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Separation of the Long Lived Radionuclides: Current Status and Future R&D Program in France

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Abstract –In the frame of the 1991 French national law on waste management, the CEA has launched research and development studies on the separation of some long-lived radionuclides (LLRN)s from high active waste issuing from the reprocessing of nuclear spent fuel. Six LLRN)s are the targets of these studies; they are: (i) the minor actinides, neptunium, americium and curium, (ii) the fission products, technetium, iodine and cesium. The reference strategy for separating these elements from the spent fuel is based on an adaptation of the PUREX process for Np, Tc and I separation, and on the development of new liquid-liquid solvent extraction processes for Am, Cm and Cs. The scientific feasibility (i.e. the concept validation) of the processes developed has been demonstrated on genuine radioactive solutions by the end of 2001 [1,2], and the CEA has selected a route for the demonstration of the long-lived radionuclides separation technological feasibility to be done before 2006. This paper deals with the current status and future R&D program in France on the separation of these LLRN)s.

I. INTRODUCTION

In December 1991 the French parliament passed a law identifying three areas of research concerning long-lived and high-level radioactive waste management. The first of these areas covers processes capable of separating long-lived radionuclides (LLRN)s: technetium, iodine, cesium (Tc, I and Cs) and the minor actinides neptunium, americium and curium (Np, Am and Cm). The reference strategy for separating these elements from the spent fuel is based on an adaptation of the PUREX process for the separation of Np, Tc, and I and the development of new liquid-liquid solvent extraction processes for the others (Am, Cm and Cs).

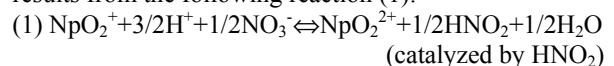
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II. SEPARATION OF LLRN)s BY MODIFIED PUREX PROCESS

II.A. Separation of Neptunium

In the first-cycle extraction/scrubbing operation of the La Hague plants, though the major fraction of the Np inventory are co-extracted with uranium and plutonium [3], significant fraction of the Np inventory are still found in the high active raffinate. In the uranium/plutonium splitting operation, nearly all the co-extracted neptunium follows the uranium into the solvent and is then separated

from uranium in the “uranium purification cycle” [3]. So, the objective of the studies was to increase the extraction yield of Np at a value higher than 99 % by a modification, as limited as possible, of the extraction/scrubbing flowsheet. In this operation, neptunium is present in two oxidation states, Np(V) for which TBP exhibits a very low affinity and Np(VI) which can be extracted by TBP with an affinity close to the one observed for U(VI). The ratio between these two oxidation states of neptunium results from the following reaction (1):



In spent fuel dissolution liquor, the neptunium is mostly present as Np(V) (~ 80-90 %). So the observed behavior of the neptunium within the extraction/scrubbing operation is explained by the shift of reaction (1) to the right due to the extraction by the TBP of Np(VI) and nitrous acid. It must be noted that the oxidation of Np(V) to Np(VI) by nitric acid (reaction (1)) requires the presence of nitrous acid, HNO₂, which acts as a catalyst of the reaction. In the 1st cycle, nitrous acid is always present to a certain extent owing to the radiolysis of the medium.

Using the PAREX simulation code of the PUREX process, it has been shown that an increase of the nitric acid concentration in the PUREX feed solution should lead to a high neptunium extraction yield (> 99%), thanks to an increase in Np(V) oxidation kinetics (reaction (1)). This positive effect of the nitric acid concentration on the extraction yield of neptunium has been verified through an alpha active test in a small pilot facility equipped with pulsed columns of 25 mm in diameter and 4 m high.

For the demonstration of the technological feasibility of this new PUREX flowsheet, an experiment based on these extraction conditions will be carried out in 2004 in the new shielded cell CBP facility of ATALANTE using 15 kg of LWR irradiated fuels. This shielded cell is equipped with 3 pulsed columns of 15 mm in diameter and 4 m high and mixer settlers.

In this flowsheet, two pulsed columns are devoted to the extraction operation in order to be representative of the residence time of the corresponding industrial extraction pulsed column which is 8 m high.

