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Development of New Hydrometallurgical Processes for Actinide Recovery: GANEX concept.

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ABSTRACT: In the future, energy producing systems will be mainly based on the use of nuclear reactors of the 4th generation, which will be developed to fulfil some criteria such as sustainability, economic efficiency, safety and resistance to proliferation risks. As a consequence, these reactors will burn fuels containing a large range of actinide elements: major actinides, such as U and Pu, but also minor actinides, such as Np, Am and Cm. This implies to master the management of all actinide elements within the overall fuel cycle and thus to develop new processes for their selective recovery and purification. This article describes the options, currently studied at CEA, to selectively recover all actinides together from the fission products by implementing hydrometallurgical processes, in order to further convert them into new targets or recycled fuels.

KEYWORDS: Gen(IV), actinide, hydrometallurgy, group extraction, recycling.

I. INTRODUCTION

Dealing with Gen(IV) future fuel cycles, CEA is involved in the definition of new chemical processes to recover the actinides from the spent fuels and to produce new fuels or targets containing mixtures of actinides. Among the possible chemical separation processes, CEA teams are essentially focussing their works on the two following types: hydrometallurgical and pyrometallurgical processes. In this paper attention will be paid to the development of new hydrometallurgical processes, which could be applied to the actinide group recovery from the dissolution liquors of irradiated fuels.

II. GENERAL STRATEGY

The design of fuel cycle technologies (spent fuel reprocessing and new fuels or targets refabrication) relies on two determining issues: the choice of a strategy for the inventory management (in coherence with the capacity of the available park of reactors to use them efficiently), and the choice of the fuel object itself (nature, composition and morphology), which is specific to a given nuclear system. The fuel is the backbone of the cycle and its choice is strictly connected to that of the processes developed and used for its treatment and (re)fabrication. Nevertheless, for all the nuclear systems involving a closed fuel cycle, some key criteria raise up, allowing a core of researches to be identified, mostly related to recycling technologies. These criteria are those of future nuclear systems:

- economic efficiency,
- safety,
- sustainability,
- resistance to proliferation risks,

the two latter stakes being largely borne by the fuel cycle itself, in particular the conservation of natural resources and the minimization of environmental impacts. On the one hand, the valuation of uranium and plutonium potential energies in fast neutron reactors is the key factor of resource conservation and, on the other hand, the recycling of plutonium and minor actinides minimizes waste potential harmfulness as well as their long-term heat generation characteristics. From these assessments can be deduced the first and main driving force of future nuclear fuel cycles: sustainability means a recurring full recycling of all actinides, although some options remain open regarding the number of elements to be considered among the transplutonics (according to their inventory, their properties, their impact and the difficulties their recycling could entail). A general line seems clearly identified and leads to the scheme pictured in Figure 1.

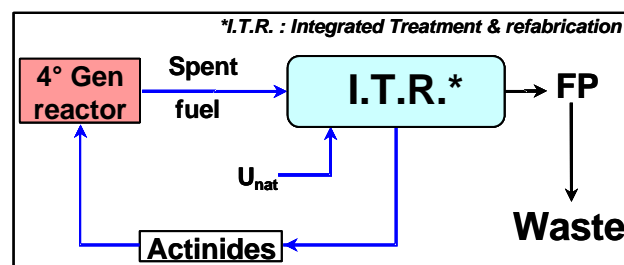


Figure 1: General scheme for Gen(IV) fuel cycle

Other less evident or less unanimous orientations can also be put forward:

- Recycling the actinides altogether not only avoids the recovery of the targeted elements in a particular

and isolated way, which increases proliferation risks, but also simplifies the management of the recycled materials, thus leading to better economic efficiency;

- Compact technologies reduce capital costs;
- Clean technologies should be favoured, that is to say: minimizing as much as it is reasonably achievable the rejected effluents and the secondary technological waste.

