



Less radiotoxic ultimate waste?

In spent fuel, once the – recyclable – plutonium has been removed, minor actinides form, among the long-lived radionuclides present, the major source for the residual long-term radiotoxicity of nuclear waste. They thus stand as the prime target for a specific management strategy, involving “enhanced separation.” CEA researchers have indeed developed molecules having the ability to effect such “tunable” partitioning, or even, possibly, at a later date, to effect the joint separation of these actinides, to feed the nuclear systems of the future, having the ability to recycle them fully.



The shielded process line (CBP: *Chaîne blindée procédé*) in Atalante, used for the demonstration trials of minor actinide separation processes.

Spent nuclear fuel contains a wide variety of **nuclides**, exhibiting **radioactive half-lives** that may range from the very short to the very long (see Box B, *Waste from the nuclear power cycle*). So-called “**long-lived**” **radionuclides**, i.e. those for which the radioactive half-life, or that of one of the decay products, is greater than 30 years, are responsible for the potential long-term radiological toxicity of irradiated fuel. These elements comprise the residual **uranium** (U), **plutonium** (Pu), **minor actinides** (MAs), and, in part – about one tenth – **fission products** (FPs) and **activation products** (APs) (see Table 1).

Inasmuch as they raise highly specific issues, which may be deemed problematical in the context of safety analyses for long-term **nuclear waste** management options, particularly with respect to **disposal in deep geological strata**, investigations have been set in

train. These seek to evaluate the feasibility, on the one hand, and potential benefit, on the other, of a specific management of long-lived radionuclides, in particular their separation, with a view to effecting their **transmutation** into stable nuclides, or **short-lived** nuclides.

A wide-ranging research program was set in place, under CEA oversight, in the early 1990s, under the aegis of the French Act of 30 December 1991 (see Box 2, in *Radioactive waste management research: an ongoing process of advances*). The initial step in a specific management strategy for long-lived radionuclides consists in *selectively recovering them from spent fuel*, to yield **ultimate waste** freed of the main part, if not all, of what makes it potentially hazardous for the long term. Consequently, a major part of that research program, dubbed SPIN (Separation

P. Stroppa/CEA

nature	element	isotope	half-life (years)	quantity (g/tiU)	isotope content (%)
minor actinides	neptunium	237	2,140,000	916	100
	americium	241	432	490	62.4
	americium	243	7,380	294	37.4
	curium	245	8,530	11	8
fission products	selenium	79	1,100,000	8	8
	zirconium	93	1,500,000	1,250	24
	technetium	99	210,000	1,410	100
	iodine	129	15,000,000	308	82
	cesium	135	2,300,000	769	17
activation products	zirconium	93	1,500,000	81	0.04
	niobium	94	20,300	2	0.4

Table 1.

Characteristics of the main long-lived radionuclides present in spent UOX fuel (once the uranium and plutonium have been extracted), **enriched** to 4.95% uranium 235, discharged with a burnup rate of 60 GWd/t. Quantities, expressed in grams per tonne of initial uranium (g/tiU), and isotope content are given as prevailing after 5 years' cooling time subsequent to fuel discharge.

Incineration), launched as early as 1992, was devoted to investigations on "enhanced" separation of long-lived radionuclides.

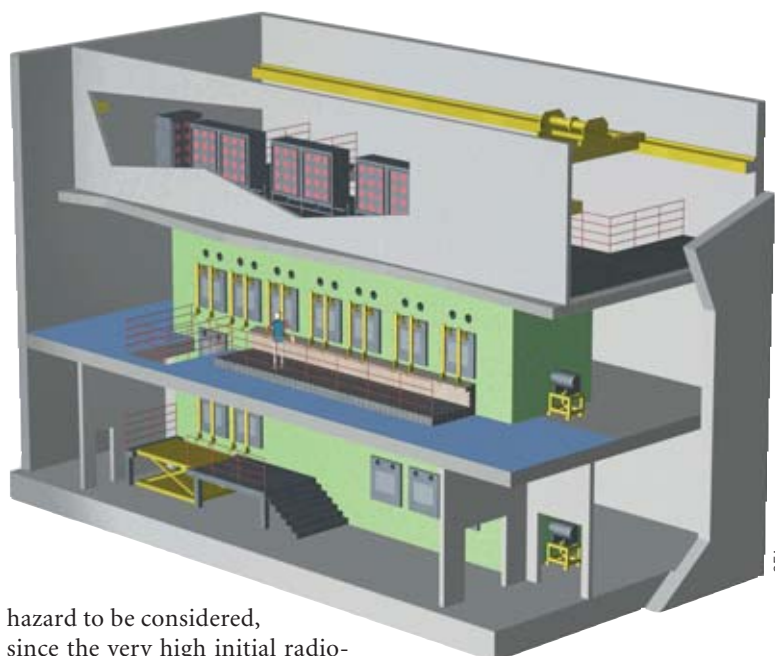
Investigations on enhanced separation

Bearing in mind the diversity of the elements potentially involved (several tens of long-lived radionuclides are present in irradiated fuel, namely FPs and MAs), and the range of techniques that may be considered to partition them, a research strategy had to be defined, seeking to answer two essential queries. What radionuclides would be concerned by the investigations? (Indeed, it would have been unthinkable to seek to investigate the separation of every element featuring, whether directly or in the guise of one of its descendents, a radioactive **isotope** having a long half-life. All MAs, and close to a third of the total mass of FPs would have been involved!). And what criteria should be taken up, for the selection of separation methods?

What elements should be partitioned?

The first consideration to take on board is that of the respective contributions the various constituents of spent fuel make to its long-term "**radiotoxicity**." The radiotoxicity of a material is the radiological detriment, i.e. the **effective dose** delivered, that would be sustained by individuals incorporating that material through ingestion, or inhalation. This depends, of course, on the radioactive characteristics of the radionuclide, or radionuclides, present in the incorporated material, but equally – and crucially – on the metabolism of these nuclides inside the organism. Thus, for example, for an equivalent radioactivity, effects of a radically different extent will be obtained, depending on whether this radioactivity is incorporated, respectively, when borne by krypton nuclei (a rare gas, chemically inert, not fixed by the organism), or iodine nuclei (which are liable to be fixed, in particular, in the thyroid).

Radiotoxicity may be seen as an appropriate criterion to evaluate the (potentially) hazardous character of nuclear waste in the long term. Indeed, in the case of a disposal facility, at the end of a very long timespan, external irradiation is not the main



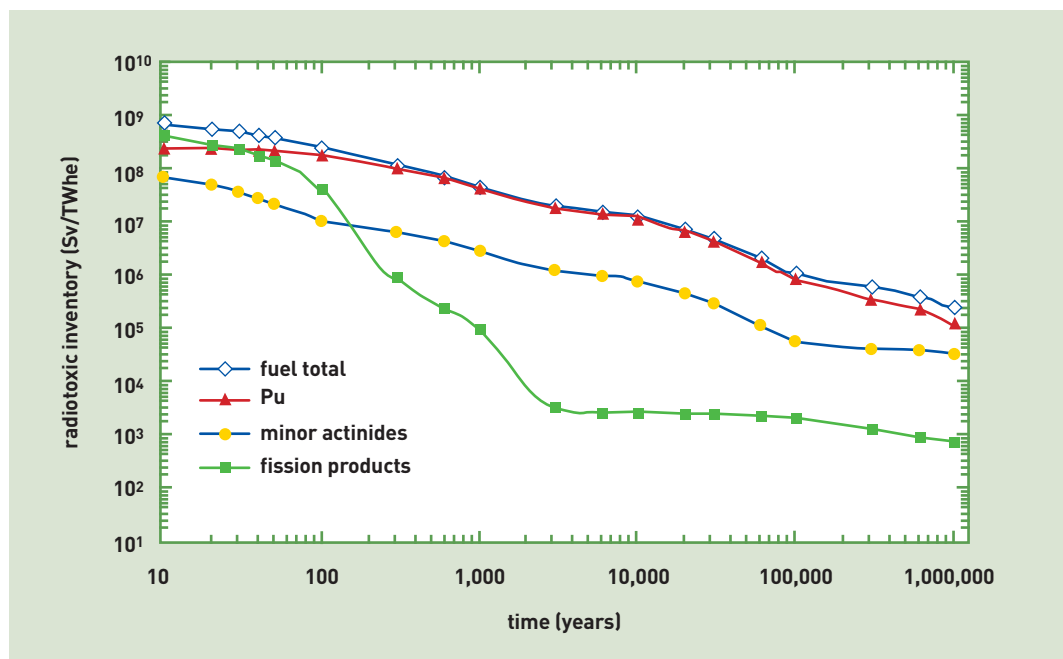
hazard to be considered, since the very high initial radioactivity will have very sharply decreased after a few centuries, and in any event durable protection shields are available. Rather, the issue, as shown by various safety evaluation exercises for disposal facilities, carried out internationally and, in France, by **ANDRA**, is the risk of incorporation, at a very low level, of radioactive elements present as trace elements in drinking water, at the outcome of a very slow solubilization and migration process.

Analysis of the residual radiotoxicity of spent nuclear fuel, after a few centuries (see Figure 1), shows this is predominantly due, primarily and by far, to the quantities of Pu present, then those of MAs, weaker by about one order of magnitude, and, finally – several orders of magnitude weaker – those of FPs. A strategy for the reduction of the long-term radiotoxicity of waste yielded by the **reprocessing** of spent fuel should thus, first and foremost, be concerned with extracting the Pu. Which is both feasible, and indeed carried out, by means of the **Purex** process, and through the strategy of **recycling** Pu in **MOX** fuel, a strategy the benefit of which, in this respect, may thus be measured (see *Spent fuel reprocessing: a fully mastered pathway*).

The shielded process line (CBP: *Chaîne blindée procédé*), set up in Atalante, is one of CEA's major facilities for experiments on radioactive materials. This instrument allows, in particular, trials of spent fuel reprocessing processes carried out on significant quantities, and over long periods, using technologies representative of those to be deployed on an industrial scale.



Figure 1.
Evolution of the
radiotoxic inventory,
expressed in sieverts per
terawatt-hour electrical
(Sv/TWhe), of spent fuel.
Pu stands out as
the main contributor to
spent fuel radiotoxicity.

