

### Radiation chemistry at the core of the spent nuclear fuel recycling

**Abstract** In the current energetic context, nuclear energy plays an important role as a carbon emission abating energy source: a wave of renewed interest has been observed worldwide. To develop a clean and sustainable energy and obtain the general public acceptance, management of the nuclear waste has been optimized by recycling valuable elements such as uranium and plutonium. Since its first industrial implementation in 1954, the PUREX (Plutonium Uranium Redox Extraction) process has been at the center of nuclear industry as a reference for spent nuclear fuel reprocessing. This process is still under development, aiming at recovering the minor actinides, but it always relies on the use of the tributylphosphate (TBP) ion in hydrocarbon solvents and nitric acid as extractant media. For further enhancement of extraction efficiency, separation factors and effective storage of nuclear waste, a predictive understanding of the radiolytic degradation of these solvents is required. This paper presents the ionizing radiation induced chemical processes on these ligands, and the issues posed by the presence of highly reactive intermediate species and/or the generation of degradation products that control for instance the solvent extraction efficiency.

**Keywords** Reprocessing, radiolysis, TBP,  $\text{HNO}_3$ , solvent extraction efficiency, La Hague.

#### Résumé La chimie des rayonnements au cœur du recyclage du combustible nucléaire

Dans le contexte énergétique actuel, l'énergie nucléaire connaît un regain d'intérêt dans le monde entier, qui vient notamment du fait qu'elle émet très peu de gaz à effet de serre. Pour développer une énergie propre et durable et obtenir l'acceptation du public, le recyclage de certains éléments radioactifs du combustible nucléaire des centrales a été mis au point et optimisé. Le procédé PUREX est ainsi devenu le procédé de référence pour le retraitement du combustible nucléaire irradié. Depuis sa première mise en service industrielle en 1954, il repose sur le principe de l'extraction liquide/liquide de l'uranium et du plutonium en milieu acide nitrique par le tributylphosphate (TBP) dissout dans un solvant organique. Pour assurer la sûreté du procédé, remplacer les solvants au moment optimal, améliorer l'efficacité de l'extraction, augmenter les facteurs de séparation et optimiser le stockage des déchets nucléaires, une compréhension fine de la dégradation radiolytique de ces solvants soumis aux rayonnements ionisants des isotopes est nécessaire. Cet article présente les mécanismes chimiques induits par les rayonnements ionisants sur ces ligands, ainsi que les problèmes posés par la présence d'espèces intermédiaires fortement réactives et par la formation de produits de dégradation qui peuvent s'accumuler dans les solvants.

**Mots-clés** Retraitement, radiolyse, TBP,  $\text{HNO}_3$ , solvant, efficacité d'extraction, La Hague.

#### Why choose nuclear energy?

The 2016 Paris agreement signed by 175 countries represents an engagement to strengthen the global response to the threat of global warming and to keep a temperature rise this century of less than 2 °C above the pre-industrial level [1]. By acknowledging the climate change as a common threat for humankind, it draws attention to the need for a new technological framework to be put into place. In accounting for anthropogenic emissions, the largest source of greenhouse gas emissions from human activities is from burning fossil fuel for electricity, heating and transportation, underlining the need for an enhanced deployment of renewable energy. According to the Intergovernmental Panel on Climate Change, worldwide emissions of  $\text{CO}_2$  yield  $27 \times 10^9$  tons (Gt) from multiple sources, with electrical power generation contributing to 10 Gt, or 37% of global emissions, without taking into account an estimated electricity demand increase of 48% over the next 20 years [2]. An assessment of the greenhouse gas emissions of different electricity generation sources (nuclear, coal, natural gas, oil, etc.) has shown that the nuclear energy's lifecycle emissions represents only 7% of the emission intensity of natural gas and 3% of coal based power plants. The European current strategy places renewable energy (wind and solar) in a key role; it represents

about 25% of the electricity production mix today, with its market share predicted to increase. Recent simulations based on 2015 hourly data from France's electricity transmission network operator show that an over-injection of subsidized renewable intermittent energy sources will destabilize the energy market [3]. Therefore, there is a real need for the establishment of a reform of the energy market, where the nuclear energy would still play an important role as a virtually  $\text{CO}_2$  benign source [4], by providing access to clean, reliable and affordable energy. This kind of energy currently supplies 75% of the total electricity in France, and 10% in the world (data in 2019) [2]. Currently, 30 countries use nuclear power and 28 other are considering, planning or actively working on including it in their energy mix. Countries like Bangladesh, Turkey and Egypt have already started to construct nuclear reactors, while Belarus and United Arab Emirates are opening their first reactors in 2020 [5].

