

## 3 Nuclear fuel and fuel cycle

[B. Barré]

### 3.1 The nuclear fuel cycle(s)

In the conventional sense, a fuel is a substance which can be combined with oxygen to produce heat, by combustion. By extension, the nuclear fuel is a substance which can produce heat by fission of its heavy nuclei by neutrons.

Cars do not burn crude oil straight out of the well, and light bulbs are not plugged directly on hydro-electric dams. For fissile nuclei to produce heat by undergoing fission in reactor cores, they must follow a “fuel cycle”, combining many different industrial steps in a sequence [81Mar, 96Wil, 99Coc].

Fuel cycles differ from reactor type to reactor type, and according to the choice of the fissile/fertile nuclei involved. Let us first describe the most usual fuel cycle, the uranium cycle for light water reactors (LWR). It encompasses the following steps:

- uranium ore mining;
- ore concentration (milling) as “yellowcake”, at the mine mouth;
- conversion to uranium hexafluoride ( $\text{UF}_6$ );
- isotopic enrichment of the uranium;
- fuel fabrication;

(fuel irradiation in the reactor)

- intermediate storage;
- spent fuel management.

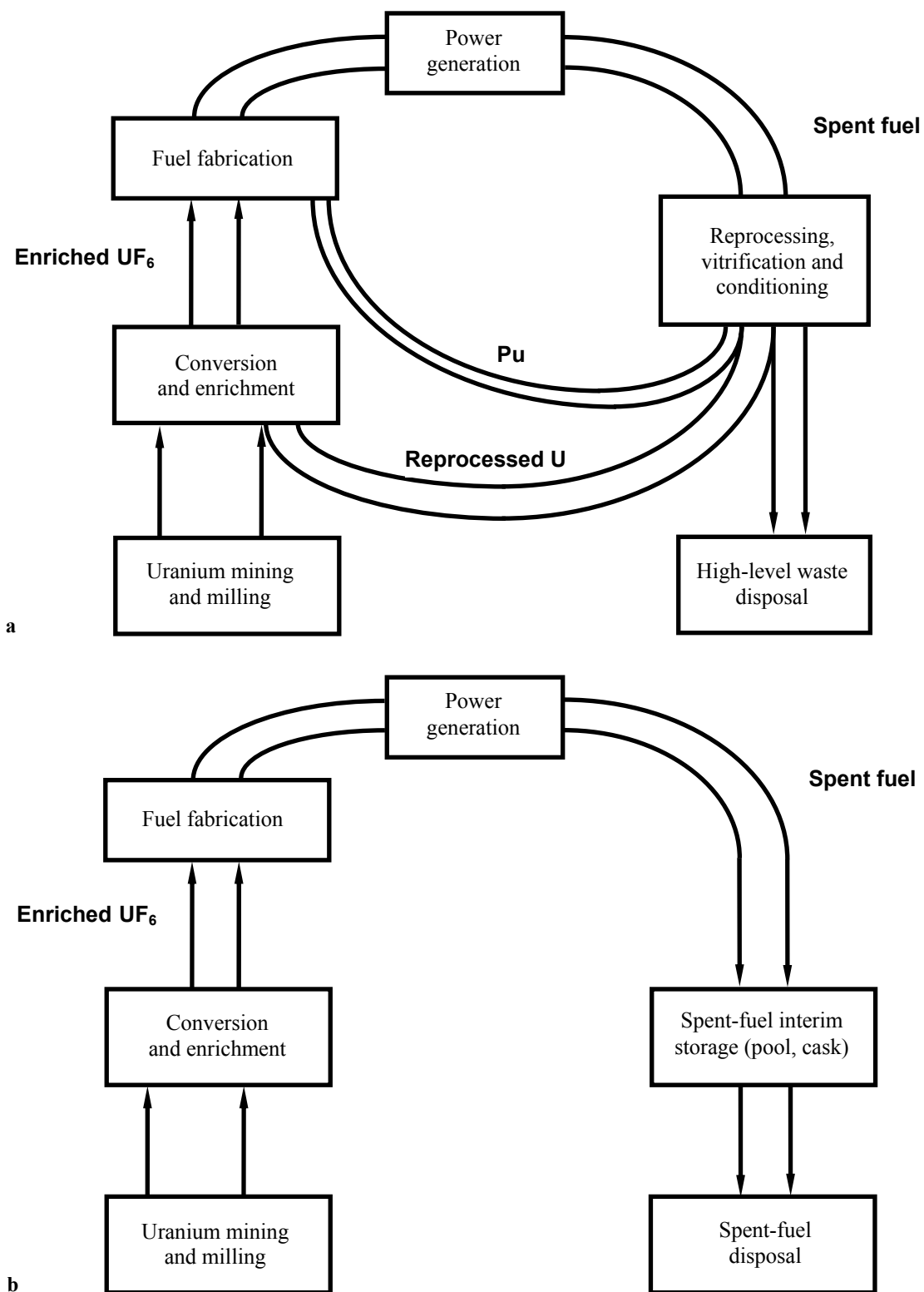
Between these steps there are many controls and quite a number of transportation stages. Each step is, by itself, a complete industrial process which will be described in more detail hereafter. The last step, spent-fuel management, splits itself into two options, which actually lead to two different fuel cycles, the “closed” cycle (from which the term “cycle” was minted), and the “open” cycle.

In the closed cycle, we find the following subsets:

- fuel reprocessing, and fissile/fertile materials recovery for recycling;
- wastes conditioning;
- wastes disposal.

The open cycle – which is not a cycle at all – ends with direct disposal of the spent fuel, considered as a final waste. Figure 3.1 schematizes both closed and open cycles.

For reactors using natural uranium and for reactors recycling plutonium or  $^{233}\text{U}$ , the enrichment step is by-passed. The fuel fabrication is the most reactor-specific process.



**Fig. 3.1.** Schemes of LWR fuel cycles. **(a)** Closed cycle. **(b)** Open cycle.

The choice between open or closed cycle relates to three different considerations:

- Physical consideration: When the “spent” fuel is unloaded from the reactor core, it still has a high content of both fissile ( $^{235}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Pu}$ ) and fertile ( $^{238}\text{U}$ ) nuclei, respectively. From a physical point of view, it makes sense to recover them.
- Economical consideration: The cost of reprocessing and recycling must be compared to the cost of the raw materials saved. High costs of uranium favor the closed cycle, low costs do not.
- Ecological consideration: Usually saving materials and energy is considered valuable, even at a cost (for example, recycling the lead in batteries costs more than using “fresh” lead).

As a matter of fact, as we shall see, neither cycle goes to the ultimate disposal. The open cycle ends today with interim storage of the spent fuel – which can still be reprocessed later – and the closed cycle is only partial, as shown in Fig. 3.2.

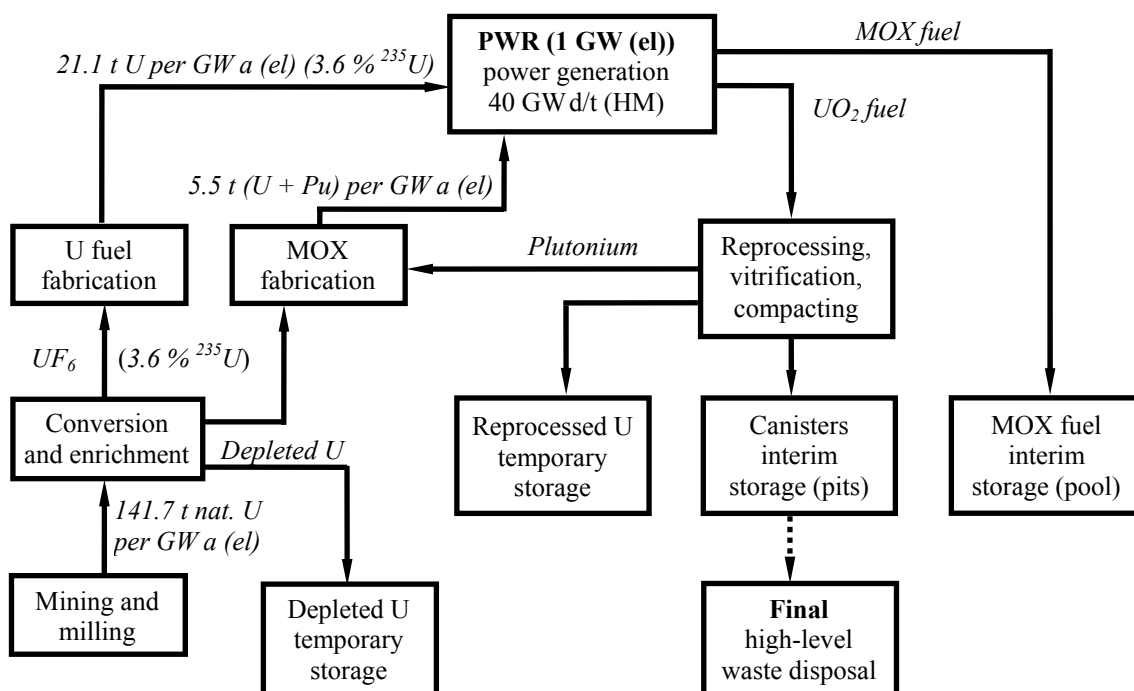


Fig. 3.2. Partly closed fuel cycle. GW d/t (HM) denotes gigawatt-days per ton of heavy metal (U, Pu).

## 3.2 Fissile and fertile materials procurement

### 3.2.1 Uranium and thorium

Uranium and thorium ores are the raw-material natural resources of nuclear power. They are neither abundant nor very rare metals in the earth’s crust: their abundance is comparable to that of tin, tungsten or molybdenum, of the order of 3 g/t for uranium and 7 g/t for thorium.

Discovered in 1789 by Klaproth, uranium, atomic number 92 of the periodic classification of Mendeleev, is the heaviest naturally occurring element on earth. As a metal, its volumic mass is 19 g/cm<sup>3</sup>, and its melting temperature is 1133 °C. It is naturally radioactive and consists of a mixture of two main iso-

topes, both radioactive, 99.28 %  $^{238}\text{U}$  and 0.715 %<sup>1</sup>  $^{235}\text{U}$ . Without this tiny fraction of  $^{235}\text{U}$ , there would probably be no nuclear power today because  $^{238}\text{U}$  has a low probability of being fissioned by neutrons, at least in the energy range of the neutrons released in the fission process, while  $^{235}\text{U}$  is easily fissioned by neutrons of any energy.

On the other hand,  $^{238}\text{U}$  is very useful because it captures neutrons and then undergoes a series of  $\beta$  decays leading to  $^{239}\text{Pu}$ , a fissile isotope of plutonium, analogous to  $^{235}\text{U}$ :  $^{238}\text{U}$  is “fertile”. The specific activity of uranium is 24.4 kBq/g (0.66  $\mu\text{Ci/g}$ ), half of which is due to  $^{238}\text{U}$  and half to  $^{234}\text{U}$ , the contribution from  $^{235}\text{U}$  being negligible.

Uranium is well distributed in the earth’s crust<sup>2</sup>, usually associated with oxygen, and with its decay products (Table 3.1). The average U content of granite is 4 to 5 parts per million (ppm). It is also found in sea-water, in huge quantities, perhaps of the order of 4 to 5 billion tons, but with a very low concentration of  $\approx 3$  parts per billion (ppb). Uranium is only mined from deposits where its concentration exceeds 0.1 %, unless it is a by-product of some other mineral production such as phosphates, gold or copper. Some uranium deposits, in veins, are extremely rich: mines in Saskatchewan reach 10 % uranium, but most mines exploit ores close to 0.2 % U. This is why uranium ores must be concentrated at the mine mouth before transportation.

Uranium is a significant constituent of about 100 different minerals, but most mineable ores belong to a dozen minerals, which are listed in Table 3.2. Usually, uranium deposits are classified in 4 types: vein-type deposits (Canada, Australia), uranium in sandstones (USA, Niger), uranium in conglomerates (South Africa, Canada), and other deposits (like the pegmatites of Namibia, and most phosphates deposits). Most of the deposits formed during the Precambrian era ( $> 600$  million years), or during orogenic events like the Hercynian and Alpine mountain formations in Europe (300 and 50 million years ago, respectively).

One distinguishes between “primary” minerals, usually black or blackish, formed at some depth inside the crust, where uranium is tetravalent (pitchblende, uraninite, coffinite, brannerite) and “secondary” minerals, derived from the former by surface oxidation. Secondary minerals are brightly colored, in green, yellow or orange, and uranium is hexavalent.

Thorium, element 90 in the periodic classification, is present in nature with only one isotope,  $^{232}\text{Th}$ , which is fertile like  $^{238}\text{U}$ , giving birth to fissile  $^{233}\text{U}$  after a neutron capture.  $^{232}\text{Th}$  is radioactive ( $\alpha$ ), with a half-life of  $1.41 \times 10^{10}$  a. As thorium has no fissile isotope, it cannot start a fuel cycle on its own. One needs  $^{235}\text{U}$  or plutonium to start the thorium cycle (Fig. 3.3).

Though it is roughly 4 times more abundant than uranium, thorium is an essential constituent of only a few minerals: thorite ( $\text{ThSiO}_4$ ), thorianite ( $\text{ThO}_2$ ) and monazite ( $\text{Ce,La,Nd,ThPO}_4$ ). The beach sands of India, Brazil and Madagascar are rich in monazite, and thorium is sometimes a by-product of uranium mining. As thorium has few applications – thoria is a highly refractory ceramic, and was also used for luminescent gas lights, but is now abandoned because of its radioactivity – reserves and resources of thorium have not been assessed with the same precision as those of uranium.

<sup>1</sup>) To be precise, there is also 0.006 %  $^{234}\text{U}$ . This characteristic composition of natural uranium is found everywhere in the world but in OKLO, Gabon, where “natural reactors” operated for thousands of years 1.7 billion years ago. More will be said on OKLO in the section devoted to wastes disposal.

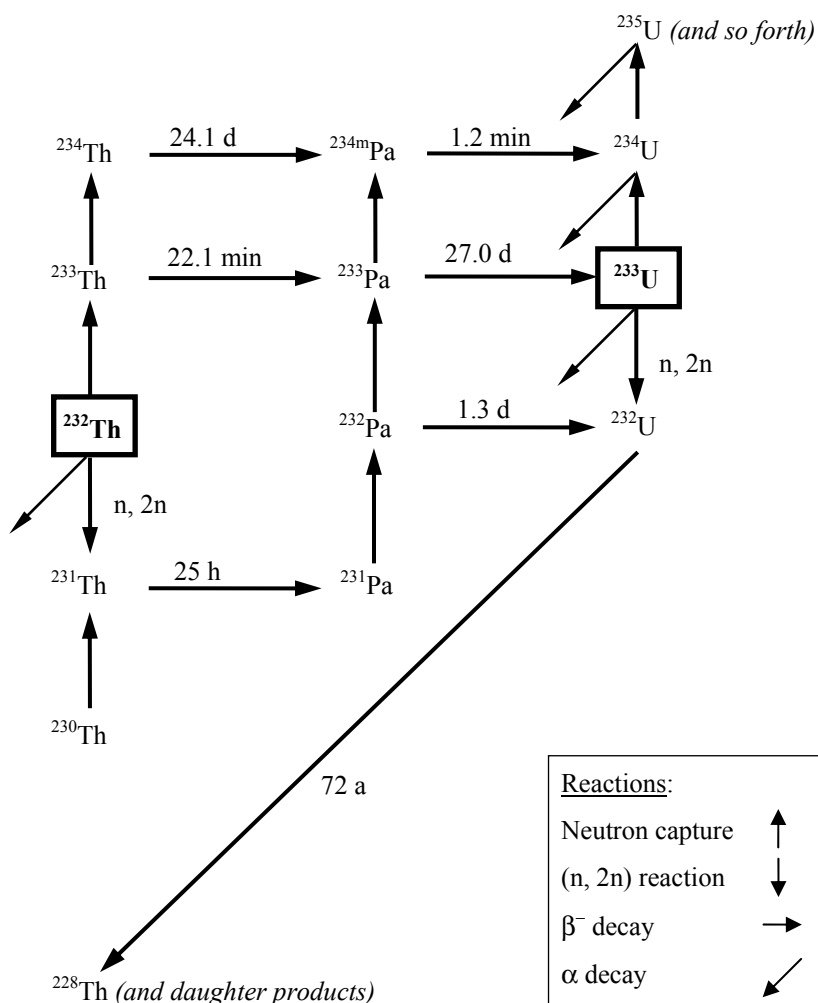
<sup>2</sup>) Once upon a time... uranium was born in a dying star. It is inside stars that light elements combine, “fuse”, to produce heavier elements, liberating energy in the process: hydrogen produces helium, which produces carbon, and so on, until one reaches atomic mass 56, i.e. the element iron. The iron nucleus is the most stable of all, with a binding energy of 8.7 MeV per nucleon. To synthesize nuclei heavier than iron, you need to capture neutrons in an extremely high flux, and these endothermic reactions need a lot of added energy : these neutrons and this energy are found during the explosions of supernovae, which, in addition, disperse these heavy elements throughout the interstellar space. The uranium in the earth’s crust was therefore born in an old star, during the last cataclysmic seconds of its existence. The dispersed matter must have been used later to form the solar system. In that way, fission energy can be said to be the fossil energy of the stars as coal and oil are the fossil energy of past organic life on earth.