II.B. Separation of Iodine

During the fuel dissolution step (figure 1), the main part of iodine is oxidized into the molecular iodine form I_2 that is trapped (as a mixture of I^- and IO_3^- ions) from the dissolver off-gases by washing with a soda aqueous solution. The so-recovered iodine (~ 97 %) is presently discharged into the sea. At different steps of the PUREX process, some iodine is trapped onto "iodine filters" loaded with silver nitrate. So very low fractions of iodine inventory are released into the atmosphere. In order to increase the iodine global recovery yield up to 99%, a process has been developed to strip I from these solid filters.

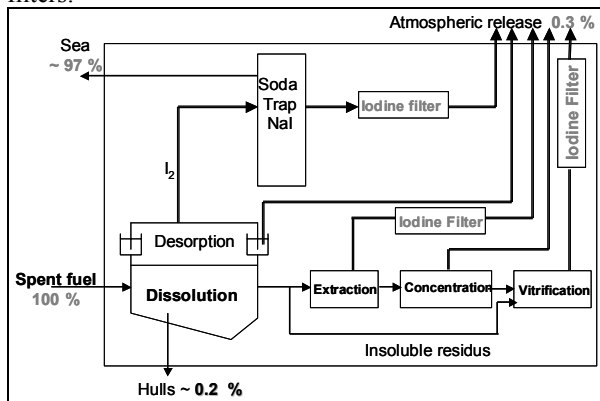


Figure 1. Behavior of iodine within the industrial operations at Cogema La Hague.

This process [4] is based on a reductive scrubbing of these solid filters using sodium ascorbate in soda medium:
 $AgI(s) + Red(aq) \rightarrow Ag(s) + I^-(aq)$

Decontamination factor higher than 100 has been obtained on simulated filter. The next step will be the test of this process on samples from iodine filters of La Hague plants. Test results are expected for the end of 2004.

Moreover, a selective process has been designed to recover and purify molecular iodine desorbed during the fuel dissolution step. This process is based on a reductive acid scrubbing of the dissolver off-gases with hydroxylammonium nitrate followed by an oxidation with hydrogen peroxide to obtain selective desorption. The

technological feasibility of this process has been demonstrated in 2001 by a test performed in a small pilot facility with an iodine recovery yield of 99 % from the dissolver off-gases [5].

II.C. Separation of Technetium

The technetium dissolution yield varies from 50 to 90 % of the Tc inventory, according to the fuel burn-up and the dissolution conditions. Technetium exists within the spent fuel dissolution liquors as Tc(VII), in the form of TcO_4^- aq, and can be co-extracted with zirconium, uranium and plutonium by TBP. As technetium catalyses the destruction of hydrazine by nitric acid, technetium can cause major dysfunctions in the uranium/plutonium splitting operation, where hydrazine is used as a Pu(III)-U(IV) stabilizer. So the flowsheet of the extraction-scrubbing operation of the 1st PUREX cycle, employed at Cogema La Hague plants, has been optimized [3] in order to minimize the technetium co-extraction with uranium and plutonium (figure 2).

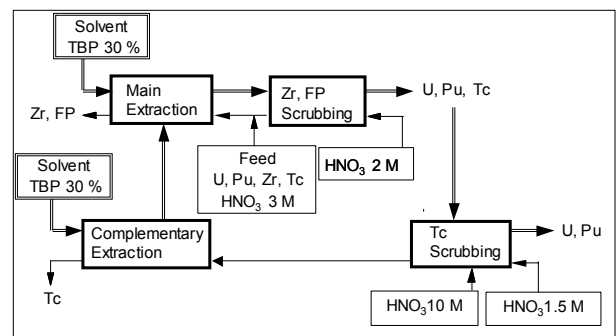


Figure 2. Flow-sheet of the 1st PUREX extraction cycle employed at Cogema La Hague.

At the exit of the "Complementary extraction step", (figure 2) more than 95 % of the soluble fraction of Tc are found purified. The research done in this field by the CEA aims at validating the process flowsheet, which should insure a Tc recovery yield corresponding to 99% of its soluble fraction. Moreover, increasing the Tc dissolution yield is also an objective to be pursued.