Turning to nuclear energy as driver of economic growth and mitigator of climate change means management of increasing spent fuel arising from nuclear power production. This issue is important due to the associated political, economic and societal implications and due to the public acceptance as a critical factor. Proposals set forth by the IAEA (International Atomic Energy Agency) and other different governments or governmental associations worldwide underline the need for

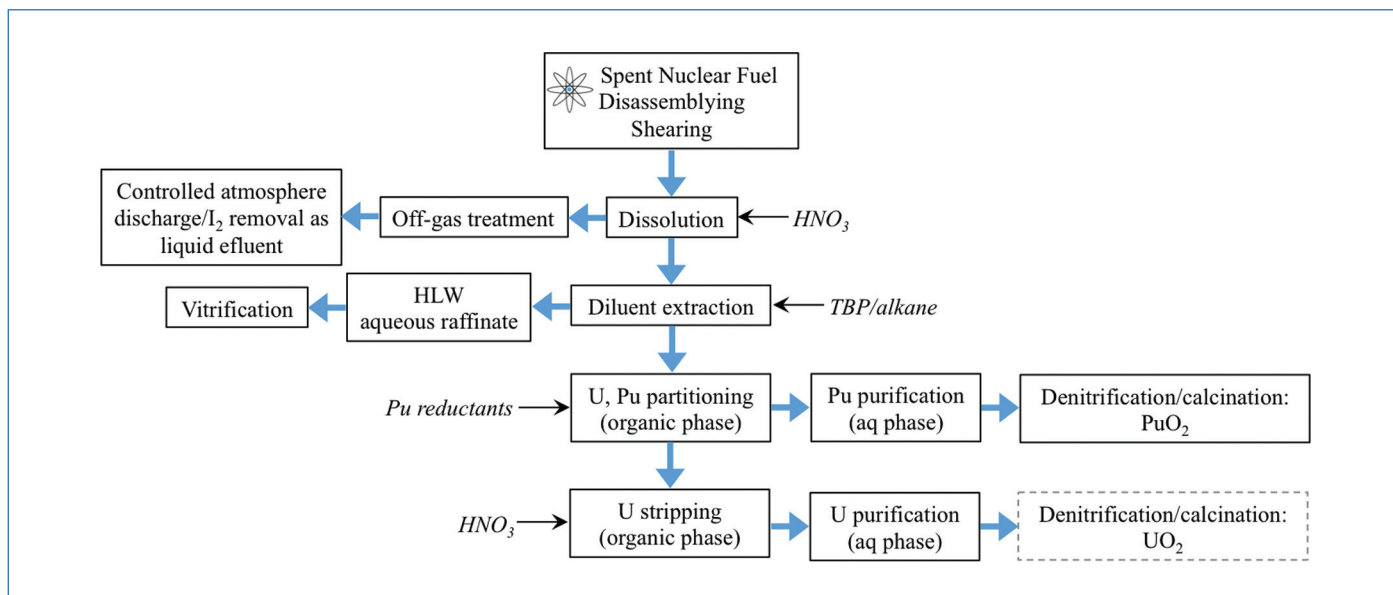


Figure 1 - PUREX technology flowsheet (dashed area: separated U to  $\text{UO}_2$  conversion is operating plant-dependent).

development of innovative means for closing (as much as possible) the nuclear fuel cycle for a sustainable nuclear development. The back-end of the fuel cycle concerns the safe, secure and sustainable management of spent fuel, by either storing or disposing it. After withdrawal from the nuclear power plant, spent fuel is reprocessed in order to recycle the valuable uranium and plutonium elements to manufacture new fuel and to vitrify the non-valuable nuclear material to dispose the waste in geological repositories [6].