**Table 3.1.**  $^{238}\text{U}$  decay chain.

Nuclide	Decay mode and energy [MeV]			Half-life
	$\alpha$	$\beta$	$\gamma$	
$^{238}\text{U}$	4.19		0.048	$4.51 \times 10^9$ a
$^{234}\text{Th}$		0.19	0.03, 1.001	24.1 d
$^{234}\text{Pa}$		0.14	0.043	6.75 h
$^{234}\text{U}$	4.77		0.053	$2.47 \times 10^5$ a
$^{230}\text{Th}$	4.69		0.068	$8.0 \times 10^4$ a
$^{226}\text{Ra}$	4.78		0.186	1602 a
$^{222}\text{Rn}$	5.49			3.82 d
$^{218}\text{Po}$	6.00			3.05 min
$^{214}\text{Pb}$		0.67	0.053	26.8 min
$^{214}\text{Bi}$		1.51	0.61, 1.76	19.7 min
$^{214}\text{Po}$	7.69			$1.64 \times 10^{-4}$ s
$^{210}\text{Pb}$		0.015	0.046	22 a
$^{210}\text{Bi}$		1.16		5.01 d
$^{210}\text{Po}$	5.31			138.4 d
$^{206}\text{Pb}$	stable			
$^{235}\text{U}$	4.46		0.168	$7.04 \times 10^8$ a
$^{232}\text{Th}$	4.08		0.063	$1.41 \times 10^{10}$ a

**Table 3.2.** Common uranium ores.

Mineral	Chemical composition
Uraninite (pitchblende)	$\text{UO}_2$
Coffinite	$(\text{USiO}_4)_{1-x}(\text{OH})_x$
Brannerite	$(\text{U}, \text{Y}, \text{Ca}, \text{Fe}, \text{Th})_3\text{Ti}_5\text{O}_{16}$
Betafite	$(\text{U}, \text{Ca})(\text{NbTaTi})_3\text{O}_9 \cdot n\text{H}_2\text{O}$
Davidite	$(\text{Fe}, \text{Ce}, \text{U})(\text{Ti}, \text{Fe})_3 (\text{O}, \text{OH})_7$
Uranothorite	$(\text{Th}, \text{U})\text{SiO}_4$
Uranothorianite	$(\text{Th}, \text{U})\text{O}_2$
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-9\text{H}_2\text{O}$
Torbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-12\text{H}_2\text{O}$
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$
Uranophane	$\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$



**Fig. 3.3.** The thorium cycle.

### 3.2.2 Exploration

In the early days of the atomic era, prospecting for uranium was a pioneer's job, for lonesome adventurers roaming the deserts of Colorado or Wyoming with their horse and their Geiger-Müller counter. Today, things are less romantic and more organized, but the basics are the same: detecting the  $\gamma$  rays of some of the decay products of  $^{238}\text{U}$ , mostly  $^{234}\text{Th}$ ,  $^{222}\text{Rn}$  and  $^{214}\text{Bi}$ , or some gaseous products of spontaneous fission like  $^{85}\text{Kr}$  or  $^{135}\text{Xe}$ .

Nowadays, one starts with the geological study of a large area to detect favorable conditions for deposit formation, notably with the help of satellite cartography (since the first ERTS and LANDSAT satellites in the early seventies).

If a given area looks interesting, the next step is aerial radiometric survey, with planes or helicopters carrying large and sensitive scintillation counters or  $\gamma$  spectrometers, and flying over stripes of land about 1 kilometer wide. This method allows for a rapid identification of the regions having the highest uranium content, and worth further exploring. Radiometric methods, when properly interpreted, will detect uranium ores, but will not give information on the quantity and concentration of the uranium.

If the radiometric measurements are promising enough, geologists go on the spot to analyze ground samples and ground water, as well as to extract soil samples by drilling to establish the precise stratigraphy.

### 3.2.3 Mining and concentration (milling)

According to the size and the location of the ore body, three methods can be used: open-pit mining when the ore is close to the surface, underground mining, or in-situ leaching [95Rig, 97Val].

Open pit mining is very common for copper, for instance. After removing the topsoil and the overburden with scrapers, the ore is excavated with hydraulic shovels and front loaders, and carried to the mill by trucks traveling on a long helical ramp from the ore bed to ground level. After exploitation, the overburden will be pushed back into the pit and covered by the topsoil for rehabilitation (see below).

Underground mining is commonly used for coal or iron. What is specific to underground uranium mining is the additional hazard caused by the radon gas  $^{222}\text{Rn}$  accumulated in the galleries: a powerful ventilation must be maintained to keep the radon concentration at an acceptable level and prevent miners' irradiation. Given the cost of underground mining, it is used for relatively high grade ore. Some ores have such a high uranium concentration, in Saskatchewan for instance, that remote mining techniques are used.

In-situ leaching (ISL), sometimes called solution mining, is a relatively inexpensive way to exploit underground ores in arid and secluded areas where possible underground water pollution is less of a concern: Wyoming, Australia, Uzbekistan. Several wells are drilled to reach the ore location, then a leaching solution (usually acidic,  $\text{pH} \approx 2\text{--}3$ ) is injected in one well and pumped from the surrounding wells (Fig. 3.4). A new mine in South Australia, with reserves in excess of 20 million tons U, will produce approximately 1 million tons U per year from 84 wells, with a total manpower of less than 50 people.

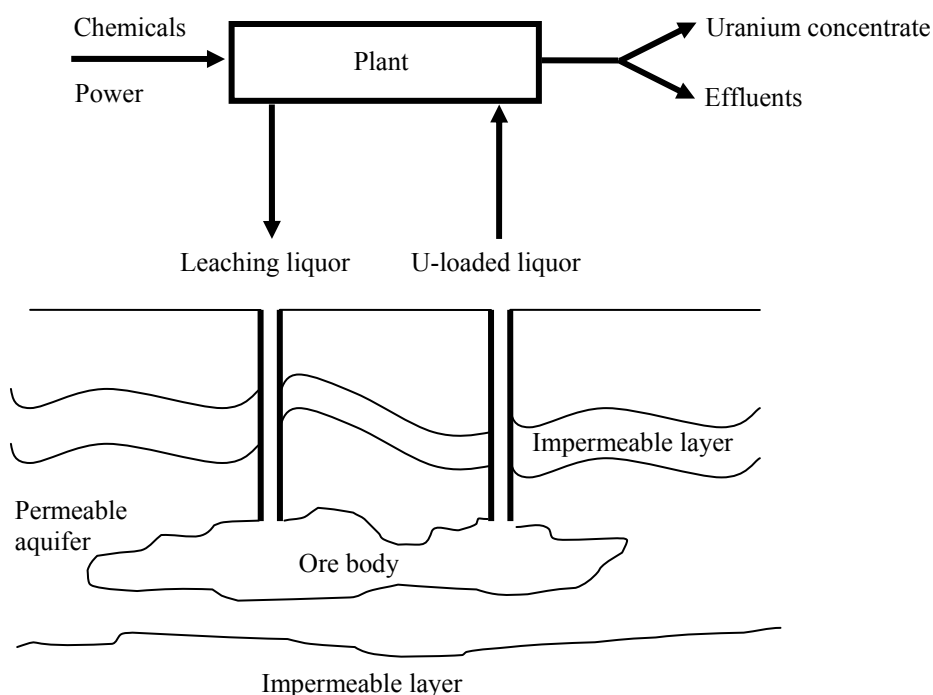


Fig. 3.4. In-situ leaching.

One should mention a fourth method of uranium extraction which bears no resemblance to mining: extraction from seawater is technically possible and has been developed on a laboratory scale, notably in Japan, using either resins (Asahi) or other specific adsorbents (JAERI). It is too early to evaluate the possible costs involved, but they will be much higher than the presently depressed commercial prices. One specific problem is the huge volumes of seawater to handle in the process: most prospective designs consider floating plants anchored in the middle of strong oceanic currents.

After the uranium has been mined, it is concentrated in a mill located close to the mine mouth. Figure 3.5 schematizes the various concentration processes.

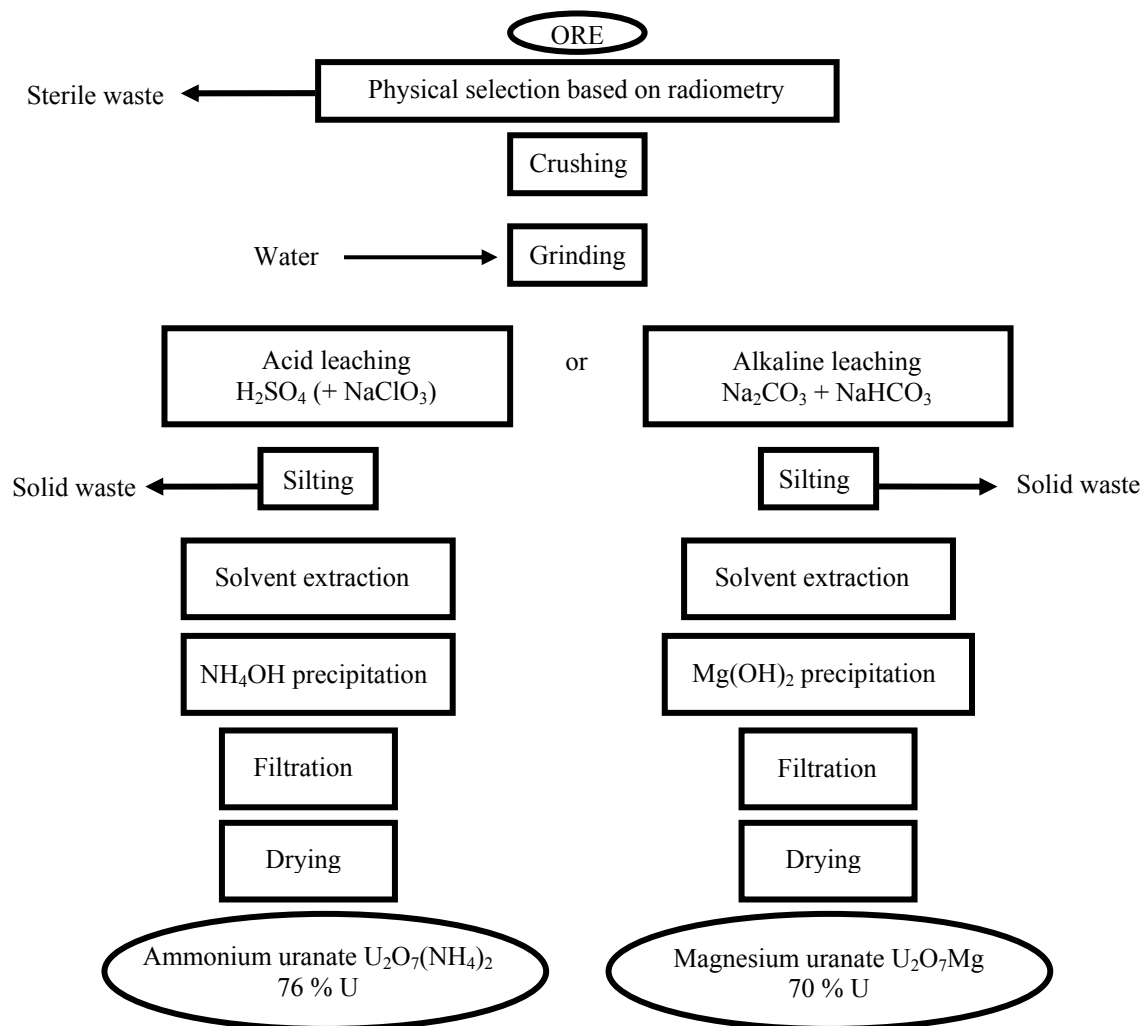


Fig. 3.5. Schematic flow chart of milling processes.

### 3.2.4 Sites rehabilitation

At the end of the commercial exploitation, mining operations leave a significant impact on the environment:

- open pits, and underground galleries;
- left-over buildings and pieces of equipment from the mill;
- excavated materials and *mill tailings*, usually in tailings ponds. Mill tailings, in huge quantities, contain all the radionuclides of the uranium decay family, including radium and radon.

Before leaving the site, the operator must therefore “rehabilitate” it, at his expenses and subject to strict regulatory rules and close scrutiny. Rehabilitation includes the following operations:

For the mine site itself: filling it with sterile excavated materials, or, alternatively, transforming open pits into artificial lakes, and thereafter remodeling the landscape, tree plantations, etc.



For the mill: complete dismantling of the plant buildings, with the possible exception of some office buildings which can be converted to other uses after clean-up, and storage of uranium-contaminated equipment together with the tailings, followed by the monitored clean-up of any contaminated soil.

The most important aspect is the safe disposal of the mill tailings. During operation, they are stored in pits or ponds, and controlled as “ICPE”<sup>3</sup> in the French legislation. After termination, the operator must assure their durable containment, to safeguard the surrounding environment from radioactive contamination and prevent exposure of people to unwanted radiation<sup>4</sup>: covering with soil to delay – and therefore limit by decay – radon release, and resist erosion and rain seepage; reinforcement of the levees, water drainage, treatment if needed, and monitoring; suitable plantations.

In addition, there shall remain for a long period of time a regular monitoring of air, water and food chains in the neighborhood.

### 3.2.5 Plutonium

Element 94 of the periodic classification, plutonium exists only as traces in nature, but is produced when uranium fuel is irradiated in reactors, through neutron capture in  $^{238}\text{U}$ . Spent fuel elements are therefore analogous to “plutonium mines”, from which plutonium is extracted by “reprocessing”.

There are five major isotopes of plutonium, ranging in atomic mass from 238 to 242. Neutron capture in  $^{238}\text{U}$  produces  $^{239}\text{Pu}$ , and further neutron captures produce the higher isotopes, while  $^{238}\text{Pu}$  comes from a series of reactions (Fig. 3.6). The amount of  $^{238}\text{U}$  converted to plutonium will increase with the time the fuel stays in the reactor, and, similarly, the longer the irradiation time, the greater the proportion of higher plutonium isotopes.

$^{239}\text{Pu}$  and  $^{241}\text{Pu}$  are fissile isotopes, similar to  $^{235}\text{U}$ , while  $^{240}\text{Pu}$  can be considered “fertile” like  $^{238}\text{U}$ , and  $^{242}\text{Pu}$  just captures neutrons to produce higher actinides. Globally, the longer the irradiation time, the less fissile the plutonium (Table 3.3).

**Table 3.3.** Isotopic composition of discharged plutonium in PWR fuel after three years cooling time, given in units of weight % [95Rig].

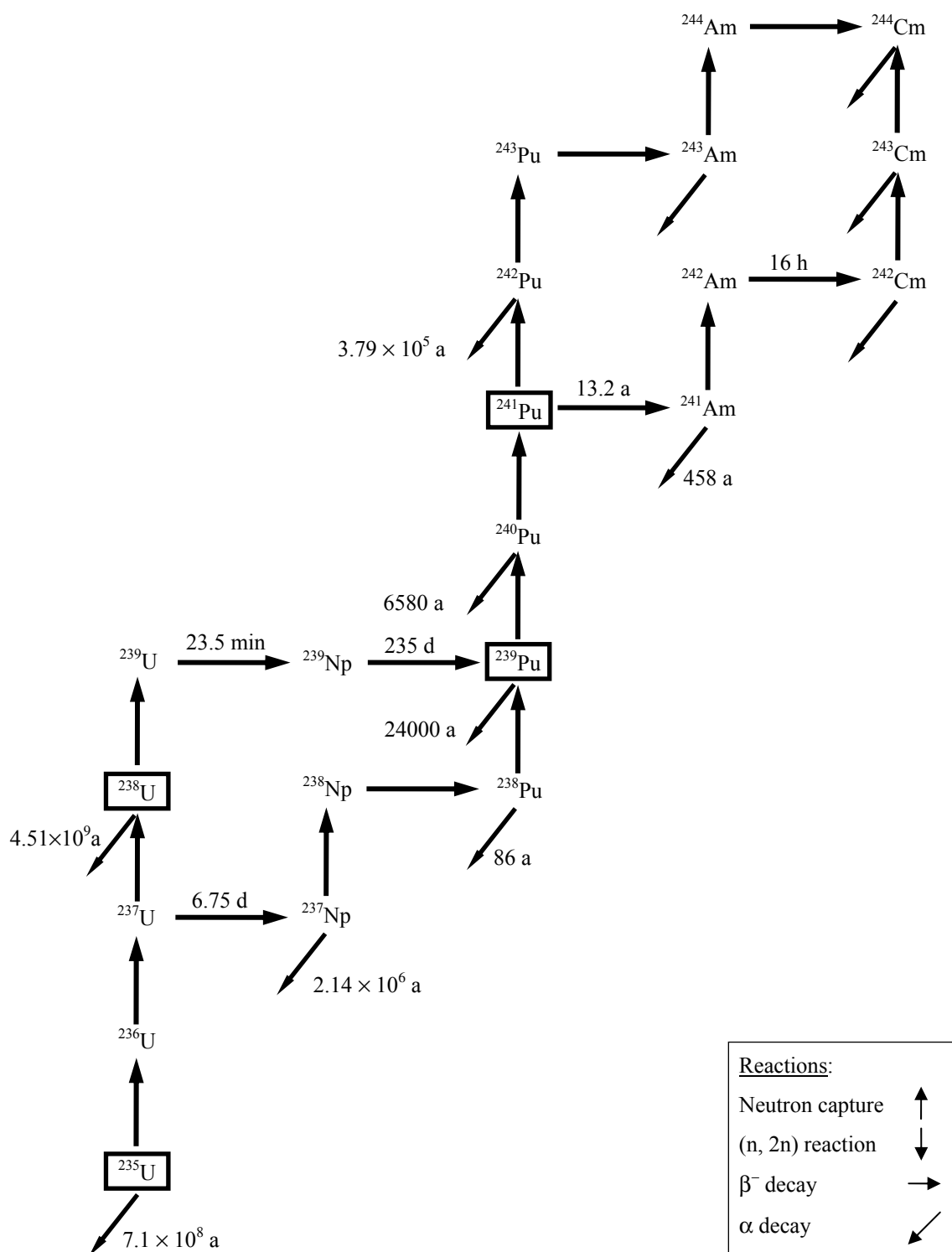
Burn-up	$^{238}\text{Pu}$	$^{239}\text{Pu}$ <sup>a)</sup>	$^{240}\text{Pu}$	$^{241}\text{Pu}$	$^{242}\text{Pu}$	Pu fiss.
33 GW d/t (HM) <sup>b)</sup>	1.7	57.2	22.8	12.2	6.0	69.4
60 GW d/t (HM)	3.9	49.5	24.8	12.9	8.9	62.4

<sup>a)</sup> By comparison, weapon-grade plutonium of low irradiation would be over 90 %  $^{239}\text{Pu}$ .

<sup>b)</sup> Gigawatt-days per ton of heavy metal (U, Pu).

<sup>3)</sup> Facility regulated for environmental protection.

<sup>4)</sup> Less than 1 mSv/a for the most exposed group.



**Fig. 3.6.** Uranium, plutonium and minor actinides.

### 3.2.6 World uranium resources and market

The concept of “resources”, or “reserves”, must be qualified, because behind any specific figure there are many hypotheses, not always explicit: hypotheses concerning the costs of extraction (the higher the accepted costs, the largest the resources because of access to lower-grade ores), and hypotheses concerning the state of the technologies of exploration, detection, and production. For instance, resources of petroleum have been vastly increased over the last decades by “secondary extraction” technologies.

Table 3.4 describes the standardized classification used by OECD/NEA and IAEA to give figures of uranium resources, always related to *recoverable* metric tons.

**Table 3.4.** NEA-IAEA classification of uranium resources.

Cost of recovery [\$ per kg U]	130...260				
	80...130	Reasonably assured	Additional 1 estimated	Additional 2	Speculative
	40...80	Reasonably assured	Additional 1 estimated		
	< 40	Reasonably assured	Additional 1 estimated		

If we take the four marked classes of assured resources and additional resources of the first category [97Oec], recoverable at a cost inferior or equal to 80 \$/kg U, commonly called *reserves*, the world total figure is around **2.5 million t U**.