The concepts of selective recovery of all actinides together trying to take advantage of some of their physical properties do not meet with the development one could expect. If the idea to separate the heaviest elements (actinides) from the others (FPs) is attractive, only exploratory studies have been done so far, as for example: ultra centrifugation at LANL, action of an electromagnetic fields on a plasma at LLNL. The objective of actinide group recycling could give a new impetus to the research in this field, but the technological depth to be filled is considerable. That is why the CEA's current strategy deals with chemical process potentialities, usually shared between hydrometallurgical processes (aqueous route) and pyrometallurgical ones (dry route).

Thanks to their long industrial experience in spent fuel reprocessing application, hydrometallurgical processes use a mature technology (solvent extraction), allowing very high separation performances (recovery rates and decontamination factors) to be reached, while generating few technological waste. They offer large adaptation freedoms to fuel characteristics (and also to recycling specifications, as shown in recent studies on minor actinide partitioning) and real improvement potentialities, notably in process compactness. Thus, they appear as the reference way for the development of advanced recycling concepts for Gen(IV) reactors.

However, great efforts should be directed towards:

- **The adaptation of the processes to actinide group separation (and conversion):** this passes through the search for new molecular architectures and appropriate flow-sheets. Such a concept, named GANEX, has been proposed recently by the CEA (see sketch on Fig. 4): firstly, major fraction of uranium contained in the spent fuels should be extracted. Then, the remaining uranium, all plutonium and minors actinides (neptunium, americium, curium) would be separated altogether by implementing an adapted version of the processes that have been worked out in the frame of French studies on Partitioning & Transmutation (first axis of French act from December 1991).
- **The evolution of the extracting solvent formulation:** the strengthening of their resistance towards radiolysis would allow short cooling-time (which has a direct impact on the nuclear material inventory) fuels to be treated.
- **The evolution of the equipments:** equipments and their implementation constitute a determining R&D domain, in which the compactness of the processes can be improved. This deals with unit operations of the processes (where remarkable progresses have been obtained already, with the development of short residence time liquid/liquid contactors), but also with their integration.

III. URANIUM RECOVERY

The GANEX concept is based on the preliminary partial separation of uranium from the nitric acid dissolution liquors, and then on the recovery of the remaining uranium and of all the other actinides by solvent extraction technique. To achieve the selective extraction of uranium, two main routes have been identified:

- The UREX process developed in the United States¹, which uses the same extractant as the PUREX process. In order to get only the extraction of uranium, the feed is adjusted in acidity and aceto-hydroxamic acid (AHA) is added to act as a reducing and complexing compound, blocking the extraction of neptunium and plutonium by TBP.
- The use of uranyl cation (UO_2^{2+}) selective extractants such as the monoamides, especially *versus* neptunium and plutonium (the other An(III) elements being only little extracted). In previous studies led by the CEA², the molecule DOiBA (Fig. 2) was chosen for its good selectivity towards U(VI) vs Pu(IV). Since then, a Japanese team³ has improved its molecular design and new formulations of monoamides with branched alkyl chains have shown better selectivity than DOiBA.

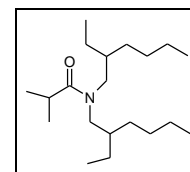


Figure 2. DOiBA (N,N-di-(2-ethyl-hexyl)-*iso*-butanamide).

Figure 3 presents the separation scheme which is currently under study at the CEA. The main goal of this process is to recover at least 80 % of the uranium present in the spent fuel dissolution liquors.

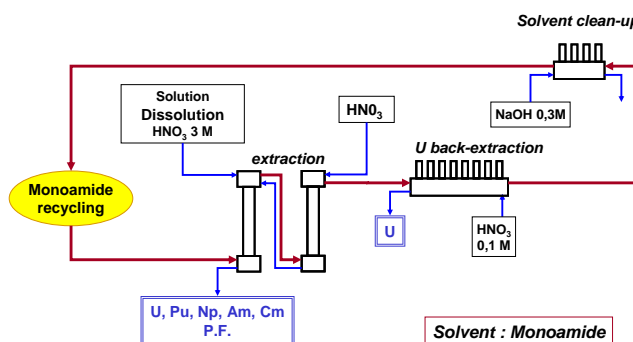


Figure 3: Uranium selective extraction using monoamides

As uranium is the major actinide compound in the dissolution liquor, the performances of the process (recovery yields) will be increased as much as possible in order to ease the implementation of the next separation step: the selective recovery of the transuranic elements.

