

LONG-LIVED RADIONUCLIDES PARTITIONED AT WILL

The differences between the most important radionuclides making up nuclear waste in terms of toxicity and lifetime call for the use of special processing methods for actinides or fission products, which represent most of the long-term potential harmful effects involved. In order to transmute them or condition them as extremely stable compounds, they must first be sorted. CEA research teams, in cooperation with the scientific community not only in France and Europe, but also in Russia and Japan, are working to develop a comprehensive range of hydrometallurgical processes to implement the advanced separation methods required – whatever the management strategies adopted downstream.

Shielded cell at the Atalante facility, CEA/Valrhô-Marcoule. This facility is at the forefront of research into advanced partitioning of long-lived radionuclides.



Even further partitioning for better management

The elements formed in nuclear **fuel** when it is irradiated in a reactor (see box B, **Waste from the nuclear power cycle**) not only present extremely diverse chemical properties and physical forms (oxides, metals, gases), but also the extremely wide range of **radioactive** properties of several hundred nuclides (which may be stable or radioactive, **alpha**, **beta** or **gamma** emitters, and with a **half-life** ranging from very short to very long). The combination of all these different properties makes short- or long-term management of spent fuel a particularly complex task.

The first step in defining a management strategy is to identify what waste should include (see box A, **What is radioactive waste?**). Nearly 96% of nuclear spent fuel is made up of material that can be reused to generate energy (residual uranium U, and plutonium Pu). The spent-fuel **reprocessing** method adopted in France to date consists in separating U and Pu from other **radionuclides (minor actinides and fission products)**. The presence of radioactive nuclei with a very long half-life in separation residue (i.e. waste) raises a number of particular questions concerning the long-term



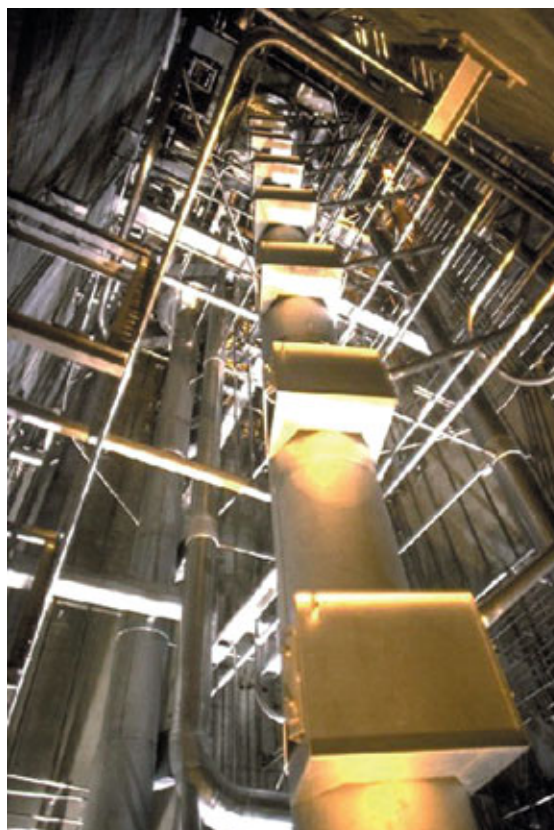
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safety of management methods. Research has now made even more progress in providing answers to these questions, which nonetheless point to the need for a more advanced management concept. Within this context, the need has arisen to study and consider the possibility of reprocessing different long-lived **radioelements** in different ways. This would first entail carrying out additional partitioning of long-lived radionuclides in what is currently the final waste (advanced separation concept), then studying specific management strategies for the isolated elements obtained (creating specific, extremely stable compounds or adopting a more radical approach, transmuting elements into nuclei with a much shorter half-life).