85 % of these reserves are in the following nine countries:

Australia	24 %	South Africa	9 %	USA	4 %
Kazakhstan	17 %	Russian Federation	6 %	Niger	3 %
Canada	13 %	Namibia	6 %	Uzbekistan	3 %

Notably absent are big consumers like Japan and the European countries, not to mention India and China. The highest figure for the “ultimate” recoverable resources might be of the order of **15 million t U**.

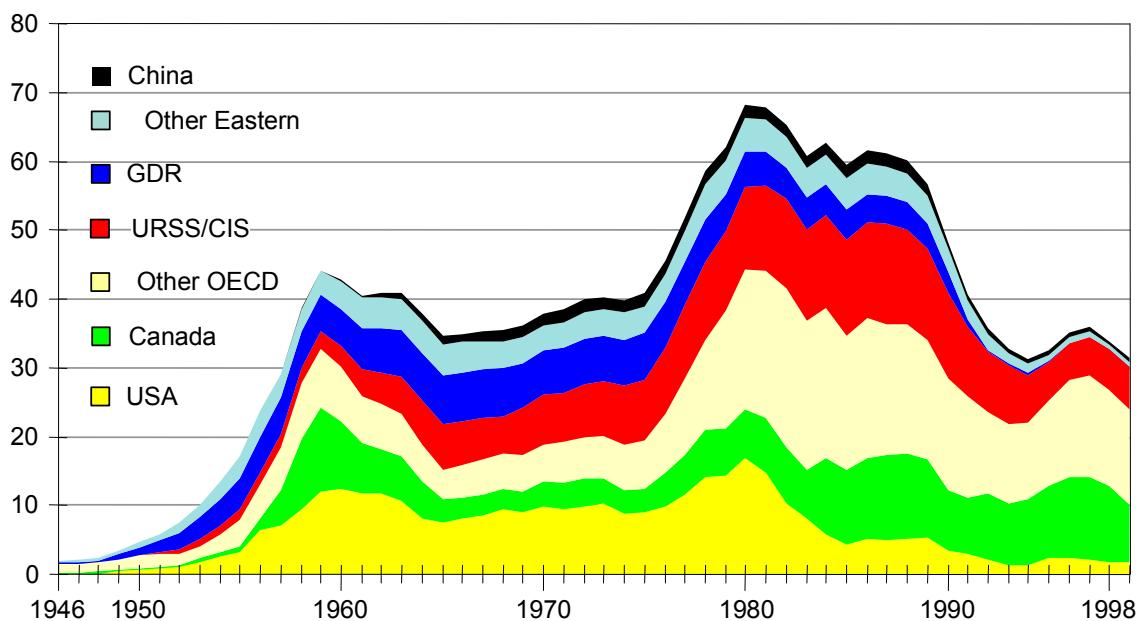
During the 1990s, the world production oscillated between 30 000 and 35 000 t U per year, but it reached close to 70 000 t in 1980. Since the origins of the nuclear era, approximately **2 million t U** have been produced, a quantity close to the “reserves” estimated today. Of these, only 1.15 million t U have been used in the supply of nuclear fuel for civilian nuclear reactors; 85 % of the remaining 850 000 t are in military stockpiles. The history of uranium production (Fig. 3.7) has been rather hectic:

- huge growth from 1946 to 1960, for military purposes;
- slump from 1960 to 1970 when the needs of the emerging nuclear power industry could not match the decrease in the military needs;
- growth – and overproduction – in the 70s, fueled by excessive expectations of nuclear power development, and aggravated by the US policy of requiring “feed” delivery by the utilities 10 years in advance of the delivery of enriched uranium (over which the US government had a monopoly);
- slow decrease during the 80s, reflecting the lowered nuclear expectations throughout the world and the numerous cancellations of nuclear projects in the USA;
- **crisis**, since 1990, with production around or below 35 000 t/a versus a stabilized demand close to 60 000 t/a [97Val], and a technical capacity around 45 000 t/a.

“Spot” prices reflect these variations: below 7 \$/lb  $\text{U}_3\text{O}_8$  in 1972, they jumped above 40 \$/lb in the mid 70s, to crumble after 1980. They have been meandering around 12 \$/lb since 1995. Till 1993, the main reason was overproduction and resale of the inventory of canceled power plants. Since that date, the “civilization” of Russian and American military stockpiles, due to the end of the Cold War and the reduction of nuclear arsenals, is adding around 200 000 t U to the overflowing civilian stockpiles. As a result, many mines have closed, exploration has dramatically slowed down, and many mergers and acquisitions have shaken the uranium mining community.

From 1985 to 2000, the number of production sites worldwide has decreased from 102 to 46, and the number of companies involved in uranium mining has shrunk from 38 to 23.

Uranium production [kilotons/year]



**Fig. 3.7.** Annual production of uranium. The total amount of uranium produced worldwide by the end of 1999 is 2.04 million t, including 0.82 million t produced by the former Eastern block and China.

### 3.3 Uranium enrichment

Maintaining a chain reaction with natural uranium is not easy because many neutrons are captured by  $^{238}\text{U}$ . It is only possible in thermal reactors moderated by graphite or heavy water ( $\text{D}_2\text{O}$ ). Early British (MAGNOX) and French (UNGG) reactors used graphite as a moderator and were fueled with metallic natural uranium. The Canadian CANDU reactors are moderated by  $\text{D}_2\text{O}$  and use the dioxide of natural uranium ( $\text{UO}_2$ ) as fuel. This is because the UK, France and Canada started their nuclear power generation program at a time when enrichment was only mastered by the United States where it had been developed for military purposes during the Manhattan Project.

The capacity to enrich uranium [79Vil], i.e. to increase the isotopic proportion of fissile  $^{235}\text{U}$ , allowed for the use of ordinary water ( $\text{H}_2\text{O}$ ) as moderator in the reactors of the nuclear submarines, to be followed by all the LWRs, which constitute 85 % of the nuclear power plants in the world today. One needs almost pure  $^{235}\text{U}$  to make nuclear weapons, whereas the LWR fuel is enriched only to between 2 % and 5 % in  $^{235}\text{U}$ .

### 3.3.1 Principle, cascade, SWU, HEU, LEU

Enrichment is the partial separation of “feed” natural uranium into its two main isotopes,  $^{238}\text{U}$  and  $^{235}\text{U}$ , to yield a “product” containing a mole fraction  $N_P$  of  $^{235}\text{U}$  higher than the naturally occurring  $N_F = 0.71\%$ , leaving a “waste” fraction depleted to a  $^{235}\text{U}$  concentration  $N_W$ . An enrichment facility can be considered as a black box with one intake and two exits, each one characterized by a mass flow ( $F$ ,  $P$  or  $W$ ) and by a concentration in  $^{235}\text{U}$  ( $N_F$ ,  $N_P$  or  $N_W$ ) as shown in Fig. 3.8.

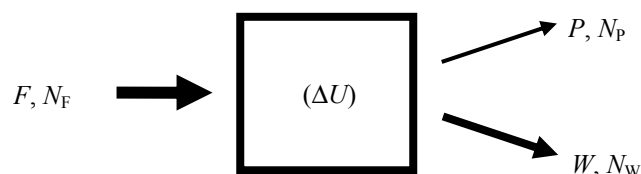


Fig. 3.8. Principle of an enrichment facility.

The equilibrium is described by the following equations:

$$F = P + W \quad \text{mass conservation} \quad (3.1)$$

$$F \cdot N_F = P \cdot N_P + W \cdot N_W \quad \text{isotopic conservation} \quad (3.2)$$

$$(\Delta U = P \cdot V(N_P) + W \cdot V(N_W) - F \cdot V(N_F)) \quad \text{value conservation (see below)} \quad (3.3)$$

Instead of using the mole fraction  $N$ , one often uses the abundance ratio  $R = N/(1 - N)$ ; the efficiency of the separation is characterized by the separation factor  $\alpha = R_P/R_F$ .

Most of the physical properties of a pure element – such as density, fusion and vaporization temperature, etc. – exhibit slight but measurable differences according to the element’s isotopic composition, but very few of these differences can be the basis for isotopic enrichment. The same can be said of the chemical properties. Even for the most efficient methods,  $\alpha$  is usually very close to unity, and one must constitute “cascades” by coupling many elementary stages to reach the desired enrichment  $N_P$ , as schematized in Fig. 3.9. In order to minimize the feed supply, the cascade is divided into two sub-cascades: most of the stages are used to enrich the product, while a few are devoted to deplete the tails to reach  $N_W$ , an operation known as “stripping”.

The simplest way to constitute a cascade is to feed stage “ $n$ ” with the product of stage  $(n - 1)$  and the tail of stage  $(n + 1)$ . Of course, not to remix what has been painfully separated, the assay of product  $n - 1$  and tail  $n + 1$  must be identical: this condition determines the optimum flow in each stage of the cascade, the optimum “shape” schematized in Fig. 3.10.

The choice of  $N_P$  is, of course, determined by reactor physics, by the burn-up to be reached in the fuel. The choice of  $N_W$  results from an economic optimization between the cost of feed uranium and the cost of the enrichment service: the higher the value of  $N_W$ , the more feed you need to obtain a given product quantity. To carry out this optimization, one introduces the concept of “separative work”, denoted by  $\Delta U$ , which derives from the increase of a “value function”  $V$ :

$$V(N) = (2N - 1) \ln(N/(1 - N)) , \quad (3.4)$$

$$\Delta U = P \cdot V(N_P) + W \cdot V(N_W) - F \cdot V(N_F) , \quad (3.5)$$

where  $\Delta U$  has the same dimension as  $F$ ,  $P$  and  $W$ , and is expressed in *Separative Work Units* (SWU). Figure 3.11 illustrates typical values of these parameters optimized for the economic conditions of the 1990s.

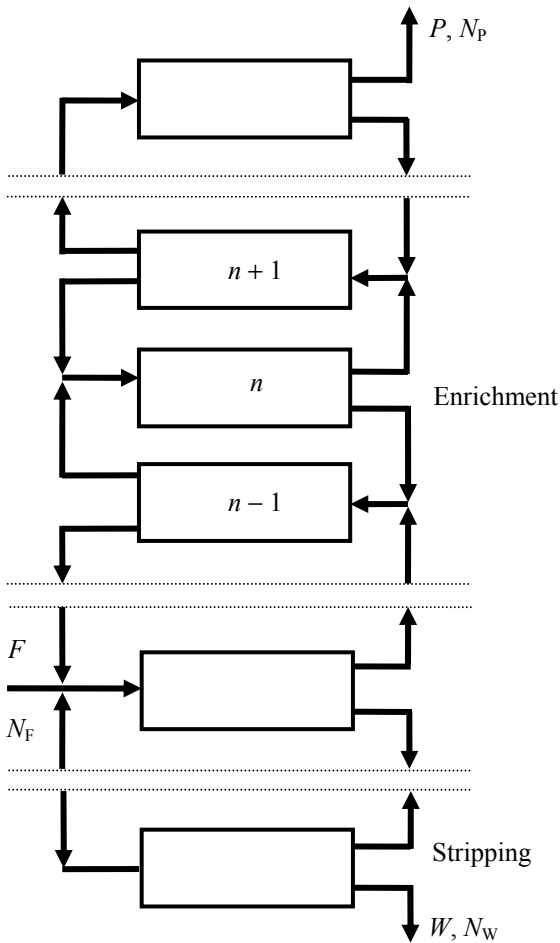


Fig. 3.9. Coupling stages to form a cascade.

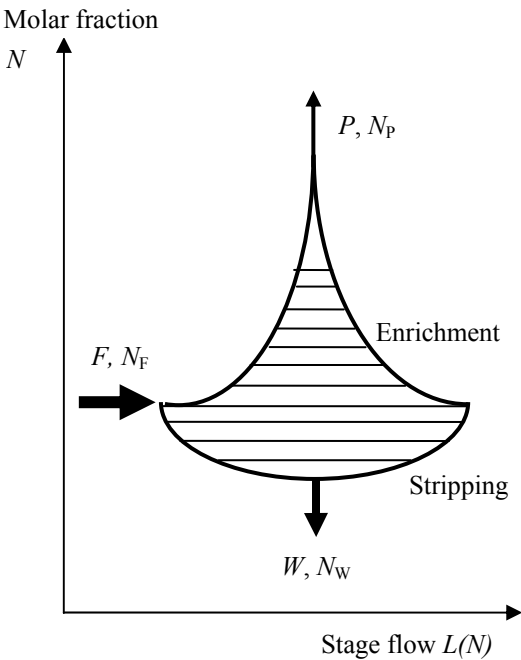


Fig. 3.10. "Profile" of an ideal cascade.

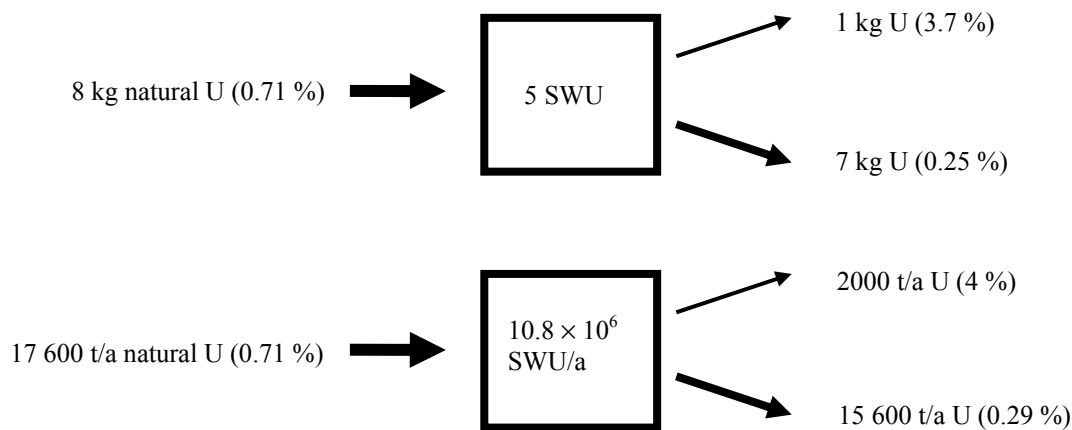


Fig. 3.11. Typical SWU values required for uranium enrichment. The respective  $^{235}\text{U}$  concentrations are given in brackets. The bottom part of the figure corresponds to the EURODIF plant.

A typical assay for a PWR fuel capable of reaching 45 GWd/t is 3.7 %  $^{235}\text{U}$ . From 1 % to 5 %  $^{235}\text{U}$ , one refers to *Low Enriched Uranium* (LEU). Above 20 % and up to weapon grade 93 %, it is called *Highly Enriched Uranium* (HEU) and subject to very strict safeguards and export restrictions to prevent risks of proliferation of nuclear weapons. The usual enrichment for research and irradiation experimental reactors fuel is 19.8 %, just below the HEU threshold.

To obtain 1 kg of commercial LEU, one needs typically 5 SWU, while 1 kg of weapon-grade HEU requires around 200 SWU. A 1 GW (el) PWR needs of the order of 100 000 SWU per year.

### 3.3.2 Enrichment technologies

There are many possible classifications of the various uranium enrichment processes, according to the property one wants to emphasize, for instance: statistical processes like gaseous diffusion or centrifuge versus selective processes like AVLIS, reversible processes like most chemical processes versus irreversible processes like calutrons, etc. One can also distinguish between established processes and processes under development, or according to the proliferation resistance, which itself calls for several criteria (ease and time to reach HEU, size and visibility of the facilities, hold-up inventory, criticality limitations, need for power, etc). Of course, for civilian purposes, economics is the key criterion, with its components: plant depreciation, operation and maintenance, power consumption.

It all started with mass spectrographs, the giant “calutrons” of the early stages of the Manhattan Project, surprisingly revived by Iraq for its clandestine military program. Then gaseous diffusion (GD) dominated the market, followed by ultra centrifuge (UC). Some development was carried out on aerodynamic processes (the German nozzle process and the South African Helicon) and on chemical isotopic separation methods (the French CHEMEX and the Japanese Asahi), but today the only developments going on appear to center around laser enrichment.

Both GD and UC operate in the gaseous phase. The only gaseous uranium compound with a significant vapor pressure at room temperature is *uranium hexafluoride*,  $\text{UF}_6$ . Fortunately, fluorine has only one stable isotope,  $^{19}\text{F}$ , whose atomic mass is much smaller than that of uranium.

At 20 °C, the saturation pressure of  $\text{UF}_6$  is 80 torr, and it reaches the atmospheric pressure of 760 torr at 55 °C: DG and UC plants operate around 50...65 °C. The phase diagram of  $\text{UF}_6$  is schematized in Fig. 3.12.

At room temperature,  $\text{UF}_6$  is a solid (density 4.68 g/cm<sup>3</sup>), which facilitates storage and handling. It reacts violently with water and most organic fluids or solids (one cannot use lubricants or rubber seals with it). Both uranium and fluorine being toxic, as well as the decomposition product HF, all containers or circuits carrying  $\text{UF}_6$  must be leaktight, with metallic seals.  $\text{UF}_6$  also corrodes most metals except for aluminium and nickel and some of their alloys.

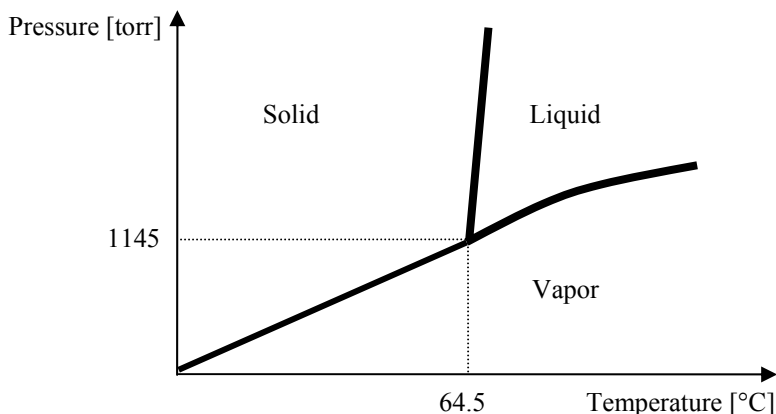


Fig. 3.12. Phase diagram of uranium hexafluoride,  $\text{UF}_6$ .

### 3.3.2.1 Gaseous diffusion

According to Knudsen's law, at a given temperature  $T$  in a gas, the molecules move with an average speed  $V_i$  inversely proportional to the square root of their molecular mass  $M_i$ :

$$V_i = [8 RT/(\pi M_i)]^{1/2}, \quad (3.6)$$

where  $R$  denotes the universal gas constant.

