CHAPTER 21

The Nuclear Fuel Cycle

Contents

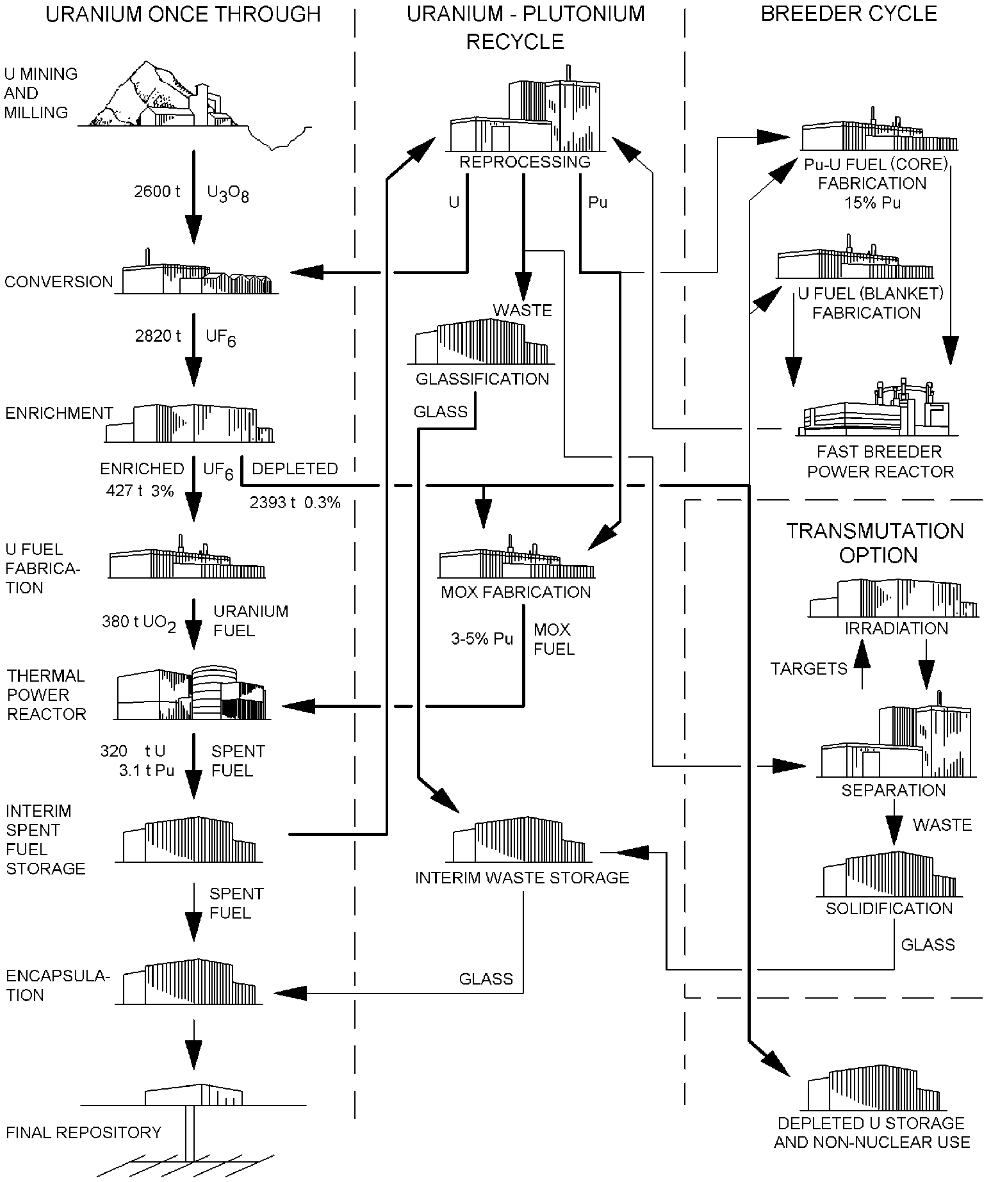

FIG. 21.1. Fuel cycle alternatives. Annual flows of materials in a 10 GW_e LWR UOT program are indicated.

The nuclear fuel cycle comprises the handling of all fissile and fertile material necessary for nuclear power production and of the radioactive products formed in this process (Fig. 21.1). The fuel cycle is suitably divided into a front end and a back end part, where the nuclear power station is the dividing line. The front end comprises uranium exploration, mining, and refining (§5.5), isotope enrichment (§2.8), and fuel element fabrication (§21.1). Reactor operation involves fuel behavior during operation, canning corrosion etc., while the back end involves reprocessing and radioactive waste ("radwaste") handling. Health and environmental aspects are important in all these steps, but being of a more general nature (see Ch. 18 and 22), they are not considered as "steps" in the nuclear fuel cycle.

The nuclear fuel used in almost all commercial reactors is based on uranium in the form of UO_2, either enriched so that the ^{235}U content has been increased to a few percent, or – less commonly – with the natural 0.7% abundance of the fissile isotope ^{235}U. Some power reactors also use fuel containing depleted uranium (~ 0.3% ^{235}U) in which plutonium is bred and/or Pu mixed with ^{238}U as a replacement for ^{235}U ("mixed oxide fuel"). ^{232}Th, in which fissile ^{233}U is bred, has also been used in a few cases.

Whether based on uranium, thorium, or plutonium, a fuel must be capable of resisting temperatures considerably above 1000°C without physical or chemical deterioration due to heat or to radiation. Metallic fuels have the high heat conduction necessary to minimize temperature gradients. Uranium melts at 1130°C and plutonium at 640°C. Moreover, metallic uranium has three and plutonium six allotropic forms between room temperature and their melting points. As a consequence, either the separate or combined effects of the radiation field, the high pressure during operation, and the high temperature can cause recrystallization into different allotropic forms with significantly different volume. Volume changes within the fuel element during operation cause mechanical deformations, reduce the mechanical strength, and increase the problem of corrosion even if the elements are clad in another corrosion resistent metal.

With the exception of some older gas cooled reactors, power reactors use ceramic pellets of UO_2, PuO_2, and ThO_2, or a mixture of these oxides, as fuels. UC has also been tested in some reactors. The size of the cylindrical pellets is ~ 1 × 1 cm (diameter × height). Fuel rods consisting of ceramic fuel pellets stacked in metallic tubes of zircaloy or stainless steel are quite temperature resistant, do not have the phase transformations of the metals, and have greater resistance to radiation effects. Unfortunately, the heat conduction is not as good as in the metallic fuel elements, and as a result rather high temperature gradients (up to 300°C mm^{-1}) often exist in the ceramic elements.

21.1. Production of fuel elements

The normal raw material for production of UO_2 based fuels is enriched uranium in the form of UF_6, which is delivered in special containers. By heating the container to ~ 100°C it is possible to transfer the hexafluoride as gas to the conversion plant, where UO_2 powder is produced, see Fig. 21.2. Several possible reactions can be used, e.g. hydrolysis of UF_6 by dissolution in water

$$UF_6(g) + 2H_2O \rightarrow UO_2F_2(aq) + 4HF(aq)$$

followed by precipitation with ammonia

$$2UO_2F_2(aq) + 6NH_4OH(aq) \rightarrow (NH_4)_2U_2O_7(s) + 4NH_4F(aq) + 3H_2O$$

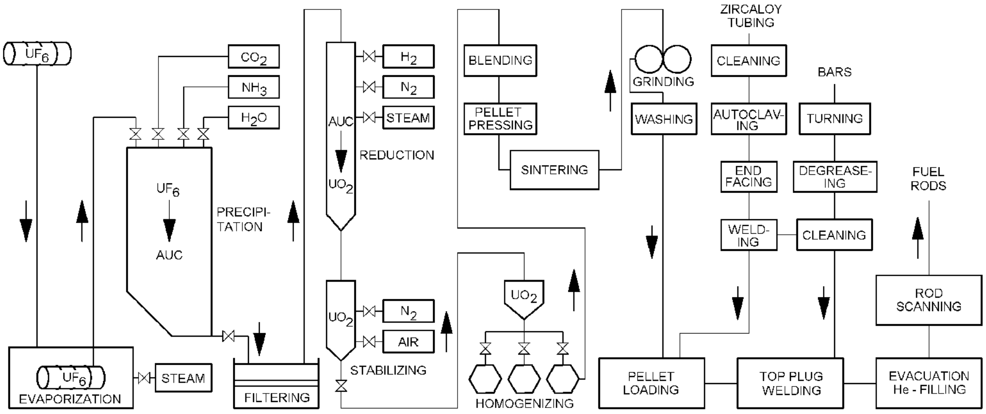

FIG. 21.2. Production of UO_2-fuel rods.

after filtration, washing and drying the diuranate is converted to UO_2 by reduction with hydrogen at 820°C.

Another often used reaction sequence begins with the formation and precipitation of ammonium uranyl carbonate (AUC) by reaction of UF_6 with water, CO_2 and NH_3, see Figure 21.2. The AUC is reduced to UO_2 by reduction in a fluidized bed using a mixture of hydrogen, nitrogen and steam and cooled to room temperature in a mixture of air and nitrogen.

The UO_2 powder is pressed into "green" pellets of slightly larger dimensions than the final product. These have ~50% of the theoretical density. The green pellets are sintered at ~1700°C in a dry H_2 atmosphere which gives a small controlled oxygen excess in the product; UO_{2+x}, where x ~0.05 is normally desired for best fuel performance. As exact dimensions of the pellets are needed in order to fit into the cladding tubes, the sintered pellets are ground to final shape.

Typically a density of ~10 400 kg m^{-3} is desired, which corresponds to a porosity of ~5%. If the density is too high the pellets swell excessively during irradiation due to the volume of the fission products gaseous at the operating temperature. Strongly swelling pellets may cause deformation, and failure, of the can. On the other hand a too low density can cause an initial shrinking of the pellet leading to an increased pellet – can gap, thereby reducing the heat transfer coefficient and increasing pellet temperature.

The finished pellets are put into a zircaloy tube with a welded bottom plug. Thereafter the pellet column hold-down spring and top plug are fitted and the resulting fuel pin sealed by electron beam welding, see Figures 19.12 and 21.2.

In order to improve heat transfer between pellets and can and to reduce pressure induced strain during operation, the space between pellets and tube is usually first evacuated and then pressurized with helium through a hole in the top end plug. It important to remove all traces of water as remaining water may form hydrogen by reaction with hot UO_2 during operation. The hydrogen reacts with the inside of the can forming zirconium hydride which may cause can failure.

Heat conduction between fuel and can is further improved by using *bonding materials* such as molten sodium, graphite powder, etc. The bonding material should also provide some lubrication between pellets and can. The canning material itself must not only be corrosion resistant to the coolant at all temperatures but should react with neither the fuel nor the bonding material.

The can should be as thin as possible, consistent with satisfactory mechanical strength and corrosion resistance (Fig. 19.12(a)). To reduce the danger of hydride formation a protective oxide layer can be produced by autoclaving the tube before filling it with pellets. In case of UO_2 pellets in zircaloy, the bonding material, e.g. graphite, is put onto the inner surface of the zircaloy tubes before the pellets are introduced. In case of stainless steel clad fast reactor fuel the production and assembly is similar, but the bonding is usually by sodium metal.

The purpose of cladding the fuel is to protect it against corrosion and to protect the coolant from radioactive contamination by the fission products from the fuel element. Aluminum has been used in water-cooled reactors, but at temperatures $> 300°C$ zirconium alloys show superior strength. At steam temperatures $> 400°C$ zirconium absorbs hydrogen, which increases brittleness, so stainless steel becomes preferable. In sodium cooled fast reactors, stainless steel is normally used. The most common alloys are zircaloy-2 (containing 1.58 Sn and 0.3% Cr, Ni, and Fe) and stainless steel type 302B (containing 10% Cr and 8% Ni). Stainless steel is not used at lower temperatures because of its larger neutron capture cross-section: σ 0.23 b for Al, 0.18 b for zircaloy-2, and about 3 b for 302B steel.

Metallic uranium is usually produced by conversion of UF_6 to UF_4 followed by metallothermic reduction of UF_4 by magnesium or calcium metal; however, several other methods exist. Metallic fuel is encased in a canning (cladding) of aluminum, magnesium, or their alloys. Fuel for high flux research reactors based on highly enriched uranium ($> 10\%$ ^{235}U) is often made in the form of uranium metal alloys (or compounds like USi_2) canned in aluminum to improve mechanical and thermal stability.

The fuel elements for use in high temperature gas cooled reactors consist of graphite rods or balls filled with oxide or carbide kernels produced by the sol-gel process. The kernels are covered by several layers of graphite and silicon carbide achieved by pyrolyzing methane or acetylene in a fluidized bed of the kernels.

Fuel cost and performance is an important part of the economy of power reactors. Approximately 20% of the expense of the electrical production in a power reactor can be attributed to the cost of the fuel. This is due about equally to the expense of the consumption of fissile material and to the production and, when applicable, reprocessing costs or intermediate storage costs. In the fast breeder reactors, it is anticipated that fuel costs would be substantially lower because of a higher burn-up.

When mixed uranium-plutonium oxide (MOX) fuel elements are used as, for example, in plutonium recycling ($< 5\%$ PuO_2) in LWRs or in fast breeders ($\leq 15\%$ PuO_2), the UO_2–PuO_2 mixture must be very intimate. This can be achieved by coprecipitation of the tetravalent actinides, normally as oxalates, followed by calcination. However, in industrial scale production of MOX fuel a rich mixture containing 15–20% PuO_2 is first very finely ground and then diluted with coarse grained pure UO_2. The final mixture is pressed into pellets and sintered similarly to UO_2-fuel pellets. This yields a fuel which can be dissolved to 99% (or better) in nitric acid. MOX fuel elements have been regularly added to the cores of many European LWRs for many years without any technical difficulties. Mixed uranium and thorium oxide fuels have also been used in a few heavy water reactors, see §20.1.1.

Instead of ground powders, spherical fuel particles can be used as a starting material. This has advantages with respect to fabrication, reactor utilization, and fuel reprocessing. These oxide or carbide particles are very small, < 1 mm in diameter. The particles are produced by the *sol–gel process*, which in principle consists of the following steps:

(i) An aqueous colloidal solution or the actinide or actinide mixture is prepared. The actinide(s) may be in the form of a hydrated complex of high concentration (3–4 M).

(ii) The solution is added to an inert solvent, which dehydrates the complex and causes the droplet to gelate. In one technique, hexamethylenetetramine, $(CH_2)_6N_4$, is added to the aqueous solution, which is added dropwise to a hot (~ 95°C) organic solvent. The heat causes the amine to decompose, forming NH_3, which leads to hydroxide precipitation in the droplet. The droplet dehydrates and solidifies rapidly, forming a "kernel".

(iii) The kernels are washed, air dried at 150-200°C, and - in the case of uranium - reduced by hydrogen gas at higher temperature to form UO_2.

(iv) The kernels are sintered at high temperature in an inert atmosphere.

Kernels of actinide carbides can be made in a similar manner. In many cases the kernels are covered by the addition of protective layers of graphite, silica or silicon carbide. The kernels are placed in fuel rod cans, pressed into pellets, or incorporated in a graphite matrix for use in high temperature reactors.

21.2. Power generation

During operation a large amount of heat is generated inside the fuel and has to be transferred to the coolant. Assuming a constant power per unit volume in the fuel, and fuel pins so long that longitudinal conduction can be neglected, the temperature profile can be estimated from the *specific power* (p, W m^{-3}) in the fuel from the following equations using the notation for radii from Figure 21.3.

Inside the fuel

$$T(r) = T(r_f) + p\,(r_f^2 - r^2)\,(4\,k_f)^{-1} \tag{21.1}$$

where $T(r)$ (°C) is the temperature at radius r (m) inside the fuel pellet, $T(r_f)$ (°C) the temperature at the pellet surface, r_f the pellet outer radius (m) and k_f the heat conductance in the fuel (W m^{-1} K^{-1}).

Across the gap between fuel and can

$$\Delta T_{gap} = p\,r_f\,(r_i - r_f)\,(2\,k_g)^{-1} = p\,r_f\,(2\,\alpha_g)^{-1} \tag{21.2}$$

where ΔT_{gap} is the temperature difference across the fuel - can gap (°C), r_i the inner radius of the can (m), k_g the heat conductivity across the gap (W m^{-1} K^{-1}) and α_g is the heat transfer coefficient across the gap (W m^{-2} K^{-1}).

For a thin can

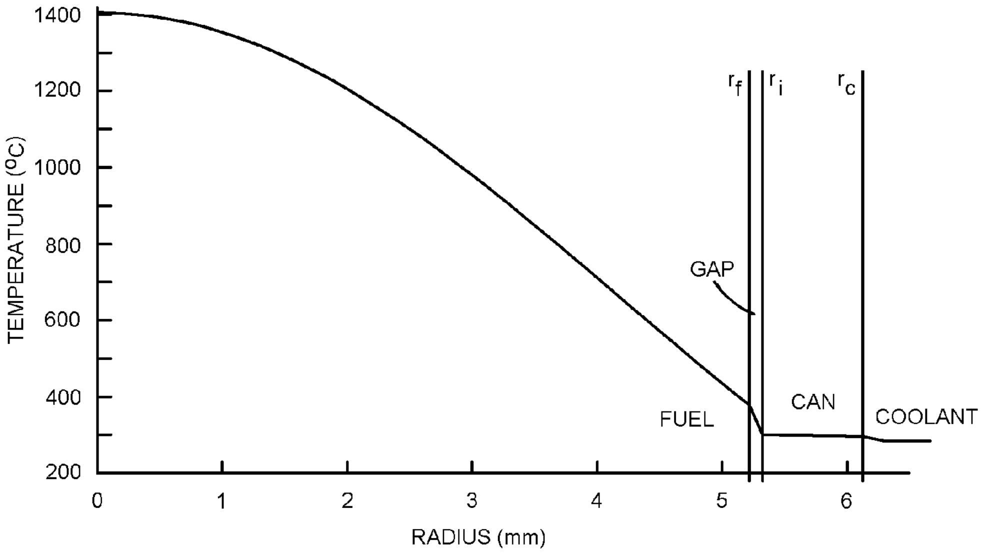

FIG. 21.3. Calculated temperatures in a BWR UO_2-fuel pin during operation at high load.

$$\Delta T_{\text{can}} = p\, r_f^2\, (r_c - r_i)\, (2\, r_i\, k_c)^{-1} \tag{21.3}$$

where ΔT_{can} is the temperature difference across the can (°C), r_c the outer radius of the can (m) and k_c the heat conductivity in the can (W m^{-1} K^{-1}).

Between the can surface and coolant,

$$\Delta T_o = p\, r_f^2\, (2\, r_c\, h)^{-1} \tag{21.4}$$

where ΔT_o is the temperature difference between the outer surface of the can and the coolant (°C) and h the film coefficient for heat transfer between can and coolant (W m^{-2} K^{-1}). The film coefficient is affected by the coolant velocity along the surface, the temperature gradient and also by the onset of boiling in a BWR.

Temperatures are best calculated by starting with eqn. (21.4) and proceeding inward to the center. A typical temperature profile is shown in Figure 21.3. However, in a more accurate calculation we must also consider the variation in specific power with fuel radius (because of self-screening effects etc.), the variation of heat conductivity (and film coefficient) with temperature, the change in heat conductivity of the fuel caused by accumulation of fission products, by pellet breakup, and by the densification of the fuel caused by high operating temperatures; the heat conductivity of UO_2 as function of temperature is shown in Figure 21.4 and some typical data at room temperature are given in Table 21.1.

As a result of these heat gradients it has been found that ceramic fuel elements may melt in the center (2865°C mp for pure UO_2) at high loading even though the surface temperature is much below the melting point. High center temperatures, especially in

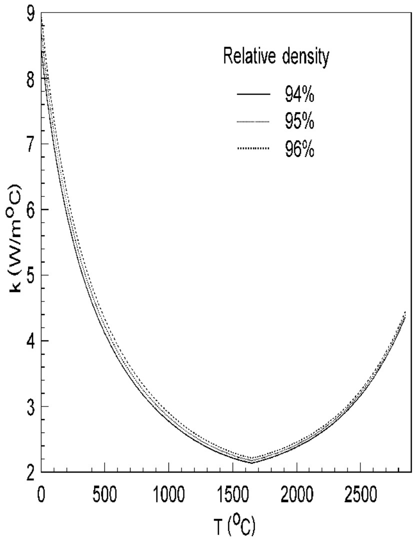

FIG. 21.4. The heat conductivity of UO_2 as function of temperature.

breeder fuel, may cause so much densification that a central hole is formed during operation.

The steep temperature gradients in the fuel during operation can cause a gradient of thermal expansion in the pellet; the expansion increasing from the surface to the center. The

TABLE 21.1. *Data (25°C) on some materials used in making nuclear fuel*

Material	Density ($kg\ m^{-3}$)	Melting point (K)	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Heat capacitivity ($J\ kg^{-1}\ K^{-1}$)	Thermal linear expansion coeff. (K^{-1})
Th (metal, α-)	11 720	2023	41	118	11.2×10^{-6}
ThO_2	10 001	3663	0.56	256	
U (metal, α-)	19 070	1405	25	116	13.5×10^{-6}
UO_2	10 970	3138	Fig. 21.4	360	14×10^{-6}
Pu (metal, α-)	19 860	912.5	8	137	57×10^{-6}
PuO_2	11 510	2663	~ 6	258	11.0×10^{-6}
Aluminum	2 700	933.4	238	903	23.2×10^{-6}
Magnox A12[‡]	1 740	~ 650	~ 167	~ 1 024	26×10^{-6}
SS (type 304)	8 030	1673	19	500	18×10^{-6}
Zircaloy 2[†]	6 550	~ 2090			5.2×10^{-6}
Zircaloy 4[‡‡]	6 440	~ 2120	16	330	4.4×10^{-6}

[†] Zr + 12-17‰ Sn, 0.7-2‰ Fe, 0.5-1.5‰ Cr, 0.3-0.8‰ Ni; [‡‡] Zr + 12-17‰ Sn, 1.8-2.4‰ Fe, 0.7-1.3‰ Cr; [‡] 0.8% Al, 0.01% Be; cf. Magnox ZA with 0.5-0.65% Zr

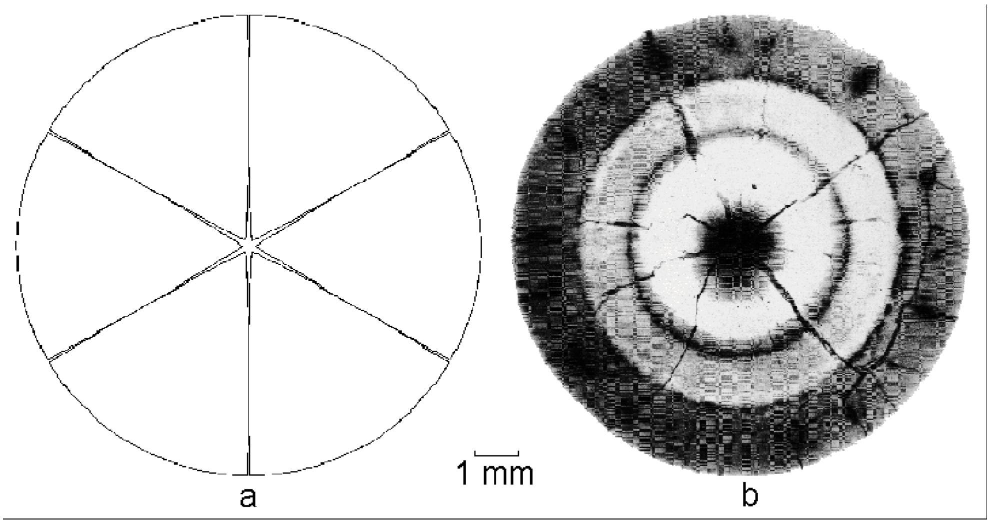

FIG. 21.5. (a) Schematic drawing of fuel pellet deformation during operation and (b) autoradiograph of a cut spent fuel pellet showing the typical pattern of cracks.

induced stresses lead to formation of a series of radial and annular cracks in the pellet and a deformation during operation, see Figure 21.5(a). Upon cooling the cracks close, but the characteristic pattern of cracks can be seen when a used fuel pin is cut and inspected, see Figure 21.5(b).

