DU COMBUSTIBLE NUCLÉAIRE AUX DÉCHETS : RECHERCHES ACTUELLES
FROM NUCLEAR FUELS TO WASTE: CURRENT RESEARCH

Separation of long-lived radionuclides from high active nuclear waste

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Abstract   The management of vitrified high activity waste issued from the reprocessing of spent nuclear fuel is often made questionable by the presence within this waste of long-lived radionuclides (LLRNs). New management scenarios of this waste are under study at the CEA since the beginning of the 1990s, involving the development of separation processes for some LLRNs. Six LLRNs are the targets of these studies; they are: (i) the minor actinides: neptunium, americium and curium; (ii) the fission products: technetium, iodine and caesium. The present paper highlights the main achievements of the research performed at the CEA in this field. ***To cite this article: C. Madic et al., C. R. Physique 3 (2002) 797–811.***
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nuclear waste / reprocessing / partitioning / long-lived radionuclides / liquid–liquid extraction

Séparation de radionucléides à vie longue des déchets nucléaires de haute activité

Résumé   La gestion à très long terme des déchets de haute activité vitrifiés issus du retraitement des combustibles nucléaires usés est souvent mise en question par la présence dans ces déchets de radionucléides à vie longue (RNVL). De nouvelles méthodes de gestion de ces déchets sont à l'étude au CEA depuis le début des années 1990, qui ont conduit à la mise au point de procédés de séparation de certains RNVL. Six RNVL font l'objet de ces recherches, ce sont : (i) les actinides mineurs : neptunium, américium et curium, et (ii) les produits de fission : technétium, iode et césium. Cet article fait le point de l'état d'avancement des recherches menées au CEA dans ce domaine. ***Pour citer cet article : C. Madic et al., C. R. Physique 3 (2002) 797–811.***
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déchets nucléaires / retraitement poussé / radionucléides à vie longue / extraction liquide–liquide

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DOSSIER

1. Introduction

High activity waste coming from the reprocessing of spent nuclear fuels is today conditioned industrially in a glass matrix for its subsequent future disposal in a deep underground repository. Even if this nuclear waste management strategy appears to be rational, the law voted by the French Parliament on 30 December 1991, asks for proposals for possible new nuclear waste management strategies [1]. If we consider, as an example, the evolution of the radiotoxic inventory of an UOx1 spent nuclear fuel (in Sieverts per TeraWatt·hour – TWhe – of produced electricity) with a burn-up of 33 GWd/$t_{\text{initial U}}$, as shown in Fig. 1, we can observe that plutonium isotopes are the major contributors, and this for a period of time up to 10^6 years. Of course, these radionuclides are not actually found in the vitrified high activity waste, because they are partially reused in the form of MOX fuels for electricity production. So, for a period of time exceeding ~70 years (see Fig. 1), the main contributors to the long-term radiotoxic inventory of the vitrified high activity waste are the α-emitting long-lived radionuclides (LLRNs) belonging to the so-called minor actinides (MAs) family:

(i)   neptunium (Np),
(ii) americium (Am) and
(iii) curium (Cm).

If we consider the situation where these long-lived radioelements would not be included in the vitrified waste, the radiotoxic inventory of this waste will be, after the few centuries time required for the decay of the most important short lived fission products, FPs (^{90}Sr and ^{137}Cs), lower than that of the quantity of natural uranium used to produce one TWhe (see Fig. 1). Consequently, the removal of the MAs from waste to be vitrified in view of their subsequent destruction into short lived and stable fission product nuclides by nuclear 'incineration' should simplify considerably the long-term management of nuclear waste. Considering now another aspect of the management of nuclear waste, i.e., the possible release and migration of radionuclides in the case of invasion of water into the deep underground repository where the vitrified waste should have been disposed, it was demonstrated that the main contribution to the dose which would be delivered in a far future to inhabitants living nearby the exhaust of the contaminated water would be given by three long-lived fission product β^- emitting radionuclides:

(i) ^{99}Tc ($t1/2 = 2.14 \times 10^5$ years),
(ii) ^{129}I ($t1/2 = 1.57 \times 10^7$ years) and
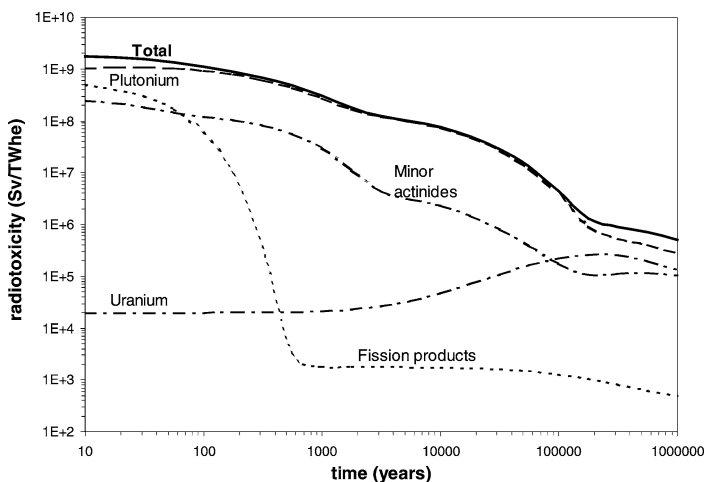(iii) ^{135}Cs ($t1/2 = 3 \times 10^6$ years).

Figure 1. Evolution of the inventory of radiotoxicity (in Sv/Twhe) of an UOx1 spent nuclear fuel (burn-up $= 33$ GWd/$t_{\text{initial U}}$).

So, the separation of the elements: technetium (Tc), iodine (I) and caesium (Cs) should also improve the long-term impact in terms of the dose of the high activity vitrified nuclear waste. For these elements, two strategies can be considered after their separation:

(i) transmutation into a stable nuclide by neutron irradiation, for ^{99}Tc,

(ii) conditioning into highly stable crystalline matrices, for I and Cs;

because for these two elements the transmutation of their long-lived radionuclides is considered too complex for an industrial implementation. So, at the beginning of the 1990s, the CEA launched a programme for the definition of processes for the separation from spent nuclear fuel of the following six elements having disturbing LLRNs:

(i) Tc,

(ii) I,

(iii) Cs,

(iv) Np,

(v) Am and

(vi) Cm.