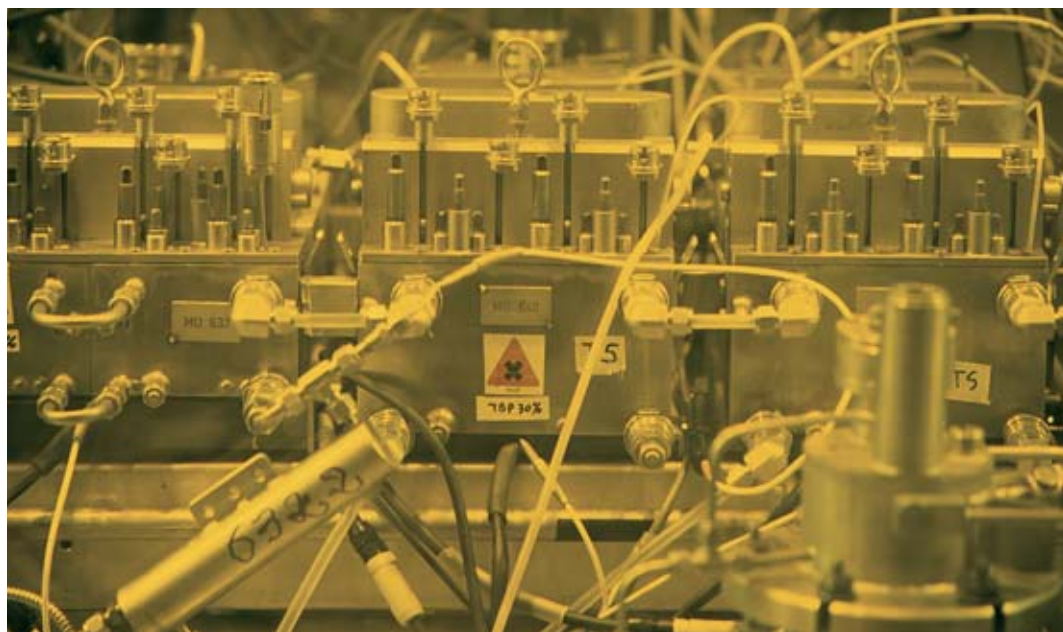


Once the Pu is extracted, MAs – essentially, neptunium (Np), americium (Am), and curium (Cm) – i.e. about one thousandth of the mass of spent fuel, thus form the main source of residual toxicity. To arrive at a further diminution in waste long-term radiotoxicity, these elements, known as “minor” actinides owing to their lesser abundance, will thus be the main “target” of an enhanced separation strategy.

Use of this sole radiotoxicity criterion results in only considering the potentially hazardous character of nuclear waste, while not taking any account of the **barriers**, which, in the various management options, are interposed between waste and populations. This criterion is thus independent of any decision as to management options, the aim being to minimize the **radiotoxic inventory** of the materials subject to management. However, in the disposal facility case, the **matrix** containing the radio-

active elements, together with the properties of the ambient environment, will obviously play a major part in preventing, or delaying, dissemination of the radionuclides. **Actinides (An)** turn out to be the least mobile, whereas certain long-lived FPs may prove more mobile, due to their being more highly soluble, and less readily **sorbable** on rocks traversed by the aquifers. Safety assessments for disposal facilities highlight the fact that nuclides such as iodine 129 (¹²⁹I), or, to a lesser extent, depending on the environments investigated, cesium (Cs), technetium (Tc), and some others yet, while inherently far less radiotoxic than MAs, may compensate for this by their greater mobility, and thus ultimately prove to be heavier contributors to the dose delivered at the **outlet**.

For that reason, the Enhanced Separation Program also took on board research on, and evaluation of, separation processes for I, Cs, and Tc.



View of mixer-settler
units during trials
carried out
in the shielded
process line (CBP).

P. Stroppa/CEA

Two major points should be noted, however. First, it is essential to achieve accurate measurement of the low level of doses that may be delivered, in the very long term (several tens of thousand years), by these elements, conditioned as they are in HLW-LL and ILW-LL waste packages, as estimated by investigations carried out on the issue (less than one **microsievert**, in normal conditions of evolution for a disposal facility). Second, advances in research on disposal, over the past 15 years, have allowed certain contributions to be better ascertained. Thus, the latest investigations, concerned with scenarios of disposal in clay, while they corroborated previous assumptions as to I mobility, at the same time invalidated those regarding Cs, and those for Tc even more. Contributions from these two elements do not now appear to be as decisive as they did, when the program was launched!

What processes should be used to carry out separations?

Taking on board the operational feedback for the Purex process of U and Pu recovery – achieving as it does very high separation performance, both in terms of amounts recovered, and purification rates achieved, with limited yield of **technological waste** – together with the 2006 deadline set by the Act of 30 December 1991 – leading to giving pride of place to a certain degree of maturity, and thus technological continuity – selective extraction (or **solvent extraction**) approaches were prioritized. Aside from this main avenue of research, in order to open up investigations to possible options, particularly with regard to long-term prospects, other alternatives were also considered, mainly pyrochemical processes, which might offer significant benefits, in a number of respects.

The elected research strategy consists in seeking to take advantage of the Purex process's partition potential, particularly with respect to Np, I, and Tc, going on to design further separation steps, using novel extraction agents, for those elements for which the Purex process extractant exhibits no affinity (this being the case with Cs, Am, and Cm), and, finally, evaluate the potentials of other technologies (see Figure 2).

What are the main stages in the program?

Research work on the main avenue for investigation, concerning extraction of the target elements, has gone through two main stages.

The initial years were mainly devoted to the quest for suitable concepts, and molecular architectures, for the extraction of Am, Cm, and Cs. This was a particularly fruitful stage, with the synthesis of very many extractants, in a context of broad opening up of the work, mobilizing a large scientific community, both in France, with the PRACTIS, then PARIS research groups (GDRs: *groupements de recherche*), and at the European level, under the aegis of the NEWPART, then PARTNEW projects (see Box 3, in *Radioactive waste management research: an ongoing process of advances*). This initial, exploration, stage, involving laboratory experiments on the milligram scale, allowed a number of extractants to be selected, having the potential to prove suitable, with respect to the

very many criteria that have to be taken on board. Such extractants must exhibit high affinity, selective with regard to the elements of interest; tunable, reversible extraction capabilities, offering appropriate kinetics; and further prove resistant in operational conditions, particularly with regard to **radiolysis** processes.

During the second stage, the aim was to verify the actual ability of the molecules identified to lend themselves to industrializable processes. Research workers reproduced on the laboratory scale, in particular in the **Atalante** facility, possible process configurations for the recovery of the various elements concerned, testing their validity on actual spent fuel samples, of a few hundred grams or so. These experiments, mainly carried out around 2000, made it possible to further narrow down selection of the various “candidate” concepts, and develop their conditions of use. Research workers are currently conducting experiments of the same kind, concerned with MA extraction, on a larger scale however (involving a fuel batch of nearly 15 kg), more representative of industrial conditions, in particular as regards technologies. The latter series of experiments, the outcome of over 15 years' research effort, was initiated with the completion, in April 2005, of a successful Np extraction trial, going on, at the end of 2005, to conclusive recovery trials of the Am and Cm contained in the fuel.

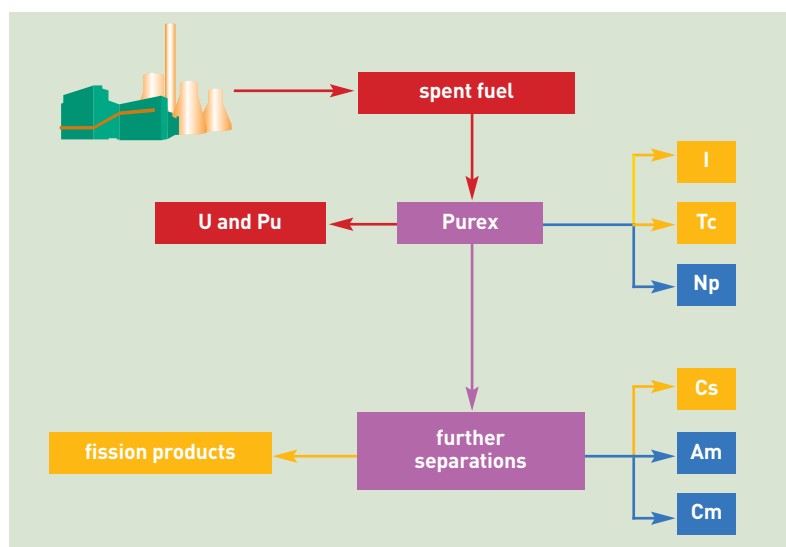


Figure 2.
Principle schematic
of enhanced separation.

Separation of minor actinides: main results

While Np separation was investigated on the basis of modifications to the Purex process, separation of Am and Cm required looking for entirely new processes.

Separation of neptunium

Np held in irradiated fuel is dissolved in bulk by nitric acid (HNO_3), in the Purex process. Two main species are found in the solution yielded by nitric dissolution: NpO_2^+ and NpO_2^{2+} . The extractant used in the Purex process, tributyl phosphate (TBP), exhibits a fairly high affinity for NpO_2^{2+} , and rather weak affinity for NpO_2^+ . Consequently, the fraction of Np

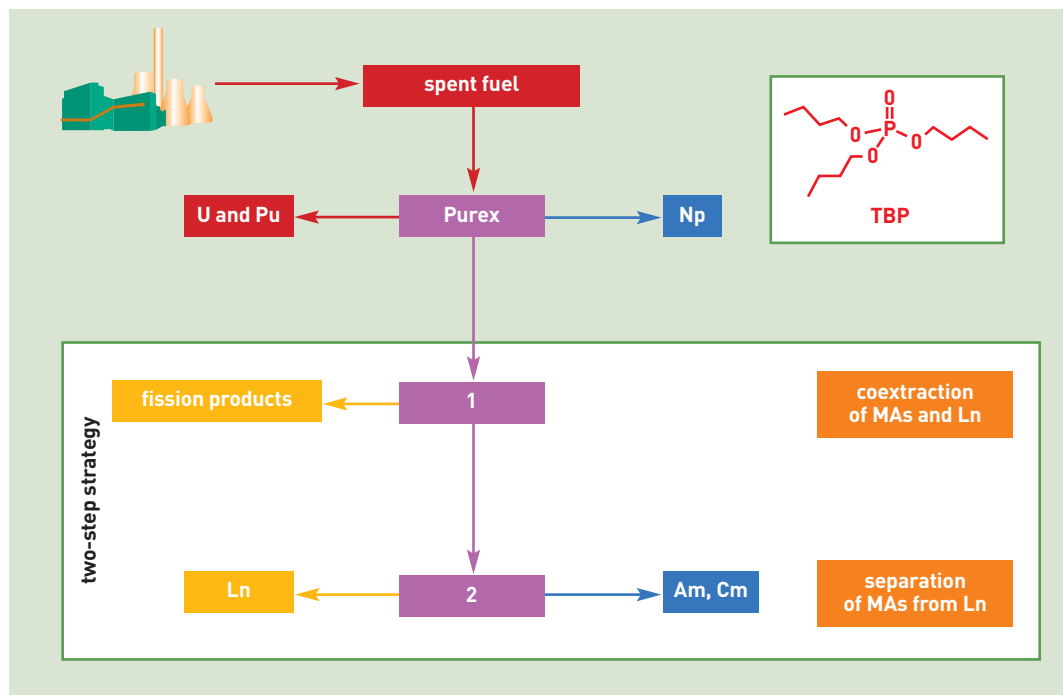


Figure 3.
Steps in the separation
of minor actinides.

extracted by means of TBP depends on the respective quantities of the two species in the feed solution, and on possible changes in their respective proportions in the course of extraction.