During operation, a slow corrosion of the can is unavoidable. As long as the corrosion products stick to the surface, corrosion rates drop with time. For zircaloy clad fuel in water cooled reactors the corrosion rate follows a parabolic equation (in the normal operating temperature range)

$$ds/dt = (k / s)\, e^{-u} \tag{21.5a}$$

where s is the thickness of the zirconium dioxide layer (m), t is the exposure time (s), k the rate constant (3.937×10^{-5} m^2 s^{-1}) and u is given by

$$u = \Delta E\, (\mathbf{R}\, T_c)^{-1} \tag{21.5b}$$

where $\mathbf{R}$ is the gas constant (8.318 J mole^{-1} K^{-1}), ΔE the activation energy (1.905×10^5 J mole^{-1}) and T_c the surface temperature of the can (K). The zirconium - steam reaction becomes very violent above ~ 1200°C, see §19.15. At about the same temperature a less well studied reaction between UO_2 and Zr begins in the fuel - cladding gap leading to the formation of a metallic U + Zr melt and ZrO_2.

Accumulation of the various fission products (and other impurities) occur where their chemical potential is at minimum. In contrast to an isothermal system where concentration gradients tend to disappear, the large temperature differences in operating nuclear fuel can result in a lower chemical potential at a higher concentration leading to an increase in the concentration gradient. Hence, some fission products, e.g. the noble gases, Cs and I, migrate to the fuel - cladding gap (lowest temperature), whereas others, e.g. Zr and Nb, migrate to the center line (highest temperature), cf. Fig. 21.5(b). A penetration of the can during reactor operation thus leads to an initial rapid release of those fission products which accumulated in the gap followed by a slow release of fission products present in the cracks and at grain boundaries and finally by a much slower dissolution and release of fuel (U, other actinides and other fission products).

The high concentration of uranium (and/or Pu) atoms in the fuel in combination with strong resonance peaks at certain neutron energies also leads to self-screening effects (n-flux depression at energies with large reaction cross sections), especially for $^{238}U(n,\gamma)$, $^{239}Pu(n,\gamma)$ and $^{239}Pu(n,f)$ (see Fig. 19.3). Thus, most of the Pu formed is located near the fuel surface and relatively little at the fuel center. This is easily seen in α-autoradiographs of spent fuel pins where most of the α:s are found in a ring near the fuel surface. Hence, thinner fuel pins yield a better fuel utilization than thicker pins, but thinner pins means higher fuel fabrication costs for the same amount of uranium. In practice an economic compromise results in pin diameters slightly less than 1 cm.

Radiation effects and oxidation causes changes in the tensile properties of the canning material. Fresh fuel has a can that is very ductile whereas the can of spent high burn-up fuel normally is hard and brittle.

In an operating power reactor, only part of the fuel is replaced annually; e.g. 1/5 to 1/4 of the total number of fuel elements. The most burnt up fuel elements are removed from the core as spent fuel and replaced by fresh fuel. In order to achieve as even as possible heat generation in the core (permitting the highest power output), the fresh fuel elements are mostly loaded in the outer core regions whereas partly spent fuel is moved in towards the center. This results in a checker board pattern of fuel of varying age in the reactor.

21.3. Composition and properties of spent fuel elements

The composition of spent reactor fuels varies as a function of input composition (kinds and amounts of fissile and fertile atoms), neutron spectrum, flux, fluency (or burnup), design of the pins and fuel elements, positions occupied in the reactor during operation, and the cooling time after removal from the reactor. A harder neutron spectrum increases fertile to fissile conversion (Fig. 19.3). Hence, after refuelling, some BWRs are initially operated at the highest possible void fraction in order to maximize conversion of ^{238}U to plutonium. This permits a higher final burnup of the fuel. Increased burnup increases the concentration of fission products and larger amounts of higher actinides are formed (Figs. 16.4 and 19.7). Thinner fuel pins increases conversion to and burning of plutonium due to less self screening. A high neutron flux results in more high order reactions (§15.3), while a long irradiation time produces relatively larger amounts of longlived products. With increased cooling time the fraction of shortlived products is reduced.

Because of such effects, spent uranium fuel elements from PWR, BWR, HWR, GCR and FBR differ in composition both from each other and between fuel batches from the same reactor. Furthermore, the composition differs between pins in the same fuel element and for each pin also along its length, especially when initial burnable poison concentration and enrichment is graded along pins. The difference is not so large that very different fuel

TABLE 21.2. *Calculated composition after 10 y cooling of 1 t U as 3.2% enriched UO_2 fuel with 33 MWd/kg U burnup at a mean flux of 3.24×10^{18} n m^{-2} s^{-1} in a typical PWR*

H $6\cdot10^{-5}$ *17.3*		Straight figures are weight in kg/t IHM. Italics are radioactivity in TBq/t IHM. Total weight is 34 kg FPs and 9.7 kg transuranium elements.															He
Li	Be											B	C 0.088 *0.022*	N	O 67.2 *0*	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn $4\cdot10^{-11}$ *$2\cdot10^{-4}$*	Ga $9\cdot10^{-10}$ *0*	Ge $7\cdot10^{-4}$ *0*	As $2\cdot10^{-4}$ *0*	Se 0.056 *0.015*	Br 0.022 *0*	Kr 0.36 *183*
Rb 0.35 *$8\cdot10^{-7}$*	Sr 0.77 *2180*	Y 0.46 *2130*	Zr 3.62 *0.068*	Nb $4\cdot10^{-6}$ *0.028*	Mo 3.35 *2.10^{-5}*	Tc 0.77 *0.49*	Ru 2.18 *22.2*	Rh 0.47 *22.1*	Pd 1.37 *0.004*	Ag 0.076 *0.007*	Cd 0.13 *1.31*	In 0.003 *0*	Sn 0.096 *0.036*	Sb 0.020 *45.4*	Te 0.48 *11.2*	I 0.24 *0.001*	Xe 5.33 *0*
Cs 2.38 *3230*	Ba 1.73 *2900*		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra $4\cdot10^{-10}$ *$2\cdot10^{-4}$*		Rf	Db	Sg	Bh	Hs	Mt									

Lantanides	La 1.22 *0*	Ce 2.37 *6.30*	Pr 1.12 *6.38*	Nd 4.03 *0*	Pm 0.011 *363*	Sm 0.86 *12.0*	Eu 0.13 *228*	Gd 0.12 *$5\cdot10^{-5}$*	Tb 0.003 *0*	Dy 0.001 *0*	Ho 0.001 *$9\cdot10^{-5}$*	Er $6\cdot10^{-5}$ *0*	Tm $6\cdot10^{-8}$ *$9\cdot10^{-7}$*	Yb	Lu
Actinides	Ac $7\cdot10^{-11}$ *$2\cdot10^{-7}$*	Th $8\cdot10^{-6}$ *0.013*	Pa 4.10^{-7} *0.024*	U 956 *0.067*	Np 0.45 *0.64*	Pu 8.69 *2990*	Am 0.58 *63.4*	Cm 0.013 *39.0*	Bk $4\cdot10^{-14}$ *$2\cdot10^{-9}$*	Cf $1\cdot10^{-10}$ *$8\cdot10^{-8}$*	Es	Fm	Md	No	Lr

cycles (e.g. other reprocessing schemes) are required as long as the fuel is based on uranium metal or uranium dioxide. In the following subsections we mainly discuss uranium dioxide fuel elements, and, more specifically, LWR elements. Fission product and actinide yields for a typical PWR fuel are given in Table 21.2.[1] The uranium once through part of Figure 21.1 shows the annual materials flow in a mixed BWR–PWR conglomerate with a total average power of 10 GW_e (i.e. about twelve 1000 MW_e plants) running at full power for 7000 hours per year (load factor ~ 80%).

21.3.1. *Fission products*

About 34 kg fission products (FP, including gaseous) are formed in each initial ton of uranium irradiated to 33 MWd/kg. To accommodate mixed oxide fuels (i.e. fuels initially containing both U and Pu), burnup, composition, activities, etc, are usually normalized to the amount of *initially present heavy metal*, *IHM*. The composition of spent fuel varies with burnup, power history and reactor. The formation rates of the various primary fission products depend on the fission rate, chain yields of the fissioning nuclide and on the corresponding charge distribution (Ch. 14). Increased fission of heavier actinides displaces the lower mass peak in the yield curve towards higher mass numbers while the heavier mass peak remains about the same (Fig. 14.9). An increased contribution from fast fission increases the yield in the valley between the peaks. Because of the continued n-irradiation, secondary n,γ-reactions occur with the primary fission products and their daughters (Ch.

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[1] As the exact composition of spent fuel varies considerably and depend on many factors, the reader will find slightly varying figures in this text.

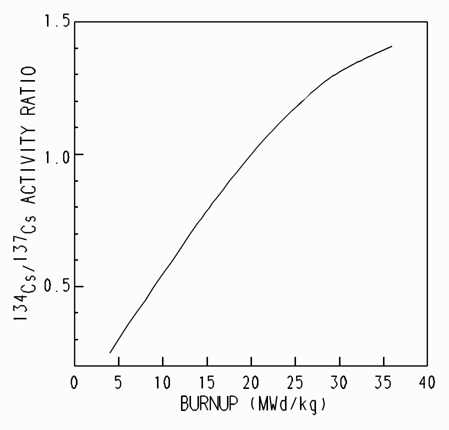

FIG. 21.6. Typical variation of the ratio between the ^{134}Cs and ^{137}Cs radioactivities with fuel burnup.

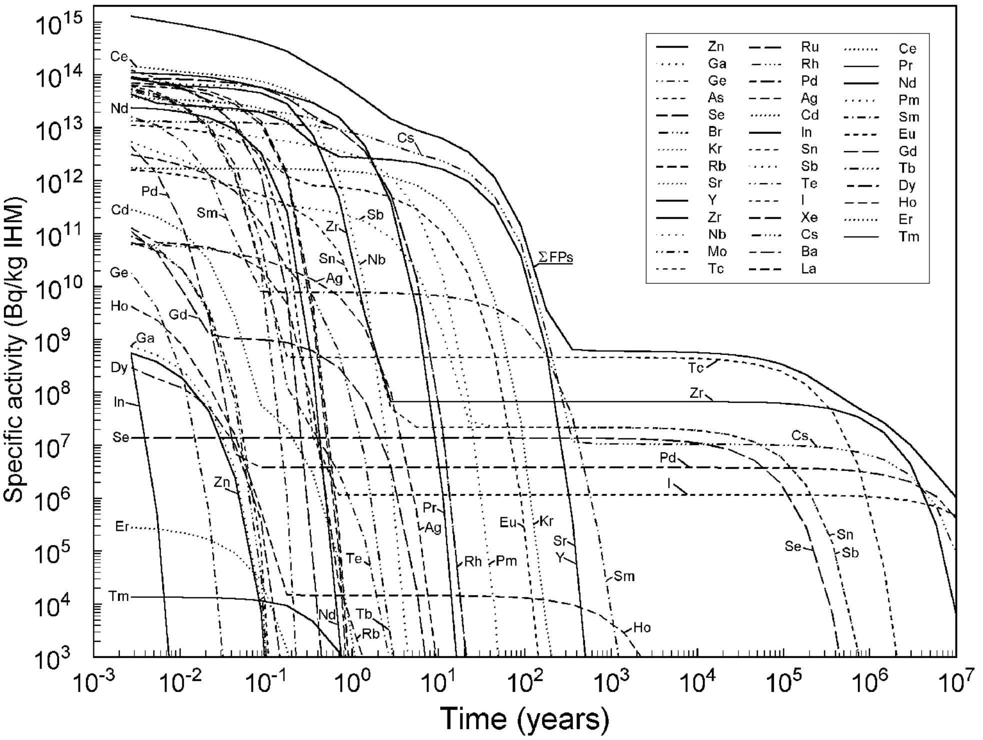

FIG. 21.7. Radioactivity of fission products per kg IHM in spent PWR fuel at 33 MWd/kg burnup. Inflexion points indicate the existence of several radioisotopes.

15). As an example, ^{134}Cs is not formed to any appreciable extent in fission because it is shielded by the stable ^{134}Xe. Hence, no ^{134}Cs is normally observed in the remains after a nuclear explosion in the atmosphere. However, primary fission products in the *A* 133 isobar chain have time to decay to stable ^{133}Cs during reactor operation and ^{134}Cs is produced by the reaction ^{133}Cs (n,γ) ^{134}Cs. Given the cooling time, the ratio between the decay rates of ^{134}Cs and ^{137}Cs can be used to estimate the burnup of fuel from a given reactor, see Figure 21.6.

Using effective cross-sections and yield values the amounts and radioactivities in Figure 21.7 and Table 21.2 were calculated. It is seen that Xe, Zr, Mo, Nd, Cs, and Ru, which are the elements formed in largest amounts in thermal fission (both by mole percent and by weight), constitute about 70% of the fission product weight after a cooling time of 10 y.

At cooling times 10–1000 y the activities of ^{90}Sr and ^{137}Cs (with daughters) dominate among the fission products. Later the fission product activity is due to very longlived nuclides of low activity (Figure 21.7, Table 21.3). ^{131}I, which for very short cooling times is one of the most hazardous FPs because of its affinity to the thyroid gland, has practically

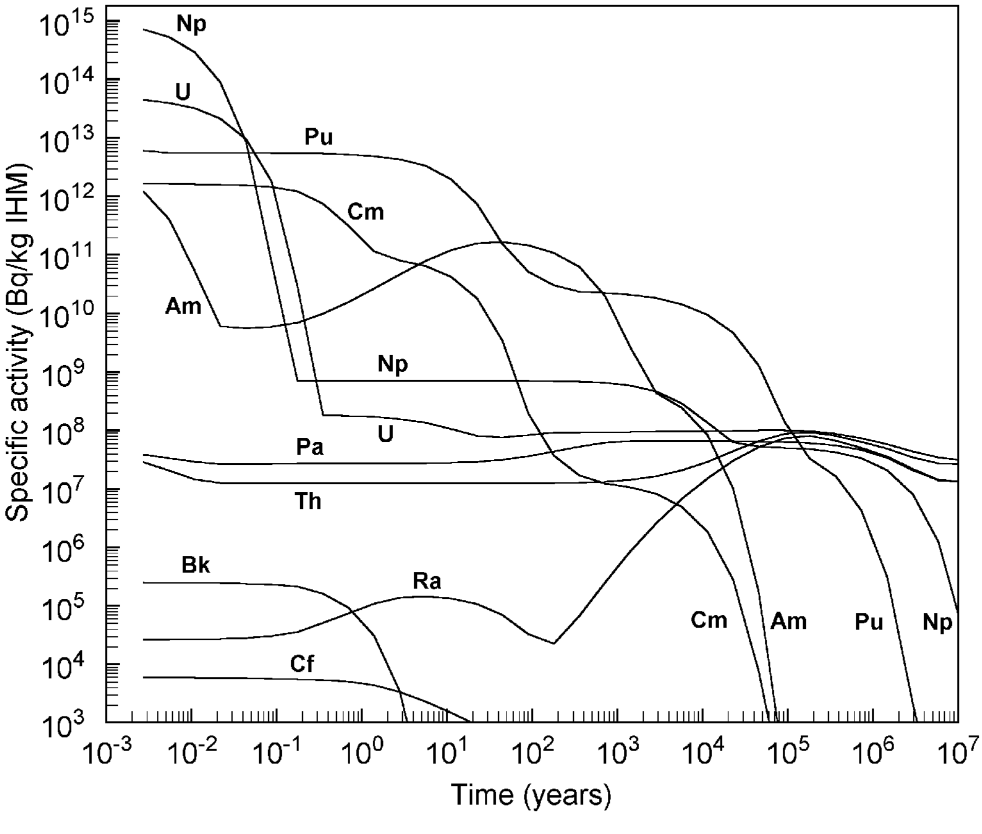

Fig. 21.8. Radioactivities of actinides and radium per kg IHM in spent PWR fuel after 33 MWd/kg burnup (see Tab. 21.2). Inflection points indicate the presense of several radioisotopes of the element.

Table 21.3. Some long-lived radionuclides produced in fission; t_{cool} 10 y, data as in Table 21.2.

Nuclide	Half-life (years)†	Decay; β^- (energy MeV)‡	Thermal fission yield(%)††	Thermal fission activity (TBq/t U)
^{79}Se	$< 6.5 \times 10^4$	0.1509	0.0443	0.0151
^{85}Kr	10.72	0.6874	1.318	183
^{87}Rb	4.8×10^{10}	0.2823	2.558	7.7×10^{-7}
^{90}Sr → ^{90}Y	28.5	0.5462 + 2.2815	5.772	2180
^{93}Zr → ^{93m}Nb	1.5×10^6	0.0905	6.375	0.068 + 0.028
^{99}Tc	2.13×10^5	0.2936	6.074	0.484
^{107}Pd	6.5×10^6	0.033	0.147	0.0042
^{126}Sn → ^{126m2}Sb	$\sim 1 \times 10^5$	0.368 + 3.670	0.0536	0.029
* ↘ ↓				
* ^{126m1}Sb				
* ↓				
. → ^{126}Sb				
^{129}I	1.57×10^7	0.192	0.757	0.0012
^{134}Cs	2.062	2.0585	0	201
^{135}Cs	3.0×10^6	0.205	6.536	0.0098
^{137}Cs → ^{137m}Ba	30.0	0.5134	6.183	3060
^{151}Sm	90	0.0763	0.4196	12
^{154}Eu	8.8	1.9689	0	169
^{155}Eu	4.96	0.2527	0.0320	59

† Only for the longer lived mother nuclide. ‡ Decay energy, not particle energy (see decay schemes).
†† Thermal fission of ^{235}U (fission of ^{238}U, fission of Pu isotopes and n,γ-reactions are important effects in a nuclear reactor).

disappeared after a cooling time of 6 months. The $A = 95$ isobar chain, which is formed in highest yield (6.52%), leads to ^{95}Zr ($t_{1/2}$ 64 d) → ^{95}Nb($t_{1/2}$ 35 d) → ^{95}Mo (stable).

From Table 21.2 it is seen that only stable isotopes remain for some fission elements at $t_{cool} \geq 10$ y (Ga, Ge, As, Br, In, Xe, La, Nd, Tb, Dy and Er), while some others are of very low activity (Zn, Se, Rb, Mo, Pd, Ag, Sn, I, Gd, Ho, and Tm). Some of the more active ones after 10 y have disappeared almost completely at 100 y (T, Sb, Ce, Eu, Pm, Ru, Rh, and Kr), leaving essentially only the ^{90}Sr-^{90}Y and ^{137}Cs-^{137m}Ba pairs and ^{151}Sm.

21.3.2. *Actinides*

Neutron capture and β-decay lead to the formation of higher actinides. This is illustrated in Figs. 16.2, 16.3, 19.5 and 19.7. ^{239}Pu and ^{241}Pu also fission, contributing significantly to the energy production (Fig. 19.8). Truly, all plutonium isotopes lead to fission, since the n-capture products and daughters, ^{241}Am, ^{242}Am, ^{243}Cm, ^{245}Cm, and most other actinides are either fertile, fissible or fissile.

Fast neutrons in the reactor induce (n,2n) reactions, e.g. ^{238}U (n,2n) ^{237}U (β^-) ^{237}Np (n,γ) ^{238}Np (β^-) ^{238}Pu (n,γ) ^{239}Pu (see Fig. 19.5), as well as fast fission. ^{237}Np is also formed through the reaction ^{235}U (n,γ) ^{236}U (n,γ) ^{237}U (β^-) ^{237}Np. These reactions are the main sources of neptunium and of ^{238}Pu.

TABLE 21.4. *Production of plutonium (kg/MW$_e$y) in various reactor types*

Reactor type	Total Pu	Fissile Pu
Light water reactors	0.26	0.18
Heavy water reactors	0.51	0.25
Gas-graphite reactors	0.58	0.43
Advanced gas-cooled reactors	0.22	0.13
Liquid metal fast breeder reactors	1.35	0.7–1.0

Many actinides formed are fissile but have a short half-life. The ratio, x, of the amount fissioned to the amount decayed or reacted with neutrons at constant flux and steady state is given by

$$x = \phi\, \sigma_f / [\lambda + \phi\, (\sigma_f + \sigma_{n,\gamma})] \qquad (21.6)$$

where ϕ is the neutron flux, σ_f the effective fission cross-section, $\sigma_{n,\gamma}$ the effective cross-section for radiative capture and λ the decay constant. As can be seen from (21.6) a higher fraction of the nuclide will fission in a very high neutron flux ($x \rightarrow \sigma_f/(\sigma_f + \sigma_{n,\gamma})$ when $\phi \rightarrow \infty$), whereas most of it will disappear by decay in a low flux ($x \rightarrow 0$ when $\phi \rightarrow 0$). As an example, practically all ^{238}Np formed by ^{237}Np(n,γ) ^{238}Np will fission when $\phi\sigma_f \gg \lambda$ ($\sigma_f = 2070$ b, $\sigma_{n,\gamma} \sim 0$ b and $\lambda = 3.8 \times 10^{-6}\ \mathrm{s}^{-1}$). Hence, the buildup of many higher actinides is less efficient in a high flux reactor than in a reactor with a more moderate neutron flux although the total buildup rate might still be higher in the higher flux. This is accentuated in fast breeder reactors where the combination of a very high neutron flux and a hard neutron spectrum (increased effective σ_f for fissible nuclides) strongly reduces the amount of higher actinides formed (at a given burnup) compared to a thermal reactor.

From the fission and capture cross-sections, and half-lives the radioactivity of each actinide element in one kg spent fuel (and radium) has been calculated and shown in Fig. 21.8 for a PWR UO_2 fuel with a burnup of 33 MWd per kg IHM. Due to the use of a log-log scale in Figure 21.8, the decay curve of any single nuclides is s smooth curve bending downwards. Inflexion points indicate the existence of several radioactive isotopes of the same element with different half-lives.

