

## THE SPIN PROGRAMME – ASSETS AND PROSPECTS

### Abstract

The French research programme on Separation-Incineration (SPIN) complies with the requirement by law to study ways to separate and destroy long-lived radionuclides contained in waste. Today's experience shows that the separation of actinides and their fission in a power reactor is theoretically feasible, and even though many difficult points remain they are being studied. Fission products could be only partially separated and transmuted by technologies extrapolated from those available today. Research is being continued to assess the reductions in long-lived radionuclide inventories which are possible based on the various techniques.

### 1. Introduction

With a park of 56 reactors, nuclear power provides three quarters of France's electricity. The nuclear industry, like any other, produces waste. Its peculiarity lies in the fact that some of these wastes which contain only short-lived radionuclides lose their radioactivity after a few centuries. Others contain long half-life radionuclides and the natural reduction of the radioactivity in these wastes is illusory. So law-makers required, in line with the December 30, 1991 law, that "solutions enabling the separation and transmutation of the long-lived radionuclides contained in high level long-lived radioactive waste be investigated". CEA is conducting the SPIN (Separation – Incineration) programme with its industrial partners COGEMA and EDF and its results are regularly submitted to the French National Assessment Commission in charge of evaluating these studies.

### 1.2 Long-lived radionuclides and the wastes containing them

The annual discharge from a 1300 MWe pressurised water reactor operating at 33 000 MWd/t is 36 metric tons of spent fuel. After cooling for three years, this fuel consists on average of 955 kg of uranium, 10 kg of plutonium, 1 kg of so-called minor actinides (neptunium, americium, curium) and 34 kg of fission products per initial ton of uranium (see Table C1). Most of these elements are multi-isotopic.

Some of these fuels, in today's French industrial strategy, are reprocessed (about 850 t/year out of 1200 t/year produced) in order to separate the plutonium and to recycle it as MOX fuel in PWR 900 reactors (today in eight reactors, ultimately in the 28 reactors for which recycling is possible). The separated uranium is stored. The other radionuclides are considered as waste and conditioned in glass without any further separation. Various low-contaminated wastes are also produced during reprocessing (fuel hulls, technological wastes, etc.), the so-called B wastes. The unprocessed spent fuel (including 135 t/year of MOX) is stored. Table C2 gives an overall picture by the year 2010 of the long-lived radionuclides produced and of their distribution.

At first, the very large majority of long-lived radionuclides will be found in the unprocessed spent fuels and then in waste from reprocessing (mainly glass).

### **1.3 By year 2006. Contribution to the global assessment report**

The SPIN programme has two facets: the first, PURETEX, consists in reducing the amount of waste produced during reprocessing without significantly changing the radionuclide inventory. The goal is  $\approx 0.5 \text{ m}^3$  of waste per ton of heavy metal reprocessed. The second facet, ACTINEX, studies ways to separate and then to eliminate the long-lived radionuclides. Such processing cannot be totally effective. This is why different scenarios are studied along with the ACTINEX programme.

The contribution to the waste management assessment study scheduled for 2006 consists of quantifying the possible reductions in inventory and in shedding light upon the technical separation and transmutation operations which would make it possible to achieve this goal.

Research must aid the choices. In the end, the decision will be political, economic and industrial.

## **2. The PURETEX programme**

The general scheme adopted for processing solid waste from reprocessing consists in:

- considering decontamination every time it allows the inventory of radionuclides to be significantly reduced and, of course, every time it proves possible to downgrade the waste;
- searching for the techniques best suited to each type of waste, in order to reduce their volume and improve the chemical stability of the terminal waste, such as:
  - incineration of fuel waste;
  - compacting of compressible waste;
  - melting of metallic waste;
  - mineralization of burnable waste.