As a consequence, in gaseous  $\text{UF}_6$ , molecules of  $^{235}\text{UF}_6$ , mass 349, will travel more rapidly than molecules of  $^{238}\text{UF}_6$ , mass 352, and in a given time interval they will hit upon the walls around them more often. If the walls are porous,  $^{235}\text{UF}_6$  molecules are slightly more likely to sneak their way through the pores than  $^{238}\text{UF}_6$  molecules, at least if the pore diameter is much smaller than the mean free path of the molecules. If there was a pressure difference between the two faces of the porous wall, the low-pressure side would therefore be slightly enriched in  $^{235}\text{UF}_6$ . Ideally, in pure Knudsen regime, the separation factor across the pore would be proportional to the square root of the ratio of the masses, in our case  $\alpha_0 = 1.0043$ . The ideal enrichment factor,  $\epsilon_0 = 4.3 \times 10^{-3}$ , is very small. *In reality, several perturbing factors lower the actual enrichment factor to around  $2 \times 10^{-3}$ .*

Gaseous diffusion, schematized in Fig. 3.13, implements this phenomenon to enrich  $\text{UF}_6$  by pushing it through a very thin porous "barrier" deposited over a porous support (with larger pores) which can withstand the pressure difference.

The elementary separative stage consists of three basic components (Fig. 3.14):

- the "diffuser", a cylindrical container in which several barriers are set up in parallel, inside their cylindrical support tubes. These barriers define two compartments inside the diffuser, a high-pressure compartment inside the barriers and a low-pressure compartment outside them;
- the compressor which circulates the gas and gives it the right pressure entering the diffuser;
- a heat exchanger to remove the calories produced by the compression.

Of course, one also needs a series of ducts and valves, etc.

In the old US plants, diffusers were horizontal, and barrier supports were made of sintered nickel. In the Tricastin EURODIF plant, the most modern GD plant, diffusers are vertical and barrier supports are made of ceramic. The actual layout of a EURODIF enrichment stage is shown in Fig. 3.15, together with the actual cascade profile, to be compared with Fig. 3.10: with such a small enrichment factor, one needs as many as 1400 stages to reach commercial LEU assay (< 5 %). It would be quite uneconomical to build 1400 stages of different sizes, so the cascade is "squared", using only three diffuser sizes, and slightly adjusting the mass flows.

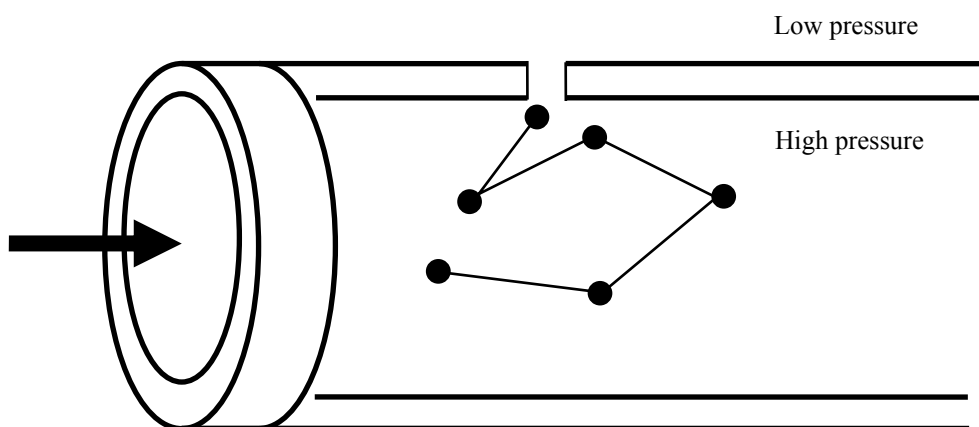


Fig. 3.13. Gaseous diffusion (elementary process).



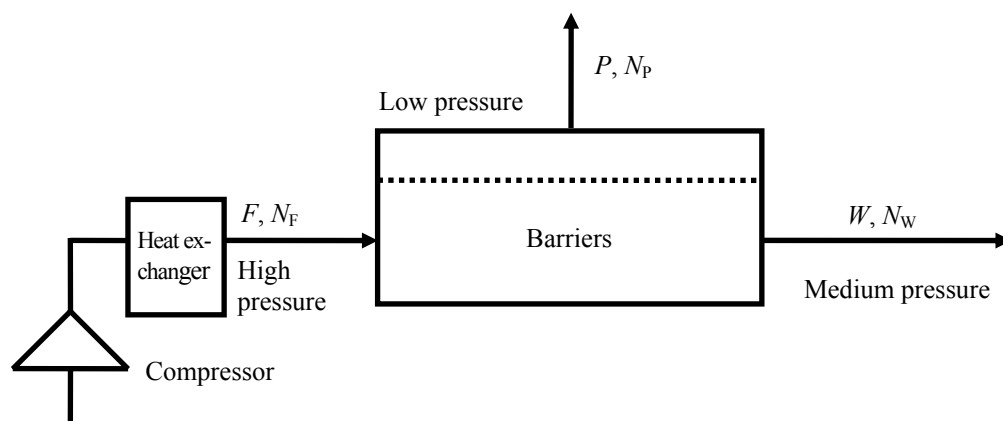


Fig. 3.14. Gaseous diffusion (schematic).

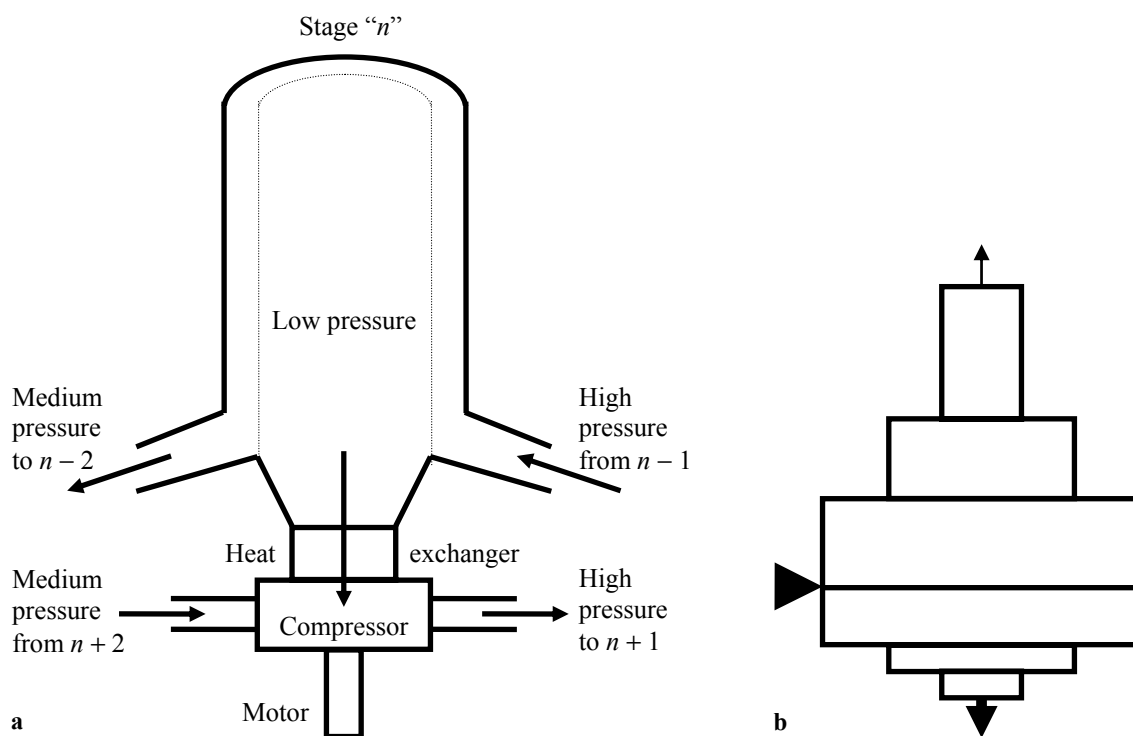


Fig. 3.15. (a) EURODIF layout (schematic). (b) Actual cascade profile.

Gaseous diffusion requires a lot of power for the compressors, around 2400 kWh per SWU: to power its 10.8 million SWU per year, EURODIF needs the full output of three 900 MW (el) PWR plants located just nearby. On the other hand, it can supply enriched uranium for 100 similar PWR plants. GD plants need a long time to reach equilibrium and have a very significant quantity of uranium “held up” inside the cascade. Furthermore, once a cascade is set up, it is extremely difficult to rearrange it to reach a significantly higher enrichment: a civilian GD plant cannot easily be made to fabricate HEU, and certainly not without a high visibility and a long delay.

### 3.3.2.2 Ultra centrifugation

Early work on the gaseous centrifuge method was carried out by G. Zippe in Germany during World War II. In the 60s, this process began to appear competitive for large-scale enrichment; it is the process used in Russia and by the Anglo-German-Dutch Company URENCO.

When a gas rotates with angular velocity  $\omega$ , its molecules (of mass  $M$ ) are subject to a centrifugal force which results in a pressure gradient  $P$  perpendicular to the rotation axis:

$$P(r) = P(0) \exp[M\omega^2 r^2 / (2kT)], \quad (3.7)$$

where  $r$  is the distance from the axis,  $T$  denotes the gas temperature, and  $k$  is the Boltzmann constant. Under this pressure gradient, a separation appears, the heavier molecules concentrating at the periphery, while the lighter species migrate preferentially toward the center, where the gas density is near zero. Assuming a centrifuge of radius  $R$ , the separation factor at a distance  $r$  from the axis would be:

$$\alpha_0 = \exp[(M_8 - M_5) \omega^2 (R^2 - r^2) / (2kT)], \quad (3.8)$$

where  $M_8$  and  $M_5$  denote the masses of  $^{238}\text{UF}_6$  and  $^{235}\text{UF}_6$  molecules, respectively. With  $\omega R = 800$  m/s,  $T = 300$  K, and  $r = 0.7 R$ , the separation factor for  $\text{UF}_6$  would be equal to 1.23, much larger than the value for gas diffusion – but the mass flow is much smaller.

To improve the performance of the centrifuge very significantly, one creates a vertical counter-current circulation at the periphery (see Fig. 3.16), with a thermal gradient for instance: it is somewhat equivalent to creating an internal cascade, the upward current being progressively enriched in  $^{235}\text{U}$  while the downward current is progressively depleted. With this set-up, one shows that the separative capacity of a single rotating bowl, expressed in SWU, can be written:

$$\text{SWU} \approx LD (\omega R)^4 (M_8 - M_5)^2 / T^2, \quad (3.9)$$

with  $L$  and  $D$  denoting the length and diameter of the bowl, respectively.

One should therefore use a long bowl and rotate it at the highest possible peripheral speed inside a vacuum case to prevent heating (and contain the fragments of an exploding bowl). But there are constraints: the bowl material must resist the enormous strain of the centrifugal force on its thin wall, it must also withstand the operating temperature and resist  $\text{UF}_6$  corrosion. The drum must be extremely well balanced. Reaching the rotational speed is very tricky because one must “pass” a number of critical resonance values. The gas temperature must not go below the solidification point because any plating of solid  $\text{UF}_6$  would unbalance the rotor and cause it to explode, etc.

The mass flow is so small that one needs a huge number of centrifuges, but as the enrichment factor is significant, one needs a limited number of stages, each constituted by many parallel centrifuges. The most advanced centrifuges, with composite materials and peripheral speeds of more than 700 m/s, are credited with an individual separative power ranging between 30 and 100 SWU/a<sup>5</sup>. Even with the latter value, a 5 million SWU/a plant would need 50 000 machines to constitute parallel cascades of less than 10 stages. Such a large number of machines requires a very high level of reliability.

Since isotopic separation in a centrifuge is a thermodynamically reversible process, it requires a lot less energy than gaseous diffusion, at least ten times less, perhaps fifty times. The cost structure of the SWU is therefore very different between the two methods.

<sup>5</sup>) From 1977 to 1985, the US almost completed a large enrichment plant (8.8 MSWU/a), GCEP at Portsmouth, which had huge centrifuges, more than 10 meters high, and were believed to have an individual capacity of several hundred SWU/a. No technical reason was given when the project was discontinued, but such “monsters” were probably not reliable enough and, therefore, uneconomical.

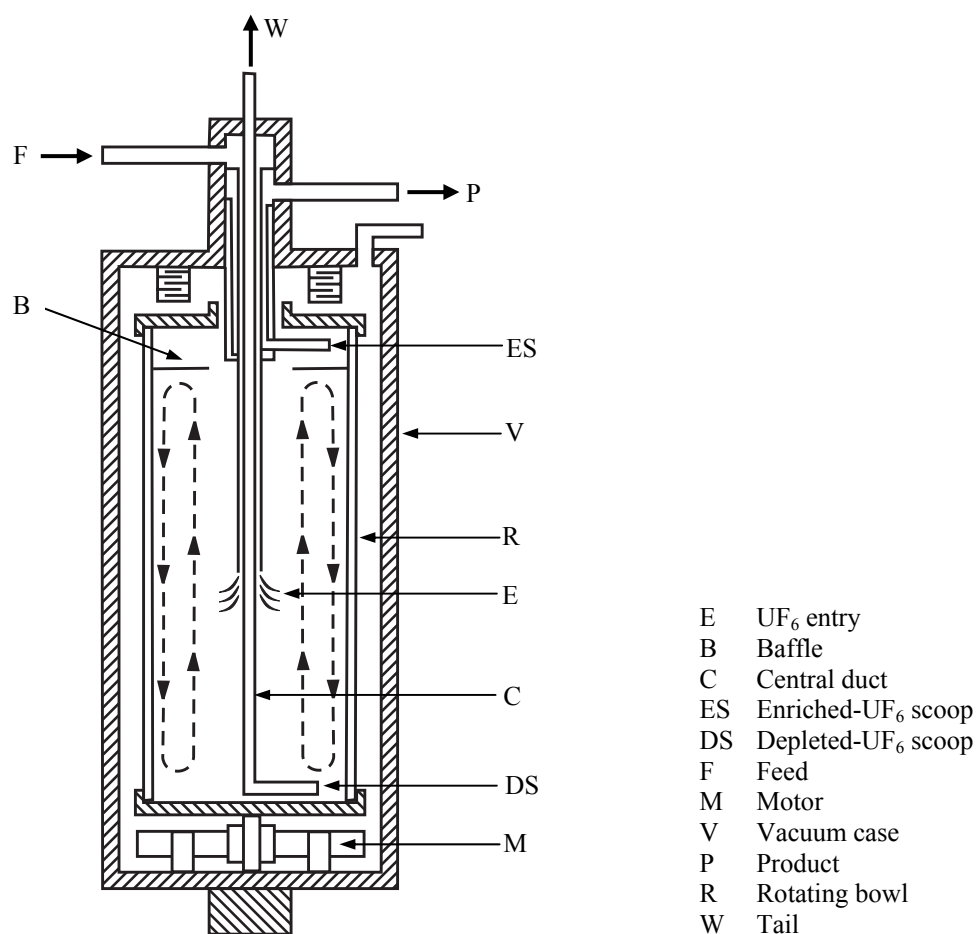


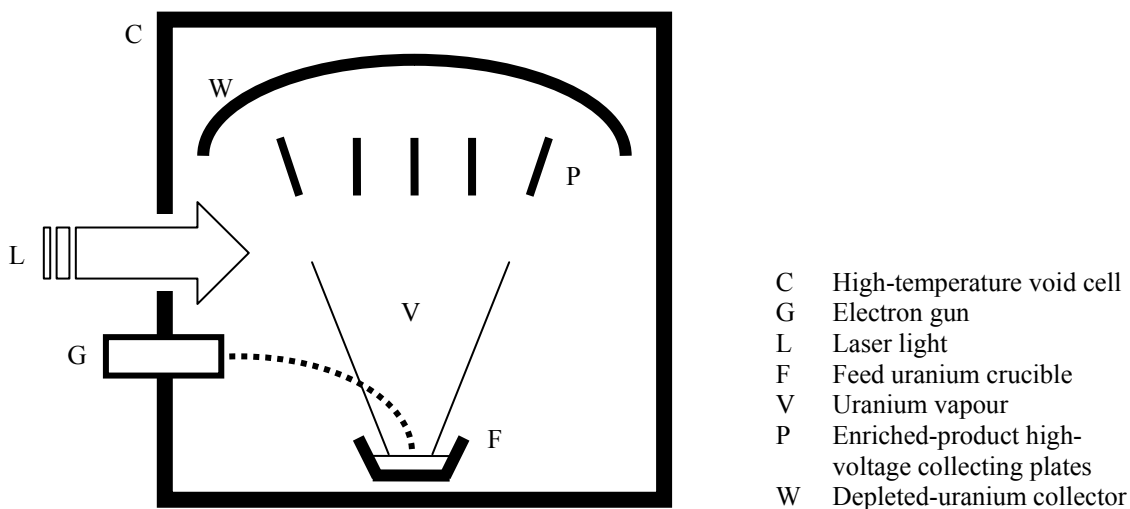
Fig. 3.16. Schematic drawing of a gas centrifuge.

### 3.3.2.3 Laser isotopic separation (AVLIS)

The AVLIS process (Atomic Vapor Laser Isotopic Separation, in French SILVA) is based on the selective ionization of the uranium atom by a laser light of convenient wavelength. The electronic spectrum of the uranium atom, with its 92 electrons, comprises many excitation levels, ranging in wavelength from infrared to ultraviolet. Because of the complexity of the interactions between the nucleus and the electrons, some of the excitation levels are not identical for  $^{235}\text{U}$  and  $^{238}\text{U}$ . The difference in energy is small, but sufficient to be used for isotopic separation [80Mai, 90Sch].

The ionization energy for the uranium atom is about 6 eV, which cannot be easily provided in one quantum: one will reach the ionization level in three stages, two successive excitations of about 2 eV each, and a final ionization from the most highly excited level. This kind of energy can be supplied by yellow-orange dye lasers. The separation process would therefore be the following (Fig. 3.17):

Uranium is melted in a crucible by electron bombardment. The atomic vapor is irradiated by laser rays of the proper wavelengths which ionize the  $^{235}\text{U}$  atoms.  $^{235}\text{U}$  ions are then deflected by a high-voltage electrical field toward the collector plates (which collect also a certain percentage of the vapor). The remaining vapor, depleted in  $^{235}\text{U}$ , is condensed on a collecting roof. Taking into account the isotopic dilution on the collecting plates, one should be able to enrich natural uranium to commercial LEU ( $\approx 5\% \text{ } ^{235}\text{U}$ ) in one single step.