Note that the quantities of these elements to be separated are rather limited. As an example, in the case of UOx1 spent nuclear fuel, with a burn-up of 33 GWd/$t_{\text{initial U}}$ and after a cooling period of 3 years, the quantities of these elements to be separated are (in g of element, and g of the LLRN(s), per tonne of initial U):

(i) Tc (822),

(ii) I (209, 170),

(iii) Cs (2680, 353),

(iv) Np (416),

(v) Am (323) and

(vi) Cm (26).

As hydrometallurgy, and especially the liquid–liquid solvent extraction method, is a highly efficient method which has been selected for all the facilities existing world-wide for the reprocessing of nuclear spent fuels (i.e., the so-called PUREX process), the initial strategy chosen by the CEA to define separation processes for the six elements noted above consists in:

(i) the exploitation of the capabilities of the PUREX process to separate some of these elements; this is the case for Np, I and Tc;

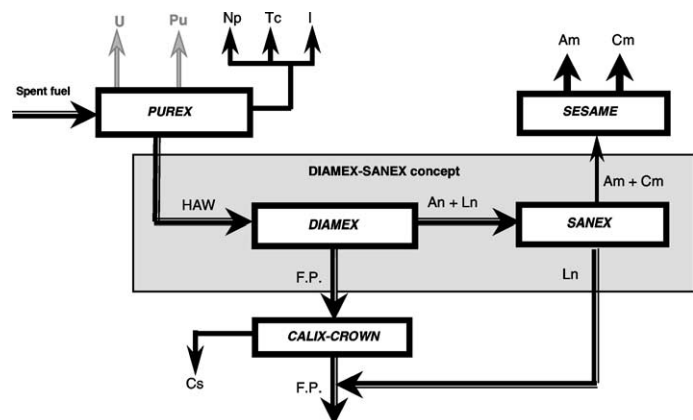(ii) the definition of new liquid–liquid solvent extraction processes for the remaining three elements: Am, Cm and Cs.

Figure 2. CEA's strategy for the partitioning of LLRNs by hydrometallurgical solvent extraction processes.

The general sketch of the processes is presented in Fig. 2. Since 1998, the CEA also considers the possibilities of pyrochemistry for the definition of separation processes for the MAs. Nevertheless, here, we will highlight only the main achievements obtained to-date in the definition of hydrometallurgical separation processes.

2. Separation of LLRNs by the PUREX process

2.1. General considerations

As mentioned above, three elements can possibly be separated using an adapted version of the PUREX process. They are:

(i) Np,

(ii) I, and

(iii) Tc.

Before describing the research done for the separation of these elements, one should recall the general chemical principles of the PUREX process. After dissolution of the spent nuclear fuel in a concentrated aqueous nitric acid solution, the dissolution liquor is contacted counter-currently with a solvent made up of a 30 vol% solution of *tri-n*-butylphosphate (TBP = $(C_4H_9O)_3P=O$) in an industrial aliphatic diluent (hydrogenated tetrapropene, TPH). For these experimental conditions, the affinity of the solvent for uranyl (U(VI)) nitrate and for plutonium(IV) (Pu(IV)) nitrate is high. The extraction of these salts proceeds according to a solvation mechanism corresponding to the following equation:

$$M^{n+}_{aq} + n\,NO^-_{3\,aq} + m\,\overline{TBP} \leftrightarrow \overline{M(NO_3)_n(TBP)_m}. \tag{1}$$
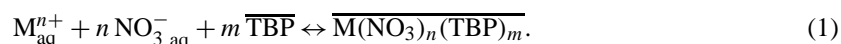
For U(VI) and Pu(IV) extracted solvates, two TBP molecules ($m = 2$) are bound to the metal ion through their phosphoryl oxygen atoms. For a high aqueous nitrate ion concentration, as found in the spent fuel dissolution liquor, the affinity of the solvent for these metallic nitrates is high. On the other hand, if the solvent containing U(VI) and Pu(IV) TBP solvates is contacted with an aqueous solution with low nitric acid concentration, the affinity of the solvent for U(VI) and Pu(IV) is low and consequently these elements are back-extracted (stripped) from the solvent. Moreover, the affinity of the solvent for most of the fission products and for the trivalent minor actinides, Am(III) and Cm(III), is low. These properties are exploited for the definition of the solvent extraction cycles of the PUREX process.

2.2. Separation of neptunium

In spent fuel dissolution liquor, Np is mostly present as Np(V) ion, $NpO^+_{2\,aq}$, for which TBP exhibits a very low affinity, whatever the nitric acid concentration of the aqueous solution. However, Np can also exist in the tetravalent (Np(IV)) and hexavalent (Np(VI)) states of which the corresponding nitrates can be extracted by TBP with affinities close to those observed for Pu(IV) or U(VI), respectively. In fact, at the La Hague plants, 25% of the Np inventory are found in the high active raffinate of the 1st PUREX extraction cycle, whereas 75% of the Np inventory are extracted and then separated from uranium at the 'uranium purification cycle'. This behaviour of the neptunium within the PUREX extraction cycles can be explained as follows. In aqueous solution, Np(V) can be oxidised by nitric acid according to Eq. (2):

$$NpO^+_{2\,aq} + \frac{3}{2}H^+_{aq} + 1/2\,NO^-_{3\,aq} \leftrightarrow NpO^{2+}_{2\,aq} + 1/2\,HNO_2 + 1/2\,H_2O. \tag{2}$$
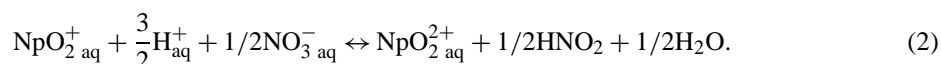
The oxidation of Np(V) to Np(VI) by nitric acid (Eq. (2)) requires the presence of nitrous acid, HNO_2, which acts as the source of the reaction catalyst. In spent fuel dissolution liquor, nitrous acid is always present to a certain extent owing to the radiolysis of the medium. In the presence of the PUREX solvent, the oxidation reaction (Eq. (2)) is shifted to the right because Np(VI) nitrate is extracted by the TBP. So,

for a better neptunium extraction yield (99% at least is expected to be extracted in the new Np management scenario), it has been calculated at Marcoule that an increase of the nitric acid concentration of the spent fuel dissolution liquor, from at present $3 \ \text{mol} \cdot \text{L}^{-1}$ to $4 \ \text{mol} \cdot \text{L}^{-1}$, will be sufficient to reach the objective of the quasi quantitative extraction of the neptunium. A demonstration of the effectiveness of the new PUREX flow-sheet will be carried out in 2003 in a hot-cell in ATALANTE facility at the CEA/Marcoule.