Identifying the elements to be separated out

Radionuclides with a half-life in excess of thirty years are those liable to remain a significant factor in the radioactivity of waste several centuries later. Analysis of spent-fuel composition shows that these radionuclides account for about 10% of the overall residual mass (see box B, **Waste from the nuclear power cycle**) once the U and Pu have been separated out, which in itself already calls for a special management strategy. This category concerns all the minor actinides (neptunium Np, americium Am, and curium Cm), of which each **isotope** either has a long half-life, or at least one daughter product with a long half-life. Some fission or **activation** products also fall into this category. These are both numerous and varied, not only in terms of their abundance but also because of their respective chemical properties. Given this degree of diversity, it therefore seems difficult, if not impossible, to design a “blanket” separation process for all the radionuclides potentially concerned. An “element-by-element” approach is essential, meaning that the main elements to be included in the process must first be identified, keeping objectives in mind.

Analysis of how the contribution of each element to the **radiotoxic inventory** of spent-fuel changes over time (see box C, **Radio-toxicity of spent fuel**) shows Pu to be the main contributor. From this, it is clear that aiming for a management strategy for long-lived radionuclides means defining a Pu management strategy! This explains the importance of **recycling** in reactors the Pu obtained from spent-fuel reprocessing as practiced today. Apart from Pu, minor actinides are the most radiotoxic component of spent-fuel radiotoxic inventory. For this reason, they must appear as the chief “target” of any selective management strategy for long-lived radionuclides. Studying the separation of Np, Am, and Cm, the three principal members



Sidney Jezequel/Cogema

The Purex process, used to recover uranium and plutonium from spent fuel, can also be adjusted to extract iodine, technetium, and neptunium. Shown here are pulsed columns in the T2 high-activity extraction unit at Cogema's UP3 waste-reprocessing plant at La Hague.



of the minor actinide group, was therefore included in research priorities in the field of long-term nuclear waste management.

Some long-lived fission or activation products, however, have particular chemical properties that make them potentially mobile in the **geosphere** and **biosphere** (relatively speaking, of course) under certain **disposal** scenarios, for example in deep geological formations. Iodine (I) and technetium (Tc) are more soluble and less prone to **sorption** on the surrounding rocks than the **actinides**, which can to some extent counteract their far lower intrinsic toxicity in impact assessments. This has led researchers to investigate the possibilities of separating out certain potentially more “mobile” fission products containing a long-lived isotope, such as iodine and, to a lesser extent, technetium and cesium (Cs).

Advanced separation processes

In theory, many different avenues can be explored for advanced separation processes (physical processes, chemical processes), and the research work undertaken in this area does indeed cover a wide variety of possible alternatives. Nonetheless, research must be pursued with a twofold objective. Firstly, it must focus on requirements relating to performance, safety, reliability, cost, and the need to minimize secondary waste, in other words, on all the criteria that should apply to a modern separation process. Secondly, it

must take into account the deadline (2006) specified in the Act promulgated on December 30, 1991 (see *Radioactive waste management research*, Box 1), which implies studying options based on industrial realities as seen today, to submit properly supported assessment data by that deadline.

Drawing on the maturity of the Purex process

The research program conducted by CEA for the past ten years is now clearly a part of this initiative. The main research theme under consideration for separating long-lived radionuclides is selective extraction from an aqueous solution in which all the components of spent fuel are dissolved (**hydrometallurgical** processes). This choice is based on several criteria. Firstly, the **Purex** spent-fuel reprocessing process, currently used to recover U and Pu, and exploiting the properties of tributyl phosphate (TBP), which has a selective affinity for these elements, is a process of this type. Secondly, as we have already seen, a process for separating long-lived radionuclides can only be effective if it is complementary to a similar strategy for plutonium. This justifies investigating additional separation objectives downstream from this key phase. Furthermore, the relative imminence of the deadline argues in favor of processes of tried and tested industrial maturity, which is the case of hydrometallurgical processes. Finally, the operating feedback from the Purex process in