**Fig. 3.17.** The AVLIS process (schematic).

The huge laser power needed is supplied by batteries of high-power yellow-green lasers (copper vapor lasers or doubled YAG), the wavelength being adjusted by tuneable color lasers downstream.

The physics of the process has been demonstrated at the laboratory scale, but the technology is very demanding, especially concerning the collector materials. The power requirements, notably for uranium vaporization, are slightly larger than for the centrifuge process, but far smaller than for gaseous diffusion. One drawback of this promising concept is that it breaks the  $\text{UF}_6$  “chain” from refining to fuel fabrication, introducing a metal technology “link” in-between.

This is why a sister technology has been pursued for some time, called MLIS for molecular laser isotopic separation. Infrared lasers would selectively excite  $^{235}\text{UF}_6$  molecules in a gaseous mixture of  $\text{UF}_6$  and a lighter gas at low temperature ( $\approx 100$  K), excited molecules would later be broken into solid  $\text{UF}_5$  and fluorine by an ultraviolet laser. This process was not completely demonstrated when abandoned in the mid 80s.

### 3.3.3 World enrichment capacities and market

The world market for enrichment services [99Oec1] is characterized in the turn of the century by a large production overcapacity, made worse by the commercialization of ex-military stockpiles.

The annual needs are about 32 MSWU. The total capacity available for commercialization is 45 MSWU/a, but the production amounts to only 30 MSWU/a, and the dilution of the 500 tons HEU purchased by the USA from Russia is equivalent to an additional 5 MSWU/a during 20 years. Furthermore, those 500 tons do not constitute, by far, the total stockpile.

The enrichment suppliers are:

- USEC, in the USA, which operates two state-owned gaseous diffusion plants, at Portsmouth and Paducah, with a total capacity of 19 MSWU/a. USEC has announced the closure of the Portsmouth plant in 2001, and commercializes the diluted Russian-origin HEU.
- EURODIF, a French-led European consortium, operates a 10.8 MSWU/a gaseous diffusion plant located in Tricastin. The next French plant, ca 2012, will be centrifuge.
- URENCO, a trinational European consortium (UK, D, NL) operates ultracentrifuge plants with a total capacity of 4.5 MSWU/a.
- TENEX commercializes on the Western market enriched uranium produced in centrifuge plants formerly used for military purposes. It can market about 10 MSWU/a.

### 3.3.4 Conversion

According to its specific process, a uranium mill would deliver concentrates

- usually made of uranates (magnesium, sodium or ammonium uranates) like  $\text{Mg}_2\text{U}_2\text{O}_7$ , containing up to 65 % uranium; and
- sometimes made of oxides, containing up to 80 % uranium: black  $\text{UO}_2$ , orange  $\text{UO}_3$  or yellow  $\text{U}_3\text{O}_8$ ;

in 200 liter barrels or 1 m<sup>3</sup> containers. Some stringent standards must be met in terms of concentration for some impurities: boron content, for instance, must be strictly below 0.1 %, and preferably < 0.005 %.

Before fuel fabrication, these concentrates must be transformed either into metallic uranium (MAGNOX metal U fuels, or feed for AVLIS), into pure uranium dioxide,  $\text{UO}_2$ , or into uranium hexafluoride,  $\text{UF}_6$  (other enrichment processes). Most usually, the name “conversion” refers to the latter operation.

There are two families of conversion processes [95Rig], according to whether the purification step takes place at the head end, by solvent extraction, or at the back end of the flow chart, by distillation (Fig. 3.18).

The dry route, often used in the USA, is simpler and produces no liquid effluent, but it is only practical if the concentrates used are  $\text{U}_3\text{O}_8$ . COMURHEX in France has selected the more versatile wet road, where tributylphosphate extraction gives pure (< 0.1 ppm total impurities) uranyl nitrate at an early stage in the process<sup>6</sup>.

## 3.4 Fuel fabrication

### 3.4.1 Elements of fuel design

With few exceptions – molten salt reactors for instance – the nuclear fuel is fabricated into discrete objects called “elements”, “bundles”, “assemblies” or “sub-assemblies”, where the nuclear materials are inserted inside mechanical, usually metallic, structures. A set of fuel elements constitutes the core of the reactor.

In the reactor, the fuel performs two essential functions: It supplies the heat in the core, and it prevents the radioactive fission products from migrating into the primary coolant circuit (it is the “first barrier” in the safety analysis). It must therefore have the capability to sustain for several years the chain reaction in a stable manner while keeping its structural integrity. As a consequence, fuel design must take into account the requirements issued from the core physics and from the coolant chemistry.

Core physics defines the fuel composition, the proper mixture of fissile, fertile and control materials in order to achieve the required burn-up, i.e. the quantity of energy supplied by the fuel during its lifetime, expressed in GW d/t, gigawatt-day per metric ton of heavy metal contained in the fuel. Core physics determine also the fuel geometry, taking into account the neutronic and thermal-hydraulic properties of the coolant, as well as the neutronic properties of the structural materials (cladding, other fuel structures as may be the case).

Coolant chemistry dictates some properties of the cladding like corrosion resistance at operating temperature or above, and even of the fuel material itself, which must not interact chemically with the coolant in case of cladding failure.

Beyond these generic considerations, fuel design and fuel fabrication are very specific to a given reactor type [99Bai].

<sup>6</sup>) For historical reasons, relating to the early UNGG program, conversion is performed in two separate plants: from concentrates to  $\text{UF}_4$  in Malvesi, and final fluorination in Pierrelatte.

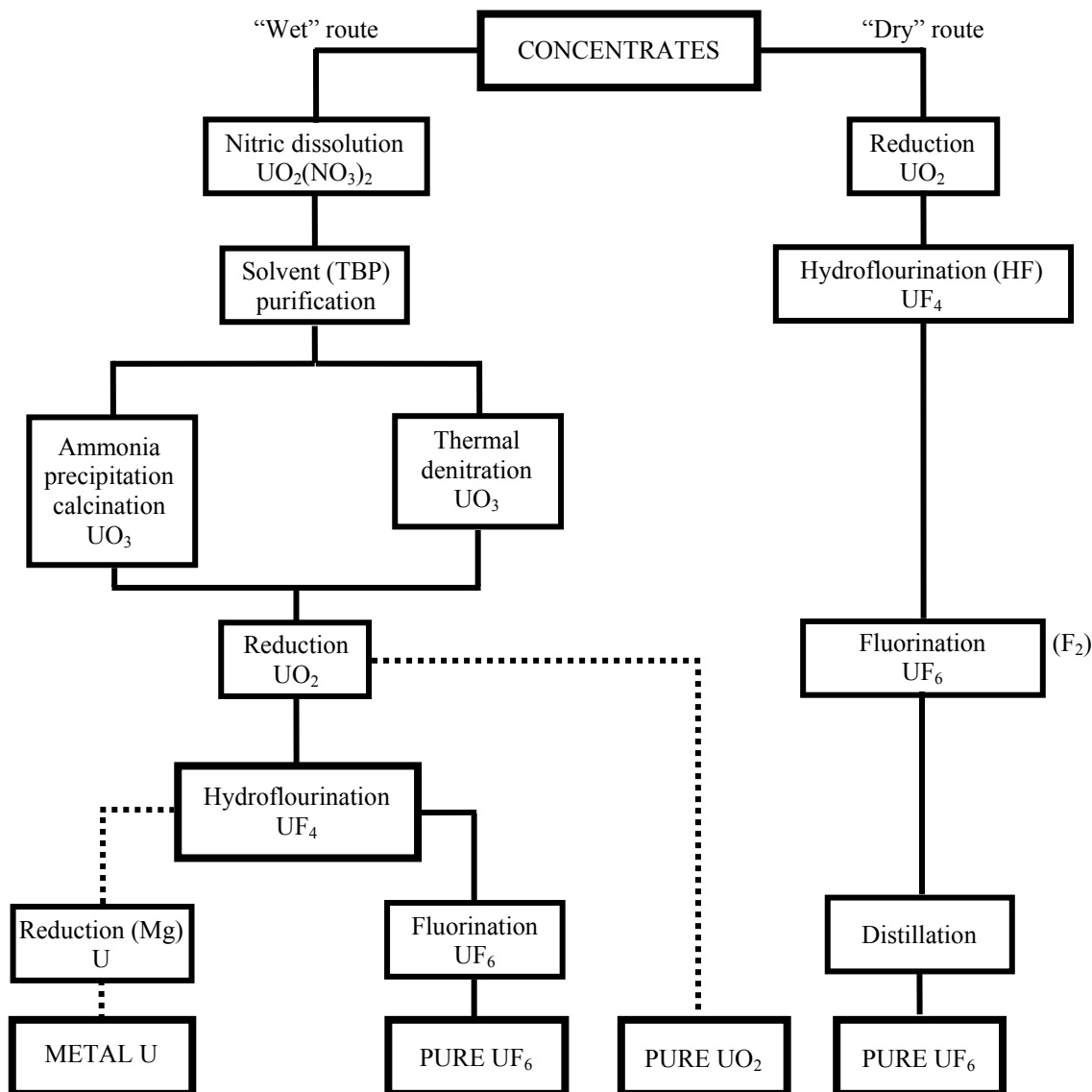


Fig. 3.18. The two conversion routes.

### 3.4.1.1 Fissile/fertile couple

With few exceptions (HEU fuel for some research or space applications reactors), the fuel is a mixture of fissile and fertile nuclides, and the conversion of fertile into fissile during the irradiation partially makes up for the fissile depletion, thus extending the lifetime of the fuel.

We have seen that natural uranium itself is a mixture of fissile  $^{235}\text{U}$  and fertile  $^{238}\text{U}$ , but with a very low concentration in fissile nuclei which severely limits its uses. Any combination, in the proper proportion, of one of the three fissile nuclides  $^{233}\text{U}$ ,  $^{235}\text{U}$  and plutonium (actually a mixture of  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$ ) with one of the two main fertile nuclides  $^{238}\text{U}$  and  $^{232}\text{Th}$  can provide the basis for a fuel cycle.

### 3.4.1.2 Fuel material

The simplest fuel material is uranium in the metal form. It is still used in gas-cooled MAGNOX power reactors, because only the metal can sustain the chain reaction in a natural uranium/graphite core where the neutron balance is tight, and in some experimental and irradiation reactors. It may also be used as a metallic alloy in fast-neutron reactors. Uranium is a highly reactive metal which oxidizes rapidly in air at room temperature. At temperatures below 600 °C, uranium crystallizes in the orthorhombic system ( $\alpha$  phase) which is anisotropic: when the metal is formed by rolling or extrusion, the crystals orient themselves along preferred directions which results in dimensional changes when the metal is irradiated (the so-called growth) or subjected to a thermal cycle.

In most other occurrences, the fuel material is ceramic: it can be uranium carbide or uranium nitride, but most often, by far, it will be uranium dioxide,  $\text{UO}_2$ . The latter has a number of qualities: it is refractory (its melting temperature is 2865 °C), it is structurally stable and does not interact with high temperature water, and its oxygen content has a very low capture cross section for thermal neutrons. The density of  $\text{UO}_2$  is 10.97 g/cm<sup>3</sup>, and it has a poor thermal conductivity (around  $2 \times 10^{-3}$  W/m/K at 1000 °C).

### 3.4.1.3 Cladding materials

The fuel cladding serves several purposes: it contains the fission products, it protects the fuel against corrosion by the coolant and it provides a heat exchange surface with the coolant, and it must do so for extended periods of time (from several weeks to several years) during which it is submitted to irradiation by fast neutrons. In addition, it must have a low neutron-absorption cross section<sup>7</sup> in order not to impair the neutron economy in the core. To provide a good heat transfer, the cladding material must have a good thermal conductivity and a good bonding with the fuel. If such bonding is not possible, an intermediate layer must be introduced: high-pressure gas (most often), liquid metal or pyrocarbon in some occurrences. With the exception of the silicon carbide coating of HTR particles (see Sect. 3.4.5), most cladding is made of metal or metallic alloys. Table 3.5 gives the thermal-neutron cross section values for several metals used as cladding or entering into the composition of cladding alloys.

Beryllium would appear ideal but its mechanical properties, especially under irradiation, are not good. Magnesium alloy MAGNOX is used in namesake reactors but would not withstand a water environment. Aluminium is used in low-temperature MTR irradiation reactors but would not resist corrosion at higher water temperatures. Alloyed zirconium is the basic choice for LWR and CANDU fuels. Stainless steel was used in LWRs and is the cladding for the sodium-cooled FBR (with fast neutrons, absorption in the cladding is negligible).

**Table 3.5.** Thermal-neutron absorption cross sections,  $\sigma$ , for different cladding metals.

Material	$\sigma$ [barn]
Beryllium	0.01
Magnesium	0.06
Zirconium	0.18
Aluminium	0.23
Tin	0.63
Niobium	1.1
Iron	2.6
Molybdenum	2.7
Chromium	3.1
Copper	3.8
Nickel	4.6

<sup>7</sup>) The cross section, expressed in barns (1 barn =  $10^{-24}$  cm<sup>2</sup>), is a measure of the probability for a given reaction to take place when a given nuclide is irradiated with neutrons.

### 3.4.1.4 Absorber materials

A reactor loaded with fresh fuel is supercritical<sup>8</sup>, if one considers only the reactivity of the fuel: this excess reactivity, which will wear out during irradiation, is necessary to compensate for a number of effects, as summarized in Table 3.6 for LWRs.

To keep the chain reaction just critical and the power level constant, a combination of neutron absorbers must be introduced in the core, taking into account that most of the above-mentioned reactivity effects happen within a few days, only the burn-up effect lasting over the complete power cycle.

**Table 3.6.** Reactivity balance, given in %, for typical LWRs [96Wil].

Changes in the core	PWR	BWR
Fuel temperature defect, from cold to hot, full power	1.5	1.5
Moderator effect (same)	2.5	2.0
Equilibrium fission-product poisoning	3.5	3.3
Burn-up compensation	10.0	6.5
Control margin and xenon-samarium override	1.2	1.0
Shutdown margin	1.0	1.0
Total	19.7	15.3

Neutron absorbers, usually referred to as “control poisons”, may be chemical compounds of boron, cadmium, gadolinium, erbium or hafnium. These poisons may be homogeneous in the coolant (soluble boric acid in PWR primary water), homogeneous in the fuel (“burnable” gadolinium oxide in BWR fuel pellets), or heterogeneous in movable “control rods” or fixed burnable absorber rods.

### 3.4.1.5 PWR and BWR fuel assemblies

The fuel assemblies of both families of light water reactors, PWR and BWR, share a lot of characteristics, which reflects the fact that both use the same material – ordinary water – as coolant as well as moderator:

- The nuclear material is a ceramic made of sintered dioxide of low-enriched uranium (LEU) or of mixed uranium and plutonium dioxide, manufactured in cylindrical “pellets”.
- The pellets are inserted inside leaktight metallic “rods” (or “pins”). The rods are pressurized with helium, both for thermal bonding and mechanical resistance.
- The rods are assembled inside a metallic “skeleton” which insures the mechanical stability in the core and during handling and transportation.

Early cladding material was stainless steel, but now cladding is usually made of zirconium-based alloys: zirconium has a low capture cross section (see Table 3.5), a high melting temperature (1845 °C) and a good resistance to corrosion by high-temperature water. It is relatively abundant, but must be purified from any trace of hafnium which comes with it and is a powerful neutron absorber. Alloying materials, varying in proportion from design to design, are used to improve the mechanical properties of zirconium and minimize its growth under irradiation. The various “Zircaloy” alloys use tin (1.2...1.7 %), iron, chromium and nickel; niobium is used in advanced cladding materials. Tin improves the mechanical properties, and the other additives are used against corrosion.

Typical parameters of PWR and BWR fuel assemblies are given in Table 3.7.

<sup>8</sup>) This means it has more fissile material in the core than would strictly be necessary to maintain the fission chain reaction going.



**Table 3.7.** Typical fuel assemblies (FA) of different reactor types.

Characteristics	PWR	BWR <sup>a)</sup>	CANDU	Superphénix
Burn-up [GWd/t]	45...60	40...50	7	> 120
Pellet diameter [mm]	8.2	9.5	12	7.1
Pellet length [mm]	13.5	11.5	16	
Cladding material	Zircaloy 4	Zircaloy 2	Zircaloy 4	Austenitic steel
Pin outer diameter [mm]	9.5	12.3	13	8.5
Cladding thickness [mm]	0.57	0.89	0.4	0.56
FA length [m]	4.8	4.1	0.495	5.4
Rod length [m]	4.5	4.5	0.493	2.7 (1.0 fuel)
Number of rods/pins	264	72 (8 tie rods)	37	271
Average fuel rating [kW/m]	17.9	15.4	57 (peak)	200
Geometry	17 × 17	9 × 9	Circular array	Hexagonal array
Structure	Rods maintained by spacer grids around a skeleton made of guide-tubes	4 bundles with spacer grids inside a wrapper tube	Bundle with spacers	Pins separated by helical spacer wire inside hexagonal wrapper tube
Control absorbers	Rods within guide-tubes	Cruciform between 4 FA	Metal rods (steel, Cd)	B <sub>4</sub> C in special sub-assemblies

<sup>a)</sup> BWR fuel is zoned axially, both in enrichment and in burnable poison, to accommodate for the change in water density between the bottom and the top of the fuel.

### 3.4.2 LWR fabrication technology

#### 3.4.2.1 Fuel pellet production

UF<sub>6</sub> is supplied by the enrichment plant to the fabrication plant as a solid stored in steel containers. There, the containers are heated to release gaseous UF<sub>6</sub>. From then on, the following operations are performed:

- *Conversion*: UF<sub>6</sub> is heated in an oven with water vapor and hydrogen, to produce UO<sub>2</sub> powder, according to the reaction  $\text{UF}_6 + 2 \text{H}_2\text{O} + \text{H}_2 \rightarrow \text{UO}_2 + 6 \text{HF}$ .
- *Mixing*: UO<sub>2</sub> is oxidized to U<sub>3</sub>O<sub>8</sub> and mixed with a “porogen” material to adjust the final density.
- *Pre-compaction*: the mixture is pre-compacted, then crushed and made into small granules, which flow easily.
- *Pelletization*: the granules and a lubricant (zinc stearate) are pressed into pellets under high pressure.
- *Sintering*: the “green” pellets are sintered at 1700 °C in a continuous oven and in a hydrogen atmosphere. In the process, the pellet density increases to ≈ 94 % of the theoretical value.
- *Grinding*: the pellets are ground to the design diameter and “cupped” at the ends. Each of them is then automatically checked for dimensions, shape and surface aspect. The finished pellets are finally out-gassed in vacuum at high temperature to remove any trace of moisture and organic contaminants.