2.3. Separation of iodine

During industrial operations at La Hague reprocessing plant, the essential part of the iodine inventory of the spent fuel is oxidised into the I(0) form which is transferred as molecular iodine I_2 to the dissolver off-gases. Iodine is then trapped (as a mixture of iodide, I^- and iodate, IO_3^-, ions) from the dissolver off-gases by washing them with a soda aqueous solution. The iodine so-recovered is actually discharged into the sea. Very low fractions of the iodine inventory are:
 (i) trapped into I solid filters, initially loaded with silver nitrate;
(ii) released into the atmosphere.
So, the research carried out presently by the CEA consists in the definition of processes for the recovery of I from the Ag solid filters present in various workshops in the plant in order to increase the I recovery yield up to $\sim$99%. Then, the recovered iodine could be precipitated for instance as PbI_2.

2.4. Separation of technetium

The behaviour of technetium within the industrial operations at Cogema La Hague is complex. Depending on the reprocessing campaigns, the Tc dissolution yield was found to vary between 50 and 100% of the Tc inventory, whereas at the laboratory scale at the CEA, Tc dissolution yield of 90% has been observed for the treatment of an UOx1 spent nuclear fuel. During industrial operations, it was observed that between 80 to 90% of the Tc soluble fraction are recovered within the 'Tc aqueous product', which is then mixed with the high active raffinate of the first PUREX extraction cycle and then directed towards the vitrification step. In fact, Tc exists within the spent fuel dissolution liquor as Tc(VII), in the form of the pertechnetate anion, $TcO_{4 \ aq}^-$. As this anion possesses a low negative charge density, it is less solvated by water than the nitrate anion, and can thus compete with NO_3^- for the formation of TBP metallic salt solvates extracted into the organic phase. It has been shown that TcO_4^- is mainly co-extracted with the zirconium fission product ion (Zr^{4+}) at the first PUREX extraction cycle according to Eq. (3) (note that Zr^{4+} is only partly co-extracted with U and Pu):

$$Zr_{aq}^{4+} + 3 \, NO_{3 \ aq}^- + TcO_{4 \ aq}^- + m \, \overline{TBP} \leftrightarrow \overline{Zr(NO_3)_3(TcO_4)(TBP)_m}. \tag{3}$$
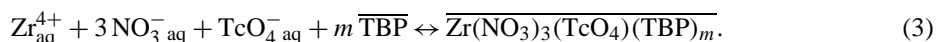
To understand better the behaviour of Tc within the PUREX process, the flow-sheet of the 1st extraction cycle is presented in Fig. 3. After the extraction step, which shows the co-extraction of Tc(VII) with Zr(IV) in the organic solvent loaded mostly with U(VI) and Pu(IV), the solvent is washed with a $2 \ \text{mol} \cdot \text{L}^{-1}$ nitric acid aqueous solution. The decrease of the concentration of the nitric acid compared with that of the feed induces a decrease of the affinity of the solvent for Zr(IV) which is tranferred back to the aqueous phase. Finally, the zirconium goes to the aqueous high active raffinate (HAR). At that step, Tc(VII) moves to an U(VI) or Pu(IV) solvate where it displaces a nitrate anion. Consequently, after the 'Zr(IV) scrub', Tc(VII) still remains in the solvent. To separate Tc from U and Pu, the solvent is then washed by a 10 mol/L nitric acid solution where, owing to the strong competition between NO_3^- and TcO_4^- anions, Tc(VII) is stripped into the aqueous solution. Small fractions of U(VI) and Pu(IV) are also stripped with Tc owing to the decrease of their distribution ratios due to the strong competition effect of nitric acid; they are then extracted by washing the Tc aqueous solution with a small flux of solvent. At the exit of the 'Complementary extraction step', most of the soluble fraction of Tc is found purified. The research done by the CEA in this field has the goal to validate the process flow-sheet aiming of being able to insure a Tc
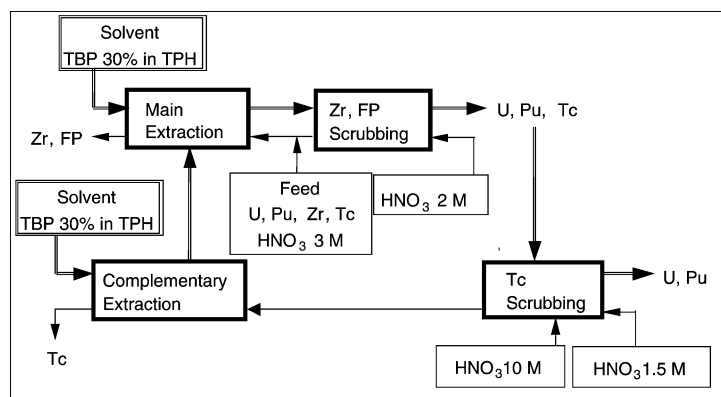
Figure 3. Flow-sheet of the 1st PUREX extraction cycle used at Cogema La Hague highlighting Tc behaviour.

recovery yield corresponding to 99% of its soluble fraction. Moreover, increasing the Tc dissolution yield is also an objective to be pursued.