A large part of the PURETEX programme is carried out in direct association with Cogéma in the framework of three industrial projects:

- new management of low and medium level effluents on the La Hague site, which, starting in 1995, resulted in phasing out the earlier co-precipitation process and its associated production of bituminous waste;
- replacement, before the year 2000, of the grouting of fuel structure waste (hulls and end-pieces) by a more efficient compacting process;
- the construction of a facility for processing by-products and  $\alpha$ -waste generated by reprocessing (in La Hague) and the MOX fuel manufacturing plants (MELOX in Marcoule and CFCA in Cadarache).

## **3. The ACTINEX programme—separation**

At present, the spent fuel (UOX), when reprocessed, is almost totally dissolved. The reusable materials U and Pu are separated and purified (with a recovery yield of about 99.9%). Iodine and the other fission gases (krypton, etc.) are discharged. The fission products and minor actinides (Np, Am,

Cm) are contained in a high activity acidic effluent containing 98% of the  $\beta$ - $\gamma$  activity and the  $\alpha$  activity exclusive of plutonium. This effluent is vitrified.

Therefore, the separation study is aimed at:

- guaranteeing the reprocessibility of future fuels: UOX with a high burn-up, MOX, etc. to separate the plutonium, uranium and iodine;
- studying the separation of minor actinides and fission products with long half-life isotopes, from the high level acidic effluent.

### **3.1 *Reprocessibility of future fuels***

MOX fuel (mixed uranium and plutonium oxides) is little different from UOX fuel as far as reprocessing is concerned. MOX fuel does have a higher plutonium and curium content. Plutonium oxide is kinetically inert to nitric acid, but the  $\text{UO}_2$ - $\text{PuO}_2$  homogeneous mixture is soluble. Today, the industrial manufacture of MOX fuel offers satisfactory characteristics for reprocessing. It is tricky to incorporate curium into glass and studies defining the incorporation limits have been undertaken.

### **3.2 *Adaptation of the PUREX process***

More than 95% of iodine is retained in a gas scrubbing effluent and its separation may be considered proven.

Technetium displays unique behaviour during uranium and plutonium separation operations. In solutions as an anionic pertechnetate ( $\text{TcO}_4^-$ ), it is co-extracted with cations of the  $\text{Zr}^{4+}$  type. This mechanism, counteracted in the PUREX process, could be useful in separating technetium. However, a significant fraction of the technetium ( $\approx 20\%$  for a UOX fuel) is not dissolved.

Zirconium can be extracted as neutral  $\text{Zr}(\text{NO}_3)_4$  but to a lesser extent than uranium and plutonium.

Neptunium has a V valency, non-extractable, and a VI valency which is extractable. Adjusting the redox conditions in the PUREX process would result in 99% separation.

### **3.3 *Search for complementary separation processes***

The PUREX process offers no potentiality for separating some radionuclides, such as americium, curium and caesium. The behaviour of the other fission products with long-lived isotopes (Pd, Se, Sn) is unknown. Important research has been launched to separate more than 99% of minor actinides and caesium (see Figure C1).

The first step, DIAMEX, is a co-extraction of the actinides and lanthanides by a bidentate extractant of the malonamide family which creates co-ordination bonds with the cations, even in an acidic medium, and which offers the advantage of not requiring a modifier like CMPO in TRUEX. The scientific feasibility has been demonstrated (99.9% extraction). The problem of the co-extraction of ruthenium must still be solved and the purification of the solvent specified.

The second step in actinide-lanthanide separation is more difficult. Extractive molecules derived from TPTZ (tripyrityltriiazine) are able to discriminate between the two families owing to their co-ordination site containing three atoms of nitrogen. Their affinity toward actinides in a 0.1 M medium

is too small, however. The possibility of including, in the extracted complex, the lipophilic anion of an organic acid and of adjusting the acidity to as low a level as possible is being investigated.

The third step concerns americium-curium separation by the SESAME process which consists of stabilising the americium in the VI oxidation state by means of a lacunar heteropolyanion (phospho or silicotungstate) capable of decreasing the apparent normal potentials of the redox pairs concerned. Extraction is then possible with TBP. The stability of the oxidised americium during extraction remains a sensitive point to study. It should be mentioned that this process could also be implemented following DIAMEX and permit the recovery of americium alone, with the curium remaining in the stream sent to waste.