The total amount of plutonium formed in various reactors is given in Table 21.4. The old gas-graphite reactors and heavy water reactors are the best thermal plutonium producers. They have therefore been used in weapons fabrication. The fast breeder reactor is also an efficient Pu producer. Whereas thermal reactors (except at very low burnup) produce a mixture of odd and even A Pu isotopes, a fast breeder loaded with such a mixture, by a combination of fission and n-capture increases the relative concentration of Pu isotopes with odd A in the core and produces fairly pure ^{239}Pu in the blanket. Hence the combined Pu product from core and blanket elements has a much higher concentration of fissile Pu isotopes than plutonium from a thermal reactor (the fast breeder not only produces more Pu than it consumes but also improves Pu quality, i.e. increases the concentration of fissionable isotopes). The LWR and AGR are the poorest plutonium producers.

Composition of spent fuel varies somewhat with cooling time, e.g. the amount of ^{241}Am increases because it is the daughter of 14.4 y ^{241}Pu; 116, 280 and 579 g/t IHM of Am after

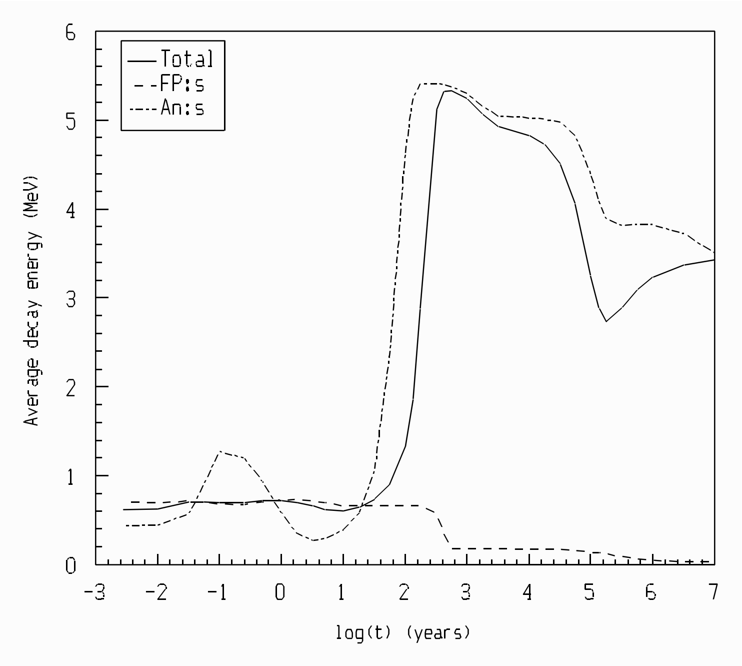

FIG. 21.9. Average energy per decay in spent PWR fuel (fuel data according to Table 21.2).

0, 3 and 10 years, respectively.

TABLE 21.5. *Decay heat from unpartitioned fuel, fission products and actinides* (Basic data as in Table 21.2)

	Decay heat (W/kg initial U)		
Cooling time	Total	Fission products	All actinides
1 d	193	146	47
90 d	30	29	1.1
180 d	19	18	0.81
1 y	10.8	10.3	0.46
5 y	2.1	1.9	0.18
10 y	1.4	1.2	0.19
100 y	0.32	0.13	0.19
10^3 y	0.054	0.000021	0.054
10^4 y	0.013	0.000019	0.013
10^5 y	0.0010	0.000012	0.0010
10^6 y	0.00038	0.0000009	0.00038

21.3.3. *Decay heat and physical properties*

As the radioactivity of the FP and actinides decreases by time, so does the energy absorbed in the shielding material (and by self-absorption) which is seen as *decay heat*. Table 21.5 gives data on the decay heat with contributions separately for the fission products and the actinides. Figure 21.9 shows the variation of the average energy per decay with time. The maxima and minima in the total and actinide curves in Figure 21.9 are caused by the presence of both α- and β,γ emitters with different activities and half-lives and also by the evolution in some decay chains. For cooling times $> 10^3$ y the decay heat from the actinides and their daughters dominates.

The decay heat is considerable at short cooling times due to the very high decay rate (see Fig. 19.15). Before unloading spent fuel from a reactor, the used fuel elements are first allowed to cool in the reactor by forced circulation. Within a few weeks they are then transferred under water to the cooling basin at the reactor site for an additional cooling time, usually 6–12 months, after which they may be transferred to a central spent fuel storage facility. In the absence of such facilities, spent fuel elements can be stored in the reactor pools for many years. During this time the radiation level and heat production decrease considerably.

21.4. Management of spent fuel

21.4.1. *Transport of spent reactor fuel*

The storage capacity of reactor pools is normally several years' production but can be increased by adding neutron absorbers to the storage racks. Eventually the fuel assemblies must be transferred in special transport flasks to (interim) storage sites, sent for reprocessing or to final disposal.

The loading of used fuel the assemblies in the transport flask requires shielding and remote handling, and the heat continual cooling. Therefore, almost all operations are carried out under water. Because each transport is expensive the transport flasks are designed to carry several assemblies of different types. A 30 t (gross weight) flask may carry 4 PWR or 9 BWR assemblies (~1 t U), a 100 t flask ~12 PWR or ~30 BWR assemblies (~6 t U). The inner cavity of such flasks is normally surrounded by a neutron absorbing shield; see Figure 21.10. They have shock absorbers, and sometimes cooling fins on the outside. A filled 100 t flask with 1 year old fuel develops ~60 kW heat; the design cooling capacity of the flask is ~100 kW. The cavity in some flasks is filled with water because the flasks are loaded and unloaded under water, and the water functions as heat conducting and neutron absorbing material (several actinides decay by spontaneous fission; α,n-reactions occur with light target atoms). Figure 21.10 shows a fuel cask for dry transport of 7 PWR or 17 BWR assemblies by special trucks, by rail, or by sea in special RO-RO type ships.

The flasks are designed for exceedingly severe treatment: free fall from 9 m onto a concrete floor, 30 min gasoline fire (~800°C), submersion into 15 m of water, etc., without being damaged.

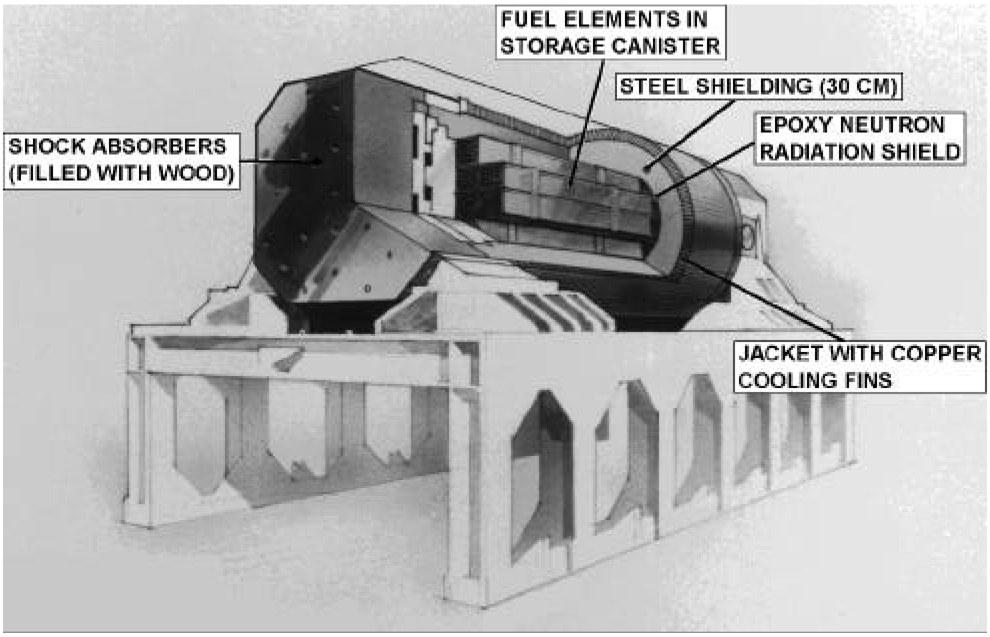

FIG. 21.10. Transport cask TN-17 for 7 PWR or 17 BWR fuel elements; ϕ 1.96 m, length 6.15 m, empty weight 76 tons (SKB, Sweden).

After loading a flask the outside of the flask must be decontaminated; often it is quite difficult to remove all activity, and a removable plastic covering is used. Before unloading, water filled flasks are flushed to remove any activity leaked from the fuel or suspended crud, which is present on the used fuel elements from BWRs and most PWRs. Further decontamination is carried out after the flask has been emptied.

Dry air filled flasks are used in many countries. They are either cooled by filling with water before unloading (the escaping steam is collected and condensed) or unloaded hot and dry by remote handling. In the former case, further handling is the same as for water filled flasks.

Shielded transport is also required for solidified high level waste, hulls, plutonium containing material, and for some intermediate and α-active waste. Special containers are used for each type. As an example, in the United Kingdom plutonium containers made of wood and cadmium are limited to carrying 10 kg Pu; the container weighs 175 kg, is 1.3 m high, and 0.8 m in diameter.

21.4.2. *Interim storage facilities*

In the once-through fuel cycle, or with a limited capacity for reprocessing, separate spent fuel element interim storage facilities become compulsory. These facilities are either of the wet pool type (Czech Republic, Finland, Germany, Japan, Sweden, United Kingdom) or of the dry vault type (France, Germany, United Kingdom). The pool types consist of large water filled basins containing a geometrically safe (with regard to criticality) lattice of stainless steel racks for the spent fuel elements. The water is circulated for cooling. In general such pools are either located in a building at ground level or underground at 30–50 m depth.

Zircaloy clad oxide fuel elements can be stored for decades in storage pools with very little risk of leakage. Metal fuels, especially those canned in magnesium or aluminum alloys, are less resistant and should not be stored as such in this manner for a prolonged time. The corrosion resistance of aluminum or magnesium clad fuel can be improved by electrolytic treatment yielding a protective oxide layer.

Some of the stringent requirements on the storage pools are: $k_{\mathrm{eff}} < 0.95$ (even if unused fuel elements are introduced), earthquake safety, no possible water loss, water level automatically kept constant, adequate leakage and radiation monitoring systems, water temperature $< 65°\mathrm{C}$, acceptably low radiation level in working areas, etc.

Dry vault storage may also be used. The fuel elements are stacked horizontally or vertically in concrete pipes which allows cooling of the fuel elements by air convection (forced or natural).

For long term storage ($\gg$10 y) the fuel elements must be recanned. For this purpose single fuel elements or bundles are placed in cylindrical containers, and the void is filled with some suitable material like lead, which has good heat conductivity and also provides some radiation protection. Depending on the external condition at the final storing place (humidity, temperature, etc.) the canisters are surrounded by an additional container to improve the lifetime of the fuel elements, which – preferably – should not be exposed to the biosphere until all radioactivity has disappeared.

21.5. Alternative fuel cycles

Fission energy can be obtained from uranium, using the *uranium once-through* option and the *uranium-plutonium fuel cycle*, and from thorium, by the *thorium-uranium fuel cycle*. Each fuel cycle offers a number of alternative routes with respect to reactor type, reprocessing, and waste handling. Although the uranium based cycles are described with special reference to light water reactors, the cycles also apply to the old uranium fueled gas cooled reactors.

21.5.1. *The uranium once-through (UOT) option*

The heavy arrows in Fig. 21.1 indicate the steps in the nuclear fuel cycle presently used on a large commercial scale. The cycle stops at the spent fuel interim storage facility; from here two alternative routes are available, one leading to the uranium-plutonium fuel cycle (reprocessing of the spent fuel elements, as described in the next section) and another leading to final storage of the unreprocessed spent fuel elements. The latter is referred to as the *once-through fuel cycle* (UOT) option.

In the UOT option, the energy content of unused ^{235}U, fertile ^{238}U, and fissile and fertile plutonium is not retrieved for future use, and the "waste" contains large amounts of these and other α-emitting nuclides. At present this is the cheapest option and also withholds plutonium from possible diversion to weapons use.

In 1994, only three countries (Canada, Sweden, USA) have decided to use the UOT strategy, while all other nuclear power countries either were undecided or had elected to use the reprocessing strategy. The technical aspects of the UOT option are further discussed in §21.13.

21.5.2. *The uranium-plutonium (U-Pu) fuel cycle*

"Cycle" infers to some mode of recirculation of material. The term "fuel cycle" was originally used for the steps in which fissile and fertile material was isolated from used fuel elements (*reprocessing*) and returned to the front end of the process for use in new fuel elements, see Figure 21.1. The proper time to start reprocessing is a balance between loss of fissile material (^{241}Pu $t_{1/2}$ 14.4 y), economic interest loss on unused fissile and fertile material and storage costs of the unprocessed fuels, on one hand, and, on the other hand, savings due to simplified reprocessing and waste handling. Originally a 180 d cooling time was considered appropriate (this time has been said to have been used in military programs). Presently the average cooling time for commercial fuel elements is 7–10 y because of lack of reprocessing capacity.

The fissile fractions in spent LWR fuel elements amounts to ~0.9% ^{235}U and 0.5–0.7% $^{239+241}$Pu. By recovering these and returning them to the LWR fuel cycle the demand for new uranium and enrichment services is reduced by ~30%. The uranium recovered may either be re-enriched and used in normal uranium oxide fuel or blended with the plutonium recovered to form *mixed oxide* (MOX) fuel elements (§21.1). MOX fuel can also be made from recovered plutonium and depleted uranium. MOX fuel elements for LWRs contain up to 5% ^{239}Pu + ^{241}Pu. Many tons of plutonium have already been used as MOX fuel in LWRs.

The re-enrichment of recovered uranium leads to a small contamination of the enrichment plant by ^{232}U, ^{233}U and ^{236}U, which are introduced as part of recovered uranium. Today, most batches of enriched uranium contain small amounts of these uranium isotopes.

In this cycle "old" plutonium from earlier production is successively exposed to increasing neutron fluency, which changes its isotopic composition. This is shown in Table 21.6 for both virgin plutonium and virgin + recycled plutonium. The fissile fraction (^{239}Pu + ^{241}Pu) decreases, requiring successively increased plutonium fractions in the MOX elements. The concentration of the most toxic isotope, ^{238}Pu, increases substantially. Its short half-life (88 y) results in a high specific radioactivity which increases the heat evolution and radiolysis of the reprocessing solutions. ^{238}Pu, ^{240}Pu, and ^{242}Pu all decay partly through spontaneous fission, with the emission of neutrons ($\sim 2 \times 10^{6}$ n kg^{-1} s^{-1}). This makes the MOX elements more difficult to handle. (All these changes also make the plutonium less suitable for weapons use.) ^{241}Pu has a critical mass of about half that of ^{239}Pu, so as ^{241}Pu builds up, criticality risks increase. The buildup of other actinides by recycling high mass isotopes in LWR fuel further increases reprocessing, handling, fuel manufacturing and waste problems.

Another possibility is to recycle only uranium, while the plutonium is left with the waste. This would produce a waste with a very high concentration of plutonium, except for highly

TABLE 21.6. *The isotopic composition of plutonium (weight %) as function of number of recycles as MOX fuel in a PWR with a burnup of 33 000 MWd/t IHM per cycle.*

Recycles	^{236}Pu	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{244}Pu	Fraction left
0	7.2×10^{-7}	1.5	56.6	26.0	10.8	5.2	0.0004	1.00
1	4.6×10^{-8}	4.7	32.2	33.7	10.0	19.5	0.0013	0.47
2	6.6×10^{-8}	5.9	22.7	25.5	7.9	38.1	0.010	0.23
3	9.2×10^{-8}	4.4	19.8	20.2	5.0	50.6	0.020	0.12
4	1.1×10^{-7}	2.9	18.2	19.9	3.9	55.1	0.040	0.066
5	1.2×10^{-7}	2.3	17.6	20.3	3.6	56.1	0.080	0.036
6	1.2×10^{-7}	2.1	17.4	20.4	3.6	56.3	0.16	0.020
7	1.2×10^{-7}	2.1	17.4	20.5	3.5	56.3	0.29	0.011
8	1.2×10^{-7}	2.1	17.4	20.4	3.5	56.1	0.53	0.006
9	1.2×10^{-7}	2.0	17.3	20.4	3.5	55.8	0.96	0.003

The recycling is assumed to be in the form of 5% Pu and 95% depleted U.

enriched uranium fuel; the weight ratio of plutonium to fission products would be 10:35 (kg/t U, Table 21.2).

The reuse of plutonium in LWRs would only be temporary if fast breeder reactors would become common (Fig. 21.1). FBRs are designed with a core, containing ~ 15% fissile Pu and ~ 85% ^{238}U (as depleted uranium) in the form of mixed oxides or carbides surrounded by a blanket of depleted uranium. In such a fast reactor, the presence of ^{235}U is undesirable as it reduces the neutron energy considerably by inelastic scattering. The actinide and fission product contents in discharged FBR fuel (core and blanket) and discharged LWR fuel are roughly the same on a GW$_e$y basis. Also the masses of total discharged fuel per GW$_e$y are comparable because the high burnup in the core is balanced by a very low burnup in the blanket. Breeding occurs only in the blanket (cf. §20.3). The burnup in the core elements is ~ 3 times higher than in LWRs, and the fraction of fission products is also 3 times larger. Since only a small part of the plutonium is burnt and the remainder has a high content of the fissile Pu isotopes, the used core fuel elements retain a high economic value, making it desirable to reprocess them after a short cooling time. Used FBR core elements may have a tenfold greater specific radioactivity than spent LWR fuel elements at the time of reprocessing and a much higher content of plutonium. Hence, criticality risks require a special reprocessing plant for core elements. The FBR blanket elements are simpler to handle because of a lower content of fission products and plutonium and they may be reprocessed in plants for LWR fuel elements. However, if the core elements are sufficiently diluted with blanket elements such a mix may be reprocessed in a "conventional" plant for LWR fuels.

In the FBR, ^{238}U is consumed both by fission (i.e. energy production) and by ^{239}Pu formation. Because the α-value of ^{239}Pu is 0.42, at least 70% ($100(1 + \alpha)^{-1}$) of all ^{238}U is useful for energy production in the U-Pu cycle. This value should be compared with the fairly small fraction, $\leq$ 0.7%, of the natural uranium which is used in the UOT cycle (taking enrichment also into account), or $\leq$ 1% in the LWR MOX fuel recycle. The FBRs not only increase the useful energy of natural uranium by a factor of ~ 100, they also make it possible to burn current stockpiles of depleted uranium amd also make it economic to mine low grade uranium ore, vastly extending the available uranium resources.

In 1994, 15 nuclear energy countries had decided to use reprocessing as part of their strategy for spent fuel management (Argentina, Belgium, Brazil, Bulgaria, China, Finland, France, Germany, Hungary, India, Japan, the Netherlands, Switzerland, Russia and the United Kingdom).

21.5.3. *The thorium-uranium (Th-U) fuel cycle*

Nuclear energy cannot be produced by a self-sustained chain reaction in thorium alone because natural thorium contains no fissile isotopes. Hence the thorium-uranium cycle must be started by using enriched uranium, by irradiation of thorium in a uranium- or plutonium-fueled reactor or by using a strong external neutron source, e.g. an accelerator driven spallation source.

Fertile ^{232}Th can be transformed into fissile ^{233}U in any thermal reactor. The reactions in ^{232}Th irradiated by neutrons are given in Fig. 20.3. Of the thermally fissile atoms ^{233}U has the highest $\sigma_f / \sigma_{n,\gamma}$ ratio, i.e. highest fission efficiency. The η-value is high enough to permit breeding in the thermal region. Capture of neutrons in ^{233}U is not a serious drawback as a second capture (in ^{234}U) yields fissile ^{235}U, but reduces the breeding gain because two neutrons are consumed without a net increase in fissile material. Since σ_{tot} increases with neutron energy (from ~ 7 b at 0.025 eV to ~ 26 b for reactor conditions; cf. also Fig. 19.3) the slightly harder neutron spectrum in PHWR and GCR make such reactors the prime candidates for a thorium-uranium fuel cycle together with the molten salt reactor (§20.3). The fuel may be arranged in a core (^{233}U) and blanket (^{232}Th) fashion, or mixed fissile and fertile material as, for example, in the HTGR prototype (High Temperature Gas-cooled Reactor) graphite matrix fuels, or as a metal fluoride melt. The initial ^{233}U must be produced from thorium in reactors fueled with ^{235}U (or ^{239}Pu) or in special accelerator driven devices. After sufficient amounts of ^{233}U have been produced, the Th-U fuel cycle may become self sustaining, i.e. thermal breeding is established.

The advantage of the Th-U fuel cycle is that it increases nuclear energy resources considerably because thorium is about three times more abundant on earth than uranium and almost as widely distributed. In combination with the uranium fuel cycle it could more than double the lifetime of the uranium resources by running the reactors at a high conversion rate (~ 1.0) and recycling the fuel. Very rich thorium minerals are more common than rich uranium minerals. The presence of extensive thorium ores has motivated some countries (e.g. India) to develop the Th-U fuel cycle.

No full-scale Th-U fuel cycle has yet been demonstrated and reprocessing has only been demonstrated on an experimental scale. The fuel cycle has to overcome the high activity problems due to the presence of ^{228}Th formed in the thorium fraction and ^{232}U formed in the uranium fraction (Fig. 20.3). The Th-U fuel cycle has a rather specific advantage over the U-Pu cycle in that its high active waste from reprocessing contains a much smaller amount of longlived heavy actinides, and thus constitutes a smaller long term hazard. With regard to nuclear weapons proliferation ^{233}U is almost as good a weapons material as ^{239}Pu and easier to produce as a single isotope by continuous withdrawal of protactinium, since it is the decay product of ^{233}Pa ($t_{1/2}$ 27 d), see also §21.7.

21.6. Reprocessing of uranium and mixed oxide fuels

The main purpose of commercial reprocessing is:

(1) to increase the available energy from fissile and fertile atoms;
(2) to reduce hazards and costs for handling the high level wastes.

Two other reasons are sometimes mentioned:

(3) to reduce the cost of the thermal reactor fuel cycle;
(4) to extract valuable byproducts from the high active waste.

The 30% savings in natural uranium for LWR and similar reactors and the hundredfold energy resource expansion for FBRs when reprocessing spent fuel, has already been discussed in the previous section. The economic advantage of reprocessing depends on the cost and availability of natural ("yellow cake") uranium, on enrichment and other front end activities, and on the prevailing energy price (mainly based on fossil fuels). At present, cheap uranium is abundant.

The reprocessing plants at La Hague, France, have a total capacity of ~ 1600 tons IHM/y, the Magnox reprocessing plant and the THORP (THermal Oxide Reprocessing Plant) at Sellafield, UK, have capacities of ~ 1500 and ~ 850 tons IHM/y, respectively. A commercial reprocessing plant under construction in Japan is designed to have a capacity of 800 tons IHM/y. In Siberia, a large russian reprocessing plant is under construction. A number of smaller, older plants are also in operation in several countries.