The process described above is the “dry” route. Conversion can also be “wet” through precipitation of ammonium diuranate, (NH<sub>4</sub>)<sub>2</sub> U<sub>2</sub>O<sub>7</sub>, followed by calcination of the precipitate. Rejected pellets are crushed and reintroduced in the pre-compaction stage.

### 3.4.2.2 Fuel rod fabrication

Zirconium is delivered as a “sponge”, which is first melted under vacuum in an arc furnace where alloying elements are added, and poured as ingots. Ingots are forged and quenched to preserve the microstructure, then drilled, rolled and annealed to obtain a long tube of the right diameter and thickness. The tube is 100 % controlled for dimensions and internal defects, using ultrasonic transducers. Cut to the design length, the tubes are fitted with a welded bottom plug.

The pellets are introduced inside the tubes up to the proper fuel length, and maintained in place by a spring introduced in the upper plenum, designed to provide room for the release of fission gases during fuel irradiation. The top plug is then welded to the tube; this plug has a small hole through which helium is introduced, around 25 bar, before closure of the hole. The completed fuel rod is then controlled: leak-tightness of the welds, length of the pellet column, etc.

### 3.4.2.3 Assembly

The skeleton is first partially assembled with the inconel bottom end piece, the zircaloy guide tubes (for PWR) and the zircaloy spacer grids. The rods are pulled into place through the grids by a special machine, and the top end piece is fitted. Complete fuel assemblies are then checked for dimensions and rod spacing, and stored in vertical position, waiting for transportation to the reactor site. Figure 3.19 shows a typical PWR fuel assembly.

### 3.4.2.4 MOX fuel

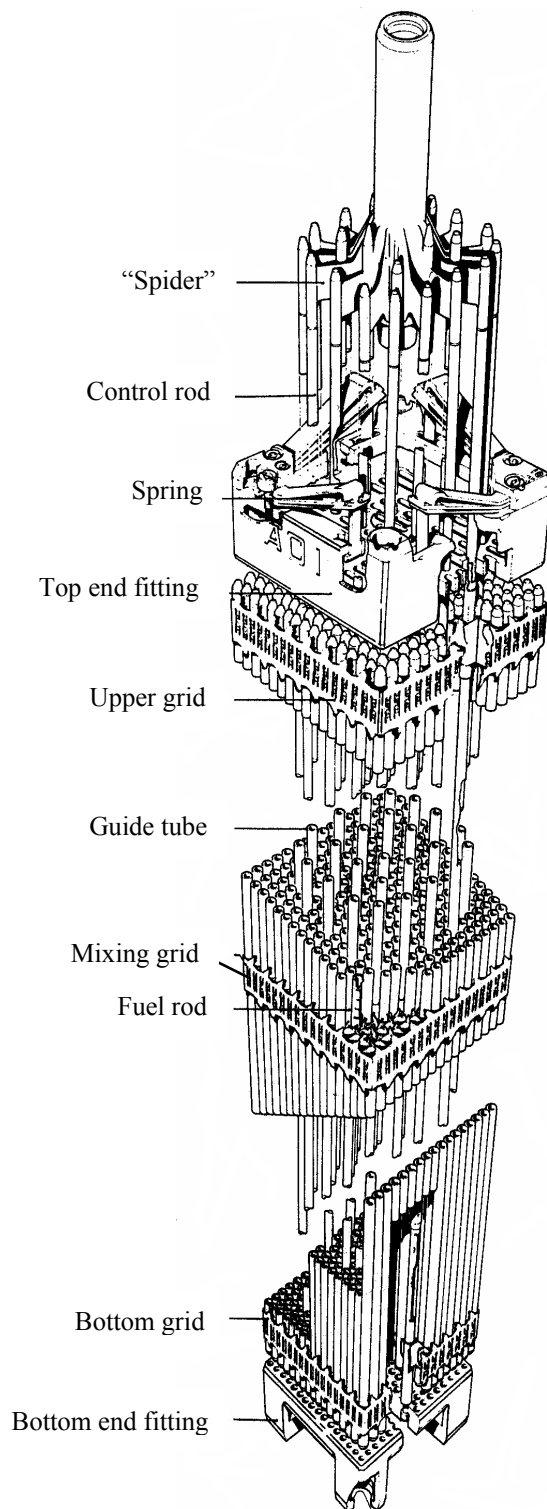
Recycling of plutonium in LWRs is performed by loading in the core a given percentage of “MOX” fuel assemblies along with the standard LEU fuel assemblies. MOX fuel has a structure identical to standard fuel: the only difference is that pellets are made from a mixture of depleted uranium oxide and plutonium oxide (U, Pu)O<sub>2</sub>. To protect the operators from the radiotoxicity of plutonium, MOX fabrication must be performed remotely, inside glove boxes.

Because of very large resonances in the neutron-absorption cross sections of the plutonium isotopes at low energy (0.3 and 1 eV, respectively), the neutron spectrum is “harder” in MOX/water media than in uranium/water. The concentration of plutonium must therefore be lowered at the periphery of a MOX assembly to adapt the neutron flux with LEU neighbors and thus avoid power heterogeneity. The average concentration Pu/(U + Pu) in a MOX assembly is roughly the double of the <sup>235</sup>U enrichment of a LEU assembly in the same batch.

The basic ingredients are UO<sub>2</sub> and PuO<sub>2</sub>, the latter coming from the reprocessing plant after oxalic precipitation of the plutonium nitrate and calcination of the oxalate. Simple mixing of the two powders would not provide enough homogeneity: this is ensured by simultaneous milling at the head-end of the process. After milling, the powder does not flow easily and must be granulated. MELOX, the only industrial-size MOX fabrication plant, located in Marcoule (France) and operated by COGEMA uses the MIMAS (Micronised MASTer blend) process shown in Fig. 3.20, where a first master mixture of rather high plutonium concentration is later adjusted by mixing additional UO<sub>2</sub>.

A typical recycle scheme would have reloads with 30 % MOX assemblies, but it is planned to realize 100 % MOX reloads in the future Ohma Japanese ABWR plant. The savings in enriched uranium more or less balance the increase in fabrication costs due to the remote operation and maintenance of the plant.

With the end of the Cold War, as was already pointed out, significant inventories of weapon-grade fissile materials have been released. To “civilize” weapon plutonium, recycling as MOX is the preferred way, though some of it might be disposed of by mixing ceramic plutonium “pucks” with vitrified high-level waste.



**Fig. 3.19.** 17 × 17 PWR fuel assembly AFA-2G.

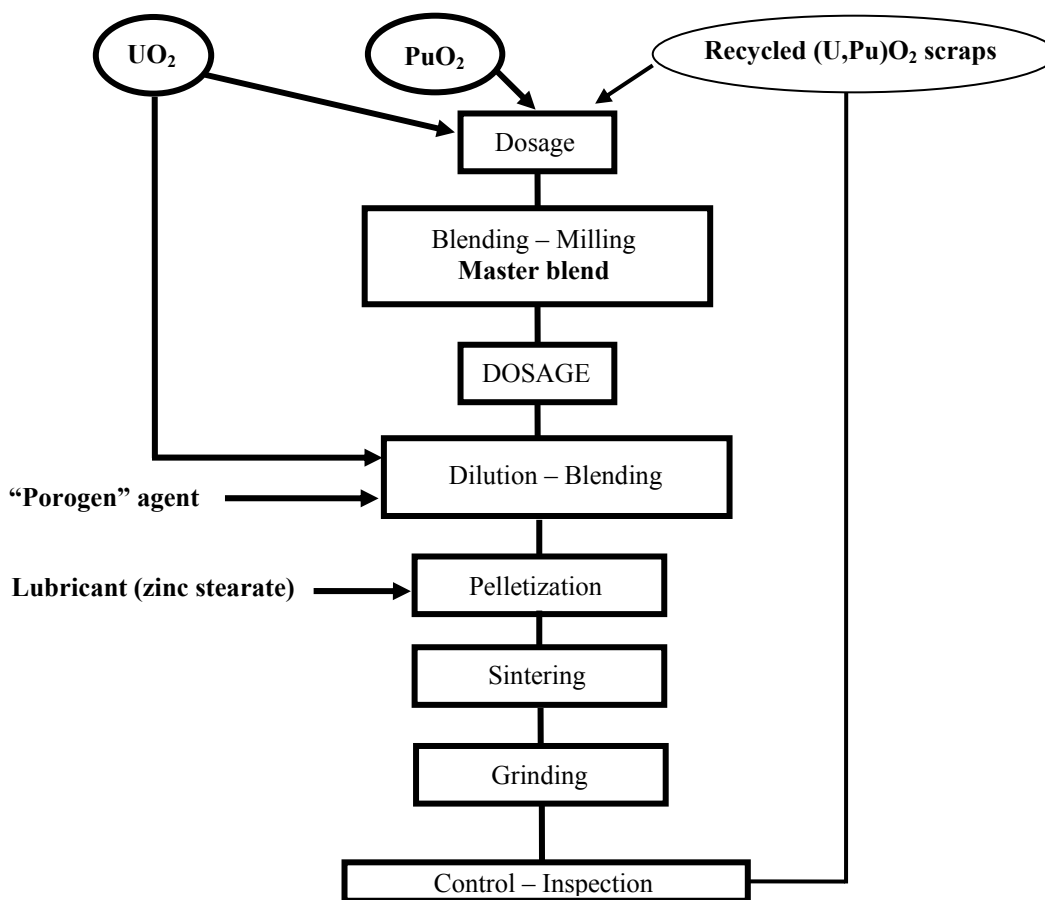


Fig. 3.20. MIMAS flow chart.

### 3.4.3 LWR fuel fabrication capacity and market

For many years, the LWR fuel fabrication industry has been carrying substantial excess capacity, due to an initial overestimation of the nuclear development throughout the world, but also due to the significant progresses achieved in fuel burn-up (the number of FA to be fabricated for a given power production is inversely proportional to the burn-up). In 2000, it is estimated that, on a worldwide basis, the average utilization factor of the fabrication plants is around 67 %, slightly higher for the PWR than for the BWR. It remains to be seen how the current trend of mergers and acquisitions will affect this situation.

Table 3.8 describes the LWR fuel vendors operating on the Western and Asian markets, as well as their production capacity, in the year 1998 (before the current mergers). After the mergers, only three groups are left: Framatome-Siemens, BNFL-Westinghouse-ABB and GE-Hitachi-Toshiba (plus Minatom-TENEX for the WWR). MOX fuel is mostly manufactured by COGEMA, in association with Belgonucléaire and BNFL [99Oec1].

**Table 3.8.** LWR fuel vendor capacities, given in tons of uranium per year.

Vendor	PWR	BWR
Europe		
Fragema/FBFC	1300	0
Siemens	500	150
ENUSA	200	100
ABB Atom	100	250
United States		
WELCO	1200	0
GNF (GE-Hitachi-Toshiba)	0	1100
SPC	400	450
FCF	400	0
ABB-CE	400	0
Total	4500	2050

### 3.4.4 Other fuel

#### 3.4.4.1 CANDU

As shown in Table 3.7, CANDU fuel bundles have the same basic components from the same basic materials as LWR fuel assemblies, though they use natural uranium oxide. The fuel bundles, loaded horizontally in the force tubes, are much shorter, and the pellets are thicker.

#### 3.4.4.2 FBR

When a neutron interacts with a heavy nucleus, it can either fission it, or be captured in a number of different reactions. Very schematically, when the energy of the neutron is higher (“fast” neutron, rather than “thermal” or “slow”), the total probability of interaction is smaller, but the relative probability of fission is higher. In addition, in the fission process,  $^{239}\text{Pu}$  emits 2.9 neutrons on the average, versus 2.5 for  $^{235}\text{U}$ . This explains why plutonium-fueled fast-neutron reactors have a better neutron economy than LEU-fueled thermal reactors like LWRs. As a consequence, with a proper core design, fast-neutron reactors can breed *more*  $^{239}\text{Pu}$  from  $^{238}\text{U}$  than they burn plutonium: this is called breeding, and those reactors are called breeders (FBR). Breeding allows, with a number of successive recycles, to progressively extract almost all the energy content of uranium, versus less than 1 % in LWR. On the other hand, breeders are expensive and will only become competitive when uranium prices are far higher than today. As the total probability of interaction is smaller, the fissile inventory in the core must be larger.

In order to keep the neutron fast, the coolant in the core must not slow down the neutrons exiting from the fuel: it cannot be water (ordinary or heavy), it can be a gas or a liquid metal. Only liquid sodium has been used to a significant degree in “liquid-metal fast breeders” (LMFBR), like BR2 in the USA, Phénix and Superphénix in France, PFR in the UK, BN 600 in Russia and Monju in Japan.

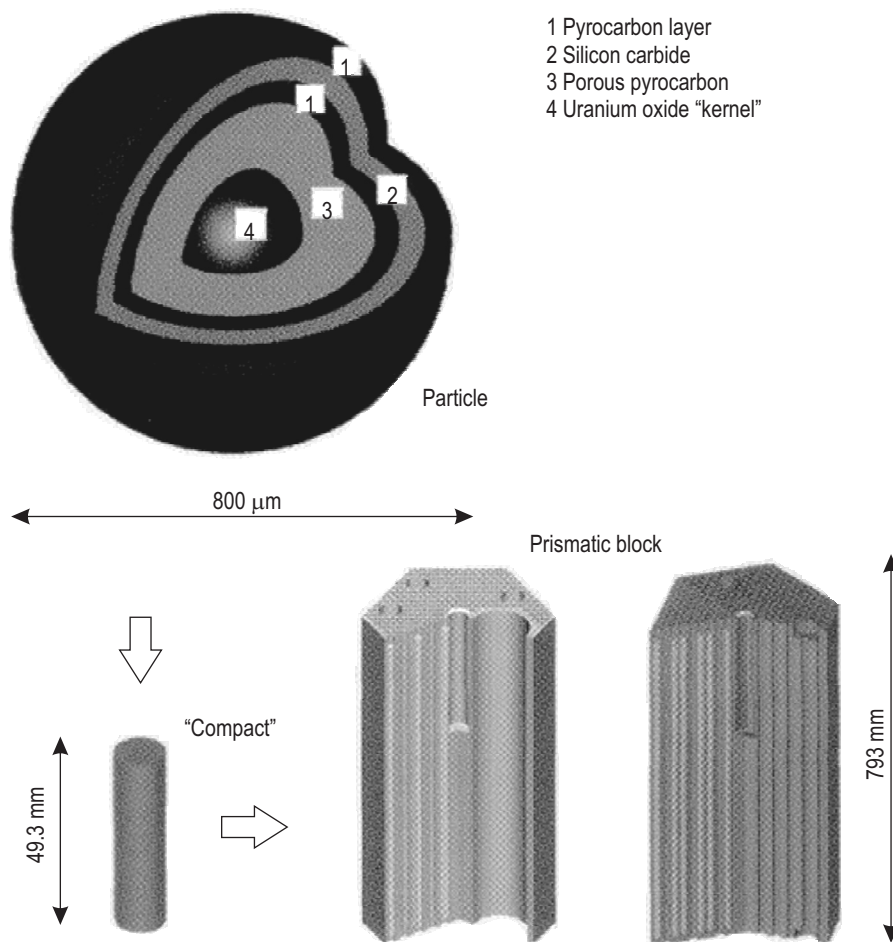
The basic LMFBR fuel is a MOX with much higher plutonium concentration (20 %). If one wants to breed, the core itself is surrounded by a “blanket” of pure  $\text{UO}_2$  fuel. In a LMFBR neutron spectrum, captures in the cladding do not matter much, but the material must be compatible with high-temperature molten sodium and resist to the irradiation by high fluxes of fast neutrons: the choice is austenitic stainless steel. The pellet fabrication process is slightly different from LWR MOX, in that the pellets are smaller (Table 3.7), and there is no “mother mixture” and no need for grinding.

### 3.4.4.3 HTR

High temperature reactors (HTR), first developed during the 1970s and 1980s in Germany and the USA, may be doing a comeback based on their high thermal efficiency and their very high degree of “intrinsic” safety.<sup>9</sup> These characteristics derive from the use of helium gas as coolant, graphite as moderator, and, above all, a very unusual type of fuel.

The equivalent of a “fuel rod” in other reactors is a tiny ceramic particle of uranium (or plutonium, or thorium) oxide or carbide, the “kernel”, coated with a number of layers, acting together like a cladding. The diameter of a fully coated fuel particle is of the order of 1 mm. There would be around 10 billion of such particles in the core of a large reactor!

Those particles are “assembled” in a graphitized matrix, either to form spherical pebbles of 6 cm diameter directly loaded in a heap inside the core cavity of a *pebble bed* reactor, or to form cylindrical “compacts” piled up in columns inside holes drilled in graphite prismatic blocks which act as “fuel assemblies” (see Fig. 3.21). The whole core is therefore entirely refractory: core meltdown is excluded, and it has been shown experimentally that the coating of the particles retains its integrity up to 1600 °C.



**Fig. 3.21.** HTR fuel element.

<sup>9</sup>) Very high temperature reactors (VHTR) are considered as a promising future source of hydrogen.

Fertile or fissile kernels are manufactured by powder aggregation or by a sol-gel process, and the layers are deposited around the kernel by pyrolytic cracking of gases in a fluidized-bed reactor. From the inside to the outside one finds:

- a buffer layer of porous carbon to prevent interaction between the hot kernel and the outer layers;
- a first layer of dense pyrocarbon;
- a layer of silicon carbide which stops the diffusion of fission products (mainly caesium and strontium) outside the coated particle;
- a second layer of dense pyrocarbon. Together, the two pyrocarbon layers act as a pressure vessel against the gases released during the fission.

### 3.5 In-reactor PWR fuel behavior

While in the reactor, the fuel undergoes series of transformations interacting with one another, inside the pellets, in the cladding material and at the interface [99Coc]. The net result of these numerous transformations determines the useful life of a fuel assembly and its “burn-up”, which is the quantity of energy the fuel can produce before being considered as “spent”.