The fourth step concerns the separation of caesium by macrocycles of the calixarene type, functionalized by etheroxide chains. These compounds offer pre-organised co-ordination sites, adapted to the dimensions of the  $\text{Cs}^+$  ion, which gives them high affinity and very high selectivity. Scientific feasibility has been demonstrated and only rubidium is co-extracted (1 to 2%) with caesium from a real high-level acidic effluent.

## **4. ACTINEX–Transmutation**

### **4.1 *Advantages and limitations of transmutation for actinides***

Incineration-transmutation is a combination of phenomena with the disappearance and the creation of nuclei: the limits of the process therefore have to be clearly defined.

Chemical separation leads to radioisotope mixes. Each one interacts with neutrons in a specific way, which is the only interaction possible today to transmute on a large industrial scale.

Actinides may undergo fissions generating radioactive fission products, as well as neutron captures which produce other actinides.

#### **4.1.1 *Physical feasibility***

Studies to date have shown that it would be possible theoretically, and apart from any question of industrial and economic feasibility, to reduce very appreciably the final production of radiotoxic heavy nuclei (plutonium and minor actinides) resulting from the supply of electricity, using fission reactors in a park of reactors that produce and consume these heavy nuclei. Such a park is said to be balanced (in mass and isotopic composition) when it reaches a steady state in which all the radiotoxic heavy nuclei it produced are fissioned.

Various scenarios of multiple recycling of plutonium alone or with minor actinides in 60 GWe parks (consisting of current PWRs using MOX fuel with depleted or enriched uranium support, highly moderated PWRs also using MOX fuel, or FRs) have been studied to strike a balance between production and consumption of actinides, hence a net zero production within the park.

These studies tend to show that there are neither outstanding nor even significant differences between scenarios to recycle plutonium alone. They all result in balanced Pu inventories in the cycle, of the same order of magnitude (a few hundred tons). The amount of plutonium sent to waste (20 to

30 kg/year compared with 12 ton/year in an open cycle) in these scenarios depends only on the separate performances of the cycle, although the production of minor actinides is increased by a factor more than two (3 ton/year instead of 1.5 ton/year, Table C.3).

These studies also indicate that the evolution of the systems is very slow (about 100 years to reach isotopic equilibrium) and that a controlled phasing out of nuclear power must also be provided to progressively eliminate the plutonium inventory in the cycle. This phase can take more or less decades according to the different scenarios.

The same theoretical studies began with the recycling, besides plutonium, of the minor actinides. They started with a study of the reactivity of various reactor cores and verifying the main safety parameters. Thus the acceptable limit in minor actinides was set at 5% in FRs and 1 to 2% in PWRs when the minor actinides are homogeneously distributed within the  $\text{UO}_2\text{-PuO}_2$  mixture in the ceramic fuel. These cores result in actinide incineration performances of 18 to 27% in FRs and from 6 to 9% in PWRs at standard burn-ups and allow a positive balance in the consumption versus the production of minor actinides. Multiple recycling scenarios are studied. The same type of result is obtained as with the recycling of Pu alone, slightly more contrasted depending on the reactors. The Pu inventory in the fuel cycle increases by 40% and that of minor actinides reaches about 100 tons. The amount of Pu and MAs sent to the wastes is in the range of 40 to 50 kg/year.

The management of curium is difficult owing to its strong neutron and  $\gamma$  emission. Interim storage may be envisaged (100 years) and then transmutation of the plutonium from daughter. A different strategy consists of strongly reducing its production while fissioning americium. This could be achieved by separating the americium and by an optimised once-through recycle in targets. Fission of more than 90% americium needs a long residence time in reactor for the target ( $\geq 10$  years).