Figure 21.11 is a schematic representation of reprocessing of spent LWR fuel. The main steps are: (i) the *head end* section, in which the fuel is prepared for chemical separation; (ii) the main fractionation (partitioning) of U, Pu, and FP; (iii) purification of uranium ; (iv) purification of plutonium; (v) waste treatment; and (vi) recovery of chemicals. These steps are described in the following sections.

21.6.1. *Head end plant*

Figure 21.12 is a simplified drawing of one of the French oxide fuel head end plants at La Hague. The flasks with the used fuel assemblies are lifted by a crane into water-filled pits, where the flasks are unloaded and decontaminated. The assemblies are stored for a desired time and then transferred to a shielded dismantling and chopping section. Some BWR fuels have end parts, which can be mechanically dismantled; this is not the case for PWR fuels, in which the end parts have to be cut off. The fuel pins are cut into pieces 3–5 cm long, either under water or in air. At THORP, UK, and in the newest part of the La Hague plant, dry charging and chopping are used.

The chopping is usually achieved with a shearing knife (cutter), but other techniques for removing or opening up the zircaloy (or stainless steel) cans have been tried. Previously, chemical decanning was used at some plants, e.g. Hanford and Eurochemic, but such techniques increase the amounts of active waste considerably.

The chopped pieces are transferred to the dissolver unit, where the oxide fuel is leached by boiling in 6–11 M HNO_3 (the cladding hulls do not dissolve) in thick stainless steel

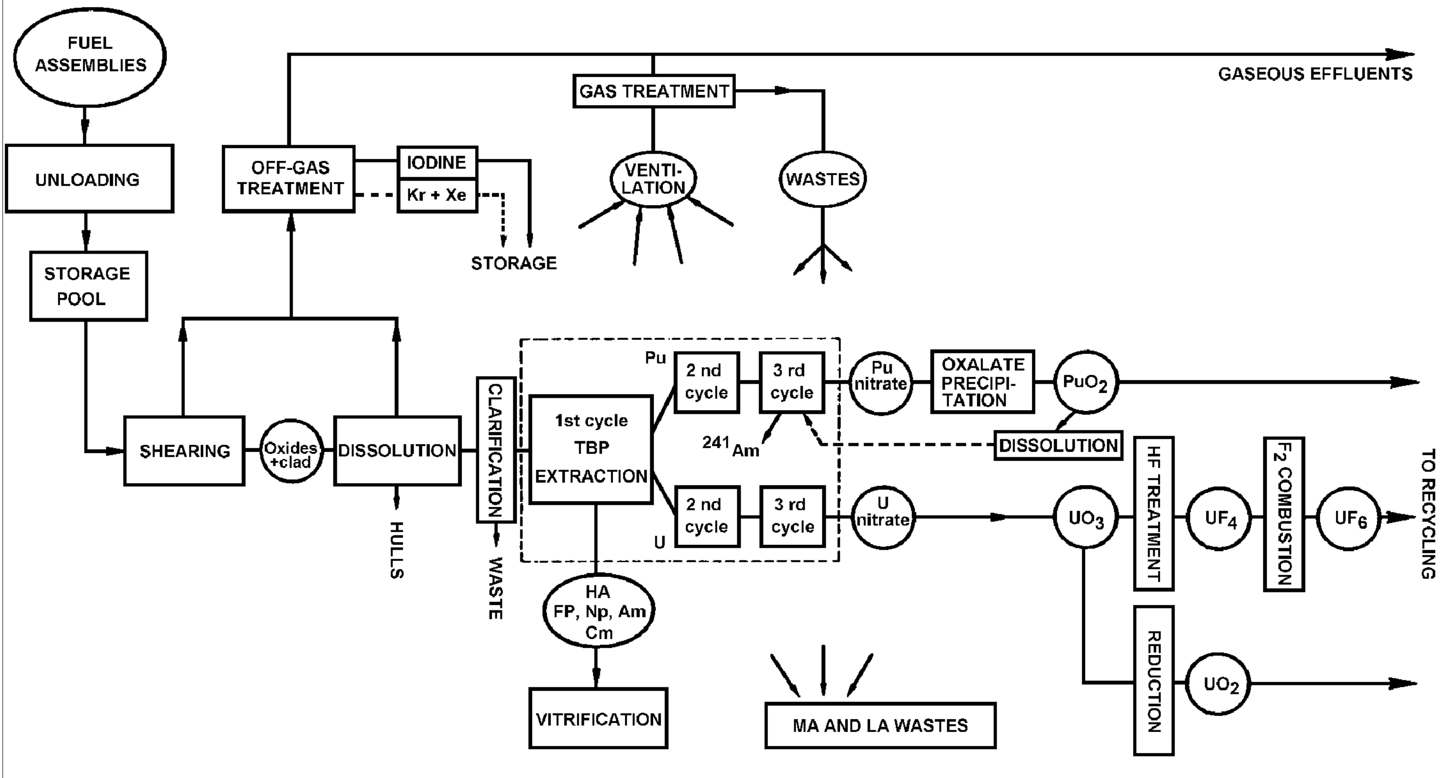

FIG. 21.11. Schematic representation of the reprocessing of spent LWR fuel (From Musikas and Schulz).

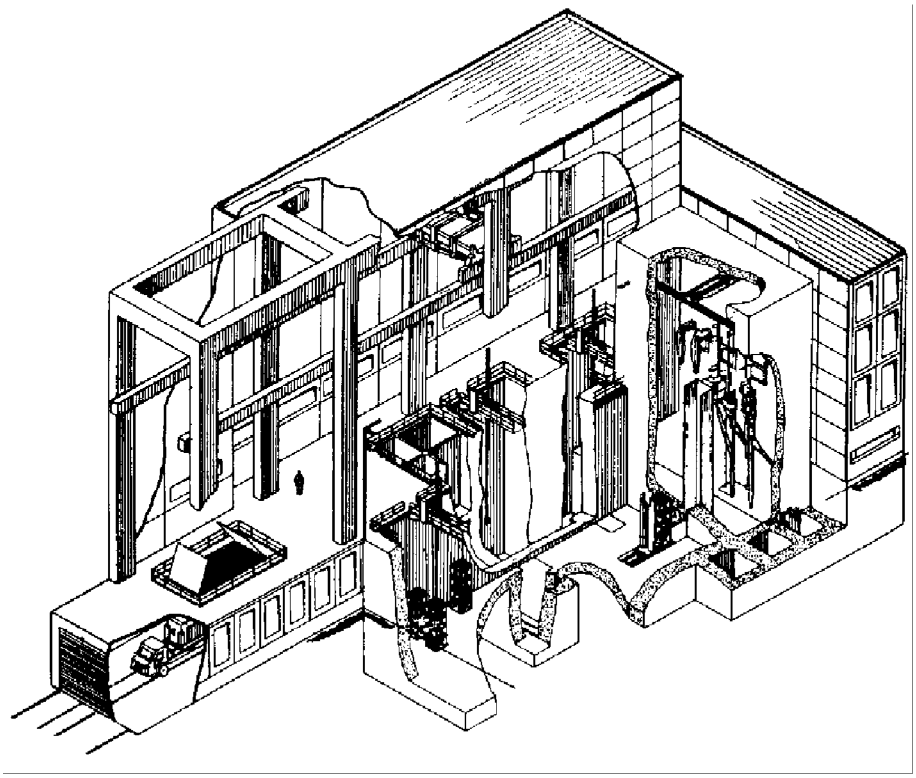

FIG. 21.12. Head end oxide fuel building at La Hague, France.

vessels provided with recirculation tubes and condenser. The hulls are measured for residual uranium or plutonium, and, if sufficiently clean of fissile material, are discharged to the waste treatment section of the plant. To improve the dissolution, some fluoride ($\leq$ 0.05 M AlF_3) may be added to the HNO_3. The F^- forms strong complexes with some metal ions such as zirconium, while its corrosion of the stainless steel equipment has been found to be negligible. Soluble poisons, such as cadmium or gadolinium nitrate, are often added to the nitric acid to assure the criticality control of the dissolution operation.

High burnup of fissile material leads to a high fission product content in the fuel elements resulting in the formation of seminoble metal fission product alloys, which are insoluble in boiling nitric acid. The insoluble material consists of mm sized metal particles of Ru, Rh, Tc, Mo, and Pd. These metal particles usually contain negligible amounts of uranium and plutonium and can be filtered as high level solid waste, HLSW.

When the fuel pins are cut, the volatile fission products contained in the gas space between the fuel oxide pellets and the canning is released (mainly ^{85}Kr, ^{3}H, ^{129}I, and ^{131}I). These gases are ducted to the dissolver off-gas treatment system. Gases released during dissolution are Kr, Xe, I_2, T_2, THO, RuO_4, CO_2, minor amounts of fission product aerosols, and large amounts of H_2O, HNO_3, and nitrogen oxides. Oxygen or air is fed into

TABLE 21.7. *Specifications for reprocessed uranium and plutonium* (From IAEA 1977)

Uranyl nitrate:
Uranium concentration 1–2 M
Free $HNO_3 \geq 1$ M
Impurities: Fe, Cr, Ni $\leq$ 500 ppm
Boron equivalents $\leq$ 8 ppm[†]
Fission products $\leq$ 19 MBq/kg U
α-activity (excluding uranium) $\leq$ 250 kBq/kg U

Plutonium nitrate:
Plutonium concentration ~ 1 M
Free HNO_3 2–10 M
Impurities: Metallic $\leq$ 5000 ppm
Uranium $\leq$ 5000 ppm
Boron equivalents $\leq$ 10 ppm
Sulfate $\leq$ 1000 ppm
Fission products ($t_{1/2} > 30$ d) $\leq$ 1.5 GBq/kg Pu[‡]
^{241}Am content (9 months after delivery to MOX-plant) $\leq$ 5000 ppm

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[†] The equivalent values are B 1.0, Cd 0.4, Gd 4.4, Fe 0.0007, etc. The amount measured for each of these elements multiplied by the factor indicated must not be more than 8 ppm.
[‡] ^{95}Zr–Nb $\leq$ 185 MBq/kg Pu.

the off-gas stream to allow recovery of part of the nitrogen oxides. The overall dissolution stoichiometry is

$$UO_2 + 2HNO_3 + \tfrac{1}{2}O_2 \rightarrow UO_2(NO_3)_2 + H_2O$$

The gas streams pass to a condenser which reclaims and returns some nitric acid to the dissolver. The noncondensibles are discharged to the off-gas treatment system.

When the dissolution is completed, the product solution is cooled and transferred to the input measurement–clarification (filter and/or centrifuge) feed adjustment unit. At this point the uranium is in the hexavalent state, and plutonium in the tetravalent.

21.6.2. *Separation methods*

The specifications for purified uranium and plutonium to be recycled are summarized in Table 21.7. Comparing these data with those presented before shows that at $t_{cool} \sim 1$ y the fission product activity must be reduced by a factor of $\sim 10^7$ and the uranium content in plutonium by a factor of $\sim 2 \times 10^4$. The large number of chemical elements involved (FPs, actinides *and* corrosion products) make the separation a difficult task. Additional complications arise from radiation decomposition and criticality risks and from the necessity to conduct all processes remotely in heavily shielded enclosures under extensive health protection measures. As a result reprocessing is one of the most complicated chemical processes ever endeavored on an industrial scale.

The problem encountered by the chemists of the Manhattan Project in the 1940's was the selection of satisfactory separation techniques. Advantage was taken of the relative stability of the oxidation state of uranium (+6) and most fission products, and the redox lability of plutonium (+3, +4, and +6). In the earliest process, only plutonium was isolated by precipitating plutonium in the reduced state as PuF_3 or PuF_4 together with all insoluble FP fluorides. This was followed by a second stage dissolving the precipitate, oxidizing plutonium to the +6 state, and a new fluoride precipitation, leaving relatively pure plutonium in the supernatant. In a final step plutonium was again reduced and precipitated as fluoride. This principle was used for the first isolation of hundreds of kilograms of plutonium at the Hanford Engineering Works, USA, with phosphate precipitation of Pu(+3) and Pu(+4), but not of Pu(+6) which does not form an insoluble phosphate. Since Bi^{3+} was used as a carrier for the precipitate, it is referred to as the *bismuth phosphate process*.

This principle of oxidizing and reducing plutonium at various stages of the purification scheme has been retained in all subsequent processes. No other element has the same set of redox *and* chemical properties as plutonium, though some elements behave as Pu^{3+} (e.g. the lanthanides), some like Pu^{4+} (e.g. zirconium) and some like PuO_2^{2+} (e.g. uranium). Numerous redox agents have been used, e.g. $K_2Cr_2O_7$ (to PuO_2^{2+}), $NaNO_2$ (to Pu^{4+}), hydrazine, ferrous sulfamate, and U^{4+} (to Pu^{3+}), cf. §16.3.

The precipitation technique is not suitable for large-scale, continuous remote operations in which both uranium and plutonium have to be isolated in a very pure state from the fission products. It was therefore replaced in the late 1940's by *solvent extraction* in which the fuels were dissolved in nitric acid and contacted with an organic solvent which selectively extracted the desired elements. The technique has been mentioned in §§9.2.6, 9.4.3 and 16.3.3 but is described in more detail in Appendix A.

The first solvent to be adopted at Hanford was methylisobutylketone ("MIBK" or "Hexone"). This solvent forms *adduct compounds* with coordinatively unsaturated compounds like the actinide nitrates, e.g. $Pu(NO_3)_4S_2$, where S represents the adduct molecule

$$Pu^{4+} + 4NO_3^- + 2S(org) \rightarrow Pu(NO_3)_4S_2(org)$$

The corresponding adduct compounds for 3- and 6-valent actinides are $An(NO_3)_3S_3$ and $AnO_2(NO_3)_2S_2$. These chemically saturated neutral compounds are soluble to different extent in organic solvents like kerosene, and – in the case of hexone – by hexone itself. The process using hexone is referred to as the *Redox process*.

In the United Kingdom, β,β'-dibutoxydiethylether ("dibutyl carbitol" or "Butex") was selected as organic solvent; it forms the same kind of adduct compounds as hexone. Though more expensive, it was more stable, less flammable and gave better separations.

Many other similar solvent systems, as well as *chelating agents*, have been tested. Thenoyltrifluoroacetone (HTTA) was found to form strong complexes with the actinides (e.g. $Pu(TTA)_4$, $UO_2(TTA)_2$), which show very high distribution ratios in favor of organic solvents. Though useful in the laboratory they were not found suitable for large scale commercial nuclear fuel reprocessing. One of the most useful recent extraction agents for actinide separation is di-2-ethylhexylphosphoric acid (HDEHP) which has found several industrial uses outside the nuclear energy industry, e.g. separation of rare earth elements.

A drawback of hexone and butex is the need to use salting-out agents (salts like $Al(NO_3)_3$ added to the aqueous phase) in order to obtain sufficiently high extraction factors. Such salt additions increase the liquid waste volumes. Further, hexone was unstable at high nitric acid concentrations. All this led to the search for a better extractant.

Presently, tributyl phosphate (TBP) is the extractant in all reprocessing plants. It acts as an adduct former and is normally used as a 30% solution in kerosene. It forms the basis for the *Purex process* (Plutonium Uranium Redox EXtraction). TBP is cheaper than Butex, more stable, less flammable, and gives better separations.

Other extractants, especially tertiary amines, have been tested for some steps in reprocessing. The amines form organic soluble complexes with negatively charged metal complexes (used in uranium purification, §5.5.3). The use in the basic Purex cycle of a secondary extractive reagent can improve the decontamination factor[1].

As alternatives to the aqueous separation processes, "dry" techniques have also been studied, but none has been used on an industrial scale. Examples are the following:

(a) *Halide volatility*. Many FP and the high valency actinides have appreciable vapor pressures; this is particularly true for the fluorides. In *fluoride volatilization* the fuel elements are dissolved in a molten fluoride salt eutectic ($NaF + LiF + ZrF_4$, 450°C) in the presence of HF. The salt melt is heated in F_2, leading to the formation of UF_6, which is distilled; it may be possible also to distill PuF_6, though it is much less stable. The process has encountered several technical difficulties.

(b) *Molten salt extraction*. The fuel is dissolved as above or in another salt melt. With a heat resistant solvent of low volatility (e.g. 100% TBP), actinides and FP distribute themselves between the two phases analogous to solvent extraction. This technique is of interest for continuous reprocessing of molten salt reactor fuel or partitioning in an accelerator driven transmuter (§20.3.1). An advantage is the higher radiation resistance of the nonaqueous system.

(c) *Molten salt transport*. The fuel is dissolved in a metallic melt, e.g. a molten Cu-Mg alloy, which is in contact through a stirred molten chloride salt at about 800°C with another metallic melt containing a reductant, e.g. a molten Zn-Mg alloy. Noble metal FPs are retained in the Cu-containing melt, whereas U and/or Pu is collected in the Zn-containing melt. The less noble FPs concentrate in the molten salt.

(d) *Molten salt electrorefining*. The spent fuel acts anode in a molten salt also containg a pure metal cathode. By applying an electric field between the anode and cathode, material is dissolved at the anode and deposited at the cathode. Careful control of the applied potential makes it possible to obtain an extremely pure cathode product. The process was initially developed for purification of plutonium metal alloys proposed as fuel for the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE).

(e) *Molten metal purification*. Metallic fuel elements can be molten and/or dissolved in molten metals (e.g. a zinc alloy). In the presence of (deficient amounts of) oxygen, strongly electropositive fission elements form oxides, which float to the surface of the melt as slag and can thus be removed, while volatile FPs distill. The residual melt would mainly contain U, Pu, Zr, Nb, Mo, and Ru ("fissium alloy") and can be reused in new fuel elements. This melt refining technique has been tested on metallic breeder reactor fuel elements. Molten chlorides have also been used to remove americium from molten plutonium metal scrap.

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[1] The decontamination factor is defined as (concentration before separation)/(concentration after separation).

21.6.3. *Purex separation scheme*

The distribution of uranium, plutonium, and some FPs between 30% TBP (in kerosene) and aqueous solutions of varying HNO_3 concentration is shown in Figure 16.8. D_{Sr} and D_{Cs} are $\ll 0.01$ for all HNO_3 concentrations. The distribution of the trivalent lanthanides and actinides fall within the Eu-Am area. Many fission products (most I, II, III, V, and VII-valent species) are not extracted, i.e. $D \leq 0.01$; see §16.3.3 and Appendix A. Thus at high HNO_3 concentration Pu(IV), Pu(VI), and U(VI) are extracted but very little of the FPs. At low HNO_3 concentration the *D*-value for actinides of all valency states is $\ll 1$, and consequently the tetra- and hexavalent actinides are stripped from the organic phase by dilute HNO_3. This chemistry is the basis for the Purex process.

The Purex process is presented schematically in Figure 21.11, where the solvent extraction steps are within the dotted frame. Three purification cycles for both uranium and plutonium are shown. High levels of beta and gamma activity is present only in the first cycle, in which > 99% of the fission products are separated. The principle of the first cycle is shown in Fig. 21.13. The two other cycles are based upon the same chemical reactions as in the first cycle; the purpose is to obtain additional decontamination and overall purity of the uranium and plutonium products. Each square in Figure 21.13 indicates a number of solvent extraction stages of the particular equipment used: pulsed columns, mixer-settlers, etc. (see Appendix A).

In the first cycle > 99.8% U and Pu (in VI and IV state, respectively) are co-extracted from 3-4 M HNO_3 into the kerosene-TBP phase, leaving > 99% of the FP in the aqueous raffinate. In the *partitioning* stage, plutonium is reduced to the III state by a solution containing a suitable reductant, e.g. U(IV) nitrate or Fe(II) sulfamate; the plutonium is stripped to a new aqueous phase and transferred to the plutonium purification section. Uranium, which as U(VI) (and U(IV)) stays in the organic phase, is stripped by dilute HNO_3 in a third stage. After concentration by evaporation it is sent to the uranium purification section.

The uranium purification contains two extraction-stripping stages. Plutonium tracers are removed by a reducing agent, e.g. U(IV):

$$U^{4+} + 2Pu^{4+} + 2H_2O \rightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+$$

U(IV) is preferred over Fe(II)-sulfamate in some plants as it avoids the introduction of foreign substances. The final, concentrated uranium solution may be percolated through a column filled with silica gel, which removes residual FP, particularly Zr-Nb.

The plutonium purification may be achieved by additional TBP extraction cycles. U(IV) cannot be used as reductant in this part of the process. The final uranium and plutonium products are nitrate solutions whose conversion to oxides, fluorides, etc., have been described earlier (§5.5.3).

The chemical problems encountered in the solvent extraction are:

(i) The choice of diluent: A mixture of aliphatic hydrocarbons, and occasionally pure dodecane, are most common; improper choice of diluent may lead to formation of a third liquid phase, slow extraction kinetics, difficult phase disengagement (i.e. separation of the organic and aqueous phases in the extraction equipment), etc.

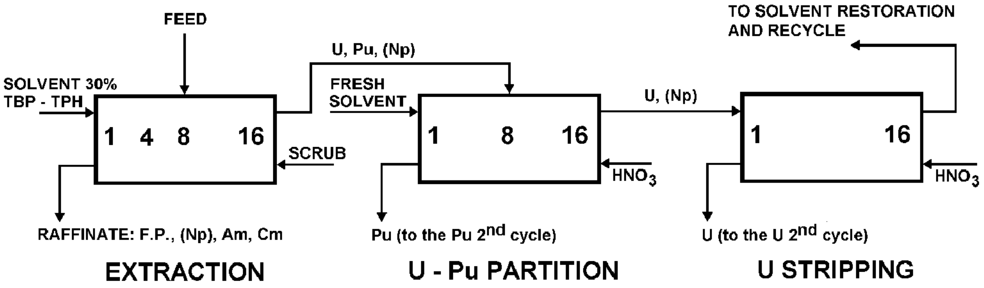


FIG. 21.13. Flowsheet of the first purification cycle in the Purex process; TPH, tetrapropylene, is a commercial dodecane. (From Musikas and Schulz.)

(ii) The choice of reductant for the reaction Pu(IV) → Pu(III): The use of U(IV) as reductant for Pu(IV) introduces new uranium in the streams; Fe(II) sulfamate ($Fe(SO_3NH_2)_2$) adds objectionable inorganic salts to the aqueous high level waste; hydroxylamine (NH_2OH) is a kinetically slow-reducing agent; electrolytic reduction of Pu(IV) to Pu(III) is lacking experience.

(iii) Solvent degradation: Radiation decomposes TBP into lower phosphates and butyl alcohol. The main products are dibutyl phosphate (DBP, $(BuO)_2POOH$) and monobutyl phosphate (MBP, $BuOPO(OH)_2$) which form strong complexes with many of the fission products as well as plutonium. As these radiolysis products are formed the decontamination efficiency decreases and losses of fissile material to the aqueous waste streams increase. The solvent is treated to remove the degradation products prior to recycle in the process, e.g. by washing the TBP solution successively with Na_2CO_3, NaOH, and dilute acid solutions.