III. SEPARATION OF LLRNS BY NEW SOLVENT EXTRACTION PROCESSES

III.A. Separation of Americium and Curium

Owing to the complexity of the separation of americium and curium from the fission products – and notably from lanthanides – in the acidic high active raffinate, three variants of the DIAMEX-SANEX process have been studied until 2001 for the scientific feasibility demonstration step [2].

The process selected for the technological feasibility demonstration is based on:

- co-extraction of actinides and lanthanides using the DMOHEMA (DiMethyl-DiOctyl-HexylEthoxy MalonAmide), like in the extraction step of the DIAMEX process,
- followed by a selective stripping of the trivalent actinides from loaded diamide solvent using an aqueous selective complexing agent,
- and finally the stripping of the lanthanides.

This process allows the trivalent actinides and lanthanides to be coextracted and separated in a single liquid-liquid extraction cycle.

The scientific feasibility of this process has been demonstrated (recovery yield of An ~99.9 % and less than 0.3 % in mass of Ln in An) by testing a flowsheet (figure 3) in which the DIAMEX solvent was supplemented by an acidic extractant, diethylhexylphosphoric acid (HDEHP), to ensure effective extraction at pH > 2. A mixture of HEDTA (actinide-selective polyamino-carboxylate complexing agent) and citric acid (pH 3 buffer) was selected for the selective stripping of the trivalent actinides [2].

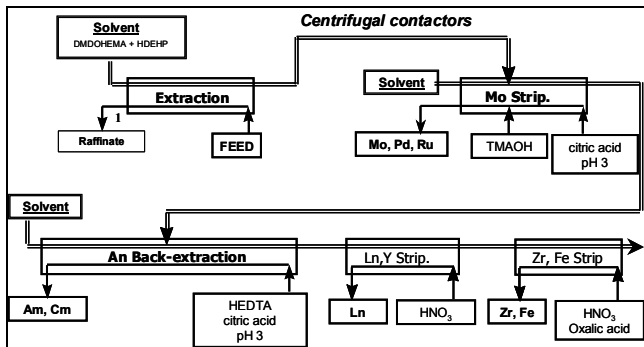


Figure 3. Flowsheet of the DIAMEX-SANEX process tested on genuine solution in 2000.

The main drawback of this flowsheet is due to the presence of the acidic extractant in the extraction step, and then the need of additional steps (figure 3) for back-extracting molybdenum, palladium and ruthenium before selectively stripping the actinides and for back-extracting zirconium and iron after lanthanides stripping. This process has been recently improved in order to remove these additional steps which induce large volumes of effluents.

This goal has been reached by splitting the solvent in two parts (acidic extractant and diamide in diluent), after the stripping of the lanthanides. The improved flowsheet is the following (figure 4):

- selective co-extraction-scrubbing of actinides and lanthanides using only the diamide in an aliphatic diluent

(first extraction-scrubbing step of the "classical" DIAMEX process [2]),

- selective stripping of the actinides with introduction of the acidic extractant at this step,
- stripping of the lanthanides,
- splitting of the two extractants, the diamide being recycled in the first step and the acidic extractant in the second step.

Acidic extractant presently under study for this process belongs to the family of dialkyl-phosphoric acids.

A new flowsheet, designed using the PAREX code, will be tested on surrogate solution by the end of 2003 in the C17 ATALANTE facility and on genuine PUREX raffinate by mid-2004 in the CBP ATALANTE facility.

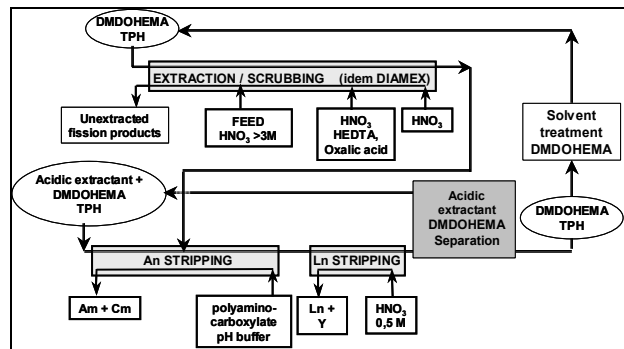


Figure 4. Principle of the improved flowsheet for the DIAMEX-SANEX process.