## 3. Separation of LLRNs by new solvent extraction processes

3.1. Separation of americium and curium

#### 3.1.1. *General considerations*

Americium and curium are present in the acidic high active raffinates issued from the PUREX process at the trivalent oxidation state, Am(III) and Cm(III) (named thereafter actinides(III) = An(III)). The selective extraction of these An(III) nitrates is made complex owing to the large competition effect due to the presence within the high active raffinates (HARs) of the PUREX process of a high concentration of both nitric acid and trivalent lanthanide (Ln(III)) fission products, which have almost similar chemical properties to those of the An(III), and which represent about a third of the total mass of the FPs inventory. For example, the molar ratio Ln(III)/An(III) for an UOx1 spent fuel is close to 60. So, owing to the complexity of the problem, it was decided to split it into different steps. The first step consists in the co-extraction of the An(III) with the Ln(III) aiming to eliminate 2/3 of the FPs and most of the nitric acid. This step was made possible by the extraction of An(III) and Ln(III) nitrates using a diamide (malonamide) extractant: this is the so-called DIAMEX (DIAMide EXtraction) process. The second step, which consists in the An(III)/Ln(III) group separation, is certainly the most difficult to define because, as mentioned above, An(lII) and Ln(III) ions have very similar chemical properties. It was decided at the CEA to develop several processes aiming to selectively extract the An(III) from the {An(III) + Ln(III)} mixture. The common acronym chosen for these processes is SANEX, meaning Selective ActiNide EXtraction. The extractants or ligands chosen for the definition of these processes all possess soft nitrogen atoms that prefer to bind An(III) over Ln(III). The third and last step of the process consists in the separation between Am and Cm by the selective extraction of Am, by a TBP organic solvent, after its oxidation in the form of Am(VI). This process was named SESAME. The state of development of these processes is presented briefly below.

3.1.2. *The DIAMEX process*

The extraction of trivalent actinide nitrates from an HAR issued from the reprocessing of nuclear spent fuel according to the PUREX process, requires an efficient extracting agent for which the strong competition between the nitric acid and the An(III) nitrates will be minimised. The choice which was made by CEA concerns the diamide family of molecules, and particularly the malonamides (L), with the semi-developed formula:

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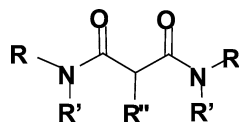
with R, R$'$ and R$''$ = alkyl, aryl or oxy-alkyl groups. It was shown that the malonamides L are bound to the An(III) and Ln(III) extracted metal ions through their two carbonyl oxygens. L extractants are thus bidendates. The extraction of M(III) (M = An and Ln) nitrates by L, in solution in the aliphatic diluent TPH, can be represented, in a first approximation, by the following equation:

$$M^{3+}_{aq} + 3\,NO^-_{3\ aq} + \overline{2L} \leftrightarrow \overline{M(NO_3)_3L_2}. \tag{4}$$
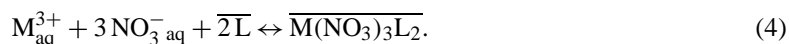
Numerous malonamide molecules were studied with different R, R$'$ and R$''$ groups, in order to optimise the extracting properties of L. The main criteria selected for the optimisation of L were:

 (i) good affinity for M(III) nitrates from acidic HARs;
 (ii) low affinity for M(III) nitrates when the loaded solvent is contacted with diluted nitric acid aqueous solution (this permits the stripping of the M(III) nitrates from the loaded solvent and then the recycling of the solvent);
 (iii) minimisation of the occurrence of third phase formation (i.e., the splitting of the organic solvent in two layers) when nitric acid and/or M(III) nitrates are extracted;
 (iv) good hydrolytic and radiolytic stabilities;
 (v) effectiveness of degraded solvent clean-up procedures by aqueous washings.

The best malonamide extractant defined so-far is the dimethyldioctylhexylethoxymalonamide (DMDO-HEMA), with R = CH$_3$, R$'$ = C$_8$H$_{17}$ and R$''$ = C$_6$H$_{13}$OC$_2$H$_4$. Several tests of the DIAMEX process based on the use of the DMDOHEMA extractant were performed in ATALANTE facility at CEA/Marcoule. The flow-sheet of the last test of the DIAMEX process, performed in 2000, and carried out with a genuine HAR in a test-loop consisting of miniature centrifugal extractors developed at Marcoule, is presented in Fig. 4 with the main results of the test. The An(III) losses in the raffinates were < 0.1% and the An(III) recovery yields > 99.9%. Of course, Ln(III) and Y(III) nitrates were extracted and found in the An(III) product solution, but the rest of the FPs was found separated, as expected, especially for the three main disturbing ones: Zr, Mo and Pd. The non-extraction of these three FPs is mainly due to the use of aqueous complexing agents, i.e., oxalic acid (for Zr and Mo removal) and hydroxyethylenediaminetriacetic acid, HEDTA (for Pd removal). Moreover, it was shown that the DMDOHEMA degradation products, generated by hydrolysis and radiolysis, are quite limited and do not exert disturbing effects on the DIAMEX process implementation. It was also demonstrated that the principles of the degraded solvent clean-up procedures are valid.

Figure 4. Flow-sheet of the DIAMEX process hot test carried out at CEA/Marcoule in 2000.
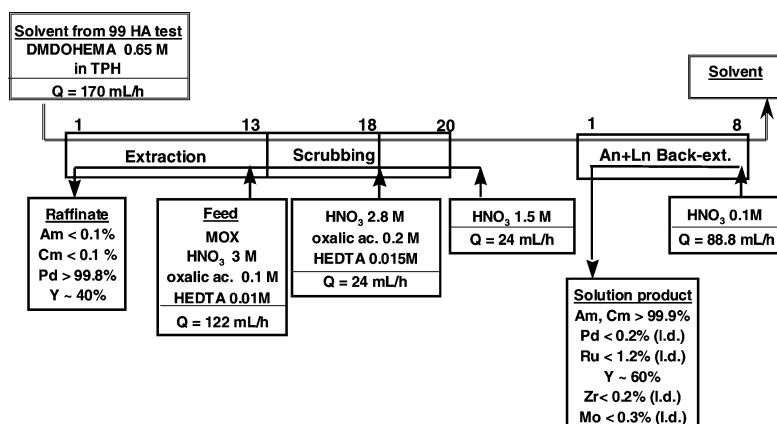
One can now conclude that the scientific feasibility of the DIAMEX process was demonstrated [2]. The present and future works in this field concern the definition of the industrial implementing conditions of the process.