It was thus seen it should be possible to achieve bulk recovery of Np through adjustment of the classic Purex process, by favoring **oxidation** of NpO_2^+ to NpO_2^{2+} . Experiments carried out at the laboratory level resulted in specifying the assumed mechanisms, and the kinetics of NpO_2^+ oxidation by nitric acid (**catalyzed** by nitrous acid $[\text{HNO}_2]$). This made it possible to suggest a modified Purex operation scheme, for bulk recovery of Np, simply based on a moderate increase in nitric acid concentration in the feed solution (see Figure 3). The findings from computations, carried out by means of the **PAREX code**, simulating the process, warranted the estimate that some 99% of Np could be extracted in these conditions. This was verified in the experiment carried out in Atalante, using 15 kg of spent fuel.

Separation of americium and curium

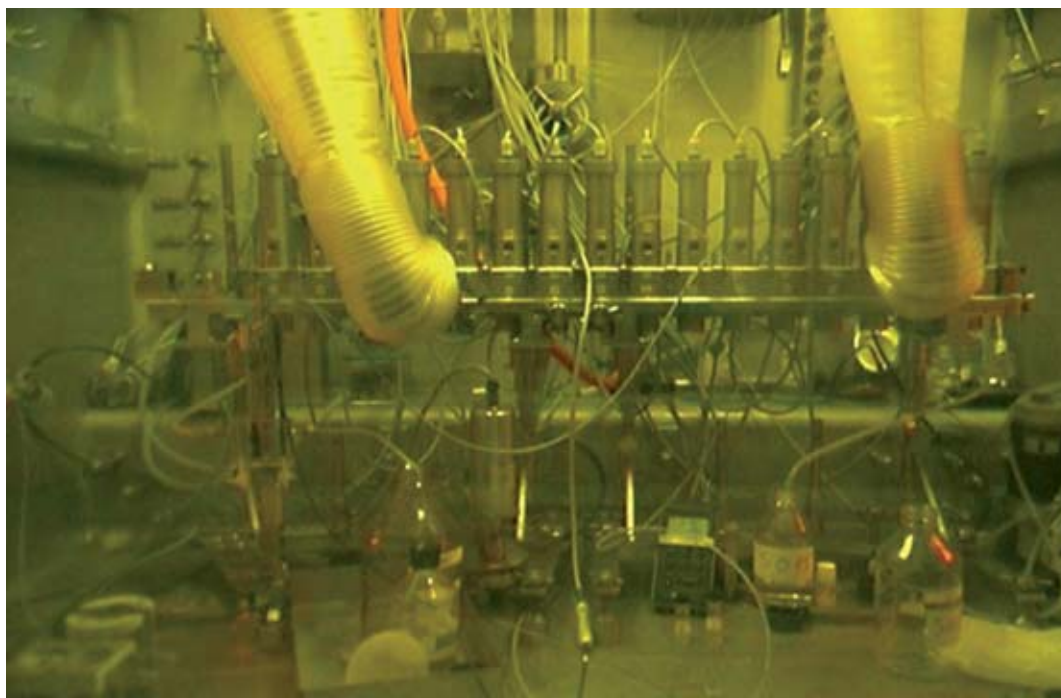
Am and Cm exhibit very low affinity for TBP, and are thus not amenable to recovery by the Purex process. The species present after dissolution are, respectively, Am^{3+} and Cm^{3+} , which remain in bulk in the aqueous solution along with the FPs, even as uranium (UO_2^{2+}) and plutonium (Pu^{4+}) are extracted. Many attempts were made in the past to develop specific extraction processes, to separate Am and Cm from FPs. Development of such concepts turned out to be difficult. The first reason for this relates to the extreme diversity of chemical properties exhibited by the FPs involved, with the presence, in particular, in solutions yielded by dissolution of irradiated fuel, of large quantities of **lanthanide (Ln)** elements (up to 50 times larger than for MAs), exhibiting behaviors very close to those of MAs. The second reason has to do with the rather high nitric acid concentrations, in solutions yielded by the Purex process. This results in unfavorable “competition” effects,

between (highly abundant) H^+ ions and the actinide ions, candidates for extraction by potentially selective extractants.

It was decided to operate in two steps (see Figure 3). First, the joint separation of MAs and Ln from other FPs (**Diamex** process), followed by the separation of MAs from the Ln, in appropriate chemical conditions, i.e. at low nitric acid concentration, in a medium freed from other elements that might interfere with the operation (**Sanex** process).

The prime aim of the research effort was to select extraction systems having the ability to carry out these operations, and further meeting the requirements outlined above. In order to minimize secondary waste yielded by the process, it was deemed advantageous to focus investigations on reactants that might be fully incinerated, solely comprised of atoms of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). This is one of the major original features of the work carried out by CEA.

Extraction agents featuring donor atoms, such as oxygen, and exhibiting two such functions, such as diamides, and most conspicuously among these malonamides, proved highly effective for the extraction of f elements from strongly acidic solutions. Consequently, investigations concerned with the first step, of coextraction of MAs and Ln, were soon directed to this family of molecules. A major effort was devoted to identifying the extraction mechanisms and ascertaining extraction kinetics, solubility limits and degradation rates under the effect of radiolysis, to optimize the **formulation** of the extractant. The initial choice was to use dimethyl dibutyl tetradecyl malonamide (DMDBDMA), its effectiveness being verified in a series of trials in a radioactive environment, carried out at laboratory level, on actual fuel samples, as early as 1993. It was subsequently shown that this molecule could be enhanced in various respects. After synthesizing some tens of molecules, dimethyl dioctyl hexaethoxy malonamide (DMDOHEMA) was adopted, in 1998, as the



Laboratory centrifugal extractors used in Atalante's shielded lines.

new "reference molecule" (see Figure 4). This was subsequently tested in a series of trials with actual samples, along with the design of a process taking advantage of its properties. Efficiency of some 99.9% was achieved for MAs (and Ln), together with outstanding purification performance with respect to other FPs.

For the second step, corresponding to the separation of MA from Ln elements, use of a variety of **ligands** was successively investigated. Chemists sought to develop extractants having the ability to make use of very slight differences in behavior between MAs and Ln, namely the greater propensity of the former to be involved in **bonds** of a **covalent** nature. This is found, in particular, in extractants where the donor atom is a nitrogen atom, contrary to what is the case for diamides, where the oxygen atom only participates in **ionic bonds**, precluding any differentiation between MAs and Ln.

Many trials were carried out, in the context of a very broad collaborative effort. Fairly high selectivity was often achieved between MA and Ln elements, however, in most instances, only for very low nitric acid concentration rates in the aqueous solution, for the reasons mentioned above.

The synthesis of bis-pyridine-triazine substitution molecules heralded a major new stage. Indeed, these molecules appeared to be able to bring about highly selective MA extraction, even from strongly acidic media. This crucial discovery, made by Zdenek Kolarik, a researcher at the Forschungszentrum Karlsruhe (FZK, Germany), under the aegis of the PARTNEW research program, in 1998, led to several series of trials on actual samples. The main results of these trials were outstanding, as regards performance, with very high recovery and purification rates. Unfortunately, difficulties, insuperable at that stage, emerged with respect to extraction kinetics, the solubility of **trivalent** actinide ions when surrounded by solvent molecules in the organic phase, and, most importantly, the very poor stability of the extractant.

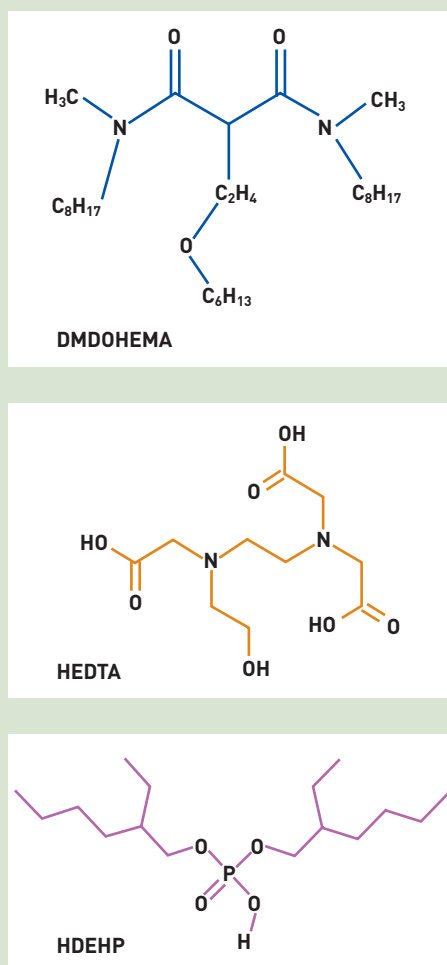


Figure 4. The extractants selected for the separation of americium and curium. DMDOHEMA is the reference molecule for the Diamex process; HEDTA (hydroxyethyl ethylene diamine triacetate) and HDEHP (di-ethylhexyl phosphoric acid) are also used in the Sanex process.