### Development of reprocessing technologies

Since the 40's, nuclear fuel has been reprocessed for military purposes using the bismuth phosphate ( $\text{BiPO}_4$ ) co-precipitation process [7] developed at the University of California Berkley/RadLab. The inability to recover uranium and the large volumes of waste generated using this process shifted the research direction to hydrometallurgical processes. The first redox processes for U/Pu separation used methyl(isobutyl) ketone in aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ ) [8-9] and was deployed on an industrial scale in the Hanford plant (Washington, USA). In the UK, the first reprocessing plant started operating in 1952 at Sellafield, using a process based on dibutyl carbitol (Butex process) as solvent and nitric acid [10]. The next step in reprocessing technology was the use of the extractant tri-n-butyl phosphate that has been proved to be a better solvent than the previous ones used. It is moreover relatively cheap, more stable and hardly flammable, yielding better separation factors and limiting the losses of Pu to waste streams [11-12]. The PUREX (Plutonium Uranium Redox Extraction) process, which still remains the industry standard, quickly took over and was used in 1954 at Aiken (South Carolina, USA), and the first commercial reprocessing plant was commissioned in the USA in 1966. Many countries have commissioned their own reprocessing plant: France in 1958, UK in 1964, Russia in 1948 and in 1977, Japan in 1977 and Belgium along with a consortium of 13 OECD countries between 1957 and 1974. Currently, the largest reprocessing capacity exists in France and in the UK. The La Hague site in France consists of two reprocessing plants (UP-2 and UP-3) with a combined capacity of 1700 tHM<sup>(1)</sup>/year. In the UK,

the Thermal Oxide Reprocessing Plant (THORP) and the B205 plant at Sellafield have a nominal capacity of 1200 tHM of LWR (light water reactor) and 1500 tHM/year of Magnox spent fuels, respectively. The composition, heat discharge and radioactivity per tHM of spent fuel depend on the burn-up and on its initial composition, on the design of the pins and the fuel elements, their positions in the reactor during operation, as well as the cooling time after removal from the reactor [13-14].

The PUREX chemical process aims at partitioning and separating the fissile nuclides  $^{235}\text{U}$  and  $^{239}\text{Pu}$  to be reused for the fabrication of mixed-oxide fuel (MOX) or of inert matrix fuel (IMF) [15]. This process uses tributylphosphate ( $\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$ , TBP) dissolved in an aliphatic diluent (called TPH, a mixture of various alkanes) to co-extract U(VI) and Pu(IV) from a nitric acid solution (3-4 M  $\text{HNO}_3$ ) leaving the bulk of the non-volatile fission products, including the trivalent lanthanides, in the aqueous phase [16]. The PUREX process produces two streams: one containing the chemically purified uranium, and the other containing the chemically purified plutonium. The aqueous refining waste stream contains the vast majority of the fission products, the minor actinides, and traces of U and Pu lost during the processing. This aqueous refining waste stream is treated as long-lived high-level nuclear waste (LL-HLW<sup>(2)</sup>): it is evaporated to dryness and the residue is melted with inert glass, forming solid vitreous LL-HLW packages.

The PUREX process starts with the shearing of spent nuclear fuel (SNF), removal of the cladding and dissolution of the oxide fuel in nitric acid [17]. During this step, particles,  $\text{NO}_x$  and volatile fission products (Kr, Xe,  $\text{I}_2$ , tritium and  $\text{RuO}_4$ ) are released and treated in an off-gas scrubber system designed to limit their emissions to legally authorized quantities. The dissolution step in nitric acid is followed by the extraction and partitioning of Pu(IV) and U(VI) in the first extraction cycle using 30% TBP in an alkane diluent; then Pu(IV) and U(VI) are purified using a multiple cycle process. Finally, depending on the operating facility, both U and Pu fractions, or only Pu fraction are converted to oxides by denitrification followed by calcination [18-19]. A simplified diagram of the principles of the PUREX reprocessing technology is presented in figure 1.