3.1.3. An(III)/Ln(III) group separation: the SANEX processes

3.1.3.1. *General considerations*

It is well known that the actinides ($5f$ elements) and the lanthanides ($4f$ elements) possess close chemical properties in their trivalent oxidation states:
 (i) the size of the ions are similar;
 (ii) they are highly hydrated in water, with 9 to 8 water molecules in the inner-shell of ion co-ordination sphere, from the beginning to the end of the series of elements;
(iii) they react principally with O-bearing ligands, as they are considered as hard acids in the Pearson classification of 'hard and soft acids and bases' (HSAB) [3].

Nevertheless, possibilities exist to discriminate between these two series of M(III) ions owing to the fact that the spatial extension of the $5f$ orbitals of the An(III) ions are slightly larger than those of the $4f$ orbitals of the corresponding Ln(III) ions. This property can be exploited to design specific ligands for An(III). In fact, it has been shown that soft donor ligands, bearing several N or S atoms, prefer to bind An(III) over Ln(III) [4]. At the CEA, we have chosen N-ligands and studied three systems for the design of An(III)/Ln(III) group separation processes, known as SANEX processes:
 (i) the first system, which uses a N-ligand, is able to perform the separation by selectively extracting the An(III) from an acidic feed ($[HNO_3] = 0.5$ to $1\ mol \cdot L^{-1}$) containing the {An(III) + Ln(III)} mixture which is the product generated by the DIAMEX process;
 (ii) the second system also uses a nitrogen ligand L for the selective An(III) extraction, but in this case, as L is not an extractant able by itself to extract An(III) nitrates, it is consequently mixed with an acidic extractant, a lipophilic carboxylic acid. To obtain sufficient An(III) extraction distribution ratios $D_{An(III)}$, it is necessary to neutralise the nitric acid of the {An(III) + Ln(III)} mixture issued from the DIAMEX process, and to use a pH buffer;
(iii) the third system studied is totally different from the two others. It consists in a modification of the DIAMEX process, with the addition of an acidic organophosphorous extractant to the diamide DMDOHEMA in the solvent. In this case, the An(III)/Ln(III) separation is carried out by the selective stripping of the An(III) from the loaded solvent under the complexing effect of a N-bearing aqueous selective ligand.

The main achievements obtained for these three routes for An(III)/Ln(III) separation are briefly presented below.

3.1.3.2. *SANEX, route 1: the BTPs*

The Bis-Triazinyl-Pyridine (BTP) extractants have been discovered by Kolarik et al. [5] in the framework of the NEWPART European research programme (1996–1999) co-ordinated by CEA-Marcoule [2]. The semi-developed formula of the BTPs is the following:
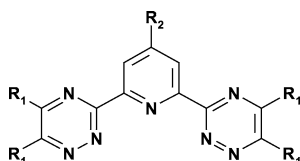
where R_1 and R_2 are alkyl groups.

The BTP ligands are able to extract selectively the An(III) nitrates from nitric acid solutions up to $2\ mol \cdot L^{-1}$. The separation factor (SF) between two corresponding M(III) ions, e.g., Am(III) and Eu(III), ($SF_{Am/Eu} = D_{Am}/D_{Eu}$, with D_{Am} and D_{Eu} the distribution ratios of Am(III) and Eu(III), respectively), is

more than two orders of magnitude, which is unique for highly acidic conditions. The extraction of An(III) nitrates by BTPs (L) in octanol corresponds to the following equation:

$$An_{aq}^{3+} + 3\,NO_{3\ aq}^{-} + \overline{3\,L} \leftrightarrow \overline{AnL_3(NO_3)_3}. \tag{5}$$
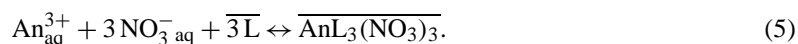
Note that octanol was chosen as the diluent instead of a more traditional aliphatic one, owing to solubility reasons of the BTP extractant and its solvates (poor solubilities observed in aliphatic diluents).

Crystal structures of U(III) and Ln(III) BTP solvates have been determined [6,7]. These structures show that:

(i) the three BTP ligands are each bound to the M(III) ion through 3 nitrogen atoms. BTP is thus a tridendate extractant;

(ii) the co-ordination sphere of the M(III) ions are composed exclusively of N atoms from the BTP molecules, leading to a co-ordination number (CN) equal to nine;

(iii) the nitrate ions are not bound to the M(III) ions;

(iv) the average M(III)-N distances are shorter for U(III)-BTP complex than for the Ce(III)-BTP corresponding complex.

This should correspond to the fact that, in case of An(III) complexes, part of the bonds with the BTP nitrogen atoms are of a covalent nature. This is correlated to the property mentioned above of the largest spatial extension of the $5f$ orbitals of the An(III) ions compared to those of the $4f$ orbitals of the corresponding Ln(III) ions.

SANEX processes based on the use of BTP extractants have been designed and tested. The first process used the nPr-BTP (with $R_1 = n$-propyl group and $R_2 = H$). If the main results of the hot tests performed both at CEA/Marcoule and ITU (FZ-Karlsruhe, Germany) were satisfactory, it was found that the stability of the nPr-BTP was not as good as expected. Laboratory studies then undertaken demonstrated that the fragile points of the nPr-BTP molecule with respect to hydrolysis and radiolysis are the carbon atoms in α positions on the R_1 groups. So, a second BTP ligand was chosen with branched R_1 groups, the iPr-BTP ($R_1 = i$-propyl group and $R_2 = H$), with steric hindrance on the R_1 α-carbons to minimise the degradation of the ligand. Laboratory experiments demonstrated the good stability of this BTP molecule. To design a SANEX process based on the use of iPr-BTP, it was necessary to define a solvent formulation including a phase transfer catalyst, in order to speed-up the kinetics of extraction of An(III) nitrates. The phase transfer catalyst selected was the malonamide, DMDOHEMA, the extractant of the DIAMEX process. In fact, when used alone in an aliphatic/alcohol mixture solvent, iPr-BTP was found to extract slowly An(III) nitrates, while for the same conditions An(III) extraction by nPr-BTP was rapid. Up to now, we do not have any explanation to interpret these differences in the kinetics of An(III) extraction with, apparently, very similar extractants.