To reduce some of these difficulties and to generally improve the efficiency of the U and Pu extraction (leaving a waste almost free of these elements) as well as the decontamination factors, other extractants than TBP have been suggested, for example dialkylamides, R-CON-R'$_2$ where R may be C_3H_7 and R' is $CH_2CHC_2H_5C_4H_9$, "DOBA". The advantages of this type and other proposed alternatives to TBP are that they are completely incinerable (while TBP leaves a phosphate waste), the radiolytic products are not deleterious for the process performance, and that no reducing agent is necessary to partition uranium and plutonium. Finally, the ash from combustion could be leached and its content of actinides recovered and returned to the process - further reducing the content of these elements in intermediate level waste.

During the decontamination steps, acid streams containing small amounts of actinides and fission products are produced. These streams are evaporated to concentrate the metal ions and recycle them. Nitric acid is recovered from the condensates and recycled. Excess HNO_3 may be destroyed by formaldehyde. Fission product concentrates are routed to the aqueous raffinate of the first extractor of the partitioning cycle which contains > 99% of the FP. This constitutes the *high level liquid waste* (HLLW, or alternatively called HAW, *high active waste*). All other liquid wastes can be subdivided into *intermediate level waste*

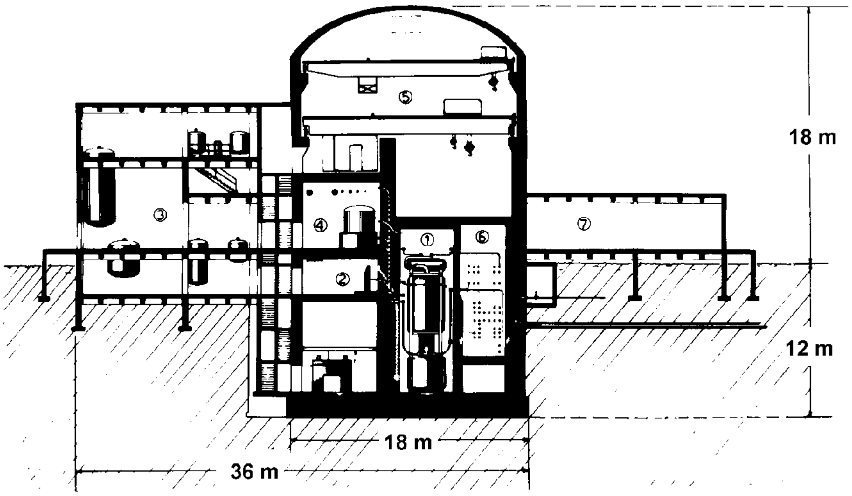


FIG. 21.14. Principle of a reprocessing plant with remote maintenance. 1, canyon with process equipment; 2, control room; 3, feed preparations; 4, feed input; 5, cranes; 6, piping; 7, analytical section.

(ILW or MLW) or *low level waste* (LLW). It is an important goal in all reprocessing operations to reduce the amount of intermediate and low level waste streams as far as possible and to route most of what remains to the HLLW stream. Waste treatment is discussed in §21.8 ff.

21.6.4. *Engineering aspects and operation safety*

All operations in a reprocessing plant have to cope with the necessity of preventing nuclear criticality and of protecting operations personnel and the environment from exposure to or contamination by radioactivity. Thus all equipment has dimensions which are safe against criticality, as, for example, annular or pipe shaped tanks for liquid storage instead of conventional tanks, or are provided with neutron absorbers. All equipment is made of stainless steel and is installed in concrete cells with wall thicknesses up to 2 m at the head end, partitioning, and waste treatment sections. All operations are carried out in airtight enclosures at reduced pressure relative to working areas.

In the event of failure of equipment within a radioactive area, three courses of action may be taken: (i) switching to duplicate equipment, (ii) replacing or repairing equipment by remote methods; *remote maintenance*, or (iii) repairing by *direct maintenance* after decontamination.

Plants were originally constructed for either completely remote maintenance or completely direct maintenance. Figure 21.14 illustrates the principle of a plant for remote maintenance. All equipment is installed in a large canyon with piping in a parallel corridor. The equipment can be replaced by an overhead crane operated from a shielded room;

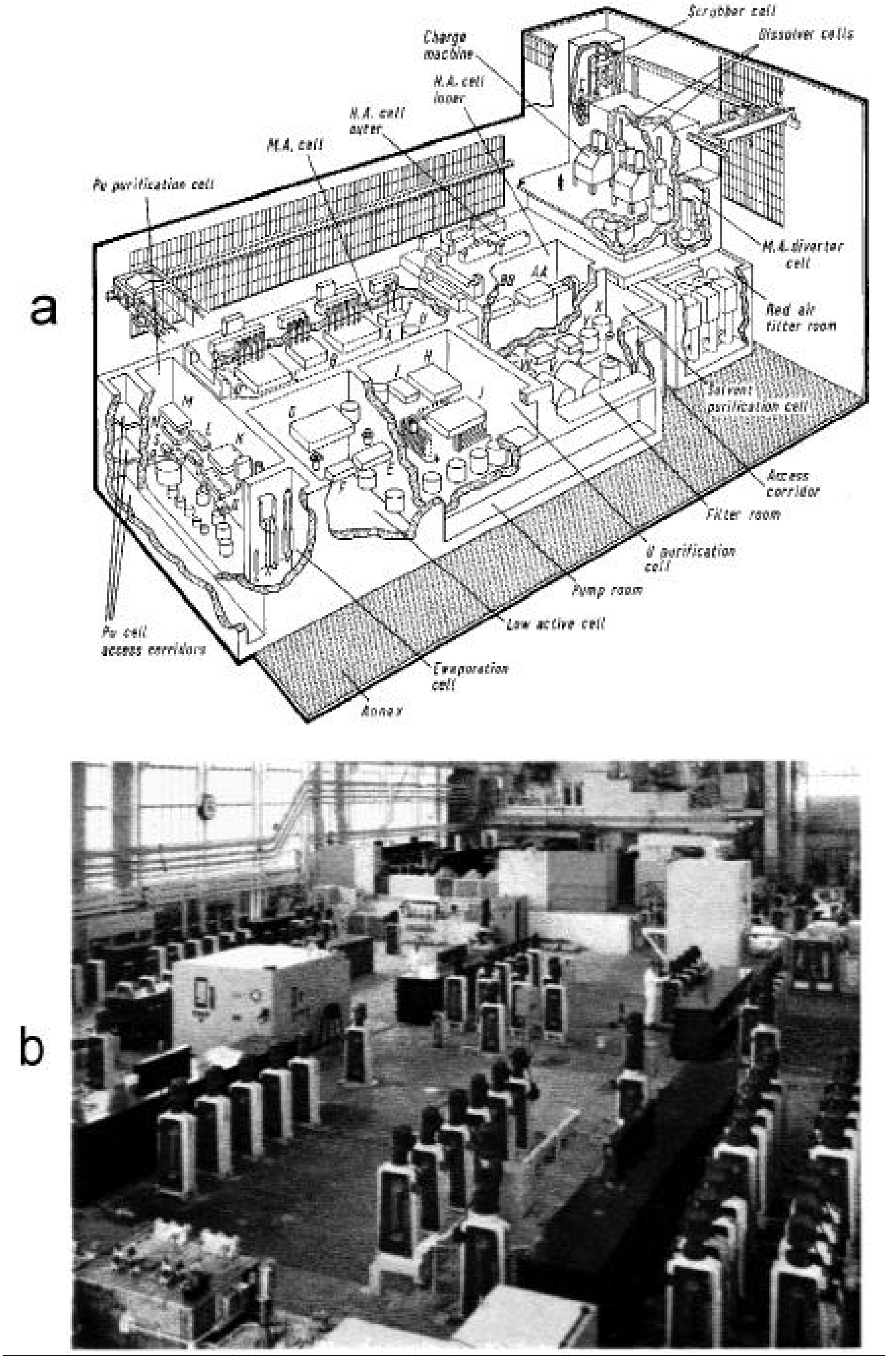


FIG. 21.15. (a) General layout of BNFL Magnox reprocessing plant at Sellafield, UK. (b) Cell top of primary separation plant showing stirrer motors for mixer-settlers below.

malfunctioning equipment could be transferred to a decontamination and repair unit or to an equipment "grave". With this philosophy conventional type chemical plant equipment can be used, though redesigned for the remote replacement. Of particular importance in such plants are good joints for piping, electricity, etc., for remote connection.

The British Nuclear Fuels Plc. (BNFL) Magnox and THORP plants at Sellafield, UK, are designed for no maintenance, which in practice might mean either direct maintenance or remote maintenance; Fig. 21.15. All kinds of common reasons for failure in chemical plants have been eliminated or minimized by using welded joints and no moving parts. Thus there are no leaking fittings, frozen valves, or stuck pumps. All welding is carefully controlled by ultrasound or radiography. Active liquids are transported by gas (usually steam) jets or lifts, or by vacuum. Liquid levels and volumes are measured by differential pressure gages and by weighing. Samples for analysis are remotely withdrawn and analyzed in shielded boxes or glove boxes depending on their activity outside the enclosure.

Even such systems may fail and dual equipment is therefore sometimes installed in parallel cells. With the process running on the spare equipment, the failing equipment must be repaired. This requires efficient decontamination both on inside and outside of the equipment, provisions for which must be incorporated in the original design. This design requires dividing the plant in a large number of cells so that the repair workers are protected from the radiation of the functioning plant.

Remote maintenance is more expensive, but may be safer for the personnel and desirable from the standpoint of continuity of operations because equipment replacements can be carried out quickly and interruption of operation is relatively brief. Modern robot technology simplifies such remote maintenance.

21.7. Reprocessing of thorium fuels

The thorium-containing fuels of present interest are only those of the kind used in HTGR and HWR; in the future fuel from MSR-like (or other) transmutation devices may become important. In the HTGR fuel elements the fertile ThO_2 and fissile $^{235}UO_2$ (or $^{233}UO_2$) particles are coated differently and embedded in a graphite matrix.

In case of the HTGR, the spent graphite fuel elements are mechanically crushed and burned to eliminate the graphite matrix and pyrolytic carbon coating from the fuel particles. Leaching permits separation of the fissile and the fertile particles because the fissile particles have a silicon carbide coating which remains intact during burning and leaching, while the all-pyrolytic carbon coatings on the fertile particles are burned away, allowing the oxide ash to be dissolved by a leach solution, consisting of HNO_3 and F^-. The solution is clarified and adjusted to proper acidity for solvent extraction (paragraph (i) below). The undissolved residue resulting from clarification is dried and classified for further treatment (paragraph (ii) below). The burner off-gas streams are passed through several stages of filtration, scrubbing, and chemical reaction to remove the entrained and volatile fission products, as well as ^{14}C containing CO_2, prior to atmospheric discharge.

In case of oxide fuel, it has to be cut and dissolved in a way similar to that described for uranium fuels.

(i) The *acid Thorex solvent extraction process* is used to purify and to separate the ^{233}U and the thorium. Three solvent extraction cycles are used. In the first, the uranium and thorium are coextracted by 30% tributyl phosphate (TBP) from ~ 5 M HNO_3 and then stripped into an aqueous phase. In the second cycle, the uranium and thorium are separated by controlling the extraction conditions using ≤ 1 M HNO_3. The uranium is extracted and processed by an additional solvent extraction cycle for final purification, while the thorium remains in the aqueous raffinate stream. Following concentration and assay, the uranium is ready for fuel refabrication. The partially decontaminated thorium is concentrated and stored.

(ii) The separated silicon-carbide coated fissile particles from the head end process for HTGR fuel are mechanically crushed to expose the fuel and are burned to remove carbon and oxidize the fuel material: the ash is leached to separate the fuel and fission products from the coating waste. The ^{235}U is separated from the fission products by solvent extraction using a Purex flowsheet. An organic solvent containing only 3-5% TBP is used in order to avoid criticality problems. A reductant such as Fe(II) sulfamate is added to the feed in order to force the small amount of plutonium present into the aqueous raffinate stream. The waste streams are treated as in the Purex process.

The process is plagued by both chemical and nuclear difficulties. The decay chain ^{233}Th → ^{233}U forms 27 d half-life ^{233}Pa. For a complete decay of all ^{233}Pa to ^{233}U, the spent fuel elements must be cooled for about a year. A still considerable amount of longlived ^{231}Pa is present in the spent fuel (about 1/2000 of the amount of ^{233}U); protactinium complicates the reprocessing chemistry and constitutes an important waste hazard.

The ^{233}U isolated contains some ^{232}U formed through reactions indicated in Figure 20.3. Since the half-life of ^{232}U is rather short and its decay products even shorter lived, a considerable γ-activity will grow in with the ^{233}U stock, complicating its handling. Since the first decay product is ^{228}Th, some ^{228}Th forms in the fuel elements, making the ^{232}Th contaminated by this isotope. Thus neither the ^{233}U nor the ^{232}Th produced can be free from γ-activity.

21.8. Wastes streams from reprocessing

Fuel reprocessing generates a large variety of wastes which can be classified in categories according to activity (low, medium and high), physical state (gas, liquid or solid package), or decay characteristics (shortlived, longlived), each treated separately. The amounts of different categories are given in Table 21.8; these wastes are treated internally at the plant and not released to the environment. Because reprocessing plants vary considerably the amounts of wastes produced also differs, especially for the liquid medium and low level categories. In this section we briefly discuss the various waste streams appearing at the plant and the treatment methods.

21.8.1. *Gaseous wastes*

Gaseous wastes originate mainly from the chopping and dissolution operations. In current practice the volatile radionuclides are discharged to the stack after scrubbing with sodium hydroxide and filtration through a special zeolite or charcoal filter. The hydroxide scrubbing removes the acidic nitrous oxides which pass through the recombination unit above the

TABLE 21.8. *Typical annual amounts of waste arising in a reprocessing plant (per t IHM and 3 years cooling time)*

Type	Form	Volume (m^3)	β,γ-activity (TBq)	Pu-content (kg)
HLLW	liquid	5	10^5	~ 0.05
MLLW	liquid	5		
LLLW	liquid	100		
HLLW	conc. liquid	0.5	10^5	0.05
Fission products	glass	0.15	10^5	0.05
Hulls	concrete	0.8	400	0.01
Ion/exch., precip.	bitumen	0.8	~ 100	0.008
Iodine	concrete	0.03	< 0.01	–
ML and LL α	solid	0.1		
Technical waste	concrete	3.2	~ 0.5	~ 0.01

dissolver. The silver impregnated zeolite or charcoal removes remaining traces of iodine.

The most hazardous volatile constituents are the iodine and ruthenium fission products. Though more than 95% of the iodine is volatilized in the dissolver (as I_2, HI and HIO mainly) most of it is caught in the off-gas scrubber and most of what remains is removed by the filters. With these techniques the retention of iodine in the plant is > 99.5%.

Ruthenium forms volatile RuO_4 in the dissolver. Almost all RuO_4 is retained in the gas purification system. As an additional feature some plants use a steel wool filter (after the nitric acid recombination) to catch the RuO_4.

Of the noble gases, radioactive xenon has completely decayed after 1 y cooling, but krypton contains ^{85}Kr with 10.7 y half-life. This isotope is produced in appreciable amounts, and though commonly it has been released to the atmosphere, this is no longer acceptable. Many processes have been devised for krypton removal. Krypton in dry, clean air is effectively trapped on a charcoal filter at cryogenic temperature; however, because of explosion risk (due to reaction between radiolytically formed ozone and carbon), the favored process is condensation by liquid N_2 (krypton boils at $-153°C$) followed by fractional distillation. This removes > 99% of ^{85}Kr. The krypton can be stored in pressurized cylinders until ^{85}Kr has decayed (> 100 years).

The amount of tritium released in reprocessing is considerable. In the chopping section it is released as T_2, but as HTO in the dissolver, where > 90% of all tritium formed is present. While T_2 can be caught (particularly if chopping is done in air), a recovery of the HTO formed in the dissolver would be expensive. Where it cannot be released to the environment the tritium can be trapped. In one process, called Voloxidation, the chopped fuel elements are treated with oxygen at 450-700°C before dissolution. Tritiated water is generated which should be relatively free of ordinary water and consequently occupy a much smaller volume than tritiated wastes do in present plants. Voloxidation may collect ~ 99% of the tritium present in unprocessed fuel. Even when all tritium is released to the environment, some precautions against its spreading in the plant are usually necessary in order to reduce the dose to operators. By proper design of the first extraction cycle most of the tritium can be confined to this part of the plant.

TABLE 21.9. *Composition of HLLW waste from Purex reprocessing of 1 t IHM LWR fuel with a burnup of 33 000 MWd/t IHM and a cooling time of 3 years.*

Component		Weight (kg) in original waste volume (~ 5 m^3)	Approx. molarity in 0.5 m^3 concentrate
H^+		1.4	~ 1.0
NO_3^-		900	~ 2.4
Fission products:	Group I (Rb, Cs)	2.94	0.046
	Group II (Sr, Ba)	2.37	0.041
	Group III (Y, Ln)	10.31	0.15
	Zr	3.54	0.076
	Mo	3.32	0.068
	Tc	0.77	0.016
	Group VIII (Ru, Rh, Pd)	4.02	0.078
	Te	0.48	0.0075
	Others	0.35	0.004
	Total fission products	28.1	0.487
Corrosion products:	Fe	1.1	0.04
	Cr	0.2	0.008
	Ni	0.1	0.003
	Total corrosion products	1.4	0.051
Phosphate (from TBP)		0.9	0.02
Actinides:	U (~ 0.5%)	4.8	0.040
	Np (~ 100%)	~ 0.44	0.0037
	Pu (~ 0.2%)	~ 0.018	0.00015
	Am (100%)	~ 0.28	0.0023
	Cm (100%)	~ 0.017	0.00014
	Total actinides	5.5	0.047
Neutron poison (e.g. Gd)		12	0.15

^{14}C is formed through the $^{14}N(n,p)^{14}C$ reaction in the nitrogen contained in the fuel elements. It is released mainly as CO_2 at the dissolution. Though only a small amount is formed (~ 40 GBq/GW$_e$y for each ppm nitrogen in the fuel), its release to the environment, makes it the dominating dose commitment of the fuel cycle back end (from reprocessing in 1989, 97 manSv from ^{14}C, and 98 manSv from all other nuclides). Presently $^{14}CO_2$ is released to the atmosphere, but techniques for its retention are available. It will probably finally be caught as $CaCO_3$, with a retention of ~ 80%.

21.8.2. *Liquid wastes*

The high level liquid Purex waste (HLLW) contains typically > 99.5% of the FPs, < 0.5% of the U and < 0.2% of the Pu present in the fuel as ~ 1 M HNO_3 solution, see Table 21.9. It is pumped to storage tanks as discussed further in §21.10. Total actual Pu losses during reprocessing is presently ≤ 0.2% of the feed.

The medium level liquid waste (MLLW) results essentially from evaporating various streams from the chemical process, such as solvent clean-up, off-gas scrubbers, product concentration, etc; Table 21.8. It may contain up to 0.5% of the uranium and up to 0.2%

of the plutonium processed. The radioactivity is usually < 40 GBq/l (an average value is 4 GBq/l). The solutions also contain appreciable amounts of solids (e.g. $NaNO_3$, iron, etc.). The waste may be neutralized and is stored in steel tanks at the reprocessing site.

Liquid waste is generated in numerous places with activities < 0.1 GBq/ m^3. Such waste is classified as low level. Some of these liquids may be clean enough to be released directly into the environment. Others are cleaned by flocculation, ion exchange, sorption, and similar processes. The general philosophy for liquid wastes is to concentrate all radioactivity to the next higher level because the waste volumes decrease in the order LLLW > MLLW > HLLW. Thus, in principle, the three kinds of wastes are reduced to two (HLLW and MLLW) and cleaned aqueous effluent. The MLLW and residues from LLLW cleaning are treated as the wastes of the nuclear power stations, i.e. concentrated and put into a disposal matrix such as concrete or bitumen (see §20.4.3). At some coastal sites it has been the practice to release the LLLW to the sea, with official permission. The nuclides of main concern are ^{3}H, ^{90}Sr, ^{137}Cs, ^{106}Ru, and the actinides.

21.8.3. *Organic wastes*

The liquid organic waste consists of spent TBP diluent mixtures originating from the organic solvent clean-up circuits and from the diluent (kerosene) washings of the aqueous streams (to remove entrained solvent); in addition to degradation products of TBP and the diluent it contains small amounts of actinides (mainly U and Pu) and FP (mainly Ru, Zr, and Nb).

This type of waste is disposed of by incineration or decomposed by hydrolysis and pyrolysis leading to the formation of inactive hydrocarbons, which are distilled, and active phosphoric acid, which is treated together with other aqueous wastes.

21.8.4. *Solid wastes*

High level solid waste (HLSW) originates at the dissolver. The hulls from the dissolution contain activation products and small amounts of undissolved fuel ($\leq$0.1%). The dissolver solution contains finely divided particles of undissolved seminoble metal alloys (Ru, Rh, Mo, Pd, etc.). This suspension is treated by filtering or centrifugation prior to the solvent extraction. Past practice in the USA and the USSR has been to put the HLSW in shielded containers which are transported to and stored at a dry disposal site. In the future the same disposal is expected to be used for the HLSW as for the solidified HLLW (§21.12).

Medium and low level solid wastes are produced at numerous places. They are divided in various ways: combustible, noncombustible, α-bearing, non-α-bearing, etc., and treated independently, when possible, to reduce volume. The wastes are then fixed in the disposal matrix (§20.4.3). Table 21.8 gives the relative amounts of solid waste produced in reprocessing. The final deposition of these wastes is further discussed in §21.13.

TABLE 21.10. *Annual releases to the environment from some reprocessing plants*

Source		Half-life (y)	Sellafield[†] (TBq)	Purex[‡] (TBq/GW$_e$y)
^{3}H	airborne	12.33	222	41
	liquid		1050	643
^{14}C	airborne	5730	4.1	2.0
	liquid			0.54
^{85}Kr	airborne	10.72	26000	12300
^{90}Sr		28.5	600	11
^{95}Nb		0.0958	150	
^{95}Zr		0.175	150	
^{99}Tc		2.13×10^{5}	180	
^{106}Ru		1.02	810	39
^{129}I	airborne	1.57×10^{7}		0.006
	liquid		0.074	39
^{131}I	airborne	0.022		0.0007
	liquid			0.032
^{137}Cs	airborne	30.0		0.002
	liquid		4090	13
^{144}Ce		0.781	100	
^{241}Pu		14.4	1800	
U			11000 (kg)	

[†] Releases in 1978 only; 1.8 GW$_e$ produced from fuel reprocessed. [‡] Average for 3 plants normalized to 1985-1989; La Hague, France, Sellafield, UK, and Toka-Mura, Japan. (From UNSCEAR 1993.)