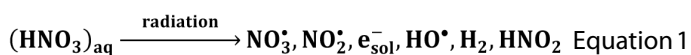
The activity levels associated with the reprocessing of SNF are very high, and the solvents involved in the PUREX process will undergo radiolysis and degrade, leading to modified organic molecules in the process phases and to accelerated corrosion rates of equipment used in the technological process [20-21]. The ionizing radiation comes mainly from the actinides solutions: high activity levels of  $\beta$  and  $\gamma$  radiation are coming from short and intermediate-lived fission products (FP) ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ) and high LET<sup>(3)</sup>  $\alpha$  radiation arises from long-lived FP ( $^{239}\text{Pu}$ ,  $^{237}\text{Np}$ ). However, radiation originates also from the solid phase and the gas phase associated with  $\alpha$  emitters like  $^{242}\text{Cm}$  and  $^{238}\text{Pu}$ .

All these degradation products from the extractant, the organic diluent and  $\text{HNO}_3$  can interfere with the separation process, decreasing fission products decontamination efficiency; this implies that their quantification is necessary for defining safety regulations [22-23]. An efficient partitioning process requires knowledge of the mechanisms and kinetics of radiolysis, the effects of ionizing radiation on the separation process itself and on the materials used in the process: it may be a critical factor in the design of the separation materials and implementation of the process. Two possible pathways have been identified in relation to radiation effects on a solute: direct and indirect radiolysis. Direct radiolysis is characterized by the breaking of bonds in the solute itself by the action of the ionizing rays, whereas in the indirect radiolysis case, the reactive species are created in the solvent and these reactive species diffuse into the bulk solution to react with the solute. In separation processes, the most commonly used solvents are, as mentioned, TBP and  $\text{HNO}_3$ , and in the following we will discuss the radiation chemistry of these two diluents.

## Solvents radiolysis

### Radiolysis of $\text{HNO}_3$

Its redox and metal complexation properties made nitric acid central to the SNF reprocessing technology [24]. In the different stages of the PUREX process,  $\text{HNO}_3$  is in aqueous solutions of concentrations varying from 0.1 to 10 M. With such a concentration range, and as the different by-products of  $\text{HNO}_3$  radiolysis may affect the separation performance, both direct and indirect effects of ionizing radiation need to be understood for optimizing the extraction efficiency. The radiolytic decomposition of  $\text{HNO}_3$  has been extensively investigated and its mechanism has been fully elucidated under low LET irradiation ( $\beta$  and  $\gamma$  rays) [25-26]. Renewed interest in  $\text{HNO}_3$  radiolysis has been observed in the recent years either through the perspective of lack of information on the yields in high LET radiation chemistry [27-29], which makes up a great fraction of SNF, or through the perspective of gaining information on the nitrate radicals ( $\text{NO}_3^\cdot$ ) reaction mechanisms [30-32], as principal driver of chemical change in nitric acid/nitrate solution media. Equation 1 and figure 2 summarize the behavior of aqueous solutions of  $\text{HNO}_3$  under irradiation:



The radiolysis of  $\text{HNO}_3$  solutions leads to the formation of nitrogen oxides, nitrous acid and molecular hydrogen that are important in the context of SNF reprocessing as they can change the physical-chemical properties of aqueous  $\text{HNO}_3$

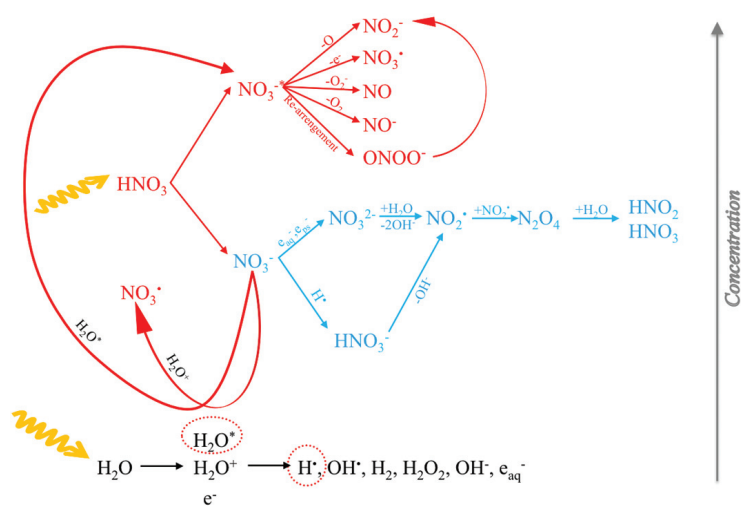


Figure 2 - Time evolution of the various steps of the radiolysis of nitric acid in dilute and concentrated solution.