Radiotoxicity of spent fuel

The main elements found in spent fuel are long-lived **radionuclides**: uranium U, plutonium Pu, **minor actinides** (neptunium Np, americium Am, curium Cm) and **fission products**. These highly **active** radionuclides emit **alpha**, **beta**, and **gamma** radiation, and are characterized by a radioactive decay period that can cover several thousand, or even several hundred thousand years. **Radioactivity** (Bq), which corresponds to the number of radioactive atoms disintegrating per second, is a measure of the disintegration dynamics of an unstable nuclide. The term **radiotoxic inventory** refers to the weighted sum of the toxic ingredients of all the elements contained in the spent fuel. The term **potential radiotoxicity** is often used with the same meaning. This measure of the harmful potential of a certain quantity of radioactive material is assessed by considering it in terms of the dose that would be received by all the members of a group of people who had incorporated the material in question⁽¹⁾. To convert the activity of the inhaled or ingested radionuclide into a human dose (in Sv), it must be multiplied by a **dose factor** (or DPUI, dose per unit intake) expressed in sieverts per becquerel (Sv/Bq). Dose factors take into account the metabolism

of radionuclides in the organism once inhaled or ingested, the type and energy level of the emitted radiation, and the radiosensitivity of tissues, etc. They are evaluated using models describing the movement of radionuclides through the different parts of the body. A dose factor table is regularly updated by the International Commission on Radiological Protection (ICRP). Generally, the values assigned are several orders of magnitude greater for actinides than for fission products (table).

The change in radiotoxicity (or radiotoxic inventory) of a spent fuel over time (diagram) shows that:

- The **global** radiotoxic inventory of the spent fuel obviously decreases over time and, after about 250,000 years, drops back to the radiotoxicity level of the initial uranium ore.
- **Plutonium** is the largest contributor to the long-term radiotoxic inventory of

spent fuel. After 300 years, it represents more than 80% of the global **residual radiotoxic** inventory, this figure rising to nearly 90% after 500 years.

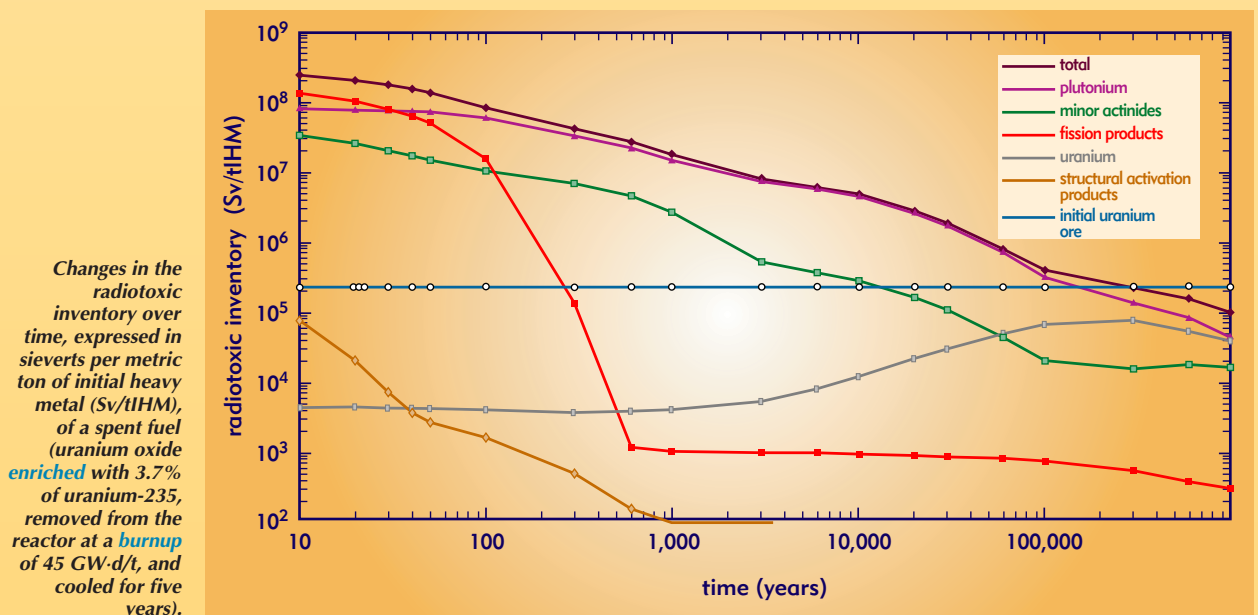
● After plutonium, the **minor actinides** make the next-largest contribution (about one order of magnitude, or 10 times, less than that of plutonium, but **three orders of magnitude**, or 1,000 times, **greater than that of fission products** after a few centuries).