The manufacture of plutonium fuels has already reached the industrial level, and their in-reactor performances mastered. Fuels also containing neptunium raise little difficulty (an experimental assembly was produced for SPX). On the other hand, the americium targets require further fundamental research on the chemical nature of americium compounds ( $\text{AmO}_2$ ,  $\text{AmO}_{2-x}$ ,  $\text{Am}_2\text{O}_3$ ), and of the inert matrix able to behave properly under irradiation (choice of the material  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgO}$ , ...). It is also necessary to improve the behaviour of the cladding under long irradiation and very great deformation of the ceramics.

#### *4.1.2 Technical and technological feasibility*

Several scenarios should be selected, chosen for their technical and industrial credibility and the broad range of choices offered to decision-makers, and technical work should be performed on the feasibility of reactors, the feasibility of the cycle, the dynamics of the systems, the inventories per cycle and the wastes, and the consequences for the risks and costs. Transient state periods will deserve special attention.

#### *4.2 Advantages and limitations of transmutation for fission products*

Long-lived fission products can be transmuted by neutron capture only. Therefore, a system must be used that produces a large available excess of neutrons. This is why fission reactors (in the theoretical parks mentioned above) are not very efficient for transmuting long-lived fission products.

Each fission product must be studied individually to assess the technical feasibility of its transmutation in reactors or in innovative dedicated systems. Sensitive points appear: the making of thermally stable iodine targets able to withstand the irradiations, the isotopic separation of caesium (without this separation,  $^{133}\text{Cs}$  generates more  $^{135}\text{Cs}$  than is transmuted, besides the occurrence formation of the highly radioactive  $^{137}\text{Cs}$ ). The case of the transmutation of  $^{99}\text{Tc}$  appears more favourable, and this has been confirmed by the preliminary experiments achieved in the Petten reactor in the frame of the EFTTRA programme (rather good behaviour, without significant damage of metallic targets for representative transmutation levels).

### 4.3 *Hybrid systems*

Many concepts of hybrid systems have been suggested, combining a spallation neutron source with a sub-critical reactor (accelerator driven). The characteristics of the different systems are being evaluated by various laboratories, whose results must be regarded with caution for several reasons:

- non-negligible uncertainties remain in the data and software;
- some results are obtained by extremely simplified approaches and yield only approximate figures;
- the studies quite often ignore (or barely consider) the technological limits, which are unclear in many cases owing to the lack of experimental data in the operating ranges considered. In fact, this point is crucial for concepts using advanced technologies.

For waste incineration, physical studies show that hybrid systems with a fast neutron spectrum offer a neutron surplus which could be used in the following cases:

- transmutation of long-lived fission products;
- transmutation of minor actinides: this case corresponds to a scenario in which Pu is multi-recycled in the nuclear park. Hybrid systems are dedicated to incinerating minor actinides (Am, Cm). In this case 5% to 7 % of installed power consisting of hybrid systems is sufficient to transmute minor actinides produced into the nuclear park. The main advantage of the “hybrid option” is to take advantage of the subcriticality to handle exotic fuels with unfavourable reactivity characteristics (positive reactivity coefficients and lower delayed neutron fraction).

## 5. **Classification of the radionuclides**

The radiotoxicity of a radionuclide takes into account the specific data on the radiation emitted and the metabolism of the particular element in man.

The actinide family is very homogeneous as it consists of elements having a similar chemical behaviour emitting  $\alpha$  particles with similar energy. The radiotoxicity of the actinides is, as a first approximation, linked mainly to their half-life. Those with the longest half-lives are the least noxious (Table C4). However, none of them decays rapidly enough to turn into a stable element. Therefore, the inventory of long-term noxious radionuclides must include the short half-life elements ( $^{243}\text{Cm}$ ,  $^{244}\text{Cm}$ ,  $^{238}\text{Pu}$  having half-lives of less than 100 years) and  $^{241}\text{Pu}$ , a  $\beta$ -emitter, since all their daughter products will be radiotoxic  $\alpha$ -emitters. The radioactive decay chains of actinides are very long and result in stable isotopes of lead and bismuth.