solutions [33]. Three pathways for the formation of  $\text{NO}_3^\cdot$  radicals have been identified from the earliest studies on the radiolysis of nitric acid: via direct ionization [34], the reaction between  $\text{HO}^\cdot$  radicals and undissociated  $\text{HNO}_3$  molecules [35], or through water hole trapping reaction [36]. Nitrogen dioxide radicals are introduced in the system through hydrolysis of  $\text{NO}_3^{2-}$ , formed by nitrate anion reduction. The radiolytic species formed in the decomposition of  $\text{HNO}_3$  are important as they can diffuse into the organic phase and affect the stability of the ligands, forming secondary radiolytic products or oxidizing important metal ions, that can have deleterious effects on plant operation [37-38]. Nitrogen oxide radicals can undergo H abstraction, charge transfer or addition onto C-centered radicals, accelerating the degradation of ligand or organic molecules, such as TBP.

Uranous nitrate, U(IV) is used to separate U from Pu by the reductive stripping of Pu [39], but accumulation of  $\text{HNO}_2$  can oxidize U(IV) nitrate to U(VI) [39]. At the same time,  $\text{HNO}_2$  formed from  $\text{HNO}_3$  radiolysis can re-oxidize Pu(III) into Pu(IV) through a self-catalyzing reaction that leads to the production of more  $\text{HNO}_2$  than it consumes [40]. As effective extraction and partitioning of U and Pu rely on controlling their oxidation state,  $\text{HNO}_3$  stabilizing agents are introduced in the PUREX process meant to consume the  $\text{HNO}_2$  present in the organic stream. Among the proposed agents we find butyraldehyde oxime, hydrazinium nitrate, hydroxyl-imine alkanolic acids, hydroxylammonium nitrate, hydroxylammonium sulphate and sulphamic acid [41-44]. These anti-nitrous agents have to be radiation resistant and should not interfere with the process operation, and constant efforts are made towards discovering new molecules for this use.

Another radiolytic product closely linked to major safety concerns in the nuclear industry is molecular hydrogen. The yield of  $\text{H}_2$  can be reduced in nitric acid media by the nitrate ions' scavenging capacity. Literature values show a decrease of the yield of  $\text{H}_2$  with increasing concentrations of the nitrate solutions, to its complete suppression in highly concentrated solutions, due to the scavenging of  $\text{H}_2$  precursors by nitrate radicals [45-46].

The complete quantitative characterization of the major radiation effects on  $\text{HNO}_3$  and ligands, their robustness to radiation is critical for optimal plant operation in terms of separation efficiency.