Figure 5. Flow-sheet of the SANEX-iPrBTP process tested at CEA/Marcoule in 2001.
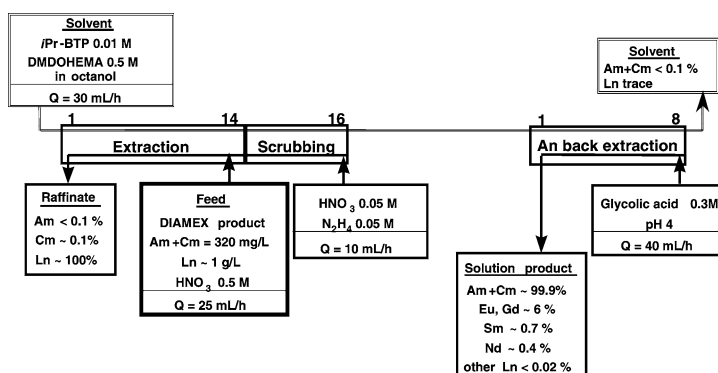
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Fig. 5 shows the flow-sheet of the test of the 'SANEX, route 1' process, performed at CEA/Marcoule in June 2001. Results of the tests were quite encouraging: (i) high An(III) recovery yields; and (ii) high An(III) decontamination with respect to Ln(III), were obtained. Nevertheless, the iPr-BTP was found slightly degraded after the test. So, more work is needed in this 'SANEX route 1' domain in order to design a more robust BTP extractant.

3.1.3.3. *SANEX, route 2*

The synergistic mixture used for the selective An(III) extraction for this 'SANEX route 2' process is composed of:

(i) a terdendate nitrogen ligand (L), the 2-(3,5,5-trimethylhexanoyl-amino)-4,6-di(pyridyl-2-yl)-1,3,5 triazine (TMHADPTZ) with the following semi-developed formula:
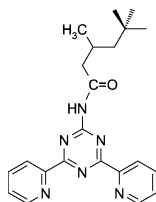
(ii) the octanoïc acid, $C_7H_{15}COOH$, (HA), which is present in a dimeric form $((HA)_2)$ in the solvent.

This mixture of extractants is dissolved in TPH. It was shown that the An(III) extraction proceeds through a cation exchange mechanism according to the following equation:

$$An_{aq}^{3+} + \overline{L} + \overline{3(HA)_2} \leftrightarrow \overline{AnL(HA_2)_3} + 3\,H_{aq}^+. \tag{6}$$
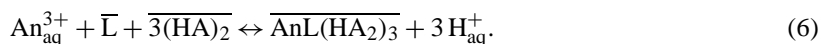
To obtain distribution ratios for An(III) ions sufficient for their extraction, the acidity of the mixture of {An(III) + Ln(III)} must be adjusted in the pH range. Without the use of a pH buffer for doing this, the $D_{An(III)}$ values will vary with the third power of pH; in this case, $D_{An(III)}$ will be very difficult to control within the process. So, for pH control, a pH buffer was selected. It consists of a glycolic acid/Na glycolate mixture. For this system, moderate $SF_{An/Ln}$ (close to 10) were obtained, being one order of magnitude lower than those corresponding to the BTP extractants, but nevertheless sufficient for designing an An(III)/Ln(III) separation process. Of course, more extraction stages will be required for implementing this second SANEX process. Fig. 6 presents the flow-sheet of the 'SANEX route 2' process which was developed and tested on genuine HAR at CEA/Marcoule. Fig. 6 shows also the main experimental results:

(i) losses of Am and Cm within the raffinate;

(ii) recovery yields of Am and Cm;

(iii) level of contamination of the Am + Cm product with respect to some Ln(III) ions. These results are excellent, but it was noted that the implementation of the process is difficult.

3.1.3.4. *SANEX route 3: the PALADIN process*

The third SANEX route for An(III)/Ln(III) separation, named PALADIN, is totally different from the two other routes. It consists in using a modified DIAMEX solvent and to perform the An(III)/Ln(III) separation by the selective strip of the An(III) under the complexing effect of an aqueous ligand. The solvent used for this system consists of a mixture of DMDOHEMA, malonamide used for the DIAMEX process, and *di*-2-ethylhexylphosphoric acid, the well-known extractant HDEHP in TPH. When the solvent is contacted with an HAR, An(III) and Ln(III) nitrates are extracted by the DMDOHEMA, but other metal ions of the FPs, such as, Mo(VI), Pd(II), Zr(IV), and Fe(III) (corrosion product), are also extracted by the HDEHP. Then, the loaded solvent is submitted to several stripping steps:

(i) the first strip concerns Mo(VI) and Pd(II) which are back-extracted under the complexing action of a citrate aqueous solution;

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Figure 6. Flow-sheet of the SANEX, route 2 process tested at CEA/Marcoule in 2000.
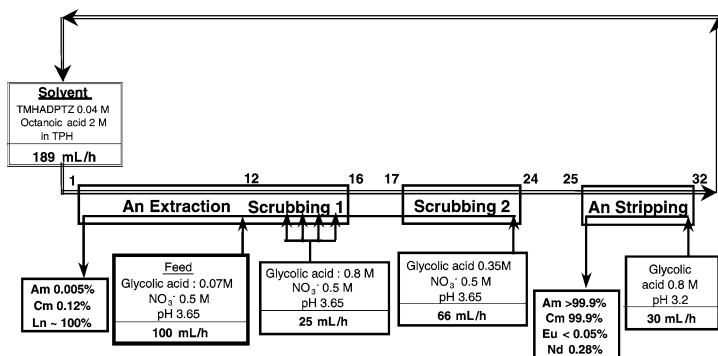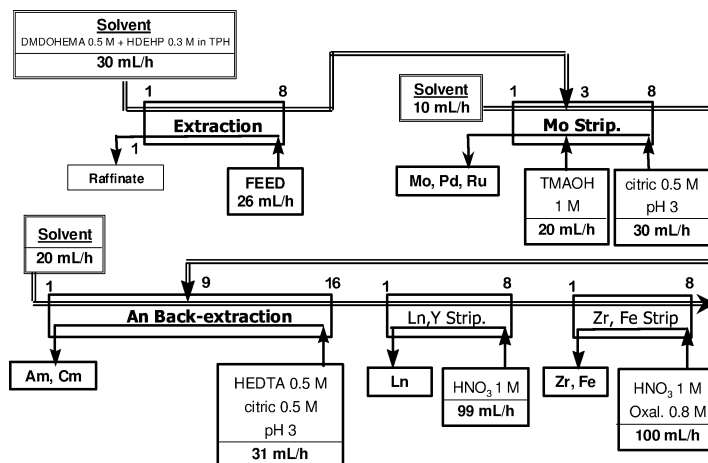
Figure 7. Flow-sheet of the PALADIN process tested at CEA/Marcoule in 2000.