Investigations were carried through, and are still currently ongoing, on this extractant family, seeking to resolve these issues through an appropriate formulation. However, research workers have redirected their attention, as regards the reference path, to an alternative, based on use of two associated extractants: a diamide, having the ability to extract trivalent MAs and Ln from strongly acidic solutions, and an organic acid, with the ability to extract these trivalent ions at low acidities (see Figure 4). One such concept was successfully tested in the laboratory, and, recently, on a larger scale. This appears highly advantageous, since it makes it possible to consider, once optimized, bringing together in one and the same cycle the two operations that heretofore were to be carried out in two successive steps.

Separation of Am from Cm has also been investigated, in the event that differentiated management of these elements be contemplated. The issue, in this case, is less complex. It is possible – as verified empirically – to take advantage of differences in the respective affinities of each of these elements for extractants such as diamides, to achieve their separation.

Separation of fission products: main results

The approach followed for the separation of I and Tc consists in an adjustment to the Purex process. On the other hand, Cs separation required development of a specific extraction process.



Extraction equipment
in the shielded
process line (CBP).

Separation of iodine

Operation of the Purex process results, nowadays, in the effective, and efficient, recovery of iodine from irradiated fuel. This iodine is mainly released in the form of gaseous diiodine (I_2) when the fuel is dissolved, and trapping of this gas occurs, first, in an **alkaline** solution, in which it is **reduced** to soluble iodide (I^-), followed by **adsorption** on **amorphous** materials impregnated with silver nitrate ($AgNO_3$). These steps result in the formation, and retention on these substrates, of iodine in the form of AgI and $AgIO_3$. More than 98% of iodine is thus recovered.

Separation of technetium

Tc is only partly dissolved during the spent fuel dissolution step, since it is mainly present in the latter in the form of polymetallic alloys, dissolution of which is a complex issue. The dissolved fraction, amounting to some 85% of the total quantities of Tc, in standard **UOX** fuel, is so dissolved in the form of the pertechnetate **anion** (TcO_4^-). This soluble fraction of Tc may be extracted, and recovered, in bulk, through extraction by tributyl phosphate (TBP), as TcO_4^- can substitute for NO_3^- in extracted **complexes** of U, Pu, and zirconium (Zr) (see *Spent fuel reprocessing: a fully mastered pathway*). The behavior of Tc in the Purex process was targeted by a major research effort in the 1980s, precisely in order to achieve purification from Tc of the recovered U and Pu. The chemistry of the system is nowadays deemed to be fairly well mastered, and reprocessing models have been developed, and tested. These provide chemists with the ability to set up Purex extraction cycles allowing selective recovery of over 95% of the soluble fraction of the Tc present in irradiated fuel.

Separation of cesium

The Purex process has no potential for selective recovery of Cs, this being dissolved in bulk, in an aqueous solution, in the form Cs^+ , which however is not amenable to extraction by TBP. At the same time, selective extraction of Cs, at fairly low concentrations, in the presence of large quantities of H^+ ions, is equally a difficult issue. The idea was mooted, of making use of sophisticated, preorganized, molecular architectures. Interesting extraction results were achieved with 1,3-dimethoxycalix[4]arene-crown-6. Very many investigations, carried out in the European collaborative framework, made it possible to select functionalized calixarene configurations, exhibiting remarkable properties, in terms of selectivity and radiolysis resistance. The effectiveness of selective Cs recovery by means of these extraction agents was verified in series of preliminary trials, in the laboratory, on actual samples, and at various scales. Recovery rates achieved are higher than 99.9%.

Pyrochemical processes, another enhanced separation path

Pyrochemical processes, consisting in separation at high temperature in molten salts, could provide an interesting alternative to the **hydrometallurgical** processes selected as the “reference path” for the enhanced separation of long-lived radionuclides. Indeed, they are well known for bringing high compactness (with higher concentrations than feasible in aqueous solutions, and a reduced number of basic steps required), and major potentials in terms of effecting chemical transformations. At the same time, they are equally highly attractive for operations on radioactive elements, insofar as they do not involve use of radiosensitive compounds, as is the case – to an extent chemists are indeed seeking to minimize – of the organic extractants used in the concepts described above. This would allow, in particular, reprocessing fuel elements or transmutation targets involving high **burnup rates**, and/or short cooling times.

On the other hand, major uncertainties remain, as to separation performance, on the one hand, and industrial deployment of such processes, on the other. Indeed, these processes involve particularly aggressive media, and could thus result in greater quantities of technological waste.

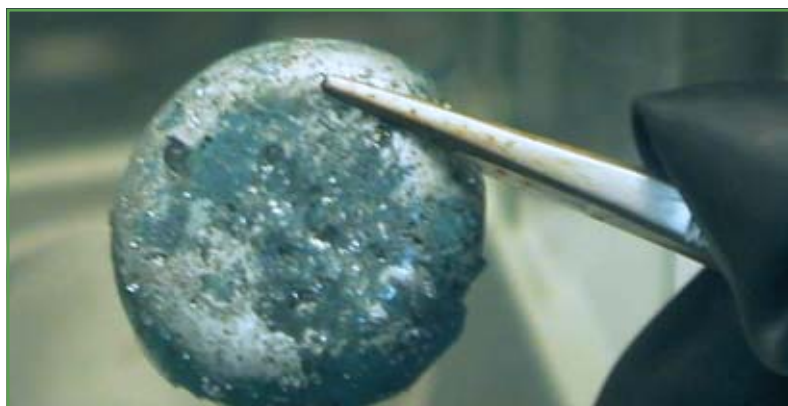
Various pyrochemical concepts have been investigated, developed, and tested around the world, in some cases at pilot plant scale. In a number of countries, for close to a decade, there has been a marked surge in interest for this type of process. The generic approach consists in effecting the dissolution of irradiated fuel elements in a **eutectic** of molten salts, at a temperature of around 500–800 °C, this being followed by recovery, which chemists are striving to make selective, of the desired elements. A number of media, and a wide variety of techniques, have been, and are currently being, investigated: chloride or fluoride media, separation through extraction by means of molten metals, through electrolytic deposition, or **precipitation**. Concepts effected in a chloride medium, developed for metallic fuels at **Argonne National Laboratory** (United States), or for oxide fuels, developed at the Scientific Research Institute of Atomic Reactors (Russia), stand, to date, as the most notable achievements in this area, with the reprocessing of several tonnes through this technique, carried out at the “Fuel Cycle Facility” pilot unit, at **Idaho National Laboratory**, Argonne-West (United States).

A research program was set up, from the late 1990s, here again in a broad collaborative context, seeking to explore a large number of options, and, bearing in mind the lesser maturity of these processes, with a view to applications in the longer term. The aim was, first, to verify to what extent the elements identified as targets for enhanced separation might be effectively separated by means of such concepts, then to seek the most suitable media and technologies, and, finally, to develop schemes for such processes, and test them on actual spent fuel samples.

As of now, in the light of the results achieved over the past few years, it is not yet possible to draw conclusions on any of these points. Many investigations still need to be carried out, before such concepts can be brought to maturity, for their application to the intended separations. Nevertheless, highly encouraging preliminary findings have been arrived at in the laboratory, in extraction trials, using a mix of an aluminum and copper melt, and An dissolved in a bath of molten fluorides. High extraction factors for all of the An, and very low factors for FPs, were achieved, which bodes well for potentially outstanding selectivity!

Answers, and a new momentum

At the outcome of nearly 15 years’ research effort on enhanced separation of long-lived radionuclides, scientists can thus avail themselves of separation techniques validated on actual spent fuel samples. The demonstration of selective, bulk recovery of MAs was effected at the end of 2005 in Atalante, on a larger-scale facility, through an experiment on some 10 kg of fuel, which should yield an approximation



In an extraction trial using an aluminum-copper alloy melt (78% Al–22% Cu), researchers were able to achieve selective extraction of plutonium and americium from a solution of molten fluorides (85% LiF–15% AlF₃) that contained, apart from those elements, lanthanides. This concept could allow “group” recovery of all actinides. Shown here, the saline and metallic phases, after cooling and withdrawal from the mold: at center, the withdrawn block, and (top) the underside of the metallic phase.

nature	element	extraction coefficient
actinides	plutonium	197
	americium	144
lanthanides	cerium	0.142
	samarium	0.062
	europium	< 0.013
	lanthanum	< 0.06

(at 1/500 scale) of what an industrial separation process might be.

The alternatives investigated, notably pyrochemical processes, while of interest in various respects, are currently far from presenting a degree of maturity such as to warrant the conclusion they could be applied to the enhanced separation of MAs. Their development should rather be seen as a longer-term prospect, in the context of new fuel and materials cycle options.

These investigations, beyond the important answers they provide, in the context of the French Act of 30 December 1991, have brought new momentum to the research effort on the chemistry of actinide separation, contributing, in particular, to the setting up of the European ACTINET “Network of Excellence,” and investigation of novel recycling concepts for the nuclear systems cycles of the future, such as, for instance, the **Ganex** concept of grouped recycling of all actinides.

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A What is radioactive waste?

According to the **International Atomic Energy Agency (IAEA)**, **radioactive waste** may be defined as “any material for which no use is foreseen and that contains **radionuclides** at concentrations greater than the values deemed admissible by the competent authority in materials suitable for use not subject to control.” French law in turn introduces a further distinction, valid for nuclear waste as for any other waste, between waste and final, or “ultimate,” waste (*déchet ultime*). Article L. 541-1 of the French Environmental Code thus specifies that “may be deemed as waste any residue from a process of production, transformation or use, any substance, material, product, or, more generally, any movable property left derelict or that its owner intends to leave derelict,” further defining as ultimate “waste, be it the outcome of waste treatment or not, that is not amenable to further treatment under prevailing technological and economic conditions, in particular by extraction of the recoverable, usable part, or mitigation of its polluting or hazardous character.”

Internationally, experts from IAEA and the **Nuclear Energy Agency (NEA)** – an OECD organization – as those in the **European Commission** find that long-lived waste produced in countries operating a nuclear power program is stored securely nowadays, whilst acknowledging a final solution is required, for the long-term management of such waste. They consider burial in deep geological structures appears, presently, to be the safest way to achieve final disposal of this type of waste.

What constitutes radioactive waste? What are the volumes currently involved?