21.8.5. *Environmental releases from reprocessing plants*

As described in §21.8.1 relatively large amounts of radioactive gases with a low hazard index (^{3}H, ^{14}C and ^{85}Kr) are released to the environment, see Table 21.10. Other large non-gaseous activities are contained within the plant, but small releases occur to the environment according to limits set by the regulating authorities. These releases were rather large in earlier days, but have been considerably reduced as improved procedures and equipment are coming into operation, see Table 21.10. The authorized releases in the UK in 1978 were 10^{4} TBq β-emitters (excl. T) per year. The ^{137}Cs release produced ~ 1000 Bq/l water in the middle of the Irish Sea (~ 150 km SW Windscale), and could be traced as far away as in the Baltic Sea. The release into the Atlantic in 1978 was $\leq$10 000 TBq. Not counting releases from plants in the US, USSR and India, it is assumed to be < 1000 TBq in 1992. It should be noted that the release of radionuclides into the sea from nuclear power operations is dominated by the effluents from a few reprocessing plants. It is, however, only a small fraction of the natural radioactivity in the oceans.

21.9. Treatment and deposition of low and medium level wastes

It has become a common practice at reprocessing plants to store low level solid waste (and sometimes higher level wastes) in trenches dug from the soil. These trenches, which

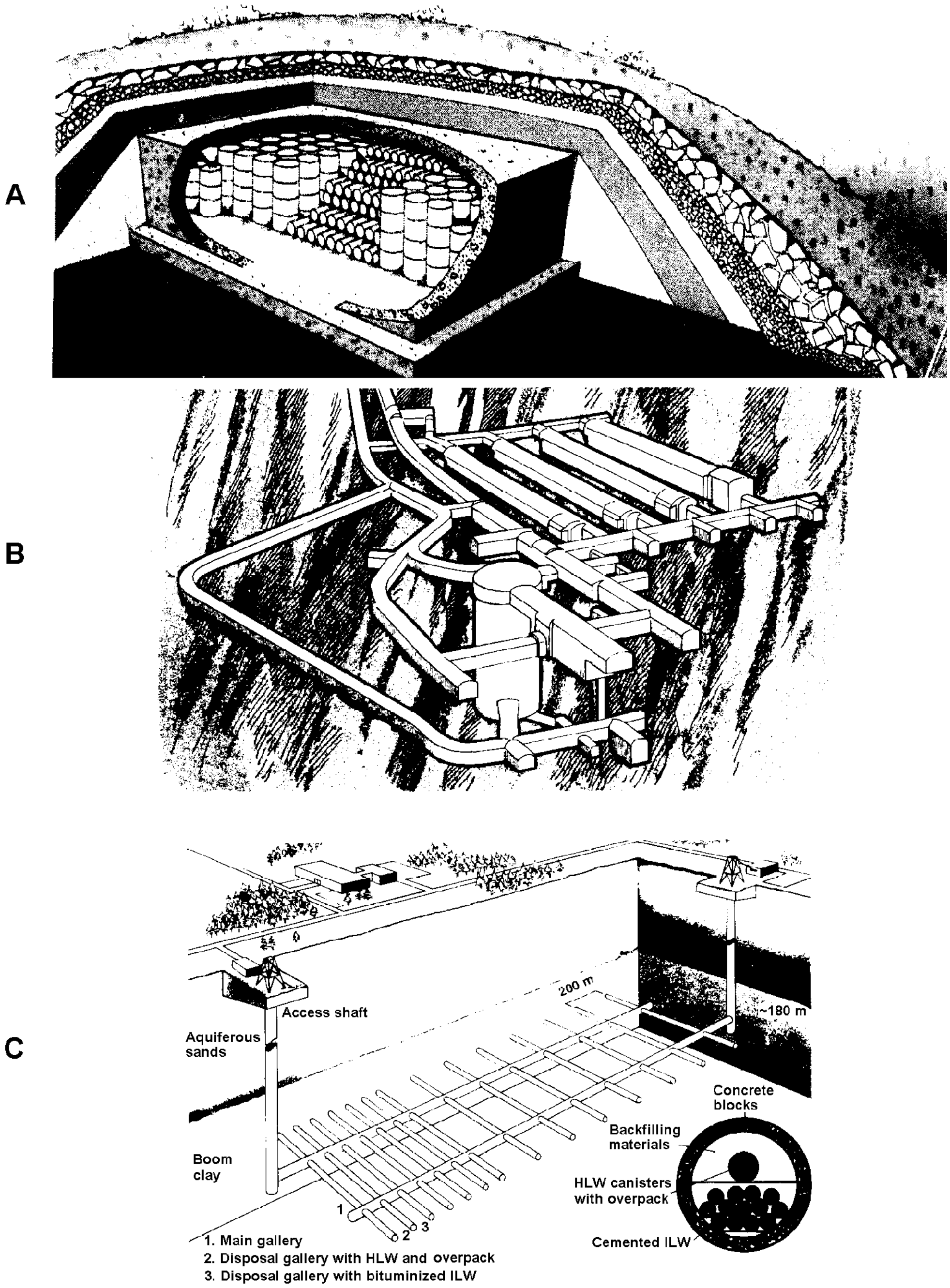


FIG. 21.16. (A) Storage of solid LLW (La Hague, France); (B) Storage of LLW and ILW (Forsmark, Sweden); (C) Suggested repository for solid ILW and HLW (Belgium).

commonly are 5-8 m deep, are sometimes lined with concrete or simply have a gravel bottom. For this purpose dry areas are selected (deserts, when available) or isolated areas with controlled groundwater conditions with respect to water table depth, flow rate, and direction. The disposed material normally should not exceed a dose rate of 1 mGy h^{-1} at 0.3 m distance, or contain a specific activity exceeding 1 MBq kg^{-1}. However, this varies, and may be a factor of 10 higher or lower in some places. When the trench is full, it is backfilled with earth, after which the surface dose rate usually is < 0.01 mGy h^{-1}. Trenches of this kind are used in the USA, the UK, France, Russia, etc., where tens of thousands of cubic meters have been disposed annually; Fig. 21.16(A).

Since some of the waste products are longlived, and the physical protection of the waste in surface trenches is poor, radioactivity may ultimately leak into the groundwater, see Ch. 22. Therefore, in many countries repositories for final deposition of solid intermediate and low level wastes have been or are being built. The Swedish repository at Forsmark for ILW and LLW from reactors, hospitals, research facilities, etc. has been in operation since 1988; Fig. 21.16(B). It is located in solid granite rock below 50 m of sea water at the Baltic Sea coast. This underground site contains large concrete silos for the ILW and storage tunnels for ILW and LLW containers. The space between the concrete walls and the rock is filled with clay (bentonite). The repository is partly operated by remote control. Fig. 21.16(C) shows Belgian plans for a mixed ILW and HLW repository located in a large clay deposit. Also in this repository, concrete and clay are the main protective barriers. Geologic barriers are discussed in §21.13.

21.10. Tank storage of high level liquid wastes

The main part of the HLLW is aqueous raffinate from the Purex cycle. It contains ~ 99.9% of the nonvolatile FPs, < 0.5% of the uranium, < 0.2% of the plutonium, and some corrosion products. For each ton of uranium reprocessed about 5 m^3 of HLLW is produced. This is usually concentrated to 0.5-1 m^3 for interim tank storage; specific activity is in the range 10^7 GBq m^{-3}. The amounts of various elements in the waste and their concentration in 0.5 m^3 solution is shown in Table 21.9. The HNO_3 concentration may vary within a factor of 2 depending on the concentration procedure. The metal salt concentration is ~ 0.5 M; it is not possible to keep the salt in solution except at high acidity. The amounts of corrosion products, phosphate, and gadolinium (or other neutron poison added) also may vary considerably. Wastes from the HTGR and FBR cycles are expected to be rather similar.

The HLLW stainless steel tanks have a volume of 50-500 m^3. They are rather elaborate (Fig. 21.17); they contain arrangements for cooling ($\leq 65°C$ to reduce corrosion) and stirring, removal of radiolytic gases, and for control of liquid level, pH, and radioactivity. The tanks are usually double-walled, have heavy concrete shielding, and are often placed underground. Storage in stainless steel tanks has been used in the last 40 y without failure. The philosophy is that tank storage is only an interim procedure and will not last for more than a few years, but the capacity for solidification has often been insufficient, so in practice tank storage has been of much longer duration.

Tank storage has not been without failure. The mild steel tanks built in the 1940's at Hanford, USA, were later (in the 1960's) found to leak due to corrosion. The waste

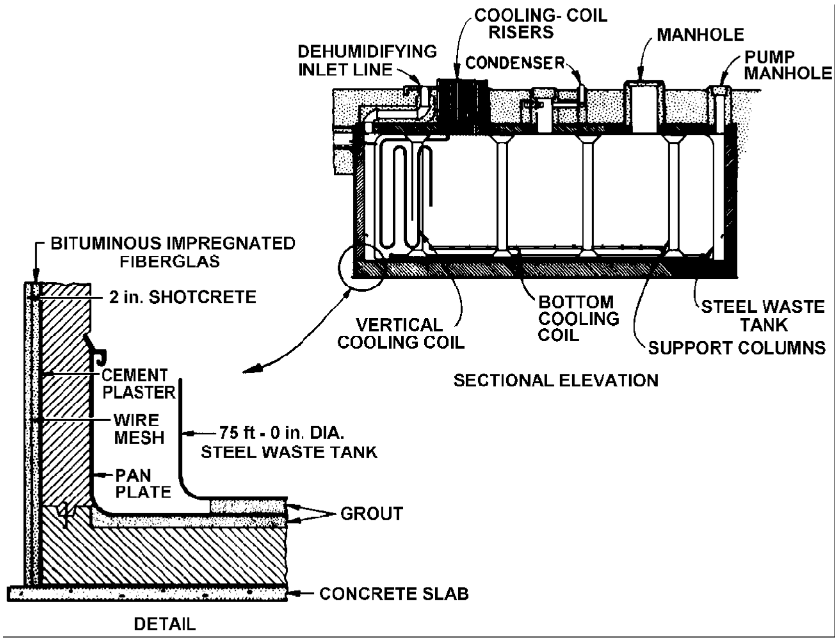


FIG. 21.17. Stainless steel tank for storage of HLLW.

nuclides seeped into the soil, some ultimately reaching ground water; NO_3^-, Ru and Cs were found to have moved hundreds of meters, while Sr, Rare Earths and Pu were less mobile in decreasing order.

In 1957 (possibly also in 1967) a serious accident occurred near Chelyabinsk (*Kyshtym*), south of Ekaterinburg, in the former USSR, probably a chemical explosion between organic wastes and nitric acid, in a high-level waste storage facility (tank or underground repository), leading to the contamination of approx. 1600 km^2 by 8×10^{16} Bq fission products. Local values as high as 10^{10} Bq/m^2 and values of 2×10^8 Bq/m^2 for ^{90}Sr and ^{137}Cs have been reported. A large area is now excluded to the public.

21.11. Options for final treatment of high level wastes

Many concepts are being studied to treat the high level liquid waste from reprocessing so that the environment is protected against short and long term radiation damage. The final treatment concepts are:

(a)dispersion to achieve environmentally acceptable concentrations;
(b) partitioning followed by
    (i) nuclear transmutation;
    (ii) disposal into space;
    (iii) burial in a nonaccessible place;

© solidification followed by geologic deposition.

In principle, dispersion is only applicable for the gaseous and liquid wastes, which would need negligible pretreatment. The limitations are practical (how efficient is the dispersion into air and sea?), radiological (what radioactive concentrations are acceptable in air and sea?) and political/legal (can it be permitted?).

The options (b) are not feasible for all high level waste products, and therefore has to be limited to the most hazardous ones. It would require an isolation of these products, usually referred to as partitioning, or fractionation, of the HLW.

Option (c) is the main route considered for high level wastes from reprocessing. Because of its importance it is discussed in greater detail in a separate subsection (§21.12). Geologic deposition is also the main choice for unreprocessed spent fuel elements.

21.11.1. *Dispersion into sea and air*

The main danger in release of radioactive waste is the risk of ingestion or inhalation. As the hazard differs considerably between the various waste products, depending on their activity, half-life, and biochemical properties, each radionuclide can be assigned a radiotoxicity value (In), §18.13.6, defined by

$$In_w = A/\text{ALI (man-years/kg spent fuel)} \qquad (21.7a)$$

and

$$In_a = A/\text{DAC (m}^3\text{ air/kg spent fuel)} \qquad (21.7b)$$

where A is the radioactivity (Bq) of a particular nuclide (cf. Fig. 21.7 and 21.8) and ALI and DAC values are taken from Tables like 18.12; see also §18.13.6. Figure 21.18 shows the radiotoxicity values for ingestion (In_w) and inhalation (In_a) according to the ALI and DAC values recommended by the ICRP for the most hazardous fission products and actinides in 1 kg of unreprocessed spent PWR fuel at a burnup of 33 MWd/kg as a function of time. It is seen that ^{90}Sr and ^{137}Cs dominate for the first 10 y, then followed by various actinides. The values for spent BWR fuel are approximately the same.

The ocean water volume needed to contain all water soluble radionuclides and the volumes of atmosphere needed to contain the gaseous waste products from all nuclear power in the world at a level below the DAC and ALI values recommended by the ICRP for safe breathing and drinking can be estimated. The basic data are the total toxicity values (In_w and In_a), which have to be compared with the global (free ocean) water volume (1.4×10^{18} m^3) and the atmospheric volume (the troposphere volume up to 12 km is 6×10^{18} m^3).

Taking all nuclides into account and multiplying by 15 000 000 (assumed to be the amount in kg/year of spent fuel removed from nuclear power plants around the turn of the century) one finds that the water volume needed is $< 0.1\%$ of the ocean water volume. Thus in principle the ocean capacity much exceeds the dispersion demand for quite a long time. Similarly, one finds that the air volume needed is only a small fraction of the global air volume, assuming all gaseous products to disperse evenly, i.e. the air volume can accommodate all nuclear power gaseous waste products without approaching the DAC value; however, this is not the case if all nuclides including the actinides were dispersed

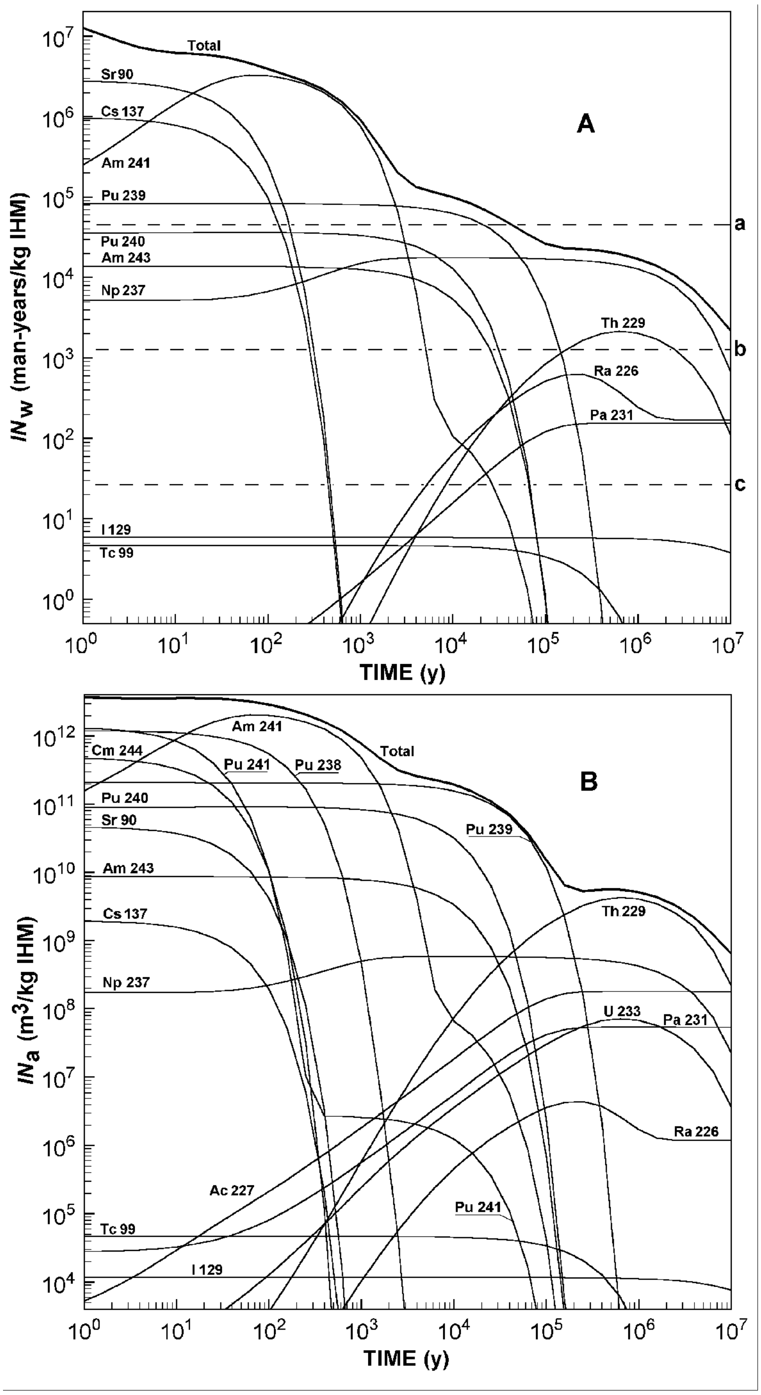


FIG. 21.18. Radiotoxicity of the dominating nuclides in spent fuel; (A) for ingestion based on ALI and (B) for inhalation based on DAC. Fuel data according to Table 21.2.

in the air. There is, however, no process for such a dispersal.

Considering that uniform dispersion is impossible, and that biological processes may enrich some radionuclides, local concentrations would be expected leading to unacceptable doses by exceeding the ALI and DAC values. Therefore only limited amounts are allowed to be disposed of into air and the sea, and within strict rules on the kind and amount of nuclide and the packaging prescribed by the London Convention (cf. §5.10.4).

The London Convention on the prevention of marine pollution by dumping of wastes (1972) limits the amounts to 100 Ci y^{-1} for ^{226}Ra, 10 Ci t^{-1} for other α-active waste of $t_{1/2} > 50$ y, 10^6 Ci t^{-1} for tritium, 100 Ci t^{-1} for ^{90}Sr + ^{137}Cs, and 1000 Ci t^{-1} for other β,γ-waste at any site. These figures are based on a dumping rate of not more than 100 000 t y^{-1} at each site. Dumping is controlled by the IAEA. (N.B., 1 Ci is 37 GBq.)

In the diagram (Fig. 21.18(A)), the horizontal dashed lines indicate the In_w values for the uranium involved in the fuel cycle. The three lines refer (a) to 7 kg natural U (i.e. the potential hazard from the amount of ore that must processed in order to produce 1 kg U enriched to ~ 3.3% in ^{235}U), (b) 1 kg enriched U, and (c) ~ 0.041 kg U (the amount $^{235+238}$U consumed in 1 kg IHM at 33 MWd/kg); in the calculation of the *In* values all uranium daughters were taken into account. It may be argued that when the radiotoxicity value for the waste goes below such a line, the potential hazard is not greater than the natural material provided the external conditions (*Ex*, eqn. (18.9)) can be made the same. The In_w line for HAW from reprocessing, shown in Figure 21.19, and for 1 t natural U cross each other at a decay time about 10^5 y. Thus if the HAW is evenly dispersed and equally well fixed as the original uranium and daughters in the mine, it does not constitute any greater hazard than the uranium ore itself. Consequently, it has been proposed to mix the HAW with cement and/or mine refuse, or, in a more elaborate scheme, to mix it with rock-forming materials and convert it into a "synthetic rock" (SYNROCK), and dispose of it in empty mines or natural underground cavities.

21.11.2. *Partitioning*

The term partitioning is used in two senses: in §21.6.3, to indicate steps in the Purex cycle where U and Pu are separated; here, to indicate a separation of the most hazardous products from the high level waste. Figure 21.19 shows that the hazard of the HAW is dominated by a few fission products (mainly ^{90}Sr and ^{137}Cs) and the remaining actinides; the actinides in the HLW consists of $\leq$0.5% U, $\leq$0.2% Pu and all Np, Am and Cm. In a successful partitioning cycle, the U and Pu recovered will be recycled, leaving "the minor actinides" Np, Am and Cm, which amount to about 0.8 g kg^{-1} y^{-1} spent fuel from a 1000 MW_e LWR reactor; the corresponding amount of Sr + Cs is about 3.7 g kg^{-1} y^{-1}.

The amount of the minor actinides is small enough to make special disposal of them interesting. If they could be removed from the HLW, the waste hazard would be considerably reduced in time, see Fig. 21.19. Presently, research is directed towards the complete removal of all longlived actinides from the reprocessing waste, followed by their "elimination" through the alternatives described later.

These separation projects go under different names: in The US the approach is referred to as the CURE (Clean Use of Reactor Energy), in which the TRUEX (TRansUranium EXtraction; also Truex) process is used; the Japanese have the OMEGA (Option for

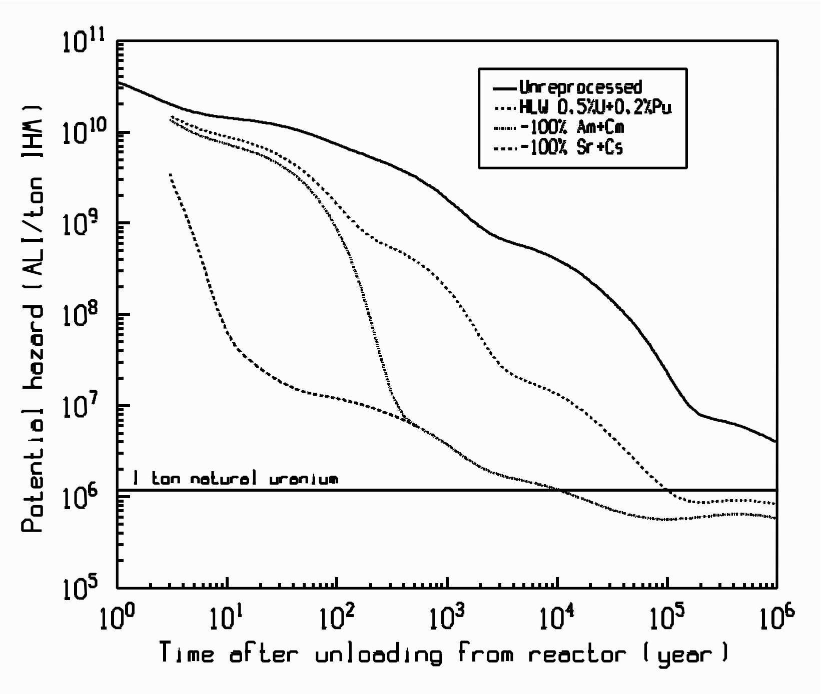


FIG. 21.19. Relative radiotoxicity after 3 y cooling. From top: spent fuel, HLW, HLW after removal of all Am and Cm, and after additional removal of all Sr and Cs.