Actinides (Pu, Np, Am, and Cm) are therefore the main contributors to the radiotoxic inventory of spent fuel. Some fission products, such as iodine (I), and, to a lesser degree, technetium (Tc) and cesium (Cs) contribute much less to this inventory. They must nonetheless be taken into account, because their relative mobility in the **geosphere** can – *all things considered* – make them more liable to present a hypothetical risk of ingestion.

(1) Therefore, it is not a measurement of risk, but simply a way of expressing the total quantity of toxic material to be managed.

	isotope	DPUI (Sv/Bq)
actinides	plutonium-239	2.5×10^{-7}
	americium-241	2.0×10^{-7}
	neptunium-237	1.1×10^{-7}
fission products	zirconium-93	1.1×10^{-9}
	technetium-99	6.4×10^{-10}
	samarium-151	9.8×10^{-11}

Table. Some DPUI values taken from ICRP 72, representing ingestion by an adult. For the same level of radioactivity, actinides have a greater impact than fission products.



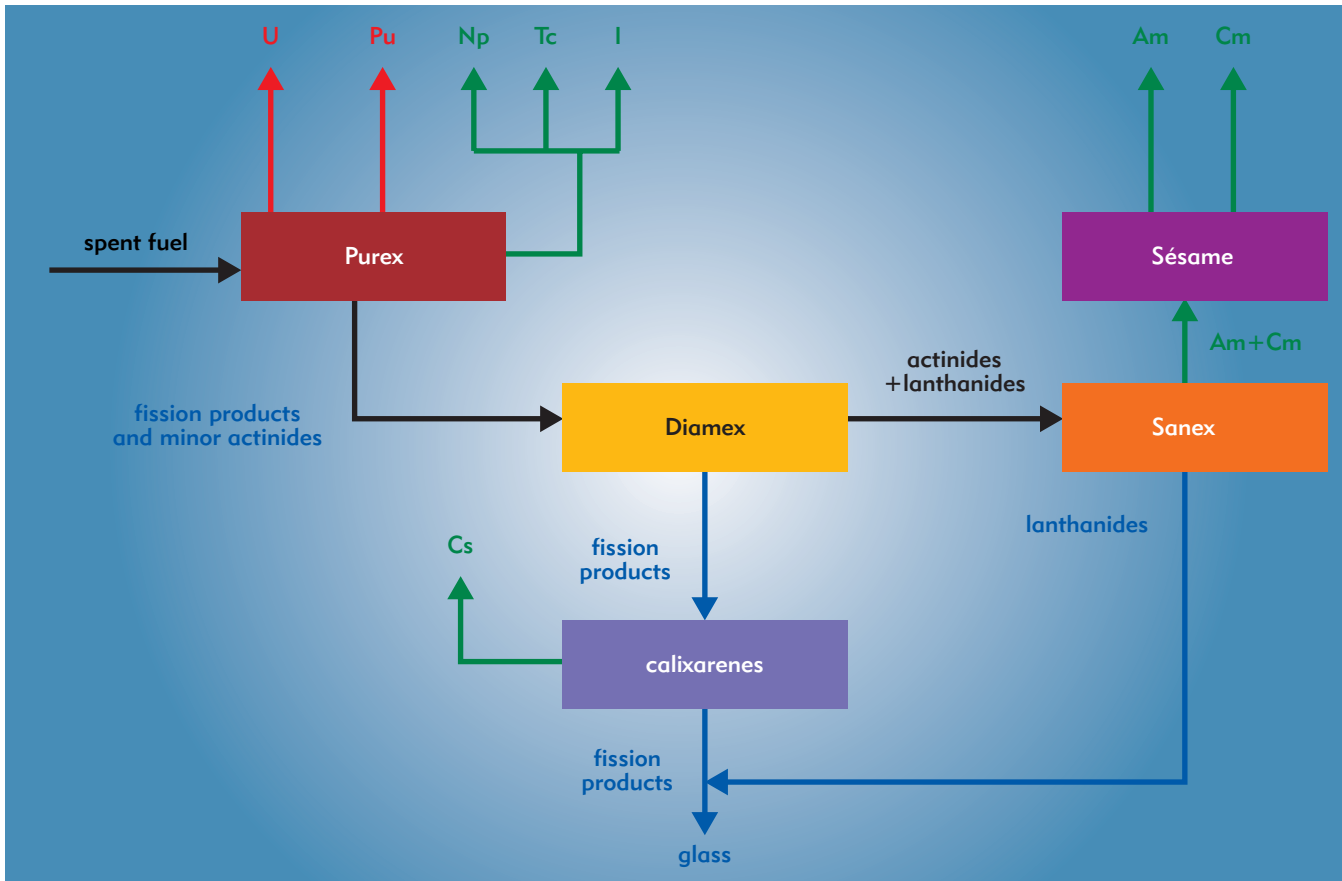


Figure 1. Reference scheme for long-lived radionuclide separation.



Cogema's plants at La Hague (Manche département) demonstrates that processes of this type can offer outstanding separation performance (quantity and selectivity of target elements recovered), while generating very little technological waste. This is a great advantage in view of the main assessment criteria considered earlier.

New extractant molecules

The strategy of the research program conducted by CEA on the separation of long-lived radionuclides involves exploring areas complementary to the industrial strategy currently implemented for spent-fuel reprocessing, and exploiting the full potential of the Purex process. Investigations of this process have already paid off for some elements, such as iodine I, which is found in gaseous form and can be recovered using various "trapping" devices, or Tc and Np, whose particular chemical properties mean that they can be quantitatively extracted using TBP. Researchers now estimate that nearly 99% of the iodine found in spent fuel can be recovered. As for elements that cannot be separated out using the Purex process, research teams are investigating complementary operations downstream involving the use of new extractants (this is the case for Am, Cm, and Cs). This is the area where the really challenging scientific research is found, with the development of original

molecular architectures capable of providing effective and selective separation techniques for these elements, while meeting the criteria discussed earlier relating to industrial practicability (e.g. stability with respect to the chemical and radiolytic hazards of the media concerned). These aspects, in particular the problems posed by selective extraction of Am and Cm in the presence of large quantities of elements from the lanthanide group found in spent fuel, which have very similar chemical properties, are discussed in the article entitled A "master key" to chemical separation processes. Specific molecules called calixarenes have been developed to extract Cs (see "Crown molecules" for separating cesium).

The scheme in which these studies take place is illustrated by figure 1. There are two milestone dates in development work: 2001 for selecting and qualifying extractant systems, and 2005 for demonstrating the feasibility of processes resulting from these concepts.