Radioactive waste is classified into a number of categories, according to its level of radioactivity, and the radioactive **period**, or **half-life**, of the radionuclides it contains. It is termed **long-lived waste** when that period is greater than 30 years, **short-lived waste** otherwise. The French classification system involves the following categories:

- **very-low-level waste (VLLW)**; this contains very small amounts of radionuclides, of the order of 10–100 Bq/g (**becquerels** per gram), which precludes considering it as conventional waste;
- **short-lived low and intermediate level waste (LILW-SL)**; radioactivity levels for such waste lie as a rule in a range from

a few hundred to one million Bq/g, of which less than 10,000 Bq/g is from long-lived radionuclides. Its radioactivity becomes comparable to natural radioactivity in less than three hundred years. Production of such waste stands at some 15,000 m³ per year in France;

- **long-lived low-level waste (LLW-LL)**; this category includes radium-bearing waste from the extraction of **rare earths** from radioactive ore, and graphite waste from first-generation reactors;

- **long-lived intermediate-level waste (ILW-LL)**, this being highly disparate, whether in terms of origin or nature, with an overall stock standing, in France, at 45,000 m³ at the end of 2004. This mainly comes from **spent fuel** assemblies (cladding **hulls** and **end-caps**), or from operation and maintenance of installations; this includes, in particular, waste conditioned during spent fuel reprocessing operations (as from 2002, this type of waste is compacted, amounting to some 200 m³ annually), **technological waste** from the operation or routine maintenance of production or fuel-processing plants, from nuclear reactors or from research centers (some 230 m³ annually), along with sludges from effluent treatment (less than 100 m³ annually). Most such waste generates little heat, however some waste of this type is liable to release gases;

- **high-level waste (HLW)**, containing **fission products** and **minor actinides** partitioned during spent fuel reprocessing (see Box B), and incorporated at high temperature into a glass **matrix**. Some 120 m³ of “nuclear glass” is thus cast every year. This type of waste bears the major part of radioactivity (over 95%), consequently it is the seat of considerable heat release, this remaining significant on a scale of several centuries.

Overall, radioactive waste conditioned in France amounts to less than 1 kg per year, per capita. That kilogram consists, for over 90%, of LILW-SL type waste, bearing but 5% of total radioactivity; 9% of ILW-LL waste, less than 1% HLW, and virtually no LLW-LL waste.

What of the waste of tomorrow?

From 1991, **ANDRA** compiled, on a yearly basis, a geographical inventory of waste present on French territory. In 2001, ANDRA was asked by government to augment this “National Inventory,” with the threefold aim of characterizing extant stocks (state of conditioning, processing

traceability), predicting future waste production trends to 2020, and informing the public (see *An inventory projecting into the future*). ANDRA published this reference National Inventory at the end of 2004. To meet requirements for research in compliance with the directions set out in the French Act of 30 December 1991 (see *Radioactive waste management research: an ongoing process of advances*), ANDRA, in collaboration with waste producers, has drawn up a Dimensioning Inventory Model (MID: *Modèle d’inventaire de dimensionnement*), for the purposes of arriving at estimates of the volume of waste packages to be taken on board in research along direction 2 (**disposal**). This model, including as it does predictions as to overall radioactive waste arisings from the current reactor fleet, over their entire lifespan, seeks to group waste types into families, homogeneous in terms of characteristics, and to formulate the most plausible hypotheses, with respect to conditioning modes, to derive the volumes to be taken on board for the purposes of the investigation. Finally, MID sets out to provide detailed stocktaking, intended to cover waste in the broadest possible fashion. MID (not to be confused with the National Inventory, which has the remit to provide a detailed account of actual waste currently present on French territory) thus makes it possible to bring down the variety of package families to a limited number of representative objects, and to specify the requisite margins of error, to ensure the design and assessment of disposal safety will be as robust as feasible, with respect to possible future variations in data.

To ensure consistency between investigations carried out in accordance with direction 2 and those along direction 3 (**conditioning and long-term storage**), CEA adopted MID as input data. MID subsumes waste packages into standard package types, then computes the number and volume of HLW and ILW-LL packages, according to a number of scenarios, all based on the assumption that current nuclear power plants will be operated for 40 years, their output plateauing at 400 **TWhe** per year.

Table 1 shows the numbers and volumes for each standard package type, for the scenario assuming a continuation of current strategy, with respect to spent fuel reprocessing: reprocessing of 79,200 **UOX** fuel **assemblies** and storage of 5,400 **MOX**

MID standard package types	Symbols	Producers	Categories	Number	Volume (m ³)
Vitrified waste packages	CO — C2	Cogema*	HLW	42,470	7,410
Activated metal waste packages	B1	EDF	ILW-LL	2,560	470
Bituminized sludge packages	B2	CEA, Cogema*	ILW-LL	105,010	36,060
Cemented technological waste packages	B3	CEA, Cogema*	ILW-LL	32,940	27,260
Cemented hull and end-cap packages	B4	Cogema*	ILW-LL	1,520	2,730
Compacted structural and technological waste packages	B5	Cogema*	ILW-LL	39,900	7,300
Containerized loose structural and technological waste packages	B6	Cogema*	ILW-LL	10,810	4,580
Total B				192,740	78,400
Total overall				235,210	85,810

* renamed Areva NC in 2006

Table 1.

Amounts (number, and volume) of waste packages, as predicted in France for 40 years' operation of the current fleet of reactors, according to ANDRA's Dimensioning Inventory Model (MID).

assemblies discharged from the current PWR fleet, when operated over 40 years.

What forms does it come in?

Five types of generic packages (also found in MID) may be considered:

- **cementitious waste packages:** ILW-LL waste packages employing hydraulic-binder based materials as a conditioning matrix, or as an immobilizing grout, or yet as a container constituent;
- **bituminized sludge packages:** LLW and ILW-LL waste packages, in which bitumen is used as confinement matrix for low- and intermediate-level residues from treatment of a variety of liquid effluents (fuel processing, research centers, etc.);
- **standard compacted waste packages** (CSD-C: *colis standard de déchets compactés*): ILW-LL packages obtained through compaction conditioning of structural waste from fuel assemblies, and technological waste from the La Hague workshops;
- **standard vitrified waste packages** (CSD-V: *colis standard de déchets vitrifiés*):

HLW packages, obtained mainly through vitrification of highly active solutions from spent fuel reprocessing;

- spent fuel packages: packages consisting in nuclear fuel assemblies discharged from reactors; these are not considered to be waste in France.

The only long-lived waste packages to be generated in any significant amounts by current electricity production (see Box B) are vitrified waste packages and standard compacted waste packages, the other types of packages having, for the most part, already been produced, and bearing but a small part of total radioactivity.

What is happening to this waste at present? What is to be done in the long term?

The goal of long-term radioactive waste management is to protect humankind and its environment from the effects of the materials comprised in this waste, most importantly from radiological hazards. Any release or dissemination of radioactive

materials must thus be precluded, through the lasting isolation of such waste from the environment. This management is guided by the following principles: to produce as little waste as practicable; limit its hazardous character as far as feasible; take into account the specific characters of each category of waste; and opt for measures that will minimize the burden (monitoring, maintenance) for future generations.

As for all nuclear activities subject to control by the French Nuclear Safety Authority (*Autorité de sûreté nucléaire*), fundamental safety regulations (RFSs: *règles fondamentales de sûreté*) have been drawn up with respect to radioactive waste management: sorting, volume reduction, package confinement potential, manufacturing method, radionuclide concentration. RFS III-2.f, in particular, specifies the conditions to be met for the design of, and demonstration of safety for an underground repository, and thus provides a basic guide for disposal investigations. Industrial solutions (see *Industrial solutions for all low-level waste*) are currently available for high on 85% (by volume) of waste, i.e. VLLW and LILW-SL waste. A solution for LLW-LL waste is the subject of ongoing investigation by ANDRA, at the behest of waste producers. ILW-LL and HLW waste, containing radionuclides having very long half-lives (in some cases, greater than several hundred thousand years) are currently held in storage installations coming under the control of the Nuclear Safety Authority. What is to become of this waste in the long term, beyond this storage phase, is what the Act of 30 December 1991 addresses (see Table 2).

For all of these waste types, the French Nuclear Safety Authority is drawing up a National Radioactive Waste Management Plan, specifying, for each type, a management pathway.

	Short-lived Half-life < 30 years for the main elements	Long-lived Half-life > 30 years
Very-low-level waste (VLLW)	Morvilliers dedicated disposal facility (open since 2003) Capacity: 650,000 m ³	
Low-level waste (LLW)	Aube Center (open since 1992) Capacity: 1 million m ³	Dedicated disposal facility under investigation for radium-bearing waste (volume: 100,000 m ³) and graphite waste (volume: 14,000 m ³)
Intermediate-level waste (ILW)		MID volume estimate: 78,000 m ³
High-level waste (HLW)	MID volume estimate: 7,400 m ³	

Table 2.

Long-term management modes, as currently operated, or planned, in France, by radioactive waste category. The orange area highlights those categories targeted by investigations covered by the Act of 30 December 1991.

■ (1) According to the Dimensioning Inventory Model (MID)

B Waste from the nuclear power cycle

Most high-level (high-activity) **radio-active waste (HLW)** originates, in France, in the irradiation, inside nuclear power reactors, of **fuel** made up from **enriched uranium oxide (UOX)** pellets, or also, in part, from mixed **uranium** and **plutonium** oxide (**MOX**). Some 1,200 tonnes of **spent fuel** is discharged annually from the fleet of 58 **pressurized-water reactors (PWRs)** operated by **EDF**, supplying over 400 **TWh** per year, i.e. more than three quarters of French national power consumption.