The “family” of long-lived fission products and of activation products ( $\beta$ -emitters) is much less consistent, and the biochemical behaviour of these compounds may be very different. Their toxicity is lower than that of actinides having the same activity level (ratio of about a hundredfold, see Table C5). Some are accompanied by isotopes which, when stable, provide an isotopic dilution which reduces their specific radiotoxicity. In general, their daughter products are stable right from the first radioactive decay.

If only the inventory of radionuclides in waste or in fuels is considered, a “radiotoxic inventory” can be defined which weights the mass of each radionuclide by a “radiotoxicity” coefficient, or more accurately by the effective dose coefficient in ingestion (or inhalation). This informative representation allows us to foresee the “radiotoxic inventory” as a function of time as it results from a reactor park supplying electricity, and to assess the impact on this “radiotoxic inventory” of strategies for recycling all or part of the long-lived radionuclides.

As an example, Figure C.2 shows that, for the spent UOX fuel, the most significant contributors beyond 500 years are plutonium and americium, and then curium (up to  $3 \times 10^4$  years), uranium, neptunium and finally the fission products.

If we consider a system for protecting the human being, such as long-term interim storage or underground geological disposal, the study of its evolution with time and the releases that may lead future generations to ingest or inhale radionuclides may draw attention to the more mobile elements in the ground (for example, some long-lived fission products) and modify the classification of the major contributors. The criterion then becomes an effective dose delivered to a population and is no longer a “radiotoxic inventory”. The radioelements that migrate most are iodine and, to a lesser extent, caesium.

## **6. Conclusions**

There is no complete waste management system today describing the specifications of the packages accepted on an underground disposal site or on a long-term interim storage site, nor is there a total authorised inventory per site for each radionuclide.

SPIN studies will make it possible to clarify, by 2006, for the various partial or complete recycling options of plutonium and minor actinides in a power reactor park, the nature and amount of waste produced, to define the technical operations to be performed and to assess their cost in a time-frame by random choices.

A P&T strategy in a reactor park really makes sense only if it is mastered from beginning to end. Any sudden interruption in nuclear programme would heavily penalise the expected gains. Times for nuclear incineration in a P&T strategy are counted in centuries. The problem of limited uranium resources in a PWR park will then be acutely felt. In this regard, the position of FRs is much more favourable.

The SPIN programme will also pave the way to prospective analyses of newer systems than the incineration of actinides or the transmutation of fission products.

Table C.1 The spent fuel taken as reference for the reprocessing process diagrams is an uranium oxide enriched to 3.5% in isotope 235, irradiated to 33 000 MWd/t in a PWR and cooled for three years. Its composition is given for one ton of uranium metal prior to irradiation.

	Amount (kg/tU)
<b>Uranium</b>	<b>955</b>
<b>Plutonium</b>	<b>10</b>
<b>Minor actinides</b>	<b>1</b>
including: neptunium	0.4
americium	0.3
curium	0.03
<b>Fission products</b>	<b>34</b>
including: rare gases (Kr, Xe)	5
alkalines (Cs, Rb)	4
alkaline-earth (Sr, Ba)	2
yttrium and lanthanides	10
zirconium	4
chalcogens (Se, Te)	0.5
molybdenum	3
halogens (I, Br)	0.2
technetium	1
Ru, Rh, Pd	4
Others (Ag, Cd, Sn, Sb)	0.3
<b>Structural materials</b>	<b>300</b>
900 MWe PWR: cladding, grids, end pieces, etc.	