The first series concerns the neutron physics, the reactivity of the fuel:

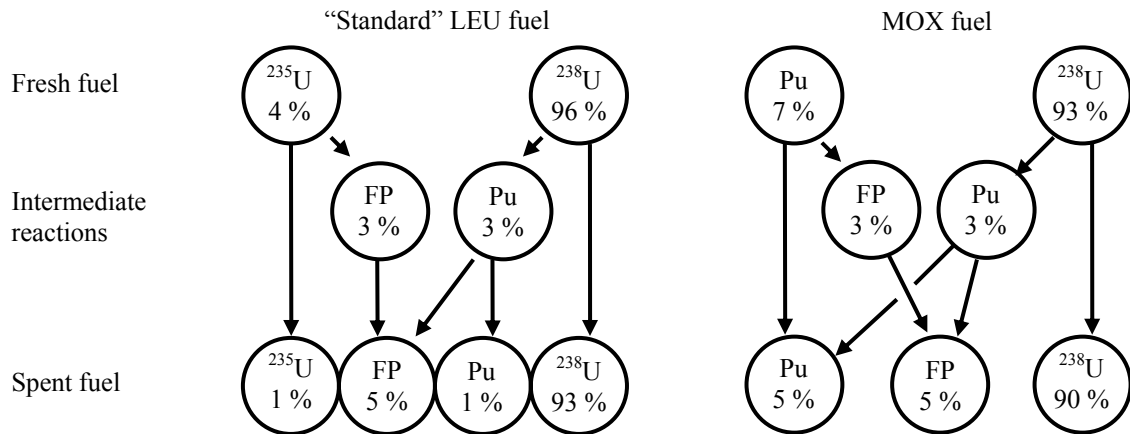
- As irradiation proceeds, the fissile nuclei are progressively consumed, while some of the fertile nuclei are transmuted into fissile nuclei. The balance between these two transformations is usually negative – with the exception of “breeder” reactors – and the fuel gets depleted in fissile nuclei (Fig. 3.22).
- In parallel, fission generates fission products. Some of those fission products, or their daughter nuclei, capture neutrons efficiently, thus “poisoning” the fuel by impairing the fission reaction.
- Consequently, the reactivity of the fuel decreases throughout its lifetime, until it is no longer capable of sustaining the chain reaction<sup>10</sup>. The “spent” fuel must then be unloaded from the core.

The higher the burn-up to be reached, the higher the initial concentration in fissile nuclei required, i.e. the higher the initial enrichment of LEU fuel or the higher the initial plutonium/uranium ratio in MOX fuel. Conversely, the higher the burn-up, the fewer fuel assemblies to manufacture and to reprocess for a given energy output. The optimum burn-up is therefore the result of an economic compromise between the costs of enriched uranium supply, fuel fabrication and reprocessing. But this is not enough: one must demonstrate that, under normal and accidental conditions, the fuel retains its integrity even at its highest burn-up. This is where the other transformations mentioned above play a crucial role.

The structural integrity of the pellet itself is affected in many ways by the irradiation:

- Most of the energy released by the fission phenomenon appears as kinetic energy communicated to the two fission fragments: their slowing down which produces heat inside the fuel produces also a lot of point defects in the fuel pellet crystallites.
- As a result, the fuel pellets swell, fragmentize, and come in close contact with the cladding.
- Many of the fission products have chemical properties different from those of uranium and plutonium, and alter the stoichiometry of the uranium and plutonium oxides.
- Some of the fission products are gases which either contribute to pellet swelling or permeate outside and increase the internal pressure inside the cladding.
- At high burn-ups, transmuted plutonium accumulates at the outer “rim” of the pellet, transforming in effect a thin annulus of the pellet into MOX fuel, with a possible loss of cohesion at the interface.

<sup>10)</sup> To compensate for this “reactivity swing” in the fuel assemblies, fresh fuel must be – deliberately – poisoned, and those control poisons are progressively removed, or burned in situ, to keep the average reactivity of the whole core constant throughout a cycle of production. As control poisons one uses cadmium alloy rods inserted inside the fuel element, and boric acid diluted in the primary coolant water. In addition, to reach very high burn-ups, “burnable” poisons, gadolinium or erbium compounds, are incorporated in the fuel pellets themselves.



**Fig. 3.22.** Schematic representation of physical processes in PWR fuel assemblies (45 GWd/t (HM)).

Even more important, the cladding, which constitutes the first safety barrier containing the radioactive elements produced in the fuel, must retain its leaktightness. During its life in the reactor core, the cladding material experiences many "aggressions":

- Corrosion is the first aggression. Even in the absence of irradiation, zirconium reacts actively with oxygen and reduces water to form an oxide, zirconia,  $\text{ZrO}_2$ . At low temperature, a thin coating of an impermeable zirconia layer protects the alloys from further oxidation (not unlike aluminium), but at reactor temperatures, above 300 °C, the corrosion goes on, together with a secondary hydride formation by the hydrogen released in the water reduction reaction. Under irradiation, this phenomenon is accelerated, and the corrosion rate becomes a limiting factor of lifetime (the zirconia layer is not allowed to exceed 100 micron). Some alloying elements drastically decrease the corrosion rate of zirconium, but their choice remains rather empirical.
- The difference of pressure between the inside of the fuel rod (initially pressurized with helium) and the water of the primary circuit induces a creep which closes the internal gap between pellet and cladding, sometimes during the second irradiation cycle<sup>11</sup>. From then on, deformations of the pellet, notably during rapid variations of power – so-called ramps – interact with the cladding and threaten its integrity, a phenomenon known as pellet-cladding interaction (PCI).
- Neutron irradiation itself induces hardening and anisotropic growth of the zirconium. In addition, fission-produced iodine may attack the cladding from the inside and induce stress-corrosion, etc. One could add that alteration of the mechanical properties under irradiation affects also spacer grids, especially springs, and guide tubes of the fuel assemblies, thereby also limiting the fuel lifetime.

All in all, the proper choice of the cladding alloy and its mechanical and thermal treatments is of key importance in the competition between nuclear fuel vendors for optimum burn-up, optimum performance for their utility customers.

<sup>11</sup>) To optimize neutron economy, at each reload, only part of the core is replaced by fresh fuel. The period between two reloads is a "cycle". A typical PWR fuel assembly stays in the core during 4 one-year cycles.



## 3.6 Spent-fuel management

After being unloaded from the reactor core, fuel assemblies spend several years to several decades stored under water in pools, either at the reactor site or in centralized storage pools, usually located in the reprocessing plants. After a few years, when the decay heat has decreased, fuel assemblies can also be stored for decades in dry-storage devices, often similar to the heavily shielded casks used for transportation. Wet or dry, these storage devices are only used ad interim: sooner or later, a choice must be made as to their final fate.

### 3.6.1 Disposal or reprocessing and recycle

The fuel elements of early gas-cooled reactors, after irradiation, could only stay in the spent-fuel pools for a limited period of time before the cladding, designed for a CO<sub>2</sub> environment, began to deteriorate under water. Interim storage had to be short, with reprocessing of the spent fuel as the only logical and practical issue. In addition, concerns about medium term uranium supply provided a strong incentive to recover the un-burnt fissile materials. This is why France and the UK took the lead in civilian reprocessing during the 70s, as well as in the development of the fast-neutron breeder, which makes the best use of the recovered plutonium and can burn the huge resources of depleted uranium.

LWR fuel, designed for a high-temperature water environment, and despite the weakening of its structure under irradiation, can stay undamaged for decades in the spent-fuel pools. Interim storage is a matter of capacity, costs and regulations: it is not a technical problem. Furthermore, with the present forecasts of rather modest nuclear power development, uranium supply does not appear a short-term concern any longer, and reprocessing is just one of the options for spent-fuel management.

For countries embarking upon a nuclear program, interim storage makes sense until the amount of spent fuel forces to face the choice between reprocessing-recycle, the closed-cycle option, and direct disposal, the open-cycle option. Countries with significant on-going programs are split: among the three leading nuclear programs, France and Japan champion the recycle option, while the United States advocates the direct disposal.

Economics does not seem to be a discriminating element in the decision: MOX recycle in LWR balances more or less the higher fabrication costs against uranium and SWU savings. A recent OECD/NEA study for OSPAR [00Oec] shows that the environmental impacts of both open and closed fuel cycles are very similar (and very minute): this is not a determining factor either. There is a significant volume reduction between encapsulated spent fuels and conditioned HLW from reprocessing, but it is difficult to assess how much that will affect the final disposal costs, which may be more sensitive to the heat load than to the volume of the packages.

Non-proliferation was the official motive which led to the “indefinite deferral” of reprocessing and recycle decided by the US President in 1976. This issue was hotly debated during the two-year INFCE, the International Nuclear Fuel Cycle Evaluation, which followed the US decision, and the international community did not endorse the US view. Commercial reprocessing plants in La Hague and Sellafield are under safeguards and scrutiny not only by the IAEA, but also by EURATOM.

Any interim storage must end with recovery and handling of the package. If spent LWR fuel can be safely interim-stored for decades, it remains a “used” object, the long term stability of which is much more difficult to assess than that of new dedicated waste packages.

The deepest reason for choosing one way or the other is probably the *sustainability* issue. For those who consider nuclear power a short parenthesis in the history of energy, the simplest solution is direct disposal of what will be a limited amount of spent fuel. For those who believe that nuclear power is a sustainable option, here to stay for a long period of time, reprocessing is the best way to keep all options open.

### 3.6.2 Reprocessing technology

Whatever the technology used, the basis of reprocessing is always the same: get rid of the inert structures of the fuel assembly, and separate by a chemical process the materials which have a value, to be used, recycled or stored, from the wastes, which are to be conditioned and disposed of [00Bar].

Today, only the fissile materials are recovered, residual uranium and converted plutonium, but in the past, caesium was recovered to make sealed radiation sources and in the future it is conceivable that rare elements may become of interest (palladium for instance).

#### 3.6.2.1 PUREX

The only industrial process in use for LWR fuel is the so-called PUREX process, which stands for **Pluto**nium **UR**anium **EX**traction. After chopping the fuel assembly and dissolving the fuel pellets in hot concentrated nitric acid, a series of redox<sup>12</sup> reactions allows for separating the nitric solution, by solvent extraction, into three separate streams: pure (99.9 %) uranium, pure (99.9 %) plutonium and all the remaining elements together, fission products and actinides (see Sect. 3.6.5). Around this core process, many auxiliary processes are used for off-gas treatment, clarification, acid and solvent recycling, etc (Fig. 3.23).

PWR and BWR fuel assemblies are transported in casks, by railways, trucks or specialized boats, to the reprocessing plant. These casks have a heavy shielding against  $\gamma$  and neutron rays from the spent fuel, radiator fins to evacuate the residual heat, and they are leaktight and extremely sturdy: they are characterized and tested to survive crashes, drops and fires of extreme severity. To give an order of magnitude, a typical PWR transport cask contains 12 assemblies with a combined weight of approximately six tons, but the cask itself weighs 120 tons.

In a dedicated facility, the casks are opened and the fuel elements are unloaded one by one, checked<sup>13</sup>, cooled, and loaded in baskets, while the empty cask is closed, checked for contamination and sent back for a new shipment.

The baskets are transferred to the next facility and stored under water in stainless steel lined seism-resistant pools, where the water is purified, cooled and continuously monitored. The fuel assemblies remain a few years in the pool (under continuous monitoring by the IAEA, for safeguard purposes).

When the fuel owner asks for it, the fuel assemblies are removed from the pool, checked, and sent to the head-end facility. There, they are chopped by a hydraulic shearing machine which removes the top and bottom end fittings and cuts the fuel rods into pieces a few centimeters long. The end fittings are rinsed in nitric acid and stored for conditioning.

The rod segments are dropped into a dissolver, where hot concentrated nitric acid dissolves the fuel pellets, leaving the cladding “hulls” intact. At the end of the dissolution (several hours), all the uranium, plutonium and minor actinides inventory is dissolved as nitrates  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{PuO}_2(\text{NO}_3)_2$ , etc, together with about 80 % of the fission products. The remaining 20 % are either in the off-gases (krypton, xenon and iodine) or in insoluble “fines” (zirconium, molybdenum, technetium, ruthenium and the platinum family).

The off-gases are treated, notably to trap any  $\text{UO}_2$  dust and to remove from the stream iodine and nitrous oxides. The nitric solution is “clarified”, the insoluble fines are sent to the vitrification, and the clarified solution is transferred to the separation unit.

The principle of the solvent extraction in PUREX is to force contact between an aqueous phase containing all the various chemical species and a non-miscible organic phase (a hydrocarbon containing the solvent TBP, tri-n-butyl phosphate), and to extract in the organic phase the species of interest. The same basic process is used three times in a row:

- (1) to co-extract U and Pu from the clarified solution: the fission products stay in the aqueous phase;
- (2) to partition Pu from U: plutonium is reduced from  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  by uranium IV. Plutonium III is “de-extracted” by the aqueous phase while uranium remains in the organic phase, from which it is later “de-extracted” by adjusting the pH of the aqueous phase;
- (3) to purify the plutonium before conversion to  $\text{PuO}_2$ .

<sup>12</sup>) A series of reductions and oxidations to selectively adjust the valence of the elements to be separated later.

<sup>13</sup>) Any fuel assembly found leaky would be put in a leak-proof “bottle”, before going to the storage pool.

The contact between the two non-miscible phases is realized in chemical reactors, mixer-settlers, pulsed columns or centrifuge extractors. What is specific in these otherwise standard chemical operations is the presence of high fluxes of radiation which forces to carry them out remotely behind very thick concrete walls, and which deteriorate the solvent.

Reprocessed uranium is still slightly enriched – depending upon the actual burn-up reached by the fuel. Separated uranium nitrate is stored before shipment for re-enrichment. Plutonium is converted to oxide powder, and stored before shipment to a MOX fabrication plant.

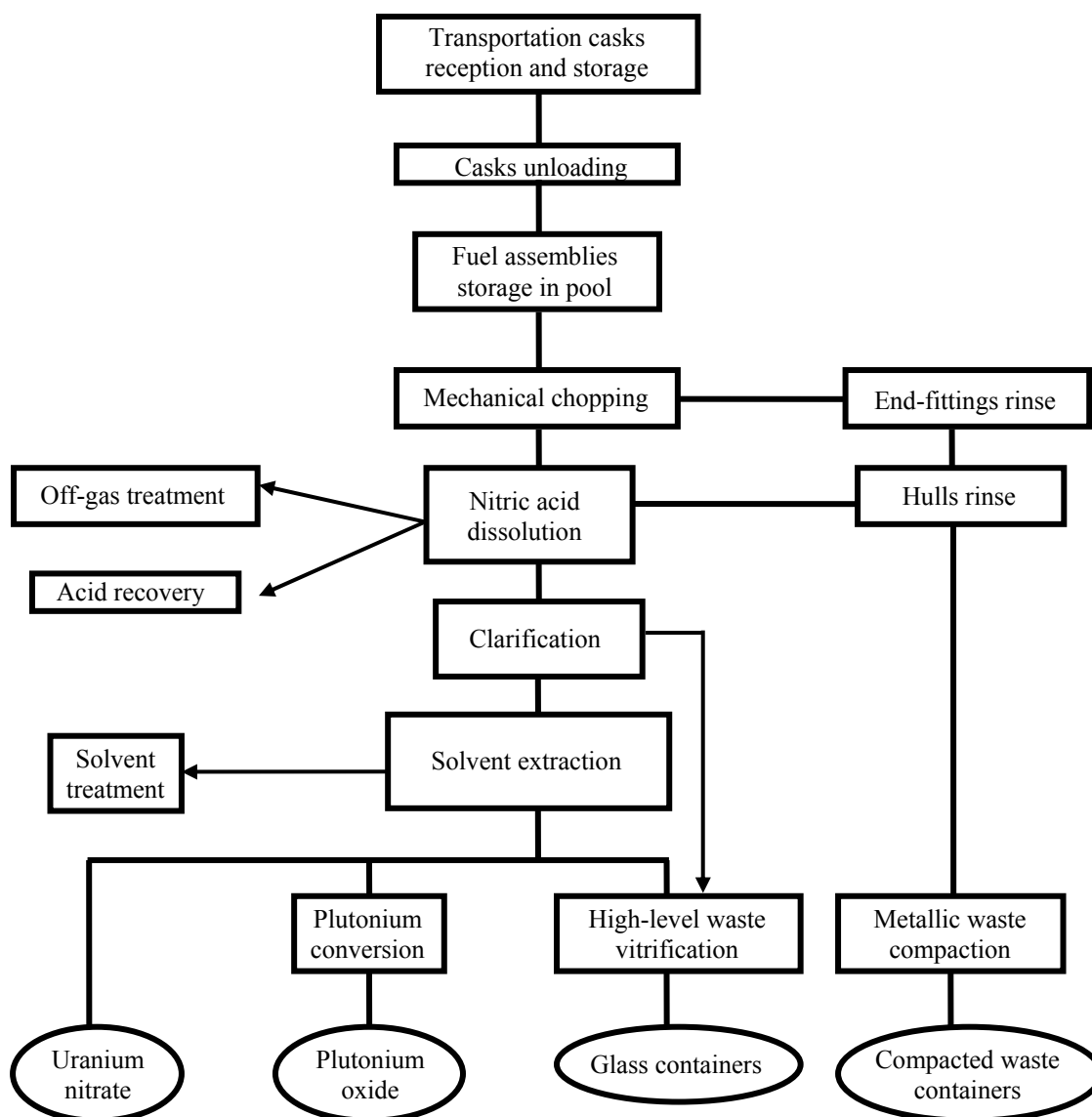


Fig. 3.23. Simplified flow chart of a modern reprocessing plant for LWR fuel.

### 3.6.2.2 Waste management

Beside retrieving fissile materials for recycling, and removing plutonium from the waste stream bound for disposal at a later time, reprocessing provides specific and adequate conditioning for the actual ultimate high-level wastes contained in the spent fuel [00Doq].

Modern reprocessing plants, like La Hague UP3, produce only two standardized HLW packages: glass blocks incorporating in the matrix the fission products as well as the residues from the process itself, and compacted metallic wastes (end fittings, hulls and technological wastes). Both types of wastes are contained in stainless steel canisters of identical geometry.

R&D performed in the 50s by the CEA (French Atomic Energy Commission) led to the selection of borosilicate glass as the most suitable matrix to confine the wastes issued from spent-fuel reprocessing. Glass is the best answer to a combination of three requirements: accept in the matrix a very wide variety of chemical elements, retain its integrity under severe irradiation and resist to water leaching. Modern vitrification facilities (R7 and T7 in La Hague) derive from the COGEMA AVM facility which started operation in 1978, in Marcoule (Fig. 3.24).

The concentrated nitric acid solution containing the fission products, with some additive to adjust its composition, is fed to a rotary “calciner” where it is heated to 600 °C. After evaporation, the calcine is heated under air and most of the nitrates are transformed into oxides.