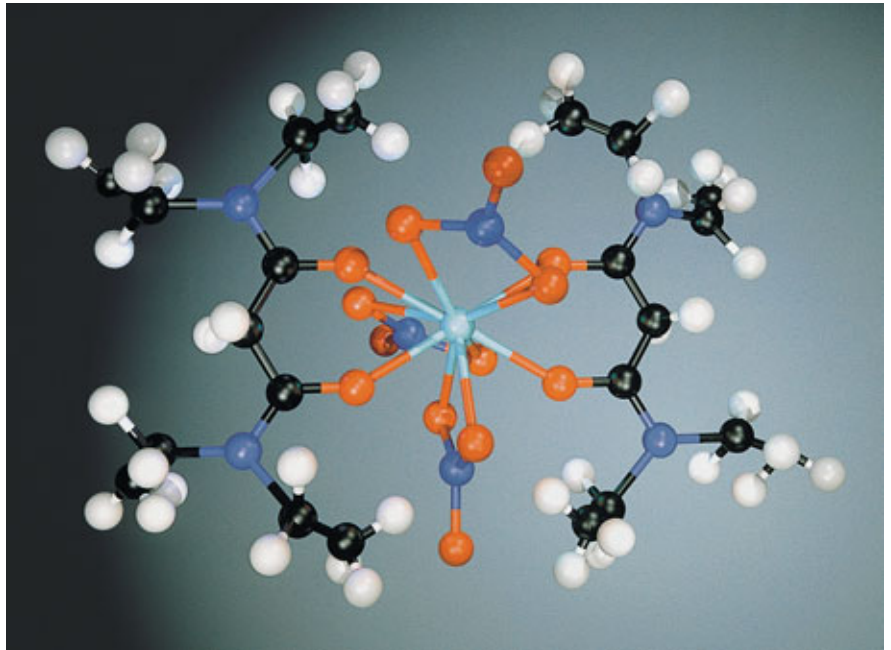
In view of the difficulties mentioned above, today's approach to Am and Cm recovery is based on a three-stage process. The first stage involves direct and combined quantitative extraction of actinides and lanthanides, to separate them from the rest of the fission products. Molecules from the diamide family currently seem the best choice for this operation (Diamex process). The purpose of the second stage is to separate actinides from

lanthanides (Sanex concept) by exploiting the slight differences in their chemical properties and using discriminating extractants, such as the molecules in the bis-triazinyl-pyridine family. The conditions for obtaining the required degree of selectivity are more "delicate" here than in the previous stage. However, as the other fission products have now been removed, particular chemical conditions can be selected without running the risk, for example, of precipitation phenomena occurring in an element with a special type of behavior. The third stage entails separating Am from Cm. This may be required if it is planned to manage these two elements differently, an option which remains to be confirmed. Several concepts are studied, the current reference model being the Sesame process based on oxidation and selective complexation of Am.

Some encouraging results

Many studies have been carried out both at the fundamental, exploratory level and at the applied experimentation level. At the end of 2001, CEA researchers conducted laboratory experiments on all these concepts using solutions obtained by dissolving real spent fuel,

Molecules from the diamide family have been developed for combined actinide and lanthanide separation from solutions resulting from the reprocessing of spent fuel according to the Diamex process. Shown here is the structure of the $Am(NO_3)_3 \cdot 2$ diamide complex, where the diamide is tetraethylmalonamide.



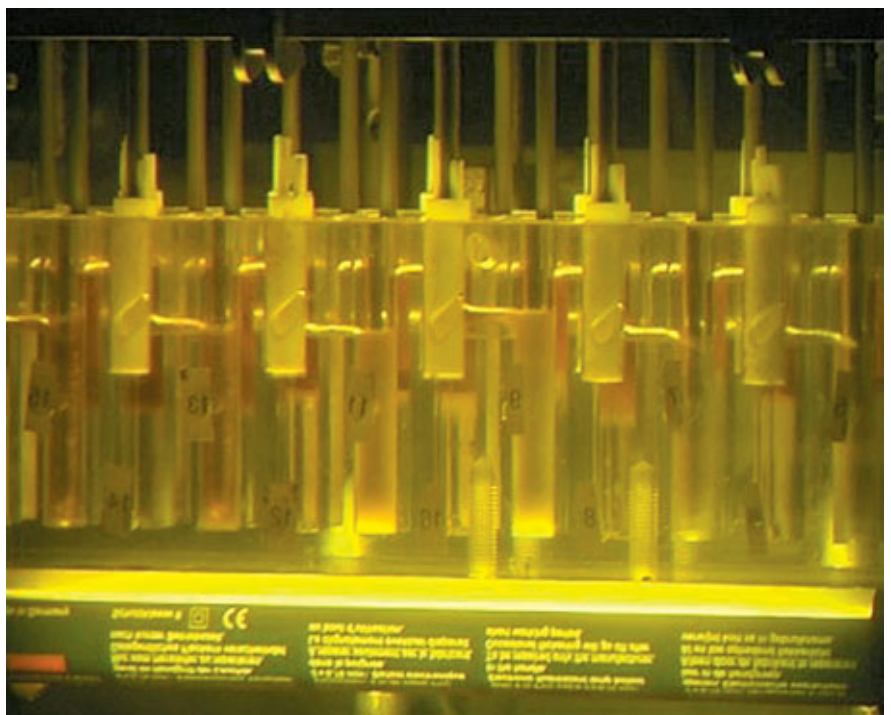
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thus under representative conditions. The results already obtained are considered significant and very encouraging in terms of submitting qualified separation processes by the year 2005. The Diamex process has demonstrated recovery efficiencies of more than 99.9%. The various versions of the Sanex concept recently passed scientific feasibility trials. It proved capable of extracting more than 99.9% of minor actinides found in a sample of waste.