IV Actinide recovery

Assuming a first cycle devoted to the selective recovery of most of the uranium inventory, a second cycle process is still needed to extract the other transuranic actinides (Np, Pu, Am, Cm and Cf) and the residual uranium. The main objectives of this process are:

- selective extraction of all actinides together vs lanthanides and other fission products,
- use of easily recycled reagents (after solvent treatment), which implies a good hydrolytic and radiolytic stability,
- limitation of secondary waste production,
- compactness and ease of industrial scaling-up of the designed process.

The most challenging issue of course is to find an extracting molecule (or a mixture of molecules) allowing the selective extraction of all the actinides present in the solution, whatever their oxidation degrees, ranging from +III to +VI. Actually, if such a selective and stable extractant was found, the implementation of the process would simplify to three stages only: (i) actinide extraction, (ii) washing of the loaded organic phase, and finally, (iii) actinide back-extraction, as shown on Figure 4.

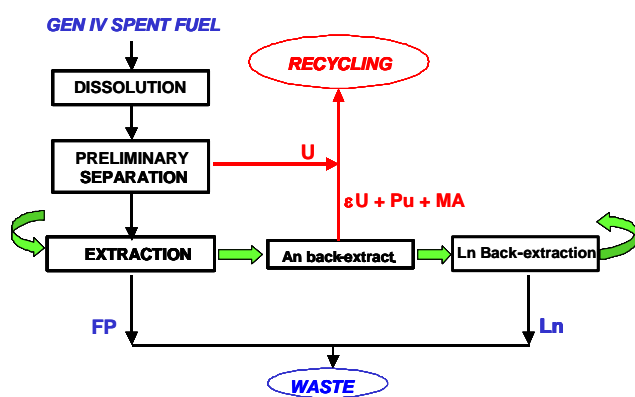


Figure 4: General scheme for actinide recovery

However, such an ideal process requires a comprehensive program of applied and fundamental studies to understand, on the one hand, the coordination, complexation and extraction phenomena of the actinide elements, and, on the other hand, the degradation mechanism of the extractant(s) under acidic hydrolysis and alpha radiolysis.

Taking advantage of the successful results obtained during the past decade at the CEA (in the frame of the studies on Partitioning & Transmutation: 1st axis of the French act from December 1991), an adapted version of the DIAMEX SANEX process is currently being developed, attempting to simplify the corresponding process flow-sheet, which generates rather large volumes of waste.

Moreover, other processes are also being investigated at the European level. In fact, an important work has been done during several successive European collaboration projects, led by the CEA on Partitioning & Transmutation (e.g.: NEWPART, PARTNEW, and presently, EUROPART), all aiming at defining new molecules for the selective extraction of Am(III) and Cm(III) from fission products, including

trivalent lanthanides. Among the molecules synthesized and tested so far, the tridentate Bis-Triazine-Pyridines (BTPs) appear very interesting, but they lack a large loading capacity towards actinides because of a poor solubility in aliphatic diluents and, worst of all, present a too weak radiolytic stability to fulfill the GANEX concept requirements.

For example, an An(III)/Ln(III) separation process flow-sheet, based on the use of the *iso*-propyl derivative of the BTPs (*i*Pr-BTP, see Figure 5), was designed and successfully tested on a genuine highly active solution (i.e.: "An(III) + Ln(III)" product issued from the implementation of a DIAMEX process on a PUREX raffinate) during PARTNEW project⁴. However, despite a satisfactory hydrodynamic behavior of the solvent and very good results in terms of separation performances (the recovery yields of Am(III) and Cm(III) exceeded 99.8% and the An(III)/Ln(III) global decontamination factor reached 150), this process pointed out the poor radiolytic stability of the *i*Pr-BTP molecule, which could not be recycled in the process battery.