III.B. Americium-Curium Splitting

The process chosen for this separation is based on the difference of the affinity of the DIAMEX solvent (DMDOHEMA) for americium and curium (Am/Cm separation factor ~ 1.6). As this difference is relatively small, this process requires a large number of stages and the performances are then sensitive to flowsheet parameters. However, such a flowsheet has been successfully tested in 2002 using surrogate solution without significant difficulties.

The performances obtained during this test were as good as those calculated:

- 0.6% of Am within Cm product solution
- 0.7% of Cm within Am product solution
- 0.02% of Am and 0.01% of Cm within the stripped solvent

The technological demonstration test of this process is planned for the end of 2004 in the CBP ATALANTE facility on genuine solution issuing from the DIAMEX-SANEX test.

III.C. Separation of Cesium

The selective separation of cesium by a solvent extraction process (CCCEX) based on the use of calix-crown molecules has been studied at CEA/Cadarache.

Two tests of the following systems:

- 1,3 [di-octyloxy]-2,4-crown-6-calix[4]arene = 0.062 mol/L, TBP 1,5 mol/L in TPH,
- 1,3 [(2-4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene = 0.1 mol/L, methyloctyl-2-dimethyl-butanamide = 1 mol/L in TPH,

using a genuine HA raffinate have been carried out in the ATALANTE facility.

The flowsheet tested for the second system is presented in figure 5.

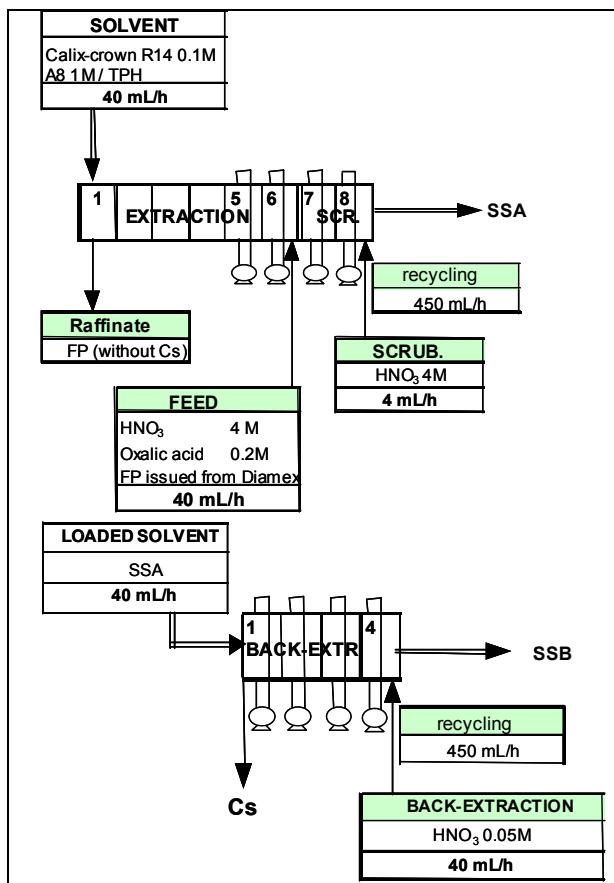


Figure 5. Flowsheet for system 2 - 1,3 [(2-4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene 0.062 M, methyloctyl-2-dimethyl-butanamide 1 M in TPH

Excellent results were obtained with the two systems tested (Cs extraction yield > 99%), thus demonstrating the scientific feasibility of the CCCEX process. For the technological demonstration feasibility of this process, hydrodynamic tests in a pulsed column and solvent degradation studies are under progress.

IV. CONCLUSION

A panel of effective partitioning processes is now available to fulfill one of the requirements of the French law of 1991, relative to high active waste management. It is now planned to demonstrate the technological feasibility of these processes through the treatment of 15 kg of genuine spent nuclear fuel in the ATALANTE facility in 2004.

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