Alongside this main area of exploration, which is perfectly compatible with the legally-imposed 2006 deadline and implements currently mature technologies, research work of a more forward-looking nature is in progress in other areas. Pyro-

chemical processes for example (box) would seem to offer considerable potential for meeting the criteria defined. These options are already being closely followed, albeit for applications in the more distant future. They are far more innovative in terms of theory and implementation – which probably means that no decision concerning them can be taken by 2006 – and also appear particularly well suited to more “integrated” cycle concepts (e.g. recycling close to the reactor). Pyrochemical processes are currently studied mainly as part of the quest for solutions for future-generation nuclear systems equipped with more advanced devices for managing the waste they produce.

View of the extraction-scrubbing sections of the Sanex concept designed to separate actinides from lanthanides. The scientific feasibility of this concept has been demonstrated.



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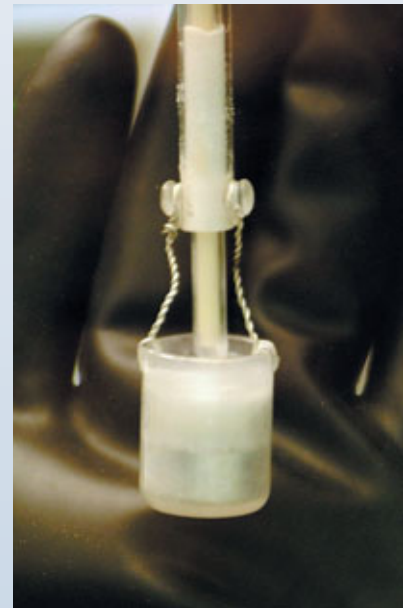
Pyrochemistry: a process for the future

Pyrochemical processes include metallurgical operations (extraction, making alloys, oxides, or even nitrides) carried out at high temperatures in non-aqueous media. In most cases, they are used when **hydrometallurgy** offers no solution, as is the case in the aluminum industry, for example, as aluminum does not have enough affinity for electrons (i.e. it is too electropositive) for it to be deposited by **reduction** of its **cation** in aqueous solution.

Pyrochemists use molten salt media, chiefly alkaline and alkaline-earth halogenides (LiCl-KCl, NaCl-KCl, NaCl-CaCl₂, etc.), and **reducing** or **oxidizing** alloys with a low melting point. Their very good resistance to irradiation, and the absence of neutron **moderators**, make these **solvents** attractive reaction media for the processing of nuclear objects in the civil or military fields. So, it could be possible

to process uncooled, or slightly cooled, irradiated objects and increase the quantity of **fissile** material for a given volume. Not only would this enhance compactness, it would also make it possible to recover all the **transuranic elements** together (plutonium + **minor actinides**).