(ii) the second strip concerns the An(III). This was achieved by contacting the solvent with an aqueous solution containing the An(III) selective complexing ligand, hydroxy-ethylenediaminotriacetic acid (HEDTA) (in presence of a citric acid buffer). For the pH selected (equal to 3), the Ln(III) ions, which were initially bound to the malonamide extractant, DMDOHEMA, remained in the solvent bound to the HDEHP extractant. It is why HDEHP is needed;

(iii) the third strip concerns the Ln(III) ions. This was achieved by using a 1 mol/L nitric acid aqueous solution;

(iv) the last strip concerns Zr(IV) and Fe(III) ions.

Fig. 7 presents the flow-sheet of this PALADIN process which was tested on genuine HAR at the CEA/Marcoule. The overall performance of the test was excellent:

(i) Am recovery yield > 99.9%;

(ii) Cm recovery yield > 99.7%;

(iii) (Am + Cm) decontamination factor for Ln > 800.

The main drawback identified for this process concerns the large volume of aqueous effluents generated: about ten times the volume of the treated HAR. In spite of this drawback, this process is considered as having large potentialities for improvement. Work in this direction is in progress at the CEA/Marcoule.

3.1.4. *Am/Cm separation: the SESAME process*

Contrary to Cm, Am can be oxidised in aqueous solutions at oxidation states higher than III, i.e., IV, V and VI. Nevertheless, these Am oxidation states are thermodynamically unstable in acidic aqueous solutions. The way selected to design an Am/Cm separation process consists in:

 (i) defining an efficient oxidation step of Am(III) to Am(VI) ($AmO_2^{2+}{}_{aq}$ ion) from nitric acid solution. During this step, Cm will remain on the initial Cm(III) form;

 (ii) the selective extraction of Am(VI) by a TBP solvent. Am(VI) nitrate extraction behaviour is similar to that of the U(VI) nitrate (cf. the PUREX process and Eq. (1)).

To permit the oxidation step, lacunary heteropolyanion, such as the phosphotungstate, $P_2W_{17}O_{61}^{10-}$ or the silicotungstate, $SiW_{11}O_{39}^{8-}$ (named hereafter PW, and SiW, respectively), were added to the nitric acid solution containing the {Am(III) + Cm(III)} mixture in order to decrease drastically the redox potential of the Am(IV)/Am(III) couple, owing to the large stability of the Am(IV) complexes formed with the PW and SiW ligands, and then to allow possible the oxidation of Am(III) to Am(IV) (complexed) by electrochemical or chemical means. The electrochemical method was chosen, but Ag(I) ion was added to the solution in order to serve as a redox mediator (Ag(II)/Ag(I) redox couple) for Am oxidation. If Am is oxidised into the 1/1 Am(IV)-PW (or SiW) complex, this complex evolves and Am is transformed into Am(VI) americyl ion, $AmO_2^{2+}{}_{aq}$, not bound to PW nor to SiW ligands. Thus, after a 100% conversion of Am into Am(VI), its extraction by TBP can be carried out. If too much PW or SiW ligand is added to the solution, Am is oxidised into the *bis* Am(IV)(PW)$_2$ (or Am(IV)(SiW)$_2$) complex which does not evolve into Am(VI). So, a precise control of the molar ratio PW(or SiW)/Am in the solution to be oxidised is required. The extraction step is also difficult to implemente because of the redox instability of Am(VI) which can be reduced back to Am(V) or Am(III), which are not extracted by TBP. To prevent such a drawback, the extraction steps should be carried out as quickly as possible with contactors such as centrifugal extractors with low residence time of the two phases. Several tests of the SESAME process have been carried out at Marcoule [8]. If the results of these tests were encouraging, the process was nevertheless not sufficiently robust; so the CEA is now considering the development of a novel option for the Am/Cm separation.

3.2. Separation of caesium: the calix-crown process

In order to selectively extract Cs^+ from acidic HARs, Dozol at CEA/Cadarache chose to design extracting agents in the domain of supramolecular chemistry. This work was part of a European research programme co-ordinated by Dozol [9]. The family of molecules which was selected consists of the well known crown-ethers, possessing ether-O atoms able to saturate the inner co-ordination sphere of the Cs^+ ion. As the caesium aqua complex possesses six water molecules in the inner co-ordination sphere $(Cs(H_2O)_6^+)$, six ether-O were selected for the crown-ether expected to be able to displace the six water molecules when extracting Cs^+. Moreover, in order to pre-organise the crown-ether for better Cs affinity and selectivity, the crown-ether moiety was branched onto a 1,3 alternate calix[4]arene platform. One or two crown-ether moieties were grafted on the lower rim of the calixarene platform leading to the new calix-*mono*-crown and calix-*bis*-crown ligands. It was found that 10^{-2} mol $\cdot$ L^{-1} calix-crown solution in the diluent nitrophenylhexylether possesses large affinity for Cs^+ from HARs with high nitric acid concentrations, and small affinity for Cs^+ when the nitric acid concentration of the aqueous solution is low. These properties are well suited for the definition of a Cs extraction process:

 (i) extraction of Cs^+ from acidic HAR;

(ii) stripping of Cs^+ from the loaded solvent with water.