The fuel's composition alters, during its irradiation inside the reactor. Shortly after discharge, fuel elements contain, on average,⁽¹⁾ some 95% residual uranium, 1% plutonium and other **transuranic elements** – up to 0.1% – and 4% of products yielded by **fission**. The latter exhibit very significant radioactivity levels – to the extent this necessitates management safety measures requiring major industrial resources – of some 10¹⁷ **Bq** per tonne of initial uranium (tiU) (see Figure 1). The **uranium** found in spent fuel exhibits a makeup that is obviously different from that of the initial fuel. The greater the irradiation, the higher the consumption of **fissile** nuclei, and consequently the greater the extent by which the **uranium** will have been **depleted** of the fissile **isotope** ²³⁵U. Irradiation conditions usually prevailing in reactors in the French fleet, with an average fuel residence time inside the reactor of some 4 years, for a

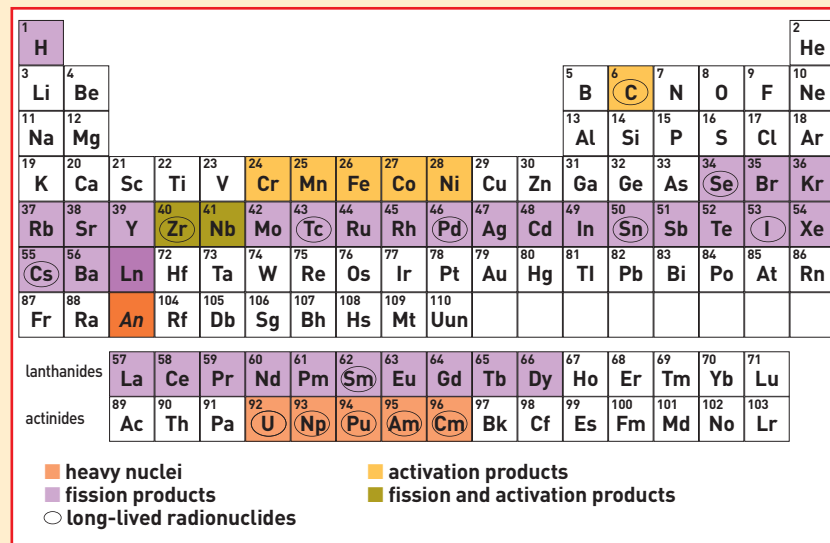


Figure 1.
The main elements found in spent nuclear fuel.

burnup rate close to 50 **GWd/t**, result in bringing down final ²³⁵U content to a value quite close to that of **natural uranium** (less than 1%), entailing an energy potential very close to the latter's. Indeed, even though this uranium remains slightly richer in the fissile isotope than natural uranium, for which ²³⁵U content stands at 0.7%, the presence should also be noted, in smaller, though significant, amounts, of other isotopes having adverse effects in neutronic or radiological terms (²³²U, ²³⁶U), that had not figured in the initial fuel (see Table 1).

The **plutonium** present in spent fuel is yielded by successive **neutron capture** and **decay** processes. Part of the Pu is dissipated through fission: thus about one third of the energy generated is yielded by "in situ recycling" of this element. These processes further bring about the formation of **heavy nuclei**, involving, whether directly themselves, or through their daughter products, long **radioactive half-lives**. These are the elements of the **actinide** family, this including, essentially, plutonium (from ²³⁸Pu to ²⁴²Pu, the odd-numbered isotopes generated in part undergoing fission themselves during irradiation), but equally neptunium (Np), americium (Am), and curium (Cm), known as **minor actinides (MAs)**, owing to the

(1) These figures should be taken as indicative values. They allow orders of magnitude to be pinpointed for enriched-uranium oxide fuel, taken from the main current French nuclear power pathway; they do depend, however, on a number of parameters, such as initial fuel composition and irradiation conditions, particularly irradiation time.

element	isotope	half-life (years)	UOX 33 GWd/tiU (E ²³⁵ U: 3.5%)		UOX 45 GWd/tiU (E ²³⁵ U: 3.7%)		UOX 60 GWd/tiU (E ²³⁵ U: 4.5%)		MOX 45 GWd/tihm (Ei Pu: 8.65%)	
			isotope content (%)	quantity (g/tiU)	isotope content (%)	quantity (g/tiU)	isotope content (%)	quantity (g/tiU)	isotope content (%)	quantity (g/tihm)
U	234	246,000	0.02	222	0.02	206	0.02	229	0.02	112
	235	7.04·10 ⁸	1.05	10,300	0.74	6,870	0.62	5,870	0.13	1,070
	236	2.34·10 ⁷	0.43	4,224	0.54	4,950	0.66	6,240	0.05	255
	238	4.47·10 ⁹	98.4	941,000	98.7	929,000	98.7	911,000	99.8	886,000
Pu	238	87.7	1.8	166	2.9	334	4.5	590	3.9	2,390
	239	24,100	58.3	5,680	52.1	5,900	48.9	6,360	37.7	23,100
	240	6,560	22.7	2,214	24.3	2,760	24.5	3,180	32	19,600
	241	14.4	12.2	1,187	12.9	1,460	12.6	1,640	14.5	8,920
	242	3.75·10 ⁵	5.0	490	7.8	884	9.5	1,230	11.9	7,300

Table 1.
Major actinide inventory for spent UOX and MOX fuel after 3 years' cooling, for a variety of enrichment and burnup rates. Burnup rate and quantity are expressed per tonne of initial uranium (tiU) for UOX, per tonne of initial heavy metal (tihm) for MOX.

B (next)

lesser abundance of these elements, compared with that of U and Pu, the latter being termed **major actinides**.

Activation processes affecting nuclei of non-radioactive elements mainly involve structural materials, i.e. the materials of the tubes, grids, plates and end-fittings that ensure the mechanical strength of nuclear fuel. These materials lead, in particular, to formation of **carbon 14** (^{14}C), with a half-life of 5,730 years, in amounts that are however very low, much less than one gram per tonne of initial uranium (g/tiU) in usual conditions.

It is the *products yielded by fission* of the initial uranium 235, but equally of the Pu generated (isotopes 239 and 241), known as **fission products (FPs)**, that are the essential source of the radioactivity of spent fuel, shortly after discharge. Over 300 **radionuclides** – two thirds of which however will be dissipated through radioactive decay in a few years, after irradiation – have been identified. These radionuclides are distributed over some 40 elements in the periodic table, from germanium (^{32}Ge) to dysprosium (^{66}Dy), with a presence of **tritium from fission**, i.e. from the fission into three fragments (ternary fission) of ^{235}U . They are thus characterized by great diversity: diverse radioactive properties, involving as they do some highly radioactive nuclides having very



Magnum/Harry Gruyaert

After discharge, spent fuel is stored in cooling pools, to allow its radioactivity to come down significantly. Shown here is a storage pool at Areva's spent fuel reprocessing plant at La Hague.

family	UOX 33 GWd/tiU (E ^{235}U : 3.5%)	UOX 45 GWd/tiU (E ^{235}U : 3.7%)	UOX 60 GWd/tiU (E ^{235}U : 4.5%)	MOX 45 GWd/tiU (Ei Pu: 8.65%)
	quantity (kg/tiU)	quantity (kg/tiU)	quantity (kg/tiU)	quantity (kg/tiU)
rare gases (Kr, Xe)	5.6	7.7	10.3	7
alkali metals (Cs, Rb)	3	4	5.2	4.5
alkaline-earth metals (Sr, Ba)	2.4	3.3	4.5	2.6
Y and lanthanides	10.2	13.8	18.3	12.4
zirconium	3.6	4.8	6.3	3.3
chalcogens (Se, Te)	0.5	0.7	1	0.8
molybdenum	3.3	4.5	6	4.1
halogens (I, Br)	0.2	0.3	0.4	0.4
technetium	0.8	1.1	1.4	1.1
Ru, Rh, Pd	3.9	5.7	7.7	8.3
miscellaneous: Ag, Cd, Sn, Sb...	0.1	0.2	0.3	0.6

Table 2.
Breakdown by chemical family of fission products in spent UOX and MOX fuel, after 3 years' cooling, for a variety of enrichment and burnup rates.

short lifespans, and conversely others having radioactive half-lives counted in millions of years; and diverse chemical properties, as is apparent from the analysis, for the "reference" fuels used in PWRs in the French fleet, of the breakdown of FPs generated, by families in the periodic table (see Table 2). These FPs, along with the actinides generated, are, for the most part, present in the form of oxides included in the initial uranium oxide, which remains by far the majority constituent. Among some notable exceptions may be noted iodine (I), present in the form of **cesium iodide**, rare gases, such as krypton (Kr) and xenon (Xe), or certain **noble metals**, including ruthenium (Ru), rhodium (Rh), and palladium (Pd), which may form metallic inclusions within the oxide matrix.

Pu is **recycled** nowadays in the form of MOX fuel, used in part of the fleet (some 20 reactors currently). Residual U may in turn be re-enriched (and recycled as a substitute for mined uranium). Recycling intensity depends on market prices for natural uranium, the recent upturn in which should result in raising the current recycling rate (about one third being recycled at present).

Such U and Pu recycling is the foundation for the **reprocessing** strategy currently implemented in France, for the major part of spent fuel (some two thirds currently).

For the 500 kg or so of U initially contained in every fuel element, and after partitioning of 475 kg of residual U and about 5 kg Pu, this "**ultimate**" waste amounts to less than 20 kg of FPs, and less than 500 grams MAs. This waste management pathway (otherwise known as the **closed cycle**), consisting as it does in reprocessing spent fuel now, to partition recoverable materials and ultimate waste, differs from strategies whereby spent fuel is conserved as-is, whether this be due to a wait-and-see policy (pending a decision on a long-term management model), or to a so-called **open cycle** policy, whereby spent fuel is considered to be waste, and designated for **conditioning** into **containers**, and **disposal** as-is.

In the nuclear power cycle, as it is implemented in France, waste is subdivided into two categories, according to its origin. Waste directly obtained from spent fuel is further subdivided into **minor actinides and fission products**, on the one hand, and **structural waste**, comprising **hulls** (segments of the cladding tubes that had held the fuel for PWRs) and **end-caps** (fittings forming the end-pieces of the fuel assemblies for these same PWRs), on the other hand. The process used for spent fuel reprocessing, to extract U and Pu, also generates **technological waste** (operational waste, such as spare parts, protection gloves...) and **liquid effluents**.

c What stands between waste and the environment?

Raw, solid or liquid **radioactive waste** undergoes, after characterization (determination of its chemical and radiological makeup, and of its physical-chemical properties), **conditioning**, a term covering all the operations consisting in bringing this waste (or spent **fuel assemblies**) to a form suitable for its transport, **storage**, and **disposal** (see Box D). The aim is to put radioactive waste into a solid, physically and chemically stable form, and ensure effective, lasting confinement of the **radionuclides** it contains. For that purpose, two complementary operations are carried out. As a rule, waste is immobilized by a material – whether by encapsulation or homogeneous incorporation (liquid or powdered waste, sludges), or encasing (solid waste) – within a **matrix**, the nature of, and performance specification for which depend on waste type (cement for sludges, evaporation concentrates and incineration ashes; bitumen for **encapsulation** of sludges or evaporation concentrates from liquid effluent treatment; or a vitreous matrix, intimately binding the nuclides to the glass network, for **fusion product** or **minor actinide** solutions). This matrix contributes to the confinement function. The waste thus conditioned is placed in an impervious **contai-**



A. Gomin/CEA

Cross-section of an experimental storage borehole for a spent fuel container (the lower part of the assembly may be seen, top right), in the Galatée gallery of CECER (Centre d'expertise sur le conditionnement et l'entreposage des matières radioactives: Radioactive Materials Conditioning and Storage Expertise Center), at CEA's Marcoule Center, showing the nested canisters.

ner (cylindrical or rectangular), consisting in one or more **canisters**. The whole – container and content – is termed a **package**. Equally, waste may be compacted and mechanically **immobilized** within a canister, the whole forming a package.

