co-extraction is highly advanced. It remains to be optimized, by examining the behavior of ruthenium, which appears as an undesirable element.

Work on separating actinides and lanthanides appears to be making headway thanks to the use of synergistic extraction systems. Conditions will have to be found in which these systems comply with *the CHON principle* and remain effective in slightly more acidic media than today.

These investigations are in the laboratory stage for the time being, and much obviously remains to be done before they can be applied industrially.

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