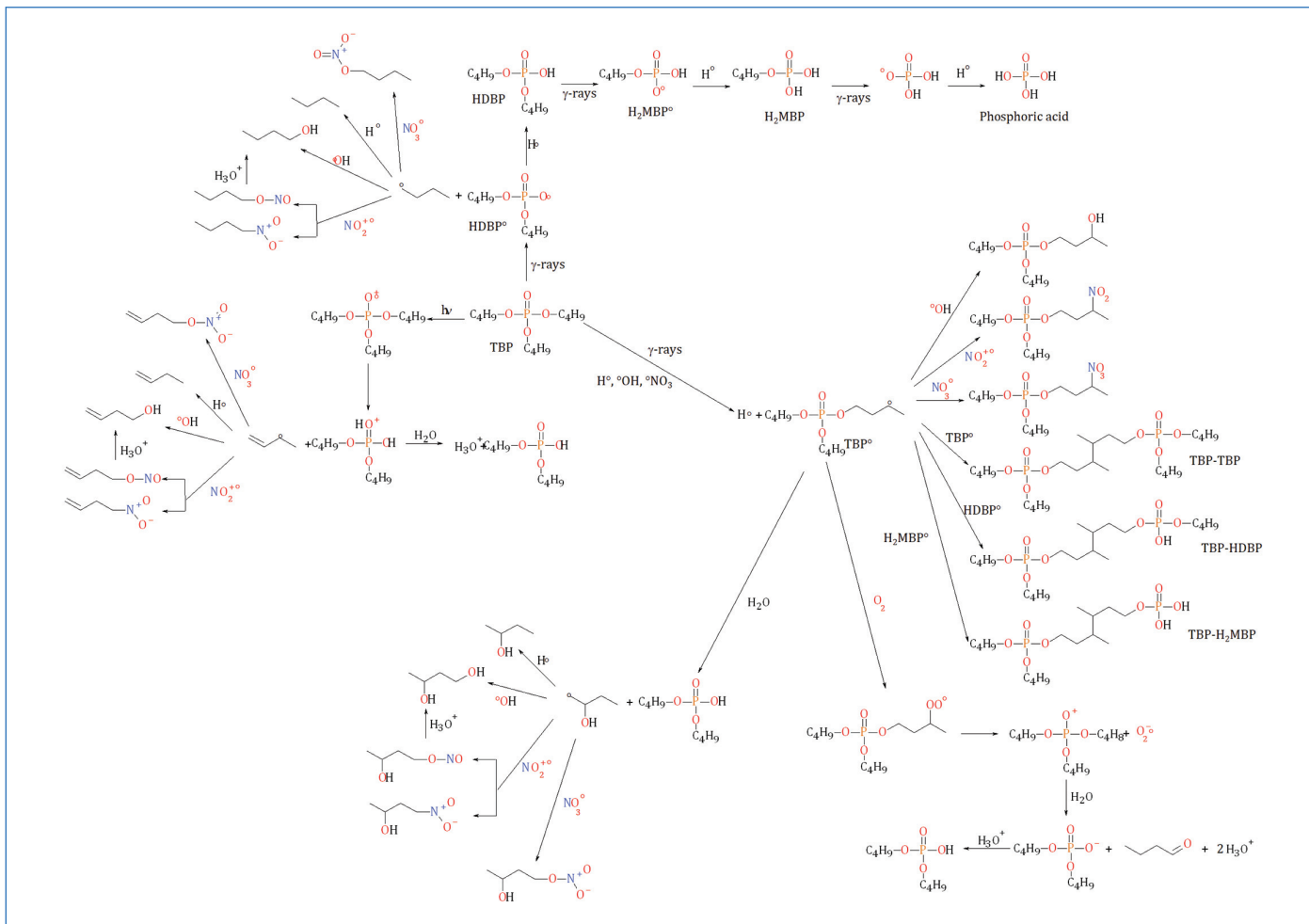


Figure 3 - Non-exhaustive scheme of degradation of TBP/TPH contact with nitric acid.

## Radiolysis of TBP

Tributylphosphate is used in the PUREX process because it is a good and selective extractant for tetra- and hexavalent actinides over the tri- and pentavalent actinides, and because of its stability under strong acidic conditions [47-48]. However, it is radiolytically instable and subsequent degradation products will be released in the solution. Direct radiolysis of TBP leads to the formation of HDBP (dibutyl phosphoric acid), H<sub>2</sub>MBP (monobutyl phosphoric acid), butyl alcohol, butyl ether, phosphoric acid, hydrocarbons and polymer, with hydrogen release; HDBP and H<sub>2</sub>MBP being the main degradation products [49]. When the mixture TBP/TPH is also in contact with nitric acid, additional radiolytic products include alkane oligomers, dodecanols, aliphatic ketones, acids, nitrosoparaffins, nitroparaffins and hydroxamic acids [17, 50]. A non-exhaustive scheme of degradation of TBP/TPH contact with nitric acid is given on *figure 3*.