Making Extra Gain from Actinides) program; the French the SPIN and ACTINEX (for Separation Project Incineration Nucleair, and ACTINide EXtraction), etc. Many of these projects are expected to run for decades before they can be realized.

It is a difficult task to isolate the higher actinides in the HLW, particularly to separate them from the lanthanides, because these elements all are present in solution as trivalent ions of similar size and therefore have very similar chemical properties. The separation methods utilize their slightly different complex forming abilities in techniques such as solvent extraction, ion exchange, and reversed phase partition chromatography. Three solvent extraction processes have been run on a larger experimental scale:

(a) In the *Reversed Talspeak process* the extractant is di-2-ethylhexylphosphoric acid (HDEHP) in a suitable aliphatic diluent. By adding lactic acid to the aqueous phase and adjusting pH to 2.5-3.0 the actinide and lanthanides are selectively co-extracted. The actinides can then be stripped by an aqueous phase containing diethylenetriaminopentaacetic acid (DTPA) as complex former and lactic acid as kinetic promotor, leaving the lanthanides in the organic phase.

(b) The *Truex process* is based on a carbamoyl organophosphorus extractant, abbreviated CMPO (for octylphenyl-N,N-disiobutylcarbamoylmethylphosphine oxide, chemical formula $C_8H_7(C_6H_5)POCH_2CON(CH_2CH(CH_3)_2))$. CMPO is used together with TBP in a mixture of aliphatic hydrocarbons. The Truex flow sheet is shown in Fig 21.20. This process (like the other ones) is based on a common principle: combining complexation of the species in the aqueous phase with a selective extraction process or reagent.

A "complete partitioning" requires the removal of strontium and cesium from the HLW, as ^{90}Sr and ^{137}Cs dominate the waste hazard during the first 400 years. If these are removed, the waste becomes almost "harmless" (i.e. it will be quite easy to handle), see Figure 21.19.

Solvent extraction processes have been developed which effectively remove Sr and Cs. Such process have to be integrated with the actinide removal processes for an efficient back end cleaning procedure. Sr can also be removed from HLLW by the *Srex process*, in which it is very selectively extracted by a macrocyclic ether (ditertiarybutyldicyclo-hexanone-18-crown-6 dissolved in n-octanol, also ^{99}Tc is extracted). Recently another group of crown ethers, calixarenes, have shown a high selectivity for Cs: e.g. in 1 M HNO_3, D_{Cs} is ~ 20, while D_{Sr} is only 0.01. Thus improved methods are being developed for the efficient removal of Sr and Cs from high level waste.

The main point of partitioning the high level waste is that it shall lead to a safer waste (more acceptable to the public) as well as a cheaper back end fuel cycle (to the advantage of the nuclear energy industry). Koyama has analyzed the different waste handling options, Fig. 21.21, and concluded that full partitioning (actinides as well as Sr + Cs, Tc and I) will lead to the cheapest fuel cycle.

21.11.3. *Disposal into space*

Assuming 20 t IHM spent fuel are removed from a 1000 MW_e LWR annually, the partitioned waste would amount to ~ 20 kg minor actinides and ~ 80 kg Sr + Cs annually. The payload of modern rockets exceed several tons. Thus, even including the weight of packaging material, it does not seem unreasonable to assume that the minor actinides from a considerable number of LWRs (> 10) could be transported by a rocket or other means to a location off the Earth. Several different space trajectories have been considered. These include:

(i) a high Earth orbit (altitude 150 000 km); Δv 4.15 km s^{-1};
(ii) transport to the sun; Δv ~ 22 km s^{-1};
(iii) an inner solar orbit; Δv ~ 15 km s^{-1};
(iv) solar system escape; Δv ~ 52 km s^{-1}.

Δv is the incremental velocity required to leave a circular Earth orbit at 200 km and is a direct indication of the size and propulsion energy of the rockets required. Vehicles that could be used include existing rockets and the space shuttle.

A high Earth orbit has the advantage of low Δv and possible later retrieval of the waste, but it requires long term container integrity and very long orbit lifetime (not yet proven). Transport to the sun or solar escape has the advantages that the waste is permanently eliminated from the Earth, but a very high Δv is required. The inner solar orbit has the next lowest Δv but requires a very stable orbit, so that it does not return to Earth.

Space disposal has an economic disadvantage since the cost of transportation is likely to be very high, as the weight of shielding could create significant economic penalty. There

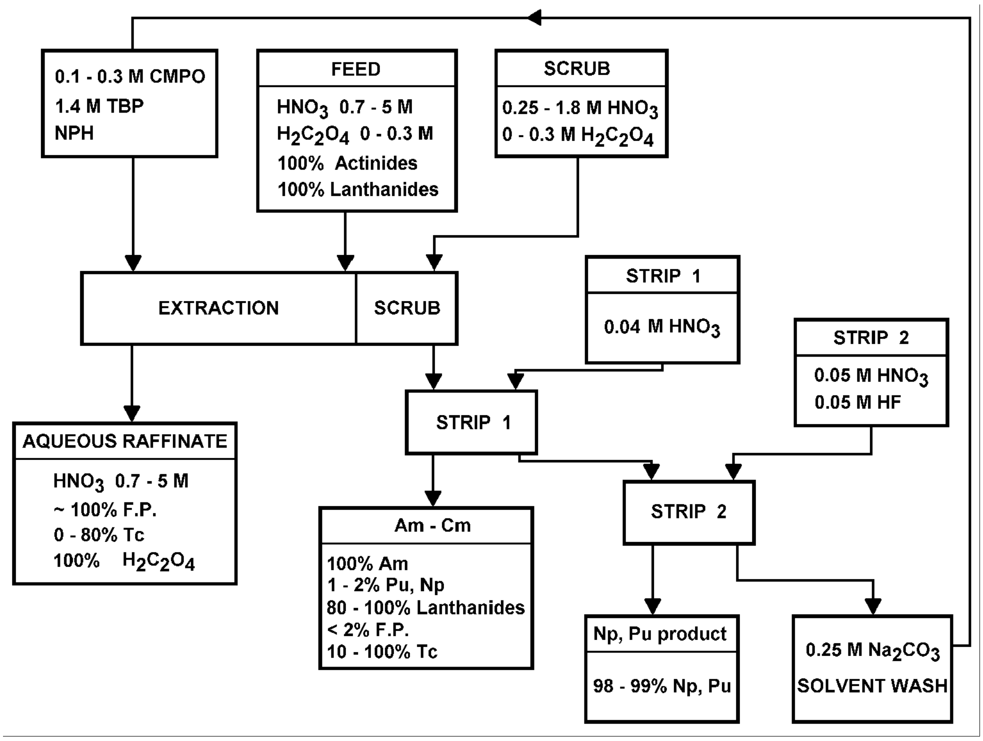


FIG. 21.20. Truex flow sheet for removal of minor actinides from HLLW (From Musikas and Schulz).

are also requirements for capsule integrity to provide a reasonable degree of assurance of survival in the case of an abort. At present, this is not considered to be a serious option. However, many kilograms of ^{238}Pu produced from ^{237}Np have already been used as a power source in deep space probes or unmanned landers (c.f. §6.9.3).

21.11.4. *Remote deposition*

It has been suggested that the most hazardous actinides be removed from the reprocessing waste and stored separately. The advantage is (i) to eliminate all actinides from the HAW, so that its hazardous potential follows that of ^{90}Sr, ^{137}Cs and ^{99}Tc, by which the main hazard is gone in about 400 years, and completely in about 100 000 y; (ii) to reduce the waste actinides to a small volume, 1/100 to 1/1000 of that of the HAW (and, of course, even much less when compared to the volume of the spent fuel elements), which will simplify the storage problem. For example, such actinide waste could be stored uniquely in very deep bore holes in the ground, eventually in the earth's molten interior. A similar procedure seems possible also for the Sr + Cs fraction.

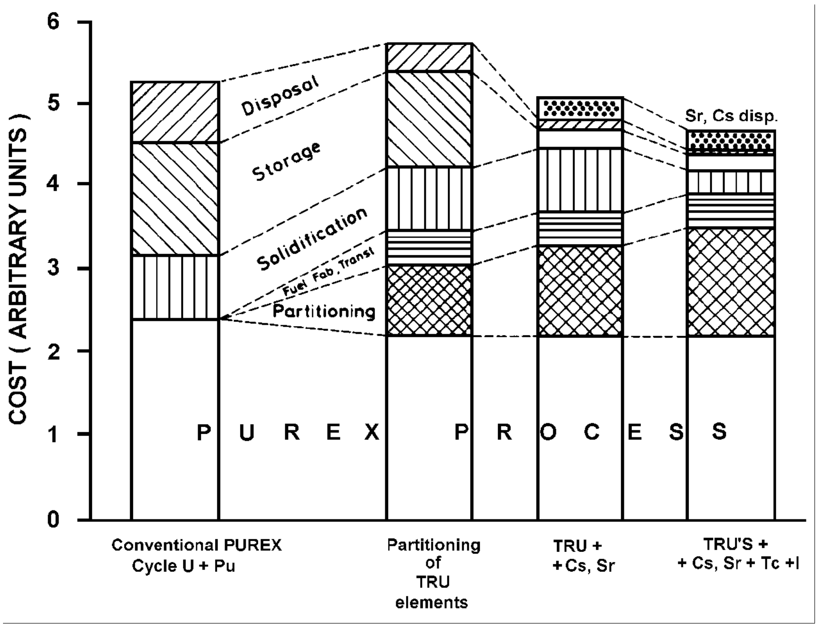


FIG. 21.21. Comparison of costs of various options for managing and disposing of Purex high-level waste. (From Koyama.)

21.11.5. *Transmutation*

The fission products ^{90}Sr and ^{137}Cs can be transformed into shorter lived or stable products by charged particle or neutron irradiation. Charged particle irradiation would be very expensive, and irradiation by reactor neutrons would produce almost as much fission products as are destroyed. Therefore the use of intense accelerator driven spallation neutron sources for transmutation by n-irradiation has been suggested. If controlled thermonuclear reactors (CTR) are developed, their excess neutrons could be used for ^{90}Sr transformation, but less efficient for ^{137}Cs.

In the long term ($\geq$600 y) the actinides dominate the risk picture. Continuous neutron irradiation of the actinides finally destroys all of them by fission (cf. Fig. 16.3). The annual production of americium and curium is ~ 5 kg in a 1000 MW$_e$ LWR, but considerably less in a FBR. Thus if pins of these elements are inserted in a FBR, more americium and curium is destroyed than formed; it is estimated that 90% will have been transformed into fission products after 5-10 y. In the future, CTRs could be used for the same purpose. As an alternative it has been suggested to leave the americium and curium in the uranium returned in the LWR cycle. Wastes from transmutation processes will contain some amount of longlived nuclides, thus a safe final repository is still needed.

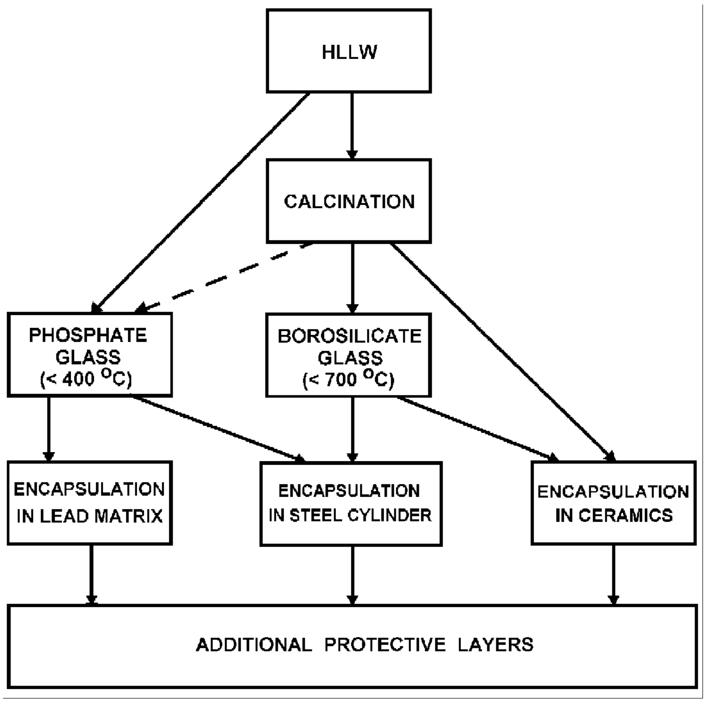


FIG. 21.22. Alternative flow sheets for HLLW solidification.

21.12. Solidification of high level liquid wastes

The solidification of HLLW, followed by geologic deposition, is presently considered as the only realistic technique to create conditions for a safe long term disposal of HAW. The objectives of solidification is to immobilize the radioactive elements and to reduce the volume to be stored. The solidified product must be nondispersable (i.e. not finely divided as a powder), insoluble, and chemically inert to the storage environment, be thermally stable, have good heat conductance (this determines the maximum radioactivity and volume of the final product), be stable against radiation (up to 10^{10} Gy), and have mechanical and structural stability.

Figure 21.22 shows the options for solidification and encapsulation of HLLW. The first step is usually a calcination in which nitrates are destroyed and all metals converted to oxides. Thousands of cubic meters of HLLW have been solidified by fluidized bed calcination. However, calcine has low leach resistance, low heat conductivity, and can be dispersed in air. It is, therefore, only considered as an interim product.

Most countries have focused development work on the fixation of the active waste in borosilicate or phosphate glass. Large continuous vitrification plants producing borosilicate waste glass are located at La Hague in France and at Sellafield in the UK. Figure 21.23 shows a rotating calciner which feeds a continuous borosilicate glass melter. Preformed and crushed borosilicate glass is continuously added near the end of calcination process. In

TABLE 21.11. *Characteristics of some solidified high level waste products*

Property	Fluidized bed calcine	Phosphate glass	Borosilicate glass
Physical form	Granular, 0.3–0.7 mm	Monolithic	Monolithic
Bulk density (kg m^{-3})	1.0-1.7	2.7-3.0	3.0-3.5
Maximum weight % FP	50	35	30
Thermal conductivity (W m^{-1} K^{-1})	0.2-0.4	1.0	1.2
Leachability (20°C, kg m^{-2} d^{-1})	1-10	10^{-5}-10^{-3} †	10^{-6}-10^{-4} ‡
Maximum center temperature (°C)	550 ††	400 *	700 *
Maximum allowable heat density (kW m^{-3}) #	45	53	127
Maximum allowable heat density (kW m^{-3}) @	38	36	92

† Devitrified (crystalline) glass has leach rates 10^{-2}-10^{-1} kg m^{-2} d^{-1}.
‡ At 100°C the leach rate is ~ 10^{-2} kg m^{-2} d^{-1}.
†† Because of risk for FP volatilization.
* Devitrifies at higher temperature.
# Forced water cooling of a cylinder; ϕ 0.3 m, surface temperature ≤100°C.
@ Natural air cooling of a cylinder; ϕ 0.3 m.

the melter the calcines and glass mixture is heated to 1000-1200°C, leading to the formation of a homogeneous glass, which is poured into stainless steel cylinders. From a chemical standpoint (stability) the glass can contain up to 30 wt% fission product oxides, but 20% is a more normal value. Thus the waste nuclides in 1 t of LWR fuel can be contained in about 200 kg glass; the exact value depends on how long time the waste has cooled. For short cooling times a high waste content in the glass could cause it to melt and possibly crystallize (at ~ 700°C), which may reduce corrosion resistance because of the larger internal surface formed. The properties of some glasses are given in Table 21.11.

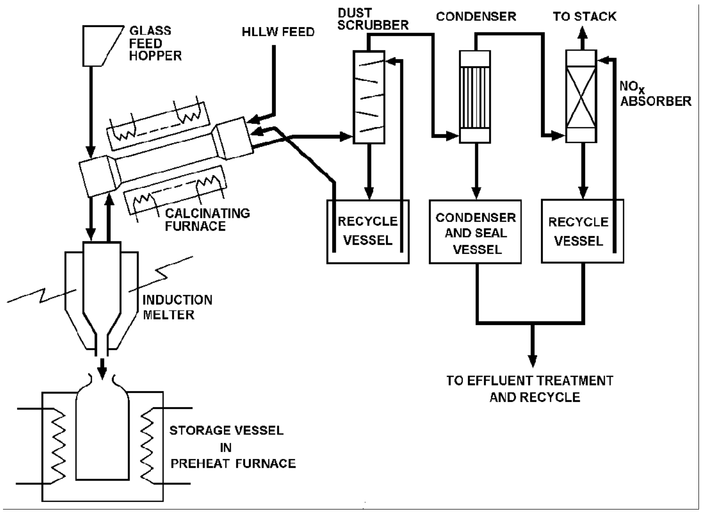


FIG. 21.23. Continuous HLLW calcination and borosilicate vitrification process.

The incorporation of the solidified waste into phosphate glass is an alternative to the use of borosilicate glass. In this case the calcination step can be bypassed. The HLLW, together with phosphoric acid, is evaporated and denitrated, and then fed to a continuous melter operating at 1000-1200°C, from where the molten glass flows into the storage pot. This process is more corrosive and produces a glass somewhat inferior to the borosilicate. Further disadvantages are that the glass recrystallizes at relatively low temperature (~ 400°C), and that the devitrified (crystallized) phosphate glass exhibits a rather high leach rate, 0.01–0.1 kg m^{-2} d^{-1}.

In the PAMELA process, earlier considered for use in Germany, granulated phosphate glass is incorporated into a metal alloy matrix in a steel cylinder. This offers high chemical and mechanical stability, as well as good heat conductivity (~ 10 W m^{-1} K^{-1} for a lead matrix; cf. 1.2 W m^{-1} K^{-1} for borosilicate glass). This decreases the central temperature and allows the incorporation of larger amounts of radioactivity (up to 35% FPs) in a single cylinder. The high heat conductivity makes it feasible to use short fuel cooling times (down to 0.5 y) and diminishes the demand for interim fuel element storage basins or HLLW storage tanks. The solidified waste glass is collected in stainless steel cylinders.

A typical waste canister may contain ~ 9% FPs, emit ~ 10 kW after 1 y, ~ 1 kW after 10 y, and ~ 0.5 kW after 40 y. They can be stored in air-cooled vaults or water-cooled pools. Before final deposition the HAW containers are reconditioned, i.e. enclosed in an additional canister of type described below. At the higher power level they are stored in water-filled pools. After > 10 y air-cooled vaults may be satisfactory; forced cooling is usually considered, but with precaution for sufficient convection cooling in case of ventilation failure.

21.13. Deposition in geologic formations

A general consensus has developed that disposal of radioactive waste should be in the country in which the nuclear energy is produced. Thus, even if the spent fuel elements are sent from one state to another for reprocessing (like spent fuel from Japanese reactors being sent to the Sellafield reprocessing plant in the United Kingdom), the producer state (Japan) must guarantee its readiness to accept the processed waste. This condition has led to intensive national investigations of the safest way to dispose of the high level waste, either in the form of solidified HLLW, or spent fuel elements in the once-through option. In these studies geologic repositories have been the prime consideration, e.g. crystalline silicate rock, clay layers, salt domes, the sea bed, etc.

21.13.1. *Properties of geologic formations*

Many geologic formations are being studied for final storage of the waste canisters: rock salt, crystalline rock (e.g. granite), volcanic tuff, clay, etc. The main requirements are:

(i) geologic stability, i.e. regions of very low seismic, volcanic, or other geologic activity;
(ii) absence of large fractures, holes, etc.;
(iii) impermeability to surface water;

(iv) negligible groundwater circulation with no flow-lines leading to nearby potential intake sources;
(v) good heat conductivity;
(vi) of little interest to and as remote as possible from human activities.

There are large geologic formations, which are very old (many hundred million years) and geologically stable, e.g. the Scandinavian and Canadian shields. These are usually fractured, even if considerably large volumes can be found (10^6 m^3) which are free of fractures. A nuclear waste storage facility will, however, for reasons given below, cover rather large areas, several km^2; thus for crystalline rock fracture zones, which carry ground water, must be taken into account. Rock salt and clay formations, on the contrary, are usually free of fractures: rock salts are dry, but clay formations are usually wet, though the water migration through the formation is extremely small (see below).

A limiting factor for geologic disposal is heat conductivity. If the thermal conductivity of the geological deposit is too poor, the material in the waste canisters may melt and react with the encapsulation, possibly destroying it. Because a safe disposal concept must rely on conduction cooling, the relatively low heat conductivity of the geologic deposit makes it necessary to disperse the waste material over a large volume. The thermal conductivity of ~ 3 W m^{-1} K^{-1} for granitic rock (compare rock salt ~ 9 and wet clay ~ 1) limits the waste heat density of the rock wall to ≤ 20 W m^{-2}. Therefore storage repositories would consist of long tunnels or deep holes at large interspace. Three concepts are under investigation: (i) very deep holes (VDH, up to 3000 m) in which waste canisters would be stacked, (ii) deep repositories (300-500 m) with parallel horizontal tunnels of moderate length (≤ 100 m), 20-100 m apart, upper part in Figure 21.24, and (iii) deep repositories with a few very long tunnels (> 1 km, VLH).

With a typical heat production of ~ 500 W per canister containing vitrified HAW (at 40 years cooling) the wall heat density would be 6-7 W m^{-2}. The internal temperature of a glass canister would then never exceed 90°C, and the surface temperature (above the storage holes, Fig. 21.24) not more than 65°C. Slightly higher temperatures can be accepted for spent fuel elements.

Such deep (geologically) repositories are safe against surface activities (including nuclear explosions) except drilling or mining. In order to avoid such an occurrence after the repository has been forgotten, it should be located in a formation of no interest to society; e.g., the formation should not contain any valuable minerals. From this point of view, location in deep seabeds has been suggested. Such a location can be chosen either deep in the bottom silt or in a bedrock under the sea floor, or, possibly, in a tectonically active trench, where with time the waste would be pulled down into the interior of the earth.

The risk for a land-based geologic repository is that a combination of more or less unpredictable circumstances could lead to rupture of the protective barriers around the waste matrix, followed by dissolution and transport of the most hazardous products by water to a place where it can enter into the food chain. Therefore a clay layer (e.g. bentonite) between the canister and the rock wall is suggested, partly to act as a mechanical buffer, so that even considerable slippage caused by earthquakes would have little effect on the mechanical integrity of the canister and partly to reduce water flow around the canister.