Table C.2 Overview for the year 2010 (as an illustration). Assessment, in 2010, of the amounts of long-lived radionuclides occurring in waste and in stored fuels

Assumption: Operating inventory of 8500 metric tons of fuel, annual amount of reprocessed fuel, 850 t/year, loss of Pu in reprocessing is 0.12% by weight. Burn-up:

1995 to 1999: 33 000 MWd/t  
 2000 to 2005: 41 200 MWd/t  
 2006 to 2010: 50 000 MWd/t

Radionuclide	Actinides (kg) excl. U				Long-lived FP (kg)						
	Pu	Np	Am	Cm	<sup>79</sup> Se	<sup>93</sup> Zr	<sup>99</sup> Tc	<sup>107</sup> Pd	<sup>125</sup> Sn	<sup>129</sup> I	<sup>135</sup> Cs
Conditioned (glass, B-waste)	140	7 650	7 100	860	80	9 700	13 700	3 700	360	90	6 340
Fuels in interim storage	223 280	6 939	17 005	2 284	77	10 965	13 831	4 449	393	3 030	7 201

- The iodine from reprocessing is discharged into the sea (about 99%).
- The B wastes contain less than 2% of the radionuclides from reprocessing (glass, more than 98%).
- “Long-lived” means a radionuclide whose radioactive half-life or that of one of its radioactive daughter products is longer than 31 years.

This table shows that, by the year 2010, the 13 840 tHM of the stored spent fuel assemblies will contain:



- nearly 223 t of plutonium (including 100 t isotopically degraded in MOX fuel assemblies);
- ≈17 t of americium (amount which should increase with the decay of <sup>241</sup>Pu);
- ≈2.3 t of curium;
- ≈6.9 t of neptunium;
- ≈40 t of long-lived fission products.

Furthermore, the following will be essentially conditioned in the 2800 m<sup>3</sup> of glass:

- ≈7 t of americium;
- ≈7.6 t of neptunium;
- nearly one ton of curium;
- more than 34 t of long-lived fission products (including 6.3 t of <sup>135</sup>Cs);
- more than 44 t of total caesium (including the <sup>135</sup>Cs).

The 70 000 m<sup>3</sup> of B-waste will contain about 200 kg of long-lived radionuclides.

**Table C.3 Multi-recycling of plutonium alone or of plutonium and minor actinide  
(Park 60 GWe – 400 TWhe)**

Park	OPEN CYCLE	PLUTONIUM RECYCLING		PLUTONIUM & M.A. RECYCLING	
	N4	N4-MOX and <sup>235</sup> U support	N4-MOX FR-CAPRA	N4-MOX and <sup>235</sup> U support	N4-MOX FR-CAPRA
% UOX	100	0	70	0	70
% MOX	0	100	16PWR-14 FR	100	10PWR-20 FR
Enrichment					
% <sup>235</sup> U	4.5	3.8	0.25	4.1	0.25
% Pu	0	2.0	10(PWR)-50(FR)	2.7	10(PWR)-55(FR)
Inventory					
Fuel Cycle (t)					
Pu		200	380	300	440
M.A.				95	90
Wastes (t/year)					
Pu	11.6	0.02	0.03	0.02	0.03
MA	1.5	3.3	3.2	0.07	0.08

Table C.4 Assessment of the radiotoxicity of ingested actinides  
(coefficients taken from the ICRP 60)

Half-Life	Radionuclides	Effective dose coefficient	Mass of radionuclides corresponding to the effective dose limit (1 mSv/yr)
		By ingestion	By ingestion
<100 years	<sup>244</sup> Cm <sup>243</sup> Cm <sup>238</sup> Pu	≈10 <sup>5</sup> Sv/g	≈10 <sup>-2</sup> μg/year
10 <sup>2</sup> to 10 <sup>5</sup> years	<sup>241</sup> Am <sup>240</sup> Pu <sup>243</sup> Am <sup>245</sup> Cm <sup>239</sup> Pu	≈10 <sup>3</sup> - 10 <sup>4</sup> Sv/g	≈0.1 - 1 μg/year
10 <sup>5</sup> to 10 <sup>8</sup> years	<sup>233</sup> U <sup>234</sup> U <sup>248</sup> Cm <sup>242</sup> Pu <sup>237</sup> Np <sup>236</sup> U <sup>244</sup> Pu	≈0.1 to 20 Sv/g	≈10 μg/yr to 0.1 g/yr
< 10 <sup>8</sup> years	<sup>235</sup> U <sup>238</sup> U	≈10 <sup>-3</sup> Sv/g	≈1 g/year