Figure 5 presents some examples of BTP structure evolution, aiming at improving the stability of these molecules, while preserving their separation performances:

- Bis-Annulated Triazinyl Pyridines (BATPs), the radiolytic stability of which is far better than that of *i*Pr-BTP, although still insufficient for GANEX process development, are the most efficient extractants studied so far: their selectivity towards An(III) vs Ln(III) sometimes exceeds 1500. They have not been applied to any genuine solution yet, but should be tested on a highly active DIAMEX stripping solution before the end of EUROPART project⁵.
- Tetradentate Bis-Annulated Triazinyl Bis-Pyridines (BATBPs), although less efficient than BATPs to extract An(III) and separate them from Ln(III), present a more favourable extraction stoichiometry: ML₂ instead of ML₃ (for the tridentate B(A)TPs), which lowers the impact of radiolysis damage on their extraction properties. Preliminary extraction tests performed on other actinides than Am(III) and Cm(III) (i.e.: Np(IV) and Pu(III)) show that BATBPs extract them quantitatively and selectively.

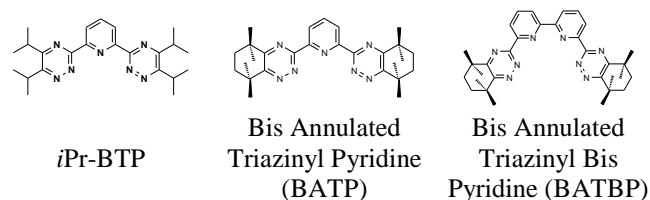


Figure 5: improvement of the BTP molecule

Nevertheless, the major drawbacks of all these Nitrogen polydentate extractants are the following:

- low solubility of the extractant in aliphatic diluents (polar diluents, such as alcohols are needed),
- sometimes too high extraction properties, which disable the stripping of the extracted actinides,

- small loading capacity, directly related to the low solubility and high extraction efficiency of the extractant,
- radiolytic weakness.

These difficulties must unavoidably be tackled and solved before any reliable GANEX process can be developed.

V. Planning of the R&D studies

The R&D program of GANEX process development has been planned at the CEA. The main milestones are:

- Experimental validation of the uranium selective recovery process on simulated dissolution liquors by the end of 2007.
- Improvement of the processes defined for the recovery of all actinides together, which will of course induce complementary studies, such as:
 - stability of the reagent(s),
 - modeling,
 - design of new extracting devices,
 - comprehensive chemistry on coordination of actinide ions,
 - redox phenomena,
 - neptunium chemistry,
 - organization of extracting molecules in organic phases.
- Test of a first separation scheme on genuine effluents by the end of 2008.

VI. CONCLUSION

Nuclear reactors of the 4th generation will be developed in the future to fulfil some criteria such as sustainability, economic efficiency, safety and resistance to proliferation risks. As a consequence, these reactors will burn fuels containing a large range of actinide elements: major actinides, such as U and Pu, but also minor actinides, such as Np, Am and Cm. This implies to master the management of all actinide elements within the overall fuel cycle and thus to develop new processes for their selective recovery and purification before nuclear target or fuel (re)fabrication. The GANEX concept is the option proposed by the CEA to address this challenging stake. It is based on, first, the separation of major part of the uranium present in the spent fuel dissolution liquors, and then, on the recovery of the remaining uranium and of all the other actinides, by implementing an adapted version of the processes that have been worked out during the past decade at the CEA to separate trivalent actinides from fission products, including trivalent lanthanides (*e.g.*: DIAMEX-SANEX process). However, these processes, which are currently developed at the CEA, require a comprehensive program of applied and fundamental studies to understand both the coordination, complexation and extraction phenomena of the actinide, and the degradation mechanism of the extractant(s) by acidic hydrolysis and alpha radiolysis.

ACKNOWLEDGMENTS

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