Most rocksalt deposits are very old. In many cases they rise in the form of a dome, the top of which may be at a few hundred meters below surface level, and with a depth up to

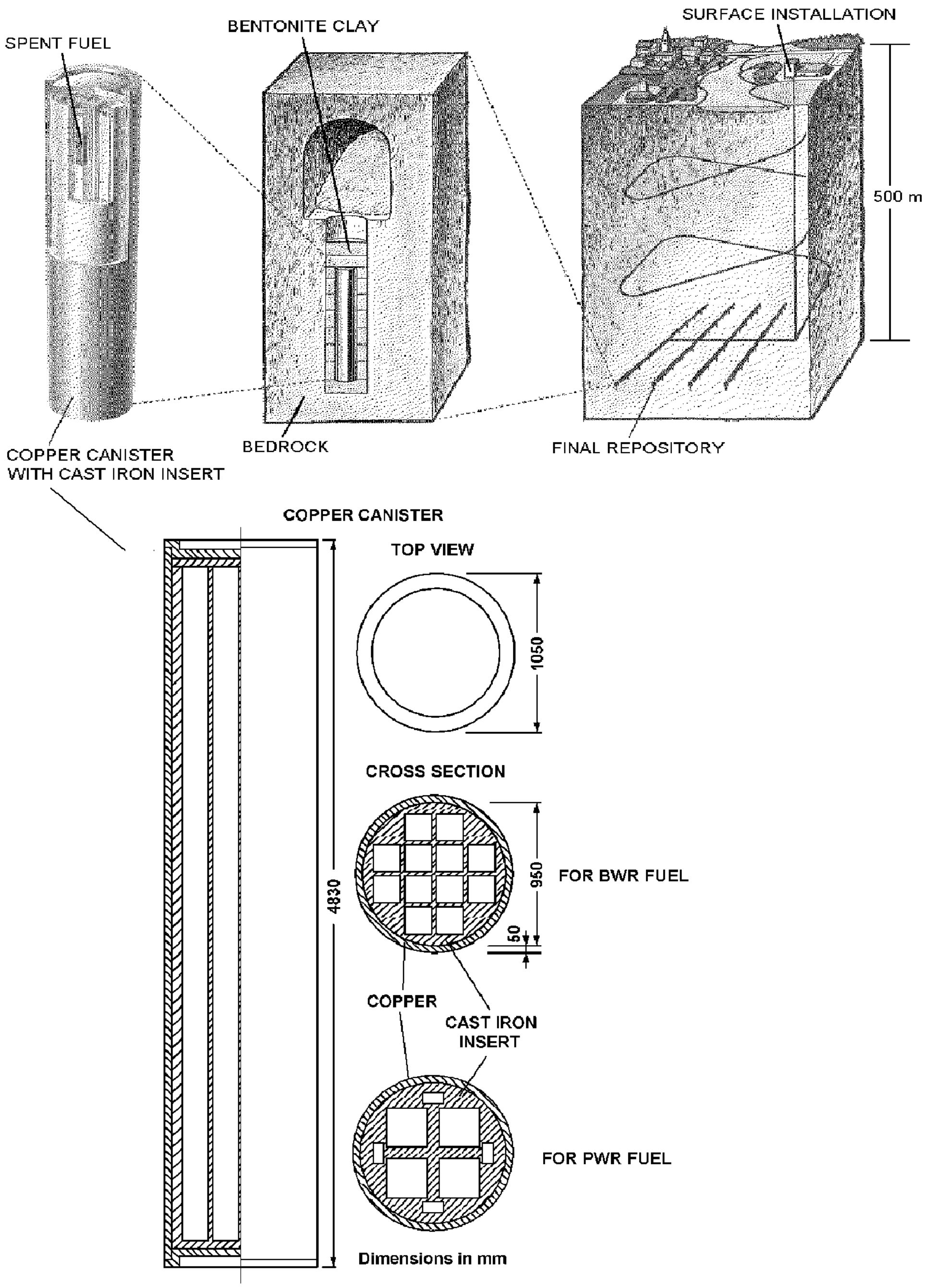


FIG. 21.24. Principles of storage of HLW: upper part, Swedish concept; lower part, canister with inserts for final storage of spent BWR fuel and spent PWR fuel (From SKB).

more than 1000 m. The dome is usually protected from groundwater by a calcite ($CaCO_3$) cap. Salt has been mined in such formations for centuries. The formation contains only microcrystalline water and is extremely dry (otherwise it would have dissolved during the geologic ages). Therefore, canisters emplaced in such formations are not believed to dissolve (as long as no water enters through the hole mined through the calcite layer). The good heat conductance allows emplacement of waste of higher power density than for deposits in clay or granite. Since the salt is plastic, the holes and corridors, which are backfilled with crushed salt, selfseal and no clay buffer is needed. The canisters would probably be crushed in the plastic salt, and therefore could be irretrievable after a hundred years.

Granite and clay formations are percolated by groundwater except at depths which presently are considered impractical. The water flow rate is given by *Darcy's law*

$$F_w = k_p\, i\, S \quad (\mathrm{m}^3\ \mathrm{s}^{-1}) \tag{21.8}$$

where k_p is the permeability (m s^{-1}), i the hydrostatic gradient (m m^{-1}), and S the flow cross section (m^2). A typical value for Scandinavian granite formations at 500 m depth is $F_w = 2\times10^{-4}$ m^3 m^{-2} y^{-1}, which gives a ground-water velocity of 0.1 m y^{-1}, and a time of 5000 y for the water to move 500 m. In this case the rock permeability is taken as 10^{-9} m s^{-1}; rock formations closer to the surface usually have higher permeabilities, but many formations with much lower values are also known (~ 10^{-13}).

Clays consist of small particles, usually < 2 µm and with an average size of < 0.1 µm, of various minerals like quartz, feldspar, montmorillonite (a hydrated aluminum silicate with high ion-exchange capacity), mica, etc. The overall chemical composition is mainly a mixture of silica, alumina, and water. The small particles in the clay give rise to a very large surface area (1 cm^3 of particles of 0.1 µm diameter have a total surface area or about 60 m^2) and correspondingly high sorption capacity for (eventually) dissolved waste products. Although the clay can take up large amounts of water (up to 70%) without losing its plasticity, the water permeability is extremely low. For the sodium bentonite clay (~ 90% montmorillonite, plenty available) considered in many projects, the permeability is 2×10^{-14} m s^{-1} (10% water in clay compacted to a density of 2100 kg m^{-3}). Such clay can be considered impermeable to groundwater. Natural clays of this type occur in many countries (the Netherlands, Italy, etc.).

21.13.2. *Waste conditioning before final storage*

The basic philosophy in storing high levels of radioactivity in geologic formations is the use of a multi barrier system to protect it against dissolution. These barriers are:

(i) The waste matrix itself, which is made highly insoluble; this is achieved by vitrification of the reprocessing HLLW as described above, while the spent unreprocessed fuel elements keep the radioactive products in a highly insoluble UO_2 matrix.

(ii) The waste matrix (glass or UO_2) is encapsulated in an "insoluble" canister.

(iii) The canister is surrounded by a clay buffer in the case of a crystalline rock deposit.

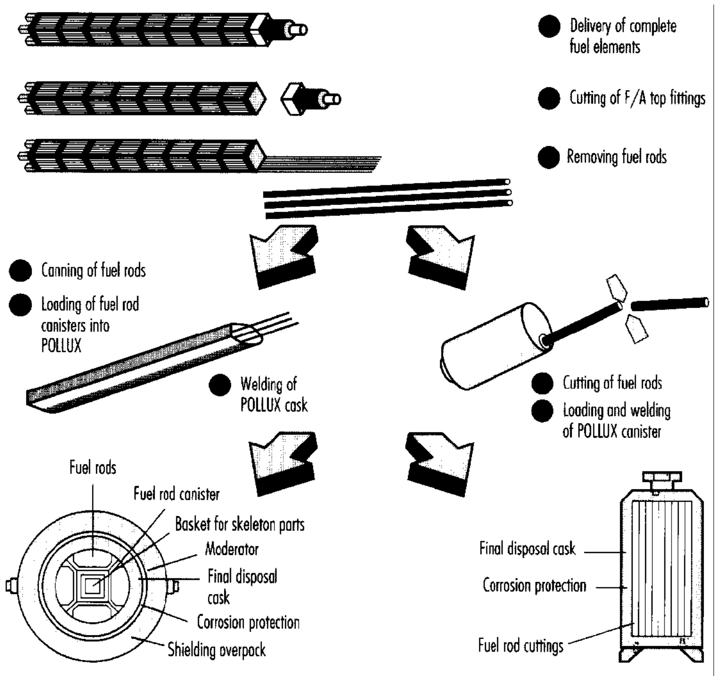
Here we shall only discuss the encapsulation, for which numerous concepts have been suggested.

(a) *Vitrified waste*. The stainless steel cylinders containing the vitrified radioactive waste are not considered to provide sufficient protection against long term corrosion in the final repository. Additional encapsulation in various corrosion resistant materials is therefore suggested: lead, titanium, copper, gold, graphite, ceramics, etc. For example, in one proposal canisters containing 170 l vitrified waste in a 3 mm thick stainless steel cylinder will be surrounded by 100 mm lead in a casing of 6 mm titanium; the overall dimensions of the cylinder will be 1.6 m long with a diameter 0.6 m. One such cylinder contains solidified HLLW from reprocessing 1 t spent fuel from a 1000 MW_e light water reactor; this corresponds to about 20 cylinders per year.

(b) *Spent fuel*. Although UO_2 dissolves more slowly than glass in groundwater, spent fuel elements must be recanned before entering the final storage facility. For this purpose single fuel elements or bundles are placed in cylindrical canisters. The lower part of Figure 21.24 shows an example. The outer part of the canister may consist of iron, stainless steel, copper, etc. selected to resist the repository environment (e.g. dry or wet). For storage in very long or deep dry holes, rounded caps are likely to be used. Waste canisters for unchopped spent fuel elements will be rather long, but it has also been suggested that the fuel is chopped as in the German Pollux concept, Fig. 21.25, which is designed for multi-purpose use, both to fit all kinds of spent fuel elements (from BWRs, PWRs, HTGRs etc) as well as vitrified high level waste. It is a double-shell concept, consisting of leak-tight welded steel; between the two steel walls is a corrosion resistent sheet of Hastelloy C4. The void is either gas filled (He) or filled with some suitable material like lead, which has good heat conductivity and also provides some radiation protection. Figure 21.24, shows the design of a spent fuel element canister where the fuel elements are inserted in a cast iron cylinder which is surrounded by 50 mm of copper metal. The thick metal layer has several purposes: (i) to simplify handling during deposition operations; (ii) to protect its content from mechanical deformation; (iii) to reduce the surface radiation to so low values that the radiolysis of groundwater will not contribute to canister corrosion; (iv) to protect, as long as possible, the waste-containing matrix from corrosion. For example, by using an outer copper wall, the lifetime of the canister is expected to greatly exceed 1000 y for oxygen containing groundwater, and 10^4 y for reducing groundwater (the lifetime of a 5 cm thick copper layer is now estimated to be $> 10^6$ y). The dissolution of waste canisters and leaching of waste is discussed in §22.10.

21.13.3. *Repository projects*

In one concept the canisters are stored in dry areas (e.g. a desert floor) after having been surrounded by concrete. A space may be left between the inner cylinder and the surrounding concrete wall to allow air convection cooling. As long as the climate stays dry the pillars will erode very slowly and last for tens of thousands of years. This procedure also allows for easy retrievability. An alternative encapsulation is achieved by using hot



POLLUX cask		POLLUX canister
~ 150 cm	Diameter	~ 43 cm
~ 5.50 m	Length	~ 134 cm
~ 65 t	Weight	~ 1 t
8 PWR-Fuel elements	Content	0.5 PWR-Fuel elements
<0.2 mSv/h	Surface dose rate	$<10^5$ mSv/h

FIG. 21.25. The proposed German POLLUX cask for final disposal of spent fuel and/or vitrified high level waste in salt.

(~1500°C) isostatic (100-300 MPa) compression to surround the fuel bundles by a homogeneous, dense ceramic material, like corundum (microcrystalline Al_2O_3) or graphite. Since corundum and graphite are natural minerals, the long term resistance should be very high, even against water.

The main concept is to store the vitrified HLW and the spent fuel elements irretrievably in deep underground geologic formations, according to designs described above. Many such formations are now being evaluated: rock salt (mainly Germany, the Netherlands and USA), crystalline rock (Canada, Finland, France, Japan, Sweden, USA), volcanic tuff (USA), clay (Belgium, Italy), etc. Cross sections of geologic repositories for HLW are shown in Figures 21.16(C) and 21.24. Also disposal into polar ice sheets (USA) and the seabed (UK, USA) have been investigated, but are no longer considered feasible.

The most advanced projects are (i) at the abandoned Asse salt mine in Germany, where drums with low and intermediate level activities have been deposited at 300 m depth in 1967-78; the repository is now used for research; a final repository in salt at Gorleben is planned to be in operation be the year 2010, (ii) the waste isolation pilot plant (WIPP) at a bedded salt deposit in New Mexico at 600 m depth; the planned repository is currently examined by the authorities for full scale operation; it will primarily be used for α-bearing military waste; in Yucca Mountain extensive studies are being made for a repository 300 m deep in dry tuff for civilian and defense nuclear waste (total capacity ~ 7000 t IHM), (iii) the Swedish KBS project for disposal in granite; the Stripa mine has been studied for more than a decade by an international team and a new underground laboratory has been built at Äspö; other hard rock laboratories are in operation in Canada, Finland and Switzerland, and (iv) a laboratory at 250 m depth in clay at Mol, Belgium, has been in operation since 1983, etc. These sites are all located in geologic formations, which have been unaltered for more than 100 million years. From the tectonic plate theory continual tectonic stability is expected for at least the next 10 million years. Although ice ages may alter surface conditions at northerly located sites, they are expected to have a negligible effect on repositories at great depth ($>$ 500 m). In 2001 the Finnish parliament gave its permission to begin construction of a KBS-like final repository for spent fuel in granite. It will be the first of its kind in the world.

21.14. Beneficial utilization of nuclear wastes

The amount of spent fuel generated during 1994 amounts to ~ 8000 t. It contains large and potentially valuable sources of metals and radioactive nuclides. Though today considered a liability it may in the future become a needed asset. Since the extraction and utilization of some of the fission products or actinides will probably not be economic after the waste has been vitrified and placed in permanent geologic storage, the nuclear fuel reprocessing scheme should therefore be designed for byproduct extraction.

Presently the most interesting products in the waste are the platinum group metals (due to their metal values) and ^{90}Sr, ^{137}Cs, ^{85}Kr, ^{237}Np/^{238}Pu, and ^{241}Am (due to their radiation properties, cf. §§7.11, 9.5, etc).

The waste contains considerable amounts of Ru, Rh, and Pd, all metals in scarce abundance on earth. These elements are used as catalysts in the chemical industry, for catalytic exhaust cleaning in cars, and as corrosion resistant materials. The United States demand exceeds the domestic production by about a factor of 100. The United States would be independent of import from year 2000 if these elements were recovered from the yearly generated spent fuel. This is particularly true if technetium is recovered, since it can often replace platinum. Some of the recovered elements would be radioactive, but the activities would be small enough to make the elements easy to handle.

Beta radiation from ^{85}Kr on phosphors causes visible light. Radiokrypton light sources have widespread applications where reliable lights are required as, for example, at airports, railroads, hospitals, etc., or where sources of electricity could cause dangerous explosions, as in coal mines, natural gas plants, etc. However, fission product krypton contains only 4% of ^{85}Kr, which makes it unsuitable for high intensity lightning applications. ^{85}Kr must therefore be enriched about a factor of 10, which presently can be done e.g. by thermal diffusion.

By the year 2000, over 100 MW heat will be produced by radiostrontium. Strontium fueled thermoelectric generators are used in several countries to power unmanned weather data acquisition systems, lighthouses, and other navigation aids, etc. Their reliability surpasses any other remote power source. The current thermoelectric generators have a thermal-to-electrical efficiency of about 5%, while recently developed thermal-to-mechanical systems show efficiencies of 25–30%. The use of such systems could be expanded vastly by increased recovery of suitable fission products and actinides.

Food sterilization by radiation is potentially of global importance (§18.7). Though this presently is done by ^{60}Co or accelerator radiation, the advent of large quantities of radiocesium recovered from nuclear wastes may have a considerable positive impact on the economics and scale of food irradiation. An almost equally important use of ^{137}Cs would be for sewage sludge treatment, which may become increasingly important as the requirements for sterilization and secondary treatment of the sludge increases. The thermoradiation of sludge may also make it useful as a sterile fertilizer.

The low penetrating radiation, long half-life, and high power density of ^{238}Pu makes it ideal for special purpose power supplies (§6.9.3). The main present use is in space research, and ~ 30 kW$_{th}$ power sources have been launched into space, ^{238}Pu has been used in heart pacemakers and is still a candidate as a power source for completely artificial hearts. Production of ^{238}Pu requires the isolation of ^{237}Np, which is then irradiated and reprocessed to produce pure ^{238}Pu.

The demand for ^{241}Am is larger than present production capacity because of its use in logging oil wells, in smoke detectors, and for various gauging and metering devices. However, the potential source is large: the annual world production is ~ 4.5 t in 1994 (after 10 years cooling, see §21.32.2) and the accumulated civilian nuclear wastes in the US contain > 20 t of americium.

If all the mentioned waste products are recovered, this would mean (a) that the waste is turned into an essential asset with benefits in food production, health, and safety, and (b) that the hazard of the remaining waste would be much lower, considerably simplifying final waste storage.

21.15. Exercises

21.1. In a BWR the minimum and maximum heat fluxes at the fuel rod surface are 0.46 and 1.08 MW m^{-2} at a coolant temperature of 283°C. The rods have an outer diameter of 12.7 mm with a cladding of 0.8 mm thick Zircaloy-4; assume a negligible fuel cladding gap and neglect the temperature drop between coolant and cladding and across the fuel-cladding gap. Assume that data in Table 21.1 are valid at all temperatures and $k_{UO2} = 4$ W/m°C. What are the highest and lowest fuel-center temperatures?

21.2. Using the data for the Würgassen reactor and the thermal neutron capture cross-section (Table 19.4) it can be calculated how many kg Pu should be formed per t U at a burn-up of 27 500 MWd/t. (a) Make this calculation assuming that plutonium disappears only through fission in ^{239}Pu. (b) According to Table 21.2 each t U from a PWR contains 8.69 kg Pu; why is your result much lower?

21.3. It is desired that 98% of all ^{233}Th formed by neutron capture in ^{232}Th decays to ^{233}U. How long a time must elapse between end of irradiation and start of reprocessing?

21.4. In a ^{233}U fueled reactor, some ^{233}U is converted into ^{235}U. Calculate the amount of ^{235}U formed in 1 t ^{233}U from neutron capture in ^{233}U and ^{234}U ($\sigma_{n,\gamma}$ 97 b) for a fluence of 10^{25} n m^{-2} (a) assuming no consumption of ^{235}U formed, (b) taking ^{235}U fission and capture into account.

21.5. Explain why ^{228}Th and ^{232}U are a nuisance in the thorium-uranium fuel cycle.

21.6. A reactor starting with 3% ^{235}U produces 6000 MWd energy/t U fuel each year. Neglecting fission in ^{238}U, (a) how much fission products have been produced after 5 years? (b) What is the ^{235}U concentration if plutonium fission also is taken into account?

21.7. In the example above, 1 t U as fuel elements is removed from the reactor after 2 years. Using Fig. 21.7, (a) what is the total radioactivity from the fission products after 1 y cooling time? (b) Which FP elements are the most radioactive ones at this time?

21.8. Calculate the decontamination factor required for (a) fission product activity, and (b) for gadolinium in commercial plutonium nitrate produced from PWR fuel (Tables 21.2 and 21.7) at t_{cool} 10 y.

21.9. 0.0015 Ci ^{239}Pu is released annually from a reprocessing plant. What will be the corresponding release of ^{238}Pu and ^{240}Pu for typical isotopic plutonium composition of LWR fuel?

21.10. Calculate the natural radiotoxicity value In_w of 1 km^3 of land (density 2 600 kg m^{-3}) containing 3 weight ppm ^{238}U with daughter products. Only ^{226}Ra has to be considered.

21.11. A tank contains 100 m^3 5 y old HLLW. Analyses show that a 1 ml sample contains 1.09 GBq of ^{90}Sr, which is the only Sr activity. (a) Calculate the heat production for a waste of composition in Table 21.9 left column. (b) How many 500 kg glass cylinders would be needed (assume the glass contains 10% FPs) to contain all the solidified waste? (c) How many 1000 MW$_e$ PWR reactor years does this waste correspond to?

21.12. Ru, Rh, and Pd are recovered from the waste from a 10 GW$_e$ program. What will the annual amounts and specific radioactivities be at t_{cool} = 10 y for each of them?

21.16. Literature

J. PRAWITZ and J. RYDBERG, Composition of products formed by thermal neutron fission of ^{235}U, *Acta Chem. Scand.* **12** (1958) 369, 377.
R. STEPHENSON, *Introduction to Nuclear Engineering*, McGraw-Hill, 1958.
J. FLAGG (Ed.), *Chemical Processing of Reactor Fuels*, Academic Press, 1961.
J. T. LONG, *Engineering for Nuclear Fuel Reprocessing*, Gordon & Breach, 1967.
K. J. SCHNEIDER and A. M. PLATT (Eds.), *High-level Radioactive Waste Management Alternatives*, Battelle Pacific Northwest Laboratories, Richland, Wash. 99352, Report BNWL-1900, NTIS, Springfield, 1974.
S. AHRLAND. J. O. LILJENZIN and J. RYDBERG, (Actinide) Solution Chemistry, in *Comprehensive Inorganic Chemistry*, Vol. 5, Pergamon Press, Oxford, 1975.
Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter - "The Definition Required by Annex I, paragraph 6 to the Convention and the Recommendations Required by Annex II, Section D", IAEA, INFCIRC/205/Add. 1, 10 January 1975.
IAEA, *Transuranium Nuclides in the Environment*, Vienna, 1976.
IAEA, *Management of Radioactive Wastes from the Nuclear Fuel Cycle*, Vienna, 1976.
ERDA, *Alternatives for Managing Wastes from Reactors and Postfission Operations in the LWR Fuel Cycle*, ERDA-76-43. NTIS, Springfield, 1976.
IAEA, *Regional Nuclear Fuel Centres*, Vienna, 1977.
NEA-OECD, *Objectives, Concepts and Strategies for the Management of Radioactive Waste Arising from Nuclear Power Programmes*, OECD, 1977.
H. A. C. MCKAY and M. G. SOWERBY, *The Separation and Recycling of Actinides*, EEC, EUR 5801e, 1977.
KBS Project, *Nuclear Fuel Cycle Back-End*, 1978, Kärnbränslesäkerhet, Fack, 10240 Stockholm.
R. G. WYMER and B. L. VONDRA, *Technology of the Light Water Reactor Fuel Cycle*, CRC-Press, 1980.
M. BENEDICT, T. H. PIGFORD and H. W. LEVI, *Nuclear Chemical Engineering*, 2nd Ed., McGraw-Hill, 1981.
C. MUSIKAS and W. SCHULZ, Ch. 11 in J. Rydberg, C. Musikas and G. Choppin, *Principles and Practices of Solvent Extraction*, Marcel Dekker, 1992.
SKB, Swedish Nuclear Fuel and Waste Management Company, Annual and other reports, Stockholm, Sweden.
Sources and Effects of Ionizing Radiation (UNSCEAR), United Nations, New York, 1993.
IAEA Bulletin **36**, No 1, 1994. (Radiation Technologies)