A research program has been proposed by the Nuclear Energy Division (CEA/DEN) to assess the potential of such processes as accurately as possible. The program covers two main aspects: special applications already identified, such as **reprocessing transmutation** targets as part of a **multirecycling** approach (see *From the critical reactor to the subcritical hybrid system*), and, as part of a wider approach, "integrated cycles" involving new systems (high-temperature reactors operating with highly refractory **fuel**).

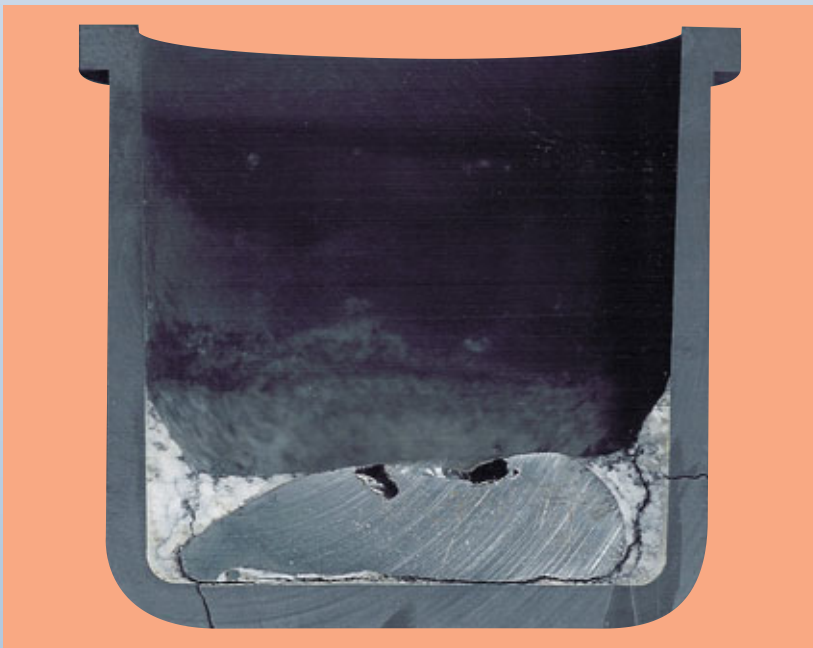


Jérôme Lacquement/CEA

Liquid-cathode device used for electrolytic recovery of actinides from a molten salt bath.

Current conventional recovery methods (electrodeposition on solid and/or liquid **cathodes**, fractional precipitation, liquid-liquid extraction between molten salts and liquid alloys) are assessed for use in recovering minor actinides (Np, Am, Cm). These studies are conducted on a laboratory scale at the **Atalante** facility at the CEA/Valrhô-Marcoule center, using molten (500–800 °C) chloride and fluoride media.

Michaël Lecomte
and **Jérôme Lacquement**
Nuclear Energy Division
CEA/Valrhô-Marcoule



Jérôme Lacquement/CEA

"Salt/metal" two-phase block coming from experiments conducted to separate actinides from lanthanides by high-temperature extraction between a molten salt and a liquid reducing alloy.

Separating long-lived radionuclides is thus at the heart of major research programs concerning nuclear waste management. It may lead on to various strategies, such as **containment** within specific matrices (see *Tailor-made matrices for long-lived radionuclides*) or **transmutation** (see chapter II). This field of research has drawn upon considerable resources, particularly within the CEA and the laboratories of the **Atalante** facility at CEA/Valrhô-Marcoule, though

also throughout the scientific community concerned. In France, examples of this effort include the **Practis** research group, which brings together 30 laboratories addressing this theme, while at the European level the **FP5 (5th technological research and development framework program) agreement** now makes considerable contributions to this area. Several research teams in Russia and Japan are also working in this field in close cooperation with the CEA. This field of

research is highly active and very open in terms of the variety of options explored and the range of skills required. From the results obtained to date, it looks quite likely that by 2006 all the scientific and technical data will be available to assess conditions for adopting this type of strategy within an industrial context. ●

Bernard Boullis
Nuclear Energy Division
CEA/Valrhô-Marcoule