When in the state they come in as supplied by industrial production, they are known as **primary packages**, the pri-

mary container being the cement or metal container into which the conditioned waste is ultimately placed, to allow handling. The container may act as initial confinement **barrier**, allotment of functions between matrix and container being determined according to the nature of the waste involved. Thus, the whole obtained by the grouping together, within one container, of a number of primary

c (next)

ILW-LL packages may ensure confinement of the radioactivity of this type of waste. If a **long-term storage** stage is found to be necessary, beyond the stage of industrial storage on the premises of the producers, primary waste packages must be amenable to retrieval, as and when required: durable primary containers must then be available, in such conditions, for all types of waste.

In such a case, for spent fuel assemblies which might at some time be earmarked for such long-term storage, or even for disposal, it is not feasible to demonstrate, on a timescale of centuries, the integrity of the cladding holding the fuel, forming the initial confinement barrier during the in-reactor use stage. Securing these assemblies in individual, impervious cartridges is thus being considered, this stainless-steel **cartridge** being compatible with the various possible future management stages: **treatment**, return to storage, or disposal. Placing these cartridges inside impervious containers ensures a second confinement barrier, as is the case for **high-level** waste packages.

In storage or disposal conditions, the waste packages will be subjected to a variety of aggressive agents, both internal and external. First, radionuclide

radioactive decay persists inside the package (**self-irradiation** process). Emission of radiation is concomitant with heat generation. For example, in confinement glasses holding high-**activity** (high-level) waste, the main sources of irradiation originate in the **alpha decay** processes from **minor actinides**, **beta decay** from **fission products**, and gamma transitions. Alpha decay, characterized by production of a **recoil nucleus**, and emission of a particle, which, at the end of its path, yields a helium atom, causes the major part of atom displacements. In particular, recoil nuclei, shedding considerable energy as they do over a short distance, result in atom displacement cascades, thus breaking large numbers of chemical bonds. This is thus the main cause of potential long-term damage. In such conditions, matrices must exhibit thermal stability, and irradiation-damage resistance.

Stored waste packages will also be subjected to the effects of water (**leaching**). Container canisters may exhibit a degree of resistance to corrosion processes (the **overpacks** contemplated for glasses may thus delay by some 4,000 years the arrival of water), and the confinement matrices must be proven to exhibit high chemical stability.

Between the containers and the ultimate barrier provided, in a radioactive waste deep disposal facility, by the geological environment itself, there may further be interposed, apart, possibly, from an overpack, other barriers, so-called **engineered barriers**, for backfill and sealing purposes. While these would be pointless as backfill in clay formations, they would have the capability, in other environments (granite), of further retarding any flow of radionuclides to the **geosphere**, notwithstanding degradation of the previously mentioned barriers.



Technological demonstrators of ILW-LL packages for bituminized sludges.

D From storage to disposal

The object of nuclear waste **storage** and **disposal** is to ensure the long-term **confinement** of **radioactivity**, in other words to contain **radionuclides** within a definite space, segregated from humankind and the environment, as long as required, so that the possible return to the **biosphere** of minute amounts of radionuclides can have no unacceptable health or environmental impact.

According to the Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management, signed on 5 September 1997, "storage" means "the holding of spent fuel or of radioactive waste in a facility that provides for its containment, with the intention of retrieval." This is thus, by definition, an interim stage, amounting to a delaying, or wait-and-see solution, even though this may be for a very long time (from a few decades to several hundred years), whereas disposal may be final.

Used from the outset of the nuclear power age, industrial storage keeps spent fuel awaiting reprocessing, and conditioned **high-level waste (HLW)**, or **long-lived intermediate-level waste**

(**ILW-LL**) in conditions of safety, pending a long-term management mode for such waste. Retrieval of stored packages is anticipated, after a period of limited duration (i.e. after a matter of



CEA design study for a common container for the long-term storage and disposal of long-lived, intermediate-level waste.

years, or tens of years).

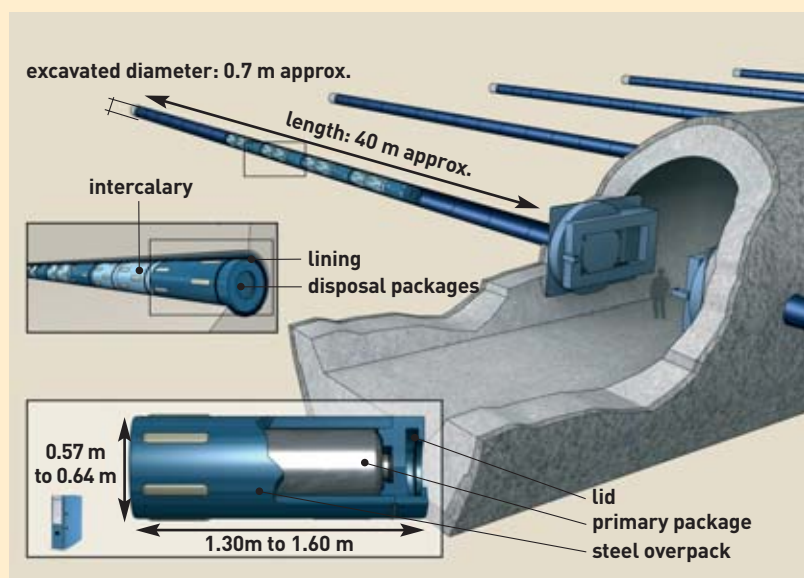
Long-term storage (LTS) may be contemplated, in particular, in the event of the deferred deployment of a disposal facility, or of reactors to carry out

recycling-transmutation, or simply to turn to advantage the natural decay of radioactivity (and hence the falling off of heat release from high-level waste), before putting the waste into **geological disposal**. By "long term" is meant a timespan of up to 300 years. Long-term storage may take place in a **surface** or **sub-surface** facility. In the former case, the site may be protected, for instance, by a reinforced-concrete structure. In the latter case, it will be located at a depth of some tens of meters, and protected by a natural environment (for instance, if buried in a hill-side) and its host rock.

Whichever management strategy is chosen, it will be imperative to protect the biosphere from the residual ultimate waste. The nature of the radioelements the latter contains means a solution is required that has the ability to ensure their confinement over several tens of thousand years, in the case of long-lived waste, or even longer. On such timescales, social stability is a major uncertainty that has to be

taken on board. Which is why disposal in deep geological strata (typically, 500 m down) is seen as a reference solution, insofar as it inherently makes for deployment of a more passive technical solution, with the ability to stand, with no increased risk, an absence of surveillance, thus mitigating a possible loss of memory on the part of society. The geological environment of such a disposal facility thus forms a further, essential barrier, which does not exist in the storage case.

A disposal facility may be designed to be **reversible** over a given period. The concept of reversibility means the design must guarantee the ability, for a variety of reasons, to access the **packages**, or even to take them out of the facility, over a certain timespan, or to opt for the final closure of the disposal facility. Such reversibility may be envisaged as a succession of stages, each affording a decreasing "level of reversibility." To simplify, each stage consists in carrying out one further technical operation bringing the facility closer to final closure, making retrieval more difficult than at the previous stage, according to well-specified criteria.



ANDRA design for the disposal of standard vitrified waste packages in horizontal galleries, showing in particular the packages' various canisters, and some characteristics linked to potential reversibility of the disposal facility.

E What is transmutation?

Transmutation is the transformation of one nucleus into another, through a reaction induced by particles with which it is bombarded. As applied to the treatment of nuclear waste, this consists in using that type of reaction to transform **long-lived radioactive isotopes** into isotopes having a markedly shorter life, or even into stable isotopes, in order to reduce the long-term **radiotoxic** inventory. In theory, the projectiles used may be **photons, protons, or neutrons**.

In the first case, the aim is to obtain, by bremsstrahlung,⁽¹⁾ through bombardment of a target by a beam of electrons, provided by an accelerator, photons able to bring about reactions of the (γ, xn) type. Under the effects of the incoming **gamma** radiation, x neutrons are expelled from the nucleus. When applied to substances that are too rich in neutrons, and hence unstable, such as certain **fission products** (strontium 90, cesium 137...), such reactions yield, as a rule, stable substances. However, owing to the very low efficiency achieved, and the very high electron current intensity required, this path is not deemed to be viable.

In the second case, the proton-nucleus interaction induces a complex reaction, known as **spallation**, resulting in fragmentation of the nucleus, and the release

of a number of particles, including high-energy neutrons. Transmutation by way of *direct* interaction between protons is uneconomic, since this would involve, in order to overcome the Coulomb barrier,⁽²⁾ very-high-energy protons (1–2 **GeV**), requiring a generating energy greater than had been obtained from the process that resulted in producing the waste. On the other hand, *indirect* transmutation, using very-high-energy neutrons (of which around 30 may be yielded, depending on target nature and incoming proton energy), makes it possible to achieve very significantly improved performance. This is the path forming the basis for the design of so-called **hybrid reactors**, coupling a **subcritical** core and a high-intensity proton accelerator (see Box F, *What is an ADS?*).

The third particle that may be used is thus the neutron. Owing to its lack of electric charge, this is by far the particle best suited to meet the desired criteria. It is “naturally” available in large quantities inside nuclear reactors, where it is used to trigger **fission** reactions, thus yielding energy, while constantly inducing, concurrently, transmutations, most of them unsought. The best **recycling** path for waste would thus be to reinject it in the very installation, more or less, that had produced it...

When a neutron collides with a nucleus, it may bounce off the nucleus, or penetrate it. In the latter case, the nucleus, by absorbing the neutron, gains excess energy, which it then releases in various ways:

- by expelling particles (a neutron, e.g.), while possibly releasing radiation;
- by solely emitting radiation; this is known as a *capture reaction*, since the neutron remains captive inside the nucleus;
- by breaking up into two nuclei, of more or less equal size, while releasing concurrently two or three neutrons; this is known as a *fission reaction*, in which considerable amounts of energy are released.