The equation for the extraction of Cs^+ by a calix-crown extractant L is the following:

$$Cs^+_{aq} + NO_3^-{}_{aq} + \overline{L} \leftrightarrow \overline{CsL^+, NO_3^-}. \qquad (7)$$
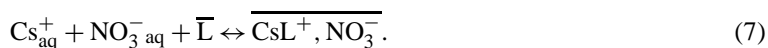
Owing to the fact that the diluent possesses a high dielectric constant, the Cs nitrate extracted complex is likely to be of the form of an ion-pair. Crystal structures of Cs-calixcrown complexes have been determined. These structures show that Cs^+ is within the crown cavity bound to the six ether-O atoms of the crown moiety. Moreover, it seems that two phenyl rings of the calix platform also interact with the Cs^+ leading certainly to a higher interaction energy between the ion and the ligand and also to a better selectivity. Note that the selectivity for Cs^+ of these calix-crown molecules is tremendously high. For example $SF_{Cs/Na}$ equal to $\sim 5 \times 10^4$ have been observed for some extractants, which is a unique property [10].

Simon and Dozol at CEA/Cadarache developed a Cs^+ liquid-liquid extraction process. Two calix-crown were chosen for this study:
 (i) 1,3 [di-octyloxyl]-2,4-crown-6calix[4]arene (L^1); and
 (ii) 1,3 [(2-4diethyl-heptylethoxy)oxy]-2,4-crown-6calix[4]arene (L^2).
Two solvent compositions were studied:
 (i) $L^1 = 0.1$ mol/L, TBP $= 1.5$ mol$\cdot L^{-1}$ in the industrial aliphatic diluent TPH;
 (ii) $L^2 = 0.1$ mol$\cdot L^{-1}$, methyloctyl-2-dimethylbutanamide $= 1$ mol$\cdot L^{-1}$ in TPH.
In these solvent formulations, the TBP and the monoamide serve only as modifiers in order to prevent third phase formation. A test of the system 2, implemented using genuine HAR, has been carried out at CEA/Marcoule in the framework of a collaboration between Cadarache and Marcoule teams. Excellent results were obtained demonstrating the scientific feasibility of the calix-crown Cs^+ extraction process. Work is now underway to define the industrial implementation conditions of the process.

4. Conclusions

Much progress has been made in the domain of the separation of LLRNs from HAR issued from the reprocessing of nuclear spent fuels. It was shown that the potentialities of the PUREX process can be exploited for the recovery of Np, I and Tc. The efficiencies of the new solvent extraction processes that have been developed for the separation of Am, Cm and Cs have most often been demonstrated during tests performed with genuine effluents. Nevertheless, some efforts are still required for solving the few problems which remain. All the research work carried out by CEA benefited from numerous collaborations, such as in France:
 (i) the Groupe de recherches named PRACTIS, co-sponsored by CNRS (IN2P3 and DSC), EdF, ANDRA and CEA (DEN), which involves 38 laboratories from the CNRS, Universities and the CEA,
 (ii) Université Louis Pasteur, Strasbourg,
 (iii) École Nationale Supérieure de Chimie, Paris (ENSCP);
In Western Europe with the collaborations:
 (i) NEWPART (1996–1999),
 (ii) PARTNEW (2000–2003) and
 (iii) CALIXPART;
In the rest of the world:
 (i) JNC and JAERI in Japan, and
 (ii) IPC Moscow, Russia.
New collaborations also have been established recently with the American DOE. So, if required, it will certainly be possible in the future to define new nuclear waste management scenarios including the partitioning of LLRNs.

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Discussion

Questions de J.P. Martin

(1) Quelle est la durée de vie de l'iode rejeté en mer ?
(2) Quel est l'intérêt de séparer les actinides mineurs ?
(3) Et le Césium ?

Réponse de C. Madic

(1) La période radioactive de l'iode-129 (^{129}I), actuellement rejeté en mer, est égale à 15,7 millions d'années.
(2) L'intérêt de séparer les actinides mineurs, neptunium, américium et curium, est de permettre leur transmutation ultérieure en nucléides stables ou à vies courtes, ce qui aura pour effet de diminuer de manière drastique la radiotoxicité à long terme des déchets ultimes vitrifiés.
(3) Le césium séparé n'est pas destiné à être transmuté car ceci se traduirait par une augmentation de la quantité du nucléide à vie longue posant problème, ^{135}Cs, de période radioactive égale à $t1/2 = 2,3$ millions d'années, par capture de neutrons par les nucléides de césium de masse inférieures. Il n'est pas envisagé de réaliser une séparation isotopique de ^{135}Cs car une telle opération serait certainement trop onéreuse. Le devenir du césium séparé est d'être conditionné dans une matrice solide, sans doute cristalline, dont les capacités de confinement du césium serait meilleure que celle du verre nucléaire industriel actuel.

Remarque de R. Dautray

La radioactivité totale de l'iode 129 dans le stockage est très faible, quelques dizaines de Ci, à comparer aux milliards de Ci qui y sont stockés.

Réponse de C. Madic

Je n'ai pas de réponse suite à la remarque de M. Dautray. Je propose néanmoins que le temps futur soit employé pour les verbes de la remarque de M. Dautray.

Remarque de H. Métivier

Pour aller dans le sens de M. Dautray, je rappellerai que si seul l'isotope 1129 de l'iode existait, la thyroïde qui contient au maximum 10 à 15 mg d'iode, contiendrait au maximum de 65 000 à 100 000 Bq d'iode 129.

Un scénario très pessimiste a été étudié par Malarbet et al. (Radioprotection 1998, 33 (1) 15–33); il correspond à l'incorporation dans l'eau de boisson quotidienne de 100 μg d'iode (80 % iode 129, 20 % iode 127) qui viendraient s'ajouter à l'iode non radioactif dans l'alimentation solide : la dose équivalente engagée à la thyroïde est de 370 μSv et la dose efficace engagée de 18,1 μSv.

Réponse de C. Madic

Je n'ai pas de réponse suite à la remarque de M. Métivier. Il faudrait néanmoins demander à M. Métivier de préciser quelle est la durée prise en compte pour les valeurs de doses engagées mentionnées (370 μSV et 181 μSV).