Table C.5 Assessment of the radiotoxicity of ingested fission products and activation products (coefficients taken from ICRP 60)

Radionuclides	Half-life (years)	Effective dose coefficient	Mass of radionuclides corresponding to the effective dose limit (1 mSv/year)
		By ingestion	By ingestion
<sup>151</sup> Sm <sup>14</sup> C	9×10 <sup>1</sup> 5.7×10 <sup>3</sup>	≈100 Sv/g	10 μg/year
<sup>79</sup> Sc <sup>126</sup> Sn <sup>129</sup> I <sup>99</sup> Tc <sup>93</sup> Zr <sup>135</sup> Cs	6.5×10 <sup>4</sup> 10 <sup>5</sup> 1.6×10 <sup>7</sup> 2.1×10 <sup>5</sup> 1.5×10 <sup>6</sup> 2.3×10 <sup>6</sup>	≈0.1 to 5 Sv/g	0.1 mg/yr 0.2 mg/yr 1.5 mg/yr 2.5 mg/yr 10 mg/yr 12 mg/yr
<sup>107</sup> Pd	6.5×10 <sup>6</sup>	7×10 <sup>-4</sup> Sv/g	1.4 g/yr

Figure C.1 SPIN/ACTINEX technical flow sheet

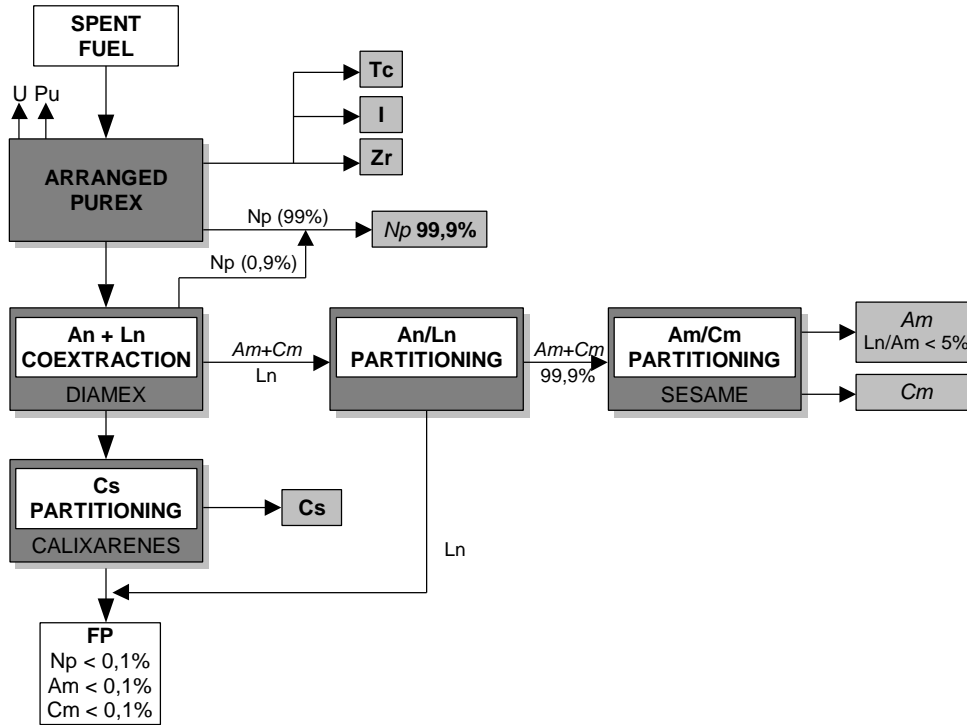


Figure C.2 Radiotoxic inventory of UOX fuel as a function of time (3.7%  $^{235}U$ , 45 GWd/tHM).