Transmutation of a **radionuclide** may be achieved either through neutron capture or by fission. **Minor actinides**, as elements having large nuclei (**heavy nuclei**), may undergo both fission and capture reactions. By fission, they transform into radionuclides that, in a majority of cases, are short-lived, or even into stable nuclei. The nuclei yielded by fission (known as fission products), being smaller, are only the seat of capture reactions, undergoing, on average, 4 radioactive decays, with a **half-life** not longer than a few years, as a rule, before they reach a stable form. Through capture, the same heavy nuclei transform into other radionuclides, often long-lived, which transform in turn through natural decay, but equally through capture and fission.

(1) From the German for “braking radiation.” High-energy photon radiation, yielded by accelerated (or decelerated) particles (electrons) following a circular path, at the same time emitting braking photons tangentially, those with the highest energies being emitted preferentially along the electron beam axis.

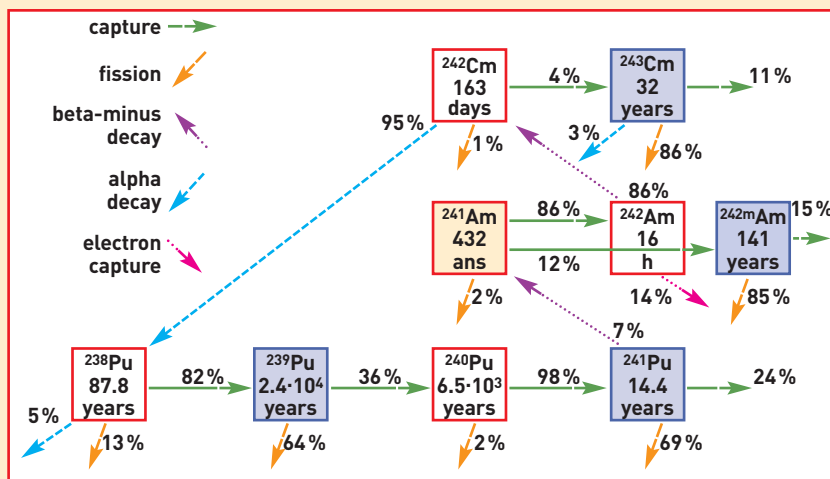
(2) A force of repulsion, which resists the drawing together of same-sign electric charges.

E

For a neutron having an energy lower than 1 eV (in the range of slow, or thermal, neutrons), the capture cross-section

Two reactor pathways may be considered, according to the neutron energy range for which the majority of fission reactions occur: **thermal-neutron** reactors, and **fast-neutron** reactors. The ther-

In a fast-neutron reactor, such as Phénix, neutrons yielded by fission immediately induce, without first being slowed down, further fissions. There is no moderator in this case. Since, for this energy range, cross-sections are small, a fuel rich in fissile radionuclides must be used (up to 20% uranium 235 or plutonium 239), if the neutron multiplication factor is to be equal to 1. The flux in a fast-neutron reactor is ten times larger (of the order of 10^{19} neutrons per square meter, per second) than for a thermal-neutron reactor.



Simplified representation of the evolution chain of americium 241 in a thermal-neutron reactor (shown in blue: radionuclides disappearing through fission). Through capture, ^{241}Am transforms into ^{242m}Am , this disappearing predominantly through fission, and into ^{242}Am , which mainly decays (with a half-life of 16 hours) through beta decay into ^{242}Cm . ^{242}Cm transforms through alpha decay into ^{238}Pu , and through capture into ^{243}Cm , which itself disappears predominantly through fission. ^{238}Pu transforms through capture into ^{239}Pu , which disappears predominantly through fission.

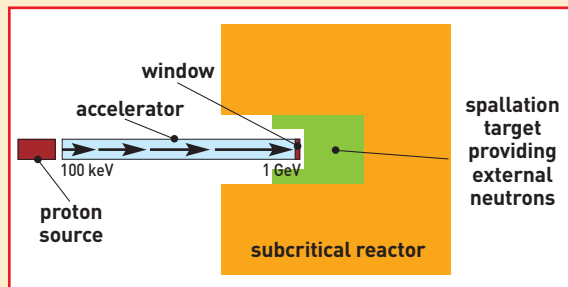
F What is an ADS?

An **ADS** (accelerator-driven system) is a **hybrid system**, comprising a nuclear reactor operating in **subcritical** mode, i.e. a reactor unable by itself to sustain a **fission chain reaction**, “driven” by an external source, having the ability to supply it with the required complement of **neutrons**.⁽¹⁾

Inside the core of a nuclear reactor, indeed, it is the fission energy from **heavy nuclei**, such as **uranium 235** or **plutonium 239**, that is released. Uranium 235 yields, when undergoing fission, on average 2.5 neutrons, which can in turn induce a further fission, if they collide with a uranium 235 nucleus. It may thus be seen that, once the initial fission

is initiated, a chain reaction may develop, resulting, through a succession of fissions, in a rise in the neutron population. However, of the 2.5 neutrons yielded by the initial fission, some are captured, thus not giving rise to further fissions. The number of fissions generated from one initial fission is characterized by the **effective multiplication factor** k_{eff} , equal to the ratio of the number of fission neutrons generated, over the number of neutrons disappearing. It is on the value of this coefficient that the evolution of the neutron population depends: if k_{eff} is markedly higher than 1, the population increases rapidly; if it is slightly higher than 1, neutron multiplication sets in, but remains under control; this is the state desired at reactor startup; if k_{eff} is equal to 1, the population remains stable; this is the state

for a reactor in normal operating conditions; and, if k_{eff} is lower than 1, the neutron population dwindles, and becomes extinct, unless – as is the case for a hybrid system – an external source provides a neutron supply.



Principle schematic of an ADS.

From the effective multiplication factor, a reactor’s **reactivity** is defined by the ratio $(k_{\text{eff}} - 1)/k_{\text{eff}}$. The condition for stability is then expressed by zero reactivity. To stabilize a neutron population, it is sufficient to act on the proportion of materials exhibiting a large **neutron capture** cross-section (neutron absorber materials) inside the reactor.

In an ADS, the **source** of extra neutrons is fed with **protons**, generated with an energy of about 100 **keV**, then injected into an accelerator (linear accelerator or cyclotron), which brings them to an energy of around 1 **GeV**, and directs them to a heavy-metal target (lead, lead-bismuth, tungsten or tantalum). When irradiated by the proton beam, this target yields, through **spallation** reactions, an intense, high-energy (1–20 **MeV**) neutron flux, one single incoming neutron having the ability to generate up to 30 neutrons. The lat-

ter then go on to interact with the fuel of the subcritical neutron **multiplier medium**, yielding further neutrons (fission neutrons) [see Figure].

Most hybrid system projects use as a core (of annular configuration, as a rule) **fast-neutron** environments, since these make it possible to achieve neutron balances most favorable to **transmutation**, an operation that allows waste to be “burned,” but which may equally be used to yield further **fissile** nuclei. Such a system may also be used for energy generation, even though part of this energy must be set aside to power the proton accelerator, a part that is all the higher, the more

subcritical the system is. Such a system is safe in principle from most reactivity accidents, its multiplication factor being lower than 1, contrary to that of a reactor operated in critical mode: the chain reaction would come to a halt, if it was not sustained by this supply of external neutrons.

A major component in a hybrid reactor, the **window**, positioned at the end of the beam line, isolates the accelerator from the target, and makes it possible to keep the accelerator in a vacuum. Traversed as it is by the proton beam, it is a sensitive part of the system: its lifespan depends on thermal and mechanical stresses, and corrosion. Projects are mooted, however, of windowless ADSs. In the latter case, it is the confinement constraints, and those of radioactive spallation product extraction, that must be taken on board.

■ (1) On this topic, see *Clefs CEA*, No. 37, p. 14

The industrial context

1

The characteristics of the major part of the **radioactive waste** generated in France are determined by those of the French nuclear power generation fleet, and of the spent **fuel** reprocessing plants, built in compliance with the principle of reprocessing such fuel, to partition such materials as remain recoverable for energy purposes (**uranium** and **plutonium**), and waste (**fission products** and **minor actinides**), not amenable to recycling in the current state of the art.

58 **enriched-uranium pressurized-water reactors (PWRs)** have been put on stream by French national utility **EDF**, from 1977 (Fessenheim) to 1999 (Civaux), forming a second generation of reactors, following the first generation, which mainly comprised 8 **UNGG** (**natural uranium**, graphite, gas) reactors, now all closed down, and, in the case of the older reactors, in the course of decommissioning. Some 20 of these PWRs carry out the industrial recycling of plutonium, included in **MOX** fuel, supplied since 1995 by the **Melox** plant, at Marcoule (Gard *département*, Southern France).

EDF is contemplating the gradual replacement of the current PWRs by third-generation reactors, belonging to the selfsame pressurized-water reactor pathway, of the **EPR** (European Pressurized-Water Reactor) type, designed by **Areva NP** (formerly **Framatome-ANP**), a division of the **Areva** Group. The very first EPR is being built in Finland, the first to be built in France being sited at Flamanville (Manche *département*, Western France).

The major part of spent fuel from the French fleet currently undergoes reprocessing at the **UP2-800**⁽¹⁾ plant, which has been operated at La Hague (Manche *département*), since 1994, by Areva NC (formerly Cogema,) another member of the Areva Group (the UP3 plant, put on stream in 1990–92, for its part, carries out reprocessing of fuel from other countries). The waste **vitrification** workshops at these plants, the outcome of development work initiated at Marcoule, give their name (**R7T7**) to the “nuclear” glass used for the confinement of **long-lived, high-level** waste.

A fourth generation of reactors could emerge from 2040 (along with new reprocessing plants), a prototype being built by 2020. These could be **fast-neutron** reactors (i.e. fast reactors [**FRs**]), either sodium-cooled (SFRs) or gas-cooled (**GFRs**). Following the closing down of the Superphénix reactor, in 1998, only one FR is operated in France, the Phénix reactor, due to be closed down in 2009.

■ (1) A reengineering of the **UP2-400** plant, which, after the **UP1** plant, at Marcoule, had been intended to reprocess spent fuel from the UNGG pathway.