At the outlet of the calciner, the calcine falls directly into a melter, along with glass frit, to be vitrified. The melter, heated by induction to 1150 °C, is fed continuously and batch poured. Each canister is filled with two batches of 200 kg of glass. A “fresh” canister may contain up to 760 000 Ci of radioactive wastes, mostly  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ . After cooling, a lid is welded to the canister, which is then decontaminated, controlled and sent to interim dry storage. After a few years of forced cooling, glass canisters are interim-stored under natural air circulation.

As indicated above, empty hulls, end fittings and technological wastes are compacted under high pressure and put in similar canisters. Table 3.9 illustrates the progress achieved in waste production during reprocessing operations.

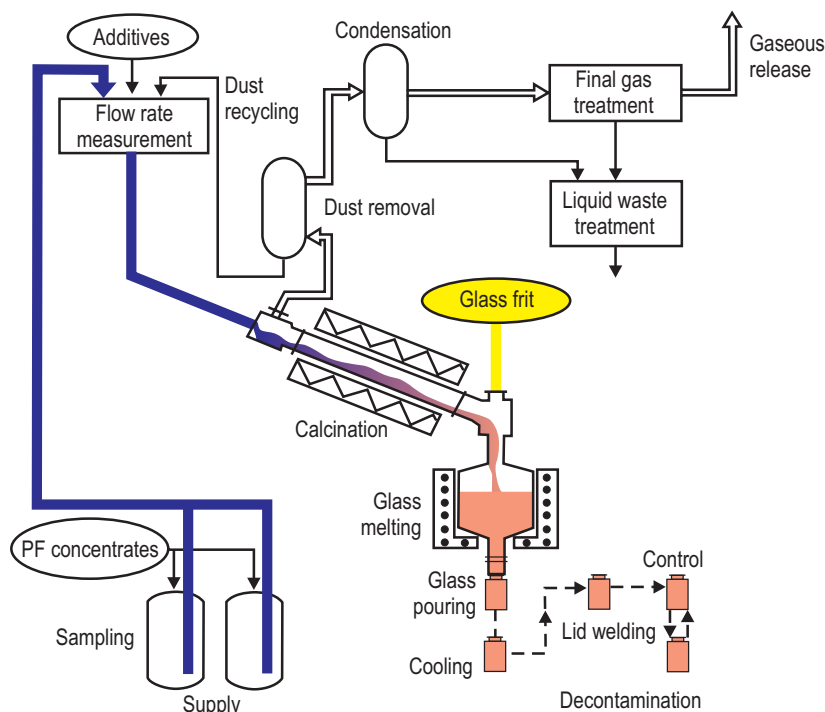


Fig. 3.24. The AVM-R7 vitrification process.

**Table 3.9.** Volume of HLW and MLW, given in units of  $\text{dm}^3$  per ton of spent fuel reprocessed.

Residues	Reprocessing: design (1980s)	Reprocessing: actual (2000)	Direct disposal
Bitumen	630	0	
Technological waste	1700	} < 350	
Hulls and end-fittings	600		
Glass	130	115	
Encapsulated spent fuel			$\approx 2000$
Total	3060	< 465	$\approx 2000$

### 3.6.2.3 Other processes

Today, all industrial plants in operation or under construction are based on the PUREX process. This process evolved from earlier aqueous (or hydro-metallurgical) processes developed in the USA and in the UK (REDOX, BUTEX), and further modifications of PUREX are under exploratory development for more sophisticated nuclides separation (see Sect. 3.6.5).

However, other non-aqueous processes have been developed or are under study: they are called “dry” or “pyrochemical” processes [00Cea]. Dry processes are usually more compact and are not sensitive to the decomposition of the reactants by the radiation emitted by the fission products (“radiolysis”). On the other hand, separation factors are usually mediocre to say the least. This poor decontamination is now considered to be a plus by those who fear proliferation and diversion of pure fissile materials – though reactor operators are unlikely to be enthused by the prospect of having to handle very radioactive “fresh” recycled fuel...

As an example of pyrochemical process, a method developed at Argonne National Laboratory uses electro-refining to reprocess fuel from the EBR 2 LMFBF. Dismantled spent-fuel segments are placed in a stainless steel basket inside an electrolyser filled with a molten cadmium chloride bath atop a layer of liquid cadmium, at  $\approx 500^\circ\text{C}$ . The spent fuel is dissolved in the molten salt, and the actinides are selectively deposited on the cathodes by electrolysis.

If today pyrochemical reprocessing does not seem very attractive, apart from a non-proliferation point of view, it might, in the future, become necessary to process very high burn-up fuel or very radioactive transmutation targets, with a high potential for hydrolysis.

### 3.6.3 Reprocessing capacities and market

There are very few industrial LWR reprocessing plants in the world:

- COGEMA operates in La Hague (France) two plants with a total capacity of 1700 tons of heavy metal per year (t (HM)/a). One plant is dedicated to French fuel from Electricité de France PWR plants, the other reprocesses fuel from Japan, Germany, Belgium, Switzerland and the Netherlands.
- BNFL operates the 800 t (HM)/a THORP plant in Sellafield (UK), for foreign customers.
- JNFL is building a 800 t (HM)/a plant in Rokkasho (Japan), to be commissioned around 2005. A small plant is also operated by JNC in Tokai (Japan).

(Russia performs reprocessing in ex-military plants, but does not yet commercialize reprocessing services outside the Federation.)

All contracts are for reprocessing services only: fissile materials (eventually as MOX fuel) and properly conditioned reprocessed wastes are returned to the spent-fuel owner. Over the last decade, both La Hague plants have operated very successfully, the volume of liquid and gaseous effluents has drastically decreased, and the radiological dosis, both individual and collective, to the operators is now extremely low.

### 3.6.4 Final repository

The disposal of radioactive waste is not an issue restricted to the wastes issued from the nuclear fuel cycle, nor is it restricted to the field of nuclear power: radiation sources used in the industry, radio-elements used in medicine, tracers used in many sectors of R&D, notably biotechnology, become radioactive wastes and must be disposed of after use. And, of course, weapon activities did produce a huge amount of radioactive wastes, especially in Russia and the United States.

In France, a complete nation-wide inventory of radioactive wastes is kept up to date by ANDRA, the agency in charge of waste management, using a classification somewhat more sophisticated than the old distinction based solely on activity (Table 3.10).

**Table 3.10.** Classification of radioactive wastes, according to their ultimate disposal destination [00Aut].

	Short half-life (main nuclides < 30 a)	Long half-life (main nuclides > 30 a)
Very low level of activity (VLLW)	Wastes from dismantling	Mine residues
Low level of activity (LLW)	Stored in existing surface disposal site	Radium bearing wastes
Medium level of activity (MLW)		Compacted hulls,...
High level of activity (HLW)	Glass canisters or encapsulated fuel	

Specific to the fuel cycle are the mine residues (very low activity and huge volumes) and the long-lived MLW and HLW, which constitute modest volumes but concentrate the bulk of the radioactivity. Over the world, only short-lived LLW and MLW, properly conditioned, are routinely disposed of in licensed surface disposal sites, under several layers of cover. Recently, the USA have opened a site in an underground salt bed, the WIPP in Carlsbad (NM), to dispose of long-lived medium-activity wastes issued from defence activities.

For encapsulated spent fuels or (civilian) reprocessing wastes, there is no licensed disposal method as of today. Alternative methods have been considered: shooting the wastes into the sun or outside the solar system, burying wastes into deep ocean bed sediments far from the tectonically active zones, or disposal in “subduction” zones at the limit between tectonic plates. None of the above seems practicable or acceptable today. Most of the developments are dedicated to burial in deep land strata (salt, clay, shales or granite) which have proven to be stable over extended periods of time. It is expected that suitably encapsulated waste emplaced deep into a carefully chosen geological formation can be effectively isolated “forever” from the biosphere – “forever” meaning: until its radio-toxicity has decreased to negligible levels. Such underground repositories exist for hazardous chemical wastes.

Given that a repository is constructed in such a stable rock formation, and sealed off<sup>14</sup>, the only natural process through which radionuclides can reach the surface is dissolution of the waste, and transport by ground water. The design and safety analysis of a repository project copes with the ground-water transport issue with a number of choices pertaining to the waste matrix, the overpack material, the engineered barriers, etc.

The Swedish, for instance, rely on high-integrity pure copper coffins to encapsulate un-reprocessed spent fuel, because copper is impervious to corrosion by ground water in the granite environment they consider for their project.

<sup>14</sup>) Today, the question of *when* to seal off a repository is pretty much open, as it relates to philosophical options:

The first option could be formulated like this: “Let us not leave to future generations those wastes of which we are responsible”. To this philosophy, ultimate disposal is the answer.

The second statement could be: “Let us leave to future generations the possibility of managing those wastes in a better way than we can imagine today”. To this philosophy, long-term interim storage is the answer.

Both points of view have their values, but they do not induce the same technical solution. Nowadays there appears to be a convergence towards a concept of “somewhat reversible” disposal...

Many other designs rely on a multiple barrier approach: ground water would take time to corrode the containers, then to leach the radionuclides out of the matrix (glass, for instance, in addition to its good resistance to corrosion, develops, when attacked by water, a “gel” outside layer which considerably delays further leaching), bentonite clay in the engineered barrier slows down ground water, allowing it to reach saturation which considerably reduces its corrosive power, bentonite traps quite a number of heavy elements, and so on. And for radioactive nuclides, delay means decay!

Each repository project is a unique case to be evaluated for its own merits, based on in-situ geological characterization, but the difficulty is that this evaluation must cover millennia. A huge effort of characterization in representative underground laboratories is being carried out in quite a number of countries, and results are exchanged and made available throughout the world: the wealth of data is considerable and gives confidence in the results of the modeling and simulation “round robin”.

Some of the issues to be covered are rather tricky: for instance, after a few centuries, the bulk of the radio-toxicity in a repository will be concentrated in the heavy elements (actinides), but those are not very mobile in ground water as was amply demonstrated by the Oklo reactors, over almost 2 billion years. As a result, any modeling shows that the first elements to eventually reach the surface, after many thousand years, would be the long-lived fission products, which are not very radio-toxic...

Even though many projects are under development or demonstration, even though monitored interim storage of conditioned HLW can be demonstrated safe over decades and decades, even though volume is not an issue because the wastes are so concentrated, as long as no repository will be in operation, the feeling will be strong in the public that there is no technical solution to the management of radioactive wastes, and that, therefore, nuclear power is not sustainable. We must close the “missing link” in the fuel cycle.

### 3.6.5 Partitioning and transmutation

There is a wide consensus within the scientific and technical community that geological disposal of long-lived radioactive wastes, in one form or another, is a practical, sound and safe solution to protect mankind and its environment for the foreseeable future. However, this conviction is not shared to the same degree by the public at large: difficulties encountered in many countries in siting, construction and licensing of repositories have caused extensive delays in the development of these facilities<sup>15</sup>. But, as mentioned above, there are few alternatives.

The quantities of spent fuel or HLW are far in excess of the capability of any program for disposal in outer space or in the sun – assuming that the reliability of the launchers could become such as to make negligible the risk of accidental contamination. Sub-seabed disposal is politically incorrect, and disposal in a tectonic subduction<sup>16</sup> area appears hardly predictable.

This is why research programs on partitioning and transmutation, P&T, are presently carried out in a number of countries [99Oec2]. The key word is “long-lived”. From the hundreds of nuclides produced during the fission and of their daughter products, very few have half-lives exceeding a few decades, which means that after four or five centuries, they will have decayed into stable, non-radioactive isotopes. After such a period, only remain active the actinides (from uranium and above) and a handful of long-lived fission products (LLFP) like <sup>99</sup>Tc, <sup>129</sup>I or <sup>135</sup>Cs.

During the reprocessing of spent fuel, as we have seen, some 99.9 % of the “major” actinides, uranium and plutonium, are recovered for recycle, while the minor actinides (MA) neptunium, americium and curium remain with the fission products to be vitrified. The MA and their decay products would constitute the bulk of the long term “potential” radio-toxicity of the glasses in a repository.

The aim of the current P&T programs is to evaluate the feasibility of selectively separating all the long-lived nuclides from the wastes stream during the reprocessing, and to transmute them by neutron

<sup>15</sup>) In 2000, only one repository was in operation in the world, the Waste Isolation Pilot Plant, WIPP, in Carlsbad, dedicated to the disposal in a salt bed of transuranic wastes issued from the US nuclear weapons program. The first waste package was accepted some twenty years after the shaft was drilled! The Russians were also injecting liquid HLW in a deep underground sand strata at Krasnoyarsk, but this would not be licensed in the West.

<sup>16</sup>) Where one tectonic plate dives under another.

irradiation into a mixture of stable and short-lived nuclides. Ideally, if the separation and transmutation efficiencies were 100 %, one would no longer need geological disposal: surface or sub-surface repositories could be used, which would require monitoring for a few centuries only before the radioactivity decreases to insignificance (Of course, if you do not recycle plutonium, there is no point in bothering about other nuclides! P&T has no meaning in an open fuel cycle.)

For the transmutation, the irradiation could take place in “classical” power reactors, which would have to accept very active fuel, or in dedicated “actinide burners” with high fluxes of fast neutrons. These burners could be reactors or accelerator-driven subcritical systems, ADS<sup>17</sup>, such as the concept popularized by Carlo Rubbia in the 90s. Some of the nuclides could be incorporated in the fuel itself, neptunium for instance, others would have to be fabricated into specific “targets”.

The first P&T program, called OMEGA for Options Making Extra Gains from Actinides, started in Japan in 1988; P&T was also one of the R&D “axes” defined by the French law on radioactive-waste management in 1991; P&T is also part of the 1999 US DOE “road mapping”. All these programs are well documented and results are regularly exchanged during international symposia. What can be said in 2000 is the following:

- Because separation and, especially, transmutation cannot reach 100 % efficiency, P&T will not suppress the need for geological disposal of HLW, but it can reduce the quantities to be disposed of.
- Implementation of P&T, if decided, would require long lead-times and large investments in dedicated burners, extension and sophistication of the reprocessing plants, and construction of remotely operated facilities to fabricate fuel and targets. It would involve handling highly active “fresh” fuel at the reactor site.
- Partitioning methods have been successfully developed, at the laboratory scale.
- Multiple recycling of plutonium and MA is a long-term endeavor which may take decades to reach equilibrium of inventories, but it can stabilize the inventory of these nuclides in a nuclear power park.
- A possible option, either for geological disposal or for future transmutation, is the conditioning of separated long-lived nuclides in very specific matrices, even more corrosion resistant than glass<sup>18</sup>.

It should be emphasized that P&T is still a subject for R&D, whose feasibility remains to be demonstrated before a cost-benefit analysis can be carried out in terms of economics, doses to operating personnel, and potential doses reduction to repository neighbors in the very very long term.

### 3.7 Economics

The economics of electricity generation from various sources vary significantly from country to country... and according to the period the comparison was made. Nuclear energy is usually the most competitive in countries which have implemented large programmes and which do not have access to very cheap fossil resources, like France, Japan or Finland. As an example, Table 3.11 presents the results of periodic evaluations by the French government’s services of the costs of baseload power produced by nuclear, coal and natural-gas plants, if they were just to be ordered, and leveled over their entire lifetime. [97Dge]

All costs have decreased between 1990 and 1997, but especially gas. It should be emphasized that only nuclear power costs account fully for externalities [98Eur], though coal or gas take no account of their “spent fuel” management, i.e. greenhouse gases and pollutants. Following the Kyoto protocol, it is possible, but not at all certain, that some kind of “carbon tax” significantly alter the picture, tipping the scales in favor of nuclear power.

A similar Finnish study [00Ris] finds 21.5 €/MWh for baseload nuclear power, versus 24.08 for coal and 26.08 for gas.

<sup>17</sup>) ADS could allow for a high concentration of MA in the core – thus minimizing the number of burners needed for a given nuclear park – because the extraneous source of neutrons can facilitate the control of the reactivity of such cores, with a low proportion,  $\beta_{\text{eff}}$ , of delayed neutrons.

<sup>18</sup>) For instance, <sup>135</sup>Cs cannot be transmuted as long as companion <sup>137</sup>Cs has not decayed.



**Table 3.11.** Costs of baseload electric power, where  $cF_{XX}$  denotes French “centimes” in the year 19XX.

Publication date	1997	1997	1993	1990
Monetary unit	$cF_{96}/\text{kWh}$	$cF_{96}/\text{kWh}$	$cF_{93}/\text{kWh}$	$cF_{88}/\text{kWh}$
Discount rate (p.a.)	5 %	8 %	8 %	8 %
Nuclear	16.7...17.2	20.7...21.2	24.1...25.8	21...22
Coal (fluidized bed)	22.1...26.6	22.1...26.5	28.8...34.8	27...32
Combined-cycle gas and steam turbine	18.2...27.2	19.1...28.2	29.4...35.7	28...43

In all cases, the cost of nuclear investment is high, and the nuclear fuel cost is low. Furthermore, the share in fuel cost of the uranium itself is low: overall nuclear power generation costs are relatively insensitive to uranium price variations, in a striking difference with fossil power costs (this is why the brackets given for nuclear costs are narrower). Conversely, the high capital cost of the nuclear kWh explains why existing, partly or totally amortized, plants are extremely competitive, and why life extension is attractive.

For the evaluation of fuel cycle costs, we refer to the 1994 OECD study [94Oec, 97Ste], as shown in Table 3.12. They show a slight penalty for the closed cycle, but the uncertainty margins overlap each other.

The latest figures come from Japan [99Mit], where imported fossil fuels are rather costly. According to this study, the (closed) fuel cycle cost represents 28 % of the busbar nuclear cost of 5.9 yen/kWh.

**Table 3.12.** PWR fuel cycle costs, in units of million US\$<sub>91</sub> per kWh.

	Fuel cycle	
	Closed	Open
Uranium	1.64	1.64
Conversion	0.21	0.21
Enrichment	1.85	1.85
Fabrication	1.00	1.00
<i>Front-end subtotal</i>	<i>4.70</i>	<i>4.70</i>
Transportation	0.11	
Reprocessing/vitrification	1.66	
Wastes disposal	0.02	
Transportation/storage		0.51
Encapsulation/disposal		0.25
<i>Back-end subtotal</i>	<i>1.79</i>	<i>0.76</i>
U credit	−0.18	
Pu credit	−0.08	
<i>Total (base case)</i>	<i>6.23</i>	<i>5.46</i>
Brackets	<i>5.17...7.06</i>	<i>4.28...6.30</i>

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In addition to the very comprehensive books quoted in [81Mar, 96Wil, 99Coc], this chapter draws heavily from material gathered by L. Patarin et al. for the Nuclear Fuel Cycle section of the “Génie Atomique” course at the Institut des Sciences et Techniques Nucléaires, to be published by EDP.

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