All these molecules formed under radiolysis are drawbacks to use TBP, because they alter the PUREX process efficiency. HDBP is a strong monoprotic acid that can act as surfactant: the presence of this radiolytic product leads, when accumulated, to the formation of a third stable phase between the organic and the aqueous one. Consequently, this third phase leads to the clogging of the process pipes and of the concentrator plug [48]. It causes also a reduction in the attainable decontamination factor due to the zirconium and niobium complexes which can be formed and cannot be scrubbed out by the nitric acid washes [48-49]. H<sub>2</sub>MBP poses also a very important problem as it forms a complex with plutonium

insoluble in aqueous and in organic solvent phases; this complexes deposition in the process pipes can induce critical problems if not taken into account [49].

Acidic phosphate radiolysis products are removed during process extractions by solvent washing with aqueous Na<sub>2</sub>CO<sub>3</sub>, NaOH and dilute acids solutions [17, 20]. The liquid organic waste contains the TBP degradation products, a small amount of actinides (mainly U, Pu) and fission products (mainly Ru, Zr and Nb). This type of waste is disposed of by incineration or decomposed by hydrolysis and pyrolysis, forming inactive hydrocarbons which are distilled, active phosphorous acid being treated together with other aqueous waste [51]. This is the second main drawback of the use of TBP: phosphorous compounds are not incinerable [52] which increases the quantity volume of wastes to be processed, stored and disposed [47-48].

Finally, some of the degradation products, very probably the high molecular weight ones coming from the addition of two molecules of TBP, of HDBP, of alkane solvent radicals and so on [17], are not removed by the solvent recycling. Their accumulation decreases the extraction performance, the phase separation efficiency, the mass transfer coefficient and the separation fission product/actinide separation factors. For instance, TBP dimers and TBP-HDBP adducts have high organic phase solubility and can retain plutonium.

The understanding of the TBP/TPH/nitric acid system degradation mechanism allows optimizing the PUREX process; degradation products are known and quantified, so the number of solvent washing before to change it can be

deduced. This leads to significant gains in safety, in process efficiency and in waste management.

## Best optimization options

Radiation chemistry is the heart of spent nuclear fuel reprocessing understanding and efficiency. This article shows that PUREX is a process which has been optimized as much as possible, from the point of view of the solvent renewal as well as from the safety.

The recycling technology is amendable to further improvement to make the nuclear fuel cycle more sustainable through simplified operations, improved fuel quality and inherent enhanced proliferation resistance. The main driving force is the reduction of the intrinsic radiotoxicity by separation and recovery of the small actinides. Examples of such technologies include UREX1, designed to separate U, Pu, Np, Tc and minor actinides [43], GANEX, designed to separate the actinides from lanthanides/fission products, EXAm extracting americium before the PUREX process, SANEX, separating americium associated with curium before applying PUREX to separate uranium and plutonium, DIAMEX and TRUOX, aiming at separating all transuranic elements and TALSPEAK that involves separation of minor actinides from lanthanides.

For these new processes, to further decrease the quantity of waste to be disposed of, new extractants are under study. Alkylamides and diamines are for instance under evaluation to replace TBP, because of their great efficiency as extractant [53]. They present three non-negligible advantages compared to TBP: their degradation products are harmless in nature (carboxylic acids and amines) [54]; these molecules being only composed of C, H, O, N atoms (called the CHON principle), they are easily incinerable, which greatly simplifies the disposal of the spent fuel solvents [17, 54]; their physical-chemical properties can be managed by the choice of the alkyl groups [54]. Nowadays, one of the most promising N-bearing molecules is DHOA (N,N-dihexyloctanamide). This molecule respects the CHON principle, dissolves easily in dodecane and has no surfactant property; it cannot cause any third phase between the aqueous and the organic phases and its extractant properties have been demonstrated to be better than those of TBP [54].

## Notes and references

La liste détaillée des références (avec leurs titres) est donnée dans l'annexe téléchargeable librement sur [www.lactualitechimique.org](http://www.lactualitechimique.org) à partir de la page liée à cet article.

(1) tHM : ton of heavy metal.

(2) LL-HLW : for actinides with half-life higher than 31 years.

(3) LET : linear energy transfer.

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